Deviations from Stoichiometric Proportions in Cuprous Iodide

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Deviations from Stoichiometric Proportions in Cuprous Iodide*

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The absorption of iodine by cuprous iodide has been studied by means of a quartz micro-balance. At 132.1°C the concentration of absorbed iodine varies as the square root of the pressure of iodine vapor in equilibrium with the sample. The temperature dependence of the the reaction at constant iodine vapor pressure indicates a heat of reaction of 0.24 ev per atom absorbed. The electrical conductivity of cuprous iodide at 132.1°C varies approximately as the 4/3 power of the concentration of the absorbed iodine.

INTRODUCTION

A FUNDAMENTAL problem in the investigation of semi-conducting compounds is the dependence of the electrical conductivity upon the deviation from stoichiometric proportions. This deviation is ordinarily so small as to prohibit direct measurement by chemical or physical methods.

In 1909, Baedeker[1] discovered that cuprous iodide, at room temperature, will absorb as much as 10^{-3} gram of excess iodine per gram of cuprous iodide. The resulting electrical conductivity was electronic in nature but of the "defect" type, the Hall constant being anomalous in sign. Nagel and Wagner[2] have shown that, if cuprous iodide is in equilibrium with iodine vapor, at constant temperature, the conductivity is a complicated function of the iodine vapor pressure.

In the light of Baedeker's results it seemed feasible to determine the concentration of excess iodine in cuprous iodide, as a function of the equilibrium iodine pressure and of the temperature, by direct weighing with a micro-balance. Since equilibrium between the cuprous iodide and iodine vapor is established in a time of the order of minutes, it is necessary to operate the microbalance in an atmosphere of iodine vapor.

EXPERIMENTAL PROCEDURE

The balance, illustrated in Fig. 1, is an adaptation of the type successfully used for the comparison of gas densities.[3,4] It was constructed of fused quartz, which was the only material exposed to the iodine vapor. The balance was operated as a null instrument, remote control being achieved in the manner described by Blewett.[5]

The frame, *A*, was of heavy fused quartz rod. The beam, *B*, was constructed of six pieces of half-millimeter quartz rod which were fused together, mutually at right angles, with the aid of a graphite jig. Two of the pieces formed the beam proper and the two short vertical rods were used to adjust the center of gravity. The remaining two quartz rods were cut off short and quartz fibers fused to them. These quartz fibers supported the beam, being fused to the heavy frame. The fibers were slightly slack so as to exert negligible restoring torque. The fiducial pointer, *C*, established the zero of the balance. The iron cylinder *E*, which was sealed in a thin-walled quartz capillary made an angle of about
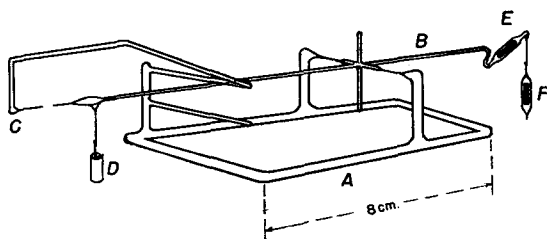

FIG. 1. Quartz microbalance.

* Publication No. 12 of the Solar Energy Conversion Research Program.
** Now at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania.
[1] K. Baedeker, Ann. d. Physik **29**, 566 (1909).
[2] K. Nagel and C. Wagner, Zeits. f. physik. Chemie **B25**, 71 (1934).

[3] A. Stock and G. Ritter, Zeits. f. physik. Chemie **A119**, 333 (1926).
[4] M. Woodhead and R. Whytlaw-Gray, J. Chem. Soc. **209**, 846 (1933).
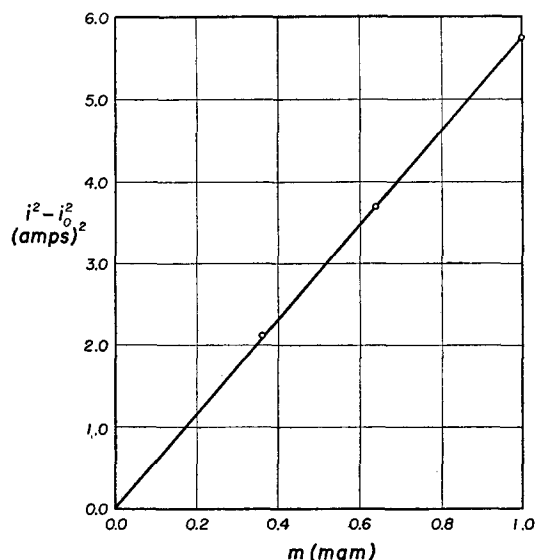[5] J. Blewett, Rev. Sci. Inst. **10**, 231 (1939).

