SOLUBILITY VII. SOLUBILITY RELATIONS OF RHOMBIC SULFUR.

BY JOEL H. HILDEBRAND AND CLARENCE A. JENKS.

The solubility relations of sulfur are of considerable interest in the light of the theory of solubility set forth in the previous papers of this series[1] because liquid sulfur, Sλ, has a rather high internal pressure compared with most liquids and the solubilities of rhombic sulfur should therefore serve well to illustrate the decreasing solubility to be expected as the internal pressure of the solvent decreases.

The solubilities of sulfur have been the subject of frequent investigation. We have data by Étard[2] for hexane, benzene, ethylene bromide and carbon bisulfide; by Gerardin[3] for stannic chloride in the neighborhood of the melting point of sulfur; by Aten[4] for sulfur monochloride; by Smith and Carson[5] for iodine; by Cossa[6] for chloroform, ethyl ether, benzene, carbon disulfide and toluene; by Retgers[7] for methylene iodide; by Brönsted[8] for benzene, iodobenzene and chloroform; by Hoffman[9] for carbon tetrachloride, dichloro-ethylene, ethylene chloride, pentachloro-ethane, perchloro-ethylene, trichloro-ethylene and tetrachloro-ethane. There are other data for more or less polar solvents, including phenol,[10] naphthol[10] and alcohols[11,3] but the only polar solvent we shall consider is ammonia, for which we have data by Ruff and Hecht.[12]

Some of the data referred to are obviously not very accurate, and many of the determinations were made only at one temperature. Accordingly it has been desirable to check certain portions and to supplement others. We have measured solubilities in carbon tetrachloride, benzene, toluene, m-xylene, heptane and ethylene chloride.

The sulfur was purified by sublimation. The ethylene chloride was purified by distillation. The carbon tetrachloride, heptane and benzene used were from the stocks

[1] Hildebrand, THIS JOURNAL, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919); Hildebrand and Jenks, ibid., 42, 2180 (1920); Hildebrand and Beuhrer, ibid., 42, 2213 (1920). Hildebrand, ibid., 43, 500 (1921).

[2] Étard, Ann. chim. phys., [7] 2, 571 (1894).

[3] Gerardin, ibid., [4] 5, 129 (1865).

[4] Aten, Z. physik. Chem., 54, 86, 124 (1905).

[5] Smith and Carson, ibid., 61, 200 (1909).

[6] Cossa, Ber., 1, 38 (1868).

[7] Retgers, Z. anorg. Chem., 3, 347 (1893).

[8] Brönsted, Z. physik. Chem., 55, 371 (1906).

[9] Hoffman, Ber., 43, 188 (1910).

[10] Smith, Holmes and Hall, THIS JOURNAL, 27, 805 (1905).

[11] de Bruyn, Z. physik. Chem., 10, 781 (1892).

[12] Ruff and Hecht, Z. anorg. Chem., 70, 61 (1911).

purified for the recent investigation by us of the solubilities of iodine. The toluene was purified by the method used by Richards and Coombs.[13] The m-xylene was purified by a modification of the method described by Levinstein.[14] The o- and p-xylenes occurring in ordinary xylene were oxidized by treatment with 40% nitric acid until about a third of the original xylene had been destroyed. The o- and p-toluic acids are formed more readily than the meta variety. The xylene remaining was washed with sodium hydroxide and water to remove the acids. Nitro bodies were also formed in this process, which were removed by long reduction, first by hydrochloric acid and tin, then by sodium hydroxide and zinc dust. The liquid was then treated with conc. hydrochloric acid and distilled with steam. The distillate was fractionated thrice, giving a constant fraction boiling at 139.0°.

TABLE I.

SOLUBILITIES OF SULFUR.

