[CONTRIBUTION FROM THE DIVISION OF MINERAL TECHNOLOGY, UNIVERSITY OF CALIFORNIA]

The Vapor Pressure of Gold and the Activities of Gold in Gold–Copper Solid Solutions[1,2]

BY LEWIS D. HALL[3]

The data in the literature on the vapor pressure and heat of vaporization of gold[4–5] are contradictory, and no satisfactory basis exists for choosing between the various results. The data of Harteck,[4] which have been generally accepted as being the most valid, consist of five values covering a temperature range of 27°. The data of Bauer and Brunner,[5] which are considered by some to be equally good, cover a much wider temperature range, but consist of only four values. Because of these discrepancies in the existing data, it was considered advisable to establish, by an equilibrium effusion method,[6] the vapor pressure of gold over as wide a temperature range as possible. In addition, it was desired to determine the activities of gold in solid gold–copper alloys of various compositions, by measurements of the gold partial pressures.

In order to overcome some of the difficulties connected with effusion measurements, a method which employed the radioactive isotope Au^{198} as a tracer was developed and used in the present investigation. The method permitted operating at lower temperatures than was formerly possible and gave an unambiguous means of analysis of gold deposits which were of the order of 10^{-8} g.

The essential features of the effusion method of evaporation have been described by Knudsen[6] and others[7] and will not be reviewed here. It should be mentioned, however, that proper cognizance of the condensation coefficient was taken in the present work. This quantity gives the fraction of vapor molecules striking the inner surface of the cell which stick to the surface upon impact. In order to obtain equilibrium between the solid gold and the gold vapor in the Knudsen cell, the ratio of orifice area to total subliming area must be small. If the condensation coefficient is large compared with the ratio of orifice area to total subliming area, the measured pressure will be approximately equal to the equilibrium vapor pressure. Therefore, if the vapor pressure is found to be independent of orifice area, within the limits of experimental error, it may be concluded that equilibrium has been essentially attained. In the present work, tests were made with two different hole sizes, whose areas were in the ratio 2:1, and it was found that the measured vapor pressure was independent of the hole size.

The quantity of material effusing can be calculated from kinetic theory.[8] It can be shown that the number of moles of gas, n, effusing in unit time through an orifice of area A is

$$n = 1.013 \times 10^6 pA/\sqrt{2\pi MRT} \qquad (1)$$

where p is the pressure in atmospheres, M is the molecular weight, R is the gas constant in ergs/°C. mole and T is the absolute temperature. From Knudsen's cosine law it can be shown that the ratio of the number of molecules N_θ emerging from the cell within a cone of semi-apex angle θ to the total number effusing is given by

$$N_\theta/N = \sin^2 \theta \qquad (2)$$

However, Clausing[9] has shown that for the case in which the ratio l/a is finite, where l is the length of the orifice and a is its radius, equation (2) must be modified. In effect, the total amount of material effusing in unit time is decreased, the deviation from the cosine law increasing with increasing angle of emergence. Hence from equations (1) and (2), after transposing and collecting constants, we have

$$p = q_1 \csc^2 \theta \sqrt{T/M}/44.4KA \qquad (3)$$

where q_1 is the mass of gold striking the collector plate, in grams per second, and K is less than unity, having a value of 0.98 in the present work.

Equation (3) assumes that all of the gold atoms which strike the plate stick, *i.e.*, the condensation coefficient is unity, an assumption which was verified in the following manner:

A piece of molybdenum plate was placed in the chamber in such a position that gold atoms could strike it only upon reflection from the collector plate, which was 0.0003 in. aluminum, 1 in. in diameter. A run was made, after which the molybdenum plate and collector plate were counted under the Geiger counter. No gold could be detected on the molybdenum plate. It was therefore concluded that the condensation coefficient of the collector plate was substantially unity.

