

condition for the equilibrium determination of the vapor pressure.⁴ Unfortunately, the system broke down at the beginning of these measurements and only one datum of value was obtained.

TABLE II

| Temp., °K. | Press., atm. ^a | Mean free path, cm. | Diameter of orifice of Knudsen cell, cm. | Ratio of mean free path to orifice diameter |
|------------|---------------------------|---------------------|--|---|
| 795 | 1.34×10^{-4} | 0.78 | 0.11012 | 7.06 |
| 781 | 6.5×10^{-5} | 1.64 | .11010 | 14.9 |
| 766 | 8.39×10^{-5} | 1.24 | .11004 | 13.7 |
| 736 | 3.54×10^{-5} | 2.85 | .11002 | 25.9 |
| 692 | 6.7×10^{-6} | 14.4 | .10996 .13248 | 131.0 108.5 |

^a The pressures given are taken from the run measurements.

Experimental Errors

For reaction (3) we may write

$$\Delta F = -RT \ln K = -RT \ln P_{\text{B}_2\text{O}_3} \quad (4)$$

From the kinetic gas theory

$$\log P = K + \log \Delta W + \frac{1}{2} \log T = \log A_{\text{orif}} - \log t_{\text{eff}} \quad (5)$$

where P = pressure, K = a constant, ΔW = loss in weight for a run, T = absolute temperature, A_{orif} = area of the orifice, t_{eff} = effective time of run. From the known sources of error in temperature measurements, the measured area of the black body hole, the measurement of the time, and the measurement of the weight loss, it was calculated that

the standard deviation of the experimental $\log P$'s should be 0.02. The actually observed standard deviation from the least squares curve is 0.14.

It is felt that the discrepancy between the calculated error and the actual average error is due primarily to an uncertainty in ΔW . By experiment it was found that a long period of storage in the desiccator resulted in a weight gain of the sample of only 0.006 g. which cannot account for an error of 0.14. The procedure in handling the sample during each run was standardized as much as possible; however, the atmospheric humidity and the length of time of exposure of the vapor pressure system itself to the atmosphere varied widely from run to run. It is felt that this variation accounts for the uncertainty in ΔW , since the sample itself may have received some moisture from the system after being placed in the apparatus.

It was mentioned previously that the length of the degassing period (when there was no heating in the system) had no apparent effect on the experimental results; however, during the heating periods it was observed that the pressure in the system rose, initially, to maximum values that varied among the runs, but later returned to the usual equilibrium value of $\sim 1 \times 10^{-4}$ mm. This is probably associated with varying amounts of adsorbed water held by the sample.

Acknowledgment.—We wish to acknowledge the suggestions of Dr. James W. Edwards in the design of the cell.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE BATTELLE MEMORIAL INSTITUTE]

The Solubility of Carbon and Oxygen in Liquid Bismuth

BY C. B. GRIFFITH^{1a} AND M. W. MALLETT^{1b}

RECEIVED OCTOBER 29, 1952

Analytical methods for determining carbon and oxygen in bismuth are described. Using these methods, the solubility limits of oxygen (400 to 750°) and carbon (300 to 750°) in liquid bismuth were determined. The solubility of oxygen in liquid bismuth varies with temperature according to the equation, \log_{10} weight per cent. oxygen = $-(3400/T) + 1.48$. An equation for the variation of liquid solubility of carbon in bismuth with temperature is, \log_{10} weight per cent. carbon = $-(360/T) - 3.17$.

Introduction

In melting bismuth in a Vycor crucible, in a vacuum, an evolution of gas occurred. Analysis of the gas showed it to be CO₂ with traces of CO, N₂ and H₂O.

A search of the literature showed new data on gases in bismuth. Sieverts and Krumbhaar observed no occlusion of hydrogen^{2a} or nitrogen^{2b} by bismuth at temperatures up to 600°. Smith³ states that occlusion of hydrogen by bismuth is improbable on general consideration.

No data on the solubility of oxygen in bismuth were found.

(1) (a) Based on work performed under AEC Contract No. W-7405-eng-92. (b) Battelle Memorial Institute, Columbus, Ohio.

(2) (a) A. Sieverts and W. Krumbhaar, *Ber.*, **43**, 896 (1910); (b) **43**, 894 (1910).