Solvent.	0° %	0° mol %	25° %	25° mol %	35° %	35° mol %	45° %	45° mol %	54° %	54° mol %
Carbon	0.340	0.204	0.827	0.498	1.156	0.697	1.567	0.946	2.010	1.212
tetrachlo-	0.337	0.202	0.834	0.502	1.153	0.695	1.561	0.942	2.005	1.211
ride	...	...	0.832	0.501	1.157	0.698	...	...	...	...
Av.	0.339	0.203	0.831	0.500	1.155	0.697	1.564	0.944	2.008	1.212
Heptane	0.124	0.048	0.362	0.141	0.510	0.200	0.698	0.274	0.925	0.363
	0.123	0.048	0.362	0.141	0.514	0.201	0.698	0.274	0.925	0.363
	...	...	...	...	...	...	0.697	0.273	0.928	0.364
Av.	0.124	0.048	0.362	0.141	0.512	0.201	0.698	0.274	0.926	0.363
Toluene	0.901	0.326	2.015	0.734	2.725	0.996	3.620	1.330	4.86	1.800
	0.892	0.322	2.000	0.727	2.720	0.994	3.620	1.330	4.85	1.796
	...	...	2.040	0.743	2.720	0.994	...	...	4.83	1.791
	...	...	...	...	...	...	...	...	4.86	1.800
Av.	0.897	0.324	2.018	0.735	2.722	0.995	3.620	1.330	4.85	1.797
m-Xylene	...	...	1.970	0.825	...	...	3.610	1.525	...	...
	...	...	1.970	0.825	...	...	3.605	1.524	...	...
	...	...	1.978	0.828	...	...	3.590	1.518	...	...
	...	...	1.965	0.823	...	...	3.610	1.525	...	...
	...	...	1.963	0.822	...	...	...	...	...	...
Av.	...	...	1.969	0.825	...	...	3.604	1.523	...	...
Benzene	...	...	2.072	0.640	...	...	...	...	5.145	1.626
	...	...	2.072	0.640	...	...	...	...	5.170	1.633
	...	...	2.078	0.642	...	...	...	...	5.170	1.633
	...	...	...	...	...	...	...	...	5.180	1.636
	...	...	...	...	...	...	...	...	5.160	1.629
Av.	...	...	2.074	0.641	...	...	...	...	5.165	1.631
							40°		79°	
Ethylene	...	...	0.824	3.195	...	...	1.380	0.537	5.43	2.17
chloride	...	...	0.825	3.202	...	...	1.380	0.537	...	...
	...	...	0.830	3.220	...	...	1.380	0.537	...	...
									97.5°	
	...	...	...	...	...	...	...	...	9.97	4.10
Av.	...	...	0.826	3.206	...	...	1.380	0.537	...	...

---

[13] Richards and Coombs, THIS JOURNAL, **37,** 1668 (1915).

[14] Levinstein, Ber., **17,** 444 (1884).

The solubility determinations were made by the aid of the vessel described in the previous investigation, except that the solutions were blown into "ducks" similar to those described in "Physiko-Chemische Messungen," by Ostwald-Luther. In the earlier experiments these "ducks," after weighing, were placed upon an electrically heated plate where the solvent was evaporated. The weight of the sulfur remained constant, upon further heating after the evaporation of the solvent. In the later experiments the solvent was evaporated without heating by blowing a current of air through the vessel. Before weighing, the sulfur was heated to fusion.

Table I contains the results of the determinations from 0° to 54°, expressed in weight percentages, grams of sulfur per 100 g. of solution, and expressed also in mol percentages, mols of sulfur, S_8, per 100 mols of solution. The figures in the last row for each solvent are the average values. Further observations were made at higher temperatures with benzene, toluene and m-xylene, respectively, by making up solutions of known composition and noting the temperature at which a minute residual crystal neither increased or diminished in size when observed through a low-power microscope. These results are given in Table II.

TABLE II.

	Benzene.	Toluene.	m-Xylene.
t.	84°	83.5°	80°
Wt. per cent........	13.02	11.64	10.29
Mol. per cent.......	4.36	4.52	4.53

The results of our own experiments together with most of those of other observers, previously cited,[15] are plotted in Fig. 1, using as ordinate the logarithm of the solubility expressed in terms of mol-fraction, and as abscissa, the reciprocal of the absolute temperature. The significance and value of this method of plotting solubility has been explained in the fifth paper of this series.[16]

Discussion.

