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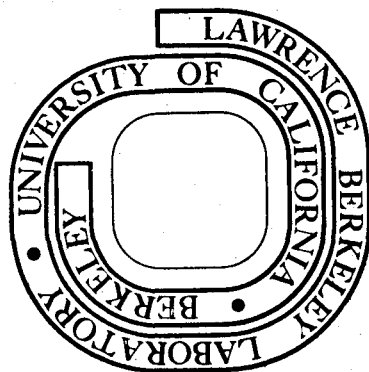
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THE KINETICS OF ENDOTHERMIC DECOMPOSITION REACTIONS:
II. EFFECTS OF THE SOLID AND GASEOUS PRODUCTS

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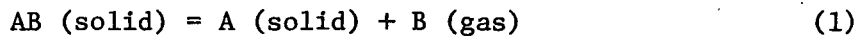
ABSTRACT

Decomposition rates are predicted to decrease linearly with increased pressure of the product gas if a chemical step for the gaseous component of the reaction is rate limiting, but to be a constant function of the difference between the reciprocals of the equilibrium decomposition pressure and the product gas pressure if a step for the solid reaction component is rate limiting. An equation which was derived by T. D. Sandry and F. D. Stevenson to describe the effect of tubular capillaries on the rates of vaporization from surfaces of known vaporization coefficients is adapted to describe the effect of porous solid barriers on the rates of decomposition reactions. Dependences of product fluxes on barrier thickness and of barrier thickness on time are also predicted to be different when a chemical step for the solid reaction component is slowest from the dependences when a step for the gaseous component is slowest. Equations are also described for use when both the product gas pressure and barrier thickness influence the reaction rate. The various rate equations are functions only of the activities of the reaction components, of measured rates in vacuo with negligible barriers, and of measurable transmission properties of the barriers. The theory is applied to interpret data for calcite decomposition.

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INTRODUCTION

Decomposition reactions, that is reactions which can be described by the general equation



where symbols A and B represent not only the two reaction products but also the two chemical components of a binary or pseudo-binary system, have probably been studied as much as any class of heterogeneous reactions. None-the-less, in a 1974 monograph of solid state reactions Schmalzried commented, "There is no general theory of decomposition reactions."¹

Recently, we provided the central elements of a general theory by identifying the four essential steps of a decomposition reaction, by deriving rate equations for six possible rate limiting processes in vacuo and by evaluating the effect of a metastable solid product on the rate equations.² Here we complete the theory for the post-nucleation period of reaction by deriving expressions for the dependence of decomposition rates on pressures of product gases and on thickness of layers of porous solid products or alternately on the time periods during which the product layers have grown.

The resulting equations predict two distinct classes of dependence of rates on pressure and on product layer thickness. In the discussion section we will briefly illustrate for calcium carbonate some applications and tests of the theory.

The Effect of Pressure of the Gaseous Product

With few exceptions, the solid products of decomposition reactions form as porous layers at the surfaces of the reactant particles. For reaction 1 to proceed when the product layer is porous requires four necessary substeps (see Fig. 1).² (a) A flux j_B formed from that portion of chemical component B which is at an interface between the solid reactant phase AB and the solid product phase must undergo solid state diffusion to the surface at a pore. (b) A flux J_B of component B must transfer from the AB surface to the gas phase. (c) A flux j_A formed from that portion of chemical component A which is at the AB surface fronted by a pore must diffuse on or in the AB phase to a particle of the solid product phase A. (d) A flux J_A must transfer from the AB phase across the interface to the solid product phase. Using the symbols i for interface, s for surface, and g for gas, these four reaction steps can be written in the order described as



