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The Inert Gas Effect on the Rate of Evaporation of Zinc and Cadmium

P. C. S. WU, T. J. O'KEEFE, AND F. KISSLINGER

An experimental study has been made to investigate the effect of argon and helium on the rate of evaporation of zinc and cadmium under one atmosphere pressure at temperatures ranging from 500 to 850°C. The experimental results were compared with the maximum rates calculated using the effusion formula as well as with values obtained using two different types of equations based on kinetic theory, diffusion theory, and empirical data. Equations have been derived for expressing the rate of evaporation of zinc and cadmium in both argon and helium as functions of temperature of the liquid zinc and cadmium. It was found that the rates of evaporation of zinc and cadmium were higher in helium than in argon, with the difference increasing with increasing temperature. It was also found that the experimental results obtained in argon agree with the calculated values better than those obtained in helium.

THE maximum rate at which molecules of a vapor can leave the surface of a liquid during evaporation is given by the effusion formula, derived from the kinetic theory of gases:¹

$$W_o = P_o(M/2\pi RT)^{1/2} \quad [1]$$

where:

W_o is the rate of evaporation in gm/cm²-s,
 P_o is the vapor pressure of the liquid at temperature T in dynes/cm²,
 M is the molecular weight of the liquid, in g,
 R is the gas constant, in cal/mol-degree Kelvin, and
 T is the absolute temperature, in degrees Kelvin.

The maximum evaporation rate would be obtained if a perfect vacuum could be maintained over the liquid. However, in order to account for the probability that some of the molecules are "reflected" during evaporation, Knudsen² has inserted alpha, the "evaporation coefficient" into Eq. [1]. Since zinc and cadmium evaporate as monatomic gases, it is reasonable to assume that the evaporation coefficients are unity in the present investigation.

Evaporation in the presence of a foreign gas has been discussed in a number of papers.^{3,4} Under these circumstances the phase transition is followed by diffusion into the foreign gas. In the case of steady-state conditions both processes, the phase transition and the diffusion, occur at the same rate.

Luchak and Langstroth^{3,4} have derived an equation giving the rate of evaporation of a substance from a liquid surface when air is present (assuming no oxidation of the liquid surface) as:

$$W_2 = (9.60)(10)^{-4} (P_o) (MD/\lambda T) \quad [2]$$

where:

W_2 is the Luchak rate of evaporation of a substance, in g/cm²-min,

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P_o is the vapor pressure of the liquid at temperature T , in mm Hg,
 M is the molecular weight of the substance being evaporated in g,
 D is the diffusivity of the substance, in cm²/s,
 T is the absolute temperature, in degrees Kelvin, and
 λ is the distance between the evaporating and condensing surfaces, in cm.

Diffusivity, D , may be calculated from the following equation which has been derived by Maxwell⁴ from the kinetic theory of gases:

$$D = \frac{kT^{3/2} (1/M_A + 1/M_B)^{1/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \quad [3]$$

where:

D is the diffusivity in the gas, cm²/s,
 k is the constant, ranging from 0.0038 to 0.0047 (Ref. 5),
 M_A is the molecular weight of the metal A , in g,
 M_B is the molecular weight of the residual gas B , in g,
 P is the total pressure, in atm,
 T is the absolute temperature, in degrees Kelvin,
 V_A is the molal volume of the metal A in liquid state at its normal boiling point, in cm³/g-mol, and
 V_B is the molal volume of the residual gas B , in liquid state at its normal boiling point, in cm³/g-mol.

According to the Maxwell-Stefan⁶ law of molecular diffusion, the rate of diffusion of the metal A through a residual gas B is given as follows:

$$W_3 = \frac{(60)(P)(D)(P_{A1} - P_{A2})(M_A)}{(\lambda)(R)(T_{A1} - T_{A2})(P_{BM})} \quad [4]$$

where:

W_3 is the Maxwell rate of diffusion of the metal A , in a stagnant gas B , in g/cm²-min,
 P is the total pressure in atm,
 D is the diffusivity of the metal A in a stagnant gas B , in cm²/s,

P_{A_1} is the partial pressure of the metal A at the evaporating surface for a given temperature T_{A_1} , in atm,
 M_A is the molecular weight of the metal A, in g,
 λ is the distance between the evaporating and condensing surface, in cm,
 R is the gas constant, 0.082 (l-atm)/mol-degree Kelvin,
 T_{A_1} is the absolute temperature of the metal A at the evaporating surface, in degree Kelvin,
 T_{A_2} is the absolute temperature of metal A at the condensing surface, in degree Kelvin,
 P_{BM} is the log mean partial pressure of the residual gas B, that is, $(P_{B_2} - P_{B_1}) \ln(P_{B_2}/P_{B_1})$, where P_{B_1} and P_{B_2} are the partial pressures of the residual gas B at evaporating and condensing surface respectively, in atm.

