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Publication Date

1975-08-01

LBL-4120
Preprint c/

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THE EFFECT OF POROUS BARRIERS ON THE MOLECULAR
COMPOSITION AND TOTAL FLUX OF A REACTIVE GAS MIXTURE

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ABSTRACT

It is shown that the theoretically expected molecular exit fluxes through a porous barrier of a gas mixture that is governed by a pressure dependent equilibrium are functions of the equilibrium constant and of the atomic concentrations at the exit face of the barrier rather than of molecular weights and impingement pressures as are the relative escape molecular fluxes of a non-reactive gas mixture under Knudsen flow conditions. It is shown that the ratio of the total atomic escape flux of each elemental constituent to the total atomic impingement flux of that element for Knudsen flow should be a/ℓ where a is the same constant, of the order of the average diameter of barrier pores, for each element of a gas mixture whether or not the gas mixture is reactive and ℓ is the barrier thickness.

The equilibrium prediction is confirmed for the sodium chloride monomer/dimer equilibrium mixture passed through alumina barriers with pores of the order of 1 to 10 micron diameter and various thicknesses. Measured dimer fluxes are reduced by the barriers to less than 10^{-3} times the dimer fluxes in conventional effusion yet the measured fluxes agree to within about 30% with predictions from the measured monomer fluxes and the monomer/dimer equilibrium constant. The predicted equation for relative total atomic flux reduction is confirmed by measurement with

barriers of different thicknesses of flux reductions for sodium chloride vapor and for zinc vapor. The influence of porous barriers on the apparent heats of vaporization of monomers and dimers and the possibility of significant influence of surface diffusion on the experimental measurements are discussed.

I. Introduction

The catalysis by porous solids of reactions between non-equilibrium constituents of gas mixtures has been the subject of very extensive study. But the fact that a mixture of gases that is already at chemical equilibrium can undergo large changes in molecular composition as a consequence of Knudsen flow through a porous solid seems to have escaped notice.

The relative fluxes of any two non-reacting molecular species that pass through a porous barrier by Knudsen flow are related by

$$\frac{J_1}{J_2} = \frac{P_1^0}{P_2^0} \sqrt{\frac{M_2}{M_1}} \quad (1)$$

where J_1 , J_2 refer to the exit fluxes of molecules 1 and 2, respectively, P_1^0 , P_2^0 are the corresponding partial pressures on the source side of the barrier and M_1 and M_2 are the molecular weights.¹ However, we have reported in a preliminary communication evidence that if a pressure-dependent chemical reaction occurs between two (or more) molecular species of an equilibrium gas mixture, Eq. (1) is no longer valid.²

A related problem was analyzed by Voronin,^{3,4} who derived, on the assumption dimer and monomer vapor molecules equilibrate on the walls of a cylindrical effusion orifice, angular distributions of the monomers and dimers which differ from predictions of the Clausing equation. Grimley et al.^{5,6} obtained data on KCl and AgCl that were consistent with Voronin's predictions, but which they initially considered might also be otherwise explained. Further study^{7,8} gives good support to Voronin's

analysis.

Berkowitz et al.⁹ used a porous nickel barrier to reduce the total pressures of alkali halide vapors in the effusion chamber of a double oven cell but did not discuss the possibility of changes in the molecular compositions in the barrier. Their experimental results would be essentially independent of any effect of the barrier on composition because equilibration is expected in the effusion chamber.

In the following section of this paper an equation is derived for Knudsen flow through a porous barrier. The equation reduces to Eq. (1) for non-reacting gases but is also valid when reactions occur among components of the gas mixture, while Eq. (1) can then no longer be applied. The remainder of the paper reports an experimental study of the effects of porous alumina barriers on the total vapor flux and on monomer and dimer concentrations in sodium chloride vapor and then compares the theoretical predictions to the experimental findings.