Experimental

The vacuum chamber, Fig. 1, was a brass, water-cooled tank, 3.5 in. in diameter and 8 in. long, with a 1 in. opening in the side for the collector plate, which was cemented to the underside of a steel cover plate. The chamber was connected to a glass vacuum system by means of a deep annular brass ring silver-soldered to a Sylphon bellows, into which the glass tubing fitted. The space between the glass and the brass ring was filled with de Khotinsky cement.

Water-cooled copper electrical leads entered the vacuum tank through Wilson seals in a bakelite end-plate. The heating element, which was connected across the ends of the leads, was a molybdenum coil of about 1 in. diameter. The diameter of the wire was 0.080 in. and the pitch was 0.110 in. The voltage across the coil was varied by means of a Variac, model 50A, rated at 45 amp. maximum, the output of which was fed through a welding transformer. Stable line voltage of 115 volts was provided by a Sola line voltage

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(1) For detailed tables supplementary to this article order Document 2923 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

(2) Abstracted from a dissertation submitted by Lewis D. Hall to the Division of Mineral Technology of the University of California, Berkeley, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) General Electric Company Charles A. Coffin Fellow, 1947–1949. Institute for the Study of Metals, University of Chicago, Chicago, Illinois.

(4) P. Harteck, *Z. physik. Chem.*, **134**, 1 (1928).

(5) Bauer and Brunner, *Helv. Chim. Acta*, **17**, 958 (1934).

(6) Knudsen, *Ann. Physik*, **28**, 75 (1909).

(7) Holden, Speiser and Johnston, THIS JOURNAL, **70**, 3897 (1948).

(8) Knudsen, "Kinetic Theory of Gases," Methuen and Company, London, 1935.

(9) Clausing, *Z. Physik*, **66**, 471 (1930).

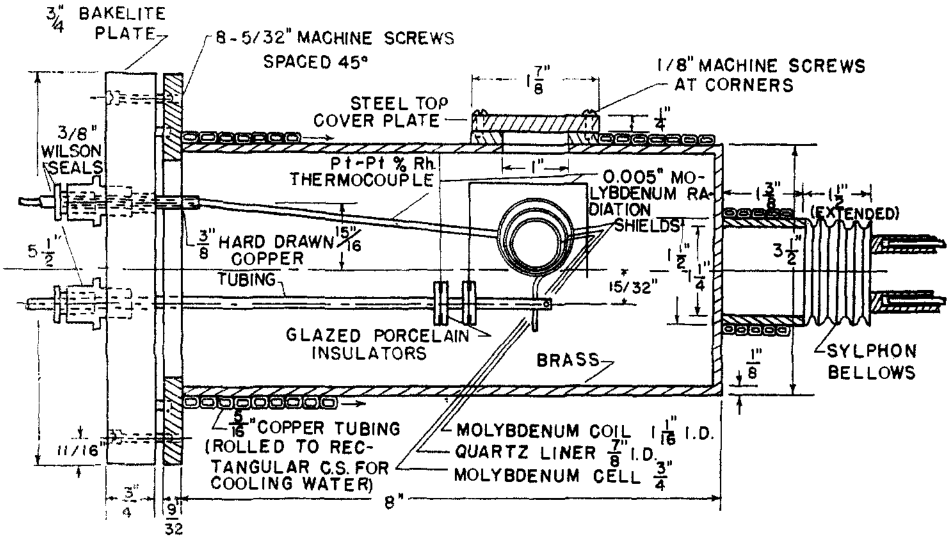

Fig. 1.—Vacuum chamber cross-sectional view.

regulator. The maximum power consumption of the coil was about 800 watts.