Most previous studies of evaporation phenomena were carried out under vacuum. In this investigation the evaporation of liquid zinc and cadmium was studied under one atm pressure of argon and helium at temperatures ranging from 500 to 850°C. The purpose of this investigation was to study the effect of argon and helium on the evaporation of liquid metals. Previous work by Su⁷ indicated that the rate of evaporation could be affected by the nature of the residual gas used. Since his work included reducing gases, it was necessary to evaluate the phenomena by comparing results in only inert gases. Aside from gaining more insight into evaporation mechanisms, there is also the possibility of deriving practical benefits. If the rate is truly dependent on such things as mass or size of residual gas, and this effect differs for various metals, then it might be possible to selectively refine certain metal combinations by varying the residual gas atmosphere and pressure.

EXPERIMENTAL AND RESULTS

A series of evaporation experiments was made to determine the rates of evaporation of zinc and cadmium in argon and helium atmosphere at temperatures ranging from 500 to 850°C. The apparatus used in this investigation consisted of three major components: 1) resistance furnace and temperature controller, 2) evaporation unit-boiler and condenser, and 3) gas purifying system. The schematic diagram of the apparatus is shown in Fig. 1. Blank runs were made to determine the amount evaporated during heating and cooling at each temperature, and the evaporation rates were calculated by subtracting the appropriate blank from the amount evaporated in the experiment and dividing this difference by the product of the time and the evaporating surface area of 11.4 cm². The weight of the graphite crucible did not change from run to run. Therefore, it did not affect the rate of evaporation. In addition, it was observed that the rate of evaporation was essentially independent of the length of the run.

Nine measurements were made at a given temperature, and the average observed evaporation rates along with the calculated values based on Eqs. [1], [2], and [4] are plotted as Arrhenius curves in Fig. 2 for Zn. The experimental results obtained on Cd are plotted in Fig. 3. The relative standard deviation for the evaporation rates was less than 5 pct in most cases.

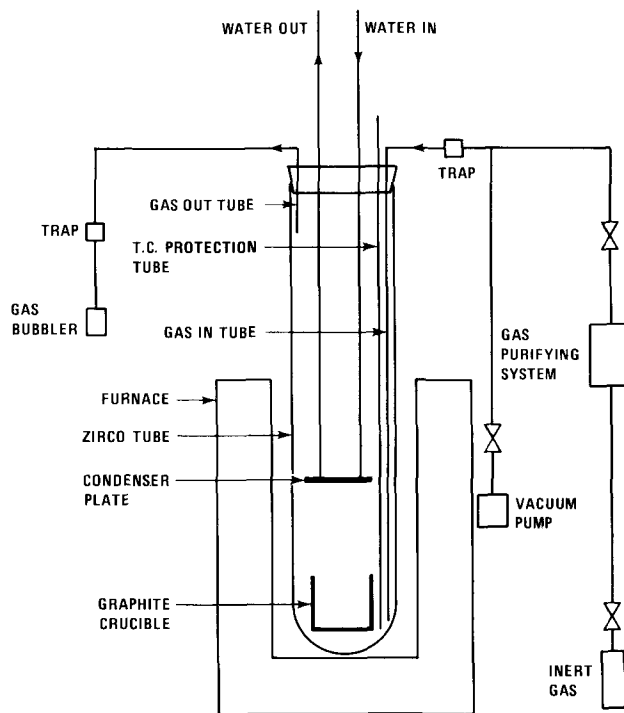


Fig. 1—Schematic of the experimental apparatus.

