Anthracene.

Heat of fusion. l.	Specific heat of liquid. c.	From equations (temp. ranges. 20–290°; 20–320°).
38.8	0.502	$l + 5.5c = 41.6$
		$l + 37.8c = 57.8$
38.6	0.515	$l + 4.9c = 41.1$
		$l + 38.1c = 58.2$

The corresponding values for the heats of fusion per mol of substance are as follows: triphenylmethane, 4340 cals.; anthraquinone, 7780 cals.; anthracene, 6890 cals.

Summary.

The following specific heats have been determined: pyrex glass, $0.174 + 0.00036t$; quartz glass, between 20° and 320°, 0.2161; triphenylmethane, solid $0.186 + 0.00277t$, liquid 0.479; anthraquinone, solid $0.258 + 0.0007t$, liquid 0.66; anthracene, solid $0.280 + 0.0007t$, liquid 0.509.

The following heats of fusion have been determined; triphenylmethane, 17.8 cals.; anthraquinone, 37.4 cals.; anthracene, 38.7 cals.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SOLUBILITY AND INTERNAL PRESSURE.

BY JOEL H. HILDEBRAND.

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In a recent paper entitled "Solubility"[1] it was shown by the writer that deviations from Raoult's law, with accompanying effects upon the solubilities of gases, liquids and solids, appear to be governed by the internal pressures and polarities of the substances involved. Over one hundred instances were cited where the behavior of mixtures in this respect accorded with the theory. In the present paper is presented additional experimental evidence of the validity of this point of view.

Where Raoult's law is obeyed by the solution, the solubility of a solid at the absolute temperature T may be calculated by the aid of the equation

$$\log N = \frac{-LTT_m}{4.58\,(T_m - T)},$$

where N is the solubility expressed in terms of mol-fraction, L is the molal heat of fusion, and T_m the melting temperature of the solute on the absolute scale. The difference between the specific heats of the solid and liquid forms of the solute is seldom known with sufficient accuracy to make it worth while to consider L as a function of the temperature.

Values of N so calculated for certain solids are given in Table I. Experimental values of the solubility are available mostly at 25°, hence N represents the solubility at that temperature, except for triphenylmethane

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[1] THIS JOURNAL, 38, 1452 (1916).

where the temperature is 20°, for better comparison with existing experimental values. The heats of fusion of anthracene, anthraquinone and triphenylmethane are taken from the preceding paper, that of *p*-dibromobenzene from the publication of Bogojawlenski,[1] that of phenanthrene from Robertson.[2]

TABLE I.

	Anthracene.	Anthraquinone.	*p*-Dibromo-benzene.	Phenan-threne.	Triphenyl-methane.
I	6890	7780	4790	4450	4340
Melting point	216.6°	282.0°	87.05°	100°	92.3°
N	0.00107	0.0023	0.248	0.221	0.229
Calc. at	25°	25°	25°	25°	20°

We will now compare these values of N, together with that for iodine, previously published, with the experimental values in various solvents. In the previous paper on this subject it was shown that the following conclusions concerning the solubility of solids may be expected to hold: (1) The solubility of a non-polar substance in a non-polar liquid of equal internal pressure is that calculated on the basis of Raoult's law. (2) Where the internal pressures are unequal, the solubility is less to an extent depending on the difference in internal pressures. (3) When one substance is polar and the other non-polar, the solubility is less than that indicated by Raoult's law. (4) When both substances are polar (leading frequently to the formation of recognizable compounds) the solubility is usually greater than that indicated by Raoult's law. The solutes here considered may be regarded as nearly non-polar except anthraquinone, which possesses a polarity due to the carbonyl group. The solvents, except alcohol, are relatively non-polar, hence we have to do mainly with the effects of differences in internal pressure.

In Table II are given a number of solubilities taken from the preceding paper, except as noted, but expressed now in terms of mol fraction of solute. The solvents are arranged in order of increasing internal pressures towards the bottom of the table; the values of internal pressure calculated from Walden, as given in the earlier paper on solubility, are added for reference.

