

ence in their molal volumes, 147.5 cc. for C_7H_{16} and 227 cc. for C_7F_{16} .

Finally, let us return to the question stated at the outset, which mainly prompted this investigation, the slope of the curve for the solution in ethylene bromide. We see, first of all, from the values in Table III, that the solvent power of ethylene bromide at 25° appears in no way exceptional. As to its change in going to higher temperatures, we cannot rely upon Equation 1 for more than the first order effect of temperature in the term $RT \ln(x_2^f/x_2)$; the second order effects involved in changes in $\delta_2 - \delta_1$ are not accurately reproduced by δ -values derived from energies of vaporization. We can, however, adopt the procedure used by Hildebrand and Negishi¹⁷ in connection with the solubility of SnI_4 in $SiCl_4$ over a large temperature range and by Hildebrand¹⁸ similarly for iodine in carbon tetrachloride, in which the values of $\delta_2 - \delta_1$ obtained from the solubility data are plotted against temperature. Upon doing this we find that the slope of the line for ethylene bromide agrees well with the slopes of all of the neighboring lines for violet solutions except carbon disulfide. Moreover, the high temperature points for the carbon disulfide solutions are somewhat scattered, as can be seen from Fig. 1, and the last three are for temperatures near its boiling point, where evaporation could have made

(17) J. H. Hildebrand and G. R. Negishi, *THIS JOURNAL*, **59**, 339 (1937).

(18) See ref. 1(c).

the figures for solubility too high, particularly in view of the procedure used by Arctowski.¹⁹ We have therefore drawn the smooth curve in Fig. 1 a little below these points, bringing the whole family of regular solutions into accord.

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Summary

The solubility of iodine has been determined in perfluoro-*n*-heptane at 25° and in 1,2- and 1,1-dichloroethanes and *cis*- and *trans*-dichloroethanes over a range of temperature. All of these solutions fit into family of violet, regular solutions of iodine, with solubilities in satisfactory accord with internal pressures. This is true even for the fluoroheptane solution, where the Raoult's law solubility is 1400 times the actual solubility.

An apparent anomaly in the temperature coefficient of the solubility of iodine in 1,2-dibromoethane reported earlier is shown to be due instead to inaccuracies in the data for carbon disulfide solutions.

The different dipole moments of the dichloroethanes and dichloroethylenes used are not of primary significance in determining their solvent powers for iodine.

(19) H. Arctowski, *Z. anorg. Chem.*, **6**, 404 (1894).

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The Magnetic Susceptibility of Atomic Iodine^{1,2}

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The magnetic susceptibility of paramagnetic free atoms has been treated theoretically by Van Vleck.⁴ To date, the only experimental value which may be used to test the validity of the equation derived by Van Vleck for the paramagnetism of free atoms is the value given by Gerlach⁵ for potassium vapor between 600 and 800° . The work of Gerlach was of limited accuracy and did not constitute a direct measurement of the susceptibility. Therefore it was with the purpose of verifying experimentally the equation given by

Van Vleck that the determination of the magnetic susceptibility of atomic iodine was begun.

Atomic iodine has a normal state of $^2P_{3/2}$, which indicates a resultant J and therefore it should exhibit paramagnetism. Accurate equilibrium data for the reaction $I_2 \rightleftharpoons 2I$ have been obtained⁶ and indicate that the pressure of atomic iodine becomes appreciable as low as 1000° . Information indicating a magnetic moment for atomic iodine in accordance with theory has been obtained by Taylor and Phipps,⁷ using the Stern-Gerlach beam method.

The Van Vleck equation for the case of spin multiplet separation large compared to kT is

$$\chi_{\text{mol.}} = (Ng^2\beta^2/3kT) J(J+1) + N\alpha \quad (1)$$

where g is the Lande splitting factor, β the value of the Bohr magneton, and the other terms have their usual significance. The $N\alpha$ term involves the con-

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(3) Research Fellow in Chemistry, Cottrell Fund of the Research Corporation, Oregon State College.

