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Publication Date

1974-10-01

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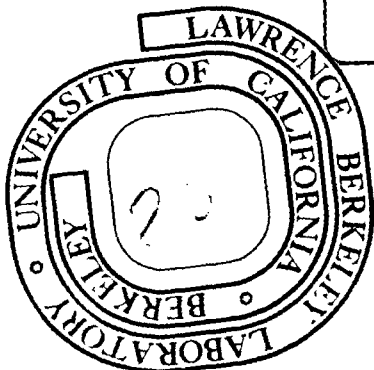
Alan W. Searcy and Dario Beruto

October, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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THE KINETICS OF ENDOTHERMIC DECOMPOSITION REACTIONS:

I. STEADY STATE CHEMICAL STEPS

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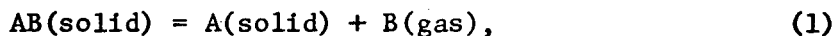
ABSTRACT

When the solid product of an endothermic decomposition reaction is porous, the rate limiting chemical step is usually assumed to be a surface step of the gaseous product or of a precursor of that product. It is shown, however, that the rate of such a reaction may also depend upon (a) rates of diffusion in the reactant phase, (b) the rate of transfer of the solid reaction product at the reactant-product interface, and/or (c) the thermodynamic stability of the solid product. A general rate equation for steady state decomposition in vacuum is derived in terms of the rate constants for four substeps of the overall reaction and of the thermodynamic activity of the solid product. Solutions are given for six limiting cases when either a single substep or a coupled pair of steps of a decomposition reaction significantly influence its rate. The dependence of the apparent activation enthalpy for decomposition on activation enthalpies for individual reaction steps and the enthalpy of formation of the solid reaction product are found for limiting cases. The rate equations are compared with recent measurements of the rate of

decomposition of calcite single crystals in vacuum. Those experimental data are most simply explained as reflecting formation of a metastable modification of calcium oxide with near equilibrium activities for each reaction step except desorption of carbon dioxide. An experiment to test this possible mechanism is suggested.

I. Introduction

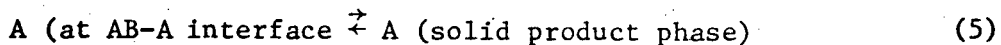
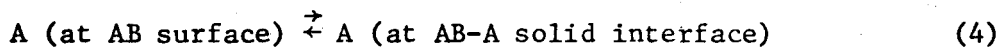
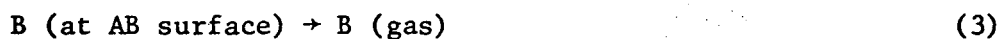
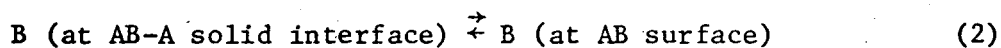
Reactions in which a single solid reactant yields a new solid phase plus a gaseous product, that is, reactions which can be described by the general equation



are usually called decomposition reactions. The kinetics of exothermic and endothermic decomposition reactions are very different from each other, and the kinetics of endothermic decomposition reactions which yield a porous solid product are characteristically different from those which yield non-porous solids.¹

A model of Polanyi and Wigner² and models derived from absolute reaction rate theory³ are used by recent reviewers^{4,5} to interpret the kinetics of endothermic decomposition reactions when the solid decomposition product is porous. These models assume that the rate limiting chemical step is a surface or desorption step of the eventual gaseous reaction product. Surface steps of the eventual gaseous products are also assumed to determine the kinetics of congruent vaporization reactions.^{6,7} We expected, therefore, that a transition state model which has proved useful for interpreting the kinetics of congruent vaporization⁸⁻¹¹ should be directly applicable to interpretation of endothermic decomposition reactions. After study, however, we have come to disbelieve the assumption that only surface steps need be considered in analyzing rate data for endothermic decomposition reactions.

Consider Figure 1, which is a schematic drawing of the relationship between the reactant solid AB and the porous product solid phase of reaction (1) during the period after nucleation is complete when such a reaction often proceeds at a constant rate per unit area of reactant.^{1,4} These spatial relationships can be maintained and reaction (1) can proceed at a constant rate only if at least the following separate steps occur at coupled net rates:



For convenience in discussing these steps later, they can be rewritten in symbolic form as



The arrows are written to indicate that, when the reaction is carried out in vacuum, the surface step for the eventual gaseous product (3') is necessarily unidirectional, but the other steps may have significant reverse fluxes. A complete list of symbols and their definitions is given in Appendix B.

For steady state decomposition to continue, those atoms or molecules of B that happen to be initially located in a volume element of AB phase which is replaced by a particle of solid product A must diffuse in the AB phase or along the interface between AB and the solid product phase to a pore, eq 2. Similarly, those atoms or molecules of A that are in a volume element of the AB phase which is replaced by a pore must diffuse to a growing particle of the solid product. Furthermore, growth of a solid phase by addition of atoms or molecules from another solid phase may sometimes be slow.¹² Equation 5 describes this interface transfer process.

Equations 2 through 5 are the minimum number of steps required to describe the steady state decomposition process. The surface step, (3), can be viewed as made up of a series of substeps of the same kinds as envisaged in the terrace-ledge-kink model for vaporization.^{6,7} Furthermore, when a complex solid decomposes, the particles that diffuse may not be the neutral molecules that constitute the eventual gaseous product, but a set of atoms or ions for which coupled diffusion has the net effect of movement of the molecules. For example, when calcite (CaCO_3) decomposes, diffusion of CO_3^- ions toward the pores and of an equal number of O^- and Ca^{++} ions away from the pores would have the same net effect as movement of equal fluxes of carbon dioxide molecules and calcium oxide molecules. For such a solid, eqs 2 and 3 express the net effect of the coupled processes.

