[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Solubility Studies. V. The Validity of Henry's Law for the Calculation of Vapor Solubilities[1]

BY J. H. SAYLOR, J. M. STUCKEY AND P. M. GROSS

The solubilities in water of over forty slightly soluble organic substances have been determined in this Laboratory. On first inspection the data seemed to be devoid of regularity and impossible of correlation. The use of a corrected or vapor solubility, however, has brought out important regularities.

The solubility C of a solute is defined as the concentration in a given solvent in equilibrium with excess solute at a given temperature. The vapor solubility is defined as that concentration C_s in equilibrium with a standard fugacity p_s of the solvent vapor at the same temperature. In general the direct determination of vapor solubilities is difficult for slightly soluble organic solutes (solubilities less than 100 millimoles/1000 g. of H_2O) in water and not many determinations are available in the literature. Henry's law has been assumed in these cases and the vapor solubility at a standard fugacity calculated by means of it from the partial pressure at saturation.[2] While there seems to be little doubt of the validity of Henry's law as applied to these cases, it seemed preferable to establish this experimentally for dilute aqueous solutions of substances of the types we have measured since the further interpretation of the solubility results depends on a knowledge of the vapor solubilities. The present paper gives the experimental justification for the use of Henry's law in such cases.

If p_c is the fugacity of the solute in equilibrium with the saturated aqueous solution of concentration C and if Henry's law holds over the fugacity and concentration ranges under consideration then $p_c/C = p_s/C_s$. For the range of vapor pressures of the substances under consideration, the partial vapor pressures may be used for the fugacities with negligible error. Furthermore, for these systems it is possible to place the vapor pressure of the pure liquid solute as equal to the partial pressure of the saturated aqueous solution with but little error as the solubility of water in these liquids is very small. Thus $p_c = p_e$ where p_e is the vapor pressure of the liquid solute at the temperature in question. Provided Henry's law holds

$$C_s = (p_s/p_c) \times C$$

The applicability of Henry's law was tested by three different methods. In the first, direct determinations of the pressure of benzene, ethylene chloride and diethyl ketone above their respective solutions at concentrations below saturation were made. These compounds were chosen as they are of varied types; a non-polar aromatic hydrocarbon, a polar halogenated aliphatic hydrocarbon and the ketone with a polar group containing oxygen.

Experimental

These compounds together with the diphenyl and nitrobenzene used in the second and third methods were carefully purified by the methods in use in this Laboratory, which have been described previously.[3] The benzene used had a freezing point of 5.48°, the ethylene dichloride a boiling point of 83.53 to 83.56° and the diethyl ketone a boiling point of 101.6 to 101.8°. The nitrobenzene used melted at 5.7° and the diphenyl at 79.0°. The apparatus, which has been described previously,[3c] consisted of a differential mercury manometer each arm of which was connected to a 50-cc. bulb. Distilled water was placed in each bulb and boiled to drive out dissolved gases. The apparatus was then put in an ice-water bath and a small amount of the organic solute introduced into one bulb. The proper amount was estimated from preliminary trials and from the known solubility in water. The necks of the two bulbs were connected to a high vacuum pump and manometer, pumped down quickly and then sealed off. The amount of substance used and the extent of pumping had to be gaged properly from preliminary trials, otherwise all the volatile solute would be pumped off. This necessitated numerous trials to get the desired ranges of concentrations below the saturation value. The apparatus was then placed in a large thermostat at 30 ± 0.01° and shaken until all of the organic substance went into solution. This required from a few minutes to several days depending on the substance and its concentration. After solution was complete the manometer was read with a cathetometer on successive days until equilibrium had been attained. The apparatus was removed from the bath, the bulb opened and the solution was analyzed. The analyses were made by comparing the readings of the solution in a Zeiss combination interferometer with those of known standards made by dissolving weighed quantities of the particular solute in

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(1) Taken in part from the thesis of J. M. Stuckey submitted in partial fulfilment of the requirements for the M.A. degree at Duke University, 1937.

(2) *Cf.* Butler, Ramchandani and Thomson, *J. Chem. Soc.*, 280 (1935).

(3) (a) Gross and Saylor, THIS JOURNAL, **53**, 1747 (1931); (b) deBruyne, Davis and Gross, *ibid.*, **55**, 3937 (1933); (c) Rintelen, Saylor and Gross, *ibid.*, **59**, 1139 (1937).

known weights of water as has been described previously.[3a] From repeated trials of the differential manometers with approximately the same concentrations it seems safe to assume that the error in the pressure readings is about 2.5 mm. as a maximum and as a rule is less than this. In the case of benzene and ethylene chloride the estimated maximum error in the determination of the concentrations is ±0.05 g. per 1000 g. of water. In the case of diethyl ketone with its larger solubility the error is ±0.1 g. per 1000 g. of water. The percentage error is, however, no higher than for the benzene and ethylene chloride.

