

THERMODYNAMICS AND KINETICS

Simple Derivations of the Extramural Relations of Thermodynamics

Using Arrhenius's Rate-Constant Law*

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THERMODYNAMICS AND KINETICS

Most thermodynamic expressions in textbooks are "intramural" relations. They tell us how to determine numerical values for unfamiliar quantities, such as ΔS and ΔG (eqns. 1a,b, for example), or how one such quantity depends on another such quantity (eqns. 1c,d).

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

(a)

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

(b)

(1)

$$\Delta G = \Delta H - T\Delta S$$

(c)

$$\left[\frac{\partial (\Delta G)}{\partial T} \right]_P = -\Delta S$$

(d)

Only a few thermodynamic expressions are "extramural" relations--ones that tell us immediately something about "directly measurable" or familiar quantities: how, for example, an equilibrium pressure P , or concentration N_2 , or quotient of concentrations K or cell voltage ξ varies with temperature (eqns. 2a-d).

$$\frac{dP}{dT} = \frac{Q}{T\Delta V}$$

(a)

$$\frac{dN_2}{dT}_{\text{fp}} = \frac{-Q}{RT_{\text{nf}}^2}$$

(b)

(2)

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{Q_{\text{irrev}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

(c)

$$nF \frac{d\xi}{dT} = \frac{Q_{\text{rev}}}{T}$$

(d)

These extramural relations (2a-d) show how equilibrium parameters (P , N_2 , K , ξ) must change with temperature if perpetual motion of the second kind is impossible.

Perpetual motion of the second kind is production of work (an increase in energy of a mechanical system) solely at the expense of the energy of a thermal reservoir. In its net effect upon the environment, it is, with respect to energy transformations, precisely the opposite of friction.

The most general statement of the Second-Law-like behavior of Nature states that any process whose net effect is precisely the opposite of friction--or heat flow, or any natural event--is impossible. From that statement can be developed by relatively long and mathematically demanding arguments, as shown in many physical chemistry texts, the extramural relations (2a-d).

It is the chief purpose of this paper to show that the Clapeyron equation (2a), the colligative property relations (such as 2b), van't Hoff's relation (2c), Gibbs-Helmholtz-type equations (such as 2d) and, also (discussed later), the osmotic pressure law (eqn. 19), Boltzmann's factor (eqn. 25), and Carnot's theorem (eqn. 35) can be obtained directly from the laws of chemical kinetics, without the use of calculus.

Our kinetic derivations of the extramural relations of thermodynamics are based on Arrhenius's rate-constant expression $k = A \exp(-\Delta H^*/RT)$. It will be shown that the derivations depend ultimately, therefore, on van't Hoff's thermodynamic equilibrium-constant expression $K = C \exp(-\Delta H/RT)$. Thus, the kinetic derivations are not, in a logical sense, a substitute for the usual thermodynamic arguments. It is often illuminating, however, to see abstract expressions (such as those of thermodynamics) emerge seemingly unexpectedly from more concrete equations (those of chemical kinetics).

The mathematical procedures in this paper can be used, also, in purely thermodynamic arguments. With no change in the algebraic steps given below, one can derive the extramural relations of thermodynamics directly from the thermodynamic expression $K = C \exp(-\Delta H/RT)$. Thus one can move rigorously and easily from one extramural relation to another without employing calculus and the entropy function

(or the chemical potential), or Carnot cycles. This simplification of the syntax of thermodynamics serves to emphasize an essential point: There is essentially only one physically independent extramural thermodynamic relation. There is only one Second Law. Expressions (2a-d), the osmotic pressure rule (19), and Boltzmann's factor (25) are all special instances of Carnot's theorem (35).

In summary the present discussion is, simultaneously: a set of novel applications to thermodynamics of Arrhenius's rate-constant expression; a non-calculus review from several new points of view of the central expressions of classical (and, briefly, statistical) thermodynamics; and, in closing, a brief account of the origins in kinetics and thermodynamics of activated complex theory.

Henry's Law and Raoult's Law

Many texts give this kinetic interpretation of the Laws of Henry and Raoult.

Consider the change



Let $R_{f(b)}$ represent the rate of the forward(backward) reaction, specific rate constant $k_{f(b)}$. Let C_X be the concentration (in any units) of X in the condensed phase, N_X its mole fraction therein, P_X its partial pressure in the gas phase, P_X° the vapor pressure of pure X. On the assumption that

$$R_f = k_f C_X \quad (4a)$$

$$R_t = k_b P_X, \quad (4b)$$

one has that at equilibrium ($R_f = R_b$)

$$P_X = (k_f/k_b)C_X = K_{eq} C_X \quad (5)$$

$$K_{eq} = P_X | C_X = 1 \quad \text{Henry's Law} \quad (5a)$$

$$= P_X | C_X = N_X = 1 \quad \text{Raoult's Law} \quad (5b)$$

$$\equiv P_X^\circ \quad \text{" "}$$

Similar derivations of mathematical expressions for other colligative properties can be achieved by introducing Arrhenius's expression for the dependence upon temperature (and pressure) of the specific rate constants k_f and k_b .

