Kinetics of Steady State Phase Transitions

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A fundamental investigation of the departure from equilibrium in steady-state phase transitions has been made in terms of irreversible thermodynamics and absolute rate theory. The present status of the concept of accommodation coefficients was reviewed and hypotheses were advanced for the reconciliation of opposing viewpoints. Formulas for the magnitude of the departure from equilibrium were derived for single- and multicomponent systems. The deviation from equilibrium appeared to be small for ordinary rates of phase change, but interpretation of the available data was hampered by lack of a detailed molecular picture of the phase-change process.

The purpose of the present treatment is to investigate the thermodynamics and kinetics of steady-state phase transitions from a fundamental point of view, to ascertain the nature and magnitude of the departure from equilibrium. On examination of the nature of phase transitions, it appears obvious that an interface across which a net flow of matter is occurring cannot be in equilibrium. An example is a closed container of a pure liquid in equilibrium with its vapor and governed by the usual equilibrium relations, that is, equal chemical potentials in both phases. A necessary corollary of equilibrium is that the system be in a time-invariant condition; that is, the rates of evaporation and condensation at the liquid surface must be equal. However if one imagines the ends of the container removed and liquid supplied at one end and vapor removed at the other, one or both of the rates must change. Thus the conventional equilibrium conditions, such as the Clausius-Clapeyron equation, should not apply. A relatively simple treatment should still be possible if a steady state can be assumed. A steady (or stationary) state is the time-invariant condition of an open system, in contrast to equilibrium, the time-invariant condition of a closed system. *A priori*, it would be expected that the departure from equilibrium would be small in view of the very large (unidirectional) rates of most phase changes relative to net rates of mass transfer between phases; however, the departure would also be expected to be greater for high rates of material flow in particular cases of interest, for example, propellant burning. An example of the model considered above is given in the work on burning ethyl nitrate by Hildenbrand and others (*1*), who measured the surface temperature at sufficiently low rates (~0.1 cm./cm./sec.) to ensure meaningful thermocouple measurements and found it to be about 30°C. less than the corresponding boiling point at the bomb pressure. (The ethyl nitrate apparently volatilizes intact below about 10 atm.) The difference is not especially quantitative in view of the uncertainty of the surface location, but it does indicate a measurable departure from equilibrium conditions. The difference would be expected to be greater for higher burning rates.

A fundamental treatment of steady-state phase transitions will have wide application not only in propellant burning but also in conventional mass transfer processes such as extraction, humidification, and distillation. A usual assumption in these latter processes is thermodynamic equilibrium at the transfer interface. There have been numerous attempts to investigate this assumption, but none have employed the recent developments in steady-state irreversible thermodynamics.

A result which may be interpreted as the maximum rate of evaporation from a surface at equilibrium is given by the Knudsen equation (*2*):

$$G = \alpha\left(\frac{W}{2\pi RT}\right)^{\frac{1}{2}}P \qquad (1)$$

This relation comes from kinetic theory and gives the number of molecules striking (and remaining on) the surface. Hence it may be equated to the evaporation rate *only* at equilibrium. The accommodation coefficient is the ratio of the actual rate to the number of molecules striking the surface. Unfortunately, there is no way to predict it *a priori*.

