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THE EFFECT OF POROUS BARRIERS ON THE MOLECULAR
COMPOSITIONS OF REACTIVE GAS MIXTURES

Piroot Mohazzabi
(Ph. D. thesis)

February 1975

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

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THE EFFECT OF POROUS BARRIERS ON THE MOLECULAR
COMPOSITIONS OF REACTIVE GAS MIXTURESContents

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THE EFFECT OF POROUS BARRIERS ON THE MOLECULAR
COMPOSITIONS OF REACTIVE GAS MIXTURES

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ABSTRACT

In Part I of the thesis, the effect of a porous barrier on the molecular composition of a gas mixture, when a pressure-dependent chemical reaction can take place among the components of the gas, is deliberately studied for the first time. A theoretical analysis shows that when a pressure dependent chemical reaction can take place in the pores of a porous barrier, then the ratio of the total mass flux at the outlet side of the porous barrier to that at the inlet side, should be independent of the particular gas mixture and vary inversely with the thickness of the porous layer, provided that the thickness of the layer is much larger than the dimensions of the pores. Furthermore, when the assumption of equilibration of the species throughout the porous barrier is made and the theory is applied to the gaseous monomer-dimer reaction, it is found that the ratio of the gas flux of the dimer to that of the monomer should also vary inversely with the thickness of the porous layer, a useful phenomenon whenever enrichment is desired in the simpler molecules of a reactive gas mixture. Mass spectrometric studies on sodium chloride monomer-dimer reaction through porous alumina were employed to verify the predictions experimentally. The fact that both sodium chloride and zinc showed the same transmission coefficient through a porous layer indicates that probably for both of these materials, simple pore effusion

is the only significant mode of transport through the porous barriers.

In Part II of the thesis, the technique developed in Part I is used to reduce the ratio of dimer to monomer of lithium fluoride. The mass spectrometric fragmentation pattern of the monomer was then studied in order to re-examine a reported deviation from the mass spectrometric specificity rule for the monomer.

Surface diffusion was found to be the dominant mode of transport of lithium fluoride through porous alumina and therefore nickel powder was used as the porous barrier. The apparent heats of vaporization of the monomer and the dimer through nickel powder are found to be higher than the reported equilibrium values, which indicates that surface diffusion may also be an important mode of transport for lithium fluoride through the nickel powder. However, a reduction of the order of 20 in the ratios of dimer intensities to monomer intensities was achieved. The main source of Li^+ ions was found to be the monomer, in agreement with the previous reports, but the deviation of the monomer from the specificity rule was much less than that reported previously.

PART I. DEVELOPMENT OF THE THEORY AND TECHNIQUE

I. INTRODUCTION

The effect of a porous barrier on the steady state ratio of the molecular fluxes of a non-reactive gas mixture at a fixed temperature in the Knudsen flow regime has been known for a long time; it is given by¹

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

where J_1 , J_2 refer to the fluxes of components 1 and 2, respectively. P_1^0 , P_2^0 are the partial pressures of these species on the source side of the barrier and M_1 and M_2 are the molecular weights of components 1 and 2, respectively. However, if a pressure dependent chemical reaction occurs between the two (or more) components of the diffusive gas, Eq. (1) will no longer be valid. In particular, if a near equilibrium composition of the diffusive components is maintained in the porous barrier, then a new equation of flow can be derived.

The fact that molecular composition of a reactive gas mixture may change greatly in a porous barrier seems not previously to have been explicitly predicted or tested. Berkowitz et al.² used a nickel porous barrier to reduce total pressures 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 rather insensitive to such a possible change in composition because of new equilibration in the effusion chamber. Voronin^{3,4} predicted theoretically that if a reactive gas mixture can equilibrate on the walls of a

cylindrical effusion orifice, then the angular distribution of the species would be different from that of the cosine law and Clausing distribution. Grimley et al.^{5,6} obtained data on KCl and AgCl that were consistent with Voronin's predictions, but which they considered might also be otherwise explained. Walbeck,⁷ however, agrees with Voronin that the data of Grimley and co-workers reflect equilibration in the flux gradient of an effusion channel. In retrospect, it is apparent that Voronin's analysis, or at least his assumptions for reactive effusion, could be considered to imply the predictions made and tested in this study.

This communication reports what is apparently the first deliberate study of the influence of a porous barrier on the molecular compositions and total mass flux of a gas mixture that is capable of undergoing a pressure dependent reaction.

In the following section, equations are derived (a) for prediction of the dependence on barrier thickness of the molecular composition of a gas mixture which undergoes a pressure-dependent change in its equilibrium composition, and (b) for prediction of the influence of changes in molecular composition on total mass flux when transport through a barrier is by Knudsen flow. The remainder of Part I of this thesis describes experimental tests of these predictions and comparisons of predictions with experiment.

II. THEORETICAL

Knudsen flow of a single gas from a source chamber through a capillary tube of length L and cross-sectional radius R , provided that $\frac{L}{R} \gg 1$, is governed by the equation⁸

$$\frac{J}{J^0} = \frac{8R}{3L}$$

where J^0 is the flux that strikes the barrier and J is the exit flux. Adzumi⁹ regarded a porous plate as a network of capillaries which are connected both in series and in parallel. He also considered that all pores of a porous plate could be viewed as having a uniform radius $\bar{R}$ and being normal to the surface of the porous plate. Under these assumptions and when molecular flow is the only mode of transport, the flux through a porous plate is given by^{10,11}

$$\frac{J}{J^0} = \frac{K}{\ell} = \frac{P}{P^0} \quad (2)$$

where ℓ is the thickness of the porous plate and K is a geometry factor which depends only upon the nature of the pores. P and P^0 are the pressures corresponding to J and J^0 , respectively.

