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The Law of Mass Action

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With 80 Figures

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Preface

'Why are atoms so small?' asks 'naive physicist' in Erwin Schrödinger's book '*What is Life? The Physical Aspect of the Living Cell*'. 'The question is wrong' answers the author, 'the actual problem is why we are built of such an *enormous number* of these particles'.

The idea that everything is built of atoms is quite an old one. It seems that Democritus himself borrowed it from some obscure Phoenician source[1]. The arguments for the existence of small indivisible units of matter were quite simple. According to Lucretius[2] observable matter would disappear by 'wear and tear' (the world exists for a sufficiently long, if not infinitely long time) unless there are some units which cannot be further split into parts.

However, in the middle of the 19th century any reference to the atomic structure of matter was considered among European physicists as a sign of extremely bad taste and provinciality. The hypothesis of the ancient Greeks (for Lucretius had translated Epicurean philosophy into Latin hexameters) was at that time seen as bringing nothing positive to exact science. The properties of gaseous, liquid and solid bodies, as well as the behaviour of heat and energy, were successfully described by the rapidly developing science of thermodynamics.

Despite this attitude of physicists, chemists of the same period employed the concept of atoms in the description of the transformation of matter by chemical reactions. Not only were the dependencies of properties of compounds on their atomic composition and arrangements of atoms within a molecule established but also all known chemical elements were systematised in Mendeleev's Periodic Table. This allowed for the prediction of the existence of yet undiscovered types of atoms and of the properties of their compounds. Even the number of atoms in a given amount of a substance of known atomic (elemental) composition had at that time been correctly estimated.

However, when describing quantitatively the ability of a compound to take part in a chemical reaction, chemists have had to apply the rules of formal thermodynamics. For such practical purposes thermodynamics supplied excellent tools which effectively substitute the relationships between molecules by the relationships between thermodynamic functions (free energy, entropy, *etc.*), their

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[1] Sextus Empiricus, '*Adversus mathematicos*' IX, 363

[2] The works of Democritus are mainly known from commentaries of his opponents. The only coherent exposition of the ancient atomistic theory available is the poem of Lucretius "*De rerum natura*".

partial derivatives, temperature, volume, pressure and the numbers of *moles*. Among these parameters the latter alone has some reference to the molecular (atomistic) concepts of chemistry.

One of these rules, the *law of mass action,* which defines the relationship between the numbers of moles of products and reactants in chemical equilibrium, is extremely important for chemists. Historically it was first established from experimental observations on the *rates* of chemical reactions employing the *dynamic interpretation of chemical equilibrium*. Therefore it is very often considered as an *empirical rule* and/or as a consequence of the *kinetic law of mass action*. In fact, the equilibrium law of mass action follows from *the fundamental laws of thermodynamics* and thus is an empirical rule to the same extent as is the first law of thermodynamics.

The law of mass action in its widely known form can be formulated only for reactions in ideal gases and ideal crystals although, in practise, real gases at low density and crystalline solids at low temperatures approximate to these ideal states. For *non-ideal systems* approximating equilibria in any other real aggregate state there are two possible ways of establishing a relationship between the amounts of reactants and products. The first is to derive a specific form of the law of mass action for a given non-ideal system. Another, more successful approach was suggested by Lewis [1], in which the universal ideal form of the law of mass action is retained but, instead of concentrations, functions of these called *activities* are to be used. The parameters of these functions (activity coefficients) once established for one reaction were found to be applicable in the description of a series of similar reactions. Hence, by making use of a limited number of reference equilibria it was possible to obtain the empirical data necessary for the calculation of activities for a very large number of practically important reactions.

An inquisitive '*naive chemist*' would probably ask why a proper law of mass action for a non-ideal system could not be derived? The problem, in fact, is not in the derivation but in the practical applicability of the equations so obtained. The mathematics of the ideal law of mass action is very simple, activities are (or assumed to be) linear or polynomial functions of concentrations. This formalism was very attractive to chemists who, at the beginning of *this* century, were not accustomed to logarithmic functions. In fact, by the time activities were generally adopted by chemists all the basic theoretical relationships had already been developed within the *molecular theory of solutions*. However, a large amount of data on activities was obtained before this theory assumed a form allowing either practical calculations or an easy interpretation.

The molecular theory of solutions has thus been developing without any competition with the empirical approach of Lewis in the field of *practical calculations*. Furthermore, the molecular theory of solutions has been largely used to explain the physical significance of activity coefficients. In other words, instead of producing its own formalism this theory was, regrettably, employed to explain the meaning of parameters arising from empirical relationships!

The molecular theory of solutions had quite early succeeded in a semi-quantitative description of many phenomena that are outside the scope of an empirical approach. Phase transitions, for example, play an important role in chemical processes, determining their apparent irreversibility when one of the products 'drops out' or escapes into a gaseous or a separate liquid phase. This leads sometimes to a misinterpretation of processes involving a phase transition. For example, the substitution of fatty acids in the form of their salts by carbonic acid (when saturating aqueous solutions of their sodium salts with CO_2) is often interpreted as evidence of the stronger acidic properties of carbonic acid. It is completely forgotten that free fatty acids form a separate phase at lower temperatures (although they can be miscible with water at higher temperatures). A theory taking into account molecular interactions predicts such phenomena and the corresponding formalism can be incorporated into the law of mass action.

In biochemistry it is considered as a great wonder that small variation of the energy of hydration (of about 1 kcal mole^{-1}) compared to the absolute magnitude of *ca.* 100 kcal mole^{-1} can switch biological processes in membranes. However, according to the molecular theory of solutions, this should not be surprising because phase separation in liquid solutions occurs when the difference in energies between hetero- and homo-molecular interactions is above $2RT$.

It is all too often believed that the activity coefficient, like a *deus ex machina,* will always allow for the application of a pseudo-ideal form of the law of mass action or of the van't Hoff and Arrhenius equations. A colleague of one of the authors complained once about the loss of large amounts of reagent in a pilot reactor when the synthesis of ethyleneglycol diacetate from ethylene oxide and acetic anhydride proceeded *in a jump*, bearing all the signs of a branched chain reaction. The real origin of this misfortune could well have been a problem of *scaling* (a tub full of hot water cools down more slowly than does a glass full!). But it is also possible that the 'jump' is connected with critical phenomena originating in molecular interactions (this case will be repeatedly considered in this book).

The molecular theory of solutions is based on a *statistical mechanical* description of collections of large numbers of molecules. Unfortunately the principles of statistical mechanics are all too often omitted from textbook discussions of reactions in solutions. Although they cover practical methods of calculation of equilibrium and rate constants for simple gas-phase reactions 'employing spectroscopic data' the fundamentals of these methods are usually neglected. That statistical mechanical methods can successfully be applied to reactions in non-ideal condensed systems is openly disbelieved (not, it must be admitted, entirely without ground). Until recently there were no examples of a chemical equilibrium in the condensed state better described by the formalism of the molecular theory of solution than by the use of empirical activity coefficients.

It was in 1972 that a spin crossover equilibrium in the solid state was successfully described by a law of mass action derived for a strongly non-ideal system [2]. This equilibrium presents unique possibilities for the checking of theoretical models of processes in the condensed phase exhibiting, as it does, a large number of the effects of molecular interactions yet, at the same time, remaining a homogeneous system. In fact, spin crossover apparently plays an important role in oxidation processes when it is necessary to convert a paramagnetic dioxygen species into the singlet state. In this book various descriptions of ideal and non-ideal systems will be illustrated by reference to examples of such spin crossover systems.

The statistical mechanical approach to the description of matter gives an answer to the question of the '*naive physicist*' mentioned above: the bodies of human beings must necessarily consist of very large numbers of particles in order to avoid *fluctuations*. This phenomenon (completely neglected by formal thermodynamics) also gives rise to some doubts concerning the applicability of the law of mass action to small systems such as bacteria (*i.e.* a *breakdown of the law of mass action* is to be expected). Indeed, the law of mass action applied to the water ionisation equilibrium in vesicles containing 10^7 molecules of water would apparently result (at pH = 7) in the number of ions per vesicle being either one or zero. Calculation of the mean concentration of ions over an ensemble of such vesicles then results in values considerably different from those predicted by the law of mass action. Whether or not this discrepancy has any connection with fluctuations becomes clear when we consider the origin of the law of mass action from a statistical thermodynamics point of view.

The aim of the present book is to give the reader a consecutive and coherent chain of reasoning leading to the formulation of the law of mass action for ideal and non-ideal systems accompanied by the necessary complementary materials.

The first two Chapters and the Appendix are an aid to those who are not sufficiently well acquainted with statistical mechanics. Chapter 1 begins *ab ovo* with the ideas relating entropy to probability and a derivation of the Maxwell – Boltzmann distribution law. One of the main tasks of statistical mechanics: the calculation of mean and most probable values of mechanical parameters is explained using several examples.

Chapter 2 explains the Gibbs approach to statistical thermodynamics and outlines the derivation of the relationship between the thermodynamic properties and partition functions of canonical distribution.

Chapter 3 concerns the derivation of the law of mass action for an ideal gas and an ideal crystal. Various forms of this law employing molar concentrations, mole fractions and the numbers of molecules as basic variables are derived and their applicability is discussed. The origin of standard free energy, enthalpy and entropy of reaction is explained and referred to the corresponding terms in the statistical mechanical expression for equilibrium constants. Specific problems of the liquid state are then discussed and a model of an 'ideal liquid' is suggested in order to derive two types of the law of mass action applicable to liquid mixtures and to clarify the choice of a proper variable (concentration) in the law of mass action. The case of the so-called 'breakdown' of the law of mass action is critically analysed.

Chapter 4 introduces improvements into the description of chemical equilibria in liquids. These improvements are based on accounting for a finite volume of molecules (*i.e.* repulsive interactions). The law of mass action is derived for mono-molecular (spin crossover) and bimolecular (formation of weak molecular complexes) equilibria. The concept of free volume and corresponding theories of the liquid state are then discussed. The law of mass action is derived employing the concept of free volume and additivity of the energy of attractive interactions. Singularities predicted by this law of mass action are discussed.

Chapter 5 gives a brief survey of the description of molecular interactions using a Lennard-Jones binary potential in its various forms. The Lennard-Jones and Devonshire model of the liquid state is also outlined.

Chapter 6 considers the problem of molecular interactions in gases using the Virial Theorem as well as a statistical mechanical treatment of a gas with weak binary interactions. The equation of state of a gas with weak binary interactions is compared with the van der Waals equation and the laws of mass action for equilibria in such systems are analysed. The conditions leading to simplification of the law of mass action and its reduction to an ideal form are discussed.

Chapter 7 concerns reactions in the solid state. An original method of calculation of free energy in a solid system of interacting molecules (suggested by ABK) is described and applied to the description of spin crossover equilibria in the solid state. This formalism (reducible under simplifying conditions to that of the theory of regular solutions) is then used to modify the Bragg – Williams approximation of ordered systems, which provides for a quantitative description of the two-step spin crossover.

Chapter 8 analyses (employing formalisms described in preceding Chapters) the physical backgrounds of empirical correlations including Linear Free Energy Relationships (or LFER's), IsoEquilibrium Relationships (IER) and IsoKinetic Relationships (IKR).

Appendices include the elements of classical mechanics in Hamilton's form, some explanations of the basics of statistical mechanics and complementary materials to other Chapters.

The writing of this book would not have been possible without the fact that the Authors were able to meet regularly in the Institut für Anorganische Chemie der Technischen Universität Wien due to appointment of ABK and RFJ as visiting professors in the Institute.

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1 Maxwell – Boltzmann Statistics

1.1
Thermodynamics and probability. The Boltzmann – Planck theorem

The original explanation of the action of a thermal engine was a very mechanistic one: heat or *phlogistic fluid* falls from a higher to a lower temperature. This model was developed by the French scientist *Sadi Carnot* who actually himself found it to be not completely correct: it leads to the principle of conservation of heat (which in fact does not hold). The correct answer was given later by *Clausius*: the temperature is not the coordinate playing the role of potential (the vertical coordinate in the case of falling material bodies) but rather an analogue of a *force*. Notwithstanding its incorrectness, the idea that the passing of heat from high temperature bodies to low temperature bodies must be connected with a kind of 'work' was very fruitful. Thermodynamics as a branch of physics explaining specific laws of the 'movement' and transformation of heat is based on this idea.

In contrast to purely mechanical devices (a water mill, for example) the elementary *work* done by a thermal (steam) engine, δw, is not, in general, represented by a complete differential and this work is thus not a function of state. The elementary quantity of *heat* transformed, δQ, is also not a complete differential. However, their sum (the *internal energy*, E) *is* a function of state and is therefore a complete differential. The first law of thermodynamics specifies the complete differential of internal energy dE as:

$$dE = \delta Q + \delta w \tag{1.1}$$

The symbol of variation (δ) signifies that neither elementary heat nor elementary work are in general complete differentials. However, for processes not involving transformation of heat ($\delta Q = 0$) the elementary work *does* equal the differential of internal energy and is therefore also a complete differential. It can then be represented as a sum of elementary work arising from *generalised forces*[1], A_i, 'performed' along the *generalised coordinates*, a_i, coupled with their

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[1] Including, in general, *gravitational forces* but also *surface forces* (if there is an interface), *electric and magnetic forces* (in the presence of corresponding fields), *etc.*

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corresponding forces. The first law of thermodynamics is often (but not completely correctly) written as:

$$dE = \delta Q + \sum_i A_i da_i \tag{1.1a}$$

The internal energy is also known as the *total energy*. We shall later see that it is '*total*' in *two* senses: in thermodynamics it is a sum of free and bound energies and in statistical mechanics it corresponds to the average Hamiltonian function, *i.e.* the sum of kinetic and potential energies. Among the types of elementary work, we shall be mainly interested in the *mechanical work* done by a system against external pressure $-pdV$ (negative) and in the 'chemical work' $+\mu dN$, *i.e.* the work done by (chemical reaction) changing the number of molecules:

$$dE = \delta Q - pdV + \mu dN \tag{1.2}$$

in which μ is 'the driving force' of a chemical transformation called (perhaps not very rationally) the *chemical potential*. As a *potential force* (and thermodynamics, both formal and statistical, considers the potential forces alone, see Chapter 5) it must be a partial derivative of thermodynamic potential with respect to a 'chemical coordinate', *i.e.* the number of molecules of a given kind:

$$\mu = \frac{\partial}{\partial N}(Thermodynamic\ Potential) \tag{1.3}$$

The *thermodynamic potential* is a thermodynamic function of state (depending on the actual conditions it can be entropy, internal energy, enthalpy, Helmholtz or Gibbs functions, see below) characterising the *amount of disposable energy*. The chemical coordinate is dimensionless which makes the dimension of *chemical potential* identical to that of energy, justifying to a certain extent its name.

When a system does not perform any work (*i.e.* a system of constant volume and constant number of particles) the variation of heat equals the differential of internal energy and is therefore itself a complete differential. It may therefore be represented as a product of a force times the differential of the coordinate. The generalised force corresponding to the transformation of heat proved to be the absolute temperature whilst the coordinate connected with the performing of 'thermal work' was a new function called by Clausius *entropy*, S, such that:

$$T\delta S = \delta Q \tag{1.4}$$

The general condition under which the variations of entropy and heat can be considered as differentials is that the processes in which these variations occur are *reversible*. Now *thermodynamic reversibility* is somewhat different from reversibility of a chemical reaction. A thermodynamically reversible process is one that admits the return of an isolated system to the initial state *without any change in the environment*. For example, the expansion of gas from a cylinder into an evacuated vessel is an *irreversible* process because we must afterwards perform the work of compression. On the other hand, if we pass the expanding gas through a turbine that lifts a given weight to a given height (all these appliances being parts of the isolated system) then we are able to compress the gas to its initial state by allowing this weight to fall.

The concept of *reversibility* is, however, closely connected with the concept of equilibrium. The *state of equilibrium* in thermodynamics is such that a system remains unchanged in all aspects, *without assistance of external processes,* for an indefinitely long time (classical thermodynamics does not consider *fluctuations*). The *stationary state* of a house wall keeping a *constant* difference of temperatures inside and outside is *not* a state of equilibrium because it requires a constant flow of heat for its existence. If we change reversibly the state of a system by going through an infinite number of infinitely close states of equilibrium (the time required is of course infinitely long) the *work done by the system* (which is, of course, negative) is *maximal.* This gives us a very important indicator of the state of equilibrium, namely that it must correspond to an *extremum of thermodynamic potential.*

For reversible processes entropy is a function of state, *i.e.*:

$$dS = dQ/T \tag{1.4a}$$

A mathematical theorem demonstrating the existence of an integrating denominator for elementary heat and showing it to be the absolute temperature is known under the name of the *Principle of Caratheodori* (see, for example, Margenau and Murphy [1]). The first law of thermodynamics for reversible processes may now be written as:

$$dE = TdS + \sum_i A_i da_i \tag{1.5}$$

Entropy appears in this expression as a *thermodynamic coordinate* coupled with *thermal force* (which is absolute temperature). The Principle of Caratheodori also shows that entropy is a function of state and an additive quantity, *i.e.* the entropy of a system is the sum of the entropies of its constituent parts. In isolated systems this coordinate may *play the role* of a potential.

The work, $\Sigma A_i da_i$, in (1.5) is distinguished from the term *TdS* by the fact that the former can be directed to increase the potential energy of other systems (*e.g.* lifting weights) whilst the heat or 'thermal work', *TdS*, can only increase the internal energy of the considered system. From this point of view *heat* and *work* are two *distinct* forms of the *transfer of energy* [2]. The term *TdS* can then be called the *bound energy* whilst the amount of all possible work given by the term $\Sigma A_i da_i$ can be called the *free energy* and generally plays the role of a thermodynamic potential. A change in internal energy of a system is thus divided between the changes in bound and free energies:

$$dE = dE_{bound} + dE_{free} \tag{1.6}$$

We immediately realise that it could be of enormous practical importance to be able to calculate *a priori* the amount of bound energy for a given system. Formal thermodynamics establishes relationships between parameters of a system without any implication as to the nature of the system itself. This can be considered as an advantage of the thermodynamic approach: we can determine thermodynamic parameters of known gases, liquids and solids and calculate (sometimes with astonishing accuracy) thermal properties of their mixtures and chemical compounds. However, such a result is not entirely satisfactory since it is often desirable to know the *origin* of these effects (for example, in order to estimate thermodynamic parameters associated with particular *theoretical molecular structures*). In other words, the drawback of formal thermodynamics is that its validity is independent of the molecular structure of material objects.

When molecules are taken into account the concept of heat must be considered from a slightly different point of view, namely as one of the forms of transformation of the *kinetic and potential energy of molecules* resulting in the increase of internal energy alone. The problem is that the number of molecules contained in the least tangible amount of matter is very large (at least 10^7). Even if the potential energy of interaction is neglected and only the exchange of kinetic energy at molecular collisions taken into account, the problem remains very complicated. Treating this problem in detail *Boltzmann* found that a solution can be obtained if we take into account the *statistical properties* of collections of large numbers of objects.

Statistical properties constituted a completely new element in the description of mechanical systems. The behaviour of classical mechanical systems is uniquely determined by the laws of mechanical motion which are derived from one basic principle known as the *principle of least action* (see Appendix 10.1). The *Hamilton* or *Canonical Equations* (*ibid.*) constitute one of the most general formulations of the laws of mechanical motion in the classical approximation. If we employ the concepts of the *theory of probability* then any mechanical state of a system becomes connected with a certain probability. Whether extremely large or extremely small a probability is still a probability! It took a long time for the crystallisation of the general idea that statistical elements *do not change the deterministic laws of mechanical motion* but are connected with a completely *undetermined nature of initial conditions* (coordinates and momenta at time $t = 0$).

The basic idea of *statistical* thermodynamics is that the thermodynamic function reflecting the statistical properties of macroscopic systems is entropy. That entropy is an additive function whilst the probability is a multiplicative one gives us a hint that such a relationship must be logarithmic. This will be exactly demonstrated by the Boltzmann – Planck theorem presented below. A function S (which is proportional to the logarithm of probability) will then be used in the derivation of the *most probable distribution*. Analysing this distribution we shall come to the important conclusion that the differential of the function S is similar to the differential of entropy as the latter appears in the first law of thermodynamics.

1.1.1
The Boltzmann – Planck theorem

Suppose we have two *non-interacting* systems A and B (*e.g.* two widely separated stars) with the probability that the system A is in the state '1' is W_1. Similarly, the probability that the system B is in the state '2' is W_2. The absence of interaction between the systems 'A' and 'B' means that the state of 'A' is independent of the state of 'B', *i.e.* W_1 and W_2 are *independent variables*. The probability of the joint occurrence of the system A being in the state '1' and the system B being in the state '2' then is:

$$W = W_1 \times W_2 \tag{1.7}$$

Let us denote some *additive property* S related to the probability, W as:

$$S = f(W); \qquad S = S_1 + S_2$$

$$S_1 = f_1(W_1); \qquad S_2 = f_2(W_2) \tag{1.8}$$

Accordingly:

$$f(W) = f(W_1 \times W_2) = f_1(W_1) + f_2(W_2) \tag{1.9}$$

The *partial* derivative of W with respect to W_1 according to (1.7) is W_2, therefore differentiating $f(W)$ with respect to W_1 yields:

$$\frac{\partial f}{\partial W_1} = \frac{df}{dW}\left(\frac{\partial W}{\partial W_1}\right)_{W_2} = \frac{df}{dW} \times W_2 \tag{1.10}$$

and with respect to W_2:

$$\frac{\partial f}{\partial W_2} = \frac{df}{dW}\left(\frac{\partial W}{\partial W_2}\right)_{W_1} = \frac{df}{dW} \times W_1 \tag{1.11}$$

Differentiating any of these equations, for example (1.10), for a second time *crosswise* we find that:

$$\frac{\partial^2 f}{\partial W_1 \partial W_2} = \frac{df}{dW} + W_2\left(\frac{\partial}{\partial W_2}\left(\frac{df}{dW}\right)\right)_{W_1} = \frac{df}{dW} + W_2 \frac{d}{dW}\left(\frac{\partial f}{\partial W_2}\right)_{W_1} \tag{1.12}$$

However, according to the preceding equation the last partial derivative is $W_1(df/dW)$, therefore:

$$\frac{\partial^2 f}{\partial W_1 \partial W_2} = \frac{df}{dW} + W_1 W_2 \frac{d^2 f}{dW^2} = \frac{df}{dW} + W \frac{d^2 f}{dW^2} \tag{1.13}$$

However, *because events* '1' *and* '2' *are independent* (1.13) must be zero:

$$W\frac{d^2f}{dW^2}+\frac{df}{dW}=0 \tag{1.14}$$

Integrating this equation we obtain initially[2]:

$$\frac{df}{dW}=\frac{k}{W} \tag{1.15}$$

and then:

$$f=k\ln W+k' \tag{1.16}$$

The second integration constant, k', depends on the way in which we define the probabilities. If we assume k' to be zero then for $S = 0$ we get $W = 1$, which at first sight is a strange probability for the lowest amount of entropy. However, the probability of the state of a system is not necessarily the ratio of the number of events *favouring* its realisation to the number of *all possible* events. In systems containing large numbers of particles it is even practically impossible to estimate the number of all possible events. Therefore, instead of the usual probability normalised to unity, the so-called *thermodynamic probability, W,* has been introduced which is just equal to the *number of events favourable* to the realisation of a given state. Zero value of S (with $k' = 0$) corresponds then to a system which can be realised in just one way ($W = 1$), *i.e.* the lowest possible probability. Under these assumptions we have:

$$S=f=k\ln W \quad \text{or} \quad W=e^{\frac{S}{k}} \tag{1.17}$$

If we identify S with entropy we can then say that the most probable state corresponds to the state characterised by a maximum in entropy. Maximal entropy of a system possessing a constant amount of internal energy corresponds to a minimum of free energy and hence to the state of equilibrium. The observed properties of a macroscopic system in such a state (temperature, volume, energy, *etc.*) must in some way be connected with molecular parameters. This relationship is obtained by deriving the most probable *distribution law.*

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[2] Equation (1.14) can be converted into the first-order differential equation $(1/x)(dy/dx) + y = 0$, the solution of which has the form $y = k/x$. A clue to this result follows from the fact that the derivative dy/dx must have dimension $[y/x]$.

1.2
The Maxwell – Boltzmann distribution law

One of the most important macroscopic parameters is, of course, energy. The energy of a system *is defined* if all coordinates and momenta of the molecules are known. This knowledge is, however, mostly redundant: it is quite sufficient to know the *law governing the distribution* of molecules over the main variables of statistical mechanics and these are the coordinates and momenta.

Suppose we have some number of fixed energy states that may be populated by molecules. A distribution law can be defined in the form of a Table: n_1 particles have the energy ε_1, n_2 have the energy ε_2, and so on; finally n_M have the energy ε_M. There are N particles in total. We may say *that molecules are distributed among M cells in a certain way.* A given macroscopic state of a system (a *macrostate*) can be achieved by an apparently very large number of arrangements of molecules over the cells. Each such arrangement we call a *microstate.* The thermodynamic probability of a given macrostate can then be defined as the number of *microstates* (Boltzmann called them 'complexions') in which this macrostate can be realised. According to Boltzmann, the thermodynamic probability of the macrostate with given n_1, n_2,...n_M (which defines the total energy as $E = \Sigma n_i \varepsilon_i$), can be computed similarly to the calculation of the number of ways in which *N passengers can be distributed among M boats having* n_1, n_2, n_3,...n_M *individual seats.* The solution of this problem is well known:

$$W = \frac{N!}{n_1!n_2!\dots n_M!} \tag{1.18}$$

(One must bear in mind that 0! = 1, so there is no mathematical problem if some energy levels (or boats!) remain unoccupied; see also Appendix 10.6). The function S of such a state is then:

$$S = k\ln W = k\ln N! \; - \sum_{i=1}^{M} \ln n_i ! \tag{1.19}$$

Using the Stirling formula $\ln N! \approx N\ln N - N$ (which will not be correct for small individual n_i) we get:

$$S = k\left(N\ln N - N - \sum_{i=1}^{M} n_i \ln n_i + \sum_{i=1}^{M} n_i \right) = k\left(N\ln N - \sum_{i=1}^{M} n_i \ln n_i \right) \tag{1.20}$$

Let us find now the set of n_1, n_2, ... n_M, corresponding to the *most probable distribution* which must correspond to the *maximum of S.*

If the statistical function S is identical with entropy then the *most probable state* is identical with the state of *equilibrium.* Formal thermodynamics defines the state of equilibrium as corresponding to an *extremum* of a *thermodynamic potential*. For a system *completely isolated* from the outer world *i.e.* when the *total energy is constant* and *the number of particles is constant*, then the entropy plays the role of thermodynamic potential and the extremum of entropy corresponds to the state of equilibrium.

The problem of a *conditional extremum* of some function is solved by the method of the *calculus of variations*[3] called the *Lagrange method of undetermined multipliers*. The conditions of conservation of energy and number of particles we write as:

$$\sum_i n_i = N = const \tag{1.21}$$

$$\sum_i n_i \varepsilon_i = E = const \tag{1.22}$$

The third equation required is the above expression for the function S:

$$S = k\left(N \ln N - \sum_i n_i \ln n_i\right) \tag{1.23}$$

The most probable distribution *corresponds* to zero variation of this function. The variations of N and E are also zero and may be multiplied by any *finite multiplier* ($-\alpha$ and $-\beta$, for example):

$$-\alpha \times \delta N = -\alpha \times \sum_i n_i = 0 \tag{1.24}$$

$$-\beta \times \delta E = -\beta \times \sum_i n_i \varepsilon_i = 0 \tag{1.25}$$

To these equations we add the variation of the function S:

$$\delta S = k\delta\left(N \ln N - \sum_i n_i \ln n_i\right) = -k\sum_i\left[\delta n_i \ln n_i + n_i \delta(\ln n_i)\right] = 0 \tag{1.26}$$

The term $n_i\delta(\ln n_i) = 1$ and usually $\ln(n_i) >> 1$, which means that the condition (1.26) can be written as:

$$-\sum_i \delta n_i \ln n_i = 0 \tag{1.27}$$

Summing (1.24), (1.25) and (1.27) we obtain:

$$-\sum_i \left(\ln n_i + \alpha + \beta\varepsilon_i\right)\delta n_i = 0 \tag{1.28}$$

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[3] Some explanations concerning variational problems are given in Appendix 10.1

The variations δn_i being non-zero (see Appendix 10.1), means that the expression in brackets *for each i* must be zero:

$$\ln n_i + \alpha + \beta\varepsilon_i = 0 \tag{1.29}$$

This equation defines the most probable distribution of molecules over *energy levels* which is known as the Maxwell – Boltzmann distribution. It can be written in an exponential form as:

$$n_i = e^{-(\alpha + \beta\varepsilon_i)} \tag{1.30}$$

The parameter α can be found directly from the normalisation procedure:

$$\sum_i n_i = N = e^{-\alpha} \sum_i e^{-\beta\varepsilon_i} \tag{1.31}$$

Accordingly:

$$\alpha = -\ln N + \ln \sum_i e^{-\beta\varepsilon_i} \tag{1.32}$$

It is convenient to introduce the constant A into the distribution law (1.30) such that:

$$A = e^{-\alpha} = \frac{N}{\sum_i e^{-\beta\varepsilon_i}} \tag{1.33}$$

The sum:

$$z = \sum_i e^{-\beta\varepsilon_i} \tag{1.33A}$$

is called the *partition function* (*Zustandsumme* or *statistical sum*). It is *one of the most important inventions of statistical mechanics*. It will become obvious later (p. 19) that it represents *the effective number of accessible states*. Using partition functions the Maxwell – Boltzmann distribution law can be written as:

$$n_i = \frac{N}{\sum_{i=1}^{M} e^{-\beta\varepsilon_i}} e^{-\beta\varepsilon_i} \tag{1.34}$$

The expression for entropy in terms of partition functions can be obtained in the following way: Substituting n_i *under the logarithm* in (1.23) by its value from (1.30) we have:

$$S = k\left(N \ln N - \sum_i n_i \ln n_i\right) = k\left(N \ln N + \alpha \sum_i n_i + \beta \sum_i n_i \varepsilon_i\right) \tag{1.35}$$

Taking into account that $\Sigma n_i \varepsilon_i = E$ we get:

$$S = k\left(N\ln N + \alpha N + \beta E\right) \tag{1.36}$$

Writing α in terms of partition functions we obtain:

$$S = k\left[N\ln N + N\left(\ln\sum_i e^{-\beta\varepsilon_i} - \ln N\right) + \beta E\right] \tag{1.37}$$

i.e.

$$S = kN\ln\sum_{i=1}^{M} e^{-\beta\varepsilon_i} + \beta E \tag{1.38}$$

In many books on statistical mechanics one can find 'demonstrations' of the identity of the statistical function S and entropy. These demonstrations are usually solutions of the problem: 'what might be the parameter β of the Maxwell – Boltzmann distribution and what relationship exists between partition functions and thermodynamic functions if we assume such an identity?' In fact, the identity of the statistical function S and entropy should be considered as an *empirically based postulate* similar to the first law of thermodynamics. The empirical observations leading to this postulate are of a very general kind: the properties of a macroscopic system at equilibrium are constant to a very high degree of precision. The basis of this argument is given in Section 2.2 of the next Chapter.

The parameter β and relationships between thermodynamic and partition functions are found by comparing partial derivatives of the entropy and the statistical function S. In formal thermodynamics entropy is defined in a differential form (1.4a). Therefore it will be sufficient to show that the complete differential of the function S is similar to the complete differential of entropy. Taking into account the work done against the pressure and 'chemical' work connected with the changes in numbers of particles the differential of entropy can be represented as (see (1.5)):

$$dS = \frac{dE + pdV - \mu dN}{T} \tag{1.39}$$

When differentiating the statistical function S (1.38) we notice that it is obviously a function of the energy E and of the *number of molecules*, N (hence it will contribute to chemical potential). It is also an *explicit function* of volume because the upper index of summation, M, (the number of cells) is directly proportional to the volume of the system. Accordingly, the complete differential of the function S can be written in a form similar to the differential of entropy[4]:

$$dS = k\beta dE + kN\frac{\partial \ln z}{\partial V}dV + k\ln(z)dN \tag{1.40}$$

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[4] The energies ε_i are *not* variables but fixed energy levels, the total energy being dependent on the *distribution* of molecules over these levels.

in which z is the partition function (1.33A). Comparing (1.39) with (1.40) we notice that $k\beta dE$ is obviously an analogue of the term dE/T. Hence the coefficient β is:

$$\beta = 1/kT \tag{1.41}$$

The last term in (1.40) corresponds to the term $-\mu dN/T$ of the formal thermodynamic expression (1.39), therefore:

$$k \ln \sum_{i=1}^{M} e^{-\beta\varepsilon_i} = -\mu/T \tag{1.42}$$

i.e.
$$\mu = -kT \ln \sum_{i=1}^{M} e^{-\beta\varepsilon_i} = -kT \ln z \tag{1.43}$$

In order to show complete identity between thermodynamic entropy and the statistical function S, the second term in (1.40) must be shown to be an analogue of the term pdV/T:

$$kN \frac{\partial \left(\ln \sum_{i=1}^{M} e^{-\beta\varepsilon_i} \right)}{\partial V} = -\frac{p}{T} \tag{1.44}$$

This allows us to express the pressure as a function of temperature and of the volume derivative of the partition function:

$$p = NkT \frac{d \ln \sum_{i=1}^{M} e^{-\beta\varepsilon_i}}{dV} \tag{1.45}$$

which is the *equation of state* of the considered system.

An analytical form of this equation of state can easily be obtained for a *continuous distribution* (see p. 11). However, the differentiation in (1.45) can also be considered in terms of finite differences by taking into account that the dependence of the partition function on volume is due to the proportionality of the upper index of summation, M, to the volume of a system. The differential can be approximated by the difference between the sums with the upper indices M and M', the latter being slightly higher:

$$d\sum_{i=1}^{M} e^{-\beta\varepsilon_i} = \sum_{i=1}^{M} e^{-\beta\varepsilon_i} - \sum_{i=1}^{M'} e^{-\beta\varepsilon_i} = \sum_{i=M+1}^{M'} e^{-\beta\varepsilon_i} \tag{1.46}$$

The differential of volume can be expressed in terms of the density of states (M/V):

$$dV = (V/M)(M' - M) \tag{1.47}$$

The equation of state can therefore be written as:

$$p=\frac{NkT}{V}\frac{M\sum_{i=M+1}^{M'}e^{-\beta\varepsilon_i}}{(M'-M)\sum_{i=1}^{M}e^{-\beta\varepsilon_i}} \tag{1.48}$$

It is not difficult to see that when the density of states is very high, and the energy levels are separated by a vanishingly small distance, then the second ratio is 1 and we get the equation of state of an ideal gas.

Assuming that the statistical function S is identical to the thermodynamic entropy implies that we have thus found explicit meanings of the parameters of the most probable (*i.e.* equilibrium) distribution:

$$n_i=\frac{N}{\sum_{i=1}^{M}e^{-\varepsilon_i/kT}}e^{-\varepsilon_i/kT}=Ae^{-\varepsilon_i/kT} \tag{1.49}$$

The larger the number of realisations of a given system the larger is its entropy. This leads to another interpretation of the relationship between internal, free and bound energy (1.6):

$$dE=dE_{bound}+dE_{free}$$

In systems having larger thermodynamic probability, W, a larger number of acts of energy exchange occur *within* the system itself and correspondingly a smaller number of acts of energy exchange is left for interaction with the outer world. This means that *the more random a system is the less work it can produce.*

Free energy, generally playing the role of thermodynamic potential, has different forms for *non-isolated* systems exchanging by heat and/or work with the environment. Systems of *constant volume* may exchange with the environment by heat but *not* by work. The thermodynamic potential for such systems is the *Helmholtz free energy or Helmholtz function, F,* (denoted also by A: from Arbeit, German for work – actually the *maximal* work):

$$F=E-TS \tag{1.50}$$

According to (1.38) this potential can be expressed in terms of partition functions as:

$$F=-kTN\ln\sum_{i=1}^{M}e^{-\varepsilon_i/kT}=-kTN\ln z \tag{1.51}$$

When a shell separating a given system from the environment is not only transparent to heat but also is elastic, then the balance of internal energy includes the work of expansion/compression and the thermodynamic potential for such systems is the *Gibbs free energy*:

$$G = F + pV = -NkT\left(\ln\sum_{i=1}^{M} e^{-\varepsilon_i/kT} - V\frac{d\ln\sum_{i=1}^{M} e^{-\varepsilon_i/kT}}{dV} \right) \qquad (1.51a)^5$$

The statistical mechanical interpretation of heat and entropy also elucidates the relationship between other forms of transformation of energy and their practical values. The highest amount of work will be done by the most non-random systems, such as *mechanical devices* built up from macroscopic parts. Indeed the efficiency of such devices approaches 99%. Other examples of systems of approximately the same efficiency are *electric* and *electro-mechanical devices*. In these cases the system performing work is the 'electron gas' and it might appear at first sight that such systems should not be efficient at all. However the work done by electrons in electric devices is connected with the *correlated motion* of electrons as a body under the action of the electric field (see also Section 1.6.4). The efficiency of a system is thus connected with the organisation of the motion of its parts. The efficiency of devices employing highly organised types of motion does not significantly depend on the magnitude of forces and potentials. *Thermal engines* employ the energy of a random molecular motion in the gaseous phase. The efficiency of thermal devices is usually small and depends on the magnitude of the driving force of thermal energy, *i.e.* the difference between initial and final temperatures of the system producing work ($(T_i - T_f)/T_i$). High-temperature energy is therefore distinguished from low-temperature energy by being more efficient. In *chemical reactions* certain rules of interactions and redistribution of particles must be obeyed (for example the equation of the chemical reaction). Therefore, *even at low temperatures* the efficiency of the transformation of internal energy into work can be quite high (*e.g.* in biochemical reactions).

The introduction of entropy as a function of state for equilibrium processes is often considered as the *first part of the second law of thermodynamics*. It can be shown that for non-equilibrium processes in *isolated systems*, for example involving the work done by non-potential forces (*e.g.* forces of *friction*), entropy may *only increase*. This second part of the second law of thermodynamics is usually written as the inequality:

$$\delta S \geq 0 \qquad (1.52)$$

in which the equality sign refers to the equilibrium processes. The entropy of an isolated system is thus (similar to time) a *unidirectional coordinate* (see also Section 2.2).

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[5] This equation, as well as equations expressing other thermodynamic functions in terms of partition functions, will be derived in Chapter 2 from the basic equations of canonical distribution.

1.2.1
Continuous Maxwell – Boltzmann distribution

The cell method of Boltzmann is (as we have seen) a very useful tool for the derivation of the fundamental formulae of statistical mechanics. However, from the point of view of classical physics a system of cells can only be considered as a model system. A transition to an infinitely small distance between energy levels is required by classical physics as a necessary step for the description of real objects (in fact we must perform a transition to very small but finite energy differences).

When the transition to a *continuous distribution* is performed the probabilities cannot be calculated using methods based on combinatorics because the probability of the event that a molecule has some *definite* value of energy is zero. We must therefore consider the molecules having energy within a small but finite range, $d\varepsilon$, around ε.

In such cases the concept of phase *space* (see Appendix 10.2) becomes very useful. The probability that a certain number of molecules possess energy within a narrow range equals the *probability of a representative point belonging to a finite elementary volume in phase space.* The Maxwell – Boltzmann distribution law defines the number of molecules having coordinates and momenta within the element $d\gamma = dp_1\, dp_2\, dp_3\, dq_1\, dq_2\, dq_3$ around the point p,q as:

$$dN = Ae^{-\frac{p_1^2+p_1^2+p_1^2}{2mkT}-\frac{U(q_1,q_2,q_3)}{kT}}dp_1dp_2dp_3dq_1dq_2dq_3 \qquad (1.53)$$

In this expression we have separated the total energy of a particle ε (*i.e.* the Hamiltonian function H) into kinetic energy, $p^2/2m$ (which is independent of the coordinates q), and potential energy U (which is independent of the momenta, p).

The evolution of a system from one microstate to another is reflected in phase space by the movement (trajectory) of a representative point. Whilst the motion of particles in physical space is governed by the *canonical equations* the motion of representative points in phase space is controlled by rules derived from the well-known *Liouville theorem.*

According to the *Liouville theorem* the volume occupied by a certain number of representative points is constant whilst its shape may change. (The exact demonstration of this theorem can be found in any of numerous books on statistical mechanics, and so will not be discussed here.) However, the truth of such a proposition can be shown by simple arguments: For any *pair* of geometrical and dynamic coordinates q_i, p_i we define the time derivative of the volume of phase space (γ) as:

$$\frac{d\gamma}{dt}=\frac{d(dp_i dq_i)}{dt}=dp_i\frac{d}{dt}dq_i+dq_i\frac{d}{dt}dp_i=dp_i d\frac{dq_i}{dt}+dq_i d\frac{dp_i}{dt} \qquad (1.54)$$

According to the canonical equations:

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}; \qquad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \tag{1.55}$$

Substituting the time derivatives in (1.54) and multiplying the first term by dq_i/dq_i and the second term by dp_i/dp_i we obtain the *difference of identical second partial derivatives* of the Hamiltonian function:

$$\begin{aligned} \frac{d\gamma}{dt} &= dp_i dq_i \frac{d}{dq_i}\frac{\partial H}{\partial p_i} - dq_i dp_i \frac{d}{dp_i}\frac{\partial H}{\partial q_i} = \\ \text{i.e.} \qquad &= dp_i dq_i \left(\frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial q_i \partial p_i} \right) = 0 \end{aligned} \tag{1.56}$$

The volume of the phase space containing representative points of a system that obeys canonical (Hamilton) equations does not change with time. It behaves like an incompressible fluid changing its shape but not its volume. This is one of the most general formulations of the laws of non-relativistic mechanical motion.

In Chapter 2 it will be shown that a statistical description can be correctly applied to the systems of non-interacting units alone. In Maxwell – Boltzmann statistics such a unit is a molecule and its state must be independent of the state of all other molecules (similar to the way in which the state of system A was independent of the state of system B in the Boltzmann – Planck theorem). Statistical independence of molecules implies zero potential energy of interaction between them. One of the most often used approximations of gaseous molecular systems is the *ideal gas* in which statistical independence is achieved by assuming very large distances between molecules, making the potential energy of intermolecular interaction vanishingly small.

Applying the Maxwell – Boltzmann distribution to such a system ($U = 0$) and integrating (1.53) over all possible values of coordinates within a vessel of volume V, *i.e.* from zero to $(V)^{1/3}$, and momenta, $p = \pm\infty$, we obtain the total number of molecules N:

$$N = A\int_0^{\sqrt{V}} dx \int_0^{\sqrt{V}} dy \int_0^{\sqrt{V}} dz \int_{-\infty}^{+\infty} e^{-\frac{p_x^2}{2mkT}} dp_x \int_{-\infty}^{+\infty} e^{-\frac{p_y^2}{2mkT}} dp_y \int_{-\infty}^{+\infty} e^{-\frac{p_z^2}{2mkT}} dp_z \tag{1.57}$$

The integration over coordinates results in the volume of the system, V. The integral over momenta is the well known *phase integral* of the kinetic theory of gases:

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\frac{p_x^2+p_y^2+p_z^2}{2mkT}} dp_x dp_y dp_z = (2\pi mkT)^{3/2} \tag{1.58}$$

We see now that the coefficient A in (1.53) and (1.57) is equal to:

$$A = \frac{N}{V}\frac{1}{(2\pi mkT)^{3/2}} \tag{1.59}$$

The *analogue* of a partition function for a mono-atomic ideal gas is, according to (1.59), proportional to volume:

i.e.
$$z_{MB} = (2\pi mkT)^{3/2} V \tag{1.60}$$

Unlike the partition function given by (1.33) the partition function z_{MB} has the dimension $[p \times q]^3$. This comes from the integration in (1.57), which is actually a summation of Boltzmann factors *multiplied by the corresponding elementary volumes of phase space.* The coefficient A transforms the whole expression (1.53) to a dimensionless form – hence the dimension of the partition function. In modified Maxwell – Boltzmann statistics (see below) the dimensionless nature of the partition function will be restored. This, however, can only be done by introducing some elements of quantum mechanics. Using (1.60), the Maxwell – Boltzmann distribution law can be written as[6]:

$$dN = \frac{Ne^{-\frac{1}{2mkT}\sum p_i^2}}{(2\pi mkT)^{3/2} V} dp_i \ldots dq_i \tag{1.61}$$

Using the relationships (1.33), (1.43) and (1.51) obtained above we get:

$$\alpha = -\ln\frac{N}{V} + \frac{3}{2}\ln(2\pi mkT) \tag{1.62}$$

$$\mu = -kT\ln(2\pi mkT)^{3/2} V \tag{1.63}$$

$$F = -kTN\ln(2\pi mkT)^{3/2} V \tag{1.64}$$

Differentiating F with respect to volume we obtain the equation of state for an ideal gas:

$$-\left(\frac{\partial F}{\partial V}\right)_T = p = \frac{kTN}{V} \tag{1.65}$$

If the velocity v (instead of momentum) is chosen as the main dynamic coordinate the expression for the distribution law will be somewhat different:

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[6] An explicit Maxwell – Boltzmann distribution over *energies* can be obtained by expressing the modulus of momentum as $p = (2m\varepsilon)^{1/2}$ and $dp = (m/2\varepsilon)^{1/2}d\varepsilon$; it can be conveniently derived employing the idea of an energy layer in the phase space of momenta, see Appendix 10.2.2.

$$dN = A' e^{-\frac{m}{2kT}\sum v_i^2} dv_i \ldots dq_i \tag{1.66}$$

in which

$$A' = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} \tag{1.67}$$

This type of distribution law will presently be used in order to obtain the most probable and mean values of molecular velocity

1.3
Calculation of most probable and mean values

One of the most common applications of distribution laws is the calculation of average and most probable values. Maxwell – Boltzmann statistics is applicable to molecules and therefore it is possible to obtain mean molecular properties such as mean molecular velocity, energy *etc.* These parameters are of considerable importance in the kinetic theory of gases and gaseous reactions.

The most probable modulus of velocity can easily be obtained if we write the distribution law in *spherical coordinates* in velocity space. Fig. 1.1 demonstrates that the element of volume in this space of velocities can be written as:

$$d\gamma_v = v^2 dv \sin\theta d\theta d\varphi \tag{1.68}$$

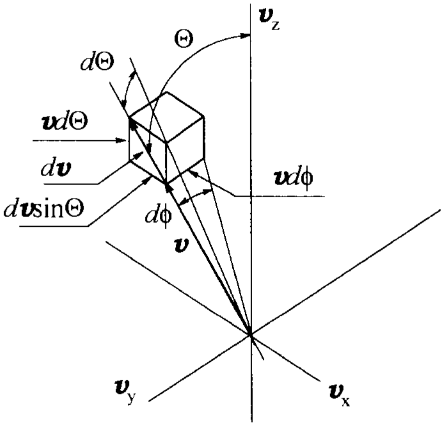

Fig. 1.1. Computation of the elementary volume of the phase space of velocities using spherical coordinates. Note that the vector dv is made to coincide with the diagonal of one face of the cube in order to simplify calculations

The distribution law with respect to velocities may then be written as:

$$dN = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv \sin\theta d\theta d\varphi \times d\gamma_q \tag{1.69}$$

The density of distribution, *i.e.* the number of particles per unit volume in the space of coordinates (γ_q) is:

$$\frac{dN}{d\gamma_q} = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv \sin\theta d\theta d\varphi \tag{1.70}$$

Integrating this function over all angles in order to get a result independent of direction we get the *distribution function* over velocities as:

$$f(v)dv = \iint_{\theta\varphi} \frac{dN}{d\gamma_q} = \frac{4\pi N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv \tag{1.71}$$

Fig. 1.2 shows several graphs of $f(v)$ corresponding to different temperatures. These distribution curves have maxima that are shifted to higher velocities at higher temperatures. The curves are obviously asymmetric and the most probable value of velocity corresponding to a maximum does not coincide with the mean value (*i.e.* the weighted average, see below).

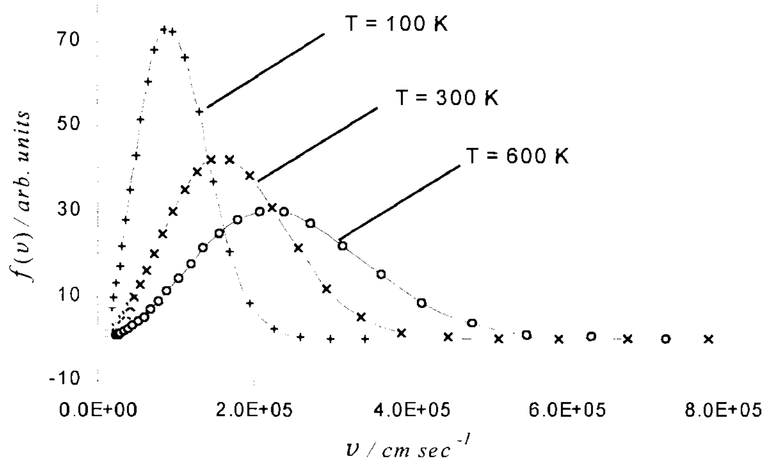

Fig. 1.2. Density of the Maxwell – Boltzmann distribution over the modulus of molecular velocity

The maximum of this function can be found from the condition:

$$\frac{d}{dv}\left(v^2 e^{-\frac{mv^2}{2kT}}\right) = e^{-\frac{mv^2}{2kT}}\left(-\frac{m}{kT}v^3 + 2v\right) = 0 \tag{1.72}$$

The most probable molecular velocity is then:

$$v_{mp} = \sqrt{\frac{2kT}{m}} \tag{1.73}$$

The mean values (*mathematical expectations*) are found as weighted averages. For example the mean molecular velocity is found to be:

$$\langle v\rangle = \frac{\sum_i v_i n_i}{\sum_i n_i} = \frac{\sum_i v_i n_i}{N} = \sum_i v_i \frac{n_i}{N} \tag{1.74}$$

in which n_i is the number of molecules possessing velocity v_i. The ratio n_i/N can be considered as the probability W_i (normalised to 1) of a particle possessing the velocity v_i. In general, for a discrete distribution, the mean value of the property U can be calculated to be:

$$\langle U\rangle = \sum_i W_i U_i \tag{1.75}$$

For example, the probability for a molecule to possess energy ε_i is:

$$W_i = \frac{n_i}{N} = \frac{A}{N} e^{-\varepsilon_i/kT} \tag{1.76}$$

Taking into account that $N = \Sigma n_i = A\Sigma e^{\varepsilon\, kT}$ we may write:

$$W_i = \frac{e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}} \quad and \quad \langle\varepsilon\rangle = \frac{\varepsilon_i e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}} \tag{1.77}$$

The factor $\exp(-\varepsilon_i/kT)$ can be taken to be the weighting factor of the state with energy ε_i. The partition function in the denominator is then the sum of weighting factors of all states in which a molecule may reside. In other words, *the partition function reflects the effective number of accessible states taking into account their probabilities.*

When the distribution law is given analytically (as a continuous distribution) the mean value of a property U is defined as:

$$\langle U\rangle = \frac{\int U(\varepsilon)e^{-\varepsilon/kT}d\varepsilon}{\int e^{-\varepsilon/kT}d\varepsilon} \tag{1.78}$$

The energy of a molecule (ε) is usually expressed as a function of the basic variables of statistical mechanics, namely coordinates and momenta. Therefore the property U must also be expressed as a function of these variables. For example, let the property U be the energy of the translational motion of a molecule along the coordinate x. The mean value of this property is then:

$$\left\langle \frac{m\dot{x}^2}{2} \right\rangle = \frac{\int \frac{m\dot{x}^2}{2} e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} \int e^{-\frac{m\dot{y}^2}{2kT}} d\dot{y} \int e^{-\frac{m\dot{z}^2}{2kT}} d\dot{z}}{\int e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} \int e^{-\frac{m\dot{y}^2}{2kT}} d\dot{y} \int e^{-\frac{m\dot{z}^2}{2kT}} d\dot{z}} \tag{1.79}$$

We need to evaluate just two integrals:

$$\int e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} \quad and \quad \int \frac{m\dot{x}^2}{2} e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} \tag{1.80}$$

The first integral is tabulated and equals:

$$\int e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} = \int e^{-a^2y^2} dy = \frac{\sqrt{\pi}}{a} = \sqrt{\frac{2\pi kT}{m}} \tag{1.81}$$

The second one is integrated in the following way:

$$\int \frac{m\dot{x}^2}{2} e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} = kT \int \frac{m\dot{x}^2}{2kT} e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} = \frac{kT}{\sqrt{\frac{m}{2kT}}} \int a^2\dot{x}^2 e^{-a^2\dot{x}^2} d\dot{x} = \frac{(kT)^{3/2}}{\sqrt{m/2}} \int_{-\infty}^{+\infty} y^2 e^{-y^2} dy \tag{1.82}$$

The last integral in (1.82) is tabulated and equals $(\pi/4)^{1/2}$, therefore:

$$\int \frac{m\dot{x}^2}{2} e^{-\frac{m\dot{x}^2}{2kT}} d\dot{x} = \frac{(kT)^{3/2}\sqrt{\pi}}{\sqrt{2m}} \tag{1.82a}$$

which results in:

$$\left\langle \frac{m\dot{x}^2}{2} \right\rangle = \frac{(kT)^{3/2}\sqrt{\pi}}{\sqrt{2m}\sqrt{\frac{2\pi kT}{m}}} = \frac{kT}{2} \tag{1.83}$$

The same result can be obtained for any other coordinate that reflects equal distribution of energy among the translational degrees of freedom ($kT/2$ per degree). A similar result can also be obtained for energy per rotational or vibrational degree of freedom. These results reflect the *principle of equi-partition of energy*. This principle is only valid in those cases in which energy is a homogeneous function of the *squares of coordinates and/or momenta* (dynamic and geometric coordinates) as in the examples considered above.

1.4
Indistinguishable molecules. The Gibbs Paradox

The values of the total energy of a system, mean energy of a molecule, and other molecular parameters calculated using expressions derived above are in more – or – less good agreement with the experimental data applicable to rarefied gases. However the values of entropy and heat capacity obtained from the formulae of the Maxwell – Boltzmann distribution as given above are wrong. The origin of this disagreement lies in an incorrect calculation of probabilities for systems of *indistinguishable* particles. Incorrect entropies of mixtures of gases are also obtained when we use the formalism of classical thermodynamics. This phenomenon is known as *the Gibbs paradox.*

Suppose we have two moles of ideal gas in a vessel with a partition dividing the total volume, $2V$, into two equal parts. The entropy of any of these parts according to classical thermodynamics is:

$$S_{1,2} = R\ln V + \frac{3}{2}R\ln T + S_0 \tag{1.84}$$

The total entropy of two moles of gas with a partition is therefore:

$$S' = S_1 + S_2 = 2R\ln V + \frac{6}{2}R\ln T + 2S_0 \tag{1.85}$$

After removing the partition we have two moles of ideal gas in double the volume. The state of the gas has not changed, *but the entropy has changed*:

$$S'' = 2R\ln 2V + \frac{6}{2}R\ln T + 2S_0 \tag{1.86}$$

The change in entropy of two volumes of a gas after removing the partition is:

$$\Delta S = 2R\ln 2 \tag{1.87}$$

No rational explanation can be given to this paradox by appealing to thermodynamics. Formally, this paradox disappears if we assume that the volume V in the above expressions is not the volume of a system but is the *volume per mole.*

The same paradox is observed when we use the statistical expression for entropy (1.38):

$$S' = 2kN \ln N + 2kN\alpha + \frac{2E}{T} \tag{1.88}$$

$$S'' = 2kN \ln 2N + 2kN\alpha + \frac{2E}{T} \tag{1.89}$$

leading to:

$$\Delta S = 2kN \ln 2 \tag{1.90}$$

In this case the paradox disappears (as has been shown by Gibbs) when the probability W (1.18) is divided by $N!$, and this is *equivalent to allowing molecules to be indistinguishable.*

It must at once be admitted, however, that molecules of *different chemical nature are distinguishable*! We shall return to this problem several times in this book.

In a system of N indistinguishable molecules distributed over m energy levels the thermodynamic probability is thus given by:

$$W = \frac{1}{n_1!n_2!\cdots n_m!} \cong \frac{1}{\prod_i^m n_i^{n_i} e^{-n_i}} \tag{1.91}$$

The statistical entropy then becomes *proportional to the number of molecules*:

$$S = k \ln W = k\sum_i (n_i - n_i \ln n_i) = kN - k\sum_i (n_i \ln n_i) \tag{1.92}$$

The processes of derivation of the most probable distribution law for systems of distinguishable and indistinguishable molecules is practically identical because the two expressions for entropy differ by a constant term ($k\ln N!$), the variation of which is in any case zero (see Table 1.1). The entropy alone ought to be calculated according to different equations:

$$S = kN \ln \sum_i e^{-\varepsilon_i/kT} + E/T \qquad \text{(distinguishable)} \tag{1.93}$$

$$S = kN \ln \sum_i e^{-\varepsilon_i/kT} + E/T - k \ln N! \qquad \text{(indistinguishable)} \tag{1.94}$$

Conventionally, however, entropy is calculated using the same equation (1.93) for both types of systems and then defining the *partition function for a system of N indistinguishable particles* so as to contain the factor ($1/N!$):

$$Z = \frac{z_{MB}^{N}}{N!} = (2\pi mkT)^{3N/2}\frac{V^{N}}{N!} \tag{1.95}$$

Such a partition function can also be represented (using the Stirling formula) as the N-th power of a modified *molecular partition function*:

$$Z = z_{m}^{N} = \left[(2\pi mkT)^{3/2}\frac{eV}{N}\right]^{N} \tag{1.96}$$

Thus the indistinguishable nature of molecules results in the addition of the factor e to the molecular partition function. This modification removes the Gibbs paradox but another modification is still required in order to get the partition function dimensionless (as it is when derived by the cell method of Boltzmann).

Table. 1.1. Derivation of the distribution law and expressions for entropy in terms of partition functions in the cases of distinguishable and indistinguishable molecules

Entropy of a system of distinguishable particles	Derivation of the distribution law	Entropy of a system of indistinguishable particles
$S = kN\ln N - k\sum n_i \ln n_i$	$\delta S = -k\sum(\ln n_i + 1)\delta n_i = 0$ $\delta N(-\alpha) = -\alpha\sum\delta n_i = 0$ $\delta E(-\beta) = -\beta\sum\varepsilon_i\delta n_i = 0$ $\sum(\ln n_i + 1 + \alpha + \beta\varepsilon_i)\delta n_i = 0$ $\ln n_i + 1 + \alpha + \beta\varepsilon_i = 0$ for $n_i >> 1$ $n_i = \exp(-\alpha - \beta\varepsilon_i)$	$S = kN - k\sum n_i \ln n_i$
Substituting n_i from the distribution law $S = kN\ln N + kN\alpha + \beta E$		*Substituting n_i from the distribution law* $S = kN + kN\alpha + \beta E$
$S = kN\ln\sum e^{\varepsilon/kT} + E/T$	Defining α and β $\sum\varepsilon_i n_i = E$ $\sum n_i = N = e^{\alpha}\sum e^{\varepsilon/kT}$ $\alpha = -\ln N + \ln\sum e^{\beta\varepsilon}$ $\beta = 1/kT$ (from $\partial S/\partial E$)	$S = kN(1 - \ln N + \ln\sum e^{\varepsilon/kT}) + E/T$

1.5
Phase volume and the number of quantum states

The partition function of a continuous Maxwell – Boltzmann distribution is given by (1.60), and in modified form by (1.96) and has the dimension $(p \times q)^{3N}$ which is the result of integration over phase space (1.57). This dimension is the dimension of *action* to the power $3N$ which suggests that the *quantum of action, i.e.* the Planck constant, should be used as a conversion denominator. A dimensionless partition function can be obtained if we divide the element of phase space $d\gamma$ in (1.53) by h^3. In doing this we convert the volume of phase space into the number of quantum states. Let us illustrate this proposition by the example of the harmonic oscillator. The phase space of a one-dimensional harmonic oscillator (see Appendix 10.2.1) is two-dimensional and can be represented graphically on a plane (see Fig. 1.3).

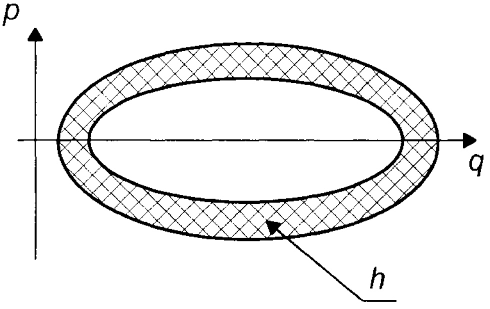

Fig. 1.3. Phase space of one-dimensional harmonic oscillator

The ellipses correspond to equi-energetic surfaces and the area between them corresponds to the volume of phase space having dimension $[p \times q]$. For a classic harmonic oscillator these two ellipses can be separated by an arbitrarily small space, but for a quantum harmonic oscillator this separation cannot be smaller than h. Such a space can be considered as corresponding to a single quantum state of the one-dimensional harmonic oscillator or to a cell in its phase space. For a three dimensional oscillator the corresponding elementary volume is h^3. By dividing the volume of phase space $\Delta\gamma$ by h^3 we get the number of quantum states of a particle oscillating in three dimensions:

$$\Delta\omega = \Delta\gamma / h^3 \tag{1.97}$$

Identical results can be obtained for a quantum particle (whose energy is a multiple of h) moving in three-dimensional space. The corresponding translational partition function for a system of N indistinguishable particles then becomes:

$$Z = \frac{z_{MB}^N}{h^{3N} N!} = (2\pi mkT)^{3N/2} \frac{V^N}{h^{3N} N!} = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{eV}{N}\right]^N = z^N \quad (1.98)$$

The number of quantum states, $\Delta\Omega$, of such a system of indistinguishable molecules is related to the volume of phase space $\Delta\Gamma$ as[7]:

$$\Delta\Omega = \Delta\Gamma / N! h^N \quad (1.99)$$

What particles can we take as distinguishable and what as indistinguishable? As mentioned above particles of different chemical nature are distinguishable[8]. In general particles are indistinguishable if they cannot be 'labelled'. Chemically identical particles are indistinguishable if they move freely within the whole volume of a system. In such a case we cannot say whether two particles exchanged sites or not because it does not bring about any change in the physical state of a system.

Even a system of *chemically* identical molecules becomes a system of distinguishable particles if such an exchange is not allowed. For example, when molecules are fixed in the cells of a crystal lattice they become distinguishable because each molecule can be labelled by the *coordinates of its cell*. The only necessary requirement is that they should not migrate from cell to cell. Such systems are called systems of *localised states*. A useful model system called the *ideal crystal* (see Chapter 3) and approximating the state of crystal solids at low temperatures is a system of localised states. Even at temperatures close to the melting point the state of a crystal solid can be considered as a system of localised states: the only requirement is that molecules do not migrate *between* the cells whatever kind of motion they perform *within* a cell. The partition function of a system of N molecules confined to their cells (within the volume V/N each) is distinguished by the absence of the factor e:

$$Z = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V}{N}\right]^N \quad (1.100)$$

We shall see later (Chapter 4) that in theories of the liquid state an interpolating factor is introduced into the partition function in order to take into account the indistinguishable nature of molecules in liquids.

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[7] When each molecule possesses f internal degrees of freedom the correct formulae for the number of quantum states are: $\omega = \Delta\gamma / h^{(3+f)}$ and $\Delta\Omega = \Delta\Gamma / N! h^{N(3+f)}$

[8] Even molecules differing by nuclear mass number should be considered as distinguishable if the reaction or process in question selects such molecules.

1.6
Quantum statistics

It is important to distinguish between the quasi-quantum corrections to Maxwell – Boltzmann statistics described above and *quantum statistics* connected with the names of Bose, Einstein, Fermi and Dirac as well as statistics based on the quantum mechanical Schrödinger equation instead of the canonical equations of classical mechanics.

Statistics employing the Schrödinger equation differs from Maxwell – Boltzmann statistics in the same way as quantum mechanics differs from classical mechanics. It allows for a more general description by taking electronic systems of molecules into consideration. *However, it does not bring anything fundamentally new to the statistical description of molecular systems.*

Bose – Einstein and Fermi – Dirac quantum statistics take into account special effects connected with an additional variable which makes some quantum states distinguishable, namely the spin, S, of a particle. An energy level can then be divided into cells corresponding to different *projections of spin* on some spatial axis, S_z.

Regarding the *spin,* there are two different types of particles. One class is made up of particles possessing *integral spin* ($S = 0, 1, 2,$ *etc.*) and the second class comprises those particles with *half-integral spin* ($S = 1/2, 3/2, ...$ *etc.*).

According to the *Pauli exclusion principle* a cell corresponding to a given quantum state cannot contain more than one particle of the second kind, whilst any number of particles of the first type may be in the same quantum state. Two different modes of the filling of cells in an energy level are thus defined corresponding to two types of *quantum statistics*, namely the *Bose – Einstein statistics* of the particles with integral spin (*bosons*) and *Fermi – Dirac statistics* of the particles with half-integral spin (*fermions*).

The majority of *elementary* particles are fermions: *electrons, protons, neutrons, positrons* ($s = 1/2$), *etc.*, as well as *compound particles* containing an odd number of fermions (the *molecule* HD, the deuterium *atom*: the electron + deutron pair). The elementary particles possessing integral spin are ***photons*** ($s = 1$), π– and K–mesons ($s = 0$). The compound particles containing an *even* number of fermions are also *bosons*, for example the hydrogen atom (the electron + proton pair), the molecule H_2, the atom of the isotope ^{4}He (two protons, two neutrons and two electrons). However, the atoms of the isotope ^{3}He are fermions.

The distinguishable nature of states characterised by different projection of spin requires a specific mode of calculation of probability. New distribution laws can thus be derived which explain a number of phenomena having no explanation within the modified Maxwell – Boltzmann statistics.

1.6.1
Bose – Einstein statistics

According to the basic assumption of Bose – Einstein statistics any number of particles may be in a given *quantum state*, *i.e.* all particles having the energy ε_i may be placed in one cell leaving all other cells (belonging to this level) empty.

Let us start with the system of N particles, having total energy E. The energies of the particles are $\varepsilon_1 \ldots \varepsilon_m$, *i.e.* particles are distributed over m energy levels. What is the number ways of distributing n_i molecules among these z_i cells? Equivalent problems are: in how many ways can n_i articles be distributed among z_i compartments, or in how many ways can the integral number n_i be represented as a *sum* of z_i integral terms? The answer is:

$$W_i = \frac{(n_i + z_i - 1)!}{n_i!(z_i - 1)!} \tag{1.101}$$

The overall probability of a system is the product of the probabilities of the distributions within the levels:

$$W = \prod_{i=1}^{m} W_i = \prod_{i=1}^{m} \frac{(n_i + z_i - 1)!}{n_i!(z_i - 1)!} \tag{1.102}$$

The entropy then is:

$$S = k \ln W = \sum_{i=1}^{m} \ln \frac{(n_i + z_i - 1)!}{n_i!(z_i - 1)!} \tag{1.103}$$

Using the Lagrange method, the following distribution law can be derived for the Bose – Einstein model:

$$n_i = \frac{z_i - 1}{e^{\alpha + \beta\varepsilon_i} - 1} \tag{1.104}$$

The meaning of the multipliers α and β are again found from the partial derivatives of entropy as:

$$\mu = -k\alpha; \qquad 1/T = k\beta \tag{1.105}$$

in which μ is chemical potential[9]. The entropy is then given by:

$$S = -\frac{N\mu}{kT} + \frac{E}{T} - k\sum_{i=1}^{m} (z_i - 1)\ln\left(1 - e^{\frac{\mu - \varepsilon_i}{kT}}\right) \tag{1.106}$$

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[9] Remember that in Maxwell – Boltzmann statistics the coefficient α, and hence the chemical potential, (in (1.32), (1.43), (1.62) and (1.63)), have been derived from differently computed probabilities.

The analogue of the partition function in Bose – Einstein statistics is:

$$\sum_i (z_i - 1)\ln\left(1 - e^{\frac{\mu-\varepsilon}{kT}}\right) \tag{1.107}$$

The factor $(z_i - 1)$ can be considered as a statistical weight or *degeneracy* of the energy level. The number of cells, z_i, in Bose – Einstein statistics is calculated similarly to the number of quantum states in an energy layer.

The volume of the energy layer of the phase space for an ideal gas corresponding to $\varepsilon = E - E + dE$ (Equation (10.77), Appendix 10.2.2) is:

$$d\Gamma(E) = \frac{3N}{2} V^N E^{\frac{3N}{2} - 1}\left(\frac{4\pi me}{3N}\right)^{\frac{3N}{2}} dE \tag{1.108}$$

The number of quantum states according to (1.99) is $d\Omega = d\Gamma(E)/N!h^{3N}$. For a gas of particles with $S = 1$ each quantum state resolves into 3 states corresponding to $S_Z = -1$, 0 and +1. Therefore:

$$z(E) = \frac{9}{2}\frac{N}{N!h^{3N}} V^N E^{\frac{3N}{2} - 1}\left(\frac{4\pi me}{3N}\right)^{\frac{3N}{2}} dE \tag{1.109}$$

Usually this value is much higher than 1, therefore the distribution law (1.104) may be written as:

$$n_i \cong \frac{z_i}{e^{-\frac{\mu - \varepsilon_i}{kT}} - 1} \tag{1.110}$$

It must be mentioned that the case of photons is a specific one. The laws of black body radiation (see Section 1.6.5) imply that the degeneracy of these particles is 2 and not 3 as should be expected from the value of their spin $S = 1$. Usually the double degeneracy of photons is explained by referring to the left and right polarisation of light. However this degeneracy must be connected with the spin-degeneracy of photons otherwise the total number of indistinguishable states would be 2 × 3 = 6. A possible explanation of this phenomenon is that these particles do not have a rest mass and are always moving in a straight line. They define therefore a natural direction in space reducing thus the number of states to *two*, with the spin in the direction of motion and in the opposite direction corresponding to the left and right circular polarisation. The case of zero projection of spin on this axis corresponds to a linear polarisation that can always be represented as a superposition of left and right circular polarisation.

1.6.2
Fermi – Dirac statistics

If we have z_i cells and n_i particles in the i-th energy level and *cells should not contain more than one particle*, then the number of ways of filling such a level is:

$$W_i = \frac{z_i!}{n_i!(z_i - n_i)!} \tag{1.111}$$

The number of ways of filling a system of such levels in an ideal gas of fermions is given by:

$$W = \prod_i W_i = \prod_i \frac{z_i!}{n_i!(z_i - n_i)!} \tag{1.112}$$

Applying the Stirling formula we get the entropy as:

$$S = k\sum_i \left[z_i \ln z_i - n_i \ln n_i - (z_i - n_i)\ln(z_i - n_i)\right] \tag{1.113}$$

After a variational procedure we obtain the Fermi – Dirac distribution:

$$n_i = \frac{z_i}{e^{\alpha+\beta\varepsilon_i} + 1} \tag{1.114}$$

The meaning of the multipliers α and β is the same as in Bose – Einstein statistics, namely:

$$-\mu / T = k\alpha; \qquad 1/T = k\beta \tag{1.115}$$

The Fermi – Dirac distribution (1.114) may then be written as:

$$n_i = \frac{z_i}{e^{-(\mu-\varepsilon_i)/kT} + 1} \tag{1.116}$$

Let us now find the limits of applicability of these three types of statistics.

1.6.3
Comparison of the three types of statistics

The distribution laws of Maxwell – Boltzmann, Bose – Einstein and Fermi – Dirac statistics can be written in one general form:

$$n_i = \frac{g}{e^{-(\mu-\varepsilon_i)/kT} + \delta} \tag{1.117}$$

and the parameters g and δ applicable to each type of statistics are given in Table 1.2.

Table 1.2. Parameters of Maxwell – Boltzmann, Fermi – Dirac and Bose – Einstein distributions

Distribution	g	δ
Maxwell – Boltzmann	1	0
Bose – Einstein	$z_i - 1$	-1
Fermi – Dirac	z_i	$+1$

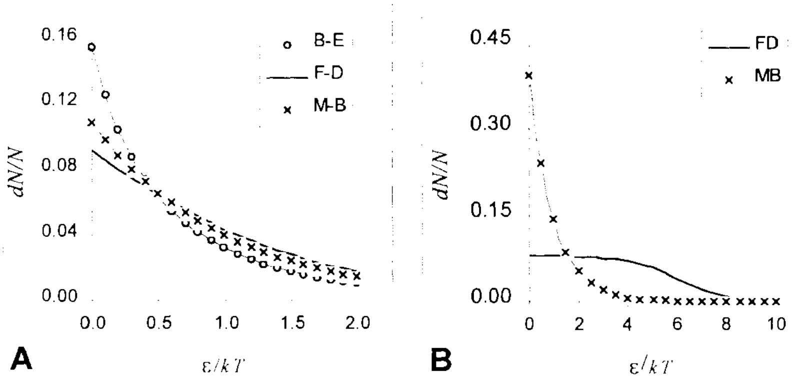

Fig. 1.4. Maxwell – Boltzmann, Fermi – Dirac and Bose – Einstein distributions computed for small negative chemical potential (**A**, $\mu = -0.6kT$) and large positive chemical potential (**B**, $\mu = +6kT$). As follows from (1.110), Bose – Einstein distribution does not allow positive μ

It therefore follows from this equation that both quantum statistics approach the Maxwell – Boltzmann distribution law when $\exp(-(\mu-\varepsilon)/kT) >> 1$. The Bose – Einstein distribution exhibits the steepest decrease in the number of particles with increasing energy (Fig. 1.4A). When $|\mu/kT| \leq 1$, the Fermi – Dirac distribution curve shows a gradual decrease with a slope smaller than that of either the Maxwell – Boltzmann or the Bose – Einstein curves (Fig. 1.4A). When the chemical potential is positive and much higher than kT the Fermi – Dirac distribution exhibits a *step* at around the value of the chemical potential (the so-called *Fermi energy*) which occurs within $2kT$ (Fig. 1.4B).

The same curves can be interpreted from the point of view of the probability of finding high or low energy particles in corresponding ensembles. The particles of *low energies* are most frequently met with in a *Bose – Einstein ensemble.* Fermi – Dirac ensembles are most rich in particles of higher energies, whilst Maxwell – Boltzmann ensembles occupy a middle position between the two quantum statistics. As a consequence, the pressure of a gas of bosons must be lower than the pressure of a gas of Maxwell – Boltzmann particles which, in its turn, is lower than the pressure of a gas of fermions. It can, however, be shown that the product pV in all three statistics is equal to $(2/3)<E>$. According to the above, both quantum statistics approach classical (Maxwell – Boltzmann) statistics when the exponential $e^{-(\mu - \varepsilon)/kT}$ is much higher than 1. This condition must hold for any energies including $\varepsilon = 0$:

$$\exp(-\mu / kT) >> 1 \tag{1.118}$$

Taking into account the factor g in (1.117) and using (1.98) the chemical potential per molecule of ideal gas can be written as:

$$-\frac{\mu}{kT} = \ln\left[g\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{eV}{N}\right] = \ln\left[g\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e\frac{kT}{p}\right] \tag{1.119}$$

Hence Maxwell – Boltzmann statistics can be employed if:

$$e^{-\frac{\mu}{kT}} = g\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e\frac{kT}{p} >> 1 \tag{1.119a}$$

Introducing numerical values of constants into (1.119) at atmospheric pressure (1.013×10^6 dyne cm^{-2}) we get:

$$0.0259 g M^{3/2} T^{5/2} >> 1 \tag{1.120}$$

in which M is the molar mass. For ^{4}He atoms ($S = 0$, $g = 1$) at T = 4.2 K, the product (1.120) equals approximately 7.5 which is considerably higher than 1. Therefore the gas of He atoms at such temperature and pressure cannot be described by Maxwell – Boltzmann statistics and Bose – Einstein (for ^{4}He) or Fermi – Dirac (for ^{3}He) distribution laws must be used. All other molecular and mono-atomic gases are described by Maxwell – Boltzmann statistics. On the other hand, electrons ($M_{\mathrm{He}}/M_e \cong 7300$) in metals form a kind of a gas, the state of which, even at high temperatures, is described by Fermi – Dirac statistics.

1.6.4
Degenerate ideal gas

The state of a gas in which it cannot be described by classical statistics is called degenerate: *a completely different concept than the degeneracy of energy levels although denoted by the same word.* The degree of degeneracy of a gas is then defined as the ratio of 1 to $\exp(-\mu/kT)$, *i.e.* it is characterised by the factor $\exp(\mu/kT)$. The chemical potential of bosons cannot be positive: in order to comply with positive n_i for low energy particles with $\varepsilon \to 0$ it must be negative or zero. In the latter case the population of the lowest energy level ($\varepsilon = 0$) is infinitely high. Fig. 1.5 shows that when μ approaches zero (*i.e.* very small negative values) the relative population of the level $\varepsilon = 0$ approaches unity leaving all other levels empty.

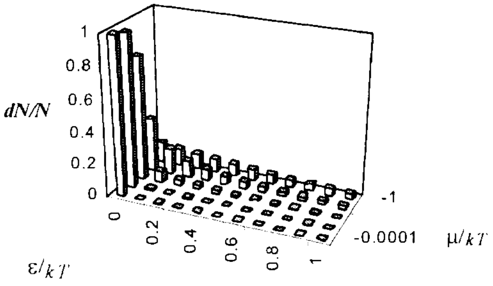

Fig. 1.5. Variation of the shape of Bose – Einstein distributions with decreasing chemical potential

Bearing in mind that for an ideal gas the chemical potential is proportional to $T^{5/2}$ (see (1.119), above) it can be guessed that with decreasing temperature the chemical potential might approach zero and *a major fraction of particles will then occupy the zero level.* They will all be in one quantum state (occupy one cell) and this state can be realised in one way. The entropy of such a state must therefore be zero. This phenomenon is called *Bose condensation.* It can be shown that a finite temperature exists below which Bose condensation becomes possible. Bose condensation explains the singular behaviour of some properties (heat capacity, heat conductivity) of ^{4}He (*bosons*) at 2.19 K which is not observed for ^{3}He (*fermions*).

A completely degenerate gas of *fermions* corresponds to a different state, namely to a consecutive *filling* of cells (*not a statistical distribution!*) starting from the cell $\varepsilon = 0$ ($p = 0$) up to the cell with maximal energy or momentum (p_m). The latter can be found from the normalisation condition of the number of quantum states filled by particles. The integral of the element of phase space $\int \ldots \int dq \ldots dp$ being multiplied by the degeneracy $g = 2S + 1$ and divided by h^3 yields the number of available quantum states. If the upper limit of integration is p_m then the number of quantum states equals the number of particles in a completely degenerate gas of fermions. In spherical coordinates an element of phase space of ideal gas can be written as (compare with (1.68)):

$$\Delta\Gamma = \int \cdots \int dxdydz \sin\theta d\theta d\varphi p^2 dp \tag{1.121}$$

The number of cells filled by particles is then:

$$N = \frac{g}{h^3}\Delta\Gamma = \frac{g}{h^3}\iiint_V dxdydz \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \int_0^{p_m} p^2 dp = g\frac{4\pi V}{3h^3}p_m^3 \tag{1.122}$$

The maximal momentum for a gas made up of particles with $S = 1/2$ and $g = 2$ is then:

$$p_m = h\left(\frac{3N}{8\pi V}\right)^{1/3} \tag{1.123}$$

The energy of such a gas is:

$$E = \frac{g}{h^3}\iiint\limits_V dxdydz\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\varphi\int_0^{p_m}\frac{p^2}{2m}p^2dp = g\frac{2\pi V}{5h^3}p_m^5 \tag{1.124}$$

and substituting p_m from (1.123) yields:

$$E = \frac{4\pi V}{5mh^3}h^5\left(\frac{3N}{8\pi V}\right)^5 = \frac{3Nh^2}{10m}\left(\frac{3N}{8\pi V}\right)^{2/3} \tag{1.125}$$

Note that the expressions (1.124) and (1.125) do not depend on temperature. The partial derivative $\partial E/\partial \mathrm{T}$ (the heat capacity) therefore does not exist. The consecutive filling of cells in a completely degenerate gas of fermions corresponds to the condition $n_i = z_i$. In such a case the thermodynamic probability is 1 and the entropy is zero:

$$W = \prod_i \frac{z_i!}{n_i!(z_i - n_i)!} = 1; \qquad S = k\ln W = 0$$

We see that at temperatures approaching zero the entropy of a gas consisting of either fermions or bosons approaches zero. The Nernst theorem can thus be derived from the basic ideas of quantum statistics. Quantum statistics gives an explanation of this phenomenon: it is a consequence of complete degeneracy of any system of simple particles having no internal degrees of freedom. In such a state *thermodynamic properties cease to exist*, which is to be expected for a system having only one possible way of realisation ($W = 1$). Such a system does possess, however, mechanical properties. For example its pressure can be calculated from:

$$p = \frac{2}{3}\frac{E}{V} = \frac{h^2}{5m}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{5/3} \tag{1.126}$$

Such completely degenerate systems may also possess electric and magnetic properties but *not thermodynamic* properties. Anything undetermined and indefinite vanishes at $T = 0$. Strictly speaking the state of complete degeneracy is achieved for an ensemble of any particles at $T \to 0$. However, as has been mentioned above, electrons in metals, due to their low mass and high density (N/V), form a practically completely degenerate gas at room temperature ($\exp(\mu/kT) \cong 10^4$ at $T = 300$ K). This explains the high efficiency of *electric* and *electro-mechanic* devices: the working body – the gas of electrons – does not have any thermodynamic properties and its motion is highly organised.

1.6.5
Applications of Bose – Einstein statistics: black – body radiation

The case of zero chemical potential can be considered as the case of a non-constant number of particles. Indeed, zero value of the multiplier α, (1.24), means that the condition of conservation of the number of particles:

$$\sum n_i = N \qquad (1.127)$$

is *not* imposed on the system. The distribution law of Bose – Einstein statistics for such a case becomes:

$$n_i = \frac{z_i - 1}{e^{\varepsilon_i / kT} - 1} \qquad (1.128)$$

This distribution law can be applied to the description of *radiation* as an ensemble of *photons* – particles with integer spin. The radiation of light and heat by a material body can be considered as a gas of photons with a non-constant number of particles not interacting between themselves. The energy of a photon is $h\nu$, and its effective mass m is $h\nu/c^2$. The momentum of a photon therefore is:

$$p = mc = h\nu/c \qquad (1.129)$$

The number of the cells corresponding to a given energy (*i.e.* frequency) is:

$$z_i = z_\nu = dxdydz\, p^2 dp \sin\theta d\theta d\varphi / h^3 \qquad (1.130)$$

Accordingly (considering $z_i >> 1$):

$$n_\nu = dV \frac{p^2 dp \sin\theta\, d\theta d\varphi}{h^3 \left(e^{\varepsilon_i / kT} - 1\right)} \qquad (1.131)$$

The number of photons with the frequency ν radiated by a macroscopic body having volume V is then:

$$dN_\nu = 2 \int_V \int_\theta \int_\varphi \frac{dV p^2 dp \sin\theta\, d\theta\, d\varphi}{h^3 \left(e^{\varepsilon_i / kT} - 1\right)} = 2 \frac{4\pi V}{h^3} p^2 \frac{dp}{e^{\varepsilon_i / kT} - 1} \qquad (1.132)$$

The factor 2 in (1.132) reflects the fact that photons of the same energy can be *left* or *right polarised*. Substituting $\varepsilon = h\nu$, $p = h\nu/c$ and $dp = (h/c)d\nu$ we reduce our expressions to one variable, ν. The energy corresponding to the frequency ν is:

$$E_\nu = \varepsilon_\nu dN_\nu = \frac{8\pi h V \nu^3 d\nu}{c^3 \left(e^{h\nu / kT} - 1\right)} \qquad (1.133)$$

This is Planck's law for black body radiation.

The variable used by Planck, the energy density per frequency unit according to (1.133), is:

$$\frac{E_\nu}{V d\nu} = \frac{8\pi h \nu^3}{c^3\left(e^{h\nu/kT} - 1\right)} \tag{1.134}$$

The latter equation is usually called *Planck's formula*. Performing the integration of E_ν/V over all frequencies we get the total energy density of radiation:

$$U = \frac{8\pi h}{c^3} \int_{\nu=0}^{\infty} \frac{\nu^3 d\nu}{\left(e^{h\nu/kT} - 1\right)} = \frac{8\pi k^4}{15c^3h^3} T^4 = \frac{4\sigma}{c} T^4 \tag{1.135}$$

which is the well known Stefan – Boltzmann law. The experimental value of Stefan's constant, σ, is in excellent agreement with that calculated *via* fundamental constants using (1.135), their ratio being 1.002. We see that in order to get this correspondence the spin degeneracy of photons was assumed to be 2 and not 3 as follows from the photon's spin of $S = 1$. Some excuse for this assumption has been produced on page 28; however, this assumption remains suspicious because it is indicative of some undiscovered fundamental properties of ensembles of photons.

1.6.6
Applications of Bose – Einstein statistics: heat capacity of solids

The thermal properties of simple crystal solids have been more or less successfully described by Einstein using a very simple model: all atoms were supposed to oscillate with identical frequency ν. They can however be in different quantum states and the partition function for such 3D oscillators is given (see Section 2.7.4) by:

$$z = \left[\frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}\right]^3 = \left[2\sinh\frac{h\nu}{2kT}\right]^{-3} \tag{1.136}$$

The total energy E of a system of N independent oscillators can be calculated in terms of partition functions (see Section 2.6) as:

$$E = NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_{V,N} = \frac{3Nh\nu}{e^{h\nu/kT} - 1} + \frac{3}{2}Nh\nu \tag{1.137}$$

Vibrational frequencies are often represented *via* characteristic temperatures, $\theta = h\nu/k$. The last term in (1.137), representing as it does the energy of zero oscillations, can be temporarily neglected and the energy and heat capacity of such a solid are given by:

$$E = \frac{3Nk\theta_E}{e^{\theta_E/T} - 1} \tag{1.138}$$

$$c_V = \frac{\partial E}{\partial T} = 3kN\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2} \tag{1.139}$$

in which θ_E is known as the Einstein temperature. Equation (1.139) provides for a generally correct description of the temperature dependence of c_V. However, at lower temperatures a statistically significant deviation of experimental data from the theoretical curve is observed (see Fig. 1.6A). Molecular (atomic) vibrations in the solid state cannot be considered as, strictly speaking, independent because, in systems of strongly bound particles, the deflection of one of them from the point of mechanical equilibrium would necessarily cause (with some delay) a similar motion of its neighbours and its neighbour's neighbours and so forth. In other words, the vibrational motion of particles is associated with the *propagation of acoustic waves*.

Based on the formalism of the theory of propagation of acoustic waves in elastic media, Debye (1913) developed a model which takes into account the fact that the frequencies of vibrations form a *spectrum*. The formalism of Debye can be deduced in a number of ways, for example, by considering elastic waves as a collection of *phonons* or *quasi-particles* analogous to photons. Similarly to photons, phonons possess spin $S = 1$ and obey therefore Bose – Einstein statistics.

The number of allowed vibrations in a solid body containing N atoms is $3N$. Similarly, in the case of radiation, the chemical potential of these *phonons* is zero, the energy is $\varepsilon = h\nu$, and the momentum is $p = h\nu/c$.

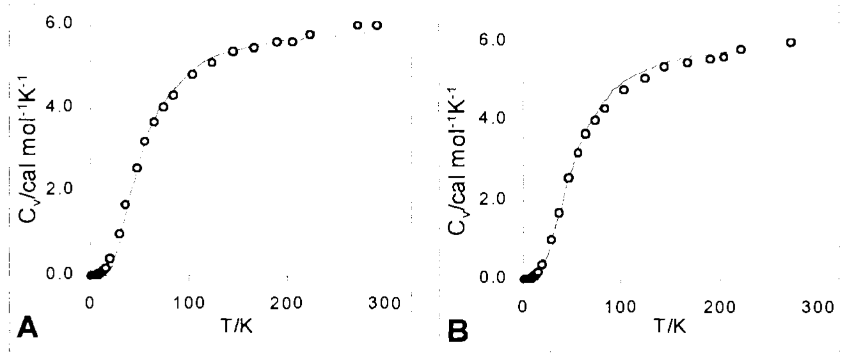

Fig. 1.6. Temperature dependence of the specific heat of silver [3, 4]. Solid curves represent the values calculated according to (**A**) the Einstein formula (1.139) with θ_E = 158 K and according to the Debye approximation (**B**) with θ_D = 200 K. The latter curve was obtained by numerical integration of (1.149) and subsequent numerical differentiation with respect to temperature

Sound waves are of two varieties, longitudinal and transversal, propagating with different velocities. The transversal waves are two-fold degenerate (right and left polarised). According to the Bose – Einstein distribution law (analogous to (1.132)) the number of vibrations in the range between ν and $\nu + d\nu$ is:

$$dn_\nu = \frac{4\pi V}{h^3} p^2 \frac{dp}{e^{h\nu/kT} - 1} \tag{1.140}$$

Taking into account that:

$$p_l^2 = \frac{h^2\nu^2}{c_l^2}; \quad p_{tr}^2 = \frac{2h^2\nu^2}{c_{tr}^2}; \quad dp_l = \frac{h}{c_l}d\nu; \quad dp_{tr} = \frac{h}{c_{tr}}d\nu;$$

we get:

$$dn_\nu = 4\pi V\left(\frac{2}{c_{tr}^3} + \frac{1}{c_l^3}\right)\frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} \tag{1.141}$$

Integrating $\varepsilon_\nu dn_\nu$ over all possible frequencies we obtain the total energy of a solid body. The *upper limit of integration must not be infinite* because the number of possible vibrations is finite ($3N$) and the number of overtones (eigenvibrations) of a body of finite dimensions is also finite.

This is a result of the assumption that an elastic body is built of atoms (molecules). We are able to characterise the vibrational spectrum of such a body by a unique ν_{max} because the vibrating particles are identical and *regularly (periodically) distributed in the structure of the crystalline solid.*

The integration of $\varepsilon_\nu dn_\nu$ must, therefore, be performed between zero and some frequency ν_{max} (the significance of this parameter will be defined below):

$$E = \int_0^{\nu_{max}} \varepsilon_\nu d\nu = 4\pi Vh\left(\frac{2}{c_{tr}^3} + \frac{1}{c_l^3}\right)\int_0^{\nu_{max}} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \tag{1.142}$$

Wave velocities can be assumed (for wavelengths much longer than the lattice constant, *i.e.* in the approximation of low temperatures) to be *independent of frequency* and they can be expressed as functions of the highest frequency ν_{max}. This can be done using the classical theory of vibrations of an elastic body. According to this theory, the number of overtones (number of elementary volumes $(\lambda/2)^3$ contained in a body) for each frequency is proportional to the cube of frequency:

$$Z = \frac{4\pi}{3}\frac{V}{\lambda^3} = \frac{4\pi V}{3c^3}\nu^3 \tag{1.143}$$

The integral of these numbers over all frequencies between zero and ν_{max} must equal $3N$. The number of vibrations corresponding to the frequencies within $\nu \rightarrow \nu + d\nu$ is:

$$dZ = \frac{4\pi V}{c^3}\nu^2 d\nu \tag{1.144}$$

For both the longitudinal and transversal waves (the latter being doubly degenerate) we get:

$$dZ = 4\pi V\left(\frac{2}{c_{tr}^3}+\frac{1}{c_l^3}\right)\nu^2 d\nu \tag{1.145}$$

The normalisation of the total number of vibrations to $3N$ yields:

$$3N = \int_0^{\nu_{\max}} 4\pi V\left(\frac{2}{c_{tr}^3}+\frac{1}{c_l^3}\right)\nu^2 d\nu = \frac{4\pi V}{3}\left(\frac{2}{c_{tr}^3}+\frac{1}{c_l^3}\right)\nu_{\max}^3 \tag{1.146}$$

and this allows us to define $\nu_{\max}$ *via* wave velocities and *vice versa*:

$$4\pi V\left(\frac{2}{c_{tr}^3}+\frac{1}{c_l^3}\right) = \frac{9N}{\nu_{\max}^3} \tag{1.147}$$

It is at least convenient to substitute two parameters by one and so exclude sound velocities. The distribution law for the eigenvibrations is then given by:

$$dZ = \frac{9N}{\nu_{\max}^3}\nu^2 d\nu \tag{1.147a}$$

The energy of a solid then becomes:

$$E = \frac{9N}{\nu_{\max}^3}\int_0^{\nu_{\max}} \frac{h\nu^3 d\nu}{e^{h\nu/kT}-1} \tag{1.148}$$

It is convenient to write this equation in terms of the dimensionless variable $x = h\nu/kT$. The upper limit of integration thus becomes $x_{max} = \theta_D/T$, where $\theta_D = h\nu_{max}/k$, and therefore:

$$E = 9NkT\frac{T^3}{\theta_D^3}\int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \tag{1.149}$$

The parameter θ_D is called the *Debye temperature*. In general this equation can only be integrated numerically. Heat capacities may be obtained from (1.149) by differentiation (either analytical or numerical).

Although both the Debye and Einstein models may be used to describe the temperature dependence of heat capacity in the region of high temperatures (as shown in Fig. 1.6 (A, B) above) the Debye approximation provides for a *significantly better agreement with experiment* at low temperatures (Fig. 1.7).

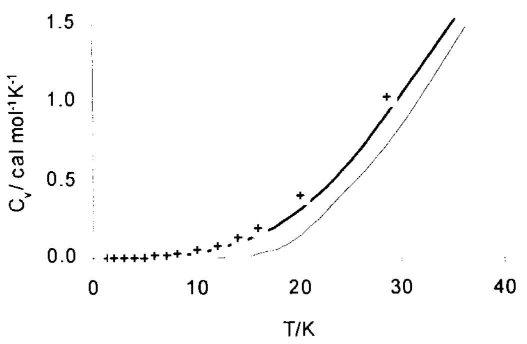

Fig. 1.7. Temperature dependencies of heat capacity of silver in the region of low temperatures (*crosses* – experimental data; *thick line* – Debye approximation (θ_D = 200 K); and *thin line* – Einstein approximation (θ_E= 158 K))

Analytical integration of (1.149) is possible for the cases of either very low or very high temperatures. At low temperatures the limit of integration θ_D/T approaches infinity and the integral in (1.149) is $\pi^4/15$:

$$E = \frac{3NkT\pi^4}{5}\left(\frac{T}{\theta_D}\right)^3 \tag{1.150}$$

The corresponding heat capacity therefore becomes:

$$C_V = \left(\frac{\partial E}{dT}\right)_V = \frac{12Nk\pi^4}{5\theta_D{}^3}T^3 \tag{1.151}$$

This is the Debye law relating heat capacities to the cube of temperature. The equation (1.149) is not exactly correct because when temperature is approaching zero the energy is not approaching zero as predicted by (1.150). Taking into account that the energy is actually:

$$\varepsilon = (n + \tfrac{1}{2})h\nu \tag{1.152}$$

the expression for energy can be obtained in a way similar to that outlined above. With this correction:

$$E = 9NkT\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} + \frac{9}{8}Nh\nu_{\max} \tag{1.153}$$

In the region of high temperatures ($x \ll 1$) the exponential in (1.149) and (1.153) can be substituted by $(1 + x)$ and the integration does not present any difficulties and results in the Dulong and Petit rule:

$$E = 3NkT + \frac{9}{8} Nh\nu_{\max} \tag{1.154}$$

An important improvement has been introduced into the Debye theory by Tarasov [5]. He has shown that the Debye law of cubes of temperature is actually a special case of a three dimensional lattice with approximately equal elastic constants for all dimensions. When the interaction between molecules in neighbouring *two-dimensional layers* is much weaker than the interaction of nearest neighbours within a layer the distribution law for eigenvibrations (1.147) becomes:

$$dZ = \frac{6N}{\nu_{\max}^2} \nu d\nu \tag{1.155}$$

Similarly when a compound forms *chain-like regular structures* ('one-dimensional crystals') the distribution law is:

$$dZ = \frac{6N}{\nu_{\max}} d\nu \tag{1.155a}$$

This leads to a general formula for the heat capacity of an *m*-dimensional crystal:

$$C_m = 3m(m+1)Nk\left(\frac{T}{\theta_m}\right)^m \int_0^{\theta_m/T} \frac{x^m dx}{e^x - 1} - 3mNk\frac{\theta_m}{T}\left(e^{\frac{\theta_m}{T}} - 1\right)^{-1} \tag{1.156}$$

When the interactions between chains and/or sheets in a crystal cannot be neglected it is possible to calculate [6, 7] the total heat capacity as a sum of contributions from 'one & three' and 'two & three' dimensional structures:

$$C_{1(3)} = C_1(\theta_1, T) - \frac{\theta_3}{\theta_1}\left[C_1(\theta_3, T) - C_3(\theta_3, T)\right] \tag{1.157}$$

$$C_{2(3)} = C_2(\theta_2, T) - \left(\frac{\theta_3}{\theta_2}\right)^2 \left[C_2(\theta_3, T) - C_3(\theta_3, T)\right] \tag{1.158}$$

in which the $C_m(\theta_m/T)$ are to be calculated according to (1.156). This formalism provides, therefore, for the determination of the type of supra-molecular structure in crystals employing heat capacity data. Experimental data and theoretical heat capacities of a crystal of HF calculated using $\theta_1 = 280$ K and $\theta_3 = 141$ K are shown in Fig. 1.8.

