# A Generalized Statement of the Law of Mass Action

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The original statement of the law of mass action is associated with the names of the two Norwegians, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900). Both were professors at the University of Christiana (now Oslo), where the former taught mechanics and the latter taught chemistry. They were not only scientific collaborators, but also twice brothers-in-law. The first family association occurred when Guldberg married Bodil Mathea Riddervold and Waage married her sister, Johanne Christiane Tandberg Riddervold. After Johanne died in 1869, they became brothers-in-law a second time when Waage married Guldberg's sister, Mathilde Sofie Guldberg (*1*).

Guldberg and Waage considered a reversible, elementary chemical reaction involving the chemical species [1]–[4],

$$\nu_1[1] + \nu_2[2] \rightleftharpoons \nu_3[3] + \nu_4[4] \qquad (1)$$
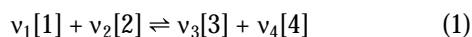
with stoichiometric coefficients ν_1–ν_4. In their law of mass action, they asserted that the net rate of reaction, r, is given by

$$r = k_f c_1^{\nu_1} c_2^{\nu_2} - k_r c_3^{\nu_3} c_4^{\nu_4} \qquad (2)$$

where c_i ($i = 1, 2, \ldots$) are the molar concentrations of the species and k_f and k_r are the rate constants (specific rates) for reaction in the forward and reverse directions, respectively. The basis for this concept appears to have occurred to Waage in 1860 while he was a guest in the Heidelberg laboratory of R. Bunsen (1811–1889). Both Guldberg and Waage seem to have been unaware, however, of the earlier work of R. Wilhelmy (1812–1864), who in 1850 used essentially the same law to analyze his data on the acid-catalyzed rate of inversion of sucrose (*2*). On the basis of this experiment, Wilhelmy is today recognized as the father of chemical kinetics.

Nonetheless, it was the careful experiments by Waage and their interpretation by Guldberg, who was trained as a mathematician, which led to the final acceptance of eq 2 (*1*). Perhaps in an attempt to get into print while avoiding controversy and rejection, Guldberg and Waage first published the law of mass action in 1864 in the Norwegian language using the *Proceedings of the Christiana Academy of Science and Letters*. This report was ignored, so in 1867 they tried again, this time writing in French in an official publication of the University of Christiana. The second attempt met the same fate as the first until J. Thomsen (1862–1909) took note of the Guldberg and Waage law (*3*), and W. Ostwald (1853–1932) discussed it in more detail (*4*). Guldberg and Waage were encouraged by this, and they published in German in 1879 their landmark paper restating eq 2 and relating it to reaction kinetics on a molecular scale (*5*).

All 19th century theoretical scientists were well versed in Newtonian mechanics, so it was probably Guldberg who introduced the distinction between the *primary forces* involved in the transfer of atoms between molecules and the *secondary forces* involved in their interaction with the environment. More than a century later, we can still recognize these forces as valence interactions and solvent interactions, respectively.

Solvent effects on chemical reactions have been widely studied experimentally and most have been analyzed on a case-by-case basis using transition state theory (*6*). Since the famous papers by Onsager (*7, 8*) on non-equilibrium thermodynamics, however, there has also been a parallel effort to understand solvent effects in terms of the generalized forces and fluxes, which appear in that theory (*9*). Within the last decade, this program appears to have come to fruition (*10*), and the results now permit chemical reaction kinetics and solvent effects to be taught in principle from a single generalized version of the law of mass action.

Generalized Law of Mass Action

For fluids behaving non-ideally from a thermodynamic point of view, Haase (*10*) has suggested that the net rate of the elementary reaction shown in eq 1 can be written

$$r = \lambda[\kappa' a_1^{\nu_1} a_2^{\nu_2} - \kappa'' a_3^{\nu_3} a_4^{\nu_4}] \qquad (3)$$

where a_i ($i = 1, 2, \ldots$) are the thermodynamic activities of the reacting species, λ is the reciprocal of the activity coefficient of the transition state, and κ' and κ'' are rate coefficients for reaction in the forward and reverse directions, respectively. For gases, κ' and κ'' are functions of temperature only, whereas for liquids both depend upon temperature and pressure. The quantity λ is a function of temperature, pressure, and composition. The thermodynamic activity of the ith reacting species is

$$a_i = y_i(c_i/\bar{c}) \qquad (4)$$

where c_i is the molar concentration, $\bar{c}$ is the standard state concentration (ordinarily a 1 M ideal solution), and y_i is the activity coefficient on the molar-concentration scale. Both a_i and y_i are conveniently treated as dimensionless quantities.