The central purpose of this paper is to derive rate equations which describe the kinetics of steady state decomposition reactions in vacuum, not only when a slow step involving the eventual gaseous product is

encountered, but when any of the other three steps may be slow enough to influence the rate. The dependence on temperature of each of the steps (2) through (5) will be analyzed, and the extent to which the nature of the rate limiting chemical step, or steps, can be deduced from rate measurements and from the temperature dependence of rate measurements will be discussed with particular reference to experimental data for calcite.¹³ In a second theoretical paper, the influence of the porous solid product layer and the effect of product gas on the rate of steady state decomposition will be analyzed.¹⁴

II. Thermodynamic Background

There is clear experimental evidence that thermodynamic activity gradients rather than concentration gradients are the driving forces in chemical reactions.^{15,16} Furthermore, for heterogeneous systems, the thermodynamic relationships between activities of a given component in different phases, and for binary systems, the thermodynamic relationships between activities of the different components of any particular phase can be used to simplify the rate equations. Consequently, rate equations for decomposition reactions will be developed in terms of activities rather than of concentrations. The pertinent thermodynamic relationships between activities of components in binary systems are reviewed in this section of the paper.

The gaseous product of a decomposition reaction in a binary or pseudo-binary system such as symbolized by reaction (1) has at any specified temperature a single equilibrium dissociation pressure. At any temperature above absolute zero, however, the binary phase is stable over a finite range of compositions and the activities of each component

of the phase are functions of composition over that composition range.¹⁷

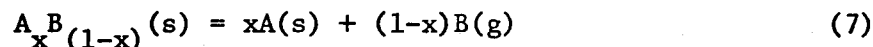
In general, the narrower the composition range over which the phase is stable, the more rapidly the activities of its components vary with composition. Thus, for example, at a temperature for which an equilibrium dissociation pressure $P_B(d)$ for reaction (1) is 10^{-6} atm, an increase of P_B to 1 atm often is associated with a change in the composition of the solid AB phase which is too small to detect. But the activity of the non-volatile component A relative to pure solid A, if equilibrium is maintained (and if the difference between the pressure and fugacity of the gas can be neglected), changes according to the equation:

$$a_A = \frac{\exp(-\Delta G_1^0/RT)}{P_B} \quad (6)$$

where ΔG_1^0 is the free energy change in reaction (1) when the AB phase of the particular composition for which the equilibrium pressure is P_B dissociates to yield pure solid A and B gas at one atmosphere pressure. Here and elsewhere in the paper it is assumed that the solubility of component B in pure solid A can be neglected so that the activity of A in the AB phase that is saturated with component A is 1. Whenever the solubility of B in pure solid A is known to be significant, corrections to the thermodynamic equations can readily be made.¹⁸

Although the activities of each component of a phase of narrow composition limits may change markedly with very small changes in composition the free energies of decomposition reactions usually do not change by measurable amounts when the reactant is initially at a composition different from that for which $a_A = 1$ and $P_B = P_B(d)$. If a particular

decomposition reaction were to show a measurable variation of free energy of formation with composition, eq 1 would take the more general form



where x is the mole fraction of component A. Then eq 6 becomes

$$a_A^x = \frac{\exp(-\Delta G_1/RT)}{P_B^{(1-x)}} \quad (8)$$

where ΔG_1 is the free energy change when $A_x B_{(1-x)}$ decomposes according to reaction (7) to pure solid A and B gas at one atmosphere pressure.

Usually the standard state for a gaseous chemical component is chosen to be the ideal gas at 1 atmosphere pressure so that the activity of the gas is numerically equal to its pressure in atmospheres. For the purposes of this paper, however, it is convenient to define the activity of B for any particular composition of the AB phase as the ratio of the partial pressure of B for that composition, P_B , to the equilibrium decomposition pressure $P_B(d)$ for each temperature. This definition combined with eq 6 yields $a_A \cdot a_B = 1$ for the AB phase when it is at internal equilibrium, not only when it is saturated with component A at unit activity, but also when the activity of A is at higher or lower values. For example, if $P_B(d) = 10^{-6}$ atm when $a_A = 1$, then when $P_B = 1$ atm, $a_A = 10^{-6}$ and, by the definition for a_B just given, $a_B = 10^6$.

A decomposition reaction can proceed at a finite rate only if the AB phase is supersaturated with respect to component A so that the activity of component A in the AB phase is greater than 1. For supersaturated solutions which are at internal equilibrium, the relationship $a_A \cdot a_B = 1$ should be essentially as good an approximation as it is for the thermodynamically stable composition range because the phase boundary does not reflect any discontinuity in properties of the AB phase but only the coincidence in activities of the chemical components in phase AB and in solid phase A.

Complete internal equilibrium cannot be achieved by a phase undergoing decomposition at a finite rate, however. The product $a_A \cdot a_B$ may remain essentially unity throughout the AB phase, but the separate activities must have gradients. If component A is to move from phase AB to solid phase A, the activity of component A must have maximum values at the AB surfaces at the centers of the pores and must have minimum values under the centers of each particle of solid A. Similarly, the activity of component B must reach a maximum under the centers of particles of the solid reaction product and a minimum at the surfaces of the AB phase at the centers of the pores.

If one of the chemical components is much more mobile than the other, the less mobile component may not be able to rearrange locally under the steady state reaction conditions to produce the atomic coordinations and distances characteristic of the equilibrium phase of the particular local composition. If local equilibrium is not maintained, the local product $a_A \cdot a_B$ will be greater than unity. Accordingly, in development of the rate equations, the equilibrium constants for reaction (1) at surfaces

and interfaces will be called K_s and K_i to recognize the possibility of significant deviations from local equilibrium.