II. Theoretical

Consider the effect of a chemically inert porous barrier on a gas mixture governed by the equilibrium reaction

where $g + h > 1$. For convenience, call the fluxes of $A_m B_n$, $A_q B_r$, and $A_s B_t$ that escape from the barrier J_1 , J_2 , and J_3 , respectively. If equilibrium is attained by the exit gas, the fluxes of J_1 , J_2 , and J_3 are related by the equilibrium constant for reaction 2 and known pressure-

independent constants:

$$K = \frac{P_2^g \cdot P_3^h}{P_1} = \frac{J_2^g \cdot J_3^h}{J_1} \frac{M_2^{g/2} M_3^{h/2}}{M_1^{1/2}} (2\pi RT)^{(g+h-1)/2} \quad (3)$$

where the Hertz-Knudsen-Langmuir equation¹⁰ is used to make substitutions of the kind $P_i = J_i (2\pi M_i RT)^{1/2}$, where M_i is the molecular weight of molecule i , R is the gas constant and T is the absolute temperature. Whether equilibrium is attained or not can be tested, therefore, by comparing measured fluxes of exit gases through porous barriers with the predictions of Eq. (3).

We will now prove that if a mixture described by reaction 2 passes through a barrier by equilibrated Knudsen flow, J_1 , J_2 , and J_3 are defined functions of the equilibrium constant for the reaction, of a transmission constant of the barrier for a non-reacting gas, and of the total flux of atomic components of reaction (2) that impinge on the barrier.

The flux J_i of a non-reacting gas that passes by Knudsen flow through a porous barrier is

$$J_i = c(M_i T)^{-1/2} P_i^o \quad (4)$$

where c is a temperature-independent constant for the particular barrier, P_i^o is the partial pressure of the gas at the source side of the barrier, and M_i is its molecular weight. The Hertz-Knudsen-Langmuir equation can be used to transform Eq. (4) into

$$J_i = C J_i^0 \quad (5)$$

where J_i^0 is the flux which strikes the high pressure face of the barrier when the partial pressure is P_i^0 and $C = c(2\pi R)^{1/2}$ is a new temperature-independent transmission constant.

Now we consider the change in molecular composition of the reactive mixture described by (2) at point x in the barrier characterized by arriving molecular fluxes J_{1x} , J_{2x} , and J_{3x} and by departing fluxes $J_{1x} + \delta J_{1x}$, $J_{2x} + \delta J_{2x}$, and $J_{3x} + \delta J_{3x}$. It is a characteristic of Knudsen flow that the probability that a molecule which leaves a given point will travel through the vapor until it collides with a surface at a particular second point y is independent of the nature of the molecule¹¹ so that the fluxes of molecules 1, 2, and 3 that leave point x and arrive at a second point y are $\phi(J_{1x} + \delta J_{1x})$, $\phi(J_{2x} + \delta J_{2x})$, and $\phi(J_{3x} + \delta J_{3x})$, where ϕ is the same number for each molecule.

The total fluxes of A and B atoms that leave point x, j_{Ax} and j_{Bx} , can be related to the molecular fluxes by means of Eq. (2).

$$j_{Ax} = m(J_{1x} + \delta J_{1x}) + gq(J_{2x} + \delta J_{2x}) + hs(J_{3x} + \delta J_{3x}) \quad (6)$$

$$j_{Bx} = n(J_{1x} + \delta J_{1x}) + gr(J_{2x} + \delta J_{2x}) + ht(J_{3x} + \delta J_{3x}) \quad (7)$$

The total fluxes of A and B atoms that leave point x and travel to point y are ϕ times the right hand sides of Eqs. (6) and (7) respectively.

