tractive forces. These forces may be further enhanced by electronic polarization of the two groups and to a much smaller extent by atomic polarization. However, in the benzene–methanol and cyclohexane–methanol systems no such parallel colinear dipoles can be formed. The attractive forces between the unlike molecules must be due primarily to electronic polarization of the benzene or cyclohexane in the field of the oxygen–hydrogen dipole.[1] Atomic polarization may also occur to some extent. A relative comparison of the magnitudes of these forces may be obtained from the differences of the energy of evaporation of methanol to an ideal gas and the partial molal heat of mixing of methanol at infinite dilution in the non-polar solvents. These differences would then give the change of energy on transferring one mole of methanol from the ideal gas state to an infinitely dilute solution of methanol in the non-polar substances. Such differences are -7200 cal. for carbon tetrachloride–methanol, and -6200 cal. for benzene–methanol, and -4600 cal. for cyclohexane–methanol. Due to the uncertainties in the heats of mixing, especially in the cyclohexane–methanol system, too great an emphasis should not be placed on the numerical value. It seems quite certain, however, that they are of this order of magnitude. It is striking in view of the different molecular structures of the three non-polar substances that these energies are so much the same.

The author wishes to thank Professor George Scatchard for his helpful criticisms of this paper.

Summary

The changes of the free energy, enthalpy and entropy on mixing at constant pressure for the cyclohexane–methanol system have been calculated from the measurements of the liquid–liquid equilibria reported by Eckfeldt and Lucasse. The excess changes of these functions over those of an ideal solution are all positive over the entire range of composition except the entropy which appears to become slightly negative in the very rich methanol solution at 31°.

The thermodynamic functions of the four systems, benzene–methanol, carbon tetrachloride–methanol, cyclohexane–methanol and chloroform–ethanol, are very similar. The behavior of these systems is considered to be due to rather strong attractive forces operating between the unlike molecules. A relative estimate of these attractive forces between methanol and carbon tetrachloride, benzene or cyclohexane shows that they decrease in this order but that they are of the same magnitude.

NEW HAVEN, CONN. RECEIVED MAY 31, 1946

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF VERMONT]

The Conductance of Iodine in Liquid Hydrogen Sulfide

BY EDGAR E. LINEKEN[1]

Iodine dissolves in liquid hydrogen sulfide to form a solution which conducts the electric current. Quam and Wilkinson[2] report the specific conductance of the saturated solution. They suggest that iodine forms both positive and negative ions and they cite a transference experiment in support of that explanation. Walden[3] has similarly explained the conductivity of iodine solutions. Chipman and McIntosh[4] have measured the conductance of solutions of iodine in liquid hydrogen sulfide throughout a range of concentration. They found no evidence of a reaction between liquid hydrogen sulfide and iodine.

It seemed worth while to repeat the work of Chipman and McIntosh using modern bridge technique and making measurements on solutions more dilute than those prepared by the above authors.

Experimental

Apparatus.—The measuring bridge differed in no essential from that described by Lineken and Wilkinson[5] which in turn was very like that described by Shedlovsky.[6] A direct balance was permitted up to 10^6 ohms. Resistances higher than 10^6 ohms were calculated from the measured parallel resistance of the solution and a 10^6-ohm resistor.

A one-tube oscillator employing a conventional circuit was used. The oscillator coil was a Western Electric 211B input transformer which was electrostatically and electromagnetically shielded. By changing the capacitance of the circuit the the frequency could be varied from 470 to 2640 cycles per second.[7] Power was taken from the oscillator directly from the plate and the oscillator

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(1) Present address: Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

(2) Quam and Wilkinson, THIS JOURNAL, **47**, 989–994 (1925).

(3) Walden, *Z. physik. Chem.*, **43**, 358 (1903).

(4) Chipman and McIntosh, *Proc. Trans. Nova Scotian Inst. Sci.*, **16**, (pt. 4), 189–195 (1926).

(5) Lineken and Wilkinson, THIS JOURNAL, **62**, 251–256 (1940).

(6) Shedlovsky, *ibid.*, **52**, 1793–1805 (1930).

(7) The author is indebted to Professor E. R. McKee of the Department of Electrical Engineering at the University of Vermont for the loan of the coil and the condensers used in constructing the oscillator, for suggesting the circuit to be employed, and for his help in constructing and in calibrating the oscillator.

ground without the use of a pick-up coil. The oscillator, therefore, was grounded only to the galvanized iron box in which it was placed. The bridge and its shields were grounded as previously described.[5]

A diagram of the conductance cell used is shown in Fig. 1. The cell was constructed of Jena glass.[8] The electrodes were platinum disks 45 mm. in diameter separated at about 1.5 mm. Several glass insulators near the circumferences of the disks held them in fixed positions relative to each other. No platinization was used. The resistance measurements were made with the cell immersed in a solid carbon dioxide–ether mixture at −78.5°.[9] Mercury contacts were used to connect the short platinum leads shown in the diagram to copper leads extending to the bridge. The mercury was solid at this temperature and made excellent electrical contact. The tops of the lead tubes were closed either with small rubber stoppers or with rubber policemen through which the copper lead wires extended. The volume of solution in the cell was determined by measuring the distance of the meniscus below the top of the neck and reading the volume from a calibration curve. Volumes so measured could vary between 161 and 173 ml. The cell constant was about 0.01. The cell was standardized by measuring the resistance of water in the cell and also in another cell at 25.0°.