Decomposition reactions often yield as the direct solid product, not the stable crystal modification of the solid product, but a metastable crystal modification or an amorphous form of the solid.^{1,4} In either event, the activity of the product, which can be called a_{Ap} , is not unity but

$$a_{Ap} = \exp(\Delta G_p / RT) \quad (9)$$

where ΔG_p is the positive free energy of formation of the metastable form of solid A from the stable form. When the interphase transfer of component A by eq 5 is a near equilibrium process, the activity of component A on the AB-side of the interface, which can be called a_{Ai} , approaches as a limit a_{Ap} , and then, if local equilibrium is assumed in the AB phase at its interface with the solid product,

$$a_{Ai} \cdot a_{Bi} \cong a_{Ap} a_{Bp} = \exp(\Delta G_p / RT) a_{Bp} \quad (10)$$

where a_{Bi} is the activity of B on the reactant side of the interface and a_{Bp} is the activity of B that would be reached in the solid product if B were brought to equilibrium in that phase. As long as the solubility of B in the solid product phase is small, the value of a_{Ap} is insensitive to whether or not component B reaches its equilibrium concentration in the solid product phase. If a_{Ai} approaches a_{Ap} then a_{Bi} can approach a_{Bp} whether or not component B reaches its small solubility limit in

product A. Equation 10 shows that, when the solid reaction product is metastable, the maximum activity that can be attained by component B, regardless of reaction mechanism, is not unity but $\exp(-\Delta G_p/RT)$ where the exponential has a value less than unity.

III. The Rate Equations for Steady State Decomposition

Consideration of the spatial relations when the reaction front is advancing at a constant rate into the decomposing solid phase (Figure 1) shows that the average diffusion distances that must be traversed by particular atoms or molecules are functions of their initial positions relative to the advancing pores and particles of the solid reaction product. For example, an A atom or molecule originally located in a volume element of the AB phase that is swept through by a growing particle of the solid reaction product need not diffuse at all. (There must be at least a small variation of the activity of component A in phase AB with position relative to distance from the center of the interface between each solid product particle and the AB phase.) And the minimum distance over which an A atom or molecule that is originally under a pore must diffuse is its distance to the boundary between the pore and the solid product phase.

Suppose that the flux of component A that must diffuse per unit area of that part of the surface of AB which is fronted by pores is j_A . That flux is described by a family of equations

$$j_A = \sum_n (f_n a_{Asn} - f_n' a_{Ain}) \quad (11)$$

where, for example, f_n is the rate constant for movement in the forward direction over one of the characteristic steady state paths, f'_n is the rate constant for the reverse direction over the same path, a_{Asn} is the activity of component A at the particular point of the AB phase surface at which the n'th diffusion path is initiated, and a_{Ain} is the activity of A at the point in the interface between the solid reactant and solid product at which the n'th path is terminated.

To simplify eq 11, it will be assumed that each activity of the kinds a_{Asn} and a_{Ain} can be replaced by average activities at the surface, a_{As} , and interface, a_{Ai} , respectively. The summation $\sum f_n$ can be called k_4 and the summation $\sum f'_n$ can be called k'_4 . Then the diffusion flux of component A is $j_A = k_4 a_{As} - k'_4 a_{Ai}$, where the rate constants k_4 and k'_4 are identified as summations that depend upon the assumption that the activities at the ends of the various diffusion paths can be approximated by average values. Similarly, if j_B is defined as the flux of component B that must diffuse per unit area of interface between the solid product phase A and the reactant then $j_B = k_2 a_{Bi} - k'_2 a_{Bs}$ where k_2 and k'_2 are composite rate constants for diffusion reaction (2).

The rate of the surface step for component B which is described by reaction (3) can be written $J_B = k_3 a_{Bi}$ where J_B is the total flux of B leaving each unit area of AB phase. For reaction (5), the step of transfer of component A at the interface between solid product and solid reactant, the reverse flux may not be negligible. The net flux of component A that leaves each unit area of the AB phase is $J_A = k_5 a_{Ai} - k'_5 a_{Ap}$ where k_5 and k'_5 are the forward and reverse rate constants for step 5.

The steady state decomposition of AB is thus characterized by four interdependent rate equations. The equations that describe steps 2 through 5 of the overall reaction are respectively:

$$j_B = k_2 a_{Bi} = k_2' a_{Bs} \quad (12)$$

$$J_B = k_3 a_{Bs} \quad (13)$$

$$j_A = k_4 a_{As} - k_4' a_{Ai} \quad (14)$$

$$J_A = k_5 a_{Ai} - k_5' a_{Ap} \quad (15)$$

There are four important restrictions on the steady state reaction:

$$J_A = J_B \quad (16)$$

$$j_A = j_B \quad (17)$$

$$a_{Ai} \cdot a_{Bi} = K_i \quad (18)$$

$$a_{As} \cdot a_{Bs} = K_s \quad (19)$$

Equation 16 expresses the requirement imposed by the stoichiometry: the flux per unit area of A and that for B must be equal during steady state decomposition. Equation 17 relates the steady state diffusion fluxes of components A and B in or on the AB phase. Equations 18 and 19

express the relationships between activities and equilibrium constants at the interface i between the reactant and solid product and at the AB surfaces bounded by pores.

In Appendix A it is shown that the four restrictions on the steady state system can be used to obtain a general solution in which all the activities other than the activity of the product phase have been eliminated. However, the physical meaning of the general equation is not easy to grasp. Here we derive the solutions that describe the kinetics for six limiting cases. When component A is mobile enough to maintain the activity of component A near equilibrium for the expression

