believe that the former can donate hydroxyl radicals to a reducing agent, and that alkaline permanganate solution reacts essentially as a very dilute solution of hydroxyl radicals; this view provides a simple explanation for the oxygenating action of the permanganate-to-manganate reaction, for example, sulfite to sulfate, as well as the rapid exchange of manganate and permanganate.[3] The investigation of these reactions is continuing.

Summary

The decomposition of alkaline permanganate to manganate has been shown to involve an equilibrium reaction in one of its steps

$$\text{I} \quad MnO_4^- + H_2O \rightleftarrows MnO_4^- + HO + H^+$$

The slow step in the decomposition is taken to be the combination of the hydroxyl radicals. The equilibrium nature of reaction I was proved by carefully controlled experiments which demonstrated that the presence of products of reaction I affected the rate of the decomposition.

The data do not allow a decision on whether equilibrium I is homogeneous or heterogeneous, but in either case it is likely that a reducing agent, particularly a negatively-charged one, is oxidized through the agency of the hydroxyl radical.

Solubility of Iodine in 1,2- and 1,1-Dichloroethanes, cis- and trans-Dichloroethylenes and Perfluoro-n-heptane

BY H. A. BENESI* AND J. H. HILDEBRAND

Solutions of iodine offer unusually valuable tests of the theory of solution of non-electrolytes by reason of the reliability of the analytical procedure used, the distinction between "chemical" and "physical" effects afforded by color, and the high London forces of iodine molecules, giving a wide spread in its solubilities in ordinary solvents. These solutions have been discussed by the senior author and collaborators in a series of papers.[1] The solubility curves, plotted as log x_2 vs. $1/T$, where x_2 is the mole fraction of iodine, fall into two types, corresponding to color, those of the violet solutions obviously belonging to a family. This suggested the now familiar designation of such solutions as "regular." The curves for the red, yellow and brown solutions, on the other hand, all have smaller and individual slopes and all the evidence points to varying degrees of solvent-solute interaction.

Solutions in ethylene bromide (1,2-dibromoethane) seemed to straddle the above distinctions; they are pure violet in color but, like the curve for the red solutions in benzene, the solubility curve has a slightly smaller slope than the one that was drawn through the adjacent experimental points for carbon disulfide. This investigation was undertaken, in part, in order to throw light upon the reason for the apparent discrepancy. It is now well known that the dipole moments of 1,2-dichloro- and dibromoethanes[2,3,4] vary with tem-

perature and, when in solution, with the solvent used, due possibly to shifts in the relative amounts of cis- and trans-configurations, and it was thought that perhaps the interaction of the two forms with iodine might be different and hence cause an anomalous temperature coefficient of solubility. In order to magnify such a possible difference, chlorides were selected rather than bromides, and we decided to compare the solubility of iodine in (a) 1,2-dichloro- and 1,1-dichloroethanes, and (b) cis- and trans-1,2-dichloroethylenes. A preliminary report of the solubility of iodine in normal perfluoroheptane which was made for another purpose is included in this communication.

Materials and Purification

Reagent grade iodine by General Chemical Company was used without further treatment.

Ethylene chloride (1,2-dichloroethane) by Eastman Kodak Company showed a negative test for chloride ion and was carefully distilled through a 15-plate fractionating column. The first and last portions were discarded and the middle portion, boiling at 83.0–83.1° at 752 mm., was collected and stored in a dry, glass-stoppered flask. After all solubility measurements had been carried out, the remaining ethylene chloride still showed a negative test for chloride ion.

cis- and trans-1,2-dichloroethylene (acetylene dichlorides) were prepared by fractionally distilling 500 cc. of the commercially prepared mixture of the isomers through a 30-plate fractionating column at a reflux ratio of 30:1. The original mixture showed a negative test for chloride ion. Two fractions were obtained boiling at 60.0–60.2 and 47.7–48.0° at 755 mm. The low boiling trans-isomer decomposed and gave a positive test for chloride ion upon standing. This isomer was therefore shaken with sodium carbonate solution, washed with distilled water, dried over "Drierite" and redistilled just before using. After the solubility measurements were made, both the cis- and trans-isomers were recovered and redistilled. The boiling points had not changed; therefore no appreciable isomerization had occurred.

A sample of pure perfluoro-n-heptane which we had in the laboratory was distilled and boiled at 81.9–82.0°.