(3) D. P. Smith, "Hydrogen in Metals," The University of Chicago Press, 1948, p. 286.

Incidental to vapor pressure studies, Ruff and Bergdahl⁴ obtained the following estimates of the solubility of carbon in bismuth.

| Temp., °C. | 1385 | 1408 | 1490 |
|---------------|-------|-------|-------|
| Carbon, wt. % | 0.012 | 0.017 | 0.023 |

Because the principal gas extracted from liquid bismuth is CO₂, a study was made of the solubilities of the constituents, carbon and oxygen, from which it is derived. The investigation was limited to the temperature range 300 to 750° in order to avoid interference from the vaporization of bismuth which occurs at higher temperatures.

The method of analysis for carbon used by Ruff and Bergdahl was rather insensitive and the experimental technique is questionable. Because of this and the wide intervening temperature range between the temperatures used by them and those

(4) O. Ruff and B. Bergdahl, *Z. anorg. allgem. Chem.*, **106**, 91 (1918).

used for the present study, no comparison of results was attempted.

Experimental

A quenching method was used to determine the solubilities of carbon and of oxygen in liquid bismuth. The liquid metal was held in contact with either graphite or Bi_2O_3 until equilibrium was reached, and then rapidly cooled, trapping the dissolved carbon or oxygen in the ingot. The amount of the solute constituent contained in the metal was determined by special analytical techniques.

Apparatus.—The apparatus used in this work consisted of a simple Vycor furnace tube with a side arm for sample storage, attached to the analytical section of a vacuum-fusion apparatus. A similar analytical train has been described by Derge.⁵ This equipment was used both to prepare solubility samples and to analyze them for carbon and oxygen.

Materials.—The bismuth metal used in this study was produced by the American Smelting and Refining Company as cast billets analyzing 99.98 weight per cent. bismuth. The principal metallic impurities of the billets as received were 0.01% silicon and 0.005% lead by weight. During the course of experimentation, the concentration of each of these elements dropped to < 0.005% and no pickup of other impurities occurred. Further analysis of the starting material, using the methods developed in the course of this investigation, showed that the metal also contained about 0.00072% oxygen and 0.00038% carbon by weight.

The bismuth trioxide powder used as a source of oxygen was 99.96% pure.

The graphite crucibles were machined from AGX grade graphite (National Carbon Company, Inc.).

Solubility of Oxygen in Liquid Bismuth

Sample Preparation.—The carbon content of the bismuth was reduced to < 0.0001 weight per cent. by heating the metal with Bi_2O_3 in a Vycor crucible at 750° for one hour in a vacuum of 10^{-4} mm.

After reducing the residual carbon to a minimum, the sample was cooled to the desired saturating temperature and held for three hours to establish equilibrium between the oxide and the solution. During the holding period, the liquid bismuth was agitated frequently to aid the precipitation and removal of excess oxide dissolved at the higher temperature. Thus the equilibrium concentration of the solute was in all cases, except that at 750°, reached from a higher concentration by precipitating and liquating the excess solute element. Upon reaching equilibrium the melt was rapidly quenched by immersing the Vycor furnace tube in cold water. The sample was removed from the crucible and the bismuth oxide adhering to the surface was removed by abrading.

Analysis.—The oxygen-saturated samples were analyzed by heating in a graphite crucible at 750° and analyzing the evolved gas for CO and CO_2 . About 20 g. of sample and a piece of steel were stored in the side arm of the furnace tube and a graphite crucible containing 0.2 g. of graphite powder was placed in the vertical section of a Vycor furnace tube. The furnace tube was then evacuated to about 10^{-4} mm. and outgassed at 850° until a negligible rate (< 0.01 ml. per hour) of gas evolution was established. The furnace was lowered and the bismuth samples pushed into the graphite crucible with a piece of steel manipulated by a magnet. The crucible was again heated to 750°. The gases formed by the reduction of the oxygen in bismuth by graphite were continuously pumped, by means of a mercury diffusion pump, into the analytical section of a vacuum-fusion apparatus until the gas evolution stopped. In the analytical train, the gas was analyzed for CO_2 and CO by the fractional-freezing method. The oxygen content of the sample was calculated from the volumes of CO and CO_2 obtained.