$a_A = 1/a_B$ throughout the reactant and solid product phases during steady state decomposition, the rate may be limited only by a surface step for the gaseous product, eq 3, or only by the rate of diffusion of the eventual gaseous product in the AB phase, eq 2. No limiting rate equation depends solely on a step for component A because the driving force for endothermic decomposition is the activity gradient between component B in the reactant and in the vacuum. But when the net flux that would result for component A if the activity gradients were established solely by slow processes for component B are less than the net flux for component B, the activities of the two components must change until the fluxes become equal. There are in consequence four limiting rate equations which depend on the coupled fluxes that result from pairing one of the two possible slow steps for component B with one of the two possible slow steps for component A. Then, from eqs 12 and 13

$$(k_2 a_{B1} - k_2' a_{Bs}) = k_3 a_{Bs}$$

so that

$$a_{Bs} = k_2 a_{Bi} / (k_2 + k_3)$$

and from (13)

$$J_B = \frac{k_2 k_3 a_{Bi}}{k_2 + k_3} \quad (20)$$

If diffusion were an elementary (single step) reaction, consequences would be that $k_2 = k_2'$ and $k_4 = k_4'$ because for elementary reaction steps the forward rate constant divided by the reverse rate constant is equal to the equilibrium constant^{19,20} and here the definitions of activities make the equilibrium constant for each diffusion process equal to unity. Diffusion is a process that reflects the sum of a sequence of steps so that the proof for elementary reactions is not directly applicable. We expect, however, that usually $k_2 \cong k_2'$ and $k_4 \cong k_4'$, and we will assume these equalities to simplify eq 20. When component A in the reactant phase at its interface with the solid product is assumed to be at equilibrium with solid product A, $a_{Bi} = a_{Bp} = K_i / a_{Ap}$ and eq 20 yields two limiting solutions. For $k_2 = k_2' \gg k_3$, that is when the rate constant for diffusion of component B is large relative to its rate constant for desorption,

$$J_B = k_3 a_{Bp} = k_3 \exp(-\Delta G_p / RT) \quad (21)$$

If the solid product is the thermodynamically stable form of solid A this reduces to

$$J_B = k_3 \quad (21a)$$

Equation 21a is the form usually assumed for steady state decomposition reactions,^{1,2} but if the solid product is metastable, (21) applies with $a_{Bp} = 1/a_{Ap}$ where $a_{Ap} > 1$ so that $a_{Bp} < 1$. When $k_2 \ll k_3$

$$J_B = k_2 a_{Bp} = k_2 \exp(-\Delta G_p/RT) \quad (22)$$

Two more limiting equations are obtained from eq 20 when diffusion of component A is assumed to be rapid so that equilibration of A with component B in the reactant phase is essentially maintained but transfer of component A to the product phase by step 5 is assumed to be irreversible so that $k_5 a_{Ap}$ can be neglected relative to $k_5 a_{Ai}$. Then substitution of eqs 18 and 15 into 20 yields

$$J_A \cdot J_B = \frac{k_2 k_3 k_5 K_1}{k_2 + k_3}$$

Since $J_A = J_B$, this expression has the solution

$$J_B = (k_3 k_5 K_1)^{1/2} \quad (23)$$

when $k_2 = k_2 \gg k_3$ or

$$J_B = (k_2 k_5 K_1)^{1/2} \quad (24)$$

when $k_2' \ll k_3$.

When diffusion of component A and desorption of component B are assumed to be slow, the product $J_A \cdot J_B$ is $(k_4 a_{As} - k_4' a_{Ai})(k_3 a_{Bs})$. Then if $k_4' a_{Ai} \ll k_4 a_{As}$, that is if the reverse flux for diffusion of component A is small compared to the forward flux.

$$J_A = J_B = (k_4 k_3 K_s)^{1/2} \quad (25)$$

The sixth limiting expression is obtained by use of eqs 17, 18 and 19 to eliminate unknown activities in the two diffusion equations, (12) and (14). The result is a quadratic equation in a_{Bs} and a_{Bi} ,

$$a_{Bs}^2 - a_{Bs} \left[\frac{k_2}{k_2'} a_{Bi} + \frac{k_4' K_i}{k_2 a_{Bi}} \right] + \frac{k_4' K_s}{k_2} = 0. \quad (26)$$

If $K_s \cong K_i \cong K$, $k_2 \cong k_2'$, and $k_4 \cong k_4'$, eq 26 has two solutions

$$a_{Bs}' = a_{Bi} \quad (27)$$

and

$$a_{Bs} = \frac{k_4 K}{k_2 a_{Bi}} = \frac{k_4 a_{Ai}}{k_2} \quad (28)$$

If the activities, a_{Bs} and a_{Bi} are identical, there can be no net diffusion flux. Equation 28 can be regarded, however, as describing the limit that is approached when diffusion in the AB phase is rapid enough relative to the interphase transfer processes at the surface and at the

reactant-solid product interface so that activity gradients in the reactant phase are negligible, and some step other than diffusion is rate limiting.

The value of a_{Bs} must always be less than that of a_{Ai} during the progress of decomposition so the solution $a_{Bs} = k_4 a_{Ai} / k_2$, eq 28, can be physically meaningful only when $k_4 < k_2$, that is when component A diffuses more slowly than does component B.

Substitution of (22) into (13) with $a_{Ai} \cong a_{Ap}$ yields

$$J_B = \frac{k_3 k_4 a_{Ap}}{k_2} \quad (29)$$

for the predicted flux when diffusion of component B is slow and the rate constant for diffusion of component A is smaller than that for component B.

IV. Temperature Dependence of the Rate Equations

Comparison of measured temperature dependences of the rates of decomposition reactions with rates which are predicted for the various limiting rate equation may help to identify the rate limiting processes as do such comparisons for vaporization reactions.⁸⁻¹¹ Accordingly, predicted temperature dependences are derived in this section of the paper. The temperature dependence of the rate constants of the surface and interfacial steps of the overall reaction can be evaluated by means of transition state theory²¹ and for the diffusion steps by means of an atomistic interpretation of Fick's first law of diffusion.²²

Transition state theory assumes that, during reaction, equilibrium is maintained between the reactant(s) and an activated complex. The

flux in the forward direction of any elementary reaction step then is assumed to be the product of the concentration of the activated complexes and the average frequency with which they decompose to yield the reaction product(s). When the reverse reaction of an elementary step cannot be neglected, the net flux in the forward direction can be assumed to be the difference between the forward flux produced by the process just described and a reverse flux which is assumed to be governed by an independent equilibrium between the product(s) of the forward reaction and activated complexes.