Ethylidene chloride (1,1-dichloroethane) from Eastman

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(1) (a) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL 42, 2180 (1920); (b) J. H. Hildebrand, ibid., 51, 66 (1929); (c) G. R. Negishi, L. H. Donally and J. H. Hildebrand, ibid., 55, 4793 (1933); (d) J. H. Hildebrand, ibid., 57, 866 (1935); (e) ibid., 59, 2083 (1937): (f) Science, 90, 1 (1939); (g) J. H. Hildebrand, "Solubility of Non-Electrolytes," 2nd Ed., Reinhold, New York, N. Y., 1936, pp. 153–157.

(2) G. I. Bloom and L. E. Sutton, J. Chem. Soc., 727 (1941).

(3) C. T. Zahn, Phys. Rev., 38, 521 (1931); 40, 291 (1932).

(4) L. Onsager, 58, 1486 (1936).

Kodak Company showed a positive test for chloride ion. The hydrogen chloride that presumably was present was removed by shaking with sodium carbonate solution. The liquid was then washed several times with distilled water, dried over "Drierite," and carefully distilled through a 15-plate fractionating column. A 300-cc. fraction boiling at 57.2° (757 mm.) was collected and showed a negative test for chloride ion.

Apparatus and Procedure

The solubility of iodine in the various solvents was determined by means of the apparatus of Hildebrand and Jenks[5] with slight modification. A solubility determination was carried out by adding 15 g. of iodine to 50 cc. of the pure solvent in a dry solubility flask. The flask was stoppered and immersed in a large beaker of water at a temperature of *ca.* 45°. The flask was agitated for ten minutes to facilitate the solution of the iodine. The stoppered solubility flask was then immersed in the thermostat in a rocking device. The supersaturated solution of iodine soon deposited solid iodine crystals and reached equilibrium very quickly. The ground glass stopper was then replaced by a weighed pipet, the assembly immersed in the thermostat, and the weight pipet filled with 10 cc. of saturated iodine solution. The pipet was removed quickly, the excess liquid wiped off, a glass tube fitted over the end, and then weighed. After weighing, the contents of the pipet was washed into a flask with purified carbon tetrachloride and titrated with standardized sodium thiosulfate solution.

Results

The results are given in Table I,

TABLE I
SOLUBILITY OF IODINE

Temp., °C.	15.0 Wt. %	15.0 Mole %	25.0 Wt. %	25.0 Mole %	35.0 Wt. %	35.0 Mole %
Ethylene chloride	3.909 3.914	1.563	5.45 5.42	2.20	7.38 7.40	3.02
Ethylidene chloride			3.828 3.824	1.531	5.241 5.249	2.112
cis-Dichloroethylene	2.597 2.597	1.008	3.682 3.690	1.441	5.170 5.176	2.041
trans-Dichloroethylene			3.626 3.630	1.417	5.048	1.990
Perfluoro-n-heptane			0.0120	0.0185		

TABLE II
DIPOLE MOMENTS

Solvent	$\mu \times 10^{18}$ (e. s. u. — cm.)
cis-$C_2H_2Cl_2$	1.89[6]
trans-$C_2H_2Cl_2$	0.00[7]
CH_2ClCH_2Cl	1.18 (35.2°)[8]
CH_3CHCl_2	2.07[6]
CH_2BrCH_2Br	0.81 (65.4°)[8]

(5) See ref. 1(a).

(6) A. A. Maryott, M. E. Hobbs and P. M. Gross, THIS JOURNAL, **63**, 659 (1941).

(7) G. P. Mikhailov and D. V. Tishchenko, *J. Gen. Chem. (U. S. S. R.)*, **9**, 782 (1939).

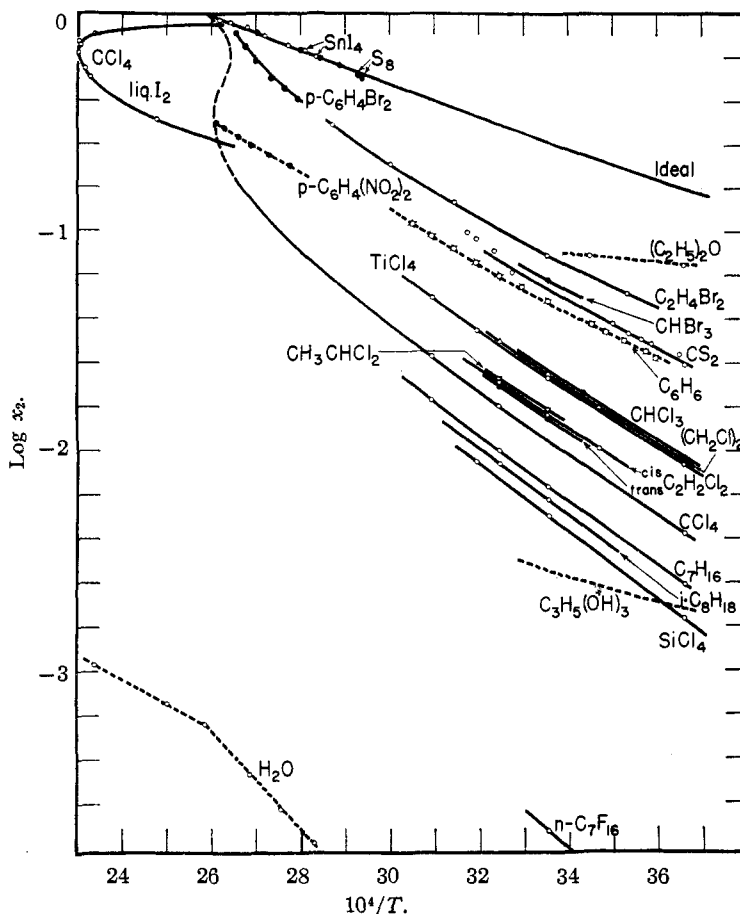(8) G. I. Bloom and L. E. Sutton, *J. Chem. Soc.*, 727 (1941).

