In Fig. 3 are plots showing the rate of electrolysis with two different initial concentrations of europium. With the smaller initial concentration of europium, the deviation from ideality was great only at the beginning of the electrolysis. Thus the deviation must have been caused by a high concentration of europium ion at the amalgam surface. With the higher initial concentration, the rate did not become normal until after the amalgam was removed and replaced. Here the average concentration of europium in the bulk amalgam as well as the concentration of the europium in the amalgam surface was high prior to the time amalgam was removed.

The upper plots in Fig. 3 show the change in cathode potential with time at constant current density. The potential during the first part of the electrolysis was low because of the buffering action of the europium in the amalgam, but eventually reached the value for dilute solutions of europium.

Separation of Samarium from Neodymium.—The purchased samarium oxide was analyzed with 10 cm. cells in the Cary Spectrophotometer and found to contain 0.07% neodymium oxide. The samarium which was electrolyzed into the mercury simultaneously with the europium was kept separate from that remaining in the electrolyte. After re-electrolysis to remove the last traces of europium, analysis with the Cary showed that no neodymium was present. Thus the electrolysis of samarium into mercury separates it from neodymium, which remains in the electrolyte. Purity of the samarium oxide fraction which was recovered from the mercury phase is believed to be >99.98% with respect to other rare earths.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Dependence of Dissociation Pressure Measurements by the Knudsen Effusion Method on Effusion Hole Area. The Dissociation Pressure of Mo$_3$Ge[1,2]

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The pressure of germanium measured by the Knudsen effusion method for the reaction $\text{Mo}_3\text{Ge(s)} = 3\text{Mo(s)} + \text{Ge(g)}$ depends on the effusion hole area in the Knudsen cell. This dependence appears to arise from depletion of Mo$_3$Ge at the sample surface. An equation is derived by means of which the equilibrium dissociation pressure is calculated from the apparent pressures obtained with effusion holes of different areas. The calculated pressures are in good agreement with pressures measured by use of a sample of high effective surface area. The dissociation pressure is given by the equation $\log P = -2.14 \times 10^4/T + 6.68$. The heat of formation of Mo$_3$Ge from solid molybdenum and liquid germanium at 1800°K. is -14.5 ± 5.0 kcal. per mole.

The Knudsen effusion method,[4] which was developed for determination of vapor pressures, can be applied to measurement of dissociation pressures for reactions of the type

$$-\text{MX}_m(\text{s}) = -\text{M(s)} + \text{X(g)}$$

The pressure P inside a chamber whose lid is pierced by a small hole is given by $P = Z(2\pi MRT)^{1/2}$ where Z is the weight loss per unit time per unit area through the hole, M is the molecular weight of the escaping vapor, R is the gas constant, and T is the absolute temperature.

The dissociation pressures of rhenium silicides were measured by the Knudsen method in this Laboratory with no difficulties that are not encountered in measuring vapor pressures in the same high temperature range.[5] Difficulty has arisen, however, in application of the method to measurement of the germanium dissociation pressure established by the reaction $\text{Mo}_3\text{Ge(s)} = 3\text{Mo(s)} + \text{Ge(g)}$. Equilibrium pressures could not be obtained inside the effusion cell, apparently because of depletion of Mo$_3$Ge at the surface of the samples with consequent reduction in the effective areas of vaporization. The effect of surface depletion apparently has not been noted previously in dissociation pressure measurements by the Knudsen method.

In this paper an equation is derived by means of which the equilibrium dissociation pressure can be calculated from the results of pressure determinations with effusion cells of different hole areas. The calculated pressures are compared with pressures obtained by use of a sample of high effective area.

Experimental

Molybdenum powder of stated 99.5% purity was obtained from Fansteel Metallurgical Corporation. Bar germanium was obtained from Eagle-Picher Company and crushed to powder for our experiments. Spectroscopic examination of these materials showed iron, probably to the extent of less than 0.1%, to be the major impurity in the molybdenum, while the germanium showed only trace amounts of other elements. Mixtures of the metal powders were heated *in vacuo* to cause reaction, and the phases produced were identified by X-ray diffraction investigation of the products. Mixtures of molybdenum and Mo$_3$Ge,[6] an easily identified cubic phase, were used for the dissociation pressure measurements. Before dissociation pressure determinations were made, the samples were heated *in vacuo* to drive out any volatile impurities.

For experiments with high effective vaporization area, molybdenum sheet cut into pieces $^1/_4$ in. × $^1/_8$ in. × 0.001

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(2) Supported by the Office of Naval Research.