Because total atomic fluxes are conserved in any chemical reaction, $m \delta J_{1x} + gq \delta J_{2x} + hs \delta J_{3x} = 0$ and $n \delta J_{1x} + gr \delta J_{2x} + ht \delta J_{3x} = 0$, so that the total atomic fluxes that travel from x to y are independent of the extent of chemical reaction at x. This conclusion is independent of the choice of the initial point x or of the final point y, so that fluxes of the atoms A and B transported between any points in the barrier by Knudsen flow are independent of possible changes in molecular composition. In particular, the total flux of any kind of atom that escapes through the barrier is independent of reactions among gas molecules in the barrier: Knudsen flow of a gas mixture through an inert porous barrier, whether or not a chemical reaction occurs, is described by

$$j_A = C j_A^o,$$

$$j_B = C j_B^o, \quad (8)$$

$$j_i = C j_i^o$$

where j_A^o , for example, is the total flux of A atoms that strike the barrier and C is the same constant that appears in Eq. (5) for non-reacting gases. Equations (6) and (7) (with δ 's = 0) plus Eqs. (3) and (8) define the exit fluxes in terms of C, j_A^o , j_B^o , and K for reaction 2.

A corollary of Eq. (8) is a generalized equation for Knudsen flow in porous barriers: The ratio of the total flux of any atomic component of a gas that passes through a non-reacting porous barrier by isothermal

Knudsen flow to the total incident flux of that atomic component on the barrier is independent of the complexity of the gas, of reactions among molecules of the gas, and of the temperature.

$$j_A/j_A^0 = j_i/j_i^0 = C \quad (9)$$

For an alkali halide dimer/monomer equilibrium the fluxes of halogen and alkali atoms are both equal to the flux of alkali halide monomer units j_{mu} , where j_{mu} is the flux of monomer molecules J_m plus two times the flux of dimer molecules J_d . If zinc vapor, which is atomic, and sodium chloride vapor both travel through a given barrier by Knudsen flow, then according to Eq. (9)

$$j_{mu}/j_{mu}^0 = j_{Zn}/j_{Zn}^0 \quad (10)$$

where j_{mu}^0 is the total flux of monomer units that strike the barrier.

Provided that fluxes are written, not per unit area of the total cross-sectional area of a barrier, but per unit area of the average cross-sectional area that consists of pores, the constant C in equations (5), (8), and (9) is the average Clausing factor^{12,13} for Knudsen flow through all the channels of the barrier. Clausing factors for long tubes of constant cross-sections vary inversely with length regardless of particular cross-sectional geometry and the proportionality constants have magnitudes of the order of the average cross-sectional dimension of the channel.¹⁴ It follows that for a porous barrier with constant average pore geometry and with a thickness large compared to average

cross-sectional width of the pores, the constant C can be replaced by a/ℓ where a is a new constant that can be expected to have a value of the order of the average cross-sectional diameter of the pores. Experiments with non-reacting gases show that the constant usually lies within one order of magnitude of the value that is calculated for a collection of cylinders of a length equal to the barrier thickness and of the same average cross-sectional area.^{15,16} Substituting $C = a/\ell$ in (9) gives

$$j_A/j_A^0 = j_i/j_i^0 = a/\ell, \quad (11)$$

which predicts that the total atomic flux for each chemical component that passes through a particular porous material by Knudsen flow, whether reactive or non-reactive, should vary inversely with the barrier thickness.

For equilibrated Knudsen flow of a monomer/dimer mixture, Eq. (3) can be solved for the ratio of escape monomer molecule flux J_m to escape dimer molecule flux J_d . Then in a mass spectrometer the ratio of ions that originate from electron collisions with a monomer, I_m , to ions that originate from a dimer, I_d , is

$$I_m/I_d = (2\pi RT)^{-1/2} K(M_d^{1/2}/M_m)(f_m/f_d)(1/J_m) \quad (12)$$

where the f 's are proportionality constants between fluxes and ion intensities. Under experimental conditions that make J_d small relative to J_m , the total escape flux of monomer units is essentially equal to the monomer molecule escape flux and the ratio I_m/I_d should increase linearly

with the length ℓ of the porous barrier

III. Experimental

Sodium chloride vapor was chosen as the subject for experimental study because it was expected that near equilibrium compositions would be achieved throughout the porous barrier. This expectation is based on evidence that the monomer and dimer of sodium chloride both have vaporization coefficients, α_v , close to unity.¹⁶ A near unit value for α_v reflects nearly complete equilibration of particles of the sodium chloride in the self-adsorption layer,¹⁷ which in turn implies a low free energy barrier to equilibration of sodium chloride monomer and dimer on a sodium chloride surface.¹⁸ During steady state effusion through the pores of a solid, sodium chloride must be adsorbed on the surfaces in concentrations that are proportional to the local thermodynamic activity of sodium chloride. It seemed probable, in light of known equilibration of sodium chloride monomers and dimers in the self-adsorption layer of sodium chloride, that equilibration would also result from the many collisions of molecules of the sodium chloride vapor in the adsorption layer of a porous solid.