The effusion cell was constructed by drilling out a $^3/_4$ in. molybdenum rod. The length of the cell was 1 in. and the wall thickness $^1/_{32}$ in. In operation, the cell lay horizontally inside a quartz liner in the heater coil, the gold vapor passing through the orifice in the side of the cell, thence through an opening in the quartz liner and between the two central turns of the coil, which had been spread slightly apart. The effusion orifice was a hole drilled in a 0.005 in. molybdenum band which encircled the outside of the cell and covered a $^1/_4$ in. diameter opening in the cell wall. The diameters of the orifices used were, respectively, 0.107 and 0.152 cm. One of the conditions for equilibrium is that all parts of the effusion cell must be at the same temperature. This condition was attained by making the coil 1.25 in. longer than the cell and reducing end losses by means of molybdenum radiation shields.

The cell temperatures were measured by a Pt-Pt-13% Rh thermocouple which entered into a well in a plug which was inserted into one end of the cell. The measuring couple was thoroughly annealed, then calibrated using the melting points of zinc, aluminum and copper (in a reducing atmosphere) before the investigation and again after the measurements had been completed. Pure Bureau of Standards metals were used in the calibration, the apparatus being similar to that used in the Bureau of Standards and described elsewhere.[10] The thermal e.m.f.'s were read with a Leeds and Northrup No. 8662 precision potentiometer.

Temperature control was accomplished by means of a Wheelco Capacitrol controller, with proportioning action, which was actuated by the e.m.f. of a chromel-alumel thermocouple whose hot junction was inside the heater coil and at the other end of the cell from the measuring couple.

The radioactive isotope Au^{198}, with a half-life of 2.7 days,[11] was obtained periodically from Oak Ridge in the form of foil weighing about 16 mg. The initial specific activity, at the pile, of this isotope is about 5000 millicuries per g. The gold was weighed, as received, on a sensitive Heusser balance which permitted weighing to within ±0.0025 mg. After weighing the bulk foil, a small portion, from 0.75 to 1.5 mg., was cut off and weighed for use in making up standards for counting. This piece was then dissolved in aqua regia and the solution diluted to 500 ml. Following the procedure recommended by Calvin[12] and co-workers, aliquot portions of this solution with a volume of about 0.40 ml. each were evaporated on 0.0003 in. plates of aluminum foil, 1 in. in diameter. The evaporation was accomplished in 10 or 15 minutes, without sputtering. Twelve to eighteen such standards were made up from each shipment of gold, an average value being calculated from their counting rates. After the standards had been counted, only one of them was used henceforth in all counting, the rest being discarded.

For the vaporization of pure gold, the foil was placed in the effusion cell after the portion had been removed for the standard. For the vaporization of copper-gold alloys, the gold was alloyed with spectroscopically pure oxygen-free copper, of 99.999+% purity. This was accomplished by heating the metals together in a quartz tube, in a hydrogen atmosphere, the heating being performed with an oxygen-gas flame. After the melting, the fused alloy bead was removed and rolled into foil, then heated for 15 to 20 hours *in vacuo* at 820°, to homogenize it. In the vapor pressure runs, the metal or alloy was placed in the effusion cell, the chamber evacuated, and the cell brought to operating temperature. A pressure of about 10^{-4} mm. as measured by a McLeod gage was obtained within 30 to 45 min. after heating had begun. The actual pressure in the vicinity of the effusing vapor was not known, but the fact that it was low enough to permit "molecular streaming" was evidenced by the sharp patterns formed on the collector plate by the impinging molecules of various types.

It was possible in some instances to make two runs in a 24-hour period, one in the daytime and one at night. The daytime runs averaged about 5 or 6 hours in length, while the night runs extended for 12 to 14 hours or longer. The times of heating to operating temperature and also of cooling from that temperature were very short in comparison with the total evaporating time, hence were neglected in the calculations of vapor pressures. Temperature readings were taken every 15 or 20 min. during the day. For the night runs, the usual practice was to read temperatures for a half-hour at the beginning and again at the end of the run, the temperature variation during the night being recorded on a Leeds and Northrup Micromax recorder.