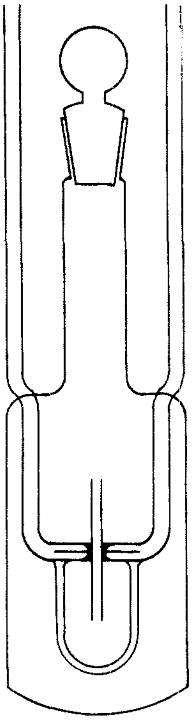

Fig. 1.—Conductance cell.

This other cell was of the Jones and Bollinger type L[10,11] having a cell constant of about 5 and was standardized with 0.01 *D* potassium chloride solution.[12] Corrections were made for a slight polarization effect[13] when measuring the resistance of the potassium chloride solution and for a slight capacitative shunt effect[10] when measuring the resistance of water in this cell. The magnitude of the polarization correction was 0.2% of the value of 1000 cycles per second and the magnitude of the capacitative shunt effect was less than 0.1% of the value at 1000 cycles per second. When measuring the resistance of water in the cell designed for the hydrogen sulfide solutions, resistances were independent of frequency to within at most one part in 2500.

Chemicals.—Purified hydrogen sulfide was liquefied directly in the cell exactly as previously described.[5]

Two sources of iodine were used. For preliminary work reagent grade iodine was sublimed once with the addition of potassium iodide and again without the potassium iodide. Solution numbered 3 (Table I) was prepared from this sample of iodine.[14] This sample of iodine was stored over calcium chloride in an ungreased desiccator. The other samples of iodine were prepared by heating finely pulverized mixtures of potassium iodide and potassium dichromate.[15] These samples were stored over phosphorus pentoxide in an ungreased desiccator and were used for all measurements reported except that on the one solution already mentioned.

Procedure.—Conductance measurements were made exactly as described by Lineken and Wilkinson.[5] Briefly,

TABLE I

CONDUCTANCE OF IODINE IN LIQUID HYDROGEN SULFIDE[a]

No.	C	$k_s \times 10^6$	$k \times 10^6$	Λ
1	0.000043	0.00084	0.0980	2.28[b]
2	.000076	.00088	.1613	2.12[c]
3	.000245	.....	.316	1.29[d]
4	.000280	.00055	.2792	.997[b]
5	.000471	.00084	.3095	.657
6	.001511	.00055	.5926	.3922
7	.003399	.00055	.7987	.2348
8	.004544	.00084	.6516	.1434
9	.008869	.00055	.9299	.1049
10	.01562	.00084	.9389	.06011
11	.02388	.00084	1.082	.04531
12	.02431	.00055	1.146	.04715
13	.03778	.00084	1.275	.03375
14	.04520	.00079	1.337	.02958[c]
15	.06109	.00084	1.556	.02547
16	.06738	.00055	1.400	.02078

[a] C is concentration on moles per liter. (When calculating C, the molecular weight of diatomic iodine was used.) k_s is the specific conductance of the solvent and k is that of the solute. Λ is the molar conductance. [b] First of a series of solutions. [c] Solutions not members of a series. [d] Conductance after solution had stood for forty-three hours. The value of k is that of the solution for this sample.

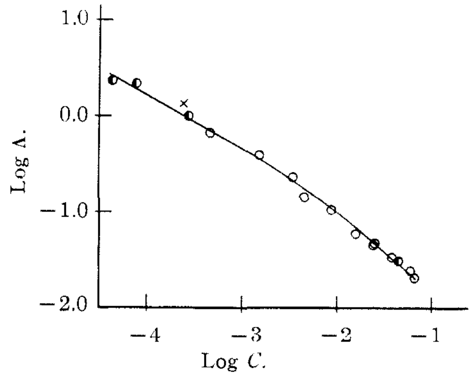

Fig. 2.—Molar conductance of iodine in liquid hydrogen sulfide.

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(8) The cell was fabricated by glass blowers of Eimer and Amend, New York, N. Y.

(9) A. Theil and E. Schultz, *Z. physik. Chem.*, **96**, 312 (1920).

(10) Jones and Bollinger, THIS JOURNAL, **53**, 411–451 (1931).

(11) This cell was fabricated for the author by Dr. G. H. Burrows, deceased.

