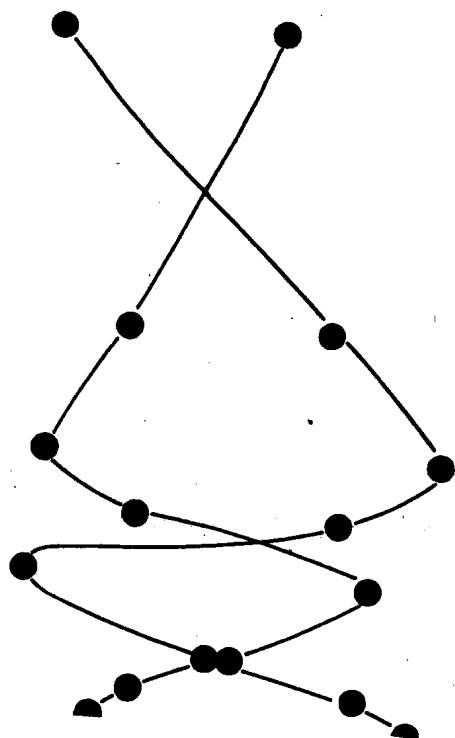


# RATES AND EQUILIBRIA OF ORGANIC REACTIONS

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ERNEST GRUNWALD



# **Rates and Equilibria of Organic Reactions**

*As Treated by Statistical, Thermodynamic,  
and Extrathermodynamic Methods*

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# Preface

Organic reactions usually involve complex molecules reacting in the liquid phase. The theoretical analysis of their rates and equilibria is necessarily less exact than that of small molecules reacting in the gas phase, for it is rarely possible to establish the relevant sets of energy levels with sufficient accuracy or completeness by direct measurement or by quantum mechanical calculation. An approximate treatment can be made from either of two points of view. In one, the formal framework of the complete microscopic analysis is retained, but various simplifying assumptions concerning the microscopic fine structure of the system are made in order to render the calculations tractable. In the other approach, the starting point is a macroscopic or thermodynamic analysis to which is added just enough microscopic detail to allow explicitly for structural and medium effects.

The point of view emphasized in this book belongs very definitely in the latter category. We make extensive use of the concept of *subspecies* because this allows us to introduce into the formal thermodynamic analysis such ideas as conformational isomerism or solvation without having to go all the way to the ultimate treatment in terms of the individual energy levels. A major part of the book is devoted to extrathermodynamic relationships (relationships not directly resulting from the axioms of thermodynamics alone) among free energies or other thermodynamic quantities. The derivation of extrathermodynamic relationships requires the introduction of microscopic detail, but the amount of microscopic information actually needed is surprisingly little. For example, in the derivation of linear free energy relationships for substituent or medium effects on reactions, we need to postulate that microscopic interactions exist, *but we do not need to identify the mechanisms of the interactions.*

We devote so much space to extrathermodynamic relationships because we are ourselves greatly impressed not only by the usefulness of such relationships in predicting rates and equilibria but also by the generality of the underlying theory and by the ease and versatility of its application. The theory provides a logical framework that encompasses all of the known empirical extrathermodynamic relationships and classifies them naturally,

thus tying together a lot of seemingly independent relationships into a single coherent and rational structure. The logical framework is sufficiently general to go beyond existing facts; it provides a useful basis for predicting new extrathermodynamic relationships that can then be tested by experiment; it also provides a useful starting point for the investigation of the actual mechanisms of substituent or medium effects.

In addition to the largely thermodynamic material, we have included chapters on very fast rate processes that occur as elementary steps in many reactions, and on solid state phenomena, two subjects we personally find exciting.

We would like to acknowledge the help and encouragement of our wives and to thank a number of people who have read and criticized our manuscript at various stages, especially George S. Hammond, Charles F. Jumper, Leo Mandelkern, Saul Meiboom, Robert W. Taft, Jr., and Edel Wasserman.

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# Glossary of Symbols

Our symbols are based on the current journal literature and reflect that salutary lack of coordinated planning that is typical of active research fields. We have, however, tried to introduce a measure of order through the use of distinctive typography. Extrathermodynamic parameters and variables are represented by sans serifs or by SMALL CAPITALS. Thermodynamic quantities are represented by *italics*. Generic chemical symbols, such as *RX* or *RBH<sup>+</sup>*, are in *italics*.

