In Fig. 1 is shown the observed variation of combined paramagnetic and diamagnetic volume susceptibility with temperature, compared to that calculated by the use of the Van Vleck equation, the diamagnetism of sulfur, and the equilibrium constants of Preuner and Schupp.

The relative probable error in the measurements based solely upon the distribution of values of the force of the field upon the sample, as a result of four or five determinations at each temperature, was about 3% at 850° and increased progressively to about 20% at 550° where the force was much smaller. Errors in temperature, field strength, and equilibrium data would increase the relative error at 850° to perhaps 7% but would be swamped by the observational error at the lower temperature. The error in the average $\chi_M T$ (excluding values at 550°) is thus about 10%.

The theory of Van Vleck[7] predicts that the molar susceptibility of molecules in the $^3\Sigma$ state, having small multiplet intervals, is

$$\chi_M = \frac{N\beta^2}{3KT}[4S(S + 1)] = \frac{0.993}{T}$$

At 850° this leads to a value of 8.83×10^{-4} unit, in good agreement with the observed average of the two samples, $9.0 \times 10^{-4} \pm 0.6 \times 10^{-4}$. Neel[3] reported 5.4×10^{-4} unit.

The average value of $\chi_M T$, excluding the values at 550°, is 0.91 ± 0.09, compared to the theoretical value of 0.993.

These data serve to show that the ground state of diatomic sulfur is undoubtedly the triplet state, and further that the equilibrium data of Preuner and Schupp predict quite satisfactorily the proportion of S_2 in sulfur vapor between 550 and 850°.

A similar study of the ground state of Se_2 is to be undertaken by this laboratory in the near future.

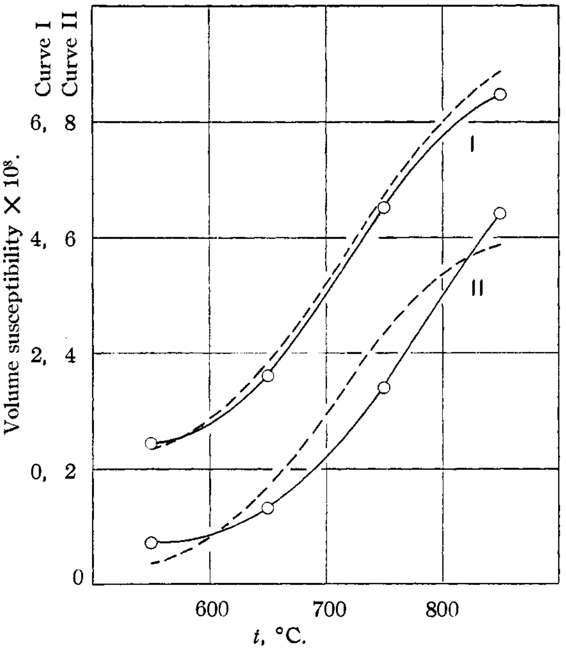

Fig. 1.—Volume susceptibility of S vapor: I, density 5.76 mg./cc.; II, density 4.74 mg./cc.; broken curves, calculated.

Summary

The molar susceptibility of S_2 at temperatures between 550 and 850° has been measured and found to agree with the theoretical value within the limits of experimental error. The existing equilibrium data predict satisfactorily the proportion of S_2 in sulfur vapor between 550 and 850°.

CORVALLIS, OREGON RECEIVED APRIL 21, 1949

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[7] J. H. Van Vleck, "Electric and Magnetic Susceptibilities. Oxford University Press, Oxford, England, 1932, p. 266.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Solubility of Nitrogen in Carbon Disulfide, Benzene, Normal- and Cyclo-hexane, and in Three Fluorocarbons

BY J. CHR. GJALDBAEK[1] AND J. H. HILDEBRAND

Introduction.—The extraordinary solubility relations of fluorocarbons have been the subject of three recent papers from this Laboratory; Scott[2] assigned figures for the "solubility parameters" needed in order to apply the modern theory of regular solutions, and showed their general consistence with the initially fragmentary data. Benesi and Hildebrand[3] determined the solubility of iodine in perfluoro-*n*-heptane, finding a value which, although only 0.027 of its solubility in normal heptane, is nevertheless consistent with theory. Hildebrand and Cochrane[4] determined liquid–liquid solubility curves for perfluoromethylcyclohexane with five organic liquids and likewise found reasonably good agreement with theory. The most illuminating investigation to undertake next appeared to us to be the solvent powers of these substances for gases. Their exceedingly low solvent power for a substance such as iodine implies high solvent power for gases, but there remained the question

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[1] Holder of a scholarship from the Danish Council for applied Science. Home address, Department of Inorganic Chemistry, the Pharmaceutical College of Denmark, Copenhagen.