Thus for the elementary step described by reaction (5)

$$J_A = g_5 C_5^* - g_5' C_5'^* \quad (30)$$

where g_5 is the frequency with which activated complexes of concentration C_5^* which are produced by equilibrium with the reactants, decompose to yield reaction products, and g_5' and $C_5'^*$ are the corresponding terms for the reverse reaction. The equilibrium assumption of transition state theory can be used to eliminate the unknown concentrations of activated complexes from the equation. The result for reaction (5) when the most general thermodynamic formulation of transition state theory²¹ is used is

$$J_A = g_5 a_{Ai} \exp(-\Delta G_5^*/RT) - g_5' a_{Ap} \exp(-\Delta G_5'^*/RT) \quad (31)$$

where ΔG_5^* and $\Delta G_5'^*$ are the free energies of activation for the forward and reverse reactions.

For the surface transfer process described by reaction (5), further simplification of eq 31 is possible. It has been proved that the kinetic factor, such as g_5 , for the forward direction of any elementary reaction step is equal to the kinetic factor for the reverse of the same elementary step, here g_5 .²⁰ Furthermore, the free energy of activation for the forward reaction minus the free energy of activation for the reverse reaction equals the free energy of the reaction. But here at equilibrium $a_{Ap} = a_{Ai}$ so the free energy of reaction is zero and $\Delta G_5^* = \Delta G_5'^*$. Consequently,

$$J_A = g_5 \exp(-\Delta G_5^*/RT) (a_{Ai} - a_{Ap}) \quad (32)$$

The expression for the surface step, reaction (3), which is obtained in the same manner, is simpler because in vacuum there is no significant reverse reaction.

$$J_B = g_3 \exp(-\Delta G_3^*/RT) a_{Bs} \quad (33)$$

A diffusion flux, such as that which is produced by reactions (2) or (4) can be described by the equation²²

$$J = b \exp(-\Delta G_c^*/RT) \frac{dC}{d\ell} \quad (34)$$

where b is the product of kinetic and geometrical terms, ΔG_c^* is a free energy of activation and $dC/d\ell$ is the concentration gradient of the diffusing species. When activity gradients rather than concentration

gradients are assumed to be the driving forces for diffusion, the flux must be described by an equation of the same form but with a different free energy of activation because activities are products of concentrations and activity coefficients. The activity coefficients are exponential functions which modify the calculated free energy of activation. Thus a diffusion flux is described by

$$J = b \exp(-\Delta G^*/RT) \frac{da}{d\ell} \quad (35)$$

With the assumptions for steady state decomposition (a) that the free energy of activation ΔG^* is independent of activity in the activity gradient between source and sink of the diffusing species, and (b) that the activity gradient is constant over the total path distance between source and sink, eq 35 becomes

$$J = b \exp(-\Delta G^*/RT) \frac{\Delta a}{\Delta \ell} \quad (36)$$

Then for reactions (2) and (4)

$$j_B = h_2 \exp(-\Delta G_2^*/RT) (a_{Bi} - a_{Bs}) \quad (37)$$

and

$$j_A = h_4 \exp(-\Delta G_4^*/RT) (a_{As} - a_{Ai}) \quad (38)$$

where h_2 and h_4 are new constants which incorporate the constant path lengths l_2 and l_4 .

Each of the rate constants that must be known in order to evaluate the temperature dependence of the rate equations for endothermic decomposition reactions has now been demonstrated to be the product of a term of the form $\exp(-\Delta G^*/RT)$, of a kinetic factor, and perhaps of a geometrical factor. The present paper will not attempt an evaluation of the various possible geometrical and kinetic factors that might be considered appropriate for the various rate constants, but only remarks on their sensitivity to the temperature of reaction.

The frequencies of decomposition of surface and condensed phase activated complexes are usually assumed to be either independent of temperature or to vary directly with temperature.²³ When desorption or separation from an activated surface site or particle is rate limiting, the kinetic factor varies with $T^{-1/2}$.¹⁰ Geometrical factors should be nearly independent of temperature. An exponential of the form $\exp(-\Delta G/RT)$ can always be rewritten as $\exp(\Delta S/R)\exp(-\Delta H/RT)$, where ΔS and ΔH are the entropy and enthalpy changes of the process. For any particular chemical process or mechanism of diffusion ΔS and ΔH are essentially independent of temperature.

Temperature variations with $T^{-1/2}$, T^0 , and T^1 power are normally negligible in comparison to those that arise from an exponential in $-\Delta H/RT$. It can be concluded, therefore, that if decomposition rates are measured for a reaction for which the limiting rate eq 21a applies, the slope of a plot of $\ln J_B$ versus $1/RT$ is $-\Delta H_3^*$, where ΔH_3^* is the enthalpy of activation for the surface step of the gaseous component B. When the

product phase is metastable and the reaction is governed by rate eq 21, the same kind of plot yields $-(\Delta H_3 + \Delta H_p)$ where ΔH_3^* is the enthalpy of the slow surface step for the gaseous reaction product B and ΔH_p is the enthalpy of formation of the metastable solid phase A from the stable form of solid A. Similarly for decomposition reactions which are governed by the limiting rate eqs 23 or 29 plots of $\ln J_B$ versus $1/RT$ yield respectively $-(\Delta H_3^* + \Delta H_5^*)/2$ if $(K_1 \cong 1)$ and $-(\Delta H_3^* + \Delta H_4^* - \Delta H_2^* + \Delta H_p)$, respectively.

A particular decomposition reaction may be governed by one of the limiting rate laws in one temperature range, but by another in a different temperature range. Over the intermediate range between the two regions governed by the limiting laws, curvature should be found in plots of $\ln J_B$ versus $1/RT$ because the total apparent activation enthalpies characteristic of the various limiting laws will almost never have the same values.¹¹

V. Discussion

It has been shown in this paper that diffusion and an interface transfer step from reactant to solid product are essential elements of a decomposition reaction, and these steps may in principle influence the reaction. For three of the limiting rate equations derived, the rate depends upon the thermodynamic stability of the solid product.