In calculating the partial pressure of the solute the assumption is made that the lowering of the vapor pressure of the water is that calculated by Raoult's law. This lowering for such dilute solutions is very small, being but a few tenths of a mm. in all cases here considered and therefore negligible compared to the experimental errors. With this assumption the manometer reading gives directly the partial pressure of the organic solute from the solution. The data are collected in Table I and plotted in Fig. 1. If Henry's law is valid the ratio p/C given in the last column should be constant. It is evident that within the accuracy of the determinations both benzene and ethylene dichloride follow Henry's law, while diethyl ketone deviates somewhat from a linear relationship.

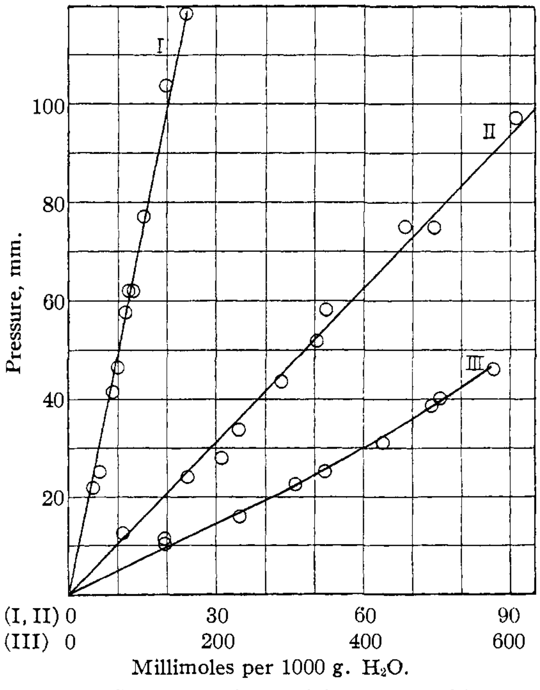

Fig. 1.—Curves for the partial pressures of benzene (I), ethylene chloride (II) and diethyl ketone (III) from aqueous solutions at 30°.

Second Method

Because of the experimental difficulties in the direct method and the necessity of making the assumptions indicated in calculating the partial pressures, as an additional check, data to test this relation were obtained for benzene solutions in water by an independent experimental method. A large quantity of benzene–naphthalene solution of known composition is brought to equilibrium with a limited quantity of water in order that the small amount of benzene dissolved by the water may not materially change the composition of the benzene–naphthalene solution. The solubility of naphthalene (0.3 millimole per 1000 g. of water)[4] is so small that the scale reading for a saturated solution of pure naphthalene in water is very small compared to readings for the benzene–naphthalene solutions. The benzene content of the water layer may then be determined by the interferometer without appreciable error by making a small correction for the dissolved naphthalene. Since benzene and naphthalene form an ideal solution, the partial pressure of benzene in equilibrium with the known benzene–naphthalene solution can be calculated by Raoult's law. This also will be the partial pressure of benzene in equilibrium with the aqueous layer, thus giving the data to test the dependence of the concentration in solution on pressure in the vapor phase. The data are set

Table I

Partial Pressures from the Aqueous Solutions at 30°

C, millimoles/1000 g. H_2O	p, partial pressure of solute	p/c
	Benzene	
5.1	21.9	4.3
6.3	25.2	4.0
8.7	41.5	4.8
9.7	46.6	4.8
11.4	57.7	5.1
12.1	64.1	5.3
13.0	64.2	4.9
15.2	77.2	5.1
19.6	103.7	5.3
23.7	118.4	5.0
	Average	4.9
	Ethylene Dichloride	
10.9	12.8	1.17
24.2	24.1	0.996
31.0	28.0	.903
34.4	33.8	.983
43.1	43.7	1.01
50.3	51.8	1.03
52.2	58.2	1.12
68.3	75.0	1.10
74.2	74.9	1.01
90.9	97.4	1.07
	Average	1.04
	Diethyl Ketone	
129.8	10.2	78.6
130.2	11.5	88.3
231.4	16.0	69.1
307.2	22.6	73.4
346.6	25.2	72.7
427.0	31.1	72.8
491.5	38.7	78.7
504.0	40.1	79.6
576.0[a]	46.1[a]	80.3
	Average	77.1

[a] Value obtained by J. C. Rintelen, Jr., working in this Laboratory.