Fig. 1.—Solubility of iodine.

and in Fig. 1 are added to the iodine solubilities previously studied. We call attention, first, to the fact that the solubilities bear little or no relation to the dipole moments of the solvent molecules, shown in Table II.

The two dichloroethylenes, for example, have almost identical solvent powers despite the fact that the *cis*-form has a moment of 1.89 e.s.u. and the *trans*-form a zero moment. This is in accord with the finding of Hildebrand and Carter[9] that the three dinitrobenzenes all show the same deviation from ideal behavior in solution in benzene.

We may note, second, that all of these solutions show a pure violet color; hence there is no evidence of solvation. This is further confirmed by the parallelism of the curves for these solutions with those for such non-polar solvents as carbon tetrachloride and titanium tetrachloride.

Third, the order of solubilities is in accord with the internal pressures of the solvents as indicated by the "solubility parameters," $\delta_1 = (\Delta E_1^V / v_1)^{1/2}$, where ΔE_1^V is the molal energy of vaporization and v_1 the molal volume of the liquid solvents. A quantitative test can be made by the method

(9) J. H. Hildebrand and J. M. Carter, *Proc. Natl. Acad. Sci.*, **16**, 285 (1930); also, ref. 1(g), pp. 82–83.

previously used in these studies[10] by the aid of the solubility equation for solids

$$4.575 \; T \log (x_2^i/x_2) = v_2\phi_1^2 (\delta_2 - \delta_1)^2 \quad (1)$$

where x_2 is the mole fraction of the solute in a saturated solution, x_2^i its ideal solubility, calculated from its heat of fusion, v_2 is the molal volume, extrapolated, of liquid solute, and ϕ_1 is the volume fraction of the solvent. We substitute in this equation the necessary quantities and calculate δ_2, the solubility parameter for liquid iodine at 25°. The figures obtained are given in the last column of Table III.

TABLE III

IODINE SOLUTIONS, 25°

Solvent	Mole. vol., cc.	Mole % I₂	x_2^i/x_2	δ_1	δ_2
n-C₇F₁₆	227	0.0185	1400	5.7	14.2
n-C₆H₁₄	131.6	.456	56.6	7.3	13.7
SiCl₄	115.3	.499	51.8	7.6	13.9
i-C₅H₁₂	166.1	.592	43.6	6.9	13.1
n-C₇H₁₆	147.5	.679	38.0	7.4	13.4
CCl₄	97.1	1.147	22.5	8.6	14.2
$trans$-C₂H₂Cl₂	77.4	1.417	18.2	9.0	14.5
cis-C₂H₂Cl₂	75.8	1.441	17.1	9.1	14.5
1,1-C₂H₄Cl₂	84.7	1.531	16.9	9.1	14.4
1,2-C₂H₄Cl₂	79.5	2.20	11.7	9.8	14.9
TiCl₄	110.5	2.15	12.0	9.0	14.1
CHCl₃	80.7	2.28	11.3	9.3	14.3
CS₂	60.6	5.46	4.73	9.9	14.1
CHBr₃	87.8	6.16	4.19	10.5	14.1
1,2-C₂H₄Br₂	86.6	7.82	3.30	10.4	14.1
				Av.	14.1
I₂	59.0	25.8	1.00	$(\Delta E^V/v)^{1/2}$	13.6

For purposes of comparison, a similar study of iodine solubilities in ten other solvents[11] has been included, together with revised values of their solubility parameters.