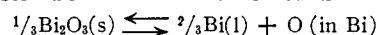
The accuracy of this analytical method was checked by adding a weighed amount of Bi_2O_3 to a sample of bismuth metal and analyzing the mixture for oxygen. The oxygen content of the CO_2 and CO collected agreed with that of the Bi_2O_3 addition.

The solubility of oxygen in bismuth increases from 0.00034 weight per cent. at 400° to 0.016 weight per cent. at 750° (see Table I). These values fall on a straight line when the

logarithm of the solubility is plotted *versus* the reciprocal of absolute temperature. The equation for this line was determined by the method of least squares to be

$$\log_{10} \text{ weight per cent. oxygen} = -(3400/T) + 1.48$$

The change in standard⁶ free energy per mole of atomic oxygen dissolved in bismuth for the reaction



may be expressed by the equation

$$\Delta F^0 = 15400 - 6.77T \text{ calories per mole}$$

The heat of solution is $15,400 \pm 700$ calories per mole.

TABLE I

SOLUBILITY OF OXYGEN IN LIQUID BISMUTH

Sample weight: approximately 20 g. in all cases

| Sample number | Temp., °C. | Oxygen, weight per cent. ^a |
|---------------|------------|---------------------------------------|
| O-A | 400 | 0.00034 |
| O-B | 500 | .0012 |
| O-C | 600 | .0029 |
| O-D | 675 | .0096 |
| O-E | 750 | .016 |

^a Experimental errors are believed to be $\pm 5\%$ of these values. Errors are estimated from the sample weight and the limitation in measuring the gas volume during analysis.

Solubility of Carbon in Liquid Bismuth

Sample Preparation.—Ingots of bismuth were saturated with carbon at various temperatures, using a technique similar to that used for oxygen. In the first attempts to determine the solubility limits of carbon in liquid bismuth, the solubility appeared to decrease with increased temperature. This was contrary to expectations. Subsequent analysis showed the presence of small amounts of residual oxygen which may have caused this discrepancy. In a new set of experiments the oxygen content was reduced to < 0.0001 weight per cent. by heating the metal in a graphite crucible at 750° in a vacuum for one hour. The bismuth was then cooled to the desired saturating temperature, held at the temperature for three hours, and quenched. The ingot was removed from the vacuum and the metal surface freed of any excess graphite by abrading.

Analysis.—The carbon content of the carbon-saturated samples was determined by heating the specimen with Bi_2O_3 in a Vycor crucible at 750° and collecting and analyzing the evolved gases for CO and CO_2 in the analytical section of a vacuum-fusion apparatus.

The analytical method was not checked by means of standard samples because of the difficulty of duplicating the carbon distribution of the experimental samples. However, because essentially the same reaction is involved in both oxygen and carbon analyses, the carbon values are believed to be correct. It should be noted that the magnitude of the carbon values is much lower than is measurable by combustion methods.

Carbon was found to have a solubility of 0.00016 weight per cent. in liquid bismuth at 300°. The solubility increases slightly with temperature (see Table II) to 0.00030 weight per cent. at 750°. The equation

$$\log_{10} \text{ weight per cent. carbon} = -(360/T) - 3.17$$

represents the variation of carbon solubility with temperature.

TABLE II

SOLUBILITY OF CARBON IN LIQUID BISMUTH

Sample weight: approximately 20 g. in all cases

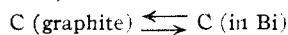
| Sample number | Temp., °C. | Carbon, weight per cent. ^a |
|---------------|------------|---------------------------------------|
| C-A | 300 | 0.00016 |
| C-B | 400 | .00020 |
| C-C | 500 | .00024 |
| C-D | 750 | .00030 |

^a Experimental errors are believed to be $\pm 5\%$ of these values. Errors are estimated from the sample weight and the limitation in measuring the gas volume during analysis.

(5) G. Derge, W. Peifer and J. Richards, "Metals Technology," TP2362, June, 1948.

(6) The standard state in this case is the hypothetical 1% solution.

The expression for the change in standard free energy, ΔF° , in the reaction,



was calculated to be

$$\Delta F^\circ = 1640 + 14.5T \text{ in calories per mole}$$

The heat of solution of carbon in bismuth is 1640 ± 200 calories per mole.