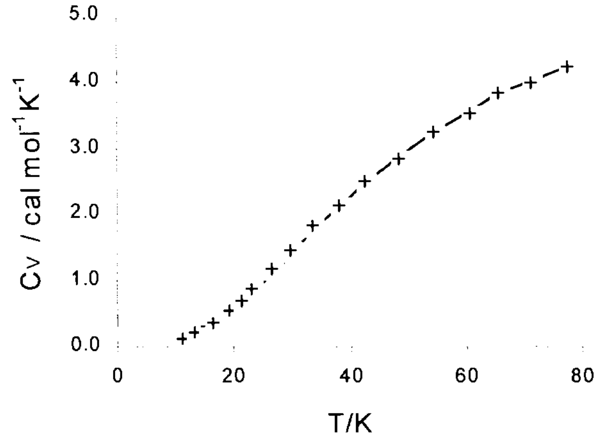

Fig. 1.8. Heat capacities of crystalline HF (experimental (*crosses*) and calculated (*line*) according to Tarasov's model)

The value of the characteristic temperature for a one-dimensional structure ($\theta_1 = 280$ K, *i.e.* $\nu_{max} = 200\ \mathrm{cm}^{-1}$) corresponds to a proton vibration in the hydrogen bond. It is interesting, therefore, that the heat capacity data above indicate the existence of chains of hydrogen-bonded molecules of HF in crystalline hydrofluoric acid at low temperatures.

The Tarasov theory is based on a model having clear physical significance and employs a small number of parameters for the description of temperature dependencies of heat capacities deviating from a simple Debye law. It must, however, be mentioned that both the Debye and Tarasov formalisms are derived assuming an independence of sound velocities on frequencies. They are therefore valid in the region of long-wave vibrations (compared to interatomic distances), *i.e.* at low temperatures.

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2 Ensembles, Partition Functions, and Thermodynamic Functions

2.1

Gibbs' approach, or how to avoid molecular interactions

Maxwell – Boltzmann statistics, with corrections for the quantum character of energy changes and the indistinguishable nature of molecules, works perfectly well when we consider systems of non-interacting molecules. If particles are interacting with each other, then the description of such systems by Maxwell – Boltzmann statistics becomes extremely difficult if not impossible. For example, consider a system of positive and negative ions interacting *in pairs*. The potential energy of such a system is:

$$U = \sum_i \sum_j \frac{e_i e_j}{2r_{ij}} \tag{2.1}$$

The potential energy of the positive ion labelled as '1' in a pair depends on the coordinates of the negative ion which is generally outside the elementary volume $d\Gamma q_1 = dx_1 dy_1 dz_1$. In order to write a distribution law for just a single ion in a pair we must introduce a second element of the coordinate space $d\Gamma q_2 = dx_2 dy_2 dz_2$. We cannot then consider interacting particles separately and the distribution law for a single pair must be written as:

$$dN_1 dN_2 = Ae^{-\frac{1}{2mkT}\left(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2\right) + \frac{e_1 e_2}{kTr_{12}}} d\gamma_1 d\gamma_2 \tag{2.2}$$

in which $r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$. With an increasing number of interactions the number of potential energy terms will increase to $N(N-1)/2$. The dimension of the phase space of coordinates increases correspondingly:

$$dN = Ae^{-\frac{1}{2mkT}\sum_{i=1}^{N}\left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2\right) + \frac{1}{2NkT}\sum_{i=1}^{N}\sum_{j=1}^{N-1}\frac{e_i e_j}{r_{ij}}} d\gamma_1 d\gamma_2 \ldots d\gamma_N \tag{2.3}$$

If we take interactions between pairs into account, the situation becomes much more complicated, and indeed makes the practical application of such a distribution law impossible.

A.B. Koudriavtsev et al., *The Law of Mass Action*

Note, however, that by using Maxwell – Boltzmann statistics it is in fact possible to describe the interaction of a single molecule with another one, while neglecting the interactions with all other molecules. The first molecule is then placed at the origin of the coordinate system and considered as fixed. The distribution law will then be:

$$dN = Ae^{-\frac{1}{2mkT}\left(p_{2x}^2+p_{2y}^2+p_{2z}^2\right)+\frac{e_1e_2}{r_{12}}}dp_{2x}dp_{2y}dp_{2z}r^2dr\sin\theta\,d\theta\,d\varphi \qquad (2.4)$$

A second consideration is connected with the fact that the Boltzmann – Planck relationship between entropy and probability (hence all the derived expressions for thermodynamic properties) was obtained by assuming that the state of an individual constituent of a system is independent of the actual states of the other constituents. In Maxwell – Boltzmann statistics such a constituent is a molecule (a particle). *Therefore it is in principle wrong to introduce molecular interactions into Maxwell – Boltzmann statistics.*

The reasons shown above are true, not only for a Maxwell – Boltzmann distribution, but for any statistical description. Therefore, statistical mechanical methods should only be applied to systems of non-interacting units. It is possible to circumvent this problem by selecting, in a system of interacting molecules, the units, which are at least approximately, statistically independent. Such a unit can be part of a system sufficiently large so as to make the energy of molecular *interactions at boundaries* negligibly small when compared to the energy of interactions within the unit itself.

In order to illustrate this, Fig. 2.1 shows a collection of 64 atoms of sodium forming a distorted simple cubic lattice. In such a lattice the number of spheres contained in the cube with n atoms along its side is n^3 and the number of atoms on the surface is $6n^2 - 12n + 8$. The fraction of atoms on the surface therefore is $6/n - 3/4n^2 + 4/n^3$. For the cluster shown in Fig. 2.1A ($n = 4$) it is 0.875 but for a cube of 100 molecular diameters it is 0.05 (see the curve in Fig. 2.1B). In fact, a 99% statistically independent unit must have *ca.* 500 atoms along the side of the cube. It will contain 1.25×10^8 atoms (or molecules).

According to Gibbs, the statistical mechanics of real systems must therefore employ such units as its elements. Another concept in statistical mechanics is that the development of a system over time can be substituted by a static picture of *an ensemble of systems*. A statistical ensemble is a collection of a large number of macroscopic systems, identical in nature, existing under identical external conditions. These systems are imaginary replicas of one another having identical laws of interaction between particles. They differ by the actual values of the momenta and the coordinates of each particular molecule and thus represent all possible microstates of a system.

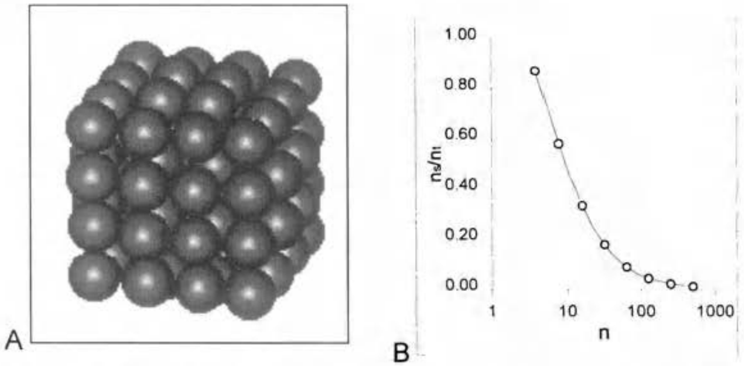

Fig. 2.1. A unit containing 64 atoms of sodium. Only a small number of atoms is confined within the unit and therefore such a collection of atoms strongly interacts with its neighbours. The right-hand graph shows the ratio of the number of surface atoms to the total as a function of the number of atoms along the side of the cube.

During the process of a measurement of any macroscopic property, a system is developing from one microstate to another in succession. The parameters of real macroscopic systems measured experimentally are therefore the time-averaged mean values. This process can be investigated theoretically employing a model system of some number of particles and performing 'molecular dynamics' calculations. In this case the mean values of parameters[1] over time are computed. We can also find the mean over the ensemble values of the same parameters, provided the distribution law for the ensemble is known The main hypothesis of statistical physics, called the *ergodic hypothesis*[2], is that the *mean over time is equal to the mean over the ensemble.*

Several forms of the distribution law can be obtained depending on the assumed type of interaction of a system with the 'outer world'. A system can be *imagined* as

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[1] One can try the HyperChem® program on a small collection of atoms (*e.g.* over the range 10 – 20 atoms).

[2] Note that Boltzmann's definition of the ergodic hypothesis was as follows. A representative point of a system necessarily goes through all possible states corresponding to a given energy before returning to the initial point. It is equivalent to the suggestion that the phase trajectory of an isolated system goes through every point of the hypersurface corresponding to constant energy. Today it is known that the phase trajectory cannot cover all points of a surface without crossing itself and it has also been shown that *the means over time are the means over the phase trajectory.* In order.to show the truth of the ergodic substitution it is then necessary to know *how these trajectories are arranged in an energy layer.* This is the subject of the *ergodic theory* developed by Birkhoff, Neumann and Kolmogorov. It has been demonstrated that the ergodic theorem holds if the considered system is *metrically transitive, i.e.* the corresponding *phase space can not be divided into finite regions containing whole trajectories.* The criterion of ergodicity was thus substituted by the criterion of transitivity. Unfortunately all efforts to find a definite criterion of ergodicity are not yet crowned with success, in fact, the results seem to be negative, *i.e.* there are several demonstrations that the suggested criteria do not work. Therefore up to now the ergodic hypothesis remains a hypothesis or postulate.

being completely isolated from the surroundings without any exchange either by energy or by matter. The amount of energy is the same for all systems in such an ensemble; they differ, however, by the actual values of *coordinates and momenta* of the molecules. Gibbs called this statistical ensemble a *microcanonical ensemble.* It cannot in reality be physically modelled, however, as collections of identical numbers of molecules encapsulated in absolutely insulating shells.

It is also possible to allow a system to exchange with its surroundings by energy but not by matter. Such a system can be imagined by separating a small part of a large system with an elastic shell impenetrable for molecules but transparent to energy. This ensemble can be physically modelled using *liquid membranes*, or *vesicles* (Fig. 2.2) which are formed when an appropriate surfactant is added to a mixture of an oil and water (or aqueous solution) in certain proportions. The vesicles are dispersed in the aqueous continuous phase which plays the role of a heat reservoir or 'outer world'[3] The *canonical ensemble* corresponds to the case when the volume, or rather the heat capacity, of the heat reservoir is much higher than the heat capacity of the systems contained within shells. The energy exchange between systems and the heat reservoir does not then change the temperature of the latter.

If shells become penetrable to the molecules confined within vesicles (in the model discussed here it can be easily achieved by adding some transport mediator to the oil) then we get an ensemble of *open systems* which are able to exchange particles with the surroundings (the continuous phase). The *grand canonical ensemble* corresponds to such a system if the number of exchanging particles in the continuous phase is much larger than that in vesicles (exchange does not then alter the composition of the surroundings).

The details of the mathematical formalism of statistical thermodynamics can be found in numerous textbooks. Hence only the main concepts and an outline of the arguments leading to the relationships between thermodynamic parameters and partition functions in systems of interacting molecules will be given below.

Statistical mechanics in the form suggested by Gibbs does not employ 'thermodynamic probabilities', it uses the probabilities normalised to unity and expressed in terms of the *probability density* $\rho(p,q,t)$:

$$dW(p,q,t) = \rho(p,q,t)dp\ldots dq \tag{2.5}$$

in which dW is the probability of a mechanical state of a system to be characterised by the values p,q within the range $dp\ldots dq$ at time t. The probability W is normalised to unity:

$$\int\ldots\int\rho(p,q,t)dp\ldots dq = 1 \tag{2.6}$$

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[3] Real vesicles contain different numbers of molecules and so a statistical ensemble cannot be accurately modelled in this way. They do, however, represent many of the features of such an ensemble.

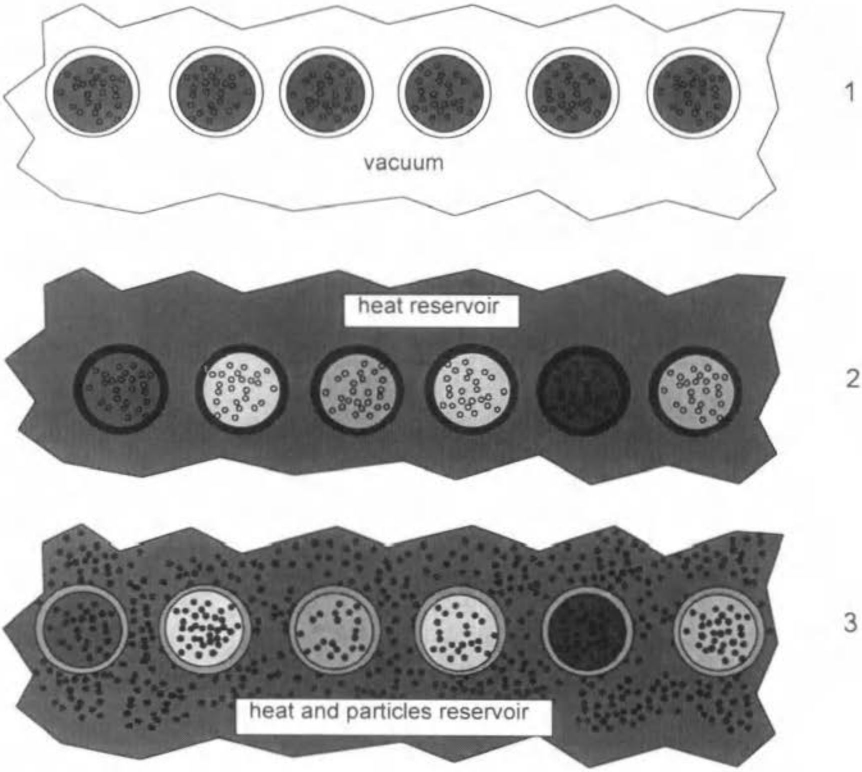

Fig. 2.2. Physical models of microcanonical (1), canonical (2) and grand canonical (3) ensembles. In the cases of *microcanonical* and *canonical* ensembles, each shell contains *the same number of particles*. The shell of a system of the *canonical* ensemble is *energy-transparent*. The shell of a system belonging to a *grand canonical* ensemble is penetrable by both *energy and particles*. The varying shades of canonical and grand canonical ensembles represent the *fluctuations* of the mean energy. The systems of grand canonical ensembles also experience fluctuations in the number of particles.

The probability density, ρ, then has the dimension $[p \times q]^{-3N}$. Being multiplied by $N!h^{3N}$ it becomes a *dimensionless multiplicative* quantity called the *normalised probability density*:

$$\widetilde{\rho} = N!h^{3N}\rho \tag{2.7}$$

The probability dW is equal to the fraction of representative points to be found within the given element of phase space, $d\Gamma = dp... dq$, in the vicinity of the point p, q:

$$dW = \delta\ell(p,q,t)/\ell \tag{2.8}$$

in which ℓ is the number of systems in an ensemble (ℓ being a very large number),

$\delta\ell$ is the number of systems the state of which is determined at the given time t by the values of momenta and coordinates belonging to the element $dp...dq$ in the vicinity of p,q. The *density of representative points* $P(p,q,t)$ is then defined as:

$$\delta\ell(p,q,t) = P(p,q,t)dp\ldots dq \tag{2.9}$$

The relationship between ρ, P and ℓ is thus given by:

$$\rho(p,q,t) = \frac{\delta\ell(p,q,t)}{\ell\, dp\ldots dq} = \frac{P(p,q,t)}{\ell} \tag{2.10}$$

A state characterised by a given amount of energy (E) corresponds to a number (which might be very large) of all possible combinations of p and q, *i.e.* to some number of *phase points* forming a surface (or, rather, a *layer* of thickness $dp = (2mdE)^{1/2}$) in phase space. A function characterising the distribution of molecules over different energy layers is called the *energy distribution function* $f(E)$. It is defined *via* the probability of a phase point belonging to an energy layer:

$$dW(E) = f(E)dE = \rho d\Gamma(E) \tag{2.11}$$

in which $d\Gamma(E)$ is the volume of the energy layer in phase space. This type of distribution can also be characterised by the corresponding density, namely the *energy density of states* $g(E)$ defined by:

$$g(E) = \frac{d\Gamma(E)}{dE} \tag{2.12}$$

$$f(E) = \rho\frac{d\Gamma(E)}{dE} = \rho g(E) \tag{2.13}$$

The actual form of the energy density of states can be found for a given model system. Using the derivation for the ideal gas shown in Appendix 10.2.2 results in:

$$g(E) = \frac{3N}{2}V^N E^{\frac{3N}{2}-1}\left(\frac{4\pi me}{3N}\right)^{\frac{3N}{2}} \tag{2.14}$$

The energy density of states is a sharply rising function of volume and energy as well as of the number of molecules.

When a distribution law is known it is possible to calculate the *mean over the ensemble* value of any property $U(p,q)$ at a given time t:

$$\langle U(t)\rangle = \int\limits_p\int\limits_q U(p,q)\rho(p,q,t)dp\ldots dq \tag{2.15}$$

The experimental value of the same property is the *mean over the observation period* τ. From the point of view of a statistical ensemble it can be written as:

$$U_\tau = \frac{1}{\tau}\int_t^{t+\tau} U(p,q)dt(p,q) \tag{2.16}$$

According to the *ergodic hypothesis*, these two types of mean value *are identical:*

$$\langle U(t)\rangle \equiv U_\tau \tag{2.17}$$

In general, experimental values might be functions of both the actual time t and the measurement time τ. (The use of proper techniques, however, enables the latter dependence to be ignored.) But it must be noted that a system, even under perfectly constant external conditions, might be developing over time, *i.e.* the *observed properties might be changing.*

2.2.
The process of equilibration and increasing entropy

A generally accepted rule (based on experimental observations) is that after a sufficiently long time a macroscopic isolated system will come to a state characterised by *stationary* and *uniform* parameters in which it can remain for an indefinitely long time (without any 'external assistance'). This state is called the *state of equilibrium.* The probability density ρ in a state of equilibrium is therefore independent of time (the measured value of any property (U) is then also independent of time). Mathematically, this means that the *partial* derivative of ρ with respect to time is zero:

$$\left(\frac{\partial \rho}{\partial t}\right)_{pq} = 0 \tag{2.18}$$

$$\rho = \rho(p,q) \neq f(t) \tag{2.19}$$

The time required for a system to come to the state of equilibrium is called the *relaxation time.* An important property of the relaxation time is that it is *longer* for systems containing *larger* number of particles.

Considering a large isolated system developing from a state of non-equilibrium we notice that at some intermediate time separate *parts* of the whole system must achieve equilibrium because they contain *smaller* number of particles. We can then describe the whole system (still in a non-equilibrium state) as divided by partitions into a number of subsystems each being in the state of *local equilibrium.* The number of microstates in which the whole system can realise itself is certainly smaller than that of a system with uniform parameters because we are not able to arrange partitions in any other way.

In other words the phase volume corresponding to these states is certainly only a part of the phase volume corresponding to the system in its (final) equilibrium state (when we may arrange partitions in an arbitrary manner and all subsystems will still be in a state of local equilibrium). The probability of a system being in equilibrium is thus always higher than the probability of the same system being in any one of the possible non-equilibrium states. This means that the most probable ensemble corresponds to the state of equilibrium in the isolated system. According to formal thermodynamics, equilibrium in an isolated system is characterised by a maximum value of the entropy. The maximum of probability corresponds then to a maximum in the thermodynamic entropy.

We have in this way demonstrated the *identity of statistical and thermodynamic entropies*. The starting point was the *empirical postulate* of the constancy of properties of macroscopic systems in equilibrium and the assumption (which can be justified logically) that the relaxation time is longer for systems containing larger number of molecules.

The *Liouville theorem* demonstrates that in any case the *complete derivative* of the probability density is zero:

$$\frac{d\rho}{dt}=\left(\frac{\partial\rho}{\partial t}\right)_{pq}+\sum_i\left[\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i\right]=0 \tag{2.20}$$

This means that the density of phase points remains constant *during their motions along phase trajectories*. Employing the Hamilton equations (see Appendix 10.1), (2.20) can be transformed into:

$$\frac{d\rho}{dt}=\left(\frac{\partial\rho}{\partial t}\right)_{pq}+\sum_i\left[\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i}-\frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right]=0 \tag{2.21}$$

Under the conditions of statistical equilibrium, when the partial derivative $(\partial\rho/\partial t)_{p,q}$ is also zero, the Liouville theorem yields the following condition:

$$\sum_i\left[\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i}-\frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right]=0 \tag{2.22}$$

From this condition it follows that the probability density at equilibrium can only be a function of the *integrals of motion* (see Appendix 10.1). For a closed system at equilibrium the probability density is assumed to be a continuous function of only *one* of the integrals of motion *viz.* the Hamiltonian function, *i.e.*:

$$\rho=\rho(H(p,q)) \tag{2.23}$$

The reason for the latter assumption lies in the fact that energy alone characterises a system as a whole, as well as its constituent parts. This is important because $\ln\rho$ is then an *additive* function. The momenta are connected with the motion of a system as a whole, but do not describe (notwithstanding the fact that they are also additive values) the statistical state of the parts of a system. For example, a system confined within a hard immovable shell does not need the values of its momenta for its description because in such a case they are not integrals of motion. The energy (Hamiltonian function) remains for such a system the sole integral of motion. This means that the probability density within a *given energy layer* is constant. It may also be said that the phase points of an *ensemble of isolated systems in equilibrium* are *evenly* distributed over the corresponding energy layer.

2.3.
Microcanonical distribution

A microcanonical ensemble is an ensemble of systems possessing identical amounts of energy. It is a model reflecting the properties of *isolated systems*. Each system is characterised by exactly the same values of total energy H, the number of particles N, and the volume V. The probability density must be zero at all points beyond that corresponding to the actual $H = E$. However, the integral over $\rho d\Gamma$ must be normalised to 1 which makes ρ infinitely high at this point. This inconvenience can be avoided employing δ-functions or by supposing there to be a very small but finite thickness of the energy layer $H = E-(E+\Delta E)$. The probability density ρ is then defined as being constant within this small range and zero beyond it. The normalisation to unity of the probability of finding the system in the energy layer $E-(E+\Delta E)$ leads to:

$$\int \rho d\Gamma = \rho_0 \int_{E \le H \le E + dE} d\Gamma = \rho_0 \Delta\Gamma(E) = 1 \tag{2.24}$$

Accordingly the probability densities are:

$$\rho_0 = 1/\Delta\Gamma(E) \tag{2.25}$$

Similarly the energy distribution function for systems of a microcanonical ensemble is equal to some finite constant within $H = E-(E+\Delta E)$ and zero beyond it, *i.e.* $f(E)$ is given by:

$$\begin{aligned} f(E) &= \rho_0 g(E) = const && at \quad E < H < E + \Delta E \\ f(E) &= 0 && at \quad E > H > E + \Delta E \end{aligned} \tag{2.26}$$

This distribution therefore defines, very sharply, possible values of the energy and other macroscopic properties, which might be convenient for exactly acting mechanisms or organisms. Unfortunately, this type of ensemble is inconsistent with the idea of life.

2.4
Canonical distribution

A canonical ensemble is a model reflecting the properties of a system in a thermostat. The shell of a canonical ensemble is impenetrable by particles but transparent to energy. The combined system including the canonical ensemble and its surroundings (heat reservoir) is treated as an isolated system, *i.e.* belonging to a microcanonical ensemble. Under these conditions the distribution law can be derived (see Appendix 10.3) in the following form:

$$dW(p,q) = \frac{A}{N!h^{3N}} e^{\beta H(p,q)} dp, dq \tag{2.27}$$

where $dW(p,q)$ is the probability of the microstate characterised by a set of coordinates and momenta q and p; A is an integration constant and β is some parameter characterising both the system in question and the heat reservoir. The probability, W, can then be normalised to unity:

$$\frac{A}{N!h^{3N}} \int \cdots \int e^{\beta H(p,q)} dp, dq = 1 \tag{2.28}$$

Simple arguments show that β must be negative: for large positive H the normalisation (2.28) is only possible when $\beta < 0$. The coefficient β is then defined as:

$$\beta = -1/\theta \tag{2.29}$$

in which θ is the *modulus of canonical distribution.* The probability density then becomes:

$$\rho(p,q) = \frac{A}{N!h^{3N}} e^{-\frac{H(p,q)}{\theta}} \tag{2.30}$$

The integration constant A can be defined as:

$$A = e^{\frac{F}{\theta}} \tag{2.31}$$

in which F is some unidentified function. The probability density then becomes:

$$\rho(p,q) = \frac{1}{N!h^{3N}} e^{\frac{F - H(p,q)}{\theta}} \tag{2.32}$$

Separating the term e^{F} and applying the normalisation condition (2.28) leads to:

$$\int \cdots \int \rho(p,q) dp,dq = \frac{e^{\frac{F}{\theta}}}{N!h^{3N}} \int \cdots \int e^{-\frac{H(p,q)}{\theta}} dp,dq = 1 \tag{2.33}$$

and hence:

$$e^{-\frac{F}{\theta}} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\frac{H(p,q)}{\theta}} dp,dq \tag{2.34}$$

The expression on the right hand side of (2.34) is an analogue of the partition function of the modified Maxwell – Boltzmann statistics:

i.e.

$$Z = e^{-\frac{F}{\theta}} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\frac{H(p,q)}{\theta}} dp,dq \tag{2.35}$$

The function F can then be expressed as:

$$F = -\theta \ln Z \tag{2.36}$$

This is readily seen to be a statistical analogue of the Helmholtz function (1.51). The *energy distribution function* for a system of a canonical ensemble thus becomes:

$$f(E) = \rho g(E) = \frac{e^{\frac{F-E}{\theta}}}{N!h^{3N}} g(E) \tag{2.37}$$

The energy density of states $g(E)$ is an increasing function of energy (see (2.14) above) whilst the other part of the distribution function, $e^{(F-E)/\theta}$, is a decreasing function of energy. Therefore *f(E)* has a maximum at the *most probable energy* of a system, E^*. Using (2.14) for the energy density of states $g(E)$, and assuming (a little ahead of the explanation given later) that $\theta = kT$ and $R = Nk$, the expression for the energy distribution function *f*(E) can be written as:

$$\begin{aligned} f(E) &= \frac{e^{\frac{F-E}{\theta}}}{N!h^{3N}} \frac{3N}{2} V^N E^{\frac{3N}{2}-1} \left(\frac{4\pi me}{3N}\right)^{\frac{3N}{2}} = \\ &= \left[e^{\frac{F-E}{RT}} \left(\frac{E}{RT}\right)^{\frac{3}{2}}\right]^N \left(\frac{E}{RT}\right)^{-1} \frac{3N}{2RT} e^{\frac{3N}{2}} \left[\frac{eV}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]^N \end{aligned} \tag{2.38}$$

We have already calculated the last term in square brackets for a gas at atmospheric pressure (Chapter 1, page 31) as 0.0259 $M^{3/2}T^{5/2}$. It is therefore not difficult to simulate the distribution function $f(E)$ for given T, V, M and N (see Fig. 2.3).

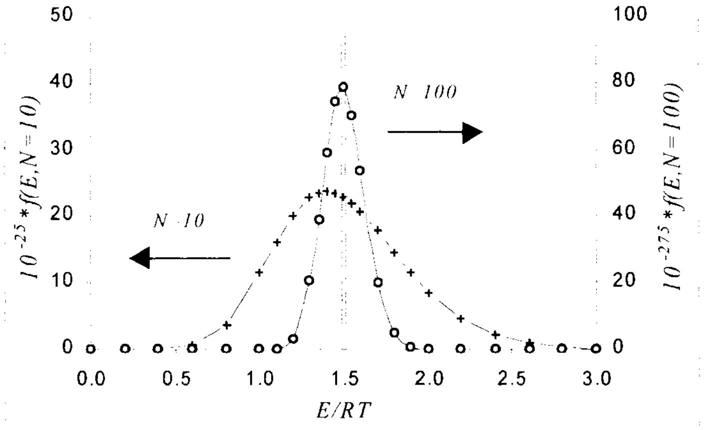

Fig. 2.3. Energy distribution functions of canonical ensembles containing 10 and 100 particles (note the difference in scales) characterised by $F = 0$ and $M = 32$ at $T = 300$ K. The energy distribution function for a microcanonical ensemble is given for comparison, using an arbitrary scale

The dependence of $f(E)$ on energy is given by the term:

$$e^{-\frac{NE}{RT}} E^{\frac{3N}{2}-1} \tag{2.39}$$

This function has a maximum at $E^*/RT = (3N-2)/2N$, *i.e.* approaching the (expected) value of $E^* = (3/2)RT$ at $N >> 1$. When the number of molecules, N, is small, the curve $f(E)$ is asymmetric. With increasing N the 'linewidth' of this distribution decreases and this means that for systems containing about one mole of a substance the canonical distribution will be as sharp as for a microcanonical distribution. Then the most probable energy E^* would equal the mean energy $<E>$ to very high precision.

2.5
The probability of a macrostate

A macroscopic state may be considered as defined if we have a knowledge of a certain number of parameters forming the vector $\mathbf{X}(X_1,X_2,X_3,..X_P)$. A very large number of combinations of coordinates and momenta of molecules correspond to one and the same vector **X**. In phase space, therefore, a macrostate is depicted by an element of volume $\Delta\Gamma(\mathbf{X})$ containing a large number of representative points. The larger this volume the higher is the probability of the corresponding macrostate:

$$W(\mathbf{X}) = \int_{\mathbf{X}}^{\mathbf{X}+\Delta\mathbf{X}} \rho \, d\Gamma(\mathbf{X}) \tag{2.40}$$

In the case of a microcanonical distribution the probability density is constant and can therefore be moved outside the integral in (2.40), which results in:

$$W(\mathbf{X}) = \int_{\mathbf{X}}^{\mathbf{X}+\Delta\mathbf{X}} \rho_0 \, d\Gamma(\mathbf{X}) = \rho_0 \, \Delta\Gamma(\mathbf{X}) \tag{2.41}$$

Next, the *statistical weight* of a macrostate corresponding to the energy E can be defined as the *fraction of the phase volume* that it occupies in the energy layer. For a microcanonical distribution ($\rho = const$) we then get a simple relationship:

$$W(\mathbf{X}) = \frac{\Delta\Gamma(\mathbf{X})}{\Delta\Gamma(E)} \tag{2.42}$$

At equilibrium, measurable parameters of macroscopic homogeneous bodies are constant and uniform to a very high degree of precision. This empirical observation indicates that the *macrostate characterised by a set of equilibrium parameters* has the highest probability (approaching 1). Otherwise significant deviations of measurable parameters from their equilibrium values would be regularly observed. We can thus say that *the most probable macrostate corresponds to the state of equilibrium* and representative points belonging to this macrostate occupy nearly the whole energy layer:

$$W(\mathbf{X}^*) = \frac{\Delta\Gamma(\mathbf{X}^*)}{\Delta\Gamma(E)} \approx 1 \tag{2.43}$$

$$\Delta\Gamma(\mathbf{X}^*) \cong \Delta\Gamma(E) \tag{2.44}$$

The deviations of parameters from their equilibrium values (normally very small for macroscopic systems) are called *fluctuations*. The larger the number of particles the smaller are the fluctuations. It will be shown later (Section 2.8) that the *relative* fluctuations of energy in an ideal gas are about $N^{-1/2}$.

2.6

Thermodynamic functions derived from a canonical distribution

Let us consider a macrostate characterised by a single parameter, namely the mean energy $<E>$. According to the principles discussed above, the 'statistical entropy' of any macroscopic system must be proportional to the logarithm of the normalised volume of the phase space containing representative points, *i.e.* to the number of quantum states of the system:

$$\Delta\Omega = \Delta\Gamma / N! h^{3N} \tag{2.45}$$

Representative points of the macrostate characterised by <*E*> occupy the volume of phase space ΔΓ(<*E*>). Two features of this macrostate *in equilibrium* are important: (i) the fluctuations of energy are very small, therefore the mean and most probable energies coincide (<*E*> ≅ *E**), and (ii) the probability of such a macrostate approaches unity:

$$\rho(E^*)\Delta\Gamma(E^*) \cong 1 \tag{2.46}$$

The volume of phase space ΔΓ(*E**) is then just the inverse of the probability density:

$$\Delta\Gamma(E^*) \cong 1/\rho(E^*) \tag{2.47}$$

The statistical entropy for such a state can then be written as:

$$S = k \ln\left(\Delta\Gamma / N! h^{3N}\right) = -k \ln\left[N! h^{3N} \rho(E^*)\right] \tag{2.48}$$

Using the expression for the probability density for canonical distribution (2.32) we get:

$$S = -k(F - E^*)/\theta \tag{2.49}$$

in which *E** = <*E*> is the canonical mean of the internal energy, which, according to the ergodic hypothesis, is equal to the observed (*mean with respect to time*) internal energy *E*. The entropy *S* (we have demonstrated the identity of statistical and thermodynamic entropies above) is then obtained as:

$$S = -k(F - E)/\theta \tag{2.50}$$

The partial derivative of entropy with respect to internal energy is thus the inverse modulus of the canonical distribution. In formal thermodynamics this derivative is $1/T$:

$$\partial S/\partial E = k/\theta = 1/T \tag{2.51}$$

The modulus of canonical distribution is thus $\theta = kT$. The function, *F*, of the canonical distribution then becomes identical with the Helmholtz free energy:

$$F = E - TS \tag{2.52}$$

The Helmholtz free energy can thus be expressed, *via* the partition function of canonical distribution, (2.33) and (2.36), as:

$$F = -k \ln Z \tag{2.53}$$

in which:

$$Z = e^{-\frac{F}{\theta}} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\frac{H(p,q)}{\theta}} dp, dq \qquad (2.54)$$

Equation (2.54) is the main relationship between the partition function of a canonical distribution and the thermodynamic functions. All other relationships are obtained *via* F and its derivatives using the corresponding formulae of thermodynamics:

Entropy	$S = -(\partial F/\partial T)_{V,N}$	$= k[\ln Z + T(\partial \ln Z/\partial T)_{V,N}]$	(2.55)
Pressure	$p = -(\partial F/\partial V)_{T,N}$	$= kT(\partial \ln Z/\partial V)_{T,N}$	(2.56)
Internal energy	$E = F + TS$	$= kT^2(\partial \ln Z/\partial T)_{V,N}$	(2.57)
Enthalpy	$H = E + pV$	$= kT[T(\partial \ln Z/\partial T)_{V,N} + V(\partial \ln Z/\partial V)_{T,N}]$	(2.58)
Gibbs free energy	$G = F + pV$	$= -kT[\ln Z - V(\partial \ln Z/\partial V)_{T,N}]$	(2.59)
Chemical potential	$\mu_i = (\partial F/\partial n_i)_{T,V,nj}$	$= -kT(\partial \ln Z/\partial n_i)_{T,V,nj\neq i}$	(2.60)
Specific heat	$C_V = (\partial E/\partial T)_V$	$= k[T^2(\partial^2 \ln Z/\partial T^2)_V + 2T(\partial \ln Z/\partial T)_V]$	(2.61)

2.7
Some molecular partition functions

The fundamental significance of the relationships obtained in the preceding Section is that they show the possibility of a statistical mechanical description of systems of interacting molecules. For practical purposes this formalism gives very little directly: the partition function of a canonical distribution defined by (2.54) does not refer to molecular parameters but suggests that the Hamiltonian function of a system is known (as a function of the coordinates and momenta of the molecules). As it will be shown in Chapters 4 – 7, the derivation of formulae for the calculation of thermodynamic functions for even the simplest model of non-ideal systems is extremely complicated. Fortunately, the systems of interacting particles can be considered (at least over a narrow range of variation of conditions and parameters) as *perturbed* ideal systems of *independent molecules*. The total partition function Z (to be used in calculations of thermodynamic functions) is then the product of the partition functions of molecules:

$$Z = \prod_{i=1}^{N} z_i \qquad (2.62)$$

In such cases the building block of a statistical description is the *molecular partition function, z*. Several important partition functions will be derived below.

2.7.1
Degeneracy

If the energy levels of a molecule are so close together that the difference $\delta\varepsilon = \varepsilon_i - \langle\varepsilon\rangle$ is always negligibly small then the sum over ε_i within this range can be substituted by the term $g\exp(-\langle\varepsilon\rangle/kT)$ where the *degeneracy factor* g plays the role of the statistical weight of an energy level. What energy differences can be considered as negligible? The lowest limit is obviously set by the fluctuations, and at the end of this Chapter we shall consider this limit in some detail. In practice however the precision of the calculation of the partition function plays the crucial role. If the variation of energy within a level $\delta\varepsilon$ is such that $g\exp(|\delta\varepsilon|/kT)$ is smaller than the required relative precision of the calculation of the partition function, then such a level can be considered as degenerate.

The energy levels of molecules having *rotational degrees of freedom* are $(2J+1)$ times degenerate (J is the rotational quantum number), each state corresponding to different orientation of the angular momentum of such a molecule. Similarly the orientation of the *nuclear spin* of each atom in a molecule results in a separate state. However, this type of degeneracy is usually not taken into account because nuclear spin is not changed in chemical reactions (an exception is the *ortho – para* hydrogen equilibrium in which the interactions between nuclear spins are significant).

Degeneracy of a molecule (atom) is often connected with *electronic degeneracy*. In highly symmetrical systems, electronic energy levels are usually degenerate, but external fields and distortions of symmetry may remove this degeneracy. For example, the state of a free ion of a transition metal containing one electron in the *d*-level is 10 times degenerate. In other words, an electron can be placed in any of the 5 *d*-orbitals of such an ion with the projection of *electronic spin* $S_z = \pm\frac{1}{2}$ and the energy will be the same.

In *octahedral* complexes the energy level of the *d*-electrons is split in the field created by the ligands into a doubly degenerate e_g sub-level and a triply degenerate t_{2g} sub-level. The unpaired electron in a Ti(III) octahedral complex may therefore occupy any of the t_{2g} orbitals (d_{xy}, d_{xz} or d_{yz}), all these states having identical energy that is lower than the energy of the e_g orbitals. In the absence of an external magnetic field the states corresponding to $S_z = \pm\frac{1}{2}$ are also degenerate and hence the total degeneracy of the ground state of an octahedral Ti(III) complex is 6.

Quite common distortions of octahedral symmetry destroy the *orbital degeneracy* and the remaining spin-degeneracy ($g = 2$ corresponding to $S_z = \pm\frac{1}{2}$) may be removed by an external magnetic field including the magnetic field of the Earth. In Section 2.8 we will discuss these possibilities.

In the majority of cases the degeneracy factor is all that is left of the electronic partition function. The distances between ground state and first (and further) excited states of molecules are so large that the ground state alone is populated to any extent and:

$$z_{el} = g_0 e^{-\varepsilon_0/kT} \tag{2.63}$$

The energy of an electronic system in this state can be taken as *the zero point of the energy scale* ($\varepsilon_0 = 0$) that is:

$$z_{el} = g_0 \tag{2.64}$$

However, in a system containing molecules of different kinds the ground state of only one type of molecule can be taken as corresponding to zero potential energy. Therefore the representation of the electronic partition function by the degeneracy factor alone might be misleading. Also in those cases where the first excited state is not much above the ground state the electronic partition function (assuming $\varepsilon_0 = 0$) is:

$$z_{el} = g_o + g_1 e^{-\varepsilon_1/kT} \tag{2.65}$$

This relationship is sometimes interpreted as a temperature dependence of the degeneracy factor.

2.7.2
Translational motion

The energy of one-dimensional motion is generally given by:

$$\varepsilon = mv^2/2 = p^2/2m \qquad \text{(2.66}$$

We have, however, to deal with systems of finite dimensions, *i.e.* confined to a vessel with some characteristic length l. For a particle in a uni-dimensional potential well of length l the energy may also be written using the de Broglie wavelength λ:

$$\varepsilon = (h/\lambda)^2/2m\,; \qquad \lambda = 2l/n; \qquad n = 1,2,3,\ldots \tag{2.67}$$

Therefore:

$$\varepsilon = h^2n^2/8ml^2 \tag{2.68}$$

The partition function:

$$z = \sum_{n=1}^{\infty} \exp\left(-\frac{h^2n^2}{8ml^2kT}\right) \tag{2.69}$$

may be approximated (except in the case of particles of low mass at low temperatures) by the integral:

$$z = \int_0^{\infty} e^{-an^2}\,dn \tag{2.70}$$

in which $a = h^2/8ml^2kT$.

This integral equals $(\pi/4a)^{1/2}$, and therefore:

$$z = \left(\frac{2\pi mkT}{h^2}\right)^{1/2} l \tag{2.71}$$

When a molecule is allowed to move in *two dimensions*, the corresponding partition function is the product of the partition functions for one-dimensional motion along each coordinate (the movement along each coordinate is considered independent):

$$z = \left(\frac{2\pi mkT}{h^2}\right)^{1/2} l_1 \left(\frac{2\pi mkT}{h^2}\right)^{1/2} l_2 = \frac{2\pi mkT}{h^2}\Omega \tag{2.72}$$

The same is true for *three-dimensional motion* in a cubic *cell* with side of length l or volume v. If we have N particles in the volume $V = Nv$ and *each particle is confined* to such a cell, then:

$$z_{cell} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} v = q_{cell} v \tag{2.73}$$

In a collection of N particles moving in the volume V, the average volume per molecule can be equal to the volume of a cell, $v = V/N$. However, the molecular partition function in such a case will have an additional factor arising from the indistinguishable nature of molecules. Suppose that we have a crystal at the temperature of melting, but still a crystal (Fig. 2.4). The molecules are confined to their cells, each of volume $v = V/N$. This is a system of *localised states* and the partition function for seven non-interacting molecules in adjacent cells of the first row is $(q_{cell}v)^7$. When we apply a little heat, the molecules in the surface layer begin to move freely in this layer. This results in (i) the molecules of this layer becoming *indistinguishable* and (ii) the volume accessible for any one molecule becoming correspondingly larger.

We must therefore divide the partition function by the number of indistinguishable combinations and take into account the increased volume. For the seven molecules shown in Fig. 2.4 the partition function will be $(q_{cell}7v)^7/7!$. When all N molecules move freely within the volume Nv the partition function becomes $(q_{cell}Nv)^N/N!$ Using the Stirling approximation we get the partition function of a system of N molecules in the volume vN and in the state of an ideal gas:

$$Z = z^N = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} ev\right]^N \tag{2.74}$$

This means additional entropy of such a system compared to that calculated employing the partition function (2.73).

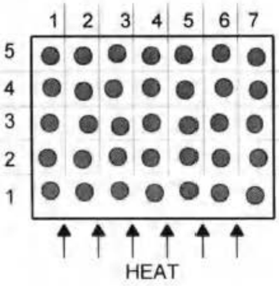

Fig. 2.4. The result of free migration of molecules

2.7.3
Free rotation

In general, the allowed values of the energy of a rotating particle having a non-zero moment of inertia I are:

$$\varepsilon_J = \frac{J(J+1)h^2}{8\pi^2 I}; \qquad J = 1,2,3\ldots \tag{2.75}$$

The rotational energy levels are degenerate: each energy level characterised by the quantum number J can be realised in $2J + 1$ ways corresponding to different orientations of the angular momentum vector of a molecule. The partition function contains, therefore, a corresponding statistical weight (degeneracy factor):

$$z = \sum_J (2J+1)\exp\left(-\frac{J(J+1)h^2}{8\pi^2 IkT}\right) \tag{2.76}$$

The energies of rotation are in general comparable with kT. We may not therefore expand exponents into series, although it is possible to substitute summation by integration because rotational levels lie close together (separated by energies of the order of hundreds of GHz). On substituting $J + ½ = x$, and $h^2/8\pi^2 IkT = b$ the rotational partition function may be written as:

$$z = \int_0^\infty e^{-bx^2}\, 2x dx = 1/b = 8\pi^2 IkT/h^2 \tag{2.77}$$

When a molecule is symmetric with respect to the rotational axis, some states are indistinguishable and the partition function must therefore be divided by the symmetry number σ:

$$z = 8\pi^2 IkT/\sigma h^2 \tag{2.78}$$

For a molecule with three unequal moments of inertia $I_{A,B,C}$ the rotational partition function becomes:

$$z_r = \pi^{1/2}\left(8\pi^2 kT\right)^{3/2}\left(I_A I_B I_C\right)^{1/2}/\sigma h^3 \tag{2.79}$$

2.7.4
Vibrational motion: linear harmonic oscillator

The vibrational motion in an ideal gas belongs exclusively to the internal degrees of freedom. On the other hand in an ideal crystal it is the *only* type of motion allowed for particles constituting such a crystal. The simplest vibrating unit is a diatomic molecule which (being in lower excitation states) may be described as a *harmonic oscillator.* The allowed energy levels of a harmonic oscillator are:

$$\varepsilon = (j + 1/2)h\nu; \qquad j = 0,1,2\ldots \tag{2.80}$$

The partition function may therefore be written as:

$$z = \sum_{j=0}^{\infty} e^{-(j+1/2)h\nu/kT} = e^{-h\nu/2kT}\left[1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \cdots\right] \tag{2.81}$$

The expression in brackets is the expansion of $(1 - e^{h\nu kT})^{-1}$, hence:

$$z = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} = \frac{1}{e^{h\nu/2kT} - e^{-h\nu/2kT}} = \left[2\sinh\frac{h\nu}{2kT}\right]^{-1} \tag{2.82}$$

There is another way of representing vibrational partition functions, namely by employing energies measured from the zero vibrational level, $h\nu/2kT$ (see [2] for example):

$$q_V = 1/\left(1 - e^{-h\nu/kT}\right) \tag{2.83}$$

This method has an advantage in that the partition function for large frequencies (low temperatures) is just 1, reflecting the fact that the molecule can only be in its lowest vibrational state. In a system containing several oscillators each such partition function enters with a weighting factor $\exp(-h\nu_i/2kT)$.

Although in some cases the form (2.83) can advantageously be used, the expression (2.82) is of general validity and will be used throughout this book.

For low energies and high temperatures $\varepsilon \ll kT$ and both expressions are reduced to the *classical statistical integral for a harmonic oscillator*:

$$z \cong kT/h\nu \tag{2.84}$$

The total number of vibrations in a molecule can be calculated from a balance of the available degrees of freedom. In a molecule containing M atoms there are

$3M$ degrees of freedom, of which 3 are connected with the translational motion of the molecule as a whole and another 3 correspond to the rotation of the molecule as a whole. These 6 degrees of freedom per molecule are sometimes referred to as *external degrees of freedom*. The total number of *internal* degrees of freedom is, therefore, $3M-6$. Among them there may be some number (n) of internal rotational degrees of freedom. The remainder, $(3M-6-n)$, are vibrational degrees of freedom.

Translational degrees of freedom are generally considered as statistically independent of internal and rotational degrees of freedom. If an excitation of an internal degree of freedom does not significantly change moments of inertia the *external rotational degrees* of freedom are also statistically independent. If an excitation of an internal degree of freedom does not change moments of inertia and the vibrational frequency of other degrees of freedom, then all *internal degrees of freedom* can be considered as statistically independent. At not very high temperatures these conditions are generally obeyed and the total partition function *of a molecule* can be calculated as the product:

$$z = g\frac{(2\pi mkT)^{3/2}e\upsilon}{h^3}\,\frac{\pi^{\frac{1}{2}}(8\pi^2kT)^{\frac{3}{2}}(I_A I_B I_C)^{\frac{1}{2}}}{\sigma h^3}\prod_{j=1}^{n} z_{jr}\prod_{i=1}^{3M-6-n}\left(2\sinh\frac{h\nu_i}{2kT}\right)^{-1} \tag{2.85}$$

2.7.5
Total partition function of an ideal system

For a collection of N statistically independent particles the total partition function is, of course:

$$Z = z^N \tag{2.86}$$

Some problems arise, however, when taking into account spin degeneracies of paramagnetic molecules. For example, the formulae for the free energy of an ideal crystal given in the book by Moelwyn-Hughes ([1], page 558) suggest that the partition function of a molecule (atom) occupying a centre of a crystal lattice is:

$$z = [g/2\sinh(h\nu/2kT)]^3 \tag{2.87}$$

This expression implicitly assumes that each vibration along a normal coordinate is g-times degenerate. Indeed, when we consider a *molecular crystal* of a neutral paramagnetic complex, for example [Eu(acac)$_3$], the vibrations of the paramagnetic molecule as a whole (lattice vibrations) might be considered as g-times degenerate because the unpaired electron belongs to the central atom and is effectively shielded (f-element) from outer orbitals participating in the formation of chemical bonds. The total partition function in such an interpretation is given by:

$$Z = \left[g/2\sinh(h\nu/2kT) \right]^{3N} \tag{2.88}$$

There are however some weighty arguments against this interpretation, namely that one and the same particle cannot possess simultaneously three different orientations of a spin. On the other hand, there are some experimental facts in favour. The *lowest* experimental value of the entropy of spin crossover (see Sections 3.5 and 7.10) in solids is exactly three times higher than the value expected for z proportional to the first power of g. If we employ (2.88), then the lowest entropy of spin crossover corresponds to the change in electronic degeneracy alone.

In ionic crystals the concept of a molecule cannot be applied and vibrations correspond to the motion of atomic nuclei independent of the electronic system. In such a case the total partition function:

$$Z = g^N / \left[2sh(h\nu/2kT) \right]^{3N} \tag{2.89}$$

corresponds to the molecular partition function proportional to the first power of the degeneracy factor:

2.8
Fluctuations

The empirically based postulate that the parameters of a macroscopic system in equilibrium are constant to a very high precision is not the *whole truth* about equilibria. In fact, this is only true for homogeneous single-phase systems. In the case of two phases in equilibrium, very large variations of parameters can be observed under (seemingly) identical conditions. Let us for example consider a mixture of ice and water in a thermostat at exactly zero Celsius and under atmospheric pressure. Under such conditions, the amounts of the two phases are *completely indeterminate*, being dependent not on temperature but on the amount of heat conveyed to the system! Such a system exhibits a peculiar property indicating large fluctuations, namely an *infinitely high specific heat*. The heat absorbed by a system results not in an increased temperature but in a change of the amounts of coexisting phases. This is an analogue of an indifferent mechanical equilibrium of a ball resting on a horizontal plane whose coordinates are completely indeterminate. Another example of a system exhibiting large fluctuation is a gas/liquid system at the critical point. An infinitely small change of temperature or pressure results in the formation of *observable* quantities of liquid and/or gas phases. This resembles the completely unstable equilibrium of one ball balanced on top of another!

Maxwell – Boltzmann distribution predicts that *individual molecules* may possess energies quite different from the most probable or mean values. According to the concept of canonical distribution, macroscopic quantities of substances may have properties differing from mean values, but only over a very narrow range.

Consider a large isolated system: the energy of such a system is exactly defined (a system belonging to a microcanonical ensemble) and we cannot expect any fluctuation of energy as long as the system remains isolated. However within such a system we can detect small but macroscopic parts (identical in mass, number of molecules *etc.*) whose energy differs from the mean value. These parts constitute either a *canonical ensemble* if they only differ by energy or a *grand canonical ensemble* if they also differ in the numbers of molecules. The *observed* variations of energy and other macroscopic parameters are the corresponding means of deflections and can be predicted on the basis of the actual distribution law. With respect to the system as a whole they are *local fluctuations* and only such fluctuations are allowed for a system of a microcanonical ensemble.

A system belonging to a canonical ensemble may have fluctuations of energy, which we will consider now in some detail.

In general, the mean deflection of a property of a system of canonical ensemble is zero:

$$\langle \Delta\varepsilon \rangle = \langle \varepsilon - \langle \varepsilon \rangle \rangle = \frac{\int \ldots \int \varepsilon\, e^{-H/kT} d\Omega}{\int \ldots \int e^{-H/kT} d\Omega} - \langle \varepsilon \rangle = 0 \tag{2.90}$$

The information about fluctuations is provided by the variance of energy or the mean of the square of deflection:

$$\langle \Delta\varepsilon^2 \rangle = \langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle = \frac{\int \ldots \int \varepsilon^2\, e^{-H/kT} d\Omega}{\int \ldots \int e^{-H/kT} d\Omega} - \frac{2\langle \varepsilon \rangle \int \ldots \int \varepsilon\, e^{-H/kT} d\Omega}{\int \ldots \int e^{-H/kT} d\Omega} + \langle \varepsilon \rangle^2 \tag{2.91}$$

This results in:

$$\langle \Delta\varepsilon^2 \rangle = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = V(\varepsilon) \tag{2.91a}$$

A connection between fluctuations and thermodynamic functions can be obtained by employing the statistical expression for Helmholtz free energy (2.54). The fluctuations should not alter the values of thermodynamic potentials and other functions that determine the equilibrium state of a system; note that formal thermodynamics *does not consider fluctuations at all.* They might, however, affect the *derivatives* of these functions. The derivative of the Helmholtz free energy with respect to temperature is entropy:

i.e.

$$\frac{\partial F}{\partial T} = -S \tag{2.92}$$

This is a *function of state* and can play the role of a potential. It should also be independent of fluctuations. The second derivative of F, on the other hand, is a quantity proportional to the specific heat at constant volume:

$$\frac{\partial^2 F}{\partial T^2} = -\frac{dS}{dT} = -\frac{\delta Q/T}{dT} = -\frac{C_V}{T} \tag{2.93}$$

This parameter is *not a thermodynamic potential* and might be connected with fluctuations of energy. This can be demonstrated directly:

Free energy defined *via* a canonical distribution is:

$$F = -kT \ln \int \ldots \int e^{-\frac{H}{kT}} d\Omega \tag{2.94}$$

The first differentiation yields:

$$\frac{\partial F}{\partial T} = -k \ln \int \ldots \int e^{-\frac{H}{kT}} d\Omega - \frac{1}{T} \frac{\int \ldots \int H e^{-\frac{H}{kT}} d\Omega}{\int \ldots \int e^{-\frac{H}{kT}} d\Omega} \tag{2.95}$$

The second term in (2.95) is proportional to the canonical mean of internal energy ($\langle E\rangle = \langle H\rangle$). Performing a second differentiation we get:

$$-\frac{\partial^2 F}{\partial T^2} = -\frac{\frac{1}{T^2} \int \ldots \int H e^{-\frac{H}{kT}} d\Omega + \frac{-1}{T^2} \int \ldots \int H e^{-\frac{H}{kT}} d\Omega}{\int \ldots \int e^{-\frac{H}{kT}} d\Omega} + \\ + \frac{1}{kT^3} \frac{\int \ldots \int H^2 e^{-\frac{H}{kT}} d\Omega \int \ldots \int e^{-\frac{H}{kT}} d\Omega - \int \ldots \int H e^{-\frac{H}{kT}} d\Omega \int \ldots \int H e^{-\frac{H}{kT}} d\Omega}{\left(\int \ldots \int e^{-\frac{H}{kT}} d\Omega \right)^2} \tag{2.96}$$

The first term on the right hand side of (2.96) is obviously zero; what is left gives us a quantity proportional to the variance of the Hamiltonian function:

$$-\frac{\partial^2 F}{\partial T^2} = \frac{1}{kT^3} \left[\frac{\int \ldots \int H^2 e^{-H/kT} d\Omega}{\int \ldots \int e^{-H/kT} d\Omega} - \left(\frac{\int \ldots \int H e^{-H/kT} d\Omega}{\int \ldots \int e^{-H/kT} d\Omega} \right)^2 \right] = \frac{\langle H^2 \rangle - \langle H \rangle^2}{kT^3} \tag{2.97}$$

Comparing the statistical and thermodynamic second derivatives of F with respect to temperature, (2.93) and (2.97), we get the variance of the total energy

$V(H) = V(E)$ as:

$$V(E) = kT^2 C_V \tag{2.98}$$

Note that this equation is of general applicability, both in ideal and in non-ideal systems. For an *ideal gas* containing N molecules $C_V = (3/2)Nk$ and the variance of energy becomes:

$$V(E) = \frac{3}{2} N k^2 T^2 \tag{2.99}$$

The *relative* mean square deviations of the total energy of such a system (taking into account the fact that $E = (3/2)NkT$) are equal to the inverse square root of the number of particles:

$$\frac{\sqrt{V(E)}}{E} = \frac{kT\sqrt{(3/2)N}}{(3/2)kTN} = \sqrt{\frac{2}{3N}} \cong \frac{1}{\sqrt{N}} \tag{2.100}$$

They are very small for systems containing macroscopic numbers of molecules, and therefore we are able to measure parameters of such systems with very high precision.

Fluctuations, being connected with the second derivatives of thermodynamic potentials, determine the *nature of the change* of these quantities when some parameter (temperature, as in the example above) is varied. This shows that the *stability* of thermodynamic potentials and their derivatives (hence of equilibrium itself) is connected with the magnitude of fluctuations. The larger the fluctuations the less *stable* is the equilibrium, which means that it is easier for a parameter to deviate from its equilibrium values.

When fluctuations become comparable with the equilibrium values of the parameters then the system is *unstable* or is in a state similar to that of mechanical *indifferent equilibrium* as in examples considered at the beginning of this Section. Again, under these conditions the heat capacity approaches infinity, which is observed at the critical point and in phase transitions.

Another asymptotic case is the state of matter at absolute zero: fluctuations are infinitely small $C_V \to 0$ and the energy of a system does not fluctuate from its "average". Any collection of (identical) molecules at absolute zero loses its statistical character.

We have mentioned in the preceding Chapter that devices employing highly organised types of motion are extremely efficient. From this point of view a device working at absolute zero must have maximal efficiency. Indeed electric devices are very close to this ideal situation because the state of an electron gas at room temperature is but slightly different from that at absolute zero.

A living organism cannot be imagined in such a state and therefore its efficiency and determinate behaviour must originate from some other source. We have seen that determined values of parameters of molecular systems can only be expected for systems containing large numbers of molecules (providing for low fluctuations of parameters). The problem worrying '*naive physicist*', and properly formulated by Schrödinger (above), is in fact solved by taking fluctuations into account. A living creature is a self-acting unit showing astonishing reliability and deterministic behaviour incompatible with large fluctuations in the parameters of any part of such an organism or also of a mechanism. Therefore the smallest organisms and/or self-sustaining parts of larger organisms (cells) contain at least $10^7 - 10^9$ molecules. Would these molecules be in the state of an ideal gas, then this number would allow for relative fluctuations of energy of about 10^{-3}, *which is probably not sufficient even for a bacterium* (see also Section 3.7).

The fact that living organisms exist exclusively in the condensed (liquid) state might apparently indicate smaller fluctuations as compared with those in the gas phase. However, the heat capacities of equal amounts of water in the liquid and the gaseous state (18 cal mole^{-1} K^{-1} and $(3/2)R \cong 3$ cal mol^{-1} K^{-1} respectively) yield, according to (2.98), a larger variance of energy for liquid water. The fact is (and we have employed it implicitly deriving the square root rule!) that the *relative* deviation of energy is *inversely* proportional to the square root of heat capacity:

$$\frac{\sqrt{V(E)}}{E} = \frac{\sqrt{kT^2C_V}}{C_VT} = \sqrt{\frac{k}{C_V}}$$

The difference between the gaseous and liquid phase is then in favour of the latter by the factor $\sqrt{6}$, which is not very much. Therefore other factors are also of importance for the preferential existence of life in liquid media. Among these is the possibility of the comparatively easy building of 'shells' separating a living unit from the outer world and thus keeping it in a non-equilibrium state.

Another problem connected with fluctuations is the problem of the degeneracy of energy levels. Let us consider an example of spin-degeneracy in a paramagnetic compound containing one unpaired electron. All chemical experiments (except those carried out in space laboratories) are affected by the magnetic field of the Earth and that, in principle, removes this degeneracy. The resonance frequency (ESR) of such a system in the magnetic field of the Earth is of the order of 3 MHz and this resonance can be observed on samples containing $N \cong 10^{-2} N_L$ molecules. The energy of such an ESR transition is much larger than the fluctuation of energy (calculated using an average heat capacity (100 cal K^{-1}) of 0.01 mol of a compound of elements of the first half of the Periodic Table with molecular mass $M = 300$ g):

$$Nh\nu = 6.02\times10^{21}\times6.62\times10^{-27}\times3\ 10^6 = 119.5 \text{ erg}$$

$$V(E) = kT^2C_V = 1.38\times10^{-16}\times9\times10^{-4}\times100\times4.18\times10^7 = 5.19\times10^{-4} \text{ erg}^2$$

and $$\sigma(E) = 2.27\times10^{-2} \text{ erg}$$

Therefore at room temperature and in the Earth's magnetic field the degeneracy connected with electronic spin is, strictly speaking, removed. However the energy difference between the evolved states with the spin oriented parallel and antiparallel to magnetic field is very small compared to kT:

$$\exp\left(\frac{h\nu}{kT}\right)=\exp\left(\frac{6.62\ 10^{-27}3\ 10^{6}}{1.38\ 10^{-16}300}\right)=\exp\left(1.4\ 10^{-6}\right)\cong 1.4\ 10^{-6}$$

This means that in statistical mechanical calculations we can safely consider such a state as degenerate. The electronic partition function can either be computed as $\exp(-\varepsilon_0/kT+0.7 10^{-6})+\exp(-\varepsilon_0/kT-0.7 10^{-6})$ or just $2\exp(\varepsilon_0/kT)$. The difference between these two modes of calculation only becomes significant below $T=0.001$ K.

2.9
Conclusions

In this Chapter we followed the derivation of the connection between thermodynamic functions and the properties of statistical ensembles, both from the conceptual point of view and giving some guidelines for practical applications. The main conceptual result is summarised by the equation connecting the Helmholtz free energy (Helmholtz function) with the partition function of the canonical ensemble (2.54).

We have also found that a statistical approach introduces a new variable into the thermodynamic description of macroscopic systems, namely fluctuations. The latter give a mechanistic interpretation of the values of the second derivatives of thermodynamic potentials (*e.g.* heat capacity), characterising the stability of thermodynamic equilibrium.

In the next Chapter we shall apply this formalism to the description of chemical equilibria in ideal systems.

References

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3 The Law of Mass Action for Ideal Systems

3.1
The law of mass action, its origin and formal thermodynamic derivation

One of the peculiarities of the development of science was that the law of mass action was at first established as the *kinetic law of mass action.* In fact, chemists were anxious to find some parameter that would characterise the ability of compounds to react and form the required products. The reaction rates seemed to provide such a parameter but it was not that simple. The history of chemical discoveries that led to the formulation of the law of mass action is very important for an understanding of the contemporary interpretation of this rule. Glasstone [1], after mentioning the names of Albertus Magnus, Boyle, Newton and other precursors, described it as follows (italics are ours):

> But it is to C. L. Berthollet (1799) that the credit must be given for the first clear emphasis of the importance of mass or concentration. He showed that whereas in the laboratory sodium carbonate and calcium chloride reacted to form calcium carbonate, the reverse process was occurring in certain Egyptian lakes on the shores of which sodium carbonate was actually crystallising. This reversal was attributed to the large amount of sodium chloride in the lake water.... The conclusion based on these experiments was stated by Berthollet (1803) in the following way: "the chemical activity of a substance depends on the *force of its affinity and upon the mass which is present in a given volume*"...The work of H. Rose (1842), on the decomposition of alkaline-earth sulphides by water and on the reversible reaction between a soluble carbonate and insoluble sulphate, once more centred attention on the influence of mass, and in 1850 L. Wilhelmy, in the course of a study of the inversion of sucrose in the presence of acid, showed that the rate of the reaction at any instant was proportional to the amount of sucrose remaining unchanged at that instant. The effect of mass on chemical reaction was also brought out clearly by M. Berthelot and P. St. Gilles (1862 – 63) who studied the reversible formation of ester from ethyl alcohol and acetic acid; they found that the reaction did not go to completion, but the proportion of acid converted into ester increased as the amount of alcohol was increased.... Berthelot and St. Gilles also observed that the rate of formation of ester in any mixture of alcohol and acid was proportional to the products of the masses of reactants, and inversely proportional to the total volume; in other words, the rate of reaction was found to be approximately proportional to the concentrations of the reactants, but this important result was not generalised. Although it was commonly realised prior to this that many reactions were reversible, in the sense that they could occur in either direction according to

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> experimental conditions, and that a state of equilibrium was attained in which the reaction was not complete, it was considered that that the equilibrium was static and that in this state all reactions ceased. As a consequence of his interpretation of the mechanism of the etherification of alcohol by concentrated sulphuric acid, A.W. Williamson (1850) was led to the view that chemical equilibrium was *dynamic* and the reaction appeared to be stationary because both direct and reverse processes were taking place at the same rate... It appeared to C. Guldberg and P. Waage (1864 - 67) that a reversible reaction involving dynamic equilibrium provided the best conditions for the comparison of chemical affinities, and this led them to what is now known as *the law of mass action* and to formulate mathematically the influence of mass on chemical activity.

Now, the starting point for Guldberg and Waage was the earlier discovered empirical rule that the rate of a chemical reaction is proportional to the product of the *active masses*, *i.e.* the molecular concentrations of reactants. Assuming that the proportionality coefficient must characterise the *affinities of reactants* meant that the rates of reaction could serve as a measure of chemical affinity, provided the concentrations are known. The most accurate values of concentrations of the components of a reaction mixture can be obtained for the state of chemical equilibrium. As the concentrations of reactants at chemical equilibrium are not zero, the rate of chemical reaction must also be non-zero, which can only be explained (in agreement with the initial assumption) by interpreting chemical equilibrium *dynamically*, *i.e.* as corresponding to *equality of the rates of forward and reverse reactions*:

$$k_+ R_1 R_2 \ldots = k_- P_1 P_2 \ldots \tag{3.1}$$

in which R_1, R_2..., P_1, P_2... are the *active masses* of reactants and products respectively. The experimentally determined ratio of the products $(P_1P_2...)/(R_1R_2...)$ equals then the ratio of the 'affinity coefficients' or 'coefficients of velocity' of the direct and reverse reactions k_+/k_-. This ratio is known as the *equilibrium constant* and thus provides for a *relative measure of chemical affinity.* Again, this rule enables the calculation of the composition of an equilibrium reaction mixture on the basis of a *known equilibrium constant* and *known initial quantities* of reactants and products.

We can see that this empirically based postulate (that the rates of chemical reactions are proportional to the product of the active masses of reactants, *i.e.* the *kinetic law of mass action*) leads to the dynamic interpretation of chemical equilibrium and thus to the *equilibrium law of mass action.* The latter could therefore be considered as an empirical postulate similar to the First and Second laws of thermodynamics. In fact, however, the equilibrium law of mass action can be derived from these laws by considering the state of chemical equilibrium as a special case of thermodynamic equilibrium in a system involving transformations of molecules of one kind into another.

The state of *chemical equilibrium* corresponds thus to the minimum of thermodynamic potential with respect to chemical composition, *i.e.* the numbers of molecules of different chemical nature. Such a state is then characterised by zero complete differential of the thermodynamic potential including partial differentials with respect to the numbers of all kinds of molecules present. When a reaction is investigated under the conditions of constant volume and constant temperature the Helmholtz free energy may be used as the thermodynamic potential. When we carry out a reaction under constant pressure and constant temperature the work of a system against the external pressure (pdV) must be taken into account and the Gibbs free energy should be used. However, statistical thermodynamic formulae based on the Helmholtz free energy are much simpler than those employing Gibbs free energy. In fact, we do not in any case lose significantly any generality of approach by making this choice (any gas phase reaction can be investigated in a closed vessel, and when reactions in the liquid or solid state are studied under constant pressure the volume of the reaction mixture remains sensibly constant). This allows us to present a comparatively simple chain of derivations of various forms of the law of mass action for gaseous, solid and liquid systems[1].

The condition for the minimum of free energy at constant volume and temperature for the reaction:

$$\zeta_{R_1} R_1 + \zeta_{R_2} R_2 + \ldots + \zeta_{R_k} R_k \Leftrightarrow \zeta_{P_1} P_1 + \zeta_{P_2} P_2 + \ldots + \zeta_{P_m} P_m \tag{3.2}$$

can be written as:

$$dF = \sum_i \mu_{R_i} dn_{R_i} + \sum_j \mu_{P_j} dn_{P_j} = 0 \tag{3.2a}$$

in which n_{Ri} and n_{Pj} are *actual* (*current*) numbers of molecules as opposed to the *initial* (*analytical*) numbers of molecules N_{Ri} and N_{Pj}. The chemical potentials, μ_{Ri} and μ_{Pj}, are partial derivatives of free energy with respect to the corresponding numbers of molecules under the condition of constant V, T and *numbers of all other molecules*:

$$\mu_{R_i} = \left(\partial F / \partial n_{R_i}\right)_{V,T,n_{R_{k \neq i}},n_P} ; \qquad \mu_{P_j} = \left(\partial F / \partial n_{P_j}\right)_{V,T,n_{P_{k \neq j}},n_R} \tag{3.3}$$

The law of mass action can be obtained from (3.2a) by introducing a single variable, namely, the degree of conversion, ξ, representing the amount of substance transformed in the chemical reaction:

$$dn_{R_i} = -\zeta_{R_i} d\xi \tag{3.4}$$

According to the equation of the chemical reaction (3.2) the transformation (disappearance) of dn_{Ri} of a reactant results in the appearance of $(\zeta_{Pj}/\zeta_{Ri})dn_{Pj}$, therefore for any product:

$$dn_{P_j} = -\zeta_{P_j} d\xi \tag{3.4a}$$

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[1] It will be shown in the next Chapter (page 108) that in fact the substitution of Gibbs free energy by Helmholtz free energy in the derivation of the law of mass action for reactions in the condensed state brings about a negligibly small error – even for pressures of up to tens of bars.

We can then write (3.2a) with respect to this single variable:

$$\left(-\sum_i \zeta_{R_i}\mu_{R_i} + \sum_j \zeta_{P_j}\mu_{P_j}\right)d\xi = 0 \tag{3.5}$$

or:

$$-\sum_i \zeta_{R_i}\mu_{R_i} + \sum_j \zeta_{P_j}\mu_{P_j} = 0 \tag{3.6}$$

This is *the most general expression of the law of mass action* in which the relationship between the amounts (*numbers of moles*) of products and reactants is hidden in the dependencies of chemical potentials on these variables.

The dependence of chemical potential on the number of moles can be derived in the following way. The First Law of thermodynamics:

$$dE = TdS - pdV \tag{3.7}$$

defines partial derivatives of entropy as:

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}; \qquad \left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \tag{3.8}$$

Partial differentials of entropy can therefore be written as:

$$dS_V = \left(\frac{\partial S}{\partial E}\right)_V dE = \frac{1}{T}dE = \frac{C_V dT}{T} \tag{3.9}$$

$$dS_E = \left(\frac{\partial S}{\partial V}\right)_E dV = p\frac{dV}{T} \tag{3.9A}$$

Now we can introduce the numbers of moles employing the *equation of state*. For a system containing n moles of a substance in the form of an *ideal gas* the equation of state is well known and is $pV = nRT$. The differentials (3.9) then become:

$$dS_V = nc_V\frac{dT}{T} \tag{3.10}$$

$$dS_E = nR\frac{dV}{V} = nR\frac{d(V/n)}{(V/n)} = nR\frac{dv}{v} \tag{3.10A}$$

in which $v = V/n$ is the molar volume and c_V is the molar heat capacity. The substitution of volume by molar volume could be considered as an arbitrary division of numerator and denominator by n, but, in fact such an operation was suggested by the Gibbs paradox (Section 1.4) and to some extent by the equation of state itself. These differentials on integration yield the entropy as:

$$S = nc_V \ln T + nR \ln v + C = n(c_V \ln T + R \ln v + s_0) \qquad (3.11)$$

in which $C = ns_0$ is an integration constant. The Helmholtz free energy of this system (note that $E = nc_V T$) is:

$$F = E - TS = n\left[c_V T(1 - \ln T) - Ts_0 - RT \ln \frac{V}{n}\right] \qquad (3.12)$$

The free energy of a mixture of molecules of different kinds in the state of ideal gas is additive:

$$F = \sum_i F_i = \sum_i n_i \left[c_{V_i} T(1 - \ln T) - Ts_{0_i} - RT \ln \frac{V}{n_i}\right] \qquad (3.13)$$

The chemical potential of the i-th species in such a mixture is:

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right) = c_{V_i} T(1 - \ln T) - Ts_{0_i} + RT \ln \frac{n_i}{V} + RT = \mu_i^0 + RT \ln \frac{n_i}{V}$$

in which:

$$\mu_i^0 = c_{V_i} T(1 - \ln T) + RT - Ts_{0_i} \qquad (3.14)$$

The law of mass action (3.6) can then be written as:

$$-\sum_j \zeta_{P_j} \mu_{P_j}^0 + \sum_i \zeta_{R_i} \mu_{R_i}^0 = RT\left[\sum_j \zeta_{P_j} \ln \frac{n_{Pj}}{V} - \sum_i \zeta_{R_i} \ln \frac{n_{Ri}}{V}\right] \qquad (3.15)$$

or, in exponential form:

$$\frac{\prod (n_{P_j}/V)^{\zeta_{P_j}}}{\prod_i (n_{R_i}/V)^{\zeta_{R_i}}} = \exp\left(-\frac{\sum_j \zeta_{P_j} \mu_{P_j}^0 - \sum_i \zeta_{R_i} \mu_{R_i}^0}{RT}\right) = K(T) \qquad (3.16)$$

Note that the numbers of moles were introduced after we had substituted pressure by *molar* volume using an equation of state. The use of *molar* volume (partial molar volume in a mixture) was suggested by the Gibbs paradox. We see that in order to derive the law of mass action within the framework of formal thermodynamics we had to make use of the equation of state.

In classical thermodynamics equations of state are fundamental assumptions or definitions: the ideal gas state is defined as obeying the equation of state of an ideal gas. When we consider the same problem from the point of view of statistical thermodynamics the equation of state becomes an integrated part of the general formalism easily obtained for an ideal gas as a collection of statistically independent particles from the respective expression for free energy (see (1.65), Chapter 1). The Gibbs paradox is not merely solved by statistical mechanics, but a rational interpretation is obtained as a consequence of the indistinguishable nature of molecules. Statistical thermodynamics provides, therefore, for a general and rational description of the origin and possible forms of the law of mass action.

In the following Sections we shall derive a number of forms of the law of mass action for gaseous, solid and liquid systems. During these derivations it is important to keep in mind the dependencies (sometimes not explicitly shown) of *all terms* on the numbers of molecules or concentrations. Some valuable hints concerning the form in which equations should be arranged might be obtained when the free energy is expressed as a function of one variable, namely the concentration (number of molecules) of a component of the reaction mixture.

The *current* numbers of molecules or moles (denoted by small n's) in a reaction mixture *are not independent variables*. They are interrelated by a system of *material (mass) balance equations*, for example:

$$n_{R_i} = N_{R_i} - \left(\zeta_{R_i}/\zeta_{P_1}\right)\left(n_{P_1} - N_{P_1}\right) \tag{3.17}$$

$$n_{P_j} = N_{P_j} - \left(\zeta_{P_j}/\zeta_{P_1}\right)\left(n_{P_1} - N_{P_1}\right) \tag{3.18}$$

The free energy of a reaction mixture can thus be expressed as a function of one variable, namely the number of particles of one of the products or reactants:

$$F\left(n_{R_1},\ldots n_{R_k}, n_{P_1},\ldots n_{P_m}\right) = F'\left(N_{R_1},\ldots N_{R_k}, N_{P_1},\ldots N_{P_m},\ n_{P_1}\right) \tag{3.19}$$

in which the initial numbers of molecules, N_i, are constants for a reaction mixture of given initial composition. The differential of the free energy F' with respect to n_{P1} is, therefore, a *complete differential*. The condition of equilibrium (minimum free energy) corresponds to zero for the *complete* derivative:

$$dF'/dn_{P_1} = 0 \tag{3.20}$$

This approach provides a clearer physical significance of these relationships. Two pictures on the cover of this book illustrate the versatility of the complete derivative (3.20) compared to the use of chemical potential in the derivation of the law of mass action. A free energy surface for a binary mixture does not directly show that there is a minimum of free energy corresponding to the state of equilibrium. It is quite difficult to guess that there is one by analysing the 'slices' parallel to vertical coordinate planes (*i.e.* employing chemical potentials). On the other hand, the cross-section along the main diagonal – an operation equivalent to the application of the mass balance equation resulting in (3.20) – immediately reveals the minimum of free energy corresponding to equilibrium.

3.2
Statistical formulae for free energy

The Helmholtz free energy of a system of N *indistinguishable interacting molecules* without internal degrees of freedom can be written, (2.53) and (2.54), as:

$$F = -kT \ln\left[\frac{1}{h^{3N}N!}\int\cdots\int e^{-H(p,q)/kT}dp_1 \ldots dp_N dq_1 \ldots dq_N\right] \tag{3.21}$$

in which H is the *Hamiltonian function* of momenta (p) and coordinates (q) of all particles. The integral in (3.21) can be *divided into kinetic and potential* energy terms:

$$F = -kT \ln\left[\frac{1}{h^{3N}}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty} e^{-\varepsilon_{kin}/kT}dp_1 \ldots dp_N \; \frac{1}{N!}\int_V\cdots\int_V e^{-U(q)/kT}dq_1 \ldots dq_N\right] \tag{3.22}$$

The integration over momenta (omitting the contributions from internal degrees of freedom) yields the *translational partition function*:

$$\frac{1}{h^{3N}}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty} e^{-\varepsilon_{kin}/kT}dp_1 \ldots dp_N = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \tag{3.23}$$

The term:

$$Z_{conf} = \frac{1}{N!}\int_V\cdots\int_V e^{-U(q)/kT}dq_1 \ldots dq_N \tag{3.24}$$

is called the *configurational integral*. The factor ($1/N!$) arises from the indistinguishable nature of molecules, which is an essential property of both gaseous and liquid states. Hence, for a gas made up of particles without internal degrees of freedom:

$$F = -kT \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \frac{1}{N!}\int_V\cdots\int_V e^{-U(q)/kT}dq_1 \ldots dq_N\right] \tag{3.25}$$

When some internal degrees of freedom are changed by reaction they must be taken into account and the free energy of such a system becomes therefore:

$$F = -kT \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \times Z_{\text{int}} \times \frac{1}{N!}\int_V \cdots \int_V e^{-U(q)/kT} dq_1 \ldots dq_N\right] \qquad (3.26)$$

in which the total partition function for internal degrees of freedom, Z_{int} is:

$$Z_{\text{int}} = \prod_{i=1}^{N}\prod_{j=1}^{f_i} z_{i,j} \qquad (3.27)$$

in which f_i is the number of internal degrees of freedom of the i-th molecule. In the case of identical molecules

$$Z_{\text{int}} = \left(\prod_{j=1}^{f} z_i\right)^N = z_{\text{int}}^N \qquad (3.28)$$

One of the internal degrees of freedom is connected with the electronic system for which the corresponding partition function is very simple because usually only the ground state is populated (provided that the temperature is not too high):

$$z_{el} = g_0 e^{-\frac{\varepsilon_0}{kT}} \qquad (3.29)$$

in which g_0 is the degeneracy factor and ε_0 the energy of the ground state of the electronic system. The exponential in (3.29) gives rise to a very important term in the partition function *reflecting that part of the potential energy of a molecule that is independent of the state of other molecules*[2]. The terms independent of the numbers of molecules in (3.26) can be combined:

$$q = z_{\text{int}}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} g e^{-\frac{\varepsilon_0}{kT}} \qquad (3.30)$$

This term has the dimensions of concentration $[1/V]$ and is not exactly a partition function (as it is sometimes called in this book as well as elsewhere). It should also be distinguished from the coordinates q_i in the configurational integral. The free energy can then be written as:

$$F = -kT \ln\left[q^N \times \frac{1}{N!}\int_V \cdots \int_V e^{-U(q)/kT} dq_1 \ldots dq_N\right] \qquad (3.31)$$

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[2] If vibrational partition functions are calculated with respect to the energy of the zero vibrational level, (2.83), then this term also includes the sum of all zero vibrational energies. In this book, however, vibrational partition functions are calculated as $[2\sinh(h\nu/2kT)]^{-1}$, and therefore are on the absolute scale of energies.

Further derivation of the law of mass action involves some simplifying assumptions concerning the calculation of the configurational integral that we are able to introduce for ideal systems. In formal thermodynamics *ideal systems* are defined phenomenologically as those obeying the *equations of state* (that is a *P-V-T* relationship) for an *ideal gas*, an *ideal crystal* or an *ideal solution*. From the point of view of *molecular theory* an ideal system is a collection of *statistically independent molecules*. In Chapter 1 we derived the distribution law and equation of state for such a system (an ideal gas) having zero energy of molecular interactions. As we shall see later, the observable properties of an ideal crystal can also be derived from its definition as a system of independent particles.

3.3
Statistical formulae for ideal systems

The calculation of the configurational integral for ideal systems does not present insurmountable problems. If the potential energy of a molecule is independent of the coordinates of other molecules then:

$$Z_{conf} = \frac{1}{N!}\prod_i \int e^{-\frac{U(q_i)}{kT}} dq_i \tag{3.32}$$

in which the potential energy of a molecule $U(q_i)$ is dependent on the coordinates of *this molecule alone*. In the absence of external fields the potential energy of the molecules of an ideal gas is zero[3] and:

$$Z_{conf} = \frac{1}{N!}\prod_i \int e^{-\frac{0}{kT}} dq_i = \frac{V^N}{N!} \tag{3.33}$$

This is a system of indistinguishable molecules as indicated by the factor ($1/N!$). Zero potential energy also *implies zero radii of molecules*, otherwise a repulsive interaction would have to be admitted for molecules at certain finite distances. In the language of statistical dependence this would mean that the presence of a molecule at the point with coordinates (x,y,z) would exclude the possibility of any other molecule being within a finite radius around this point. The molecules of an ideal gas are thus material points moving freely within the *whole volume* of a system.

The total partition function for an ideal gas containing N chemically identical molecules is:

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[3] When molecules collide with each other, then the potential energy of repulsive interaction is supposed to be transformed instantly into the kinetic energy of the same particles moving along new trajectories.

$$Z = q^N Z_{conf} = q^N \frac{V^N}{N!} \tag{3.34}$$

When we have a mixture of chemically *distinguishable* molecules A, B, ... K in the quantities n_A, n_B,...n_K, the total partition function is:

$$Z = \prod_{i=A}^{K} V^{n_i} \frac{q^{n_i}}{n_i!} \tag{3.35}$$

A statistical independence of molecules can also be imagined for a system in the state of a crystal with molecules fixed in lattice centres. Molecules do not migrate from cell to cell and this is what makes them *distinguishable* (any molecule can be labelled by the coordinates of its centre). A molecule in such a state may perform *oscillations of small amplitude* not affecting the state of other molecules. (Appendix 10.4 presents an alternative way of deriving the formulae for an ideal crystal resulting in an interesting relationship between the translational and vibrational partition functions.)

The partition function of a three-dimensional oscillator approximating the oscillations of a spherical molecule (as a whole) in a centre of a simple cubic lattice is given by:

$$z_{vib} = \left[\frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}}\right]^3 = \left[2\sinh\left(\frac{h\nu}{2kT}\right)\right]^{-3} \tag{3.36}$$

The partition function of a molecule in such a centre can be written as:

$$z = g\, z_{vib} z_{\mathrm{int}}\, e^{-\varepsilon_0/kT} \tag{3.37}$$

in which g is the *degeneracy* factor, z_{int} is the partition function for internal degrees of freedom and the exponential $\exp(-\varepsilon^0/kT)$ reflects the electronic energy as well as the *potential energy in the mean field* of the neighbours of the molecules concerned. This *mean* field is static by definition and does not destroy the statistical independence of molecules. Such a state approximates the state of molecules in crystals at low temperatures and is called an *ideal crystal*.

If such a crystal is built of molecules of one chemical kind it can be realised in one way and the partition function of a crystal built of N such molecules is:

$$Z_{ic} = z^N \tag{3.38}$$

The *distinguishable* nature of molecules is indicated by the absence of the factor $(1/N!)$.

When several kinds of molecules are present in such a crystal the number of realisations is given [2] by:

$$W = \frac{(n_A + n_B + n_C + \ldots + n_K)!}{n_A! n_B! n_C! \ldots n_K!} \tag{3.39}$$

The total partition function for such a crystal is then:

$$Z_{ic} = W \times z_A^{n_A} z_B^{n_B} z_C^{n_C} \cdots z_K^{n_K} \tag{3.40}$$

The factor W brings about the contribution to entropy, $k \ln W$, called the *entropy of mixing* or the *configurational entropy*. The configurational entropy of a *random*[4] mixture of the molecules A and B is thus:

$$S_{conf} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!} \cong -k(N_A + N_B)(X_A \ln X_A + X_B \ln X_B) \tag{3.41}$$

in which $X_{A(B)} = N_{A(B)}/(N_A + N_B)$ is the mole fraction of the component $A(B)$.

The case of the liquid phase is the most difficult: molecular interactions are approximately as strong as in solids and at the same time molecules move within the volume of a system. There is, however, the possibility of constructing at least a *pseudo-ideal* model of a liquid, which can be helpful in the interpretation of relationships observed for liquid state equilibria.

3.4
The law of mass action for ideal gases

Taking into account (3.31) and (3.33), the Helmholtz free energy of an ideal gas is:

$$F_{ig} = -kT \ln \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} \left(g z_{\text{int}} e^{-\frac{\varepsilon_0}{kT}} \right)^N \frac{V^N}{N!} \right\} = -kT \ln \frac{q^N V^N}{N!} \tag{3.42}$$

Applying the Stirling formula yields:

$$F_{ig} = -kT \{ N \ln q + N \ln(eV) - N \ln N \} \tag{3.43}$$

From the statistical independence of the particles in an ideal gas it follows (partition functions being multiplicative) that the free energy of an ideal gas is an additive property. Therefore, when we have a mixture of molecules of different kinds forming an ideal gas the free energy of such a mixture may be calculated as the sum of the free energies of the components:

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[4] Equation (3.39) holds when the particles A, B, ... K are of the same size and their interactions are of the same magnitude, otherwise either ordered sequences (such as $Na^+Cl^-Na^+Cl^-$ in a rock-salt crystal), separate clusters ($AAAA$ and $BBBB$), or even phases would be preferentially formed.

$$F_{ig} = \sum N_i F_i = -kT \sum \left[N_i \ln q_i + N_i \ln V - N_i \ln N_i + N_i \right] \tag{3.44}$$

Note that the logarithm of the number of particles, ln$N$, in (3.43) and (3.44) appears because the molecules in an ideal gas are indistinguishable (ln$N!$).

We now derive the law of mass action for a reversible reaction of the most general type:

$$\zeta_{R_1} R_1 + \zeta_{R_2} R_2 + \cdots + \zeta_{R_k} R_k \Leftrightarrow \zeta_{P_1} P_1 + \zeta_{P_2} P_2 + \cdots + \zeta_{P_m} P_m \tag{3.45}$$

The state of equilibrium corresponds to a minimum of free energy, *i.e.* zero complete differential dF. Under the condition of constant temperature and constant volume the partial differentials with respect to numbers of molecules alone should be taken into account:

$$dF = \sum_i \left(\frac{\partial F}{\partial n_i} \right)_{T,V,n_{j \neq i}} dn_i = \sum_i \mu_i dn_i = 0 \tag{3.46}$$

According to (3.6) the condition of equilibrium of the reaction (3.45) is:

$$\sum_i \zeta_{R_i} \mu_{R_i} - \sum_j \zeta_{P_j} \mu_{P_j} = 0 \tag{3.47}$$

The free energy of a reaction mixture forming an ideal gas being additive, the chemical potentials can easily be obtained by differentiating the following expression for free energy:

$$-\frac{F}{kT} = \sum_{i=1}^{k} n_{R_i} \left[\ln q_{R_i} + \ln V - \ln n_{R_i} + 1 \right] + \sum_{j=1}^{m} n_{P_j} \left[\ln q_{P_j} + \ln V - \ln n_{P_j} + 1 \right] \tag{3.48}$$

The result:

$$\mu_{R_i} = -kT \left(\ln q_{R_i} + \ln V - \ln n_{R_i} \right) \tag{3.49}$$

applied to (3.47) yields the law of mass action as:

$$\sum_i \zeta_{R_i} \left[\ln q_{R_i} + \ln V - \ln n_{R_i} \right] - \sum_j \zeta_{P_j} \left[\ln q_{P_j} + \ln V - \ln n_{P_j} \right] = 0 \tag{3.50}$$

If we separate in this equation just the *numbers of molecules*, then the arguments of all logarithmic functions will be dimensionless which is (at least) convenient:

$$\sum_j \zeta_{P_j} \ln n_{P_j} - \sum_i \zeta_{R_i} \ln n_{Ri} = \sum_j \zeta_{P_j} \ln q_{P_j} V - \sum_i \zeta_{Ri} \ln q_{R_i} V \quad (3.51)$$

Note that the right-hand side of (3.51) contains logarithms of the dimensionless function $q_i V$, which is actually a partition function multiplied by the number of molecules of corresponding kind. The logarithm itself must therefore be proportional to free energy. This fact will be used a little later when we introduce standard free energies of reaction (Section 3.4.3).

The exponential form of the law of mass action is obtained from (3.51) as:

$$\frac{\prod_j n_{P_j}^{\zeta_{Pj}}}{\prod_i n_{R_i}^{\zeta_{R_i}}} = \frac{\prod_j q_{P_j}^{\zeta_{P_j}}(T)}{\prod_i q_{Ri}^{\zeta_{R_i}}(T)} V^{\left(\sum \zeta_{P_j} - \sum \zeta_{R_i}\right)} = K_n(T,V) \qquad (3.52)$$

The law of mass action (3.51) and (3.52) is thus written with respect to the *numbers of molecules* and not with respect to either molar concentrations or mole fractions. The equilibrium constant K_n is *dimensionless for any reaction* but related to the actual system occupying the volume V. It is therefore convenient to use this form of the law of mass action for equilibria in systems confined to a vessel of constant volume. In order to get comparable equilibrium constants both the volume and temperature must be standard.

3.4.1
Conversion to molar concentrations

Within a gaseous reaction mixture we can always *mentally* select a region of unit volume. The numbers n_i become then *numerically equal* to molar concentrations. This is equivalent to combining n_i and V in (3.51) and (3.52):

$$\sum_j \ln\left(\frac{n_{P_j}}{V}\right)^{\zeta_{P_j}} - \sum_i \ln\left(\frac{n_{Ri}}{V}\right)^{\zeta_{R_i}} - \sum_j \ln q_{P_j}^{\zeta_{P_j}} + \sum_i \ln q_{R_i}^{\zeta_{Ri}} = 0 \quad (3.53)$$

and:

$$\frac{\prod_j \left(n_{P_j}/V\right)^{\zeta_{Pj}}}{\prod_i \left(n_{R_i}/V\right)^{\zeta_{R_i}}} = \frac{\prod_j q_{P_j}^{\zeta_{P_j}}}{\prod_i q_{Ri}^{\zeta_{R_i}}} = K_C(T) \qquad (3.54)$$

The equilibrium constant in (3.54) is a function of temperature alone and *independent of the volume* of the system and this can also be very convenient. However, the arguments of the logarithmic functions in (3.53) are *no longer dimensionless.*

Now, we must state clearly and explicitly that ***there is nothing implicitly wrong in the taking of the logarithm of a quantity having dimensions***. Such an operation is merely connected with an implicit assumption that the logarithm of a *conversion factor* (the inverse *unit* in which this quantity *is measured*) is zero. Even when we compare the logarithms of two quantities having different dimensions (units) we assume that the logarithm of the ratio of two units is zero. For example the difference of the logarithms of the numbers of apples and the number of people is not something nonsensical – it is just the logarithm of the number of apples per person (which might be related with the probability of finding an apple being eaten!). The only 'problem' arising in such operations is that the results depend on the *choice of units* (*e.g.* bottles or half-bottles of wine).

It is therefore not at all necessary to relate a quantity to some standard state just in order to get a dimensionless argument of a logarithmic function. On the other hand, it is very useful to check the dimensions of the results of mathematical operations during the derivation of a mathematical formalism in order to detect possible dependence of the results of calculations on the choice of units, *i.e.* to make use of 'quantity calculus'.

In the conversion of the law of mass action to the form with respect to molar concentrations we have chosen a unit volume (one litre) and have thus implicitly introduced the conversion factor $(1\,litre)^{\Sigma\zeta_{P_j}-\Sigma\zeta_{R_i}}$ into the equilibrium constant. This results in a dependence of the numerical value of the equilibrium constant on the *units of concentration*, in other words, when we use non-conventional concentrations we must be prepared to obtain different values of equilibrium constants. For example using concentrations expressed in terms of 10^{-3} M (millimolar or mol m^{-3}) we get an equilibrium constant which equals the one based on litres multiplied by

$$\left(10^{-3}\right)^{\Sigma\zeta_{P_j}-\Sigma\zeta_{R_i}}.$$

Therefore, in order to obtain comparable equilibrium constants, *two parameters, namely the units of concentration and the temperature must be standardised.*

3.4.2
Conversion to mole fractions

Dividing the numbers of molecules by volume we have normalised them to a quantity derived from the configurational integral, *i.e.* the sum of the statistical weights of all configurations of molecules. Another possibility is to refer the numbers of molecules of each kind to the total number molecules. We will then get the law of mass action written with respect to mole fractions. For equilibria in ideal gases a straightforward linear transformation is required because V and N are related *via* the equation of state as:

$$V = NkT/p \tag{3.55}$$

Equation (3.54) can then be written as:

$$\frac{\prod_j n_{P_j}^{\zeta_{P_j}}}{\prod_i n_{R_i}^{\zeta_{R_i}}} = \frac{\prod q_{P_j}^{\zeta_{P_j}}}{\prod q_{R_i}^{\zeta_{R_i}}} \left(\frac{NkT}{p}\right)^{\left(\sum\zeta_{P_j}-\sum\zeta_{R_i}\right)} = K_x(T,p) \qquad (3.56)$$

The numbers of molecules can be transformed into mole fractions (x_i) by moving the factor $N^{(\Sigma\zeta_{P_j}-\Sigma\zeta_{R_i})}$ into the left-hand part of (3.56). The logarithmic and exponential forms of the law of mass action become:

$$\sum_j \ln\left(x_{P_j}\right)^{\zeta_{P_j}} - \sum_i \ln\left(x_{R_i}\right)^{\zeta_{R_i}} - \sum_j \ln\left[q_{P_j}\frac{kT}{p}\right]^{\zeta_{P_j}} + \sum_i \ln\left[q_{R_i}\frac{kT}{p}\right]^{\zeta_{R_i}} = 0 \qquad (3.57)$$

$$\frac{\prod_j x_{P_j}^{\zeta_{P_j}}}{\prod_i x_{R_i}^{\zeta_{R_i}}} = \frac{\prod_j q_{P_j}^{\zeta_{P_j}}}{\prod_i q_{R_i}^{\zeta_{R_i}}} \left(\frac{kT}{p}\right)^{\left(\sum\zeta_{P_j}-\sum\zeta_{R_i}\right)} = K_x(T,p) \qquad (3.58)$$

The equilibrium constant in such a case is temperature and pressure dependent. It is convenient, therefore, to use this form of the law of mass action for reactions under *constant pressure* (being prepared to obtain quite different values of the equilibrium constants at different pressures). Again, in order to obtain comparable equilibrium constants temperature and pressure must be standardised.

3.4.3
Standard states and standard free energies of reaction

Note the symmetry in the expressions of the law of mass action when we use mole fractions (for equilibria at constant pressure) and numbers of molecules (for equilibria at constant volume). In both cases equilibrium constants are *dimensionless* and dependent on two parameters: temperature and either pressure (mole fractions) or volume (numbers of molecules).

In the derivation of the law of mass action, above, we have not used an exactly complete differential of the free energy, but that applicable under the conditions of either constant volume and temperature, or constant pressure and temperature. As a result the equilibrium constants so obtained can only be compared if these pairs of parameters are standardised. In the case of an equilibrium constant expressed in molar concentrations this dependence reveals itself in the standardisation of the units of concentration (which is equivalent to the standardisation of the units of volume).

By employing standard states it is also possible to introduce a very versatile parameter characterising chemical equilibrium, namely the *standard free energy of reaction.*

Let us investigate how this parameter appears in thermodynamic equations. Suppose that $F^0_{R(P)}$ is the free energy of N_L (the *Avogadro Number*) molecules of a reactant or product in the ideal gas state occupying volume V at temperature T (the pressure is completely defined by the values of N, V and T):

$$F^0 = -kTN_L \ln\frac{qVe}{N_L} \tag{3.59}$$

Let us use the law of mass action with respect to the numbers of molecules. Even in such a case we can introduce a *measure* or a *standard*: for example, consider N_L as a *unit* of the number of molecules and call it *one mole*. The *standard free energy of one mole of a reactant or a product* is:

$$F^0 = -RT\ln[qVe] \tag{3.60}$$

in which $R = N_L k$ is the 'gas constant' for one mole of molecules. The introduction of a *measure* results in the subtraction of $-RT\ln N_L$, *i.e.* in the introduction of a conversion factor. The *standard free energy for the reaction* (3.45) becomes:

$$\Delta F^0 = \sum_j \zeta_{\mathrm{P_j}} F^0_{\mathrm{P_j}} - \sum_i \zeta_{\mathrm{R_i}} F^0_{\mathrm{R_i}} = -RT\left[\sum_j \zeta_{\mathrm{P_j}} \ln q_{\mathrm{P_j}} Ve - \sum_i \zeta_{\mathrm{R_i}} \ln q_{\mathrm{R_i}} Ve\right] \tag{3.61}$$

We see that the standard free energy of a reaction in the units of RT is *numerically* equal to the negative logarithm of the equilibrium constant:

$$\frac{\Delta F^0}{RT} = -\sum_j \zeta_{\mathrm{P_j}} \ln[q_{\mathrm{P_j}} Ve] + \sum_i \zeta_{\mathrm{R_i}} \ln[q_{\mathrm{R_i}} Ve] = -\ln K_n(V,T) \tag{3.62}$$

$$\ln K_n(V,T) = -\frac{\Delta F^0}{RT} \tag{3.63}$$

Knowing the standard free energies of the components of a reaction mixture, therefore, makes it possible to calculate the equilibrium constant: a result of considerable importance. Employing the thermodynamic expression for free energy (1.50) enables the equilibrium constant to be written as:

$$\ln K_n(V,T) = -\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} \tag{3.64}$$

in which the standard free energy of reaction is divided into 'temperature dependent' and 'temperature independent' parts. This relationship is known[5] as the *van't Hoff plot.* The statistical mechanical relationships in (3.30), (3.53) and (3.54) show that (3.64) is a *linear approximation* of a more complicated temperature dependence of the equilibrium constant. Such a linearisation is in fact only possible over a *narrow range* around some given temperature T_0.