The rate equations that correspond to the chemical process 2-5 are respectively

$$j_B = k_2 a_{Bi} - k_2' a_{Bs} \quad (6)$$

$$J_B = k_3 a_{Bs} - k_3' a_{Bg} \quad (7)$$

$$j_A = k_4 a_{As} - k_4' a_{Ai} \quad (8)$$

$$J_A = k_5 a_{Ai} - k_5' a_{Ap} \quad (9)$$

where each k is the rate constant (or for diffusion, the composite rate constant) for the forward direction of the reaction step indicated by the subscript and each k' is a rate constant (or composite rate constant) for the reverse of one of the four steps. a_{Bi} , for example is the thermodynamic activity for component B at the interface between the reactant and the solid product, and a_{Bs} is the activity of B on the surface of the reactant at the bottom of a pore. The diffusion flux j_B is defined as the flux of B per unit area of that part of the reactant which forms an interface with the solid product and j_A is defined as the diffusion flux of A per unit area of that part of the reactant which is fronted by pores, while J_A and J_B are fluxes per unit of total reactant surface plus interfacial area. It should be noted that these definitions are contrived to make all four fluxes numerically equal during steady state decomposition even though the numbers of A and B particles that must diffuse are not equal to each other or to the number of A and B particles that undergo reaction.

The rate constants for the forward direction of an elementary reaction divided by the rate constant for the reverse direction equals the equilibrium constant for any fixed set of experimental conditions³ even if the reaction is far from equilibrium and reactants and/or products have activity coefficients that differ from those found at equilibrium.⁴ For the reactions 2 through 5, the equilibrium constants are all unity, and 3 and 5 are elementary reactions so k_3 equals k_3' and k_5 equals k_5' . Reactions 2 and 4 are diffusion reactions which require a sequence of steps which may not have the same activation free energy

barriers at all points along the diffusion path. But for decomposition reactions the diffusion paths are short, and we will use the reasonable assumptions $k_2 \approx k'_2$ and $k_4 \approx k'_4$.

Suppose first that there is no significant pressure gradient of B along the pores through the product and that diffusion of component B in or on the reactant is slower than any of the other three necessary steps of the reaction. Then all steps of the overall reaction except step 6 have nearly equal forward and reverse fluxes, so that 1) component A can be expected to be essentially the same activity on both sides of the reactant-solid product interface, that is $a_{Ap} \approx a_{Ai}$, and 2) when the activity of B in the gas phase is made as high or higher than the activity of B in the surface in vacuo, the surface activity becomes almost the same as that of the gas, that is $a_{Bs} \approx a_{Bg}$.

Integral free energies of formation of the binary phases which undergo decomposition reactions usually change only negligible amounts with changes in composition of the phase, but the activities of the components can change by many orders of magnitude.^{5,6} It is convenient to assign unit activities to the solid reaction product when it is formed in its thermodynamically stable form and to the gaseous product, not when its pressure is 1 atm, but instead when its pressure has the equilibrium value for the decomposition of AB (solid) to the stable form of A (solid). With these definitions of activities, the product of the activities in a local region of the AB phase, for example at the reactant-solid is close to unity. Thus, $a_{Ai} \times a_{Bi} \approx 1$, and $a_{Bi} \approx 1/a_{Ai} \approx 1/a_{Ap}$. Substitution of $a_{Bi} \approx 1/a_{Ap}$ and $a_{Bs} \approx a_{Bg}$ into equation 6 gives for the net flux of B or A

-5-

$$J = k_2 \left(\frac{1}{a_{Ap}} - a_{Bg} \right) \quad (10)$$

If AB is at equilibrium with the stable form of solid A during decomposition, $a_{Ap} = 1$ and equation 10 reduces to

$$J = \frac{k_2}{P_{Beq}} \left(P_{Beq} - P_{Bg} \right) \quad (10')$$

where P_{Beq} is the equilibrium decomposition pressure for reaction 1. If AB is at equilibrium with the metastable form of solid A during decomposition, $a_{Ap} > 1$ and $a_{Bi} \approx 1/a_{Ap} < 1$. Then

$$J = \frac{k_2}{P_{Bm}} \left(P_{Bm} - P_{Bg} \right) \quad (10'')$$

where P_{Bm} , the equilibrium decomposition pressure for formation of metastable solid A, is less than P_{Beq} .

Equation 10'' predicts that if diffusion of B is rate limiting and a metastable form of solid A is produced, the rate of decomposition will be reduced to zero by a pressure P_{Bm} of the product gas which is lower than the equilibrium decomposition pressure. In practice, a decomposition reaction which is governed by 10'' at low pressures of background gas is likely at higher pressures to yield the stable solid product and follow equation 10' because the net flux for 10'' reaches zero when $P_{Bg} = P_{Bm}$ while the net flux for 10' is finite until P_{Bg} reaches $P_{Beq} > P_{Bm}$.