Equation 3 can be shown to be consistent with transition state theory. Consider eq 1 for the moment only in the forward direction where reactants [1] and [2] pass through the transition state [∗] on their way to products [3] and [4]:

$$\nu_1[1] + \nu_2[2] \rightarrow [∗] \rightarrow \nu_3[3] + \nu_4[4] \qquad (5)$$
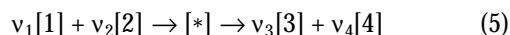
In transition state theory, reactants [1] and [2] are considered to be in dynamic equilibrium with [∗]. Their thermodynamic activities are related by

$$K' = \frac{a^*}{a_1^{\nu_1} a_2^{\nu_2}} \qquad (6)$$

where a^* is the activity of $[*]$ and K' is the equilibrium constant for the formation of $[*]$ from $[1]$ and $[2]$. Using eq 4 to evaluate a^*, eq 6 can be rewritten as

$$K' = \frac{y^* \left(c^*/\bar{c} \right)}{a_1^{\nu_1} a_2^{\nu_2}} \qquad (7)$$

where y^* and c^* are the activity coefficient and concentration of $[*]$, respectively. We can solve eq 7 to obtain

$$c^* = \frac{K' \bar{c}}{y^*} a_1^{\nu_1} a_2^{\nu_2} \qquad (8)$$

In the forward direction, the reaction in eq 5 proceeds at the rate

$$r' = \nu' c^* \qquad (9)$$

where ν' is the specific rate (s^{-1}) at which $[*]$ decays into products. Ordinarily, ν' is set equal to $k_B T/h$, where k_B is Boltzmann's constant, T is the absolute temperature, and h is Planck's constant. Upon substitution of eq 8 into eq 9, there results

$$r' = \frac{\kappa'}{y^*} a_1^{\nu_1} a_2^{\nu_2} \qquad (10)$$

where κ' is defined by

$$\kappa' = \nu' K' \bar{c} \qquad (11)$$

By the principle of detailed balance (11), the reaction in eq 5 must proceed in the reverse direction via the same transition state $[*]$ that it traversed in the forward direction. An analysis that is the analog of eqs 6–11 can be applied to eq 5 in the reverse direction. The result is

$$r'' = \frac{\kappa''}{y^*} a_3^{\nu_3} a_4^{\nu_4} \qquad (12)$$

where r'' is the reverse reaction rate,

$$\kappa'' = \nu'' K'' \bar{c} \qquad (13)$$

and

$$K'' = \frac{a^*}{a_3^{\nu_3} a_4^{\nu_4}} \qquad (14)$$

Since the net reaction rate is $r = r' - r''$, eqs 10 and 12 can be combined to obtain eq 3 where the definition of λ is (10)

$$\lambda = 1/y^* \qquad (15)$$

Note that by virtue of eqs 11 and 13, both κ' and κ'' have the dimension mol L^{-1} s^{-1}, as does r, since in eq 3, λ and the activities, a_i ($i = 1, 2, \dots$), are all dimensionless.

The net rate of reaction, r, is directly measured by the time rate of change of the "extent of reaction", ξ. If the initial concentration of reacting species is $c_i(0)$, then the concentration, c_i, at any time t can be expressed in terms of ξ by

$$c_i = c_i(0) \pm \nu_i \xi \qquad (16)$$

where the upper sign applies to products and the lower sign to reactants. Equation 16 implies that $\xi = 0$ when the time $t = 0$. The rate of reaction is then (12)

$$\frac{d\xi}{dt} = -\frac{1}{\nu_1}\frac{dc_1}{dt} = -\frac{1}{\nu_2}\frac{dc_2}{dt} = \frac{1}{\nu_3}\frac{dc_3}{dt} = \frac{1}{\nu_4}\frac{dc_4}{dt} = r \qquad (17)$$

This equation has the advantage that r is defined independently of whichever of the concentrations, c_i, is used to monitor the rate.