A sodium chloride sample of 99.9% purity from J. T. Baker Chemical Co. was used. The barriers were porous alumina disks which were placed on top of a high density alumina cell and were masked by a molybdenum lid which was pierced by a tapered orifice of 3.8 mm minimum diameter. Two different preparations of porous alumina were used. The first, of relative density 0.442, was prepared from randomly packed tabular alumina particles which had dimensions of the order of 10 μ in two directions and

1 μ in the third. The second, of relative density 0.555, was formed of rounded particles of average diameter of the order of 1 μ . Disks of thicknesses 0.28, 0.389, 0.599, 0.69 and 0.838 mm were prepared from the porous alumina of 0.442 relative density.

The effusion cell was heated by direct radiation from three tungsten filaments in a Nuclide mass spectrometer. Temperatures were measured with a Pt:Pt-10% Rh thermocouple located at the bottom of the cell. Temperatures of the barriers were calibrated against this thermocouple in experiments in which another thermocouple of the same kind was pinned inside the porous layer.

In all of the experiments on sodium chloride with porous disks, sodium chloride condensed on the lower surface of the disk because the temperatures were about 15°K lower than temperatures at the bottom of the cell. The flux generated by the sodium chloride deposit on the bottom of the disks should be the equilibrium flux for the disk temperature because sodium chloride has a unit vaporization coefficient.¹⁶

With each disk a run was made in which the ion intensities of NaCl⁺ (from NaCl gas) and Na₂Cl⁺ (from Na₂Cl₂ gas)¹⁹⁻²² were measured over a range of temperatures below the melting point of sodium chloride. To compare data obtained in these runs with equilibrium data for sodium chloride effusion, a run with a conventional effusion cell was also completed. The orifice diameter in this run was 0.55 mm and the channel length was 1.1 mm.

In order to establish whether equilibrium was achieved in the exit vapors from the porous barriers, separate weight-loss runs were made at

1025°K with the 0.28, 0.389 and 0.838 mm porous disks of 0.442 relative density and with a 0.30 mm disk of 0.555 relative density.

Finally, in order to compare the transmission constants of the disks for sodium chloride vapor with those for a non-reactive, single component gas, weight-loss runs were also made with zinc using porous disks 0.389 and 0.838 mm thick and relative density 0.442. Before the zinc runs, these disks, which were previously used for sodium chloride, were washed with hot water and baked in the mass-spectrometer until the ion peaks corresponding to sodium chloride vapor molecules disappeared from the spectrum.

In order to measure the apparent heat of vaporization of zinc through the porous layers, the temperature dependence of the ion intensities produced from the zinc atoms vaporized through the porous layer of 0.389 mm thickness was measured. There was already a condensate of zinc metal on the interior side of this lid from the weight-loss experiments. The disk temperature was again used as the temperature of vaporization; zinc also has a unit vaporization coefficient.²³

Our studies with porous disks reported below support earlier conclusions¹⁹⁻²² that Na^+ and NaCl^+ are formed essentially exclusively from NaCl and that Na_2Cl^+ is from Na_2Cl_2 . From slopes of log IT vs $1/T$ data which we obtained with the conventional Knudsen effusion cell without a porous disk (Fig. 1) are calculated the mean values for vaporization of 48.9 ± 0.4 Kcal/mole (from Na^+) and 48.4 ± 0.7 Kcal/mole (from NaCl^+) for ΔH_m^0 and 51.2 ± 0.7 Kcal/mole for ΔH_d^0 . The JANAF²⁴ values are 52.2 Kcal/mole for ΔH_m^0 and 56.9 Kcal/mole for ΔH_d^0 .