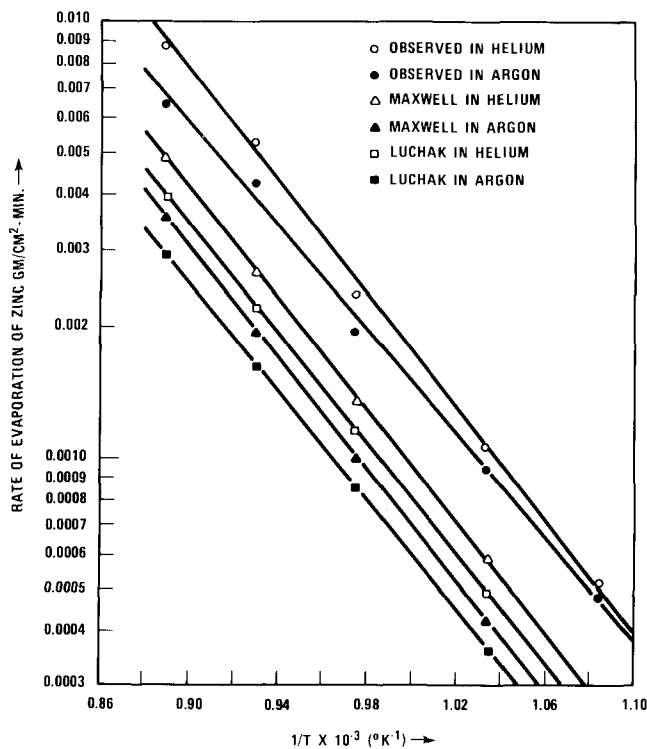


Fig. 2—Comparison of the observed and calculated rate of zinc evaporation.

Analytical expressions were derived, by using the least squares analysis, for the evaporation of zinc in helium and argon as Eqs. [5] and [6], respectively:

$$\log W_{Zn(He)} = -\frac{6555}{T} + 3.793 \quad [5]$$

$$\log W_{Zn(Ar)} = -\frac{6005}{T} + 3.175 \quad [6]$$

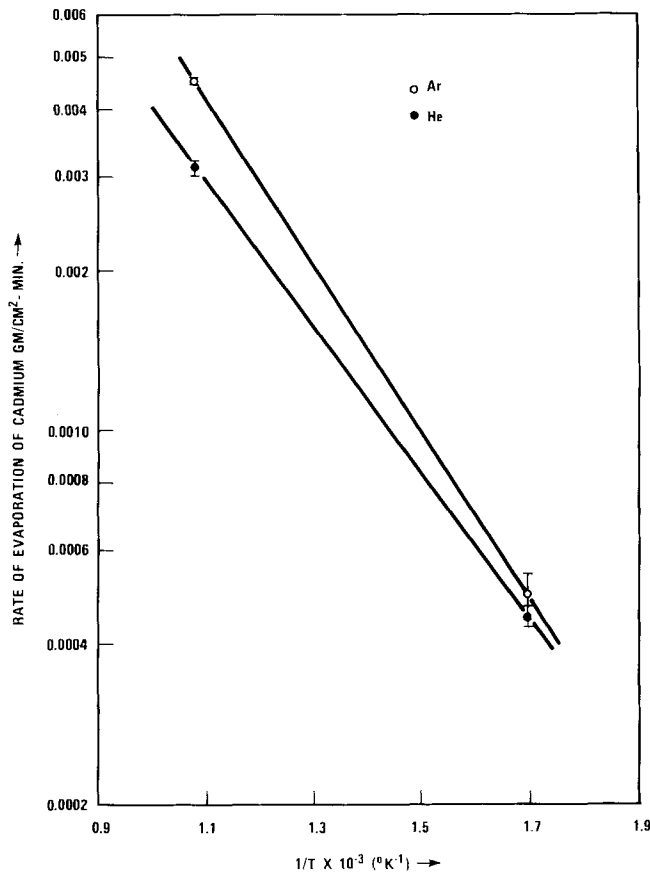


Fig. 3—The observed rate of evaporation of cadmium in argon and helium.

Since there were only two temperatures studied in the case of cadmium, the least squares method was not used to derive analytical expressions. The significance of the slope of the Arrhenius curves and the reason for the higher evaporation rate in helium atmosphere are discussed in the next section.

DISCUSSION

In plotting the rate of evaporation *vs* reciprocal temperature, as shown in Fig. 2, a straight line is obtained. From the slope of the straight line the activation energy of evaporation can be calculated. The Arrhenius equation is of the form:

$$\log W = -\frac{\Delta Q}{2.303R} \frac{1}{T} + C \quad [7]$$

where:

- W is the evaporation rate, in $\text{g}/\text{cm}^2\text{-min}$,
- T is the absolute temperature, in degrees Kelvin,
- ΔQ is the activation energy of evaporation, in kcal/mol ,
- R is the gas constant, $\text{cal}/\text{mol-deg Kelvin}$, and
- C is an integration constant.

By comparing Eqs. [5] and [7] we get ΔQ for zinc in helium to be 30.1 kcal/mol . Similarly, by comparing Eqs. [6] and [7], the ΔQ for zinc in argon is obtained to be 27.5 kcal/mol .

The maximum rate of evaporation of zinc can be calculated based on Eq. [1] and the vapor pressure data reported by Baker.⁸ The line of best fit for the maximum rates is also calculated by the least squares method and is of the form:

$$\log W_{\text{Zn(max)}} = -\frac{5900}{T} + 7.801 \quad [8]$$

By comparing Eqs. [7] and [8] one gets the apparent ΔQ for zinc in vacuum for the temperature range 650 to 850°C to be 27.06 kcal/mol .