FIG. 2. Calibration curve of quartz microbalance.

20 degrees with the beam. This iron cylinder was 5.0 mm long and 1.0 mm in diameter.

The horizontal magnetic field of a pair of Helmholtz coils was used to create the torque upon the iron cylinder which deflected the beam. A set of storage batteries supplied the current for the coils.

An important detail in the construction of the balance was the method of suspending the specimen, D, and its counterweight, F, from the beam. They were hung on quartz fibers which were fused to the beam. Only in this manner was it possible to maintain the lever arm of the balance constant and avoid erratic apparent changes in weight of the specimen.

The counterweight, F, was a piece of platinum wire sealed in a quartz capillary. Its density was adjusted to within a few percent of the density of cuprous iodide so as to avoid buoyancy effects.

The balance was calibrated by placing known weights of aluminum wire on the specimen hook and determining the current necessary to bring the beam back to its zero. The aluminum wire was weighed upon an Ainsworth microbalance. The calibration was performed by first placing upon the specimen hook an unknown mass sufficient to bring the beam pointer slightly below the fiducial pointer. The current to balance the beam was i_0. The known mass, m, was then

added to the specimen hook and the current for balance was i. Figure 2 shows a calibration curve. In agreement with the theory of the balance, $i^2 - i_0^2$ was proportional to m. The zero of the balance was observed over a period of several weeks and remained constant within a fraction of a microgram.

The reliability and precision of the instrument were tested by mounting it in a Pyrex tube with a molybdenum weight on the specimen hook. At room temperature, the apparent change in weight of the molybdenum was determined as a function of the pressure of dry nitrogen in the tube. The data are shown in Fig. 3.

Figure 4 shows the experimental arrangement for determining the dependence of the weight of a cuprous-iodide specimen upon the equilibrium pressure of iodine vapor. The balance was in the Pyrex tube, T. The Helmholtz coils H, surrounded the Pyrex tube. The entire assembly was in the electrically heated oven, O. Two small, double-walled, mica windows permitted observation of the beam and fiducial pointer. A simple lens giving a magnification of 5-fold was used for this purpose. The Pyrex tube, E, which connected the balance tube with the iodine reservoir, A, was wrapped with a heating element and kept at a temperature intermediate of that of the balance and iodine.

Before assembly of the apparatus a sample of 0.5-mil copper foil was suspended from the specimen hook. The weight of foil chosen was such as to yield a weight of cuprous iodide approximately 10^{-5} gram in excess of that necessary to balance the counterweight. The capsule, D,
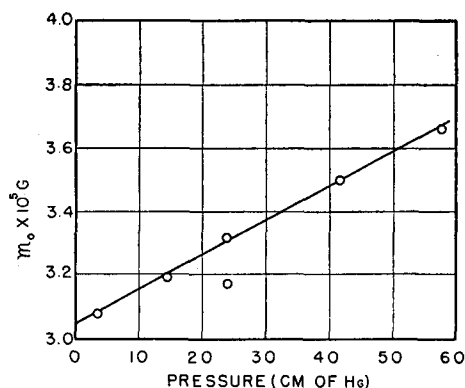

FIG. 3. Test of quartz microbalance

contained iodine which had been presublimed in a stream of dry nitrogen. After evacuating the tube through B, the capsule D was opened by dropping the glass-enclosed iron hammer S, on the thin-walled glass tip, C. The iodine was then distilled into the lower part of the tube E. Finally, after pumping the tube to a pressure of 10^{-6} mm Hg, it was sealed off at A.