Apparently the only previous attempt at a fundamental study of nonequilibrium at phase interfaces was that of Schrage (*3*), who recognized the necessity of such a situation and developed many interesting ideas. The significance of his results, however, is lessened by several questionable assumptions, notably that the departure from equilibrium in the gas phase may still be found from an equilibrium velocity-distribution function, with a consequent modification of the rate of condensation. Also, he employs classical kinetic theory throughout, effectively limiting the treatment to monatomic molecules and excluding the more powerful and searching techniques of absolute-rate theory. Penner, from absolute-rate theory (*4*), derived an expression for the (unilateral) rate of evaporation which agreed with the Knudsen equation within a factor of e. The activated complex was assumed to be a molecule moving gaslike in two degrees of freedom in an area $(V^*)^{2/3}$. The other translational degree of freedom is along the reaction coordinate. The internal degrees of freedom are, at first, assumed to be equal in the initial state and activated complex. The simple free-volume theory is used for the initial liquid state. The result is an equation for the rate of evaporation larger than the Knudsen equation by a factor of e. Penner attributes this to lack of equilibrium between the initial state and the activated complex (a fundamental postulate of rate theory) and employs Hirschfelder's simple, nonequilibrium rate theory (*5*), which reduces the rate by a factor of approximately $1/e$. However, as Penner notes, there are no compelling reasons for using Hirschfelder's particular nonequilibrium formulation (between initial state and activated complex, *not* the general steady-state departure from equilibrium). It would seem that there are better places to look to improve the simple-rate-theory picture: the nature of the activated complex, the detailed molecular picture of the evaporation process, and improvements in the description of the liquid state. If a good expression for the evaporation process is obtained, it should be possible to relate the transmission coefficient of rate theory to the accommodation coefficient of the Knudsen equation.

The question as to whether the accommodation coefficient is close to unity or appreciably less has been the subject of much discussion and experimentation since the advent of the Knudsen equation (ca. 1880). Schrage has reviewed the older literature and concludes that the evidence for an accommodation coefficient less than unity is unreliable. Some careful and thorough work by Hickman and coworkers (*6*) on the absolute rate of vaporization of glycerol, water, and high-boiling phthlate esters in high-vacuum falling-film stills indicates that the accommodation coefficient is essentially unity, even for polar molecules such as glycerol and water, at least for a moving, fresh surface. They found that the vacuum-evaporation rate decreased markedly if the surface was contaminated or not continually renewed. This observation explains the low results obtained with many "stagnant" surfaces in the past. Penner, on the other hand, has drawn attention to the quantitative correlation between the accommodation coefficient as measured by several different workers, techniques for stagnant systems, and the free-angle ratio of Eyring and Kincaid (*7*). In a rough model the free-angle ratio may be interpreted as the ratio of the rotational partition function in the gas and liquid phase and thus is a measure of the hindered rotation of polar molecules in the liquid. It may be found by several methods, the most reliable being the comparison of free volumes from vapor pressure and velocity-of-sound data. The former should include the hindered rotation (or vibration) effect, but the latter should not. In Penner's absolute-rate theory of evaporation, the free-angle ratio becomes a multiplier of the Knudsen equation [Equation (1)]. The accompanying table illustrates the agreement obtained (*8*).

Liquid	Experimental Accommodation coefficient	Theoretical Free-angle ratio
CCl_4	1.0	1.0
C_6H_6	0.90	0.85
$CHCl_3$	0.16	0.54
C_2H_5OH	0.020	0.018
CH_3OH	0.045	0.048
H_2O	0.036–0.040	0.04
glycerol	0.052–0.105	0.077

These two well-substantiated but apparently conflicting situations for the evaporation can be explained by either of two hypotheses. (1) The lowered evaporation (or sublimation) rate is due in many cases to a lowering of the temperature of the evaporating surface because of the heat of vaporization, which is supplied by radiation from the surroundings. Littlewood and Rideal (*9*) have emphasized this point of view and have shown that the *accommodation coefficients* they found for several long-chain acids and alcohols could be explained by a few degrees of temperature difference. Other subsidiary experiments are cited to support this contention, such as the rise in evaporation rate when the phase change took place on a mercury droplet, which presumably improved the heat supply to the surface. (2) Alternately, an ordered layer (of unknown thickness) exists on stagnant surfaces of polar molecules which exhibits the expected hindrance to evaporation, but as the surface becomes turbulent or is constantly renewed some of the liquid forces disappear and the evaporation becomes normal, that is, approaches the maximum Knudsen rate. Thus there should be a hydrodynamic effect on the interphase mass transfer, at least for polar liquids. Emmert and Pigford (*10*), in studying gas absorption in flowing liquids, found the accommodation coefficient more or less proportional to the Reynolds number of the flowing liquid (water). It is not apparent why the molecular constitution of the condensed phase should be important for liquids and not for solids.