Let now a reactive gas mixture flow through the porous plate of thickness ℓ . Furthermore, consider the pressure dependent chemical reaction between them of the form

in which $A_{m,n}$ and A_n are two different polymers (or a polymer and the monomer) of the same element or chemical compound. At any thickness, ℓ , we can write

$$dJ_{A_{m,n}} = - \frac{KJ_{A_{m,n}}^o}{\ell^2} d\ell + dJ_{A_{m,n}}^* \quad (4)$$

$$dJ_{A_n} = - \frac{KJ_{A_n}^o}{\ell^2} d\ell + dJ_{A_n}^* \quad (4a)$$

where in each of these equations the first term on the right hand side refers to the contribution from non-reactive Knudsen flow (Eq. (2)) while the second term gives the contribution to the differential of the total flux from the chemical reaction. But Eq. (3) shows that

$$dJ_{A_n}^* = - m dJ_{A_{m,n}}^* \quad (5)$$

Substituting in Eqs. (4) and (4a) for $dJ_{A_n}^*$ from Eq. (5) and manipulating the coefficients gives

$$dJ_{A_{m,n}} = - \frac{KJ_{A_{m,n}}^o}{\ell^2} d\ell + dJ_{A_{m,n}}^*$$

$$\frac{1}{m} dJ_{A_n} = - \frac{KJ_{A_n}^o}{m\ell^2} d\ell - dJ_{A_{m,n}}^*$$

Adding up these equations we obtain

$$d(J_{A_{m.n}} + \frac{1}{m} J_{A_n}) = - (J_{A_{m.n}}^o + \frac{1}{m} J_{A_n}^o) \frac{K}{\ell^2} d\ell$$

Integration gives

$$J_{A_{m.n}} + \frac{1}{m} J_{A_n} = (J_{A_{m.n}}^o + \frac{1}{m} J_{A_n}^o) \frac{K}{\ell} + C$$

where C, the constant of integration, is zero because as $\ell \rightarrow \infty$ each and every flux should go to zero. Therefore we obtain the final equation

$$J_{A_{m.n}} + \frac{1}{m} J_{A_n} = (J_{A_{m.n}}^o + \frac{1}{m} J_{A_n}^o) \frac{K}{\ell} \quad (6)$$

It is important to note that Eq. (6) has been derived without appealing to any assumption concerning chemical equilibration inside the porous plate. Now if we introduce the assumption of equilibration on the walls of the pores, throughout the porous barrier, i.e.^{3,4}

$$\frac{J_{A_n}^m}{J_{A_{m.n}}} = \kappa \quad (7)$$

where κ is the equilibrium constant in terms of fluxes, on the walls of the pores (and one would expect κ to be equal to the equilibrium constant in terms of fluxes of the reaction in the gas phase, if it could occur, and at the same temperature).

Equations (6) and (7), when applied to specific reactions will give some important and interesting information which we explore by

examining a special case of Eq. (3), i.e., a monomer-dimer gas flow through a porous layer.

For the particular case

$$D \rightleftharpoons 2M$$

where D is the dimer and M is the monomer, then from Eq. (6) we have

$$J_D + \frac{1}{2} J_M = (J_D^0 + \frac{1}{2} J_M^0) \frac{K}{\ell}$$

and if the temperature is constant we can absorb the quantity $(J_D^0 + \frac{1}{2} J_M^0)$ into the constant K' and write

$$J_D + \frac{1}{2} J_M = \frac{K'}{\ell}$$

or

$$J_M \left(\frac{J_D}{J_M} + \frac{1}{2} \right) = \frac{K'}{\ell} \quad (8)$$

But from Eq. (7) we have

$$\frac{J_M^2}{J_D} = \kappa$$

or

$$J_M = \kappa \frac{J_D}{J_M}$$

Substituting for J_M from this equation into Eq. (8) we obtain

$$\kappa \left[\left(\frac{J_D}{J_M} \right)^2 + \frac{1}{2} \left(\frac{J_D}{J_M} \right) \right] = \frac{\kappa'}{\ell}$$

and if $\frac{J_D}{J_M} \ll 1$ then the last equation becomes

$$\frac{J_D}{J_M} = \frac{h}{\ell} \quad (9)$$

where $h = \frac{2\kappa'}{\kappa} = \frac{\kappa(2J_D^0 + J_M^0)}{\kappa}$, a constant at constant temperature. Therefore the dimer to monomer ratio would drop inversely with length of the porous barrier, or stated otherwise, the monomer to dimer ratio would increase linearly with length of the porous barrier. For non-reactive flux the dimer to monomer ratio (or monomer to dimer ratio) would according to (1) be independent of barrier thickness.

In the above analysis we have assumed that the only significant mode of transport is Knudsen effusive flow. If surface diffusion is important, the linear dependence of flux on $1/\ell$ that is predicted by Eq. (9) cannot be expected, but the prediction that a pressure dependent reaction, if it remains at chemical equilibrium in a porous barrier, will have a molecular composition that depends for a particular reaction only on the initial fluxes and on the reduction in total flux is retained. This prediction depends on the assumption that the flux leaving the outlet face of the barrier depends only on equilibration of the vapor species at their reduced activities at the barrier face and is, therefore, independent of the mechanism of transport through the barrier.