<i>A</i>	pre-exponential factor in the Boltzmann equation, the Arrhenius equation, and some other equations of analogous mathematical form.
<i>a, b</i>	coefficients in extrathermodynamic relationships by linear combination of two model processes.
<i>a<sub>i</sub></i>	activity of the <i>i</i> th component.
<i>B, B<sub>A</sub>, B<sub>B</sub></i>	slope in the Brønsted relationship.
<i>B<sub>i</sub></i>	intrinsic term for the <i>i</i> th component in the power-series expansion of the free energy of a solution.
<i>b</i>	ionic radius.
<i>C<sub>p</sub></i>	heat capacity at constant pressure.
<i>C<sub>v</sub></i>	heat capacity at constant volume.
<i>c<sub>i</sub></i>	concentration of the <i>i</i> th component (in moles or formula weights per liter).
<i>D</i>	dielectric constant.
<i>D<sub>A</sub></i>	diffusion coefficient of the molecular species <i>A</i> .
<i>E</i>	energy.
<i>E</i>	activation energy.
<i>E<sup>o</sup></i>	standard partial molar energy.
<i>E<sub>s</sub></i>	steric substituent constant of the acyl group in ester hydrolysis.
<i>e</i>	magnitude of the electric charge of the electron.
<i>F</i>	Gibbs free energy.
<i>F<sub>i</sub></i>	partial molar free energy of the <i>i</i> th component.

$F_i^\circ$	standard partial molar free energy of the $i$ th component.
$F_R, F_X$	independent additive terms (per mole) in the formal representation of $F_{RX}^\circ$ .
$f$	force of retraction in a stretched fiber; tension.
$f(x)$	a function of $x$ .
$g_i$	number of quantum levels having an energy value $\epsilon_i$ ; degeneracy factor for $\epsilon_i$ .
$H$	enthalpy.
$\bar{H}_i^\circ$	standard partial molar enthalpy of the $i$ th component.
$H_0, H_0',$ $H_-, H_R$ }	acidity functions.
$h$	Planck's constant.
$\mathcal{I}$	ionization potential.
$l_{R,X}$	first-order interaction term for the interaction between $R$ and $X$ in the formal representation of $F_{RX}^\circ$ .
$l_{R,M}$	first-order interaction term for the interaction between $R$ and the medium $M$ in the formal representation of $F_{RX}^\circ$ in $M$ .
$l_R, l_X, l_M$	independent factors in the approximate representation of first-order interaction terms.
$ll_{R,X,M}$	second-order interaction term in the formal representation of $F_{RX}^\circ$ in the medium $M$ .
$ll_R, ll_X,$ $ll_M$ }	independent factors in the approximate representation of $ll_{R,X,M}$ .
$J$	rate of application of shear energy.
$j$	rotational quantum number.
$K$	equilibrium constant.
$K_c$	equilibrium constant in terms of molar concentrations.
$K_a$	equilibrium constant in terms of activities.
$K_0$	equilibrium constant for the standard reference reaction.
$K_A$	acid dissociation constant.
$K_B$	base dissociation constant.
$K_\gamma$	$\gamma_{\text{products}}/\gamma_{\text{reactants}}$ .
$k$	rate constant.
$k_0$	rate constant for the standard reference reaction.
$k$	force constant of a bond.
$k$	Boltzmann's constant.
$L$	length of a fiber.
$L_i$	length of a fiber in the isotropic or unstrained state.
$l'$	length of a "statistical element" of a polymer chain.
$M_i$	molecular weight of the $i$ th species.
$M$	interaction variable characteristic of the medium.