[2] R. L. Scott, THIS JOURNAL, **70**, 4090 (1948).

[3] H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

[4] J. H. Hildebrand and D. R. F. Cochrane, *ibid.*, **71**, 22 (1949).

whether the gases, at the one end of the scale, would fit the theory as well as does iodine, at the other.

Since the theory has been derived from a model process in which two pure liquids are mixed, the reference of the activity of a gas to a hypothetical liquid above its critical temperature has made the values for ideal solubility[5] heretofore used rather uncertain. An additional uncertainty is introduced by the large discrepancy between the molal volumes of nitrogen and the solvents, particularly the fluorocarbons.

Apparatus and Procedure.—The apparatus and procedure were approximately those of Lannung.[6] The volume of the gas buret was 7 cc., that of the flask, 55 cc. The temperature of the air thermostat was constant within 0.05° in the range 25–50° and within 0.1° at the lowest temperatures, which were in the neighborhood of 2°.

Materials.—The nitrogen was from Stuart Oxygen Co. (99.996% N_2). The three fluorocarbons, from E. I. du Pont Co., were fractionated by distilling in a Vigreux column and the middle portions used showed the following boiling points: perfluoro-*n*-heptane (C_7F_{16}) 82.3–82.4° (753.7 mm.), perfluoromethylcyclohexane (C_8F_{14}) 76.5–76.6° (760.0 mm) and perfluorodimethylcyclohexane (C_8F_{16}) 102.4–102.6° (760.0 mm.). Carbon disulfide ("analytical reagent") by Mallinckrodt showed a negative test for polysulfides and a fraction was used boiling at 45.80–45.85° (750.1). *n*-Hexane ("research grade") by Phillips Petroleum Company was used without further treatment. Cyclohexane by Paragon Testing Laboratories was fractionated by distillation and a portion with boiling point 80.63–80.66° (755.7 mm.) was taken. The benzene was that used by Benesi and Hildebrand.[3]

It is necessary to know the vapor pressure of the solvent in each experiment in order to calculate the solubility of the solute gas at a partial pressure of one atmosphere. For the three fluorocarbons we used the values given by Fowler and co-workers.[7] Their values for perfluoro-*n*-heptane are in good agreement with those of Barber.[8] For the other solvents, we used the values given in "International Critical Tables."

The densities of perfluoro-*n*-heptane were those of Grosse and Cady[9]; for perfluoromethylcyclohexane we determined $d^{25.0}$ 1.7859, and for perfluorodimethylcyclohexane $d^{25.0}$ 1.8400, $d^{35.1}$ 1.8126 and $d^{46.8}$ 1.7834. The other densities needed were taken from the "International Critical Tables."

Results.—The results are expressed in Table I in terms of the Bunsen absorption coefficient, $\alpha = 760\ V^g/pV^1$; V^g referring to the volume of the gas measured at the temperature of the experiment in the volume, V^1 that of the solvent. Pressure is in mm. mercury. An example of the calculation is given in detail in an earlier paper.[10] The table gives, also, values of x_2, the mole fraction of the dissolved gas, at 0, 25, and 50°, derived from the observed values.

TABLE I

SOLUBILITIES OF NITROGEN EXPRESSED IN BUNSEN ADSORPTION COEFFICIENT, α, AND MOLE FRACTION, x_2

Solvent	t, °C.	α	Interpolated or extrapolated value t, °C.	α	$x_2 \cdot 10^4$
	1.98	0.406 (1)[a]	0	0.411	40.1
	2.13	.409 (1)			
	2.45	.404 (2)			
	4.10	.406 (1)			
C_7F_{16}	24.90	.384 (2)	25	.385	39.1
	24.97	.387 (1)			
	46.91	.362 (2)			
	48.60	.362 (1)	50	.360	38.0
C_7F_{14}	24.90	.371 (1)			
	25.00	.384 (2)	25	.375	31.8
	25.00	.324 (1)			
C_8F_{16}	25.00	.329 (2)	25	.328	33.0
	37.97	.330 (2)			
	40.52	.319 (1)			
	47.10	.319 (2)	50	.317	31.9
	24.95	.239 (2)			
n-C_6H_{14}	24.95	.241 (2)	25	.239	14.0
	25.30	.237 (1)			
	24.98	.156 (1)			
c-C_6H_{12}	24.98	.155 (2)	25	.156	7.55
C_6H_6	25.0	.124 (1)	25	.124	4.48
CS_2	24.89	.0822 (2)			
	24.96	.0823 (1)	25	.0823	2.23

[a] (1) indicates that the experiment was performed from the same charge of solvent and gas; (2) indicates experiments with a new charge.