Examples

We now demonstrate that some of the principle results of chemical kinetics can be derived starting from eq 3.

Example 1: The Kinetic Law for Ideal Gas Reactions and for Reactions in Dilute Ideal Solution

In both of these cases, $\lambda = 1 = y_i$ and $a_i = c_i/\bar{c}$ for all i. Equation 3 becomes

$$r = (\kappa'/\bar{c}^{\nu_1+\nu_2}) c_1^{\nu_1} c_2^{\nu_2} - (\kappa''/\bar{c}^{\nu_3+\nu_4}) c_3^{\nu_3} c_4^{\nu_4} \qquad (18)$$

Equation 18 is identical to the Guldberg–Waage statement of the law of mass action (eq 2), if we identify

$$k_f = \kappa'/\bar{c}^{\nu_1+\nu_2} \qquad (19)$$

and

$$k_r = \kappa''/\bar{c}^{\nu_3+\nu_4} \qquad (20)$$

In the forward directions, the overall molecularity is $\nu_1 + \nu_2$, while in the reverse direction it is $\nu_3 + \nu_4$. Equations 19 and 20 conform to the ordinary convention that the rate coefficient for a reaction with overall molecularity n should have the units $(L\ mol^{-1})^{n-1} s^{-1}$.

Example 2: The Relation between Rate Constants and the Equilibrium Constant

At equilibrium, $r = 0$, and each thermodynamic activity, a_i, assumes its equilibrium value, a_i^e. Equation 3 implies

$$\frac{\kappa'}{\kappa''} = \frac{\left(a_3^e\right)^{\nu_3}\left(a_4^e\right)^{\nu_4}}{\left(a_1^e\right)^{\nu_1}\left(a_2^e\right)^{\nu_2}} \equiv K \qquad (21)$$

where K is the equilibrium constant for the reaction. By contrast, had we set $r = 0$ in eq 2, we would have found K to be determined by the equilibrium concentrations, c_i^e. Although such a result is adequate in the case of ideal gases and dilute ideal solutions, it is inapplicable in general. Equation 21 further illustrates the meaning of κ' and κ'' and confirms that both must have the same dimensions, since K is dimensionless.

Example 3: Solvent Effects on Reaction Rates

Let us assume that eq 1 is irreversible, so that we can set $\kappa'' = 0$ in eq 3; then by use of eqs 4 and 15, eq 3 becomes

$$r = \frac{\left(y_1\right)^{\nu_1}\left(y_2\right)^{\nu_2}}{y^*} \kappa'\left(\bar{c}\right)^{-(\nu_1+\nu_2)} c_1^{\nu_1} c_2^{\nu_2} \qquad (22)$$

Since the observed forward rate is $k_{obs} c_1^{\nu_1} c_2^{\nu_2}$, eq 22 implies that

$$k_{obs} = \kappa'\left(\bar{c}\right)^{-(\nu_1+\nu_2)} \frac{\left(y_1\right)^{\nu_1}\left(y_2\right)^{\nu_2}}{y^*} \qquad (23)$$

which is a standard formula for estimating solvent effects.

In particular, consider the case of a reaction between ionic species in the presence of an inert, strong electrolyte.

The ionic strength, I, of the solution is defined by

$$I = \frac{1}{2}\sum_j c_j Z_j^2 \tag{24}$$

where Z_j is the valence of the jth ionic species, and the sum is computed over all values of j. According to Debye and Hückel, in the case of a dilute solution,

$$\ln y_j = -B Z_j^2 \sqrt{I} \tag{25}$$

where

$$B = \left(\frac{2\pi N e^6}{1000(\varepsilon k_B T)^3}\right)^{1/2} \tag{26}$$

and T is the absolute temperature, N is Avogadro's number, e is the electron charge, and ε is the solvent dielectric constant. The quantities in eq 26 are in the cgs units preferred for theoretical work, where e has the units esu (erg cm)$^{1/2}$, k_B has the units erg K^{-1}, N has the units mol^{-1}, 1000 has the implied units of cm^3 L^{-1}, and ε is dimensionless. The resulting units of B are then L$^{1/2}$ mol$^{-1/2}$ (*13*).