If a surface or desorption step of B is the slowest of the four steps necessary to the overall reaction, a similar line of argument leads to $a_{Bs} \approx a_{Bi} \approx 1/a_{Ai} \approx 1/a_{Ap}$ and the net flux of B is given by

$$J = k_3 \left(\frac{1}{a_{Ap}} - a_{Bg} \right) \quad (11)$$

Equation (11) can be expressed in alternate forms that differ from 10' and 10'' only in that k_3 replaces k_2 .

If the rate constant k_5 for the interfacial transfer step for component A is smaller than the rate constants for both of the steps for component B, a very different dependence on the pressure of B is predicted. Let k_B equal $k_2 k_3 / (k_2 + k_3)$, which reduces to k_2 if $k_3 \gg k_2$ or k_3 if $k_3 \ll k_2$. Then $k_5(a_{Ai} - a_{Ap}) = k_B(a_{Bi} - a_{Bg})$. When decomposition is carried out in vacuo, a_{Bg} is zero and $a_{Bi} = 1/a_{Ai}$ falls until the reduced activity for B and increased activity for A at the interface make J_A equal J_B .

Pressures of B gas only influence the reaction rate significantly when a_{Bg} is of the magnitude of a_{Bi} in vacuo or higher. Then $a_{Ai} = 1/a_{Bi} \approx 1/a_{Bg}$ and

$$J = k_5 \left(\frac{1}{a_{Bg}} - a_{Ap} \right) \quad (12)$$

If the solid product is the stable form, equation 12 can be written

$$J = k_5 P_{Beq} \left(\frac{1}{P_{Bg}} - \frac{1}{P_{Beq}} \right) \quad (12')$$

If the solid product is metastable, the equation in terms of pressures is

$$J = k_5 P_{Beq} \left(\frac{1}{P_{Bg}} - \frac{1}{P_{Bm}} \right) \quad (12'')$$

If diffusion of A is assumed to be the slowest process necessary to decomposition, a similar line of argument can be applied to yield equations that are identical to 12, 12' and 12'' except that k_4 replaces k_5 .

Effects of a Porous Solid Product

Sandry and Stevenson⁸ have derived an equation for the unit flux J

that will escape from a tube of Clausing correction C^9 when the source of the vapor is a surface of condensation coefficient (or vaporization coefficient⁴) α . Their equation can be put in the form

$$\frac{J}{J_0} = \frac{C}{C+(1-C)\alpha} \quad (13)$$

where J_0 is the unit flux that would escape from the surface if no tube impeded the Knudsen flow.

Actually, equation 13 can sometimes be used even though surface diffusion or hydrodynamic flow is the dominant mode of transport through a tube. If the tube is found experimentally to have a transmission coefficient C for a particular gas supplied from a reversible source (such as a bulb of the gas), then provided that C and α are independent variables, equation 13 gives the effective transmission coefficient from a source that emits a fraction α of the flux emitted by an equilibrium source.

Sandry and Stevenson's equation can be adapted for use in analysis of the effect of a porous product layer on decomposition rates by evaluating C as a function of layer thickness and by replacing α by a measure of the irreversibility of the slowest step for the gaseous component of the reaction. For relatively thick porous barriers, C has been shown experimentally to be equal to cf/ℓ , where f is the fraction of the cross-sectional area occupied by pores, ℓ is the barrier thickness, and c is a constant of the order of an average cross-sectional dimension of a pore if transport is by Knudsen flow or larger if surface diffusion is the dominant mode of gas transport.¹⁰ We will use $C = cf/(\ell + cf)$, to force J to approach J_0 , rather than infinity as ℓ approaches zero. An

alternate expression, $C = cf/(l+c)$, which forces J to approach fJ_0 as l approaches zero, is perhaps theoretically superior to the one we use, but leads to more cumbersome mathematical expressions. Differences in predictions of the two expressions are probably not measurable.