(4) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, Oxford, England, 1932, pp. 226-238.

(5) W. Gerlach, *Atti congresso inter. fisici*, **1**, 119 (1927).

(6) M. L. Perlman and G. K. Rollefson, *J. Chem. Phys.*, **9**, 362 (1941).

(7) J. B. Taylor and T. E. Phipps, *Phys. Rev.*, **29**, 904 (1927).

tribution of the diamagnetism and temperature independent paramagnetism to the susceptibility. Since the multiplet separation between the ground state and next higher state for iodine atoms⁸ is 7600 cm.^{-1} , which indicates an energy separation large compared with kT , equation (1) is the appropriate equation for the case here. The $N\alpha$ term contributes very little to the value of the susceptibility for atoms with very large multiplet separations.

The value of g depends on the coupling scheme. The work of Deb⁸ indicates that the coupling in atomic iodine is $j-j$; thus the appropriate value of g is 1.38.

Experimental

Susceptibility measurements were made by means of the Gouy method.⁹ In order to obtain a reasonable pressure of atomic iodine it was necessary to work at a temperature not less than 1000° and at a total pressure of about 3 atm. This necessitated inclosing the sample in a relatively heavy fused quartz bulb. A calculation based on equation (1) shows that the force on a

sample of 0.5 sq. cm. cross section from readily obtainable fields would be of the order of 0.1 mg., whereas the total weight of the sample bulb could not be much less than 15 g. which imposed severe requirements on the sensitivity of the balance.

Torsion Balance.—It was found that a torsion balance, using a phosphor-bronze suspension and astatized by an inverted pendulum, possessed sufficient sensitivity and at the same time was only slightly affected by thermal disturbances and vibration. The measuring apparatus is shown in Fig. 1. The brass frame and floor plate of the torsion balance were mounted on leveling screws resting on a 1" marble slab. The slab was supported by a heavy wooden frame suspended from a reinforced concrete ceiling beam. A no. 27 B. & S. phosphor-bronze wire, 19 cm. long, supported a horizontal aluminum beam of length 15 cm., upon which was mounted a vertical brass rod carrying a mirror *M*. Sensitivity was regulated by means of a movable lead weight on the brass rod. A small electro-magnet *E* was provided to lift a 1 mg. iron calibrating weight from the conical cup placed approximately midway between the fulcrum and the end of the beam. The sample bulb was counterpoised by an adjustable brass rider. The balance was inclosed in a 9" bell jar sealed to the brass base by means of a rubber gasket. This made possible the evacuation of the system to about 3 mm. to reduce thermal disturbances.

The sample tube was 7.95 mm. average i. d. quartz tubing, 19 cm. in length and having a closure 7 cm. from the lower end. In the upper end was placed the iodine sample, and the bulb was suspended so that the closure was in the center of a homogeneous magnetic field. The lower portion of the bulb extended below the field and served to nearly neutralize the force of the field on the bulb alone.

To detect beam displacements, an optical system providing a magnification of more than 2500X was devised. Light from a 200 w. source was passed through a condensing system, a narrow slit and a long focal length lens, and after reflection from the balance mirror and a second stationary mirror was brought to a focus on a camera 9.5 m. distant. The shutter of the camera consisted of a vertical slit which was driven slowly across the film by a small motor. The small vertical motions of the balance beam were thus registered on the film as a sinusoidal curve; the equilibrium position of the beam was determined by the locations of the troughs and crests of the curve in the same manner that right and left swings determine the equilibrium position of an analytical balance beam. Kodak Super XX film pack, $9 \times 12 \text{ cm.}$, was used, mounted in a movable rack behind the slit so that nine exposures could be made on each film.

The developed films were projected, with an enlargement of 20X, upon a large sheet of coordinate paper from which the equilibrium positions of the curves were read to the nearest 0.01° . The sensitivity of the balance was such that 1 mg. change in mass of the sample resulted in about 4° change in position of the projected image.