Most reactions to which eq 23 can be applied are bimolecular, such as the electron transfer reaction

$$Fe^{2+} + Hg^{2+} \rightarrow Fe^{3+} + Hg^+ \tag{27}$$
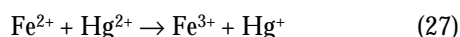
Since in a bimolecular reaction $\nu_1 = \nu_2 = 1$, the reacting ions, $[1]^{Z_1}$ and $[2]^{Z_2}$, form a transition-state species $[*]^{Z_1+Z_2}$, having valence $Z_1 + Z_2$. According to eq 25, the activity coefficient of $[*]^{Z_1+Z_2}$ is given by

$$\ln y^* = -B(Z_1 + Z_2)^2 \sqrt{I} \tag{28}$$

while the activity coefficients of the reacting ions are

$$\ln y_1 = -B Z_1^2 \sqrt{I} \tag{29}$$

and

$$\ln y_2 = -B Z_2^2 \sqrt{I} \tag{30}$$

respectively. Setting $\nu_1 = \nu_2 = 1$ and using eqs 28–30, the logarithm of eq 23 becomes

$$\ln k_{obs} = \ln k_f + 2 Z_1 Z_2 B \sqrt{I} \tag{31}$$

where $k_f = \kappa'/(\bar{c})^2$ is the specific rate when $I = 0$. Equation 31 is the Brönsted–Bjerrum result for the "*primary* kinetic salt effect", which is discussed in many elementary physical chemistry textbooks (*14–20*).

In the primary salt effect, ions from the inert electrolyte form a charged atmosphere (Debye–Hückel space charge) around each of the reacting ions $[1]^{Z_1}$ and $[2]^{Z_2}$ and their transition state $[*]^{Z_1+Z_2}$. The net charge of the atmosphere is equal and opposite to that of the charge of the central ion. The electrostatic energy stored in the atmosphere makes the ions behave as non-ideal solutes and causes the activity coefficients to depend upon I, as shown in eq 25. The atmosphere is stable because the net current of inert ions moving toward a central ion owing to their Coulomb interactions is balanced by the net current of inert ions moving away from a central ion by Brownian motion. The range of the mutual electrostatic interaction

between the reacting ions $[1]^{Z_1}$ and $[2]^{Z_2}$ (surrounded by their atmospheres) depends upon $I^{-1/2}$, which decreases with increasing concentration of the inert electrolyte. Specifically, when Z_1 and Z_2 have the same sign, the ion atmospheres reduce the *repulsive* electrostatic force acting between $[1]^{Z_1}$ and $[2]^{Z_2}$, which accelerates the rate of their mutual reaction; hence, as predicted by eq 31, $\ln k_{obs}$ increases with increasing ionic strength. By contrast, when Z_1 and Z_2 have opposite signs, the atmospheres reduce the *attractive* electrostatic force between $[1]^{Z_1}$ and $[2]^{Z_2}$, which according to eq 31 decelerates their mutual rate of reaction, so that $\ln k_{obs}$ decreases with increasing ionic strength.

There is, incidentally, a related *secondary* salt effect, which occurs in the case of a reaction catalyzed by a weak acid or a weak base. In this case, an increase in the concentration of an inert electrolyte enhances the ionization of the acid (or base) and increases the concentration of the active catalyst species, H$^+$ (or OH$^-$). This secondary salt effect is not kinetic in nature but depends instead upon the effect of the ion atmosphere on an ionic equilibrium (*21*).