Arrhenius's Rate-Constant Law

According to Arrhenius (in modern notation), for forward and backward reactions

$$k = Ae^{-\Delta H^*/RT} \quad (6)$$

where, over small temperature intervals, A and ΔH^* may be treated as constants, and where, Fig. 1,

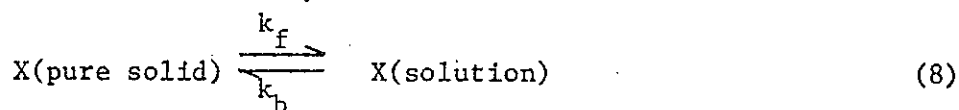
$$\Delta_f H^* - \Delta_b H^* = \Delta H \quad (7a)$$

$$= H_{\text{products}} - H_{\text{reactants}}$$

$$= \Delta E + \Delta(PV). \quad (7b)$$

The Ideal Solubility Equation and Freezing Point Depressions

To illustrate the use of the Arrhenius Rate-Constant Law to obtain by a kinetic analysis expressions normally obtained through reasoning based on thermodynamic principles, consider the solution, or melting, of a pure solid.



On the assumption that $R_f = k_f$ and $R_b = k_b N_x$, one has that, at equilibrium, $k_f = k_b N_x$ or, on using the Arrhenius expression, (6), that $A_f \exp(-\Delta_f H^*/RT) = N_x A_b \exp(-\Delta_b H^*/RT)$. Rearrangement and use of (7a) yields

$$\frac{A_f}{A_b} = N_x e^{\Delta H/RT} \quad (9)$$

ΔH is the enthalpy of solution, or melting, of X. Taking the natural logarithm of both sides of (8), one obtains

$$\frac{\Delta H}{RT} + \ln N_x = \ln \frac{A_f}{A_b}, \text{ a constant} \quad (9a)$$

$$= \frac{\Delta H}{RT} \Big|_{N_x = 1} \quad (9b)$$

$$= \frac{\Delta H}{RT_{\text{nfp}}} \quad (9c)$$

From (9c),

$$\ln(N_x/1) = \frac{\Delta H}{R} \left(\frac{1}{T_{\text{nfp}}} - \frac{1}{T} \right) \quad (10)$$

For $N_x \approx 1$, $\ln N_x \approx -(1-N_x) \equiv -N_2$, $T \approx T_{\text{nfp}}$, and eqn. (10) reduces to

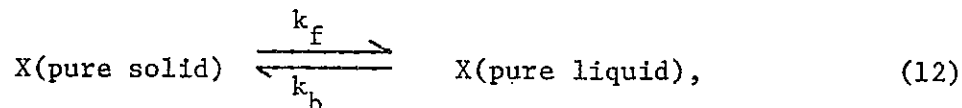
$$N_2 = \frac{-\Delta H}{2RT_{\text{nfp}}} (T - T_{\text{nfp}}) \quad (11)$$

Eqn. (10), the ideal solubility equation, is a special case of eqn. (2c).

Eqn. (11), the thermodynamic expression for freezing point depressions, is an integrated form of eqn. (2b).

Clapeyron's Equation

If a pure solid dissolves (melts) in its *pure* liquid,



$N_X = 1$ and, in place of eqn. (9), one has that, at equilibrium, $(A_f/A_b) = 1 \cdot \exp(\Delta H/RT)$.

Taking the natural logarithm of both sides, one obtains in place of eqn. (9a)

$$\begin{aligned} \frac{\Delta H}{RT} &= \ln \frac{A_f}{A_b}, \text{ a constant} \\ &= \frac{\Delta E + P\Delta V}{RT}. \quad [\text{by (7b)}]. \end{aligned} \quad (13)$$

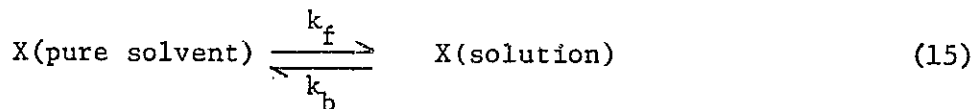
If the pressure and temperature change from values P and T that satisfy eqn. (13) to new values $P + dP$ and $T + dT$, for equilibrium to be maintained, dP and dT must be such that

$$\frac{\Delta E + (P + dP) \Delta V}{R(T + dT)} = \frac{\Delta E + P\Delta V}{RT} \quad (14)$$

In writing eqn. (14) it has been assumed that, like (A_f/A_b) , ΔE and ΔV are temperature- and pressure-independent. Simplification of (14) yields, on solving for the ratio of dP to dT , eqn. (2a), where $Q = \Delta E + P\Delta V = \Delta H$. A kinetic analysis of the similar but slightly more complicated case of the vaporization of a liquid (or solid) is given in Appendix 1, together with a kinetic analysis of the effect on a vapor pressure of squeezing a liquid (the Gibbs-Poynting effect), with an application to osmosis.