Decomposition rates measured for single crystals in vacuum must depend upon the chemical steps rather than upon vapor phase transport, which probably commonly determines rates measured for powders heated in inert atmospheres.^{24,13} But the relative importance of the various essential chemical steps cannot be determined from the vacuum decomposition

rates alone because kinetic factors and free energies of activation can be assumed for each of the limiting rate equations that will reproduce any experimentally observed rate data.

Comparison of the rate data with thermodynamic data for the reaction, however, can serve to distinguish whether or not all reaction steps except desorption of thermally equilibrated gaseous products are near equilibrium processes. If so, special forms of eq 21 or 21a must describe the kinetics. The arguments will be illustrated with our recent data for calcite (CaCO_3) decomposition.¹³

Just as a maximum possible flux for vaporization in vacuum can be calculated from the Hertz-Knudsen-Langmuir (H-K-L) equation and the equilibrium vapor pressure,^{6,8} a maximum possible flux in vacuum, J_{max} can be calculated from the H-K-L equation and the equilibrium dissociation pressure for a decomposition reaction:

$$J_{\text{max}} = \frac{P_B(d)}{(2\pi M_B RT)^{1/2}} \quad (39)$$

where M is the molecular weight of the gaseous decomposition product.

Equation 39 is a special case of eq 21. For a decomposition reaction to occur at the rate given by eq 39 requires that all steps of the overall reaction except desorption of the gaseous product in its equilibrium state be essentially at equilibrium--the reasons for this conclusion are essentially the same as given for congruent vaporization reactions in reference 10. If the measured decomposition flux is identical with that predicted by eq 39 from the equilibrium dissociation pressure $P_B(d)$ for the stable form of solid A, then eq 21 with

$k_3 = (2\pi M_B RT)^{-1/2} P_B(d) = (2\pi M_B RT)^{-1/2} \exp(-\Delta G_d/RT)$ and $a_B = 1$, i.e. eq 21a would be the correct rate equation for decomposition.

The experimental data for calcite do not agree with the predictions of this form of eq 21. The measured rate was found to be only about 2% of the calculated maximum rate for the midpoint of the experimental range, and the apparent enthalpy of the decomposition reaction was 49 Kcal compared to 41.5 Kcal for the equilibrium decomposition reaction.

Agreement is not expected, however, because a 30 micron thick layer of a metastable form of calcium oxide was found to separate the decomposing calcite surface from a growing layer of calcium oxide in its stable crystalline form. Stable calcium oxide cannot be at thermodynamic equilibrium with either the metastable modification of calcium oxide or with the calcite on the opposite side of the layer of metastable calcium oxide; metastable modifications of solids transform exothermally and irreversibly to their stable modifications. Rao et al.²⁵ have observed that an exothermic reaction occurs when the initial product of calcite decomposition is heated. Transformation of the metastable oxide to the stable form probably takes place irreversibly whenever the stress produced by mismatch of the lattice planes of the metastable oxide to the (10 $\bar{1}$ 1) plane of the calcite on which the metastable oxide grows epitaxially exceeds a critical value. For the single crystals and temperature range studied, the stress level apparently is reached when the metastable oxide layer is about 30 microns thick.

It is reasonable to hypothesize that all steps of decomposition to the metastable calcium oxide except desorption to thermally equilibrated

carbon dioxide are near equilibrium with the calcite. This hypothesis can be tested if the heat and enthalpy of formation of the metastable oxide is determined. If the hypothesis is correct, then eq 21 with $k_3 = (2\pi M_B RT)^{-1/2}$ is the appropriate rate equation and the activity $a_{A_p} = 1/a_{B_p}$ in eq 21 is

$$a_{CaO} = \frac{J_{max}}{J_o} = \exp[(\Delta S_d^o - \Delta S^*)/R] \exp[-(\Delta H_d^o - \Delta H^*)/RT] \quad (40)$$

where J_o is the experimentally observed flux and ΔS^* and ΔH^* are the apparent activation entropy and enthalpy obtained from the intercept and slope of a plot of $\ln J$ versus $1/T$. Substitution of known values of ΔS_d^o and ΔH_d^o into (40) yields 7.5 Kcal for the predicted molar enthalpy of formation of the metastable form of calcium oxide from the stable modification and 1 cal per degree for the molar entropy of formation. These values are of the correct sign and of appropriate magnitude for formation of metastable solids.

A test of this assumed mechanism by means of a calorimetric determination of the thermodynamic stability of the metastable calcium oxide might be difficult because the metastable oxide may not be easy to prepare except in the presence of excess stable calcium oxide. But the stability might be determined by measuring the back pressure of carbon dioxide that must be introduced to bring to zero the rate of decomposition of calcite to the metastable oxide. For that pressure $P_B(d,m)$ the activity of B is a_{B_p} whether or not the suggested interpretation is correct so that the free energy of formation of the metastable oxide is $-RT \ln P_B(d,m)/P_B(d)$. The ratio $P_B(d,m)/[J_o(2\pi M_{CO_2} RT)^{1/2}]$ should be 1

independent of temperature if the suggested interpretation is correct, but less than 1 if some step other than desorption of carbon dioxide is not maintained near equilibrium.

In our second theoretical paper we will show that the effect on decomposition rates of pressures of the product gas in the range between the apparent decomposition pressure of the reactant in vacuum and the equilibrium decomposition pressure can be used to further delineate the influence of the different substeps of the overall reaction on the reaction rate.

Acknowledgment

We appreciate advice on this study by Alfred Büchler and David J. Meschi. Support was provided by the United States Atomic Energy Commission.