(12) Jones and Bradshaw, THIS JOURNAL, **55**, 1780–1800 (1933).

(13) Jones and Christian, *ibid.*, **57**, 272-280 (1935).

(14) Data on solution 3 were measured in a cell differing from that described above in that glass insulators were not used between the electrodes and the cell was equipped with filling tubes. This cell was accidentally broken and was replaced with the one previously described.

(15) Vanino, "Präparative Chemie," I Band, zweiter Auflage.

after measuring the conductance of the solvent, a weighed amount of iodine was added and the resistance and volume of the solution were noted as soon as solution was complete. When making a series of measurements, another weight of iodine was added and the process was continued until the series was completed.

Results and Discussion

Results are shown in Table I and in Fig. 2.

The conductance of the pure solvent showed a somewhat erratic variation of about 1% as the frequency was changed. (Calculations were made for only one sample of solvent.) This variation with frequency was probably within the precision of measurement of such high resistances (9.3 × 10^6 to 17.5 × 10^6 ohms for the samples reported in Table I). Since the conductance of the solvent was less than 1% of that of the solute for the most dilute solution measured, the solvent conductance at 1000 cycles per second was sufficiently accurate for correcting the conductance of the solution for that of the solvent. The resistances of the solutions were independent of the frequency of the current used to within at most 0.1%.

The conductance of a given solution of iodine in liquid hydrogen sulfide does, however, increase with time. The change with time is slow and iodine dissolves rapidly in the solvent. Measurements 1 and 4 (Table I) are first members of a series and 2 and 14 are on independently prepared solutions. These four solutions are indicated by half-shaded circles in Fig. 2. Solution 3 (Table I) is a solution which was prepared by liquefying hydrogen sulfide in the cell which already contained a weighed sample of iodine. The resistance of that solution was followed for forty-three hours. At the end of that time the solution's resistance was nearly constant. The final conductance of solution 3 is indicated by a cross in Fig. 2. Those solutions indicated by circles were prepared by adding iodine to a more dilute solution.

Distillation of the hydrogen sulfide from iodine solutions (in one case the solution had stood for one week) through an adequate spray trap into water formed a water solution containing an iodine compound, presumably hydrogen iodide. The presence of this compound was shown by boiling the aqueous solution to eliminate hydrogen sulfide, and then adding carbon disulfide, and potassium dichromate and sulfuric acid solutions. Sufficient iodine was liberated to color the carbon disulfide. Solutions of iodine in liquid hydrogen sulfide contained volatile iodine compounds when prepared from iodine from each source previously mentioned. This is not in accord with the observations of Chipman and McIntosh.[4]

A slow reaction of iodine with dry liquid hydrogen sulfide would account for the lack of perfect constancy of the conductivity of the solutions. Circumstances do not permit a detailed study of the reaction at present. That the slow change in conductance did not appreciably affect the values reported can be seen by referring to Fig. 2 where the conductances of more concentrated solutions prepared by adding iodine to more dilute solutions fall in line with the conductances of solutions prepared by adding iodine to solvent. Also, the conductance of a solution which had stood for forty-three hours is not very greatly out of line with the others.

After this paper was written it was noticed that Antony and Magri[16] have determined the solubility of iodine in liquid hydrogen sulfide. Their value is 1.14 g. in 100 cc. of the liquid. This would mean that the saturated solution would be 0.045 molar. Solutions 15, 16, and possibly 14 (Table I) are shown as being more concentrated than that. The specific conductance data probably show a tendency to level off at about 0.045 molar but whether they really do that is impossible to tell since the specific conductance of solution 15 is considerably higher while that of solution 16 (more iodine involved) is only slightly higher than solution 14 (0.0452 molar). When making these experiments, the constancy of resistances with agitation of the solutions (except for the slow changes previously mentioned which take place without agitation) was accepted as evidence of completed solution. It was not expected at that time that the amounts of iodine used were sufficient to saturate the solutions[2,4] and it is conceivable that undissolved material could have been over-looked when discarding the densely colored solutions involved. If these few solutions were saturated, the use of solution 14 as evidence that the slow change of resistances with time did not greatly affect the values is still valid. In that event, the fact that the specific conductance of an approximately saturated solution prepared with one addition of iodine reached a similar value as compared with those prepared by making successive small additions would be evidence that the longer time required for the second process had not significantly changed the final result.—(Received June 1, 1946).

Summary

The conductance of iodine dissolved in liquid hydrogen sulfide has been measured over a considerable range of concentration. Evidence is presented for a slow reaction between iodine and liquid hydrogen sulfide.

SOMERVILLE, NEW JERSEY RECEIVED APRIL 5, 1946

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[16] Antony and Magri, *Gazz. chim. ital.*, **35**, 206 (1905) [*Chem. Zentr.*, **76**, I, 1691 (1905)].