Figure 2 shows that when a porous barrier is used, the relative intensities of NaCl^+ , from the monomer, and Na_2Cl^+ , from the dimer, are drastically different from relative intensities found in conventional effusion. Linear least squares analyses of these data and similar data for four other barrier thicknesses yield the apparent heats of vaporization listed in columns 2 and 3 of Table I. Column 4 gives the NaCl^+ to Na_2Cl^+ ion intensity ratios calculated at 1025°K from the least squares curve for each run. These ratios are shown in Fig. 3 to vary linearly with disk thickness.

Weight losses through four different porous disks (Table II) were used with intensity ratios measured in the Knudsen effusion experiment to calculate monomer and dimer pressures from the intensity data obtained with the porous disks. The $\text{NaCl}^+/\text{Na}_2\text{Cl}^+$ intensity ratio which was measured in the effusion experiment was used to determine the proportionality constant k in the expression $P_m/P_d = k (I_m^+/I_d^+)$ from values of the equilibrium pressures of monomer P_m and dimer P_d reported in the JANAF tables. The partial pressure of monomer was calculated in each constant temperature weight loss experiments with porous disks by means of the Hertz-Knudsen-Langmuir equation.¹⁰ For these calculations, the effective area of vaporization, A , was taken to be that area of the exposed surface of the porous layer that was covered by the pore mouths, i.e. $A = \pi R^2 (1-D_r)^{2/3}$ where πR^2 is the total exposed area of the disk and $(1-D_r)^{2/3}$ is the two-dimensional pore fraction of the surface (R being, in this equation, the radius of the exposed area and D_r the relative density of the porous alumina layer).

The quantities $j_{Zn}/j_{Zn}^0 = C$ for two porous barriers are given in Table III with the corresponding values of the fractional reduction in total monomer unit flux for sodium chloride calculated from Table II for comparison.

The temperature dependence of Zn^+ ions produced from zinc atoms that vaporized through the 0.389 mm porous layer gave an apparent heat of vaporization of 28.7 ± 0.8 Kcal/mole. The reported heat of vaporization of zinc at the mid-point of the temperature range of study is 30.7 Kcal/mole.²⁵

IV. Discussion

The alumina particles of the barriers used in most of the experiments had tabular shapes with their two longer dimensions usually less than ten microns but occasionally as great as twenty microns. The maximum pressure at the high pressure faces of the barriers was less than 10^{-3} atm. The hard sphere model can be used to calculate that pressures were, therefore, well within the Knudsen flow regime.¹⁴

Fluxes of sodium chloride monomer were reduced almost two orders of magnitude by these porous barriers. The $Na^+/NaCl^+$ ion intensity ratios at 1025°K are the same as those found in ordinary effusion experiments to within about 2%. This result confirms earlier conclusions¹⁹⁻²² that molecules other than the monomer are negligible sources of both Na^+ and $NaCl^+$ ions. The $Na_2Cl^+/NaCl^+$ ion ratios, however, are very much reduced from those found in ordinary effusion experiments and decrease with increasing barrier thickness. This result contradicts the prediction of the equation for non-reactive Knudsen flow (Eq. (1)) that the dimer/monomer ion ratio should be identical with that for ordinary Knudsen

effusion regardless of barrier thickness and shows that a new equation of flow is required between sodium chloride monomers and dimers in the barriers. Attainment of equilibrium is confirmed by Table II, in which the dimer pressures calculated from weight losses and ion flux ratios for four different barriers are compared with the dimer pressures predicted from the accepted equilibrium constant for dimer dissociation and from the measured monomer pressures. Measured dimer pressures agreed with predicted pressures to within an average deviation of 28% even though these dimer pressures are all less than 10^{-3} times the dimer pressures in the saturated vapor. Further confirmation is provided by the observation (Fig. 3) that the ratio of monomer to dimer ion peak intensities varies linearly with barrier thickness as predicted by Eq. (12).

