DIFFUSION MEASUREMENTS USING A MODIFIED KNUDSEN TECHNIQUE

by

D. J. Fray*

ABSTRACT

By measuring the weight loss out of a Knudsen cell the vapor pressure of the escaping species can be calculated. If the only way this species can enter the Knudsen cell is by diffusion through a foil, the steady state weight loss is also the diffusion flux. The composition of the surface of the foil in the cell is given by the vapor pressure in the cell and the thermodynamics of the system. The composition of the other foil surface can be controlled by the external vapor pressure of the diffusing material. Using the above data and the foil thickness, the diffusion coefficient can be calculated from Fick's first law. This technique has been used to study the diffusion of zinc through thin silver foil in the temperature range 500-800°C.

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* Assistant Professor, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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INTRODUCTION

Diffusion in metals and alloys is of fundamental importance as well as being of practical interest. A considerable number of solid state reactions are diffusion controlled. However, in some cases, the bulk diffusion coefficient does not give an accurate prediction of the mass transport. For example, the diffusion of zinc out of brass is 5 times faster than the diffusion of zinc into brass[1]. Many industrial processes rely on the diffusion of matter through a thin foil or layer, where both inward and outward diffusion occurs, and, in this case, the bulk diffusion coefficient may be insufficient for calculating the useful lifetime of metals and alloys. In an attempt to study this problem, it was decided to measure the diffusion of metallic vapor through thin non-volatile foils. The Knudsen method used in this work was originally developed by Meadowcroft and Cuny[2].

From the measured weight loss out of a Knudsen cell, the efflux vapor pressure can be calculated and by using a series of alloys of different composition, a relationship between composition and the equilibrium vapor pressure at a particular temperature can be determined. If, however, a foil is placed between the alloy and the orifice so that the only path for the vapor into the Knudsen cell is through the foil, the flux leaving the cell is also the diffusion flux. Under steady state conditions Fick's first law,

$$J = -D \frac{\partial C}{\partial X} \tag{1}$$

where J is the flux per unit area, D is the diffusion coefficient

[redacted]

and $\frac{\partial C}{\partial X}$ is the concentration gradient in the x direction, is valid. It is assumed that the composition of one side of the foil will be that of an alloy held in equilibrium with the foil, and the composition of the other side is given by the weight loss and thermodynamics of the diffusing species. The weight loss, therefore, gives the inner foil composition and by measuring the thickness and area of the foil, the diffusion coefficient may be found directly.

The Knudsen expression for calculating vapor pressures from the flux through a small orifice is given by

$$P(\text{atm}) = 2.255 \times 10^{-2} \times \frac{w}{W_o tA}\sqrt{\frac{T}{M}} \tag{2}$$

where P is the vapor pressure in atmospheres, w/t is the weight loss in gm/sec, W_o is the Clausing factor to correct for absorption and subsequent remission of atoms in the orifice, A is the orifice area in sq cm, T is the absolute temperature and M is the molecular weight.

Provided the vapor pressure and the thermodynamics of the alloy system concerned are known, the concentration of the diffusing species on the outside of the foil can be calculated from

$$\frac{P}{P_o} = a \tag{3}$$

and

$$a = N\gamma \tag{4}$$

where P is the vapor pressure given by expression (2), P_o is the vapor pressure of the pure substance at the temperature under consideration, N is the atom fraction, a is the activity and γ is the activity coefficient.

One of the limitations of this technique is that the vapor pressure of the diffusing element must be at least two orders of magnitude higher than that of the metal through which diffusion occurs. Under this condition, it can be assumed that only the vapor of the diffusing element leaves the cell. Secondly, in order that the weight loss be measured accurately, the flux must be at least 10^{-9} gm/sec. Also, the weight loss should not be greater than 10^{-6} gm/sec; otherwise, the Knudsen expression no longer holds for an orifice of approximately 10^{-4} cm^2. This range of measurement is roughly the same as given by the sectioning technique.

The system chosen for study is the diffusion of zinc through silver. The zinc-silver system was selected as the thermodynamics of the system are known and other diffusion data exist for comparison. In order to avoid complications that would result if compounds formed, it was decided to study diffusion in the α-solid solution region.

Experimental Procedure

The experimental arrangement was essentially the same as that used by Boyer and Meadowcroft[3] in their studies of surface diffusion in a Knudsen cell. The only modifications were the addition of a thermocouple (enclosed in an alumina tube to prevent contamination from zinc vapor) just below the crucible and more radiation shields to improve the temperature profile. Preliminary measurements showed that an even temperature zone (±1°C) of at least 1" existed in the furnace over the temperature range studied. A constant voltage source was used and the temperature was kept within ±2°C during a run.

The success of the cell rested upon obtaining a leak-tight seal between the foil and the cell and having a well-defined foil area. The cell consisted of a tantalum container which fitted perfectly into the molybdenum cylinder containing the orifice

The foil was stretched over the tantalum portion and the unit was assembled at room temperature. On heating to the operating temperature, the tantalum container expands tightly against the molybdenum portion to form a gas-tight seal as the coefficient of expansion for tantalum exceeds that for molybdenum. The area of the foil was taken to be the area defined by the knife edges of the tantalum container. As data was not available for zinc surface diffusion on molybdenum, a conical orifice was used, to which a Clausing factor was applied.

The foil and the silver used to make up the alloys was 99.90% pure, while the zinc was 99.98% pure. Silver-zinc alloy chips were used as a source of volatile zinc vapor. The zinc concentration was known to ±0.05 wt%. This was determined by chemical analysis, and successive determinations of the same sample were accurate to the above figure.