$m$	mass per molecule.
$m$	substrate parameter in the mY equation.
$N$	number of molecules.
$N_i$	number of molecules to be found in the $i$ th energy level.
$N_A, N_B \dots$	number of molecules belonging to the species or subspecies $A, B \dots$ .
$N_0$	Avogadro's number.
$N_i$	mole fraction of the $i$ th component.
$n$	number of collisions in an encounter ( $Z/Z_E$ ).
$n_i$	number of moles of the $i$ th component.
$n$	nucleophilic parameter based on the reactions of methyl bromide.
$n'$	number of "statistical elements" in a polymer chain.
$P$	pressure.
$P$	probability factor in collision theory.
$P$	probability that an encounter between the reactant molecules will lead to reaction.
$\mathcal{P}$	time-dependent property of a solution.
$\mathcal{P}_{  }$	component of $\mathcal{P}$ which is in phase with a changing variable of state.
$\mathcal{P}_\perp$	component of $\mathcal{P}$ which is $90^\circ$ out of phase with a changing variable of state.
$p$	operator, $\equiv -\log_{10}$ .
$Q$	partition function.
$R$	gas-constant per mole.
$R$	interaction variable characteristic of the substituent.
$r$	temperature-independent interaction variable characteristic of the substituent.
$R$	mixing parameter in the Yukawa-Tsuno equation.
$r$	length of a polymer chain.
$S$	entropy.
$S_i^\circ$	standard partial molar entropy of the $i$ th component.
$s$	average distance a molecule diffuses in time $t$ .
$s$	reaction parameter in the $sE_s$ equation for steric effects.
$s$	substrate parameter in the $ns$ equation for nucleophilic reactivity.
$T$	absolute temperature.
$t$	time
$V$	volume.
$\bar{V}_i$	partial molar volume of the $i$ th component.
$v$	potential energy.



$V_0$	minimum value of the potential energy function of a harmonic oscillator.
$v$	velocity.
$v_2$	volume fraction of polymer in a network which is swollen or diluted by solvent.
$W$	work.
$w$	substrate parameter in the Bunnett equation.
$X$	interaction variable characteristic of the reaction zone.
$x_i$	concentration of the $i$ th solute species or subspecies (in arbitrary units).
$Y, Y_0, Y_-$	solvent parameters in the mY equations.
$Z$	collision frequency at unit concentrations.
$Z_E$	encounter frequency at unit concentrations.
$Z_{ij}$	average number of collisions experienced by a molecule in a vibrational level $\epsilon_i$ before transition to $\epsilon_j$ takes place. The translational energies are thermally distributed.
$Z$	transition energy of the charge-transfer absorption band of 1-ethyl-4-carbomethoxypyridinium iodide ion pair.
$z_i$	charge number of the $i$ th ionic species.
$\alpha$	polarizability.
$\alpha$	parameter in the rate-equilibrium relationship ( $= \delta \Delta F^\ddagger / \delta \Delta F^\circ$ ).
$\alpha_i$	fraction of the formal species which exists in the form of the $i$ th subspecies.
$\beta$	isokinetic temperature ( $= \delta \Delta H^\ddagger / \delta \Delta S^\ddagger$ for a single interaction mechanism).
$\beta_1, \beta_2$ $\beta', \beta''$ $\beta_{ij}$	values of $\beta$ for individual interaction mechanisms.
$\gamma_i$	pairwise interaction term for components $i$ and $j$ in the power-series expansion of the free energy of a solution.
$\Delta$	activity coefficient of the $i$ th component.
$\Delta F^\ddagger, \Delta H^\ddagger, \Delta S^\ddagger$	reaction operator; e.g., $\Delta F^\circ = F^\circ_{\text{product}} - F^\circ_{\text{reactant}}$ .
$\delta_L$	free energy, enthalpy, and entropy of activation.
$\delta_R$	operator, for changing the length of a fiber of constant composition; e.g., $\delta_L F = F_L - F_{L_0}$ .
	substituent stabilization operator; e.g.,