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in. reacted with germanium powder to yield a mixture of molybdenum and Mo_3Ge in sheets which could be loosely piled in an effusion cell. After dissociation pressure determinations there was no diffraction evidence of reaction between the samples and the graphite crucibles. Graphite was not expected to react with Mo_3Ge because no germanium carbides are stable at the temperatures employed[7] and the molybdenum carbides have very low free energies of formation.[8]

The areas of the carbon and tungsten effusion holes were corrected for thermal expansion. Apparatus and experimental procedure were the same as described by Searcy and McNees.[5]

Results and Discussion

Pressure data obtained from the mixtures of Mo_3Ge and molybdenum powders are summarized in Table I. Clausing constants listed in the table must be divided into the pressures calculated from the basic Knudsen equation to correct for the use of effusion holes of finite instead of infinitesimal lengths.[9]

TABLE I

APPARENT DISSOCIATION PRESSURE OF Mo_3Ge

Temp., °K.	Time, sec.	Wt. loss, mg.	Pressure, atm.
1981[a]	1670	18.9	2.48×10^{-5}
1969[a]	1690	12.0	1.55×10^{-5}
1936[a]	3910	7.4	3.99×10^{-6}
1923[a]	1530	8.2	1.16×10^{-5}
1878[a]	5290	8.5	3.42×10^{-6}
1866[a]	3450	8.1	4.99×10^{-6}
2020[b]	1670	12.7	6.57×10^{-5}
1915[b]	4640	10.29	1.87×10^{-5}
1909[b]	5210	8.43	1.36×10^{-5}
1865[b]	4150	6.08	1.22×10^{-5}
1989[c]	2560	17.6	5.77×10^{-5}
1980[c]	2580	12.1	3.91×10^{-5}
1968[c]	2450	11.1	3.77×10^{-5}
1951[c]	2620	9.9	3.13×10^{-5}
1904[c]	3520	5.4	1.29×10^{-5}
1897[c]	3280	6.8	1.69×10^{-5}
1840[c]	7110	6.2	7.02×10^{-6}
1829[c]	7010	4.7	5.37×10^{-6}

[a] Graphite crucible. Area of hole at room temperature 0.0794 cm.^{2}, Clausing constant 0.68. [b] Graphite crucible. Area of hole at room temperature 0.0308 cm.^{2}, Clausing constant 0.45. [c] Molybdenum crucible. Area of hole at room temperature 0.0308 cm.^{2}, Clausing constant 0.45.

The dissociation pressure data obtained by use of a carbon crucible are in excellent agreement with those obtained by use of a molybdenum crucible with an effusion hole of nearly identical effective area. Pressures calculated from experiments that employed the larger effusion hole area, however, are lower than the pressures obtained with use of the smaller hole areas.

The pressure dependence on hole area could arise because of a slow step in the vaporization of germanium from Mo_3Ge. A surface that does not yield atoms or molecules to the vapor phase at as great a rate as the vapor atoms or molecules strike the surface at equilibrium is said to have a low vaporization coefficient. The pressure measured by the Knudsen equation P_k is actually not exactly the equilibrium pressure P_e because escape of vapor through the hole in a Knudsen cell reduces the pressure below the equilibrium value. Motzfeldt has discussed the relationship between equilibrium pressure and the dimensions of a Knudsen cell.[10] For cells of the dimensions used, his equation can be reduced to $P_e = P_k(1 + A/fS)$ where A is the effusion hole area divided by the Clausing constant, f is the vaporization coefficient, and S is the vaporizing surface area of the sample.

In this research the ratio A/S was about 10^{-2} for the smaller holes. A vaporization coefficient that was about 10^{-2} could explain the observed pressure variations. Vaporization coefficients are usually very close to unity, however, for evaporation of atoms from metal surfaces,[11] and Searcy and Freeman have shown that germanium vapor is predominantly monoatomic.[12]

A more probable explanation of the observed pressure variation is that the quantity of Mo_3Ge present at the sample surface was insufficient to maintain the equilibrium germanium pressure in the cell above the sample surface. X-Ray examination of material from the surface of the sample after heating showed a very low concentration of Mo_3Ge, while the center of the crusted sample showed almost pure Mo_3Ge. Furthermore, the first run or two after the sample was removed from the crucible and crushed gave higher pressures than prior or later runs. These observations suggest that a steady state is established for which the equilibrium dissociation pressure can be found only at the interior of the sample where the concentration of Mo_3Ge is high.

On the assumption that the germanium pressure above the sample is established by effusion of vapor through pores from the interior of the sample, the observed pressure P_k can be related to the equilibrium pressure P_e. The pores of the sample can be considered as the equivalent of a single effusion channel of unknown cross section and length. At the low pressures studied, the net weight g of germanium transported per unit time outward through the pores of the sample will be proportional to the pressure difference so that

$$g = B(P_e - P_k) \qquad (1)$$

where B is a constant for a given temperature and geometry. But under the steady state of an effusion cell, g is also the weight loss per unit time through the cell effusion hole. A more detailed analysis of the transport relationships by Sears[13] yields an equation that reduces to equation 1 for constant pore geometry and constant temperatures.