The copper foil was slowly transformed to cuprous iodide by holding the balance oven at 150°C and the iodine oven at 80°C.

The oven temperatures were held constant by mercury thermoregulators and relays and the vapor pressure of the iodine in the tube was determined from the temperature of the iodine oven by use of the vapor pressure data of the *International Critical Tables*.

While taking data, the zero of the balance was checked periodically by immersing the iodine in liquid air and thus reducing the vapor pressure of iodine in the tube to a negligible value.

Figure 5 shows the dependence of the density of absorbed iodine atoms upon the pressure of the iodine vapor in equilibrium with the cuprous iodide. The temperature of the cuprous iodide was 132.1°C. The density of the absorbed iodine was calculated from the initial weight of the pure cuprous iodide and its measured change in weight. Since the initial weight of the copper foil was 29.414 milligrams, the initial weight of the cuprous iodide was taken as 88.14 milligrams. At all but the lowest iodine vapor pressures, the density of iodine atoms is proportional to the

FIG. 4. Apparatus for investigation of absorption of iodine by cuprous iodide.

square root of the iodine vapor pressure.

$$d = d_0 p_{I_2}^{\frac{1}{2}}. \qquad (1)$$

Figure 6 shows the dependence of the density of absorbed iodine atoms upon the temperature
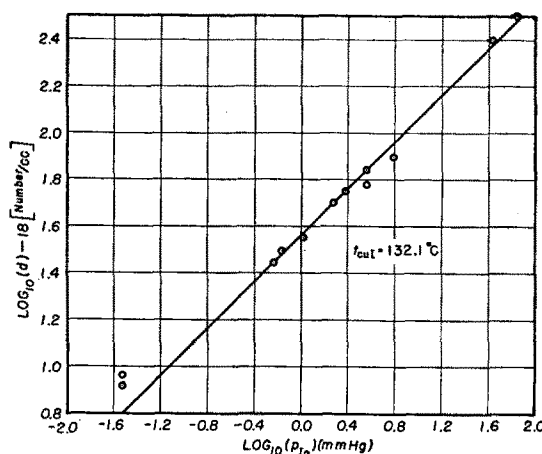

FIG. 5. The density of absorbed iodine atoms as a function of the equilibrium pressure of iodine vapor at constant temperature, $t = 132.1$ degrees C.

of the cuprous iodide for a constant equilibrium vapor pressure of iodine of 1.55 mm Hg. Over the narrow temperature interval examined, the density of absorbed iodine atoms is an exponential function of the reciprocal of the absolute temperature. The slope of the $\log_{10} d$ *versus* $1/T$ curve shown in Fig. 6 gives the heat of reaction as 0.24 electron volts per atom absorbed.

ELECTRICAL CONDUCTIVITY

The electrical conductivity of cuprous iodide was also measured as a function of temperature and of the equilibrium pressure of iodine vapor. Nagel and Wagner have shown that the increased conductivity, which results from the absorption of iodine, is electronic in nature. The electrolytic conductivity (due to the Cu^+) is also increased but is negligible. The experimental arrangement, which was essentially that of Nagel and Wagner,[2] is illustrated in Fig. 7. Platinum-foil electrodes were spot welded to two strips of copper foil, whose dimensions were 2.0 cm×0.5 cm×1.2×10^{-3} cm. The copper foils were suspended on platinum springs, spot welded to the electrodes, inside a sealed-off, evacuated Pyrex tube. Iodine, which had been
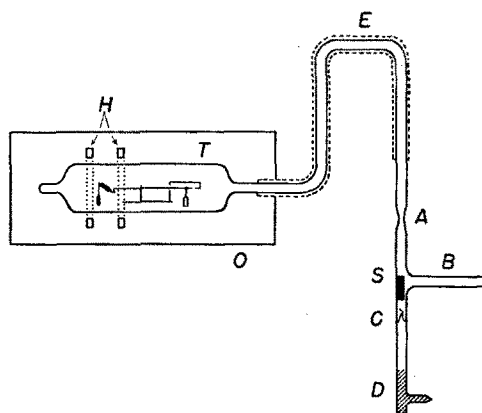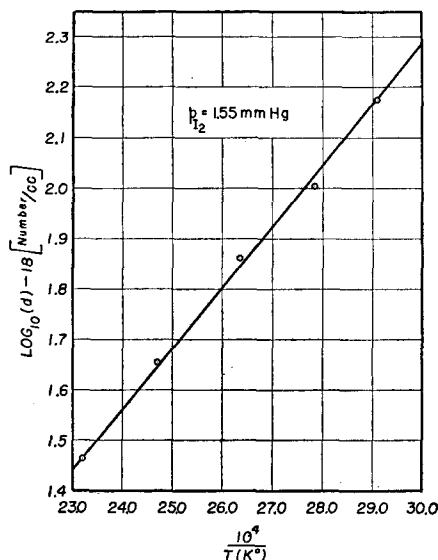
FIG. 6. The density of absorbed iodine atoms as a function of the temperature at constant iodine pressure. $p_{I_2} = 1.55$ mm Hg. Heat of reaction $= 0.24$ ev per atom absorbed.