With the fact clearly established by the results just quoted that transport of sodium chloride through alumina barriers in the Knudsen flow regime is equilibrated, we can examine the transport data for its consistency with the equations that we have derived for reactive Knudsen flow. We will then briefly discuss the extent to which the experimental observations might also be consistent with the interpretation that surface diffusion is the major mode of vapor transport. Previous studies of gas transport through porous solids in the Knudsen flow regime show that usually surface diffusion is only important when pores have diameters some two orders of magnitude smaller than the 1 to 10μ pores used in the present study.²⁶ But we have found that our alumina barriers give much smaller reductions in lithium fluoride vapor fluxes²⁷ than of sodium chloride or of zinc. Surface diffusion must be the principal mode of transport for the lithium fluoride vapor and might also be the principal

mode of transport for sodium chloride and zinc vapors.

Equation (10) predicts that the fractional reduction in total monomer unit flux through any given barrier is independent of composition, temperature, or gas pressure in the Knudsen flow range and depends only on the geometry of the barrier. This prediction is confirmed by data of Table III. The ratios of monomer unit escape fluxes to impingement fluxes for sodium chloride vapor are found to deviate by an average of only 16% from the corresponding ratios for zinc atoms in the same barriers.

The prediction of Eq. (11) that transmission constants defined by $a = \ell j/j^0$ will be independent of barrier thickness are not convincingly confirmed by the weight loss data. Values of a for sodium chloride are calculated to be 4.6×10^{-3} , 6.8×10^{-3} , and 9.4×10^{-3} mm for the 0.28, 0.389, and 0.838 mm thick barriers, respectively. For zinc the two longer barriers give $a = 9.0 \times 10^{-3}$ and $a = 10.1 \times 10^{-3}$ mm, respectively. The calculated transmission constants apparently increase somewhat with barrier thickness.

The fact that monomer to dimer ion intensity ratios were found to vary linearly with barrier thickness, however, strongly supports the prediction that values of $\ell j/j^0$ is a constant for sodium chloride vapor in the tabular alumina of constant average pore geometry. Equation (12) shows that the exit flux for monomers is inversely proportional to the monomer ion/dimer ion intensity ratio if equilibrium is maintained, as it has been proved to be for our experimental conditions, and the proportionality constants are independent of the geometry of the barrier. But Fig. 3 shows that the monomer/dimer ion intensity ratio varies

linearly with ℓ so that the monomer exit flux must be inversely proportional to ℓ . The monomer molecule exit flux J_m is, to within a few percent, equal to the total exit flux of monomer units, j_{mu} , so that $J_m/j_{mj}^0 \approx j_{mu}/j_{mu}^0$, and therefore, the ratio of j_{mu}/j_{mj}^0 is also inversely proportional to ℓ . The data of Fig. 3 scatter very little from a straight line and, therefore, confirm the form of Eq. (11).

It seems probable that values of a calculated from the weight loss data may be influenced by a leakage error that increases in relative importance when the flux reductions are greatest. The ion intensity ratio is relatively insensitive to leaks because it is measured for a collimated beam that is generated from the center of the exposed upper surface of the porous alumina barrier. We conclude that the magnitude of a as determined by this study for sodium chloride and zinc are uncertain by a factor of two, but that the constancy of a is established to within 10% for variations of barrier thicknesses by a factor of three.

Because the focus of this research was on examining the effects of porous barriers on a reactive gas mixture at a single temperature, measurements in the various runs were made over only about a 40° temperature interval--too small a range at 1000°K to yield accurate measurements of apparent heats of vaporization from the temperature dependences of the intensities. Nonetheless, it has proved instructive to compare the experimentally measured apparent heats with theoretical predictions.