Osmotic Equilibrium

Consider, next, diffusion of a pure solvent at pressure P through a rigid, semi-permeable membrane into a solution at pressure $P + \pi$,



Pressure:	P	$P + \pi$
Mole Fraction:	$N_x = 1$	$N_x < 1$

The kinetic analysis $R_f = k_f = R_b = k_b N_x$ yields with Arrhenius's relation, (6), expressions identical to (9) and (9a). In this instance, at least approximately, $\Delta E = \Delta V = 0$. Thus for (15)

$$\Delta H = \Delta(PV) = (P + \pi)\bar{V}_x - P\bar{V}_x = \pi\bar{V}_x. \quad (16)$$

Substitution from (16) into (9a) yields

$$\frac{\pi\bar{V}_x}{RT} + \ln N_x = \ln(A_f/A_b), \text{ a constant.} \quad (17)$$

For $N_x = 1$, $\pi = 0$ (at equilibrium). In this instance, therefore,

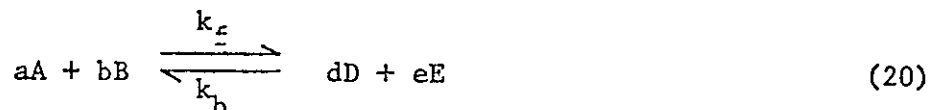
$$\ln(A_f/A_b) = 0. \quad (18)$$

Substitution from (18) into (17) yields for dilute solutions ($\ln N_x \approx -N_2$) the usual thermodynamic expression for a solution's osmotic pressure π :

$$\pi \approx \frac{RTN_2}{\bar{V}_x} \approx RTc_2 (\text{moles/liter}). \quad (19)$$

Chemical Equilibrium

By the *Principle of Microscopic Reversibility* one has that for the chemical change



the rate at which A and B disappear by the (perhaps unlikely) *mechanism* $aA + bB$, rate law $R_f = k_f C_A^a C_B^b$, is *at equilibrium* equal to the rate at which A and B appear by the mechanism $dD + eE$, rate law $R_b = k_b C_D^d C_E^e$ ¹. Thus, from $R_f = R_b$ one obtains the familiar Law of Mass Action, eqn. (21) below, which with eqns. (6) and (7) yields eqn. (22), from which can be obtained directly eqn. (2c) ($Q_{irrev} = \Delta H$).

$$\left. \frac{C_D^d C_E^e}{C_A^a C_B^b} \right|_{\text{equil.}} = \frac{k_f}{k_b} = K_{eq} \quad (21)$$

$$= \frac{A_f}{A_b} e^{-\Delta H/RT} \quad (22)$$

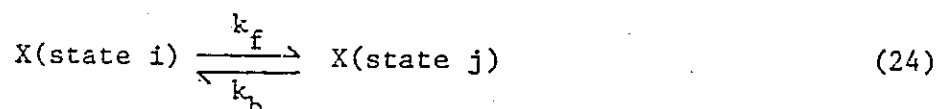
For later reference, we note that, from eqns. (21) and (22),

$$K_{eq} = \frac{A_f}{A_b} e^{-\Delta H/RT} \quad (23a)$$

$$= e^{-[\Delta H - RT \ln(A_f/A_b)]/RT} \quad (23b)$$

Boltzmann's Factor

A particularly simple "chemical" change is the transition of a molecule X in a quantum state i , energy ϵ_i , to a quantum state j , energy ϵ_j .



¹ For a further discussion of this point see, Frost, A. A., and Pearson, R. G., "Kinetics and Mechanism," John Wiley and Sons, Inc., 1953, Ch. 8; or Frost, A. A., J. Chem. Educ., 18, 272 (1941).

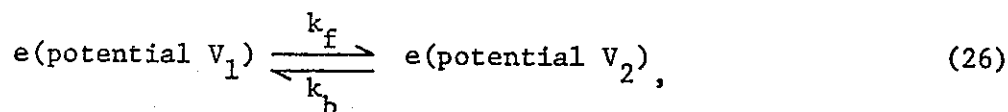
By arguments identical to those given in the preceding section, one obtains expressions of the form (21) and (22). In this simple instance $K_{eq} = C_j/C_i [C_{j(i)} = \text{concentration of molecules in state } j(i)], \Delta H = N_o(\epsilon_j - \epsilon_i) [\Delta(PV) = 0], \text{ and } A_f = A_b$. Thus, for a system that is at equilibrium with respect to the change indicated in (24)

$$\frac{C_j}{C_i} = e^{-\frac{(\epsilon_j - \epsilon_i)}{kT}} \quad (k \equiv R/N_o) \quad (25)$$

From the Boltzmann Factor expression (25) can be obtained directly by summation partition functions and thence, by differentiation and the taking of logarithms, the other standard expressions of statistical thermodynamics.