Example 4: Reaction Kinetics and Non-Equilibrium Thermodynamics

According to non-equilibrium thermodynamics, a "flux" is the net rate of some process and a "driving force" is the disturbance that produces it. Examples of fluxes and their respective forces are electric current density and electric field (Ohm's law); diffusive mass flux and gradient of chemical potential (Fick's law); volume flux of a liquid and pressure gradient (Poiseuille equation) (*22*). Close to equilibrium, a flux, J, is found to be linearly dependent upon its conjugate force, X; hence, one writes $J = LX$, where L is termed the "Onsager coefficient" (*22*). Indeed, when X is zero, J is also zero, and the process is at equilibrium.

Slightly away from equilibrium, however, molecules in forward motion still are nearly balanced by molecules in reverse motion (*11*), and this is the basis for extending thermodynamics to non-equilibrium phenomena. In the case of chemical reactions, the flux may be chosen as the net reaction rate, r. We can use eq 3 to show that the driving force is the reaction "affinity", A. Introduced by DeDonder, the affinity is just the negative of the instantaneous Gibbs free energy, ΔG, of reaction.

To demonstrate the dependence of r upon A, we first factor $\kappa' a_1^{\nu_1} a_2^{\nu_2}$ from eq 3 and write

$$r = \lambda \kappa' a_1^{\nu_1} a_2^{\nu_2}\left[1 - \frac{\kappa''}{\kappa'} \cdot \frac{a_3^{\nu_3} a_4^{\nu_4}}{a_1^{\nu_1} a_2^{\nu_2}}\right] \tag{32}$$

The molar chemical potential, μ_i, of the ith species is

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{33}$$

where R is the gas law constant, and μ_i° is the chemical potential of that species in its standard state. We define as usual

$$\Delta G = \nu_3\mu_3 + \nu_4\mu_4 - \nu_1\mu_1 - \nu_2\mu_2 \tag{34}$$

and

$$\Delta G^\circ = \nu_3\mu_3^\circ + \nu_4\mu_4^\circ - \nu_1\mu_1^\circ - \nu_2\mu_2^\circ \tag{35}$$

Combining eqs 33–35, we obtain the familiar result

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_3^{\nu_3} a_4^{\nu_4}}{a_1^{\nu_1} a_2^{\nu_2}} \qquad (36)$$

In eq 36, the argument of the log is the reaction function

$$Q = \frac{a_3^{\nu_3} a_4^{\nu_4}}{a_1^{\nu_1} a_2^{\nu_2}} \qquad (37)$$

Substituting eqs 21 and 37 into eq 32, we obtain

$$r = \lambda \kappa' a_1^{\nu_1} a_2^{\nu_2}\left[1 - \frac{Q}{K}\right] \qquad (38)$$

which is a result obtained by Castellan (23).

At equilibrium, where each $a_i = a_i^e$ and $\Delta G = 0$, we obtain from eqs 21 and 36 another familiar result,

$$\Delta G^\circ = -RT \ln K \qquad (39)$$

Using eqs 37 and 39, eq 36 can be rewritten

$$\Delta G = RT \ln(Q/K) \qquad (40)$$

Upon substitution of eq 40 into eq 38, we obtain the rate law

$$r = \lambda \kappa' a_1^{\nu_1} a_2^{\nu_2}[1 - \exp(-A/RT)] \qquad (41)$$

where we have set $A = -\Delta G$. Equation 41 demonstrates that the driving force for a reaction is the affinity; indeed, when $A = 0$, the net reaction rate, $r = 0$. When the reaction is so close to equilibrium that $A/RT << 1$, we can then approximate the exponential by $e^x = 1 - x$ and replace λ, a_1, and a_2 by their equilibrium values λ^e, a_1^e, and a_2^e, respectively, so that eq 41 takes the form

$$r = \frac{\lambda^e \kappa' \left(a_1^e\right)^{\nu_2}\left(a_2^e\right)^{\nu_2}}{RT} A \qquad (42)$$

Equation 42 confirms the premise of non-equilibrium thermodynamics that near equilibrium, the flux, r, should depend linearly upon its conjugate force, A. We can identify in eq 42 the Onsager coefficient

$$L = \frac{\lambda^e \kappa' \left(a_1^e\right)^{\nu_2}\left(a_2^e\right)^{\nu_2}}{RT} \qquad (43)$$

where $\lambda^e \kappa' (a_1^e)^{\nu_1}(a_2^e)^{\nu_2}$ is the rate of the forward reaction at equilibrium.