$$\delta_R F^\circ = F^\circ_{RX} - F^\circ_{R_0X}.$$

$\delta_M$	solvent stabilization operator; e.g., $\delta_M F_i^\circ = F_{i, \text{ in solvent M }}^\circ - F_{i, \text{ in standard solvent }}^\circ$
$\delta f$	half-width of a spectral line (in cycles/sec). See figure 5-6.
$\epsilon_i$	energy of the $i$ th energy level.
$\zeta(x)$	a function of $x$ .
$\eta$	viscosity.
$\eta_{ij}$	pairwise interaction term for components $i$ and $j$ in the power-series expansion of the entropy of a solution.
$\kappa$	transmission coefficient in transition-state theory.
$\lambda$	critical distance for bond-breaking in a polymer chain.
$\mu$	reduced mass of a two-particle system [= $m_1 m_2 / (m_1 + m_2)$ , where $m_1$ and $m_2$ are the masses of the particles].
$\mu$	ionic strength $\left( = \frac{1}{2} \sum c_i z_i^2 \right)$ .
$\bar{\mu}$	dipole moment.
$\nu$	number of polymer chains.
$\nu$	frequency.
$\nu_{\text{osc}}$	characteristic frequency of a harmonic oscillator.
$\nu_{\text{max}}$	(in absorption spectroscopy) frequency of maximum absorption of energy.
$\xi$	friction coefficient.
$\rho$	reaction parameter in $\rho\sigma$ and $\rho\sigma^+$ relationships for aromatic reactions.
$\rho', \rho''$	reaction parameters for individual interaction mechanisms.
$\rho'$	reaction parameter for side-chain reactions at the 1-position in the 4-X-bicyclo-[2.2.2] octane system.
$\rho^*$	reaction parameter for polar effects in aliphatic reactions.
$\sigma$	substituent parameter in the $\rho\sigma$ relationship for aromatic side-chain reactions.
$\sigma', \sigma''$	substituent parameters for individual interaction mechanisms.
$\sigma^+$	substituent parameter for reactions in which a formal positive charge is produced on, or adjacent to, an aromatic ring.
$\sigma^-$	substituent parameter for reactions in which a non-bonding pair of electrons is produced on, or adjacent to, an aromatic ring.

$\sigma^o$	“normal” aromatic substituent parameter.
$\sigma'$	substituent parameter for the 4-X-bicyclo [2.2.2] octane -1 series.
$\sigma^*$	polar substituent parameter for aliphatic reactions.
$\sigma_{AB}$	collision diameter; i.e., sum of molecular radii of <i>A</i> and <i>B</i> .
$\tau$	transmission coefficient for aromatic substituent effects.
$\tau$	relaxation time.
$\tau$	mean time that a molecule can spend in a given state.
$\tau_\mu$	dielectric relaxation time per molecule.
$\phi_i$	volume fraction of the <i>i</i> th component.
$\phi(x)$	a function of <i>x</i> .
$\chi_{ij}$	pairwise interaction term for components <i>i</i> and <i>j</i> in the power-series expansion of the enthalpy of a solution.
$\psi(x)$	a function of <i>x</i> .

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# Equilibrium from the Statistical Point of View

*As far as I can see, the only foundation of the doctrine of probability, which (though not satisfactory for a mind devoted to the "absolute") seems at least not more mysterious than science as a whole, is the empirical attitude: The laws of probability are valid just as any other physical law in virtue of the agreement of their consequences with experience.*

Max Born  
*Experiment and Theory in Physics*

The course of any chemical system, the major and minor reactions that take place, and the composition of the system as a function of time are predictable if the values of the rate and equilibrium constants are predictable. Since rate constants are treated most conveniently by the transition-state theory, which is itself an extension of theories dealing with equilibrium, the study of equilibrium is the logical starting point for an understanding of chemical reactions. In this chapter we shall discuss equilibrium from the microscopic or molecular-statistical point of view. In the next chapter we shall discuss equilibrium from the thermodynamic point of view, and we shall show the relationships between the two treatments. In the statistical or microscopic treatment of equilibrium the fundamental concept is that of probability. In the thermodynamic treatment of equilibrium we again encounter probability, in the guise of entropy.

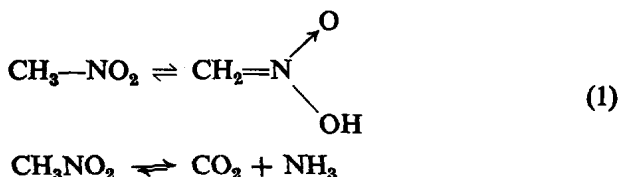
## EQUILIBRIUM AS AN EXERCISE IN PROBABILITY

A system at equilibrium may be defined as being in a state of maximum probability. The various possible physical states, from which it is our task to select the most probable one, are defined in macroscopic terms. When each of these possible states is examined in microscopic detail, it is found that the same macroscopic properties (i.e., the same macroscopic state) can

be produced by a large number of different microscopic arrangements of the molecules and the energy. The number of such different arrangements is the measure of the probability of a given macroscopic state.