Electrochemical Equilibrium

For the flow of electrons from a potential V_1 to a potential V_2 ,



in an *electrochemical* circuit, cell voltage $\xi = V_2 - V_1$, one has that at equilibrium (a "balanced circuit"), $R_f = k_f = R_b = k_b$. Thus, by the Arrhenius relation, (6), *at equilibrium*

$$\frac{A_f}{A_b} = e^{\frac{(\Delta_f H^* - \Delta_b H^*)}{RT}} \quad (27)$$

The activation enthalpies ΔH^* contain, in this instance, two contributions: one from the enthalpy of activation of the *chemical* change to which the electron flow is coupled in an electrochemical cell; the other from the enthalpy of activation for the *physical* transfer of electrons across a potential difference ξ . Thus,

in this instance,

$$\frac{\Delta_f H^* - \Delta_b H^*}{RT} = \frac{\Delta_{rx} H + nF\xi}{RT} \quad (28a)$$

$$= \ln \frac{A_f}{A_b}, \text{ a constant.} \quad (28b)$$

At equilibrium the right-hand-side of (28a) is equal to $\ln(A_f/A_b)$, a constant, eqn. (28b). If the temperature and voltage change from values T and ξ that satisfy eqns. (28) to new values $T + dT$ and $\xi + d\xi$, for equilibrium to be maintained, dT and $d\xi$ must be such that

$$\frac{\Delta_{rx} H + nF(\xi + d\xi)}{R(T + dT)} = \frac{\Delta_{rx} H + nF\xi}{RT} \quad (29)$$

In writing eqn. (29) it has been assumed (again) that, like A_f/A_b , $\Delta_{rx} H$ is temperature independent. Simplification of (29) yields on solving for the ratio of $d\xi$ to dT

$$nF \frac{d\xi}{dT} = \frac{\Delta_{rx} H + nF\xi}{T}. \quad (30)$$

Eqn. (30) is, in disguise, eqn. (2d). For consider this universe (or isolated system): a chemical system σ , an atmosphere atm, mechanical surroundings wt, and thermal surroundings θ [for example, as here, a chemical cell σ at constant temperature (owing to thermal contact with θ) and constant pressure (owing to mechanical contact with atm) performing useful work $nF\xi$]. Application of the First Law (the conservation of energy) to the universe $\sigma + atm + wt + \theta$ yields, on introducing the definitions of P , $\Delta_{rx} H$, and Q , the expressions in (31).

$$\Delta E_{\text{total}} = \Delta E_{\sigma} + \Delta E_{\text{atm}} + \Delta E_{\text{wt}} + \Delta E_{\theta} = 0$$

$$\underbrace{\Delta E_{\sigma}}_{\Delta H_{\sigma} = \Delta_{\text{rx}} H} + nF\xi - Q = 0 \quad (31)$$

Thus, for a universe σ (a chemical cell) + atm + wt + θ , $\Delta_{\text{rx}} H + nF\xi = Q$. When the universe is in internal equilibrium [change (26) reversible], one may write

$$\Delta_{\text{rx}} H + nF\xi_{\text{rev}} = Q_{\text{rev}} \quad (32)$$

Substitution from (32) into (30) yields (24).

Carnot's Theorem

The previous results can be generalized. The work obtained from a spontaneous chemical change need not appear as electrical energy. Replacing $nF\xi$ in eqn. (28a) by W , any useful work, one has for reversible changes that

$$\frac{\Delta H + W_2}{T_2} = \frac{\Delta H + W_1}{T_1} \quad (33)$$

In writing (33) it has been assumed (again) that ΔH is independent of temperature, i.e., that

$$C_p(\text{products}) = C_p(\text{reactants}). \quad (34)$$

W_2 and W_1 represent the work obtained at, respectively, temperatures T_2 and T_1 .

Consider now this partial cycle (a cycle for a composite chemical system $\sigma_1 + \sigma_2$, not, however, for its thermal and mechanical surroundings): A chemical reaction for which the change in enthalpy is ΔH advances *forward* reversibly at temperature T_2 in a system σ_2 in contact with a thermal reservoir θ_2 performing useful work W_2 with $Q_{\text{rev}} \equiv Q_2 = \Delta H + W_2$ (by 32). Next the reaction is run *backward*

reversibly at a lower temperature T_1 in a system σ_1 (except for its temperature, identical with σ_2) in contact with a thermal reservoir θ_1 consuming useful work W_1 . Finally, with a graded series of external thermal reservoirs the products in σ_1 (chemically identical to the reactants in σ_2) are *warmed* reversibly from T_1 to T_2 and, using the same set of thermal reservoirs, but in the opposite order, the products in σ_2 (chemically identical to the reactants in σ_1) are *cooled* from T_2 to T_1 . By (34), the individual external reservoirs suffer no net change. The net work obtained from the overall, reversible process (cyclic for $\sigma_1 + \sigma_2$) is $W_2 - W_1$. By (33), $W_1 = (T_1/T_2)(\Delta H + W_2) - \Delta H$. Thus

$$W_2 - W_1 = \underbrace{(W_2 + \Delta H)}_{Q_2} \left(1 - \frac{T_1}{T_2}\right)$$

Division of both sides by Q_2 , the energy absorbed from the warmer thermal reservoir, yields Carnot's theorem.

$$\left. \frac{W}{Q_2} \right|_{\text{rev}} = 1 - \frac{T_1}{T_2} \quad (35)$$

Our discussion of the kinetic derivation of the *extramural* relations of chemical thermodynamics concludes with (35) and its companion

$$\frac{dW_{\text{rev}}}{dT} = \frac{Q_{\text{rev}}}{T} \quad (36)$$

obtained, after replacing $nF\xi$ by W , from (30) and (32). All the second-law based relations of thermodynamics are essentially special instances of (35) or (36).

