261. *A Thermodynamic Study of Some Iodine Solutions.*

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The partial pressure, partial molar volume, and solubility of iodine have been measured for solvents with which it forms molecular complexes. All three properties show clearly the effects of the formation of complexes. The partial molar volume at infinite dilution is greatly reduced by such association, the values at 25° varying from 67·9 ml. in *cyclo*hexane to 48·3 ml. in ethyl ether. Measurements of the partial pressure of solid iodine in the presence of the solvent vapours show that small concentrations of complex-forming solvents reduce the iodine concentration in the gas phase. It is suggested that this is due to the formation of a coherent surface phase. Larger concentrations of vapour increase the iodine concentration owing to interaction in the gas phase between iodine and solvent.

THE solubility of iodine in organic solvents and the colour of these solutions have long been used to distinguish between substances with which iodine forms molecular complexes and substances to which it is inert. The solutions containing complexes are generally red or brown and the normal solutions violet. The solutions containing complexes show very strong and broad absorption bands in the near-ultraviolet region, which are now generally interpreted as charge-transfer spectra in a binary complex in which the iodine acts as an electron acceptor and the solvent as the donor.[1, 2] Aromatic compounds, ethers, alcohols, and amines have all been found to act as donors. Very weak complexes have been reported between iodine and saturated hydrocarbons,[3] but the effects of these on the physical properties of the solutions are probably negligible. A study of the solubility of iodine in normal solvents was an important part of the work which led Hildebrand to formulate his theory of "regular solutions." He found that such solubilities were always less than ideal by an amount which depended on the energy of vaporisation per unit volume of the solvent.[4] The solubilities in complex-forming solvents, though still less than ideal, were greater than those calculated for a regular solution. However, thermodynamic properties other than solubilities have been little studied, possibly on account of the difficulties of working in conventional apparatus with material which reacts with both mercury and tap-grease. In this paper we report some measurements of the partial pressures and partial molar volumes of iodine in solution and of the partial pressures of solid iodine in the presence of vapours of organic substances at total pressures less than the saturation pressure. The partial pressures were measured in a sealed all-glass apparatus by using radio-iodine to determine the iodine concentration in the vapour phase. The solvents used were *cyclo*hexane, benzene, fluorobenzene, chlorobenzene, bromobenzene, mesitylene, pyridine, ethyl bromide, ethyl iodide, and diethyl ether. All but *cyclo*hexane showed evidence of molecular complexes.

EXPERIMENTAL

Purification of Materials.—Iodine ("AnalaR") was used without further purification, except for the density measurements for which it was finely powdered and stored over phosphoric oxide.

Radioactive iodine, ^{131}I, was obtained from the Radiochemical Centre, Amersham, in 2 mc batches as a carrier-free solution of sodium iodide. This solution was brought to equilibrium with an ethereal solution of normal iodine by 24 hours' shaking. The ether was removed by evaporation in a current of dry air, and the iodine separated from involatile material by vacuum-distillation in a short-path still. The final activity was about 0·25 mc/g.

*cyclo*Hexane (from Messrs. Howards) was freed from aromatic substances by shaking it with a nitrating mixture, then washed with alkali and with water, dried, and fractionally distilled.

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[1] Andrews, *Chem. Rev.*, 1954, **54**, 713.
[2] Orgel, *Quart. Rev.*, 1954, **8**, 437.
[3] Evans, *J. Chem. Phys.*, 1955, **23**, 1424.
[4] Hildebrand and Scott, "The Solubility of Non-Electrolytes," Reinhold, New York, 1950.

Benzene (" AnalaR ") was fractionally crystallised three times and dried.

Fluorobenzene, chlorobenzene, and bromobenzene (from British Drug Houses Ltd.) were dried and fractionally distilled.

Mesitylene (from Genatosan Ltd.) was converted into the sulphonic acid, and the crystals were washed with 70% sulphuric acid. The mesitylene was regenerated by refluxing the acid with 15% hydrochloric acid, followed by steam-distillation. It was then dried and fractionally distilled.

Pyridine (" AnalaR ") was dried and fractionally distilled from " Anhydrone."