The total probability of all the possible macroscopic states is of course unity. However, for systems containing a large number of particles the probability of the most probable state is so very close to unity that once the equilibrium has been achieved the macroscopic system is never observed to depart from it. That is to say, a state differing from the equilibrium state in its macroscopic properties by even a very small amount has already a negligibly small probability. A system on its way to the equilibrium state proceeds through macroscopic states of progressively higher probability.

In predicting the most probable state of the system, we must eliminate from consideration not only those states that are incompatible with the given physical conditions (such as constant volume and energy) but also those states that are merely inaccessible because the rate of attaining them is prohibitively slow. Most chemical problems concern states of metastable or quasi equilibrium, and the true or infinite-time equilibrium state may be excluded from consideration among the possible states because of the lack of a sufficiently fast mechanism for attaining it. For example, if we are interested in the equilibrium (1) between nitromethane and its *aci*-form, we will neglect the extremely slow reaction leading to carbon dioxide and ammonia.



## FACTORS ENTERING THE PROBABILITY CALCULATION

Besides the fundamental idea of probability, equilibrium calculations make use of the concept of quantized energy levels. An *energy level* is a complete description of the state of a molecule (or of a set of atoms) and makes use of *all* the quantum numbers. The value of the energy,  $\epsilon$ , is an important *property* of the energy level but does not suffice to describe it completely. Since molecules in different energy levels differ by at least one quantum number, they also differ in at least one observable property and can therefore be distinguished even when the energies happen to be the same. A *chemical species* in the usual sense is a mixture of many different energy levels; these energy levels can be regarded as isomers constituting the chemical species.

The problem of calculating the equilibrium state of a system is essentially this: Given the possible energy levels of an isolated system, distribute the finite amount of matter and energy in the system among those energy levels and do so in the most probable way.

## THE BOLTZMANN DISTRIBUTION

For simplicity let us first consider a system consisting of a single chemical species in which *no* chemical reaction occurs at an appreciable rate. Even though the molecules all belong to the same chemical species, they can be classified still further by assignment to quantized energy levels. The energies of all the molecules must add up to the total energy of the system, but there are many ways in which that amount of energy can be apportioned among the molecules. For example, Figure 1-1 shows some of the ways in which 30 molecules could be distributed among five levels equally spaced in energy so that the total energy remains constant. When the system contains a large number of molecules, one of the distributions is very much more probable than all the others, and this is to all intents and purposes the way the energy will be distributed at equilibrium. By counting permutations or

Energy of the Level (energy units)	Number of Molecules in Each Level					
5	0	1	3	0	0	0
4	0	3	1	3	2	1
3	0	5	5	6	7	9
2	30	7	5	9	10	9
1	0	14	16	12	11	11
Total molecules	30	30	30	30	30	30
Total energy units	60	60	60	60	60	60

Figure 1-1. Six of the possible distributions of 30 molecules having a total energy of 60 units among 5 equally spaced energy levels. Each distribution corresponds to a different macroscopic state of the system. Some distributions can be achieved in more ways than others. For example, the first distribution shown can be achieved in only one way, while the second distribution can be achieved in many ways: any one of the thirty molecules could occupy the fifth level, any three of the remaining twenty-nine molecules could occupy the fourth level, and so on.

the number of distinguishable ways of achieving a given distribution of the energy, it can be shown that the Boltzmann distribution (equation 2) is in fact the most probable or equilibrium distribution.

$$N_i = Ae^{-\epsilon_i/kT} \quad (2)$$

$$A = \frac{N}{\sum e^{-\epsilon_i/kT}} \quad (3)$$

In these equations  $N_i$  is the number of molecules to be found in the level of energy  $\epsilon_i$  and  $N$  is the total number of molecules.