ΔS and ΔG

(Clausius-Gibbs Thermodynamics)

The major *intramural* relations of chemical thermodynamics are obtained by introducing the abbreviation

$$R \ln \frac{A_f}{A_b} = \Delta S. \quad (37)$$

From the present viewpoint eqn. (37) may be considered a definition of ΔS .

Use of (37) in (13) yields for the melting-freezing equilibrium

$$\Delta S = \frac{\Delta H}{T}. \quad (38)$$

Use of (37) in (23b) yields

$$K_{eq} = e^{-\frac{(\Delta H - T\Delta S^{\circ})}{RT}} \quad (39)$$

The superscript $^{\circ}$ on S in (39) is added to indicate that in this instance the numerical value of ΔS calculated from (37) will depend on the units used to express the concentrations of, for example, A and B, since the latter will determine, in part, the numerical value assigned to the kinetic parameter A_f in the rate law

$$R_f = [A_f \exp(-\Delta_f H^*/RT)] C_A^a C_B^b.$$

Use of (37) in (28a,b) yields (with $nF\xi = W$)

$$\frac{\Delta H + W_{rev}}{T} = \Delta S. \quad (40a)$$

Or,

$$W_{rev} = -(\Delta H - T\Delta S). \quad (40b)$$

Taken with (32), (40a) yields (1a), which, with (36) yields

$$\frac{dW_{rev}}{dT} = \Delta S. \quad (41)$$

Together, (40a) and (41) yield $dW_{\text{rev}}/dT = (\Delta H + W_{\text{rev}})/T$ or

$$\frac{d\left(\frac{W_{\text{rev}}}{T}\right)}{dT} = \frac{\Delta H}{T^2} \quad (42)$$

This last relation is an extramural relation. The symbols S and/or G do not appear in it. It can be obtained directly from (36) and (32; with $nF\xi_{\text{rev}} = W_{\text{rev}}$).

Introduction of the abbreviation (1c), a definition of ΔG , yields with (39) (and the ideal-solution theory approximation that ΔH is concentration independent) eqn. (1b). Use of (1c) in (40b) yields $W_{\text{rev}} = -\Delta G$. The latter with (41) yields (1d) and, with (42), the Gibbs-Helmholtz equation:

$$\frac{d\left(\frac{\Delta G}{T}\right)}{dT} = -\frac{\Delta H}{T^2} \quad (43)$$

Equivalence of the Inter- and Extra-Mural Relations of Thermodynamics

Introduction of the symbols ΔS and ΔG with the assigned properties

$$\begin{array}{lll} \Delta S = \frac{Q_{\text{rev}}}{T} & \Delta G = \Delta H - T\Delta S & \frac{\partial \Delta G}{\partial T} = -\Delta S \\ (1a) & (1c) & (1d) \end{array}$$

does not increase the physical content of thermodynamics, namely that -

$$\begin{array}{ll} Q = \Delta H + W & \frac{dW_{\text{rev}}}{dT} = \frac{Q_{\text{rev}}}{T} \\ (32) & (36) \end{array}$$

The First Law ²

The Second Law

² For a universe $\sigma + \theta + \text{atm} + \text{wt}$.

With definitions (1c) and (1a), (32) and (36) imply (1d):

$$\Delta G = \Delta H - T\Delta S = \Delta H - Q_{\text{rev}} = -W_{\text{rev}} \implies \frac{\partial \Delta G}{\partial T} = -\Delta S.$$

(1c) (1a) (32) (36,1a) (1d)

Conversely, with definitions (1c) and (1a), (31) and (1d) imply (36). *The intramural and extramural relations of thermodynamics are logically equivalent to each other.*

To write (1b)

$$-RT \ln K_{\text{eq}} = \Delta G^{\circ}$$

is, with (1d) (and 1c), equivalent, mathematically, to writing the van't Hoff relation (2c) in its differential form

$$\frac{d \ln K_{\text{eq}}}{d T} = \frac{\Delta H}{RT^2}$$

The position in the above, hierarchical arrangement of ideas of the expression $\Delta S_{\text{total}} \geq 0$ is described in Appendix 2.

Summary and Conclusions

Equations of classical (and statistical) thermodynamics based on the Second Law can be divided into two classes: those that contain the symbols S and/or G (or A) (the intramural relations) and those that do not (the extramural relations). The latter relations, those of immediate practical use, can be obtained quickly and easily, without calculus, from simple kinetic arguments based on Arrhenius's Rate-Constant Law and the assumptions of ideal solution theory (ΔH independent of concentration; activities of solvents equal to mole fractions, those of gases to partial pressures); the assumption, or approximation, that $\Delta C_p = 0$; and, in some

instances, the Principle of Microscopic Reversibility. The kinetic treatment is, thus, a complement to, not a complete substitute for, the usual thermodynamic derivations of, for example, Clapeyron's equation and Carnot's theorem, which are valid relations even for non-ideal systems and for systems for which $\Delta C_p \neq 0$.

Arrhenius's Law is the non-thermodynamically inclined chemist's friend. While not encompassing the full content of the Second Law, and probably precisely because of that fact, Arrhenius's Rate-Constant Law embodies in a form immediately and easily applicable to many problems (both classical and statistical) those implications of the Second Law of particular interest to chemists. One may wonder how Arrhenius was led to an expression that captures so simply yet effectively the chemically significant features of the Second Law of thermodynamics.