presublimed in a stream of dry nitrogen, was distilled into the tube prior to its final evacuation and sealing off. That part of the tube containing the copper foils was surrounded by an electrically heated oven, O_1. The tube, E, which connected the specimen chamber, S, with the iodine reservoir, D, was wrapped with an electrical heating element and kept at a temperature intermediate of that of the ovens, O_1, and O_2. The oven temperatures were controlled by thermoregulators and measured with thermocouples and mercury thermometers. The resistance of the cuprous iodide was measured with a Leeds and Northrup Wheatstone bridge. The independence of the resistance of the cuprous iodide of the magnitude and sign of the d.c. voltage across the sample was checked. The resistance as measured with 60-cycle alternating current was the same as the d.c. resistance, within the precision of measurement.

The data are collected in Fig. 8. The agreement between these results and those of Nagel and Wagner is good except at the lowest iodine pressures where Nagel and Wagner's conductivities are as much as 50 percent lower than those found in these experiments.

By interpolation, the conductivity of cuprous iodide as a function of iodine pressure for a cuprous-iodide temperature of 132.1°C, can be obtained from the data of Fig. 8. In conjunction with the results of Fig. 5, the conductivity as a function of the density of absorbed iodine atoms, can be plotted. This is done in Fig. 9. Over the range of excess iodine concentration investigated, the conductivity varies approximately as the 4/3 power of the density of the absorbed iodine atoms.

$$\sigma = \sigma_0 d^{4/3}. \qquad (2)$$

DISCUSSION

Nagel and Wagner have proposed a mechanism for the absorption of iodine by cuprous iodide, similar to that which has been used, to successfully describe the behavior of cuprous oxide. They assume that two cuprous ions and two electrons wander to the surface of the solid for each iodine molecule absorbed. The result is an extension of the cuprous-iodide lattice, the formation of two vacancies in the cuprous ion lattice, and a defect of two electrons. This mechanism is plausible because the slight electrolytic conductivity of cuprous iodide is entirely due to the mobility of the Cu^+ ion. The reaction can be described by the chemical equation

$$2\ Cu^+ + I_2(g) \rightleftharpoons 2\ Cu^+ + 2I^- + 2V + 2h, \qquad (3)$$
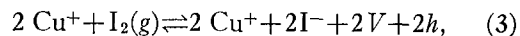
where the symbol, V, denotes a cuprous ion vacancy and the symbol, h, a defect of an electron or a "hole." The concentration of "holes" will then be proportional to the fourth root of the iodine vapor pressure, if the "holes"
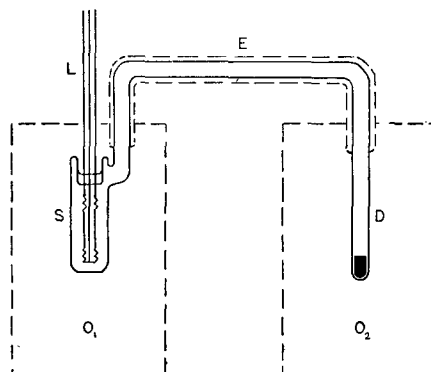