Ethyl bromide (from British Drug Houses Ltd.) was washed with concentrated sulphuric acid to remove alcohol, with sodium hydrogen carbonate solution, and with water. It was dried and fractionally distilled.

Ethyl iodide (from Messrs. Whiffen) was purified in small batches immediately before use by distillation through a column packed with copper turnings to remove hydrogen iodide, then dried and fractionally distilled.

Ethyl ether (" AnalaR ") was dried and fractionally distilled.

Partial Pressure of Iodine.—The relative concentration of radio-iodine in the vapour phase above a solution of known total iodine concentration was determined by means of a Geiger counter outside, but adjacent to, the glass apparatus. This concentration was compared with that of the vapour from a sample of pure solid iodine prepared from the same batch of radioactive material. The vapour pressure of solid iodine has been measured directly by Gillespie and Frazer.[5] The apparatus, shown schematically in Fig. 1, consisted of a closed circuit of 8 mm. glass tubing connecting the bulb *A* containing the iodine solution, a horizontal tube *B* which enclosed a glass stirrer that was moved magnetically, and an annular vessel *C* which surrounded the Geiger counter *D*. The glass circuit was immersed in two thermostats T_1 and T_2, the temperature of the former being about 3° higher than that of the latter. The parts of the circuit outside the thermostats were heated electrically to a temperature about 10° above that of T_2. A weighed amount of iodine was placed in *A* and the apparatus evacuated. A weighed amount of solvent was then distilled on to the iodine through one of the side-arms near *A*, and the apparatus sealed. The stirrer in *B* caused a rapid mixing of the vapour phase (as shown by its colour) and caused sufficient vibration to keep the liquid in *A* well-mixed. A small correction was applied to the calculated liquid composition to correct for the amounts of solvent and solute which passed into the vapour. The counter and the annular vessel *C* were shielded by 1—2 inches of lead (not shown) from cosmic rays and from direct radiation from the iodine in *A*. Usually over 90% of the observed count-rate was due to vapour in *C*. Once equilibrium had been reached (usually after about 5 hr.) the count-rate was independent of whether or not the vapour was being stirred.

A similar apparatus was used to measure the amount of iodine in the vapour when solid iodine was in contact with the unsaturated vapours of the solvents, but here the solid iodine was in a tube heated to a constant temperature in a vapour-jacket. The original intention was to cover a wider temperature range than could be covered by a liquid thermostat.

Densities of Iodine Solutions.—These were measured under the same conditions and in the same pyknometer as the densities measured by Thacker and Rowlinson.[6]

Solubilities.—Measurements were made by sampling a saturated solution, through a sintered-glass plate, with a small pipette. The whole assembly, including the pipette, was kept for 8 hr. in a thermostat, the temperature of which was measured on a thermometer calibrated by the N.P.L. All solutions were saturated at a temperature about 10° higher than this before being placed in the thermostat. The solution in the pipette was weighed, washed out with carbon tetrachloride, and titrated in triplicate with standard thiosulphate. The method is similar to that of Hildebrand and Jenks.[7] The apparatus was modified for those solutions in ether whose total vapour pressure exceeded atmospheric by using an evacuated and sealed saturator and pipette.

Estimation of iodine in pyridine solution was difficult. Titration with thiosulphate was not possible because of the unfavourable pH, while titration with sodium arsenite gave, at the supposed end-point, a yellow pyridine layer which was not discoloured by excess of arsenite. That this layer contained iodine was shown by acidifying it, for the excess of iodine could then be extracted by carbon tetrachloride. In view of the reported reaction of iodine with pyridine[8]

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[5] Gillespie and Frazer, *J. Amer. Chem. Soc.*, 1936, **58**, 2260.

[6] Thacker and Rowlinson, *Trans. Faraday Soc.*, 1954, **50**, 1036.

[7] Hildebrand and Jenks, *J. Amer. Chem. Soc.*, 1920, **42**, 2180.

[8] Kleinberg, Colton, Sattizahn, and VanderWerf, *ibid.*, 1953, **75**, 442.

this chemical method was abandoned and the iodine concentration determined, in freshly made solutions, by using radio-iodine as a tracer.

The solubility of iodine in iodobenzene could not be measured, as the mixture apparently reacted chemically, depositing lemon-yellow crystals.