Magnet.—The magnet was an electro-magnet energized by a 220 v. d. c. shunt-wound generator. The magnet core was made from a laminated mild-silicon-steel transformer reactor core, of 25 sq. in. cross-section. It had pole faces of 9 sq. in. area and an adjustable gap. The magnet coils contained approximately $15,000'$ of no. 12 and no. 16 B. & S. copper magnet-wire, and drew a current of about 9 amp. The field was held constant by passing the current through a 0.01 ohm oil-cooled manganin resistance across which a potentiometer was connected. The potential drop across the resistance was kept at any desired value by manually adjusting the field rheostat of the generator. The field controlled in this manner was found to stay very constant since only very large deflections of the potentiometer galvanometer would indicate any appreciable current change. Field measurements were made with certain fixed gaps and potentiometer settings, so that fields could easily be reproduced. For the measurements on atomic iodine, a gap of 2.93 cm. and a field of 8080 oersteds were used. Measure-

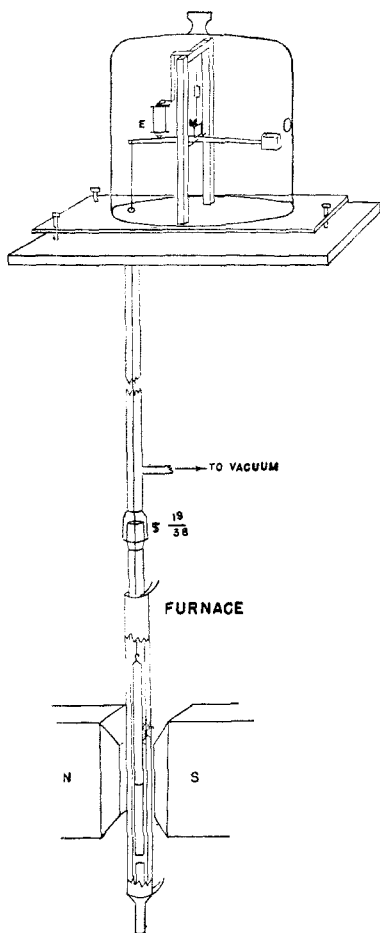


Fig. 1.—Diagram of apparatus.

(8) S. C. Deb, *Proc. Roy. Soc. (London)*, **139**, 380 (1933).

(9) L. G. Gouy, *Compt. rend.*, **109**, 935 (1889).

ment of the field strength was done by the Gouy⁹ method using a micro-balance with water as a calibrating agent. The susceptibility of water at 20° was assumed to be -0.720×10^{-6} unit per gram.

Furnace.—The furnace shown in Fig. 1 was made of 18 mm. o.d. quartz tubing, 42 cm. long. Extending 6 cm. into the lower end was sealed a piece of 10 mm. o.d. quartz tubing to serve as a thermocouple well. The large quartz tube was wrapped with 11' of chromel ribbon, having a resistance of 0.4 ohm per foot extending 33 cm. up the tube from the bottom. The furnace insulation was kept to a minimum to keep the magnet pole gap as small as possible. The resistance ribbon was covered with a one-eighth inch layer of an asbestos-alundum mixture, around which was wrapped a sheet of 0.005" brass. The upper end of the quartz furnace was ground to fit a standard taper joint $\frac{1}{8}$ 19/38. This joint connected the furnace to a 50 cm. long 18 mm. o.d. Pyrex tube which made a vacuum tight joint to the floor plate of the torsion balance. The temperature gradients of the furnace were investigated at the temperatures to be used. Over a length of 12 cm. in the central portion of the furnace, the maximum temperature difference was 38°. The bulb temperature was taken as the average temperature throughout its length. The difference between the temperature of the bulb position and the temperature in the thermocouple-well was determined by having one thermocouple in the well and another in the bulb position. By knowing this difference, the temperature of the bulb could be found.