BASIC RELATIONS FOR A ONE-COMPONENT SYSTEM

Initially a pure liquid evaporating in a steady-state system will be considered, but many of the relations developed will be valid for any phase transition. Two relatively uncommon variables will be found convenient: ξ, the progress of reaction, and A, the affinity (not to be confused with the Helmholtz free energy); both parameters were introduced by DeDonder (*11*, *12*) in his formulation of thermodynamics to include the irreversibility of chemical reactions. ξ usually describes the fractional extent of completion of a chemical reaction but may be used with physical transformations such as phase changes and order-disorder transitions in alloys. The affinity A is a thermodynamic state function which is closely related to the irreversibility in the system, owing to the chemical reaction of certain physical changes as above. It is defined by

$$dQ' = A d\xi \geqq 0 \qquad (2)$$

where dQ' is the quantity needed to make the Second Law an equality. For a reversible process

$$dS = dQ/T$$

dQ' is then defined by

$$dS - \frac{dQ}{T} \equiv \frac{dQ'}{T} > 0 \qquad (3)$$

for an irreversible process. dQ is the energy the system exchanges with its environment, and dQ' arises from irreversible changes in the interior of the system. Thus dQ' and A are always positive (or zero). The usual array of thermodynamic relations may be derived involving the affinity (see references *11* and *12* for details). In particular, the affinity may be expressed in terms of the chemical potentials (μ_i) of the chemical components or phases undergoing the changes being considered

$$A = -\sum \nu_i \mu_i \qquad (4)$$

Also, the temperature and pressure dependence are given by

$$\frac{\delta}{\delta T}\left(\frac{A}{T}\right)_{P,\xi} = \frac{1}{T^2}\left(\frac{\delta H}{\delta \xi}\right)_{T,P} \qquad (5)$$

and

$$\left(\frac{\delta A}{\delta T}\right)_{T,\xi} = -\left(\frac{\delta V}{\delta \xi}\right)_{T,P} \qquad (6)$$

It is now possible to derive an expression for the affinity of a phase change in a steady-state system. The affinity will then be related to the net and unilateral rates of the transformation. The starting point is the total differential of A/T in the variables T, P, and ξ. The variable ξ here measures the transition liquid $\longrightarrow$ gas.

$$d\left(\frac{A}{T}\right) = \left[\frac{\delta\left(\frac{A}{T}\right)}{\delta T}\right]_{P,\xi} dT + \left[\frac{\delta\left(\frac{A}{T}\right)}{\delta P}\right]_{T,\xi} dP + \left[\frac{\delta\left(\frac{A}{T}\right)}{\delta \xi}\right]_{P,T} d\xi \qquad (7)$$

In terms of dA Equation (7) becomes, with the aid of Equations (5) and (6),

$$dA = \frac{A + \left(\frac{\delta H}{\delta \xi}\right)_{T,P}}{T} dT - \left(\frac{\delta V}{\delta \xi}\right)_{T,P} dP - \left(\frac{\delta A}{\delta \xi}\right)_{P,T} d\xi \qquad (8)$$

Two important properties of open steady-state systems are now utilized: time independence of all properties, that is, $dA = 0$; and the fact that an open system which undergoes a change with all composition variables constant behaves like a closed system with ξ constant; that is, $d\xi = 0$. In other words, the problem is to find the variation of dP with dT in the system at constant affinity and composition. Equation (8) thus becomes

$$\frac{A + (\delta H/\delta\xi) dT}{T} = \left(\frac{\delta V}{\delta \xi}\right) dP \qquad (9)$$

For evaporation of a pure liquid

$$\frac{\delta H}{\delta \xi} = Q_{vap}, \qquad \frac{\delta V}{\delta \xi} = \Delta V_{vap} \qquad (10)$$

An equation analogous to the Clausius-Clapeyron equation results, but for an open system:

$$\frac{dP}{dT} = \frac{A + Q_{vap}}{T \Delta V_{vap}} \qquad (11)$$

With the usual approximations of the ideal gas law and neglect of the liquid volume compared to the gas volume, Equation (11) becomes

$$\frac{dP}{P} = (A + Q)\frac{dT}{T^2} \qquad (12)$$

For a closed system (no net mass transfer) $A = 0$, and Equation (12) reduces to the conventional Clausius-Clapeyron equation. Both A and Q in Equation (12) are always positive quantities, and so the effect of a nonzero value of A is to increase the effective heat of vaporization. On an ln P vs. $1/T$ plot, therefore, the line for an open system will lie above the static vapor pressure. This is precisely the situation in burning ethyl nitrate (below about 10 atm.).