Another important aspect of Eq. (6) for Knudsen flow is that if we write it in the form

$$\frac{J_{A_{m.n}} + \frac{1}{m} J_{A_n}}{J_{A_{m.n}}^o + \frac{1}{m} J_{A_n}^o} = \frac{K}{\ell}$$

then the R.H.S. of this equation is only a function of the porous layer, i.e. the L.H.S. of the equation should be independent of any particular reaction. In the example that we just considered, i.e. the monomer-dimer reaction, the equation is

$$\frac{J_D + \frac{1}{2} J_M}{J_D^o + \frac{1}{2} J_M^o} = \frac{K}{\ell}$$

and if we write this equation in terms of mass fluxes we get

$$\frac{j_D + j_M}{j_D^o + j_M^o} = \frac{K}{\ell}$$

where j 's are the mass fluxes. Consider now the flow of a single component, A, through the same porous layer. We will have from Eq. (2)

$$\frac{j_A}{j_A^o} = \frac{K}{\ell}$$

and therefore we must have

$$\frac{j_D + j_M}{j_D^o + j_M^o} = \frac{j_A}{j_A^o}$$

This equation makes the important prediction that for Knudsen flow, although equilibration in a porous barrier may greatly change the molecular composition of a mixture of monomer and dimer, the fractional reduction in total mass flux is identical with that for a single chemical species in the same barrier. This result would not apply to surface diffusion which depends upon the specific chemical interactions of each vapor species with the surface. Consequently, one means for determining whether or not surface diffusion is a significant mode of transport for a particular mixture of reactive gases through a particular barrier is to compare its fractional reduction in total mass flux to that for a reference gas for which surface diffusion has been shown to be negligible.

The effect of surface diffusion on gas flow through porous membranes has been extensively studied.¹²⁻¹⁹ Barrer et al.¹⁹ studied the diffusion of a number of gases through carbolac and graphon of different BET areas. For convenience in comparing data for different gases, they define a permeability, K ($\text{m}^2 \cdot \text{s}^{-1}$), for a micro-porous membrane as

$$K = \frac{J\ell}{A_c \Delta C_g} \quad (10)$$

where

J = flux (molecules/sec)

A_c = cross-sectional area of the porous barrier normal to the direction of flow

ΔC_g = concentration drop in the gas phase (molecules. m^{-3}) from $x = 0$ to $x = \ell$ where x is the normal distance from the inlet face of the porous barrier, and

ℓ = thickness of the barrier.

For steady state flow, if surface diffusion is a negligible mode of transport for a gas, then the quantity $\frac{K}{\sqrt{T}}$ should be independent of temperature for that gas, as long as the inlet flux of the gas is held constant (the outlet end is in vacuum). In particular, the quantity $K \sqrt{\frac{M}{T}}$ should be the same for all gases and independent of temperature if the above conditions are satisfied. They found experimentally that the quantity $\frac{K}{\sqrt{T}}$ for helium is independent of temperature and hence helium passes through the micro-porous membranes by effusional flow. By comparing the behavior of other gases with that of helium, they were able to study the contribution of surface diffusion to the total flux, and they measured the activation energy for the surface diffusion of a number of gases through carbolac and graphon.

If the vapor source for a porous barrier is equilibrium vapor of a condensed phase instead of a gas flux (as used by Barrer et al.), then the $\frac{K}{\sqrt{T}}$ test for surface diffusion cannot be directly applied because the equilibrium flux of a vapor is not constant but increases exponentially with temperature. However, by comparing the apparent heat of vaporization of the material through the porous barrier to the heat of the equilibrium vaporization reaction, it is possible to determine whether

or not surface diffusion is a significant mode of transport through the porous barrier. Whenever a barrier produces a significant reduction in flux, the heats should be identical if surface diffusion is negligible, but should usually be different if surface diffusion is the major source of transport.

III. EXPERIMENTAL

Experimental studies were carried out with a Nuclide model HT-12-60 mass spectrometer.^{20,21} The molecular beam was generated in an effusion cell which was heated by direct radiation from three tungsten filaments. Temperature was measured with a Pt:Pt-10% Rh thermocouple located at the bottom of the cell. Temperatures of the barriers were calibrated versus the thermocouple at the bottom of the cell in experiments in which another thermocouple of the same kind was pinned inside the porous layer. The intensity of each ion measured is related to the partial pressure of the corresponding species in the high temperature effusion cell through the equation²¹

$$P_i = \frac{K_o I_i^+ T}{\sigma_i \gamma_i \Delta E_i} \quad (11)$$

where

P_i = partial pressure of species i

K_o = machine constant depending upon the geometry of the machine

I_i^+ = intensity of the species i

T = absolute temperature

σ_i = ionization cross-section of the species i

γ_i = number of secondary electrons produced by the conversion
dynode due to species i

ΔE_i = difference between the electron energy and the appearance
potential of the species i .

Clearly during a run K_o is constant, and for a species σ_i , γ_i and ΔE_i is constant.

Sodium chloride vapor was chosen as the subject for experimental study because it was expected that in the diffusion of sodium chloride monomer and dimer through a porous barrier near equilibrium composition of the species would be approached throughout the porous barrier. This expectation is based on evidence that the monomer and dimer of sodium chloride have a vaporization coefficient, α_v , close to unity.²² The near unit value for α_v reflects nearly complete equilibration of the particles of the sodium chloride in the self-adsorption layer,^{23,24} which in turn implies a low energy barrier to equilibration of sodium chloride monomer and dimer on a sodium chloride surface.²⁵ In a pressure range that makes the ratios of mean-free-path of the molecules to the average dimensions of the pores large (that is, under Knudsen flow conditions), it seemed probable that equilibration would result from the many collisions of molecules of the sodium chloride vapor with the surface of a porous solid.

Sodium chloride samples of 99.9% purity from J. T. Baker Chemical Co. were used. The barriers were porous alumina disks which were placed on the top of a high density alumina cell and were masked by a molybdenum lid (Fig. 1). Two different preparations of porous alumina were used. The first of relative density 0.442 was prepared from irregular alumina particles of the order of 10μ average diameters. The second, of relative density 0.555 was formed of more rounded particles of average diameter of the order of 1μ . (See Fig. 2.) 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. With each disk a run was made in which the ion intensities of NaCl^+ (from NaCl gas) and Na_2Cl^+ (from Na_2Cl_2 gas)²⁶⁻²⁹

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Figure 1. High temperature cell assembly.