The reproducibility of the solubilities was better than 1%, but for pyridine solutions there must be some doubt as to the chemical state of the dissolved iodine.

Heat of Dilution.—Only in one solvent, ethyl iodide, was the solubility at 25° great enough for a determination of the heat of dilution. This was measured in a calorimeter similar to that of Thacker and Rowlinson[6] except that their U-tube containing mercury was replaced by two coaxial tubes, the inner of which contained the solution and the outer the solvent. The inner tube was sealed by a microscope cover-slide held in place by a trace of Silicone grease until the mixing took place, by inverting the calorimeter, the cover-slide being then broken by a glass bead in the inner tube.

RESULTS

Partial-pressure Measurements.—The solvents used in these measurements were *cyclo*hexane, benzene, fluorobenzene, and mesitylene at 55·3°, and diethyl ether at 35·0°, 45·0°, and 55·3°. Ethyl iodide was not used because of the possibility of exchange with the radio-iodine.

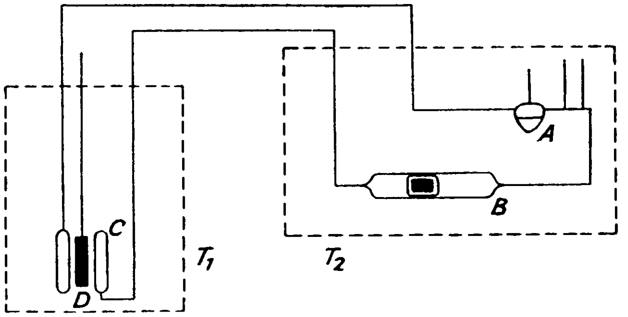


FIG. 1. *Apparatus used for partial-pressure measurements.*

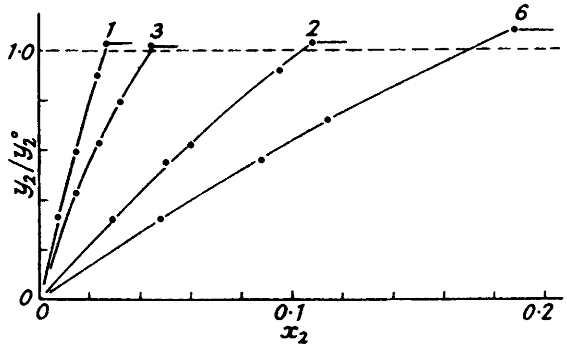


FIG. 2. *Relative concentration of iodine in the vapour phase above liquid solutions at 55·3° for the solvents,* cyclo*hexane* (1), *benzene* (2), *fluorobenzene* (3), *and mesitylene* (6).

The results are shown in Figs. 2 and 3. The function $(y_2/y_2°)$ is the ratio of the mole fraction of iodine in the vapour phase to the mole fraction in a vapour mixture containing the same concentration as the vapour from pure solid iodine. This function is plotted against x_2, the mole fraction of the iodine in the liquid phase. In every solution the highest value of x_2 is that corresponding to saturation. These measurements were made on solutions containing excess of solid iodine.

The amount of iodine in the vapour phase when solid iodine is in equilibrium with unsaturated vapours is shown in Figs. 4 and 5 for air and for the vapours of *cyclo*hexane, benzene, fluorobenzene, pyridine, and ether at 56°. The function $(y_2/y_2°)$ is here plotted against the pressures of the added vapours, which are assumed to be perfect.

Density Measurements.—Fig. 6 shows V_2' the apparent molar volume of iodine in liquid solutions at 25°, defined by

$$V_2' = (v - v_1)/n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

FIG. 3. *Relative concentration of iodine in the vapour phase above liquid solutions of ethyl ether* (10) *at, from left to right,* 35·0°, 45·0°, *and* 55·3°.