An expression for the affinity in terms of the rates of the phase change may be derived from Equation 4. In this case

$$A = \mu_L - \mu_G \qquad (13)$$

If the phases are in equilibrium, $A = 0$ and $\mu_L = \mu_G$. Otherwise the chemical potentials in the two phases are not equal. For a chemical reaction it may readily be shown that Equations (4) and (13) take the form

$$A = RT \ln \frac{K}{Q} \qquad (14)$$

It may now be supposed that the rates of phase changes may be written in terms of rate constants and concentration factors.

$$M_f = k_f F_f(C)$$
$$M_b = k_b F_b(C) \tag{15}$$

for the forward and back *reaction* rates. In terms of these rates, Equation (14) becomes

$$A = RT \ln \frac{k_f/k_b}{[F_b(C)/F_f(C)]} \tag{16}$$

since $K = k_f/k_b$ and $Q = F_b(C)/F_f(C)$
M is given by

$$M = M_f - M_b = M_f\left(1 - \frac{M_b}{M_f}\right)$$
$$= M_f\left(1 - \frac{k_f F_b(C)}{k_f F_f(C)}\right) \tag{17}$$

If the affinity is introduced with the aid of Equation (16), Equation (17) becomes

$$M = M_f\left[1 - \exp\left(-\frac{A}{RT}\right)\right] \tag{18}$$

Equation (18) is a general relation between reaction rate and affinity. It is usually nonlinear, in contrast to other irreversible processes such as diffusion and heat conduction. Only when $A/RT \ll 1$ does Equation (18) yield a linear relation between rate (flux) and affinity (force):

$$M = M_f \cdot \frac{A}{RT}, \quad \frac{A}{RT} \ll 1 \tag{19}$$

For a measurable nonequilibrium effect in phase changes, the exponential relation, Equation (18), must be used. Solving Equation (18) for A and substituting in Equation (12), one obtains

$$\frac{d \ln P}{d(1/T)} = \frac{-Q}{R} + T \ln\left(1 - \frac{M}{M_f}\right) \tag{20}$$

The second term on the right of Equation (20) is a correction to the Clausius-Clapeyron equation. M_f is usually quite large compared with M, and the correction is quite small, but each particular case must be investigated. Especially in propellant burning, there are likely to be appreciable departures from equilibrium at the high phase-change (burning) rates.

The vapor pressure and bomb pressure are functions of temperature and surface temperature in Figure 1 for burning ethyl nitrate, the departure from equilibrium of the surface temperature being outside the limits of experimental error. The expected effect on the basis of the value of M_f from the Knudsen equation is not so great. For $M = 0.028$ cm./sec., $t_{surface} = 105$°C., there results from Equation (1) for $EtONO_2$

$$M_f^e = 23.7\phi \text{ cm./sec.} \tag{21}$$

where M_f^e is the forward (evaporation) rate *at equilibrium*, and ϕ is the free-angle ratio or accommodation coefficient. The best estimate of ϕ is 0.07; therefore the correction term in Equation (20) is negligible. Equation (21) applies only at equilibrium and hence is an upper limit to the true value of the evaporation rate.

In principle one should be able to calculate both M and M_f in Equation (20) from absolute-rate theory, but this is not possible with the present knowledge of the structure of the liquid and the detailed molecular picture of the evaporation process.