Consider a simple non-isomolar equilibrium in an ideal gas:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{3.65}$$

The equilibrium constant $K_n(V,T)$ of this reaction can be written, separating temperature independent and temperature dependent terms, as:

$$\ln K_n(V,T) = \ln\left[\left(\frac{h^2}{2\pi k}\frac{m_C}{m_A m_B}\right)^{3/2}\frac{1}{Ve}\right] + \ln Q_{\mathrm{int}} - \ln T^{3/2} - \frac{\varepsilon_C - \varepsilon_A - \varepsilon_B}{kT} \tag{3.66}$$

in which:

$$\ln Q_{\mathrm{int}} = \ln\frac{z_{iC}}{z_{iA} z_{iB}} \tag{3.66a}$$

The partition functions for internal degrees of freedom *are* generally temperature dependent and the term $\ln Q_{\mathrm{int}}$ is a function of temperature. In some cases, however, the lowest level alone is populated (similar to an electronic system). These degrees of freedom contribute then to the exponential term in the partition function and may otherwise be disregarded.

The function (3.66) can be linearised with respect to T^{-1} in the vicinity of T_0^{-1} (omitting for simplicity the symbol of the volume dependence of K_n) as:

$$\ln K_n(T) \cong \ln K_n(T_0) + \left(\frac{\partial \ln K_n(T)}{\partial T^{-1}}\right)_{T=T_0}\left(T^{-1} - T_0^{-1}\right) \tag{3.67}$$

The *standard entropy* and *standard internal energy* of this reaction then are:

$$\Delta S^0 = R\left\{\ln K_n(T_0) - \left(\frac{\partial \ln K_n(T)}{\partial T^{-1}}\right)_{T=T_0} T_0^{-1}\right\} \tag{3.68}$$

$$\Delta E^0 = -R\left(\frac{\partial \ln K_n(T)}{\partial T^{-1}}\right)_{T=T_0} \tag{3.69}$$

The derivative in (3.69) is:

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[5] Rather confusingly the same relationship is also called the '*isotherm of chemical reaction*', or the '*van't Hoff isochore*'.

$$\left(\frac{\partial \ln K_n(T)}{\partial T^{-1}}\right)_{T=T_0} = \frac{3}{2}T_0 - \frac{\varepsilon_C - \varepsilon_A - \varepsilon_B}{k} + \left(\frac{\partial \ln Q_{\text{int}}}{\partial T^{-1}}\right)_{T=T_0} \tag{3.70}$$

The standard entropy and internal energy[6] of (3.65) can thus be written explicitly as:

$$\frac{\Delta S^0}{R} = \ln\left[\frac{1}{Ve}\left(\frac{m_C}{m_A m_B}\frac{h^2}{2\pi k T_0}\right)^{3/2} Q_{\text{int}}(T_0)\right] - \frac{3}{2} - \frac{1}{T_0}\left(\frac{\partial \ln Q_{\text{int}}}{\partial T^{-1}}\right)_{T=T_0} \tag{3.71}$$

$$\Delta E^0 = N_L(\varepsilon_C - \varepsilon_A - \varepsilon_B) - \frac{3}{2}RT_0 - R\left(\frac{\partial \ln Q_{\text{int}}}{\partial T^{-1}}\right)_{T=T_0} \tag{3.72}$$

We see that both the standard entropy and the standard internal energy are temperature dependent. The translational partition function contributes largely towards the standard entropy of a gas phase reaction. The standard internal energy of a gaseous reaction originates mainly from the difference of electronic energies of the ground states of products and reactants.

The temperature dependence of the internal degrees of freedom constitutes an important part of both the standard internal energy and the standard entropy of reaction as defined by (3.71) and (3.72). This fact predetermines a certain parallelism in the variations of these parameters in a reaction series leading to the phenomenon known as the *compensation effect* or *iso-equilibrium relationship* (IER) showing that the effects of molecular interactions play a considerable role in these phenomena. This will be analysed in detail in Chapter 8.

The concept of a standard state is also useful when describing the behaviour of *non-ideal* systems. Expressions for the free energy of such systems contain terms dependent on squares and higher powers of the numbers of molecules or concentrations. However, over a *narrow range of concentrations* it can be approximated by (3.44) containing only linear and logarithmic terms, thus reducing the law of mass action to a pseudo-ideal form (see Chapters 4 and 7). This operation is usually referred to as the introduction of a hypothetical standard state (for example, that at infinite dilution). We consider such terminology confusing, misleading and unnecessary!

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[6] For reactions in solutions (under constant pressure) the *Gibbs free energy* is universally used as the thermodynamic potential resulting in the *enthalpy* of reaction as the factor determining the temperature dependence of equilibrium constants. As mentioned above, the difference between enthalpy and internal energy in the condensed state is negligibly small for pressures of up to tens of bars. Therefore the parameter statistically calculated as internal energy is often called the enthalpy (the latter notation being conveniently shorter). We think, however, that it is better to avoid inaccuracies – even at the risk of appearing pedantic!

3.5

The law of mass action for an ideal crystal. Spin crossover equilibria

The number of possible types of reactions in the ideal crystal state is limited. First of all, any non-isomolar reaction would create either new centres or vacancies or change the type of the crystal lattice. Real solid state reactions are often accompanied by the formation of new phases (gaseous, liquid or solid) and the cases of homogeneous solid state reactions are quite rare. There is, however a class, of 'nearly' chemical transformations in the solid state ideally suited to the purpose of checking the theoretical descriptions of such reactions. This is the so-called *spin crossover equilibrium* occurring between high spin (HS) and low spin (LS) forms of a transition metal complex [3]. It can be described by a simple monomolecular equilibrium:

$$\mathrm{A(LS)} \rightleftharpoons \mathrm{B(HS)} \tag{3.73}$$

The free energy of the reaction mixture (3.73) of the molecules A and B in the state of an ideal crystal, according to (3.21), (3.40) and (3.41), is given by:

$$F = F_A + F_B - TS_{conf} = -kTN\left[x_A\left(\ln z_A - \ln x_A\right) + x_B\left(\ln z_B - \ln x_B\right)\right] \tag{3.74}$$

in which z_A and z_B are partition functions given by (3.36) and (3.37) for the particles A and B respectively and $N = n_A + n_B$. We see that free energy is dependent on the logarithms of the *mole fractions* and not on $\ln(N_i/V)$ as in the case of an ideal gas, (3.43). Let us write the free energy of such a crystal as a function of one variable, namely the number of molecules A (n_A):

$$F = -kT\left\{n_A \ln z_A - n_A \ln\frac{n_A}{N} + (N_A - n_A)\ln z_B - (N - n_A)\ln\frac{N - n_A}{N}\right\} \tag{3.75}$$

Differentiating (3.75) with respect to n_A yields the condition of equilibrium as:

$$\frac{dF}{dn_A} = -kT\left\{\ln\frac{z_A}{z_B} - \ln\frac{n_A}{N - n_A}\right\} = 0 \tag{3.76}$$

This results in a conventional law of mass action:

$$K(T) = \frac{z_B}{z_A} = \frac{N - n_A}{n_A} = \frac{n_B}{n_A} = \frac{x_B}{x_A} \tag{3.77}$$

This equation can be written with respect to the numbers of molecules alone but, the free energy being a function of mole fractions, the same variables should be used in the law of mass action. The thermal behaviour of such systems is usually simulated by expressing ln$K$ *via* the standard energy and entropy of reaction. According to (3.64) and (3.77):

$$\ln \frac{x_B}{1-x_B} = \ln K(T) = \ln \frac{z_B}{z_A} = -\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} \qquad (3.78)$$

As in the case of the ideal gas, this is just a linear approximation (linear van't Hoff plot) of a more complicated temperature dependence. Taking into account the actual form of the partition function of a molecule in an ideal crystal (3.36), (3.37), the standard internal energy, ΔE^0, originates in the exponential term arising from the difference in electronic energies and in potential energies in the molecular field. The standard entropy of reaction in the crystal state originates mainly in changes of vibrational frequencies (both lattice and internal vibrations) but may also include a contribution from different degeneracy factors of products and reactants (as occurs in spin crossover).

Spin crossover can be observed experimentally on changing temperature as well as on light irradiation and pressure changes [3]. Most spin crossover compounds are Fe(II) complexes with the associated crystal fields formally intermediate between weak and strong. The state of an Fe(II) ion in a strong octahedral crystal field is diamagnetic (singlet $^1A_1$). In a weak octahedral crystal field the ground state of Fe(II) ions is paramagnetic (5-fold spin-degenerate term $^5T_2$). This state may be orbitally degenerate: in an isotropic complex a hole in the t_{2g} orbitals may be placed with equal probability in any of them, and therefore the total degeneracy may be $3 \times 5 = 15$ (orbital degeneracy is connected with the orbital contribution to magnetic moment). However distortions of the crystal field usually remove orbital degeneracy. The HS and LS species differ not only in magnetic moment but the LS species also have significantly shorter (by 0.11 – 0.24Å [3]) bond lengths.

The energy difference, ΔE_{sc}, in spin crossover compounds is small – of the order of 1 – 2 kcal mol^{-1}. Variation of temperature causes a variation in the populations of LS and HS states of such complexes, hence changes in the observed magnetic properties. An interesting feature of the complexes exhibiting such *thermally induced* spin crossover is that the LS state is always the ground state ($E_0^{(\mathrm{HS})} > E_0^{(\mathrm{LS})}$). This property is connected with the higher degeneracy of the HS state and lower vibrational frequency in HS complexes. Let us consider this problem in some detail:

The partition function to be used in the calculation of the equilibrium constant of spin crossover can be written as:

$$z_{HS} = e^{-\varepsilon^0_{HS}/kT} \times z_{\mathrm{int}\,HS} \times g_{HS} \times \left[2\sinh\left(\frac{h\nu_{HS}}{2kT}\right)\right]^{-3} \qquad (3.79)$$

(A similar partition function may be written for a molecule in the LS state.) Components of this partition function and corresponding contributions to the standard entropy of spin crossover can be estimated using various experimental data. It has already been mentioned that the energies ε^0 for HS and LS states differ by *ca.* 1 – 2 kcal mol^{-1}. The degeneracy factor of an Fe(II) complex is 5 in the HS state and 1 in the LS state. Vibrational spectra show that intramolecular Fe–ligand stretching vibrations are considerably affected by spin crossover. For example, the Fe–N stretching vibrations in [Fe(Phen)$_2$(NCS)$_2$] [4] show an approximately double decrease in frequency upon LS → HS transition. Table 3.1. shows the process of evaluation of vibrational contributions to the standard entropy of spin crossover.

Table 3.1. Calculation of the vibrational contributions (at 200 K) to the standard entropy of spin crossover according to literature data on vibrational frequencies

	Lit.	ω_{HS} (cm^{-1})	ω_{LS} (cm^{-1})	$n_v \ln z_v$ (HS)	$n_v \ln z_v$ (LS)	$\ln Q_v$	$(1/T)d\ln Q/dT^{-1}$	$\Delta S^0/R$
Fe–NCS	[4]	252	533	–1.457	–3.791	2.334		
Fe–Phen	[4]	220	379	–2.246	–5.182	2.937		
sum						5.271	2.917	2.354
lattice vib.	[5]	93	108	1.146	0.670	0.476	0.040	0.436
lattice vib.	[6]	96	67	1.054	2.173	–1.119	–0.061	–1.058

There are two Fe–NCS and four Fe–N(phenanthroline) vibrations per complex; the corresponding weighting factors to the logarithms of the partition functions (n_v) are therefore 2 and 4. For lattice vibrations of the complex as a whole (characterised by Debye temperatures θ_D obtainable from Mössbauer spectra) the corresponding factor is 3 (3-dimensional oscillator). The latter contribution is not known for [Fe(Phen)$_2$(NCS)$_2$] and the data shown in Table 3.1 are on two different spin crossover compounds presented here for illustration. The temperature derivative of the vibrational partition functions was calculated by computing $\Sigma\{n_{vi}[\ln(\sinh(\omega_{HSi}/2kT) - \ln(\sinh(\omega_{LSi}/2kT)]\}$ at 180, 200 and 220 K and estimating parameters of the corresponding linear regression equation. According to (3.71) the difference $\ln Q - (1/T)d\ln Q/dT^{-1}$ represents the contribution of vibrations into the standard entropy of spin crossover in units of R.

The changes in intra-molecular vibrational frequencies contribute considerably to the entropy of spin crossover. On the other hand, the temperature dependence of the intramolecular vibrational partition function significantly decreases this contribution. The effect of lattice vibrations is small and can be either positive or negative. However, the total sum of contributions to the entropy of spin crossover is positive:

$$\frac{\Delta S^0}{R} = 1.609 + 2.35 + \left\{ \begin{matrix} +0.44 \\ -1.06 \end{matrix} \right. = 3.96 \left\{ \begin{matrix} +0.44 \\ -1.06 \end{matrix} \right. \tag{3.80}$$

in which $1.609 = \ln 5$ represents the contribution of spin-degeneracy. This estimate, $\Delta S^0 = (2.8 - 4.4)\,R$, is still less than the lowest level of experimental entropy of spin crossover in the solid state ($\Delta S^0 > 6R$).

The data given above show that the entropy of spin crossover is generally positive. If a substance exhibits spin crossover, *i.e.* if a mixture of equal amounts of the HS and LS forms can be observed at some temperature, then the difference of energies of the HS and LS states must be positive. When $x_{\text{HS}} = x_{\text{LS}} = 0.5$ the equilibrium constant is 1 and the standard free energy is zero. The temperature corresponding to such a state is called the *transition temperature* or temperature of spin crossover $T_{1/2}$ (T_{SC}):

$$\Delta F^0 = \Delta E^0 - T_{1/2}\Delta S^0 = 0 \tag{3.81}$$

i.e.

$$\Delta E^0 = T_{1/2}\Delta S^0 > 0 \tag{3.81a}$$

The *ground state of a substance exhibiting spin crossover is thus the LS state.* There are a large number of molecules with HS ground state and the excited LS state may be quite close to the ground state. However, following the reasons given above, this excited state cannot be accessed by heating. Irradiating the molecules with light of an appropriate wavelength can, however, populate such states. A well-known example of such excitation is molecular oxygen (O_2), which is HS (triplet) in the ground state. Its excited LS (singlet) state, inaccessible thermally, plays an important role in numerous *photochemical* reactions.

A paramagnetic molecule might also be converted into the diamagnetic state by changing its symmetry. For example, four-coordinated complexes of Ni(II) may often exist in either square planar (diamagnetic) or tetrahedral (paramagnetic) conformations in equilibrium. The standard enthalpy of transition from square planar to tetrahedral conformations in a series of Ni(II) complexes is small and positive ($0 - 5\ \text{kcal mol}^{-1}$, [7]). These complexes behave formally, therefore, as conventional spin crossover compounds with the HS state populated at higher temperatures. However, these equilibria are not a thermally induced spin crossover because by changing temperature we do not populate excited states but change the 'average degeneracy' of the ground state. Furthermore, square planar complexes of Ni(II) can be solvated by donor molecules, which results in paramagnetic octahedral complexes. Standard enthalpy of solvation of bis-salicylaldoximatonickel(II) by DMSO [8] is negative ($-13.5\ \text{kcal mol}^{-1}$) and at higher temperatures the LS state is more populated. However, it is the result of decreasing (due to the dissociation of solvates) number of molecules in the paramagnetic ground state and not of the population of exited states.

The law of mass action for an ideal crystal can be applied to spin crossover equilibria when the species in equilibrium are statistically independent. This is possible in two cases: (i) when the properties of HS and LS particles are very similar so that the transition of a given molecule from one state to another does not affect the states of molecules in its neighbourhood, and (ii) in diluted systems, for example in crystals of mixed metal complexes such as Fe/Zn coordination compounds. In the latter instance a molecule is mainly surrounded by molecules of 'solvent' and hence any spin transition of a given molecule can be considered not to affect the state of any other spin crossover complex.

The volumetric properties of HS and LS species are significantly different due to the presence of additional (unpaired) electrons in antibonding e_g orbitals in the HS state which causes the above mentioned increase of molecular radius by up to 10%, *i.e.* an increase in molecular volume by *ca.* 30%. Such a transformation must affect the neighbours of the said molecule. It creates mechanical strain, and this changes the potential energy of neighbouring and even remote molecules (up to the range of the characteristic length of lattice relaxation). The behaviour of pure, crystalline, spin crossover compounds must significantly deflect from that predicted by the law of mass action for ideal crystals[7]. It is generally observed experimentally in the form of a *steep spin crossover* and other deviations from ideality that will be considered in detail in Chapter 7. In amorphous solids and crystals with a high defect content (for example, after grinding in a ball-mill) spin crossover transitions approach those predicted by (3.78). In fact, vacancies in the crystal lattice can be considered as a third component of a considerably smaller molecular volume. The presence of such species partly compensates the effects of the volumetric changes accompanying spin crossover.

In 'magnetically diluted' systems spin crossover very often follows the law of mass action for ideal crystals. Fig. 3.1 shows a *practically* linear van't Hoff plot for the spin crossover equilibrium in highly magnetically diluted crystal of $[Fe_yZn_{1-y}(ptz)_6](BF_4)_2$ [9], corresponding to $y = 0.005$.

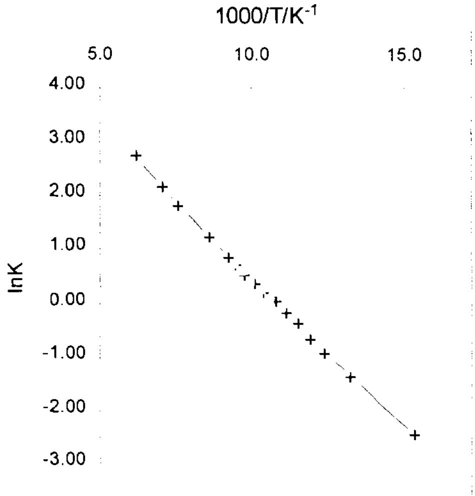

Fig. 3.1. Van't Hoff plot for spin crossover in magnetically diluted $[Fe_yZn_{1-y}(ptz)_6](BF_4)_2$, $y = 0.005$. *Crosses*: experimental data [9], *solid line*: theoretical curve

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[7] In some cases (especially at low temperatures) *magnetic interactions* between HS species (absent for LS species) must also be taken into account.

In diluted mixed crystals the species involved in chemical equilibrium are at very large distances, which excludes their direct interactions. Nevertheless the van't Hoff plot in Fig. 3.1 is slightly curved which can be explained by taking into account the temperature dependence of z_v for the lattice vibrations of a molecule as a whole:

$$\ln\frac{z_B}{z_A} = -\frac{\varepsilon_B^0 - \varepsilon_A^0}{kT} + 3\ln\frac{\sinh(\theta_A/2T)}{\sinh(\theta_B/2T)} + \frac{\Delta S^0}{R} \tag{3.82}$$

where $\theta = h\nu/k$ is the Einstein characteristic temperature and:

$$\frac{\Delta S^0}{R} = \ln\frac{g_B z_{\text{int}\,B}}{g_A z_{\text{int}\,A}} \tag{3.83}$$

The entropy ΔS^0 can, to a first approximation, be considered as temperature independent (higher temperatures are required to excite internal vibrational degrees of freedom). When we approximate the observed temperature dependence of $\ln K$ by a linear van't Hoff plot the regression error is about ± 0.063. A reliable estimation of θ_A θ_B from this set of data is impossible. However, by setting $\theta_B = 40$ K, $\theta_A = 180$ K and adjusting $\Delta\varepsilon^0$ and ΔS^0 we obtain reasonable estimates of these parameters ($N_L\Delta\varepsilon^0 = 1.634 \pm 0.005$ kcal mol^{-1}, $\Delta S^0/R = 2.74 \pm 0.03$)[8] with a regression error of $\ln K = \pm 0.024$. In the spin crossover complex with 2-picolylamine $[\mathrm{Fe}_y\mathrm{Zn}_{1-y}(2\text{-pic})_3]\mathrm{Cl}_2.\mathrm{EtOH}$ [10] the curvature of the van't Hoff plot is more pronounced and requires 15 internal degrees of freedom (apparently corresponding to 15 vibrational modes of an octahedron) to be taken into account in order to get an adequate description.

The phenomenon of spin crossover is often represented not by van't Hoff plots but by *transition curves*, $x_{\mathrm{HS}} = f(T)$. The equation of the transition curve for a spin crossover in an ideal crystal (Fig. 3.2) can be written in terms of ΔE^0 and $T_{1/2}$ as:

$$x_{HS} = \frac{1}{1+K^{-1}} = \left\{1 + \exp\left[\frac{\Delta E^0}{R}\left(\frac{1}{T} - \frac{1}{T_{1/2}}\right)\right]\right\}^{-1} \tag{3.84}$$

When analysing such curves, it is important to remember that the highest limit of x_{HS} might be considerably smaller than 1. According to (3.84) the asymptotic value of x_{HS} corresponding to infinitely high temperatures is:

$$x_{HS}^{\infty} = \left[1 + \exp\left(-\frac{\Delta E^0}{RT_{1/2}}\right)\right]^{-1} \tag{3.85}$$

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[8] Note that this value does not contain the contribution from lattice vibrations and it is still higher than the pure electronic degeneracy entropy ($R\ln 5$).

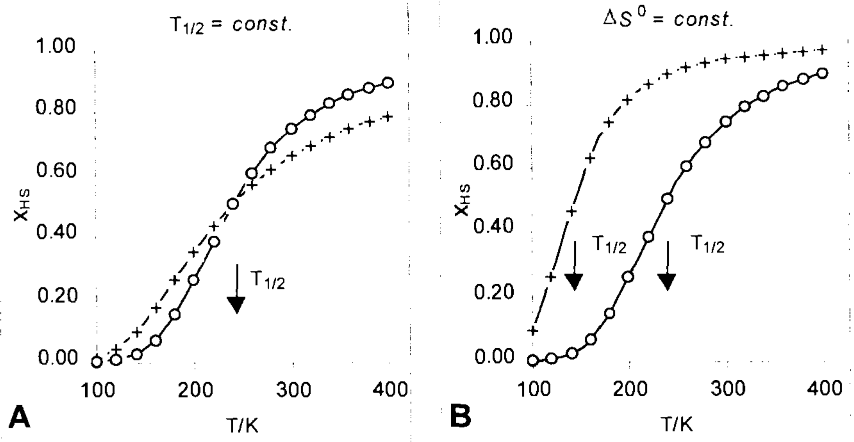

Fig. 3.2. Simulated spin crossover curves corresponding to a gradual LS → HS transition with ΔE^0 = 1.5 kcal mol^{-1} (*crosses*) and 2.5 kcal mol^{-1} (*circles*). The graph **A** illustrates the case of a constant transition temperature $T_{1/2}$ = 240 K (and varying ΔS^0), whereas the graph **B** shows the curves corresponding to identical ΔS^0 = 10.42 cal mol^{-1}K^{-1} (resulting in varying $T_{1/2}$)

For the curves shown in Fig. 3.2 this value is 0.995 (ΔE^0 = 2.5 kcal mol^{-1}), and 0.959 (ΔE^0 = 1.5 kcal mol^{-1}) but for lower energies of transition it may differ more significantly from 1.

3.6
Liquids

The difficulties in constructing an ideal model of the liquid state are connected with strong molecular interactions and migrations of molecules making the integration over coordinates a necessary and quite complicated procedure. These difficulties are alleviated by two circumstances. First of all, in systems of uncharged particles (excluding, therefore, solutions of electrolytes) the interactions between nearest (and perhaps next nearest) neighbours are alone really important. Secondly, the number of nearest neighbours of a given molecule is large (the coordination number is *ca.* 10) providing for an efficient averaging of interactions. A useful approximate model of the liquid state can be constructed on these assumptions: molecules can be considered as mainly residing in the cells of a quasi-crystal lattice. Within these cells they may perform various types of motion in the *average field* created by their neighbours. The mean field within a cell can be considered as approximately static. The motion within the volume of a system is achieved by comparatively rare and very fast jumps of molecules from cell to cell. The state of a molecule is then determined by its coordinates within a cell *independently of the coordinates of all other molecules*. Such a system can be considered as pseudo-ideal.

This model is actually based on the experimental observation that liquids have much more in common with solids than with gases. The only feature common for liquids and gases is the indistinguishable nature of molecules. On the other hand, the volumetric properties of liquids and solids are quite similar: their densities may differ by a maximum of 15%, whilst the density of the gaseous phase in equilibrium with liquid is *ca.* 1000 times smaller. Even the mode of molecular motion in liquids at temperatures close to the melting point resembles that in solids: molecules perform motion mostly within their cells with occasional jumps from cell to cell whilst in solids such jumps can be neglected.

The concept of the volume itself is completely different in the cases of the condensed and gaseous states. The volume of a gas is the volume of the vessel containing it. Liquids as well as solids have their own volume and as a consequence they also possess surfaces (or interfaces). The volume of a gas at a given pressure is proportional to the *number of molecules* whereas the volume of liquid at a given pressure is proportional to the *quantity of matter*. Liquids are usually considered as incompressible and therefore, at pressures not exceeding tens of bars, the *specific volume* of a liquid is approximately constant and determined by the *elemental composition of the system*. The densities of liquids, either organic or inorganic, composed of specified types of atoms lie in a narrow range. For example, the liquids composed of atoms of hydrogen, carbon, nitrogen and oxygen vary between 0.7 – 1.2. Higher densities are achieved by the introduction of heavier elements in which matter is made compact by the *'strong'* nuclear interactions.

When we look at an equilibrium reaction mixture we notice that it is composed of the same atoms and in the same numbers as the initial mixture. Therefore a non-isomolar reaction in the condensed state does not significantly change its volume. In contrast, a non-isomolar gas phase reaction (at constant pressure) is connected with volume changes proportional to the change in the number of molecules.

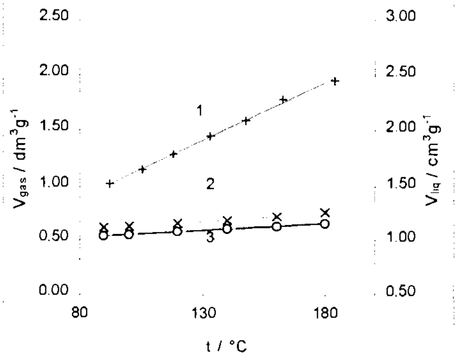

Fig. 3.3. Specific volumes of gaseous (1) and liquid (3) acetic acid. Curve (2) shows the specific volume of liquid methyl formate as reference

A simple example illustrates this proposition. The density of the vapour of acetic acid (Fig. 3.3) is strongly temperature dependent because of a dimerisation equilibrium (*via* hydrogen bonding) with ΔH^0 = 14.3 kcal mol^{-1} (see p. 896 in [11]). In the liquid phase the same dimerisation equilibrium exists and NMR investigations show that the enthalpy is of the same order of magnitude or even higher [12]. Despite this fact, the specific volume of liquid acetic acid is but slightly increasing with temperature, at a rate similar to the thermal expansion of liquids not exhibiting hydrogen bonding (such as methyl formate, curve 2, Fig. 3.3).

3.6.1
The law of mass action for an 'ideal liquid'

Let us derive the law of mass action for a liquid state reaction taking into account only one particular feature of the liquid state, *viz.* the invariance of the total volume of a reaction mixture under constant pressure. The molecules we consider as material points moving freely in the *whole total volume V*. The latter condition actually means that molecules *are* material points, otherwise some space would be forbidden for a given molecule. The volume of a liquid system of constant mass is independent of the number of molecules. The molecules are supposed to interact with a uniform molecular mean field which actually causes them to be confined within the volume *V*. This model seems to be more applicable to a highly compressed gas in a vessel placed in a strong external force field than to a liquid. The difference is that the pressure in such a gaseous system is proportional to the number of particles whilst in a liquid it is constant. Molecules are statistically independent and indistinguishable except by their chemical nature. The partition function of such a binary liquid mixture (see p. 687 in [11]) is:

$$Z = \left(\frac{(2\pi m_A kT)^{\frac{3}{2}}}{h^3} \frac{eV}{N_A} \right)^{N_A} z_{iA}^{N_A} e^{-\frac{N_A \varepsilon_A^0}{kT}} \left(\frac{(2\pi m_B kT)^{\frac{3}{2}}}{h^3} \frac{eV}{N_B} \right)^{N_B} z_{iB}^{N_B} e^{-\frac{N_B \varepsilon_B^0}{kT}} \quad (3.86),$$

where the exponential factors account for the possibility of migration of a molecule within the whole volume of a system, ε^0 is the potential energy comprising the electronic energy and potential energy in the mean field, and z_i is the product of partition functions for internal degrees of freedom. The total volume V being independent of composition we can write the free energy as:

$$F = -kT \ln Z = \left[N_A (\ln q_A - \ln N_A) + N_B (\ln q_B - \ln N_B) \right] \quad (3.87)$$

in which 'partition functions' q_A and q_B are independent of composition. Under the condition of V = const they are determined by the 'intramolecular' properties of corresponding molecules:

$$q_A = \left(\frac{(2\pi m_A kT)^{3/2}}{h^3} eV \right) z_{iA} e^{-\frac{\varepsilon_A^0}{kT}} \tag{3.88}$$

The expressions (3.87) and (3.88) are similar to (3.30) and (3.43) for an ideal gas. The latter yielded the law of mass action, (3.51) – (3.54), with respect to the numbers of molecules or molar concentrations. A reaction in the liquid state under constant pressure is therefore described by the law of mass action of a gas phase reaction at constant volume. We are not able, however, to perform a conversion to mole fractions because the equation of state is unknown and the volume V is *not* proportional to the number of molecules.

Fortunately, it can be easily shown that the form with respect to *mole fractions* corresponds to the invariance of the *volume per molecule.* By substituting in (3.86):

$$V = (N_A + N_B)v \tag{3.89),}$$

in which v is the volume per molecule and by applying the Stirling formula the partition function (3.86) can be transformed into:

$$Z = \frac{(N_A + N_B)!}{N_A! N_B!} \left(\frac{(2\pi m_A kT)^{3/2}}{h^3} ev \right)^{N_A} z_{iA}^{N_A} e^{-\frac{N_A \varepsilon_A^0}{kT}} \left(\frac{(2\pi m_B kT)^{3/2}}{h^3} ev \right)^{N_B} z_{iB}^{N_B} e^{-\frac{N_B \varepsilon_B^0}{kT}} \tag{3.90}$$

The corresponding expression for free energy becomes:

$$F = -kT \ln Z = \left[N_A \left(\ln q_A - \ln \frac{N_A}{N_A + N_B} \right) + N_B \left(\ln q_B - \ln \frac{N_B}{N_A + N_B} \right) \right] \tag{3.91),}$$

in which:

$$q_A = \left(\frac{(2\pi m_A kT)^{3/2}}{h^3} ev \right) z_{iA} e^{-\frac{\varepsilon_A^0}{kT}} \tag{3.92}$$

It is when the volume per molecule v is independent of N_A, N_B that the condition $dF = 0$ results in the law of mass action of an ideal gas with respect to mole fractions.

The invariance of the volume per molecule in the liquid phase implies an equality of molar volumes of components. In fact, *Raoult's Law* when formulated in terms of mole fractions is only applicable to mixtures of molecules of approximately equal volumes.

We see that by considering a liquid as a system of statistically independent material points and taking into account the invariance of the specific volume of liquids of the same elemental composition, a general rule can be derived: *molar concentrations should be used as variables in the law of mass action.* An additional condition is that the quantity of matter remains unchanged, *i.e.* nothing escapes into another phase (gaseous, solid or liquid). The state of infinite dilution is a good approximation to a reaction in an 'ideal liquid' because reacting particles are randomly distributed and surrounded mostly by solvent molecules. The *volume* of such a system is determined by the volumetric properties of the solvent and is independent of the degree of conversion.

3.7
'Breakdown' of the law of mass action

Liquid phase equilibria strongly shifted to one side present the problem that only small numbers of molecules are involved in the equilibrium when the volume of the reaction mixture is small. It is now nearly a decade since the first publication appeared [13] declaring a breakdown of the law of mass action in vesicles containing $10^7 - 10^9$ water molecules. The law of mass action indeed predicts for such systems (at pH = 7) that the number of pairs of H^+ and OH^- ions must be less than one. Such a result has been interpreted by Blumenfeld *et al.* [14] as meaning that some of the vesicles dispersed in bulk water contain one or more pairs of ions whereas others contain none of them. The average numbers of dissociated water molecules in vesicles computed in [14] proved to be completely different from that given by the law of mass action for bulk water. One of the consequences of such behaviour might be a gradient of thermodynamic potential across the membrane separating vesicle from bulk water. The authors produced some experimental data on the smallest living units supporting this discovery and explained the breakdown of the law of mass action by the effects of *fluctuations*.

However, this interpretation is suspicious because fluctuations affect the second derivatives of thermodynamic potential (see Chapter 2) whereas the law of mass action represents the first derivative. Fluctuations should not therefore affect the mean values of concentrations predicted by the law of mass action – although they determine the ease with which mean values may deviate from the most probable values by variations in temperature, pressure, *etc.* Secondly, the fluctuations in living organisms should not be large according to the answer given by Erwin Schrödinger to 'naive physicist' (see Introduction). In fact, the expected relative fluctuations for an *ideal gas* containing 10^6 molecules are of the order 10^{-3} whilst the deviations from the law of mass action predicted by the formulae of Blumenfeld *et al.* are much larger. This 'breakdown of the law of mass action' was critically considered by Sokirko [15] whose (clearer) presentation of the problem we shall now analyse.

Consider water ionisation equilibrium occurring in a closed volume containing N molecules:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \tag{3.93}$$

The ions H_3O^+ and OH^- are present in small quantities and are therefore separated by distances of several tens of nanometers, which provides for the validity of the ideal gas laws for such a system. The equilibrium constant of this reaction is the ionic product divided by the square of water concentration, *i.e.* it is *ca.* 3.2×10^{-18}. The equations of the law of mass action and material balance for (3.93) may be written with respect to the numbers of ions as:

$$m = n_+ = n_- = (N - n_0)/2 \tag{3.94}$$

$$\ln K = \ln\frac{q_+q_-}{q_0^2} = \ln\frac{m^2}{(N-2m)^2} \tag{3.95}$$

in which (neglecting to a first approximation the contributions from rotational and vibrational partition functions, see Appendix 10.5):

$$q_i = \left(\frac{2\pi\mu_i kT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{\varepsilon_i}{kT}} \tag{3.96}$$

and μ_i is the mass of the corresponding particle. Taking into account (3.96) the equilibrium constant of (3.93) can be written as:

$$\ln K = \ln\left(\frac{\mu_{H_3O^+}\mu_{OH^-}}{\mu_{H_2O}^2}\right)^{\frac{3}{2}} \exp\left(-\frac{\varepsilon_{H_3O^+} + \varepsilon_{OH^-} - 2\varepsilon_{H_2O}}{kT}\right) \tag{3.97}$$

The masses of the particles involved in the equilibrium (3.93) are practically identical (μ = 17, 18 and 19) and therefore the equilibrium constant is mainly determined by the exponential term in (3.97). According to (3.95) the equilibrium value of the number of dissociated molecules m can be found as a solution of the quadratic equation:

$$m^2(1-4K) + 4KNm - KN^2 = 0 \tag{3.98}$$

$$m = \frac{2KN^2}{4KN \pm \sqrt{16K^2N^2 + 4(1-4K)KN^2}} = \frac{N\sqrt{K}}{2\sqrt{K}\pm 1} \tag{3.98a}$$

For small equilibrium constants (such as considered here) the number of pairs of ions is approximately proportional to the square root of K. This number is less than one when $N\sqrt{K} < 1$, *i.e.* when the number of water molecules in a vesicle is less than 5×10^8.

Blumenfeld *et al.* then considered an ensemble of such vesicles and calculated the *mean number of vesicles containing a dissociated molecule* ($<m>$). Neglecting rotational and vibrational contributions the partition function for the equilibrium mixture (3.93) in a vesicle was written as:

$$Z_{ves} = (q_+V)^m (q_-V)^m (q_0V)^{(N-2m)} \frac{1}{m!}\frac{1}{m!}\frac{1}{(N-2m)!} e^{-\frac{(N-2m)\varepsilon_0 + m(\varepsilon_+ + \varepsilon_-)}{kT}} \tag{3.99}$$

The masses of particles involved (H_2O, H_3O^+ and OH^-) being nearly identical, the first three terms equal $(q_0V)^N$. The factorial $(N-2m)!$ for large N and small m may be approximated as:

$$(N-2m)! \cong (N-2m)^{N-2m} e^{-(N-2m)} \cong (N/e)^N (N/e)^{-2m} \tag{3.100}$$

Therefore the partition function (3.99) may be written[9] as:

$$Z_{ves} = \left(\frac{q_0 e V}{N}\right)^N e^{-\frac{N\varepsilon_0}{kT}} \left(\frac{1}{m!}\right)^2 e^{-\frac{m(\varepsilon_+ + \varepsilon_- - 2\varepsilon_0)}{kT}} e^{-2m} N^{2m} \tag{3.101}$$

The mean over the ensemble value of m was then calculated *using partition function* (3.101) as a *statistical weight*:

$$\langle m \rangle = \frac{\sum\limits_{m=0}^{\max} m Z_{ves}}{\sum\limits_{m=0}^{\max} Z_{ves}} = \frac{\sum\limits_{m=0}^{\max} \frac{m}{(m!)^2} \left[e^{-\frac{\Delta\varepsilon}{kT}} \frac{N^2}{e^2} \right]^m}{\sum\limits_{m=0}^{\max} \frac{1}{(m!)^2} \left[e^{-\frac{\Delta\varepsilon}{kT}} \frac{N^2}{e^2} \right]^m} \tag{3.102}$$

in which $\Delta\varepsilon = \varepsilon_+ + \varepsilon_- - 2\varepsilon_0$. For large $\Delta\varepsilon/kT$ and complying with the condition:

$$\left(\frac{N}{e}\right)^2 e^{-\frac{\Delta\varepsilon}{kT}} < 1 \tag{3.103}$$

the series in (3.102) converge fast and the first two terms corresponding to $m = 0$ and $m = 1$ are sufficient for a reliable calculation of $<m>$ (see Table 3.2). The mean number of vesicles containing one dissociated water molecule can then be calculated as:

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[9] Note that a certain manipulation has been performed when approximating the factorial $(N - 2m)!$. The difference $N - 2m$ was assumed to equal N as the base but not as the power. In this case it is permissible, but in general a separation of a small value from a large one can be dangerous.

$$\langle m\rangle = \frac{e^{-\frac{\Delta\varepsilon}{kT}}e^{-2}N^2}{1+e^{-\frac{\Delta\varepsilon}{kT}}e^{-2}N^2} \tag{3.104}$$

Table 3.2 The ratio of the mean values of *m* calculated using the first 2 and the first 12 terms in the sums in (3.102) at different values of $\alpha = (N/e)^2\exp(-\Delta\varepsilon/kT)$

α	0.8	0.6	0.4	0.2	0.1
$m(2)/m(12)$	0.753	0.796	0.848	0.914	0.954

The exponentials in (3.104) *equal the equilibrium constant as defined by the law of mass action* (3.95), therefore:

$$\langle m\rangle = \frac{KN^2/e^2}{1+KN^2/e^2} \cong KN^2/e^2 \tag{3.105}$$

On the other hand, when $(N/e)^2\exp(-\Delta\varepsilon/kT) > 1$ the series in (3.102) can be substituted by their largest term and both sums cancel out resulting in the mean value becoming identical with the most probable value $<m> = m^*$ (corresponding to the maximum of the partition function). This condition ($d\ln Z/dm = 0$), as we know, results in a conventional law of mass action which yields:

$$m^* = \frac{N\sqrt{K}}{2\sqrt{K}+1} \cong N\sqrt{K} \tag{3.106}$$

As has been pointed out by Sokirko [15], (3.105) has been obtained for an ensemble of *essentially closed systems*. Such an ensemble when considered as one system is *not* in thermodynamic equilibrium because it is separated by partitions impenetrable to molecules. *The law of mass action cannot be applied to such a system*. For a collection of bacteria or cells exchanging water molecules and ions with bulk water the averaging must be performed over an ensemble of open systems (grand canonical ensemble). In such a case the averaging results in an expression identical to that given by the law of mass action [15].

In a *single* small isolated system ionisation equilibria can be considered as a stochastic process occurring in time. The mean number of dissociated molecules per vesicle then corresponds to the number of events of dissociation normalised to the total number of trials.

These problems are not of purely theoretical interest because the formalism of Blumenfeld *et al.* predicts a considerable difference (not connected with surface effects) in the concentrations of charged particles in bulk water and in small capsules. These concentrations must differ by the factor $\sqrt{K}$, *i.e.* 10^{-9} for water, which would proportionally affect the rates of reactions catalysed by protons and hydroxyls. Although for water ionisation equilibrium the size of a system complying with (3.103) is too small to be investigated (1.5×10^{-15} cm^3, *i.e.* a cube with sides of 2.5×10^{-4} mm) there are several quite tangible systems complying with this condition. The ionic product of saturated hydrocarbons is estimated [16] as *ca.* 10^{-40} mol^2 l^{-2}, *i.e.* there must be less than one dissociated proton in under 0.17 ml. There are also some very stable complexes of transition metals: the first stage of dissociation of $[Hg(CN)_2]$ is characterised by $K_1 \cong 10^{-16}$ mol l^{-1}; $K_2 \cong 10^{-17}$ mol l^{-1} [17]. The concentration of free mercury ions in a solution containing 1 mol l^{-1} of $HgCN_2$ and 1 mol l^{-1} of KCN is then 10^{-33} mol l^{-1}. One needs therefore to go through at least 1.6×10^9 litres of such a solution in order to find a single free mercury ion!

A *single* event of dissociation of a molecule can hardly be detected using any direct non-invasive method but the rates of $^1H/^2H$ isotope exchange must be proportional to the number of dissociated protons/deuterons. This provides for an indirect method of estimating the mean number of acts of dissociation in small systems. For example, in a solution of deuterated cyclohexane in an excess of protonated benzene (or *vice versa*) one can expect to observe (after a sufficiently long time) an increase in the intensity of the PMR signal of C_6HD_{11} (CHD_5). The limiting stage of the deuteron-proton in such a solution is the dissociation of the deuteron/proton. Therefore the rate of protonation (easier observed than the rate of deuteration) must be different in a small sample (less than 0.2 ml C_6D_{12} in an excess of C_6H_6) for which (3.105) holds and in a two-litre flask for which the law of mass action is valid. The difference is rather dramatic: the rate of protonation in the large flask must be larger by the factor $\sqrt{K}$, *i.e.* 10^{20}! To our knowledge no evidence of such behaviour[10] has ever been made public.

Theoretically, a process involving rare events can be described using the Poisson distribution. Observing for a long time a single 'small' system we detect (or rather accumulate in the form of protonated cyclohexane) a certain number (m) of events of dissociation. For small degrees of conversion the probability of such a result follows the Poisson distribution:

$$P_{m,n} \cong \frac{(pn)^m}{m!} e^{-np} \tag{3.107}$$

in which $P_{m,n}$ is the probability of detecting dissociation in m trials out of n and p is the probability of a single rare event approaching zero at finite pn. The number of trials can be identified with the number of oscillations of a deuteron/proton made during the observation period *i.e.* $n \cong 10^{14}\tau$ (τ in seconds). For large[11] $m \gg 1$ the

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[10] A rather serious disadvantage of this method is that several years must elapse before a meaningful answer is obtained and experiments must be carried out deep under the Earth's surface in order to exclude the background effects of cosmic rays!

[11] Observing a small change in the intensity of a PMR signal of a deuterated compound means that m *is* large because the sensitivity of PMR is 10^{15} protons (events of dissociation) at best.

Poisson distribution can be written using the Stirling approximation as:

$$P_{m,n} \cong \left[\frac{pn}{m} e^{1-\frac{pn}{m}}\right]^m \tag{3.108}$$

This probability approaches 1 when $pn/m = 1$, that is

$$\frac{m}{n} = p \tag{3.109}$$

i.e. the expected value of m is pn, a well-known result in the theory of random processes. The probability of a single act of dissociation can be expressed similarly to the equilibrium constant as $\exp(-\Delta\varepsilon/kT)$ and in this sense (3.109) formally agrees with (3.105). However, the physical significance of $\Delta\varepsilon$ in (3.109) is completely different: it is not the standard energy of reaction but the *height of the potential barrier* in the reaction path of heterolytic bond cleavage. This comparison shows that the mode of computation of mean numbers employed by Blumenfeld *et al.* was essentially stochastic and implied the use of parameters different from those of thermodynamic formulae.

It is also possible to derive the law of mass action in a form mathematically correct for small numbers of particles by representing the factorial in terms of the Γ–function. This approximation results (see Appendix 10.6) in the law of mass action:

$$\ln\frac{q_+q_-}{q_0^2} - \ln\frac{(m+0.52)^2}{N^2} \cong 0 \tag{3.110}$$

which predicts that in small systems ($KN^2 \le 0.52^2$) no (thermally actuated) ionisation would take place. According to this, the protonation of C_6D_{12} (if observed) in such small systems can only be due to the radiation effects of light and cosmic rays! In other words (3.110) predicts the irreversibility of chemical reactions, which contradicts the initial assumptions employed in the derivation of the law of mass action. It must be remembered that the Γ–function is just an approximation providing for the smoothest interpolation of a function of essentially integral arguments. The same problem arises if we try to correct the Maxwell – Boltzmann distribution by taking into account that some of the filling numbers n_i (p. 7) are small and $n_i!$ should be represented in terms of the Γ–function. Such a correction would result in the distribution:

$$n_i + 0.52 \cong e^{-\alpha-\beta\varepsilon_i} \tag{3.111}$$

Again, this law actually puts a limit on the possible energy of a particle corresponding to the condition:

$$0.52e^{\alpha} \le e^{-\beta\varepsilon_i} \tag{3.112}$$

which does not have any physical significance. This shows that the cell method of Boltzmann, allowing for the derivation of the main formulae of statistical mechanics and thermodynamics, is not completely correct; particularly in the use of combinatorics formulae for the distribution over the energy levels, some of which can be empty. This method, however, is based on an extremely clear physical model, and, as has been emphasised by Sommerfeld [18], its results are correct.

In fact, the general applicability of the law of mass action to the description of *chemical equilibria* in small macroscopic objects is not questioned by any of the singularities described above. A chemical equilibrium also imposes restrictions on the composition of the reaction mixture in the form of the *mass balance equation*. The numbers of particles are not independent variables and, mathematically, the choice of a variable can be correct or incorrect (fortunate or unfortunate). For small systems, the law of mass action should be written with respect to the numbers of non-dissociated molecules:

$$\ln K = \ln \frac{q_+ q_-}{q_0^2} = \ln \frac{(N - n_0)^2}{n_0^2} \tag{3.113}$$

For small KN but large N this equation yields $n_0 \cong N$ to an *extremely high degree of precision.*

3.8
Conclusions

In this Chapter we have shown that the law of mass action is not an empirical relationship but a fundamental law originating from the dependence of free energy on the composition of reaction mixtures. The general variables of the law of mass action in an ideal gas are the numbers of molecules that can be converted to either molar fractions or molar concentrations resulting in specific forms applicable to the cases of constant volume and constant pressure. The equilibrium constant is a function of *two* parameters in all cases, namely temperature together with either volume (K_n), pressure (K_x) or chosen units of concentration (K_C). This fact determines the concept of the *standard state* that includes a standard temperature and either standard volume, pressure, or concentration. Chemical affinity can be uniformly characterised by the standard free energies of reactions that can be calculated from the standard free energies of the components of a chemical equilibrium.

The use of a van't Hoff plot to describe the temperature dependence of equilibrium constants corresponds to a linear approximation of a rather complicated relationship in the vicinity of the standard temperature.

The free energy of an ideal crystal has been derived as a function of mole fractions, thus indicating that this quantity should be used as the main variable in the law of mass action for solid state reactions. The examples of spin crossover equilibria show that the ideal form of the law of mass action can only be applied in diluted solid systems (when the species in equilibrium are separated from each other).

By taking into account specific volumetric properties of liquids (*viz.* the invariance of volume with respect to the number of particles in a system of constant mass), the general applicability to liquid systems of the law of mass action with molar concentrations as the main variable has been demonstrated. Note that the law of mass action with respect to mole fractions can only be applied to liquid mixtures of molecules of approximately equal molecular volume.

The 'breakdown' of the law of mass action predicted for pseudo-ideal diluted systems by statistical analysis has its origins in the incorrect mode of calculation of the probabilities. The fluctuations *cannot change the mean values of the first derivatives of thermodynamic potentials*, one of which is represented by the law of mass action. Real deviations from ideality are connected with molecular interactions. In the next Chapter we introduce them by employing a semi-empirical approach.

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4 Reactions in Imperfect Condensed Systems. Free Volume

4.1

Additive volume: a semi-empirical model of repulsive interactions

One of the earliest theories of the liquid state developed by Jäger [1] described an 'ideal liquid' as a collection of hard spheres of finite diameters comparable to the distances between their centres and held together by cohesive internal pressure. As has been mentioned in Chapter 3, the admission of finite diameters of molecules introduces repulsive interactions and the system of such particles cannot be considered as ideal. In fact, the ideal liquid of Jäger is a slightly imperfect liquid in which repulsive interactions are accounted for in the semi-empirical form of the finite volumes of molecules. Attractive interactions in the form of cohesive internal pressure are introduced irrespective of any molecular model.

It must be emphasised that the separation of molecular interactions into repulsive and attractive contributions is only possible within a theoretical model employing a certain (simplified) intermolecular potential (see Section 4.3). In reality the volume of a liquid always reflects a balance between repulsive and attractive forces. It is the *difference* in the steepnesses of the repulsive and attractive potentials that makes it possible to consider volume as reflecting mainly the repulsive interactions (see Chapter 5).

The volume of a 'Jäger' liquid under constant external pressure can be considered as an additive property with respect to the numbers of molecules *provided their diameters do not differ too much.* The volume of a mixture of molecules of approximately equal size may then be calculated as:

$$V = \sum_i n_i v_i \tag{4.1}$$

in which v_i is the volume per molecule of the i-th kind. As the result of finite molecular volumes the volume of a reaction mixture becomes a *function of composition* and we must take it into account when deriving the law of mass action. We will do this presently neglecting at first another possible contribution from non-ideality connected with the energy of attractive interactions.

A.B. Koudriavtsev et al., *The Law of Mass Action*

4.1.1
Binary equilibrium in a liquid with repulsive interactions

Consider a simple monomolecular equilibrium (*e.g.* spin crossover) in the liquid state without a solvent:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{4.2}$$

When deriving a law of mass action for a system exhibiting volume changes the *Gibbs free energy* must be employed as the thermodynamic potential. The Gibbs free energy ($G = F + pV$) of such a reaction mixture is given by:

$$-\frac{G}{kT} = (N - n_B)[\ln q_A + \ln eV - \ln(N - n_B)] + n_B[\ln q_B + \ln eV - \ln n_B] - \frac{pV}{kT} \tag{4.3}$$

in which $N = n_A + n_B$ is the total number of molecules. The condition of equilibrium of such a reaction in the liquid phase corresponds to $dG/dn_B = 0$. Taking into account any possible dependence of volume on composition $V = f(n_B)$ we get:

$$\begin{aligned} -\frac{1}{kT}\frac{dG}{dn_B} &= -\ln q_A - \ln eV + \ln(N - n_B) + (N - n_B)\left[\frac{d\ln V}{dn_B} + \frac{1}{N - n_B}\right] \\ &\quad + \ln q_B + \ln eV - \ln n_B + n_B\left[\frac{d\ln V}{dn_B} - \frac{1}{n_B}\right] - \frac{p}{kT}\frac{dV}{dn_B} = 0 \end{aligned} \tag{4.4}$$

We see that although the terms $\ln V$ cancel out, those containing the derivative of volume with respect to n_B do not, and the law of mass action must therefore be written as:

$$\ln\frac{q_B}{q_A} - \ln\frac{n_B}{n_A} + \frac{N}{V}\left(1 - \frac{pV}{NkT}\right)\frac{dV}{dn_B} = 0 \tag{4.5}$$

We also see that the work against external pressure is represented in the law of mass action by the term:

$$\frac{pV}{NkT}\frac{dV}{dn_B}$$

The ratio pV/NkT equals 1 when all N molecules are in the ideal gas state. The volume of a liquid or solid system containing N molecules is *ca.* 1000 times smaller. Therefore, for pressures of up to 10 bars, the error connected with the use of the Helmholtz free energy instead of the Gibbs free energy would not exceed 1%. Neglecting, therefore, the term pV/NkT modifies equation (4.5):

$$\ln\frac{q_B}{q_A} - \ln\frac{n_B}{n_A} + \frac{N}{V}\frac{dV}{dn_B} = 0 \tag{4.6}$$

The changes in volume expected for a liquid system of constant elemental composition are small. Therefore the last term in (4.6) can be considered as a small parameter and represented in logarithmic form[1], that is $\pm\delta \cong \ln(1 \pm \delta)$. When taking into account that $N = n_A + n_B$, the non-ideality term can be transformed into activity coefficients:

$$\ln\frac{q_B}{q_A} - \ln\left[n_B\left(1 - \frac{n_B}{V}\frac{dV}{dn_B}\right)\right] + \ln\left[n_A\left(1 + \frac{n_A}{V}\frac{dV}{dn_B}\right)\right] = 0 \tag{4.7}$$

Note that the activity coefficients for products and reactants have different signs: a result of differentiation with respect to one variable ($dn_B/dn_A = -1$). This law of mass action can be written with respect to one type of variable, *viz.* molar concentrations, by adding and subtracting $\ln V$ in the left-hand part of (4.7).

If the volume V is additive with respect to the numbers of molecules of components, then:

$$V = (N - n_B)\upsilon_A + n_B\upsilon_B = N(\upsilon_A + x_B\Delta\upsilon) \tag{4.8}$$

in which υ_A and υ_B are molecular volumes of the components and $\Delta\upsilon = \upsilon_B - \upsilon_A$. The derivative dV/dn_B then equals $\Delta\upsilon$ and the law of mass action (4.6) becomes[2]:

$$\ln\frac{q_B}{q_A} - \ln\frac{x_B}{1 - x_B} + \frac{\Delta\upsilon}{\upsilon_A + x_B\Delta\upsilon_B} = 0 \tag{4.9}$$

We may use mole fractions or numbers of moles (the reaction is isomolar) as variables in the ideal part of (4.9) but volumetric properties remain important as indicated by the non-ideality term. In order to describe the thermal behaviour of this equilibrium the term $\ln(q_B/q_A)$ can be represented as:

$$\ln\frac{q_B}{q_A} = -\frac{\Delta E}{RT} + \frac{\Delta S}{R} \tag{4.10}$$

The parameters ΔE and ΔS are the 'ideal parts' of the standard internal energy and entropy of (4.2). They correspond to zero volume changes and are controlled exclusively by intramolecular parameters. Calculating the temperatures corresponding to given x_B values thus enables transition curves to be simulated:

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[1] In other words expanding $\exp[(N/V)dV/dn_B]$ into a power series and truncating it at the linear term.

[2] Note that the derivatives in (4.6) and (4.7) are *complete*, and not *partial*, derivatives. The latter are $\partial V/\partial n_A = \upsilon_A$, $\partial V/\partial n_B = \upsilon_B$.

$$T = \frac{\Delta E}{\Delta S^0 - R\ln\frac{x_B}{1-x_B} + \frac{R\Delta\upsilon}{\upsilon_A + x_B\Delta\upsilon}} \tag{4.11}$$

Note that, theoretically, the tangent to the transition curve at the deflection point can be vertical when:

$$x(\Delta\upsilon/\upsilon_A + 2) + \Delta\upsilon/\upsilon_A = 0 \tag{4.12}$$

However, the roots of (4.12) are either negative (*i.e.* $x < 0$) or $x > 1$, both of which are meaningless.

Fig. 4.1 shows that the transition curves simulated according to (4.11) run slightly steeper when $\Delta\upsilon > 0$. Corresponding van't Hoff plots (Fig. 4.1B) show that the non-zero balance, $\Delta\upsilon$, affects mainly the entropy of transition ($\Delta S^0 = 10.41$ cal mol^{-1} K^{-1} *vs.* 10.0 cal mol^{-1} K^{-1} in an ideal solution). The standard energy of spin crossover is changed to a lesser extent ($\Delta E^0 = 2.473$ kcal mol^{-1} *vs.* 2.5 kcal mol^{-1} in an ideal solution)[3]. Van't Hoff plots remain practically linear and only a slight decrease in apparent energy of reaction can be expected for large volume changes (2.309 *vs.* 2.500 kcal mol^{-1} for $\Delta\upsilon/\upsilon_A = 1$). Reactions in the condensed state are, in general, accompanied by comparatively small changes in volume. For example, spin crossover equilibria are characterised by $\Delta\upsilon/\upsilon_A \leq 0.3$ which can result in a small contribution to the standard entropy of reaction. Significant deviations of van't Hoff plots from linearity (steep spin crossover) cannot therefore be explained by volume changes.

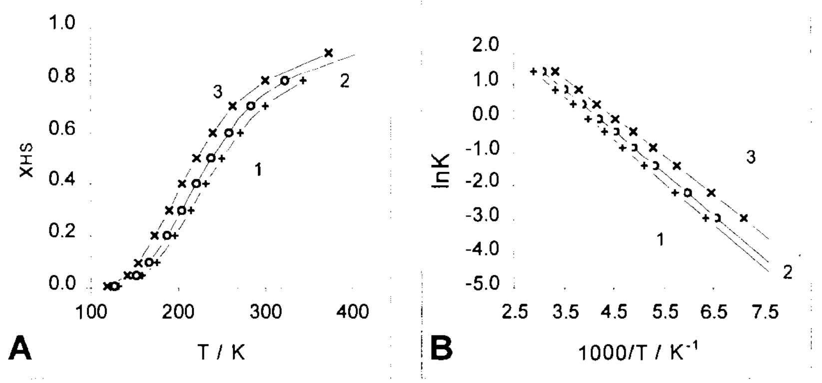

Fig. 4.1. Transition curves (**A**) and van't Hoff plots (**B**) simulated for a spin crossover system with $\Delta E = 2.5$ kcal mol^{-1}, $\Delta E/\Delta S = 250$ K. Curve 1 corresponds to an ideal solution ($\Delta\upsilon = 0$). Curve 2 corresponds to $\Delta\upsilon = 0.3\,\upsilon_{LS}$ and curve 3 to $\Delta\upsilon = \upsilon_{LS}$

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[3] These values are the standard (apparent) internal energy and entropy of reaction and include the effects of non-ideality.

4.1.2
Non-isomolar equilibrium in liquid with repulsive interactions

One of the most intensively studied types of reaction in the liquid phase is the formation of weak molecular complexes in solutions [2, 3, and 4]:

$$A + B \rightleftharpoons C \tag{4.14}$$

Equilibria of this type are usually investigated by measuring some property such as optical density, shift of band maximum, NMR chemical shifts, *etc.* as a function of the initial concentrations C_A, C_B. The dependencies so obtained are then analysed either by non-linear regression or by employing some linearised regression equations. It is of interest to find out what might be the effects of non-ideality in such systems.

Consider, for example, the formation of the molecular complex of $CHCl_3$ (acid) with *tri*-butylphosphate (base) in cyclohexane (solvent) which can be followed by measurements of the chemical shift of the $CHCl_3$ proton. The dependence of the exchange averaged chemical shift of the $CHCl_3$ proton originates from a simple additivity rule:

$$\delta_{obs} = \delta_A + (\delta_C - \delta_A)\frac{[C]}{C_A} \tag{4.15}$$

in which δ_A is the chemical shift of $CHCl_3$ in the absence of base, δ_C is the chemical shift of $CHCl_3$ in its complex with TBP. Employing the ideal form of the law of mass action, the concentration of complex $[C]$ is obtained as the real positive root of the quadratic equation:

$$K(C_A - [C])(C_B - [C]) - [C] = 0 \tag{4.16}$$

Under the condition of a large excess *of base*, $C_B \gg C_A$ (hence $C_B \gg [C]$), this equation becomes linear:

$$[C] = \frac{KC_AC_B}{1 + KC_B} \tag{4.17}$$

The observed (averaged) chemical shift (c.s.) is then a simple function of the equilibrium constant, the chemical shifts in free and complexed states (δ_A and δ_C), and the analytical concentration of the base C_B:

$$\delta_{obs} = \delta_A + (\delta_C - \delta_A)\frac{KC_B}{1 + KC_B} \tag{4.18}$$

This equation can be transformed into the so-called Foster – Fyfe plot [3] which is an NMR version of the Benesi – Hildebrand equation employed in optical spectroscopy [4]:

$$(\delta_{obs} - \delta_A)^{-1} = \frac{C_B^{-1}}{K(\delta_C - \delta_A)} + \frac{1}{(\delta_C - \delta_A)} \tag{4.19}$$

The equilibrium constant, K, and the difference of chemical shifts ($\delta_C - \delta_A$) can be obtained from the slope and intercept of (4.19). This method is applicable to the study of *weak complexes* when a considerable amount of free acid is present in solutions containing an excess of base. Experimental data [5] on the dependence of the chemical shift (c.s.) of the $CHCl_3$ signal on the concentration of tributylphosphate (TBP) are shown in Table 4.1. According to the regression equation shown in Fig. 4.2, the equilibrium constant of complex formation is $K = 4.13$ l mol^{-1}.

Using this value we can calculate the composition of a reaction mixture within the investigated region of concentrations and in the actual solvent alone. (Whether it may be employed at other concentrations and in other solvents is not completely clear.) Equilibrium constants for the self-association of alcohols in inert solvents were found to be dependent on the molar volume of solvent [6]. That such behaviour can be a rule will presently be demonstrated by analysing the law of mass action in liquid mixture of molecules of finite diameters.

Table 4.1. Chemical shifts of $CHCl_3$ in cyclohexane solution containing additions of TBP. The concentration of $CHCl_3$ is constant and equal to 0.01 mol l^{-1}

C_B/mol l^{-1}	0.1	0.2	0.3	0.4	0.5	0.6	0.7
δ/ppm	7.635	7.843	7.979	8.072	8.139	8.184	8.229

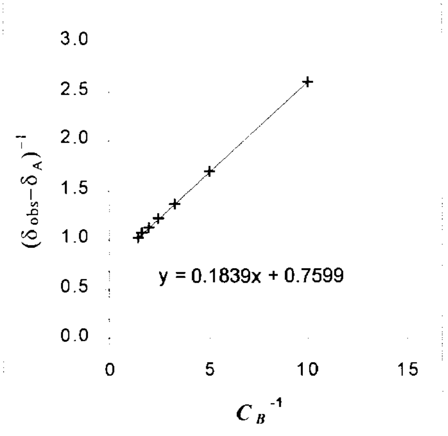

Fig. 4.2. Foster – Fyfe plot of the data from Table 4.1

The free energy of such a reaction mixture, written as a function of the number of molecules of the product (n_C), is:

$$\begin{aligned}-\frac{F}{kT} &= (N_A - n_C)[\ln q_A + \ln eV - \ln(N_A - n_C)]\\ &+ (N_B - n_C)[\ln q_B + \ln eV - \ln(N_B - n_C)]\\ &+ n_C[\ln q_C + \ln eV - \ln n_C]\\ &+ N_S[\ln q_S + \ln eV - \ln N_S]\end{aligned} \tag{4.20}$$

in which N_A, N_B are the initial numbers of molecules (or moles) of reactants and N_S is the number of molecules (or moles) of solvent. Considering the volume, V, as a *function of composition* (n_C) the law of mass action can be obtained from the condition that $dF/dn_C = 0$:

$$\ln\frac{q_C}{q_A q_B} - \ln V - \ln\frac{n_C}{(N_A - n_C)\,(N_B - n_C)} + n\frac{d\ln V}{dn_C} = 0 \tag{4.21}$$

in which n is the current number of molecules in a system, *i.e.* where $n = N_A + N_B + N_S - n_C$. The volume of the reaction mixture (4.14) of molecules having finite diameters can be written as:

$$V = N_A v_A + N_B v_B + N_S v_S + n_C(v_C - v_A - v_B) \tag{4.22}$$

The derivative $d\ln V/dn_C$ is then:

$$\frac{d\ln V}{dn_C} = \frac{v_C - v_A - v_B}{V} = \frac{\Delta v}{V} \tag{4.23}$$

The law of mass action becomes:

$$\ln\frac{q_C}{q_A q_B} - \ln V - \ln\frac{n_C}{(N_A - n_C)\,(N_B - n_C)} + \frac{n\Delta v}{V} = 0 \tag{4.24}$$

The equilibrium constant computed *via* the numbers of molecules ($K_n = n_C/n_A n_B$) is dependent on the volume *i.e.* on the initial quantities of reactants and solvent. This can be rather inconvenient and therefore the law of mass action with respect to molar concentrations is usually preferred. By adding and subtracting $\ln V$, (4.24) can be written in terms of the concentration $[C] = n_C/V$:

$$\ln\frac{q_C}{q_A q_B} - \ln\frac{[C]}{(C_A - [C])\,(C_B - [C])} + \frac{n\Delta v}{V} = 0 \tag{4.25}$$

in which C_A and C_B are the initial (analytical) molar concentrations of reactants and $[C]$ is the current concentration of product.

Note that the last term in (4.24) and in (4.25) is actually the ratio of the volume balance $\Delta\upsilon$ and the *mean volume per molecule*, $\langle\upsilon\rangle$:

$$\langle\upsilon\rangle = V/n \tag{4.26}$$

In general, the mean volume per molecule, $\langle\upsilon\rangle$, is a function of $[C]$. Equation (4.25) can then be written in the following form:

$$\ln\frac{q_C}{q_A q_B}e^{\frac{\Delta\upsilon}{\langle\upsilon\rangle}} - \ln\frac{[C]}{(C_A-[C])\,(C_B-[C])} = 0 \tag{4.27}$$

When the volume balance $\Delta\upsilon$ is zero, the law of mass action, (4.25) – (4.27), is obviously reduced to an ideal form (in terms of molar concentrations)[4]. This condition implies that the volume of products equals the volume of reactants, *i.e.* molecular volumes are additive:

$$\upsilon_C = \upsilon_A + \upsilon_B \tag{4.28}$$

Equation (4.28) is approximately obeyed and corresponds to the *Kopp* rule [7,8] of the additivity of molar volumes. According to this rule, the molar volumes of liquids at the boiling point can be estimated from their molecular formulae by using Kopp's 'atomic volumes'. However, the type of bonding (single, double, *etc.*), which is often changed in chemical reactions, also contributes to molecular volumes. For example, Kopp's volume for oxygen in C=O is 12 whilst in OH it is 7.8 [8]. This example illustrates to what extent rule (4.28) may be obeyed.

In the state of *infinite dilution* ($N_S \gg N_A$, N_B), the mean volume per molecule is approximately the molecular volume of the solvent, which is independent of composition:

$$\ln\frac{q_C}{q_A q_B}e^{\frac{\Delta\upsilon}{\upsilon_S}} - \ln\frac{[C]}{(C_A-[C])\,(C_B-[C])} = 0 \tag{4.29}$$

This is an *almost* ideal law of mass action with an *equilibrium constant containing the additional factor* $\exp(\Delta\upsilon/\upsilon_S)$ controlled by the volumetric properties of the solvent and the actual balance of molecular volumes of reactants and products.

These parameters determine, at least in part, the observed *solvent effects* in complexation equilibria in dilute solutions. In fact, at infinite dilution one should expect to obtain *quite different values of the equilibrium constant in solvents having different molar volumes.*

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[4] When the balance $\Delta\upsilon$ is zero, the volume V is independent of the current composition and is controlled by the initial quantities of components. In the case of non-zero $\Delta\upsilon$, concentrations should be measured with respect to the equilibrium volume of the reaction mixture.

These effects contribute towards the difference in the values of equilibrium constants of complex formation in solutions obtained by optical spectroscopy and NMR studies. The ranges of concentrations employed in these types of experiments are drastically different, $10^{-5} - 10^{-4}$ M in the case of optical spectroscopy and 10^{-2} – 1 M in the case of (early) NMR studies. The mean volume per molecule is different in these cases and this results in different equilibrium constants.

In concentrated solutions the mean volume per molecule is a function of current composition and the law of mass action therefore deviates from the ideal form. When the balance of molecular volume, $\Delta\upsilon$, is small these deviations can be described in terms of *activity coefficients*. Molar concentrations introduced in (4.25) are already non-linear functions of the numbers of molecules:

$$[A]=\frac{n_A}{V}=\frac{n_A}{V_0}\left(1+n_C\frac{\Delta\upsilon}{V_0}\right)^{-1}=\frac{n_A}{V_0}\left(1+(N_A-n_A)\frac{\Delta\upsilon}{V_0}\right)^{-1} \tag{4.30}$$

in which $V_0 = N_A\upsilon_A + N_B\upsilon_B + N_S\upsilon_S$. Using the material balance and separating the constant number of molecules of solvent (N_S) means that (4.25) can be written as:

$$\ln\frac{q_C}{q_Aq_B}-\ln\frac{[C]}{[A]\,[B]}+\left\{\,[A]+[B]+[C]\,\right\}\Delta\upsilon+C_S\Delta\upsilon=0 \tag{4.31}$$

If the products [A]$\Delta\upsilon$, [B]$\Delta\upsilon$ and [C]$\Delta\upsilon$ are small compared to 1 they can be represented in logarithmic form ($\pm\delta \cong \ln(1\pm\delta)$) and introduced under the logarithm:

i.e.
$$\ln\frac{q_C}{q_Aq_B}e^{C_S\Delta\upsilon}-\ln\frac{[C](1-[C]\Delta\upsilon)}{[A](1+[A]\Delta\upsilon)\,[B](1+[B]\Delta\upsilon)}=0 \tag{4.32}$$

This law of mass action defines activities as polynomial functions of concentrations that in their turn are polynomial functions of the numbers of molecules.

The thermal behaviour of the equilibrium (4.14) can be conveniently analysed using (4.25) expressed in terms of the dimensionless parameters related to the sum of initial concentrations of reactants ($N = N_A + N_B$) and the molecular volume of one of the reactants (*e.g.* υ_A):

$$\ln\frac{q_C}{q_Aq_B\upsilon_A}-\ln V_r-\ln\frac{x}{(X_A-x)(X_B-x)}+\frac{\Delta\upsilon}{\upsilon_A}\,\frac{X_A+X_B+X_S-x}{V^*}=0 \tag{4.33}$$

in which the reduced volume V^* is:

$$V^*=X_A+X_B\frac{\upsilon_B}{\upsilon_A}+X_S\frac{\upsilon_S}{\upsilon_A}+x\frac{\Delta\upsilon}{\upsilon_A} \tag{4.34}$$

and:

$$x = \frac{n_C}{N_A + N_B}; X_S = \frac{N_S}{N_A + N_B}; X_A = \frac{N_A}{N_A + N_B}; X_S = \frac{N_B}{N_A + N_B} \tag{4.35}$$

Note that the x-values are *not* mole fractions and X_S can be higher than 1. The first term in (4.33) can be expressed in terms of the 'ideal' standard energy and entropy of reaction (see above):

$$-\frac{\Delta E}{RT} + \frac{\Delta S}{R} - \ln V^* - \ln \frac{x}{(X_A - x)(X_B - x)} + \left(\frac{\Delta v}{v_A}\right) \frac{X_A + X_B + X_S - x}{V^*} = 0 \tag{4.36}$$

Van't Hoff plots can easily be simulated by calculating equilibrium temperatures for given values of x instead of obtaining numerical solutions of (4.36):

$$T = \frac{\Delta E}{\Delta S - R\left\{\ln V^* + \ln \frac{x}{(X_A - x)(X_B - x)} - \left(\frac{\Delta v}{v_A}\right) \frac{X_A + X_B + X_S - x}{V^*}\right\}} \tag{4.37}$$

The simulations carried out according to (4.37) show (see Fig. 4.3A) that a visible curvature of the van't Hoff plot should be expected in non-dilute mixtures characterised by very large positive $\Delta v / v_A > 2$ or negative $\Delta v / v_A$ approaching –2 (*i.e.* when the volume of product is approaching zero). Neither event, however, is very probable. The value $\Delta v / v_A < 0.6$ for $X_A = X_B$ and $v_A = v_B$ seems to be an upper limit. Furthermore, Fig. 4.3B shows that the curvature of the van't Hoff plot disappears when small amounts of solvent are added to the mixture of reactants. Therefore the only effect of the non-ideality considered here is a modest contribution to the standard entropy of reaction (to the extent of about $R\Delta v / \langle v \rangle$).

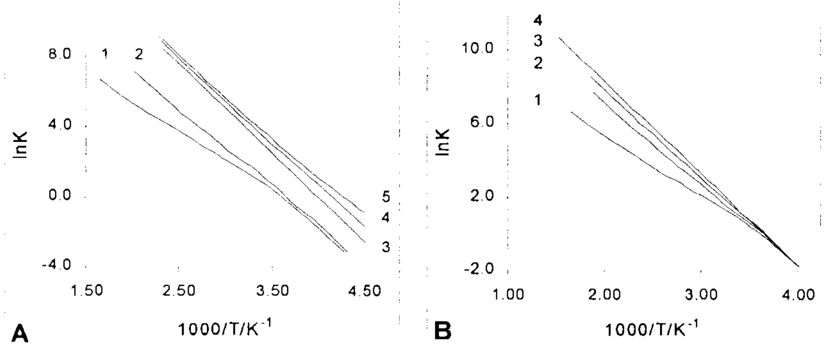

Fig. 4.3. Van't Hoff plots simulated according to (4.37) for the reaction (4.14) with $\Delta E = 10$ kcal mol^{-1}, $\Delta S = 40$ cal mol^{-1} K^{-1}; $v_A = v_B = v_S$; $X_A = X_B = 0.5$; and $\Delta v / v_A = -1.7$ (1), –1.5 (2), 0 (3), +1 (4), +2 (5) at $X_S = 0$ (**A**). The right-hand side graph, (**B**), shows the effects of solvent on van't Hoff plots of the same system with $\Delta v / v_A = -1{,}7$ and $X_S = 0$ (1), 0.3 (2), 1 (3) and 10 (4)

4.2
Lattice theories of the liquid state

Using a semi-empirical model based on the additivity of the volume of reaction mixtures, we have analysed the possible effects of repulsive *molecular interactions*. We have clarified the nature of activity coefficients and obtained a comparatively simple form of the law of mass action applicable to imperfect systems such as Jäger's 'ideal liquid'. The same problem can be approached on the basis of a molecular theory of the liquid state that takes into account both repulsive and attractive interactions. In this Section we consider some theoretical models of the condensed state leading to refined forms of the non-ideal law of mass action.

The main problem to be solved by any theory of the condensed state is the calculation of the configurational integral. It can be done in a direct way by employing computational methods and performing an integration of $\exp(-U(r)/kT)$ over randomly generated spatial configurations of molecules for a given type of intermolecular potential $U(r)$. This is the substance of the well-known Monte-Carlo method. On the other hand, analytical solutions are also possible for simple *models* that represent liquids as systems of pseudo-independent particles in the *mean molecular field*[5]. Such analytical solutions have been found within two types of models, namely, the '*cell theory of liquids*' and the '*hole theory of liquids*'. The former is associated with the names of Lennard-Jones and Devonshire and the latter was developed by Eyring and his co-workers. Both these theories are based on the *method of cells* in which the liquid is considered as a molecular assembly retaining, to a large extent, crystal structure. Therefore they are also known as *lattice theories* of the liquid state.

The configurational integral of an ideal gas is merely the N-th power of volume. When we introduce molecular interactions the analogue of the volume becomes not the whole configurational integral but only that part of it connected with the energy of displacement of a molecule from the position of mechanical equilibrium.

A system of N molecules can be imagined in a state in which all molecules are in the centres of their cells corresponding to the minima of potential energy, $u(0)$ called the *lattice energy* [9].

Any deflection of molecules from these positions brings about an increase in potential energy. Considering all molecules identical and pseudo-independent we may move the factor $\exp(-u(0)/kT)$ from under the integral:

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[5] The advanced theories of the liquid state operating with *radial distribution functions* and *pair correlation functions* also admit of analytical solutions [10] in the form of integral equations. Solutions of the latter for given potentials approach the results of computational methods. Here we are interested, however, in a simple model illustrating the origin of the concepts of free volume and lattice energy and providing for an approximate description of reaction mixtures.

$$Z_{conf} = \frac{1}{N!} e^{-\frac{Nu(0)}{kT}} \int \ldots \int \ldots \int e^{-\frac{u(\mathbf{r})-u(0)}{kT}} d\mathbf{r}_1 \ldots d\mathbf{r}_N = \frac{V_f^N}{N!} e^{-\frac{Nu(0)}{kT}} \tag{4.38}$$

in which $\mathbf{r}_i$ is a vector of the coordinates of the i-th molecule with respect to the centre of its cell. The integration in (4.38) results in the N-th power of the parameter V_f that is termed the *free volume*. The difference $u(\mathbf{r}) - u(0)$ is always positive, making the free volume always smaller than the volume V. The free volume can be interpreted as the volume in which the *centres of mass of the molecules can move*. The term $\exp(-u(0)/kT)$ manifests itself in the corresponding equation of state in the form of the *internal pressure*.

In the original Lennard-Jones and Devonshire model, all cells were considered as occupied and molecules did not 'explicitly' migrate between cells. The availability of the whole volume to molecules, and hence their indistinguishable nature, was accounted for by the introduction of the so-called '*communal entropy factor*', s. This varies between e (the whole free volume is available for any molecule) and 1 (V_f/N is available for each molecule, as in the system of localised states). A refined treatment of molecular motion in the framework of the Lennard-Jones and Devonshire model resembles the theory of ordered structures in the solid state (see Chapter 7). Molecules are supposed to be distributed between two types of position (α and β) representing occupied and vacant centres. In the solid state the α centres alone are occupied making such a system completely ordered. In the liquid state some molecules can move into β-centres and thus migrate over the whole volume of a system. The availability at the melting point of N additional centres explains the commonly observed entropies of fusion of monatomic liquids.

In Eyring's model, molecules are also distributed between two types of 'states': the actual centres of a quasi-crystal lattice and the 'holes'. The behaviour of molecules in these states is supposed to be different: in the centres of the quasi-crystal lattice the molecules perform oscillations of small amplitude (as in the solid state), whilst in 'holes' they move freely (similar to gas-phase molecules) within the volume assigned to the 'holes'. The entropy of melting of a crystal containing N molecules is identified with the entropy of mixing of N centres and n_h holes. The ratio of the number of holes to the number of molecules ($\gamma = n_h/N$) thus estimated varies from 1.3 for Ar to 0.7 for Hg. Another adjusting parameter employed in this model is the volume fraction of holes estimated from the volume changes on melting ($f_G = (V_L - V_S)/V_S$). A liquid reaction mixture is thus represented as a superposition of gaseous-like and solid-like reactions. Employing two interpolation coefficients as mentioned above, it is possible to derive the law of mass action for such a model. However the equations obtained in this way are extremely cumbersome and contain too many parameters.

The Lennard-Jones and Devonshire model on the other hand allows for the derivation of a practical law of mass action taking into account both the repulsive and the attractive interactions between molecules.

4.3
The Lennard-Jones and Devonshire model

Consider a solid in equilibrium with a liquid phase at the melting point. Molecular motion in both phases must be similar and can be described as *free movement within a cell* (molecules are supposed to have neither rotational nor internal degrees of freedom). The partition function for the solid phase then is:

$$Z_S = \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]^N Z_{ConfSol} \tag{4.39}$$

The state of a given molecule being independent of the state of all other molecules implies that the configurational integral for such a solid is to be taken over the volume of *all cells independently*:

$$Z_{ConfSol} = e^{-\frac{Nu(0)}{kT}} \int \ldots \int_{\Delta=V/N} \ldots \int e^{-\frac{u(\mathbf{r})-u(0)}{kT}} d\mathbf{r}_1 \ldots d\mathbf{r}_N = \left(\frac{V_f}{N}\right)^N e^{-\frac{Nu(0)}{kT}} \tag{4.40}$$

in which **r** is the vector of the coordinates of a molecule *with respect to the centre of its cell.* This expression defines the *free volume per molecule* as:

$$v_f = \frac{V_f}{N} = \iiint_{\Delta} e^{-\frac{u(\mathbf{r})-u(0)}{kT}} d\mathbf{r} = \int_0^{r_{\max}} e^{-\frac{u(r)-u(0)}{kT}} 4\pi r^2 dr \tag{4.41}$$

in which $r_{\max}$ is the maximum possible deflection of the centre of mass of a molecule from its position of equilibrium and Δ signifies integration over the volume of a cell.

When such a solid melts, any point within the free volume of a system becomes accessible to *any molecule* thus making molecules *indistinguishable* and the factor ($1/N!$) must be added to the configurational integral. The integration, on the other hand, must be performed over the *whole volume* of the system:

$$Z_{ConfLiq} = \frac{1}{N!} e^{-\frac{Nu(0)}{kT}} \int \ldots \int_V \ldots \int e^{-\frac{u(\mathbf{r})-u(0)}{kT}} d\mathbf{r}_1 \ldots d\mathbf{r}_N = \frac{V_f^N}{N!} e^{-\frac{Nu(0)}{kT}} \tag{4.42}$$

The free energies of the solid and liquid phases at the melting point are, according to the above:

$$F_S = -kT \ln\left\{\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \left(\frac{V_f}{N}\right)^N e^{-\frac{Nu_S(0)}{kT}}\right\} \tag{4.43}$$

$$F_L = -kT\ln\left\{\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}\frac{V_f^N}{N!}e^{-\frac{Nu_L(0)}{kT}}\right\} \tag{4.44}$$

The ratio of N^N to $N!$ is e^N and therefore the entropy of fusion must be Nk per mole. In fact, the entropy of fusion of many metals lies within 1.7 – 2.3 cal mol^{-1} K^{-1}. In order to obtain better agreement, the *communal entropy, s,* was introduced as an interpolation factor between the systems of distinguishable and indistinguishable particles:

$$F_L = -kT\ln\left\{\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}\left(\frac{sV_f}{N}\right)^N e^{-\frac{Nu_L(0)}{kT}}\right\} \tag{4.45}$$

When $s = e$, (4.45) is identical to the expression (3.42) for the free energy of ideal gas with volume substituted by *free volume* (V_f). The calculation of the free volume thus becomes an important part of the theoretical description of the thermodynamic properties of liquids.

The free volume can be calculated according to (4.41) for a given binary potential and geometry of a cell using either computational methods or obtaining an analytical solution (see Section 5.6). A rough estimate of free volume can also be obtained by considering it as a space within which the free motion of the centres of mass of hard spheres is allowed. The simple geometrical model shown in Fig. 4.4 yields the following equation (σ being the molecular diameter):

$$\upsilon_f = \left[2\upsilon^{1/3} - 2\sigma\right]^3 = 8\left[\left(\frac{V}{N}\right)^{1/3} - \sigma\right]^3 = 2\kappa\left[\left(\frac{V}{N}\right)^{1/3} - \sigma\right]^3 \tag{4.46}$$

Similar expressions can be obtained for other types of lattices which actually differ by the factor 2κ where κ is the *structural constant* connecting the volume of a crystal with the lattice constant *a* (see Table 4.2):

$$V = N\kappa a^3 \tag{4.47}$$

The free volume thus obtained is smaller than the volume but its temperature dependence is not shown explicitly by this equation. It can be established by deriving the corresponding equation of state. The pressure derived from (4.45) comprises two terms arising from the derivatives of *free volume* and *lattice energy*, both being functions of volume:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = NkT\frac{\partial \ln V_f}{\partial V} - N\frac{\partial u(0)}{\partial V} \tag{4.48}$$

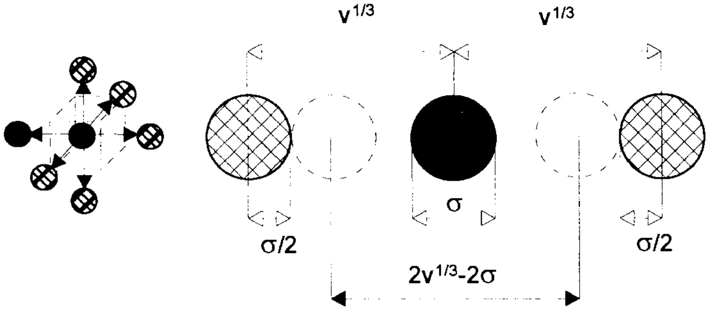

Fig. 4.4. Estimation of the free volume from a geometrical model in a simple cubic lattice.

Table. 4.2. Coordination numbers and structural constants for several types of crystal lattice

Type	cubic	space centred	face centred	hexagonal	tetrahedral
Coordination number, c	6 (NaCl)	8 (alkali metals)	12 (noble gases)	12 (hard spheres)	4 (diamond)
Structural constant, κ	1	$4/3\sqrt{3}$	$1/\sqrt{2}$	$1/\sqrt{2}$	$(2/\sqrt{3})3$

The derivative of free volume by volume is easily obtained from (4.46) as:

$$\frac{\partial V_f}{\partial V} = 3N(2\kappa)^3\left[\left(\frac{V}{N}\right)^{1/3}-\sigma\right]^2 \frac{1}{3N^{1/3}V^{2/3}} = 2\kappa\left(\frac{V_f}{V}\right)^{2/3} \tag{4.49}$$

The *derivative of lattice energy* with respect to volume in (4.48) is actually the *internal pressure* $p_{int} = -\partial u(0)/\partial V$. The equation of state can now be written as:

$$p - p_{\text{int}} = p + N\frac{\partial u(0)}{\partial V} = NkT\frac{2\kappa}{V_f^{1/3}V^{2/3}} \tag{4.50}$$

and the free volume then becomes:

$$V_f = \frac{1}{V^2}\left[2\kappa NkT\Big/\left(p+N\frac{\partial u(0)}{\partial V}\right)\right]^3 \tag{4.51}$$

The lattice energy increases upon expansion, therefore the cohesive internal pressure is negative. On the other hand, the internal pressure can be considered as mainly responsible for the reduction of volume from $V_{gas} = NRT/p$ to $V_{cond} = NRT/(p_{int} + p)$. This reduction (V_{gas}/V_{cond}) is *ca.* 1000-fold and therefore $|p_{int}| >> p$.

The term $N\partial u(0)/\partial V$ can be approximated as the density of potential (lattice) energy U/V and hence, approximately, the *vaporisation energy* per unit volume. Neglecting the external pressure in the denominator of (4.51) yields:

$$V_f = \frac{1}{V^2}\left[2\kappa NkT \Big/ N\frac{\partial u(0)}{\partial V}\right]^3 = V\left[\frac{2\kappa NkT}{U}\right]^3 \tag{4.52}$$

Note that the free volume cannot be larger than the total volume of a system, therefore the molar energy of vaporisation must be higher than $2\kappa RT$. We see that free volume is proportional to the volume of a system and to the *cube* of the *ratio* of the *thermal energy* (NkT) to lattice energy. The latter appeared when we calculated pressure as the volume derivative of free energy *i.e.* took into account the dependence of lattice energy on the *size of a cell.*

This *cubic* dependence is an important feature determining, as we will see later, critical phenomena in condensed systems. It originates from the three-dimensional model for which the free volume was estimated (see (4.46) and Fig. 4.4). If we consider the motion of a molecule in a *two-dimensional* lattice, then the resulting expression for free 'volume' is:

$$V_f = V\left[\frac{2\kappa NkT}{U}\right]^2 \tag{4.53}$$

For motion in a *one-dimensional* lattice (chain-like polymeric molecules) the free 'volume' would be proportional to the first power of the ratio of thermal and lattice energies.

4.4
Chemical equilibria in Lennard-Jones and Devonshire liquids

At first glance the substitution of volume by free volume should not substantially change anything in the derivation of the law of mass action for a reaction in the liquid phase. One can assume the additivity of free volume and obtain a non-ideality term in the form of $\Delta v_f/\langle v_f\rangle$. However, free volume and lattice energy are *not independent variables*: they are connected *via* the equation of state (4.48). Free volume is a function of both repulsive and attractive interactions as reflected by (4.51). The stronger the *attractive* interactions (U) the less space is left for free movement of the centres of masses of the molecules. To a first approximation, both the *volume* and the *lattice energy* can be considered as *additive* quantities. Chemical equilibria in such a (seemingly ideal) model liquid are described by the law of mass action [11] containing non-ideal terms.

For a mixture of two types of molecules in chemical equilibrium in solution:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{4.54}$$

the additivity of the lattice energy can be written as:

$$U = Nu_A + N_S u_S + n_B(u_B - u_A) = Nu_A + N_S u_S + n_B \Delta u \qquad (4.55)$$

in which u_A, u_B and u_S are the molecular lattice energies of components (the symbol (0) has been dropped for convenience) and $N = n_A + n_B$. The free energy can be written (assuming a 'communal entropy' factor equal to e) as:

$$\begin{aligned} -\frac{F}{kT} &= (N - n_B)\left[\ln q_A eV + 3\ln\frac{2\kappa(N+N_S)kT}{Nu_A + N_S u_S + n_B(u_B - u_A)} - \ln(N - n_B)\right] \\ &+ n_B\left[\ln q_B eV + 3\ln\frac{2\kappa(N+N_S)kT}{Nu_A + N_S u_S + n_B(u_B - u_A)} - \ln n_B\right] \\ &+ N_S\left[\ln q_S eV + 3\ln\frac{2\kappa(N+N_S)kT}{Nu_A + N_S u_S + n_B(u_B - u_A)} - \ln N_S\right] \end{aligned} \qquad (4.56)$$

The term $\ln q_i$ includes the contributions from translational and internal partition functions as well as the factor $\exp[-(\varepsilon_i + u_i)/kT]$, where ε represents the electronic energy of a molecule. As a result of the assumed additivity of V and U, the molecular parameters v_i and u_i are *independent of composition.* For lattice energies this is only a rough approximation and the formalism we are developing now accounts, therefore, for only a part of the non-ideality. The case of non-additive lattice energy will be considered in detail in Chapter 7.

We have considered the effects of finite volumes of molecules in preceding Sections and now, therefore, for simplicity we assume $\Delta v = 0$ and investigate the effects of internal pressure alone. The law of mass action derived from the condition $dF/dn_B = 0$ contains the derivative of the lattice energy with respect to n_B:

$$\ln\frac{q_B}{q_A} - \ln\frac{n_B}{N - n_B} - \frac{3(N + N_S)}{U}\frac{dU}{dn_B} = 0 \qquad (4.57)$$

According to the assumed additivity of lattice energy (4.55) this derivative is $\Delta u = u_B - u_A$, and therefore (4.57) can be rewritten as:

$$\ln\frac{q_B}{q_A} - \ln\frac{n_B}{N - n_B} - \frac{3\Delta u(N + N_S)}{Nu_A + N_S u_S + n_B \Delta u} = 0 \qquad (4.58)$$

Approximating $\ln(q_B/q_A)$ by $-\Delta E/RT$ (arising from the terms $\exp[-(\varepsilon + u)/kT)]$) and $\Delta S/R$ (originating in the contribution from partition functions) we get:

$$-\frac{\Delta E}{RT} + \frac{\Delta S}{R} - \ln\frac{n_B}{N - n_B} - \frac{3\Delta u(N + N_S)}{Nu_A + N_S u_S + n_B \Delta u} = 0 \qquad (4.58a)$$

Dividing numerators and denominators by N we can re-write the law of mass action (4.58) with respect to the *degree of conversion*, $x = n_B/N$:

$$-\frac{\Delta E}{RT}+\frac{\Delta S}{R}-\ln\frac{x}{1-x}-\frac{3\Delta u\left(1+N_S/N\right)}{u_A+(N_S/N)u_S+x\Delta u}=0 \qquad (4.58b)$$

By relating the lattice energy balance Δu to u_A we get the law of mass action with respect to dimensionless variables:

$$-\frac{\Delta E}{RT}+\frac{\Delta S}{R}-\frac{3\left(\Delta u/u_A\right)\left(1+N_S/N\right)}{1+(N_S/N)(u_S/u_A)+x\left(\Delta u/u_A\right)}-\ln\frac{x}{1-x}=0 \qquad (4.58c)$$

Transition curves can therefore be simulated by expressing the temperature as a function of x. Fig 4.5 shows such transition curves computed for a non-diluted ($N_S = 0$) system with varying Δu. A zero or small Δu obviously results in an ideal law of mass action. Negative Δu increase the slope of the transition curves (Fig. 4.5, left-hand graph) whilst small positive Δu decreases it. However, at $\Delta u/u_A > 1$ the maximal slope increases with increasing positive Δu. Equation (4.58c) predicts a vertical tangent to the transition curve when:

$$3\alpha^2(1-x)x-(1+\alpha_E x)^2=0 \qquad (4.59)$$

in which $\alpha = \Delta u/u_A$. For $x = ½$ we have two values of α_E that correspond to a vertical tangent $\alpha = 1 \pm \sqrt{3}$ *i.e. ca.* 2.7 and -0.7. Equation (4.59) has a single (meaningful) solution with respect to α at $x = ¾$ corresponding to the balance of lattice energy $\Delta u = -(2/3)u_A$. At more negative Δu, the transition curves become *S*-shaped, *i.e.* over a certain region of temperatures there are two possible equilibrium compositions of such a system (Fig. 4.6). Similar *S*-shaped transition curves and van't Hoff plots are expected for positive $\alpha > 2$ (see Fig. 4.7).

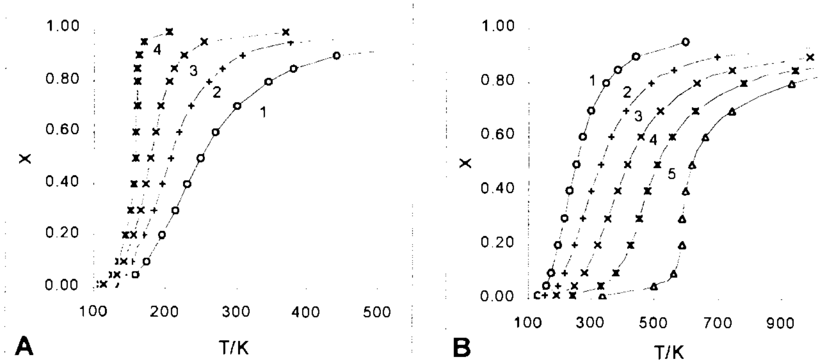

Fig. 4.5. Transition curves simulated for the system (4.54) characterised by $\Delta E = 2.5$ kcal mol^{-1}; $\Delta E/\Delta S$ = 250 K; N_S = 0 with negative (left-hand graph **A**); $\Delta u/u_A$= 0 (1), –0.3 (2), –0.5 (3), -0.66 (4) and positive (right-hand graph **B**) $\Delta u/u_A$ = 0 (1), 0.5 (2), 1.0 (3), 1.5 (4), 2.0 (5)

This situation is incompatible with the *homogeneity* of the considered system, and therefore these effects correspond to the *separation of two condensed phases*. An *S*-shaped curve can only be obtained by computing *T* as a function of *x*. When we solve the equation of the law of mass action with respect to *x* using a numerical method we obtain a sharp transition from one branch to another as shown in Fig. 4.6. Two pathways obtained by searches starting from higher and lower values of *x* imitate cooling and heating of the reaction mixture that must exhibit, therefore, *hysteresis*.

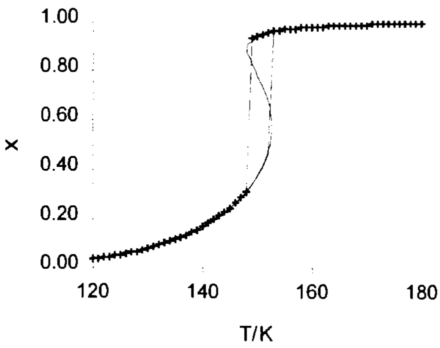

Fig. 4.6. Transition curves calculated by numerical solution of (4.58c) with respect to x for a non-ideal binary system ($\Delta E = 2.5$ kcal mol^{-1}; $\Delta E/\Delta S$ = 250 K; N_S = 0; $\Delta u/u_A$ = -0.7). The *S*-shaped curve was obtained by simulating temperatures

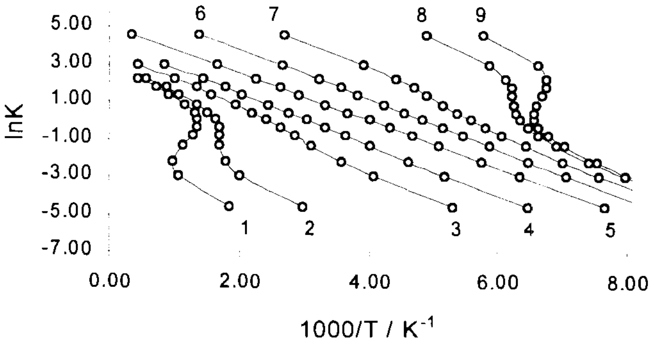

Fig. 4.7. Van't Hoff plots calculated for a non-diluted spin crossover system: $N_S = 0$; $\Delta E = 2.5$ kcal mol^{-1}; $\Delta E/\Delta S = 250$ K with varying balance of lattice energy; $\alpha = +2.5$ (1), 2(2), +1 (3), +0.5 (4), 0.0 (5), −0.3 (6), −0.5 (7), −0.66 (8) and −0.7(9)

Table 4.3. Approximation of the curves in Fig. 4.7 by linear van't Hoff plots

$\Delta u/u_A$	ΔE^0 (kcal mol^{-1})	ΔS^0 (kcal mol^{-}1 K^{-1})	$T_{1/2}$ (K)
2	4.54	5.97	760.6
1	3.11	7.27	427.9
0.5	2.68	8.13	329.5
0	2.49	9.99	249.9
–0.3	2.638	12.80	206.0
–0.5	3.11	17.68	176.0
–0.66	4.45	29.74	149.7

Steep transition curves, sometimes exhibiting hysteresis, similar to those shown in Fig. 4.6 are experimentally observed in non-diluted *crystalline* spin crossover compounds but *not in the liquid state.* In fact, up to now no pure liquid spin crossover compound has ever been synthesised. Known examples of spin transitions in the liquid state (gradual spin crossover) have been observed for very dilute solutions and, in principle, there is no reason why a steep spin crossover should not be observable in the liquid state.