Origin of Arrhenius's Rate-Constant Law

"In his notable book *Studies in Chemical Dynamics* van't Hoff gives a theoretically-based formulation of the influence of temperature on the rate of reaction," wrote Arrhenius in 1889 in a paper (his chief contribution to chemical kinetics) *On the Reaction Velocity of the Inversion of Cane Sugar By Acids* (1).

"It may be proved, by means of thermodynamics," van't Hoff had written (2), "that the values of k_1 and k_2 [our k_f and k_b] must satisfy the following equation: -

$$\frac{d \log k_1}{d T} - \frac{d \log k_2}{d T} = \frac{q}{2T^2} \quad (44)$$

[Today we usually write \ln for \log , ΔH for q , R for 2 .]

"Although this equation does not directly give the relationship between the constants k and the temperature," continued van't Hoff, "it shows that this

relationship must be of the form

$$\frac{d \log k}{d T} = \frac{A}{T^2} + B \quad (45)$$

where A and B are constants" (2).

Implicit in van't Hoff's remarks is the understanding that $A_1 - A_2 = q$ (cf. eqn. 7a) and that $B_1 = B_2$.³

"It is, however, easily seen," notes Arrhenius, "that B can be any function, F(T), of the temperature... [provided only that] the F(T) belonging to two reciprocal reactions are the same" (1).

"Since F(T) can be anything at all," continues Arrhenius, "it is not possible to proceed further without introducing *a new hypothesis*, which is in a certain sense *a paraphrase of the observed facts*" [emphasis added].

Noting that the influence of temperature on specific reaction rates is very large, much larger than increasing gas-phase collision frequencies or decreasing liquid-phase viscosities, Arrhenius suggests by analogy with the "similar extraordinary large change in specific reaction velocity (k)...brought about by weak basis and acids" [an effect arising from the catalytic effect of often an *infinitesimal amount* of H^+ or OH^-] that in, for example, the inversion of cane sugar, the rate of which is sharply temperature dependent, the "actual reacting substance is not [ordinary] sugar, since its amount does not change with temperature, but is another hypothetical substance... which we call 'active cane sugar' [today, 'activated cane sugar']...that is generated [in small amounts, by activation] from [ordinary, inactive] cane sugar...and must [be supposed to] increase rapidly in quantity with increasing temperature."

³ In absolute rate theory $k = (\kappa T/h) e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$. Hence, for $\Delta C_p^\ddagger = 0$, $d \ln k/dT = \Delta H^\ddagger/RT + 1/T$ and $B = 1/T$. More generally, if, empirically, one has $k = aT^n e^{A/T}$, a, A, constants, then, by (45), $B = n/T$.

Continuing with his paraphrase of the observed facts, Arrhenius writes that "since the reaction velocity is approximately proportional to the amount [concentration] of [ordinary] cane sugar...the amount [concentration] of 'active cane sugar', M_a , must be taken to be approximately proportional to the amount of inactive cane sugar, M_i . The *equilibrium condition* [emphasis added] is thus:

$$M_a = k M_i \quad (46)$$

"The form of this equation shows us that a molecule of 'active cane sugar' is formed from a molecule of inactive cane sugar either by a displacement of the atoms or by addition of water", whose amount is constant; its concentration, therefore, does not appear in eqn. (46).

The constant k in (46) wears two hats. It is simultaneously a thermodynamic parameter and a rate parameter. It is the thermodynamic equilibrium constant for the postulated equilibrium between active and inactive cane sugar molecules (It would be written today as K^* or K^\ddagger). And, if the rate of inversion is, as postulated, proportional to M_a , k is proportional to the kinetic rate constant for the inversion of cane sugar.

Carrying over in this way to kinetics a thermodynamic relation, Arrhenius applies van't Hoff's *thermodynamic* expression (44) for the temperature variation of an equilibrium constant $K (= k_1/k_2)$ to the thermodynamic-kinetic constant k of (46). In the spirit of modern absolute rate theory, he writes that "Thus for the constant k (or what is the same thing M_a/M_i) we have the equation

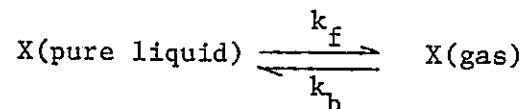
$$\frac{d \log_{\text{nat}} k}{dT} = \frac{q}{2T^2}, \quad (47)$$

which on integration yields, with $q = \Delta H^\ddagger$ (and $2 = R$), eqn. (6).

That Arrhenius's Rate-Constant Law captures for chemistry the essential features of the Second Law of thermodynamics is, thus, no mystery. It is a plausible application, based on a selective if brief axiomatization of nearly universal features of chemical reaction rates, of van't Hoff's thermodynamic relation (44), which is a special instance--THE CHEMICAL INSTANCE--of the Gibbs-Helmholtz equation (43), which in turn is a general instance, if not quite the complete embodiment of Carnot's theorem (35, 36), itself THE most general mathematical statement of the Second-Law - like behavior of nature. As we have shown, however, in many chemical problems Arrhenius's Law (6) is a more quickly and easily used expression of the Second Law than is Carnot's more widely applicable and, though mathematically simpler, chemically more remote theorem (35).