The thermocouples used were Pt-Rh(10) calibrated at the freezing points of C.P. sodium chloride, C.P. sodium sulfate, and Bureau of Standards tested copper.

Preparation of Iodine.—C.P. iodine crystals were purified by sublimation and stored in a desiccator over P_2O_5 .

Method of Measurement.—The upper section of the sample bulb, which was of volume 5.671 cc. and cross-sectional area 0.498 sq. cm., was filled with 37.8 mg. of iodine, sufficient to give a pressure of about 3 atm. at 1000°, then rapidly evacuated and sealed. The iodine was weighed on introduction into the bulb and determined after the experiment by titration with standardized sodium thiosulfate. The bulb was suspended from the balance arm by a platinum wire and freed from any contact with the walls of the furnace by a positioning screw which moved the lower end of the furnace until it was ascertained that the bulb was hanging freely.

Data were obtained at each of three temperatures, 470, 1030 and 1127°. As it was desired to measure the change in weight of the sample bulb in the magnetic field, the equilibrium position of the balance beam was determined photographically first with the calibrating weight in the cup, second with the weight lifted, and third with the weight dropped and the field applied. This process yielded three closely-spaced curves; upon projection, the distance from the first equilibrium position to the third was divided by the distance from the first to the second to give the ratio of the change in weight due to the field to that due to lifting the calibrating weight. All data were recorded in terms of this ratio; it was readily convertible to the weight change due to the magnetic field. By recording a calibrating curve with each field measurement, errors due to change in balance sensitivity and to shrinkage and expansion of film were eliminated. Some 300 practice measurements

were made in developing the most reliable technique.

Since the lower end of the bulb, though out of the region of high field strength, was in a weak non-homogeneous field, the force exerted on the bulb was considerably dependent upon its position. To obtain a value for the force of the field on the bulb itself, it was decided to obtain the force upon the iodine-filled bulb at 470°, where the dissociation constant of iodine¹⁰ is approximately 5×10^{-6} . By applying a small correction for the diamagnetism of the molecular iodine and using an approximate value for the paramagnetism of the small amount of atomic iodine present, the force on the bulb alone was computed. Since the diamagnetism of quartz is virtually independent of temperature, this value could be used as the force upon the empty bulb at the two higher temperatures, and eliminated the considerable error which would be introduced by removing and re-suspending the bulb in the apparatus. The temperature independence of the susceptibility of the quartz was verified by a number of measurements on the empty bulb at all three temperatures.

Results and Discussion

Because of the very small force to be measured and the relative magnitude of the observational errors, a rather wide range of values for the force due to the magnetic field was found at each temperature. Consequently, a number of determinations were made at each temperature in groups of from 6 to 18, and alternating between the low and the high temperatures. At 470°, forty-eight values were taken and at 1030°, seventy-six were taken. At 1127°, numerous difficulties were encountered and only 18 values were obtained which could be considered representative. The data at all three temperatures fell upon a probability distribution curve, as shown in Fig. 2 with curve 1 representing

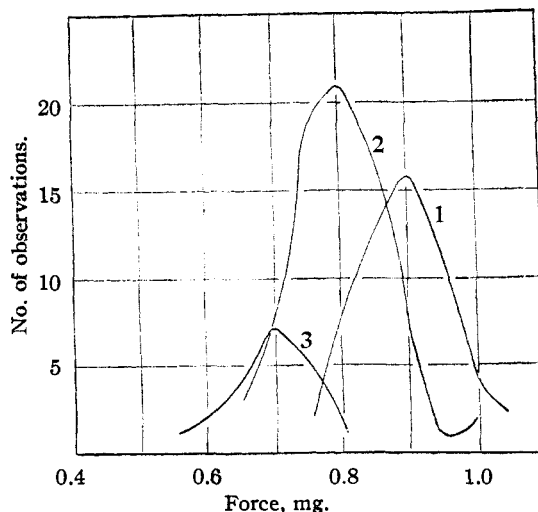


Fig. 2.—Probability distribution curves.