The choice of the zero point for the energy is arbitrary. As can be derived from equation 3, a change in the choice of zero point is canceled in its effect on the actual distribution because of its occurrence in the pre-exponential as well as in the exponential term. The value of the proportionality constant  $A$  is fixed by the fact that the sum of the molecules in all the energy levels must equal the total number,  $N$ , of molecules.

$$\sum N_i = N = A \sum e^{-\epsilon_i/kT} \quad (4)$$

The Boltzmann equation has two important qualitative properties. The first of these is that at constant temperature a given energy level will contain fewer molecules the higher the energy of the level. The reason for this is the finite constant amount of total energy at constant temperature. The other important property is that the difference in the relative populations of levels of high and low energy is less pronounced at higher temperatures. For example, at an infinitely high temperature the exponential term  $e^{-\epsilon_i/kT}$  would become unity and each level would be populated by the same number of molecules as any other level, whereas at a very low temperature all of the molecules would have to be in the lowest levels.

### Application of the Boltzmann Distribution to Chemical Reactions

When we consider systems in which chemical reactions occur, we find that the reactions do not alter the nature of the problem at all. Equation 2 continues to apply to the population of the  $i$ th energy level *regardless of the chemical species to which the  $i$ th level happens to belong*. This should not be surprising, since the notion of molecular or chemical species is completely arbitrary. A chemical species is a collection of energy levels, and we may include or exclude any energy levels we choose. In practice, the degree of difference we demand between two energy levels before we are willing to call them members of different molecular species depends on the time scale of the experiments that we propose to do. Thus 1,2-dichloroethane is a single chemical species to the person who is subjecting it to fractional distillation but a mixture of *trans* and *gauche* forms to the spectroscopist who is subjecting it to high-frequency radiation. At room temperature the



# EQUILIBRIUM FROM THE STATISTICAL POINT OF VIEW

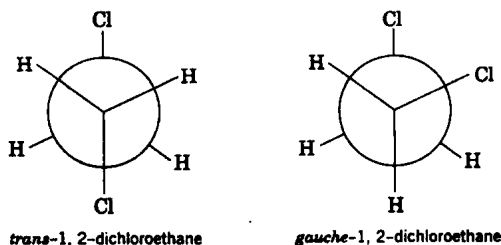


Figure 1-2. Subspecies of 1,2-dichloroethane.

average time between conversions from one form into the other is about  $10^{-10}$  sec.

Since we usually wish to know how many molecules of a particular chemical species are present in a reaction mixture rather than how many molecules are in a particular energy level, we must specify which energy levels are to be counted as members of the chemical species in which we are interested. For example, if *gauche*-1,2-dichloroethane is the species in question, we count only those energy levels having the *gauche* configuration. But if we are interested simply in 1,2-dichloroethane, we must include not only *gauche* and *trans* energy levels but also higher energy levels which because of free rotation have no assignable configuration.<sup>1</sup>

For a simple system in which there are only two substances *A* and *B* in the equilibrium mixture, the equilibrium constant is the number of molecules in all the levels that are considered to belong to species *B* divided by the number of molecules in all the levels that are considered to belong to species *A*. The equilibrium constant is obtained by dividing the Boltzmann expression for the populations of the *B* species by that for the populations of the *A* species, as in equation 5.

$$\begin{aligned}
 N_A &= A \sum e^{-\epsilon_{iA}/kT} \\
 N_B &= A \sum e^{-\epsilon_{iB}/kT} \\
 K &= \frac{N_B}{N_A} = \frac{\sum e^{-\epsilon_{iB}/kT}}{\sum e^{-\epsilon_{iA}/kT}} \quad (5)
 \end{aligned}$$

It is convenient to recast equation 5 into an equivalent form which stresses the difference between the energy of the *i*th level and that of the lowest level for each species. The result is equation 6.

$$K = \frac{N_B}{N_A} = e^{-(\epsilon_{0B}-\epsilon_{0A})/kT} \times \frac{\sum e^{-(\epsilon_{iB}-\epsilon_{0B})/kT}}{\sum e^{-(\epsilon_{iA}-\epsilon_{0A})/kT}} \quad (6)$$

<sup>1</sup> The higher energy levels alluded to are by themselves a chemical species, namely the transition state for the interconversion of the *trans* and *gauche* isomers. Their population is quite small in comparison to that of either of the isomers.