For vaporization or condensation reactions α is the fraction of those vapor molecules which upon striking the surface of their condensed phase come to complete equilibrium with the condensed phase rather than desorbing before equilibrium is complete.¹¹ In decomposition reactions, if diffusion of B is slower than its surface steps, equilibrium will only be maintained at the reactant-solid product interfaces. For such reactions we define a decomposition coefficient for the gaseous component as

$$\alpha_B = \frac{k_B (P_{Bg}/P_{Beq})}{(2\pi MRT)^{1/2} P_{Bg}} = \frac{k_2 k_3}{k_2 + k_3} \frac{1}{LP_{Beq}} = \frac{k_B}{LP_{Beq}} \quad (14)$$

where $(2\pi MRT)^{-1/2} P_{Bg}$ is the Hertz-Knudsen-Langmuir expression for the flux that strikes a surface when the pressure above the surface is P_{Bg} , M is the molecular weight of the gas, R is the gas constant, T is the absolute temperature, and $L = (2\pi MRT)^{1/2}$. With the definition $\alpha_B = k_B/(LP_{Beq})$, equation 13 applied to the porous barriers of decomposition reactions becomes

$$\frac{J}{J_0} = \frac{cf/(cf+l)}{cf/(cf+l) + [1-cf/(cf+l)]\alpha_B} \quad (15)$$

Equation (15) gives the predicted dependence of flux on product layer thickness if one of the two steps for component B is the slowest of the four steps of the decomposition reaction. According to (15) the product layer will have little effect so long as $\alpha_B \ll cf/(cf+l)$, but when $cf/(cf+l)$ becomes smaller than α_B , the flux will vary with $1/l$.

Suppose, however, that the interfacial transfer step (equation 5) for component A is slower than either step for B. In vacuo with a negligible porous barrier, the rate equation then is

$$J = (k_5 k_B \cdot a_{Ai} a_{Bi})^{1/2}, \quad (16)$$

where $a_{Ai} a_{Bi} \cong 1$.² The effective rate constant for the flux of B that leaves the interface, where the two components are at equilibrium, becomes the product of k_B and the right hand side of equation 15, which we will call g . Then

$$J = (k_5 k_B g)^{1/2} \quad (17)$$

which predicts that when $cf/(cf+l)$ becomes smaller than α_B (but not smaller than k_5) the flux will vary approximately as $1/l^{1/2}$.

If diffusion of A is the slowest step of decomposition in vacuo and diffusion of B is the next slowest step, the net flux when the porous barrier has negligible influence depends on the composite rate constant k_4 for diffusion of component A, and the constant k_2 for diffusion of component B. A porous barrier will then have no observable influence on the decomposition rate until the product gk_3 becomes as small as k_2 , and with smaller values of gk_3 the rate equation is

$$J = (k_4 k_3 g)^{1/2}. \quad (18)$$

Regardless of the rate equation that governs in vacuo, if l becomes sufficiently large, g will become smaller than all of the four rate constants. All steps of the decomposition except flow through the barrier will have nearly equal fluxes in both directions, and the limiting rate equation will approach

$$J = \frac{cf}{cf+l} J_o. \quad (19)$$

The Variation of Rates with Time

If the porous solid remains in place on the advancing front at which the decomposition takes place, each of the rate equations of the previous section that depends on ℓ implies a corresponding time-dependent equation. The number of moles of solid product formed per unit area of AB per unit time is $dn/dt = J$. If the reaction proceeds along a linear front, $dn = (f_A/V_A) d\ell$, where f_A is the fraction of the surface of AB that is covered by the solid product and V_A is the molar volume of the solid product phase.

When a step for component B is rate limiting, $J = gJ_o$, and therefore, $(1/g)d\ell = (V_A J_o / f_A) dt$. When the right hand side of equation 15 is substituted for g in this relation and it is integrated from zero time and thickness to time t and thickness ℓ , the relation found is

$$\frac{\alpha_B}{2cf} \ell^2 + \ell = \frac{V_A J_o}{f_A} t \quad (20)$$

Equation 20 predicts that the porous product layer thickness will be linearly dependent on time so long as cf/ℓ is large compared to α_B but that when $cf/\ell \ll \alpha_B$, then ℓ will approach a parabolic dependence on t ,

$$\ell = \left(\frac{2cfV_A J_o t}{\alpha_B f_A} \right)^{1/2} \quad (21)$$

It is interesting to note that this equation predicts that if the chemical steps of a decomposition reaction other than the final step of desorption are close to equilibrium, a growing porous coating causes the parabolic time dependence which is usually associated with non-porous, so-called protective coatings.