Table 4.3 shows the results of the linear approximations (in the vicinity of the transition point) of the van't Hoff plots shown in Fig. 4.7. Increasing magnitude of the balance of lattice energy (both positive and negative) increases the effective standard internal energy ΔE^0. A negative Δu brings about an increase in the *effective* entropy of transition whilst a positive Δu decreases it (Table 4.3). These two effects cause the transition temperature to vary over a wide range.

Similar critical phenomena may be observed in other reaction mixtures when the products of reaction are drastically different from the reactants with respect to molecular interactions. It is of interest therefore to analyse the case of a non-isomolar reaction in a highly non-ideal solution.

For the equilibrium of complex formation in solution:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{4.60}$$

the law of mass action can be written by substituting volume by free volume in (4.21) as:

$$\ln \frac{q_C}{q_A q_B} - \ln V_f - \ln \frac{n_C}{(N_A - n_C)(N_B - n_C)} + n \frac{d \ln V_f}{d n_C} = 0 \tag{4.61}$$

in which $n = N_A + N_B + N_S - n_C$ is the current total number of molecules in the reaction mixture.

Approximating free volume by (4.52) leads to:

$$\ln V_f = \ln V + 3\ln\frac{2\kappa nkT}{U} \tag{4.62}$$

Assuming the volume V to be constant (for simplicity) we get the derivative of $\ln V_f$ with respect to n_C as:

$$\frac{d\ln V_f}{dn_C} = \frac{3}{n} - \frac{3}{U}\frac{dU}{dn_C} \tag{4.63}$$

For additive lattice energy the derivative dU/dn_C equals the balance Δu:

$$dU/dn_C = \Delta u = u_C - u_A - u_B \tag{4.64}$$

and the law of mass action becomes:

$$\ln\frac{q_C}{q_A q_B} - \ln V - \ln\frac{n_C}{n_A n_B} - 3\left\{\ln\left(\frac{2\kappa nkT}{U}\right) + n\frac{\Delta u}{U} + 1\right\} = 0 \tag{4.65}$$

When $\Delta u = 0$ this law of mass action is reduced to a form which is not, strictly speaking, ideal:

$$\ln\frac{q_C}{q_A q_B V e^3} - \ln\frac{n_C}{n_A n_B} - 3\ln\left(\frac{2\kappa nkT}{N_A u_A + N_B u_B + N_S u_S}\right) = 0 \tag{4.66}$$

The numerator in the last term in (4.66) is the energy of thermal motion of molecules proportional to the *current number of molecules* (n) whilst the denominator of this term is the lattice energy which under the condition $\Delta u = 0$ is *independent* of n_C. Therefore the free volume remains composition dependent and the system behaves non-ideally[6]. This quasi-ideal form of the law of mass action can be written as:

$$\ln\frac{q_C}{q_A q_B V}\left(\frac{N_A u_A + N_B u_B + N_S u_S}{2\kappa kTe}\right)^3 - \ln\frac{n_C}{n_A n_B} - 3\ln n = 0 \tag{4.67}$$

Under the condition of excess of solvent ($N_S >> N_A$, N_B; $U \cong N_S u_S$) the complete form of (4.65) is reduced to a pseudo-ideal form:

$$\ln\frac{q_C}{q_A q_B}\left(\frac{u_S}{2\kappa kTe}\right)^3 e^{-\frac{3\Delta u}{u_S}} - \ln\frac{[C]}{[A][B]} = 0 \tag{4.68}$$

When one of the reactants is taken in excess it plays the role of solvent and similar pseudo-ideal behaviour should be expected for such systems. The factor applied to the equilibrium constant resulting from non-ideality strongly depends

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[6] This case is exclusively of 'theoretical' importance: an exact equality $\Delta u = 0$ could hardly be expected to hold in a real system at different temperatures!

on temperature (proportional to T^{3}) which distinguishes non-ideality originating in internal pressure from that arising from the finite volume of molecules.

In concentrated solutions and non-zero but small Δu the last term in (4.65) can be represented in logarithmic form ($\delta \cong \ln(1+\delta)$):

$$\ln\frac{q_C}{q_A q_B(2e\kappa)^3}-\ln\frac{[C]}{[A][B]}-\ln\left[\frac{kT}{\langle u\rangle}\left(1+\frac{\Delta u}{\langle u\rangle}\right)\right]^3=0 \tag{4.69}$$

in which the mean lattice energy per molecule is a function of composition:

$$\langle u\rangle=\frac{U}{n}=\frac{N_A u_A+N_B u_B+N_S u_S+n_C\Delta u}{N_A+N_B+N_S-n_C} \tag{4.70}$$

The non-ideality term in (4.69) can then be easily converted into activity coefficients,

e.g.
$$a_A=[A]\left[\frac{kT}{\langle u\rangle}\left(1+\frac{\Delta u}{\langle u\rangle}\right)\right]^{-3} \tag{4.71}$$

When $\Delta u/<u>$ is not a small parameter the behaviour of such a system is described by exact solutions of (4.65) which can be found by numerical methods, for example, dichotomy. Numerical methods must also be employed when the thermal behaviour of such models is investigated: it is impossible to neglect the cubic temperature dependence of the non-ideality term, therefore temperature cannot be found as an explicit function of composition.

The law of mass action in the form showing temperature dependence of the equilibrium constant can be written (remember, we have supposed $\Delta v = 0$, *i.e.* $V = const.$) as:

$$-\frac{\Delta E^0}{RT}+\frac{\Delta S^0}{R}-\ln\frac{[C]}{[A][B]}-\ln\left(\frac{kT}{\langle u\rangle}\right)^3-3\frac{\Delta u}{\langle u\rangle}=0 \tag{4.72}$$

The temperature dependence of the equilibrium constant computed according to (4.72) exhibits singularities when Δu is sufficiently large, either positive or negative (Fig. 4.8A). A 'jump' in the degree of conversion may be expected at that temperature at which the energy of molecular interactions of the product is either *ca.* twice that of reactants and ($\Delta u/(u_A + u_B) > 1$, *i.e.* $u_C > 2(u_A + u_B)$) or when it is considerably smaller than that of products ($\Delta u/(u_A + u_B) < -0.88$, *i.e.* $u_C < 0.12(u_A + u_B)$). This 'jump' is more gradual in dilute systems (Fig 4.8 B) and may disappear completely in solutions containing about 10 moles of solvent per mole of reactant.

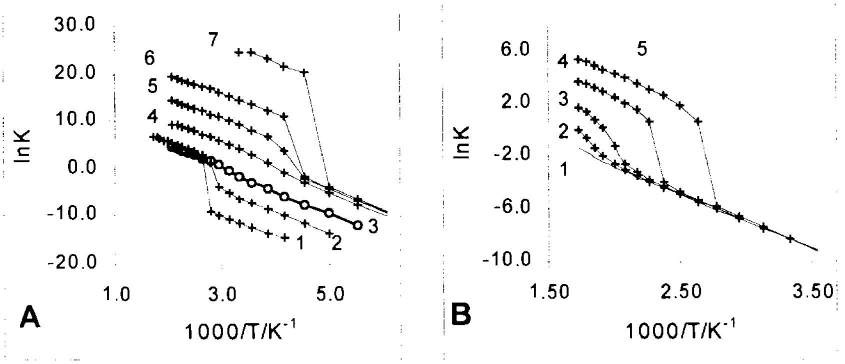

Fig. 4.8. Van't Hoff plots computed according to (4.72) for the equilibrium (4.60) with $\Delta E = 10$ kcal mol^{-1}; molar lattice energies of reactants $N_L u_A = N_L u_B = 6$ kcal mol^{-1}; $\Delta u/(u_A + u_B) = +1.5$ (1), +0.66 (2), 0.0 (3), −0.75 (4), −0.833 (5), −0.875 (6), −0.916 (7) in a mixture of pure components (plots **A**). **B** shows the effects of dilution in a strongly non-ideal system ($\Delta u/(u_A + u_B) = 1.0$; $C_A = C_B = 5.55$ (5), 3.98 (4), 2.65 (3), 2.03 (2), 1.5 (1) mol l^{-1})

These singularities draw to mind the unfortunate incident involving the synthesis of ethyleneglycol diacetate from ethylene oxide and acetic anhydride related in the Introduction to this book. An unexpected 'jump' in the degree of conversion at equilibrium could indeed bring about a very fast heating of the reaction mixture because this reaction is exothermic (*ca.* 40 kcal mol^{-1}). However the heat of vaporisation of the product is only about 25% smaller than the sum of the heats of vaporisation of reactants. Therefore the balance of the energy of molecular interactions cannot be sufficiently large to produce the discontinuities described above. Another possible explanation of this mini-disaster (besides a trivial miscalculation of the necessary amount of cooling agent!) could be that it had its origin in strongly *non-ideal kinetics* (see Section 4.6)

4.5
The non-ideal law of mass action, activities, and standard states

After considering several special cases of non-ideality we are now able to analyse in general the case of equilibria in condensed state characterised by additive volume and energy of molecular interactions. We start with the expression for the free energy of the liquid (4.45) writing it (assuming communal entropy $s = e$) as:

$$-\frac{F_L}{kT} = N \ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} + N \ln eV_f - N \ln N - \frac{N(\varepsilon + u)}{kT} \qquad (4.73)$$

The free energy of a mixture of quasi-independent molecules of different chemical kinds is given by:

$$-\frac{F_L}{kT} = \sum_i n_i \ln\left(\frac{2\pi m_i kT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{\varepsilon_i}{kT}} + \sum_i n_i \ln eV_f - \sum_i \frac{n_i u_i}{kT} - \sum_i n_i \ln n_i \tag{4.74}$$

In general, V_f and each individual lattice energy u_i may be composition dependent; therefore, the chemical potential of the i-th species is:

$$-\frac{\mu_i}{kT} = \ln q_i - \frac{u_i}{kT} + \ln V_f - \ln n_i + n\frac{\partial \ln V_f}{\partial n_i} - \sum_k \frac{n_k}{kT}\frac{\partial u_k}{\partial n_i} \tag{4.75}$$

in which $$q_i = \left(\frac{2\pi m_i kT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{\varepsilon_i}{kT}} \quad \text{and} \quad n = \sum_k n_k \tag{4.76}$$

We assumed, to a first approximation, both the *volume and (total) lattice energy to be additive* ($V = \Sigma n_i v_i$, $U = \Sigma n_i u_i$). The partial (per molecule) volumes and lattice energies (v_i, u_i) are independent of composition and $\partial u_k/\partial n_i = 0$.

Let us consider a chemical equilibrium of the most general type:

$$\zeta_{R_1} R_1 + \zeta_{R_2} R_2 + \cdots + \zeta_{R_k} R_k \Leftrightarrow \zeta_{P_1} P_1 + \zeta_{P_2} P_2 + \cdots + \zeta_{P_m} P_m \tag{4.77}$$

The law of mass action for (4.77) is:

$$\sum_j \zeta_{P_j} \mu_{P_j} - \sum_i \zeta_{R_i} \mu_{R_i} = 0 \tag{4.78}$$

By taking into account the explicit expression for the chemical potential (4.75), the law of mass action (4.78) can be written as:

$$\begin{aligned} &\sum_j \zeta_{P_j}\left[\ln q_{P_j} + \ln V_f - \ln n_{P_j}\right] - \sum_i \zeta_{R_i}\left[\ln q_{R_i} + \ln V_f - \ln n_{R_i}\right] \\ &\qquad + N\left[\sum_j \zeta_{P_j} \frac{\partial \ln V_f}{\partial n_j} - \sum_i \zeta_{R_i} \frac{\partial \ln V_f}{\partial n_i}\right] = 0 \end{aligned} \tag{4.79}$$

The first line in (4.79) is the law of mass action for equilibrium in an ideal gas in which the volume has been substituted by the free volume. The second line is the non-ideality term associated with the dependence of free volume on composition. A relationship between volume and free volume was obtained using a version of the Eyring equation of state:

$$V_f = \frac{1}{V^2}\left(2\kappa kTn \middle/ \left(p + \frac{\partial U}{\partial V}\right)\right)^3 \tag{4.80}$$

Further assumptions made were: (i) that the molecular potential is 'V-shaped' (see Fig. 4.9) and hence the internal pressure dU/dV can be substituted by the density of lattice energy $dU/dV = U/V$ and (ii) that the internal pressure is much higher than the external pressure and we can neglect p in the denominator of (4.80).

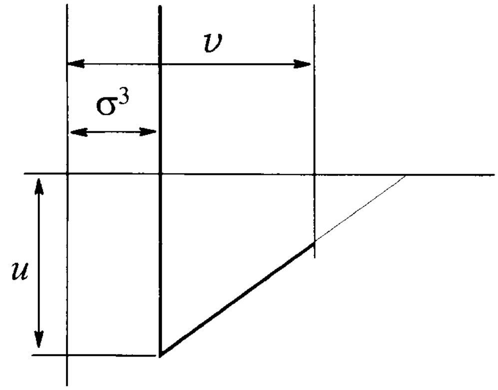

Fig. 4.9. The shape of the potential of a system of hard attracting spheres used in the derivation of (4.51)

These assumptions result in a relatively simple relationship between the volume and free volume:

$$V_f = \left(\frac{2\kappa kT\sum_i n_i}{\sum_i n_i u_i}\right)^3 V = \left(\frac{2\kappa kT\sum_i n_i}{\sum_i n_i u_i}\right)^3 \sum_i n_i v_i = \tau^3 V \tag{4.81}$$

in which $\tau = 2\kappa kT/\langle u\rangle$ and is termed (in books on the statistical theory of liquids) the *reduced temperature*. The lattice energy per molecule, u_i, has been estimated as the molecular energy of vaporisation; there are, however, other methods of estimating this parameter (see Sections 5.3 and 5.7.2).

The relationship (4.81) can be interpreted in the following way: the stronger the *attractive* forces between molecules (represented in the model of V-shaped potential by U) the *smaller* is τ, and hence the free volume. On the other hand, the *stronger* the *repulsive* forces the *larger* is the total volume V.

Under the conditions of additivity of U and V the *partial* derivative $\partial \ln V_f/\partial n_i$ is obtained from (4.81) as:

$$\frac{\partial \ln V_f}{\partial n_i} = \frac{v_i}{\sum_i n_i v_i} - \frac{3u_i}{\sum_i n_i u_i} + \frac{3}{\sum_i n_i} \tag{4.82}$$

We are now able to completely separate the ideal and non-ideal terms in the law of mass action:

$$\begin{aligned}&\sum_j \zeta_{\mathrm{P}_j}\left[\ln q_{P_j} + \ln V - \ln n_{P_j}\right] - \sum_i \zeta_{\mathrm{R}_i}\left[\ln q_{R_i} + \ln V - \ln n_{R_i}\right] + \\ &+\left(\sum_j \zeta_{\mathrm{P}_j} - \sum_i \zeta_{\mathrm{R}_i}\right)\ln \tau^3 + n\left[\sum_j \zeta_{\mathrm{P}_j}\frac{\partial \ln V_f}{\partial n_j} - \sum_i \zeta_{\mathrm{R}_i}\frac{\partial \ln V_f}{\partial n_i}\right] = 0\end{aligned} \tag{4.83}$$

The first contribution to non-ideality is connected with the reduced temperature τ, which determines the ratio of volume to free volume. This term, being logarithmic and having proper multipliers (stoichiometric coefficients), can always be introduced into the ideal part as associated either with concentrations or with the equilibrium constant. The second contribution to non-ideality (the term in square brackets) represents the balance of the effects of molecular interactions in the reaction mixture.

The second non-ideality term can be transformed into activity coefficients by employing at least two different approaches. The first route is suggested by the stoichiometric coefficients available in (4.83). The law of mass action can then be written as:

$$\begin{aligned}&\sum_j \zeta_{\mathrm{P}_j}\left[\ln q_{P_j} - \ln\frac{n_{P_j}}{V}\right] - \sum_i \zeta_{\mathrm{R}_i}\left[\ln q_{R_i} - \ln\frac{n_{R_i}}{V}\right] + \\ &+\sum_j \zeta_{\mathrm{P}_j}\left(\ln \tau^3 + n\frac{\partial \ln V_f}{\partial n_j}\right) - \sum_i \zeta_{\mathrm{R}_i}\left(\ln \tau^3 + n\frac{\partial \ln V_f}{\partial n_i}\right) = 0\end{aligned} \tag{4.84}$$

The non-ideality terms in (4.84) may then be considered as factors applicable to the corresponding concentrations. However, such activity coefficients are rather complicated functions of the numbers of molecules:

$$\gamma_i = \tau^3 \exp\left(n\frac{\partial \ln V_f}{\partial n_i}\right) = \left(\frac{2\kappa kT\sum_i n_i}{\sum_i n_i u_i}\right)^3 \exp\left(\frac{v_i\sum_i n_i}{\sum_i n_i v_i} - \frac{3u_i\sum_i n_i}{\sum_i n_i u_i} + 3\right) \tag{4.85}$$

in which the summation is to be performed over all components (solvent, reactants and products). This expression can be compactly written using the mean volume $\langle v \rangle$ and the mean potential energy $\langle u \rangle$ per molecule:

$$a_i = \frac{n_i}{V}\left(\frac{2\kappa ekT}{\langle u\rangle}\right)^3 \exp\left(\frac{v_i}{\langle v\rangle} - \frac{3u_i}{\langle u\rangle}\right) \tag{4.86}$$

The term $n(\partial \ln V_i/\partial n_i)$ is, in general, *not* a small value. We are considering mixtures of molecules of similar size and similar energy of molecular interactions, therefore, $n(\partial \ln V/\partial n_i) = nv_i/V \cong 0.5 - 2$. Hence the corresponding exponential in (4.85) cannot be readily expanded into a truncated series (which would result in an approximately polynomial activity coefficient).

This problem can be solved if we extract that part of the non-ideality term that remains constant under the given conditions. A system can be studied over a limited range of variations of $<v>$ and $<u>$ around some *standard value* $<v_0>$ and $<u_0>$. Extracting the constant part of the non-ideality term:

e.g.

$$\sum_i \zeta_{R_i} \ln e^3\tau_0^3 \exp\left(\frac{v_i}{\langle v_0\rangle} - \frac{3u_i}{\langle u_0\rangle}\right) \tag{4.87}$$

enables the variable part to be expressed as:

$$\sum_i \zeta_{R_i} \ln \frac{\tau^3}{\tau_0^3} \exp\left(v_i \frac{\langle v_0\rangle - \langle v\rangle}{\langle v\rangle\langle v_0\rangle} - 3u_i \frac{\langle u_0\rangle - \langle u\rangle}{\langle u\rangle\langle u_0\rangle}\right) \tag{4.88}$$

The terms containing the differences $<v_0> - <v>$, $<u_0> - <u>$ may, however, be small and the corresponding exponential can then be expanded into a series and truncated at the linear (or higher) term:

$$\exp\left(v_i \frac{\langle v_0\rangle - \langle v\rangle}{\langle v\rangle\langle v_0\rangle} - 3u_i \frac{\langle u_0\rangle - \langle u\rangle}{\langle u\rangle\langle u_0\rangle}\right) \cong 1 + \frac{v_i}{\langle v_0\rangle}\left(\frac{\langle v_0\rangle}{\langle v\rangle} - 1\right) - 3\frac{u_i}{\langle u_0\rangle}\left(\frac{\langle u_0\rangle}{\langle u\rangle} - 1\right) + \ldots \tag{4.89}$$

Every such term may be introduced into the ideal part of the law of mass action as an activity coefficient:

$$\gamma_i = \frac{\tau^3}{\tau_0^3}\left[1 + \frac{v_i}{\langle v_0\rangle}\left(\frac{\langle v_0\rangle}{\langle v\rangle} - 1\right) - 3\frac{u_i}{\langle u_0\rangle}\left(\frac{\langle u_0\rangle}{\langle u\rangle} - 1\right) + \ldots\right] \tag{4.90}$$

The constant term corresponding to the standard state ($<v_0>$, $<u_0>$) is added to the equilibrium constant:

$$\ln K = \ln \frac{\prod_j q_{P_j}^{\zeta_{P_j}}}{\prod_i q_{R_i}^{\zeta_{R_i}}} + \sum_j \zeta_{P_j} \ln e^3\tau_0^3 \exp\left(\frac{v_j}{\langle v_0\rangle} - \frac{3u_j}{\langle u_0\rangle}\right) - \sum_i \zeta_{R_i} \ln e^3\tau_0^3 \exp\left(\frac{v_i}{\langle v_0\rangle} - \frac{3u_i}{\langle u_0\rangle}\right) \tag{4.91}$$

This method of transformation of the non-ideality term into the activity coefficient has the advantage that every term in the original equation (4.83) appears with the correct stoichiometric coefficient. The *disadvantage* is a rather insecure expansion of exponentials around the point corresponding to a *standard state*. In the examples considered in this Chapter we have been transforming non-ideality terms into activity coefficients in a different manner.

Our method was based on approximate rules governing the changes of volume and vaporisation energy in a *reaction mixture*, *i.e.* in a mixture containing always the same numbers of atoms of each element. In the condensed state these changes are generally small which apparently always results in a *small* term in the square brackets in (4.83). This small term can be further separated into individual contributions from every species present. What is perhaps not obvious is that (as follows from the mass balance equation) the term in square brackets in (4.83) is proportional to the *complete derivative of free volume with respect to the number of any given species*:

$$\sum_i \xi_i \frac{\partial \ln V_f}{\partial n_i} = \xi_k \frac{d \ln V_f}{d n_k} \tag{4.92}$$

in which the summation is performed over both products and reactants; the stoichiometric coefficient ξ is negative when associated with a reactant and positive when it belongs to a product[7]. Taking into account that $n = \Sigma n_i$ the total non-ideality term in (4.83) can be written as:

$$\sum_k \left(\xi_k \ln \tau^3 + \xi_k n_k \frac{d \ln V_f}{d n_k} \right) \tag{4.93}$$

The complete derivative of the logarithm of the free volume of a reaction mixture reflects, as we have seen, the relative balances of volume and lattice energy and can be small. We may therefore expand the second term in (4.93) as a truncated series and write the total non-ideality as:

$$\sum_k \xi_k \left[\ln \tau^3 \left(1 + \frac{n_k}{V_f} \frac{d V_f}{d n_k} \right) \right]$$

and then define the activity coefficient of a given species (k) as:

$$\gamma_k = \tau^3 \left(1 + \frac{n_k}{V_f} \frac{d V_f}{d n_k} \right) \tag{4.94}$$

in which τ may also be a function of the corresponding number of molecules.

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[7] We are avoiding the use of this (very versatile from the point of view of mathematics) notation in order to preserve the habitual shape of the equation of a chemical reaction – one of the few links between the material of this book and chemistry!

Apparently, even when the balance of molecular volume and lattice energy is considerable, we are able to extract a constant term corresponding to the standard state (similarly to the above) and use the ideal form of the law of mass action. This shows that the concept of a *standard state is a very versatile cure* for many cases involving quite serious problems.

It must however be remembered that only a part of the possible effects of molecular interactions have been considered, whereas those leading to the non-additivity of molecular lattice energy have been neglected. The latter case will be considered in Chapter 7. Also the results above are only applicable to equilibria and do not include the effects of non-ideality in kinetics that will be considered in the next Section.

In general, frequent application of the concept of a standard state and the use of a pseudo-ideal law of mass action can promote some dangerous side effects, namely forgetting possible critical phenomena occurring when molecular interactions of reactants drastically differ from those of products. Indeed one could envisage a system that exhibited pseudo-ideal behaviour characterised by a small enthalpy and highly negative entropy (small equilibrium constants) yet at only a few kelvins above (or below) the investigated range a complete conversion to products would take place (see Figs. 4.6 and 4.8).

4.6
Kinetic law of mass action

The equilibrium and kinetic laws of mass action are in fact completely different relationships bound together by the *dynamic interpretation of chemical equilibrium* as the state in which the rate of the forward reaction equals the rate of the reverse reaction. At equilibrium the main variable of kinetics, time, disappears and, furthermore, time is completely ignored in classical thermodynamics.

Note that the *dynamic interpretation of equilibrium* logically follows from the empirically based assumption of the proportionality of reaction rates to the concentrations of reactants (see Section 3.1). In a system containing non-zero quantities of reactants, the reaction rate should not be zero and the only explanation of a stationary state (observed in experiments) is the equality of the rates of forward and reverse reactions. The dynamic interpretation of chemical equilibrium may therefore be considered as one of the general postulates of physical chemistry along with the first and second laws of thermodynamics. On the other hand, the proportionality of the reaction rates to the product of concentrations of reactants can also be explained (from a molecular point of view) as reflecting the probability of collision between reacting molecules.

The number of collisions per unit time determines the rates of chemical reactions in the gas phase. The corresponding expression is commonly derived using the so-called *collision tube* (Fig. 4.10):

$$\langle z \rangle = \sqrt{2}\frac{N}{V}\pi\sigma^2\langle c \rangle \tag{4.95}$$

in which σ is the molecular diameter and $\langle c \rangle$ is the mean molecular velocity. It shows that the number of collisions is proportional to the *volume concentration of molecules and not to the mole fraction.* By compressing a gaseous system we increase the concentrations (increasing proportionally the number of collisions) but leave the mole fractions unchanged. This, of course, can be interpreted as a dependence of a rate constant expressed in mole fractions on pressure (similar to that of the equilibrium constant (3.56)). However, such an interpretation *would merely conceal the origin of this pressure dependence,* namely the increased/decreased probability of molecular collision. This is a typical case of correlating two functions (k and p) of the same variable (the number of collisions) and declaring one of them a function of the other[8]. Mole fractions are therefore seldom used in formulating the kinetic law of mass action.

In gaseous systems we can change the volume over a wide range by applying external pressure. The volume of a system is thus an independent variable and reaction rates *always increase with decreasing volume (increasing pressure).*

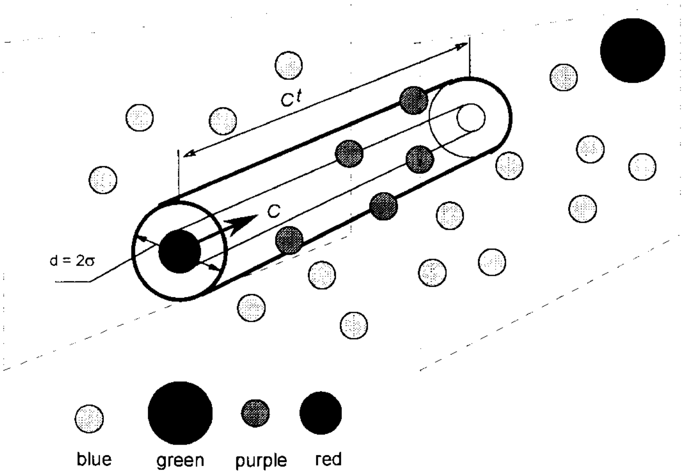

Fig. 4.10. 'Collision tube': there are 20 'blue' molecules of which five expecting to be hit by the 'red' one turned purple. The reaction, however, only occurs if the 'red' molecule is at least *red hot* and strikes at a proper angle; the result will be a large 'green' molecule visible in the corner. If we compress this gas the number of 'blue' molecules to be hit will proportionally increase

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[8] The number of 'jaywalkers' passed by a car per hour depends on the *population per mile of road* and the *speed* of a car. The life expectancy of an average jaywalker depends on ***both*** of these parameters and *not exclusively on the average number of cars per person.*

In the condensed state the situation is very different. Reaction rates are found *both to increase and to decrease* with increasing pressure. The molecules in a condensed phase are closely packed and *surrounded by an approximately fixed number of nearest neighbours* (the coordination number). The rate of occurrence of molecular collisions is the frequency of vibrations multiplied by the probability of reacting molecules being in the first coordination sphere of each other. This obviously leads to the idea of using mole fractions in formulating the kinetic law of mass action for reactions in the condensed state.

One, seemingly unimportant, point changes the situation, however:

When calculating mole fractions we must take into account not only material components but also vacancies in the first coordination sphere. According to theoretical models of the liquid state, the number of vacancies at the melting point must approximately equal the number of molecules ($N_V \cong N$ according to the Lennard-Jones and Devonshire model and $N_V \cong (0.7-1.3)N$ according to the Eyring theory). Furthermore, the thermal expansion of liquids is mainly due to an increasing number of vacancies: the mean intermolecular distance in liquids, according to X-ray diffraction experiments, does not depend on temperature [12]. It is practically impossible to get data on the total number of centres both occupied and vacant in a liquid reaction mixture, but a quantity proportional to this number is certainly the volume. Therefore molar concentrations are advantageously used in formulating the kinetic law of mass action for liquid state reactions.

This model does not, however, explain the effects of pressure on reaction rates in the liquid state. These effects are explained not by an increase/decrease of the number of vacancies and of the frequency of vibration but by a quasi-equilibrium model of the transition-state. When the transition-state is more compact than the ground state of the reactants then the pressure shifts the equilibrium towards the formation of this transition state and hence the reaction rate is increased. When the volume of the transition-state is larger than the volume of the molecules in the ground state then the effect of pressure on reaction rate is negative.

This model can be treated, at least semi-quantitatively, using the formalism developed above. According to the transition-state model the irreversible reaction:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{4.96}$$

should be written as:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}^{*} \longrightarrow \mathrm{C} \tag{4.97}$$

The rate of reaction (4.96) depends on the concentration of the transition-state or activated complex AB^*:

$$d[\mathrm{C}]/dt = [\mathrm{AB}^*]\nu_0 \tag{4.98}$$

in which the frequency of transitions of the activated complex over the potential barrier, ν_0, may be considered as proportional to the frequency of collisions (vibrations) or to a semi-quantum factor (kTe/h). The concentration of activated-complex at a given time can be obtained by a solution of the law of mass action for the equilibrium part of (4.97) and the law of mass action (4.25) may be used:

$$\ln\frac{q_{AB*}}{q_A q_B} - \ln\frac{[AB*]}{[A][B]} + ([A]+[B]+[AB*]+[C]+[S])\Delta v_{AB*} = 0 \tag{4.99}$$

in which $\Delta v_{AB*} = v_{AB*} - v_A - v_B$ and the additivity of the volume of the whole system is assumed:

$$V = v_A n_A + v_B n_B + v_{AB*} + v_C n_C + v_S N_S \tag{4.100}$$

Equation (4.99) yields the following expression for the concentration of activated complex:

$$[AB^*] = [A][B]\frac{q_{AB*}}{q_A q_B}\exp\left[\frac{\Delta v}{\langle v\rangle}\right] \tag{4.101}$$

in which the mean volume per molecule is, in general, a function of composition:

$$\langle v\rangle = \frac{n_A v_A + n_B v_B + n_C v_C + n_{AB*} v_{AB*} + N_S v_S}{n_A + n_B + n_C + n_{AB*} + N_S} \tag{4.102}$$

or:

$$\langle v\rangle^{-1} = [A] + [B] + [AB*] + C_S \tag{4.102a}$$

Correspondingly the reaction rate of (4.96) is given by:

$$\frac{d[C]}{dt} = \nu_0 \frac{q_{AB*}}{q_A q_B} e^{\frac{\Delta v}{\langle v\rangle}}[A][B] \tag{4.103}$$

Equation (4.103) signifies that, for dilute systems, we must multiply the ideal rate constant $q_{AB*}/q_A q_B$ by a constant factor higher or smaller than 1 according to the sign of Δv (in agreement with the qualitative explanations given above). In concentrated solutions one might expect a slight dependence of the term $\exp(\Delta v/<v>)$ on the concentration of reactants but this type of non-ideality does not bring about any critical phenomena.

More significant effects can be expected when we use the model that takes into account the changes in internal pressure during the formation of the activated complex. Simple qualitative arguments show that this should be the case most often met with. Experimentally it is found that, although there are some cases of decreasing reaction rates with increasing pressure, such examples are rare. Usually reaction rates are only increased significantly by application of pressures of several hundreds of bars. This indicates that the volume of the transition-state is smaller than the volume associated with reactants. On the other hand *chemical bonds* in the activated complex must be weakened and the transition-state may be viewed as a *semi-gaseous collection of atoms* or molecular fragments packed into a small volume. The internal pressure or the density of potential energy of molecular interactions in the transition state must drastically differ from that in either products or reactants. Equilibria of formation of activated complexes can therefore be characterised by large balances of lattice energy. For such systems the law of mass action (4.69) should be applied:

$$\ln\frac{q_{AB*}}{q_A q_B e^3}-\ln V_f-\ln\frac{n_{AB*}}{n_A n_B}+n\left(\frac{v_{AB*}-v_A-v_B}{V}-3\frac{u_{AB*}-u_A-u_B}{U}\right)=0 \quad (4.104)$$

in which V_f is given by (4.52), and V and U are additive functions of composition.

The concentration of the activated complex at a given moment of time can be calculated as a root of (4.104). At each given moment of time the current numbers of molecules of reactants $N_{A(B)} - n_C$ play the role of $N_{A(B)}$ in a normal equilibrium (the equilibrium between reactants and transition-state is assumed to be very fast). The product C can thus be considered as a *co-solvent*. According to the arguments given above we may assume large positive Δε for the activation equilibrium. Fig. 4.11 shows the "pseudo-van't Hoff" plots computed for the equilibrium part of (4.97) under the condition of varying content of reactants (taken in equimolar quantities) dissolved in a constant amount of solvent.

The initially small, and not very temperature sensitive, content of activated molecules AB^* exhibits a sudden increase upon reaching a certain temperature (Fig. 4.11B). Such a sharp increase in the concentration of the activated complex would cause a corresponding 'jump' in the reaction rate and, as the enthalpy of reaction is considerable, it would cause at least a local increase of temperature *etc*. However, such a system would stabilise itself because the dilution of the reaction mixture by the product shifts the critical point in the transition curves to higher temperatures (Fig. 4.11A and B).

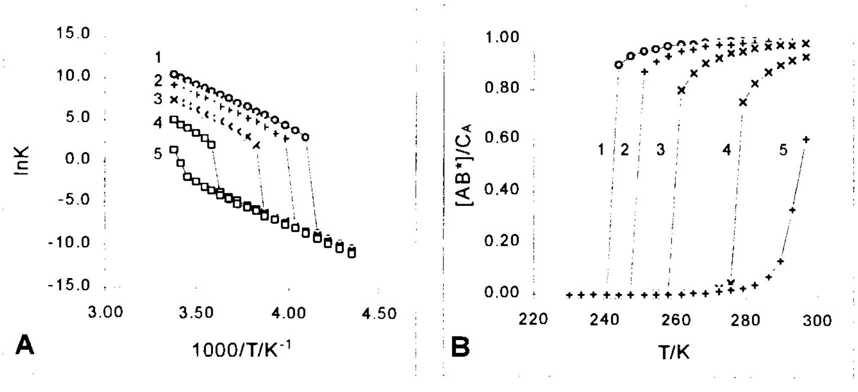

Fig. 4.11. Van't Hoff plots (A) and 'transition curves' (B) of the equilibrium of formation of activated complex (4.97) in a mixture described in Table 4.4. with varying quantities of reactants $N_A = N_B = 4$ (1), 2 (2), 1 (3), 0.5 (4), 0.25 (5) moles. The volume of activated complex was assumed to be equal to the sum of the volumes of reactants whilst the lattice energy was taken to be much higher than the additive value (Δu = 25 kcal mol^{-1})

The kinetics of such reactions can be simulated by including calculation of the reaction rate according to (4.98) and (4.101) in the procedure of numerical integration of the differential equation for the reaction (4.97). Fig. 4.12 shows the kinetic curves of the accumulation of the product C in the reaction (4.97) computed using the program 'Model' [5] (parameters of the reaction mixture are given in Table 4.4). In one case the 'ideal kinetics' was simulated and the balance of 'lattice energy' associated with the formation of the transition-state was supposed to be zero ($\Delta u^* = 0$). Corresponding kinetic curves have zero intercept and their initial slopes regularly increase with temperature (see Fig. 4.12A). The initial slope of the kinetic curve is directly proportional to the rate constant and therefore the corresponding Arrhenius plot can be drawn using the degrees of conversion at $t = 1$ min (first non-zero point in Fig. 4.12A). The curves in Fig. 4.12A thus yield an activation energy of 17.9 kcal mol^{-1} (see the Arrhenius plot in Fig. 4.13A) which is smaller than the 20 kcal mol^{-1} due to the cubic temperature dependence of V_f in (4.52). In the second instance the non-ideal kinetics was simulated corresponding to a large balance of lattice energy ($\Delta u^* = 25$ kcal mol^{-1}). These kinetic curves exhibit (Fig. 4.12 B) above certain temperature a non-zero intercept whilst the Arrhenius plot drawn from initial rates shows a well-defined step (Fig. 4.13B).

The low-temperature part of this plot yields an activation energy of 19.3 kcal mol^{-1} that is close to that for ideal kinetics. In the high-temperature region (after the step) this Arrhenius plot shows an activation energy of about twice that of the low-temperature part (40.4 kcal mol^{-1}). The logarithms of the pre-exponential factors of these parts of the Arrhenius plot are respectively 25 and 60.6 whilst that for an ideal solution is 32.8. We see that positive Δu^* always increases activation energy but may decrease (at lower temperatures) the pre-exponential factor[9].

If we disregard the intercept of the kinetic curves (supposing that some initial quantity of a product was present at $t = 0$) then the slopes of the kinetic curves in Fig. 4.12B yield an activation energy of 24 kcal mol^{-1} and $\ln v_0 = 32.45$. When the zero point is thus disregarded, a large positive Δu^* increases substantially the apparent E_a but leaves the pre-exponential factor practically unchanged

The dilution of such a system by the product of reaction stabilises the kinetics when the conditions are strictly isothermal. This can be achieved in a laboratory-scale experiment but might present a problem in larger reactors. One should expect therefore a heating of the reaction mixture proportional to the degree of conversion, which can neutralise the effects of dilution and cause an acceleration of the reaction. This has probably happened in the synthesis of ethyleneglycol diacetate from ethylene oxide and acetic anhydride mentioned above.

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[9] In a reaction series with varying Δu^* the anti-compensation effect may thus be observed (the case which up to now has admitted of no rational explanation)

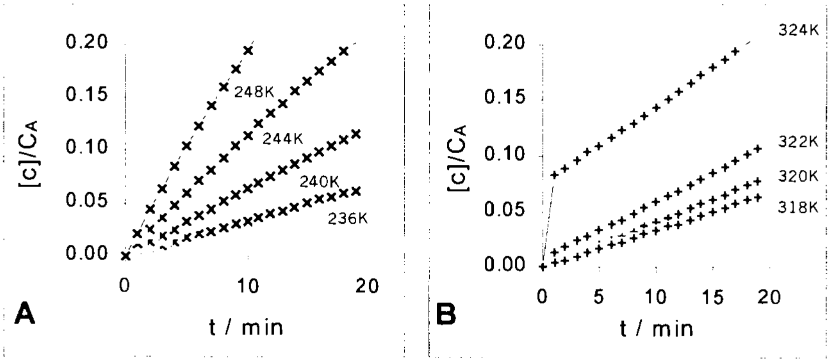

Fig. 4.12. Simulated kinetic curves for a system with an activation energy of 20 kcal mol^{-1} in the cases of ideal solution: $\Delta u^* = 0$ (**A**) and highly non-ideal solution $\Delta u^* = 25$ kcal mol^{-1} (**B**)

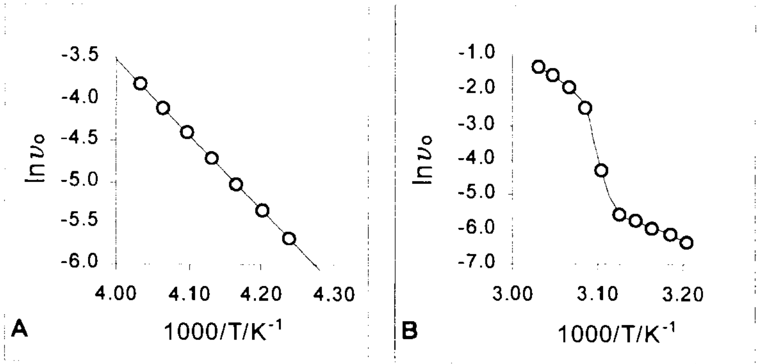

Fig. 4.13. Arrhenius plots for initial reaction rates corresponding to the kinetic curves in Fig. 4.12. The right-hand graph corresponds to a large positive Δu^*

Table 4.4. Parameters of the reaction mixture (4.97)

E_a (kcal mol^{-1})	$E_a/\Delta S_a$ (K)	ν_0 (min^{-1})	$N_A = N_B$ (mol)	N_S (mol)
20	300	0.5	1	2
v_A (l mol^{-1})	v_B (l mol^{-1})	v_{AB^*} (l mol^{-1})	v_C (l mol^{-1})	v_S (l mol^{-1})
0.05	0.1	0.15	0.15	0.1
u_A (kcal mol^{-1})	u_B (kcal mol^{-1})	u_{AB^*} (kcal mol^{-1})	u_C (kcal mol^{-1})	u_S (kcal mol^{-1})
6	9	40	15	7

The thermal effect of the reaction:

$$C_2H_4O + (CH_3CO)_2O \longrightarrow (CH_3COOCH_2)_2 \quad (4.105)$$

is considerable (*ca.* 40 kcal mol^{-1}) and the amount of steam used to heat the reaction mixture to a predetermined temperature must be exactly calculated and *controlled according to the data on the degree of conversion.* The vaporisation energies of ethylene oxide and acetic anhydride are approximately 6 and 9 kcal mol^{-1} respectively and that of the product is about 11 kcal mol^{-1}. The 'vaporisation energy' of the transition-state may well be different from those of reactants because the transition-state can be highly polar. The dipole moment of (a probable) transition-state for the reaction (4.106) shown in Fig. 4.14A is 5.769 D whilst the dipole moment of the product is 1.278 D (Fig. 4.14B)[10]. The energy of dipole-dipole interactions of these species may therefore differ by the factor $(\mu_C/\mu_{AB\bullet})^2 \cong 20$. The energy of molecular interactions of reactants is of the same order of magnitude as that of the product (the respective heats of vaporisation differ by about 25%). Therefore Δu^* for this reaction can be quite large – even if the dipole-dipole interaction is responsible for only a small part of the experimental heat of vaporisation (9 – 15 kcal mol^{-1}). According to the analysis given above, the non-ideality of the activation equilibrium sharply increases the thermal sensitivity of a reaction over a small temperature range. In laboratory experiments, carried out under practically isothermal conditions, this non-ideality might pass unobserved because the dilution of a system by the product provides for an apparent stability. The intercepts of the kinetic curves might be disregarded as originating in an impurity of the reactants. Such a misinterpretation is a result of an habitual approximation of real systems by pseudo-ideal models with activity coefficients playing the *deus ex machina*. It is important to bear in mind that this model might fail from time to time.

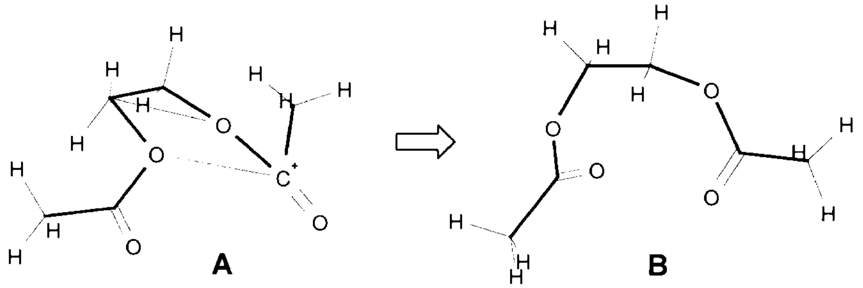

Fig. 4.14. Probable structure of the transition-state in the reaction of ethylene oxide with acetic anhydride (A) and that of the final product of this reaction (ethylene glycol diacetate), (B). Thin lines in the transition-state structure indicate the original bonds in the reactants. Structures were optimised using the Molecular Mechanics method (HyperChem3®)

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[10] The results of MNDO calculations using the HyperChem3® program.

4.7
Conclusions

In this Chapter we have derived a number of forms of the law of mass action applicable to imperfect liquid systems under the assumption of the *additivity of total volume* and of the *total energy* of attractive molecular interactions (lattice energy).

Non-ideality was introduced in a formal way by taking into account the dependence of these parameters on composition arising from this additivity. The combined action of these parameters resulted in the dependence of *free volume* on the composition of a system. Although the model was mainly empirical and approximate it predicted correctly what type of effects can be expected in systems of interacting particles and sketched a way in which they can be analysed.

This model predicted the appearance of non-ideality terms in the law of mass action in the form of relative balances of volume and lattice energy (potential energy of attractive molecular interactions approximated by the energy of vaporisation). Empirical rules, such as the Kopp rules, indicate that these balances are not large, which enables these non-ideality terms to be transformed into activity coefficients. A general form of activity coefficient arising from this type of non-ideality has been derived and involves reduced temperature and the *complete derivative* of free volume with respect to the numbers of actual species.

In dilute solutions these non-ideality terms bring about the dependence of the equilibrium constant on the volumetric and distillation properties of the solvent.

Extremely large balances of lattice energy in a reaction might cause critical phenomena related to phase transitions and manifested by singularities ('jumps') in the van't Hoff plots. Balances of such magnitude are not very probable for equilibria but may be expected for the formation of a transition state step in chemical kinetics.

The analysis given in this Chapter disregards the possible dependence of *molecular* lattice energies and volumes on composition and the derived terms only reflect a part of the effects of non-ideality. The case of non-additive lattice energy will be considered in Chapter 7 and in Chapter 9 where a general form of the law of mass action for non-ideal systems will be constructed. Chapter 6 is dedicated to an analysis of the effects of non-ideality arising from binary molecular interactions in gases. In Chapter 5 we shall consider the description of molecular interactions employing empirical binary potentials.

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5 Molecular Interactions

5.1
Introduction

In the preceding Chapter we introduced the effects of molecular interactions into the law of mass action assuming a *formal* dependence of free volume on the composition of reaction mixtures. In dilute solutions these effects reveal themselves by dependence of the equilibrium constant on molecular volume and vaporisation energy of the solvent, whereas in concentrated solutions deflections of van't Hoff plots from linearity may be observed. A theoretical description of these phenomena requires a knowledge of the actual equation of state and/or the shape of the intermolecular potential. A very rough model has been used in order to obtain the relationship between free volume, volume and internal pressure. Nevertheless, the formalism derived explained a number of deviations of the law of mass action from ideality and predicted some critical phenomena.

In this Chapter we shall consider various forms of the most widely used molecular potentials as well as sketch the way in which the equation of state can be derived based on the given shape of the potential. Also some examples will be given of how to estimate the parameters of intermolecular potentials from experimental data.

The nature of intermolecular forces (according to our knowledge of the structure of matter) is electric. The coulombic forces may however be of different ranges of action. The forces of the longest range are those between *point charges* corresponding to *ions* either in electrolyte solutions or in plasma. The interactions between *neutral particles* having asymmetrical charge distribution and hence non-zero *permanent electric moments* are of shorter range and that is reflected in the higher powers of their radial dependencies (the energy being proportional to r^{-2} for ion-dipole and r^{-3} for dipole-dipole interactions). Uncharged symmetric molecules, which possess neither dipole nor quadrupole permanent moments, are attracted to each other by the so-called *dispersive forces*. These are inversely proportional to the 6-th and higher powers of distance and originate from the interaction of *instantaneous* electric moments associated with the polarisation of electronic orbitals in external electric fields, which are created either by light (bringing about the phenomena of dispersion) or by the oscillating electrons of neighbouring molecules (causing molecular attraction). Quantum theory (London)

A.B. Koudriavtsev et al., *The Law of Mass Action*

shows that dispersive forces exist even between spherically symmetrical atoms of the noble gases where classical electrostatics fails to explain such interaction.

Repulsive short-range forces occurring at collisions of uncharged molecules originate in the Pauli principle, according to which two electrons with the same spin can not be in the vicinity of each other. These effects are called *electron correlation* effects. This results in a very steep radial dependence of repulsive forces at short distances.

The theoretical description of molecular interactions is based on the concept of the *force field* (created by a partner particle or by some number of particles). The fields considered in the theories of equilibrium properties are always *potential i.e.* there must be such a function φ that the *force* X (acting on a molecule) along a *coordinate* equals the *derivative of* φ *by this coordinate:*

$$X = -\partial\varphi/\partial x \tag{5.1}$$

Such forces are called *potential forces* and the function φ is the *potential.* Statistical mechanics deals exclusively with potential forces whilst *non-potential* forces (such as forces of friction for example) belong to other fields of science (*e.g.* the mechanical theory of heat). In many cases potential forces are also *central i.e.* derived from a spherically symmetric potential.

General electrostatics predicts the potential of *attractive* molecular interactions to be a *hyperbolic function* of distance:

$$\varphi = -Ba^{-m} \tag{5.2}$$

in which the exponent m may (theoretically) be 1, 2, 3, 4, 6 and 8 (see also Table 5.1). The constant B can be calculated for certain models theoretically but usually it is considered (as well as the exponent m) as merely an empirical constant. For repulsive interactions originating from electron correlation effects the potential is a product of exponential and polynomial, $R(r)$, functions:

$$\varphi = R(r)\, e^{-r/\rho} \tag{5.3}$$

In real molecular systems, different modes of interaction contribute to the intermolecular potential. Therefore, any general formula describing such a potential is at least an interpolation or, in fact, an empirical equation. The repulsive part, for example, is rarely described by (5.3) because of purely computational difficulties. Instead a hyperbolic term similar to (5.2) is used, with higher exponents, to account for the steep radial dependence. Electrostatics and quantum mechanics give a hint rather than provide an exact form of the intermolecular potential applicable to practical calculations.

5.2
Empirical binary potentials

An exact solution of the *equation of motion* of a system of interacting bodies can only be obtained for a two-body system. Approximate solutions can be found for systems of larger numbers of particles when it is possible to select one principal binary interaction (*e.g.* a given planet and the Sun) whilst other interactions (with other planets) can be considered as small perturbations. Molecular interactions are generally considered as if occurring within independent isolated molecular pairs. This is true if these pairs are statistically independent *i.e.* the interaction in one pair does not change the interactions in all other pairs. Such a condition might hold for rarefied gases but not for the condensed state where the interactions of molecules with molecular pairs and those between the pairs of molecules should, in principle, be taken into account.

However, the approximation of binary interactions can be used as an *effective* description, bearing in mind that the parameters of a binary potential include the contributions from higher order interactions. Such a 'neglect' of the higher order interactions results in a certain non-additivity of the energy of molecular interactions in the condensed state (see Chapter 7). With these reservations in mind, the binary potential can be considered as a building block of the theoretical description of molecular interactions. Some model potentials that are frequently used in such studies are shown in Table 5.1.

The choice of a potential depends on the nature of the calculations and involves striking a balance between the required precision and the computation time. Most potentials assume spherical symmetry of interaction, although the *Stockmayer* potential allows for the introduction of angular dependence. The '6–exp' potential gives a better description of the repulsive part but requires longer computation times than the use of hyperbolic potentials.

Table 5.1. Model intermolecular binary potentials

Rigid-core potential	$u(r) = \infty$ at $r < \sigma$; $u(r) = 0$ at $r > \sigma$
Sutherland's potential	$u(r) = \infty$ at $r < \sigma$; $u(r) = -cr^{-m}$ at $r > \sigma$
Square potential well	$u(r) = \infty$ at $r < \sigma$, $-\varepsilon$ at $\sigma < r < \lambda\sigma$, and 0 at $r > \lambda\sigma$ ($\lambda = 1.5$)
'6–exp' potential	$u(r) = be^{-ar} - cr^{-6}$
Stockmayer's potential	$u(r,\theta_A,\theta_B,\varphi_A-\varphi_B) = 4D_e[(\sigma/a)^{12} - (\sigma/a)^6]$ $-(\mu_A\mu_B/r^3)[2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos(\varphi_A-\varphi_B)]$

In this Chapter we shall be using a spherically symmetrical hyperbolic potential known as the Lennard-Jones[1] potential:

$$\varphi = Aa^{-n} - Ba^{-m} \tag{5.4}$$

In (5.4) m and n are positive integers ($n > m$, reflecting a steeper repulsive potential) and A and B are positive constants. Fig. 5.1 shows an example of the Lennard-Jones potential curve computed for a pair of argon atoms.

The Lennard-Jones potential can be written in a number of convenient forms by defining the constants A and B *via* the *coordinates of the point of mechanical equilibrium* a_e and φ_e (Fig. 5.1). At this point the derivative of potential with respect to coordinate is zero:

$$(d\varphi/da)_{a=a_e} = -nAa_e^{-n-1} + mBa_e^{-m-1} = 0 \tag{5.5}$$

Equation (5.5) reflects the balance of *repulsive and attractive forces* at the point of mechanical equilibrium. Employing this equation the constant B can be expressed in terms of the constant A and *vice versa* as:

$$B = (n/m)\left(A/a_e^{n-m}\right) \tag{5.6}$$

Equation (5.4) can thus be rewritten as:

$$\varphi = Aa^{-n} - \frac{n}{m}\frac{A}{a_e^{n-m}}a^{-m} = Aa^{-n}\left[1 - \frac{n}{m}\left(\frac{a_e}{a}\right)^{m-n}\right] \tag{5.7}$$

The potential in the point of equilibrium $\varphi_e(a = a_e)$ then equals:

$$\varphi(a_e) = \varphi_e = -Aa_e^{-n}\left[\frac{n}{m} - 1\right] \tag{5.8}$$

The constants A and B then are:

$$A = -\frac{\varphi_e a_e^n}{(n/m) - 1}; \qquad B = -\frac{\varphi_e a_e^m}{1 - (m/n)} \tag{5.9}$$

The equation of the Lennard-Jones potential (5.4) is thus transformed into:

$$\varphi = \frac{\varphi_e}{m-n}\left[m\left(\frac{a_e}{a}\right)^n - n\left(\frac{a_e}{a}\right)^m\right] \tag{5.10}$$

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[1] Actually, the general form of this equation was first suggested by the Austrian scientist *Gustav Mie* [1]. The *Lennard-Jones* potential corresponds to $m = 6$ and $n = 12$.

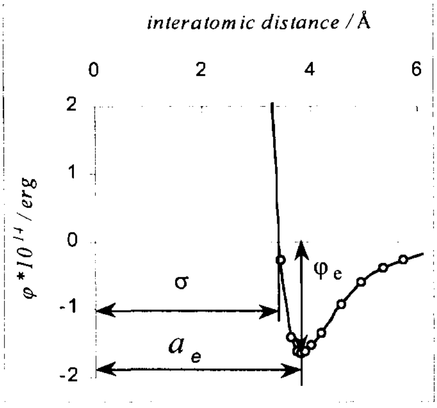

Fig. 5.1. Lennard-Jones potential for an Ar–Ar pair.

The potential energy at the equilibrium point φ_e is usually negative and its magnitude can be identified with the energy of dissociation of the molecular pair:

$$D_e = -\varphi_e \tag{5.11}$$

The potential (5.10) may then be written as:

$$\varphi = \frac{D_e m}{n-m}\left[\left(\frac{a_e}{a}\right)^n - \frac{n}{m}\left(\frac{a_e}{a}\right)^m\right] \tag{5.12}$$

Equation (5.12) can, in turn, be written in terms of volume ($v \propto a^3$):

$$\varphi = \frac{D_e m}{n-m}\left[\left(\frac{v_e}{v}\right)^{\frac{n}{3}} - \frac{n}{m}\left(\frac{v_e}{v}\right)^{\frac{m}{3}}\right] \tag{5.13}$$

The *energy of displacement* of a particle from the point of equilibrium *in an isolated molecular pair*[2] can be expressed as:

$$W = \varphi - \varphi_e = \frac{D_e}{n-m}\left\{n\left[1-\left(\frac{a_e}{a}\right)^m\right] - m\left[1-\left(\frac{a_e}{a}\right)^n\right]\right\} \tag{5.14}$$

Introducing the dimensionless parameter characterising the deviation from the position of equilibrium, $x = (a - a_e)/a_e$, yields:

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[2] A much more complicated procedure is required to obtain the average displacement energy of a molecule in a cell in the condensed state (see Section 5.5).

$$W = \varphi - \varphi_e = \frac{D_e}{n-m}\left\{n\left[1-(1+x)^m\right] - m\left[1-(1+x)^n\right]\right] \tag{5.15}$$

This equation will help us find the frequency of vibrations of a particle at the bottom of the potential well.

For *small displacements* ($x << 1$) we may expand $(1+x)^{-n}$ into a series and cut off this expansion at the square term:

$$(1+x)^{-n} \cong 1 - nx + (1/2)n(n+1)x^2 \tag{5.16}$$

The displacement energy then becomes:

$$W \cong \frac{D_e}{2}mnx^2 = \frac{D_e}{2}\left(\frac{a-a_e}{a_e}\right)^2 \tag{5.17}$$

The potential curve for *small displacements* is thus a parabola corresponding to *harmonic oscillation of a particle at the bottom of a potential well. The frequency*[3] *of such oscillations is:*

$$\nu_e = \frac{1}{2\pi a_e}\left(\frac{mnD_e}{\mu}\right)^{1/2} \tag{5.18}$$

in which μ is the reduced mass. For a molecular pair this is:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{5.19}$$

Instead of the position of equilibrium (a_e), the *distance corresponding to zero potential,* σ, (Fig. 5.1) is often employed. According to (5.10), zero potential corresponds to the following relationship:

$$a_e = \sigma\left(\frac{n}{m}\right)^{\frac{1}{n-m}} \tag{5.20}$$

The potential (5.10) can then be written in the following convenient form:

$$\varphi = \frac{D_e}{n-m}\left(\frac{n^n}{m^m}\right)^{\frac{1}{n-m}}\left[\left(\frac{\sigma}{a}\right)^n - \left(\frac{\sigma}{a}\right)^m\right] \tag{5.21}$$

The most frequently used pairs of n and m are 12 and 6 as well as 9 and 6

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[3] The idea that any potential curve with a minimum can be represented by a parabola is of course trivial. The derivation given was necessary in order to obtain the relationship between the frequency of a harmonic oscillator and the parameters of the essentially asymmetric Lennard-Jones potentials.

(depending on the nature of the actual molecular system and macroscopic properties). Accordingly the last equation can be written as:

$$\varphi = 4D_e\left[\left(\frac{\sigma}{a}\right)^{12} - \left(\frac{\sigma}{a}\right)^{6}\right]; \qquad \varphi = \frac{27}{4}D_e\left[\left(\frac{\sigma}{a}\right)^{9} - \left(\frac{\sigma}{a}\right)^{6}\right] \tag{5.22}$$

Parameters of this equation for *hetero-molecular interactions* can be calculated (for non-polar molecules) using empirical rules:

$$D_{eAB} = \left(D_{eAA}D_{eBB}\right)^{1/2}; \qquad \sigma_{AB} = \left(\sigma_{AA} + \sigma_{BB}\right)/2 \tag{5.23}$$

These rules, although of empirical origin, are supported by the theory of dispersive forces. For example, when the frequencies of electronic oscillations in both molecules are identical the constant B in the Lennard-Jones potential for a hetero-molecular pair can be calculated to be:

$$B_{AB} = \left(B_{AA}B_{BB}\right)^{1/2} \tag{5.24}$$

On the other hand, if their polarisabilities are identical, then the following rule should be used:

$$B_{AB} = 2B_{AA}B_{BB} / \left(B_{AA} + B_{BB}\right) \tag{5.25}$$

In general, the polarisabilities vary over a wider range than do those of the electronic frequencies and therefore (5.24) is commonly used.

5.3

Taking into account nearest, next nearest, and longer range interactions in the condensed phase

Binary interactions are typical for rarefied gases. A molecule in the condensed state interacts with c nearest neighbours (the coordination number) as well as with molecules outside the first coordination sphere. The total potential energy can be approximated as the *sum of energies of binary interactions* with these neighbours. In a system of N molecules there are $Nc/2$ nearest neighbour interactions (one should not count the same interaction twice!). The total potential energy of *nearest neighbour binary interactions* is thus:

$$U = \frac{Nc}{2}\varphi = \frac{Nc}{2}\left(Aa^{-n} - Ba^{-m}\right) \tag{5.26}$$

The average energy of nearest neighbour interactions *per molecule* is then one half of the energy of interaction of a selected molecule with its surrounding:

$$u = \frac{U}{N} = \frac{c}{2}\left(Aa^{-n} - Ba^{-m}\right) \tag{5.27}$$

In crystals, the interactions with molecules *beyond the first coordination* sphere can easily be taken into account because there is a strict relationship between the parameters of a cell and the number of molecules and radii of the second, third and so forth coordination spheres. For example, in a lattice of the NaCl type any ion (atom or molecule) has 6 neighbours at a distance of a. Twelve neighbours are at a distance of $a\sqrt{2}$ and 8 neighbours at a distance of $a\sqrt{3}$. The repulsive and attractive parts of the potential energy of a particle in such a lattice can thus be written as:

$$\varphi_{rep} = \frac{6A}{a^n}\left[1 + \frac{2}{2^{n/2}} + \frac{4}{3^{(n+2)/2}} + \cdots\right] = \frac{cAs_n}{a^n} \tag{5.28}$$

$$\varphi_{att} = \frac{cBs_m}{a^m} \tag{5.29}$$

in which the coefficients s_n and s_m are:

$$s_n = 1 + \frac{2}{2^{n/2}} + \frac{4}{3^{(n+2)/2}} + \cdots; \qquad s_m = 1 + \frac{2}{2^{m/2}} + \frac{4}{3^{(m+2)/2}} + \cdots \tag{5.30}$$

The potential energy is then:

$$U = \frac{Nc}{2}\left(s_n Aa^{-n} - s_m Ba^{-m}\right) \tag{5.31}$$

The coefficients s_m and s_n for several simple crystal lattices are given in Table 5.2. As is expected, the coefficients corresponding to higher exponents (m, n) are close to 1. For $c = 12$, $m(n) = 6$ and 12 means that the effects of the outer coordination spheres are just 20% and 1% respectively. However, even these contributions can change considerably the results of calculations (see the Lennard-Jones and Devonshire equation of state, page 162).

Table 5.2. Coefficients $s_{m(n)}$ for cubic lattices [2]

$m(n)$	Simple cubic lattice ($c = 6$)	Space centred lattice ($c = 8$)	Face centred lattice ($c = 12$)
6	1.4003	1.5317	1.2045
9	1.1048	1.2368	1.0410
12	1.0337	1.1395	1.0110

Table 5.3. Values of coordination numbers c, structural constants κ, and coefficients $s_{n(m)}$ for different types of the quasi-crystal lattice of liquids [2]

	c	κ	K	s_6	s_9	s_{12}
face-centred lattice	12	$1/\sqrt{2}$	$\sqrt{2}$	1.219	1.038	1.009
diamond lattice	4	$8/\sqrt{3}$	$4/\sqrt{6}$	1.449	1.103	1.057

In liquids there is no long-range order, therefore molecular interactions are taken into account in a slightly different way. They are divided into two parts: (i) those with the molecules of the first coordination sphere (described by (5.27)) and (ii) those with all other molecules. The number of nearest neighbours in liquids (the effective coordination number, c) is usually known and their contribution to the total potential energy is $Nc\varphi/2$.

The effects of molecules outside the first coordination sphere in liquids are estimated assuming these layers to be a *continuum*. If the concentration of molecules in a liquid is some constant value[4] $q = (N/V)$, then the number of molecules in a spherical layer of the radius r and thickness dr is $q4\pi r^2 dr$. The total energy of interaction of a given molecule with molecules outside the first coordination sphere can be found by integration over the distances from the radius of the border between first and second coordination spheres (R_2) to infinitely large distances:

$$\varphi_{out} = 4\pi q \int_{R_2}^{\infty} \left(Ar^{-n} - Br^{-m}\right) r^2 dr \tag{5.32}$$

The radius R_2 can be assumed to be proportional to the average distance between molecules ($R_2 = Ka$). To a first approximation the volume of the first coordination sphere can be identified with the volume of a crystal cell κa^3 whilst the concentration of molecules q is the inverse volume of a cell ($q = 1/\kappa a^3$). The values of K *and* κ for a liquid can be assumed to be the same as in a similar crystalline solid (see Table 5.3).

The integration of (5.32) then yields the energy of interaction of a molecule with its 'remote' surroundings as:

$$\varphi_{out} = \frac{4\pi}{\kappa} \left[\frac{Aa^{-n}}{(n-3)K^{n-3}} - \frac{Ba^{-m}}{(m-3)K^{m-3}} \right] \tag{5.33}$$

The total potential energy of binary interactions in liquids can be conveniently written (similar to solids) using the coefficients s_n and s_m:

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[4] Better agreement is achieved when the radial dependence of molecular concentration is taken into account, *e.g.* in the form of a *radial distribution function*. In this case, however, we must integrate it within (5.32).

$$U = \frac{N}{2}\left(\varphi_{ins} + \varphi_{out}\right) = \frac{Nc}{2}\left(s_n A^{-n} - s_m B a^{-m}\right) \tag{5.34}$$

The coefficients s_n and s_m *for liquids* are given by much simpler equations than in the case of solids, namely:

$$s_n = 1 + \frac{4\pi}{c\kappa(n-3)K^{n-3}}; \qquad s_m = 1 + \frac{4\pi}{c\kappa(m-3)K^{m-3}} \tag{5.35}$$

The potentials (5.31) and (5.34) can be expressed in terms of the coordinates of the point of equilibrium (φ_s and a_s) as has been done for binary interactions. The potential energy per molecule in a lattice is:

$$u = (c/2)\left(s_n A a^{-n} - s_m B a^{-m}\right) \tag{5.36}$$

and has a minimum at $(du/da) = 0$, hence:

$$a_s^{n-m} = nAs_n / mBs_m \tag{5.37}$$

The ordinate of the equilibrium point is then:

$$u_s = -\frac{cs_m B}{2a_s^m}\left(1 - \frac{m}{n}\right) = -\frac{cs_n A}{2a_s^n}\left(\frac{n}{m} - 1\right) \tag{5.38}$$

The expression for potential energy per molecule may therefore be written as:

$$u = \frac{u_s}{m-n}\left[m\left(\frac{a_s}{a}\right)^n - n\left(\frac{a_s}{a}\right)^m\right] \tag{5.39}$$

Note that the energy u_s can be identified with the energy of vaporisation because the gaseous state can be considered as the result of an infinite expansion of the condensed phase:

$$-u_s = u_V \tag{5.40}$$

The energy of vaporisation of a liquid can, of course, be estimated as the vaporisation enthalpy less the work of expansion (*RT* for one mole). However a better approximation is obtained when the data derived from surface tension are employed. The molecular energy of vaporisation according to Stefan's law is double the surface energy per molecule [3]:

$$u_V = 2\gamma \upsilon^{2/3} \tag{5.41}$$

in which γ is the surface tension and υ is volume per molecule. Expressing υ as V_m/N_L allows the molar vaporisation energy to be written as:

$$U_V = N_L u_V = 2\gamma V_m^{2/3} N_L^{1/3} \tag{5.42}$$

Using this approximation for u_s the velocity of sound in a large number of liquids was calculated on the basis of Lennard-Jones potentials and found to be in good agreement with experimental data (see Section 5.7.2).

5.4
Frequency of vibrations

The vibrational partition function is responsible for a considerable part of the free energy of solids and liquids. Therefore a knowledge of the frequency of vibration and its relation to the parameters of intermolecular potential is important. The movement of a particle in a potential well is always a kind of oscillation or (if the bottom of the potential well is flat) a mixture of translational motion and oscillation. A pure harmonic oscillation corresponds to a parabolic potential curve; the force acting on a particle in such a potential well ($\varphi = kx^2$) is:

$$X = -\partial\varphi/\partial x = -2kx \tag{5.43}$$

in which x is the displacement from the equilibrium point and $2k$ is the *elastic constant*. The mode of motion of a particle in a given force field can be found by integrating the equation of motion:

$$\mu \frac{d^2x}{dt^2} + 2kx = F(t) \tag{5.44}$$

in which μ is the reduced mass and the term $\mu d^2x/dt^2$ represents the 'dynamic force', whilst the term $-2kx$ is the 'returning force' derived from the potential (5.1).

The reduced mass μ in a system of a particle surrounded by a large number of neighbours is approximately the mass of this particle. The right-hand part of (5.44) contains the external force *F(t)*. Equation (5.44) is a second order linear differential equation and a general solution of this type of equation is the sum of exponentials:

$$x = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} \tag{5.45}$$

in which $C_{1,2}$ are the coefficients to be determined from the initial conditions and $\lambda_{1,2}$ are the roots of the *characteristic equation*:

$$\mu\lambda^2 + 2k = 0; \qquad \lambda_{1,2} = \pm(2k/\mu)^{1/2} \tag{5.46}$$

For a U-shaped potential well, k is positive and both roots of (5.46) are imaginary. The exponential function of an imaginary argument is a periodic function connected with the *cosine* function as follows:

$$\cos\left(t\sqrt{2k/\mu}\right)=\frac{1}{2}\left[e^{it\sqrt{2k/\mu}}+e^{-it\sqrt{2k/\mu}}\right] \tag{5.47}$$

The movement is therefore a harmonic oscillation with frequency:

$$\omega=(2k/\mu)^{1/2}; \qquad \nu=\frac{1}{2\pi}(2k/\mu)^{1/2} \tag{5.48}$$

The case of a potential in the form of a cubic parabola ($\varphi = kx^3$) corresponds to a vibrating string with a massive object fastened to its centre. A potential well of an arbitrary shape *can always be approximated in the vicinity of its minimum by a quadratic parabola.* Therefore small amplitude oscillations in the case when $\varphi = kx^3$, as well as in any other potential, may be considered as harmonic. However, a *classical* particle of mass μ that possesses energy ε in a square potential well with infinitely high walls and the width l would perform a 'saw-tooth' motion with a period $l/(\varepsilon/2\mu)^{1/2}$.

In order to calculate the vibrational frequency we must find the connection between the elastic constant and parameters of intermolecular potential. According to (5.43), the elastic constant is the second derivative of potential with respect to coordinate:

$$\partial^2\varphi/\partial x^2 = 2k = K \tag{5.49}$$

For the Lennard-Jones potential this leads (derivation see in [2]) to:

$$K=\frac{d^2\varphi}{dx^2}=\frac{2u_s mn}{3a^2(m-n)}\left[(n-1)\left(\frac{a_s}{a}\right)^n-(m-1)\left(\frac{a_s}{a}\right)^m\right] \tag{5.50}$$

The frequency of vibrations of a particle in a condensed isotropic medium is therefore:

$$\nu_s=\frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{1/2}=\frac{1}{2\pi a}\left\{\frac{2mnu_s}{3\mu(m-n)}\left[(n-1)\left(\frac{a_s}{a}\right)^n-(m-1)\left(\frac{a_s}{a}\right)^m\right]\right\}^{1/2} \tag{5.51}$$

Equation (5.51) shows that the frequency of vibration depends not only on the parameters of potential but also on the amplitude of vibrations ($a - a_s$). This should be expected for any not strictly parabolic potential. However, for *small amplitudes* ($a \approx a_s$) the vibrational frequency is given by the simple formula:

$$\nu_s=\frac{1}{2\pi a_s}\left(\frac{2mn|-u_s|}{3\mu}\right)^{1/2} \tag{5.52}$$

We now consider the relationship between the shape of the potential well in a cell in the condensed state and parameters of the Lennard-Jones potential.

5.5

The shape of the potential well in a cell

The dependence of potential energy on the distance *a* discussed above corresponds to the expansion or compression of the whole solid or liquid. On the other hand, the potential energy profile for a molecule in a cell (required for the calculation of free volume) can be found on the basis of the binary potential employing some model averaging so as to simulate the effects of molecular motion.

In the Lennard-Jones and Devonshire theory of the liquid state, the molecular motion is approximated as a random circling over a sphere of varying radius (within the allowed space). The corresponding variation of the distance between such a molecule and a fixed neighbour can easily be determined from a geometric model (Fig. 5.2). The *average* distance $\langle z \rangle = a$ remains constant and characterises the equilibrium properties. The radius of the sphere *r* is an independent variable imitating the amplitude of thermal motion.

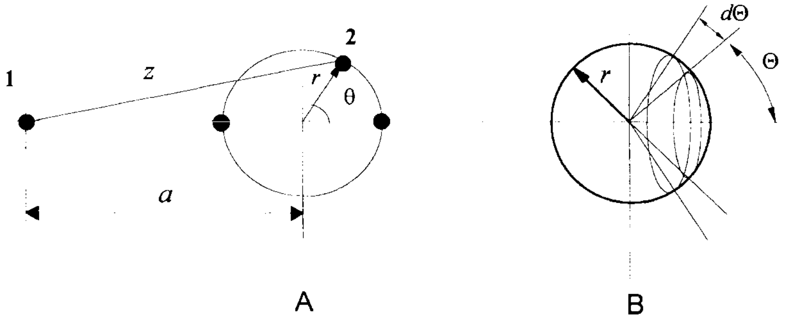

Fig. 5.2. Geometrical models of the averaging of intermolecular potential

The current distance between two molecules in this model (Fig. 5.2 A) is:

$$z = \left(a^2 + r^2 + ar\cos\theta\right)^{1/2} \tag{5.53}$$

Considering all angles θ to be of equal probability (spherically symmetrical potential) the distribution law for *z* is given by the ratio (see Fig. 5.2B):

$$\frac{\textit{element of spherical surface}}{\textit{total surface of sphere}} = \frac{2\pi r^2 \sin\theta d\theta}{\int_0^\pi 2\pi r^2 \sin\theta d\theta} = \frac{\sin\theta d\theta}{\int_0^\pi \sin\theta d\theta} = \frac{\sin\theta d\theta}{2} \tag{5.54}$$

The average potential energy of such a binary interaction is then:

$$\langle\varphi\rangle = \frac{1}{2}\int_0^{\pi}\varphi(z)\sin\theta d\theta \tag{5.55}$$

Taking into account that $dz/d\theta = -ar\sin\theta/z$, *i.e.* $\sin\theta\, d\theta = -zdz/ar$ the above expression can be transformed into:

$$\langle\varphi\rangle = -\frac{1}{2ar}\int_{a+r}^{a-r} z\,\varphi(z)dz = \frac{1}{2ar}\int_{a-r}^{a+r} z\,\varphi(z)dz \tag{5.56}$$

For the Lennard-Jones potential:

$$\varphi = \frac{A}{z^n} - \frac{B}{z^m} \tag{5.57}$$

In addition, the integration of (5.56) results in:

$$\langle\varphi\rangle = \frac{1}{2ar}\left\{\frac{A}{n-2}\left[(a-r)^{-n+2} - (a+r)^{-n+2}\right] - \frac{B}{m-2}\left[(a-r)^{-m+2} - (a+r)^{-m+2}\right]\right\} \tag{5.58}$$

Employing an effective (averaged over the whole system of molecules) coordination number c we can write the average potential energy of the molecule performing motions of amplitude r within a cell as:

$$\psi(a,r) = c\langle\varphi\rangle$$
$$= \frac{c}{2}\frac{a}{r}\left\{\frac{Aa^{-n}}{n-2}\left[\left(1-\frac{r}{a}\right)^{-n+2} - \left(1+\frac{r}{a}\right)^{-n+2}\right] - \frac{Ba^{-m}}{m-2}\left[\left(1-\frac{r}{a}\right)^{-m+2} - \left(1+\frac{r}{a}\right)^{-m+2}\right]\right\} \tag{5.59}$$

For *small displacements* $(r/a) << 1$ (taking into account the fact that $(1 \pm \delta)^k \cong 1 \pm k\delta$), the potential energy of such a molecule becomes equal to the sum of energies of its interactions with its nearest neighbours at a distance a:

$$\psi(a,0) = c\left(Aa^{-n} - Ba^{-m}\right) \tag{5.60}$$

The *displacement energy* w can then be defined as:

$$w = \psi(a,r) - \psi(a,0) = c\left(\frac{A}{a^n}\ell_A - \frac{B}{a^m}\ell_B\right) \tag{5.61}$$

in which the polynomials ℓ_A and ℓ_B represent the motion of a molecule within a cell:

$$\ell_A(a,r,n)=\frac{1}{2}\left(\frac{a}{r}\right)\frac{1}{n-2}\left[\left(1-\frac{r}{a}\right)^{-n+2}-\left(1+\frac{r}{a}\right)^{-n+2}\right]-1 \tag{5.62}$$

$$\ell_B(a,r,m)=\frac{1}{2}\left(\frac{a}{r}\right)\frac{1}{m-2}\left[\left(1-\frac{r}{a}\right)^{-m+2}-\left(1+\frac{r}{a}\right)^{-m+2}\right]-1 \tag{5.62a}$$

The constants A and B in (5.61) can be expressed in terms of the parameters D_e, and a_e, or D_e and σ (see (5.10) and (5.21)). However, expressing the displacement energy as a function of volume is also convenient. For $m = 6$ and $n = 12$ this results in:

$$w=cD_e\left[\left(\frac{v_e}{v}\right)^4\ell_A-2\left(\frac{v_e}{v}\right)^2\ell_B\right]=cD_e\left[\frac{\ell_A}{v^{*4}}-2\frac{\ell_B}{v^{*2}}\right] \tag{5.63}$$

in which $v^* = v/v_e$ is the reduced (*i.e.* normalised to the equilibrium value) volume of a cell. The polynomials ℓ_A, ℓ_B can be conveniently written with respect to the dimensionless parameter $y = (r/a)^2$. For $m = 6$ and $n = 12$ they become [4]:

$$\ell_A(y,12)=\left(1+12y+25.2y^2+12y^3+y^4\right)(1-y)^{-10}-1 \tag{5.64}$$

$$\ell_B(y,6)=(1+y)(1-y)^{-4}-1 \tag{5.64a}$$

Fig. 5.3 shows the radial dependencies of the potential energy $\psi(a, r)$ *as a function of the relative displacement* (r/a) computed for several reduced volumes.

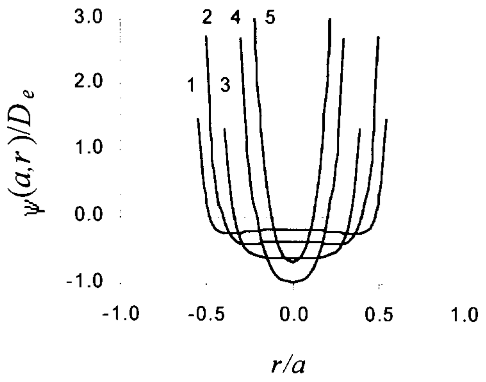

Fig. 5.3. The radial dependence of the potential energy of a molecule in a cell of the quasi-crystal lattice of a liquid: (1) $v^* = 3.2$; (2) $v^* = 2.2$; (3) $v^* = 1.6$; (4) $v^* = 1.0$; (5) $v^* = 0.8$

When the volume of a system is considerably higher than the equilibrium volume (curve 1, $\upsilon^* > 2$) the potential well resembles two Lennard-Jones binary potentials combined. This means that in a *highly expanded liquid, molecules interact mainly in pairs*. A molecule may perform oscillations around two positions of equilibrium corresponding to interaction with *either* the left- *or* the right-hand neighbour. With decreasing volume, two positions of equilibrium become less and less pronounced and a flat-bottomed potential curve determines the motion of a molecule in such a cell. The motion is then a superposition of translational movement and harmonic oscillations. When $\upsilon^* < 1.6$ there is just one minimum of potential energy and the motion can be described (at the limit of small amplitudes) as harmonic oscillation.

5.6
Free volume of a Lennard-Jones and Devonshire liquid

Consider a system where all molecules reside at the centres of their cells and have approximately the same energy close to the bottoms of potential wells (Fig. 5.4). The potential energy of such a system of quasi-independent molecules is one half the sum of the potentials $\psi(0)$:

$$U(0) = \frac{Nc}{2}\psi(0) \tag{5.65}$$

Indeed, should we remove *every second molecule* to an infinite distance the work done would be $Nc/2$ whilst the remaining $N/2$ molecules would posses approximately zero potential energy because there would be *no nearest neighbours*.

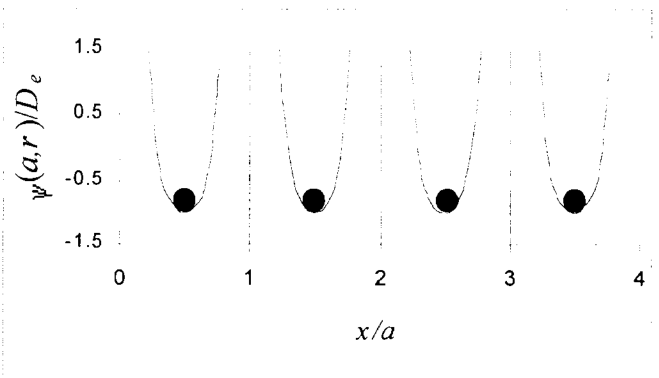

Fig. 5.4. A system of cells occupied by identical molecules at low temperatures. Potential curves correspond to $\upsilon^* = 1$. The total potential energy of this system is $Nc\psi(0)/2$.

On the other hand the *displacement energy of a molecule* (from which the free volume is derived) must be calculated with respect to the potential energy of a given molecule at the bottom of a well ($\psi(0)$):

$$w = c\left[\psi(\bar{r}) - \psi(0)\right] \tag{5.66}$$

The potential energy of a given molecular configuration (represented by the average vector of coordinates $\bar{r}$) can then be defined as:

$$U(\bar{r}) = U(0) + Nw = \frac{Nc}{2}\psi(0) + Nc\left[\psi(\bar{r}) - \psi(0)\right] \tag{5.67}$$

The displacement energy enters (5.67) with the coefficient N and not $N/2$ because it is the energy *of* a molecule and not the energy *per* molecule. Under these conditions the partition function (to be used in the derivation of the equation of state) may be written as:

$$Z = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{Nc\psi(0)}{2kT}} \left(s\upsilon_f\right)^N \tag{5.68}$$

in which s is the 'communal entropy' and υ_f is the free volume per molecule:

$$\upsilon_f = \int_0^{r_{\max}} e^{-\frac{w(r)}{kT}} 4\pi r^2 dr = 2\pi a^3 \int_0^{y_{\max}} y^{\frac{1}{2}} e^{-\frac{w(y)}{kT}} dy \tag{5.69}$$

in which $y = r^2/a^2$. Using the expression (5.61) for the displacement energy we get the free volume as:

$$\upsilon_f = 2\pi a^3 g = 2\pi a^3 \int_0^{y_{\max}} y^{1/2} \exp\left[-\frac{c}{T^*}\left(\frac{\ell_A(y)}{\upsilon^{*4}} - 2\frac{\ell_B(y)}{\upsilon^{*2}}\right)\right] dy \tag{5.70}$$

in which $T^* = kT/D_e$ is the *reduced temperature*. The upper index of integration can be roughly estimated as corresponding to $r_{max} = a_e/2$ (*i.e.* $y_{max} = 1/4$) or deduced from the actual geometry of a cell. However, this value is of no particular importance since the integral g in (5.70) becomes stable at $y > 0.2$ for $D_e/kT > 0.1$, (Fig. 5.5).

The shape of the dependence of free volume on reduced temperature (which determines the possibility of various critical phenomena, see Section 4.4) appears to be practically linear for a normal liquid (curve $\upsilon^* = 1$, Fig. 5.5B) and slightly curvilinear for a compressed liquid ($\upsilon^* = 0.8$, $g \propto (T^*)^{1.2}$). This is, however, only true for large reduced temperatures, *i.e.* weak molecular interactions. In the range of small reduced temperatures ($T^* < 0.1$, implying strong molecular interactions) the curves $g = f(T^*)$ correspond to the proportionality of g to $(T^*)^{1.5}$ – practically irrespective of compression.

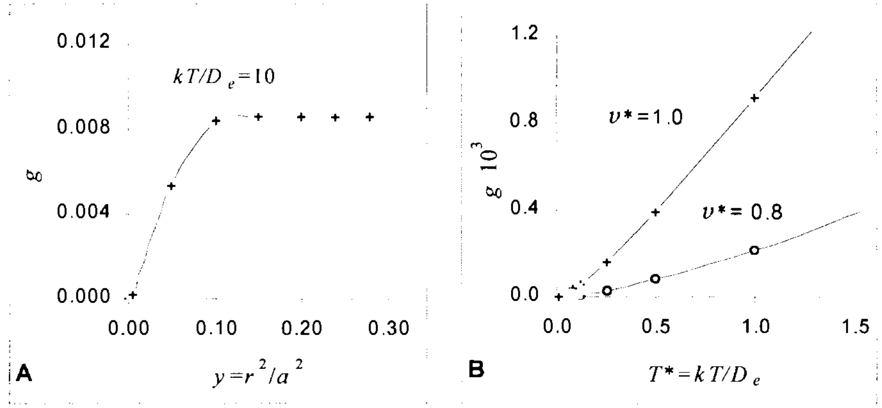

Fig. 5.5. Numerical integration of $\int e^{-w/kT}$ in the Lennard-Jones and Devonshire model ($v^* = 1$, $c = 6$) for **A**. The dependencies of the reduced free volume g on the reduced temperature for a liquid at equilibrium ($v^* = 1$) and for compressed ($v^* = 0.8$) liquid ($c = 6$) for **B**

This shows that the Lennard-Jones potential is associated with a weaker dependence of free volume on the reduced temperature compared to the '*V*-shaped' potential employed in a crude estimation of the effects of internal pressure (Section 4.3). It must, however, be remembered that the hyperbolic potential is too smooth to approximate the real repulsive interactions between molecules very well. Therefore a rough model employing *V*-shaped or square-shaped potentials might produce a better description of some properties.

The equation of state corresponding to the described model can be derived by differentiating the free energy with respect to volume:

$$p = -kT(\partial F/\partial V)_T \tag{5.71}$$

Using (4.42), (4.44) along with (5.63) – (5.70) one obtains [4] the Lennard-Jones and Devonshire equation of state:

$$\frac{pV}{NkT} = 1 + \frac{2c}{T^*}\left[\frac{1}{v^{*4}}\left(C + \frac{2g_l}{g}\right) - \frac{1}{v^{*2}}\left(D + \frac{2g_m}{g}\right)\right] \tag{5.72}$$

in which $T^* = kT/D_e$. The integrals g_l and g_m are similar to the reduced free volume g:

$$g_l(v^*, T^*) = \int_0^{y_0} \ell_A(y) y^{1/2} \exp\left[-\frac{c}{T^*}\left(\frac{\ell_A(y)}{v^{*4}} - 2\frac{\ell_B(y)}{v^{*2}}\right)\right] dy \tag{5.73}$$

$$g_m(v^*, T^*) = \int_0^{y_0} \ell_B(y) y^{1/2} \exp\left[-\frac{c}{T^*}\left(\frac{\ell_A(y)}{v^{*4}} - 2\frac{\ell_B(y)}{v^{*2}}\right)\right] dy \tag{5.74}$$

The coefficients C and D equal 1 when only the nearest neighbour interactions are taken into account and $C = s_n = 1.01$, $D = s_m = 1.205$ (see Table 5.2) when interactions with the next nearest neighbours are also taken into account. The isotherms calculated according to (5.72) are shown in Fig. 5.6. Above certain temperatures the isotherms do not show any maximum/minimum, *i.e.* such a system can only exist in the gaseous state. When calculations are performed with $C = D = 1$ (*i.e.* taking into account the nearest neighbour interactions alone) the critical reduced temperature for $c = 12$ (inert gases) is *ca.* 0.95 (Fig. 5.6A).

By introducing next nearest neighbour interactions and reducing the coordination number to $c = 10$ (*i.e.* accounting for the presence of vacancies in the quasi-crystal lattice) it is possible to obtain $T_C^* \cong 1.35$ (Fig. 5.6B) in good agreement with experimental data (see Table 5.4).

It must be mentioned here that the isotherms given by (5.72) are very sensitive to the values of the coefficients C and D. Therefore, it is not difficult to get a correct value of the critical temperature by a fine adjustment of these coefficients.

Table 5.4. Comparison of critical parameters obtained from the Lennard-Jones and Devonshire model with experimental values [4]

	$\tilde{T}_C = T_C^*$	$\tilde{v}_C = v_C / a^3$	$\tilde{p}_C = p_C a^3 / D_e$
Lennard-Jones and Devonshire	1.30	1.77	0.434
Experimental Values	1.26	3.16	0.116

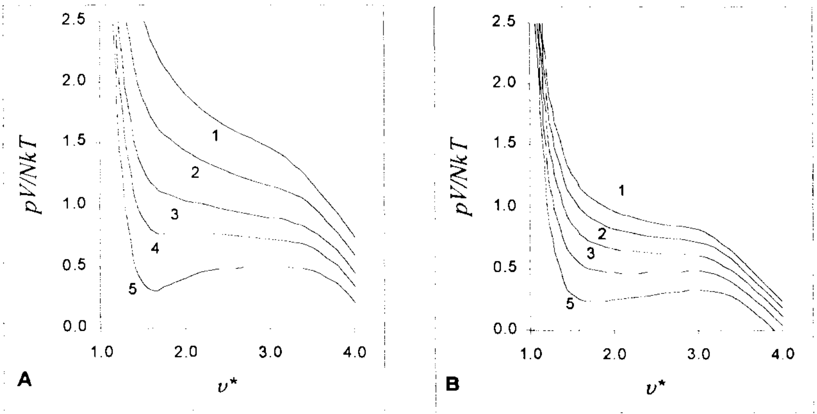

Fig. 5.6. Lennard-Jones and Devonshire isotherms (5.72) calculated for $c = 12$, $C = D = 1$ and varying reduced temperatures $T^* = kT/D_e = 1.6$ (1), 1.2 (2), 1.0 (3), 0.9 (4) and 0.8 (5) (A), and similar isotherms calculated for $c = 10$, $C = 1.01$ $D = 1.205$ and varying reduced temperatures $T^* = kT/D_e = 1.6$ (1), 1.5 (2), 1.4 (3), 1.3 (4) and 1.2 (5). The curves 4 in both graphs still exhibit extrema

However, once one parameter is adjusted the remaining ones are strictly defined. Therefore the values of critical volume and pressure given by this equation disagree considerably with experimental data (Table 5.4). It has been shown by Prigogine and Garikian [5] that the type of binary potential employed does not significantly change these results. The problem remains mainly with the original assumption that one cell is occupied by one molecule. Improvements in the cell theory are, therefore, connected with accounting for either multiple occupation of cells or for the presence of holes or vacant cells as well as with taking into account any correlated character of molecular motion in neighbouring cells.

5.7

Experimental determination of parameters of the Lennard-Jones potential

The Lennard-Jones potential is characterised by four parameters: the exponents m, n and two constants A and B (5.4). The constants A and B can be expressed in terms of the coordinates of the point of equilibrium, ϕ_e, a_e or ϕ_e, σ. (See (5.10) – (5.13) and (5.21).) Some of these parameters are usually chosen according to the assumed model of molecular interactions. In the condensed state, however, binary potentials provide for an *effective* description and some parameters must be adjusted in order to achieve an agreement with experimental data. For example, experimental data on ionic crystals can be described employing the Lennard-Jones potential with $m = 1$ and the constant B equal to the square of the ion's charge multiplied by the Madelung constant (*i.e.* the coefficient s_1) as predicted by the electrostatic model of attractive interactions [2, 6]. However the repulsive part must be completely neglected *which does not, of course, mean that repulsive interactions do not exist in ionic crystals* but is a consequence of the application of a binary potential to systems with many-centre interactions. On the other hand, an effective repulsive potential can be derived describing extremely well experimental data on molten metals and electrolyte solutions, and neglecting the attractive part [7]. Again this is merely a form of accounting for many-centre forces. In systems of uncharged particles (in the gaseous and liquid state) the value of m was at first assumed to be 3 as follows from the van der Waals equation of state. However, the theory of dispersive forces predicts for such systems $m = 6$. This value is now widely used in various applications of the Lennard-Jones potential whereas the value of n is adjusted according to the actual experimental data. The methods of experimental determination of parameters of intermolecular potential discussed in books on physical chemistry are therefore rather illustrations of the connections between macroscopic properties and theoretical models involving molecular interactions. Several examples will be given here. The method employing virial coefficients of gases will be considered in the next Chapter.

5.7.1
Compressibility: the Born – Landé method

Parameters of intermolecular potential may be determined, at least in a crystal, from the values of *isothermal compressibility extrapolated to absolute zero.* Indeed the first law of thermodynamics:

$$dE = TdS - pdV \tag{5.75}$$

defines the second derivative of internal energy with respect to volume *at absolute zero* as

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial E}{\partial V}\right)\right)_{T=0} = -\frac{\partial p}{\partial V} = \frac{1}{V\beta_{T=0}} \tag{5.76}$$

in which $\beta_T = -(\partial \ln V/\partial p)_T$ is the isothermal compressibility. Kinetic energy is not a function of volume, and therefore the derivative in (5.76) refers to potential energy and the isothermal compressibility may be found from the shape of the Lennard-Jones potential. For example, calculating potential energy per molecule and employing (5.13):

$$\varphi = \frac{\varphi_e \mu \nu}{\mu - \nu}\left[\frac{1}{\nu}\left(\frac{v_e}{v}\right)^{\nu} - \frac{1}{\mu}\left(\frac{v_e}{v}\right)^{\mu}\right] \tag{5.77}$$

in which $\mu = m/3$ and $\nu = n/3$, we get the first and second derivatives of potential energy with respect to volume as:

$$\left(\frac{\partial \varphi}{\partial v}\right)_T = \frac{\varphi_e \mu \nu}{\mu - \nu}\left[-\frac{v_e^{\nu}}{v^{\nu+1}} + \frac{v_e^{\mu}}{v^{\mu+1}}\right] \tag{5.76}$$

$$v^2\left(\frac{\partial^2 \varphi}{\partial v^2}\right)_T = \frac{\varphi_e \mu \nu}{\mu - \nu}\left[(\nu + 1)\left(\frac{v_e}{v}\right)^{\nu} - (\mu + 1)\left(\frac{v_e}{v}\right)^{\mu}\right] \tag{5.79}$$

If the deformations accompanying the measurements of compressibility are small, then we may assume $v_e/v \cong 1$ and the term in square brackets is $\nu - \mu$, which results in:

$$\left(\frac{\partial^2 \varphi}{\partial v^2}\right)_T = -\frac{\varphi_e \mu \nu}{v^2} = \frac{u_e \mu \nu}{v^2} = \frac{u_e m n}{9 v^2} \tag{5.80}$$

in which u_e is the depth of the potential well *or double the potential energy per molecule.*

Table 5.5. Initial data and results of calculations of the product *mn* from compressibility [2].

	T K	V (cm^3 mole^{-1})	$\beta_S 10^{12}$ (cm^2 dyne^{-1})	U_e (kcal mole^{-1})	mn
Hg	0	14.035	3.55	15327	55.5
Hg	273.1	14.7556	3.946	15142	53.1
LiF	273.1	9.818	1.53	238000	5.80
KCl	273.1	37.43	5.64	163000	8.75
CCl_4	0	71.5	29 ± 8	11220	51 ± 14

According to (5.76) and (5.80), *isothermal compressibility at absolute zero* is inversely proportional to the product *mn* (Born – Landé equation [2, 8]):

$$\frac{1}{\beta_{T=0}} = \frac{u_e mn}{9v} \tag{5.81}$$

The value of u_e for substances in crystalline form can be obtained using the Born – Haber [9] cycle. The extrapolation of experimental data for $9v/\beta_T u_e$ to absolute zero is quite a lawful operation for crystals. The data on Hg (Table 5.5) show that extrapolation to zero brings about a correction of about 3% relative to the value obtained at 273 K. For ionic compounds the product *mn* equals the exponent n ($m = 1$) and these values are quite small ($n = 6 - 9$).

5.7.2
Acoustic measurements: the B.B. Kudryavtsev method

The extrapolation to zero temperatures for liquids is of rather doubtful reliability. Fortunately, there is no need for such an operation because a relationship between the product *mn* and the isothermal compressibility at any temperature can be derived. Furthermore, the isothermal compressibility is related to the velocity of sound that can be measured very accurately in liquids. These are the foundations of the method of estimating the product *mn* from the data of acoustic measurements suggested by B.B. Kudryavtsev [10].

Using the first law of thermodynamics and one of the Maxwell relations:

$$(\partial S/\partial V)_T = (\partial p/\partial T)_V \tag{5.82}$$

the following equation can be obtained for the volume derivative of internal energy at any temperature:

$$\left(\frac{\partial E}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V \tag{5.83}$$

Differentiating it a second time with respect to volume we get:

$$\left(\frac{\partial^2 E}{\partial V^2}\right)_T = -\left(\frac{\partial p}{dV}\right)_T + T\left(\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)\right)_T \tag{5.84}$$

On the other hand the phenomenological theory of propagation of sound in an elastic continuum gives the following relationship between the velocity of sound (c) and isothermal compressibility:

$$c^2 = \gamma V^2 \left(\frac{\partial p}{\partial V}\right)_T = \frac{\gamma V}{\beta_T} \tag{5.85}$$

in which $\gamma = C_p/C_V$ and V is the *specific volume*, *i.e.* the considered system is of unit mass. This is one version of the *Laplace formula*, a detailed derivation of which can be found in [11]. Differentiating (5.85) with respect to temperature at constant volume yields:

$$\left(\frac{\partial (c^2)}{\partial T}\right)_V = V^2 \gamma \left(\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)\right)_T \tag{5.86}$$

Combining (5.84) and (5.86) yields the relationship between the second derivative of internal energy by volume and the velocity of sound:

$$\gamma V^2 \left(\frac{\partial^2 E}{\partial V^2}\right)_T = c^2 - T\left(\frac{\partial (c^2)}{\partial T}\right)_V \tag{5.87}$$

The kinetic energy of molecules is not a function of volume and therefore the derivative $(\partial^2 E/\partial V^2)$ refers to potential energy:

$$\left(\partial^2 E/\partial V^2\right)_T = \left(\partial^2 \varphi/\partial V^2\right)_T \tag{5.88}$$

We have already obtained the expression for the second derivative of the Lennard-Jones potential (5.80) with respect to volume:

$$V^2 \left(\frac{\partial^2 \varphi}{\partial V^2}\right)_T = -\varphi_e \mu \nu \tag{5.89}$$

The only condition was that the amplitude of a sound wave should not approach the cavitation limit and we may assume $V_e/V \cong 1$. The parameters of the Lennard-Jones potential are then directly related to the velocity of sound in the form of a differential equation:

$$\mu \nu \gamma \varphi_e = c^2 - T\left(\frac{\partial (c^2)}{\partial T}\right)_V \tag{5.90}$$

The solution of this linear differential equation is:

$$c^2 = \gamma\nu\mu\varphi_e + \alpha T + g(V) \tag{5.91}$$

The function $g(V)$ appears because the derivative in (5.90) is the partial derivative at constant volume. Its form, as well as the meaning of the coefficient α, is found from the boundary conditions corresponding to the critical state. These are (i) the velocity of sound in liquids can be assumed to be equal to the velocity of sound in vapour, (ii) the vapour phase may be treated as an ideal gas and (iii) the depth of the potential well, φ_e, equals zero. Under these assumptions and using the Laplace formula[5] we get:

$$g(V) = 0; \qquad \alpha = \gamma R/M \tag{5.92}$$

in which M is the molecular mass. The velocity of sound, therefore, is related to the parameters of the Lennard-Jones potential by:

$$c^2 = \gamma\nu\mu\varphi_e + \gamma RT/M \tag{5.93}$$

When the depth of the potential well φ_e is estimated as the heat of vaporisation (λ) this formula yields velocities of sound that are too high except for the pair $\mu = 1$, $\nu = 2$ (*i.e.* $m = 3$, $n = 6$). For these exponents (5.93) yields velocities of sound agreeing with experimental data within the range ± 16 – 20% (Table 5.6). (The heat of vaporisation must, of course, be calculated or determined at the same temperature as that at which the velocity of sound was recorded.)