FIG. 7. Apparatus for determination of the electrical conductivity of cuprous iodide as a function of temperature and equilibrium vapor pressure of iodine.

are assumed free.

$$(h) = n = n_0 p_{I_2}^{\frac{1}{4}}. \tag{4}$$

Nagel and Wagner assume that the conductivity is proportional to the concentration of "holes," or

$$\sigma = \sigma_0 p_{I_2}^{\frac{1}{4}}. \tag{5}$$

This result is not in agreement with the experimental data of Fig. 8, although there is some indication that when the equilibrium vapor pressure is very small, Eq. (5) may be valid.

The conductivity of a semi-conductor is usually discussed in terms of Lorentz's equation:

$$\sigma = (4/3)[e^2 n l/(2\pi m k T)^{\frac{1}{2}}]. \tag{6}$$

The conductivity is proportional, at constant temperature, to the product of the density of
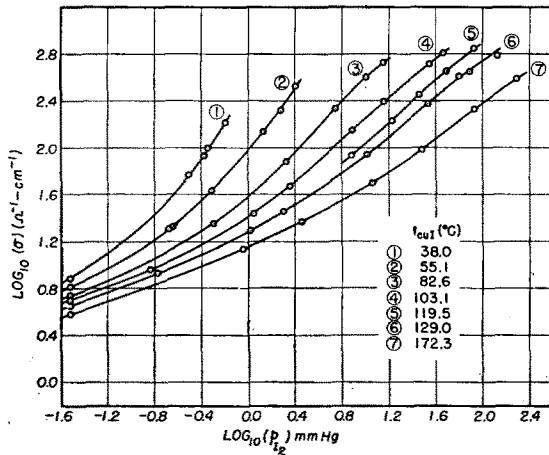
FIG. 8. The electrical conductivity of cuprous iodide as a function of temperature and equilibrium iodine pressure.
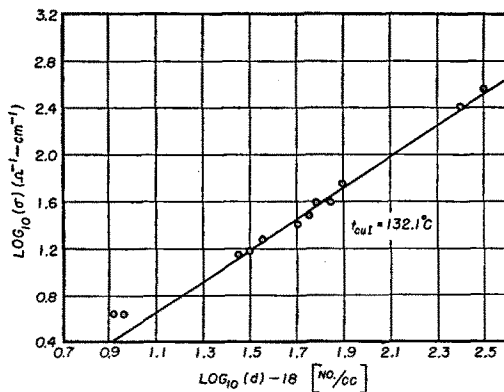
FIG. 9. The electrical conductivity of cuprous iodide as a function of the density of absorbed iodine atoms.
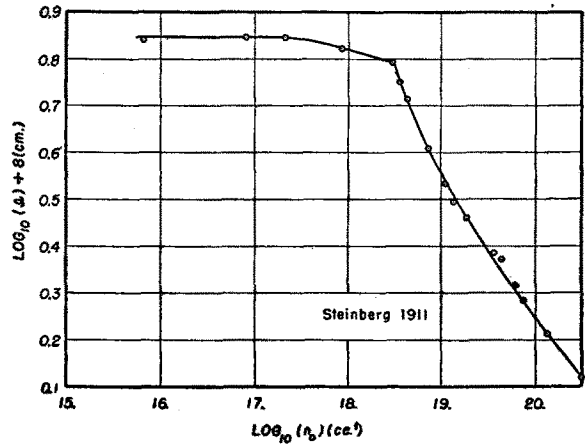
FIG. 10. The mean free path of the conducting "holes" in cuprous iodide as a function of the density of "holes." After Steinberg.