(a)

(b)

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Fig. 2. Scanning electron micrographs of the porous alumina samples.
(a) Relative density 0.442, and (b) relative density 0.555.

were measured over a range of temperature below the melting point of sodium chloride, 1074°K. The approximate average temperature of each run was 1025°K. In each experiment a circular area of the disks 3.8 mm in diameter was exposed to the vacuum. To compare the results 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. To avoid going above the region of molecular flow in the orifice channel^{11,30,31} this run was carried out at lower temperatures, 895 to 1025°K.

In order to establish whether equilibrium was achieved in the exit vapors from the porous barriers, separate weight-loss runs were made with the 0.28, 0.389 and 0.838 mm porous disks of 0.442 relative density and with a 0.3 mm disk of relative density of 0.555. In these runs the weight loss in a measured time was measured at a fixed temperature of 1025°K.

Finally to compare the transmission coefficients of the disks (defined as the ratio of total mass flux at the outlet face to that at the inlet face of a porous barrier) for sodium chloride vapors with that of 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 zinc runs these disks, which were previously used for sodium chloride, were washed with hot water and baked out in the mass-spectrometer until the ion peaks corresponding to sodium chloride vapor molecules disappeared from the spectrum.

In order to measure the 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, but since zinc also has a unit vaporization coefficient³² the results are insensitive to this condensation.

To obtain greater flexibility in the range of porous barriers which could be studied a second experimental arrangement was developed. In this design (Fig. 3) a small graphite cell containing sodium chloride powder is placed in the middle of a larger graphite cell and is covered completely by the powder of the material through which the transport of the vapors is to be studied. The thickness of the powder layer is smallest directly on the top of the small cell so that almost all the exit vapor comes exclusively from that region. A study of temperature dependence of the intensities of the ions Na^+ and NaCl^+ and Na_2Cl^+ was completed using this design with nickel powder (B&A nickel powder, code 2011) of an average about 50 μ particle size as the porous barrier. The thickness of the powder on the top of the cell was about 1.5 mm. The nickel powder in the other regions was at least 2 mm thick. The temperature was measured by a thermocouple at the bottom of the larger cell. The temperature range was about 930-1030°K.

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Figure 3.

IV. RESULTS

Intensities of the ions, Na^+ , NaCl^+ and Na_2Cl^+ obtained from the Knudsen effusion cell were multiplied by the absolute temperature, T , to give quantities proportional to the partial pressures of the corresponding neutral precursors (see Eq. (11)). Plots of $\ln I^+T$ versus $\frac{1}{T}$ are shown in Fig. 4. The slope of the straight lines so obtained is equal to

$$- \frac{\Delta H_v^0}{R} \quad (21)$$

where ΔH_v^0 is the average standard heat of vaporization of the neutral vapor molecules from which the ions are formed over the temperature range of study and R is the universal gas constant. Linear least square analysis of the points gave the slopes and intercepts, listed in Table I.

Table I. Results of sodium chloride
in Knudsen effusion cell

Ion	Slope $\times 10^{-3}$	Intercept
Na^+	-24.593 ± 0.212	34.499 ± 0.231
NaCl^+	-24.378 ± 0.364	33.926 ± 0.397
Na_2Cl^+	-25.748 ± 0.374	35.052 ± 0.412

Our studies with porous disks support earlier conclusions²⁶⁻²⁹ that Na^+ and NaCl^+ are formed essentially exclusively from NaCl and that Na_2Cl^+ is from Na_2Cl_2 . From the slopes we obtain the mean values of 48.9 ± 0.4 Kcal/mole and 48.4 ± 0.7 Kcal/mole from ΔH_v^0 of NaCl and 51.2 ± 0.7 Kcal/mole for ΔH_v^0 of Na_2Cl_2 . The JANAF³³ values are 52.2 Kcal/mole

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Figure 4. Knudsen effusion run of sodium chloride.

and 56.9 Kcal/mole for NaCl and Na₂Cl₂, respectively. The discrepancy in the heats obtained in this experiment and those reported in the JANAF tables probably comes from a temperature dependent error in the temperature measurements of the experiment. The ratio of the intensities of different ions which is the main focus of this study is insensitive to such an error in temperature measurements.

Plots of $\ln I^+T$ obtained in the same way for NaCl⁺ and Na₂Cl₂⁺ in experiments with porous disks of relative density 0.442 are shown in Figs. 5-9. Linear least square analyses of these data yield the values listed in Table II. The result of the independent run for measuring the intensity of Na⁺ ions relative to the NaCl⁺ ions above the porous disk of 0.838 mm thickness is shown in Fig. 10.

In all of the experiments on sodium chloride with porous disks, sodium chloride condensed on the lower surface of the disk because temperature of the disks, as shown by calibration measurements of disk temperatures, were about 15°K lower than the temperature 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.²²

From the data in Table II the following ratios of ion intensities of NaCl⁺ to Na₂Cl₂⁺ were calculated at 1025°K (the approximate midpoint of the runs):

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Figure 5. Vaporization of sodium chloride through the porous layer of relative density 0.442 and 0.28 mm thickness.

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Figure 6. Vaporization of sodium chloride through the porous layer of relative density 0.442 and 0.389 mm thickness.

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Figure 7. Vaporization of sodium chloride through the porous layer of relative density 0.442 and 0.599 mm thickness.

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Figure 8. Vaporization of sodium chloride through the porous layer of relative density 0.442 and 0.69 mm thickness.