Guerry[11] reported $\alpha = 0.213$ for nitrogen in *n*-hexane at 25° and 0.149 in cyclohexane, both lower than our values. Just[12] reported $\alpha = 0.0526$ for its solubility in carbon disulfide, much lower than our figure. These redeterminations were made because of gross discrepancies[5] for other gases between Guerry and McDaniel, on the one hand, and Just and Horiuti,[13] on the other. One may infer from a comprehensive survey of the data on gas solubilities that all the results published by McDaniel and by Just are somewhat low, due possibly to insufficient degassing of solvents. Our figure for benzene, $\alpha = 0.124$, agrees well with the one found by Horiuti, 0.121.

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(5) J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," third edition, Reinhold Publ. Corp., New York, N. Y., 1949;

(6) A. Lannung, *Det Kgl. Danske Vidensk. Selskab. Mat.-fys. Medd.*, **XX**, no. 3 (1942).

(7) R. D. Fowler, J. M. Hamilton, J. S. Kasper, C. E. Weber, W. B. Burford and H. C. Anderson, *Ind. Eng. Chem.*, **39**, 375 (1947).

(8) J. Barber, Thesis, University of Washington, 1948.

(9) A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

(10) J. Chr. Gjaldbaek, *Det Kgl. Danske Vidensk. Selskab. Matt.-fys. Medd.*, **XX**, no. 3 (1942).

(11) D. Guerry, Thesis, Vanderbilt University, 1944.

(12) G. Just, *Z. physik. Chem.*, **37**, 342 (1901).

(13) J. Horiuti, *Sci. Papers, Inst. phys.-chem. Research, Tokio*, **17**, no. 341, 125 (1931).

Correlation with Theory.—The senior author[14] pointed out, in 1916, that Raoult's law, $p = p^0x = 1$ atmosphere, could be used to define an "ideal" gas solubility, even above the critical temperature of the gas, by obtaining a fictitious value for p^0 by plotting log p *vs.* $1/T$ for the vapor pressure of the gas. This gives a practically straight line right up to the critical point.[5] and its extrapolation to still higher temperatures yields values of p/p^0 which are close to the measured solubilities of gases in solvents of low internal pressure such as hexane. He showed, further, that the solubility falls off regularly with increasing internal pressure of the solvent. We had long ago obtained in this way, for nitrogen $p^0 = 1000$ atmospheres and $x^i = 0.0010$ when $p = 1$ atmosphere, while Guerry reported 0.00125 in n-hexane.

In order to take into account the different internal pressures of the solvents, we may use the equation[15]

$$-\ln x_2 = -\ln x_2^i + (\bar{v}_2/RT)(\delta_1 - \delta_2)^2 \qquad (1)$$

where the subscript 2 now refers to the solute gas and subscript 1 to the solvent, and the δ's are "solubility parameters," defined, for liquid components, as the square roots of their energy of vaporization per cc. The senior author[16] found that an equation of this type, with a semi-empirical adjustment of parameters, could account well for the solubilities of argon, and Gonikberg[17,5] applied it successfully to the solubilities of hydrogen.

When pure normal liquids are mixed, the expansion is ordinarily very small, and we can set $\bar{v}_2 = v_2$ with but little error. In the case of nitrogen solutions at 25° we have no pure liquid volume but we can use the values of $\bar{v}_2$ determined by Horiuti,[13,5] who found 53 cc. per mole in both benzene and carbon tetrachloride, and values not significantly different from 53 in other solvents. Although ideally one would wish to calculate solubility from the properties of the pure components, the values obtained by Horiuti for all the gases in this class can be used in combination with the other necessary data for the practical task of calculating the solubilities of these gases in new solvents. The proper value of δ_2 to use for nitrogen solutions can best be determined, for practical purposes, from the data themselves, but if we adjust one uncertain parameter in order to fit the data we might as well adjust another also. It is possible to use $x_2^i = 10^{-3}$ and $\bar{v}_2 = 53$ cc. and to select empirically a value for δ_2 which permits the calculation of solubilities agreeing rather well with the measured ones in all solvents except the fluorocarbons, where the calculated values are definitely too small. This suggests introducing a correction of the Flory–Huggins[18] type based upon the ratio of molal volumes, which alters Eqn. 1 to

$$-\log x_2 = -\log x_2^i + \log(\bar{v}_2/v_1) + 0.434(1 - \bar{v}_2/v_1) + \bar{v}_2(\delta_1 - \delta_2)^2/4.575T \quad (2)$$

We have set $x_2^i = 1.6 \times 10^{-3}$, $\bar{v}_2 = 53$ cc., and $\delta_2 = 5.2$ to obtain the calculated values of solubility given in the fourth column of figures in Table II.