The exit flux of monomers through each barrier contains a contribution from the dimers that are converted to the monomers in the barrier. It can be shown that if only Knudsen flow is important, the apparent heat of vaporization of monomers ΔH_{am} through barriers that convert

almost all of the initial dimer flux to monomers, as do the barriers in this study, is greater than the standard heat of vaporization of monomer ΔH_m^0 in the same temperature range by

$$\Delta = \Delta H_{am} - \Delta H_m^0 = - \left(\frac{RT_2 T_1}{T_1 - T_2} \right) \ln \left(\frac{1+2^{1/2} P_{d2}^0 / P_{m2}^0}{1+2^{1/2} P_{d1}^0 / P_{m1}^0} \right) \quad (13)$$

where P_{d2}^0 and P_{m2}^0 for example, are dimer and monomer pressures on the source side of the barriers at temperature T_2 . The apparent heat of vaporization of the dimer through the barrier should exceed the standard heat of vaporization of the dimer in the same temperature range by 2Δ . The sign of Δ is positive when the heat of vaporization of dimer exceeds that of monomer and negative when the heat of vaporization of dimer is smaller than that of the monomer.

For sodium chloride at 1025°K, Δ is 1.5 Kcal. Accordingly, the apparent heats predicted for monomer and dimer effusion through the alumina barriers from the single effusion run (Fig. 1) are $48.7 + 1.5 = 50.2$ Kcal for the monomer and $51.2 + 3.0 = 54.2$ Kcal for the dimer. The averages from five measurements of intensity variations with temperature are 47.8 Kcal for the monomer and 63.7 Kcal for the dimer. There is no clear trend in either apparent heat value with barrier thickness.

The difference between measured and predicted values for the monomer probably simply reflect the high systematic error often encountered in measuring intensity variations by effusion methods, particularly from data in a limited temperature range. But the high average difference measured between dimer and monomer apparent heats, 16 Kcal compared to a

predicted difference of 6.2 Kcal, suggests that some factor must be operating besides those found in conventional measurements of effusion of saturated vapors.

The large discrepancy between the predicted and observed relative heats probably reflects the extreme sensitivity of the dimer ion signal to contributions from sodium chloride that has condensed outside the cell. In ordinary effusion studies, subtraction of the unshuttered background at any ion peak largely eliminates errors from such contributions, but with the porous barrier in place, the dimer signal is reduced more than three orders of magnitude. Consequently, the contribution to the signal from sources exterior to the cell, while negligible for the monomer, may well have been significant for the dimer. Furthermore, the extraneous signal would probably increase more rapidly with temperature than the signal from the cell, making the apparent heat of vaporization of the dimer higher than expected, because degassing effects generally increase with temperature. Fortunately, errors of this kind would always increase the measured relative dimer/monomer intensity ratio above the ratio that would be observed without extraneous vapor sources; the conclusion that essentially equilibrium dimer to monomer pressure ratios were maintained in the porous barriers is unaffected.

Equilibration of sodium chloride monomers and dimers was expected for the exit flux whether or not surface diffusion is significant. The observed proportionality between the total monomer unit flux transmission and the reciprocal of the barrier thickness does not rule out significant surface diffusion, but shows that if surface diffusion were the dominant mode of transport, the surface diffusion coefficient must be independent

of the pressure gradient through the barrier.

On the other hand, the transmission constants calculated for the barriers are of the magnitude predicted for Knudsen flow from the geometry of the pores with no contribution from surface diffusion. Furthermore, the fact that the monomer unit flux transmissions for sodium chloride and for zinc vapors were the same to within probable error for two different barriers (Table III) would be compatible with a major contribution from surface diffusion only if surface diffusion were fortuitously of equal importance for sodium chloride at 1025°K and zinc vapor at 668°K. It seems probable, but not certain, that Knudsen flow rather than surface diffusion was the principal mode of transport of sodium chloride and zinc vapors through the alumina barriers used in this research.

In future studies of the influence of porous barriers on the molecular compositions of reactive vapors it will be desirable to attempt to obtain apparent heat measurements of high reliability. Because the activated complexes for surface diffusion are bound to the surface, the apparent enthalpies of vaporization of the monomers of a monomer/dimer mixture measured through porous barriers should be reduced below the predictions of Eq. (13) when surface diffusion is the principal mode of transport through a barrier.