Appendix 1

Derivation of Clapeyron's Equation for the Phase Change



With a Note on the Gibbs-Poynting Effect and Osmotic Pressure

At equilibrium ($R_f = R_b$), $k_f = k_b P$. Using (6) and (7a), one obtains on taking logarithms.

$$\frac{\Delta H}{RT} + \ln P = \ln \frac{A_f}{A_b}, \text{ a constant.}$$

Thus, on going from an equilibrium point T, P to another equilibrium point $T + dT, P + dP$, one has that if ΔH is (in this instance) independent of T and P ,

dT must be such that

$$\frac{\Delta H}{R(T+dT)} + \ln(P + dP) = \frac{\Delta H}{RT} + \ln P.$$

Multiplying through by $R(T + dT)T$, simplifying, noting that $\ln(P + dP) - \ln P = \ln(1 + \frac{dP}{P}) = dP/P$ and that $RT^2/P = T\bar{V}^g$ and dropping the term containing $dP \times dT$, one obtains

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta H}{T\bar{V}^g} \\ &\approx \frac{\Delta H}{T\Delta V}. \end{aligned}$$

If the partial pressure on the gas, P^g , is not the same as the pressure on the liquid phase, P^l (the liquid, for example, might be squeezed--as in an osmotic experiment--behind a rigid, X-permeable barrier), the first equation above should be written

$$\frac{\Delta E + \frac{RT}{P^g \bar{V}^g} - P^{l-1}}{RT} + \ln P^g = \ln \frac{A_f}{A_b}, \text{ a constant.}$$

For vapors behaving as ideal gases, one has (as indicated) $P^g \bar{V}^g = RT$. If, now, at constant temperature, the two pressures change from values P^l and P^g that satisfy the above relation to new values $P^l + dP^l$ and $P^g + dP^g$, for equilibrium to be maintained, dP^l and dP^g must be such that

$$\frac{\Delta E + RT - (P^l + dP^l)}{RT} - \ln (P^g + dP^g) = \frac{\Delta E + RT - P^{l-1}}{RT} + \ln P^g.$$

Simplifying, one obtains the Gibbs-Poynting equation

$$dP^g = \frac{\bar{V}^l}{\bar{V}^g} dP^l.$$

Consider, now, a *squeezed, impure* liquid X in equilibrium with the pure, unsqueezed liquid, eqn. (15), equilibration occurring (in one's mind) via a common vapor phase. A finite squeeze $\Delta P^1 = \pi$ *increases* the vapor pressure (the pressure of the gas that maintains equilibrium with the liquid) by an amount (see above) $(\bar{V}^1/\bar{V}^g)\pi$. The presence, however, of a second component, 2, *decreases* the vapor pressure from that of the pure liquid, P_X^0 , by an amount (see eqn. 5b) $P_X^0 - P_X^0 N_X = P_X^0(1 - N_X) \equiv P_X^0 N_2$. Equating those two terms, one finds that the amount π an *impure* liquid must be squeezed to maintain equilibrium with the *pure* liquid is given by the expression

$$\pi = \frac{P_X^0 \bar{V}^g N_2}{\bar{V}^1} = \frac{RT N_2}{\bar{V}^1}$$

(in agreement with eqn. 19).

Appendix 2

$$\Delta S_\sigma, \Delta S_\theta, \Delta S_{\text{atm}}, \Delta S_{\text{wt}}, \text{ and } \Delta S_{\text{total}}$$

The primary implications for classical thermodynamics of the Second-Law - type behavior of nature are embodied in expression (36): $dW_{\text{rev}}/dT = Q_{\text{rev}}/T$. The variation with temperature of W_{rev} is a property jointly of the initial *and* final states of a system σ . It is, so to speak, a "double state function". *Define*, in the spirit with which (36) was introduced,

$$\begin{aligned}
 \Delta S_{\sigma} &\equiv \frac{dW_{\text{rev}}}{dT} && \text{For Convenience}^4 \\
 &= \frac{Q_{\text{rev}}}{T} && \text{By Carnot's Theorem} \\
 &= \frac{-\Delta_{\text{rev}} E_{\theta}}{T} && \text{By Definition: } Q \equiv -\Delta E_{\theta} \\
 &= \frac{\Delta H_{\sigma} + W_{\text{rev}}}{T} && \text{By the First Law}
 \end{aligned}$$

Define, also, purely for bookkeeping purposes,

$$\begin{aligned}
 \Delta S_{\theta} &\equiv \frac{\Delta E_{\theta}}{T} \\
 \Delta S_{\text{atm}} &\equiv 0 \\
 \Delta S_{\text{wt}} &\equiv 0 \\
 \Delta S_{\text{total}} &\equiv \Delta S_{\sigma} + \Delta S_{\theta} + \Delta S_{\text{atm}} + \Delta S_{\text{wt}}
 \end{aligned}$$