MULTICOMPONENT SYSTEMS

An expression for the departure from equilibrium at a phase interface in a multicomponent system may be derived from Equations (14) and (18):

$$\frac{Q_i}{K_i} = 1 - \frac{M}{M_{fi}},$$
$$M = M_{fi}\left(1 - \frac{Q_i}{K_i}\right) \tag{22}$$

where K and Q are now interpreted as the equilibrium and nonequilibrium distribution coefficients for component i. The departure from equilibrium is given by the ratio of M/M_f, as with a one-component system. The problem of comparing this equation with experiment is the same as before: lack of a means of calculating M_f. Also, in any practical system one must necessarily have *intra*phase transfer effects, which complicate the observation of *inter*phase processes. There have been several such studies in the chemical engineering field (*10*, *13*, and *14*).

One of the objects of all these studies was to determine the validity of the usual assumption in mass-transfer work of physical equilibrium at the transfer interface. The lack of agreement of the data with equations based on the equilibrium assumption was interpreted as evidence of departure from equilibrium.

Sinfelt and Drickamer employed a semiempirical equation at the transfer interface which is very similar to Equation (22):

$$M = \frac{\text{net}}{\text{flux}} = \alpha\left[C(0^-, t) - \frac{C_{0^-}^{+}}{C_{0^+}^{+}} C(0^+, t)\right] \tag{23}$$

where α is the *interface transfer coefficient*, $C(0^-, t)$ and $C(0^+, t)$ are the actual concentrations on either side of the interface, and the superscript crosses denoting equilibrium quantities. Thus for no resistance $\alpha \rightarrow \infty$, and for high resistance $\alpha \rightarrow 0$. It is readily seen on comparing (22) and (23) that

$$M_f = \alpha C(0^-, t) \tag{24}$$

that is, the unilateral forward rate is taken to be proportional to the interface concentration, and α has the nature of a rate constant. Sinfelt and Drickamer give an equation for α from absolute-rate theory and experimental barrier heights $\Delta F^{\ddagger}$ for several systems. It would be desirable to calculate these $\Delta F^{\ddagger}$'s from an *a priori* molecular model of the interface transfer process.

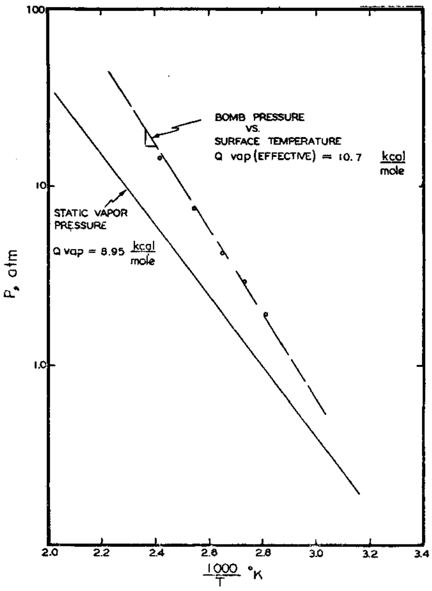

Fig. 1.

In connection with a study of the evaporation of small drops of high-boiling esters, Monchick and Reiss (*15*) have also derived an expression similar to (22). They assumed the rate of emission from the liquid surface to be given by the Knudsen equation while the condensation rate was found from the gas distribution function, modified to account for the flux to the surface. The result, in the present notation, is

$$M = \frac{M_{fi}\left(1 - \dfrac{n_i}{n_i^0}\right)}{1 - \alpha'/2}$$

where n_i is the actual number density at the surface, and n_i^0 is the equilibrium density corresponding to the surface temperature. It is not apparent how the factor $(1 - \alpha'/2)$ is to be reconciled with Equation (22).

NOTATION

A = thermodynamic state function, g./(sq. cm.)(sec.)
a = interface transfer coefficient
a = accommodation coefficient
dQ = energy the system exchanges with its environment
dQ' = uncompensated heat
G = rate of evaporation

K = usual equilibrium constant
M = net rate of phase change
n_i = number density at surface
n_i^0 = equilibrium density
P = pressure
Q = nonequilibrium concentration function
R = usual gas constant
T = absolute temperature
V^* = volume/molecule in the liquid
W = molecular weight

Greek Letters

μ_i = chemical potentials of the chemical components or phases undergoing the changes being considered
ν_i = stoichiometric coefficients

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Manuscript received Sept. 18, 1957; revised Nov. 29, 1957; accepted Nov. 29, 1957.