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Figure 9. Vaporization of sodium chloride through the porous layer of relative density 0.442 and 0.838 mm thickness.

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Figure 10. Vaporization of sodium chloride through the porous alumina disk of relative density 0.442 and 0.838 mm thickness.

Table II. Results of sodium chloride runs with porous disks
(corrected for the temperature of the porous disks)

Disk thickness mm	Slope x 10 ⁻³		Intercept		ΔH_V^+ (Kcal/mole)	
	NaCl	Na ₂ Cl ₂	NaCl	Na ₂ Cl ₂	NaCl	Na ₂ Cl ₂
0.28	-25.469 ± 1.168	-31.372 ± 1.797	33.204 ±1.143	35.239 ±1.758	50.6 ±2.3	62.3 ±3.6
0.389	-24.937 ± 0.564	-33.293 ± 2.115	32.858 ±0.554	36.879 ±2.100	49.6 ±1.1	66.2 ±4.2
0.599	-22.254 ± 1.659	-28.970 ± 2.163	29.750 ±1.625	31.883 ±2.119	44.2 ±3.3	57.6 ±4.3
0.69	-24.424 ± 0.758	-33.808 ± 2.337	31.482 ±0.737	35.921 ±2.270	48.5 ±1.5	67.2 ±4.6
0.838	-22.712 ± 1.046	-33.093 ± 2.629	30.031 ±1.018	35.301 ±2.600	45.1 ±2.1	65.8 ±5.2

<u>Disk thickness (mm)</u>	<u>$I_{\text{NaCl}^+}/I_{\text{Na}_2\text{Cl}^+}$</u>
0.28	41.4
0.389	62.3
0.599	83.1
0.69	111.6
0.838	129.

When the ratios of $I_{\text{NaCl}^+}/I_{\text{Na}_2\text{Cl}^+}$ are plotted as a function of disk thickness, ℓ , Fig. 11 is obtained.

Weight losses through three different porous disks (Table III) 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 used to determine the proportionality constant C between the monomer to dimer intensity ratio

$$\frac{I_{\text{M}}^+}{I_{\text{D}}^+}$$

and the monomer to dimer partial pressure ratio $\frac{P_{\text{M}}}{P_{\text{D}}}$ reported for equilibrium studies in the JANAF tables:

$$\frac{P_{\text{M}}}{P_{\text{D}}} = C \frac{I_{\text{M}}^+}{I_{\text{D}}^+}$$

The partial pressure of monomer was calculated in each weight loss experiment by means of the Hertz-Knudsen-Langmuir equation³⁴⁻³⁶ with the approximation that weight loss through the porous disks as dimer can be

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Figure 11. Variation of the monomer/dimer intensity ratio with the thickness of the porous alumina disks (in mm) at 1025°K.

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

Relative density of the alumina disk	Disk thickness in mm	Partial pressure of the monomer (atm)	Partial pressure of the dimer (atm)	P_M^2/P_D
0.442	0.28	3.01×10^{-6}	4.66×10^{-8}	1.94×10^{-4}
0.442	0.389	3.12×10^{-6}	3.21×10^{-8}	3.03×10^{-4}
0.442	0.838	2.03×10^{-6}	1.05×10^{-8}	3.92×10^{-4}
0.555	0.30	3.00×10^{-6}	2.50×10^{-8}	3.6×10^{-4}
JANAF	0	1.15×10^{-4}	4.78×10^{-5}	2.77×10^{-4}

neglected. (The maximum dimer intensity was $\frac{1}{41.4}$ the monomer intensity.)

$$P_M = \frac{W}{At} \left(\frac{2\pi RT}{M} \right)^{1/2}$$

where M is the molecular weight of the monomer, W is the total weight loss and t is the total time of heating. A is the effective area of vaporization, which in this study 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).

In Fig. 12 values of P_M^2/P_D from Table III are plotted against the thickness of the porous layer.

The results of the weight loss measurements on zinc at 668°K are as follow:

Disk thickness (mm)	P_{Zn} (atm)	Total mass flux, j_{Zn} (g.cm ⁻² sec ⁻¹)
(Run #1	2.12×10^{-6}	2.94×10^{-5}
0.389 (		
(Run #2	2.08×10^{-6}	2.89×10^{-5}
0.838	1.09×10^{-6}	1.51×10^{-5}
JANAF	9.05×10^{-5}	8.49×10^{-4}

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Figure 12.

The quantities j_{Zn}/j_{Zn}^o for the two porous layers, where j_{Zn}^o is the total mass flux at the inlet side of the porous layer are given in Table IV with the corresponding values of the fractional reduction in total mass flux for sodium chloride, i.e.

$$\frac{j_{NaCl} + j_{Na_2Cl_2}}{j_{NaCl}^o + j_{Na_2Cl_2}^o}$$

calculated from Table III for comparison.

Table IV. Transmission coefficients of the porous layers for sodium chloride and zinc

Disk thickness (mm)	$\frac{j_{Zn}}{j_{Zn}^o}$ at 668°K	$\frac{j_{NaCl} + j_{Na_2Cl_2}}{j_{NaCl}^o + j_{Na_2Cl_2}^o}$ at 1025°K
0.389 (Run #1	3.46×10^{-2}	2.53×10^{-2}
(Run #2	3.40×10^{-2}	
0.838	1.78×10^{-2}	1.64×10^{-2}

The temperature dependence of ion intensities produced from zinc atoms vaporized through the porous layer is shown in Fig. 13. Linear least square fit of the points 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.³⁷

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Figure 13. Temperature dependence of ion intensities produced from zinc atoms vaporized through the porous layer of relative density 0.442 and 0.389 mm thickness.