Example 5: Relaxation Time

Any small disturbance of a reaction from chemical equilibrium decays by a first-order rate law. Let ξ_e be the equilibrium value of the reaction variable and expand A in a Taylor series about $\xi = \xi_e$. To first order, the result is

$$A(\xi) = A(\xi_e) + \left(\frac{\partial A}{\partial \xi}\right)_e (\xi - \xi_e) \qquad (44)$$

After noting that $A(\xi_e) = 0$, if we substitute eq 44 into the right-hand side of eq 42 and $r = d\xi/dt$ into the left, we obtain

$$\frac{d\xi}{dt} = \frac{\lambda^e \kappa' a_1^e a_2^e}{RT}\left(\frac{\partial A}{\partial \xi}\right)_e (\xi - \xi_e) \qquad (45)$$

If we compare eq 45 with the first-order equation

$$\frac{d\xi}{dt} = -\frac{(\xi - \xi_e)}{\tau} \qquad (46)$$

defining the relaxation time, τ, we obtain

$$\frac{1}{\tau} = \frac{\lambda^e \kappa' \left(a_1^e\right)^{\nu_1}\left(a_2^e\right)^{\nu_2}}{RT}\left(\frac{\partial \Delta G}{\partial \xi}\right)_e \qquad (47)$$

where we have replaced A by $-\Delta G$.

We can illustrate the usefulness of eq 47 by considering the case of a dilute ideal solution and a reaction with $\nu_1 = \nu_2 = \nu_3 = \nu_4 = 1$. In this case, $a_i = (c_i(0) \pm \nu_i \xi)/\bar{c}$, so that eq 36 can be expanded to read

$$\Delta G = \Delta G^\circ + RT[\ln(c_3(0) + \xi) + \ln(c_4(0) + \xi) - \\ \ln(c_1(0) - \xi) - \ln(c_2(0) - \xi)] \qquad (48)$$

Term-by-term differentiation of eq 48 leads to

$$\left(\frac{\partial \Delta G}{\partial \xi}\right)_e = RT\left[\frac{1}{c_3^e} + \frac{1}{c_4^e} + \frac{1}{c_1^e} + \frac{1}{c_2^e}\right] \qquad (49)$$

where we have let $c_i^e = c_i(0) \pm \nu_i \xi_e$. For a dilute ideal solution at reaction equilibrium, $a_i^e = c_i^e/\bar{c}$ and r = 0. Equation 3 then implies for the stoichiometry under consideration,

$$\kappa' c_1^e c_2^e = \kappa'' c_3^e c_4^e \qquad (50)$$

We can substitute eqs 49 and 50 into eq 47, with $\lambda^e = 1$ (dilute ideal solution), to obtain

$$\frac{1}{\tau} = k_f\left(c_1^e + c_2^e\right) + k_r\left(c_3^e + c_4^e\right) \qquad (51)$$

where we have used eqs 19 and 20 to identify k_f and k_r, respectively. Equation 51 is the standard formula for the relaxation time in the case of an elementary reaction that is bimolecular in both directions (24).

Discussion

Although suggested by Haase (10) as a postulate, eq 3 would seem to hold wherever transition state theory is valid (25, 26). Of course, since there exists no completely satisfactory kinetic theory of the liquid state, the applicability of eq 3 to solutions must ultimately rest upon experiment.

Although we have not shown it, eq 3 can be applied to each step of a reaction involving a mechanism. In elementary steps that are fast, one invokes the steady-state approximation, $r = 0$. The algebraic equations so obtained are used to eliminate the activities of intermediates from the expression for r describing the rate-controlling step. So stated in terms of activities of stable species, the result becomes the expression for the overall rate and contains within it all possible solvent effects.

The ultimate solvent effect occurs when the solvent approaches its critical point. Since activities and activity coefficients are expected to be continuous through the critical point (27), the effect of the critical point on the relaxation time is presumably determined by $(\partial \Delta G/\partial \xi)_e$ (28). Under certain conditions near the critical point, this derivative vanishes (29), which implies that the rate of reaction must go to zero. This is called "critical slowing down".