Discussion

Oxygen reacts with liquid bismuth to form the stable compound, bismuth trioxide. Therefore, the solubility of oxygen in liquid bismuth is determined by the oxide-metal equilibrium and is practically independent of the partial pressure of oxygen over the melt.⁷ Chipman⁸ in his investigation of a similar metal-oxide system (Fe-FeO) found that the oxygen solubility was not only independent of the pressure of an oxygen atmosphere but also was virtually independent of the character of the ambient atmosphere. In the present investigation, the melts were made in a vacuum to prevent excessive oxidation of the metal. The temperatures fluctuated only about $\pm 5^\circ$ during equilibration.

The oxygen (or carbon) content of the samples represented equilibrium values only if the following

(7) C. J. Smithells, "Metals Reference Book," Interscience Publishers, Inc., New York, N. Y., 1949, p. 379.

(8) J. Chipman and K. L. Fetters, *Trans. Am. Soc. Metals*, **29**, 953 (1941).

conditions were fulfilled: (1) the liquid bismuth was saturated with the solute element, (2) this saturation amount of solute was retained quantitatively during quenching, and (3) no undissolved solute element was mechanically entrapped in the metal at the end of the holding period.

In general, the results obtained on a few exploratory melts heated for one hour and for three hours, agreed. The three hours holding period was, therefore, undoubtedly more than long enough to establish equilibrium.

Equilibrium was approached from a higher temperature (supersaturated condition) in all cases except for the melts quenched from 750° . The data show a reasonable internal consistency whether equilibrium was approached from a higher or lower temperature.

The molten bismuth solidified within one minute after cooling started. Microscopic examination of the resulting ingots showed that the precipitated solute element was present as fine dendrites and not as large agglomerates as would be the case in slow-cooled melts, or melts in which the excess solute was incompletely liquated during equilibration. As a further precaution each analytical sample was composed of the entire portion of the ingot remaining after cleaning off surface contamination.

COLUMBUS 1, OHIO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

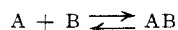
Acid Strength of Iodine Monochloride, Antimony Trichloride and Picric Acid with Reference to the Bases Pyridine and Aniline in Nitrobenzene

BY I. M. KOLTHOFF, DANICA STÖCESOČÁ AND T. S. LEE

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The dissociation constants in nitrobenzene of picric acid, pyridinium picrate, pyridine-iodine monochloride, pyridine-antimony trichloride and aniline-antimony trichloride have been determined spectrophotometrically. These constants, together with others available in the chemical literature, allow a comparison of strengths of a series of Lewis acids and bases in nitrobenzene. The magnitude and in some instances even the order, of the strengths of a series of acids depends on the base chosen as reference, and *vice versa*.

In the Brønsted-Lowry theory of acidity and basicity the strength of a base is a measure of its affinity for the proton. In the Lewis theory, which recognizes as acids other electrophilic substances in addition to the proton, the term base strength is ambiguous unless a reference acid is specified. If we consider the simplest type of acid-base reaction



one in which a soluble Lewis acid of any charge type reacts with a soluble base of any charge type to form a soluble addition compound ("neutralization product"), we may suppose on theoretical grounds that no simple relationship exists between the strengths of a series of bases toward one acid and the strengths of the same series of bases toward another acid. This supposition is based chiefly on the consideration that the energy of the bond between A and B, and also the solvation energy of AB, are in general not related in a simple or known way to the individual properties of A and B. Similarly the term acid strength might be expected to have meaning only if a reference base is specified.

An experimental comparison of the strengths of the bases, pyridine, aniline and picrate ion, and of the acids iodine monochloride, antimony trichloride, picric acid, pyridinium ion and anilinium ion was possible after the approximate determination of the dissociation constants of several addition products. The constants were calculated from results of spectrophotometric measurement of equilibrium concentrations in appropriate solutions. Nitrobenzene, which has a dielectric constant of 34.5, was used as solvent. Preliminary experiments were carried out in chloroform; however, the results of experiments involving ionic species were difficult to interpret because of the low dielectric constant (about 5) of this solvent.

Experimental

Nitrobenzene was purified by washing it successively with 1:1 sulfuric acid, water, concentrated sodium hydroxide (until washings were colorless), and finally with several portions of water. The product was dried over calcium chloride and then distilled under reduced pressure over barium oxide. Pyridine of analytical reagent grade was dried over sodium hydroxide. Picric acid of melting point $121-121.5^\circ$