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(4) Mitchell, *J. Chem. Soc.*, 1333 (1926).

forth in the first half of Table II. Column I gives the composition of the naphthalene–benzene solution, column III the partial pressure of benzene computed from Raoult's law and from the vapor pressure of benzene at 30°, and column IV the concentration of benzene in the water layer. Column V gives the ratio of pressure to concentration and the average value of this constant is seen to be about the same as the corresponding value for the direct measurements for benzene in Table I. In the latter half of Table II similar data for benzene at 35° are listed which were obtained by using benzene–diphenyl solutions instead of benzene–naphthalene solutions as the non-aqueous phase. The use of a higher temperature and of diphenyl as the second component of the ideal solution allowed a somewhat greater spread of concentrations of benzene than in the case of the naphthalene–benzene solutions at 30°.

TABLE II

Mole fraction C_6H_6	Vapor pressure C_6H_6	Partial pressure p-C_6H_6, mm.	Concn. C_6H_6 in aq. phase millimoles per 1000 g. H_2O	p/c
Benzene–Naphthalene Solutions at 30°				
0.705	118.4	83.47	16.9	4.9
.710	118.4	84.06	16.9	5.0
1.000	118.4	118.4	23.6	5.0
			Average	5.0
Benzene–Diphenyl Solutions at 35°				
0.7703	150.0	115.5	19.2	6.0
.7717	150.0	115.7	18.7	6.2
.7756	150.0	116.3	18.8	6.2
.8078	150.0	121.2	20.0	6.1
.8128	150.0	121.9	19.9	6.1
.8197	150.0	122.9	19.5	6.3
1.0000	150.0	150.0	24.3	6.2
			Average	6.2

Third Method

A search of the literature failed to reveal any suitable systems with more polar components such as nitrobenzene whose partial pressures had been determined accurately which could be used in a manner similar to the naphthalene and diphenyl–benzene cases. The applicability of Henry's law to aqueous solutions of nitrobenzene was therefore tested as follows. Nitrobenzene which melts at 5.7° was supercooled to 0° and the metastable liquid brought to equilibrium with its water solution at this temperature without crystallization occurring. The solubility thus found for the supercooled liquid at 0° was 13.5 millimoles per 1000 g. of water. Bringing crystalline nitrobenzene to equilibrium with water at 0° gave a value for its solubility of 12.6 millimoles per 1000 g. of water. Both values represent the mean of several concordant determinations. If Henry's law holds, the ratio of these two solubilities (1.07) should be the same as the ratio of the vapor pressure of supercooled liquid nitrobenzene at 0° to the sublimation pressure of crystalline nitrobenzene, also at 0°. While data for the vapor pressure of liquid nitrobenzene at low temperatures are available, they do not agree well. Also reliable data for the sublimation pressure at 0° are lacking so that an evaluation of this pressure ratio directly from experimental material is not possible. This ratio may however be determined indirectly from the heat of fusion (L_f) for which reliable data are available. From the Clapeyron equations for the vapor (p_e) and sublimation (p_s) pressures at 0° and from the vapor pressure at the melting point, 5.7°, the following equation may be derived

$$\log_{10}\frac{p_e}{p_s} = \frac{-L_f}{2.303}\,\frac{1}{R}\left(\frac{1}{T_m} - \frac{1}{T_0}\right)$$

where R is the gas constant and T_m the absolute melting point 278.9°A. and T_0 is 273.2°A. The value of L_f used was 2771 g./cal./mole.[5] This equation assumes that the heat of fusion is the same at 0° as at the melting point (5.7°) but it should give the pressure ratio with greater accuracy than that of the solubility results. The value of the ratio p_e/p_s so found is 1.11 compared to 1.07 given by the ratio of the solubilities. The difference, 4%, is but little greater than the possible combined error in the two solubility results.

Discussion

It is evident from the data that Henry's law is applicable to the solutions of benzene, ethylene and nitrobenzene within the limitations of the experimental determinations and of the assumptions made in the different cases. In the case of diethyl ketone inspection of the graph (Fig. 1) shows that there is a linear relation between pressure and concentration up to concentrations of somewhat over 400 millimoles per 1000 g. of water. Above this concentration there is a greater rate of increase in escaping tendency as the concentration increases. It is therefore probable that the failure of Henry's law in this region is to be attributed to the relatively high concentrations involved and not to the nature of the solute. These concentrations are almost eight times greater than in the case of the next lower concentrations, those of the ethylene dichloride solutions. If other ketones with lower solubilities could have been measured it is probable that Henry's law would have been applicable over the entire range up to saturation. The substances investigated involve a wide range of molecular types and differ considerably in polar characteristics as measured by such criteria as dipole moment and dielectric constant. It seems reasonable to conclude therefore that Henry's law is generally applicable to aqueous solutions of organic substances of these types provided their solubilities are sufficiently small to enable them to be classed as dilute solutions. An approximate upper limit to this dilute region might be set at from 300 to 400 millimoles per 1000 g. of water. If the validity of Henry's law is accepted

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[5] "International Critical Tables."

then it is possible to calculate the vapor solubilities in equilibrium with a standard vapor state in these cases as indicated earlier in this paper.