In the temperature dependent study of the ion intensities of Na^+ , NaCl^+ and Na_2Cl^+ , using nickel powder as the porous barrier, a decrease of the ion intensities with time was observed during about the first two hours of heating. This behavior is attributed to a settling and sintering of the nickel particles. Despite this settling and sintering, particle size and shape changes were insignificant as can be seen from the scanning electron micrographs taken before and after the experiment (Fig. 14). Least square analysis of the data taken after the intensities stabilized (Fig. 15) gives an apparent heat of vaporization of 52.3 ± 0.9 Kcal/mole for the monomer and 60.7 ± 0.9 Kcal/mole for the dimer. This compares to the values of JANAF tables which are 51.8 Kcal/mole for the monomer and 56.1 Kcal/mole for the dimer, at 975°K, the approximate average temperature of the experiment. The heat obtained from the temperature dependence of the ion intensities of Na^+ is 52.4 ± 0.5 Kcal/mole. The ratio of the ion intensities of the monomer to the ion intensities of the dimer, i.e.

$$\frac{I_{\text{NaCl}^+}}{I_{\text{Na}_2\text{Cl}^+}}$$

calculated from the least square data was 45.2 at 975°K, and the ratio

$$\frac{I_{\text{Na}^+}}{I_{\text{NaCl}^+}} \text{ was } 1.38 \text{ at this temperature.}$$

(a)

(b)

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Fig. 14. Scanning electron micrographs of the nickel particles (a) before and (b) after experiment.

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Figure 15. Vaporization of sodium chloride through nickel powder.

V. DISCUSSION

Fluxes of sodium chloride monomer through the porous alumina barriers are reduced about two orders of magnitude by the porous barriers used. The intensity ratio $I_{\text{Na}^+}/I_{\text{NaCl}^+}$ is the same as that measured for equilibrium effusion of the saturated vapor, while the intensity ratio $I_{\text{Na}_2\text{Cl}^+}/I_{\text{NaCl}^+}$ is down by about two orders of magnitude from the ratio measured for effusion and varies inversely with barrier thickness (Fig. 11). These results confirm earlier conclusions that in the fragmentation pattern of sodium chloride gaseous species, Na^+ and NaCl^+ are both essentially exclusively produced from NaCl but Na_2Cl^+ from Na_2Cl_2 .

That the ratio $I_{\text{NaCl}^+}/I_{\text{Na}_2\text{Cl}^+}$ varies linearly with barrier thickness confirms the predictions which were made on the assumptions that vapor transport would be by Knudsen flow and that equilibrium would be attained at the reduced pressures which correspond to the reduced fluxes at the outlet side of the barrier. Values of P_M^2/P_D calculated by combination of weight loss results with intensity measurements for three different barrier thicknesses confirms, to well with a factor of two, the prediction that equilibrium is attained by the outlet fluxes (Table III).

If surface diffusion were the dominant mode of transport through the porous barrier, equilibrium would still be expected at the outlet face of the barrier, and the total flux would, according to Ficks first law, be expected to vary inversely with the barrier thickness, provided that the diffusion coefficient were independent of the concentration of sodium chloride vapor.

Both sodium chloride vapor and zinc vapor show the same transmission coefficients in the total mass flux for the same porous disk (Table IV).

This result was predicted for vapors that pass through the porous barriers by Knudsen flow, even when one vapor, like sodium chloride, undergoes a pressure dependent reaction. The equality between transmission coefficients for sodium chloride vapor and zinc vapor implies that surface diffusion is not an important mode of transport for either vapor or that surface diffusion is coincidentally equally important for both. Because rates of surface diffusion must depend upon the strength of chemical interactions between a surface and each different kind of vapor, equal contributions for the two vapors are possible but unlikely. We can conclude that Knudsen flow was probably, but not certainly, the principal mode of transport of both sodium chloride and zinc vapors through the porous alumina barriers used.

The apparent heats of vaporization for the dimer (Table II) are higher than the equilibrium value, 56.9 Kcal/mole by a greater difference than expected from possible systematic errors. The difference may result because the activation energy for desorption of the dimer from the alumina surfaces is higher than that of the monomer. However, the dimer partial pressures are low and the temperature range of dimer measurements are relatively restricted. We see no explanation for these high apparent heats other than error in measurements.

The effect of porous barriers on molecular compositions of reactive gases could prove useful whenever enrichment is desired in the simpler molecules of a reactive gas mixture. For example, a porous barrier provides an easier means for enriching a molecular beam in monomer vapor species for determination of mass-spectrometer fragmentation patterns than does the double oven technique (which, however, has additional

applications).² DeMaria has commented³⁸ that porous barriers would also be useful in altering the proportions of species to be studied by matrix isolation methods. In Part II of this thesis the effect of porous barriers on molecular compositions is applied to a study of the unusual dependence of mass-spectrometer fragmentation pattern on temperature reported for lithium fluoride vapor.²

PART II. APPLICATIONS. STUDIES ON LITHIUM FLUORIDE

I. INTRODUCTION

In the determination of thermodynamic data for high temperature systems from mass spectrometer intensity measurements, it is customary to assume that when an ion is formed in the ion source of a mass-spectrometer as a result of electron bombardment of a neutral species originated in the Knudsen cell, then the ratio I_i^+T/P_i is a constant of temperature, where I_i^+ is the measured intensity of the species i originated in a Knudsen cell in which it has partial pressure P_i at absolute temperature T . This is the so-called specificity rule² in mass-spectrometry.