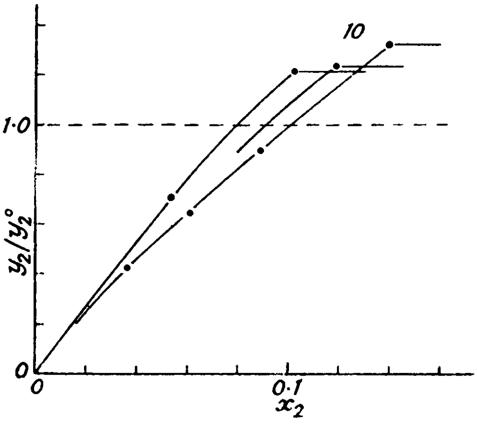


FIG. 4. *Relative concentration of iodine in the vapour phase for solid iodine at* 56° *in the presence of the vapours of* cyclo*hexane* (1), *benzene* (2), *and fluorobenzene* (3).

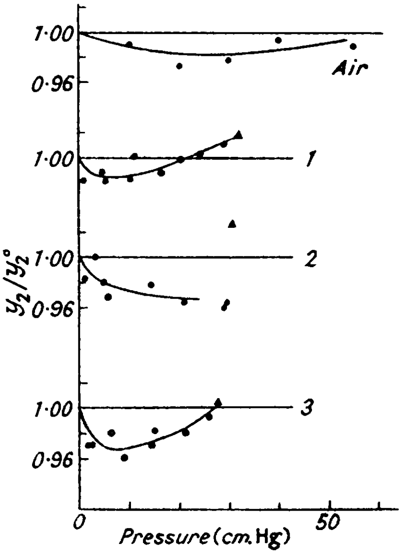


FIG. 5. *Relative concentration of iodine in the vapour phase for solid iodine in the presence of ethyl ether vapour at* 56°. *Measurement at* 35° *gave very similar results.*

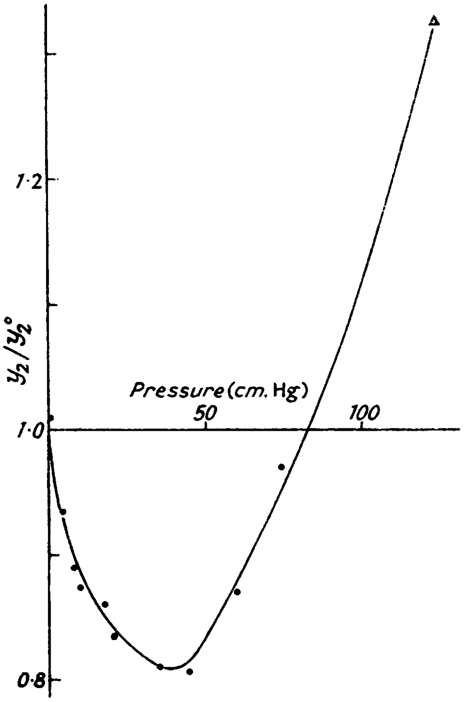
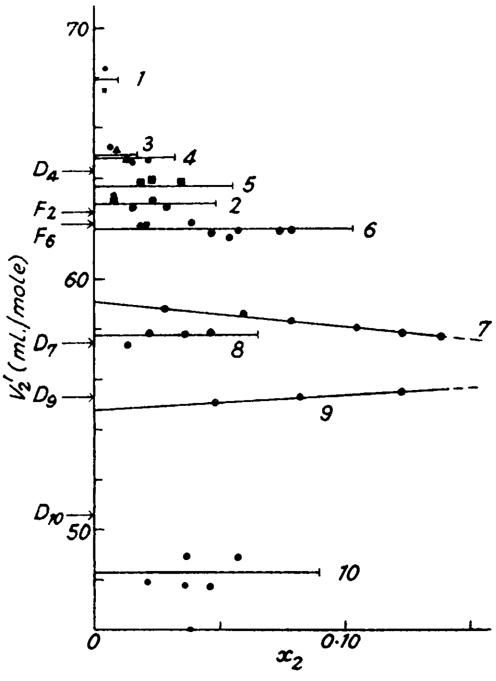


FIG. 6. *Apparent molar volume of iodine at* 25° *in solutions of* cyclo*hexane* (1), *benzene* (2) (●), *fluorobenzene* (3) (▲), *chlorobenzene* (4) (●), *bromobenzene* (5) (■), *mesitylene* (6), *pyridine* (7), *ethyl bromide* (8), *ethyl iodide* (9), *and ethyl ether* (10). *The arrows show the values of* V_2' *at high dilution as observed by Dawson* (*D*) *and Fairbrother* (*F*) *for solvents* 2, 4, 6, 7, 9, *and* 10.