charge carriers, n, and their mean free path, l. In Fig. 10, is shown the dependence of the mean free path, l, of the "holes" in cuprous iodide, upon the density of "holes." These data are calculated from the Hall effect and conductivity data of Steinberg.[6] If we assume that the density of "holes" is of the order of magnitude of the density of absorbed iodine atoms, the mean free path is a strong function of the density of "holes" for the range of densities involved in these experiments. In fact, the mean free path can be well respresented within this range, by the equation

$$l = l_0 n^{-0.3}. \tag{7}$$

If we assume that this relationship, obtained from Steinberg's measurements at room temperature, is valid at the higher temperature of the present experiments, we can combine (7) and (6) and conclude that

$$\sigma = (4/3)[e^2 l_0 n^{0.7}/(2\pi m k T)^{\frac{1}{2}}], \tag{8}$$

combining Eqs. (2) and (8), we have the result that, within the error of experiment, the density of conducting "holes" varies as the square of the density of absorbed iodine atoms,

$$n \propto d^2; \tag{9}$$

and is proportional to the equilibrium vapor pressure of iodine.

$$n \propto p_{I_2}. \tag{10}$$

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[6] K. Steinberg, Ann. d. Physik 35, 1009 (1911).

CONCLUSION

The effect of the absorption of iodine upon the electrical conductivity of cuprous iodide is not adequately explained by the mechanism of Nagel and Wagner. We plan to extend the absorption measurements to other temperatures and to determine the Hall coefficient of cuprous iodide as a function of temperature and concentration of absorbed iodine.

Low Temperature Specific Heats of α-Manganese and γ-Manganese[1]

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The specific heats of α- and γ-manganese were measured in the temperature range 52° to 298°K. The specific heat curve of α-manganese exhibited a small "hump," extending over the temperature range 63°–103°K, with the peak of the "hump" occurring about 95°K. No anomaly appeared in the specific heat curve of γ-manganese. The computed heat contents and entropies per gram-atom are as follows: α-manganese, $H°_{298.16} - H°_0 = 1193 \pm 4$ cal., and $S°_{298.16} = 7.59 \pm 0.04$ E.U.; γ-manganese, $H°_{298.16} - H°_0 = 1221 \pm 4$ cal., and $S°_{298.16} = 7.72 \pm 0.04$ E.U.

A HIGH temperature allotropic modification of a metal seldom can be obtained in a sufficiently pure and stable form to determine its low temperature specific heat. Only one instance has been reported previously in the literature; viz., gray tin.[3] γ-manganese which is stable at low temperatures has been prepared by a controlled electrolysis at the Salt Lake City Station of the Bureau of Mines. This paper presents low temperature specific heat data for this material and for α-manganese.

MATERIALS

The γ-manganese used in these measurements was prepared by David Schlain[4] by electrolysis of manganous sulfate in the absence of sulfites. In the presence of sulfites the electrolysis deposits α-manganese. The resistivity of each of forty-three strips of γ-manganese used in the measurements was determined by E. V. Potter.[5] The mean value was 45.1 microhms-cm, with a standard deviation of 0.4 microhms-cm. Previous measurements of other samples of γ-manganese showed resistivities of 42.8 ± 0.3, 45.6 ± 0.5, and 44.7 ± 0.2 microhms-cm. The resistivity of α-manganese is 185 microhms-cm. This is rather conclusive evidence of the absence of α-manganese in the γ-manganese sample; certainly it is not present to the extent of a few percent. The sample of γ-manganese was refrigerated immediately after preparation and, except for a few hours at room temperature, was kept refrigerated until the specific heat measurements were commenced. Indications are that the rate of conversion of γ- to α-manganese is very slow, even at room temperature. A 374.20-g sample of γ-manganese was used in the measurements.

After completion of the measurements on γ-manganese, the sample was removed from the calorimeter and conversion to α-manganese effected by heating gradually to 550°C in a high vacuum (10^{-4} mm Hg). Before conversion, the γ-manganese was ductile, but after conversion to α-manganese it became brittle. Specific heat measurements were then made on a 368.30-g sample of this α-manganese.

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.
[2] Chemist, Pacific Experiment Station, Bureau of Mines.
[3] F. Lange, Zeits. f. physik. Chemie 110, 343 (1924).
[4] Metallurgist, Salt Lake City Station, Bureau of Mines.
[5] Physicist, Salt Lake City Station, Bureau of Mines.