The thickness of the foil was determined by two methods. First, a known area of foil was weighed and, from the density of silver, the thickness was calculated. This method always gave good agreement with the reading given by a micrometer. The former reading was always taken, and it was assumed that the foil thickness was known within 5%.

The weight loss was given by a microbalance which was accurate to ±0.02 mg. The cell was weighed before and after each run, and the resulting weight loss was usually within ±0.0005 gm of that obtained from the microbalance charts. Because zinc vapor was lost from the cell during a run, the concentration of zinc in the container had to be continuously corrected. This was calculated from the original analysis and the weight loss given by the chart. Calculations showed that the amount of zinc in the foil was negligible at all times.

An error analysis showed that the errors in the foil area and thickness were the most important, and these gave an overall error in the diffusion coefficient of 15%. This is approximately the same error obtained by the sectioning techniques.

Results

The flux from the cell was obtained at 5 temperatures and at various initial starting conditions. About 5 runs were made at each temperature.

In order to check that diffusion was the rate-controlling step, the thickness of the foil was varied at 1000°K. For the same concentration drop, the flux is inversely proportional to the thickness, which shows that diffusion, and not the transport of zinc vapor into and out of the foil, controls the flux.

When calculating the concentration on the outside of the foil, the zinc vapor pressure data of Kubaschewski and Wittig[4] and the thermodynamic data of Birchenall and Cheng[5] were used. The latter data was available only at 600°C, and it was assumed that it was independent of temperature.

The results obtained from the experiment are the flux in gm/sec, the area and thickness of the foil, and the concentration gradient across the foil. In order to make equation (1) dimensionally correct, the LHS must be multiplied by the density of the foil. Provided the diffusion coefficient is independent of temperature, it can be calculated by direct substitution of the data in equation (1). However, when D is plotted against the concentration outside the foil, it is found that the diffusion coefficient is not independent of concentration. It is assumed that the diffusion coefficient depends on the concentration in the following way:

$$D_c = D_o\ (1 + ac + bc^2 + c'c^3) \qquad (5)$$

where D_c is the diffusion coefficient at concentration c (weight fraction), D_o is the diffusion coefficient at zero concentration and a, b and c' are constants. Substituting equation (5) into equation (1) and integrating gives

$$J\,\frac{\delta}{A} = -D_o\ [(C_o-C_i) + \frac{a}{2}\,(C_o{}^2-C_i{}^2) + \frac{b}{3}\,(C_o{}^3-C_i{}^3) + \frac{c'}{4}\,(C_o{}^4-C_i{}^4)] \qquad (6)$$

where δ is the thickness of the foil, C_i is the inside concentration and C_o is the outside concentration. In the range of concentrations used in these experiments $(C_o{}^3-C_i{}^3)$ and $(C_o{}^4-C_i{}^4)$ are very small compared to (C_i-C_o) and were, therefore, neglected. The available data were computed for the best values of D_o and a, and values of D_c calculated. When D_c is plotted against concentration, it is found that, at the lower temperatures, the diffusion coefficients obtained in this experiment are considerably greater than those obtained by Sawatsky[6], while, at the higher temperatures, there is good agreement.

Metallographic examinations were carried out on the foils, and it was found that after diffusion of the zinc the foils used at 1000°K were virtually uneffected. The foils used at low temperatures exhibited considerable porosity near the surface where the zinc leaves the foil. This effect increased markedly with decreasing temperature.

Discussion of the Results

The results found with this technique are in good accordance with the findings of other investigations. At high temperatures, the diffusion rates are approximately the same as those found by Sawatsky[6]. However, at temperatures below 960°K, the diffusion coefficient given by this method is considerably greater than that obtained by more normal methods. From the metallographs, it was seen that the increased diffusion was due to porosity at the outward edge of the foil. In similar experiments, Ballufi[7] observed porosity by evaporating copper from a copper-nickel alloy, silver from a silver-gold alloy and silver from a silver-palladium alloy into a vacuum. In the case of zinc evaporating from a brass specimen, he found that, although porosity occurred, the diffusion coefficient was unaltered.

It is probable that the larger diffusion coefficient of zinc results in zinc diffusing out of the foil faster than the silver can fill the vacant sites. These vacant sites then condense together to form pores. At 0% Zn, $\frac{D_{Zn}}{D_{Ag}}$ is 6.05 at 800°K and 4.7 at 1000°K[6,8]. Therefore, at higher temperatures, where the diffusion coefficient of silver approaches that of zinc, vacancies no longer form during the diffusion process. However, at 25 wt% Zn, $\frac{D_{Zn}}{D_{Ag}}$ is roughly 2.5[9] and is virtually independent of temperature and, providing the above reasoning is correct, one would expect the amount of porosity to decrease with increasing concentration. Becuase no runs were made at concentrations approaching 25 wt% Zn, this hypothesis could not be tested.

In the present work, it is seen that the transport of a metal through another metal having a smaller diffusion coefficient gives considerable porosity, which results in a decrease in the diffusion path with a corresponding increase in the mass transport. This is of direct importance in many industrial processes. For example, in galvanising, zinc has to diffuse through several intermetallic compounds to react with the iron and it is, therefore, anticipated that, due to the larger diffusion coefficient of the zinc, porosity will tend to occur in these layers, thereby reducing the adherence, mechanical strength and corrosion resistance of the coating.

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