The ideal solubility of iodine at 25° was calculated from the heat of fusion determined by Frederick and Hildebrand.[12] The corresponding molar volume of liquid iodine was obtained by extrapolation of the data by Drugman and Ramsey.[13] The solubility parameters of the solvents were calculated from their heats of vaporization and molar volumes at 25°. The recently compiled data on hydrocarbons[14] furnished this information in the case of the hydrocarbons. The heats of vaporization of the tetrahalides were taken from the data compiled by Kelley.[15] The remaining solubility parameters were based on calorimetrically determined heats of vaporization wherever possible. In the absence of calorimetric data, the heats of vaporization were calculated from vapor pressure data, the usual corrections being made for imperfect gas behavior.

If Equation 1 were rigid, the values of δ_2 would

(10) Ref. 1(g), p. 74.
(11) See ref. 1(g), p. 155.
(12) K. J. Frederick and J. H. Hildebrand, THIS JOURNAL, 60, 1436 (1938).
(13) Drugman and Ramsey, J. Chem. Soc., 77, 1228 (1900).
(14) "Selected Values of Properties of Hydrocarbons," Bureau of Standards Circular C461 (Government Printing Office, Washington. D. C., Nov., 1947).
(15) K. K. Kelley, Bull. U. S. Bur. Mines. 383 (1934).

agree within the experimental errors involved. The departures are not surprising in view of the various molecular sizes and shapes involved and the lack of symmetry of some of the fields of force. The formula was derived on the assumption, among others, of spherical molecular symmetry. The molecules of normal paraffins, which yield low values of δ_2, are far from spherical. Again, the equation neglects the effect of different molal volumes upon the entropy of mixing. We may use the approximate formula[16]

$$\Delta \bar{s}_2 = -R \ln \phi_2 + R\phi_1 \left(\frac{v_2}{v_1} - 1\right) \quad (2)$$

to take this into account, modifying Equation 1 to read

$$\log \frac{x_2^i}{\phi_2} = \frac{v_2\phi_1^2(\delta_2 - \delta_1)^2}{4.575 \; T} - 0.434 \; \phi_1 \left(\frac{v_2}{v_1} - 1\right) \quad (3)$$

Let us apply this to the solution in Table III which shows the biggest ratio of v_1/v_2, that of I₂ in isoöctane, where $v_1/v_2 = 2.815$. Calculating δ_2 for this solution by Equation 3 gives 13.8 instead of 13.1, close to the value 14.1 obtained for solvents like carbon disulfide, for which the volume ratio is close to unity.

In reversing the calculation to obtain solubilities from δ-values, we should not expect extremely close checks with experiment. In the first place, $(\delta_2 - \delta_1)^2$ is extremely sensitive to slight variations in the δ-values; in the second, the formula takes no account of the peculiarities of molecular architecture; in the third, this theory of solubility, like any rival it might have, is based upon theories of heat and entropy of mixing whose algebraic sum gives a free energy, and if this is in error by even a few per cent. the mole fraction calculated from it will be in error by many per cent.

Fourth, we invite particular attention to the solubility of I₂ in n-C₇F₁₆ which is only 0.0185 mole per cent., far smaller than the figure for any other "violet" solvent, and only 1/1400 of the ideal solubility; nevertheless, it yields $\delta_2 = 14.2$, practically identical with the values of δ_2 derived from solutions in other non-polar solvents such as titanium tetrachloride and carbon disulfide. Obviously, the process could have been reversed and the solubility in C₇F₁₆ calculated with remarkable accuracy from $\delta_2 = 14.1$ and $\delta_1 = 5.7$. The latter value has been deduced, in the absence of data for the vapor pressure or heat of vaporization of this substance, from a comparison of the known heats of vaporization of hydrocarbons and the analogous fluorocarbons made by our colleague, Dr. R. L. Scott, and soon to be published in a comprehensive review of the solubility relations of fluorocarbons. The striking decrease in δ_1 from 7.4 for n-C₇H₁₆ to 5.7 for n-C₇F₁₆, is to be attributed to the fact that while their molal heats of vaporization are approximately the same, the energies of vaporization per cc., δ_1^2, are very different due to the big differ-

(16) Cf. J. H. Hildebrand, J. Chem. Phys., 15, 225 (1947), for prior references.

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 $RT \ln (x_2^i/x_2)$; 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 Negishi[17] in connection with the solubility of SnI_4 in $SiCl_4$ over a large temperature range and by Hildebrand[18] 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 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.

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.

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

(18) See ref. 1(c).

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

The Magnetic Susceptibility of Atomic Iodine[1,2]

BY ALLEN B. SCOTT AND THOMAS M. CROMWELL[3]

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 Gerlach[5] 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 obtained[6] 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

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

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-