As has been mentioned above, the depth of the potential well may also be estimated from data on surface tension (5.42). This results in the following relationship for the velocity of sound:

$$c^2 = 2\mu\nu\gamma N_L^{1/3} \frac{\sigma}{M^{1/3}\rho^{2/3}} + \frac{\gamma RT}{M} \tag{5.94}$$

in which σ is the surface tension and N_L is the Avogadro number. This equation has been tested on 50 liquids of different chemical nature [8]. The best fit was obtained with $\mu = 2$, $\nu = 4$ (*i.e.* $m/n = 6/12$) assuming an average of $\gamma = 1.4$ (see Fig. 5.7).

For 12 liquids of quite different chemical nature (octane, acetone, formic acid, ethyl bromide, *tert*-BuOH, acetic acid, *etc.*) calculations produced an excellent agreement with experimental data (±5%). Similar calculations for six liquids (stearic acid, palmitic acid, octyl alcohol, cyclohexanol, aniline, ethyl aniline, and quinoline) exhibit large negative deviations from the experimentally determined velocities of sound (from –20 to –30%). The remaining 32 liquids investigated exhibit mainly negative deviations of medium magnitude (5 – 20%).

Better results can be obtained with $n = 14$ as well as by using actual values of γ instead of the average value 1.4. Using these parameters, (5.94) yields a very good

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[5] According to the Laplace equation (5.85) for one gram of a substance in the ideal gas state the velocity of sound is given by: $c^2 = \gamma p/\rho = \gamma pV = \gamma RT/M$, ($V$ is the *specific volume*).

temperature dependence of sound velocities in benzene and ethyl alcohol, fitting the experimental data within ±5%.

Table 5.6. Velocities of sound calculated according to (5.93) and assuming $\gamma = 1.4$, and $\varphi_e = \lambda/M$

	T (K)	(λ/T) [12] (cal mole^{-1} K^{-1})	c_{calc} (m s^{-1})	c_{exp} (m s^{-1})	$(c_{calc}-c_{exp})/c_{exp}$
Benzene	283	29.6	1140	1370	+0.2
CCl_4	273	29.3	800	1010	+0.2
Heptane	273	34.0	1050	1230	+0.18
$CHCl_3$	273	28.8	920	1070	+0.14

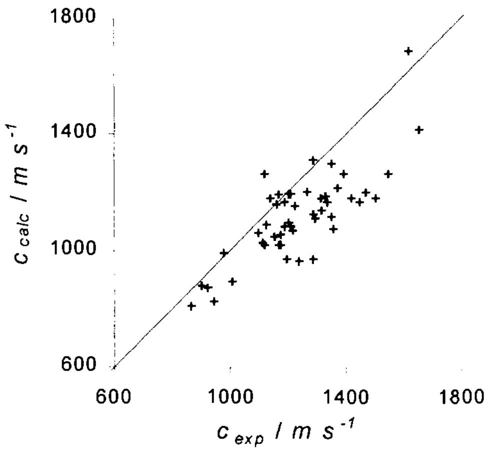

Fig. 5.7. Comparison of calculated, (5.94), and experimental sound velocities in liquids [8]

These results indicate a better coincidence of theoretical and experimental velocities of sound when the depth of the potential well is estimated from surface tension rather than from the heat of vaporisation[6].

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[6] The reason why surface tension provides a better estimate of potential energy at the minimum is not clear. Of course surface tension gives the energy and not the enthalpy (which is obtained from the heat of vaporisation). However the correction for the work of expansion is small and cannot account for the observed deviations. The heat of vaporisation probably contains a contribution from various associative equilibria especially strong, for example, in the case of carbonic acids.

5.7.3
Viscosity of gases: the Rayleigh – Chapman method

The temperature dependence of the viscosity of real gases originates from the variations with temperature of (i) the number of binary collisions and (ii) the least distance between molecules at impact. The first type of dependence is given by the kinetic theory of gases as:

$$\eta = \frac{1}{\pi\sigma^2}\left(\frac{\mu kT}{\pi}\right)^{1/2} \tag{5.95}$$

in which μ is the molecular mass and σ is the molecular diameter. The second component originates from the temperature dependence of σ. At the distance of least approach, all the kinetic energy of colliding molecules (along a given coordinate, *i.e.* kT for a pair) is transformed into potential energy:

$$kT = \varphi = \frac{A}{\sigma^n} - \frac{B}{\sigma^m} \tag{5.96}$$

At short distances (see Fig. 5.1), the positive contribution from the first term is much higher than the energy of attractive forces, and we may therefore neglect the second term in (5.96) and write:

$$\sigma = \left(\frac{A}{kT}\right)^{1/n} \tag{5.97}$$

The temperature dependence of the viscosity of gases is then given by:

$$\eta = \frac{1}{\pi}\left(\frac{kT}{A}\right)^{2/n}\left(\frac{\mu kT}{\pi}\right)^{1/2} = Const \times T^C \tag{5.98}$$

in which the constant $C = (2/n + ½)$. Such a temperature dependence is observed experimentally with C varying from 0.5 for rarefied gases to 1 for saturated vapours. This method yields n = 6.4 – 12.7 with an average value of 8.9 (see Table 5.7).

Table 5.7. Values of n estimated from viscosity of gases

He	Ne	Ar	Hg	H_2	N_2	CO	NO	O_2
12.2 ± 1.4	12.7	6.33	7.9±3.1	10.3	7.81	7.75	7.14	6.37

5.8
Conclusions

In this Chapter we have considered how the potential energy and the free volume can be represented in terms of *binary potentials*. These potentials contain parameters that can be expressed in terms of the coordinates of the point of mechanical equilibrium in a molecular pair (a_e, D_e) and the exponents (m, n) determining the range of action of the repulsive and attractive forces. When applied to molecular interactions in dense gases and condensed states these potentials give an effective description with parameters containing contributions from triple and higher order interactions. Estimates of the parameters of binary potentials depend, therefore, on both the subject under discussion (*i.e.* gaseous or condensed sates, systems of charged or uncharged particles, *etc.*) and the methods of estimation. The latter are based on measurements of physico-chemical properties, such as compressibility, viscosity, surface tension, velocity of sound, *etc.*

The potential energy of a molecule obviously depends on the nature of its environment and hence the composition of the system. The molecular lattice energies and free volumes are therefore composition-dependent and corresponding improvements must be introduced into the equations of the law of mass action for condensed state reactions. This will be done in Chapter 7, whereas in Chapter 6 we will apply the concept of binary interactions to gaseous reactions.

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6 Imperfect Gases

6.1

Introduction. The virial theorem

In this Chapter we will investigate the effects of molecular interactions on the form of the law of mass action for equilibria in the gas phase. The volume of a gaseous system is directly connected with the number of molecules, and therefore a knowledge of the actual equation of state is important for the study of reactions in gases. In an ideal gas the volume of a system at constant pressure is linearly dependent on the number of molecules. A large number of empirical equations of state have been suggested for the description of real gases, among which the *van der Waals* equation is the most famous.

A theoretical equation of state can be obtained using statistical-mechanical expressions for free energy. Alternatively, an equation of state for a gaseous system can also be derived on the basis of *the virial theorem,* which, separately from statistical mechanics, establishes a connection between macroscopic and molecular parameters. When an equation of state is obtained in this way, the corresponding expression for free energy can be derived by integration. The virial theorem provides, in some cases, an easier and more elegant way of deriving the required mathematical formalism. It is based on the concept of the *virial of forces.* Clausius[1] defined the virial of forces (it seems to have no abbreviation) as:

$$Virial = -\frac{1}{2}\sum_i \left(X_i x_i + Y_i y_i + Z_i z_i\right) \tag{6.1}$$

in which X_i, Y_i, *and* Z_i are *components* of forces acting on material points (molecules) having coordinates x_i, y_i, z_i. The *virial theorem* demonstrates that the virial of a stationary ideal gas (contained in an immovable vessel) is equal to the sum of the kinetic energies of the molecules:

$$-\frac{1}{2}\sum_i \left(X_i x_i + Y_i y_i + Z_i z_i\right) = \frac{1}{2}\sum_i mc_i^2 = \frac{3}{2}NkT \tag{6.2}$$

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[1] Boltzmann, and some other authors, apply the same name to $\sum_i \left(X_i x_i + Y_i y_i + Z_i z_i\right)$

A.B. Koudriavtsev et al., *The Law of Mass Action*

By taking into account the fact that:

$$\frac{1}{2}\frac{d^2\left(x^2\right)}{dt^2} = \frac{d}{dt}\left(x\frac{dx}{dt}\right) = x\frac{d^2x}{dt^2} + \left(\frac{dx}{dt}\right)^2 \tag{6.3}$$

the product $\frac{1}{2}Xx$ may be represented by:

$$\frac{1}{2}Xx = \frac{m}{2}x\frac{d^2x}{dt^2} = \frac{d^2}{dt^2}\left(\frac{mx^2}{4}\right) - \frac{m}{2}\left(\frac{dx}{dt}\right)^2 \tag{6.4}$$

Summing over coordinates we obtain ($x^2 + y^2 + z^2 = r^2$):

$$\frac{1}{4}\frac{d^2}{dt^2}\left(mr^2\right) = \frac{mv^2}{2} + \frac{1}{2}\left(Xx + Yy + Zz\right) \tag{6.5}$$

Summing over molecules we get:

$$\frac{1}{4}\frac{d^2}{dt^2}\sum_i\left(mr_i^2\right) = \sum_i\frac{mv_i^2}{2} + \frac{1}{2}\sum_i\left(X_ix_i + Y_iy_i + Z_iz_i\right) \tag{6.6}$$

When averaged over a sufficiently long time in a system with a fixed centre of gravity (*e.g.* molecules of a gas contained in a vessel) the left-hand part of (6.6) is zero. Therefore:

$$\overline{\sum_i\frac{mv_i^2}{2}} = -\frac{1}{2}\overline{\sum_i\left(X_ix_i + Y_iy_i + Z_iz_i\right)} \tag{6.7}$$

The *mean kinetic energy* of a molecule in an ideal gas is $kT/2$ per degree of freedom, and therefore:

$$\frac{3}{2}NkT = -\frac{1}{2}\overline{\sum_i\left(X_ix_i + Y_iy_i + Z_iz_i\right)} \tag{6.8}$$

In an ideal gas, the forces acting on molecules only originate in collisions with the walls of the vessel (resulting in the external pressure p). The mean force acting on all molecules of a monomolecular layer in the plane yz is $\langle \mathbf{X} \rangle = -pyz$ (assuming the vessel to have the shape of a cube, see Fig. 6.1A). The mean coordinate along the x-axis is $\langle x \rangle = \frac{1}{2}x$ and therefore the mean value of $\langle \mathbf{X}x \rangle$ is $-\frac{1}{2}pxyz = -\frac{1}{2}pV$. All six walls of the considered cube contribute identically and hence the average virial of the ideal gas is:

$$-\frac{1}{2}\overline{\sum_i\left(X_ix_i + Y_iy_i + Z_iz_i\right)} = \frac{3}{2}pV = \frac{3}{2}NkT \tag{6.9}$$

This is actually an *equation of state of an ideal gas.*

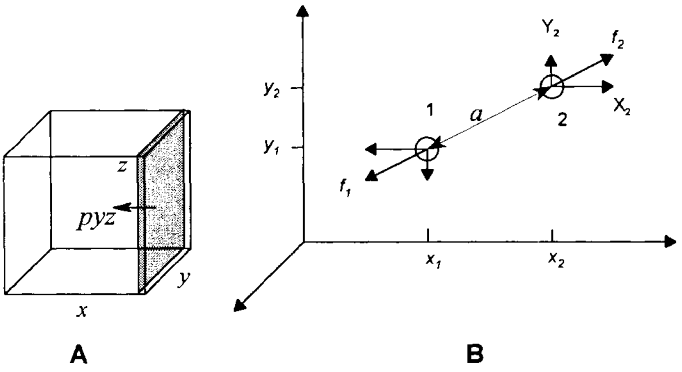

Fig. 6.1. Calculation of the virial of external (**A**) and intermolecular (**B**) forces

This equation of state is thus connected with the virial of external forces as:

$$pV = NkT = -\frac{1}{3}\overline{\sum_i (X_i x_i + Y_i y_i + Z_i z_i)} \tag{6.10}$$

Let us now consider a gas with intermolecular interactions. In such a system the virial of *intermolecular* forces must be added to the virial of the ideal gas:

i.e.

$$NkT = pV + \frac{1}{3}\overline{\sum (X_{\text{int}} x + Y_{\text{int}} y + Z_{\text{int}} z)} \tag{6.11}$$

or:

$$\frac{pV}{NkT} = 1 - \frac{1}{3NkT}\overline{\sum (X_{\text{int}} x + Y_{\text{int}} y + Z_{\text{int}} z)} \tag{6.12}$$

We can now find the actual form of the virial in a gas with binary interactions, *i.e.* when the molecules interact as *isolated pairs*. The state of a given pair is thus statistically independent of the state of any other pair. The forces acting on a molecule in such a pair are then the derivative of the *binary potential* φ along the line connecting the two molecules in a pair (Fig. 6.1B):

$$f = f_2 = -f_1 = -\frac{d\varphi}{da} \tag{6.13}$$

The component of force acting on molecule "2" along the direction x (Fig. 6.1B) is obviously:

$$X_2 = f_2 \frac{x_2 - x_1}{a} \tag{6.14}$$

The similar component of force acting on the molecule "1" is $X_1 = -X_2$. Therefore, for an isolated molecular pair:

$$X_1 x_1 + X_2 x_2 = \frac{f}{a}\left[(x_1 - x_2)x_1 + (x_2 - x_1)x_2\right] = \frac{f}{a}(x_2 - x_1)^2 \tag{6.15}$$

The same is true for other coordinates, which results in the following internal virial of a molecular pair:

$$\frac{f}{a}\left[(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2\right] = af = -a\frac{d\varphi}{da} \tag{6.16}$$

The virial of the whole system can then be written as:

$$pV = NkT - \frac{1}{3}\sum_{i=1}^{N/2} a_i \frac{d\varphi_i}{da_i} \tag{6.17}$$

in which the summation is carried out over *molecular pairs*.

6.2
The Rayleigh equation

The sum in (6.17) can be calculated by employing the distribution law and defining the number of pairs with a given distance of separation a. This number equals the number of molecules in a spherical layer around a selected molecule. The Maxwell – Boltzmann distribution law gives the concentration of molecules at distance a from a considered molecule as:

$$C_a = \frac{N}{V} e^{-\frac{\varphi(a)}{kT}} \tag{6.18}$$

The number of molecules in the spherical layer of radius a and thickness da is $C_a \times 4\pi a^2 da$. Each pair contributes $(1/3)a(d\varphi/da)$ to the virial. The total contribution can then be obtained by integration:

$$\frac{1}{3}\int_0^\infty a\left(\frac{d\varphi}{da}\right)\frac{N}{V} e^{-\frac{\varphi(a)}{kT}} 4\pi a^2 da \tag{6.19}$$

Taking into account that $d\varphi = (d\varphi/da)da$ and that the *number of pairs* is $N/2$ we may write the total virial of interactions as:

$$\frac{4\pi N^2}{6V}\int_0^\infty e^{-\frac{\varphi(a)}{kT}} a^3 d\varphi \tag{6.20}$$

The integration by parts of (6.20) (assuming $U = a^3$, and $V = -kT\exp(-\varphi/kT)$) yields:

$$\int_0^\infty e^{-\frac{\varphi}{kT}} a^3 d\varphi = -a^3 kTe^{-\frac{\varphi}{kT}}\Big|_0^\infty - \int_0^\infty -kTe^{-\frac{\varphi}{kT}} 3a^2 da \tag{6.21}$$

At large distances, the potential energy is zero and $\exp(-\varphi/kT) = 1$; at vanishingly small distances $\varphi = \infty$, and $\exp(-\varphi/kT) = 0$. The right-hand part of (6.21) therefore transforms into:

$$-kTa_\infty^3 + \int_0^\infty kTe^{-\frac{\varphi}{kT}} 3a^2 da \tag{6.22}$$

The term $-kTa_\infty^3$ can be represented as $-kT\int_0^\infty 3a^2da$, which results in the virial of interactions being expressed as:

$$\frac{1}{3}\sum_i a_i \frac{d\varphi_i}{da} = \frac{2\pi N^2}{3V}\int_0^\infty e^{-\frac{\varphi(a)}{kT}} a^3 d\varphi = \frac{2\pi kTN^2}{V}\int_0^\infty \left(e^{-\frac{\varphi(a)}{kT}} - 1\right)a^2 da \tag{6.23}$$

The complete virial of a gas with binary interactions can thus be written as:

$$pV = NkT - \frac{1}{3}\sum a\frac{d\varphi}{da} = NkT\left[1 + \frac{2\pi N}{V}\int_0^\infty \left(1 - e^{-\frac{\varphi(a)}{kT}}\right)a^2 da\right] \tag{6.24}$$

This relationship is known as the *Rayleigh equation.* Note that the integral in the Rayleigh equation is some (temperature dependent) constant having the dimensions of volume. In the case of weak interactions (φ/kT approaching zero), it is only a small fraction of the total volume of a system.

6.2.1

Virial coefficients: the Lennard-Jones method for the determination of the parameters of a binary potential

The Rayleigh equation is one of a series of equations of state of an imperfect gas of the general type:

$$\frac{pV}{NkT} = 1 + B_2\frac{N}{V} + B_3\left(\frac{N}{V}\right)^2 + \cdots \tag{6.25}$$

in which deviation from ideality is accounted for by a series of powers of density – the so-called *virial expansion.* The coefficients B_2, B_3, ... are called the second, third (and so on) *virial coefficients.* The Rayleigh equation takes into account binary interactions alone and contains one term linear in density. The integral in (6.24) becomes, therefore, connected with experimentally measurable values of the second virial coefficient. From the temperature dependence of virial coefficients it is possible to estimate parameters of the intermolecular potential:

$$B_2 = 2\pi \int_0^\infty (1 - e^{-\frac{\varphi(a)}{kT}}) a^2 da = 2\pi a_e^3 \int_0^\infty (1 - e^{-\frac{\varphi(r^*)}{kT}}) r^{*2} dr^* \tag{6.26}$$

in which $r^* = a/a_e$. Using a Lennard-Jones potential in the form (5.12) the second virial coefficient can be written (for practical calculations) as:

$$B_2 = 2\pi a_e^3 \int_0^{r^*_{\max}} \left\{ 1 - \exp\left[-\frac{D_e}{kT(n-m)} \left(mr^{*-n} - nr^{*-m} \right) \right] \right\} r^{*2} dr^* \tag{6.27}$$

in which $r^*_{\max}$ is some large value (10 – 40, depending on the type of potential) providing a good approximation of the integral to infinity. For weak molecular interactions ($D_e/kT \ll 1$) the theoretical temperature dependence of B_2 given by (6.27) is close to inverse proportionality (see Fig. 6.2). Experimental data [1] for the second virial coefficient of argon at different temperatures yield excellent agreement between theoretical and experimental values (Fig. 6.2) when analysed according to (6.27) (by using a non-linear regression method). The estimates of D_e and a_e so obtained are shown in Table 6.1. The original model of Lennard-Jones [2] involved $m = 4$ and $n = 40/3$, 20 and 24. Afterwards the same data were analysed assuming $m = 6$ as predicted by the theory of dispersive forces [3]. The regression error corresponding to different combinations of m and n is approximately the same (*ca.* 0.25 – 0.4% of the highest absolute value of B_2). It seems that the description depends mainly on the shape of repulsive potential: even the combination $m = 3$, $n = 9$ yields as good a description as the combination 6/9. However the combinations $m = 6$, $n = 9$ and $m = 6$, $n = 12$ only result in reasonable values of the constants A and B (5.4) and (5.26) coinciding with the estimates of the Born – Landé method. It must be mentioned at this point that the data for the second virial coefficient of He do not fit (6.27) (the temperature dependence of B_2 exhibits a maximum).

Table. 6.1. The estimates of D_e, a_e and the constants A and B in the Lennard-Jones potential obtained from temperature dependence of the second virial coefficient of argon (assuming different combinations of the exponents m and n)

m	n	D_e/k (K)	$a_e \times 10^8$ (cm)	Regr. error of B_2	A (erg cm^n)	B (erg cm^m)
6	9	89.86	4.059	0.0094	7.425×10^{-81}	1.66×10^{-58}
6	12	119.77	3.814	0.0097	1.568×10^{-103}	1.01×10^{-58}
6	14	135.4	3.710	0.0101	1.314×10^{-118}	8.53×10^{-59}
4	13.3	47.27	4.208	0.0108	1.339×10^{-113}	2.92×10^{-44}
4	20	65.89	3.857	0.0126	1.211×10^{-163}	2.51×10^{-44}
4	24	73.16	3.752	0.0133	1.228×10^{-193}	2.40×10^{-44}
3	6	2.512	7.871	0.0153	8.249×10^{-59}	3.38×10^{-37}
3	9	7.373	5.623	0.0094	2.861×10^{-81}	2.71×10^{-37}

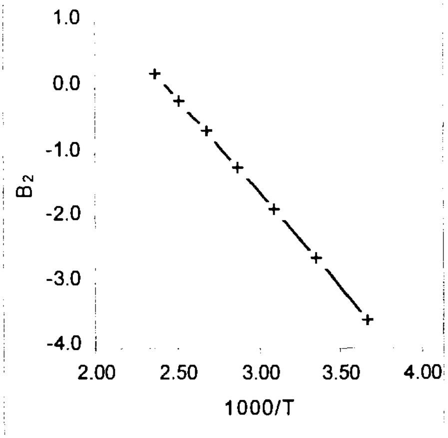

Fig. 6.2. Experimental data (crosses) for the second virial coefficient of Ar [1] and the theoretical curve (line) corresponding to $m = 6$, $n = 9$ (see Table 6.1)

The Rayleigh equation of state employing the Lennard-Jones potential is completely different from the Lennard-Jones and Devonshire equation of state considered in Chapter 5. That equation was derived for the condensed state and does not explicitly contain a term linear in density (*i.e.* the second virial coefficient is formally zero) whilst the terms proportional to υ^{*-2} and υ^{*-4} are present. However one has to take into account the volume dependence of g_l/g and g_m/g in (5.72) – (5.74) that leads (in the range of higher 'reduced temperatures') to the non-ideality terms being proportional to $\upsilon^{*-3.3}$ (repulsive term) and $\upsilon^{*-1.7}$(attractive term). This can be interpreted in terms of an additional term linear in density.

6.2.2
Free energy derived from the Rayleigh equation of state

Noticing that:

$$p = -(\partial F/\partial V)_T \tag{6.28}$$

the Rayleigh equation can be written as a differential equation with respect to free energy:

$$V\left(\frac{\partial F}{\partial V}\right)_T = -NkT\left[1 + \frac{2\pi N}{V}\int_0^\infty (1 - e^{-\frac{\varphi(a)}{kT}})a^2 da\right] \tag{6.29}$$

The solution of this differential equation (obtained in quadratures) contains some unknown function of temperature, *f(T)*, because the derivative in (6.29) was the *partial derivative*:

$$F = -kTN\left[\ln V + \frac{2\pi N}{V}\int_0^\infty (e^{-\frac{\varphi(a)}{kT}} - 1)a^2 da\right] + f(T) \tag{6.30}$$

The *nature* of this function is quite clear: when N/V approaches zero the first term approaches $-kTN\ln V$ and the function $f(T)$ represents the *volume independent part* of the free energy of an extremely rarefied gas, *i.e.* that derived from kinetic energy.

For $|\varphi(a)/kT| << 1$ and low density (N/V) the term: $(2\pi N/V)\int(e^{-\varphi(a)/kT} - 1)a^2 da$ is much smaller than 1. It can then be represented as $\delta \cong \ln(1 + \delta)$:

$$F = -kTN\ln\left\{V\left[1 + \frac{2\pi N}{V}\int_0^\infty (e^{-\frac{\varphi(a)}{kT}} - 1)a^2 da\right]\right\} + f(T) \tag{6.31}$$

In the next Section we shall obtain a similar equation employing the methods of statistical thermodynamics.

6.3
A gas with weak binary interactions: a statistical thermodynamics approach

Let us now consider the same gaseous system, where only binary interactions occur, from a statistical thermodynamics point of view. We shall take into account all such interactions – even between molecules at opposite ends of the vessel. The number of binary interactions is, therefore, $N(N-1)/2$ (the number of elements of the square matrix in the upper/lower triangles excluding the diagonal). In general, the free energy of a gaseous system with molecular interactions is given by (3.25) (Chapter 3):

$$F = -kT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{N\varepsilon^0}{kT}} \frac{1}{N!}\int_V \cdots \int_V e^{-U(q)/kT} dq_1 \ldots dq_N\right] \tag{6.32}$$

in which integration must be performed over the coordinates (q_i) of *all molecules within the volume of a system.* The potential energy of the whole system, $U(q)$, we assume to be additive with respect to the potential energies of *binary interactions:*

i.e.
$$U(q) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} U_{ij} \tag{6.33}$$

The configurational integral in (6.32) is then transformed into:

$$\frac{1}{N!}\int\cdots\int \exp\left(-\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{U_{ij}}{kT}\right)dq_1 dq_2 \ldots dq_{N-1} dq_N \tag{6.34}$$

in which dq_i represents the product $dx_i dy_i dz_i$. The integration in (6.34) can be performed consecutively, starting from the coordinates of molecule number N. The terms depending on the coordinates q_N are obviously $\exp(-\Sigma_i U_{iN}/kT)$. Resolving the exponentials $\exp(-\Sigma_i\Sigma_j U_{ij}/kT)$ into the components according to the coordinates of the molecules: N, $N-1$, ... 1, we may write the integral (6.34) as a product of integrals:

$$Z_{conf} = \frac{1}{N!}\int dq_1 \int e^{-\frac{U_{12}}{kT}} dq_2 \int e^{-\frac{U_{13}+U_{23}}{kT}} dq_3 \cdots \int e^{-\sum\limits_{i=1}^{N-2}\frac{U_{iN-1}}{kT}} dq_{N-1} \int e^{-\sum\limits_{i=1}^{N-1}\frac{U_{iN}}{kT}} dq_N \tag{6.35}$$

The integral over the coordinates of the first molecule (dq_1) is obviously the volume V and the configurational integral can be represented as:

$$Z_{conf} = \frac{V}{N!}\prod_{K=2}^{N} I_K \tag{6.36}$$

in which:

$$I_K = \int \exp\left(-\sum_{i=1}^{K-1}\frac{U_{iK}}{kT}\right)dq_K \tag{6.37}$$

This integral has the dimensions of volume and when the energy of interaction is small (for $|U_{iK}| << kT$ the exponential approaches 1) I_K must be approximately the volume of the system. For weak interactions we can, therefore, extract the small parameter and write $\exp(-U_{iK}/kT)$ in the form:

$$e^{-\frac{U_{iK}}{kT}} = 1 + f_{iK} \tag{6.38}$$

in which f_{iK} is a small parameter given by:

$$f_{iK} = e^{-\frac{U_{iK}}{kT}} - 1 \tag{6.39}$$

The term $\exp(-\Sigma_i U_{iK}/kT)$ in (6.37) can then be expressed as a product:

$$\exp\left(-\sum_{i=1}^{K-1}\frac{U_{iK}}{kT}\right) = \prod_{i=1}^{K-1}(1 + f_{iK}) \tag{6.40}$$

This product is, in explicit form, a polynomial[2] the first term being 1 and the

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[2] In the case of identical f_{iK} it will become the *Newton* binomial to the power $(K-1)$.

second the sum of all f_{iK} :

$$\prod_{i=1}^{K-1}\left(1+f_{iK}\right)=1+\sum_{i=1}^{K-1} f_{iK}+\ldots \tag{6.41}$$

We can neglect terms with higher powers of f_{iK} and the integral I_K may be expressed as:

$$I_K=\int\left(1+\sum_{i=1}^{K-1} f_{iK}\right) dq_K=V+\int \sum_{i=1}^{K-1}\left(e^{-\frac{U_{iK}}{kT}}-1\right) dq_K \tag{6.42}$$

All binary potentials U_{ik} in a system of identical molecules can be considered as identical. Therefore I_K is equal to the volume of a system plus the sum of $(K-1)$ identical integrals, β:

$$I_K=V+(K-1)\beta \tag{6.43}$$

$$\beta=\iiint\left(e^{-\frac{U\left(r_{iK}\right)}{kT}}-1\right) dx_K\, dy_K\, dz_K \tag{6.44}$$

The integral β can be calculated in a molecular coordinate system by placing the considered molecule at the origin:

$$\beta=\iiint\left(e^{-\frac{U(r)}{kT}}-1\right) r^2 \sin \theta\, d\theta\, d\varphi\, dr=4\pi \int_0^L\left(e^{-\frac{U(r)}{kT}}-1\right) r^2 dr \tag{6.45}$$

in which L is a characteristic dimension of a system (*e.g.* its radius). If the molecular interactions are short range, then the integration in (6.45) may be performed within the volume of the molecular pair (outside this volume the energy of interaction is zero):

$$\beta \approx 4\pi \int_0^\tau\left(e^{-\frac{U(r)}{kT}}-1\right) r^2 dr \tag{6.46}$$

in which τ is the *effective radius* of the molecular pair. The integral β can be divided into two parts representing the effects of repulsive and attractive forces. At distances (r) smaller than the molecular *diameter* (σ) the potential energy of repulsive interactions is infinitely high. The integration within $r=0 \rightarrow \sigma$ yields, therefore, a negative constant equal to $4\pi\sigma^3/3$, *i.e.* eight molecular volumes per pair (Fig. 6.3B). At distances larger than σ, the potential energy becomes negative and smaller (by a magnitude) than kT. The integration within $r=\sigma \rightarrow \tau$ yields a positive value dependent on temperature.

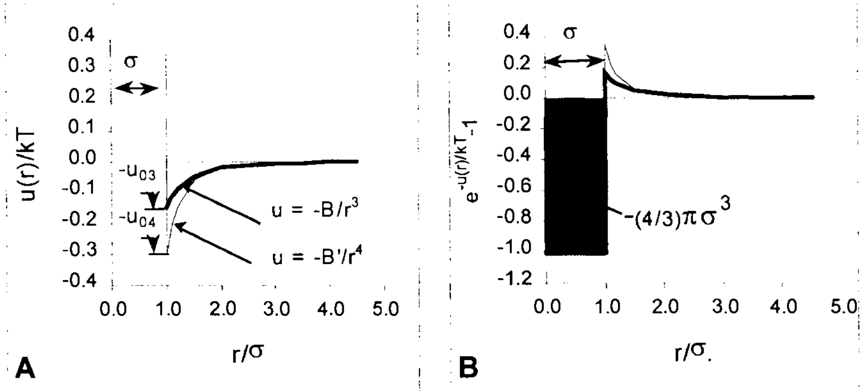

Fig. 6.3. Integration over the intermolecular distance in a pair. The potential energy (**A**) is high and positive within $r = 0 \rightarrow \sigma$, small and negative within $r = \sigma \rightarrow \tau$ and approaches zero at $r > \tau$. The radius of action of attractive forces τ was assumed to be 5σ. Two possible radial dependencies of potential energies are shown (proportional to r^{-3} and r^{-4}). Parameters of these dependencies are adjusted in a way providing for equal area under the curves $f(r) = \exp(-u(r)/kT) - 1$ (**B**)

For $|U(r > \sigma)| << kT$, the positive part of the integral β is considerably smaller than the negative part. The integral β is thus a *negative quantity* having the *dimension of volume* and its absolute value is *much smaller than the volume per molecule* (V/N).

The configurational integral for such a gas containing N molecules is:

$$Z_{conf} = \frac{V}{N!}\prod_{K=2}^{N} I_K = \frac{V}{N!}\prod_{K=2}^{N}\left(V + (K-1)\beta\right) = \frac{V^N}{N!}\left\{1 + \frac{1}{2}N(N-1)\frac{\beta}{V} + \cdots\right\} \tag{6.47}$$

The term $(K-1)\beta$ is about four times the total volume of the molecules and is much smaller than the volume of the system V if the density of the considered gas is not high. Therefore it is allowable to cut off the binomial expansion in (6.47) at the second term. The factor $N(N-1)/2$ represents the number of binary interactions. For a macroscopic system it is approximately $N^2/2$.

Using the results obtained above we get the free energy of a gas of *low density* in which molecules *interact in pairs* as:

$$F = -kT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{N\varepsilon^0}{kT}} \frac{V^N}{N!}\left(1 + \frac{N^2}{2V}\beta\right)\right] \tag{6.48}$$

Comparing this expression with the formulae for an ideal gas, (3.25) and (3.33), we see that the volume has been replaced by the *free volume*:

$$V_f = V\left[1+\frac{N^2\beta}{2V}\right]^{\frac{1}{N}} \tag{6.49}$$

The free volume as defined by (6.49) is dependent on temperature, the concentration of molecules, and the parameters of intermolecular interaction. As the integral β is small and negative the free volume of an imperfect gas is slightly less than the volume of the system as a whole. For $N^2\beta/2V \ll 1$ the root of the N-th power in (6.49) can be computed approximately ($(1+\delta)^{1/N} \cong 1+\delta/N$):

$$V_f = V\left[1+\frac{N\beta}{2V}\right] \tag{6.50}$$

The free energy then becomes:

$$F = -kT\ln\left\{\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{N\varepsilon^0}{kT}} \frac{1}{N!}\left[V\left(1+\frac{N}{2V}\beta\right)\right]^N\right\} \tag{6.51}$$

or, using (6.50) and writing β explicitly:

$$\begin{aligned} F = {} & -kT\ln\left[\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{N\varepsilon^0}{kT}}\right] \\ & -kTN\ln\left[V\left(1+\frac{2\pi N}{V}\int_0^{\tau}\left(e^{-\frac{U(r)}{kT}}-1\right)r^2dr\right)\right] \end{aligned} \tag{6.52}$$

A similar equation (6.31) has been obtained in the preceding section:

i.e.
$$F = -kTN\ln\left\{V\left[1+\frac{2\pi N}{V}\int_0^{\infty}(e^{-\frac{\varphi(a)}{kT}}-1)a^2da\right]\right\}+f(T) \tag{6.53}$$

We see that the unknown function of temperature in (6.31) is:

$$f(T) = -kT\ln\left[\frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{N\varepsilon^0}{kT}}\right] \tag{6.54}$$

We see that both the virial theorem and the statistical mechanical treatment of a gas with binary interactions result in similar formulae for free energy. Let us now compare these descriptions with that given by the van der Waals equation of state.

6.4
Van der Waals equation of state

We shall now demonstrate that a low-density gas with weak binary interactions obeys the van der Waals equation of state. The integral β consists of two parts: (i) negative, arising from repulsive short-range forces and (ii) positive, resulting from attractive intermolecular forces. If attractive interactions are *weak* ($|U_{att}|/kT << 1$) then the corresponding part can be calculated approximately by using the first two terms of the expansion:

$$e^{-\frac{U(r)}{kT}} - 1 \cong -\frac{U(r)}{kT} \tag{6.55}$$

This results in:

$$\beta = -4\pi\int_0^\sigma r^2 dr + 4\pi\int_\sigma^\tau\left(-\frac{U}{kT}\right)r^2 dr = -2b + \frac{2a}{kT} \tag{6.56}$$

where b and a are *positive constants* given by:

$$b = \frac{2}{3}\pi\sigma^3 \qquad \textit{and} \qquad a = -2\pi\int_\sigma^\tau U(r)r^2 dr \tag{6.57}$$

The constant b equals four times the volume of a molecule if taken to be a hard sphere. The *value* of the constant a depends on the functional dependence of potential energy on the intermolecular distance. For a typical hyperbolic dependence $U(r) = -B/r^m$ (see Fig. 6.3, above) the constant B can be determined *via* the potential energy u_{0m} of attractive interaction at $r = \sigma$ (the 'minimum' in Fig. 6.3):

$$B = u_{0m}\sigma^m \tag{6.58}$$

The constant a can then be represented as:

$$a = 2\pi\sigma^3 u_{0m}\int_\sigma^\tau\left(\frac{\sigma}{r}\right)^{m-2} d\frac{r}{\sigma} = 2\pi\sigma^3 u_{0m}\int_1^{\tau^*}\frac{dr^*}{(r^*)^{m-2}} \tag{6.59}$$

in which $\tau^* = \tau/\sigma$ and $r = r/\sigma$. Equation (6.59) then transforms into:

for $m = 3$
$$a = 2\pi\sigma^3 u_{03} \ln\tau^* = 3bu_{03} \ln\tau^* \tag{6.60}$$

for $m > 3$
$$a = \frac{2\pi\sigma^3 u_{0m}}{m-3}\left[1-(\tau^*)^{-m+3}\right] = \frac{3bu_{0m}}{m-3}\left[1-(\tau^*)^{-m+3}\right] \tag{6.61}$$

If the intermolecular forces are *not* short-range and τ^* approaches infinity, then the values of $m \leq 3$ result in infinite values of a. On the other hand, if the potential forces *are* short-range *i.e.* the potential energy profile is cut off at a finite (and not very large) τ^*, and $|u_{0m}|/kT << 1$, then any shape of potential can be assumed (for example, a square-shaped potential well). The constant a is in any case proportional to the potential energy in the 'minimum' (Fig. 6.3A) therefore a/kT is inversely proportional to the reduced temperature ($T^* = kT/u_{0m}$). The exponent $m \geq 4$ provides for finite values of a even when the integration is performed to infinity (see (6.61)).

Under these conditions the *integral* β *is independent of volume* and we can easily derive the equation of state. Using (6.48) for free energy:

i.e.
$$F = -kT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} e^{-\frac{N\varepsilon^0}{kT}} \frac{V^N}{N!}\left(1+\frac{N^2}{2V}\beta\right)\right]$$

the pressure as a derivative of free energy with respect to volume becomes:

$$p = NkT\left(\frac{\partial \ln V}{\partial V}\right)_T + kT\frac{\partial \ln\left(1+N^2\beta/2V\right)}{\partial V} = \frac{NkT}{V} - \frac{N^2\beta/2V^2}{1+N^2\beta/2V} \qquad (6.62)$$

Under the condition of low density, $N^2\beta/2V << 1$, the denominator in (6.62) is approximately 1 and hence:

$$p = \frac{NkT}{V} - \frac{N^2kT\beta}{2V^2} = \frac{NkT}{V}\left[1+\frac{N}{V}\left(b-\frac{a}{kT}\right)\right] \qquad (6.63)$$

This equation contains one (linear) term of the expansion with respect to density. It can be further transformed into:

$$p = \frac{NkT}{V} + \frac{N^2kTb}{V^2} - \frac{N^2a}{V^2} \qquad (6.64)$$

On the other hand, the van der Waals equation of state (for one mole of a gas) is:

$$\left(p+\frac{\boldsymbol{a}}{V^2}\right)\left(V-\boldsymbol{b}\right) = RT \qquad (6.65)$$

in which $\boldsymbol{a}$ and $\boldsymbol{b}$ are the molar *van der Waals constants*. The virial form of the van der Waals equation is:

$$\frac{pV}{RT} = \frac{V}{V-\boldsymbol{b}} - \frac{\boldsymbol{a}}{V} \qquad (6.66)$$

and this can be rewritten in terms of an infinite expansion over powers of $\boldsymbol{b}/V$:

$$\frac{pV}{RT} = -\frac{\boldsymbol{a}}{V} + 1 + \frac{\boldsymbol{b}}{V}\left\{1 + \frac{\boldsymbol{b}}{V}\left[1 + \frac{\boldsymbol{b}}{V}\left(1 + \cdots \frac{\boldsymbol{b}}{V}\frac{V}{V-\boldsymbol{b}}\right)\right]\right\} \tag{6.67}$$

This equation, (6.67), shows that, despite its simplicity, the van der Waals equation might provide a better description of the properties of dense gases than equations based on a limited number of terms in the virial expansion such as (6.64). The van der Waals equation for n moles of gas is:

$$\left(p + \frac{n^2\boldsymbol{a}}{V^2}\right)(V - n\boldsymbol{b}) = nRT \tag{6.68}$$

which can be transformed into:

$$p = \frac{nRT}{V}\left(1 + \frac{n\boldsymbol{b}}{V - n\boldsymbol{b}}\right) - \frac{n^2\boldsymbol{a}}{V^2} = \frac{nRT}{V} + \frac{n^2RT\boldsymbol{b}}{V(V - n\boldsymbol{b})} - \frac{n^2\boldsymbol{a}}{V^2} \tag{6.69}$$

Considering then the *restricted volume* $n\boldsymbol{b}$ *to be much smaller than* V, we get:

$$p = \frac{nRT}{V} + \frac{n^2RT\boldsymbol{b}}{V^2} - \frac{n^2\boldsymbol{a}}{V^2} \tag{6.70}$$

Comparing this equation with (6.64) we notice that they are identical if we assume $NkT = nR$, $n\boldsymbol{b} = Nb$, and $n^2\boldsymbol{a} = N^2a$. The equation of state of the gas with weak binary interactions becomes identical with the van der Waals equation of state *when the restricted volume is much smaller than the total volume* of the system. This condition (low density) has been used in the derivation of the expression for free energy (6.48) and the equation of state (6.64). A rarefied gas with binary interactions thus obeys an equation of state that can be considered as a special form of the van der Waals equation. The latter equation is based on a simple model not involving the condition of low density (see Appendix 10.7) *and may even be applied to liquids.*

The available volume ($V - n\boldsymbol{b}$) in the van der Waals equation *is not identical with the free volume derived for a gas with weak binary interactions* (6.49) and (6.50) because the latter also includes a contribution from attractive interactions:

$$V_f = V + \frac{N\beta}{2} = V - Nb + \frac{Na}{kT} \tag{6.71}$$

in which the term Na/kT represents the effect of attractive forces (which keep molecules closer together, thus making the free volume larger).

$$V_f = V - Nb\left(1 - 3\frac{u_{03}}{kT}\ln\tau^*\right) \tag{6.72}$$

The free volume thus defined *decreases* with *increasing reduced temperature*, which is opposite to the behaviour of the free volume of liquids. Calculations employing the van der Waals constants for N_2 show that this effect is not negligible.

The origin of this difference in behaviour of the free volume in liquids and gases lies in the different significance of the *concept of volume* in these aggregate states. The volume of a gas is always the volume of the vessel containing it, whereas the volume of a liquid is (usually) its equilibrium volume in contact with its own vapour (or other gaseous phase) at a given temperature and pressure.

6.5
Chemical equilibria in imperfect gases

In a system containing two different kinds of molecules (*e.g.* A (N_A) and B (N_B)) the number of binary interactions is $(N_A + N_B)(N_A + N_B - 1)/2 \cong (N_A + N_B)^2/2$. Of this number there are N_A^2 of AA, N_B^2 of BB and $2N_AN_B$ of AB interactions. Each type of interaction can be characterised by its integral β, β_{AA}, β_{BB} and β_{AB}. The last of these is taken over the distance apart in a hetero-molecular pair:

$$\beta_{AB} = \int_0^\infty \left[\exp\left(-\frac{U_{AB}}{kT} \right) - 1 \right] 4\pi r^2 dr \tag{6.73}$$

The free energy of such a system can then be written as:

$$F = F_{igA} + F_{igB} - \frac{kT}{2V} \left[N_A^2 \beta_{AA} + N_B^2 \beta_{BB} + 2N_A N_B \beta_{AB} \right] \tag{6.74}$$

in which:

$$F_{igA} = -kT \ln \left[\frac{2\pi m_A kT}{h^2} \right]^{\frac{3N_A}{2}} e^{-\frac{N\varepsilon_A^0}{kT}} \frac{V^{N_A}}{N_A!} = -kTN_A \left[\ln q_A(T) + \ln eV - \ln N_A \right] \tag{6.75}$$

The parameters a and b of hetero-molecular interactions are usually estimated using some empirical combination rule from a large number of suggested interpolation formulae. The most frequently encountered are the arithmetic mean for b and the geometric mean for a:

$$b_{AB} = \frac{b_{AA} + b_{BB}}{2} \tag{6.76}$$

$$a_{AB} = (a_{AA} a_{BB})^{1/2} \tag{6.77}$$

We are thus able to describe a system involving a chemical equilibrium and derive the corresponding law of mass action.

6.5.1
Isomolar equilibria in imperfect gases

Equations (6.74) and (6.75) yield the following expressions for the chemical potentials of a binary mixture in the state of an imperfect gas:

$$\mu_A = \frac{\partial F}{\partial n_A} = -kT\left[\ln q_A - \ln\frac{n_A}{V}\right] - kT\left[\frac{n_A\beta_{AA} + n_B\beta_{AB}}{V}\right] \tag{6.78}$$

$$\mu_B = \frac{\partial F}{\partial n_A} = -kT\left[\ln q_B - \ln\frac{n_B}{V}\right] - kT\left[\frac{n_B\beta_{BB} + n_A\beta_{AB}}{V}\right] \tag{6.79}$$

The condition of equilibrium of a mono-molecular reversible reaction:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{6.80}$$

requires the equality of these chemical potentials, which then yields the following law of mass action:

$$\ln\frac{q_B}{q_A} - \ln\frac{n_B}{n_A} - \frac{1}{V}\left[\,(n_B\beta_{BB} + n_A\beta_{AB}) - (n_A\beta_{AA} + n_B\beta_{AB})\,\right] = 0 \tag{6.81}$$

The last term in (6.81) describes the effects of non-ideality introduced by molecular interactions. The terms $n\beta/V$ are by definition small compared to 1 therefore they can readily be converted into activity coefficients without any further restriction. The form of the non-ideality term involving the product of integral β (volume) times concentration n/V (1/volume) suggests that the numbers of molecules in the ideal part of this law of mass action should also be converted into volume concentrations:

$$\ln\frac{q_B}{q_A} - \ln\frac{[B]}{[A]} - \left\{[B]\;\beta_{BB} + [A]\;\beta_{AB} - [A]\;\beta_{AA} - [B]\;\beta_{AB}\right\} = 0 \tag{6.82}$$

Combining terms we get:

$$\ln\frac{q_B}{q_A} - \ln\frac{[B]}{[A]} - \left\{[B]\;(\beta_{BB} - \beta_{AB}) - [A]\;(\beta_{AA} - \beta_{AB})\right\} = 0 \tag{6.83}$$

Converting small non-ideality terms into logarithms we get a pseudo-ideal form of the law of mass action with respect to activities:

$$\ln\frac{q_B}{q_A} - \ln\frac{a_B}{a_A} = 0 \tag{6.84}$$

in which activities are polynomial functions of concentrations:

$$a_A = [A] - [A]^2(\beta_{AA} - \beta_{AB}) \tag{6.85}$$

$$a_B = [B] - [B]^2(\beta_{BB} - \beta_{AB}) \tag{6.85a}$$

These activities obviously approach molar concentrations when the differences ($\beta_{AA} - \beta_{AB}$) and ($\beta_{BB} - \beta_{AB}$) approach zero:

$$\beta_{BB} = \beta_{AB}; \qquad \beta_{AA} = \beta_{AB} \tag{6.86}$$

These conditions imply that:

$$\beta_{BB} = \beta_{AA} \tag{6.87}$$

This does not however mean that molecules A and B are identical: equal integrals β_{AA}, β_{BB}, and β_{AB} may have different contributions from repulsive and attractive forces (see Fig. 6.4).

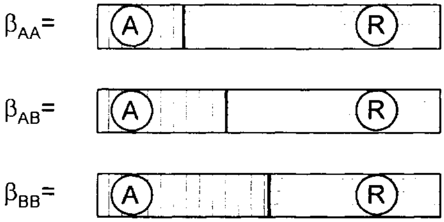

Fig. 6.4. Possible differences in the nature of molecular interactions corresponding to equal integrals β

An interesting case arises from the condition:

$$\beta_{AA} + \beta_{BB} - 2\beta_{AB} = 0 \tag{6.88}$$

i.e. the situation in which the sum of the coefficients of square terms in (6.85, 6.85a) is zero. The activities then become:

$$a_A = [A] - \gamma[A]^2; \quad a_B = [B] + \gamma[B]^2; \qquad \gamma = \frac{(\beta_{AA} - \beta_{BB})}{2} \tag{6.89}$$

In this both the product and the reactant are characterised by identical activity coefficients γ. However the law of mass action is not hereby considerably simplified:

$$\ln\frac{q_B}{q_A} - \ln\frac{[B] + \gamma[B]^2}{[A] - \gamma[A]^2} = 0 \tag{6.90}$$

In fact, any further simplification is apparently impossible. On the other hand, when we apply the condition (6.88) to the *general form* of the law of mass action (6.81) – (6.83) and not to that expressed in terms of activities, (6.84), we find that the behaviour of a system obeying (6.88) is practically ideal:

$$\ln\frac{q_B}{q_A}-\ln\frac{[B]}{[A]}-\left\{([A]+[B])\left(\frac{\beta_{BB}-\beta_{AA}}{2}\right)\right\}=0 \qquad (6.91)$$

The sum of concentrations $[A]+[B]=C_0$ and therefore the non-ideality term can be added to the equilibrium constant. We see that a general form of the law of mass action provides for a more correct way of asymptotic analysis of the behaviour of a system approaching the ideal state. *The form with respect to activities does not allow this* because too many approximate transformations have already been made in order to obtain an expression for the activity coefficients.

In fact, a direct indication of such a pseudo-ideal behaviour of a system under the condition (6.88) can be obtained when we express the free energy as a function of one concentration, let us say that of the reactant (n_A/V). By allowing for the material balance ($n_A + n_B = N$) in (6.74) we get the *excess free energy* as:

$$f_{ex}=F-F_{igA}-F_{igB}=-\frac{kT}{2V}\left[n_A^2(\beta_{AA}+\beta_{BB}-2\beta_{AB})+2Nn_A(\beta_{AB}-\beta_{BB})+N^2\beta_{BB}\right] \qquad (6.92)$$

When condition (6.88) is obeyed, *i.e.* when the parameter of hetero-molecular interaction is the arithmetic mean of the parameters of the corresponding homo-molecular interactions,

i.e. $$\beta_{AB}=(\beta_{BB}+\beta_{AA})/2\ \beta_{\mathrm{AB}} \qquad (6.93)$$

then the *quadratic* term with respect to the current number of molecules disappears. The remaining *linear* term will contribute a constant term to the law of mass action, thus changing the equilibrium constant.

Condition (6.93) repeats the combination rule (6.76) for the repulsive part of β which might constitute its major part. This means that the condition (6.93) may be expected to be generally obeyed, *i.e.* a practically ideal gas law of mass action can be applied to isomolar equilibria in a gas of low density:

$$\ln\frac{q_B}{q_A}e^{-\frac{N}{2V}(\beta_{BB}-\beta_{AA})}-\ln\frac{[B]}{[A]}=0 \qquad (6.94)$$

It requires little more imagination to guess that such a non-ideality term can also be introduced into the concentrations:

$$\ln\frac{q_B}{q_A}-\ln\frac{n_B}{V(1+N\beta_{BB}/2V)}+\ln\frac{n_A}{V(1+N\beta_{AA}/2V)}=0 \qquad (6.95)$$

Such a form implies *composition independent* free volumes of the *A* and *B* species:

$$V_{Afree} = V\left(1 + \frac{N\beta_{AA}}{2V}\right); \quad V_{Bfree} = V\left(1 + \frac{N\beta_{BB}}{2V}\right) \tag{6.96}$$

This is not, however, the whole truth concerning the possible effects of molecular interactions on equilibria in the gas phase. In fact the condition (6.88) is sufficient only for isomolar equilibria. The general case of non-isomolar reactions is a little more complicated.

6.5.2
A non-isomolar reaction in an imperfect gas

For a bimolecular reversible reaction:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{6.97}$$

the material balance equations (supposing that the product C was not initially present) are:

$$N_A = n_A + n_C; \quad N_B = n_B + n_C \tag{6.98}$$

The ideal gas free energy of the reaction mixture is:

$$-\frac{F_{ig}}{kT} = n_A\left(\ln q_A - \ln\frac{n_A}{eV}\right) + n_B\left(\ln q_B - \ln\frac{n_B}{eV}\right) + n_C\left(\ln q_C - \ln\frac{n_C}{eV}\right) \tag{6.99}$$

The contribution from molecular interactions, *i.e.* the *excess free energy* of the reaction mixture is:

$$-\frac{f}{kT} = \frac{n_A^2\beta_{AA} + n_B^2\beta_{BB} + n_C^2\beta_{CC} + 2n_An_B\beta_{AB} + 2n_An_C\beta_{AC} + 2n_Bn_C\beta_{BC}}{2V} \tag{6.100}$$

Written as a function of n_C (using material balance equations) the excess free energy becomes:

$$\begin{aligned} -\frac{f}{kT} = \frac{1}{2V} \Big\{ & n_C^2\left(\beta_{AA} + \beta_{BB} + \beta_{CC} + 2\beta_{AB} - 2\beta_{AC} - 2\beta_{BC}\right) \\ & -2n_C\left[N_A\left(\beta_{AA} + \beta_{AB} - \beta_{AC}\right) + N_B\left(\beta_{BB} + \beta_{AB} - \beta_{BC}\right) \right] \\ & + N_A^2\beta_{AA} + N_B^2\beta_{BB} + 2N_AN_B\beta_{AB} \Big\} \end{aligned} \tag{6.101}$$

As in the previous example we notice that such a system must behave pseudo-ideally when the coefficient of the quadratic term in (6.101) is zero. Applying the condition of equilibrium to this reaction we get the law of mass action:

$$\ln\frac{q_C}{q_A q_B}-\ln\frac{[C]}{[A][B]}+\frac{n_C}{V}\left(\beta_{AA}+\beta_{BB}+\beta_{CC}+2\beta_{AB}-2\beta_{AC}-2\beta_{BC}\right)$$
$$+\frac{N_A}{V}\left(\beta_{AA}+\beta_{AB}-\beta_{AC}\right)+\frac{N_B}{V}\left(\beta_{BB}+\beta_{AB}-\beta_{BC}\right)=0 \tag{6.102}$$

Taking into account that the terms $\beta n_C/V$ are small and employing material balance equations for this reactions we get the law of mass action with respect to activities:

$$\ln\frac{q_C}{q_A q_B}-\ln\frac{a_C}{a_A a_B}=0 \tag{6.102a}$$

in which:

$$a_A=\frac{n_A}{V}\left[1-\frac{n_A}{V}\left(\beta_{AA}+\beta_{AB}-\beta_{AC}\right)\right] \tag{6.103}$$

$$a_B=\frac{n_A}{V}\left[1-\frac{n_B}{V}\left(\beta_{BB}+\beta_{AB}-\beta_{BC}\right)\right] \tag{6.103a}$$

$$a_C=\frac{n_C}{V}\left[1-\frac{n_C}{V}\left(\beta_{CC}-\beta_{AC}-\beta_{BC}\right)\right] \tag{6.103b}$$

Activity coefficients as defined by (6.103) and (6.103b) are *linearly dependent on the corresponding concentrations*. The coefficients of the linear terms in square brackets in (6.103) and (6.103b) include (i) the integral of the corresponding homo-molecular interaction and (ii) the integrals of two hetero-molecular interactions with positive sign, if the interaction occurs on one side of the reaction equation, and with negative sign if the interaction occurs across the arrows.

Such a system behaves ideally if all these coefficients separately are zero (a trivial solution):

$$\beta_{AC}=\beta_{AA}+\beta_{AB};\quad \beta_{BC}=\beta_{BB}+\beta_{AB};\quad \beta_{CC}=\beta_{AC}+\beta_{BC} \tag{6.104}$$

Another solution is available when the sum of coefficients in (6.103,a,b) is zero. Such a possibility is directly indicated by (6.101) and (6.102):

$$\beta_{AA}+\beta_{BB}+2\beta_{AB}+\beta_{CC}-2\beta_{AC}-2\beta_{BC}=0 \tag{6.105}$$

The square term (with respect to n_C) in (6.101) disappears under such a condition. If we apply the 'combination rule' for hetero-molecular interactions (6.88) then the sum (6.105) does *not* become zero, but is transformed into:

$$\beta_{AA} + \beta_{BB} - \beta_{CC} \tag{6.106}$$

The additional requirement therefore is:

$$\beta_{CC} = \beta_{AA} + \beta_{BB} \tag{6.107}$$

We have obtained (similarly to the cases discussed in Chapter 4) a certain '*conservation rule*' for the parameter β characterising molecular interaction. If repulsive interactions are prevalent then the condition (6.107) expresses the additivity of molecular volumes of the products of reaction exactly as has been obtained in a semi-empirical manner in Chapter 4 (the Kopp rule of additivity of molar volume (see page 114)).

This condition did not appear for an isomolar reaction because it is fulfilled automatically when the combination rule (6.88) is applied. Under conditions (6.88) and (6.107) the law of mass action (6.102) is reduced to:

$$\ln \frac{q_C}{q_A q_B} - \ln \frac{n_C}{n_A n_B} + \ln V + \frac{1}{2V}\left(N_A \beta_{AA} + N_A \beta_{AA}\right) = 0 \tag{6.108}$$

The constant non-ideality term can either be added to the equilibrium constant or converted into a composition independent activity coefficient. The integrals β_{AA} and β_{BB} are small compared to the volume of the system per molecule (V/N) therefore the last term of (6.108) can be written in logarithmic form as:

$$\frac{1}{2V}\left(N_A \beta_{AA} + N_A \beta_{AA}\right) \cong \ln\left(1 + \frac{N_A \beta_{AA} + N_A \beta_{AA}}{2V}\right) = -\ln \gamma \tag{6.109}$$

Adding and subtracting this term to (6.108) yields the activity of any component as linearly proportional to its concentration:

$$a_A = \gamma[A] \qquad a_B = \gamma[B] \qquad a_C = \gamma[C] \tag{6.110}$$

This activity is actually the concentration calculated with respect to a composition independent free volume:

$$V_{free} = V + \left(N_A \beta_{AA} + N_B \beta_{BB}\right)/2 \tag{6.111}$$

Remember that the integral β is generally negative and the free volume is thus smaller than the volume V. It has already been mentioned that this integral is made up of a contribution of both repulsive and attractive forces which obey different combination rules. The conditions (6.88) and (6.107) have therefore different meanings for these parts of β. In order to elucidate the significance of the conditions under which a gas phase equilibrium behaves ideally, we must consider the effects of the attractive and the repulsive parts of β separately.

6.5.3
Separate conditions of ideal behaviour for attractive and repulsive molecular interactions

Consider a non-isomolar chemical reaction:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{6.97}$$

The condition (6.105) (under which such a reaction mixture behaves ideally) written separately for repulsive and attractive parts is:

$$b_{AA} + b_{BB} + b_{CC} - 2b_{AC} - 2b_{BC} + 2b_{AB} = 0 \tag{6.113}$$

$$a_{AA} + a_{BB} + a_{CC} - 2a_{AC} - 2a_{BC} + 2a_{AB} = 0 \tag{6.113a}$$

The repulsive part obeys this condition when (i) the combination rule (6.76) is valid and (ii) when the constant *b* of the product C is additive with respect to its constituent parts:

i.e.

$$b_{AA} + b_{BB} = b_{CC} \tag{6.114}$$

The combination rule for the *attractive part* of integral β is different (6.77):

$$a_{AB} = (a_{AA}a_{BB})^{1/2} \tag{6.115}$$

and therefore the condition (6.113a) is transformed into:

$$a_{AA} + a_{BB} + a_{CC} - 2\sqrt{a_{AA}a_{CC}} - 2\sqrt{a_{BB}a_{CC}} + 2\sqrt{a_{AA}a_{BB}} = 0 \tag{6.116}$$

The expression in the left-hand part of (6.116) is nothing else but:

$$\left(\sqrt{a_{AA}} + \sqrt{a_{BB}} - \sqrt{a_{CC}}\right)^2 \tag{6.117}$$

The condition (6.113a) then holds if:

$$\sqrt{a_{AA}} + \sqrt{a_{BB}} = \sqrt{a_{CC}} \tag{6.118}$$

or:

$$a_{CC} = a_{AA} + 2\sqrt{a_{AA}a_{BB}} + a_{BB} = a_{AA} + 2a_{AB} + a_{BB} \tag{6.119}$$

Equation (6.119) implies that the attractive interactions of two molecules of the product C only include two homo-molecular and two hetero-molecular interactions of the reactant molecules (see Fig. 6.5). In other words *reaction does not introduce any new attractive intermolecular forces.*

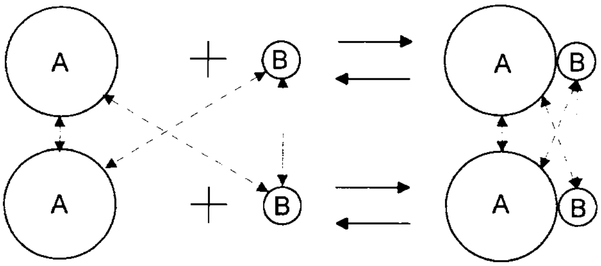

Fig. 6.5. The origin of attractive interactions between the molecules of reaction products

Under condition (6.119) *attractive* forces still contribute to the free energy:

$$-\frac{1}{2V}\left(N_A\sqrt{a_{AA}}+N_B\sqrt{a_{BB}}\right)^2 \tag{6.120}$$

but the corresponding term *does not appear in the law of mass action.*

6.5.4
Associative equilibria in the gaseous phase

Associative equilibria in the gaseous phase can be considered as a good (and perhaps the only) example of reactions obeying the rules derived in the preceding section. Let us consider a dimerisation reaction:

$$\mathrm{A}+\mathrm{A} \rightleftharpoons \mathrm{A}_2 \tag{6.121}$$

This reaction is a *special case* of reaction (6.97) – both reactants being identical. The integrals β_{ij} are therefore reduced from five to three:

$$\beta_{11}=\beta_{AA}=\beta_{BB}=\beta_{AB};\quad \beta_{12}=\beta_{AC}=\beta_{BC};\quad \beta_{22}=\beta_{CC} \tag{6.122}$$

Taking also into account that $\beta=-2b+2a/kT$ and applying the material balance for (6.121) the excess free energy, (6.101), can be re-written as:

$$\begin{aligned}-\frac{f}{kT}&=-\frac{n_2^2}{V}\left(4b_{11}+b_{22}-4b_{12}\right)+\frac{2n_2N}{V}\left(2b_{11}-b_{12}\right)\\&+\frac{n_2^2\left(4a_{11}+a_{22}-4a_{12}\right)}{VkT}-\frac{2n_2N\left(2a_{11}-a_{12}\right)}{VkT}+\frac{N^2}{V}\left(-b_{11}+\frac{a_{11}}{kT}\right)\end{aligned} \tag{6.123}$$

in which N (corresponding to N_A+N_B) is:

$$N=n_1+2n_2=const \tag{6.124}$$

The constant b_{22} can be assumed to be to be double the constant b_{11} (the volume of the dimer is double the volume of the monomer). This (along with the combination rule $b_{12} = (b_{11} + b_{22}) = (3/2)b_{11})$ results in the coefficient of the square term in the first line of (6.123) being zero:

i.e. $$4b_{11} + b_{22} - 4b_{12} = 4b_{11} + 2b_{11} - 6b_{11} = 0 \qquad (6.125)$$

The value of a is proportional to the potential of the attractive forces at the equilibrium distance and to the volume of the molecule: for $m = 6$ and a sufficiently large τ^* (6.61) gives rise to:

$$a = bu_e\left[1 - (\tau^*)^{-m+3}\right] \cong bu_e \qquad (6.126)$$

If we assume that the energy of molecular interactions per dimer (u_{22}) is double that value per monomer ($u_{22} = 2u_{11}$) then the constant a for the dimer will be:

$$a_{22} = 2b_{11}2u_{11} = 4a_{11} \qquad (6.127)$$

which is consistent with condition (6.119):

$$a_{22} = a_{11} + 2a_{11} + a_{11} = 4a_{11} \qquad (6.128)$$

This makes the coefficients of the square and linear terms in the second line of (6.123) equal to zero. The excess free energy then becomes a linear function of the current concentrations:

$$-\frac{f}{kT} = \frac{1}{V}\left[(n_2 - N)Nb_{11} + N^2\frac{a_{11}}{kT}\right] = -\frac{(n_1 + n_2)}{V}Nb_{11} + \frac{N}{V}\frac{Na_{11}}{kT}$$
$$(6.129)$$

The first term ($b_{11}N << V$) can be converted into the restricted volume and the expression for the total free energy of reaction mixture becomes:

$$-\frac{F}{kT} = n_1\left[\ln q_1 - \ln n_1 + \ln e(V - Nb_{11})\ \right] + n_2\left[\ln q_2 - \ln n_2 + \ln e(V - Nb_{11})\ \right] + \frac{N^2a_{11}}{VkT}$$
$$(6.130)$$

In other words, the system behaves as an ideal gas mixture of monomers and dimers occupying a volume slightly less than the volume of the system. The law of mass action for this system is similar to that of an ideal gas with concentrations calculated with respect to a constant free volume.

The assumption made above (that the energy of interaction of two dimeric molecules is twice the energy of molecular interactions of two monomeric molecules) implies that the energy of actual bonding (*e.g.* hydrogen bonding) should *not* be taken into account. On the other hand it also implies that the electronic system of those molecules in monomeric form and those in the dimer *do not considerably differ*.

A certain doubt might arise at this point concerning possible neutralisation of electric dipole moments of individual molecules in a dimer (as, for example, in the dimer of acetic acid).

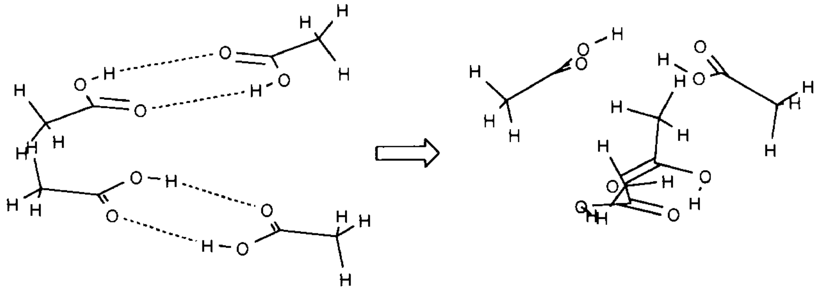

Fig. 6.6. Optimisation of the structure of an acetic acid tetramer. The energy difference between the optimised structure and a pair of separated of dimers is *ca.* 6.4 kcal

The dipole moment of such a dimer is indeed close to zero and the energy of dipole-dipole interactions of two such associates separated by large distances is zero. When four molecules of acetic acid are brought close together the distribution of electric charge in individual molecules becomes important. Fig. 6.6 shows the optimisation of the geometry of such a system starting from a pair of acetic acid dimers. The result is a complicated structure with bent hydrogen bonds corresponding, apparently, to the minimum of electric dipole-dipole interactions of individual molecules.

6.5.5
Molecular interaction *via* a chemical reaction

These questions touch on one of the fundamental problems of the description of equilibria in systems of interacting molecules: should the formation of an associate be considered as a chemical reaction or as a kind of molecular interaction? Molecular interactions, as we considered them in Chapter 5, do not result in the formation of a stable associate of an *a priori* known composition moving as a whole (at least during a certain number of periods of oscillations of its parts sufficient to detect such an aggregate by spectroscopic methods). Such an associate *may* be the result of a chemical reaction. For example when a diatomic molecule is formed a new degree of freedom appears which can be detected by the rotational structure of spectral lines and by additional contribution to the heat capacity. Molecular interactions, on the other hand, can be considered as phenomena resulting in a higher probability of two molecules to be found in the vicinity of each other. Their motion is *not correlated* and such associates do not posses a rotational degree of freedom.

Molecular dynamics simulations carried out on the dimer of acetic acid molecules show that this aggregate behaves like a chemical compound *only at very low temperatures*. Of course, the results of such simulations depend very much on the type of potential used in the calculations and can only be considered as qualitative[3]. However they are useful in elucidating the physical significance of a model describing molecular interactions employing the concept of molecular association or formation of ion pairs.

Vapours of alkali metal atoms under very low pressure present an interesting case of a system of particles interacting practically only chemically and forming dimeric molecules which can be detected spectroscopically. The state of such a system is that of an ideal gas, but chemical reaction changes the number of particles, which results in apparent deviations from the equation of state of an ideal gas. Such a reaction can be studied by measuring p–V–T relationships (actually by determining the second virial coefficient) as will be shown below.

Imagine a dimerisation equilibrium of atoms A in the ideal gas:

$$2\mathrm{A} \rightleftharpoons \mathrm{A}_2 \tag{6.131}$$

Suppose that the reaction (6.131) occurs in unit volume (1 cm^3). The total number of *molecules* is $(n_1 + n_2)$ whilst the total number of *atoms* is $N_0 = n_1 + 2n_2$. The pressure in such a system is given by the equation of state:

$$p = (n_1 + n_2)kT = \frac{N_0 + n_1}{2}kT \tag{6.132}$$

Applying the law of mass action for an ideal gas:

$$K = \frac{n_2}{n_1^2} = \frac{N_0 - n_1}{2n_1^2} \tag{6.133}$$

shows that the concentration of atoms (monomers) equals the real positive root of the quadratic equation:

$$2Kn_1^2 + n_1 - N_0 = 0 \tag{6.134}$$

i.e.

$$n_1 = \frac{\sqrt{1 + 8KN_0} - 1}{4K} \tag{6.135}$$

For a rarefied gas with $8KN \ll 1$, the square root in (6.135) can be calculated approximately as:

$$\sqrt{1+\delta} \cong 1 + \frac{\delta}{2} - \frac{\delta^2}{8} \tag{6.136}$$

The number of monomeric molecules is thus:

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[3] The 'molecular mechanics' method provides for a convenient speed of calculation thus allowing one to view the tumbling of molecules. However, It does not give a correct value of the energy of hydrogen bonding (it gives 3 – 4 kcal mole^{-1} instead of the experimental value of 20 kcal mol^{-1}). Therefore the *temperature scale* employed in such calculations is wrong!

$$n_1 = \frac{4KN_0 - 8K^2N_0^2}{4K} = N_0(1 - 2KN_0) \tag{6.137}$$

Substituting n_1 in (6.132) we find the equation of state of an 'ideal' gas involving a dimerisation equilibrium:

$$p = N_0kT(1 - KN_0) \tag{6.138}$$

Taking into account the fact that the derivation has been performed for unit volume ($N_0 = N/V$), the equation of state can be rewritten as:

$$\frac{pV}{NkT} = 1 - K\frac{N}{V} \tag{6.139}$$

The second virial coefficient in such a gas equals the equilibrium constant K and must show a considerable temperature dependence ($\ln B_2 \propto 1/T$ and not $B_2 \propto 1/T$ as for weak molecular interactions (see page 179)

6.6
Conclusions

In Chapter 5 we have considered the theoretical aspects of the description of molecular interactions. In this Chapter we have applied the concept of molecular interaction to the derivation of the equation of state and the evaluation of non-ideality terms in the law of mass action as applied to gas-phase reactions.

A specific feature of gas-phase reactions is that the non-ideality terms in the law of mass action are generally small and can easily be transformed into activity coefficients that are linearly dependent on concentrations. However this form is not to be analysed any further because it is only an approximate relationship.

By analysing the general form of the law of mass action we have found that, under certain conditions, the ideal law of mass action can describe reactions in real gases. These conditions correspond to a general *conservation rule: a reaction should not introduce any new molecular interactions.* For repulsive interactions this results in the conservation of the incompressible molecular volume. This rule is to be expected to be approximately followed over a wide range of reactions. For attractive interactions, this rule implies that molecules of the products are attracted to each other *as if they consist of independently interacting fragments of reactants.* This means that molecular interaction is expected mainly to proceed from the noble gas residue of electronic structure, excluding valence electrons. Taking into account that the constants of molecular interactions a and b are interrelated: $a \cong bu_0$, the quantitative expression of the conservation rule (6.118) for attractive interactions in the equilibrium of formation of the molecular complex results in the following relationship between the potential energies u_0:

$$\sqrt{u_{0C}\frac{b_{CC}}{b_{CC}}} = \sqrt{u_{0A}\frac{b_{AA}}{b_{CC}}} + \sqrt{u_{0B}\frac{b_{BB}}{b_{CC}}} \tag{6.140}$$

This implies that the square root of the potential energy of a molecule is additive with respect to the *volume fractions* of the constituent parts. We have thus obtained a refinement of the additivity rule for molecular vaporisation energies derived in Chapter 4.

The gas with binary interactions considered in this Chapter is, of course, a first approximation to the description of real gases. It does not take into account triple and higher order interactions (not mentioning the truncation of series carried out in the derivation of the expression for free energy). For gases, higher order interactions can be accounted for and this has been done by Mayer [4]. This theory allows, in principle, for the introduction of collisions of any order. The configurational free energy is then written in virial form (expansion over densities):

$$-kT\ln\frac{1}{N!}\int\ldots\int e-\frac{U(q)}{kT}dq1\cdots dqN = NkT\left[1+\frac{\beta_1}{2}\frac{N}{V}+\frac{2\beta_2}{3}\frac{N^2}{V^2}+\frac{3\beta_3}{4}\frac{N^3}{V^3}+\cdots\right] \tag{6.141}$$

in which the β_s are irreducible *integrals* corresponding to *irreducible ensembles* of $s + 1$ interacting molecules:

$$\beta_s = \frac{1}{s!V}\int\ldots\int\sum_{s+1>i}\prod_{j>i}(f_{iK})dq_1\ldots dq_s \tag{6.142}$$

This produces quite good agreement with experimental data for gases at high pressures. However, at densities corresponding to liquids (note the importance of volumetric properties) the series into which free energy is expanded *does not converge*. Therefore, this approach, although being fundamentally correct, cannot be applied to the liquid state due to purely mathematical difficulties.

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7 Reactions in Imperfect Condensed Systems. Lattice Energy

7.1
Exchange energy

In Chapter 4 we considered reactions in imperfect liquids on the basis of a semi-empirical and generally phenomenological model based on the assumption of the additivity of volume and energy of molecular interactions. This assumption implies the independence of *molecular volumes* and *lattice energies* of composition. It can also be said that under these conditions the energy of a molecule is independent of the nature of its surroundings. The non-ideality then reveals itself in the dependence of the *free volume* on composition. The lattice energy, when additive, contributes towards the standard internal energy of reaction and does not introduce any additional non-ideality terms into the equation of the law of mass action.

That this is a too rough an approximation for mixtures of molecules differing by the energy of molecular interactions can be illustrated by a simple argument. The energy of a polar molecule is certainly different when surrounded by similar polar molecules and in a cluster of non-polar molecules. Therefore the total lattice energy in such a mixture is non-additive and the description of non-ideality developed in Chapter 4 reflected only a part of the effects of molecular interactions.

In this Chapter we will consider the non-ideality connected with the *dependence of molecular lattice energy on the nature of the surroundings.* The formalism derived below is based on combinatorial formulae for the probabilities of molecular configurations. This limits the scope to mixtures of molecules of approximately equal size and strength of molecular interactions. Strictly speaking, solely in such cases does the probability of finding a centre of a crystal (or quasi-crystal) lattice occupied by a molecule of a given type equal the mole fraction of these molecules. However, we shall see that the derived formalism successfully describes the behaviour of mixtures of molecules considerably differing in energies of molecular interactions (by more than $2RT$).

Consider a binary mixture of molecules A and B. The potential energy of interaction of a molecule A with its surroundings (coordination number c) is then:

A.B. Koudriavtsev et al., *The Law of Mass Action*

$$u_A = c\left(x_A\varphi_{AA} + x_B\varphi_{AB}\right) \qquad (7.1)$$

in which φ_{AA} and φ_{AB} are binary potentials of AA and AB interactions. Similarly, the potential energy of interaction of a molecule B with its surroundings is:

$$u_A = c\left(x_B\varphi_{BB} + x_A\varphi_{AB}\right) \qquad (7.1a)$$

The potential energy *per molecule* is one half of the energy of interaction of a *given molecule* with its surroundings (see Chapter 5), therefore the total potential energy of $N = N_A + N_B$ molecules is:

$$U = \frac{N}{2}\left(x_A u_A + x_B u_B\right) = \frac{Nc}{2}\left(x_A^2\varphi_{AA} + x_B^2\varphi_{BB} + 2x_A x_B\varphi_{AB}\right) \qquad (7.2)$$

A rather ingenious transformation (see Appendix 9.10) allows one to express U as an additive quantity with respect to binary *homo-molecular potentials* plus an *excess term*:

$$U = \frac{Nc}{2}\left(x_A\varphi_{AA} + x_B\varphi_{BB} + x_A x_B\Delta u_{ex}\right) \qquad (7.3)$$

The excess term represents the energy of random mixing of $N/2$ molecules of A and $N/2$ molecules of B and hence Δu_{ex} is sometimes referred to as the *excess mixing energy*. However, this term has another meaning that is clarified by writing Δu_{ex} as follows:

$$\Delta u_{ex} = \frac{c}{2}\left(2\varphi_{AB} - \varphi_{AA} - \varphi_{BB}\right) = \frac{c}{2}\left(\varphi_{AB} - \varphi_{AA} + \varphi_{AB} - \varphi_{BB}\right) \qquad (7.4)$$

Equation (7.4) shows that Δu_{ex} is the energy accompanying a simultaneous transfer of molecules A and B from *hetero-molecular* surroundings into *homo-molecular* surroundings, *i.e.* it characterises an *interchange* of molecules. This excess term is also called the *cooperativity term* or *cooperativity* thus reflecting the co-operative behaviour of molecules in non-ideal mixture. Guggenheim and Fowler [1] defined *co-operative ensembles* as those where interactions are not negligibly small. However, according to (7.4), the excess term represents the *difference* in the interactions of molecules in homo- and hetero-pairs rather than the absolute strength of such molecular interactions. Therefore it is more to the purpose to call Δu_{ex}, following Moelwyn-Hughes [2], the *interchange energy*. For the sake of brevity, we call it here the *exchange energy* emphasising its analogy to the corresponding quantum mechanical parameter.

The partition function of the binary mixture considered here can be written as:

$$Z = z_A^{N_A} z_B^{N_B} \frac{N!}{N_A!N_B!} e^{-\frac{U}{NkT}} \qquad (7.5)$$

in which z is the molecular partition function.

The free energy of such a system is then:

$$-\frac{F}{NkT} = x_A\left[\ln z_A - \ln x_A - \frac{c\varphi_{AA}}{2kT}\right] + x_B\left[\ln z_B - \ln x_B - \frac{c\varphi_{BB}}{2kT}\right] - x_A x_B \frac{\Delta u_{ex}}{kT}$$

$$= -\frac{1}{kT}\left[x_A f_A + x_B f_B + x_A x_B \Delta u_{ex} + kT\left(x_A \ln x_A + x_B \ln x_B\right)\right] \tag{7.6}$$

in which $f_A = -kT\ln z_A - c\varphi_{AA}/2$ and $f_B = -kT\ln z_B - c\varphi_{BB}/2$ are the free energies of the particles of corresponding type per molecule in an ideal crystal. Equation (7.6) explains a number of phenomena and properties of non-ideal liquid and solid mixtures such as the relationship between vapour pressure and composition of liquid, phase separation in liquid mixtures, *etc.* [1, 2]. The mixtures (either solid or liquid) obeying (7.6) are called *regular solutions*. Regular ensembles are such co-operative ensembles where interactions can be represented as the sum of binary *nearest neighbour* interactions [1]. The functions φ_{AA}, φ_{BB} and φ_{AB} in (7.6) are binary intermolecular potentials, which enables an easy estimation of the effects of molecular interactions. However this model only defines the *excess mixing energy* whilst the nature of the *excess mixing entropy* remains unclear. Therefore this quantity is taken as zero for regular solutions.

Another approach to the description of imperfect mixtures in the condensed state has been recently developed by Koudriavtsev [3]. This approach is based on the statistical aspect of molecular interactions, considering them as *the dependencies of the states of molecules on the nature of their surroundings*. In the following Sections, we shall apply this approach to the description of chemical equilibria in the condensed state. It will be shown that it provides for a more general formalism than the approximation of binary interactions.

7.2

Non-ideality as a result of dependence of the partition function on the nature of the surroundings

Let us consider a crystal of simple cubic symmetry (without defects) formed by particles *A* and *B*. The molecular lattice energies and vibrational frequencies of particles in this crystal are assumed to be dependent *on the nature of the surroundings* (in contrast to the ideal crystal where they are determined by the nature of the particle alone). These variations of energy and vibrational frequency we assume to be sufficiently small to consider molecules as *randomly distributed* over all centres in the crystal lattice. In a simple cubic lattice (coordination number $c = 6$) there are seven possible types of surroundings, each having a statistical weight[1] varying from 1 to 20 (Fig. 7.1).

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[1] These statistical weights arise from the number of ways in which the given surroundings can be realised.

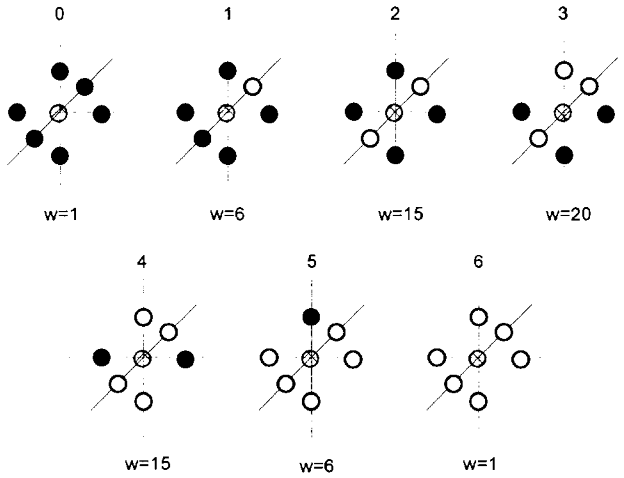

Fig. 7.1. Possible configurations in a binary cubic crystal. The values of *w* represent statistical weights

When molecules *A* and *B* are similar, the total probability of a particular environment is the weighted product of mole fractions to proper powers. The free energy of particles *A* can then be written as:

$$\begin{aligned}F_A = kTN_A\Big(&x_A^6 \ln z_{A0} + 6x_A^5 x_B \ln z_{A1} + 15x_A^4 x_B^2 \ln z_{A2} + 20x_A^3 x_B^3 \ln z_{A3} \\ &+ 15x_A^2 x_B^4 \ln z_{A4} + 6x_A x_B^5 \ln z_{A5} + x_B^6 \ln z_{A6}\Big)\end{aligned} \tag{7.7}$$

in which z_{Ai} are the partition functions of molecules in corresponding surroundings (a similar expression can be written for particles *B*). Such an initial equation promises a complicated derivation that hardly provides for an analytical solution.

The problem is considerably simplified when we consider the effects of just *two neighbours along a coordinate* (Fig. 7.2).

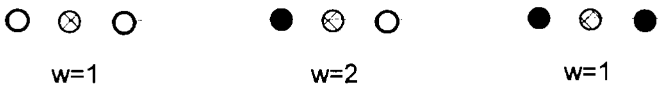

Fig. 7.2. Three types of possible environment along a coordinate in a cubic lattice

We may then sum over three coordinates and afterwards over molecules. This mode of calculation implies that the motion of molecules along three spatial coordinates is independent. This simplification is valid for not very strong interactions (such as in molecular crystals). Another implication is that this model takes into account triple interactions (which are harder to estimate than binary interactions) but of a primitive kind, *viz.* those with three interacting particles lying on one line (bond angle 180°). The free energy *per degree of freedom* of a molecule in a simple cubic lattice under the defined conditions is:

$$f_A = -kT \ln z_{iAj} \tag{7.8}$$

in which the partition function z_{iAj} is dependent on the nature of the two nearest neighbours along a coordinate, mainly through the lattice energy and the frequency of vibration:

$$z_{iAj} = e^{-u_{iAj}/3kT} \times z_{\text{int}} \times g_A e^{-\varepsilon_A^0/3kT} \times \left[2\sinh\left(\frac{h\nu_{iAj}}{2kT}\right)\right]^{-3} \tag{7.9}$$

The electronic partition function, $g_{A(B)}\exp(-\varepsilon_A^0/3kT)$, as well as other internal degrees of freedom of particles, can be considered as unaffected by the surroundings. The vibrational frequency, ν_{iAj}, is dependent on the surroundings due to the varying *depth and width* of the potential well. The factor 1/3 that is applied to the energies u_{iAj} and ε_A^0 indicates that these energies are calculated *per linear oscillator*. Molecular lattice energies, $u^0_{i*j}/3$ can be estimated as the potential energies of triple molecular interactions ($i*j$); they can also be approximated as one third of the potential energy of a molecule in the surroundings containing proportional quantities of components, A_6 ($A*A$), B_6 ($B*B$) or A_3B_3 ($A*B$) (the asterisk indicating *any* molecule).

Summing (7.8) over coordinates[2] and molecules of each kind and adding the configurational entropy, we get the free energy of a binary mixture in an isotropic crystal as[3]:

$$\begin{aligned} F = \; & -kTN\Big[3x_A\left(x_A^2 \ln z_{AAA} + 2x_Ax_B \ln z_{AAB} + x_B^2 \ln z_{BAB}\right) \\ & + 3x_B\left(x_A^2 2\ln z_{ABA} + 2x_Ax_B \ln z_{ABB} + x_B^2 \ln z_{BBB}\right) - x_A \ln x_A - x_B \ln x_B\Big] \end{aligned} \tag{7.10}$$

in which $N = N_A + N_B$ and x_A, x_B are the mole fractions of corresponding molecules. The terms $-3kTN\ln(z_{iAj})$ and $-3kTN\ln(z_{iBj})$ in (7.10) can be considered as the *standard free energies* of molecules in corresponding surroundings:

$$F_{i*j} = -3kTN \ln z_{i*j} \tag{7.11}$$

The free energy of such a system can therefore be expressed as:

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[2] If a crystal is isotropic, then the summation over coordinates is equivalent to multiplying ln*z* by 3, *i.e.* by cubing the partition function.

[3] The configurations *ABB* and *BBA* are considered to be indistinguishable (as are also *AAB* and *BAA*).

$$F = x_A\left(x_A^2F_{AAA} + 2x_Ax_BF_{AAB} + x_B^2F_{BAB}\right) + x_B\left(x_A^2F_{ABA} + 2x_Ax_BF_{ABB} + x_B^2F_{BBB}\right) + NkT\left(x_A \ln x_A + x_B \ln x_B\right) \tag{7.12}$$

Note that the standard free energies, F_{ijk}, form a three dimensional (cubic) matrix F(2 × 2 × 2) and the polynomial part of (7.9) is the sum of the products of F_{ijk} by the corresponding $x_ix_jx_k$. The coefficients 2 in (7.12) just reflect the identity of non-diagonal elements in the upper and lower 'half-cubes'.

In a mixture with a negligibly small difference in molecular interactions, we can assume that $F_{iAj} \cong F_A$, $F_{iBj} \cong F_B$. The terms in square brackets in (7.12) are then transformed into $(x_A + x_B)^2F_{A(B)} = F_{A(B)}$ corresponding (as might be expected) to an ideal crystal. A similar situation occurs in dilute solid solutions of molecules A and B in a third (inert) component S where the predominant species are SAS and SBS ($x_S \cong 1 = const.$):

$$F = x_Ax_S^2F_{SAS} + x_Bx_S^2F_{SBS} + NkT\left(x_A \ln x_A + x_B \ln x_B + x_S \ln x_S\right) \tag{7.13}$$

This equation does not contain cross terms involving both reacting species and is therefore an analogue of the expression for the free energy of an ideal crystal (see also Section 7.11)

7.3
Exchange free energy

Expressing the free energy (7.12) as a function of one variable (x_A), we get:

$$F = x_A^3\Delta^{(3)} + x_A^2\Delta^{(2)} + x_A\Delta^{(1)} + F_{BBB} + NkT\left[x_A \ln x_A + (1 - x_A)\ln(1 - x_A)\right] \tag{7.14}$$

in which:

$$\Delta^{(3)} = \left(F_{AAA} + F_{BAB} - 2F_{AAB}\right) - \left(F_{BBB} + F_{ABA} - 2F_{ABB}\right) \tag{7.15}$$

$$\Delta^{(2)} = F_{ABA} - 4F_{ABB} + 2F_{AAB} - 2F_{BAB} + 3F_{BBB} \tag{7.16}$$

$$\Delta^{(1)} = F_{BAB} + 2F_{ABB} - 3F_{BBB} \tag{7.17}$$

The coefficients of the cubic, square, and linear terms are interrelated:

$$\Delta^{(1)} = -\Delta^{(0)} - \Delta^{(2)} - \Delta^{(3)} \tag{7.18}$$

in which the term $\Delta^{(0)}$ can be identified with the ideal part of the standard free energy:

$$\Delta^{(0)} = F_{\mathrm{BBB}} - F_{\mathrm{AAA}} = \Delta E - T\Delta S \tag{7.19}$$

Equation (7.14) can then be written in the following equivalent forms, thus elucidating the nature of the non-ideality terms:

$$F = -x_A\left(1 - x_A^2\right)\Delta^{(3)} - x_A\left(1 - x_A\right)\Delta^{(2)} - x_A\Delta^{(0)} + F_{BBB} + TN\Delta s_m \tag{7.20a}$$

$$F = -x_B\left(1 - x_B\right)\left(2 - x_B\right)\Delta^{(3)} - x_B\left(1 - x_B\right)\Delta^{(2)} + x_B\Delta^{(0)} + F_{AAA} + TN\Delta s_m \tag{7.20b}$$

$$F = -x_A x_B\left(1 + x_A\right)\Delta^{(3)} - x_A x_B\Delta^{(2)} - x_A\Delta^{(0)} + F_{BBB} + TN\Delta s_m \tag{7.20c}$$

$$F = -x_A x_B\left(2x_A + x_B\right)\Delta^{(3)} - x_A x_B\Delta^{(2)} + x_A F_{AAA} + x_B F_{BBB} + TN\Delta s_m \tag{7.20d}$$

in which the mixing entropy, Δs_m, can be written as:

$$\Delta s_m = k\left[x_A \ln x_A + \left(1 - x_A\right)\ln\left(1 - x_A\right)\right] = k\left[x_A \ln x_A + x_B \ln x_B\right] \tag{7.20e}$$

Comparing (7.20c) and (7.6), we find that the coefficient $\Delta^{(2)}$ plays the role of the exchange energy. The set of four coefficients $\Delta^{(0)}$ – $\Delta^{(3)}$ in these equations represents the least number of adjustable parameters (the free energies F_{BBB} or F_{AAA} can be considered as the zero level). At first sight the coefficients $\Delta^{(1)}$, $\Delta^{(2)}$ and $\Delta^{(3)}$ as defined by (7.15) – (7.17) do not possess any explicit physical significance. They are just combinations of the free energies of molecules in different surroundings. These free energies form, however, a system of energy levels (an example of which is shown in Fig. 7.3). The diagram in this Figure implies that a particle having higher free energy causes the free energy of its neighbours to increase and inversely the particle having lower free energy decreases the free energy of its neighbours.

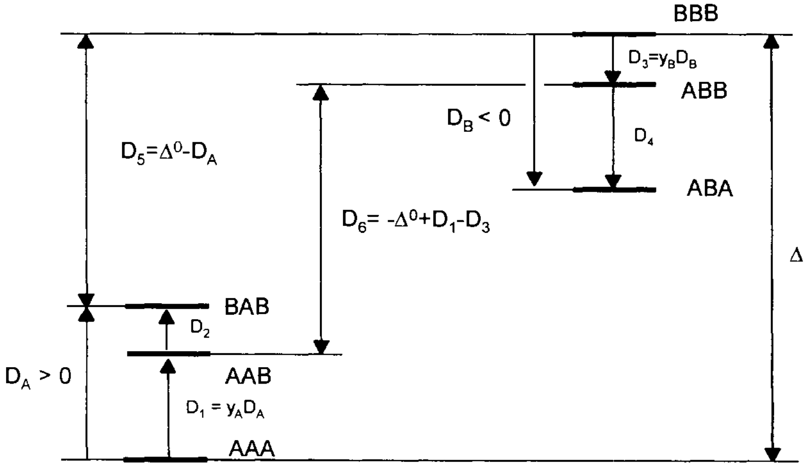

Fig. 7.3. Free energy level diagram of a binary mixture with significant non-additive influence of the nearest surroundings

Table 7.1. Representations of the coefficients Δ in (7.14) in terms of binary differences of standard free energies[4]

$D_1 = F_{AAB} - F_{AAA}$	$2D_5 = 2(F_{BBB} - F_{BAB})$	$-D_5 = F_{BAB} - F_{BBB}$
$D_2 = F_{BAB} - F_{AAB}$	$2D_6 = 2(F_{AAB} - F_{BBA})$	$2D_3 = 2(F_{BBA} - F_{BBB})$
$D_3 = F_{BBA} - F_{BBB}$	$-D_3 = F_{BBB} - F_{BBA}$	
$D_4 = F_{ABA} - F_{BBA}$	$D_4 = F_{ABA} - F_{ABB}$	
$\Delta^{(3)} = (D_2 - D_1) - (D_4 - D_3)$	$\Delta^{(2)} = 2D_5 + 2D_6 - D_3 + D_4$	$\Delta^{(1)} = -D_5 + 2D_3$
$\Delta^{(3)} = (1 - 2y_A)D_A - (1 - 2y_B)D_B$	$\Delta^{(2)} = (1 - 4y_B)D_B - 2(1 - y_A)D_A$	$\Delta^{(1)} = D_A + 2y_B D_B - \Delta^0$

An important property of the coefficients $\Delta^{(i)}$ is that they can be represented as combinations of *binary differences* of free energies as shown in Table 7.1. The coefficients $\Delta^{(1)} - \Delta^{(3)}$ can then be represented in terms of four parameters: D_A, D_B, y_A, y_B, having clear physical significance. The differences of free energies D_A and D_B characterise the effects of the formation of completely *hetero*-surroundings of the molecules A and B separately:

$$D_A = D_1 + D_2 = F_{BAB} - F_{AAA}; \quad D_B = D_3 + D_4 = F_{ABA} - F_{BBB} \tag{7.21}$$

The *dimensionless* coefficients y_A and y_B characterise the relative efficiency of the first substitution in a homo-environment:

$$y_A = \frac{D_1}{D_A} = \frac{F_{AAB} - F_{AAA}}{D_A}; \qquad y_B = \frac{D_3}{D_B} = \frac{F_{ABB} - F_{BBB}}{D_B} \tag{7.22}$$

Using these notations, (7.14) can be written as:

$$\begin{aligned} F = {} & x_A^3\left[(1-2y_A)D_A - (1-2y_B)D_B\right] + x_A^2\left[(1-4y_B)D_B - 2(1-y_A)D_A\right] \\ & + x_A\left(D_A + 2y_B D_B - \Delta^0\right) + F_{BBB} + NT\Delta s_m \end{aligned} \tag{7.23}$$

When the effects of first and second substitutions in the environment of a given molecule along a coordinate are identical:

$$F_{AAA} - F_{AAB} = F_{AAB} - F_{BAB}; \qquad F_{BBB} - F_{ABB} = F_{ABB} - F_{ABA} \tag{7.24}$$

the levels corresponding to asymmetric surroundings (F_{AAB}, F_{ABB}) lie in the middle between the levels of symmetric surroundings ($F_{AAA} - F_{BAB}$ and $F_{BBB} - F_{ABA}$). The coefficients y_A and y_B are then exactly ½. It can be said that the effects of the surroundings under these conditions are *additive* and *the standard free energy of a molecule in asymmetric surroundings is the arithmetic mean of the free energies of the same molecule in symmetric surroundings:*

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[4] There are four possible combinations of the effects of surroundings in a binary mixture ($D_A > 0$, $D_B < 0$; $D_A > 0$, $D_B > 0$; $D_A < 0$, $D_B > 0$ and $D_A < 0$, $D_B < 0$) and for each case the relationships shown in Table 7.1 hold.

$$F_{A*B} = \left(F_{A*A} + F_{B*B}\right)/2 \tag{7.25}$$

Under these conditions the coefficient $\Delta^{(3)}$ is zero irrespective of the actual signs and magnitudes of D_A and D_B whilst the other two coefficients ($\Delta^{(2)}$ and $\Delta^{(1)}$) contain only the diagonal elements of the matrix **F**:

$$\Delta^{(2)} = -\left(D_A + D_B\right) = -\left(F_{BAB} - F_{AAA} + F_{ABA} - F_{BBB}\right) \tag{7.26}$$

$$\Delta^{(1)} = -\Delta^{(0)} - \Delta^{(2)} = -\Delta^{(0)} + D_A + D_B \tag{7.26a}$$

The sum $D_A + D_B$ is obviously an analogue of the exchange energy and may be called the *exchange free energy*:

$$\Delta F_{ex} = D_A + D_B = F_{BAB} - F_{AAA} + F_{ABA} - F_{BBB} \tag{7.27}$$

A non-zero cubic term is therefore connected with a certain non-equivalence of the effects of first and second substitutions. Such a non-equivalence or non-additivity indicates an interaction not taken explicitly into account. In fact, we have assumed the independence of these effects along three spatial coordinates, which ignores any interaction 'along a diagonal'. Therefore the coefficients y_A and y_B may well deviate from ½. For example, suppose that molecule B is larger than molecule A as occurs in spin crossover reactions. The transformation $A \rightarrow B$ in a cluster of molecules A shifts the equilibrium positions of the central molecule (Fig. 7.4A). Such a transformation also changes the interaction of the central molecule A with two molecules along another coordinate. A second substitution restores the initial symmetry.