(10) Murphy, *J. Chem. Phys.*, **4**, 344 (1936).

observations at 470°, curve 2 the observations at 1030°, and curve 3 the observations at 1127°, indicating that the observational errors were random and could be treated with some confidence by the usual statistical means. The temperature was estimated to be accurate to $\pm 5^\circ$ which is less than the probable error of experimental values.

The average force upon the bulb and contents at 470° was 0.929 mg. Using Berthelot's equation of state in the form

$$PV = RT(1 + \lambda P) \quad (2)$$

the pressure of molecular iodine was calculated. The value for λ was taken as -0.0047 , from Perlman and Rollefson's⁶ data for I_2 at 450°. The pressure of iodine so computed was 1.59 atm.; the ideal gas law gave 1.60 atm. At the two higher temperatures both molecular and atomic iodine were assumed ideal. Assuming the molar susceptibility of iodine¹¹ to be -89.2×10^{-6} the force due to the molecular iodine was calculated to be 0.039 mg. from the equation

$$\text{force (g.)} = \kappa AH^2/2g \quad (3)$$

where κ is the volume susceptibility, A the cross-sectional area, H the field strength and g the acceleration due to gravity. Since slight dissociation occurs at 470°, the contribution of atomic iodine was evaluated by assuming an approximate atomic susceptibility of free iodine, based on initial calculations at 1030° and correcting for temperature change by Curie's law, of 1.4×10^{-3} . From the dissociation constant, 5×10^{-6} , the force due to atomic iodine was found to be 1.1×10^{-3} mg. and in the opposite direction from the forces on the bulb and molecular iodine. The net force on the bulb alone was thus 0.891 mg.

The average force on the bulb and contents at 1030° was 0.823 mg. The dissociation constant found by interpolation of the data of Perlman and Rollefson⁶ is 0.234. The pressure of molecular

iodine was computed to be 2.44 atm. and of atomic iodine 0.756 atm. Equation (3) was again used to evaluate the contribution due to the diamagnetism of the molecular iodine, which was 0.034 mg.; the force due to the bulb and atomic iodine was thus 0.789 mg. Comparing this force with that computed for the bulb alone at 470°, it is seen that the force upon the atomic iodine was 0.102 mg. From equation (3) the volume susceptibility of atomic iodine may now be obtained which may be converted by use of the pressure and the ideal gas law to molar susceptibility. The value found at 1030° was $8.7 \times 10^{-4} \pm 0.6 \times 10^{-4}$ c. g. s. units.

In an analogous manner the susceptibility at 1127° was calculated. The average force on the bulb and contents was 0.726 mg., K was taken as 0.603, and the force due to molecular iodine was computed to be 0.031 mg. The force due to atomic iodine was 0.196 mg., which, at a pressure of 1.21 atm., yielded a molar susceptibility of $11.2 \times 10^{-4} \pm 0.6 \times 10^{-4}$ c. g. s. units.

The probable errors in these values were computed on the basis of the distribution curves only and are of course smaller than the possible error, particularly at 1127° at which temperature the number of determinations was much smaller, and the possibility of systematic error greater.

The value computed from the Van Vleck equation not including the $N\alpha$ term is 6.84×10^{-4} at 1030° and 6.37×10^{-4} at 1127°. While the experimental values found do not check these values within the probable error, they do lie within the possible error; therefore these values may be assumed to furnish a reasonable check of the Van Vleck equation.

Summary

1. An experimental determination of the magnetic susceptibility of atomic iodine was made. Values for χ_{mol} were found to be 8.7×10^{-4} at 1030° and 11.2×10^{-4} at 1127°.
2. The apparatus and method of measurements are given in detail.

(11) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 52.