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Appendix A

Substitution of eqs 13 and 15 of the text into eq 16 and of (12) and (14) into (17) yields the relations:

$$k_3 a_{Bs} = k_5 (a_{Ai} - a_{As})$$

$$k_4 a_{As} - k_4' a_{Ai} = k_2 a_{Bi} - k_2' a_{Bs}$$

which with (18) and (19)

$$a_{As} \cdot a_{Bs} = K_s$$

$$a_{Ai} \cdot a_{Bi} = K_i,$$

put four restrictions on the steady state decomposition process. The following definitions can be adopted: $k_4 a_{As} = x$; $k_4' a_{Ai} = y$; $k_2 a_{Bi} = w$; $k_2' a_{Bs} = z$; $(k_2' k_5) / (k_4' k_3) = \mu$; $(k_5 k_2) / k_3 = \theta$; $K_i k_2 k_4 = \zeta$; and $K_s k_4 k_2' = \rho$. Then the above four restrictions become

$$z = \mu y - \theta \tag{A1}$$

$$x + z = y + w \tag{A2}$$

$$yw = \zeta \tag{A3}$$

$$xz = \rho \tag{A4}$$

Combining the four relations yields

$$\frac{\rho}{(\mu y - \theta)} y + (\mu - 1)y^2 - \theta y = \zeta \quad (\text{A5})$$

The solutions that are obtained for this equation when $\rho = \zeta$ will be compared to results obtained in the text. It is readily shown that ρ and ζ are approximately equal when

$$(k_4 a_{As} - k_4' a_{Ai}) / k_4' a_{As} \ll k_4 / k_4' \quad (\text{A6})$$

and when

$$(k_2 a_{Bi} - k_2' a_{Bs}) / k_2' a_{Bi} \ll k_2 / k_2' \quad (\text{A7})$$

But inequalities of the kinds given by (A6) and (A7) would be established when the activity gradients between the surfaces and interfaces of the AB phase are small compared to the activities themselves.

When $\rho = \zeta$ eq A5 can be factored to yield

$$y - \frac{\rho}{\mu y - \theta} = 0 \quad (\text{A8})$$

and

$$\frac{y\rho}{\mu y - \theta} - \rho = 0 \quad (\text{A9})$$

Solution of (A8) yields $J_A = J_B = (k_3 k_5 k_4)^{1/2}$, which is eq 23 of the text.

Equation A9 yields

$$y = z = \frac{\theta}{\mu - 1} \quad (\text{A10})$$

$$x = w = \frac{\rho(\mu - 1)}{\theta} \quad (\text{A11})$$

But $y = k_4' a_{Ai}$ and $z = k_2' a_{Bs}$ so that (A10) gives

$$a_{Bs} = \frac{k_4'}{k_2'} a_{Ai} \quad (\text{A12})$$

Since a_{Bs} can never be larger than $1/a_{Ap}$ and a_{Ai} can never be smaller than a_{Ap} where $a_{Ap} \geq 1$, eq A12 has physical meaning only when k_4'/k_2' is less than 1.

Combining (A12) with eqs 13 and 15 of the text yields

$$J_A = J_B = \frac{k_3 k_4' k_5 a_{Ap}}{k_2 k_5 - k_3 k_4'} \quad (\text{A13})$$

Equation A13 gives the predicted flux when $k_4'/k_2' < 1$ and when $k_2 k_5 - k_3 k_4' > 0$. When $k_3 k_4'$ can be neglected relative to $k_2 k_5$, (A13) reduces to

$$J_A = J_B = \frac{k_3 k_4'}{k_2} a_{Ap} \quad (\text{A14})$$

which, if $k_2' = k_2$ and $k_4' = k_4$, is identical to eq 29 of the text.

Appendix B

Definitions and symbols used in the text:

1 as a subscript, identifies a quantity that is a characteristic of the overall decomposition reaction $AB(\text{solid}) = A(\text{solid}) + B(\text{gas})$.

2 as a subscript, identifies a quantity characteristic of the process $B(\text{interface}) \rightarrow B(\text{surface})$ or of its reverse.

3 as a subscript, identifies a quantity characteristic of the process $B(\text{surface}) \rightarrow B(\text{gas})$.

4 as a subscript, identifies a quantity characteristic of the process $A(\text{surface}) \rightarrow A(\text{interface})$ or of its reverse.

5 as a subscript, identifies a quantity characteristic of the process $A(\text{interface}) \rightarrow A(\text{product})$ or of its reverse.

A identifies the chemical component that forms the solid phase reaction product.

a_A is the thermodynamic activity of component A, subscripts i, p, or s identify the activity as specifically in the reactant phase at its interface with the solid product phase, in the solid product phase, or in the reactant phase at the surface of a pore.

a_B is the thermodynamic activity of component B defined as the ratio of its fugacity (assumed equal to its partial vapor pressure) divided by its standard fugacity (assumed equal to its partial vapor pressure) when the reaction $AB(\text{solid}) = A(\text{solid}) + B(\text{solid})$ is at equilibrium.

Subscripts i, p, and s have the meaning described for a_A .

AB is the reactant phase in a decomposition reaction.

b is a proportionality constant in diffusion equations.

B identifies the chemical component that forms the gaseous products of a decomposition reaction.

C is concentration.

C_5^* is the concentration of activated complex for reaction 5, $A(\text{interface}) \rightarrow A(\text{product})$, that is at equilibrium with component A in the AB phase at the AB-solid product interface.

$C_5'^*$ is the concentration of the activated complex for the reverse of reaction 5. This concentration of activated complex is at equilibrium with component A in the reaction product phase.

f_n and f_n' are the rate constants for the forward and reverse directions of a particular diffusion path.

g and g' are frequencies for decomposition of those activated complexes which are respectively at equilibrium with reactants and products of an elementary reaction step.

ΔG is a change in Gibbs free energy.

ΔG_d^0 is the free energy of decomposition of AB to pure solid A in its stable modification and to B gas at 1 atm pressure.