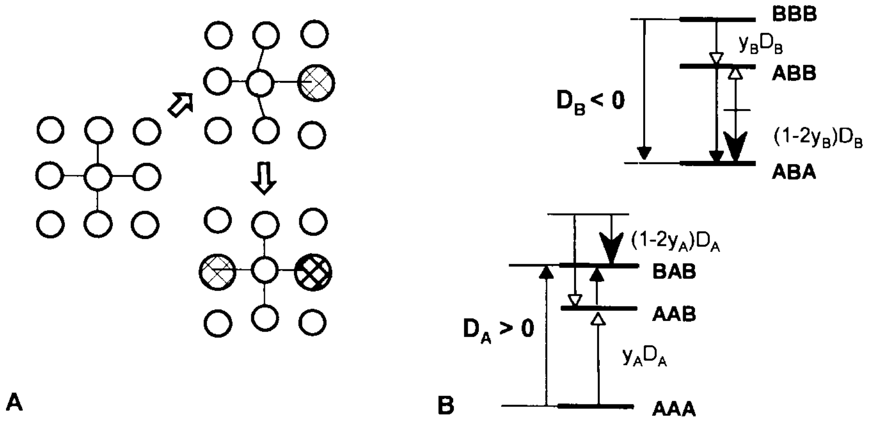

Fig.7.4. The difference in the effects of first and second substitutions in the surroundings of a molecule (**A**) and the free energy level diagram with opposite signs of D_A and D_B complying with condition (7.29) (**B**)

The cubic term in (7.23) may also be zero when $y_A \neq y_B \neq ½$: the deviations from additivity for the central molecules A and B may compensate each other (possible for either identical or opposite signs of D_A and D_B, – the latter case being illustrated in Fig. 7.4B):

$$(1-2y_A)D_A = (1-2y_B)D_B \tag{7.28}$$

Under the condition (7.28) the coefficients $\Delta^{(2)}$ and $\Delta^{(1)}$ are transformed into:

$$\Delta^{(2)} = -(2y_B D_B + D_A)\,; \qquad \Delta^{(1)} = -\Delta^{(0)} + 2y_B D_B + D_A \tag{7.29}$$

According to (7.29) the exchange free energy is smaller by $(1-y_B)D_B$, otherwise the formalism is the same as in the case of $y_A = y_B = ½$. The free energy of a binary mixture under the conditions providing for a zero cubic term can be written as:

$$F = x_A(1-x_A)\Delta F_{ex} + x_A(F_{AAA} - F_{BBB}) + F_{BBB} + NT\Delta s_m \tag{7.30}$$

or:

$$F = x_A x_B \Delta F_{ex} + x_A F_{AAA} + x_B F_{BBB} + NT\Delta s_m \tag{7.31}$$

In the approximation of regular solutions ($\Delta S_{ex} = 0$) we can substitute the exchange free energy by the exchange energy ΔE_{ex}:

$$F = x_A x_B \Delta E_{ex} + x_A F_{AAA} + x_B F_{BBB} + NT\Delta s_m \tag{7.32}$$

The equation (7.32) then becomes identical to (7.6) when:

$$F_{AAA} = -NkT \ln z_A + \frac{Nc}{2}\varphi_{AA}\,; F_{BBB} = -NkT \ln z_B + \frac{Nc}{2}\varphi_{BB}\,;$$

and:

$$\Delta E_{ex} = Nc\Delta u_{ex} \tag{7.32a}$$

The developed formalism can therefore be reduced to that of regular solution theory if we neglect (i) the contribution from triple interactions (the cubic term in (7.14)) and (ii) the effects of the surroundings on vibrational frequencies ($\Delta F_{ex} = \Delta E_{ex}$).

When the exchange energy approaches zero, we obtain the expression for free energy identical to that of *perfect solutions* [1,4]:

$$F = x_A F_{AAA} + x_B F_{BBB} + NkT[x_A \ln x_A + x_B \ln x_B] \tag{7.33}$$

The effects of the surroundings (D_A,D_B) must not necessarily be negligibly small: it is sufficient that *they are of equal magnitude and opposite sign*:

$$i.e. \qquad D_A = -D_B \tag{7.34}$$

We shall later see that such an occurrence in not anything extraordinary and practically linear van't Hoff plots in strongly non-ideal systems might originate from such a balance.

7.4
Phase separations in binary mixtures

Although the formalism presented above has been derived for imperfect crystals it can be applied (at temperatures not far from the melting point) to liquid mixtures. The restrictions placed on such extrapolations are connected with the absence of any periodic structure in liquids and amorphous solids. For example, a description of a solid body employing a single Debye temperature can only be successful for a periodic crystal. Thermodynamic properties of amorphous and liquid bodies require for their calculation a knowledge of the *Debye spectrum. So long as we do not employ features associated with the periodicity of a crystal, we may use a common formalism for liquids and for solids.*

In Chapter 3 we have shown that mole fractions may be used in the law of mass action for liquid systems when the volume per molecule remains approximately constant. The molecular partition function is then of the form (3.90):

$$z_A = \left(\frac{(2\pi m_A kT)^{3/2}}{h^3} ev \right) z_{A\,\mathrm{int}} e^{-\frac{\varepsilon_A + u_A}{kT}} \tag{7.35}$$

in which $v = V/(N_\mathrm{A} + N_\mathrm{B})$. The variation of v and z_{Aint} from surroundings to surroundings partly determines the entropy of exchange. The required independence of v thus limits possible variations of the entropic term. The lattice energy, u_A, may vary considerably depending on the surroundings, which is taken into account in the form of exchange energy. With these reservations, knowledge of an explicit form of the partition function is not required, provided that the molecular standard free energies f_A, f_B and the exchange free energy Δf_{ex} are defined.

Let us consider a liquid mixture of *non-reacting* molecules A and B in equilibrium with its gaseous phase and examine the relationship between the compositions of these phases. The gaseous phase we can treat as an ideal gas whilst the non-ideality of the liquid phase can be taken into account by applying an expression derived for an imperfect mixed crystal with additive effects of the surroundings. (We can drop three letter indices of standard free energies since they are now redundant.) Equation (7.32) can therefore be written with respect to the numbers of molecules as:

$$F = \frac{N_A N_B}{N_A + N_B} \Delta f_{ex} + N_A f_A + N_B f_B + kT\left(N_A \ln x_A + N_B \ln x_B\right) \tag{7.36}$$

Differentiating (7.36) with respect to N_A yields the chemical potential of this component in the liquid phase:

$$\mu_{AL} = \left(\frac{\partial F}{\partial N_A}\right)_{N_B,T,V} = x_B^2 \Delta f_{ex} + f_A + kT \ln x_A \tag{7.37}$$

The chemical potential of the *same molecule* in the gas phase *treated as an ideal gas* is:

$$\mu_{AG} = -kT \ln q_{AG} + kT \ln p_A \tag{7.38}$$

in which $q_{AG} = (2\pi m_A kT/h^2)^{3/2} ekT$ and p_A is the partial pressure of the component A. The chemical potential of molecules A in pure liquid component A ($x_A = 1$) is the free energy per molecule $\mu^0{}_{AL} = f_A$. At equilibrium, the chemical potentials in the gas and liquid phases are equal, therefore:

$$\mu^0_{AL} = f_A = \mu^0_{AG} = -kT \ln q_{AG} + kT \ln p^0_A \tag{7.39}$$

in which $p_A{}^0$ is the (saturated) vapour pressure over the pure component A.

In a mixture of components A and B, the chemical potentials of the component A in the liquid and the gaseous phases are:

$$\mu_{AL} = x_B^2 \Delta fex + \mu^0_{AG} + kT \ln x_A ; \mu_{AG} = \mu^0_{AG} + kT \ln\left(p_A / p^0_A\right) \tag{7.40}$$

At equilibrium they must be equal, therefore:

$$x_B^2 \Delta f_{ex} + kT \ln x_A = kT \ln\left(p_A / p^0_A\right) \tag{7.41}$$

or:

$$p_A / p^0_A = x_A \exp\left[\frac{(1 - x_A)^2 \Delta f_{ex}}{kT}\right] \tag{7.42}$$

This dependence of partial pressure on the composition of the solution has several interesting features. It may have extrema at compositions given by the roots of:

$$\frac{d\left(p_A / p^0_A\right)}{dx_A} = \frac{2\Delta f_{ex}}{kT} x_A^2 - \frac{2\Delta f_{ex}}{kT} x_A + 1 = 0 \tag{7.43}$$

i.e.

$$x_{Ae} = \frac{\alpha \pm \sqrt{\alpha^2 - 2\alpha}}{2\alpha} \tag{7.44}$$

in which $\alpha = \Delta f_{ex}/kT$. The real roots of (7.43) are obtained when $\alpha > 2$. When $\alpha = 2$ there is just one deflection point with $dp/dx_A = 0$, namely at $x_{Ae} = ½$. For $\alpha > 2$, there is a maximum and a minimum in the curve $p(x)$ (Fig. 7.5). *In such cases, three* different *compositions correspond to the same vapour pressure, which is incompatible with the idea of a homogeneous system.* This means that such a system can only exist as a mixture of separate condensed phases over a certain range of compositions. Fig. 7.5B shows how the total vapour pressure changes with the composition of such a liquid phase.

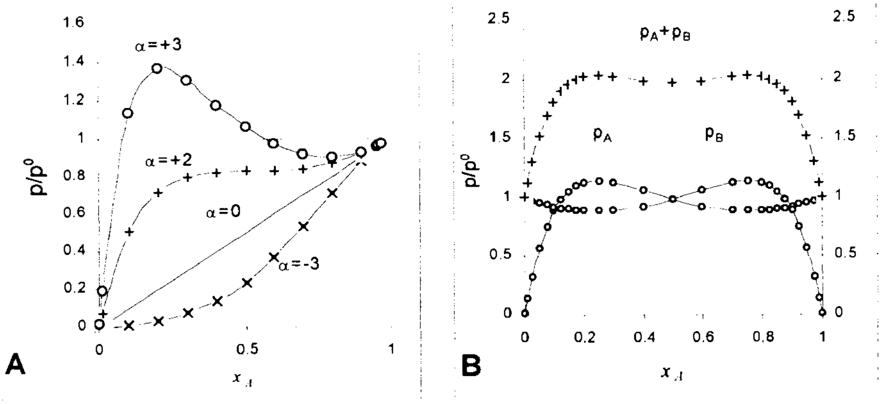

Fig. 7.5. Partial vapour pressure as a function of the composition of a binary mixture for different values of $\alpha = \Delta f_{ex}/kT$.(**A**) The right-hand graph (**B**) shows partial and total vapour pressures over the mixture with $\alpha = \Delta f_{ex}/kT = 2.7$ and with equal $p_A{}^0$ and $p_B{}^0$. Note that the total pressure is higher than that in an ideal mixture, which shows that a mixture having a tendency to phase separation would boil at lower temperature than either of its components. This phenomenon is used in the purification of organic compounds by *steam distillation*.

Phase transitions in a non-ideal binary liquid mixture ($\Delta E_{ex} \neq 0$) can be followed using the diagrams x_{Agas} *vs.* x_{Aliq}. The composition of the gas phase (ideal gas approximation) can be calculated to be $x_{AG} = p_A/(p_A + p_B)$. Fig. 7.6 shows such curves computed for a system with slightly different vapour pressures of pure components ($p_B{}^0 = 0.78 p_A{}^0$) and $\alpha = \Delta F_{ex}/kT = -3$, $+2$ and $+2.7$. For negative and small positive ($\alpha < 2$) exchange energies, a single point exists at which the composition of the vapour phase is identical to the composition of the liquid phase. This is obviously an *azeotropic* mixture. At any other composition a sample being *completely*[5] evaporated (up arrows in Fig. 7.6) *starts to condense* (down arrows in Fig. 7.6) as a liquid mixture of *another composition.* The new liquid phase is depleted/enriched in one of the components as shown in Figs. 7.6.

In the special case of a large positive exchange energy (Fig. 7.6C), there is a region of composition where two or three compositions of the liquid phase correspond to one and the same composition of the gas phase. The sample containing *ca.* 60% (molar) of the component *A* being completely evaporated, starts to condense as a mixture of solutions of *A* in *B* and *B* in *A* (solid arrows in Fig. 7.6C). These solutions are *saturated* (*i.e.* correspond to a minimum in the free energy) at the *actual temperature* of condensation. The dashed arrow indicates the composition of a non-existing (metastable) homogeneous liquid solution corresponding to the gaseous mixture containing 60% of component *A*.

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[5] *I.e.* when the composition of the gas phase is identical with the composition of the original liquid phase (the diagonal lines in Fig. 7).

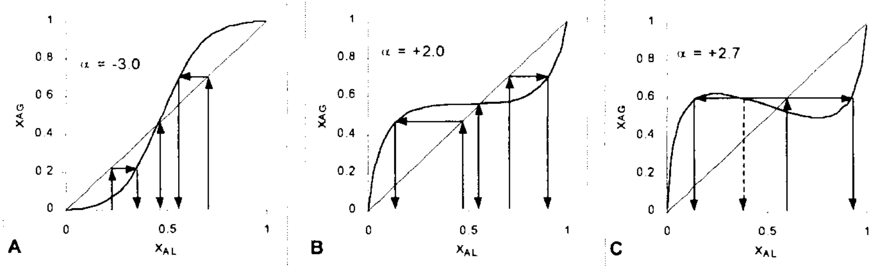

Fig. 7.6. Compositions of the vapour phase of binary mixtures with different exchange energies

This model qualitatively pictures the behaviour of the vapour pressure over mixtures of liquids with limited miscibility (*e.g.* aqueous solutions of higher alcohols). If Δf_{ex} is large and 'temperature independent' ($\Delta s_{ex} = 0$), then (7.43) implies that a temperature exists below which liquids cannot be mixed in any proportion, the so-called *critical temperature of miscibility*. Water and propylene carbonate are miscible in any proportions above 73 – 75°C but separate into two phases at lower temperatures – an effect employed in the 'homogeneous' extraction of metal salts [5].

7.5

The law of mass action for an imperfect mixture in the condensed state

Suppose now that molecules A and B can transform into each other, *i.e.* a monomolecular equilibrium exists in an imperfect system as described above:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{7.45}$$

The law of mass action for this reaction can be obtained by differentiating (7.14) with respect to x_A:

$$\frac{dF}{dx_A} = 3x_A^2\Delta^{(3)} + 2x_A\Delta^{(2)} + \Delta^{(1)} - NkT\left[\ln(1-x_A) - \ln x_A\right] \tag{7.46}$$

which leads, taking into account (7.18), to[6]:

$$3x_A^2\frac{\Delta^{(3)}}{NkT} + 2x_A\frac{\Delta^{(2)}}{NkT} - \frac{\Delta^{(0)} + \Delta^{(2)} + \Delta^{(3)}}{NkT} - \ln\frac{1-x_A}{x_A} = 0 \tag{7.47}$$

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[6] Equations of the law of mass action in this Chapter appear to be different when compared to the similar equations in Chapter 4. This is because free energies are proportional to the *negative* logarithms of the partition functions $\ln q_{A(B)}$.

This law of mass action contains linear and quadratic terms (with respect to x_A), the latter being the result of accounting for triple interactions. One can expect that when higher order interactions are taken into account, the terms with higher powers of x_A will appear in the law of mass action.

Inversely, when binary interactions only are taken into account, *i.e.* when:

$$y_A = y_B = \tfrac{1}{2}; \quad 2F_{AAB} = F_{BAB} + F_{AAA}; \quad 2F_{ABB} = F_{BBB} + F_{ABA} \tag{7.48}$$

the quadratic term in (7.47) disappears and non-ideality under these conditions is described by the linear term proportional to exchange energy:

$$-2x_A \frac{\Delta F_{ex}}{NkT} - \frac{\Delta^{(0)} - \Delta F_{ex}}{NkT} - \ln\frac{1-x_A}{x_A} = 0 \tag{7.49}$$

Equation (7.49) can also be written in the following equivalent forms:

$$(1-2x_A)\frac{\Delta F_{ex}}{NkT} - \frac{\Delta E - T\Delta S}{NkT} - \ln\frac{1-x_A}{x_A} = 0 \tag{7.50}$$

$$(1-2x_B)\frac{\Delta F_{ex}}{NkT} + \frac{\Delta E - T\Delta S}{NkT} - \ln\frac{1-x_B}{x_B} = 0 \tag{7.51}$$

in which $\Delta E - T\Delta S = F_{BBB} - F_{AAA}$. The non-ideality terms in these laws of mass action (including the general expression (7.47)) can be transformed into activities if they are much smaller than 1. The small parameter can be either x_A (dilute solutions) or the coefficients $\Delta^{(i)}$ (weak interactions with respect to kT). The law of mass action (7.47) can be reduced (see Appendix 10.9) to:

$$-\frac{\Delta^{(0)}}{NkT} - \ln\left[x_B\left(1 + x_B\frac{\Delta^{(2)}}{NkT} - x_B^2\frac{1.5\Delta^{(3)}}{NkT}\right)\right] + \ln\left[x_A\left(1 + x_A\frac{\Delta^{(2)}}{NkT} + x_A^2\frac{1.5\Delta^{(3)}}{NkT}\right)\right] = 0 \tag{7.52}$$

The effects of triple interactions introduce a certain asymmetry into the activity coefficients of reactant and product (quadratic terms have different signs). The law of mass action (7.47) written with respect to one variable shows that dilute solutions of one component in another (very small x_A) are described by a practically ideal law of mass action with the effective free energy of reaction $\Delta F^0 = \Delta^{(0)} + \Delta^{(1)} + \Delta^{(2)}$. *This does not follow from* (7.52) *employing activities.*

The laws (7.50) and (7.51) (valid for systems with zero cubic term) can also be written in a pseudo-ideal form with respect to activities (assuming $|x_A\Delta F_{ex}/kT| << 1$ and taking into account the fact that $1 - 2x_A = x_B - x_A$):

$$-\frac{\Delta E^0 - T\Delta S^0}{NkT} - \ln\frac{a_B}{a_A} = 0 \tag{7.53}$$

in which the activities are polynomials of the second order:

$$a_A = x_A\left(1 - x_A\frac{\Delta F_{ex}}{NkT}\right); \qquad a_B = x_B\left(1 - x_B\frac{\Delta F_{ex}}{NkT}\right) \tag{7.54}$$

Systems highly diluted by an inert component (S) behave similarly to perfect solutions as indicated by (7.13) above. This equation yields the following law of mass action:

$$-x_S^2\frac{F_{SBS} - F_{SAS}}{NkT} - \ln\frac{1 - x_A}{x_A} = 0 \tag{7.55}$$

In Chapter 3 we considered an example of spin crossover equilibrium in a very dilute solid solution of a spin crossover complex in its diamagnetic analogue: $[Fe_yZn_{1-y}(ptz)_6](BF_4)_2$. Equation (7.55) shows that the estimates obtained for ΔE^0 and ΔS^0 should be corrected by taking into account the factor x_S^2. It will not, however, be a significant correction for the considered spin crossover equilibrium since the fraction of 'solvent' is close to 1 ($x_S = 0.995$).

In non-diluted systems, the law of mass action can also approach that for a perfect solution when ΔF_{ex} becomes negligibly small compared to kT. The effects of the surroundings must either be small ($|D_A| << kT$ and $|D_B| << kT$) or balance each other ($D_A \cong -D_B$). The latter case is apparently realised in the spin crossover equilibrium in crystalline $[Fe(2\text{-picolylamine})_3]Cl_2CH_3OH$ exhibiting, as it does, a nearly linear van't Hoff plot over a wide range of degrees of conversion (0.03 - 0.93) (See Fig. 7.7A). It is hardly possible that the structure of this compound excludes interaction between HS and LS species: a bulkier solvating molecule C_2H_5OH results in a steep spin crossover indicating molecular interactions (Fig. 7.7B). Therefore the approximately linear van't Hoff plot for spin crossover in the methanolic solvate reflects, most probably, the approximate equality $D_A \cong -D_B$.

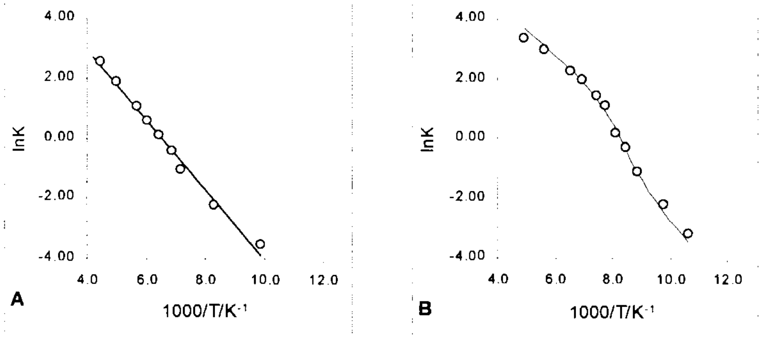

Fig. 7.7. Van't Hoff plots for spin crossover: linear in the case of $[Fe(2\text{-pic})_3]Cl_2CH_3OH$ (A) and S-shaped for $[Fe(2\text{-pic})_3]Cl_2C_2H_5OH$ (B) drawn using the data in [6]. The curve in the right-hand graph is the best fit according to (7.51) with $\Delta E^0 = 1.85$ kcal mol^{-1}, $\Delta S^0 = 15.3$ cal mol^{-1}K^{-1} and $\Delta E_{ex} = 250$ cal mol^{-1}, $\Delta S_{ex} = 0$

7.6

The regular solution model of steep spin crossover

A more pronounced curvature of the van't Hoff plot is observed for spin crossover in pure crystalline $[Fe(ptz)_6](BF_4)_2$ (see Fig. 7.8). The temperature dependence of the internal vibrational partition functions may account for a positive curvature (see page 93) but *not* for an *S*-shaped van't Hoff plot. Slichter and Drickamer [7] explained these phenomena using a phenomenological equation of the law of mass action for regular solutions:

$$(1-2x_B)\Gamma + \Delta G^0 = kTN \ln \frac{1-x_B}{x_B} \qquad (7.56)$$

in which Γ is an interaction constant and ΔG^0 is the standard Gibbs free energy of spin crossover. For not very high pressures, this equation can be considered (the term pdV being small) as identical with (7.51). The interaction constant Γ is then identical with the exchange energy ΔE_{ex} and ΔG^0 corresponds to $F_{BBB} - F_{AAA}$. Equation (7.56), in general, correctly describes transition curves and van't Hoff plots of steep spin crossover (*e.g.* that for $[Fe(ptz)_6](BF_4)_2$, Fig. 7.8A). However, in the regions of dilute solutions of one component in another, the theoretical curves deviate from experimental data. When the *relative regression error* is optimised (dashed line in Fig. 7.8A) the region of low HS content is best fitted, whereas when the *absolute error* is optimised (solid line in Fig. 7.8A) the best agreement is achieved in the region of high HS content. These deviations probably arise from insufficient accuracy when calculating equilibrium constants at very low or very high x_{HS}.

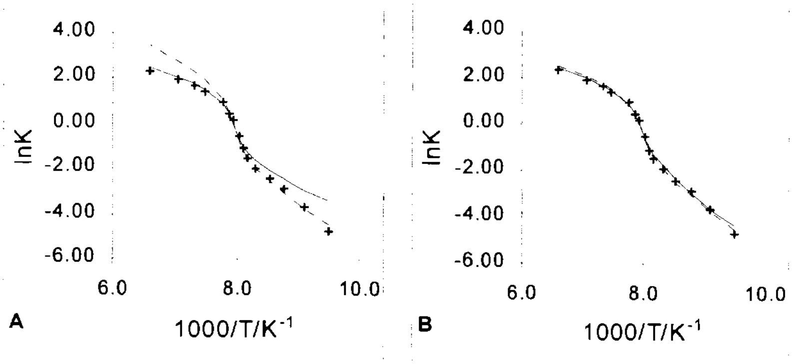

Fig. 7.8. Temperature dependence of the equilibrium constant of spin crossover in pure $[Fe(ptz)_6](BF_4)_2$ [8] described by (7.51) assuming $\Delta S_{ex} = 0$ (left-hand graph) and $\Delta S_{ex} \neq 0$ (right-hand graph) (see Table 7.2). Dashed lines correspond to optimised relative and solid lines to optimised absolute regression errors

Table 7.2. Estimates of the parameters of the spin crossover equilibrium in [Fe(ptz)$_6$](BF$_4$)$_2$ obtained from the data in Fig. 7.8 using a non-linear regression method, following (7.50)

Parameter	$\Delta S_{ex} \neq 0$		$\Delta S_{ex} = 0$	
	rel. error	abs. error	rel. error	abs. error
ΔE^0/kcal mol^{-1}	2.60 ± 0.01	2.49 ± 0.008	3.21 ± 0.015	1.82 ± 0.01
ΔS^0/cal mol^{-1} K^{-1}	20.68 ± 0.03	19.80 ± 0.05	25.5 ± 0.06	14.4 ± 0.07
ΔE_{ex}/kcal mol^{-1}	1.14 ± 0.07	1.12 ± 0.02	420 ± 19	451 ± 22
ΔS_{ex}/cal mol^{-1} K^{-1}	5.73 ± 0.5	5.62 ± 0.2	0	0

However, a very good agreement can be obtained in both regions when non-zero exchange entropy (Fig. 7.8B) is adjusted. The estimates of ΔE^0, ΔS^0, ΔE_{ex} and ΔS_{ex} are shown in Table 7.2. The fitting of these curves has been done by calculating theoretical values of x_{HS} for given temperatures using (7.51) and employing the dichotomy method.

An 'easier' way of regression analysis, by following (7.50), is to consider temperature as a dependent variable and simulate it as a function of x_{HS}:

$$T = \frac{(1 - 2x_B)\Delta F_{ex} + \Delta E}{\Delta S + R\ln[(1 - x_B)/x_B]} \tag{7.57}$$

In the following examples we assume $\Delta S_{ex} = 0$ and analyse the effects of exchange energy. Equation (7.57) predicts increasing steepness of the transition curves with increasing ΔE_{ex}. At $\Delta E_{ex} = 2RT_{1/2}$, the tangent to the transition curve at the transition point ($x_{HS} = ½$) becomes vertical and at higher ΔE_{ex} this equation yields two or three equilibrium compositions of reaction mixture at a given temperature over a certain range around the transition point (Fig. 7.9). As has been mentioned before, two equilibrium compositions indicate a possible separation of a previously homogeneous solution into individual phases. In the case of spin crossover, the separating phases are those of HS and LS species. They retain, in many cases, an identical type of crystal structure but differ in density and optical properties (colour). Such phase transitions are reversible and occur without any detectable break-up of the sample (which is remarkable!). That such a phase transition might be accompanied by hysteresis has been confirmed experimentally and follows from (7.51) and (7.57). If (7.51) is solved with respect to x_{HS} using the 'consecutive search' method then the results may be different when this search is performed from $x_{HS} = 0$ upwards and from $x_{HS} = 1$ downwards.

For systems with high $\Delta E_{ex} > 2RT_{1/2}$ there are two solutions in the region of the *S*-loop of the transition curve given by (7.57) and illustrated in Fig. 7.9. These methods of search imitate two possible pathways of spin crossover corresponding to heating and cooling of a sample respectively. Why hysteresis is not *always* observed becomes clear when we consider how the free energy of the reaction mixture depends on temperature and composition. Fig. 7.10A shows the temperature dependencies of x_{HS} and the free energy of a significantly non-ideal system ($\Delta E_{ex} \cong 2.5RT_{1/2}$). The dependencies of free energy on *composition* are shown in Fig. 7.10B. When this system is cooled down to temperatures below 246 K, the possibility of building an *LS-rich* phase arises (the second minimum in the dependence of free energy on composition curve in Fig. 7.10B).

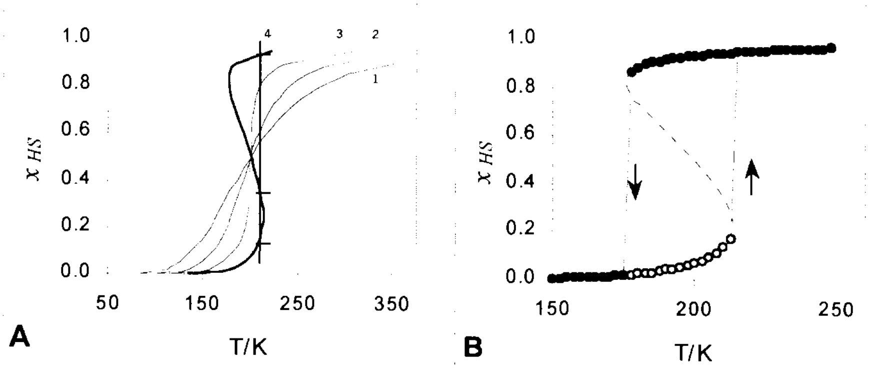

Fig. 7.9. Spin crossover transition curves calculated (**A**) according to (7.51) for $\Delta E^0 = 2.0$ kcal mol^{-1}, $T_{1/2} = 200$ K, $\Delta S_{ex} = 0$ and varying exchange energies: $\Delta E_{ex} = 0$ (1), $RT_{1/2}$ (2) $2RT_{1/2}$ (3) and $3RT_{1/2}$ (4). Graph **B** shows the transition curve for a similar system ($\Delta E_{ex} = 1.2$ kcal mol^{-1}) obtained by numerical solution of (7.51) in the 'cooling mode' (•) and 'heating mode' (o). The dashed line was obtained similarly to the curves in graph **A**

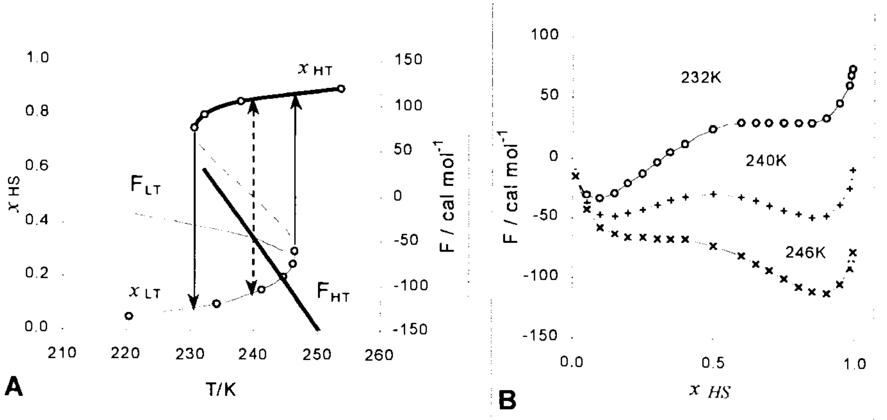

Fig. 7.10. The shape of the spin-crossover curve in the case of high exchange energies $\Delta E_{ex} = 1.2$ kcal mol^{-1}, $\Delta S_{ex} = 0$, $\Delta E^0 = 2.5$ kcal mol^{-1} and $T_{1/2} = 240$ K (**A**). Two crossing lines represent the free energies of HS-rich (HT) and LS-rich (LT) phases. The graph B shows free energy as a function of composition

The formation of an LS-rich phase under these conditions although being *possible*, is highly *improbable* because the macroscopic states corresponding to higher free energy are practically unpopulated[7]. It is only when the temperature reaches $T_{½}$ and the free energies of the HS-rich and LS-rich phases become equal that a real probability exists for the formation of a new phase. A fluctuation of energy or formation of a nucleus of a new phase (for example, an impurity of high crystal field strength that is capable of stabilising the LS state) might overcome the potential barrier between these states. However, if this barrier is high, then a sample can be super-cooled below the transition point. The dashed arrow in Fig. 7.10 indicates, therefore, a possible and probable *but not a necessary* onset of the phase transition in both the cooling and the heating branches of a transition curve.

The height of the potential barrier is proportional to the ratio $\Delta E_{ex}/RT_{½}$ and therefore systems with larger ΔE_{ex} can be more readily super-cooled – in other words, a wider hysteresis has a higher probability of being observed. At 232 K the original minimum of free energy corresponding to the HS-rich phase disappears (Fig. 7.10B) which means that at lower temperatures there is only one stable LS-rich phase. A system must therefore transform *very sharply* into this phase. This process is termed 'switching' (thus indicating its possible use in information storage devices) and is experimentally observed.

Fig. 7.11A shows experimental data on the H_2O solvate of the iron(II) picolylamine complex [7] that exhibits a wide hysteresis and a sharp transition from HS to LS state in the cooling mode.

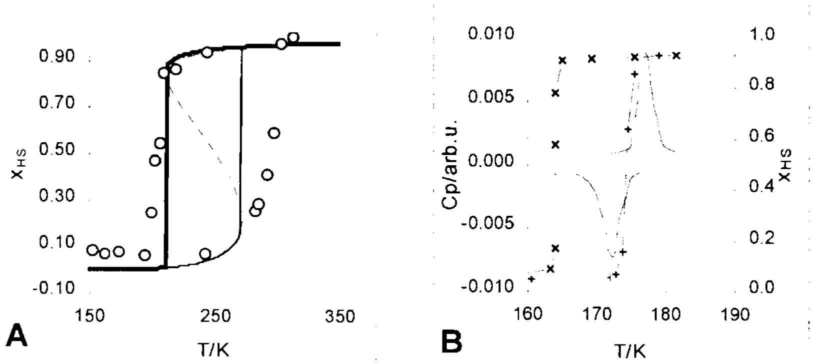

Fig. 7.11. A: Spin crossover transition curve simulated according to (7.51) (solid line) and the experimental data from [7] (o) for the spin crossover of $[Fe(2\text{-pic})_3]Cl_2H_2O$. **B**: Transition curves and heat capacity peaks for the spin crossover in the $FeL(NCS)_2$ complex with an N_4-dentate ligand [9]

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[7] In the same way, the probability that a steel ball of 1.0 g weight will of itself jump up 1 mm is negligibly small notwithstanding the fact that the energy difference between these states is only *ca.* 1 erg – *i.e.* much less than RT at 300 K.

Theoretical curves (obtained by numerical solutions of (7.51) in the 'heating' and 'cooling' modes) correspond to $\Delta E = 2.5$ kcal mol^{-1}, $\Delta E_{ex} = 1.6$ kcal mol^{-1} $\Delta S_{ex} = 0$, and $T_{1/2} = 250$ K. The transition in the heating mode observed experimentally is evidently not so sharp as in the cooling mode, the cause of which remains unclear. Theoretically, the shape of the transition curve of a steep spin crossover, especially one exhibiting hysteresis, cannot be other than a sharp switch. At the transition point ($F_{HS} = F_{LS}$) the composition of a sample is *undetermined* within the range $x_1(T_{1/2}) \leftrightarrow x_2(T_{1/2})$ as indicated by the dashed arrow in Fig. 7.10A.

The experimentally observed average composition is controlled, not by the temperature, but by the *amount of heat transferred to or abstracted from the sample.* In order to be able to discuss the shape of a steep transition curve the sample composition must be determined (by magnetochemical or Mössbauer measurements) *simultaneously* with calorimetric measurements. Unfortunately, to our knowledge no such experiments have yet been conducted. Even when one – and – the same sample is investigated *subsequently* by magneto-chemical and calorimetric measurements the results may differ.

Transition temperatures of the [FeL(NCS)$_2$] complex with N$_4$-dentate ligands of the phenanthroline type [9] determined from magnetic susceptibilities and measurements of specific heat (Fig. 7.11B) do not coincide, probably because of different modes of heating/cooling in corresponding devices. Therefore, it is possible that the shape of a transition curve reflects the impatience of an experimenter rather than reality.

Another complication might arise from the kinetics of spin crossover itself. The exchange between HS and LS states is normally fast but at low temperatures (in general, below 50 K but even at 77 K for some compounds [10]) it becomes slow and fast cooling may trap a metastable HS state. At 10 K such a metastable state can exist for a long time, the rate of the relaxation process being controlled exclusively by tunnelling through the potential barrier. Another way of trapping a metastable HS state is to irradiate a deeply cooled sample (*ca.* 10 K) by light of the appropriate wavelength. The HS state appears then as a result of a series of electron transitions involving a relaxation from the excited LS state. This effect is known as *light induced electron spin state trapping* (LIESST).

7.7
Heat capacity changes in spin crossover

The uncertainty of the composition of a spin crossover compound characterised by high exchange energy ($\Delta E_{ex} \geq 2RT$) predicted by (7.50), (7.51) or (7.57) in the region of switch indicates macroscopically large fluctuations and a first-order phase transition. Such transitions must be accompanied by (infinitely) *high peaks of heat capacity* that are observed experimentally for substances exhibiting steep spin crossover.

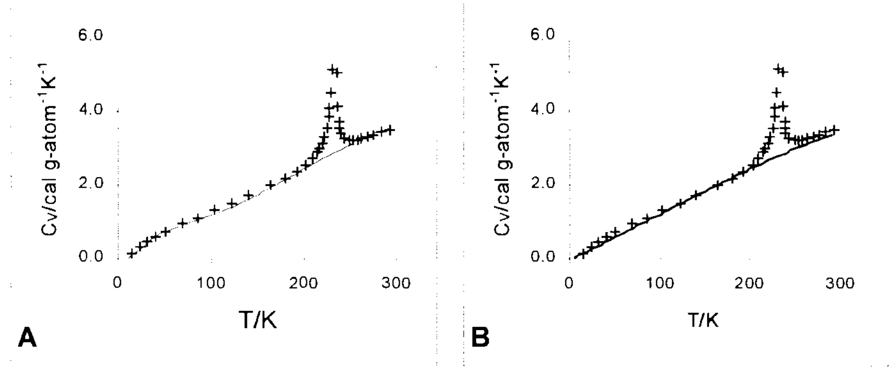

Fig. 7.12. Temperature dependence of the heat capacity of [Fe(phen)$_2$(NCSe)$_2$] drawn from the data in [11] (recalculated per gram-atom). The curve in graph **A** represents the approximation of experimental data (*crosses*) two Debye functions with θ_{D1} = 130 K and θ_{D2} = 1130 K taken in the ratio 1:5. Graph **B** shows the approximation of the same data by a single Tarasov function for one-dimensional crystal (weakly interacting chains) with θ_1 = 1100K.

One of the first observations of this kind was made by Sorai and Seki [11] in their study of spin crossover in [Fe(phen)$_2$(NCSe)$_2$] (See Fig. 7.12). In systems exhibiting *steep* spin crossover the composition of the sample below the transition point is mainly LS and above it mainly HS. The low temperature region of data shown in Fig. 7.12 can therefore be described employing the Debye or the Tarasov approximations (see Chapter 1) for a pure (LS) substance. It proved that these data cannot be described by a single Debye function, but a weighted sum of two functions with drastically different θ_D fits experimental data very well (see Fig. 7.12 A). On the other hand, the same data also fit (although with a lower precision) a single Tarasov function for a one-dimensional crystal ($m = 1$ in (1.156), see Fig 7.12 B). The latter model has the advantage of employing a smaller number of adjusting parameters and providing a clearer physical interpretation of the observed relationship. According to the Tarasov model, [Fe(phen)$_2$(NCSe)$_2$] must be built of weakly interacting polymeric chains with strong atomic interactions (θ = 1100 K) within the chain.

At the transition point there must be a step in heat capacity corresponding to the standard entropy of transition $\Delta S^0 = \Delta E^0/T_{½}$. However, this step is not considerable (0.1 – 0.2 cal g-atom^{-1}, for the system shown in Fig. 7.12).

The peak itself can be described by calculating the heat capacity as:

$$C_V = \frac{\partial}{\partial T}\left[x_{HS}E_{HS} + (1 - x_{HS})E_{LS}\right] = C_{VLS} + x_{HS}\Delta C_V + \Delta E^0\left(\frac{\partial x}{\partial T}\right)_V \quad (7.58)$$

The derivative dx/dT can easily be found from the law of mass action (7.51) $\Phi(x,T) = 0$ noticing that $dx/dT = -(\partial\Phi/\partial T)_x/(\partial\Phi/\partial x)_T$.

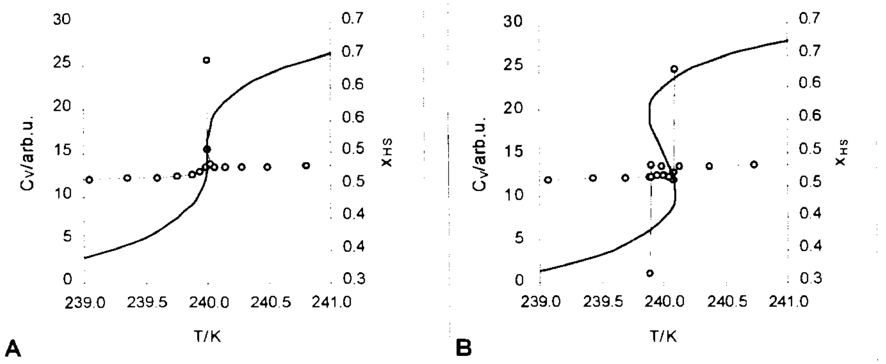

Fig. 7.13. Temperature dependencies of x_{HS} and the heat capacity calculated using (7.59) for $\Delta E = 2.5$ kcal mol^{-1}, $T_{1/2} = 240$ K, $\Delta S_{ex} = 0$ and $\Delta E_{ex} = 950$ cal mol^{-1} (**A**) and 964.25 cal mol^{-1} (**B**)

This yields the following expression for the specific heat:

$$C_V = C_{VLS} + x_{HS}\Delta C_V + \Delta E^0 \frac{x_{HS}\left(1 - x_{HS}\right)\left[R\ln\left(\frac{1 - x_{HS}}{x_{HS}}\right) + \frac{\Delta E^0}{T_{1/2}}\right]}{RT - 2\Delta E_{ex}\left(1 - x_{HS}\right)x_{HS}} \qquad (7.59)$$

in which $\Delta C_V = C_{VHS} - C_{VLS}$. Fig. 7.13 shows the temperature dependence of C_V calculated for a system characterised by exchange energies slightly below (A) and slightly above (B) the critical value of $2RT_{1/2}$.

In the first case one sharp maximum of heat capacity is predicted, whilst in the second case the heat capacity exhibits two separate peaks: one in the heating and one in the cooling modes (compare this with the experimental data in Fig. 7.13).

There are also systems exhibiting a double peak in each mode (see Fig. 7.14). Transition curves of spin crossover compounds with such a temperature dependence of heat capacity show, when examined closely, a *plateau* at $x_{HS} = ½$ (Fig. 7.14B). This is the case of so-called *two-step spin crossover.* Note a much better matching of the results of calorimetric measurements and transition curves (obtained using Mössbauer spectroscopy) carried out by different workers on different samples of $[Fe(2\text{-pic})_3]Cl_2C_2H_5OH$ as indicated by the derivative dx/dT in Fig. 7.14A than in the case of the steep spin crossover with hysteresis (Fig. 7.11B).

The phenomenon of two-step spin crossover cannot be explained by the effects of higher order molecular interactions. A non-zero quadratic term in the law of mass action (7.47) results in some asymmetry of the transition curve *but not in the step.* With increasing negative $\Delta^{(3)}$ the steepness of the transition curve increases and the "critical point" (corresponding to a vertical tangent) is achieved at lower values of $\Delta^{(2)}$. Positive $\Delta^{(3)}$ decrease the steepness of the transition curve.

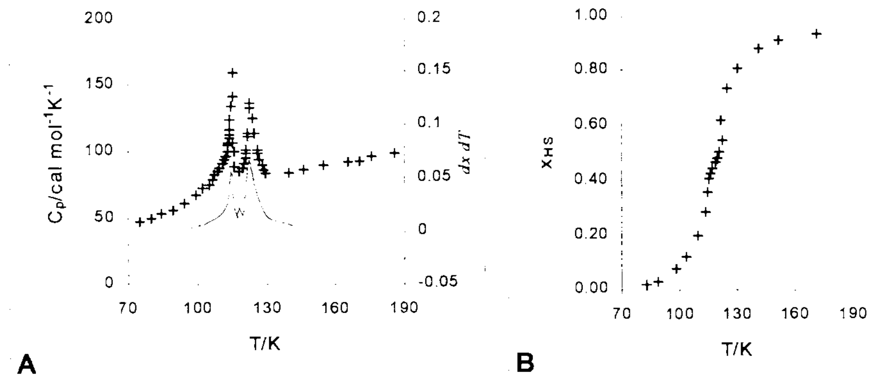

Fig. 7.14. The graph **A** shows the temperature dependence of the heat capacity of $[Fe(2\text{-}pic)_3]Cl_2C_2H_5OH$ drawn from the data in [12]. The curve below shows the derivative $\Delta x_{HS}/\Delta T$ calculated from the Mössbauer data on the same complex [13] in the right-hand graph (**B**)

The double peak of heat capacity must reflect some phase transition of either first or second order. The origin of phase separation in a steep spin crossover is the *large positive exchange energy* reflecting a much stronger interaction of molecules in homo-pairs than in hetero-pairs. Some critical phenomena should also be expected in the reverse case of molecules in hetero-pairs interacting stronger than those in homo-pairs, *i.e.* in the case of *large negative exchange energy*. The result must apparently be an ordered structure (A-B-A-B-A-B). The formalism predicting such phenomena must employ some parameter(s) characterising ordering in a binary mixture. Such a parameter is missing in the law of mass action (7.47) and therefore we cannot expect it to describe the case of two-step spin crossover.

7.8

Negative exchange energy. Ordering. The Bragg – Williams approximation

It has long been known that in binary alloys of similar metals (*e.g.* Cu-Ag) there is a tendency to form (albeit very slowly) regular sub-lattices for individual metal ions detectable by XRD without, however, an apparent formation of separate phases [2]. This indicates that an ordered structure has a lower free energy but that ordering does not involve the formation of new phases. The process of ordering can be described by taking into account the non-equivalence of centres in the crystal lattice, *i.e.* by distinguishing the centres belonging to the A and B sub-lattices. Apparently, they are characterised by different potential energies and the corresponding Boltzmann factors should be used when calculating the probability of a molecule being found in such a centre. This approach can be used in numerical simulations such as in the Monte-Carlo method[8] but it excludes the possibility of an analytical solution of this problem.

There are, however, several elegant approximate analytical solutions of the problem of ordering in binary systems developed by Bragg, Williams, Gorsky, Bethe and Kirkwood (see [1], pages 570*ff.*). The Bragg – Williams approximation is the simplest among those mentioned above. It takes into account the existence of two sub-lattices consisting of α- and β-centres equivalent from the point of view of the probability of finding either molecule A or B in any centre. However, when these centres are *regularly* filled by molecules A and B (*i.e.* an A in the α centre and a B molecule in the β-centre, or *vice versa*) the number of hetero-molecular interactions is maximal for any composition. When hetero-molecular interactions are stronger than homo-molecular interactions (negative ΔE_{ex}), such a regular distribution would also imply a minimum of potential energy of the whole system. Therefore there is a 'driving force' to bring such a binary system into an *ordered state.* This 'driving force' also includes a special configurational entropy that must take into account the existence two types of centres.

Let us consider a crystal built from the molecules A and B (with similar characteristics) in which two sub-lattices can be formed, each having the same coordination number c. N centres of such a crystal are then divided into $N/2$ α-centres and $N/2$ β-centres. These two kinds of centre form a regular lattice in which an α-centre is surrounded by c β-centres and a β centre is surrounded by c α-centres. The main simplification of the Bragg – Williams model amounts to the suggestion that molecules A and B are *randomly distributed* among the α and β centres. The ordering in such a system can be quantitatively characterised by the *degree of ordering, s,* introduced in the following way:

Consider a system of N_A particles A and N_B particles B, distributed over $N/2$ α-centres and $N/2$ β-centres ($N = N_A + N_B$). The probability p of a molecule A to get into an α-centre is:

$$p = N_A(\alpha)/N_A \tag{7.60}$$

in which $N_A(\alpha)$ is the number of molecules of type A in α-centres. In the state of complete disorder, this probability is obviously ½. The state of complete order, on the other hand, is characterised by $p_{order} = 1$ (all molecules A occupy α-centres). Note that such a situation is possible at $x_A \leq ½$. The degree of ordering is then defined as the ratio:

$$s = \frac{p - p_{disorder}}{p_{order} - p_{disorder}} = \frac{p - 0.5}{0.5} = 2p - 1 \tag{7.61}$$

Accordingly the probability p expressed in terms of s is:

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[8] Monte-Carlo simulations of a spin crossover system have shown the possibility of a two-step spin crossover [12].

$$p=(1+s)/2 \tag{7.62}$$

The number of molecules A in α-centres is:

$$N_A(\alpha)=(1+s)x_A N/2 \tag{7.63}$$

in which $x_A = N_A/N$. The state of complete order corresponds to $s = 1$ and the state of complete disorder is characterised by $s = 0$. Such a definition is exactly valid within the range $0 < x_A \leq ½$. For systems with a higher content of A molecules, the reference state with $p = 1$ is inaccessible. This leads to an *a priori* requirement that s cannot be higher than $(1 - x_A)/x_A$. On the other hand, in the range $1 > x_A > ½$ the degree of ordering can be defined in terms of the probability of a molecule B occupying a β-centre:

$$p' = N_B(\beta)/N_B \tag{7.64}$$

$$s = 2p' - 1 \tag{7.65}$$

The degree of ordering, s, is thus defined for each type of molecule, strictly speaking, on one half of the total range of compositions ($x_A = 0 - ½$). This does not affect the description of mixtures of non-reacting particles because a symmetry exists between the regions $0 < x_A < ½$ and $½ < x_A < 1$. If, however, molecules A can transform into molecules B and *vice versa* then such a symmetry disappears: one of the species is stable at high temperatures and another at low temperatures. It will be shown that this feature still does not affect the transition curve but it does change the shape of the temperature dependence of the degree of ordering.

The configurational entropy of the system defined above corresponds to the number of ways in which (N/2) α centres can be filled by $N_A(\alpha)$ A-particles and $N_B(\alpha)$ B-particles multiplied by the number of ways in which (N/2) β centres can be filled by $N_A(\beta)$ A-particles and $N_B(\beta)$ B-particles. In the approximation of random filling this leads to [2]:

$$W=\frac{(N/2)!}{(Ny_1/2)!\,(N(1-y_1)/2)!}\times\frac{(N/2)!}{(Ny_2/2)!\,(N(1-y_2)/2)!} \tag{7.66}$$

in which y_1 and y_2 are the respective probabilities of finding an α- and a β-centre occupied by a molecule A:

$$y_1=(1+s)x_A; \qquad y_2=(1\text{-}s)x_A \tag{7.67}$$

The configurational entropy defined in terms of this number of realisations is:

$$\begin{aligned} S_{conf} &= k\ln W \\ &= -\frac{Nk}{2}\{y_1\ln y_1+[1-y_1]\ln[1-y_1]+y_2\ln y_2+[1-y_2]\ln[1-y_2]\} \end{aligned} \tag{7.68}$$

An argument of a logarithmic function cannot be zero or negative and therefore

$1 - y_1 > 0$ and this leads to the *a priori* condition mentioned above:

$$s < (1 - x_A)/x_A \tag{7.69}$$

The next step is to define the potential energy of the system. This is done by counting the number of *AA*, *BB* and *AB* binary interactions characterised by the corresponding potentials (φ_{AA}, φ_{BB} and φ_{AB}). The relative number of homo- and hetero-interactions depends on the composition and degree of ordering. The potential energy of such a system thus becomes a function of the degree of ordering. It is not difficult to derive this dependence in an explicit form [1,2]. The energies of ordering and disordering resulting from such a derivation are:

$$\Delta U_{ord} = U^{(s)} - U^{(0)} = -s^2 x_A^2 \frac{cN}{2}\left[\varphi_{AA} + \varphi_{BB} - 2\varphi_{AB}\right] = -s^2 x_A^2 w \tag{7.70}$$

$$\Delta U_{dis} = U^{(s)} - U^{(1)} = \left(1 - s^2\right)x_A^2 w \tag{7.71}$$

in which:

$$w = \frac{cN}{2}\left[\varphi_{AA} + \varphi_{BB} - 2\varphi_{AB}\right] = -\Delta E_{ex} \tag{7.72}$$

The quantity w is identical with the exchange energy taken with negative sign. The interesting case of negative exchange energy corresponds, therefore, to positive w and to lower potential of an ordered structure. The *free energy* of ordering and disordering can be found by adding the configurational term ($-T\Delta S_{\mathrm{conf}}$) to (7.70) and (7.71):

$$\Delta F_{dis} = U^{(s)} - U^{(1)} - kT\ln\frac{W^{(s)}}{W^{(1)}}; \quad \Delta F_{ord} = U^{(s)} - U^{(0)} - kT\ln\frac{W^{(s)}}{W^{(0)}} \tag{7.73}$$

Now the configurational entropy of a completely disordered system is obviously:

$$k\ln W^{(0)} = -kN\left[\ x_A \ln x_A + (1 - x_A)\ln(1 - x_A)\ \right] \tag{7.74}$$

whilst that corresponding to $s = 1$ according to (7.66) is[9]:

$$k\ln W^{(1)} = -\frac{kN}{2}\left[\ 2x_A \ln 2x_A + (1 - 2x_A)\ln(1 - 2x_A)\ \right] \tag{7.75}$$

The free energies of ordering and disordering are therefore given by:

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[9] A completely ordered structure with $x = ½$ (...*ABABAB*...) can only be realised in one way and for this composition alone $W^{(1)}=1$. When calculating $W^{(1)}$ for an arbitrary composition one has to take into account that $0! = 1$, *i.e.* $0 \ln 0 = 0$.

$$\begin{aligned}\Delta F_{ord} &= x_A^2 s^2 \Delta E_{ex}\\ &+\frac{kTN}{2}\left[\ y_1 \ln y_1 + (1-y_1)\ln(1-y_1) + y_2 \ln y_2 + (1-y_2)\ln(1-y_2)\ \right]\\ &-kTN\left[\ x_A \ln x_A + (1-x_A)\ln(1-x_A)\ \right]\end{aligned} \tag{7.76}$$

$$\begin{aligned}\Delta F_{dis} &= -x_A^2(1-s^2)\Delta E_{ex}\\ &+\frac{kTN}{2}\left[\ y_1 \ln y_1 + (1-y_1)\ln(1-y_1) + y_2 \ln y_2 + (1-y_2)\ln(1-y_2)\ \right]\\ &-\frac{kTN}{2}\left[\ 2x_A \ln 2x_A + (1-2x_A)\ln(1-2x_A)\ \right]\end{aligned} \tag{7.77}$$

In a system of chemically non-reactive particles there is a certain degree of ordering corresponding to the minimum of free energy, *i.e.* the state of equilibrium characterised by:

$$(\partial \Delta F_{ord}/\partial s)_{V,T,x} = (\partial \Delta F_{dis}/\partial s)_{V,T,x} = 0 \tag{7.78}$$

Applying this condition to (7.77) yields:

$$kTN \ln \frac{y_1(1-y_2)}{y_2(1-y_1)} + 4sx_A\Delta E_{ex} = 0 \tag{7.79}$$

This equation has a trivial solution of $s = 0$ which is the *only solution for positive exchange energies.*

Non-trivial solutions of (7.79), $s = f(x_A, T)$, *can only be obtained for* large negative $|\Delta E_{ex}| > 2RT$. They form a surface with a ridge along $x_A = ½$, rising in the direction of lower temperatures (See Fig. 7.15). The transition from $s = 0$ to non-zero solutions of (7.79) with changing x_A or T is very sharp, indicating the involvement of a large number of molecules, *i.e.* cooperativity of the ordering process.

Fig. 7.16 shows diagrams of the free energies of ordering and disordering as functions of composition and temperature. Both free energies are negative because the values of s employed in calculations correspond to the minimum of F. Only half of the diagram of $F_{dis}(x,T)$ may be calculated according to (7.77) because the state $s = 1$ for molecules A can only be defined within the range $x_A = 0 - ½$. However, the degree of ordering may also be defined with respect to molecules B, therefore, the total diagram of the free energy of disordering must be symmetric. Both free energies exhibit then a global minimum at $x = ½$. The depth of this minimum increases in the direction of lower temperatures for the free energy of ordering (Fig. 7.16A) and in the direction of rising temperatures for the free energy of disordering (Fig. 7.16B).

The free energy of ordering (ΔF_{ord}, diagram in Fig. 7.16A) represents a change of free energy which would be observed if we equilibrate a random mixture of A and B molecules. In this case, there is a unique minimum of free energy. In a mixture of molecules A and B possessing equal chemical potentials the ordering would stabilise only the composition $x_A = x_B = ½$.

The free energy of disordering (ΔF_{dis}, Fig. 7.16B) represents a change of free energy that would be observed during the equilibration of a completely ordered mixture. For such a process there are other minima of ΔF (although not very deep and lying higher than the global minimum at $x = ½$) corresponding to $x_{A(B)} = 0.15 - 0.3$. This might result in a special kind of hysteresis.

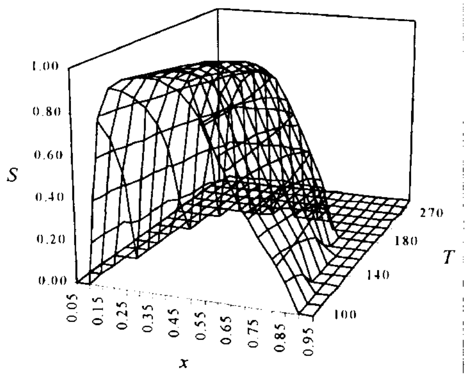

Fig. 15. The degree of ordering at equilibrium as a function of composition and temperature calculated for $\Delta E_{ex} = -1$ kcal mol^{-1}

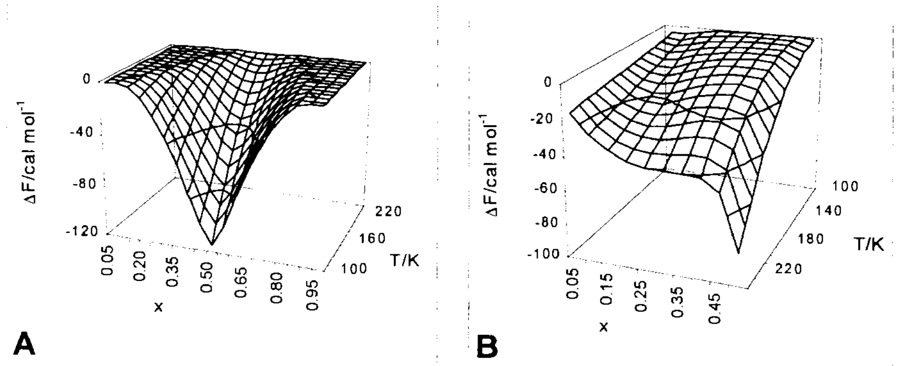

Fig. 7.16. Free energy of ordering (**A**) and disordering (**B**) as functions of T and x calculated for a binary system with $\Delta E_{ex} = -1$ kcal mol^{-1} and equilibrium values of s

7.9

Description of ordering taking into account triple interactions

Let us now apply the formalism taking into account triple molecular interactions in the condensed state to the description of a binary ordered system. We can assume that partition functions are dependent on the nature of the surroundings and consider the effects of two nearest neighbours along a coordinate. In general (*i.e.* before applying the Bragg – Williams approximation), we must distinguish between the molecules in α and β centres, therefore the following configurations should be taken into account:

$$\begin{array}{cccc} \underline{A}A\underline{A} & A\underline{A}A & ABA & \underline{ABA} \\ \underline{A}AB & A\underline{AB} & AB\underline{B} & \underline{AB}B \\ BAB & \underline{BAB} & \underline{B}B\underline{B} & B\underline{B}B \end{array}$$

The molecule A occupying an α-centre is thus denoted by A and the same molecule occupying a β-centre is denoted by $\underline{A}$. Similarly, the molecule B in an ('improper') α-centre will be denoted by $\underline{B}$.

The probabilities p_A, $p_{\underline{A}}$, p_B, $p_{\underline{B}}$ to find α- and β-centres occupied by the molecules A and B, as well as the mole fractions X_A, X_B, $X_{\underline{A}}$, $X_{\underline{B}}$ of the molecules A and B in these centres, are given in Table 7.3.

According to these assumptions, the contribution of the configuration $\underline{A}A\underline{A}$ can be written as:

$$-3NkTX_A p_{\underline{A}}^2 \ln z_{\underline{A}A\underline{A}} = (½)y_1 y_2^2 F_{\underline{A}A\underline{A}} \tag{7.80}$$

in which $X_A = N_A(\alpha)/N$ is the fraction of molecules A in α-centres, $p_{\underline{A}} = y_2$ is the probability of finding a β-centre occupied by a molecule A.

The asymmetric configuration $\underline{A}AB$ can be realised in two ways, therefore:

$$-6NkTX_A p_{\underline{A}} p_B \ln z_{\underline{A}AB} = y_1 y_2 (1 - y_2) F_{\underline{A}AB} \tag{7.81}$$

in which $p_B = (1 - y_2)$ is the probability of finding a β-centre occupied by a B molecule.

Table 7.3. Formulae for calculating the probabilities of filling lattice centres with molecules A and B. The values of X_A and X_B are mole fractions of the molecules A and B in lattice centres

	p_A	p_B	X_A	X_B
α-centre	$y_1 = (1 + s)x_A$	$1 - y_1$	$y_1/2$	$(1 - y_1)/2$
β-centre	$y_2 = (1 - s)x_A$	$1 - y_2$	$y_2/2$	$(1 - y_2)/2$

The third possible configuration with central molecule A contributes:

$$-3NkTX_A p_B^2 \ln z_{BAB} = \left(\tfrac{1}{2}\right) y_1 (1 - y_2)^2 F_{BAB} \tag{7.82}$$

Obtaining similar expressions for configurations with central molecule $\underline{A}$ and combining them with those above we obtain the free energy of molecules A (analogous computations can easily be performed for the molecules B and B̲) as:

$$\begin{aligned} 2F_A = {} & y_1 y_2^2 F_{\underline{A}A\underline{A}} + y_2 y_1^2 F_{A\underline{A}A} + 2y_1 y_2 (1 - y_2) F_{\underline{A}AB} + 2y_2 y_1 (1 - y_1) F_{A\underline{AB}} \\ & + y_1 (1 - y_2)^2 F_{BAB} + y_2 (1 - y_1)^2 F_{\underline{BAB}} \end{aligned} \tag{7.83}$$

The main assumption of the Bragg – Williams approximation is that the random distribution of molecules over α and β centres implies that the free energy of a molecule *does not depend on the nature of the centre in which it, or its neighbour, resides*. The standard free energies $F_{\underline{A}A\underline{A}}$ and $F_{A\underline{A}A}$ must, therefore, be (at least approximately) equal. The same is true for other pairs of standard free energies:

$$F_{\underline{A}AB} \cong F_{A\underline{AB}}; \quad F_{BAB} \cong F_{\underline{BAB}} \tag{7.84}$$

We may then drop the notations of 'proper' and 'improper' centres. Expressing y_1 and y_2 in terms of s and x_A (Table 7.3) and combining terms with equal powers of x_A, we can write the free energy of the whole system as:

$$\begin{aligned} F = {} & x_A^3 \left(1 - s^2\right) \left[\left(F_{AAA} + F_{BAB} - 2F_{AAB}\right) - \left(F_{BBB} + F_{ABA} - 2F_{ABB}\right) \right] \\ & - x_A^2 \left[2F_{BAB} - 2F_{AAB} + 4F_{ABB} - 3F_{BBB} - F_{ABA} - s^2 \left(F_{ABA} - F_{BBB} + 2F_{BAB} - 2F_{AAB}\right) \right] \\ & + x_A \left(F_{BAB} + 2F_{ABB} - 3F_{BBB}\right) + F_{BBB} \\ & + \frac{NkT}{2} \left[y_1 \ln y_1 + y_2 \ln y_2 + (1 - y_1) \ln (1 - y_1) + (1 - y_2) \ln (1 - y_2) \right] \end{aligned} \tag{7.85}$$

in which the last line represents the configurational entropy. (A similar expression can be obtained when the degree of order is defined with respect to molecules B, *via* $N_B(\beta)$ [3]). When the effects of the surroundings are additive: $y_A = y_B = ½$ the coefficient of the cubic term in (7.82) is zero and hence the free energy becomes:

$$\begin{aligned} F = {} & -x_A^2 \left(1 - s^2\right) \Delta F_{ex} + x_A \left(\Delta F_{ex} - F_{BBB} + F_{AAA}\right) + F_{BBB} \\ & + \frac{NkT}{2} \left[y_1 \ln y_1 + y_2 \ln y_2 + (1 - y_1) \ln (1 - y_1) + (1 - y_2) \ln (1 - y_2) \right] \end{aligned} \tag{7.86}$$

When the exchange entropy is zero ($\Delta F_{ex} = \Delta E_{ex}$) this equation gives the free energy of a regular ordered solution. It is a function of the composition of a system and of the degree of ordering. When $s = 0$ this equation becomes identical with (7.30) of regular solution theory. The differentiation of (7.84) with respect to s (at constant x_A) produces an expression identical with the (7.75) derived in the Bragg – Williams approximation.

We have thus obtained a modification of the Bragg – Williams approximation of ordered binary structures which takes into account triple interactions. The degree of ordering, s, enters the coefficients of the cubic and square non-ideality terms in the expression for free energy (7.85). The contribution from triple interactions is therefore dependent on the process of ordering.

7.10

Chemical equilibrium in ordered systems. Two-step spin crossover

When a chemical reaction takes place in a system with ordering, the state of equilibrium is determined by the minimum of free energy with respect to both composition and degree of ordering. The isotherms calculated according to (7.84) with $F_{AAA} = 0$, $F_{BBB} = +5$ kcal mol^{-1}, $\Delta E_{ex} = -1$ kcal mol^{-1}, $T_{½} = 140$ K and equilibrium values of s exhibit one minimum (Fig. 7.17), thus indicating homogeneity of the system (in contrast to systems characterised by an equally large positive exchange energy).

This minimum tends to remain in the region $x = ½$ which can be interpreted as a plateau in the transition curve. It can be explicitly shown as follows: A minimum in an isotherm in Fig. 7.17 corresponds to the state of chemical (spin crossover) equilibrium:

$$\text{A (LS)} \rightleftharpoons \text{B (HS)} \tag{7.87}$$

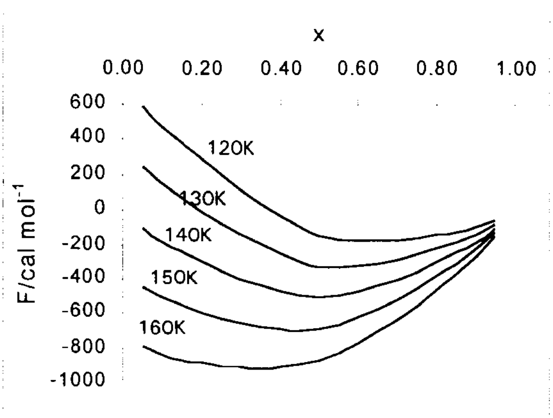

Fig. 7.17. The free energy isotherms for a spin crossover equilibrium mixture characterised by $\Delta E_{ex} = -1.0$ kcal mol^{-1}, $\Delta E = 5$ kcal mol^{-1} and $T_{1/2} = 140$ K

When we also take into account the process of ordering, the state of equilibrium corresponds to zero complete differential of free energy:

$$dF = \left(\frac{\partial F}{\partial x_A}\right)_{V,T,s} dx_A + \left(\frac{\partial F}{\partial s}\right)_{V,T,x_A} ds = 0 \qquad (7.88)$$

It implies separate equalities to zero of both partial derivatives (either considering x_A and s as independent variables or admitting that s is bound to x through the condition $\partial F/\partial s = 0$, (7.78)):

$$\left(\frac{\partial F}{\partial x_A}\right)_{V,T,s} = 0; \qquad \left(\frac{\partial F}{\partial s}\right)_{V,T,x_A} = 0 \qquad (7.89)$$

This system of equations can be solved as follows. Let us remove temperature from both these equations and equalise the expressions so obtained. Using (7.84) derived for the case of additive effects of surroundings we get:

$$T = \frac{\Delta E^0 - \Delta E_{ex}\left[1 - 2x_A\left(1 - s^2\right)\right]}{\frac{R}{2}\left\{(1+s)\ln\left(\frac{y_1}{1-y_1}\right) + (1-s)\ln\left(\frac{y_2}{1-y_2}\right)\right\} + \Delta S^0 - \Delta S_{ex}\left[1 - 2x_A\left(1 - s^2\right)\right]} \qquad (7.90)$$

$$T = \frac{2x_A s\Delta E_{ex}}{2x_A s\Delta S_{ex} - \frac{R}{2}\left\{\ln\left(\frac{y_1}{1-y_1}\right) - \ln\left(\frac{y_2}{1-y_2}\right)\right\}} \qquad (7.90a)$$

The system of equations (7.90) and (7.90a) can be solved with respect to s for a given x_A using an appropriate numerical method. The temperature can then be calculated from[10] (7.90). For positive exchange energies $\Delta E_{ex} > 0$ (7.90), (7.91) we have only the trivial solution $s = 0$. When ΔE_{ex} is negative and sufficiently large two solutions: one trivial ($s = 0$) and another non-trivial ($s \neq 0$), are possible within a certain range of composition and temperature.

Fig. 7.18 shows the transition curve and temperature dependence of the degree of ordering calculated employing (7.90) and (7.90a) for a system characterised by a large negative exchange energy $\Delta E_{ex} = -1.0$ kcal mol^{-1}. According to these data, a significant ordering must be expected between 107 K and 167 K. Over the same region of temperature the transition curve experiences an inflection similar to the plateau experimentally observed in two-step spin crossover.

The calculations using the degree of ordering s defined either in terms of $N_A(\alpha)$ or of $N_B(\beta)$ result in the *same transition curve* but the temperature dependencies of s are different for these two cases.

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[10] Equation (87a) is an uncertainty when s = 0.

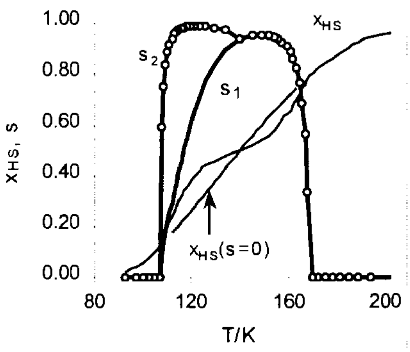

Fig. 7.18. Transition curve in a system with ordering ($\Delta E_{ex} = -1$ kcal mol^{-1}, $\Delta E = 5$ kcal mol^{-1} and $T_{1/2} = 140$ K). The curve s_1 shows the degree of ordering defined in terms of $N_A(\alpha)$; the curve s_2 (o) shows the degree of ordering defined in terms of $N_A(\alpha)$ above the transition point and in terms of $N_B(\beta)$ below it

When defined *in terms of* $N_A(\alpha)$ the degree of ordering (curve s_1 in Fig. 7.18) passes through a maximum close to $x_A = ½$ and decreases to zero with increasing content of A (lower temperatures). The degree of ordering defined *in terms of* $N_B(\beta)$ increases at $x_A > ½$ approaching $s = 1$ and then falls abruptly to $s = 0$. These phenomena can be explained as indicating a stabilisation of ordered structures at low temperatures. However, below certain temperatures the amount of the molecules B (HS) is so small that the formation of a stable ordered structure (a sub-lattice with a very large lattice constant) becomes impossible, thus causing a sharp fall in s.

Taking into account that ordered structures can be formed as sub-lattices of either A (LS) or B (HS) the combined definition of s should apparently be used, *viz.* with respect to $N_B(\beta)$ below $T_{½}$ ($1 > x_A \geq ½$) and with respect to $N_A(\alpha)$ above $T_{½}$ ($½ > x_A > 0$).

The least negative exchange energy connected with non-zero degrees of ordering depends on the energy gap between the HS and LS states ($F_{BBB} - F_{AAA}$). Observable deflections from a smooth transition curve, which can be interpreted as a plateau, occur when ordering is considerable, *e.g.* $s \cong 0.7 - 0.8$ (Fig. 7.19B). A defined plateau can be observed when s approaches 1 (Fig. 19C).

The formalism developed here qualitatively predicts the main features of experimentally observed two-step spin crossover. However, all attempts to obtain a quantitative agreement between theoretical and typical experimental transition curves have so far failed. Experimental two-step transition curves are usually just slightly modified *steep* spin crossover curves ($\Delta E_{ex} > 0$). On the other hand, the slopes of theoretical curves predicted by (7.90) for negative exchange energies beyond the region of ordering are even smaller than those expected for perfect solutions ($\Delta E_{ex} = 0$).

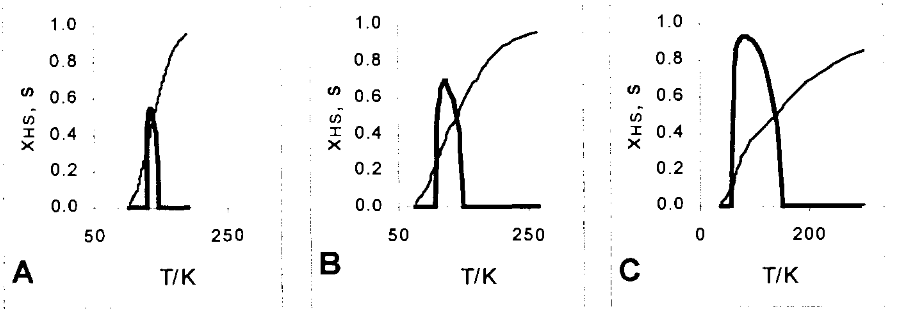

Fig. 7.19. The shape of transition curves computed at fixed exchange energy $\Delta E_{ex} = -0.6$ kcal mol^{-1} and varying $\Delta E = 1.25$ kcal mol^{-1} (**A**), 2.5 kcal mol^{-1} (**B**), and 5.0 kcal mol^{-1} (**C**)

This dilemma can nevertheless be solved within the suggested model if we consider the case of non-additive effects of the surroundings ($y_A \neq y_B \neq ½$) and take into account the possibility of different signs of these effects for molecules A and B (D_A and D_B). Under these conditions the cubic term in (7.85) is, in general, non-zero. Employing four parameters characterising molecular interactions, D_A, D_B, y_A, and y_B allows (7.85) to be written as:

$$\begin{aligned} F = {} & x_A^3\left(1-s^2\right)\left[\,(1-2y_A)D_A-(1-2y_B)D_B\right] \\ & + x_A^2\left[\,(1-4y_B)D_B-2(1-y_A)D_A+s^2\left(D_B+2(1-y_A)D_A\right)\,\right] \\ & + x_A\left(D_A+2y_BD_B-F_{BBB}+F_{AAA}\right)+F_{BBB} \\ & + \frac{NkT}{2}\left[\,y_1\ln y_1+y_2\ln y_2+(1-y_1)\ln(1-y_1)+(1-y_2)\ln(1-y_2)\,\right] \end{aligned} \tag{7.91}$$

A similar expression can be obtained for the case when s is defined in terms of $N_B(\beta)$. Applying the procedures described above, the law of mass action can be obtained and, solving numerically the equivalents of (7.90) and (7.90a), the equilibrium values of x_{HS}, s, and T can be calculated for given D_A, D_B, y_A, y_B, ΔE, and T'_2 (see in Ref. [3]).

Fig. 7.20 shows experimental [13] and theoretical (based on (7.91)) transition curves for solid [Fe(2-pic)$_3$]Cl$_2$.EtOH. The estimates of the parameters obtained by this regression are given in Table 7.4. The agreement between experimental and calculated data of x_{HS} is very good over the whole region ($x_{HS} = 0.02 - 0.94$) the standard regression error being 1.47 K (in the procedure described the dependent variable was temperature). This description is insensitive to the choice of the magnitude of D_B in the range 620 – 1000 cal mol^{-1} provided its counterpart D_A, as well as y_A, y_B, ΔE, and T'_2 are adjusted. This might indicate an over-parameterisation of a model but may also be the result of insufficient accuracy of "experimental" data (which have been read from the graph in the original paper [13]).

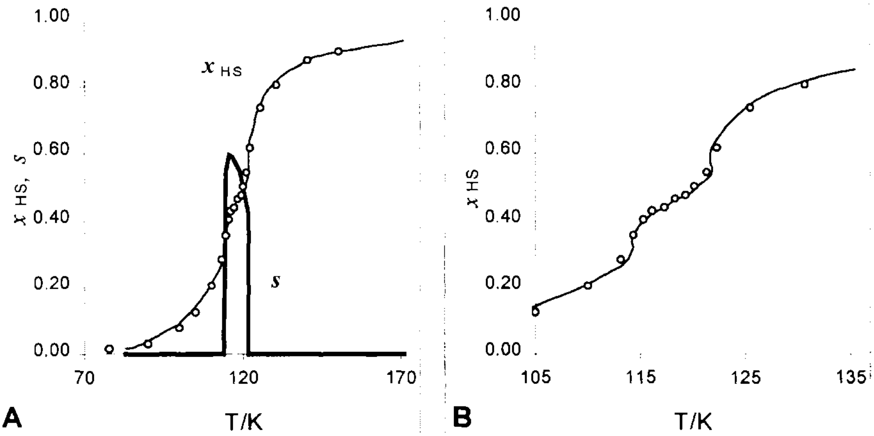

Fig. 7.20. Experimental transition curve (*circles*) of the two-step spin crossover of $[Fe(2\text{-pic})_3]Cl_2.EtOH$ [13] and the regression curve (*line*), corresponding to the parameters presented in Table 7.4. The curve *s* is the temperature dependence (computed) of the degree of ordering. The right-hand graph (**B**) shows, in detail, the central part of the transition curve

Table 7.4. The estimates of parameters in (7.91) obtained by regression of the experimental data on spin crossover in $[Fe(2\text{-pic})_3]Cl_2.EtOH$.

D_A (kcal mol^{-1})	D_B (kcal mol^{-1})	y_A	y_B	ΔE (kcal mol^{-1})	$T_{1/2}$ (K)
+0.581	−0.65	0.84	0.12	1.150	116.7
−0.64	+0.571	0.19	0.95	1.147	116.7

This mathematical model is invariant with respect to a simultaneous change of sign at D_A and D_B *provided that the coefficients* y_A and y_B *are adjusted.* In other words, practically the same regression error can be achieved for both negative D_A and positive D_B with symmetrically changed values of y_A and y_B (see Table 7.4). These two descriptions are illustrated by the energy level diagrams shown in Fig. 7.21. The diagram A in Fig. 7.21 admits a simple interpretation based on the assumption that the energy of a spin crossover molecule is largely determined by the energy of repulsive molecular interaction. In such a case the formation of a hetero-molecular surroundings of an LS molecule is connected with an increase in potential energy because HS molecules are larger than the (original) LS molecules (the ratio of radii r_{HS}/r_{LS} is usually of the order of 1.1). On the other hand, the potential energy of a large HS molecule decreases when its environment is transformed from homo-molecular to hetero-molecular (made up of smaller LS molecules).

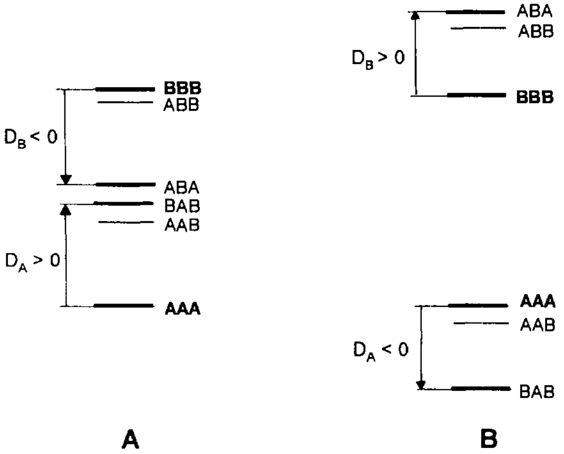

Fig. 7.21. Energy level diagrams illustrating theoretical descriptions of two-step spin crossover in $[Fe(2\text{-pic})_3]Cl_2.EtOH$. The diagrams **A** and **B** correspond to parameters in the first and second rows of Table 7.4 respectively.

Estimation of the coefficient y_A shows that the appearance of the first HS molecule in the environment of an LS molecule brings about 84% of the total free energy change that is connected to the formation of the sequence HS-LS-HS. On the other hand, the value of y_B shows that the first substitution of an HS molecule in a homo-environment of an HS molecule results in only 12% of the total energy change, which is connected with the formation of the sequence LS-HS-LS.

The first stage of a substitution of an LS molecule by an HS one creates an asymmetric environment and changes the interaction of a central molecule with other neighbours (see Fig. 7.4A, above). Therefore a higher effect is to be expected at this stage and is actually observed. On the other hand, the appearance of the first, small, LS molecule in the environment of an HS molecule might not be connected with a considerable energy change because a small molecule can easily be accommodated in a large vacancy.

When the second neighbour of an HS molecule is converted into an LS complex a large effect is observed and this is connected with the formation of regular structures. In fact, the complete formation of an LS-HS-LS structure is equivalent to the formation of an HS-LS-HS structure and the energies of these types of environment must be identical. In fact, the estimates of ΔE, D_A, and D_B confirm this within the experimental error (see Table 7.4, the diagram A in the Fig. 7.21 deviates slightly from the exact values in order to be legible).

The diagram B in Fig. 7.21 implies that the energy of an HS molecule increases when its surroundings are transformed into a hetero-molecular one. This is possible when a strong magnetic interaction exists between unpaired electrons of HS species. However, such an interaction (with a constant of *ca.* 600 cal mol^{-1}, *i.e. ca.* 200 cm^{-1}) would bring about the formation of a magnetically ordered phase at lower temperatures, which is not observed experimentally. Neither can the decrease in energy of an LS molecule upon the formation of a heteromolecular environment be explained. These arguments allow us to choose one of the descriptions in the first row in Table 7.4 as physically meaningful.

This example clearly shows that such parameters as volume and lattice energy are only *indirectly* connected with repulsive and attractive interactions. Lattice energy changes in spin crossover are mainly determined by the repulsive interactions and are therefore strongly related to the corresponding volume changes. The separation of molecular interactions into repulsive and attractive has a physical meaning in relation to forces between molecules but *not* to the energy and much less to macroscopic parameters that are determined by the balance of these forces. Therefore the concept of internal pressure, although useful in depicting a simple model of the condensed state. might be misleading when we consider its relationship to the potential energy of molecules.

It is interesting to note that the estimates of ΔE^0 and $T_{1/2}$ yield the entropy of spin crossover at the lowest experimentally observed level that is typical for such systems [14]:

$$\Delta S^0 = \Delta E^0/T_{½} = 9.86 \text{ cal mol}^{-1}\text{ K}^{-1} \tag{7.92}$$

The contribution to the entropy from change in the electronic spin-degeneracy is Rln5 = 3.186 cal mol^{-1} K^{-1} which is nearly exactly $^1/_3$ the value obtained above ($3R\ln 5 = 9.56$). Such a coincidence suggests use of the formula for entropy with the cube of the degeneracy factor [2]. By doing this we assume that vibrations are unaffected by spin crossover, which might indeed be the case for the *lowest observed entropy.*

7.11
Diluted systems

Let us now consider the effects of dilution of a reacting system in the solid state by an inert solvent. Spin crossover in magnetically diluted crystals is a good example of such a reaction:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{7.93}$$

The mass balance for this reaction can be written as:

$$N = n_A + n_B + n_S; \quad x_A + x_B + x_S = 1 \tag{7.94}$$

in which S denotes the solvent. The free energy of such a reaction mixture can be written in terms of molecular standard free energies $F_{A(B,S)} = -3kT\ln z_{A(B,S)}$:

$$F = N\left[x_A F_A + x_B F_B + x_S F_S + kT\left(x_A \ln x_A + x_B \ln x_B + x_S \ln x_S\right)\right] \tag{7.95}$$

In an ideal system these free energies are independent of the nature of molecular surroundings, whereas in an imperfect crystal we must consider the influence of the nearest (and also, perhaps, the next nearest) neighbours. Taking into account (as above) the effects of two neighbours along a coordinate we get:

$$\begin{aligned}
F_A &= x_A^2 F_{AAA} + 2x_A x_B F_{AAB} + 2x_A x_S F_{AAS} + 2x_B x_S F_{BAS} + x_B^2 F_{BAB} + x_S^2 F_{SAS} \\
F_B &= x_A^2 F_{ABA} + 2x_A x_B F_{ABB} + 2x_A x_S F_{ABS} + 2x_B x_S F_{BBS} + x_B^2 F_{BBB} + x_S^2 F_{SBS} \\
F_S &= x_A^2 F_{ASA} + 2x_A x_B F_{ASB} + 2x_A x_S F_{ASS} + 2x_B x_S F_{BSS} + x_B^2 F_{BSB} + x_S^2 F_{SSS}
\end{aligned} \tag{7.96}$$

According to (7.95) and (7.96), the chemical potentials ($\partial F/\partial x_i$) of the species A and B are given by:

$$\mu_A = \sum_{i=A,B,S}^{j=A,B,S} a_{ij} x_i x_j + kT \ln x_A \,; \quad \mu_B = \sum_{i=A,B,S}^{j=A,B,S} b_{ij} x_i x_j + kT \ln x_B \tag{7.97}$$

Table 7.5 contains the coefficients a_{ij}, b_{ij}; the sums of the corresponding columns yield the coefficients A_{ij} entering the law of mass action:

$$\begin{aligned}
\mu_A - \mu_B = A_{11}x_A^2 + A_{12}x_A x_B + A_{13}x_A x_S + A_{23}x_B x_S + A_{22}x_B^2 + A_{33}x_S^2 \\
+ kT \ln\left(x_A/x_B\right) = 0
\end{aligned} \tag{7.98}$$

None of the standard free energies repeat twice in a column of Table 7.5, and therefore, in general, the law of mass action (7.98) contains polynomial terms of up to the second power (similar to the law of mass action (7.47)). In order to analyse these polynomial terms and elucidate their physical significance let us express them as a function of x_A.

The fraction of reacting species we denote as γ:

$$\gamma = x_A + x_B \,; \qquad 1 - \gamma = x_S \tag{7.99}$$

The law of mass action (7.98) then becomes:

$$\begin{aligned}
x_A^2\left(A_{11} - A_{12} + A_{22}\right) + x_A\left[\gamma\left(A_{12} - 2A_{22}\right) + (1-\gamma)\left(A_{13} - A_{23}\right)\right] \\
+ \gamma^2 A_{22} + \gamma(1-\gamma)A_{23} + (1-\gamma)^2 A_{33} + kT \ln\frac{x_A}{1 - x_A} = 0
\end{aligned} \tag{7.100}$$

Note that the coefficient of x_A^2 in (7.100) does not contain the standard free energies of the configurations involving solvent:

$$A_{11} - A_{12} + A_{22} = 3\left[\left(F_{AAA} - 2F_{AAB} + F_{BAB}\right) - \left(F_{BBB} - 2F_{BBA} + F_{ABA}\right)\right] \tag{7.101}$$

It is identical with the coefficient $3\Delta^{(3)}$ at the square term in (7.47) obtained for a non-diluted system. This shows that the quadratic term arises from triple interactions between *reacting* species alone. This term disappears when the effects of the surroundings on the free energy of reacting species are additive.

Table 7.5. Coefficients of the $x_i x_j$ terms in the expressions for chemical potentials

	x_A^2	$x_A x_B$	$x_A x_S$	$x_B x_S$	x_B^2	x_S^2
a_{ij}	$+3F_{AAA}$	$+4F_{AAB}$ $+2F_{ABA}$	$+4F_{AAS}$ $+2F_{ASA}$	$+2F_{BAS}$ $+2F_{ABS}$ $+2F_{ASB}$	$+F_{BAB}$ $+2F_{ABB}$	$+2F_{ASS}$ $+F_{SAS}$
$-b_{ij}$	$-2F_{AAB}$ $-F_{ABA}$	$-4F_{ABB}$ $-2F_{BAB}$	$-2F_{BAS}$ $-2F_{ABS}$ $-2F_{ASB}$	$-4F_{BBS}$ $-2F_{BSB}$	$-3F_{BBB}$	$-2F_{BSS}$ $-F_{SBS}$
	A_{11}	A_{12}	A_{13}	A_{23}	A_{22}	A_{33}

The coefficient of the *linear term* can be written as a weighted sum of two contributions: one from the configurations without solvent and another from those involving it:

$$\begin{aligned}2\Delta^{(2')} &= 2\gamma\left(2F_{AAB} + F_{ABA} + 3F_{BBB} - 4F_{AAB} - 2F_{BAB}\right)\\ &\quad + 2(1-\gamma)\left(2F_{AAS} + F_{ASA} - 2F_{BAS} - 2F_{ABS} - 2F_{ASB} + F_{BSB} + 2F_{BBS}\right)\end{aligned} \tag{7.102}$$

Interestingly, when the effects of the surroundings are additive, the terms in brackets in (7.102) become identical, which results in the exclusion of the parameter γ. The linear term in (7.100) is then reduced to a very simple expression involving the effects of the reacting species alone, in fact, a *complete analogue* of the corresponding term derived for non-diluted systems in (7.50):

$$-2x_A\left(\gamma\Delta F_{ex} + (1-\gamma)\Delta F_{ex}\right) = -2x_A\Delta F_{ex} \tag{7.103}$$

in which, as usual:

$$\Delta F_{ex} = F_{BAB} - F_{AAA} + F_{ABA} - F_{BBB} \tag{7.103a}$$

The terms independent of the concentration of reacting species in (7.100) are:

$$\begin{aligned}\Delta^{(1')} &= \gamma^2 A_{22} + \gamma(1-\gamma)A_{23} + (1-\gamma)^2 A_{33} =\\ &= \gamma^2\left(A_{22} + A_{33} - A_{23}\right) + \gamma\left(A_{23} - 2A_{33}\right) + A_{33}\end{aligned} \tag{7.104}$$

They contain combinations of standard free energies not repeating twice in a term and thus cannot be further simplified. However, for *additive effects of the surroundings*, the coefficient of γ^2 in (7.104) equals zero and this term can be written as:

$$\Delta^{(1')} = \gamma\left(F_{BAB} - F_{BBB} + F_{ABA} - F_{BBB}\right) + (1-\gamma)\left(F_{SAS} - F_{SBS} + F_{ASA} - F_{BSB}\right) \tag{7.105}$$

Taking into account the physical significance of the differences of free energies in

(7.105) this equation can also be written as:

$$\Delta^{(1')} = \gamma\left(\Delta F_{ex} - \Delta F\right) - \left(1-\gamma\right)\left(\Delta F_{\infty} + \Delta F_{solv}\right) \qquad (7.105a)$$

The first term in (7.105a) is similar to that occurring in the law of mass action for non-diluted systems ($\Delta F_{ex} - \Delta F$). The second term comprises the standard free energy of reaction (7.93) in the state of infinite dilution ($-\Delta F_{\infty} = F_{SAS} - F_{SBS}$) and the change of free energy of solvent molecules due to a spin crossover in their neighbourhood ($-\Delta F_{solv} = F_{ASA} - F_{BSB}$) accompanied by the weighting factor ($1 - \gamma$).

Under the condition of the additivity of the effects of surroundings, the law of mass action is, in general, similar to that for non-diluted systems:

$$-2x_A\Delta F_{ex} + \gamma\left[\Delta F_{ex} - \Delta F\right] - \left(1-\gamma\right)\left(\Delta F_{\infty} + \Delta F_{solv}\right) + kT\ln\frac{x_A}{x_B} = 0 \qquad (7.106)$$

The exchange term is seemingly independent of dilution (γ) but this is only a *seeming independence* because the law of mass action (7.106) is written with respect to the mole fraction of x_A and not with respect to the degree of conversion. Therefore the steepness of the transition curve varies with dilution which can be demonstrated by writing (7.106) in terms of the degree of conversion $\chi_{A(B)}$, defined by the mass balance equations (7.94) and (7.99) as:

$$x_A/\gamma + x_B/\gamma = 1 \qquad (7.107)$$

hence:

$$\chi_A = x_A/\gamma; \quad \chi_B = x_B/\gamma \qquad (7.107a)$$

The complete law of mass action with respect to χ can then be written as:

$$3\gamma^2\chi_A^2\Delta^{(3)} + 2\gamma\chi_A\Delta^{(2')} + \Delta^{(1')} + kT\ln\left(\frac{\chi_A}{1-\chi_A}\right) = 0 \qquad (7.108)$$

and under the condition of additivity of the effects of surroundings:

$$\gamma\left(1-2\chi_A\right)\Delta F_{ex} - \gamma\Delta F - \left(1-\gamma\right)\left(\Delta F_{\infty} + \Delta F_{solv}\right) + kT\ln\left(\frac{\chi_A}{1-\chi_A}\right) = 0 \qquad (7.109)$$

We see that dilution (lower γ) decreases the effective exchange energy and hence diminishes the probability of critical phenomena (*e.g.* phase separation, or steep spin crossover) occurring. Experimental data on magnetically diluted spin crossover compounds [14] are in agreement with this.

According to (7.109), when exchange free energy is zero the standard free energy contains contributions from spin crossover in clusters of reacting species (ΔF), fully solvated species (ΔF_{∞}), and from changes in the state of solvent molecules due to *spin crossover in their nearest neighbourhoods* (ΔF_{solv}). In fact, the latter two contributions cannot be estimated separately as they enter (7.109) with the same coefficient $1-\gamma$. Experimental data can therefore be analysed either assuming $\Delta E_\infty = \Delta E$, $\Delta S_\infty = \Delta S$ and non-zero ΔE_{solv}, ΔS_{solv}, or assuming the latter two parameters to be zero and varying ΔE_∞ and ΔS_∞.

Fig. 7.22 shows experimental data on spin crossover in $[Fe_yZn_{1-y}(ptz)_6](BF_4)_2$ with varying content of a diamagnetic component acting as a solvent. The data on dilute solution ($\gamma \to 0$, open circles lying on a straight line in Fig. 7.22) provide for an independent estimation of $\Delta E_{inf} = \Delta E_\infty + \Delta E_{solv}$ as well as corresponding entropies. On the other hand the data on non-diluted system ($\gamma = 1$, filled circles in Fig. 7.22) yield the estimates of ΔE_{ex}, ΔE and ΔS. A good coincidence of theoretical and experimental curves indicates that the interpolation according to (7.109) is valid. Two rows of Table 7.6 show two possible estimations of the parameters of (7.109), both corresponding equally to the 'whisk-broom' pattern of experimentally observed van't Hoff plots employing the least number of adjustable parameters. However, both these interpretations of the estimates are wrong from the point of view of physically allowed values of the parameters.

It is highly improbable that the state of the Zn-complex is not changed by a transformation of its nearest surroundings from a small LS complex into a large HS complex. Due this difference in molecular volumes the energy of a Zn-complex must be increased by an LS→HS transition in its nearest neighbourhood. Therefore, ΔE_{solv} must be non-zero and positive.

In order to comply with this requirement the standard energy at infinite dilution must be considerably smaller than ΔE in the pure Fe complex. It is not improbable that the presence of the Zn-complex decreases the energy difference between LS and HS states of the Fe-complex:

$$E_{ZnBZn} - E_{ZnAZn} = \Delta E_\infty < \Delta E = E_{BBB} - E_{AAA}$$

Since the exchange energy is high and positive such a relationship implies that Zn–complex is similar to the HS species of the Fe complex (see the diagram of free energy levels shown in Fig. 7.22). These arguments lead to the following possible estimates of the parameters of (7.109): $\Delta E = 1.74$, $\Delta E_\infty = 1.1$ and $\Delta E_{solv} = 0.1$ kcal mol^{-1}.

Table 7.6. Parameters of (7.110) approximating experimental data from [8] and illustrated in Fig. 7.22 for spin crossover in $[Fe_yZn_{1-y}(ptz)_6](BF_4)_2$; ΔS_{ex} was assumed to be zero

ΔE_{ex} (cal mol^{-1})	ΔE (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔE_∞ (cal mol^{-1})	ΔS_∞ (cal mol^{-1} K^{-1})	ΔE_{solv} (cal mol^{-1})	ΔS_{solv} (cal mol^{-1} K^{-1})
480	1740	7.0	1200	6.7	0	0
480	1740	7.0	1740	7.0	–540	–0.3

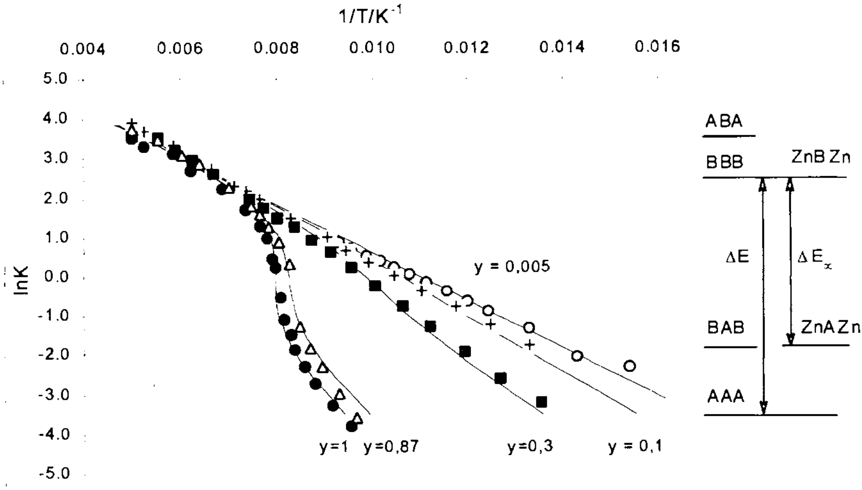

Fig. 7.22. Theoretical van't Hoff plots based on (7.109) with parameters shown in Table 7.6 describing experimental data on spin crossover in magnetically diluted $[Fe_yZn_{1-y}(ptz)_6](BF_4)_2$ [8]. The diagram in the right-hand side of the picture shows possible positions of free energy levels in non-diluted and diluted species.