While for organic molecules it is known that the specificity rule is sometimes not obeyed, the only inorganic molecule so far reported to disobey the rule is the monomer of lithium fluoride vapor,² LiF(g) . Berkowitz et al. used a porous nickel barrier between a chamber in which solid lithium fluoride was heated and a second chamber, which served as a Knudsen effusion cell. The temperature of each chamber could independently be controlled, and by this means they were able to vary the ratios of the partial pressures of the monomer to dimer, and therefore the ion intensity ratios $I_{\text{LiF}^+}/I_{\text{Li}_2\text{F}^+}$, from 1.8 to 0.24, in the effusion cell at 1093°K. They found that (a) the only source of the ion Li^+ was the monomer, LiF(g) , and (b) the specificity rule fails for the monomer in the sense that the ratio $I_{\text{Li}^+}/I_{\text{LiF}^+}$ is temperature dependent.

In Part I of this thesis we showed that a porous barrier can also cause equilibration of reactive vapor mixtures at the decreased pressures

produced by the barriers. Because the specificity rule is of crucial importance in thermodynamic studies made with mass spectrometers, we have applied the barrier effect to re-examine the influence of temperature on the mass spectrometer fragmentation pattern of lithium fluoride vapor.

II. EXPERIMENTAL

Lithium fluoride samples of optical grade were obtained from the Hudson Laboratories in Florida.

In a preliminary experiment this material was heated in a high density alumina cell covered with a porous disk of 0.4 mm thickness and relative density 0.555. The temperature dependence of the ions Li^+ and LiF^+ and Li_2F^+ were measured below the melting point of lithium fluoride, 1115°K. Two weight loss experiments were also carried out at 1015°K using the same cell assembly.

Three independent runs were made with lithium fluoride using nickel powder as the porous barrier in exactly the same form as was used in the experiment with sodium chloride. The nickel powder sample was also the same as before. In these experiments the temperature dependence of Li^+ and LiF^+ and Li_2F^+ were again measured over a range of temperature but below the melting point of lithium fluoride, and with 1053°K as the approximate average temperature for each run.

Finally to compare the results of the porous barrier experiments with those of the equilibrium experiments, and also to check the calibration of the machine, two independent runs were completed in each of which lithium fluoride was heated in a conventional effusion cell made of graphite. The orifice was a tapered one with a base diameter of 0.71 mm. Again these runs were made at temperatures below the melting point of lithium fluoride, with 1010°K as the approximate average temperature for each run.

III. RESULTS

A very strong time dependency of the Li^+ , LiF^+ and Li_2F^+ intensities were observed when lithium fluoride was heated in the alumina cells even at temperatures about $30^\circ\text{--}40^\circ\text{K}$ below the melting point of lithium fluoride. The alumina cells were found to be embrittled after heating. Furthermore, after each run, even though the temperature of the cell was maintained always at least 30°K below the melting point of lithium fluoride, some traces of lithium fluoride were found on the exterior surfaces of the alumina cell whenever a determination of temperature dependence of the ions Li^+ , LiF^+ and Li_2F^+ was attempted.

In the first weight loss experiment, in which the temperature was first raised close to the melting point of lithium fluoride (about 20°K below it), and then lowered, the following average intensities were obtained: $I_{\text{Li}^+} = 0.948$; $I_{\text{LiF}^+} = 0.204$; $I_{\text{Li}_2\text{F}^+} = 0.458$. This gives

$$\frac{I_{\text{Li}_2\text{F}^+}}{I_{\text{LiF}^+}} \approx 2.2.$$

In the second run in which the temperature was not first raised close to the melting point, the following average intensities were obtained:

$I_{\text{Li}^+} = 0.08$; $I_{\text{LiF}^+} = 0.025$; $I_{\text{Li}_2\text{F}^+} = 0.0047$. This gives

$$\frac{I_{\text{Li}_2\text{F}^+}}{I_{\text{LiF}^+}} = \approx 0.2.$$

The results of the two independent conventional effusion runs of lithium fluoride in graphite cell are shown in Figs. 16 and 17. Least square analysis of the data results in the values given in Table V, which includes, for comparison, the JANAF data for the monomer and the dimer. The results of the least square analysis give the following quantities at 1010°K, the approximate average temperature of the runs. (The intensities are normalized to $I_{\text{LiF}^+} = 100$ in each case.)

	I_{Li^+}	I_{LiF^+}	$I_{\text{Li}_2\text{F}^+}$
Run #1	432	100	683
Run #2	419	100	579

In the experiments of effusion of lithium fluoride through nickel powder, time dependency of all ion intensities, i.e. Li^+ , LiF^+ and Li_2F^+ were observed in the early periods of the experiments just as for sodium chloride. The intensities stabilized sooner than for sodium chloride, probably because the temperatures were in general higher in these experiments than in the sodium chloride experiment. However, the transient period is again attributed to settling and sintering of nickel particles (see Part I of the work). In each run the values of $\ln I^+T$ for Li^+ , LiF^+ and Li_2F^+ were plotted against $\frac{1}{T}$ and the results are shown in Figs. 18, 19, and 20. Least square analysis of the data taken after the intensities stabilized gives the results tabulated in Table VI.

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Figure 16. Knudsen effusion run (no. 1) of lithium fluoride.

Figure 17. Knudsen effusion run (no. 2) of lithium fluoride.

Table V. Results of the Knudsen effusion runs of lithium fluoride.
The JANAF values are calculated for the approximate average
temperature of the runs, 1010°K.

Run #	Slope x 10 ⁻³			Intercept			ΔH_v (Kcal/mole)		
	Li ⁺	LiF ⁺	Li ₂ F ⁺	Li ⁺	LiF ⁺	Li ₂ F ⁺	Li ⁺	LiF ⁺	Li ₂ F ⁺
1	-30.235 ± 0.300	-31.623 ± 0.496	-33.468 ± 0.287	35.762 ± 0.296	35.699 ± 0.489	39.288 ± 0.283	60.1 ± 0.6	62.8 ± 1.0	66.5 ± 0.6
2	-30.988 ± 0.451	-31.628 ± 0.561	-32.878 ± 0.329	36.114 ± 0.448	35.280 ± 0.555	38.443 ± 0.327	61.6 ± 0.9	62.9 ± 1.1	65.3 ± 0.7
JANAF	-	-	-	-	-	-	-	63.1	64.7

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Figure 18. Vaporization of lithium fluoride through nickel powder.
Run No. 1.