If for a decomposition reaction the rate constant for one of the steps of component A is smaller than gk_B , then $J = g^{1/2} J_0$ and integration yields

$$\left[\left(\frac{\alpha_B}{cf} \right)^3 \ell^3 + 3 \left(\frac{\alpha_B}{cf} \right)^2 \ell^2 + 3 \frac{\alpha_B}{cf} \ell + 1 \right]^{1/2} - 1 = \frac{3}{2} \frac{\alpha_B V_A J_0}{cf f_A} t \quad (22)$$

When $cf/\ell \gg \alpha_B$, the first two terms inside the square brackets can be neglected and equation 22 reduces to the same linear law found for small ℓ from equation 20. When $cf/\ell \ll \alpha_B$, but cf/ℓ is greater than the smaller rate constant for a step of component A, only the first term inside the square brackets need be retained. Then

$$\ell = \left(\frac{cf}{\alpha_B} \right)^{1/3} \left(\frac{3}{2} \frac{V_A J_0}{f_A} \right)^{2/3} t^{2/3} \quad (23)$$

The flux is $(f_A/V_A) d\ell/dt$. Differentiation of equation 21 yields

$$J = \left(\frac{c f f_A J_0}{2 \alpha_B V_A} \right)^{1/2} t^{-1/2} \quad (24)$$

and differentiation of equation 23 yields

$$J = \left(\frac{2 c f f_A}{3 \alpha_B V_A} \right)^{1/3} J_0 t^{-1/3} \quad (25)$$

The combined Effects of Solid and Gaseous Products

The probability that a gas molecule will traverse a porous barrier of transmission probability C and come to thermodynamic equilibrium with a surface at the opposite face of the barrier can be calculated by the same approach which was used by Sandry and Stevenson for calculating the probability of escape of a gas from a surface that has a superimposed barrier. We find for the flux of gas that condenses

$$J_c = \frac{\alpha_B C J_{Bg}}{C + (1-C)\alpha_B} \quad (26)$$

where the flux J_{Bg} which strikes the outer face of the barrier is LP_{Bg} .

The net flux when a step for B is rate limiting is then

$$J = g(J_o - \alpha_B J_{Bg}) = g\alpha_B L(P_{Beq} - P_{Bg}) \quad (27)$$

provided that g as defined by the right side of equation 15 and α_B are independent of the magnitude of forward and reverse fluxes over the range of background pressures between zero and P_{Bg} . Equation 27 should usually be valid if transport through the barrier is by Knudsen flow or by surface diffusion in a Henry's law adsorption layer. The variations of product layer thickness and of net flux with time which result from equation 27 are given by substituting $J_o - \alpha_B J_{Bg}$ for J_o in equations 21 and 23.

When the slowest step in vacuum is a step for the solid reaction component, the decomposition flux is given by equation 17 or 18 until the background pressure is as high or higher than $J_o/\alpha_B L$. The flux is then predicted by the same equation that applies when no porous layer is present, that is by equation 12 or by a similar equation in which k_4 replaces k_5 . But when the product layer has grown thick enough to make gk_B smaller than the smaller of k_4 and k_5 , equation 27 applies.

DISCUSSION

There is reason to believe that many, perhaps even most, measurements of decomposition reactions have been made under conditions for which the rates are limited by gas phase diffusion exterior to the pores of the reaction product or by thermal transport.^{12,13} Here, we will illustrate

applications and tests of the theory with our measured rates of decomposition of calcite (CaCO_3) single crystals at low reaction fluxes, which clearly should be limited by the chemical steps and/or by diffusion through pores of the solid product.¹³