The final step in the measurements was the process of counting the evaporated gold to determine the amount collected. This was accomplished with a Geiger-Muller counter. The procedure was simply that of counting background, the condensed gold on the collector plate, and the standard. The amount of gold in the standard being known, that on the collector plate was immediately calculated from the ratio of its counting rate to that of the standard.

In order to eliminate counting errors due to the geometry of the samples and other factors, certain precautions were taken. The collector plate and the standard were folded into packets about 8 mm. square, before counting, in such a manner as to minimize non-uniformities of distribution of active material across the surface of the sample. According to Calvin[11] this should reduce to negligible proportions the errors in counting caused by displacement of material outward from the axis of the counter.

The relative contributions of beta and gamma radiation to the total counting rate were determined by counting a strong sample first in the usual manner and then with an

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(10) Roeser, *J. Research Natl. Bur. Standards*, **3**, 343 (1929).

(11) Levy and Greuling, *Phys. Rev.*, **75**, 819 (1949).

(12) Calvin and associates "Isotopic Carbon," John Wiley & Sons, Inc., New York, N. Y., 1948.

aluminum absorber interposed. The density of the absorber was 391 mg. per cm.^{2}, which was just enough to absorb all beta radiation without seriously affecting the gamma radiation. The counting rates with and without absorber were in the ratio of 1 to 380, indicating that less than one-third of one per cent. of the observed counting rate was caused by gamma radiation.

Thermodynamic Calculations

a. Vapor Pressure and Heat of Vaporization of Gold.

—The heat at absolute zero, ΔH_0^0, of the reaction

$$\mathrm{Au(s)} = \mathrm{Au(g)} \qquad (4)$$

may be found as follows: for any reaction

$$\Delta F^0 = -RT \ln K \qquad (5)$$

where ΔF^0 is the standard free energy change and K is the equilibrium constant. For the reaction (4) above

$$\Delta F^0/T = -R \ln p \qquad (6)$$

where p is the equilibrium pressure of gold vapor, in atmospheres, at temperature T. Now

$$\Delta F^0/T = \Delta F^0/T - \Delta H_0^0/T + \Delta H_0^0/T \qquad (7)$$

therefore

$$\Delta H_0^0/T = -R \ln p - \Delta(F^0 - H_0^0)/T \qquad (8)$$

where $\Delta(F^0 - H_0^0)/T$ denotes the difference in the values of the function $(F^0 - H_0^0)/T$ for gold vapor and solid gold.

Values of $(F^0 - H_0^0)/T$ have been calculated from spectroscopic data for gold vapor, and from heat capacity data for solid gold. Kelley[13] has used these values to calculate $\Delta(F^0 - H_0^0)/T$ over a wide range of temperatures. Interpolating in his table, and combining with the experimental values for the vapor pressure obtained in the present work, the heat of vaporization at the absolute zero has been calculated. The results are summarized in Table I which will be published in a microfilm supplement to this paper, together with Table II. The average value for ΔH_0^0 is found to be 84.6 ± 0.8 kcal. per mole.

The results obtained for the partial pressures of gold vapor in equilibrium with gold–copper solid solutions of various compositions are listed in Table II and plotted in Fig. 2. From the figure, on which the data for pure gold have also been plotted, the activities of gold in the alloys have been calculated. Since $a_{\mathrm{Au}} = p/p^0$, where p is the pressure over the alloy and p^0 is the pressure over pure gold at the same temperature, $\log_{10} a_{\mathrm{Au}}$ may be measured directly.

In constructing the curves of Fig. 2 a straight line with slope $\Delta H^0_{1125^\circ\mathrm{K.}}$ has been drawn through the points for pure gold. Lines parallel to this have been drawn through the mean positions of the other sets of points. This procedure neglects the partial molal heat of solution of gold in the alloys and also neglects the change in ΔH^0, the heat of vaporization, over the temperature range investigated. These quantities are small in comparison with the heat of vaporization and are not revealed by the plot, since the scatter in the points is sufficient to obscure them. The activity coefficients calculated from Fig. 2 are plotted in Fig. 3 as a function of composition.