In the examples treated above, we have used eq 3 to derive

several familiar results associated with the chemical kinetics of both ideal and non-ideal solutions. Perhaps most satisfying from a pedagogical point of view was the fact that when r was set to zero, the correct thermodynamic result for K in terms of equilibrium activities was obtained.

Going further, we suggest that a chemical kinetics course might begin with eq 3. This approach would serve to reduce the ad hoc nature of the concepts currently appearing in the standard method of teaching this branch of physical chemistry.

Acknowledgments

Literature Cited

1. Haraldsen, H. In *The Law of Mass Action: A Centenary Volume, 1864–1964.* Det Norske Videnskaps-Akademi i Oslo; Universitets forlaget: Oslo. 1964; pp 19–35.
2. Lund, E. W.; Hassel, O. In *The Law of Mass Action: A Centenary Volume, 1864–1964.* Det Norske Videnskaps-Akademi i Oslo; Universitets forlaget: Oslo. 1964. pp 36–46.
3. Thomsen, J. *Ann. Phys. Chem.* **1869,** *138,* 65.
4. Ostwald, W. *J. Prakt. Chem.* **1877,** *124,* 385.
5. Guldberg, C. M.; Waage, P. *J. Prakt. Chem.* **1879,** *127,* 69.
6. Amis, E. S. *Solvent Effects on Reaction Rates and Mechanisms,* Academic: New York, 1966.
7. Onsager, L. *Phys. Rev.* **1931,** *37,* 405.
8. Onsager, L. *Phys. Rev.* **1931,** *38,* 2265.
9. deGroot, S. R.; Mazur, P. *Non-Equilibrium Thermodynamics,* Dover: New York, 1984; Chapter X.
10. Haase, R. *Z. Phys. Chem. (NF)* **1987,** *153,* 217.
11. Laidler, K. J. *Chemical Kinetics,* 3rd ed.; Harper and Row: New York, 1987; Chapter. 4.
12. Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry,* Wiley: New York, 1980; p 1118.
13. Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions,* Reinhold: New York, 1959; Chapter 3.
14. Adamson, A. *A Textbook of Physical Chemistry,* 3rd ed.; Academic: New York, 1986; p 635.
15. Alberty, R. A.; Silbey, R. J. *Physical Chemistry,* 2nd ed.; Wiley: New York, 1997; pp 727–729.
16. Atkins, P. *Physical Chemistry,* 6th ed.; Freeman: New York, 1998; pp 836–837.
17. Berry, R. S.; Rice, S. A.; Ross, J. Op. cit.; p 1160.
18. Castellan, G. *Physical Chemistry,* 3rd ed.; Benjamin/Cummings: Menlo Park, CA, 1983; pp 862–863.
19. Levine, I. N. *Physical Chemistry,* 4th ed.; McGraw-Hill: New York, 1995; pp 830–831.
20. Noggle, J. N. *Physical Chemistry,* 3rd ed.; Harper Collins: New York, 1996; pp 585–587.
21. Bell, R. P. *The Proton in Chemistry,* 2nd ed.; Cornell University Press: Ithaca, NY, 1973; pp 134–135.
22. Berry, R. S.; Rice, S. A.; Ross, J. Op. cit.; pp 734–735.
23. Castellan, G. W. *Ber. Bunsen-Ges.* **1963,** *67,* 898.
24. Berry, R. S.; Rice, S. A.; Ross, J. Op. cit.; p 1173.
25. Eyring, H.; Lin, S. W. In *The Law of Mass Action: A Centenary Volume, 1864–1964.* Det Norske Videnskaps-Akademi i Oslo; Universitets forlaget: Oslo. 1964; pp 37–46.
26. Hall, D. G. *Z. Phys. Chem. (NF)* **1987,** *153,* 213.
27. Wheeler, J. C. *Ber. Bunsen-Ges.* **1972,** *76,* 308.
28. Greer, S. C. *Int. J. Thermophys.* **1988,** *9,* 761.
29. Griffiths, R. B.; Wheeler, J. C. *Phys. Rev. A* **1970,** *2,* 1047.