On Phase Equilibrium at the Gas-Liquid Interface During Absorption

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That phase equilibrium exists at the gas-liquid interface during gas absorption is usually assumed in the analysis and design of absorption equipment, but the validity of this assumption has been in doubt since Higbie's pioneering gas-absorption studies. Accurate measurements are reported herein of the absorption rates at 25°C. of carbon dioxide into short water jets in which the liquid was in laminar flow. The jets issued from circular nozzles of about 1.5-mm. diam., flowed intact downward through an atmosphere of carbon dioxide at average velocities of from 75 to 550 cm./sec. over distances of 1 to 15 cm., and were collected in a receiver slightly larger in diameter than the nozzles. The measured absorption rates are in excellent agreement with predictions based on unsteady state diffusion theory, when one assumes interfacial equilibrium. It is concluded from these results and those of other investigators that equilibrium prevails at a freshly formed, relatively clean, carbon dioxide–water interface and that the same statement probably applies to the absorption of other slightly soluble gases in water.

Evidence is discussed which indicates that an accumulation of minute quantities of surface-active materials may seriously reduce the rate of gas absorption, either by affecting the hydrodynamic characteristics of the system or perhaps by offering resistance to the transfer of solute molecules across the interface.

That phase equilibrium exists at the gas-liquid interface has commonly been assumed in applications of the film theory (*21*, *32*) and the more realistic penetration theory (*6*, *15*, *16*, *32*) to gas absorption. In attempting to test the validity of this assumption, various previous investigators have obtained conflicting results (*4*, *7*, *8*, *11*, *16*, *23*, *25*, *35*). It seems likely that this lack of agreement is due principally to inadequate knowledge of the fluid dynamics of the different flow systems employed, although in certain cases it may arise from unknown chemical reaction effects, inaccurate diffusivity values, and so forth. Several careful studies have been published recently. From data obtained with their novel rotating-drum apparatus Danckwerts and Kennedy (*7*) concluded that there may be a small interfacial resistance to mass transfer in the carbon dioxide–water system. Lynn, Straatemeier, and Kramers (*23*) decided on the basis of their wetted-wall column experiments that interfacial equilibrium exists in the sulfur dioxide–water system. Cullen and Davidson (*4*) concluded from jet-absorber experiments that interfacial equilibrium exists in the carbon dioxide–water system, and in a companion study employing a wetted-sphere absorber (*8*) they confirmed this conclusion and found that it is probably also true in the absorption of a number of other slightly soluble gases.

The present investigation was undertaken to resolve the controversy on the basis of careful physical-absorption measurements carried out at short liquid-exposure times and with a relatively simple flow system amenable to mathematical analysis. At the time of its inception laminar liquid jets similar to those described herein had been utilized in surface-tension studies (*27*) and in a few absorption studies (*9*, *24*, *25*); subsequent applications in absorption

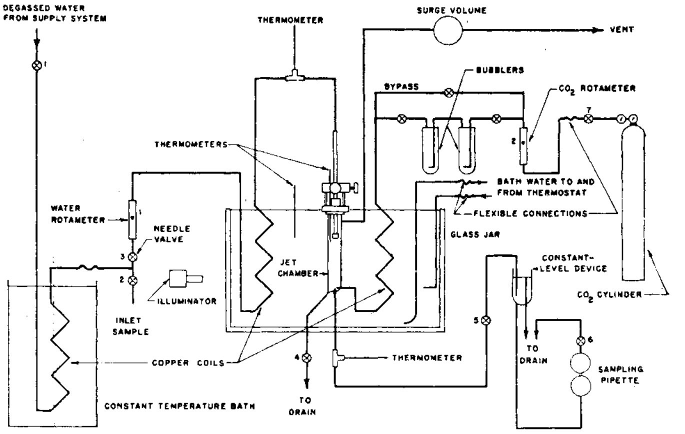

Fig. 1. Flow diagram of jet apparatus.

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