The curves in Fig. 1 show very strikingly the deviations of these solutions from the solubility that would be expected in a solvent with which sulfur obeyed Raoult's law. The line corresponding to the ideal solubility is calculated from the melting point and the heat of fusion of rhombic sulfur, using data given in a paper by Lewis and Randall[17] and corresponds to an ideal solubility for S_8 of mol-fraction 0.282 at 25°. The heat of solution of sulfur in such a solvent is the same as its heat of fusion, or, in other words, such a solvent would mix with molten sulfur with no heat effect.

The position of sulfur in the table of internal pressures given in our third paper may be determined by the aid of the following data. Toepler[18] has given the specific volume of supercooled sulfur at 20° as 0.951 times

[15] The data by Cossa are evidently of inferior accuracy and have been omitted.
[16] See also Braham, THIS JOURNAL, 41, 1715 (1919).
[17] Lewis and Randall, ibid., 36, 2468 (1914).
[18] Toepler, Wied. Ann., 47, 169 (1892)

the specific volume at 120°, which according to Pisati[19] is 0.5541. From these figures we calculate the molecular volume of liquid sulfur S_8, at 20° as 135 cc.

The surface tension of sulfur at 20° is 60.0.[20] This gives $\gamma/V^{1/3} = 11.7$, which would place sulfur close to iodine in internal pressure.

From the vapor pressure measurements of Ruff and Graf[21] we calculate the heat of vaporization of sulfur at low temperatures to be 19,100 cals.
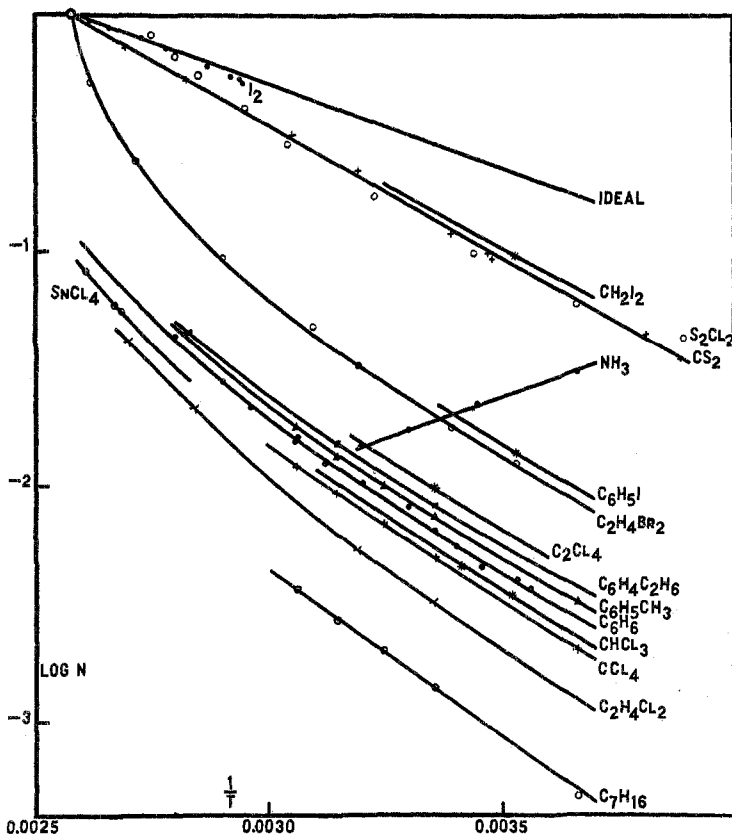

Fig. 1.—Solubilities of rhombic sulfur.

per mol. From this we get $L_v/V = 137$, which, again, would place sulfur just above iodine in internal pressure. Unfortunately, data do not exist for the calculation of the internal pressure by the more accurate method of our sixth paper.

We should thus expect that sulfur would obey Raoult's law rather closely with iodine, and that its solubility would decrease progressively as we

[19] Pisati, *Gazz. chim. ital.*, **4**, 29 (1874).
[20] Cf. Harkins, Davis and Clark, THIS JOURNAL, **39**, 541 (1917).
[21] Ruff and Graf, *Ber.*, **40**, 4199 (1907).

change to solvents of lower internal pressure.   By comparing the curves in the figure with the table of internal pressures given in our third paper the order will be seen to correspond, on the whole, very well.