A more direct way of determining the importance of surface diffusion through given kinds of barrier materials is to compare transmission of a gas in question with that of helium, for which surface diffusion is negligible on all known surfaces at high temperatures.²⁸ A second way would be to vary pore diameters while keeping the fundamental pore

geometry relatively constant, since surface diffusion should increase in relative importance when average pore diameters are decreased. We hope to employ both of these techniques in future studies. We expect that equilibrated vapor flow through porous barriers such as these results prove to occur for sodium chloride in porous alumina will be found for reactive vapor and gas mixtures whenever the activation free energies of the pressure dependent reaction are relatively low compared to RT. We have found that compositional changes such as described here for sodium chloride vapor can be produced for lithium fluoride vapor by use of porous nickel barriers and we have used these compositional changes to study the mass spectrometer ionization cross-section for the lithium fluoride monomer.²⁷

Acknowledgments

Emery Kozak and Dr. David J. Meschi provided invaluable technical help and advice. Dr. Meschi and Dr. Alfred Büchler participated in a number of valuable discussions of theory and interpretations. This research was supported by the U. S. Energy Research and Development Administration.

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Table I. Results of sodium chloride runs with porous alumina disks of 0.442% relative density

Disk thickness mm	Apparent heats of vaporization (Kcal/mole)		Ion intensity ratio $\text{NaCl}^+/\text{Na}_2\text{Cl}^+$ (1025°K)
	NaCl	Na_2Cl_2	
0.28	50.6 ± 2.3	62.3 ± 3.6	41.4
0.389	49.6 ± 1.1	66.2 ± 4.2	62.3
0.599	44.2 ± 3.3	57.6 ± 4.3	83.1
0.69	48.5 ± 1.5	67.2 ± 4.6	111.6
0.838	45.5 ± 2.1	65.8 ± 5.2	129.0

Table II. Weight loss results for sodium chloride at 1025°K .

Relative density of the alumina disk	Disk thickness (mm)	Partial pressure of the monomer (atm)	Measured partial pressure of the dimer (atm)	Calculated* partial pressure of the dimer (atm)
0.555	0.30	3.00×10^{-6}	2.50×10^{-8}	3.24×10^{-8}
0.442	0.28	3.01×10^{-6}	4.66×10^{-8}	3.27×10^{-8}
0.442	0.389	3.12×10^{-6}	3.21×10^{-8}	3.55×10^{-8}
0.442	0.838	2.03×10^{-6}	1.05×10^{-8}	1.48×10^{-8}

* Calculated from the measured monomer partial pressures and equilibrium constants in the JANAF tables.

Table III. Ratios of exit to impingement total monomer unit fluxes for zinc and sodium chloride vapor in porous alumina barriers

Disk thickness (mm)	Vapor pressures		j_{Zn}/j_{Zn}^o	j_{NaCl}/j_{NaCl}^o
	Zn (668°K)	NaCl (1025°K)	(668°K)	(1025°K)
0.389	9.05×10^{-5}	1.63×10^{-4}	$\left\{ \begin{array}{l} 2.35 \times 10^{-2} \\ 2.31 \times 10^{-2} \end{array} \right\}$	1.74×10^{-2}
0.838	9.05×10^{-5}	1.63×10^{-4}	1.21×10^{-2}	1.12×10^{-2}

Figure Captions

- Fig. 1. Relative intensities of ions from the sodium chloride monomer (Na^+ and NaCl^+) and an ion from the dimer (Na_2Cl^+) in a conventional Knudsen effusion run for sodium chloride.
- Fig. 2. Relative intensities of an ion from the sodium chloride monomer (NaCl^+) and from the dimer (Na_2Cl^+) produced by effusion through an alumina barrier of relative density 0.442 and 0.389 mm thick.
- Fig. 3. Variation of the monomer/dimer intensity ratio with thickness (in mm) of porous tabular alumina disks at 1025°K.

XBL 7412-7728

Fig. 1

XBL 7412-7730

Fig. 2

XBL 7412-7735

Fig. 3

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