On the basis of the data given in the earlier paper, it was expected that iodine, having a high internal pressure, would be much less soluble in hexane than in the other liquids for which solubility data then existed. The recent measurement of this solubility has resulted in full confirmation of this prediction, as shown in the last column in Table II. The significance of the other values has already been discussed. We may repeat merely that the apparently anomalous value for the solubility in benzene is due to the fact that in this case the solid phase is not pure iodine but a solid solution of lower melting point and hence greater solubility.

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[1] *Chem. Zentr.*, **1905**, II, 945.

[2] *Proc. Chem. Soc.*, **18**, 131 (1903).

TABLE II.

Solubilities and Internal Pressures.

Solvent.	Internal pressure.	Anthracene. 25°.	*p*-Dibromobenzene. 25°.	Phenanthrene. 25°.	Triphenylmethane. 20°.	Anthraquinone. 25°.	Iodine at 25°.
Hexane	1250	0.0018	0.086	0.042	0.030[1]	...	0.0045
Ether	1360	0.0059	0.183	0.151	...	0.00037	....
Carbon tetrachloride	1680	0.0063	0.193	0.186	...	...	0.026[3]
Benzene	1920	0.0081	0.217	0.207	...	0.0013[2]	0.047[3]
Chloroform	1950	....	....	....	0.258[1]	0.0040[2]	0.022[3]
Carbon disulfide	2400	0.0112	0.224	0.255	0.191[1]	...	0.058[3]
Bromoform	2550	....	....	....	...	...	0.066[3]
Alcohol	Polar	0.0009	0.0198	0.0125	...	0.00097	....
Calculated from Raoult's law	....	0.0107	0.248	0.221	0.229	0.0023	0.212

We have no data upon the internal pressures of the other solutes in Table II (considered as supercooled liquids) so that the test of our theory must be made by finding one solvent in which the solid in question obeys Raoult's law, and then seeing whether its solubility is less in liquids having either a greater or smaller internal pressure.

It will be seen that the solubility of anthracene in carbon disulfide is practically the same as the calculated value, which we may call briefly the ideal solubility. We may conclude from this that the internal pressure of liquid anthracene would be very close to that of carbon disulfide. It is evident, therefore, that anthracene should stand rather close to carbon disulfide in the table of internal pressures, and that its solubility should decrease as we ascend the list of solvents to those of lower internal pressure. The experimental values show that this expectation is fully realized. We may, therefore, feel considerable confidence in extending our predictions to include other solvents given in the more complete table of internal pressures previously published, and for which we have, as yet, no solubility data. For example, xylene, whose internal pressure is probably less than that of carbon tetrachloride, we should expect to be a poorer solvent for anthracene than is carbon tetrachloride. It may be noted that this violates the rule made much of by other writers on solubility, that chemically similar substances come closest to obeying Raoult's law, for xylene is surely more like anthracene, chemically, than is carbon tetrachloride.

Alcohol, it will be noted, is a poor solvent for anthracene on account of its highly polar nature, in accord with the third rule given above.

p-Dibromobenzene is very much more soluble in all of these solvents than is anthracene, because its melting point is so much lower, 87° as compared with 216.6°. The relative solubilities in the various solvents are, however, the same as with anthracene, indicating that liquid *p*-di-

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[1] Calculated from data by Etard, *Bull. soc. chem.*, [3] **9**, 82 (1893).

[2] Calculated from data by Tyrer, *J. Chem. Soc.*, **97**, 1778 (1910).

[3] From paper on solubility, *Loc. cit.*

bromobenzene would have an internal pressure greater than that of benzene, though we cannot tell, from the data at hand, whether this would be greater or less than that of carbon disulfide. We could determine this if we knew its solubility, for example, in bromoform, for if it is more soluble in this solvent than in carbon disulfide, then its internal pressure is more like that of bromoform, and *vice versa*. It is evident, however, that it should stand rather close to carbon disulfide in the table of internal pressures, whether above or below, and that its solubility should decrease as we ascend the list of solvents to those of smaller internal pressure, as is indeed the case.