Figure 19. Vaporization of lithium fluoride through nickel powder.
Run No. 2.

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Figure 20. Vaporization of lithium fluoride through nickel powder.
Run No. 3.

Table VI. Results of vaporization of lithium fluoride through nickel powder.
The JANAF values are calculated for the approximate average temperature
of the runs, 1053°K.

Run #	Slope x 10 ⁻³			Intercept			ΔH_v^+ (Kcal/mole)		
	Li ⁺	LiF ⁺	Li ₂ F ⁺	Li ⁺	LiF ⁺	Li ₂ F ⁺	Li ⁺	LiF ⁺	Li ₂ F ⁺
1	-32.498 ± 0.507	-33.749 ± 0.926	-33.575 ± 0.599	35.679 ±0.482	35.519 ±0.881	34.269 ±0.568	64.6 ±1.0	67.1 ±1.8	66.7 ±1.2
2	-33.911 ± 0.557	-34.091 ± 0.629	-38.016 ± 0.797	37.055 ±0.529	35.926 ±0.597	38.557 ±0.757	67.4 ±1.1	67.7 ±1.2	75.5 ±1.6
3	-32.777 ± 0.187	-33.655 ± 0.452	-36.277 ± 0.806	36.319 ±0.177	35.926 ±0.429	37.522 ±0.764	65.1 ±0.4	66.9 ±0.9	72.1 ±1.6
JANAF	-	-	-	-	-	-	-	62.8	64.3

IV. DISCUSSION

The fact that the transmission coefficients of lithium fluoride through porous alumina disks were much higher than for sodium chloride indicates that surface diffusion must be an important mode of transport of lithium fluoride through the porous layer. Moreover, in the experiment in which the cell was first heated close to the melting point of lithium fluoride the intensity ratios were higher than in the run at lower temperatures and reached $I_{\text{Li}_2\text{F}^+}/I_{\text{LiF}^+}$ ratios of the order of 0.35 of the equilibrium values. This high ratio can probably be attributed to the formation of a lithium fluoride film on the walls of the pores, along which lithium fluoride moves by liquid phase diffusion. The increase in ion intensities with time, especially at higher temperatures, suggests that a film spread on the alumina surface and drew lithium fluoride up to fill the pores by capillary action.

The embrittlement of alumina cells by lithium fluoride and the observation of traces of lithium fluoride on the exterior walls of the cell are further indications that lithium fluoride strongly wets alumina. Film formation might have been avoided by working at lower temperatures, but it appeared probable that in the temperature ranges over which satisfactory fluxes could be attained surface diffusion would remain an efficient mode of transport through the pores. In consequence, a reduction in vapor fluxes sufficiently large to produce the desired increase in monomer to dimer intensity ratios might not be achieved.

The nickel powder proved a more satisfactory porous barrier. The approximately 1.5 mm thick layer of powder produced a reduction of the

$I_{\text{Li}_2\text{F}}^+/I_{\text{LiF}}^+$ ratios by about a factor of 20 compared to that of the equilibrium runs. However, since the apparent heats of vaporization for monomer and dimer through the porous barrier are higher than the reported equilibrium values, surface diffusion may be an important mode of transport through the nickel powder: if only Knudsen flow were important, the apparent heats of sublimation through the powder should be the same as for equilibrium measurements because steady state Knudsen flow is not an activated process (see Eq. (2) of Part I).

The fact that the intensity ratios $I_{\text{Li}}^+/I_{\text{LiF}}^+$ stayed approximately the same for the Knudsen effusion runs and for the nickel powder experiments, where the intensity ratios $I_{\text{Li}_2\text{F}}^+/I_{\text{LiF}}^+$ were different by a factor of about 20, confirms the report by Berkowitz, et al. that the main source of Li^+ ions is the monomer, LiF(g) . The difference between the $I_{\text{Li}}^+/I_{\text{LiF}}^+$ ratios from effusion measurements and porous barrier measurements (calculated from Tables V and VI) indicates that probably 10 to 12% of the Li^+ signal may arise from fragmentation of dimer and/or higher polymers.

The Knudsen effusion results plus the nickel powder effusion results for lithium fluoride show little or no temperature dependence in the fragmentation pattern of LiF(g) . The ratios of $I_{\text{Li}}^+/I_{\text{LiF}}^+$ reported by Berkowitz, et al. are 9.0 and 4.7 at 975°K and 1050°K, respectively, but the corresponding average values calculated from the least square results of Table IV are 3.87 and 3.65. Because the corresponding ratios measured in the effusion experiments, 4.43 and 4.12, show a similar small difference, it may be that the small variation is real. But the variation is certainly little more than expected from errors in measurement.

ACKNOWLEDGMENT

I deeply acknowledge Prof. Alan W. Searcy, a gentleman and a real scientist, for his invaluable guidance and encouragement both professionally and personally throughout my graduate work.

I am indebted to Dr. David J. Meschi for his frequent technical help as well as many helpful suggestions. I also thank Dr. Alfred Büchler for his helpful suggestions. The trials of being a graduate student in science were considerably eased by the companionship of my fellow student Tushar K. Basu. Finally, my thanks are due to Emery Kozak, a master of vacuum technology, for his many technical helps. Kelly Radmilovic kindly typed this manuscript, which is, of course, appreciated.

This work was supported by the U. S. Energy Research and Development Administration.

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