ΔG^* and $\Delta G'^*$ are the free energy of activation for the forward and reverse of an elementary reaction step.

ΔG_p is the Gibbs free energy for the formation of a metastable modification of solid product phase A from its stable modification.

h is a proportionality constant in a diffusion equation.

ΔH is a change in enthalpy

i is a subscript that identifies the AB phase side of the interface between the AB phase and the solid product phase.

j_A is the molar flux of component A that diffuses at or near the reaction front during steady state decomposition per unit area of that portion of the AB surface which is fronted by pores.

j_B is the molar flux of component B that diffuses between the solid product and the pores at or near the reaction front during steady state diffusion per unit area of interface between the AB phase and the solid product phase.

J_A is the molar flux of component A per unit area of reactant phase.

J_B is the molar flux of component B per unit area of reactant phase.

J_{max} is the maximum flux of component A and component B which can be calculated from thermodynamic data for the decomposition reaction and from the Hertz-Knudsen-Langmuir equation.

J_o is the molar flux of components A and B that is experimentally observed during steady state decomposition in vacuum.

k and k' are rate constants for forward and reverse reactions.

K is the equilibrium constant given by $\frac{a_A}{a_B}$.

l is the distance between the origin and end of a diffusion path.

M is molecular weight.

n identifies one of a set of diffusion paths for which the total diffusion flux is j_A or j_B .

p is a subscript that identifies the solid product phase.

P_B is the partial pressure for component B.

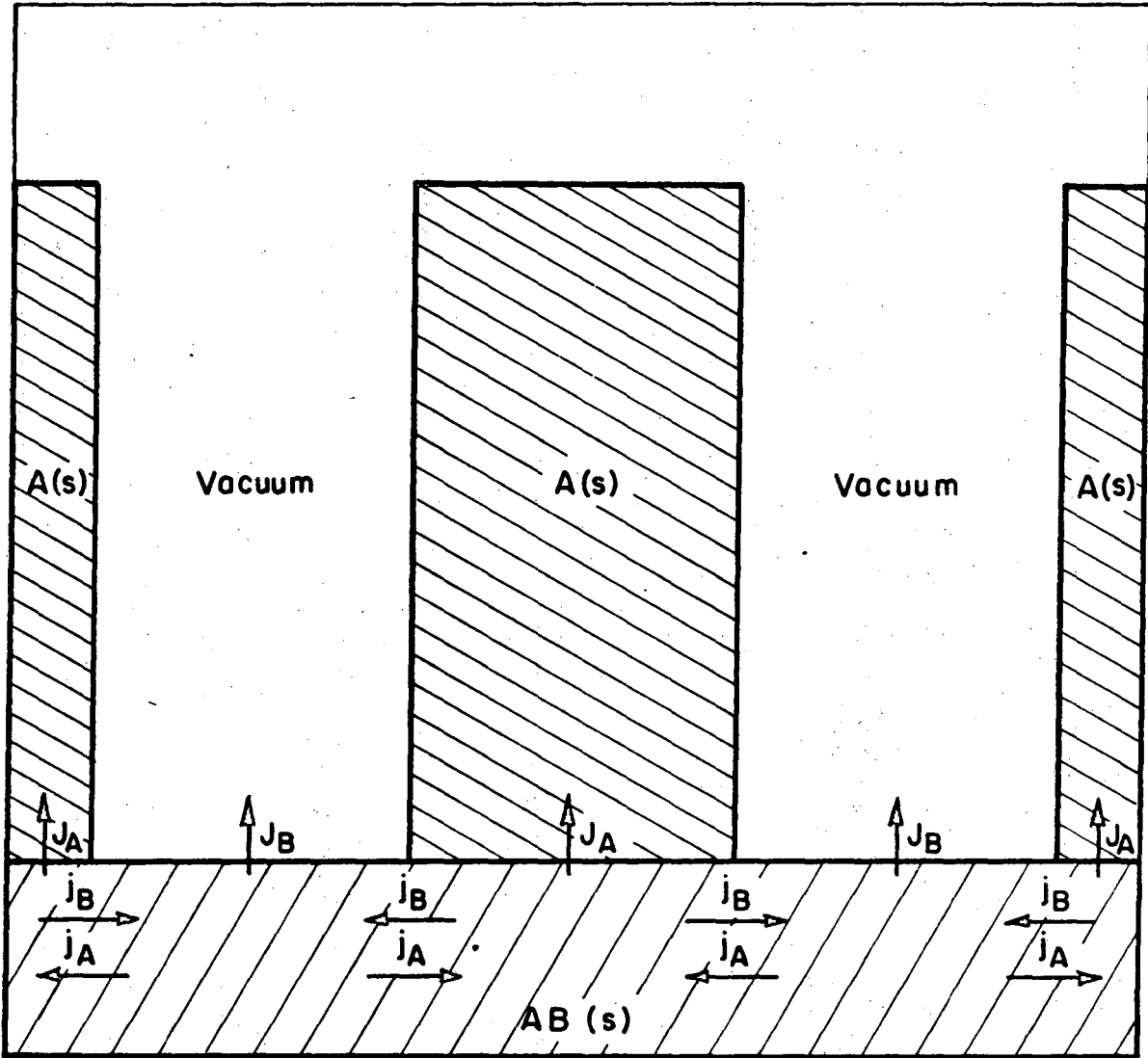
$P_B(d)$ is the partial pressure for component B when the reactant phase AB is in equilibrium with the most stable form of solid product phase A.

$P_B(d,m)$ is the partial pressure for component B when the reactant phase AB is in equilibrium with a metastable form of the solid product phase A.

R is the gas constant.

s is a subscript used to identify the surface of the reactant phase which is bounded by a pore.

ΔS is an entropy change.



XBL 748-6867

Fig. 1. Schematic drawing of the spatial relations for the steady state reaction $AB(\text{solid}) \rightarrow A(\text{solid}) + B(\text{gas})$.

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