The situations with respect to phenanthrene and triphenylmethane appear to be the same as with *p*-dibromobenzene. The fact that the solubilities of the former in carbon disulfide and of the latter in chloroform appear to be slightly greater than the ideal solubilities may be due to experimental error, though in the case of chloroform it may be due to the chemical reactivity of chloroform and its tendency to form addition compounds with many substances, as referred to later. The data indicate that the internal pressure of triphenylmethane is less than that of carbon disulfide since its solubility falls off as we descend the table from chloroform to carbon disulfide. From this we may predict that its solubility in bromoform would be found less than that in carbon disulfide, *i. e.*, less than 0.19. Similarly, we may feel confident that its solubility in ether is greater than 0.03, which is its solubility in hexane, and still greater in carbon tetrachloride.

When we come to anthraquinone we encounter the interesting complication due to the presence of the polar carbonyl group. On this account its solubility in alcohol is one-half the ideal solubility instead of only about one-tenth of it, as with the previous solutions. Moreover, the solubility in chloroform is about twice the ideal solubility. This is undoubtedly due to the formation of a solvate with the chloroform, and had been predicted by us from the analogous behavior of mixtures of chloroform and acetone.[1]

The above examples lend strong additional support to the theory that the deviations of mixtures of non-polar liquids from Raoult's law, with corresponding effects upon solubilities of gases and solids, may be considered as a function of the relative internal pressures of the two substances. In order to put this relationship upon a more quantitative basis it seems desirable, as the next step, to undertake a critique of the various methods for calculating internal pressures. This is now in progress, and will be the subject of a future communication.

Summary.

A number of solubilities of solids have been calculated on the basis of Raoult's law, and compared with experimental values. It has been shown

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[1] Dolezalek, *Z. physik. Chem.*, 64, 727 (1908).

that the deviations from the calculated value are in entire accord with predictions made upon the basis of the internal pressures and polarities of the substances involved.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SOLUBILITIES OF ANTHRACENE, ANTHRAQUINONE, PARABROMOBENZENE, PHENANTHRENE AND IODINE IN VARIOUS SOLVENTS.

BY JOEL H. HILDEBRAND, E. T. ELLEFSON AND C. W. BEEBE.

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In working upon the theory of solubility one is struck by the fact that nearly all of the determinations of solubility to be found in the literature have been made with aqueous solutions, or at least with solutions in other more or less polar solvents like alcohol. Since solutions of this type introduce complications due to association and ionization, it is desirable to have solubility data for relatively non-polar substances, whose solutions are much simpler. The following determinations were made with this end in view, the solutes chosen being those whose heats of fusion are known, for the purpose described in the following paper:

An accuracy of 1% was considered quite sufficient for our purpose, and the various factors involved were controlled to the corresponding degree. The solutes used were from a commercial source and in most cases were not further purified. The solvents were dried and carefully distilled; the portion used distilled between narrow limits.

The solid and liquid, in each case, was sealed in a tube about 2 cm. in diameter and 8 cm. long, provided with a stem several centimeters long bent at an angle with the axis of the tube. These tubes were rotated in a thermostat at 25° for one or more days, until equilibrium was attained. Except in the case of the iodine solutions the analysis was made by evaporating the solvent from a weighed portion of the solution and weighing the solid residue of solute. The vessels in which this evaporation was carried out were flat-bottomed bulbs of about 20 cc. capacity, provided with two open tubes, the bore of one of which was large enough to admit the stem of the tubes described above, which we will call the shaking tubes. The transfer of the saturated solution from these tubes to the evaporating bulbs was effected as follows: The tube was detached from the shaking device in the thermostat and held so that only the stem projected above the water in the thermostat. This stem was then opened with a file and inserted into one of the openings of the evaporating tube. A portion of the saturated solution was poured into the latter which was quickly stoppered for weighing. The angle which the stem made with