Clearly, for a reversible process $\Delta S_{\text{total}} = 0$. For irreversible processes, one has that

$$W_{\text{irrev}} = \Delta H_{\sigma} + Q_{\text{irrev}} < W_{\text{rev}} = \Delta H_{\sigma} + Q_{\text{rev}}$$

$$\begin{array}{ccc}
 \text{1}^{\text{st}} \text{ Law} & & \text{Carnot} \quad \text{1}^{\text{st}} \text{ Law}
 \end{array}$$

$$\implies Q_{\text{irrev}} < Q_{\text{rev}} \quad \text{or} \quad (Q \equiv -\Delta E_{\theta})$$

$$\Delta_{\text{irrev}} E_{\theta} > \Delta_{\text{rev}} E_{\theta}$$

$$\implies \Delta_{\text{irrev}} S_{\theta} > \Delta_{\text{rev}} S_{\theta}$$

$$\implies \Delta_{\text{irrev}} S_{\text{total}} > 0.$$

⁴ It's easier to write " ΔS " than " dW_{rev}/dT ".

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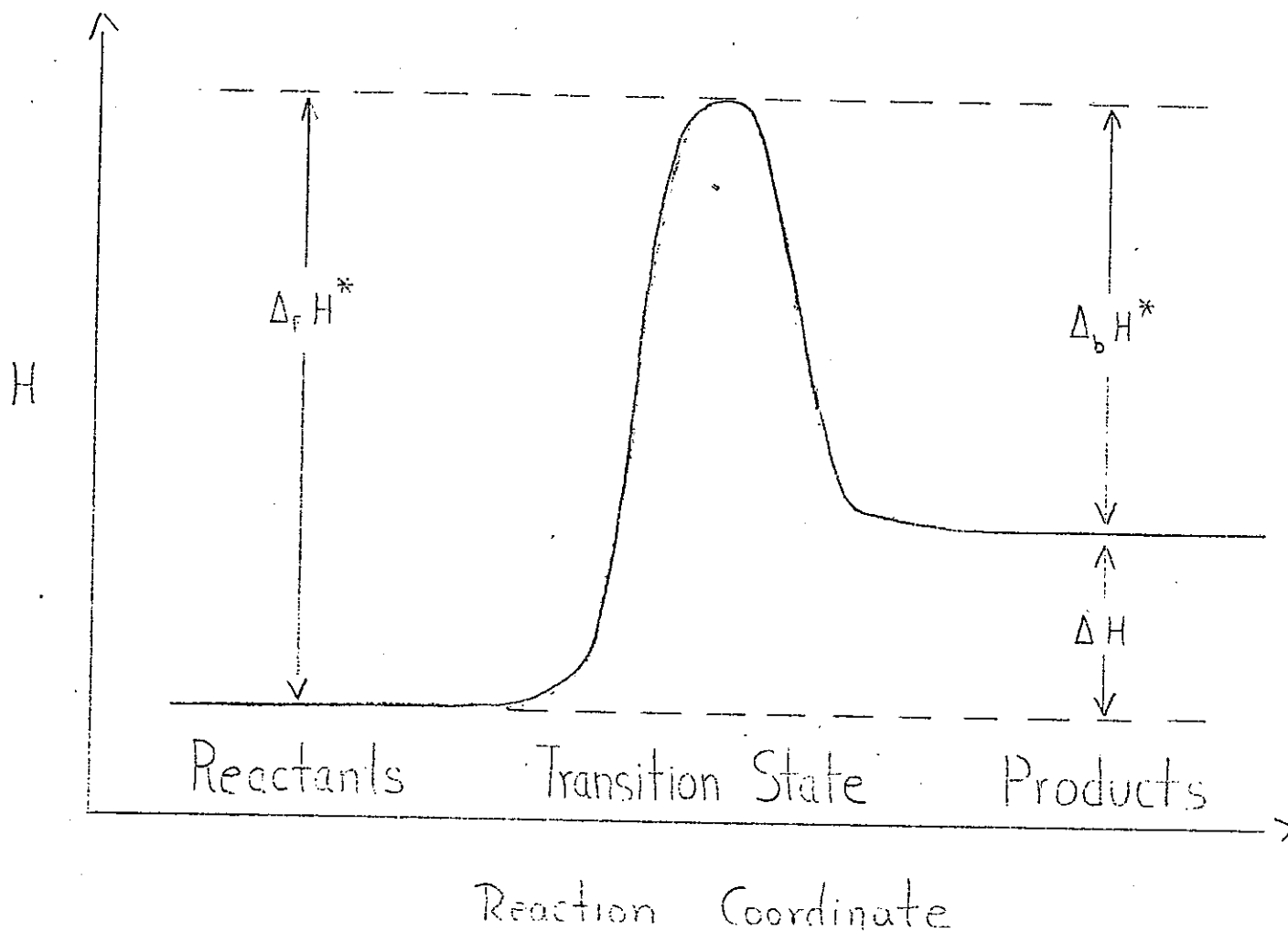


Fig. 1. The Arrhenius - van't Hoff relation between the kinetic parameters $\Delta_f H^*$ and $\Delta_b H^*$ and the thermodynamic parameter ΔH :

$$\Delta H = \Delta_f H^* - \Delta_b H^*$$