The above activation energies differ from each other in the expected manner. That is, the slope of the theoretical curve is less than those of the observed curves. This was discussed in connection with the heat of evaporation which can be obtained from these data.⁹ The difference in activation energies is not believed to indicate a difference in mechanism for the evaporation processes. Lowe's¹⁰ work shows that ΔQ is fixed for the evaporation of solid silver in oxygen, nitrogen, and vacuum. That ΔQ_{He} , ΔQ_{Ar} , and ΔQ_{Vac} are not exactly the same can be justified as follows:

1. Contamination¹¹ of the evaporating surface by an oxide film.
2. The presence of absorbed residual gas on the liquid surface might affect the local equilibrium in the activated state.¹¹
3. Changes in the accommodation coefficients of the residual gases with temperature.¹²
4. Changes in the heat conductivity of the residual gas with temperatures.
5. The data may be too few to reduce the error sufficiently.

Although a thin oxide film was found on the sample surface at room temperature, its presence above the melting point is unlikely and, therefore, should have no effect on the measurements.

Hirth and Pound¹¹ noted that inert gases may be absorbed at the liquid-vapor interface and slow the kinetics of evaporation. Since argon and helium were used in this investigation, the changes of the activation energies of evaporation of zinc and cadmium are possible.

Smoluchowski¹² found that in some gases, particularly hydrogen and helium, the amount of heat given up to the gas by the solid was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving. This fraction was called the accommodation coefficient by Knudson.¹² He also observed that the accommodation coefficients for heavier gases, such as nitrogen, carbon dioxide were several times larger than those for lighter gases. Soddy and Berry¹³ in a study of the heat conductivity of gases, found that the accommodation coefficient for argon showed an average value of 0.85 over a relatively wide temperature range; while the coefficient for helium was 0.37 at 150°C, but became lower at higher temperatures. These variations of accommodation coefficient are recognized in the field of heat transfer as mentioned previously, and are discussed below in connection with the heat of evaporation. In this investigation, because of the lower accommodation coefficient of helium especially at higher temperatures, less heat is transferred from the liquid to the helium than to argon, and the

surface temperature of the liquid metal should be higher in a helium atmosphere than in argon. Therefore, it is reasonable to believe that the metal was actually evaporating at a higher temperature in the helium atmosphere than in the argon atmosphere even though the chromel-alumel thermocouple outside the boiler indicated the same temperature. This could account for the steeper slope on the helium curve.

It was also observed in Fig. 2 that the Luchak and Maxwell values remained a relatively constant fraction of the observed values at all temperatures. Since the ratios of the Luchak and the Maxwell values to the observed values show less variation with temperature, the mechanism of the evaporation of zinc and cadmium in an inert gas appears to be the same as that assumed in the derivation of the Luchak and Maxwell equations.

The heat capacity corrections, based on the Clausius-Clapeyron equation, showed that the difference in temperature gradient at the evaporating surface is insignificant between the helium and argon atmospheres.⁹ Therefore, it is not likely that this difference would affect the evaporation rate to any appreciable extent. However, the higher evaporation rate observed in helium with respect to argon atmosphere can be explained as follows:

1. Because the diffusivity of Zn and Cd in helium is approximately 1.3 times larger than that in argon, the rate of evaporation is then expected to be higher in helium than in argon.⁹

2. As metal atoms diffuse through the residual gas, they lose energy by collision with the residual gas molecules. The force exerted by argon on Zn atoms was calculated⁹ to be 1.2 times larger than that by helium molecules. Thus zinc atoms lose more energy in argon than in helium. Wada concluded the same thing¹⁴ in his study of the preparation of fine metal powders by condensing metal vapors in various gases.

3. The thermal accommodation coefficient of helium is much lower than that of argon at all temperatures. Therefore, it is possible that the temperature of the evaporating metal surface was always higher in the helium runs than in argon runs as explained before.

CONCLUSIONS

1. The rate of evaporation of zinc and cadmium is dependent upon the heat conductivity and the accommodation coefficient of the inert gas, and it is higher in helium than in argon.

2. The Luchak and Maxwell equations give evaporation rates which are lower than the present measurements.

3. The similarity of temperature dependence of the experimental results with respect to the calculated values based on Luchak and Maxwell equations indicates that the mechanisms of evaporation in the present study is similar to the diffusion controlled mode assumed in Luchak and Maxwell equations.

4. The data on cadmium are not sufficient to allow meaningful analysis, and additional work is required regarding selectively refining metal combinations by varying the residual gas atmosphere and pressure.

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