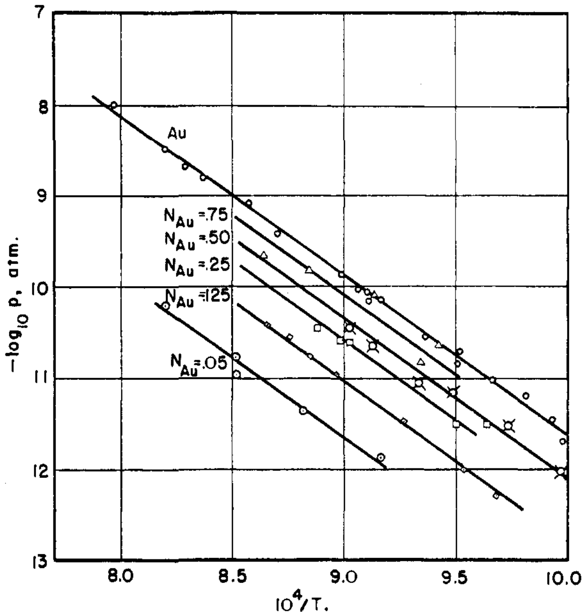

Fig. 2.—Partial pressures of gold vapor in equilibrium with pure gold and gold–copper solid solutions.

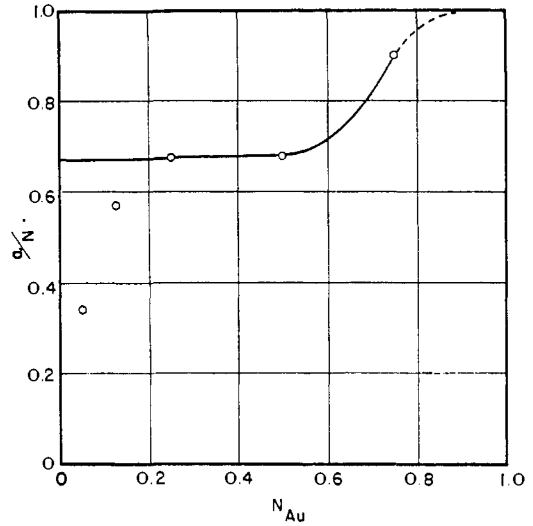

Fig. 3.—Activity coefficients of gold in gold-copper solid solutions; temperature range 1003–1219°K.

Discussion and Conclusions

The vapor pressures of gold obtained in the present work establish the heat of vaporization at the absolute zero as 84.6 ± 0.8 kcal. per mole. Calculations based on the data of Harteck[4] and of Bauer and Brunner[5] yield 90.4 and 77.5 kcal. per mole, respectively. The heat of vaporization determined in the present study thus lies about halfway between the values obtained by the earlier investigators.

The temperature measurements of Bauer and Brunner have been questioned because of their failure to make proper emissivity corrections. Brewer[14] has observed that their errors are such as to cause their observed temperatures to be

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(13) Kelley, "Free Energies and Heats of Vaporization of Inorganic Substances," U. S. Bur. Mines Bull. 383 (1935).

(14) Leo Brewer, private communication.

somewhat low, hence their pressures are probably too high. Fraser[15] has expressed the opinion that the pressures recorded by Harteck are probably too low, because of too large an orifice area in his cell. It is therefore probable that the true vapor pressures lie somewhere between the values of Harteck and of Bauer and Brunner. The results reported here confirm this view. For example, calculation of the vapor pressure of gold at 1200°K. yields the following values; Bauer and Brunner, 4.5×10^{-8}; Hall, 2.1×10^{-9}; Harteck, 1.9×10^{-10}.

Because of the large number of consistent points which were obtained over a wide temperature range and under equilibrium conditions, it is believed that the present study has established reliable values for the vapor pressure and heat of vaporization of gold.