The assumptions that the molybdenum coating is porous and that the pore geometry is constant after a short time of heating can be justified by the general results of kinetic studies. The gram molar volume of Mo_3Ge is 36 ml. compared to 28 ml. for the volume of three gram moles of molybdenum.

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[11] R. S. Bradley and P. Volans, *Proc. Roy. Soc.* (*London*), **217**, 508 (1953).

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It is well established from kinetic investigations that a porous coating results if the coating material occupies less volume than the substrate from which the coating material was produced. Furthermore, reactions involving transfer of gases through such coatings are linear with time, indicating that changes in the pore dimensions have negligible effects on the reaction velocities.[14]

If there were no experimental error, log P *vs.* $1/T$ plots should yield parallel lines for data obtained with different hole areas. Solution of equation 1 for P_e at various temperatures would then yield a line that is also parallel. But with a slight difference in the slopes of the experimental lines, the curve calculated for log P_e will have a markedly different slope because of the great sensitivity of equation 1 to changes in the ratios of the P_k values obtained with the two hole areas. The most accurate way of obtaining P_e as a function of temperature, therefore, appears to be to use the value of P_e calculated at the midpoint of the temperature range studied in combination with the experimental slope found by use of the smaller Knudsen hole (for which most data were obtained). This procedure yields the equation $\log P_e = -2.14 \times 10^4/T + 6.68$.

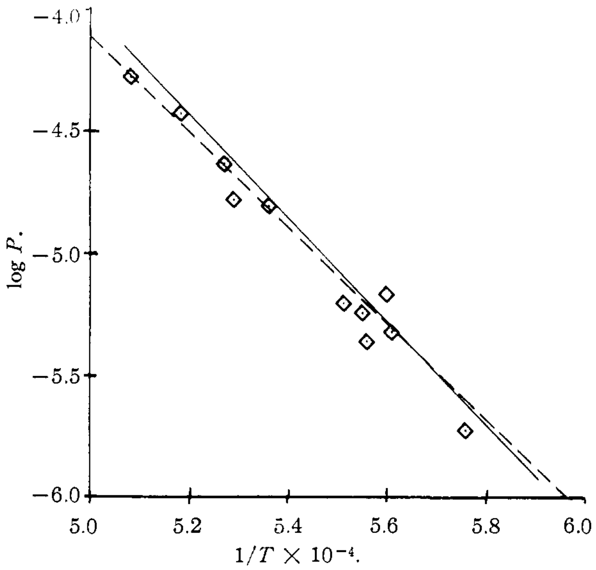

Fig. 1.—Comparison of pressure measured with sample of high effective area and calculated pressure: – –□– –, measured; ——, calculated.

The heat of dissociation of Mo_3Ge is then 98.0 kcal. per mole at 1800°K. and the entropy of dissociation is 30.6 cal. per mole per deg. If the entropy of formation of Mo_3Ge from the solid elements is estimated to be zero, the entropy of dissociation is calculated from tables of Stull and Sinke[15] for the condensed germanium phases and of Brewer[16] for germanium gas to be 32.5 cal., in reasonable agreement with the experimental value.

To check the pressures calculated for P_e from equation 1, an additional series of pressure determinations was made with the sample prepared in the form of loosely piled, thin sheets. The very loose packing that resulted should favor effusion of the germanium vapor throughout the container and consequently yield results close to the equilibrium pressure. Data for this sample are plotted in Fig. 1 with the calculated curve for P_e.

The pressures obtained by use of the loose flakes agree to within the probable error with the calculated pressure curve.

From the equation for P_e and the heat of vaporization of germanium,[10] the heat of formation of Mo_3Ge from solid molybdenum and liquid germanium is calculated to be −14.5 ± 5 kcal. mole at 1800°K.

The experimental results of this research demonstrate that for dissociation pressure measurements by the Knudsen method, data obtained by use of only one hole area should not be accepted without corroboration as yielding equilibrium pressures. Dissociation pressure measurements on systems that yield polyatomic vapors such as S_2 or P_4 should be especially carefully scrutinized. For such a system a low vaporization coefficient[17] as well as the surface depletion described here may be encountered.

BERKELEY, CAL.

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(14) *Cf.* for example, "The Corrosion Handbook," edited by H. Uhlig, John Wiley and Sons, New York, N. Y., 1948.

(15) D. F. Stull and G. C. Sinke, "The Thermodynamic Properties of the Elements in Their Standard States," The Dow Chemical Co., Midland, Mich., 1955.

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