It is more difficult to make a similar guess about the entropies ΔS_∞ and ΔS_{solv}. The difference between ΔS and ΔS_∞ in the assumption of zero ΔS_{solv} is small (0.3 cal mol^{-1} K^{-1}) and might arise from combined changes in the vibrational frequencies of Fe and Zn complexes.

We see that the model of molecular interactions employed here puts some restrictions on possible values of the parameters and thus enables us to draw additional conclusions.

The relationships obtained also explain why singularities such as steep spin crossovers are not observed in the liquid state. The quasi-crystal lattices of liquids contain a large number of vacancies that can be considered as an inert diluting component. According to lattice theories of the liquid state about 70 – 100% additional centres occur upon melting (according to the entropy of fusion of simple mono-atomic solids). This means an effective decrease of the exchange energy by a factor ($1/\gamma$) of 2, which might well prevent any possibility of observing critical phenomena in spin crossover in the liquid state. On the other hand, phase separation in liquid mixtures must, in reality, be connected with approximately double the exchange energies estimated from the critical temperature of miscibility.

7.12
Conclusions

In this Chapter we have derived various forms of the law of mass action that take into account the non-ideality connected with non-additivity of lattice energy. It has been shown that such non-additivity is a direct result of molecular interactions and can be described either on the basis of binary potentials or represented as a result of dependence of a partition function on the nature of the molecular surroundings. The latter approach yields a more general formalism than that employing the approximation of binary interactions. In fact, it provides a way by which higher order interactions in the condensed state can be taken into account.

The model of binary interactions yields the formalism of the theory of regular solutions, and this explains a number of phenomena connected with phase transitions in liquid mixtures as well as in the solid state (steep spin crossover). The improved model, taking into account triple interactions, yielded the law of mass action describing equilibria in ordered systems in the solid state such as the two-step spin crossover quantitatively. This formalism can be reduced to that of the theory of regular solutions when the effects of molecular surroundings are assumed to be additive.

The non-ideality terms thus introduced are determined by the magnitude of the exchange energy, *i.e.* the energy accompanying a simultaneous transfer of a pair of molecules from homo-molecular to hetero-molecular surroundings. When the exchange energy is positive and larger than $2RT$, singularities such as steep spin crossover (indicative of first-order phase transitions) are predicted. Other singularities predicted for binary mixtures are connected with the phenomenon of ordering originating from negative exchange energy, *i.e.* in the higher energy of hetero-molecular interactions compared to that of homo-molecular interactions.

Multi-component mixtures can also be described using the concept of exchange energy and separating the additive and non-additive parts of the lattice energy. The total potential energy $\Sigma n_i u_i$ of a mixture of m components can be written in terms of binary potentials as:

$$\sum_1^m n_i u_i = \frac{c}{2} \sum_{i=1}^m n_i \sum_{j=1}^m \frac{n_j}{N} \varphi_{ij} \qquad (7.110)$$

in which $N = \Sigma n_i$ and c is the co-ordination number. For such a system there are $m(m-1)/2$ possible types of hetero-interactions and the corresponding number of exchange energies:

$$\Delta u_{ij} = 2\varphi_{ij} - \varphi_{ii} - \varphi_{jj} \qquad (7.111)$$

Equation (7.110) can then be written as:

$$\begin{aligned}\sum_i n_i u_{0i} &= \frac{c}{4}\left(\sum_{i=1}^{m} n_i \sum_{j=1}^{m} \frac{n_j}{N}\left(\Delta u_{ij} + \varphi_{ii} + \varphi_{jj}\right)\right) \\ &= \frac{c}{4}\left(\sum_{i=1}^{m} n_i \sum_{j=1}^{m} \frac{n_j}{N}\Delta u_{ij} + \sum_i n_i \varphi_{ii} \sum_j \frac{n_j}{N} + \sum_i n_i \sum_j \frac{n_j}{N}\varphi_{jj}\right)\end{aligned} \tag{7.112}$$

The second term on the right-hand side of (7.112) equals $\Sigma n_i \varphi_{ii}$ because the sum of mole fractions of all components equals 1. The same is true for the last term: the order of summation can be changed – the indices of summation being independent. The matrix of exchange energies Δu_{ij} is symmetric and therefore the sum $\Sigma x_j \Delta u_{ij}$ is double the sum of either of the triangles:

$$\sum_i n_i u_{0i} = \frac{c}{2}\left(\sum_{i=1}^{m} n_i \varphi_{ii} + \sum_{i=1}^{m} n_i \sum_{j=i+1}^{m} \frac{n_j}{N}\Delta u_{ij}\right) \tag{7.113}$$

This equation represents the energy of molecular interactions as being made up of two parts: one additive with respect to the number of molecules and reflecting interactions with homo-molecular surroundings, and another proportional to the binary products of the numbers of molecules, this reflecting interactions in hetero-surroundings.

The part of a chemical potential arising from such a dependence of the energy of molecular interactions on composition is given by:

$$\frac{1}{kT}\frac{\partial}{\partial n_i}\left(\sum_j n_j u_{0j}\right) = \frac{c}{2}\frac{\varphi_{ii}}{kT} + \frac{c}{2}\left(\frac{N-n_i}{N}\sum_{j\neq i}\frac{n_j}{N}\frac{\Delta u_{ij}}{kT} - \sum_{j\neq i}\sum_{k\neq i,j}\frac{n_j n_k}{N^2}\frac{\Delta u_{jk}}{kT}\right) \tag{7.114}$$

Note that for a binary mixture ($i = 1$, $j = 2$), the second term in brackets disappears. The term $c\varphi_{ii}/2kT$ will contribute towards the standard internal energy of reaction whilst other terms, being concentration dependent, will contribute towards non-ideality.

It must be emphasised that the non-ideality terms considered reflect only a few of the possible effects. Another type of non-ideality terms originates from the dependence of *free volume* on composition (see Chapter 4). These terms are functions of the *relative balances* of volume and lattice energy whereas those connected with the exchange energy are referred to the energy of thermal motion. The non-ideality terms originating from free volume produce effects of a limited magnitude which are practically independent of temperature. On the other hand, non-ideality connected with the non-additivity of lattice energy, being referred to the energy of thermal motion, manifests itself especially strongly at low temperatures.

These two types of non-ideality terms have been considered up to now separately. When put together, they appear in the law of mass action as:

$$Q_n = \sum_i \xi_i \ln V_f + n \sum_i \xi_i \frac{\partial \ln V_f}{\partial n_i} - n \sum_i \xi_i \frac{\partial}{\partial n_i} \sum_j \frac{n_j u_j}{kT} \qquad (7.115)$$

in which stoichiometric coefficients ξ are positive for products and negative for reactants, each u_{0j} is a function of composition and $\Sigma n_j u_j$ is given by (7.110) and (7.112). The free volume itself is a function of lattice energy and this complicates the derivation of an explicit general form of non-ideality terms in (7.115). However, at least for a binary equilibrium, these difficulties are not insurmountable and the corresponding law of mass action can be obtained (see Chapter 9). A general form of the non-ideal law of mass action can be written as:

$$\sum_i \xi_i \ln q_i - \sum_i \xi_i \ln n_i + Q_n\left(n_{1,2..,k}, u_{1,2...k}, v_{1,2...k}\right) = 0 \qquad (7.116)$$

It includes the non-ideality term Q_n given by (7.115) and represented (in the approximations considered above) by a polynomial function of mole fractions of components. It predicts non-linear van't Hoff plots and critical phenomena corresponding to phase transitions of first- and second-order (two-step spin crossover). This law of mass action thus warns one that a reaction in the condensed state might run in a way *unpredictable by a pseudo-ideal form* of this law employing activities.

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8 Chemical Correlations

8.1
Studies of variations of chemical reactivity

The law of mass action establishes a measure of chemical affinity in the form of equilibrium or rate constants or their equivalent, the *standard free energies* of reaction or activation. This is the first step in the formulation of the rules connecting chemical structure and reactivity. Statistical mechanics explains the origin of the relationship between molecular parameters and standard free energy of reaction or activation and enables corresponding formulae to be derived. However, quantitative calculations are (or rather were) only possible for a small number of simple reactions. Therefore, for the majority of practically important cases, a number of *empirical correlations* has been developed, effectively substituting variations of chemical reactivity and modification of the reaction mixture for theoretical relationships.

Although a reaction mixture can be modified in a large number of ways, two general types of *systematic study* are quite common, namely those involving modifications of either the reactant or the solvent.

Studies involving modification of reactants may be further subdivided into two classes, namely those in which the modification is 'remote' with respect to the reaction centre (in other words involving the nearest atoms) or 'direct' (*i.e.* involving a modification of the reaction centre itself). Modification of a reaction centre leads to the largest effects but there is, for such modifications, a high probability of concomitant change in the reaction mechanism. In practice, modification is often achieved by the introduction of *substituents* into reactant molecules.

The studies of *solvent effects* can be classified according to the chemical reactivity of the solvent. A solvent can be chemically inert, it can form molecular complexes with reacting species (*i.e.* solvate them) or it can be directly involved in the considered reaction (*i.e.* behave like a reactant in large excess). The variation of solvent is therefore connected with the variation of parameters of the mean molecular field (inert solvents) and with the introduction of additional equilibria (active solvents).

Quantitatively, modifications can be characterised in two ways: Some molecular parameter or a set of parameters (molecular or ionic radii, dipole

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moment, ionisation potential, energy of LUMO or HOMO, *etc.*) as well as macroscopic physical properties (*e.g.* dielectric, constant, density, viscosity, *etc.*) can be employed to characterise the variation. This mode of characterisation normally implies a reference to the actual reaction mechanism and some theoretical relationship. However, real modifications are always connected with simultaneous changes of several molecular parameters controlling chemical reactivity that complicates the interpretation of the observed variations. In Section 8.1.4, we will consider this problem in some detail.

Another way is to characterise modifications by their effects on a reference reaction. These effects can be conveniently characterised by variations of the logarithms of the equilibrium or rate constants of reactions involving modified reference reactants. This allows one to compare the effects of modification on reactions of different orders as well as to bring together kinetic and equilibrium data. As will be shown later, however, this approach only partly solves the problem of the multidimensionality of variations of parameters.

In any case it is desirable (if not necessary for a meaningful interpretation) to have a knowledge of the physical significance of any correlation and hence to know what molecular parameters govern the chemical reactivity and in what manner they operate.

8.1.1.

Molecular parameters governing variations of chemical reactivity

Molecular parameters which control the standard free energy (or activation free energy) of reaction are in fact not very numerous. In an ideal approximation, *i.e.* taking into account purely intramolecular properties, we must expect contributions (in order of increasing importance) from rotational, translational, vibrational and electronic partition functions. For example, the reaction between two atoms resulting in a diatomic molecule:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB} \tag{8.1}$$

is accompanied by the formation of one vibrational and one rotational degree of freedom as well by a change in the potential energy of the system. The equilibrium constant of (8.1) can be expressed as:

$$\ln K = -\ln eV\left(\frac{2\pi kT}{h^2}\frac{m_A m_B}{m_A + m_B}\right)^{\frac{3}{2}} + \ln\frac{8\pi^2 I_{AB}kT}{\sigma h^2} - \ln\left[2\sinh\left(\frac{h\nu_{AB}}{2kT}\right)\right] - \frac{\Delta E}{kT} \tag{8.2}$$

in which ΔE is often referred to as the difference of the 'electronic energies' of products and reactants. In fact, ΔE is the difference of potential energy of the systems 'electrons + nuclei' of products and reactants. It corresponds to the so-called 'total energy' (sum of electronic energy and the energy of the core-core interactions) computed by quantum chemical programs such as HyperChem®.

Taking into account the fact that a reaction mixture contains the same set of atoms, the 'binding energy' (*i.e.* the total energy less the energy of isolated atoms) can also be used to calculate ΔE yielding identical results.

The moment of inertia, I_{AB}, of a diatomic molecule is:

$$I_{AB} = \frac{m_A m_B}{m_A + m_B} r_{AB}^2 = \mu_{AB} r_{AB}^2 \tag{8.3}$$

and using this we can get the standard free energy of reaction (8.1) as a function of the reduced mass (μ_{AB}), the intermolecular distance (r_{AB}), the vibrational frequency (ν_{AB}), and the change in potential energy (ΔE).

For equilibria that involve polyatomic molecules we have:

$$\sum_i \varsigma_{Ri} R_i \Leftrightarrow \sum_j \varsigma_{Pj} P_j \tag{8.4}$$

In addition, the changes in all degrees of freedom must be taken into account:

$$\ln K = \ln Q_{tr} Q_r Q_v - \frac{\Delta E}{kT} \tag{8.5}$$

in which $\ln Q = \Sigma\zeta_P \ln z_P - \Sigma\zeta_R \ln z_R$. For example, for vibrational degrees of freedom $\ln Q$ becomes:

$$\sum_{i=1}^{l} \varsigma_{P_j} \sum_{j=1}^{m_i} \ln\left(2\sinh\frac{h\nu_j}{2kT}\right)^{-1} - \sum_{i=1}^{n} \varsigma_{R_i} \sum_{j=1}^{m_i} \ln\left(2\sinh\frac{h\nu_j}{2kT}\right)^{-1} \tag{8.5a}$$

in which l and n are the numbers of products and reactants respectively, m_i is the number of vibrational degrees of freedom in the i-th molecule, and ν_j is the vibrational frequency of the j-th degree of freedom.

The number of vibrations and their corresponding frequencies can be determined from *normal mode analysis*. Such an analysis does not present any difficulties, even for complex molecules, because programs for quantum chemical calculations (such as HyperChem®) are now generally available. This program allows one to evaluate all parameters necessary for the calculation of the standard free energy including vibrational frequencies, potential energies, moments of inertia *etc.*[1].

Modifications of reactants also bring about variations in the parameters of *molecular interactions* referred to in this book as *non-ideality terms*. As the main object of making chemical correlations is to establish relationships between reactivity and molecular structure (independent of the state of all other molecules) the non-ideality terms are unwelcome participants and are usually disregarded. In

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[1] Unfortunately, semi-empirical methods (providing a reasonable time of computation) are optimally parameterised for the calculations of *one* property. The results of such calculations are therefore only illustrative.

reality, as will be shown below, they determine many features of chemical correlations in the condensed state.

To a first approximation, assuming volume and lattice energy to be additive, non-ideality can be conveniently expressed in terms of the balances of volume and lattice energy (Δv and Δu – see Chapter 4). A non-additivity of the lattice energy results in non-ideality terms expressed *via* the exchange energy (Δu_{ex}, Chapter 7). In our discussion of correlations based on a linear free energy relationship, the role of non-ideality will be illustrated in terms of the balances of volume and lattice energy. On the other hand, the phenomena of isoequilibrium and isokinetic relationships (Section 8.4) are connected with the temperature dependencies of equilibrium and rate constants where the exchange energy plays a significant role. These phenomena will therefore be analysed by applying both types of description of non-ideality.

Under the condition of additivity of volume and lattice energy the law of mass action for reaction (8.1) can be written as:

$$\ln Q - \ln\left(\frac{2\kappa ekT}{\langle u\rangle}\right)^3 + \frac{\Delta v}{\langle v\rangle} - 3\frac{\Delta u}{\langle u\rangle} = \ln\frac{n_C}{n_A n_B} = \ln K_n \qquad (8.6)$$

in which Δv, Δu are the balances of molecular volume and lattice energy and $<v>$, $<u>$ are the corresponding mean quantities per molecule. Any modification of reactants can bring about a variation in the balances and (in non-diluted systems) the mean values of v and u that contribute toward changes in the equilibrium constant.

8.1.2
Solvent effects

When a reaction is studied in a series of *inert* solvents, solvation equilibria can be disregarded and non-ideality terms alone need be taken into account. For a binary chemical equilibrium in solution with non-zero balances of volume and vaporisation energy:

$$\mathrm{R} \xrightleftharpoons{\text{Solvent}} \mathrm{P} \qquad (8.7)$$

the expression for free energy (4.56) yields the following law of mass action:

$$\ln\frac{q_P}{q_R} - \ln\frac{n_P}{N - n_P} + \frac{\Delta v}{\langle v\rangle} - 3\frac{\Delta u}{\langle u\rangle} = 0 \qquad (8.8)$$

The balances Δv, Δu have been considered (Chapter 4) as *composition independent* and the mean values $<v>$, $<u>$ as *additive properties*. Even such a quasi-ideal approximation resulted in singularities up to phase transitions in the case of large Δu. In dilute solutions, however, non-ideality terms resulted merely in a *solvent dependent* equilibrium constant:

$$\ln \frac{q_P}{q_R} e^{\frac{\Delta v}{v_S} - 3\frac{\Delta u}{u_S}} - \ln \frac{n_P}{N - n_P} = 0 \qquad (8.9)$$

in which the mean volume and mean lattice energy per molecule are determined by the corresponding solvent properties. The variation of the logarithm of the equilibrium constant of (8.7) arising from the variation of solvent can thus be described by the following expression:

$$\ln \frac{K(S)}{K(S_0)} = \Delta v \left(\frac{1}{v_S} - \frac{1}{v_{S_0}} \right) - 3\Delta u \left(\frac{1}{u_S} - \frac{1}{u_{S_0}} \right) \qquad (8.10)$$

in which S_0 denotes a reference solvent.

When solvent molecules form complexes with the molecules of reactants and products we must consider additional effects produced by *solvation equilibria* – a common component of a chemical reaction in the condensed state which is very rarely taken into account explicitly. In addition to the chemical equilibrium, one has to consider the equilibria of solvation of reactants and products. Solvation equilibria can be approximated as the formation of '1:1' molecular complexes:

$$\mathrm{R + S} \xrightleftharpoons{\mathrm{K_{SR}}} \mathrm{RS} \qquad (8.11)$$

$$\mathrm{P + S} \xrightleftharpoons{\mathrm{K_{SP}}} \mathrm{PS} \qquad (8.12)$$

Real concentrations of the components of such an equilibrium mixture can be calculated from the combined law of mass action and mass balance equations. For the system of reactions (8.7), (8.11) and (8.12) they are:

$$C_R = [R] + K[R][S] + K_{SR}[R][S]; \quad [PS] = KK_{SP}[R][S]; \quad [S] \cong C_s \qquad (8.13)$$

The equilibrium constant calculated from the concentrations of reacting species, both solvated and non-solvated (*i.e.* disregarding the solvation equilibria) depends, of course, on the strength of solvation. For the reaction (8.7) it is given by:

$$K_{eff} = \frac{[P] + [PS]}{[R] + [RS]} \qquad (8.14)$$

Taking into account (8.13), this can be transformed into:

$$K_{eff} = K \frac{1 + K_{SP} C_s}{1 + K_{SR} C_s} \qquad (8.15)$$

The effective constant is thus *higher* for strongly solvated *products* and *lower* for strongly solvated *reactants*. When $K_{SR}C_s$, and $K_{SP}C_s >> 1$, the effective equilibrium constant is roughly proportional to the ratio of the equilibrium constants of solvation of products and reactants:

$$K_{eff} \cong K\frac{K_{SP}}{K_{SR}} \tag{8.16}$$

One should not expect significant deviations of the volume and energy of vaporisation of molecular complexes from additivity (at least in a system of uncharged particles). Therefore the effects of non-ideality considered above might be important for the *chemical reaction* (8.7) but, to a first approximation, they can be neglected for the solvation equilibria. Combining the effects of non-ideality in the chemical reaction (8.7) with those of solvation, the effective equilibrium constant of (8.7) can thus be written as:

$$\ln K_{eff}(S) = \ln\frac{K_{SP}}{K_{SR}} + \frac{\Delta v}{v_S} - 3\frac{\Delta u}{u_S} \tag{8.17}$$

The terms on the right-hand side of (8.17) represent the balances of (i) the 'solvability', (ii) the volume, and (iii) the energy of molecular interaction between products and reactants. The variation of the effective equilibrium constant of a chemical reaction in a series of solvating media with respect to the reference solvent 'S_0' can then be expressed as:

$$\ln\frac{K_{eff}(S)}{K_{eff}(0)} = \ln\frac{K_{SP}}{K_{SR}}\frac{K_{S_0R}}{K_{S_0P}} + \Delta v\left(\frac{1}{v_S} - \frac{1}{v_{S_0}}\right) - 3\Delta u\left(\frac{1}{u_S} - \frac{1}{u_{S_0}}\right) \tag{8.18}$$

Although the solvability terms might constitute the major part of the variation of free energy any detailed study of solvent effects must also take into account the non-ideality terms.

8.1.3
Kinetic studies

Equilibrium constants (standard free energies of reaction) provide us with a relative (referred to the reverse reaction) measure of chemical affinity. A more direct measure (but also more difficult to obtain, either theoretically or experimentally) is the reaction rate constant (standard free energy of activation). The rates of chemical reactions can be described theoretically using approaches based on a quasi-thermodynamic model. These include, *inter alia*, the Arrhenius equation as well as the model of the transition state developed by Eyring [1]. Another description is based on the kinetic theory of gases and is known as *collision theory* (Lewis [2], Trautz [3]). Non-equilibrium thermodynamics has also been successfully applied to the description of the kinetics of chemical reactions (Kramers [4], McCoy and Carbonell [5]).

The transition-state model is based on the idea of a chemical equilibrium between the ground state of the reactants and their state on the top of the potential barrier of reaction (transition state, activated complex). The motion achieving the final transformation of the activated complex into products is taken to be an oscillation of relatively low frequency, ω^*. The rate of a chemical reaction is thus the product of the frequency ω^* and the concentration of the activated complex. The latter is calculated using the law of mass action for the activation equilibrium and statistical mechanical formulae for the corresponding 'equilibrium constant'. One of the partition functions involved is that of oscillation with frequency ω^*, *i.e.* $kT/h\omega^*$, which results in the cancellation of this frequency. This then leaves the factor kT/h as a general frequency of the attempts to pass the potential barrier for any reaction:

$$k = \frac{kTe}{h}\exp\left(-\frac{\Delta F^{\#}}{RT}\right) \tag{8.19}$$

The fundamental problem connected with this model is that the frequency of oscillations along the reaction coordinate at the top of the potential barrier, ω^*, (although cancelled in the final equation) becomes an imaginary value. Again, the rate of formation of the activated complex is arbitrarily assumed to be much faster than that of any reaction. In other respects this model provides a convenient calculation of the standard free energy of activation, $\Delta F^{\#} = \Delta E^{\#} - T\Delta S^{\#}$ by employing statistical formulae.

The molecular collision model successfully describes experimental data on a large number of gas and condensed phase bimolecular reactions [6]. The rate of reaction is calculated as the number of collisions of molecules having kinetic (energy along the line of mutual approach) higher than that of some required value E^*:

$$-\frac{d[A]}{dt} = [A][B]\left\{ (r_A + r_B)^2 (8\pi kT/\mu_{AB})^{1/2} \right\} e^{-\frac{E^*}{RT}} \tag{8.20}$$

in which μ_{AB} is the reduced mass. Due to the compensating effects of masses and radii of molecules, theoretical values of the pre-exponential factor (the term in square brackets in (8.20)) vary in a relatively narrow range $Z^0 \cong 10^{10} - 10^{11}\ \mathrm{s}^{-1}$. Pre-exponential factors higher than predicted by this theory (positive activation entropy) are explained either by invoking a chain mechanism or by the distribution of energy over a number of oscillators [6]. According to the latter model, the vibrational energy of a large number of weakly interacting oscillators may be concentrated in one crucial degree of freedom, thus causing an elementary act of chemical reaction. This theory yields the rate constant as a function of the height of the potential barrier E^* and the number of oscillators s:

$$k_2 = Z^0 e^{-\frac{E^*}{RT}} \sum_{i=0}^{s-1} \frac{(E^*/RT)^i}{i!} \tag{8.21}$$

This model was originally developed by Hinshelwood, Fowler and Rideal [7] to explain monomolecular reactions activated by molecular collisions. In general, Z^0 can be considered as the frequency of attempts to pass the potential barrier. For example, the rate constant of molecular rotation is given [8] by:

$$k_1 = \frac{2\Gamma(s+1/2)}{\Gamma(s)} \nu \left(\frac{E^*}{kT}\right)^{1/2} e^{-\frac{E^*}{RT}} \sum_{i=0}^{s-1} \frac{(E^*/RT)^i}{i!} \tag{8.22}$$

in which $\nu = (E^*/4\pi^2 I)^{1/2}$ is the frequency of rotational oscillations of a molecule in the ground state whilst for the transition state a free rotation along the reaction coordinate is assumed.

Lower than expected reaction rates (negative activation entropy) can be interpreted as arising from a specific mutual orientation of reactants being required for an elementary act of a chemical reaction. Similar factors decreasing the rate of chemical reactions with respect to that given by the number of binary collisions are steric hindrances. They can be described by introducing equilibria of structural transformation of reactants into chemically active forms. Due to the high potential energy of these forms they are present in small amounts and are practically independent of temperature. Formally, these stages contribute towards the entropy of activation alone *but only at low temperatures*[2].

For completeness, it must be mentioned at this point that reactions can also be inhibited by the 'spin conservation rule'. A good example of where this applies is in the reactions of molecular oxygen with organic compounds because such reactions must include either the occurrence of spin crossover or the formation of radicals. In other words, the spin conservation rule can be overcome either by a spark causing the atomisation of molecular oxygen followed by a radical chain reaction or by the formation of a catalytic spin crossover complex. These examples also reveal the principal difference between equilibria (independent of the reaction path) and kinetics (which is dependent on the path).

Within the framework of non-equilibrium thermodynamics, a chemical reaction is considered as a stochastic process of molecules crossing a potential barrier *via* many-quantum excitations actuated by molecular collisions. The reactants are considered as distributed among some number (s_N) of closely spaced energy levels and the molecules on the highest level are assumed to transform irreversibly into the products. The probability of transition from level to level due to interaction with the heat bath (vibrational motion of surrounding molecules) is given by the non-diagonal matrix elements of the corresponding Hamiltonian. Under steady state conditions this model yields [9] the first order reaction rate constant as:

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[2] At $kT \geq \Delta E$ the amounts of active forms become *temperature dependent*.

$$k_1 = A_0 s_N \left(\frac{\hbar\omega}{kT_{bath}} \right)^2 \exp\left(\frac{s_N \omega}{\nu} \right) \exp\left(-\frac{s_N \hbar\omega}{kT_{bath}} \right) \tag{8.23}$$

in which $\hbar\omega$ is the energy spacing between the levels of reactants and $\hbar\nu$ is the energy spacing of the heat bath. The numerator in the second exponential in (8.23) is then the height of the potential barrier. This term corresponds, therefore, to the usual exponential describing an activation process. The argument of the first exponential is the height of the potential barrier ($s_N\omega$) with respect to the energy spacing in the heat bath. By expanding the first exponential into a series and truncating it at the s_N-th term we obtain an equation similar to that of the model for the distribution of energy (8.21):

$$k_1 = A_0 s_N \left(\frac{\hbar\omega}{kT_{bath}} \right)^2 \sum_{i=0}^{s_N - 1} \frac{(h s_N \omega / h\nu)^i}{i!} \exp\left(-\frac{s_N \hbar\omega}{kT_{bath}} \right) \tag{8.23a}$$

The potential barrier height in (8.21) can be identified with $E^* = N_L \hbar s_N \omega$; the energy level spacing in the heat bath can be assumed to be of the order of RT ($\hbar\nu = kT$). Equations (8.21) and (8.23a) then yield nearly identical dependencies of the rate constant on temperature and potential barrier height. Both these models predict a certain parallelism in the variations of entropy and internal energy of activation, *i.e.* the isokinetic relationship (IKR) (which will be considered in Section 8.4).

The transition-state model seems to be the most comprehensive and comprehensible. It allows one to draw, at least qualitative, conclusions about the nature of the transition state and the mechanism of reaction. The kinetic theory of gases provides a clear physical significance of the kinetic parameters of bimolecular reactions in gases. The stochastic model, on the other hand, is more applicable to reactions in the condensed phase, where the interactions of molecules should be described using the concept of a molecular field rather than that of molecular collisions.

8.1.4
Multidimensionality of variations. Reference reactions

As has already been mentioned above, a modification of a reaction mixture is connected with a simultaneous variation of more than one of those parameters determining chemical affinity. By varying a substituent, one changes potential (electronic) energy, masses and volumes of particles and their moments of inertia as well as vibrational frequencies. In the condensed state free rotation is fairly damped and it is reduced to rotational oscillations depending on molecular properties (moments of inertia) as well as on parameters of intermolecular interactions. The latter are governed by intermolecular distances (molecular volume) and electric properties of molecules (dipole moments, polarisability).

This shows that, in studies of variations of reactivity, the independent variable is practically always a vector:

$$\mathbf{Q} = (Q_1, Q_2, \ldots Q_n) \tag{8.24}$$

As an assumption (supportable by some arguments), the variations of all components of **Q** but one can often be disregarded. Table 8.1 shows the results of calculations of the contributions from translational, rotational, vibrational (neglecting lattice vibrations) and electronic partition functions to the molecular free energy of halogen-substituted benzene:

$$\frac{f}{kT} = const - \ln m^{\frac{3}{2}} - \ln(I_A I_B I_C)^{\frac{1}{2}} - \sum \ln\left[2\sinh\frac{h\nu_{\text{int}}}{2kT}\right] + \frac{E}{kT} \tag{8.25}$$

in which m is molecular mass and I_A, I_B, I_C are the moments of inertia about the respective three axes and the subscript *int* refers to the internal vibrational degrees of freedom. The potential energy E was obtained by MNDO calculations on optimised molecular structures (HyperChem3®) as the 'total energy'; the same program was used to determine the moments of inertia and vibrational frequencies.

According to Table 8.1, the variations of the potential ('total') energy E of a molecule are indeed much higher than the variations of translational, rotational and vibrational contributions. However, the standard free energy of reaction is the *difference* of molecular free energies of products and reactants. Therefore, large variations of electronic energy can be cancelled out *whilst the variations of minor contributions* (*e.g.* moments of inertia) will not. When a reaction is studied in a number of weakly solvating solvents, the observed variation of reactivity might originate either from a variation of the molecular volume of the solvent or from a variation of the energy of weak molecular interactions.

Table 8.1. Variations[3] of energy (in kcal mol^{-1}) of molecules of mono-substituted benzene, C_6H_5X, and of translational, vibrational (for 30 normal vibrational modes) and rotational contributions to the free energy with respect to the iodine-derivative calculated at 303 K

Substituent	I	Br	Cl	F
Total Energy	0	–150.35	–311.45	–3189.64
$-RT\Sigma \ln z_v$	0	0.264	0.708	2.332
$-RT\ln m^{3/2}$	0	0.235	0.535	0.678
$-RT\ln (I_x I_y I_z)^{1/2}$	0	0.139	0.368	0.623

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[3] Data in Table 8.1 are referred to the iodine derivative (and not to the unsubstituted benzene) in order to get comparable results of semi-empirical quantum chemical calculations using the same set of orbitals (s and p).

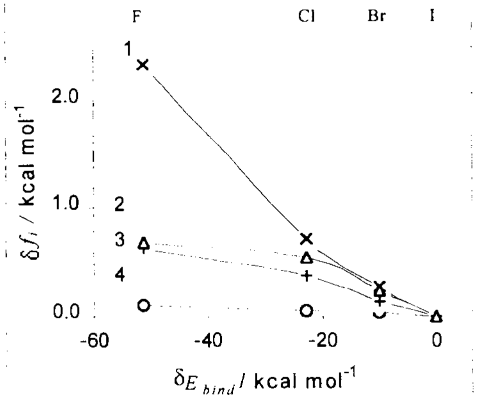

Fig. 8.1. The variations of the terms of (8.25) as functions of the variation of binding energy in halogen substituted benzene: $f_i = -RT\Sigma\ln z_v$ (1); $-RT\ln m^{3/2}$ (2); $-RT\ln(I_xI_yI_z)^{1/2}$(3); and $-RT\ln v$ (4)

Note also, that in the sequence F, Cl, Br, I several apparently independent parameters, namely molecular volume, molecular mass, vibrational temperature, moments of inertia show variations (Fig. 8.1) closely related to the variations of binding energy (total energy less the energy of isolated atoms). *All these parameters constitute a multidimensional vector* **Q**.

For any reaction, there are several parameters most strongly affecting the reactivity. They can be selected based on the actual reaction mechanism and characterised by the *parametric sensitivities* $\partial U/\partial q_i$, U denoting the standard free energy of reaction (activation) or a property directly connected with it.

Significant effects can be expected from the variations of the parameters q_i having $\partial U/\partial q_i$ above a certain level. These parameters constitute the vector **q**. The variations of reactivity observed in a given reaction series characterised by the vector **Q** thus originate in variations of the components of **Q** belonging to the intersection $\mathbf{Q}\cap\mathbf{q}$. *If this intersection is multidimensional then any results obtained cannot be unambiguously interpreted.* It is possible to reduce the number of variables characterising a reaction series to one by employing a *reference* property as an independent variable. The variation of reactivity (or some physical property connected with reactivity) R of a *reference substance in a reference reaction* can be measured for a given type of modification of reactants or solvent.

A *single empirical parameter* therefore replaces a *vector of theoretical parameters*. The behaviour of the reference property can be thoroughly investigated on the basis of a molecular model, thus providing an indirect way of theoretical interpretation of the observed variations of reactivity.

The problem of multidimensionality is thus transformed into the problem of a correct (fortunate?) choice of the reference reaction and reference property. For example, in the Gutmann scale of donicity [10], $SbCl_5$ was chosen as a reference substance and its heat of complexation with molecules in dilute solutions in dichloroethane (DCE) was taken as a reference property. In the Hammett scale of reactivity [11], substituted benzoic acids and the constants of their electrolytic dissociation were chosen as reference substance and reference property respectively. Common sense suggests that the stability of the molecular complex of an acid with a number of bases must be proportional to the donor number of the bases. On the other hand, the reactivity of a compound modified by substituents and involved in reactions of nucleophilic or electrophilic substitution must follow the Hammett rules. The reference object must, therefore, have some crucial parameter in common with the investigated reaction or, in other words, the *reference and investigated reactions must be closely related.* In such cases, we can expect a correlation between the reactivity U and reference property R.

Another requirement for the reference substance or reaction is that the corresponding vector of parameters $\mathbf{q}_R$ determining the reactivity R must be, as far as possible, *one-dimensional.* In other words, the parametric sensitivity with respect to one parameter must be much higher than those with respect to all other parameters. Having a set of such reference objects we would then be able to analyse the behaviour of the system using multidimensional regression and evaluate the contributions of different mechanisms.

One-dimensionality of variations in a reference object can be achieved by employing a reference compound showing extremely strong properties (*e.g.* a strong electron acceptor such as $SbCl_5$ for donor numbers or a strong electron donor such as tri-methylphosphine oxide for acceptor numbers [12]). On the other hand, a reaction can be virtually insensitive to any other effects but one (the electrolytic dissociation of benzoic acid is seemingly sensitive only to the electron distribution in the aromatic ring).

Suppose that the molecular parameters varied in a reaction series constitute the vector $\mathbf{Q}$. The investigated and reference properties can then be defined as functions of $\mathbf{Q}$: $U(\mathbf{Q})$ and $R(\mathbf{Q})$. The variations of these properties originate from the variation of parameters constituting the vectors $\mathbf{q}_U$ and $\mathbf{q}_R$ that correspond to the highest sensitivities. The observed changes (very rarely is an experiment designed for the observation of zero changes!) of both U and R signify that intersections of $\mathbf{Q}$ and $\mathbf{q}$ are not void:

$$\mathbf{Q} \cap \mathbf{q}_U = \mathbf{u} \neq \mathbf{Z} \text{ and } \mathbf{Q} \cap \mathbf{q}_R = \mathbf{r} \neq \mathbf{Z} \qquad (8.26)$$

in which $\mathbf{Z}$ is a void set. The *physical* significance of these observations depends, however, on whether the changes in U are caused by the intersection $\mathbf{u} \cap \mathbf{r}$ or not. If there is a non-void intersection of the vectors $\mathbf{u}$ and $\mathbf{r}$:

$$\mathbf{u} \cap \mathbf{r} = \mathbf{p} \neq \mathbf{Z} \qquad (8.27),$$

then the observed correlation might reflect a dependence $U = f(R)$. This actually happens when the observed variations of U and R are caused by variations of *the* *same* independent variable(s). The correlation of U and R can then be considered as a functional dependence defined parametrically:

$$U = f(\mathbf{p})\,;\ R = \varphi(\mathbf{p}) \tag{8.28}$$

and this situation is highly probable when the dimensions of *both* $\mathbf{q}_U$ and $\mathbf{q}_R$ are small.

On the other hand, if the dimension of $\mathbf{q}_U$ is large (the dimension of $\mathbf{q}_R$ we assume to be small) then the observed variations can be caused by the components of **u** not belonging to **p**. Unfortunately, these effects can completely mask the effects due to the components belonging to **p**. Such variations of U and R represent then a *pseudo-correlation* that arises from the multidimensionality of the variable **Q**.

Also an absence of variation of U over some range of R (a horizontal line in a graph) does not necessarily mean that $\mathbf{u}\cap\mathbf{r} = \mathbf{p} = \mathbf{Z}$. The multidimensionality of **u** might cause the effects of variations of u_i not belonging to **p** to compensate those of u_j belonging to **p**. *In order to get a physically significant correlation the vectors **u** and **r** must be of small dimensions and their intersection **p** must be not void.*

This is, in fact, a mathematical formulation of the condition that the investigated and reference reactions must be *similar*. We see that the introduction of a reference property does not solve the problem of multidimensionality. In order to obtain a *physically significant* correlation the *reference reaction must comply with the requirement of one-dimensionality and the investigated and reference reactions must be similar.*

8.2
Linear free energy relationship. Modification of reactants

Experimentally, a large number of linear relationships have been established between standard free energies of reaction (and activation). One of the best known correlations is the Hammett equation. Such relationships are known as *linear free energy relationships* (LFER). A linear relationship between standard free energies of equilibria involving identical modifications of a reactant can be established on the basis of a simple rule that the *variations of molecular free energy due to a given modification are equal for a number of similar molecules forming a class and differ by a constant factor for the molecules belonging to different classes.*

Suppose that one of the reactants taking part in the reaction of a general type:

$$\sum_i \varsigma_{Ri} R_i \Leftrightarrow \sum_j \varsigma_{Pj} P_j \tag{8.29}$$

is systematically modified by substituents. Apparently, one of the products must also be similarly modified. Let us assume that they are the reactant '1' and the product '1'. Stoichiometric coefficients corresponding to these molecules must be identical. The law of mass action for (8.29) can then be written as:

$$\sum_{j=2} \varsigma_{P_j} \ln q_{P_j} - \sum_{i=2} \varsigma_{R_i} \ln q_{R_i} + \varsigma_1 \left(\ln q_{P_1} - \ln q_{R_1}\right) - \ln \frac{\prod_j [P_j]^{\varsigma_{Pj}}}{\prod_i [R_i]^{\varsigma_{Ri}}} = 0 \qquad (8.30)$$

Separating the constant and varying parts (over the reaction series), we get the equilibrium constant of (8.29) as:

$$\ln K(S) = \sum_j \ln [P_j]^{\varsigma_{Pj}} - \sum_i \ln [R_i]^{\varsigma_{Ri}} = \ln Q + \varsigma_1 \left(\ln q_{P_1}(S) - \ln q_{R_1}(S)\right) \qquad (8.31)$$

in which the symbol 'S' signifies the modification by the substituent 'S'. The *variation* of the logarithm of the equilibrium constant with respect to the *reference substituent* '0' becomes:

$$\ln \frac{K(S)}{K(0)} = \varsigma_1 \left\{ \left(\ln q_{P_1}(S) - \ln q_{P_1}(0)\right) - \left(\ln q_{R_1}(S) - \ln q_{R_1}(0)\right) \right\} \qquad (8.32)$$

The terms in square brackets are the variations (in units of kT) of molecular standard free energies, $f_i = -kT \ln q_i$, of the product '1' and the reactant '1' modified by the same substituent. Molecules of reactant '1' and product '1' belong, most probably, to different classes and the variations of their free energies must differ by a constant factor:

$$\delta f_{P_1}(S) = f_{P_1}(S) - f_{P_1}(0) = a \delta f_{R_1}(S) \qquad (8.33)$$

This results in:

$$\ln \frac{K(S)}{K(0)} = -\varsigma_1 \left(\delta f_{P_1}(S) - \delta f_{R_1}(S)\right) = -\varsigma_1 (a-1) \frac{\delta f_{R_1}}{kT} \qquad (8.34)$$

Note that when $a = 1$, *i.e.* when the reactant and product are (nearly) identical molecules, no variation of reactivity will be observed in a reaction series.

The variation of free energy of the reactant '1' is, in its turn, linearly related to the variation of molecular free energy of some *reference compound* **R**:

$$\delta f_{R_1} = b \delta f_{\mathbf{R}} \qquad (8.35)$$

This allows us to write (8.34) as:

$$\ln \frac{K(S)}{K(0)} = -b \varsigma_1 (a-1) \frac{\delta f_{\mathbf{R}}(S)}{kT} \qquad (8.36)$$

This equation holds for *any* reversible reaction hence also for the *reference reaction* involving the reference compound. In this case $b = b_{\mathbf{R}} = 1$ and $a = a_{\mathbf{R}}$. The logarithm of the ratio of equilibrium constants of a reference reaction involving modified and 'unmodified' (substituent '0') reference compounds can therefore be used as a parameter characterising the change in chemical affinity due to such a modification:

$$\sigma_S = \ln\frac{K_{\mathrm{R}}(S)}{K_{\mathrm{R}}(0)} = -\varsigma_{\mathrm{IR}}(a_{\mathrm{R}} - 1)\frac{\delta f_{\mathrm{R}}(S)}{kT} \tag{8.37}$$

Comparing (8.36) and (8.37) we see that σ_S characterises the variation of chemical affinity in a series of equilibria of an arbitrary type involving a reactant modified by substituents:

$$\ln\frac{K_i(S)}{K_i(0)} = \rho_i\sigma_S \tag{8.38}$$

in which

$$\rho = \frac{b(a-1)}{(a_{\mathrm{R}} - 1)}\frac{\varsigma_{\mathrm{I}}}{\varsigma_{\mathrm{IR}}} \tag{8.38a}$$

Equation (8.38) is similar to the Hammett equation in which a *substituent constant*[4] σ is defined employing the equilibrium of electrolytic dissociation (reference reaction) of the substituted benzoic acid (reference compound) but applied to characterise the *rates* of chemical reactions:

$$\ln\frac{k_i(S)}{k_i(0)} = \rho_i\sigma_S \tag{8.39}$$

This equation successfully describes correlations of kinetic rate constants of a large number of reactions, which means that the principle of linear free energy relationship *can* be applied to the equilibrium of formation of the transition state. Although the effects of modification of the transition state might be thought to be completely different to those of the ground state, the general assumption of the principle of LFER holds: identical modifications of similar transition states must result in identical changes in the free energy. The ground and transition states can be considered as molecules belonging to completely different classes and the coefficient a in (8.36) can be imagined to be large and positive, large negative or zero *but not* $a = 1$ *for which no correlation would be observed.*

The physical significance of the coefficient a is quite difficult to establish. In general, even the variation of molecular free energy due to a substitution cannot be expressed explicitly because the total energy E can only be obtained as a solution of the corresponding Hamiltonian. One can *simulate* these variations using quantum chemical calculations on actual molecules and thus estimate a 'theoretical' value of a. Such an estimation is, however, just a numerical experiment. According to the data in Table 8.1 (above) the variations of the total energy calculated for halogen-substituted benzene are much higher than the

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[4] The Hammett equation employs decimal logarithms which brings about the conversion factor 2.3 ($\sigma_S = 2.3\sigma$)

variations of translational, rotational and vibrational contributions. However, the *variations* of the total energy caused by identical substitutions (modifications) of different molecules are astonishingly similar (see Table 8.2). They are practically identical for substituted benzene and naphthalene: the difference is far less than RT at 300 K. The variations in substituted ethylene molecules differ from those of the corresponding benzenes by less than $2RT$. It is only in saturated hydrocarbons that substitution by halogens brings about changes in total energy differing from those observed in aromatic compounds (by 6 – 9RT). These results show that the basic assumption of the principle of the LFER is qualitatively correct with respect to the total energy.

Table 8.2 Variations (with respect to the iodine derivative) of the total energy (MNDO calculations) due to substitution in molecules of various classes

	Br	Cl	F	Br	Cl	F	Br	Cl	F
	δE (kcal mol^{-1})			$A = \delta E/\delta E_{\mathrm{PhX}}$			$(\delta E - \delta E_{PhX})/RT$		
Ph-X	–150.3	–311.4	–3189.6	1	1	1	0	0	0
Naphth-X	–150.4	–311.5	–3189.6	1.0002	1.0001	1.0000	–0.055	–0.057	–0.028
C_2H_3X	–150.5	–312.0	–3191.0	1.0009	1.0019	1.0004	–0.219	–1.001	–2.335
C_2H_5X	–154.3	–316.7	–3192.5	1.0263	1.0170	1.0009	–6.6	–8.804	–4.951
C_3H_7X	–154.6	–317.0	–3193.1	1.0280	1.0179	1.0011	–7.019	–9.302	–5.949

Table 8.3. Variations of the main components of free energy of meta-substituted benzoic acids and corresponding anions compared to the variation of the Hammet substituent constant (at 298 K)

	I	Br	Cl	F
		Absolute values		
E_{Ac} (kcal mol^{-1})	–44997.156	–45147.546	–45308.529	–48187.051
E_{An}(kcal mol^{-1})	–44687.473	–44837.646	–44999.377	–47877.616
$(E_{An} - E_{Ac})/RT$	524.851	525.217	523.951	524.430
$\Sigma \ln Z_{vAn} - \Sigma \ln Z_{vAc}$	13.872	13.959	13.982	13.897
		Values with respect to those of the iodine-derivative		
E_{Ac} (kcal mol^{-1})	0	–150.389	–311.372	–3189.895
E_{An} (kcal mol^{-1})	0	–150.173	–311.903	–3190.143
$(E_{An} - E_{Ac})/RT$	0	0.366	–0.899	–0.420
$\Sigma \ln Z_{vAn} - \Sigma \ln Z_{vAc}$	0	0.086	0.109	0.024
$2.3\Delta\sigma$	0	0.092	0.046	–0.023

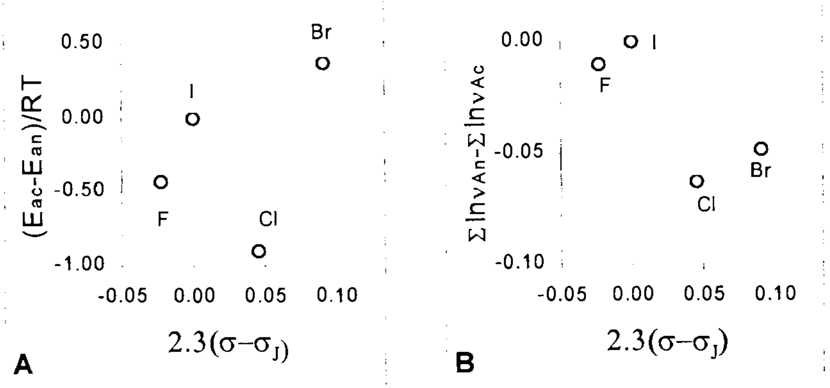

Fig. 8.2. The variation in the contributions to the standard free energy of ionisation of substituted benzoic acids from the total energy (**A**) and vibrations (**B**) as functions of Hammett substituent constants

The product and reactant molecules must, however, be drastically different in order to get a substantial variation of the standard free energy. In fact, the variations of reactivity reflected by the Hammett substituent constants correspond to *extremely small variations* of the standard free energy of dissociation of modified benzoic acids. Theoretical differences of the total energies (MNDO) of the molecules of non-dissociated benzoic acid and corresponding anion exhibit variations, (although very small compared to the variations in these molecules separately) several times higher than the expected value of $2.3\Delta\sigma$, see Table 8.3.

Furthermore, the computed variations of $\Delta E = E_{An}(S) - E_{Ac}(S)$ show no correspondence with the variations of substituent constants (Fig. 8.2). In fact, a good correlation could hardly be expected because the variations of ΔE result from a balance of very large values corresponding to non-dissociated acid and anion. The same calculations show that the vibrational contribution ($\delta\Sigma\ln z_v$) is of the same order of magnitude as the variations of experimental substituent constants (Fig. 8.2 B). Therefore, experimental values might result from a complete balance of major effects, whereas minor contributions such as vibrations, solvation and non-ideality might contribute significantly to the Hammett constants (especially as the products (ions) drastically differ from the reactant (non-dissociated acid) with respect to molecular interactions).

The variation of chemical reactivity can be also described directly by using a simplified model of interactions, *i.e.* calculating some part of the free energy whilst assuming other contributions to be constant. For example, the difference in the free energies of substituted benzoic acid in non-dissociated and dissociated forms can be represented as arising from the *electrostatic interaction* of the dipole moment of the C–X bond and the proton point charge in the molecule of non-dissociated acid [6]:

$$2.3\sigma = \frac{E_{el}}{kT} = \frac{z_H \mu_{CX} \cos\theta}{kTr_{HX}^2} \frac{1}{D} \tag{8.40}$$

in which z_H is the charge on the OH proton, μ_{CX} is the dipole moment of the C–X bond, θ is the angle between the dipole moment and the line connecting its centre with the OH proton, D is an effective dielectric constant accounting for the shielding of the electrostatic field by electronic orbitals. Table 8.4 shows the results of such calculations for meta-substituted benzoic acids. According to these data, (8.40) predicts, in some cases, the wrong sign for σ. The difference between the electrostatic component E_{el}/kT and 2.3σ increases regularly in the series F, Cl, Br, I, which indicates some unaccounted for contribution, *e.g.* the non-ideality terms which must be considerably different for a neutral molecule when compared with a solvated cation and anion.

Hammett substituent constants do not, therefore, reflect *exclusively* the intramolecular properties but contain a significant intermolecular contribution. They provide us with a measure of reactivity originating from the variation of several parameters and establish a formal scale that can be useful in predicting the behaviour of similar molecules in similar reactions. The well-known example of a linear correlation of Hammett constants with the reaction rates of methanolysis concerns the esters of substituted benzoic acids. In this case, the investigated reaction includes a heterolytic cleavage of the COO–R bond, which is very similar to the reference reaction of proton dissociation. Such a scale of reactivity can be adjusted by a selective choice of objects or by employing additional parameters determined from other reference reactions such as has been done in the Taft system [13].

Table 8.4. Charge distribution, interatomic distances (AM1 calculations[5] HyperChem3®), dipole moment of the C–X bond and the energy of electrostatic interaction of this dipole with the OH proton in molecules of meta-substituted benzoic acids. The factor $1/D$ was assumed to be 1

X	Atomic charges (electron charge)			Distances (Å)		μ (Debye)	*E*/*kT*	2.3σ
	X	C	H	X–C	X–H	X–C		
H	0.14	–0.149	0.248	1.1	5.794	1.525	0.652	0
F	–0.1	0.075	0.248	1.354	5.965	–1.137	–0.458	0.782
Cl	–0.003	–0.082	0.248	1.698	6.198	0.643	0.240	0.874
Br	0.066	–0.188	0.248	1.871	6.324	2.281	0.819	0.897
I	0.158	–0.285	0.248	2.019	6.431	4.293	1.49	0.805

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[5] The method AM1 was found to provide the best agreement between calculated and experimental values of the dipole moments of substituted benzenes.

8.3

Linear free energy relationship. Variation of solvent

One of the drawbacks of the Hammett and related systems of substituent constants is that the reference reaction exhibits very small variations of free energy and these can only be determined exactly because of the extremely high (at least in theory!) precision of electrochemical measurements. The system of *donor and acceptor numbers* developed by Gutmann and his co-workers is based on very strong electron donor/acceptor properties of the reference compounds. It can be advantageously used for predicting reactivity in solvents forming Lewis acid-base complexes with reacting species. The donor number being the heat of reaction of $SbCl_5$ with bases, measured in dilute solution in dichloroethane (DCE), corresponds to the standard *internal energy* (enthalpy) of the reaction of formation of an acid-base complex:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB} \tag{8.41}$$

The stability constant of such a complex is controlled by molecular parameters as represented by the statistical mechanical expression:

$$\ln K = \ln Q_{tr} Q_r Q_v - \frac{\Delta E}{RT} \tag{8.42}$$

in which $Q = z_{AB}/z_A z_B$ are the contributions of translational, rotational and vibrational degrees of freedom and ΔE is the (total) energy difference between the product and reactants. Neglecting rotational degrees of freedom of the reactants, the first two contributions can be written as:

$$Q_{tr} = \left(\frac{2\pi kT}{h^2}\mu_{AB}\right)^{-3/2}; \quad Q_r = \frac{8\pi^2 \mu_{AB} r_{AB}^2 kT}{\sigma h^2} \tag{8.43}$$

The vibrational contribution can be found from the frequencies of the normal vibrations of reactants and products to be:

$$Q_v = \prod 2\sinh\frac{kT}{2h\nu_A} \prod 2\sinh\frac{kT}{2h\nu_B} \Big/ \prod 2\sinh\frac{kT}{2h\nu_{AB}} \tag{8.44}$$

The standard entropy of (8.41) includes the derivatives $\partial \ln Q/\partial T^{-1}$:

$$\Delta S^0 = R\ln\left[\left(\frac{8\pi}{\mu_{AB}}\frac{h^2}{kT_0}\right)^{1/2} r_{AB}^2 Q_v(T_0)\right] - \frac{R}{T_0}\left(\frac{\partial \ln Q_{tr} Q_r Q_v}{\partial T^{-1}}\right)_{T=T_0} \tag{8.45}$$

The same quantity also enters the expression for the standard internal energy (see (3.71) and (3.72)):

$$\Delta E^0 = \Delta E - R\left(\frac{\partial \ln Q_{tr} Q_r Q_v}{\partial T^{-1}}\right)_{T=T_0} \qquad (8.46)$$

According to (8.43), the derivative for the product $Q_{tr}Q_r$ is $-\frac{1}{2}T_0$ and that for the vibrational contribution can be found by the numerical experiment of calculating $\ln Q_v$ for several temperatures around T_0 and estimating the coefficient a_v of the linear regression equation $\ln Q_v = a_v T^{-1} + b_v$.

Table 8.5 shows the computed components of the standard free energy of the reaction of $SbCl_5$ with bases *in vacuo*. The standard internal energies computed with respect to that of DCE (δE^0) are of the order of magnitude of the corresponding donor numbers and qualitatively follow (Fig. 8.3) in their variation. The absolute values (ΔE^0) calculated for DCE are apparently too high whereas those for acetone and dioxane are too small. It must be mentioned that the computed ΔE^0 is sensitive to the details of the assumed structure of the acid-base complex. For example, the molecule of formamide (*fa*) can be oriented parallel to the bond Sb – O or perpendicular to it (*fa (h)* and *fa (v)* in Table 8.3). The standard internal energy of complexation in these two cases differs by 1.5 kcal. Of the same order of magnitude (2.3 kcal mol^{-1}) is the mean square difference between the standard internal energy (*i.e.* the heat of reaction) and standard free energy.

The standard deviation of $\Delta E^0/RT_0$ (in the shown set of bases with respect to the mean value, last row in Table 8.5) is *ca.* 10.5 whilst that of $\ln Q_v$ is 2.7. Other components show much smaller variations (0.3 – 0.5) and may (to a first approximation) be disregarded.

Table 8.5. Components of the standard free energy (in kcal mol^{-1} at $T = 300$ K) of the complexation of $SbCl_5$ with several donor molecules (dichloroethane – *dce*, acetic anhydride – *acan*, dioxane – *di*, acetone – *ac*, acetonitrile – *an*, formamide – *fa*, dimethylformamide – *dmf* and dimethylsulphoxide – *dmso*), calculated using the PM3 method (HyperChem3®)

Solvent	$\Delta E/RT$	$\ln Q_r$	$-\ln Q_{tr}$	$\ln Q_v$	$-a_v/T$	$\Delta E^0/RT$	$-dS^0/R$	$-\delta E^0$ kcal mol^{-1}	$-\delta F^0$ kcal mol^{-1}	*Dn*
dce	−11.37	9.70	61.70	7.12	5.84	−5.02	41.03	0.00	0.00	0
acan	−17.51	9.53	61.73	2.72	5.64	11.36	45.83	3.76	0.91	10.5
an	−27.62	8.55	60.61	3.00	4.97	−22.15	46.08	10.17	7.17	14.1
di	−5.09	9.58	61.57	9.53	5.71	1.12	36.24	−3.65	−0.80	14.8
ac	−13.17	9.01	61.06	8.88	5.76	−6.90	39.40	1.11	2.08	17.0
fa (h)	−21.29	8.53	60.74	2.65	5.67	−15.12	45.88	5.99	3.11	24.0
fa (v)	−23.96	8.53	60.74	2.70	5.82	−17.63	45.67	7.48	4.73	24.0
dmf	−24.00	9.50	61.34	6.26	5.95	−17.54	41.61	7.43	7.08	26.6
dmso	−41.21	9.14	61.42	5.40	6.05	−34.65	42.82	17.60	16.5	29.8
Std.Dev.	10.53	0.48	0.43	2.75	0.30	10.25	3.40			

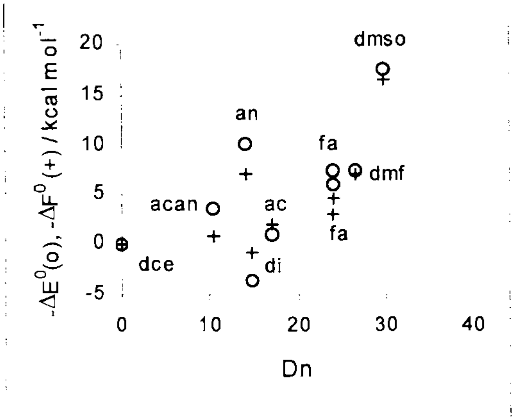

Fig. 8.3. Standard internal energy (o) and standard free energy (+) of complexation of $SbCl_5$ with bases (computed using the PM3 method, HyperChem3®) as a function of donor numbers

Vibrational contributions thus constitute the major part of the difference between the variations of ΔE^0 and ΔF^0 and in detailed studies it must be taken into account. Donor numbers characterise, therefore, the relative stability of acid-base complexes with the precision of this term, *i.e. ca.* 30%. According to the principle of linear free energy relationships, the logarithm of the equilibrium constant of reaction (8.11) (of the basic solvent S with some molecule R showing acidic properties) must be proportional to the donor number of the base Dn_S:

$$\ln K_{SR} = a_R Dn_S \tag{8.47}$$

The proportionality coefficient a_R must reflect the acidic properties of R with respect to $SbCl_5$. Acceptor numbers [12] offer such a measure and the proportionality coefficient a_R can be calculated as:

$$a_R = \alpha_R An_R / 100 \tag{8.48}$$

in which 100 is taken as the acceptor number of $SbCl_5$ and the conversion factor α_R accounts for the difference between donor numbers and $\ln K$. Donor and acceptor numbers may thus be used to characterise solvent effects in reactions. The effect of solvation on the equilibrium constant of a chemical reaction can then be expressed in terms of donor numbers as:

$$\ln \frac{K(S)}{K(S_0)} = \ln \frac{K_{SP}}{K_{SR}} \frac{K_{0R}}{K_{0P}} = \Delta a \left(Dn_S - Dn_{S_0} \right) \tag{8.49}$$

in which $\Delta a = a_P - a_R$ represents the relative balance of acidic properties of products and reactants whereas the term $Dn_S - Dn_{S_0}$ represents the donor properties of the actual solvent with respect to a reference solvent (S_0).

We have thus obtained another linear free energy relationship involving empirical parameters characterising the ability of a molecule to form molecular complexes with Lewis acids. This accounts for solute-solvent interactions of a chemical nature, *i.e.* attractive interactions acting at short distances, saturated according to the stoichiometry of solvation, and resulting in species behaving (at least during about 100 oscillation periods) like molecules. The variations of chemical reactivity due to solvation and non-ideality are then given by:

$$\ln\frac{K(S)}{K(S_0)}=\Delta a\left(Dn_{S_0}-Dn_0\right)+\Delta v\left(\frac{1}{v_S}-\frac{1}{v_{S_0}}\right)-3\Delta u\left(\frac{1}{u_S}-\frac{1}{u_{S_0}}\right) \quad (8.50)$$

The terms on the right-hand side of (8.50) represent the balances (Δ) of 'solvability', volume, and energy of molecular interaction of the molecules of products and reactants calculated with respect to a reference solvent (S_0).

8.4
Isoequilibrium and isokinetic relationships

A deeper insight into the origin of variations of chemical reactivity can be achieved when the 'temperature dependent' and 'temperature independent' components of the free energy (ΔE^0 and ΔS^0 or $\Delta E^{\#}$ and $\Delta S^{\#}$) are determined and analysed. Theoretical analysis of the contributions towards ΔE^0 and ΔS^0 of the complexation of $SbCl_5$ with organic bases (shown in Table 8.5, above) demonstrate that ΔS^0 is mainly controlled by the vibrational component whilst ΔE^0 is governed by the total energy difference between product and reactants. However, even in such a case there is a certain correlation (Fig. 8.4A) between ΔE^0 and ΔS^0 arising from a concerted variation of ΔE and the vibrational contribution.

Experimental data quite often show more pronounced correlations between ΔS^0 and ΔH^0 (see, for example, Fig. 8.4B) as well as between corresponding activation parameters which cannot be explained by the parallel variations of molecular mass, vibrational frequencies and total energy. This phenomenon is called the *compensation effect* or the *isoequilibrium* (*isokinetic*) *relationships* (*IER*, *IKR*). These correlations manifest themselves in (sometimes spectacular) intersections of van't Hoff and Arrhenius plots (hence the name *IER*, *IKR*). An intersection of several van't Hoff plots means that the equilibrium constant at a certain temperature is independent of the parameters (x_i), the variation of which brings about the observed changes in ΔE^0 and ΔS^0. Mathematically this can be written as:

$$dR\ln K=\sum_i\left(\frac{\partial\Delta S^0}{\partial x_i}-\frac{1}{T_{iso}}\frac{\partial\Delta E^0}{\partial x_i}\right)dx_i=0 \quad (8.51)$$

in which T_{iso} is the isoequilibrium temperature.

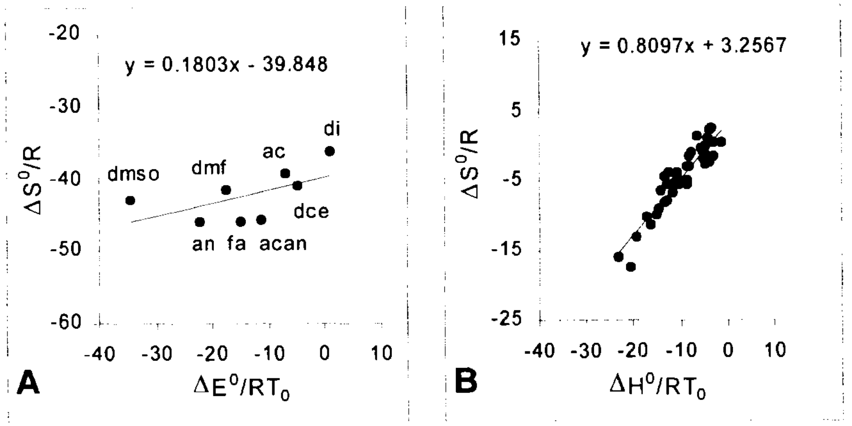

Fig. 8.4. Theoretical correlation between ΔS^0 and ΔE^0 for the reaction of SbCl$_5$ with organic bases (**A**) and experimental isoequilibrium relationship [14] for the formation of cyclodextrin inclusion complexes (**B**)

It is highly improbable that a *random variation of several independent* parameters x_i in a reaction series results in the same T_{iso}. One possibility for the observation of an IER (IKR) is that *only one parameter (x_k) is varied* in a reaction series. The condition (8.51) is then transformed into:

$$\frac{\partial \Delta S^0}{\partial x_k} dx_k - \frac{1}{T_{iso}} \frac{\partial \Delta E^0}{\partial x_k} dx_k = 0 \tag{8.52}$$

or

$$d\Delta S^0 - \frac{1}{T_{iso}} d\Delta E^0 = 0 \tag{8.53}$$

which leads to a linear relationship between ΔS^0 and ΔE^0, *provided that none of the partial derivatives in* (8.52) *is zero.* The isoequilibrium (isokinetic) temperature is then the ratio of the parametric sensitivities of ΔE^0 and ΔS^0:

$$T_{iso} = \frac{\partial \Delta E^0}{\partial x_k} \bigg/ \frac{\partial \Delta S^0}{\partial x_k} \tag{8.54}$$

The isoequilibrium temperature is thus informative with respect to the relationships controlling ΔS^0 and ΔE^0. Another possibility for an isoequilibrium (isokinetic) relationship is that several parameters in a reaction series vary in a concerted manner, so that a linear relationship exists between the variations of these parameters:

$$dx_i = a_i dx_k \tag{8.55}$$

Such a possibility must be very common, at least when parameters are varied over a narrow range[6]. In such a case (8.51) is transformed into:

$$\sum a_i \frac{\partial \Delta S^0}{\partial x_i} - \frac{1}{T_{iso}} \sum a_i \frac{\partial \Delta E^0}{\partial x_i} = 0 \tag{8.56}$$

This condition can be fulfilled provided *none of the sums* is zero. An intersection of van't Hoff plots at one point may then be observed but the isoequilibrium temperature *does not reflect exclusively the parameters of a reaction mixture*. It includes also the coefficients a_i belonging to the experimental set-up:

$$T_{iso} = \sum a_i \frac{\partial \Delta E^0}{\partial x_i} \Big/ \sum a_i \frac{\partial \Delta S^0}{\partial x_i} \tag{8.57}$$

It is even possible that for each parameter either $\partial \Delta S^0 / \partial x_i$ or $\partial \Delta E^0 / \partial x_i$ is zero but the sums in (8.56, 57) will be non-zero. This case corresponds to a pseudo-correlation arising from the multidimensionality of variations discussed above. The relationship between ΔS^0 and ΔE^0 in this case is also linear: by multiplying (8.56) by dx_k, we transform sums into complete differentials of ΔS^0 and ΔE^0, thus obtaining (8.53), which yields upon integration a linear relationship:

$$\Delta S^0 = \frac{1}{T_{iso}} \Delta E^0 + Const \tag{8.58}$$

This shows that the experimental set-up plays an important role in studies of IER and IKR (this apart from the problem of the statistical reliability of either the linearity of (8.58) or the intersection point). Unfortunately earlier theories of IKR (IER) paid little attention to the effects of experimental design and tried to find a formalism predicting an intersection of van't Hoff or Arrhenius plots irrespective of the mode in which experimental data are obtained. It was therefore assumed that an IKR can only be observed when one parameter alone is varied in a reaction series [14]. In fact, this requirement provides an easy physical interpretation of the isokinetic temperature. The necessary requirement for an IER (IKR) when only one parameter is varied is that $\partial \Delta S^0 / \partial x$ and $\partial \Delta E^0 / \partial x$ are non- zero. This means that the standard entropy and energy of reaction must depend on the same parameter varied in the actual reaction series. When several linearly related parameters are varied (which, as we have seen, is a common occurrence) the IER (IKR) can be observed but its interpretation requires the knowledge of (i) the relationship between the varied parameters (coefficients a_i) and (ii) the parametric sensitivities $\partial \Delta S^0 / \partial x_i$ and $\partial \Delta E^0 / \partial x_i$.

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[6] A periodic variation of properties might be observed when we study objects through several rows of the Mendeleev Table (which is very rarely carried out). A random variation of some parameters while others are systematically varied might, in theory, be possible but difficult to imagine.

8.4.1
Statistical-mechanical model of the IER in ideal systems

An analysis of the IER or IKR must therefore start with the determination of what parameters are really important for the actual reaction and what are the parametric sensitivities of ΔE^0 and ΔS^0. Statistical mechanics provides a detailed analysis of the possible results of variations of the parameters controlling ΔE^0 and ΔS^0 in a reaction series in *ideal systems*, *i.e.* when the state of a molecule is determined *exclusively* by intra-molecular parameters. For example, the equilibrium constant of a bimolecular reaction:

$$\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C} \tag{8.59}$$

given by (3.66):

$$\ln K_n(V,T) = \ln\left[\left(\frac{h^2}{2\pi kT}\frac{m_C}{m_A m_B}\right)^{\frac{3}{2}}\frac{1}{Ve}\right] + \ln Q_{\mathrm{int}}(T) - \frac{\Delta E}{RT} \tag{8.60}$$

indicates that, besides the simultaneous variations of ΔE and the masses of the particles, the modification of internal degrees of freedom might contribute towards the IER. Indeed the standard entropy and internal energy of this reaction according to (3.71) and (3.72) are:

$$\frac{\Delta S^0}{R} = -\ln\left[eV\left(\frac{2\pi k\mu_{AB}T_0}{h^2}\right)^{\frac{3}{2}}\right] - \frac{3}{2} + \ln\left[Q_{\mathrm{int}}(T_0)\right] - \frac{1}{T_0}\left(\frac{\partial \ln Q_{\mathrm{int}}}{\partial T^{-1}}\right)_{T=T_0} \tag{8.61}$$

$$\Delta E^0 = \Delta E - \frac{3}{2}RT_0 - R\left(\frac{\partial \ln Q_{\mathrm{int}}}{\partial T^{-1}}\right)_{T=T_0} \tag{8.62}$$

Note that T_0, *i.e.* the mean temperature around which the equilibrium constant is determined, enters both expressions. Depending on whether T_0 is kept constant or varied in a certain way, the isoequilibrium relationships can be observed or not observed.

Besides T_0, the internal degrees of freedom (including all rotations) contribute towards both ΔS^0 and ΔE^0 in the form of the derivative $(1/T_0)d\ln Q/dT^{-1}$. Among the internal degrees of freedom, rotations and *vibrations of low frequency* ($h\nu < kT$) have partition functions of identical form, $f = T/\theta$, where θ is the characteristic rotational ($\sigma h^2/8\pi^2 Ik$) or vibrational ($h\nu/k$) temperature. The logarithm of such a partition function depends on temperature as $\ln T$ and:

$$\frac{1}{T_0}\left(\frac{\partial \ln Q_{\mathrm{int}}}{\partial T^{-1}}\right)_{T=T_0} = -\frac{1}{T_0}\left(\sum_{i=1}^{p} T_0 - \sum_{i=1}^{r} T_0\right) = -\Delta n \tag{8.63}$$

in which $\Delta n = p - r$ is the balance of the number of rotational (and the low-frequency vibrational) degrees of freedom in products and reactants. We have thus defined Δn as one of the parameters which (when varied in a reaction series) may give rise to an IER. The corresponding parametric sensitivity of ΔS^0 is R whereas that of ΔE^0 is RT_0.

The total contribution of rotational and low frequency vibrational degrees of freedom to the standard entropy of reaction, $\ln Q - (1/T_0) d\ln Q/dT^{-1}$, can be written as:

$$\sum_{i=1}^{p} \ln \frac{T_0}{\theta_i} - \sum_{j=1}^{r} \ln \frac{T_0}{\theta_j} + \Delta n = \Delta n - \left(\sum_{i=1}^{p} \ln \frac{\theta_i}{T_0} - \sum_{j=1}^{r} \ln \frac{\theta_j}{T_0} \right) \tag{8.64}$$

Note that the term in brackets in (8.64) contributes towards the entropy *alone* and thus destroys any possible IER. It can be considered as a weighted difference between the logarithms of the harmonic means of the rotational temperatures of products and reactants, related to the standard temperature T_0:

$$\Delta\theta = n \left[\frac{p}{n} \sum_{i=1}^{p} \ln \left(\frac{\theta_i}{T_0} \right)^{\frac{1}{p}} - \frac{r}{n} \sum_{j=1}^{r} \ln \left(\frac{\theta_j}{T_0} \right)^{\frac{1}{r}} \right] \tag{8.65}$$

in which $n = p + r$ is the total number of rotational and low frequency vibrational degrees of freedom in products and reactants. The contribution towards the standard entropy (8.64) can then be considered as a function of two parameters, Δn and $\Delta\theta$, the latter characterising the differences in the rotational (low frequency vibrational) spectra of products and reactants. In fact, $\Delta\theta$ is a complicated function of changes in the number of degrees of freedom and corresponding characteristic temperatures.

On the other hand, vibrations of higher frequency $(h\nu/2kT_0 > 2)$ do not contribute towards the standard entropy of reaction. Over this range of frequencies, the vibrational contribution can be approximated as[7]:

$$\ln Q_{vhi} = - \left(\sum \ln 2 \sinh \frac{\theta_v}{2T_0} \right) \Bigg|_{Reactants}^{Products} \cong - \left(\sum \frac{\theta_v}{2T_0} \right) \Bigg|_{Reactants}^{Products} \tag{8.66}$$

The derivative $(1/T_0) d\ln Q_{vhi}/dT^{-1}$ approaches the same value: at $x > 2$ the hyperbolic cotangent representing $d\ln[\sinh(x)]/dx$ approaches the constant value $\coth(x) \cong 1$ and:

$$\frac{1}{T_0} \left(\frac{\partial \ln Q_{vhi}}{\partial T^{-1}} \right)_{T=T_0} = - \sum_{Reactants}^{Products} \frac{\theta_{vhi}}{2T_0} \coth \frac{\theta_{vhi}}{2T_0} \cong - \sum_{Reactants}^{Products} \frac{\theta_{vhi}}{2T_0} \tag{8.67}$$

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[7] The hyperbolic sine for large arguments ($x > 2$) approaches $0.5\exp(x)$.

The two terms contributing towards the standard entropy thus compensate each other. The derivative (8.68) represents the contribution of the higher frequency vibrations to the standard internal energy of reaction. It reflects the difference in the amount of vibrational (higher frequency) energy in products and reactants:

$$-\frac{1}{T_0}\left(\frac{\partial \ln Q_v}{\partial T^{-1}}\right)_{T=T_0} \cong \sum_{i=1}^{P_v} \frac{\theta_{vpi}}{2T_0} - \sum_{j=1}^{R_v} \frac{\theta_{vrj}}{2T_0} = \frac{\Delta E_{vhi}}{2RT_0} \tag{8.68}$$

Table 8.6 summarises the contributions towards standard entropy and internal energy from rotations and vibrations. The variation of the balance, Δn, of the number of vibrational/rotational low frequency lines can produce correlated changes in ΔS^0 and ΔE^0, and hence an IER. This type of IER corresponds to unit slope of the dependence $\Delta S^0/R$ *vs.* $\Delta E^0/RT_0$. Indeed the slope of the regression line in Fig 8.4 is *ca.* 0.8, which is not far from 1. A variation in the distribution of vibrations of higher frequencies contributes to ΔE^0 alone and thus destroys such a correlation causing a deviation of the slope of the IER from 1.

It must also be pointed out that Δn_{vlo} and θ_{vlo} are usually not independent variables: it is mainly the changes in the frequencies that cause the changes in the number of low-frequency degrees of freedom of products and reactants. However, the value of Δn_v might be controlled by the symmetry properties of molecules. For example, the temperature derivative of the vibrational contribution towards the internal energy of complexation of $SbCl_5$ computed earlier (Table 8.5) exhibits a peak towards smaller values for acetonitrile (see Fig. 8.5). This peak has its origin in the higher symmetry of the molecule of acetonitrile. This molecule has practically an axial symmetry (C_∞) that brings about the lowest possible increase in the number of vibrational modes (by 1) upon complexation.

Table 8.6. Contributions of rotations and vibrations towards the standard entropy and internal energy of reactions

	$\Delta S^0/R$	$\Delta E^0/RT_0$
Rotations	$\Delta n_r - \left(\sum_{i=1}^{P_r} \ln\frac{\theta_{ri}}{T_0} - \sum_{i=1}^{R_r} \ln\frac{\theta_{rj}}{T_0}\right)$	Δn_r
Low-freq. vibrations	$\Delta n_v - \left(\sum_{i=1}^{P_v} \ln\frac{\theta_{vi}}{T_0} - \sum_{i=1}^{R_v} \ln\frac{\theta_{vj}}{T_0}\right)$	Δn_v
High-freq. vibrations	0	$\sum_{i=1}^{P_v} \frac{\theta_{vi}}{2T_0} - \sum_{j=1}^{R_v} \frac{\theta_{vj}}{2T_0}$

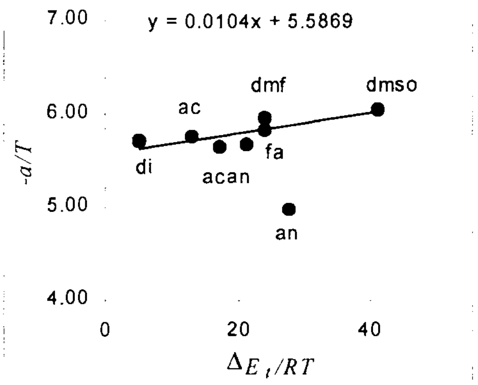

Fig. 8.5. A correlation between computed values of the temperature derivative of $\ln Q_v$ and the total energy change in the reaction of complexation of $SbCl_5$ with organic bases.

Other molecules shown in Fig. 8.5 have C_{2v} symmetry, which allows twisting modes in *$SbCl_5$–Base* complexes, which, in turn, results in an increase in the total number of vibrations by 6. A slight correlation between ΔE and a/T_0 illustrates the connection between vibrational frequency and the strength of chemical bond and hence the change of the total potential energy ΔE. A high absolute value of a_v/T_0 is apparently due to high-frequency vibrations (the last row in Table 8.6).

8.4.2
The IER in gas-phase reactions

Moelwyn-Hughes pointed out [6] that for gas phase reactions no simple and reliable correlation between ΔH^0 and ΔS^0 has been found. Large variations in the equilibrium constants of the dissociation of hydrogen halides are due to the differences in ΔH^0 whilst ΔS^0 remains approximately constant. In fact, these data (see Table 8.7) show small variations in ΔS^0 in parallel to those of ΔH^0. These changes, as well as absolute values of ΔS^0, can be explained in terms of translational, rotational and vibrational contributions. Vibrational and rotational contributions towards the equilibrium constant of the reaction of dissociation of hydrogen halides were calculated using available spectroscopic data [15]. The vibrational contribution ($\Pi[2\sinh(h\omega c/2kT)]^{-1}$) proved to be temperature dependent and the corresponding derivative (a_v/T_0) was calculated using a linear regression method. The results are shown in Table 8.8 and illustrated in Fig. 8.6A. Calculated standard entropies of reactions coincide with the experimental values (curves 3 and 2 in Fig. 8.6A) and both slightly increase with increasing ΔE^0. This correlation is not, however, caused by the variation of one parameter in a reaction series but is a result of simultaneous and sometimes compensating changes in all constituting terms (see curves 1, 4, 5, 6 in Fig. 8.6A).

Table 8.7 Thermodynamic parameters of the equilibria of dissociation of hydrogen halides in the gaseous phase at 298 K [6]

Reaction	K	ΔS^0 (cal mol^{-1} K^{-1})	ΔH^0 (kcal mol^{-1})
$2HCl \rightleftharpoons H_2 + Cl_2$	5.50×10^{-34}	–4.74	43.96
$2HBr \rightleftharpoons H_2 + Br_2$	1.05×10^{-19}	-5.07	24.38
$2HI \rightleftharpoons H_2 + I_2$	5.01×10^{-4}	-5.20	2.95

Table 8.8 Thermodynamic parameters for the equilibrium of dissociation of hydrogen halides calculated according to (8.61) and (8.62) from the spectroscopic data

HX	E_{dis} (kcal mol^{-1})	$\ln Q_{tr}$	$\ln Q_r$	$\ln Q_v$	$-a/T_0$	$\ln K$	$\Delta E^0/RT_0$	$\Delta S^0/R$
HCl	43.940	-5.426	0.612	2.511	–2.250	–76.276	71.723	–4.553
HBr	24.370	–6.599	1.264	1.632	–0.979	–44.730	40.048	–4.682
HI	2.300	-7.279	1.524	0.462	0.548	-9.165	4.420	–4.744

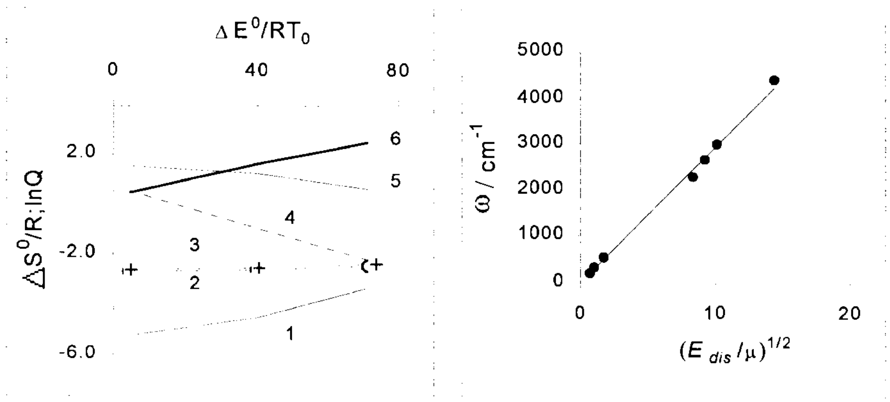

Fig. 8.6. Correlation between ΔE^0 (computed) and other components of the standard free energy of dissociation of hydrogen halides in the gaseous phase (**A**): $\ln Q_{tr}$ (1), calculated $\Delta S^0/R$ (2), experimental $\Delta S^0/R$ (3), $-(1/T)\partial \ln Q_v/\partial T^{-1}$ (4), $\ln Q_r$ (5) and $\ln Q_v$ (6). The right-hand graph (**B**) shows the correlation between vibrational frequencies and dissociation energy in diatomic molecules (X_2, HX and H_2)

The overall effect is mainly due to the contributions towards the entropy from translational and vibrational partition functions whilst the temperature dependence of the vibrational partition function $(-a_v/T_0)$ causes the variation to be in the reverse order (see Fig. 8.6A). That the vibrational contribution follows the changes in the balance of dissociation energies (controlling ΔE^0) *is not a coincidence* (which can be said about the translational contribution). For *diatomic* molecules the frequency of vibration is directly related to the square root of the ratio of the dissociation energy and reduced mass:

$$\nu = \frac{a}{\pi}\sqrt{E/\mu} \tag{8.69}$$

in which a is an empirical constant entering the Morse potential and E is the dissociation energy. This is supported by experimental data (Fig. 8.6B) and results in:

$$\ln Q_v = const + \ln E_{HX} - \frac{1}{2}\ln E_{X_2} \tag{8.70}$$

$$\Delta E = const + E_{HX} - \frac{1}{2}E_{X_2} \tag{8.71}$$

Both E_{HX} and E_{X2} are varied in the considered reaction series and these variations are concerted according to the principle of linear free energy relationships. In such a case an approximately linear relationship should exist between $\ln Q_v$ and ΔE and is observed experimentally (curve 6 in Fig. 8.6A). A concerted variation of dissociation energies and masses of molecules also contributes towards the observed IER. The observed correlation is therefore not a completely 'genuine' isoequilibrium relationship but on the other hand is not a result of a completely 'coincidental' variation of masses of particles, vibrational frequencies and binding energies. A true IER (or IKR) connected with the variation of a *single parameter is therefore not very probable for gas-phase equilibria.*

8.4.3
Isokinetic relationships

Historically, the compensation effect was mainly investigated as concerning kinetic data on reactions in solutions, so much so that the name IKR has often been applied to isoequilibrium relationships. A theoretical description of the IKR, employing the model of distribution of energy [16–19], provides a joint variation of activation energy and activation entropy when either the height of the potential barrier (E^*) or the number of oscillators (s) is varied. In other words, the corresponding parametric sensitivities of $\Delta E^{\#}$ and $\Delta S^{\#}$ in this model are non-zero. According to this model the reaction rate constant can be written as:

$$k = \nu_0 e^{-\frac{E^*}{RT}} \sum_{i=0}^{s-1} \frac{(E^*/RT)^i}{i!} = \nu_0 \exp\left(\frac{\Delta S^\#}{R} - \frac{\Delta E^\#}{RT}\right) \tag{8.72}$$

in which ν_0 is the average frequency of the attempts of reactants to pass a potential barrier; E^* is the height of the potential barrier and s is the number of oscillators. Experimental data on the temperature dependence of the activation energy of molecular rotation in ethylene glycol and water yield $s = 9$ and $s = 22$, respectively [8]. This indicates that the oscillators involved are *not* the internal degrees of freedom but are apparently connected with molecular interactions, *e.g. via* hydrogen bonding. The parameter of a purely ideal model (s) thus reflects (indirectly) the non-ideality of liquids.

This model gave the first clear physical interpretation of the isokinetic temperature. According to (8.73), the activation energy and activation entropy (standard internal energy and standard entropy of activation) can be written as[8]:

$$\Delta E^\# = -R\left(\frac{\partial \ln k}{\partial T^{-1}}\right)_{T_0} = E^*\left(1 - \sum_{i=0}^{s-2} \frac{(E^*/RT_0)^i}{i!} \Bigg/ \sum_{i=0}^{s-1} \frac{(E^*/RT_0)^i}{i!}\right) \tag{8.73}$$

$$\frac{\Delta S^\#}{R} = \ln\left[\sum_{i=0}^{s-1} \frac{(E^*/RT_0)^i}{i!}\right] - \frac{E^*}{RT_0} \sum_{i=0}^{s-2} \frac{(E^*/RT_0)^i}{i!} \Bigg/ \sum_{i=0}^{s-1} \frac{(E^*/RT_0)^i}{i!} \tag{8.74}$$

The variations of $\Delta E^\#$ and $\Delta S^\#$ resulting from the variations of the potential barrier height E^* (at constant s) and from the variations of the number of oscillators s (at constant E^*) as predicted by (8.73) and (8.74) are shown in Figs. 8.7A and 8.7B respectively.

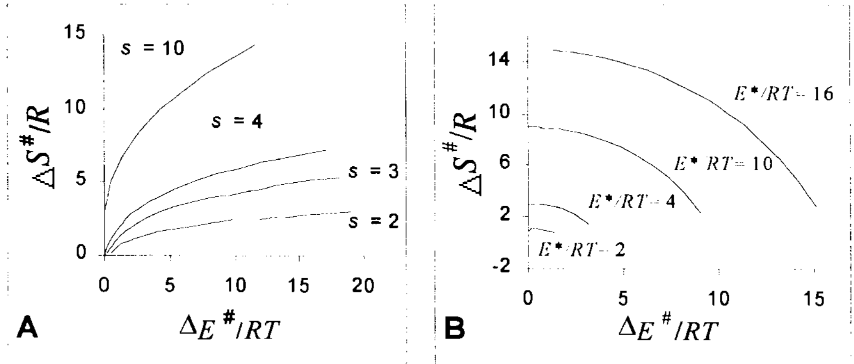

Fig. 8.7. Correlation between $\Delta S^\#$ and $\Delta E^\#$ due to the variation of potential barrier height at constant s (**A**) and due to the variation of s at constant E^* (**B**)

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[8] Assuming, to a first approximation, that ν_0 is temperature independent.

According to these curves the variation of potential barrier height at constant s generally results in positive isokinetic temperatures (positive $d\Delta S^{\#}/d\Delta E^{\#}$). The variation of s at constant and *small* E^* results in a relationship between $\Delta S^{\#}$ and $\Delta E^{\#}$ with a maximum. At higher (and constant) E^* the variation of s is connected with a decrease in $\Delta S^{\#}$ on increasing $\Delta E^{\#}$, *i.e.* it corresponds to negative isokinetic temperatures.

The physical significance of the isokinetic temperature becomes clear when we consider the case of high potential barriers. For the potential barriers $E^*/RT >> (s-1)$, (8.73) and (8.74) can be considerably simplified by substituting the sums by their largest terms. The activation energy and entropy then become:

$$\Delta E^{\#} = E^* - (s-1)RT_0 \tag{8.75}$$

$$\frac{\Delta S^{\#}}{R} = (s-1)\ln\left(\frac{E^*}{RT_0}\right) - \ln(s-1)! - (s-1) \tag{8.76}$$

The case of variations of E^* at constant s is relatively simple: The activation energy is a linear function of the potential barrier height E^*. On the other hand, the dependence (8.76) can be linearised with respect to E over a narrow range of variations around the average value E_0^* as:

$$\frac{\Delta S^{\#}}{R} = (s-1)\ln\left(\frac{E_0^*}{RT_0}\right) + \frac{(s-1)E^*}{E_0^*} - \ln(s-1)! \tag{8.77}$$

Combining (8.75) and (8.77), we get:

$$\frac{\Delta S^{\#}}{R} = (s-1)\left[\ln\left(\frac{E_0^*}{RT_0}\right) + \frac{(s-1)RT}{E_0^*} - 1\right] - \ln(s-1)! + \frac{(s-1)}{\mathrm{E}_0}\Delta E^{\#} \tag{8.78}$$

The inverse isokinetic temperature is then obtained as:

$$\frac{1}{R}\frac{d\Delta S^{\#}}{d\Delta E^{\#}} = \frac{1}{RT_{iso}} = \frac{(s-1)}{E_0^*} \tag{8.79}$$

This means that the isokinetic temperature reflects the *energy per oscillator* $E_0^*/(s-1)$ *required to pass over the average potential barrier* (in the reaction series).

A linear dependence of activation energy on temperature (8.75) can be compared to a similar relationship that follows from the Kirchhoff law:

$$\Delta E^{\#} = \Delta E_0^{\#} + \int \Delta C_v dT \cong \Delta E_0^{\#} + \Delta C_v T \tag{8.80}$$

in which $\Delta E_0^{\#}$ is the standard internal energy of activation at absolute zero and ΔC_v is the difference in heat capacities (at constant volume) of the activated complex and the ground state of the reactants. According to (8.76) and (8.81) the potential barrier height, E^*, equals the activation energy at absolute zero and the number of oscillators, s, is proportional to the difference in heat capacities of the reactants, *i.e.* to the *number of degrees of freedom which disappear in the process of activation* [16]:

$$-(s-1)=+\Delta C_v/R \tag{8.81}$$

In the case of variations of the number of oscillators the linearisation of the dependence (8.77) with respect to s is more difficult because the derivative of $\ln(s-1)!$ can not be obtained analytically. This derivative can, however, be approximated by $\ln(s-1)$ in the range of large s and by $\ln(s-0.48)$ over the range of small $s = 2 - 10$ (see Appendix 10.6). The derivative of $\Delta S^{\#}$ with respect to s is then:

$$\frac{\partial}{\partial s}\left(\frac{\Delta S^{\#}}{R}\right)=\ln\left(\frac{E^*}{RT_0}\right)-1-\ln x \tag{8.82}$$

in which $x = s - 1$ for $s > 10$ and $x = s - 0.48$ for $10 \geq s \geq 2$. The activation entropy can then be represented (in a narrow range around s_0) as a linear function of s:

$$\frac{\Delta S^{\#}}{R}=\frac{\Delta S^{\#}(s_0)}{R}+\left[\ln\left(\frac{E^*}{RT_0}\right)-1-\ln x_0\right](s-s_0) \tag{8.83}$$

Noticing that the variable $s - 1 = (\Delta E^{\#}-E^*)/RT_0$, we get a linear relationship between the activation entropy and activation energy:

$$\frac{\Delta S^{\#}}{R}=\frac{\Delta S^{\#}(s_0)}{R}+\left[\ln\left(\frac{E^*}{RT_0}\right)-1-\ln x_0\right]\left(\frac{\Delta E^{\#}}{RT_0}-\frac{E^*}{RT_0}+1-s_0\right) \tag{8.84}$$

According to this result, the inverse isokinetic temperature equals the negative inverse mean experimental temperature less some contribution depending on the ratio of the average effective number of oscillators x_0 and potential barrier height:

$$-\frac{1}{T_{iso}}=\frac{1}{T_0}\left(1-\ln\frac{E^*}{x_0 RT_0}\right) \tag{8.85}$$

The deviation of the magnitude of the isokinetic temperature from the mean experimental temperature is determined therefore by the logarithm of the *energy (in units of RT_0) per average effective oscillator required to pass the potential barrier* of reaction. A number of experimental isokinetic relationships have been explained using this model [17–19].

Mathematical formalism of the description of the IKR using a non-equilibrium thermodynamic model [9] is very similar to that just discussed because of the essential similarity of the initial equations for the kinetic rate constant (8.72) and (8.23a):

$$k_1 = A_0 s_N \left(\frac{\hbar\omega}{kT_{bath}}\right)^2 \sum_{i=1}^{s_N-1} \frac{(hs_N\omega/h\nu)^i}{i!} \exp\left(-\frac{s_N\hbar\omega}{kT_{bath}}\right) \qquad (8.23a)$$

However, the interpretation of the isokinetic temperature is quite different. First of all the potential barrier height in (8.23a) is directly related to the 'number of oscillators' s_N ($E^* = s_N\hbar\omega$). This simplifies the description but excludes the possibility of negative isokinetic temperatures (that are observed experimentally and predicted by (8.85) in the case of varying s and constant E^*).

According to (8.23a), the isokinetic temperature is determined by the energy spacing in the system of levels of the heat bath ($\hbar\nu$). This spacing was believed to be connected with a line in the vibrational spectrum of the solvent[9]. A large number of IKR and IER have been analysed according to this model [14]. It was suggested that when a statistically relevant IKR is observed the reactions involved must proceed by identical (or at least very similar) mechanisms [9]. Indeed, beyond a purely coincidental intersection of Arrhenius plots (which is *not* very probable) a linear interrelation between apparent ΔS^0 ($\Delta S^\#$) and ΔE^0 ($\Delta E^\#$) in a systematically modified series of reactions implies a single equation describing rate or equilibrium constants and hence a single mechanism. This assumption proved to be very fruitful allowing, as it does, the classification of reactions of unknown or doubtful mechanism [14].

8.4.4
Non-ideality as a source of an IER

Employing the dynamic interpretation of equilibrium, it is possible to derive isoequilibrium relationships from isokinetic relationships and apply theoretical formulae described in the preceding Section to the description of the IER [6, 20]. However, we are able to obtain an independent explanation of the equilibrium compensation effect by analysing the origin of the fact that both IER and IKR are mainly observed in the condensed state. This observation suggests that the effects of non-ideality play an important role in both IER and IKR. Indeed, the possibility of a correlation between ΔE^0 and ΔS^0 can be demonstrated straightforwardly by employing the equations of the law of mass action derived for non-ideal systems (Chapters 4 and 7). This approach allows one to obtain direct relationships between T_{iso} and parameters characterising non-ideality, whereas the models of IKR described above are essentially ideal and their parameters only indirectly reflect molecular interactions[10].

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[9] Molecular interactions are thus implicitly assumed to arise from interaction with the molecular electromagnetic field, thus excluding molecular collisions and optically inactive vibrations.

[10] In this aspect they resembled the Lewis approach in their description of non-ideal systems.

Solvation equilibria contribute directly to the standard entropy and energy of reaction and *cannot cause an IER except by a coincident correlation of parameters*. On the other hand, the non-ideality terms arising from the dependence of free volume on composition as well as those based on the exchange energy result in correlations between ΔE^0 and ΔS^0 (as will be shown below).

Let us consider a simple example of an isomolar reaction in a non-ideal system characterised by non-zero balances of molecular volume and vaporisation energy:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{8.86}$$

The law of mass action for such a reaction mixture can be written (see Chapter 4) as:

$$\ln Q - \frac{\Delta E}{RT} - \ln\frac{1-x_A}{x_A} + \frac{v_B - v_A}{(1-x_A)v_B + x_A v_A} - 3\frac{u_B - u_A}{(1-x_A)u_B + x_A u_A} = 0 \tag{8.87}$$

in which $\ln Q$ is the term arising from translational, rotational and vibrational partition functions and ΔE is the difference in potential energies between isolated molecules of products and reactants (*intramolecular* potential energies); v are molecular volumes and u are the lattice energies per molecule. At first glance the non-ideality terms are temperature independent and must contribute towards the standard entropy alone. Their variations should not then cause an isoequilibrium relationship. In reality, the temperature dependence of $x_A = (1 + K)^{-1}$ (contained in the non-ideality terms) must be taken into account and the variations of non-ideality produce changes in both the entropy and enthalpy of reaction.

For simplicity, let us consider a reaction series where the vaporisation energy alone is varied whilst molecular volume is not changed by the reaction ($\Delta v = 0$). The non-ideality of such a system can be characterised by the ratio $\alpha = (u_B - u_A)/u_B$. Under these conditions, the law of mass action can be written as:

$$\Phi = \ln Q - \frac{\Delta E}{RT} - \ln K - \frac{3\alpha(1+K)}{1+K-\alpha} = 0 \tag{8.88}$$

A *systematic* study of equilibrium constants in a series of reactions can be arranged in two different modes: keeping either the mean temperature of experiment T_0 or the mean value of $\ln K$ constant. The latter mode usually provides for optimal precision of measurements adjusted to the limited dynamic range of the measuring device. Let us analyse the results of this mode of estimation of ΔS^0 and ΔE^0 in a reaction series:

The equilibrium constant K then becomes an invariable parameter $K = K(T_0)$. Table 8.9 shows the estimates of ΔE^0 and ΔS^0 obtained from the pseudo-experimental data simulated according to (8.88) for a system characterised by $\Delta E = 1\,\mathrm{kcal\,mol^{-1}}$, $\ln Q = 5$, and varying α. Only a narrow range of degrees of conversion ($x_A = 0.4 - 0.6$, *i.e.* around $K = 1$) was used in the estimation of the standard internal energy and entropy of reaction. This resulted in a shift of the mean temperature of experiment (T_0) with varying non-ideality (see Table 8.9).