The results obtained for the gold–copper solid solutions are less certain, but the general trend of the activity coefficients is similar to that calculated from the data of Wagner and Englehardt[16] and Weibke and Quadt,[17] who measured the e.m.f.'s of electrolytic cells with electrodes of pure copper and gold–copper alloys of various compositions. Unfortunately, internal inconsistencies in their data and lack of agreement between the respective authors make quantitative comparisons very difficult. Nevertheless, the curve of Fig. 3 agrees roughly with that to be expected from calculations based on their data, which were obtained at lower temperatures.

The activity coefficient curve of Fig. 3 has been drawn so as to conform to Henry's law at the low gold compositions. The experimental points obtained at the two lowest compositions studied lie well below the curve, thus demanding some explanation. It is probable that the evaporation of copper affects the gold vapor at these concentrations, reducing the quantity of the latter which reaches the collector plate. This could conceivably occur if the copper partial pressures were high enough. The existing data for copper are ambiguous, but a recent report by Dushman[18] as well as some exploratory work by the author has indicated that the vapor pressure of copper may be several orders of magnitude higher than that of gold at the temperatures considered. The ratio between the partial pressures at the low gold compositions would be even greater, leading to a qualitative prediction of copper partial pressures which might be high enough to cause interference with the gold vapor.

The results of the present investigation show that the radioactive tracer technique is well adapted to the investigation of the vapor pressures of pure metals over large temperature ranges. In view of the large discrepancies which exist between the data of different investigators for many of the common metals, it is apparent that re-examination of these values is a fruitful field for future study.

Acknowledgments.—The author is greatly indebted to Professors E. R. Parker and Leo Brewer of the Mineral Technology Division and Chemistry Department, respectively, of the University of California, and to Dr. K. K. Kelley of the Pacific Experiment Station, U. S. Bureau of Mines, for their helpful advice and unfailing encouragement.

Summary

1. Measurements using the Knudsen method of equilibrium effusion, with radioactive gold as a tracer, have established the heat of vaporization of gold at the absolute zero as 84.6 ± 0.8 kcal. per mole, corresponding to a vapor pressure of 2.1×10^{-9} atm. at 1200°K.

2. The results of the measurements indicate that the radioactive tracer technique is well suited to the determination of metallic vapor pressures.

3. Gold–copper solid solutions were found to exhibit negative deviations from ideality. The low values obtained for the activity coefficients at the low gold compositions may be a result of interference by the copper vapor.

(15) Fraser, "Molecular Rays," Cambridge University Press, 1931.

(16) Wagner and Englehardt *Z. physik. Chem.*, **A159**, 241 (1932).

(17) Weibke and Quadt, *Z. Elektrochem.*, **45**, 715 (1939).

(18) Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 98.

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The Kinetics and Mechanism of the Reaction of Diphenyldiazomethane and Benzoic Acid in Ethanol[1]

BY JOHN D. ROBERTS, WARREN WATANABE AND ROBERT E. MCMAHON

The reactions of substituted diazomethanes with carboxylic acids have been studied mainly in nonhydroxylic solvents. In one of the earliest papers published on this subject, Staudinger and Gaule[2] reported that a variety of diazomethane derivatives reacted with substituted acetic acids in cumene at rates which depended on the strengths of the acids. Similar observations were later made by Norris and Strain[3] with di-*p*-tolyldiazomethane and substituted benzoic acids in benzene, toluene and ethyl acetate solutions. The reaction of diazoacetic ester in aprotic solvents with various carboxylic acids has also been investigated and found to be roughly second-order in acid[4,5] in

[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] Staudinger and Gaule, *Ber.*, **49**, 1897 (1916).

[3] Norris and Strain, THIS JOURNAL, **57**, 187 (1935).

[4] (a) Brønsted and Bell, *ibid.*, **53**, 2478 (1931); (b) Hartman, Hochanadel and Bobalek, *ibid.*, **68**, 2071 (1946).

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 288-289.