We pointed out in our first theoretical paper² that the simplest interpretation of data for decomposition of single crystals of calcite (CaCO_3) in vacuo is that, except for desorption of CO_2 , all steps of the reaction to form a metastable modification of calcium oxide are at equilibrium. The metastable oxide was observed as a 30μ thick layer between undecomposed calcite and a growing layer of the stable oxide.¹³ We further pointed out that if this hypothesis were correct the heat of formation of the metastable oxide from the stable oxide should be the difference between the apparent heat of activation for decomposition and the equilibrium heat of the reaction, 7.5 kcal.²

By decomposing in vacuo calcite powder ground to less than 30μ diameter we have since prepared the metastable form of calcium oxide in isolation from the stable form. The heat of formation from the stable oxide proves to be only 3 kcal.¹⁵ Accordingly, the rate of decomposition in vacuo must be limited by an irreversible chemical step.

The fact that the rate of decomposition is unaffected by growth of a porous calcium oxide layer to at least the order of 1 mm in thickness requires one of two limiting interpretations.

If a step for the solid product is the slowest chemical step, so that equation 17 or 18 is rate limiting, g of that equation must not vary significantly with l under the conditions of study. But if Knudsen flow

is assumed, $cf/(cf+l)$ is estimated from the fact that pores are not resolvable at 30,000 magnifications in a scanning electron microscope to be less than 10^{-4} when l is 1 mm, while when equation 17 or 18 applies, α_B cannot be less than the square root of the ratio of the measured flux in vacuo, J_o , to the maximum possible flux, J_m . The ratio J_o/J_m is 10^{-5} for calcite (In our experimental paper,¹³ we incorrectly calculated J_m and reported $J_o/J_m \approx 10^{-3}$). Accordingly, for Knudsen flow g should decrease markedly with l in our experimental range. For g to be independent of l would only be possible if surface diffusion of CO_2 through the calcium oxide is efficient enough to saturate the pores with CO_2 . Such efficient surface diffusion would not be expected from measurements for CO_2 or similar gases at lower temperatures,¹⁰ but it seemed possible that a chemically activated mechanism of surface diffusion may be important at high temperatures. To test this possibility - which could have important practical applications if verified - we have undertaken experimental measurements of $cf/(cf+l)$ by passing CO_2 from an equilibrium source through the calcium oxide barriers which result from complete decomposition of calcite wafers in vacuo.¹⁶

The assumption that a step for the gaseous product is rate limiting provides a much simpler explanation of why the rate is independent of l . When a step for B is rate limiting for calcite α_B is given by $J_o/J_m = 10^{-5}$. But even for $l = 1$ mm, $cf/(cf+l)$ for Knudsen flow may still be of the order of 10^{-4} if the pore diameters are not much below the 10^{-4} mm resolution limit of the scanning electron microscope. Then with α_B small compared to $cf/(cf+l)$ equation 15 reduces to $J \approx J_o$, as observed.

This simple interpretation would not appear consistent with pore diameters that are more than an order of magnitude smaller than the maximum diameters set by resolution of the scanning electron microscope. In order to test this explanation more rigorously, we plan measurements with a transmission electron microscope, which is capable of much higher resolution. We hope also to investigate the effect of product layers on the rates over a range of thicknesses which may be great enough to make equation 19 become rate limiting.

One important prediction of our theory is that decomposition rates will vary inversely with the product gas pressure if the slowest chemical step is one for the solid reaction component, while if a step of the gaseous component is slowest, the net flux will decrease linearly as the product gas pressure increases toward its equilibrium value. Two sets of investigators have reported that the rate of decomposition of calcite varies inversely with the pressure of carbon dioxide gas.^{17,18} We at first thought, therefore, that their reported pressure dependence indicated a step for the calcium oxide reaction component to be rate limiting. But new measurements¹⁹ over a much longer pressure range than employed in the published investigations, while consistent with measurements of those investigations, show the decomposition rate to be nearly independent of CO_2 pressure at low pressures, where equation 10 predicts a strong pressure dependence.

The metastable form of calcium oxide which is present during decomposition in vacuo is not found when higher pressures of CO_2 are present during decomposition.¹⁴ The apparent inverse dependence of the rate on CO_2 pressure may be a consequence of changes in the quantity or

the degree of crystallinity of the metastable calcium oxide at the reaction interface with CO₂ pressure. We will attempt to correlate measurements of the morphology and crystallinity of the oxide layer with background CO₂ pressures and decomposition rates.