Summary

Three different types of experimental tests are employed to test the applicability of Henry's law to aqueous solutions of slightly soluble organic liquids. It is concluded that Henry's law is applicable in concentration ranges below approximately 300 to 400 millimoles per 1000 g. of water. The calculation of vapor solubilities in cases where Henry's law is applicable is discussed.

DURHAM, N. C. RECEIVED DECEMBER 6, 1937

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

Experiments Establishing the Thermodynamic Temperature Scale below 1°K. The Magnetic and Thermodynamic Properties of Gadolinium Phosphomolybdate as a Function of Field and Temperature

BY W. F. GIAUQUE AND D. P. MACDOUGALL

Although summaries of the more important results described in this paper have been presented[1] several years previously, it is only recently that we have found time to prepare a full account of the work. This paper completes the presentation of the results obtained by the authors in a series of investigations over the period March, 1933–June, 1934, in which the first adiabatic demagnetization experiments producing temperatures below 1°A. were carried out and in which these low temperatures were placed on the thermodynamic scale.

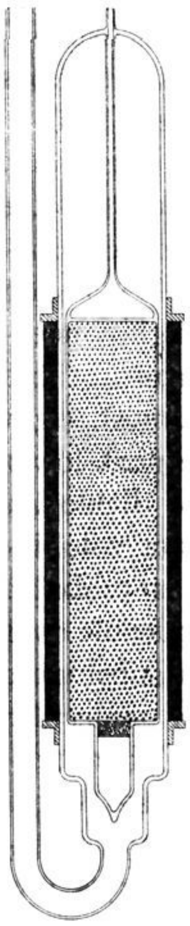

Fig. 1.

Gadolinium phosphomolybdate tridecahydrate was selected for investigation because Hoard[2] had shown that this substance is cubic, with the gadolinium atoms occupying equivalent positions in a diamond type lattice. Also this substance, $Gd(PMo_{12}O_{40})\cdot 30H_2O$, contains but one gadolinium atom in a total of 144 atoms and this dilution was expected, and was found, to lead to a closer approach to ideal paramagnetism than any of the other gadolinium compounds previously investigated. Hoard[2] has shown that the distance of closest approach of the gadolinium ions is 10.03 ± 0.02 Å.

The experimental arrangement was approximately that shown in Fig. 1 of a previous paper.[3] The sample tube, surrounded by the insulating vacuum space, and the inductance coil used for susceptibility measurements is shown in Fig. 1 of the present paper. At the upper end of the sample tube a small chamber is shown in which helium could be liquefied when desired. This permitted a temperature a little below bath temperature to be obtained at the start of demagnetization. However, this was not very useful in connection with the thermodynamic measurements as it was necessary to pump on the chamber until all the liquid helium had evaporated. The presence of an unknown amount of liquid helium in contact with the sample would have interfered with the interpretation of the measurements and when the helium was entirely evaporated the starting temperature was not accurately known when the sample was in a field. This small chamber was used as a container for an inductance heater which will be described later.

The measurement of magnetic susceptibility by means of the inductance coil has been described previously.[4] Inductance coil no. 4[3] was used for all of the measurements described in this paper. The end effect was assumed to be independent of the susceptibility. It may be well to mention here that unpublished later investigations of J. W. Stout and one of us have justified this assumption within rather small limits of error for the particular dimensions of the above apparatus and the range of susceptibility considered here.

The gadolinium phosphomolybdate was prepared by dissolving gadolinium oxide in 12-phosphomolybdic acid. The compound was then crystallized from the solution by slow evaporation of the water under vacuum at room temperature. The flask containing the solution was attached to a vacuum pump and a stream of air was allowed to pass over the surface of the liquid to facilitate evaporation. The crystals were partially dried on a filter, but it was considered desirable to leave a small excess of water since this made certain that the 30 molecules of water of crystallization were present. Analysis of a representative por-

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(1) Giauque and MacDougall, Meeting of the American Chemical Society in affiliation with the American Association for the Advancement of Science, Berkeley, California, June 18, 1934; *Phys. Rev.*, **47**, 885 (1935).

(2) Hoard, *Z. Krist.*, **A84**, 217 (1933).

(3) MacDougall and Giauque, THIS JOURNAL, **58**, 1032 (1936).

(4) Giauque and MacDougall, *ibid.*, **57**, 1175 (1935).