Table 8.9 Estimates of ΔE^0 and ΔS^0 obtained from pseudo-experimental data on the binary non-ideal equilibrium characterised by $\Delta E = 1$ kcal mol^{-1}, $\ln Q = 5$ and varying negative α

α	0	−0.5	−1	−1.2	−1.4	−1.6	−1.7	−1.8	−1.9
$1000/T_0$ (K^{-1})	9.90	12.28	13.87	14.37	14.81	15.20	15.38	15.55	15.71
ΔE^0(cal mol^{-1})	1000	1134	1494	1721	2019	2427	2688	3003	3387
ΔS^0(cal mol^{-1} K^{-1})	9.90	13.94	20.73	24.72	29.92	36.90	41.31	46.70	53.22

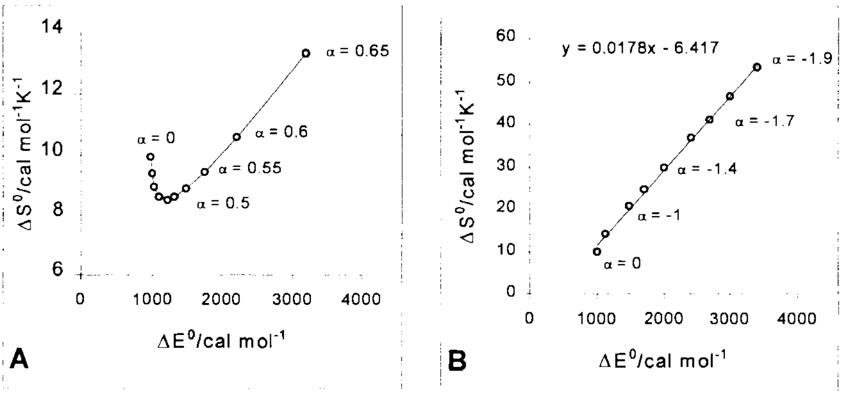

Fig. 8.8. Correlation between ΔS^0 and ΔE^0 predicted by the non-ideal law of mass action (8.88) for a system characterised by $\Delta E = 1$ kcal mol^{-1} and $\ln Q = 5$ and varying non-ideality term

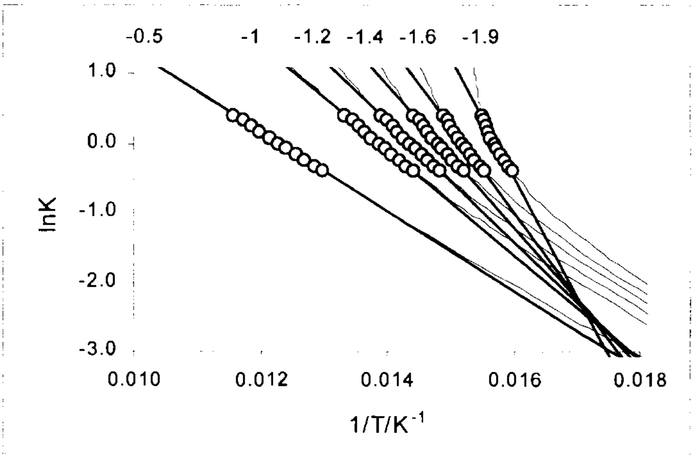

Fig. 8.9. Van't Hoff plots over *a narrow range* of compositions around the transition point of the non-ideal system characterised by $\Delta E = 1$ kcal mol^{-1}, $\ln Q = 5$ and negative α. Thin curves show the actual shapes of the van't Hoff plots

The estimates of ΔS^0 and ΔE^0 thus obtained show a pronounced correlation (Fig. 8.8) especially over the range of negative α ($\Delta u < 0$, *i.e.* a weaker molecular interaction between products than between reactants). The corresponding van't Hoff plots (Fig. 8.9) also show an intersection over a narrow range of temperatures. For a limited number of equilibria in Fig. 8.9, the point of intersection is statistically relevant[11] and thus the question arises as to what is the physical significance of the isoequilibrium temperature obtained in this way ($T_{iso} = 56.2$ K according to the regression equation in Fig. 8.8B)?

The relationship between ΔS^0 and ΔE^0 resulting from the law of mass action (8.88) can be found in the following way. The composition of the reaction mixture (8.86) is directly connected with the apparent equilibrium constant as $x_A = 1/(1+K)$. Standard internal energy and entropy are calculated as $\Delta E^0 = -(Rd\ln K/dT^{-1})_{T_0}$ and $\Delta S^0 = R\ln K(T_0) + \Delta E^0/T_0$ respectively. For any given theoretical law of mass action $\Phi(\ln K, T^{-1}) = 0$ the values of the apparent standard internal energy and entropy can then be determined according to (3.71) and (3.72) from the derivative $d\ln K/dT^{-1} = -\partial\Phi/\partial T^{-1}/\partial\Phi/\partial(\ln K)$.

Straightforward derivations according to this algorithm applied to (8.88) yield:

$$-\frac{\Delta E^0}{R} = -\frac{\Delta E}{R}\frac{[1+K-\alpha]^2}{(1+K-\alpha)^2 - 3\alpha^2 K} \tag{8.89}$$

$$\frac{\Delta S^0}{R} = \ln Q - \frac{3\alpha(1+K)}{1+K-\alpha} + \frac{\Delta E}{RT_0}\frac{3\alpha^2 K}{(1+K-\alpha)^2 - 3\alpha^2 K} \tag{8.90}$$

Combining (8.89) and (8.90) we get the following relationship between ΔE^0 and ΔS^0:

$$\frac{\Delta S^0}{R} = \ln Q - \frac{3\alpha(1+K)}{1+K-\alpha} + \frac{\Delta E^0}{RT_0}\frac{3\alpha^2 K}{(1+K-\alpha)^2} \tag{8.91}$$

In the case considered here, the equilibrium constant is invariant whereas ΔE^0, T^0 and α are variables. It is convenient therefore to substitute the ratio $\alpha/(1+K-\alpha)$ by a single parameter:

$$a = \alpha/(1+K-\alpha) \tag{8.92}$$

This parameter reflects non-ideality (α) as well as experimental set-up (K). From (8.89), it follows that:

$$\frac{\Delta E}{\Delta E^0} = 1 - 3Ka^2 \tag{8.93}$$

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[11] If the condition $K(T_0) = 1$ is not strictly obeyed, then the intersection region may be wider or narrower. By a 'careful adjustment' of the temperature range for each reaction, van't Hoff plots can be *artificially* made to intersect in one point.

Equation (8.91) then becomes:

$$\frac{\Delta S^0}{R} = \ln Q - 3(1+K)a + \frac{\Delta E^0}{RT_0} 3Ka^2 = \ln Q \pm b\left(1 - \frac{\Delta E}{\Delta E^0}\right)^{1/2} + \frac{\Delta E^0 - \Delta E}{RT_0} \tag{8.94}$$

in which $b = (1 + K)(3/K))^{1/2}$. The ± sign in (8.94) results from the fact that $a(\alpha)$ can be both positive and negative.

The chosen mode of determination of ΔE^0 and ΔS^0 (keeping $K = K(T_0) = 1$) implies that the estimates of ΔE^0, ΔS^0 and T^0 are *not independent variables* but are connected *via* $\Delta S^0 = \Delta E^0/T^0$ (one can easily check this by using the data in Table 8.9). We can therefore substitute T_0 in (8.94) by $\Delta E^0/\Delta S^0$ and obtain a direct relationship between ΔS^0 and ΔE^0 as a function of ΔE (for negative α):

$$\Delta S^0 = R\frac{\Delta E^0}{\Delta E}\left[\ln Q + b\sqrt{1 - \frac{\Delta E}{\Delta E^0}}\right] \tag{8.95}$$

The isoequilibrium temperature is then obtained as:

$$\frac{1}{T_{iso}} = \frac{d\Delta S^0}{d\Delta E^0} = \frac{R\ln Q}{\Delta E} + \frac{Rb}{\Delta E}\left[\sqrt{1 - \frac{\Delta E}{\Delta E^0}} + \frac{\Delta E/\Delta E^0}{2\sqrt{1 - \Delta E/\Delta E^0}}\right] \tag{8.96}$$

The term $R\ln Q/\Delta E$ equals the inverse transition temperature when the effects of non-ideality are zero. For the considered case ($\langle\alpha\rangle = -1.233$) it constitutes more than one half of the mean inverse isoequilibrium temperature:

$$\frac{1}{T_{iso}} = 0.0099 + [0.00451 + 0.00291] = 0.01732 \tag{8.96a}$$

The deviation (second term in 8.96) of the inverse isoequilibrium temperature from the ideal inverse transition temperature depends on both the experimenter's choice and non-ideality (the term in square brackets in (8.96)). A well-defined isoequilibrium point can be observed if T_{iso} is a constant, *i.e.* if $d(1/T_{iso})/dE^0 = 0$. The analysis of (8.96) (derived for negative α) shows that the two parts of $d(1/T_{iso})/dE^0$ compensate each other and the remaining part is relatively small:

$$\frac{d(1/T_{iso})}{d\Delta E^0} = \frac{bR}{2(\Delta E^0)^2}\frac{(\Delta E/\Delta E^0)^2}{(1 - \Delta E/\Delta E^0)^{3/2}} \tag{8.97}$$

For $\alpha = -1{,}233$, (8.97) yields $d\Delta(1/T_{iso})/d\Delta E^0 = 1.2 \times 10^{-6}$ mol cal^{-1} K^{-1} which corresponds to the deviation of $1/T_{iso}$ by a maximum of 0.0028 K^{-1} at the level 0.017 K^{-1} thus explaining the good linearity observed for the isoequilibrium relationship.

When an experiment is arranged in a way providing for a *constant mean temperature,* then the mean value of $\ln K$ varies in a reaction series. Equation (8.94) can be written explicitly with respect to K:

$$\frac{\Delta S^0}{R} = \ln Q \pm \sqrt{3}\left(\sqrt{K} + \frac{1}{\sqrt{K}}\right)\sqrt{1 - \frac{\Delta E}{\Delta E^0}} + \frac{\Delta E^0 - \Delta E}{RT_0} \tag{8.98}$$

and contains a product of two terms depending on the variable parameters K and ΔE^0. Taking into account the fact that $K = \exp(-\Delta F^0/RT)$ means that (8.98) can be written as:

$$\frac{\Delta S^0}{R} = \ln Q \pm 2\sqrt{3}\cosh\left(\frac{\Delta F^0}{2RT_0}\right)\sqrt{1 - \frac{\Delta E}{\Delta E^0}} + \frac{\Delta E^0 - \Delta E}{RT_0} \tag{8.99}$$

Although an expression for the inverse isokinetic temperature can be obtained by an implicit differentiation of (8.99) as:

$$\frac{d\Delta S^0}{d\Delta E^0} = \frac{1}{T_0} + \frac{\dfrac{R}{\Delta E^0}\dfrac{\Delta E}{\Delta E^0}2\sqrt{3}\cosh\left(\dfrac{\Delta F^0}{2RT_0}\right)}{\left[\sqrt{3}\sinh\left(\dfrac{\Delta F^0}{2RT_0}\right)\sqrt{1 - \dfrac{\Delta E}{\Delta E^0}} + 1\right]\sqrt{1 - \dfrac{\Delta E}{\Delta E^0}}} \tag{8.100}$$

It can hardly be used for the analysis of the observed correlations! A considerable contribution towards $1/T_{iso}$ arises from the mean temperature T_0 that is seldom supplied with published data. The physically meaningful part (the second term on the right-hand side of (8.100) is a complicated function of ΔE^0, ΔS^0 and non-ideality represented by the ratio $\Delta E/\Delta E^0$).

The pseudo-experimental data discussed above, when arranged in such a way as to provide for a constant mean temperature $T_0 = 70$ K, show a correlation between ΔS^0 and ΔE^0 (Fig. 8.10A) with an isoequilibrium temperature of 59.5 K. It is below the experimental range as predicted by (8.100). The simple mode of observed correlation is only apparent: when arranged in the order of increasing non-ideality these data exhibit a peculiar loop of the actual dependence of ΔS^0 on ΔE^0 (Fig. 8.10B). *This shows that although the derived equation might predict correctly the value of T_{iso} it is practically impossible to use it in the physical interpretation of the origin of an observed compensation effect.*

Similar effects are predicted for the variations of the balance of molecular volume. Neglecting the effects of lattice energy, (8.87) can be written as:

$$\ln Q - \frac{\Delta E}{RT} - \ln\frac{1 - x_A}{x_A} + \frac{3\alpha}{1 - \alpha x_A} = 0 \tag{8.101}$$

in which the non-ideality is characterised by $\alpha = (v_B - v_A)/v_B$.

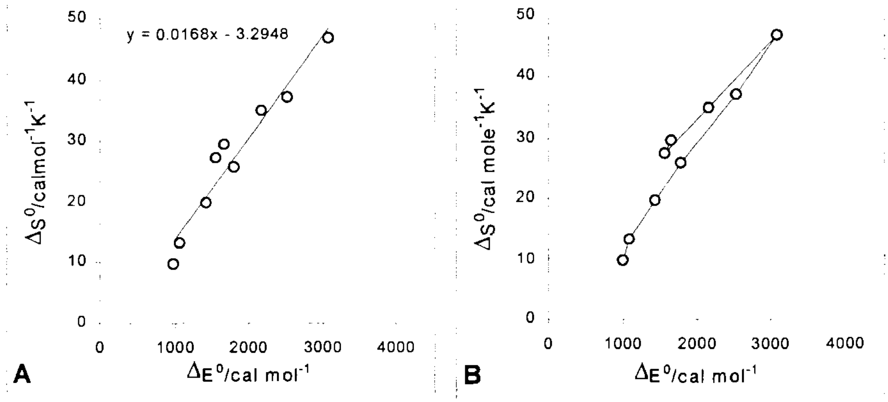

Fig. 8.10. An apparently linear relationship between ΔS^0 and ΔE^0 computed under the conditions of constant average temperature (**A**). Graph (**B**) shows the same data but connected in order of increasing non-ideality

Non-zero coefficients α (both positive and negative) cause mainly a decrease in the apparent ΔE^0 and ΔS^0, *i.e.* an IER with a positive isoequilibrium temperature. These effects (as might be expected) are in general smaller than in the case of variations of the balance of lattice energy Δu.

We see that non-ideality connected with the free volume might cause an IER with an isoequilibrium temperature lying below the experimental range, but it cannot be responsible for the cases of intersection of van't Hoff plots *within* the experimental range. A wider scope of possibilities for an observation of an IER is predicted by the theory of regular solutions.

8.4.5
IER and exchange energy

The formalism developed in Chapter 7 takes into account the effects of the molecular environment on molecular lattice energies. Under the assumption of additivity of these effects, this model can be reduced to the theory of regular solutions employing the concept of exchange energy. The law of mass action for the binary equilibrium (8.86) in such systems is given by (7.50) as:

$$(1-2x_A)\frac{\Delta F_{ex}}{NkT}-\frac{\Delta E-T\Delta S}{NkT}-\ln\frac{1-x_A}{x_A}=0 \qquad (8.102)$$

or:

$$\frac{K-1}{K+1}\frac{\Delta F_{ex}}{NkT}-\frac{\Delta E-T\Delta S}{NkT}-\ln K=0 \qquad (8.103)$$

in which ΔE and ΔS are the 'ideal' parts of the standard internal energy and entropy controlled by intra-molecular parameters of products and reactants (total energy ΔE_t and contributions from partition functions $\ln Q$).

Employing the algorithm described in the preceding section and denoting $(K-1)/(K+1) = 1-2x_A = \kappa$ and $2K/(K+1)^2 = 2x_A(1-x_A) = k$ the standard internal energy and standard entropy of reaction can be derived from (8.103) as:

$$\Delta E^0 = \Delta E\left(1-\kappa\frac{\Delta E_{ex}}{\Delta E}\right)\Bigg/\left(1-k\frac{\Delta F_{ex}}{RT}\right) \tag{8.104}$$

$$\frac{\Delta S^0}{R} = \frac{\Delta S}{R}+\kappa\frac{\Delta F_{ex}}{RT}+\frac{\Delta E}{RT}\left(k\frac{\Delta F_{ex}}{RT}-\kappa\frac{\Delta E_{ex}}{\Delta E}\right)\Bigg/\left(1-k\frac{\Delta F_{ex}}{RT}\right) \tag{8.105}$$

The actual relationship between ΔS^0 and ΔE^0 depends on the way in which these parameters are determined.

When equilibrium constants are measured in the vicinity of $K = 1$ corresponding to $x_A = ½$, $k = ½$, $\kappa = 0$ the expressions (8.104), (8.105) become very simple:

$$\Delta E^0 = \Delta E\Bigg/\left(1-\frac{\Delta F_{ex}}{2RT_{1/2}}\right) \tag{8.106}$$

$$\frac{\Delta S^0}{R} = \frac{\Delta S}{R}+\frac{\Delta E^0}{RT_{1/2}}\frac{\Delta F_{ex}}{2RT_{1/2}} \tag{8.107}$$

These equations can be used to determine the isoequilibrium point when the exchange energy is constant and ΔE is varied. Noticing that at the transition point ΔS^0, ΔE^0 and $T_{1/2}$ are interrelated as $\Delta E^0 = T_{1/2}\Delta S^0$, we get:

$$\left(\frac{\Delta S^0}{R}\right)^2\frac{\Delta F_{ex}}{2\Delta E^0}-\frac{\Delta S^0}{R}+\frac{\Delta S}{R} = 0 \tag{8.107a}$$

The relationship between ΔE^0 and ΔS^0 is non-linear and the IER is not perfect. When ΔE is constant and ΔE_{ex} is varied, (8.106) and (8.107) can be combined to yield three variables ΔS^0, ΔE^0 and $T_{1/2}$:

$$\frac{\Delta S^0}{R} = \frac{\Delta S}{R}+\frac{\Delta E^0}{RT_{1/2}}\left(1-\frac{\Delta E}{\Delta E^0}\right) \tag{8.108}$$

Again, the third variable is not independent ($\Delta E^0 = T_{1/2}\Delta S^0$) and we get:

$$\Delta S-\Delta S^0\frac{\Delta E}{\Delta E^0} = 0 \quad or \quad \frac{\Delta S}{\Delta E} = \frac{\Delta S^0}{\Delta E^0} \tag{8.109}$$

But the ratio of ΔS and ΔE is actually the inverse transition temperature and we have just demonstrated a trivial fact that van't Hoff curves in a reaction series characterised by constant ΔE and varying ΔE_{ex} intersect at the transition point (see

Chapter 7). What is more important, the tangents at equal conversion of the van't Hoff curves based on (8.102) and corresponding to constant ΔE and varying ΔE_{ex} intersect at one point, *i.e.* exhibit a perfect IER (see Fig. 8.11).

The isoequilibrium temperature can be negative when this reaction is studied over a range of high degrees of conversion. It is positive when the range of low degrees of conversion is explored and an intersection of the van't Hoff plots can be observed within the experimental range when equilibrium constants are measured around $K = 1$.

These results have been obtained for a non-diluted system. When a binary system (*e.g.* a spin crossover system) is studied in a regular solution containing an inert solvent, the law of mass action is given by (7.109) in Chapter 7 (χ being the degree of conversion):

$$\gamma(1-2\chi_A)\frac{\Delta F_{ex}}{kT}-\gamma\frac{\Delta F}{kT}-(1-\gamma)\left(\frac{\Delta F_\infty}{kT}+\frac{\Delta F_{solv}}{kT}\right)+\ln\left(\frac{\chi_A}{1-\chi_A}\right) = 0 \qquad (8.110)$$

Among the parameters entering this law of mass action ΔF_{ex}, ΔE, ΔS characterise binary equilibrium in pure components; ΔE_∞ ΔS_∞ characterise this equilibrium at infinite dilution and ΔE_{solv}, ΔS_{solv} characterise the change in the state of solvent molecules.

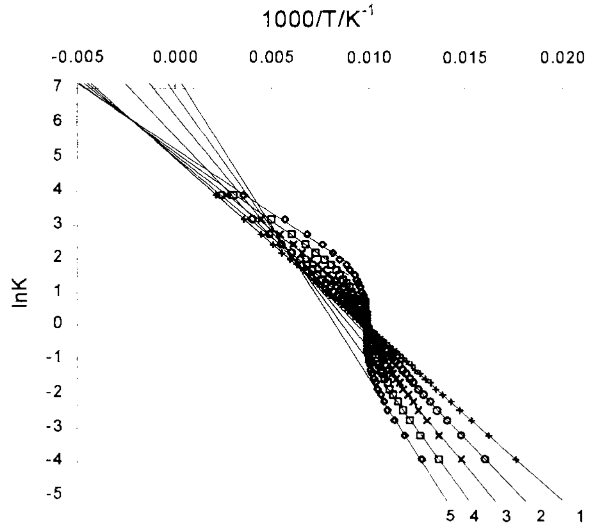

Fig. 8.11. The intersection of tangents to van't Hoff plots calculated for a system described by (8.102) with ΔE = 1000 cal mol^{-1}, $\ln Q = 5$, $\Delta S_{ex} = 0$ and varying ΔE_{ex}: 0 (1), 100 (2), 200 (3), 300(4) and 400 (5) cal mol^{-1}

Formally, two terms with the weighting factor $(1-\gamma)$ must be combined and the effective free energy change at infinite dilution ($\Delta F_{inf} = \Delta F_{\infty} + \Delta F_{solv}$) will describe the combined effect of LS–HS transitions on the molecules of solute and solvent:

$$\gamma(1-2\chi_A)\frac{\Delta F_{ex}}{kT} - \gamma\left(\frac{\Delta E}{kT} - \frac{\Delta S}{k}\right) - (1-\gamma)\left(\frac{\Delta E_{inf}}{kT} - \frac{\Delta S_{inf}}{k}\right) + \ln\left(\frac{\chi_A}{1-\chi_A}\right) = 0 \tag{8.111A}$$

Equation (8.111) predicts specific variations of the shapes of van't Hoff plots upon dilution indicative of IER-s. Fig. 8.12 shows a series of patterns of van't Hoff plots that can be observed in a system characterised by a positive exchange energy.

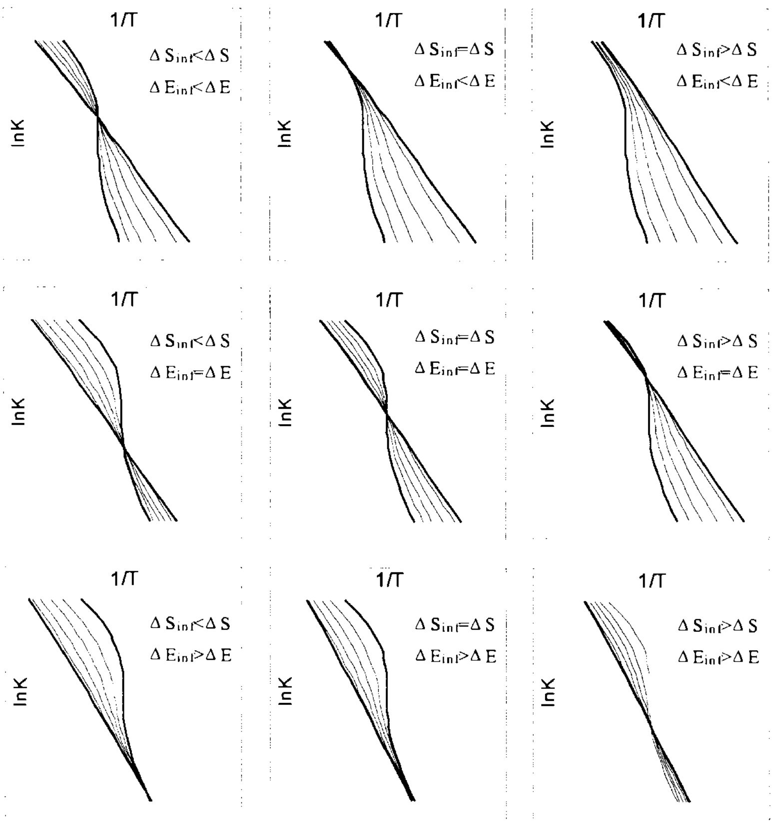

Fig. 8.12. Van't Hoff plots obtained by dilution of the reaction mixture (8.86) characterised by *positive exchange energy* $\Delta E_{ex} = +0.4$ kcal mol^{-1}, $\Delta S_{ex} = 0$, $\Delta E = 1$ kcal mol^{-1}, $\Delta S = 5R$ and varying ΔS_{inf}, ΔE_{inf}. The plots corresponding to the highest dilution approach a straight line whilst the those of non-diluted systems are curvilinear

(Similar patterns can be derived for a system characterised by negative exchange energy without, however, taking into account possible ordering. The case of ordering in a three component system is complicated and will not be discussed here.)

Depending on the ratios $\Delta E/\Delta E_{inf}$ and $\Delta S/\Delta S_{inf}$, the intersection point can be shifted within the experimental range and (in the case of tangents) beyond it. The dilution (variation of γ) effectively varies all parameters in (8.111) which results in peculiar shapes of the patterns of sets of van't Hoff plots corresponding to diluted systems. One of these patterns in the middle row of Fig. 8.12 ($\Delta S_{inf} > \Delta S$, $\Delta E_{inf} = \Delta E$) exhibits apparently two points of intersection.

It must be pointed out that a tendency of van't Hoff (Arrhenius) plots to intersect in one point does not necessarily mean an IER (IKR): this intersection must occur at finite temperatures (ether positive or negative). *An intersection at infinite temperatures (zero abscissa on the van't Hoff plot) means that the energy (it can be ΔE, ΔE_{inf} or ΔE_{ex}) is varied in a reaction series whereas the entropy is constant.* This is a result of the presence of the factor $1/kT$ in any energy term in the equation of the law of mass action (8.111). On the other hand, the variation of ΔE_{ex} necessarily brings about an intersection at the transition point and hence curves with two points of intersection. Fig. 8.13 illustrates this situation with examples of van't Hoff plots simulated for variations of exchange energy at constant dilution.

In reaction series characterised by constant exchange energy and variable ΔE and ΔE_{inf}, van't Hoff plots intersect at the infinite temperature alone (Fig. 8.14A and 8.14B). However, (due to non-zero ΔE_{ex}) such plots remain curvilinear and tangents to these curves might intersect at other temperatures, depending on the actual mode of collecting data (*e.g.* at constant mean temperature or constant mean *K*). The variation of the purely entropic part (ΔS, ΔS_{inf}) causes a parallel horizontal shift of such curves (Fig. 8.14C). An intersection of tangents to these curves at constant temperature is not so obviously possible as in the case of variations of energy.

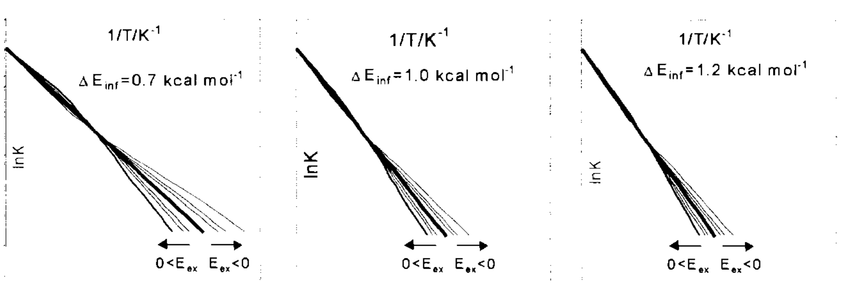

Fig. 8.13. Van't Hoff plots of the reaction mixture (8.86) characterised by $\Delta E = 1$ kcal mol^{-1}, $\Delta S = \Delta S_{inf} = 3R$, $\Delta S_{ex} = 0$, and varying ΔE_{ex}. Reacting species are diluted ($\gamma = 0.3$) by the solvent characterised by ΔE_{inf} shown in graphs. Thick straight lines correspond to zero ΔE_{ex}

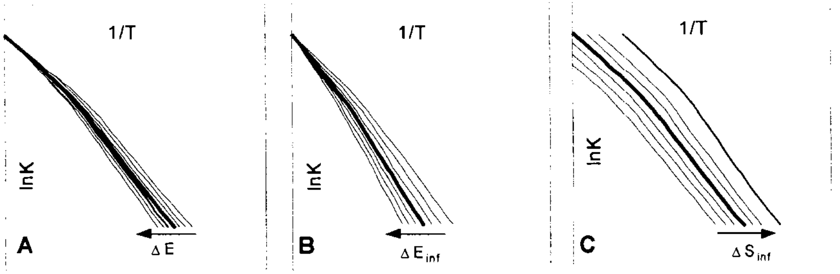

Fig. 8.14. Van't Hoff plots of the reaction mixture (8.86) characterised by $\Delta E_{ex} = 0.4$ kcal mol^{-1}, $\Delta S_{ex} = 0$, $\gamma = 0.3$ and varying ΔE, ΔE_{inf} and ΔS_{inf}. Thick lines correspond to $\Delta E = \Delta E_{inf}$ and $\Delta S = \Delta S_{inf}$

Using the algorithms described above it is not difficult to obtain expressions for the coordinates of the isoequilibrium point for any actual example. The parameters of isokinetic relationships are thus useful in the analysis of non-ideality effects – especially when the reaction can be studied over a narrow range of degrees of conversion (for example, in the liquid state where phase transitions limit the available range of temperatures). When the whole transition curve can be obtained, the data can be analysed directly according to the general equation of the law of mass action as has been done in the analysis of spin crossover in diluted systems (see Section 7.11).

8.5

Conclusions

The law of mass action derived on the basis of statistical mechanics allows one to analyse various empirical chemical correlations such as linear free energy relationships and the isokinetic and isoequilibrium relationships. Correlations between free energies exist in series of similar equilibria, *i.e.* those having the highest sensitivity to the same parameter (s). A reference reaction should be sensitive to one parameter alone or the reaction series must be arranged in a way providing for such conditions. One of these ways is to choose a reference substance possessing an exceptionally strong property such as the electron acceptor ability of $SbCl_5$. Theoretical analysis, however, shows that several parameters significantly changing reactivity are usually varied in almost all reaction series. Methods relying on a high precision of determination of a reference property (such as dissociation constants in the Hammett substituent scale) bring about a large contribution from the effects of non-ideality and solvation.

The latter two types of contributions towards the free energy of reaction must be distinguished because the solvation contribution is connected with the formation of molecule-like associates, whereas general molecular interactions just increase/decrease the probability of finding molecules of given kinds close together. Solvation contributes directly towards the standard internal energy and entropy of reaction and its effect can be predicted on the basis of donor and acceptor numbers of solvent, reactants and products of reaction. An alternative method of taking into account interactions of the 'chemical' type is to include corresponding equilibria in the general reaction scheme. Molecular interactions of 'non-chemical' type result in additional non-logarithmic terms in the law of mass action (indirectly contributing to the effective ΔE^0 and ΔS^0) and bring about a curvature of van't Hoff plots.

The correlation between temperature dependent and temperature independent parts of standard free energy, *i.e.* standard internal energy (enthalpy) and standard entropy of reaction or activation may originate from two sources. Firstly, molecular parameters such as molecular mass, moments of inertia, electronic energy, and vibrational frequency can be varied in a reaction series in a correlated manner. This brings about an IER and IKR that can be analysed on the basis of statistical mechanical expressions for free energy in an ideal approximation.

Another source of an IER and IKR is the non-ideality of equilibria in the condensed state and, connected with it, curvature of van't Hoff (Arrhenius) plots. The analysis of the non-ideal law of mass action derived using lattice theory of the liquid state shows that all known types of IER can be explained by these effects.

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9 Concluding Remarks

In the preceding Chapters several approaches to the problem of the derivation of the law of mass action for ideal and non-ideal systems based on molecular theory of solutions have been described. The main conclusions following from this material are systematised below in the most general form. Relationships presented admit an easy reduction to practically applicable equations by employing methods described in the corresponding Chapters and illustrated by numerous examples.

1. By the law of mass action we understand a *theoretical relationship* determining the amounts of reactants and products in equilibrium and obtained from the condition of the *minimum of free energy* with respect to the numbers of participating molecules. The law of mass action thus originates in *the first and the second laws of thermodynamics.* It may have different forms for systems differing by the mode of molecular interactions.

Parameters of the law of mass action (equilibrium constant, standard free energy, balances of molecular volume and lattice energy, exchange free energy, *etc.,* see below), on the one hand, characterise chemical reactivity whereas, on the other hand, they are directly connected with molecular parameters. This enables the formulation of '*structure – reactivity*' *relationships* in terms of parameters having clear physical significance.

The alternative method employing *activities* retains a *unique mathematical form* but this form can only be considered as an *empirical relationship.*

2. *Statistical mechanics* provides for a *physical interpretation* of equilibrium constants and other parameters of the law of mass action at the molecular level (Chapters 1, 2 and 8). One of the most important links provided by statistical mechanics is the *definition of ideal systems* as *systems of statistically independent molecules.* It enables the formulation (Chapter 3) of the law of mass action for *ideal gases* and *ideal crystals.* The theoretical foundations of 'structure - reactivity' relationships can therefore be firmly established for reactions in rarefied gases and crystals at low temperatures, in which the state of any one molecule is approximately independent of the state of all other molecules.

The law of mass action for the chemical equilibrium of the most general type:

$$\sum_i \xi_i R_i = 0 \tag{9.1}$$

occurring in an ideal system can be written as:

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$$\sum_i \xi_i \ln n_i = \sum_i \xi_i \ln q_i + \sum_i \xi_i \ln V \tag{9.2}$$

or:

$$\sum_i \xi_i \ln n_i = \sum_i \xi_i \ln q_i + \sum_i \xi_i \ln N \tag{9.3}$$

in which the stoichiometric coefficients ξ_i are positive for products and negative for reactants, V is the volume of the system and N is the total number of molecules. The partition functions, q_i, are determined exclusively by the 'intramolecular' parameters of the reacting species and temperature. Equations (9.2) and (9.3) readily yield an easy transformation to simple conventional forms that contain the products of concentrations to the corresponding powers.

The *main* variables of the law of mass action are *numbers of molecules*. However, it is convenient to use *concentrations* in order to get equilibrium constants independent of the absolute amounts of reactants. The dependence of equilibrium constant on the amounts of reactants (volume of a system) is then substituted by the dependence on the chosen unit of concentration or pressure.

In gas-phase reactions, both mole fractions (for reactions at constant pressure) and molar concentrations (for reactions at constant volume) may be used because the equation of state of ideal gas yields a linear relationship between V and N (see (9.2) and (9.3)).

The law of mass action for a reaction in an ideal crystal can be straightforwardly derived in the form of (9.3). This makes mole fractions the natural variables in the law of mass action of *solid-state reactions*.

In the liquid state the volume of a system is determined not by the number of molecules (as in the gas phase at constant pressure) but by the quantity of matter. The invariance of the volume of a reaction mixture in the liquid state favours the use of (9.2) and molar concentrations as variables in the law of mass action.

3. When *molecular interactions* are taken into account (Chapter 4) the volume of a system in the liquid state becomes dependent on composition and parameters of molecular interactions. Employing the model of the mean molecular field (*i.e.* the *lattice theory of the liquid state*) molecular interactions can be described in terms of *free volume* (V_f) and *lattice energy* (U). In the framework of this model the law of mass action for an imperfect system can be written as:

$$\sum_i \xi_i \ln n_i = \sum_i \xi_i \ln q_i + Q(n_i, \ldots, V_f, U) \tag{9.4}$$

The case of *additive* volume and lattice energy:

$$V = \sum_i n_i v_i \qquad U = \sum_i n_i u_i \tag{9.5}$$

(in which v_i and u_i are independent of composition) is usually considered as approaching the state of the ideal solution. However, the dependence of V and U

on composition (9.5) brings about a certain non-ideality resulting in the term Q defined as:

$$Q = \sum_i \xi_i \ln V_f + \sum_i n_i \sum_j \xi_j \frac{\partial \ln V_f}{\partial n_j} \tag{9.6}$$

The *free volume* V_f is connected with the volume of a system *via* an equation of state and can be approximated by:

$$V_f = aV\tau^{\alpha} \tag{9.7}$$

in which a is a proportionality coefficient, $\tau = NkT/U$ is the *reduced temperature*, $\alpha = 3$ for the simplified Eyring equation of state and $\alpha \cong 1.5$ for the Lennard-Jones and Devonshire equation of state. This relationship is strongly dependent on the shape of the intermolecular potential (Chapter 5).

The last term in (9.6) can be represented *via* a *complete derivative* with respect to the number of molecules of any kind. Under the condition (9.5) this derivative is a function of the *relative balances* of v and u in the actual reaction:

$$\sum_j \xi_j \frac{\partial \ln V_f}{\partial n_j} = \xi_k \frac{d \ln V_f}{dn_k} = \frac{\Delta v}{V} - \alpha \frac{\Delta u}{U} \tag{9.8}$$

in which:

$$\Delta v = \sum_i \xi_i v_i \qquad \Delta u = \sum_i \xi_i u_i \tag{9.9}$$

Although a chemical reaction always changes the volume of a reaction mixture as well as the energy of molecular interactions ($\Delta v \neq 0$; $\Delta u \neq 0$), in many cases these changes are not large. The last term in (9.6) is then small compared to 1 and that facilitates a ready transformation of the non-ideality terms into activity coefficients (Chapters 4 and 6).

4. Gaseous systems of low density with weak molecular interactions can be described in a comparatively simple way employing statistical mechanical formalism (Chapter 6). The equation of state of such a gas is identical with a simplified form of the van der Waals equation of state. The effects of non-ideality in such gas-phase reactions are generally small and can readily be taken into account in the form of activities.

5. In the condensed state the balances of the energies of molecular interactions may be large because neutral reactants might result in highly polar or charged products and *vice versa*. Therefore considerable deviations from ideality can be expected, resulting in a curvature of van't Hoff plots and even *critical phenomena*, such as a separation of two condensed phases, similar (but not identical) to those originating in the effects of *non-additivity of the lattice energy*.

The non-additivity of the lattice energy (Chapter 7) is commonly taken into account by introducing a *perturbation term*. In a binary mixture of molecules of similar size this perturbation term is dependent on the product of mole fractions of components:

$$U = N\left(x_A u_{AA} + x_B u_{BB} + x_A x_B \Delta u_{ex}\right) \tag{9.10}$$

The parameter Δu_{ex} is known under different names such as '*cooperativity*', '*excess energy of mixing*' or '*interchange energy*' reflecting different aspects of the existence of molecular interactions. Describing the non-ideality at the molecular level, it is convenient to interpret this parameter as the change in potential energy accompanying the formation of two hetero-molecular pairs from two homo-molecular species:

$$\Delta u_{ex} = 2u_{AB} - u_{AA} - u_{BB} \tag{9.11}$$

In this book it has, therefore, been termed *exchange energy*, emphasising its analogy to the well-known quantum mechanical parameter. In both cases this name refers not to any real physical process occurring in a system but to a versatile and illustrative *model*. Similar perturbed additivity rules are being applied to various properties of non-ideal systems and *inter alia* to volume. In the latter case the notation '*excess volume*' is better applicable to the parameter Δv_{ex}.

6. Equation (9.10) originates in the model taking into account *binary interactions* alone. If higher order interactions are considered then higher order terms (with respect to mole fractions of components) appear in the expressions for the potential and free energy. In Chapter 7 a formalism taking into account *triple interactions* has been derived employing a novel method that considers *molecular interactions as arising from the dependence of partition functions* of molecules on the nature of their surroundings. Considering the effects of two neighbours along a coordinate the free energy of a binary mixture is obtained as:

$$F = -x\left(1-x^2\right)\Delta^{(3)} - x(1-x)\Delta^{(2)} - x\Delta^{(0)} + F_{BBB} + kTN\left[x\ln x + (1-x)\ln(1-x)\right] \tag{9.12}$$

in which x is the mole fraction of the component A and $\Delta^{(0)} = F_{BBB} - F_{AAA}$ is the standard free energy of the transformation $A \rightarrow B$. The coefficients $\Delta^{(3)}$ and $\Delta^{(2)}$ characterising non-ideality are *combinations of binary differences of free energy* corresponding to six possible configurations of molecules A and B in triple sequences. This formalism thus provides for an easy physical interpretation of the estimates of parameters of the law of mass action. For a mixture described by (9.12) the law of mass action can be written as:

$$3x^2\frac{\Delta^{(3)}}{kT} + 2x\frac{\Delta^{(2)}}{kT} - \frac{\Delta^{(0)} + \Delta^{(2)} + \Delta^{(3)}}{kT} = \ln\frac{1-x}{x} \tag{9.13}$$

Equation (9.11) shows that non-ideality directly contributes towards the effective standard free energy of reaction (the third term in (9.13)) and also changes the shape of van't Hoff plots *via* the (composition dependent) first and second terms. The *non-ideality parameters in* (9.13) *are related to kT* and the corresponding terms can be quite large at low temperatures, resulting in *critical phenomena* actually observed experimentally.

Under certain conditions (quite often adhered to) the coefficient $\Delta^{(3)}$ vanishes and the developed formalism is reduced to that of the theory of regular solutions. The coefficient $\Delta^{(2)}$ then becomes identical with the *exchange free energy*. However, in special cases, triple interactions are important (as, for example, in two-step spin crossover) requiring for its explanation a non-zero $\Delta^{(3)}$ and a certain degree of ordering (Chapter 7).

7. A *general form of the law of mass action* for an imperfect liquid (based on the lattice model of the liquid state) must take into account the non-ideality terms originating in both the *dependence of the free volume on composition* and *non-additivity of lattice energy*. It can be written as:

$$\begin{aligned}\sum_i \xi_i \ln n_i &= \sum_i \xi_i \ln q_i + \sum_i \xi_i \ln V \\ &+ \sum_i \xi_i \ln \frac{V_f}{V} + \sum_i n_i \sum_j \xi_j \frac{\partial \ln V_f}{\partial n_j} - \sum_i n_i \sum_j \xi_j \frac{\partial}{\partial n_j} \sum_k \frac{n_k u_k}{kT}\end{aligned} \tag{9.14}$$

in which the derivative of the lattice energy is given by:

$$\frac{\partial}{\partial n_j}\left(\sum_k \frac{n_k u_k}{kT}\right) = \frac{c}{2}\frac{\varphi_{jj}}{kT} + \frac{c}{2}\left(\frac{N-n_j}{N}\sum_{k\neq j}\frac{n_k}{N}\frac{\Delta u_{jk}}{kT} - \sum_{k\neq j}\sum_{l\neq k,j}\frac{n_k n_l}{N^2}\frac{\Delta u_{kl}}{kT}\right) \tag{9.15}$$

The first line in (9.14) is the ideal gas law of mass action that can be transformed into a form with respect to molar concentrations. The second line in this equation presents the effects of non-ideality.

The first non-ideality term is proportional to the logarithm of reduced temperature and is therefore controlled by the shape of the average intermolecular potential.

The second non-ideality term is connected with the dependence of free volume on composition. To a first approximation it can be represented *via* the relative balances of volume and lattice energy. A second approximation brings about the dependence of this term on exchange (excess) volume and exchange energy.

The third non-ideality term is connected with the dependence of the lattice energy on composition. It can be derived in terms of exchange energy (see Chapter 7, Eq. (7.115)) but in some cases higher order approximation is required as in the description of the two-step spin crossover mentioned above.

8. A general condition for non-ideality terms in the law of mass action to be small is that the reaction should not significantly change the character of molecular interactions in the reaction mixture. In such a case these terms can

easily be converted into activity coefficients that are polynomial functions of concentrations.

When this condition does not hold, the non-ideality terms are large and such a transformation is, in general, not allowed. However, *over a narrow range of degrees of conversion*, the conventional form of the law of mass action can still be used: one can extract the (approximately) constant part of non-ideality terms and combine it with the equilibrium constant. This procedure is equivalent to the linearisation of an essentially curvilinear dependence (*e.g.* non-ideal van't Hoff plot) in the vicinity of a standard state.

Such a linearisation is only allowed when non-ideality terms do not bring about *critical phenomena*. In the latter case a system can exhibit an exploding behaviour within a few kelvins, while at the same time showing quasi-normal van't Hoff plots beyond the narrow critical region. Any extrapolation of the dependencies obtained on the basis of the conventional law of mass action and activity coefficients are, therefore, dangerous in every sense of this word.

9. The use of the non-ideal law of mass action is then strongly recommended – especially for non-explored systems. Although the general expressions presented above are mainly illustrative, a practical law of mass action can be derived (see numerous examples in this book) for any special case. By taking into account all possible simplifications allowed for the actual system, such a law of mass action can be reduced to a comparatively simple expression admitting a reliable estimation of parameters from experimental data.

Even the law of mass action taking into account both the *composition dependence of free volume* and *non-additivity of volume and lattice energy* (a version of the Eq. (9.14)) can be straightforwardly derived for a binary mixture (see Appendix 10.10). It contains seven parameters including the *balances*, ΔU, ΔV and exchange parameters ΔU_{ex}, ΔV_{ex}. The balances themselves do not considerably change the shape of the van't Hoff plots but they increase the sensitivity of this relationship towards the exchange parameters: the critical value of ΔU_{ex} above which phase separation can be observed is considerably lower when the balances are non-zero.

From the point of view of their physical significance the balances can be interpreted as the result of the *non-additivity of the atomic interactions* (within a molecule) whereas the exchange parameters reflect the *non-additivity of the molecular* interactions.

10. Non-ideality terms contribute towards the equilibrium constant and are therefore important for *chemical correlations* such as the *linear free energy relationships* (LFER). In Chapter 8 it has been shown that *molecular interactions play an important role in the scales of chemical reactivity* such as that of Hammett. This narrows the scope of interpretations of such correlations as representing 'structure-reactivity' relationships: their parameters reflect not the intra-molecular properties alone but are also dependent on the mode of molecular interactions.

Non-ideality terms also bring about a certain curvature of van't Hoff and Arrhenius plots, which results in formal interdependence between standard enthalpy and standard entropy of reaction and activation known as *isoequilibrium and isokinetic relationships* (IER and IKR). In fact, *all known types of IER can be explained* (see Chapter 8) on the basis of the law of mass action for systems with *non-additive lattice energy* ($\Delta U_{ex} \neq 0$).

Parameters of isokinetic and isoequilibrium relationships are also considerably affected by the mode in which experimental data are collected. A simple analysis can be done in the cases of the invariant mean equilibrium (rate) constant or the invariant mean temperature of experiment. Unfortunately these conditions are rarely obeyed in experiments providing data for an IER or IKR analysis. Therefore quantitative values of IER (IKR) parameters are of a limited validity. On the other hand, qualitatively, an observation of IER (IKR) indicates certain type of non-ideality and this indication can be important for the interpretation of other results.

A reliable estimation of the parameters of a non-ideal law of mass action is only possible when experimental data are available over a wide range of degrees of conversion. In such cases, a non-linear regression analysis according to the exact expression of the law of mass action provides a deep insight into the nature of the investigated reaction (as illustrated by the examples of two-step and steep spin crossover in the solid state given in Chapter 7).

In the liquid state, however, such experimental data can rarely be obtained because of the limited temperature region for the existence of liquid systems. In such cases an IER (IKR) analysis might provide valuable information about non-ideality in the investigated system.

10 Appendices

10.1
Lagrange equations and Hamilton (canonical) equations

The laws of mechanics formulated by Newton *only implicitly contain the concept of energy*, a concept by far more general than the velocity, momentum and coordinates of a moving body. The law of conservation energy is one of the most general laws, revealing itself not only in the *dynamics of moving bodies* but also in *electrical and chemical* processes and in the processes of *transformation of heat*. It must also be mentioned that *mathematical equations* employing the concept of energy were introduced by *Lagrange* (1788) and *Hamilton* (1834) long before the energy ceased to be called *'life force'* and the law of conservation of energy was formulated quantitatively. One of the most general principles of classical mechanics is the *principle of least action* formulated by Hamilton. According to this principle, the trajectory of a moving body corresponds to the *least value* of the integral W called the *action* or *function of action:*

$$W = \int_{t_0}^{t_1} L dt \tag{10.1}$$

The function L is the *Lagrangian function* or *kinetic potential* equal to the *difference* between kinetic and potential energies:

$$L = \frac{mv^2}{2} - U = T - U \tag{10.2}$$

The problem of finding the *functions* corresponding to an extremum of some quantity are found using the *calculus of variations* developed by *Euler*. The operation of variation is in many ways very similar to differentiation and does *commute with differentiation*. Furthermore, the variation of a function of many variables is calculated similarly to the complete differential. There are, of course, differences: *variations only exist in the defined region* of interest and *at both ends* of this region *variations equal zero*. The problem stated above is solved similarly to an ordinary search of extrema, *i.e.* by setting the variation equal o zero:

$$\delta W = \delta \int_{t_0}^{t} L dt = 0 \tag{10.3}$$

In the field of *central* forces, potential *energy* is a function of the coordinates alone, therefore:

$$L = L(q_1, q_2, \ldots q_n; \dot{q}_1, \dot{q}_2, \ldots \dot{q}_n) \tag{10.4}$$

in which q_i are coordinates and $\dot{q}_i$ the corresponding velocities. The Lagrangian function may also explicitly depend on time. The variation of action (10.3) can be written as:

A.B. Koudriavtsev et al., *The Law of Mass Action*

$$\delta W = \int_{t_0}^{t} \delta L dt \tag{10.5}$$

For all coordinates:

$$\delta L = \sum_i \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) \tag{10.6}$$

and:

$$\delta W = \int_{t_0}^{t} \sum_i \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) \tag{10.7}$$

The second part of the integral (10.7) can be transformed as follows:

$$\int_{t_0}^{t} \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i = \int_{t_0}^{t} \frac{\partial L}{\partial \dot{q}_i} \frac{d}{dt} \delta q_i \tag{10.8}$$

In addition, this integral can be integrated by parts:

$$\int_{t_0}^{t} \frac{\partial L}{\partial \dot{q}_i} \frac{d}{dt} \delta q_i = \left[\delta q_i \frac{\partial L}{\partial \dot{q}_i} \right]_{t_0}^{t} - \int_{t_0}^{t} \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \delta q_i dt = - \int_{t_0}^{t} \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \delta q_i dt \tag{10.9}$$

The expression in square brackets is zero because the variations at the ends of the path are zero. Therefore:

$$\delta W = \sum_{i=1}^{n} \int_{t_0}^{t} \left(\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i dt = 0 \tag{10.10}$$

The variation δq being non-zero within the integration range, (10.10) only holds if *every term of the sum in* (10.10) *equals zero*:

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0 \tag{10.11}$$

This system of equations is called the '*Lagrange equations*'. Lagrange equations are very useful when deriving equations of motion in various coordinate systems. For example Newton's first law can be derived from a Lagrange equation. In Cartesian coordinates the Lagrangian function is:

$$L = T - U = \frac{m}{2} \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2 \right) - U(x, y, z) \tag{10.12}$$

The components of the Lagrange equations (the derivatives of L with respect to coordinates and velocities) are:

$$\frac{\partial L}{\partial q_1} = \frac{\partial L}{\partial x} = - \frac{\partial U}{\partial x}; \quad \frac{\partial L}{\partial \dot{q}_1} = m\dot{x}; \quad \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_1} = m\ddot{x} \tag{10.13}$$

For each coordinate (x, y, z) the Lagrange equations can then be written as:

$$-\partial U/\partial x - m\ddot{x} = 0 \tag{10.14}$$

The derivatives of potential energy with respect to the coordinates are corresponding components of the force; therefore, the last equation formulates Newton's first law.

Polar or spherical coordinates are very convenient for the derivation of equations of motion in *central force fields*, and Lagrange equations can be used advantageously for this purpose. Suppose we have a body (a particle) in a central force field moving on a plane. The potential and kinetic energies are:

$$U = -\frac{A}{r}; \quad T = \frac{m}{2}\left(\dot{r}^2 + r^2\dot{\varphi}^2\right) \tag{10.15}$$

The Lagrangian function then is:

$$L = \frac{m}{2}\left(\dot{r}^2 + r^2\dot{\varphi}^2\right) + A/r \tag{10.16}$$

and the components of the Lagrange equation are:

$$\frac{\partial L}{\partial q_1} = \frac{\partial L}{\partial r} = mr\dot{\varphi}^2 - \frac{A}{r^2}; \quad \frac{\partial L}{\partial \dot{q}_1} = \frac{\partial L}{\partial \dot{r}} = m\dot{r} \tag{10.17}$$

The first and the second Lagrange equations are:

$$\frac{\partial L}{\partial r} - \frac{d}{dt}\frac{\partial L}{\partial \dot{r}_i} = mr\dot{\varphi}^2 - \frac{A}{r^2} - \frac{d}{dt}\left(m\dot{r}\right) = 0 \tag{10.18}$$

$$\frac{\partial L}{\partial \varphi} - \frac{d}{dt}\frac{\partial L}{\partial \dot{\varphi}_i} = -\frac{d}{dt}mr^2\dot{\varphi} = 0 \tag{10.19}$$

The Lagrangian function in (10.16) is *independent* of the polar angle φ therefore the derivative $\partial L/\partial\varphi$ equals zero. This signifies that:

$$\left.\begin{aligned} mr^2\dot{\varphi} &= const \\ mr\dot{\varphi}^2 - A/r^2 &= m\ddot{r} \end{aligned}\right\} \tag{10.20}$$

Using the Lagrange equations we have thus directly obtained the *integral of the equation of motion with respect to the angular momentum* ($mr^2\dot{\varphi}$). This rule is, in fact, general – whenever L is independent of some coordinate q then the derivative of the Lagrangian function with respect to the corresponding *velocity* is constant:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = 0; \quad \frac{\partial L}{\partial \dot{q}} = const \tag{10.21}$$

Such coordinates are called *cyclic coordinates*. The derivative $\partial L/\partial \dot{q}$ of the Lagrangian function with respect to the velocity corresponding to the cyclic coordinate is an *integral of motion*.

We have thus found one of the integrals of motion: it is the angular momentum. There are seven integrals of motion: energy, three components of *angular momentum* (in Cartesian coordinates), and three components of *momentum*. This method is applicable to any number of material points.

Suppose we have a *system* of material points the *potential energy of which is proportional to* *the square of displacement from the point of equilibrium*:

$$U = \tfrac{1}{2}\sum \alpha_i^2 q_i^2; \quad T = \tfrac{1}{2}\sum m_i \dot{q}_i^2 \tag{10.22}$$

then the corresponding Lagrangian function is:

$$L = \frac{1}{2}\sum \left(m\dot{q}_i^2 - \alpha_i^2 q_i^2\right) \tag{10.23}$$

By differentiating (10.23) we get:

$$\frac{\partial L}{\partial q_i} = -\alpha_i^2 q_i; \quad \frac{\partial L}{\partial \dot{q}_i} = m\dot{q}_i \tag{10.24}$$

and the Lagrange equation yields the following relationship:

$$\alpha_i^2 q_i + m\ddot{q}_i = 0 \tag{10.25}$$

Solution of this differential equation (α^2 is always positive) corresponds to harmonic oscillations. Any system for which the Lagrangian function is represented by a sum of quadratic terms with respect to coordinates and momenta (even containing cross products) is, in principle, a set of harmonic oscillators.

The approach developed by Lagrange is indeed very useful, the only drawback being that equations were derived using *velocities* and not the fundamental variable of Newtonian mechanics – *momentum*. The formulation, in the most general form, of the laws of classical mechanics in terms of momenta (*dynamic coordinate*) and coordinates (*geometrical coordinate*) is due to Hamilton. The Lagrangian function is replaced by the *Hamiltonian function*, which is the *sum of kinetic and potential energy* expressed as a function of coordinates and momenta. The generalised *momentum* (in any coordinate system) is defined as the derivative of kinetic energy with respect to *velocity*:

$$p_i = \partial T / \partial \dot{q}_i \tag{10.26}$$

A quantity similar to the momentum has *been used in Lagrange equations: the derivative of the Lagrangian function with respect to velocity*. The Hamiltonian function can be written in Cartesian coordinates as:

$$H(p,q) = T + U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + U(x,y,z) \tag{10.27}$$

In polar coordinates the kinetic energy is expressed as:

$$T = (m/2)\left(\dot{r}^2 + r^2\dot{\varphi}^2\right) \tag{10.28}$$

There are two momenta for a motion in a plane: those corresponding to the polar coordinates r and φ:

$$p_r = \partial T/\partial \dot{r} = m\dot{r}; \quad p_\varphi = \partial T/\partial \dot{\varphi} = mr^2\dot{\varphi}; \tag{10.29}$$

Expressing kinetic energy as a function of generalised momenta:

$$T = \frac{1}{2m}\left(p_r^2 + p_\varphi^2 / r^2\right) \tag{10.30}$$

we find the Hamiltonian function to be:

$$H = \frac{1}{2m}\left(p_r^2 + p_\varphi^2/r^2\right) + U(r,\varphi) \tag{10.31}$$

Kinetic energy, as can be seen from (10.12), (10.28) and (10.30), is a *homogeneous second order*[1] *function* of *velocities or momenta* and this is true for any system of material points obeying the laws of Newtonian mechanics. From the definitions of the Hamiltonian and Lagrangian functions it follows that:

$$L + H = 2T; \quad H = T + U; \quad H - L = 2U \tag{10.32}$$

According to *Euler's theorem* on homogenous functions of the n-th order:

$$nF(\xi_1, \xi_2, \ldots \xi_m) = \sum_i \frac{\partial F}{\partial \xi_i}\xi_i \tag{10.33}$$

Applying this rule to *kinetic energy* as a homogeneous function of the *squares of velocities*, we get:

$$2T = \sum\left(\frac{\partial T}{\partial \dot{q}_i}\right)\dot{q}_i \tag{10.34}$$

Remembering *the* definition of momentum $p_i = \partial T/\partial \dot{q}_i$, we find:

$$2T = \sum p_i \dot{q}_i \tag{10.35}$$

Substituting in (10.32) yields:

$$L + H = \sum p_i \dot{q}_i; \quad or \quad L = \sum p_i \dot{q}_i - H \tag{10.36}$$

From this relationship, we now derive the expression for the *action function, W*:

$$W = \int_{t_0}^{t}\left(\sum p_i \dot{q}_i - H\right)dt \tag{10.37}$$

Applying a variation procedure, we obtain a new expression of the *principle of least action*:

$$\delta W = \int_{t_0}^{t}\left(\delta \sum p_i \dot{q}_i - \delta H\right)dt = 0 \tag{10.38}$$

The variation of the Hamiltonian function is here:

$$\delta H(p,q) = \sum\left(\frac{\partial H}{\partial q_i}\delta q_i + \frac{\partial H}{\partial p_i}\delta p_i\right) \tag{10.39}$$

and:

$$\delta W = \int_{t_0}^{t}\sum\left(p_i \delta \dot{q}_i + \dot{q}_i \delta p_i - \frac{\partial H}{\partial q_i}\delta q_i - \frac{\partial H}{\partial p_i}\delta p_i\right)dt \tag{10.40}$$

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[1] A function dependent exclusively on the squares of variables (in *normal coordinates*) or on the binary products of variables (in any coordinates).

If the variations *of velocities* in this expression are now removed by using the commutative properties of differentiation and variation procedures (similar transformations have been performed when deriving the Lagrange Equations):

$$p_i \delta \dot{q}_i dt = \delta \frac{dq_i}{dt} dt = p_i \frac{d}{dt}(\delta q_i) dt \qquad (10.41)$$

Integrating then by parts:

$$\int_{t_0}^{t} p_i \frac{d}{dt}(\delta q_i) dt = p_i \delta q_i \Big|_{t_0}^{t} - \int_{t_0}^{t} \frac{dp_i}{dt} \delta q_i dt = -\int_{t_0}^{t} \frac{dp_i}{dt} \delta q_i dt \qquad (10.42)$$

Substituting this integral in (10.40) yields the variation of action:

$$\delta W = \int_{t_0}^{t} \sum \left[\left(-\frac{dp_i}{dt} - \frac{\partial H}{\partial q_i} \right) \delta q_i + \left(\frac{dq_i}{dt} - \frac{\partial H}{\partial p_i} \right) \delta p_i \right] dt \qquad (10.43)$$

The condition of extremum corresponds to $\delta W = 0$, which holds if both coefficients of the variations δq and δp separately equal zero:

$$\frac{dp_i}{dt} + \frac{\partial H}{\partial q_i} = 0 ; \qquad \frac{dq_i}{dt} - \frac{\partial H}{\partial p_i} = 0 \qquad (10.44)$$

or:

$$\dot{p}_i = \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} ; \qquad \dot{q}_i = \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \qquad (10.45)$$

These are the ***canonical equations*** of mechanics or ***Hamilton equations***.

Similarly to the Lagrange equations, the *canonical* equations are very useful in the derivation of the *equations of motion*. The first law of Newton can be obtained from Hamilton's equations as readily as from the Lagrange equations. In Cartesian coordinates the Hamiltonian function can be written as:

$$H(p,q) = T + U = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + U(x,y,z) \qquad (10.46)$$

Kinetic energy is independent of *coordinates*, therefore $\partial H/\partial x = \partial U/\partial x$. According to (10.45):

$$\frac{dp_x}{dt} = -\frac{\partial U}{\partial x} \qquad (10.47)$$

The time derivative of momentum being $\dot{p}_x = m\ddot{x}$, the last equation reflects the *balance of dynamic and potential forces* acting on a particle according to Newton's first law. In the polar coordinate system the Hamiltonian function can been written as:

$$H = \frac{1}{2m}\left(p_r^2 + p_\varphi^2 / r^2\right) + U(r,\varphi) \qquad (10.48)$$

In a field of central forces the *potential energy* is only a function of the distance and does not depend on the polar angle:

$$H = \frac{1}{2m}\left(p_r^2 + p_\varphi^2 / r^2\right) - \frac{A}{r} \tag{10.49}$$

We see that polar angle does not enter the expression for the Hamiltonian function. Such coordinates (similarly to those in Lagrange equations) are called *cyclic*. Hamilton's equations for this case can be written as follows:

$$-\frac{dp_r}{dt} = \frac{\partial H}{\partial r} = \frac{A}{r^2} - \frac{p_\varphi^2}{mr^3}; \quad \frac{dr}{dt} = \frac{\partial H}{\partial p_r} = \frac{p_r}{m}; \tag{10.50}$$

or, in a cyclic coordinate system:

$$-\frac{dp_\varphi}{dt} = \frac{\partial H}{\partial \varphi} = 0; \quad \frac{d\varphi}{dt} = \frac{\partial H}{\partial p_\varphi} = \frac{p_\varphi}{mr^2} \tag{10.51}$$

The momentum corresponding to the cyclic coordinate (φ) does not change with time and is the first integral of the equation of motion. Using this property, it is possible to exclude p_φ from the expression for the Hamiltonian function making the latter an explicit function of p_r and r. The availability of cyclic coordinates thus simplifies the integration of equations of motion.

The concept of the integral *of motion* is very important and is being used in the solution of many mechanical problems. The *integral of motion can be any function that remains constant during the motion of a particle or of a system*. The *complete* time derivative of such a function is zero:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum\left(\frac{\partial f}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial f}{\partial p_i}\frac{dp_i}{dt}\right) = 0 \tag{10.52}$$

Using the Hamilton equations (10.44) it can be transformed into:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum\left(\frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = \frac{\partial f}{\partial t} + \{f, H\} = 0 \tag{10.53}$$

The notation $\{f,H\}$ used in (10.53) is called *Poisson brackets*. If a function does not explicitly depend on time then its partial time derivative is zero and:

$$\{\varphi, H\} = 0 \tag{10.54}$$

For conservative systems $\partial H/\partial t = 0$, and using Hamilton's equations it can be found that dH/dt is also zero ({H,H} is, of course, zero). Therefore the Hamiltonian function is an integral of motion.

10. 2

Phase space

Phase space is a useful tool in the description of the mechanical state of systems containing large numbers of particles. It is a *multidimensional Euclidean space of generalised momenta (p) and coordinates (q)*, having axes $q_{11}, \ldots q_{3N}$, $p_{11}, \ldots\ldots p_{3N}$, where N is the number of particles. For particles having some number of rotational, vibrational or any other (electronic, nuclear spin, *etc.*) degrees of freedom the dimension of the phase space is correspondingly increased.

The μ*-space* is the phase space corresponding to the momenta and coordinates of a given molecule or particle; μ-space is a subspace of Γ-space. The elementary volume of μ–phase space, dγ is:

$$d\gamma = dp_1 dp_2 \cdots dp_f \, dq_1 dq_2 \cdots dq_f \tag{10.55}$$

in which f is the number of degrees of freedom ($f = 3$ in the absence of internal degrees of freedom).

The Γ*-space* is the phase space corresponding to the system of N particles. An element of Γ space is the product of elementary volumes dγ:

$$d\Gamma = \prod_{i=1}^{N} d\gamma_i \tag{10.56}$$

A microstate is the mechanical state of a system characterised by a given complete set of q_i and p_i for all particles.

A macrostate is the state of a system characterised by a given value of one or several macroscopic parameters (temperature, volume, density, *etc.*). A large number of microstates corresponds to the same macrostate.

A representative point is a point in phase space (with coordinates **q, p**) representing the coordinates and momenta of all molecules in a system which define a microstate.

A trajectory of a representative *point* in phase space describes the development of a microstate in time. For a system in equilibrium the phase trajectory does not imply any change in the macrostate. The trajectory representing the development of a part of system *never crosses trajectories of other parts; neither does it cross with itself.* Such an intersection would mean that in this point the development of a system is *completely undetermined*, the two directions being equally probable. Phase trajectories of *conservative systems* belong to a hypersurface (*energy layer*) described by:

$$H(p,q) = const. \tag{10.57}$$

10.2.1
The phase space of a harmonic oscillator.

A harmonic oscillator is a model system that is very useful in the description of many systems considered in statistical thermodynamics. A *one*-dimensional *harmonic oscillator* is a system in which the *force F acting on a particle is proportional to the displacement q*:

$$\mathbf{F} = -\alpha^2 q = -\partial U/\partial q \tag{10.58}$$

The potential energy of a harmonic oscillator is a *quadratic* function of a coordinate:

$$U = -\int F dq = \alpha^2 q^2/2 \tag{10.59}$$

The kinetic energy or a harmonic oscillator is a *quadratic* function of velocity:

$$T = m\dot{q}^2/2 \tag{10.60}$$

The momentum of a harmonic oscillator is:

$$p = \frac{\partial T}{\partial \dot{q}} = m\dot{q} \tag{10.61}$$

The Hamiltonian function (total energy) of a harmonic oscillator may then be written as:

$$H(p,q) = p^2/2m + \alpha^2 q^2/2 \tag{10.62}$$

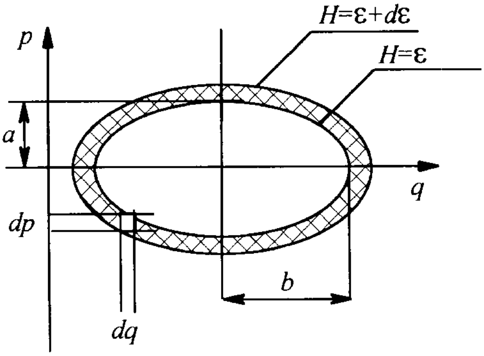

Fig. 10.1. 'Hypersurfaces' describing the states of a harmonic oscillator possessing energy ε

The angular frequency *of oscillations* performed by a harmonic oscillator is:

$$\omega = \left(\alpha^2 / m\right)^{1/2} \tag{10.63}$$

The 'hypersurface' containing representative points of all microstates of a one-dimensional *conservative* ($H = const = \varepsilon$) harmonic oscillator is an ellipse (Fig. 10.1) described by:

$$p^2/2m\varepsilon + \alpha^2 q^2/2\varepsilon = 1 \tag{10.64}$$

or:

$$p^2/2m\varepsilon + q^2 m\omega^2/2\varepsilon = 1 \tag{10.64a}$$

The half–axes of this *ellipse* are $a = (2m\varepsilon)^{1/2}$ and $b = (2\varepsilon/\alpha^2)^{1/2}$ (or $b = (2\varepsilon/m\omega^2)^{1/2}$). The area of this ellipse (volume of the phase space) contains an infinite number of possible microstates corresponding to the values of the Hamiltonian function from $H = 0$ to $H = \varepsilon$. This 'volume' is therefore a function of the *energy* of the oscillator:

$$\int p dq = \pi ab = 2\pi\varepsilon / \omega \tag{10.65}$$

A microstate of the harmonic oscillator with its energy lying between ε and (ε + $d\varepsilon$) is defined by specifying the *volume dpdq in the vicinity of the point pq belonging to the layer between two ellipses* (Fig. 10.1).

The area between the ellipses (Fig. 10.1) contains all possible states of the harmonic oscillator *with energy* ε *to* (ε + $d\varepsilon$). The *probability of a microstate* of such a harmonic oscillator is the ratio of *dpdq* to the area *of the energy layer.*

10.2.2
The phase space of an ideal gas

An *ideal gas* is a collection of *statistically independent particles moving freely within the volume of a vessel.* In an ideal gas, statistical independence results from large distances between molecules and thus the potential energy of *intermolecular interaction* approaches zero. However, the potential energy of a given particle in an ideal gas can be non-zero due to interaction with an external field (for example a gravitational field). Statistical independence of the molecules of an ideal gas implies that they have zero size, *i.e.* they are *material points.* Their particular property is that they are indistinguishable.

The total energy of ideal *gas* is the sum of the kinetic energies of the molecules (it is *additive* with respect to the kinetic energies of *molecules*):

$$H = \sum_{j}^{N} \varepsilon_j = \sum_{j=1}^{N} \frac{1}{2m_j} \sum_{1}^{3} p_i^2 \tag{10.66}$$

The μ*-space of an ideal* gas is 6-dimensional ($d\gamma = dxdydzdp_xdp_ydp_z$). *The energy of a molecule in an ideal gas is independent of the coordinates* and is a function of the *magnitude* of the momentum:

$$p = |p| = \left(p_x^2 + p_y^2 + p_z^2\right)^{1/2}; \qquad \varepsilon = p^2/2m. \tag{10.67}$$

In the phase space of momenta an energy layer of a molecule is a spherical layer of thickness $d\varepsilon$ and radius:

$$p = \sqrt{2m\varepsilon} \tag{10.68}$$

The volume of such a *spherical* layer is the product of surface by thickness:

$$d\gamma_p = Sdp = 4\pi p^2 dp \tag{10.69}$$

The elementary *volume* of an energy layer in the μ*-space* is:

$$d\gamma(\varepsilon) = \iiint_V dxdydz \int_{\varepsilon}^{\varepsilon+d\varepsilon} d\gamma_p = 4\pi V p^2 dp = 4\pi V m (2m\varepsilon)^{1/2} d\varepsilon \tag{10.70}$$

The energy density of the states of a molecule of an ideal gas is:

$$g(\varepsilon) = \frac{d\gamma(\varepsilon)}{d\varepsilon} = 4\pi V m \sqrt{2m\varepsilon} \tag{10.71}$$

The momenta of the *molecules* of an ideal gas are independent of the coordinates and therefore an element of a volume of the phase space of an ideal gas containing N molecules can be represented as a product of the elementary volumes of the p and q subspaces:

$$d\Gamma = \prod_{i=1}^{3N} dp_i dq_i = d\Gamma_p d\Gamma_q \tag{10.72}$$

The phase volume containing phase points representing systems with energy varying from zero to H can also be represented as a product of the corresponding volumes in the phase space of momenta and coordinates or *configurations* (each point in Γ_q-space represents the coordinates of all molecules, *i.e.* it is *a configuration*):

$$\Gamma(E) = \int d\Gamma = \iint_{0<H<E} d\Gamma_p d\Gamma_q = \Gamma_p \Gamma_q \tag{10.73}$$

The integration over coordinates (or configurations) yields the volume of a system to the N-th power:

$$\Gamma_q = \int \ldots \int_V \ldots \int dV_1 \ldots dV_N = V^N \tag{10.74}$$

The volume Γ_p in the space of momenta is the volume of a $3N$-dimensional *hypersphere* of radius $r = p = (2mE)^{1/2}$ described by $\sum p_i^2 = r^2$. For a hypersphere of a very large number of dimensions ($n >> 1$), the volume is given by the following *asymptotic* formula:

$$\ln V_n \cong \frac{n}{2} \ln \frac{2\pi e r^2}{n} \tag{10.75}$$

For $n = 3N$ and $r = p = (2mE)^{1/2}$, we get:

$$\Gamma(E) = V^N E^{\frac{3N}{2}} \left(\frac{4\pi m e}{3N} \right)^{\frac{3N}{2}} \tag{10.76}$$

The volume *of an energy layer* ($H = E$ *to* $E + dE$) is the difference of the volumes of two hyperspheres with the radii p and $p + dp$:

$$d\Gamma(E) = \frac{3N}{2} V^N E^{\frac{3N}{2}-1} \left(\frac{4\pi m e}{3N} \right)^{\frac{3N}{2}} dE \tag{10.77}$$

The energy density of states is:

$$g(E) = \frac{d\Gamma(E)}{dE} = \frac{3N}{2} V^N E^{\frac{3N}{2}-1} \left(\frac{4\pi m e}{3N} \right)^{\frac{3N}{2}} \tag{10.78}$$

The volume of phase-space and the energy density of states are very sharply rising functions of the number of particles and of the energy of a system.

10.3
Derivation of the canonical distribution

Let us consider a macroscopic system (system A) in a large heat reservoir (system B) with a very large (compared to system A) heat capacity. The state of system B remains unchanged irrespective of any changes occurring in system A. System B is therefore statistically independent of system A. When the heat reservoir is static (experiencing negligibly small fluctuations) the state of system A can be considered as independent of the state of the heat reservoir.

The Hamiltonian function of a system of statistically independent parts is the sum of the Hamiltonian functions of its components:

$$H(p,q) = H_A(p,q) + H_B(p,q) \tag{10.79}$$

The combined system ($A + B$) is considered as isolated, *i.e.* $H(p,q) = const$. When the systems A and B are in equilibrium *within themselves and between themselves* the combined system is also in equilibrium. The normalised probability densities ($\tilde{\rho} = N! h^N \rho$) of the quasi-independent systems A and B constitute together a system of a microcanonical ensemble and are multiplicative and their logarithms are additive:

$$\tilde{\rho}(H) = \tilde{\rho}_A(H_A) \tilde{\rho}_B(H_B) \tag{10.80}$$

$$\ln \tilde{\rho}(H) = \ln \tilde{\rho}_A(H_A) + \ln \tilde{\rho}_B(H_B) \tag{10.81}$$

Differentiating the logarithmic form (10.81) yields:

$$\frac{\partial \ln \tilde{\rho}}{\partial H} dH = \frac{\partial \ln \tilde{\rho}_A}{\partial H_A} dH_A + \frac{\partial \ln \tilde{\rho}_B}{\partial H_B} dH_B \tag{10.82}$$

The differential dH of the Hamiltonian function of the combined system (which is conservative) is zero. On the other hand it constitutes the differentials of the Hamiltonian functions of the systems A and B:

$$dH = dH_A + dH_B = 0 \tag{10.83}$$

and therefore:

$$dH_A = -dH_B \tag{10.84}$$

The condition $dH = 0$ implies that the sum in (10.82) is also zero because the derivative $\partial \ln \tilde{\rho} / \partial H$ can not be infinitely high. Taking into account (10.84) we get:

$$\left(\frac{\partial \ln \tilde{\rho}_A}{\partial H_A} - \frac{\partial \ln \tilde{\rho}_B}{\partial H_B} \right) dH_A = 0 \tag{10.85}$$

The differential dH_A being non-zero the condition (10.85) can be written as:

$$\frac{\partial \ln \tilde{\rho}_A}{\partial H_A} = \frac{\partial \ln \tilde{\rho}_B}{\partial H_B} = \beta \tag{10.86}$$

in which β *is a certain* parameter *common to both systems and independent of the microscopic variables*. The state of the system B (the heat reservoir) was defined as approximately unchangeable therefore the parameter β is a constant. We are not interested in the details of the state of the system B and will now consider the effects of the heat reservoir exclusively as represented by the parameter β. Equation (10.86) can be directly integrated with respect to the Hamiltonian function of the system A (the indices A and B now become redundant). This integration yields the *normalised probability density of the canonical distribution* as:

$$\tilde{\rho}(p, q) = A e^{\beta H(p,q)} \tag{10.87}$$

in which A is an *integration* constant. The probability of finding a representative point of a system of a canonical ensemble within *dp...dq* around the point *p,q* is then:

$$dW(p, q) = \rho d\Omega = A e^{\beta H(p,q)} \frac{dp \ldots dq}{N! h^N} \tag{10.88}$$

This is the canonical distribution, which provides for the derivation of statistical formulae for thermodynamic functions in systems of interacting molecules.

10.4

Free volume associated with vibrations

Translational motion and vibrations have many features in common. In fact, harmonic vibrations are translational motions in a force field characterised by a parabolic potential, *i.e.* under the action of a returning force linearly dependent on the deviation from the point of mechanical equilibrium:

$$u = fx^2/2 \tag{10.89}$$

in which x is the coordinate of a particle with respect to its position of equilibrium and f is the quasi-elastic constant related to the frequency of oscillations as:

$$\nu = (1/2\pi)\sqrt{f/m} \tag{10.90}$$

$$f = 4\pi^2\nu^2 m \tag{10.91}$$

Under these conditions the integration over the spatial coordinates in (3.32) results not in the volume but in the *free volume*. The molecules being independent, we are able to perform this integration for a single molecule (atom) considered as an isotropic three-dimensional oscillator:

$$v_f = \left[\int e^{-\frac{fx^2}{2kT}}dx\right]^3 \tag{10.92}$$

in which v_f is the *free volume* associated with such a vibrator. Let us define:

$$a = f/2kT = 2\pi^2 m\nu^2/kT\,; \quad u = kTax^2 \tag{10.93}$$

At *high temperatures*, the limits of integration in (10.92) can be set to be ±∞ and the free volume can be written as:

$$v_f = \left[\int_{-\infty}^{+\infty} e^{-ax^2}dx\right]^3 \tag{10.94}$$

The integral of $\exp(-ax^2)$ *from* $-\infty$ to $+\infty$ is *twice* the integral from 0 to $+\infty$. The latter is:

$$\int_0^{+\infty} e^{-ax^2}dx = \frac{1}{2\sqrt{a}}\Gamma(1/2) = \frac{\sqrt{\pi}}{2\sqrt{a}} \tag{10.95}$$

Therefore:

$$v_f = (\pi/a)^{\frac{3}{2}} = \left(kT/2\pi m\nu^2\right)^{\frac{3}{2}} \tag{10.96}$$

This expression provides for several important conclusions:

1. If we substitute, in the expression for the translational partition function, the volume v by the free volume (omitting the factor e as originating in migrations of molecules) we will get the high temperature approximation of the *vibrational partition function*:

$$z = \left(2\pi mkT/h^2\right)^{3/2} v\, e^{-\frac{\varepsilon_0}{kT}} = (kT/h\nu)^3 e^{-\frac{\varepsilon_0}{kT}} = z_{vib} e^{-\frac{\varepsilon_0}{kT}} \tag{10.97}$$

2. Extrapolating this result suggests that at low temperatures the free volume can also be determined from the equality $z_{trans}(v_f) = z_{vib}$ (10.97):

$$v_f = z_{vib}\left(2\pi mkT/h^2\right)^{-3/2} = \left[2\left(2\pi mkT/h^2\right)^{\frac{1}{2}}\sinh(\theta/2T)\right]^{-3} \tag{10.98}$$

3. We can also define the quasi-elastic constant f and potential energy *via* the free volume:

$$a = \pi/v_f^{2/3}\,; \qquad u = akTx^2 = \pi kT\,x^2/v_f^{2/3} \tag{10.99}$$

4. The *equation of state* of a collection of independent 3D oscillators can then be obtained as $p = -dU/dV$ where $U = N\pi kT < x^2 > v_f^{-2/3}$. We may assume the mean square deflection from the point of equilibrium to be independent of volume (to a first approximation). The equation of state then becomes:

$$p = \frac{2\pi}{3} NkT\left\langle x^2 \right\rangle v_f^{-5/3} \frac{dv_f}{dV} = \frac{2\pi}{3} NkT\left\langle x^2 \right\rangle v_f^{-2/3} \frac{d\ln v_f}{dV} \tag{10.100}$$

The ratio $<x^2>/v_f^{2/3}$ can be obtained from the condition of equi-partition of energy $<u> = 3kT/2$. According to (10.99):

$$\pi kT\left\langle x^2 \right\rangle / v_f^{2/3} = \frac{3}{2} kT \tag{10.101}$$

The equation of state of a collection of 3D vibrators is then:

$$p = NkT \frac{d\ln V_f}{dV} \tag{10.102}$$

These relationships illustrate the interconnections between different forms of motion.

10.5
Rotational contribution to the equilibrium constant of the ionisation of water

The moments of inertia of OH^- and H_3O^+ ions can be estimated from quantum mechanical calculations using the HyperChem® program. After optimising geometry, the vibrations are calculated, saving the results as a log. The moments of inertia obtained by MNDO calculations are shown in Table 10.1. The rotational partition function for OH– must be calculated using (2.78), whilst for H_2O and H_3O^+, because they have three moments of inertia, (2.79) must be used:

$$z = \frac{8\pi^2 IkT}{\sigma h^2} \quad (2.78); \quad z = \frac{\pi^{1/2}\left(8\pi^2 kT\right)^{3/2}\left(I_A I_B I_C\right)^{1/2}}{\sigma h^3} \quad (2.79)$$

The calculations at 300 K yield the results shown in the last column of Table 10.1. The contribution of the rotational partition function into the equilibrium constant of ionisation is therefore $\Delta S_r/R = \ln(z_{r+} z_{r-}/z^2_{r0}) = \ln 0.364 = -1.009$

Table 10.1. Moments of inertia (in 10^{-40} g cm^2), symmetry numbers, and rotational partition functions for molecules involved in the ionisation equilibrium

	I_x	I_y	I_z	σ	z_r (300 K)
H_2O	0.94	1.92	2.86	2	41
H_3O^+	2.31	2.31	4.62	3	59.5
OH^-	0	1.38	1.38	1	10.3

10.6
Forms of the law of mass action employing the Γ function approximation of the factorial

Some doubts might arise concerning the validity of the law of mass action (as well as of the Maxwell – Boltzmann distribution) for small systems on account of employing the Stirling approximation of the factorial function. In fact, there are no *mathematical* problems in approximating the factorial function of small numbers.

Employing (3.42), we can write the free energy of the reaction mixture (3.93) as:

$$-\frac{F}{kT} = m\ln q_+q_-V^2 + (N-2m)\ln q_0V - 2\ln m! - \ln(N-2m)! \tag{10.103}$$

Zero derivative of this function with respect to m will then define the law of mass action:

$$\ln\frac{q_+q_-}{q_0^2} - 2\frac{d\ln m!}{dm} + 2\frac{d\ln(N-2m)!}{d(N-2m)} = 0 \tag{10.104}$$

The factorial in the last term in (10.103), involving large numbers, may be approximated by the Stirling formula, which thus yields:

$$\ln\frac{q_+q_-}{q_0^2} - 2\frac{d\ln m!}{dm} + 2\ln(N-2m) = 0 \tag{10.105}$$

For rational positive arguments the logarithmic derivative of a factorial is defined employing the Γ-function (*e.g.* Jahnke E, Emde F (1933) Funktionentafeln. B.G. Teubner, Lepzig.). For $m > 5$ it quite closely approaches $\ln(m)$ (Fig. 10.2A). For $m = 0 - 5$ this function can be approximated by $\ln(n + 0.52)$ as shown in Fig. 10.2B. For a small number of particles involved in a chemical equilibrium the law of mass action may therefore be written in the following approximate form:

$$\ln\frac{q_+q_-}{q_0^2} - \ln\frac{(m+0.52)^2}{N^2} = 0 \tag{10.106}$$

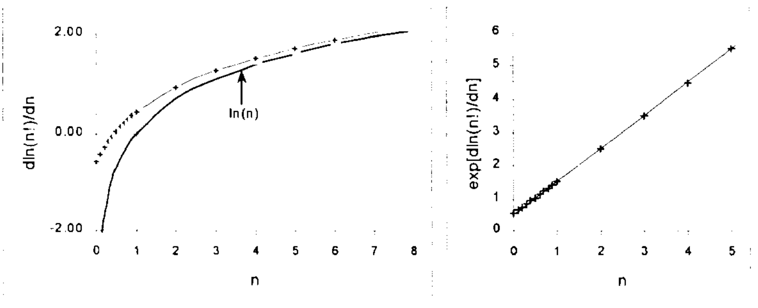

Fig. 10.2. The logarithmic derivative of the factorial (*crosses*) and the logarithmic function (*line*) in the region of small values of the argument (left-hand graph). The right-hand graph shows the approximation of the function exp($d$ln $n!/dn$) (*crosses*) by the linear relationship $y = n + 0.52$ (*line*).

With decreasing equilibrium constant and/or size of the system, the law of mass action thus predicts a gradual decrease in the number of ions to zero at finite values of the 'equilibrium constant' $q_+q_-/q_0^2 = 0.270/N^2$. In other words, this law of mass action predicts that in some systems reactions can be irreversible: for $KN^2 < 0.270$ the law of mass action does not have any solution.

10.7

Derivation of the van der Waals equation of state

Let us suppose that the average potential energy of a molecule beyond the restricted area corresponding to a direct contact of molecules has a small negative value inversely proportional to the volume of the system:

$$u = -a/NV \tag{10.126}$$

In other words the *density* of the energy of molecular interactions is assumed to be constant. Within this restricted volume, the potential energy is infinitely high and we may define the free volume per molecule as:

$$v_f = (V-b)/N \tag{10.127}$$

in which b represents the total restricted volume. The molecular partition function then becomes:

$$z = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \int_0^{v_f} e^{-\frac{u}{kT}} dv = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} v_f e^{-\frac{u}{kT}} \tag{10.128}$$

Substituting v_f and u according to their definitions, we get:

$$\ln z = \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} + \ln(V-b) + \frac{a}{VNkT} \tag{10.129}$$

For a gas of spherical particles (without internal and rotational degrees of freedom) the free energy can be written as:

$$F = -NkT\left[\frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} + \ln(V-b)\right] - \frac{a}{V} \tag{10.130}$$

The pressure of such a gas containing N molecules in volume V is:

$$p = NkT\left(\frac{\partial \ln z}{\partial V}\right)_T = \frac{NkT}{V-b} - \frac{a}{V^2} \tag{10.131}$$

This is one of the forms of the van der Waals equation, which can easily be transformed into:

$$\left(p + \frac{a}{V^2}\right)(V-b) = NRT \tag{10.132}$$

We see that the condition of small density ($V \gg b$) was *not* imposed on this system, therefore the van der Waals equation can be applied to dense gases and liquids.

10.8
Exchange energy

As in many examples considered in the preceding Chapters, a hint as to how to transform an equation is given when we express the potential energy as a function of one variable (*e.g.* the mole fraction of the component A):

$$U=\frac{Nc}{2}\left[x_A^2\left(\varphi_{AA}+\varphi_{BB}-2\varphi_{AB}\right)+x_A\left(2\varphi_{AB}-2\varphi_{BB}\right)+\varphi_{BB}\right] \tag{10.133}$$

The term $\Delta\varphi=2\varphi_{AB}-\varphi_{AA}-\varphi_{BB}$ has a clear physical significance and therefore we can express the potential of hetero-interaction, φ_{AB}, in terms of this quantity. The energy of molecular interactions then becomes:

$$U=\frac{Nc}{2}\left[-x_A^2\Delta\varphi+x_A\left(\Delta\varphi-\varphi_{BB}+2\varphi_{AA}\right)+\varphi_{BB}\right. \tag{10.134}$$

Returning to the potential energy as a function of two variables, x_A and x_B, we get a useful formula separating the additive contributions of homo-molecular interactions:

$$U=\frac{Nc}{2}\left(x_Ax_B\Delta\varphi+x_A\varphi_{AA}+x_B\varphi_{BB}\right) \tag{10.135}$$

This form provides a convenient representation of non-ideal systems as perturbed ideal systems.

10.9
Activity coefficients derived from the non-ideality resulting from triple interactions

The equation of the law of mass action (7.47) can be written as:

$$\frac{3}{2}\left[x_A^2+\left(1-x_B\right)^2\right]\frac{\Delta^{(3)}}{NkT}+\left(x_A-x_B+1\right)\frac{\Delta^{(2)}}{NkT}-\frac{\Delta^{(0)}+\Delta^{(2)}+\Delta^{(3)}}{NkT}-\ln\frac{x_B}{x_A}=0 \tag{10.139}$$

Expanding $(1-x_B)^2$ and combining the terms with identical powers of x results in the polynomial part of (10.139) becoming:

$$x_A^2\frac{1.5\Delta^{(3)}}{NkT}+x_A\frac{\Delta^{(2)}+1.5\Delta^{(3)}}{NkT}+x_B^2\frac{1.5\Delta^{(3)}}{NkT}-x_B\frac{\Delta^{(2)}+1.5\Delta^{(3)}}{NkT}-\frac{\Delta^{(0)}+\Delta^{(3)}}{NkT} \tag{10.140}$$

When $\Delta^{(3)}=0$, the polynomial part of (10.139) transforms into an expression symmetrical with respect to $\ln(x_B/x_A)$:

$$x_A\frac{\Delta^{(2)}}{NkT}-x_B\frac{\Delta^{(2)}}{NkT}-\frac{\Delta^{(0)}}{NkT}-\ln x_B+\ln x_A=0 \tag{10.141}$$

which, for small $\Delta^{(2)} << NkT$, can be transformed into the law of mass action with respect to activities:

$$-\frac{\Delta^{(0)}}{NkT}-\ln\left[x_B\left(1+x_B\frac{\Delta^{(2)}}{NkT}\right)\right]+\ln\left[x_A\left(1+x_A\frac{\Delta^{(2)}}{NkT}\right)\right]=0 \tag{10.142}$$

In the case of non-zero $\Delta^{(3)}$, the activity coefficients become asymmetric with respect to reactant and product:

$$-\frac{\Delta^{(0)}}{NkT}-\ln\left[x_B\left(1+x_B\frac{\Delta^{(2)}}{NkT}-x_B^2\frac{1.5\Delta^{(3)}}{NkT}\right)\right]+\ln\left[x_A\left(1+x_A\frac{\Delta^{(2)}}{NkT}+x_A^2\frac{1.5\Delta^{(3)}}{NkT}\right)\right]=0 \tag{10.143}$$

This shows that activities determined separately for reactant and product might be valid for the linear term alone.

10.10

The law of mass action for a binary equilibrium in a system with non-additive volume and lattice energy.

According to the model of molecular interactions represented as arising from the dependence of the partition function on surroundings, the lattice energies u and the molecular volumes v in a binary mixture can be separated into four classes corresponding to homo-molecular and hetero-molecular clusters:

$$U=n_Au_{AAA}+n_Bu_{BBB}+n_Ax_B\Delta u_{ex} \tag{10.144}$$

$$V=n_Av_{AAA}+n_Bv_{BBB}+n_Ax_B\Delta v_{ex} \tag{10.145}$$

in which:

$$\Delta u_{ex}=u_{AAA}-u_{BAB}+u_{BBB}-u_{ABA} \tag{10.146}$$

$$\Delta v_{ex}=v_{AAA}-v_{BAB}+v_{BBB}-v_{ABA} \tag{10.147}$$

We can combine two types of non-ideality *viz.* those arising from free volume and lattice energy. Free volume and lattice energy *are not independent variables* but are interrelated *via* an equation of state. According to a simplified version of the Eyring equation of state, free volume is proportional to the third power of the reduced temperature and for a binary mixture it can be written as:

$$V_f=V\tau^3;\qquad \tau=\frac{2N\kappa kT}{n_Au_{AAA}+n_Bu_{BBB}+n_Ax_B\Delta u_{ex}} \tag{10.148}$$

in which V is defined by (10.145).

The free energy of a binary system in the liquid state can be written as:

$$-\frac{F}{kT}=n_A\left[\ln z_A-\frac{\varepsilon_A+u_{AAA}}{kT}-\ln\frac{n_A}{V_f}\right]+n_B\left[\ln z_B-\frac{\varepsilon_B+u_{BBB}}{kT}-\ln\frac{n_B}{V_f}\right]-n_Ax_B\frac{\Delta u_{ex}}{kT} \tag{10.149}$$

in which V_f is a function of composition as defined above. It must be mentioned that the energies ε_A, ε_B are very large quantities comprising the total potential energy of an isolated molecule. Their difference (constituting the major part of the standard internal energy of reaction) is considerably smaller but still might reach the values of tens and hundreds of kilocalories per mole. The lattice energies u_{AAA} and u_{BBB}, as well as their differences Δu, are much smaller – the latter reaching perhaps the level of tens of kilocalories per mole. Much smaller values can be expected for the exchange energies reflecting the difference of lattice energy of molecules in (slightly) different molecular environments. It is only in special cases such as spin crossover that the exchange energy is comparable to the difference in potential energies of products and reactants. What is more important, the exchange energy in spin crossover is higher than $kT_{1/2}$ that results in the steep spin crossover.

The law of mass action obtained from (10.149) can be written with respect to the numbers of molecules of the species B as:

$$\ln\frac{n_B}{N-n_B}=\ln\frac{z_B}{z_A}-\frac{\Delta\varepsilon+\Delta u}{kT}+N\frac{d\ln V_f}{dn_B}-\left(1-2x_B\right)\frac{\Delta u_{ex}}{kT} \tag{10.150}$$

The derivative of free volume with respect to the number of molecules involves the balances and exchange parameters:

$$\frac{d\ln V_f}{dn_B}=\frac{\Delta v+(1-2x_B)\Delta v_{ex}}{V}-3\frac{\Delta u+(1-2x_B)\Delta u_{ex}}{U} \tag{10.151}$$

The balances, Δv and Δu are due to the reaction seemly occurring in completely homomolecular surroundings:

$$\Delta u=u_{BBB}-u_{AAA};\qquad \Delta v=v_{BBB}-v_{AAA} \tag{10.152}$$

The exchange parameters, on the other hand, characterise the difference of volume and lattice energy (per molecule) in homo- and hetero-molecular surroundings ((10.146) and (10.147)).

The law of mass action for a binary reaction without a solvent and written explicitly with respect to molar parameters illustrates this situation:

$$\begin{aligned}\ln\frac{x}{1-x}&=-\frac{\Delta E+\Delta U}{RT}+\frac{\Delta S}{R}-\left(1-2x\right)\frac{\Delta U_{ex}}{RT}\\&+\frac{\Delta V+\left(1-2x\right)\Delta V_{ex}}{V_A+x\Delta V+x\left(1-x\right)\Delta V_{ex}}-3\frac{\Delta U+\left(1-2x\right)\Delta U_{ex}}{U_A+x\Delta U+x\left(1-x\right)\Delta U_{ex}}\end{aligned} \tag{10.153}$$

in which the parameters ΔS and ΔE are determined exclusively by the molecular properties of products and reactants.

There are seven parameters in total, determining the shape of the transition curves obeying this law of mass action, namely ΔS, ΔE, ΔU, ΔU_{ex}, ΔV, ΔV_{ex} and U_A. The volume V_A can be cancelled out, whereas the absolute value of U_A is important because ΔU_{ex} enters two different terms in (10.153). Simulations following (10.153) show that the introduction of exchange energy into the expression for free volume has increased the sensitivity of van't Hoff plots to the effects of non-ideality. For example the critical value of ΔU_{ex} above which phase separation can be observed is considerably lower than that obtained for the law of mass action (7.50). For $U_A = 5RT$ the vertical tangent to the transition curve is achieved at $\Delta U_{ex} = 1.28RT$ *vs.* $2RT$ obtained for (7.50).

Small non-zero balances ΔU and ΔV do not produce of themselves considerable curvature of the van't Hoff plots when ΔU_{ex} is zero. However they increase/decrease significantly the curvature caused by a non-zero ΔU_{ex}.

The effects of non-zero exchange volume are formally similar to those of exchange energy: it produces varying curvature of van't Hoff plots that intersect at the transition point. Its effect on the shape of a van't Hoff plot when ΔU_{ex} is also non-zero and is more pronounced than that arising from the balance of volume. Non-zero balances make the van't Hoff plots curvilinear (or increase the curvature caused by non-zero exchange parameters) and shift them horizontally without an intersection. Non-zero exchange parameters, on the other hand, besides making van't Hoff plots curvilinear, cause them to intersect at the transition point

10.11

Physico–chemical constants and units of energy

Table 10.2. Physico-chemical constants

Velocity of light	$c = 2.99793\times10^{10}$ cm sec^{-1}
Mass of electron	$m_e = 9.1083\times10^{-28}$ g
Mass of proton	$m_p = 1.6723\times10^{-24}$ g
Charge of electron	$e = 4.80286\times10^{-10}$ CGSE
Planck constant	$\hbar = 1.05443\times10^{-27}$ erg sec
Planck constant	$h = 6.625\times10^{-27}$ erg sec
Boltzmann constant	$k = 1.38044\times10^{-16}$ erg K^{-1}
Gas constant	$R = 1.98$ cal mol^{-1}K^{-1} = 8.31 J mol^{-1}K^{-1}
Avogadro number	$N_L = 6.0249\times10^{23}$ atom mol^{-1}

Table 10.3. Energy units.

	cm^{-1}	erg	eV	kT(1K)	MHz
$N_L hc\omega$(1cm^{-1}) = 2.86 cal mol^{-1}				1.43kT equals 1 cm^{-1} ($hc\omega$)	
cm^{-1}	1	1.9862×10^{-16}	1.2398×10^{-4}	1.4388	29.979×10^{3}
erg	5.0348×10^{15}	1	6.242×10^{11}	7.244×10^{15}	1.5094×10^{20}
eV	8066.0	1.602×10^{-12}	1.	11605	2.4181×10^{8}
kT(1K)	0.69504	1.3805×10^{-16}	8.6169×10^{-5}	1	2.0837×10^{4}
MHz	3.3356×10^{-5}	6.6252×10^{-21}	4.1355×10^{-9}	4.7993×10^{-5}	1
One MHz ($h\nu$) equals 6.6252×10^{-21} erg			1cal = 4.184 J = 4.184×10^{7} erg		

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