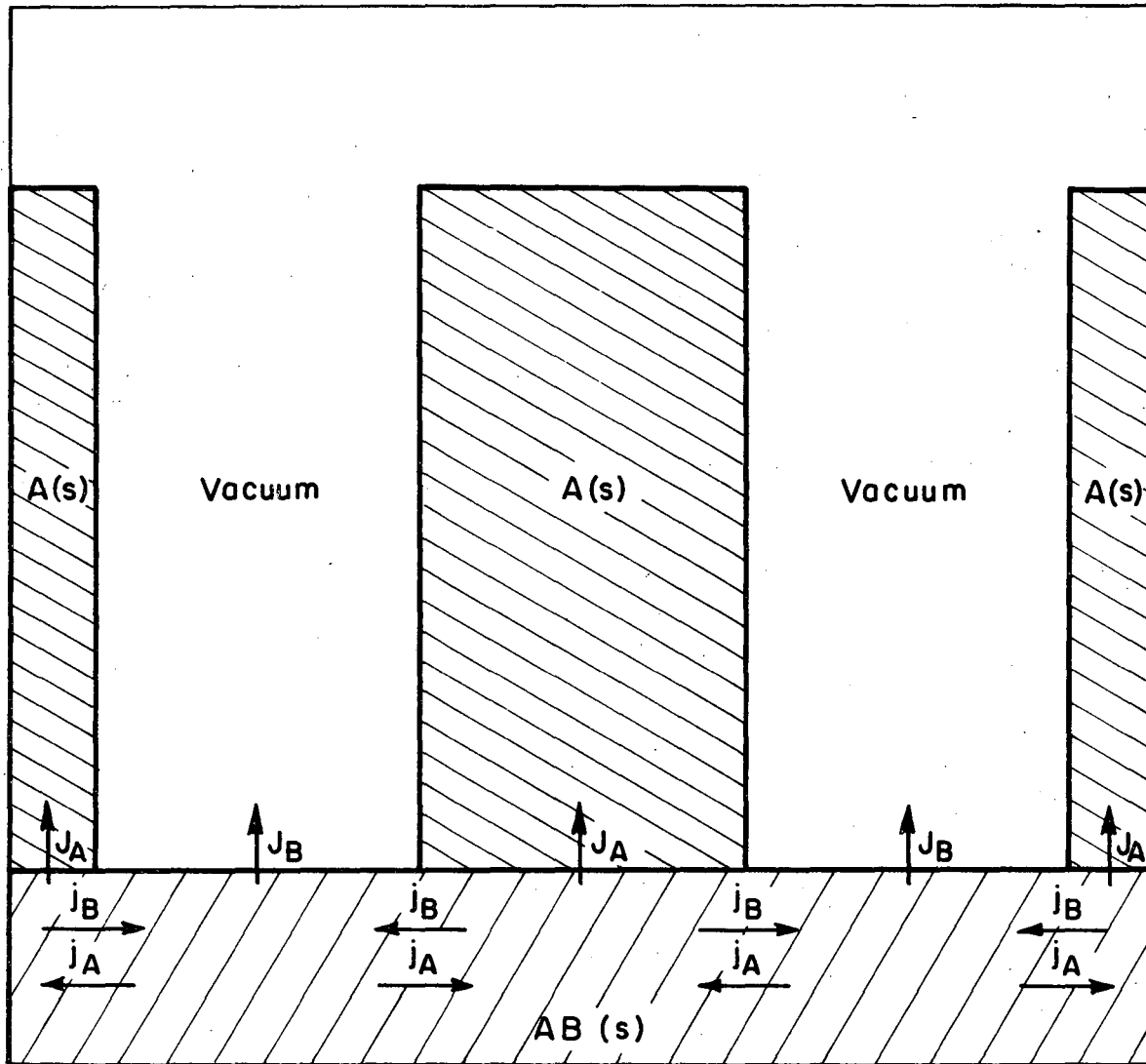
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Fig. 1. Schematic drawing of the spatial relations for the steady state reaction $AB(\text{solid}) \rightarrow A(\text{solid}) + B(\text{gas})$.

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