where v is the volume of a solution containing n_1 moles of solvent and n_2 of solute, and v_1 is the volume of n_1 moles of pure solvent. At infinite dilution, and at other concentrations if V_2' is independent of concentration, the apparent molar volume is the same as the partial molar volume. The accuracy of V_2' increases with the concentration and varies inversely with the molecular weight of the solvent. The values obtained agree moderately well with those calculated from the density measurements at higher dilutions by Dawson [9] and Fairbrother.[10]

Solubility Measurements.—The results are set out in Table 1 and compared with previous results in Fig. 7.

FIG. 7. *Solubilities as a function of temperature. The solvents are numbered as in Fig. 6. Circles denote measurements reported here and triangles the measurements of Hildebrand and others.*[4] *The broken line is the ideal solubility.*

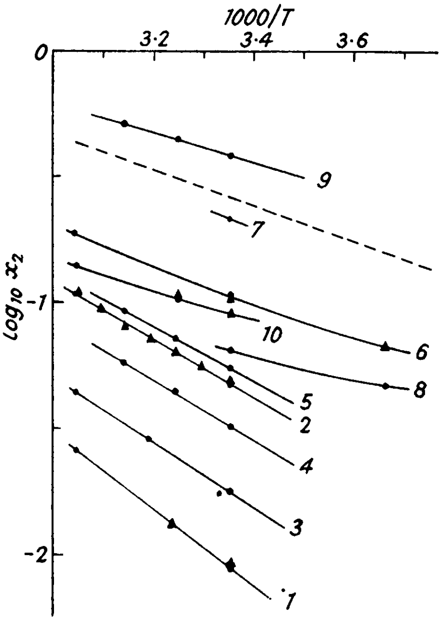


FIG. 8. *The apparent, H_2', and partial, $\bar{H}_2$, molar heats of dilution of iodine in ethyl iodide at 25°, relative to infinite dilution.*

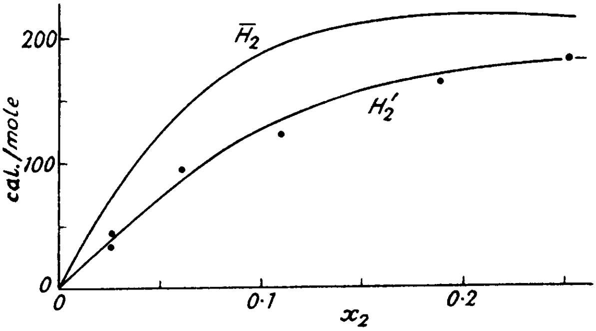


TABLE 1. *Solubility of iodine in moles/100 moles of solution.*

Solvent	0·00°	24·96°	35·07°	45·08°	55·33°
*cyclo*Hexane	—	0·91	—	—	2·69
Benzene	—	4·75	—	—	10·78
Fluorobenzene	—	1·73	2·77	—	4·45
Chlorobenzene	—	3·19	4·40	5·75	—
Bromobenzene	—	5·50	7·15	9·34	—
Mesitylene	—	10·82	—	—	19·15
Pyridine	—	21	—	—	—
Ethyl bromide	4·72	6·50	—	—	—
Ethyl iodide	—	32·8	37·9	41·7	—
Ethyl ether	—	—	10·2	—	14·0

Heat of Dilution.—The apparent and partial molar heats of dilution of iodine in ethyl iodide are shown in Fig. 8. The calculation of the partial heat from the apparent heat followed the procedure of Taylor and Rowlinson.[11]

DISCUSSION

The most obvious feature of Figs. 2 and 3 is that the values of (y_2/y_2°) are greater than unity at the saturation point. That is, the concentration of iodine in the vapour above

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[9] Dawson, *J.*, 1910, **97**, 1041.
[10] Fairbrother, *J.*, 1948, 1051.
[11] Taylor and Rowlinson, *Trans. Faraday Soc.*, 1955, **51**, 1183.

