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Rate Constants are Variables in Almost all Chemical Reactions

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Chemical reactions are almost always analyzed using rate constants assumed to be constants. Rate constants are constant if reactants do not interact and have zero excess free energy of interaction, and if spatial gradients are insignificant. Reactants in biology almost always interact strongly because charges attract or repel. Biology occurs in mixtures of ions and organic acids and bases with large permanent charge. Large partial charges are found in carbonyl, amine, and peptide bonds of biomolecules and in the solvent water itself. The energy of one charged reactant depends on all charge in the ionic atmosphere around that reactant. The atmosphere contains **all species** and so the **energy of reactants depends strongly on the concentrations of all species with significant charge**. Measuring excess free energy of interactions has been the life's work of generations of physical chemists. Rate constants in life's solutions should not be assumed constant when physical measurements show important excess interaction energy. 'Everything' interacts with everything in those cases and rate constants are variables. When rate constants are assumed to be constant, **interactions of reactants can be mistaken for conformational changes or complex reaction schemes** of an enzyme. Physical models provide alternatives that reflect known properties of ions in confined spaces. Physical models of L-type Ca channels, DEKA Na channels, and most notably Ryanodine Receptors, account for experiments, over five orders of concentration, in mixtures of many species. Anomalous Mole Fraction Effects were predicted by Gillespie in Ryanodine Receptors before they were found experimentally by Meissner and Xu. The variational calculus provides an alternative description of interactions. The Energy Variational Approach of Chun Liu [Journal Chemical Physics (2010) 133:104104] is mathematically well-defined, even unique (for a given physical model). It includes interactions and spatial gradients that allow flow.

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