A minor discrepancy exists in the cases of toluene and xylene.   These have internal pressures smaller than that of benzene so that lower solvent power for sulfur would be expected; in the case of xylene about the same as that of carbon tetrachloride.   The reason for this discrepancy will be discussed in a future theoretical communication.   We will merely note that the expected order is attained at higher temperatures with liquid sulfur. According to observations by Alexejeff[22] the critical temperature of mixing of benzene and sulfur is 163°, whereas with toluene it is 180°.   Of course, at these temperatures considerable $S\mu$ is present so that they cannot be regarded as true measures of the solubility of $S\lambda$.

Ethylene chloride, shows an abnormally low solvent power.   Its internal pressure is greater than that of benzene, but its solvent power for sulfur is considerably less than that of carbon tetrachloride.   This is undoubtedly due to its polar character, as shown by its dielectric constant of 10.4. The dielectric constant of liquid sulfur is only 3.4.   As the polar character diminishes with rising temperature we find the solvent power of ethylene chloride increasing somewhat more rapidly with temperature than does that of a normal substance such as carbon tetrachloride.   Ethylene bromide, with a smaller dielectric constant, 4.9, shows a solvent power nearly as great as its internal pressure would lead one to expect.   Tetrachloro-ethylene, C_2Cl_4, with a dielectric constant of only 2.46 has about the solvent power indicated by its internal pressure.   The other solvents investigated by Hoffman have not been included in the plot, partly because of lack of space, partly because of lack of knowledge concerning their physical constants.   In general, however, we may state that their solvent powers accord well with the theory.

The figures of Aten for sulfur monochloride show, when plotted, considerable irregularity.   Those for hexane by Étard, not included in the plot, are very close to our own for heptane, but a smaller slope than that of the other curves of the family indicates some inaccuracy.   The small solubility of sulfur in hexane makes accurate determinations difficult. Étard's figures for benzene also do not fall very closely upon the curve.

Methylene iodide, which was not given in the table of internal pressures, has a value for L/V of 136, which places it below sulfur monochloride and accords exactly with its solvent power for sulfur.

The curve for ammonia, which is included as an interesting illustration of a solvent power to be attributed to solvation, falls off at higher temperatures, quite unlike the other cases given.   The prediction of such

[22] Alexejeff, *Wied. Ann.*, **28**, 305 (1886).

behavior is outside the scope of the theory and is part of the great unsolved problem of chemistry, the prediction of chemical combination.

The deviations from Raoult's law for most of the substances here considered is sufficient to cause the existence of two liquid phases above the melting point of sulfur. Therefore, the curves below that of ethylene bromide do not converge to the melting point of sulfur but would be continued to the left as the solubility curves for liquid sulfur, ending at the critical temperatures of mixing. The data for this region are fragmentary and conflicting, so that we have not attempted to include them in this paper.

We may note the possibility offered by such a family of curves of constructing a solubility curve from a single point, as we have done in the figure for methylene iodide, iodobenzene and tetrachloro-ethylene. The solubility of sulfur in these solvents at any desired temperature can be read from such a curve. Such a procedure would not, of course, be valid in the case of a very polar solvent, or of one, like ammonia, which forms a solvate with the sulfur.

In conclusion we would point out the enormous deviations from Raoult's law which most of the solubilities of sulfur represent, the extreme case being with heptane, where the solubility at $25°$ is 0.00141, expressed as mol. fraction, while the solubility according to Raoult's law is 0.282. It is also evident that there is no justification in attempting to account for this variation by the assumption of any abnormal molecular weight for either substance. What is required is a substitute for Raoult's law for defining the ideal solution. The study of this subject is now in progress.

Summary.

Solubilities of rhombic sulfur at various temperatures have been measured in the following solvents:heptane, ethylene chloride, carbon tetrachloride, benzene, toluene, and *m*-xylene.

These data, together with many obtained by other observers in these and other solvents, have been plotted by the method previously used by us for evaluating solubility data.

It is shown that, with the exception of certain minor discrepancies, the solubilities of sulfur accord well with the internal pressure relations of the substances involved.

BERKELEY, CALIFORNIA.