these solutions is greater than that in the vapour of pure solid iodine. Such an increase in concentration is most naturally interpreted as a consequence of the departure of the vapour mixture from the perfect-gas laws. (The departure of the vapour of pure solid iodine may be neglected owing to the low total pressure.) Similar increases have been observed, although generally at higher total pressures, for many other systems in which a gas is in contact with a slightly volatile solid or liquid.[12] It has been shown that the logarithm of the ratio (y_2/y_2°) may be expressed by a series of which the first two terms are [13]

$$\ln (y_2/y_2^\circ) = \ln a_2 + p\,(V_s - 2B_{12})/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a_2 is the activity of the solute in the condensed phase (solid or solution) with respect to the pure solid in the absence of the first component; V_s is the molar volume of the solute in the condensed phase, and B_{12} is the second virial coefficient for the interaction in the gas phase between component 1 and component 2. This coefficient must be large and negative for the interaction of iodine with solvent molecules and is undoubtedly the term in this equation by virtue of which (y_2/y_2°) exceeds unity above a saturated solution, for which $a_2 = 1$ at true equilibrium. The activity of iodine in the liquid phase may therefore be calculated from this equation at all concentrations by correcting $\ln (y_2/y_2^\circ)$ by a constant amount, as p is virtually independent of the iodine concentration in the gas. The values of B_{12} calculated from this equation for the iodine–ether interaction are shown in Fig. 9. These values indicate a considerable degree of interaction between the molecules. B_{12} is -2800 ml./mole at 35°, compared with -1000 ml./mole for the ether–ether interaction [14] at this temperature.

FIG. 9. *The virial coefficient for the interaction of iodine and ethyl ether.* (▲ *from the results of Brüll and Ellerbrock.*[17])

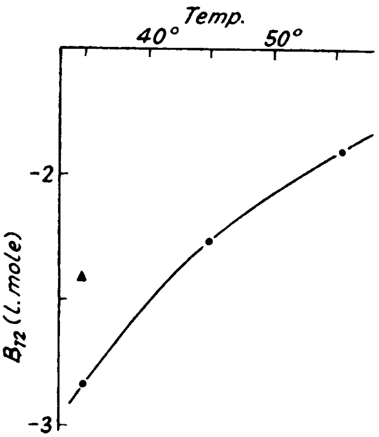
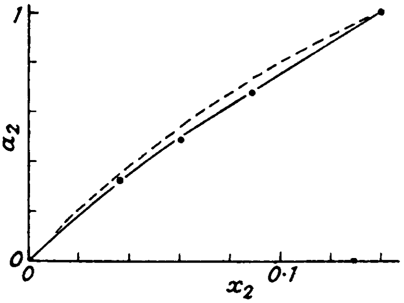


FIG. 10. *The activity of iodine in ether solution at* 55·3°.



The full line is calculated from equation 4 *and the broken line from equation* 3. *The relative positions of these lines are very similar for the other solutions.*

The activities calculated in this way are shown in Fig. 10 as functions of x_2. The curvature of these graphs is of the sign to be expected for a regular solution, for which the logarithm of the activity coefficient (referred to unit activity in the ideal solution) is proportional to the square of either the mole fraction or, in Hildebrand's formulation, the volume fraction of the solvent. These proportionalities lead directly to :

$$\ln a_2 = (x_1/x_1^{\mathrm{s}})^2 \ln (x_2^{\mathrm{i}}/x_2^{\mathrm{s}}) + \ln (x_2/x_2^{\mathrm{i}}) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\ln a_2 = (\phi_1/\phi_1^{\mathrm{s}})^2 \ln (x_2^{\mathrm{i}}/x_2^{\mathrm{s}}) + \ln (x_2/x_2^{\mathrm{i}}) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[12] *E.g.*, Diepen and Scheffer, *J. Amer. Chem. Soc.*, 1948, **70**, 4085; Webster, *Proc. Roy. Soc.*, 1952, *A*, **214**, 61.

[13] Robin and Vodar, *Discuss. Faraday Soc.*, 1953, **15**, 233; Ewald, Jepson, and Rowlinson, *ibid.*, p. 238; Bell, *ibid.*, p. 290.

[14] Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc.*, 1949, *A*, **196**, 113.

where ϕ is the volume fraction, the superscript i denotes ideal, the superscript s denotes saturation, and the state of unit activity is the saturated solution. Fig. 10 shows that the second of these equations fits the experimental results more closely than the first.

The second virial coefficient B_{12} can be measured by studying the amount of iodine in the gas phase when solid iodine is in contact with the vapours of the solvents, provided that the activity of the solid iodine is not affected by the added vapour. If a_2 is independent of p, then $\ln (y_2/y_2^{\circ})$ [and therefore (y_2/y_2°) at low p] will be a linear increasing function of p. The results recorded in Figs. 4 and 5 show that this is not so. In every case a small amount of added vapour decreases the concentration of iodine in the gas phase. This diminution was quite stable and reproducible, although the accuracy of (y_2/y_2°) was no better than $\pm 1\%$. The addition of air in the range 100—600 mm. Hg caused a slight decrease of up to 2%. *cyclo*Hexane vapour caused a similar initial fall but (y_2/y_2°) then increased and was greater than unity for pressures greater than 200 mm. If the curve is extrapolated it passes through the value of (y_2/y_2°) obtained from the saturated liquid solutions. The other vapours decreased the iodine concentration at 56° by the following amounts: benzene (4%), fluorobenzene (4%), and ethyl ether (18%). The extrapolated curves pass through the value of (y_2/y_2°), except for that of benzene—an exception for which we cannot account but which is probably an experimental error. Pyridine was found to cause a much greater decrease than ethyl ether. The addition of 5 mm. decreased the iodine concentration by 18%, and the addition of higher pressures caused a yellow solid to be precipitated throughout the apparatus. Acetone, ethanol, and methyl acetate appeared to react, for the iodine concentration in the vapour, as measured by the count-rate, rose steadily with time and gave no signs of reaching a steady value.

It is apparent that ethyl ether and pyridine, which form strong complexes with iodine, and, to a smaller extent, benzene and fluorobenzene, interact with the solid in such a way as to reduce its surface activity. This interaction could either be the formation of a new solid phase, such as mixed crystals, or the formation of a surface phase, such as a tightly bound, chemisorbed layer. The first is probably the less likely as Hildebrand and Jenks [7] showed that iodine prepared by crystallisation from benzene contained no appreciable amount of solvent, and Harris, Mack, and Blake [15] showed that a powder photograph of iodine prepared by very rapid evaporation of ether from a solution at low temperature showed no unusual features. The second explanation appears more likely. The results may be compared with those obtained by Wright and McGregor [16] and by Brüll and Ellerbrock.[17] The former used both static and flow methods, but the only quantitative result they give is a fall in the iodine concentration of 3% on the addition of air at atmospheric pressure. This agrees well with our figure. In their flow measurements they found that the organic vapours initially carried over more iodine than air but that the amount fell with time and eventually was less than that carried by air. Brüll and Ellerbrock used a flow method and found increases in the amount of iodine carried over. From their results with ethyl ether a figure of B_{12} has been calculated which is shown in Fig. 9. Neither of these sets of results is inconsistent with those reported here, for with a flow technique the problem becomes one of kinetics rather than of equilibrium measurement. The amount carried over will depend on the relative rates of the formation of the surface film and of its removal by evaporation.

The values of $(-B_{12})$ shown in Fig. 9 are therefore only minimum values. The actual values may be greater if the surface phase persists in the saturated liquid solution. At much higher pressures Braune and Strassman [18] demonstrated a considerable increase in iodine concentration in the presence of carbon dioxide, a substance which is unlikely to form a strongly adsorbed layer.

The partial molar volumes at infinite dilution (Fig. 6) show the effect of complex formation most clearly. The solvents may be arranged in order of decreasing molar volume of iodine at 25°, as follows: *cyclo*hexane (67·9 ml.), fluorobenzene (65·0 ml.), chlorobenzene

[15] Harris, Mack, and Blake, *J. Amer. Chem. Soc.*, 1928, **50**, 1583.
[16] Wright and McGregor, *J.*, 1929, 1364.
[17] Brüll and Ellerbrock, *Z. anorg. Chem.*, 1934, **216**, 353.
[18] Braune and Strassman, *Z. phys. Chem.*, 1929, **143**, 225.

(64·9 ml.), 1 : 4-dioxan (64·7 ml.), bromobenzene (63·6 ml.), benzene (63·0 ml.), *p*-xylene (62·2 ml.), mesitylene (62·0 ml.), pyridine (59·1 ml.), iodine (59 ml.), ethyl bromide (57·8 ml.), ethyl iodide (54·8 ml.), ethyl ether (48·3 ml.). The figure for iodine, as solvent, is that obtained by extrapolation [4] of the density of liquid iodine to 25°, and the figures for dioxan and xylene are from measurements by Fairbrother.[10] The range covered by these volumes is surprisingly high. It is clear that in solvents in which there is little or no complex formation the volume of the iodine is greater than in liquid iodine. There is evidence that liquid iodine itself is not a normal liquid held together only by van der Waals forces. It has an appreciable electrical conductivity which decreases with temperature [19] and may be due to an electron-transfer equilibrium,* such as :

$$2I_2 = I^+ + I_3^-$$

Thus, if the volume in *cyclo*hexane is taken as the normal volume, it follows that the formation of complexes is accompanied by a diminution of volume in every case, including that of liquid iodine itself. The position of iodine, as solvent, in this list explains Ham's observation [20] that " it seems possible that the change of volume on complexing is negative even though the volume of mixing is positive." He found the volume change for the formation of one mole of complex to be —1·5 ml. in benzene and —3·3 ml. in mesitylene, by observing the effect of pressure on the equilibrium constant, as measured spectroscopically.

The solubilities at 25° (Table 1) show that the decrease in partial molar volume is roughly parallel to the increase in solubility. The solubility in ethyl ether and in ethyl iodide confirms the great ability of these solvents to form complexes. In ethyl iodide, where the solubility is greater than ideal, the formation of complexes has been confirmed spectroscopically by Keefer and Andrews,[21] and in ethyl ether by Benesi and Hildebrand.[22] The heat of solution at saturation (the so-called last heat of solution) may be calculated from the temperature coefficient of the solubility after applying a small correction for the variation of activity coefficient with concentration.[23] The results for four of the solutions are compared in Table 2 with the heats of solution measured calorimetrically by Hartley and Skinner.[24] The latter include a small but unknown heat of dilution, so the agreement is quite satisfactory.

TABLE 2. *Heat of solution,* (1) *from solubility and* (2) *measured directly,*[24] *in kcal./mole.*

Solvent	(1)	(2)	Solvent	(1)	(2)
*cyclo*Hexane	6·5	5·8	Benzene	4·4	4·25
Chlorobenzene	4·8	4·75	Ethyl ether	1·4	1·8

Hartley and Skinner have already pointed out the relation between the heat of solution and the complex-forming power of the solvent.

In conclusion, the measurements reported here on iodine solutions and on the equilibrium between solid iodine and organic vapours show that the formation of donor–acceptor complexes affects many of the physical properties, and that any of these properties may be used to place solvents roughly in the order of complex-forming power. In increasing power, the best order is probably paraffins, halogenobenzenes, benzene, (toluene), xylenes, mesitylene, ethyl bromide, ethyl ether and pyridine, ethyl iodide. This order agrees in the main with others based on spectroscopic measurements of the equilibrium constant of the association.[1, 2, 25]

One of us (W. B. J.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

THE UNIVERSITY, MANCHESTER, 13.

[*Received, November 4th,* 1955.]

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* We are indebted to Dr. F. Fairbrother for this suggestion.

[19] Rabinovitsch, *Z. phys. Chem.*, 1926, **119**, 79.
[20] Ham, *J. Amer. Chem. Soc.*, 1954, **76**, 3881.
[21] Keefer and Andrews, *ibid.*, 1952, **74**, 1891.
[22] Benesi and Hildebrand, *ibid.*, 1949, **71**, 2703.
[23] Williamson, *Trans. Faraday Soc.*, 1944, **40**, 421.
[24] Hartley and Skinner, *ibid.*, 1950, **46**, 621.
[25] Kortum and Vogel, *Z. Electrochem.*, 1955, **59**, 16.