TABLE II

SOLUBILITY OF NITROGEN, 25°, 1 ATM., COMPARISON OF OBSERVED AND CALCULATED VALUES

			$-\log x_2$				
Solvent	v_1, cc.	δ_1	Meas.	Calcd. Eqn. 2	Δ_2	Calcd. Eqn. 1[a]	Δ_1
n-C_7F_{16}	227	5.9	2.41	2.52	+0.11	2.72	+0.31
C_7F_{14}	196	6.0	2.48	2.57	+ .09	2.73	+ .25
C_8F_{16}	217	6.1	2.50	2.54	+ .04	2.73	+ .23
n-C_6H_{14}	132	7.3	2.85	2.83	− .02	2.87	+ .02
$(C_2H_5)_2O$	105	7.45	2.90[13]	2.91	+ .01	2.90	.00
c-C_6H_{12}	109	8.2	3.12	3.06	− .06	3.05	− .07
CCl_4	97	8.6	3.19[13]	3.18	− .01	3.15	− .04
m-$C_6H_4(CH_3)_2$	123	8.9	3.21[12]	3.18	− .03	3.31	+ .10
$CHCl_3$	81	9.0	3.35[12]	3.32	− .03	3.26	− .09
C_6H_6	89	9.15	3.35	3.35	.00	3.31	− .04
C_6H_5Cl	102	9.5	3.36[13]	3.43	+ .07	3.42	+ .06
CS_2	60	10.0	3.65	3.69	+ .04	3.60	− .05

[a] With $-\log x_2^i = 2.70$.

The differences, Δ_2, between calculated and experimental values in the next column, give an idea of the errors involved. Going from C_7F_{16} to CS_2, the value of $\log \bar{v}_2 - \log v_1 + 0.434 (1 - \bar{v}_2/v_1)$ increases from −0.30 to 0.00 while the value of $\bar{v}_2(\delta_1 - \delta_1)^2/4.575T$ increases from 0.02 to 0.90. We see that Eqn. 2 accounts for solubilities greater than the ideal value in liquids with large v_1, and for solubilities less than the ideal value in liquids with large δ_1, while Eqn. 1 is only able to account for solubilities less than the ideal value since the term $\bar{v}_2(\delta_1 - \delta_2)^2/4.575\,T$, is always positive. The degree of agreement yielded by this equation with "best" values of the parameters is shown in the last two columns of Table II. A few polar but not associated liquids are included in Table II.

From a practical standpoint, the solubility of any of the super-critical gases can now be approximately predicted in any new non-polar solvent from the δ-value of the latter by simple interpolation with known solvents, since we are in possession of data for all of these gases in a series of solvents. It will be seen that the order of the measured solubilities in Table II closely follows the δ-values of the solvents. It is obvious, nevertheless, from the data in this paper, that there is much room for refinement in the present theory of gas solubility.

We may note that, having measured the solubility of nitrogen in two of the solvents at more

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(14) J. H. Hildebrand, THIS JOURNAL, **38**, 1452 (1916); **42**, 1067 (1919); also, N. W. Taylor and J. H. Hildebrand, *ibid.*, **45**, 682 (1923).

(15) For the history of this equation see ref. 5, Chapter VII.

(16) J. H. Hildebrand, "Solubility of Non-electrolytes," 3rd edition, Reinhold Publ. Corp., New York, N. Y., 1936, p. 135.

(17) M. G. Gonikberg, *J. Phys. Chem., USSR*, **14**, 582 (1940).

(18) For an account of this development, see ref. 5, also, J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

than one temperature, we are in a position to calculate the heat of solution of nitrogen in these solvents by the aid of the relation

$$\left(\frac{\partial \ln x_2}{\partial T}\right)_{p_2} = -\left(\frac{\partial \ln x_2}{\partial \ln p_2}\right)_T \left(\frac{\partial \ln p_2}{\partial T}\right)_{x_2} = \frac{-\bar{H}_2}{RT^2}$$

since the nitrogen obeys Henry's law in these very dilute solutions and therefore $(\partial \ln x_2/\partial \ln p_2)_T = 1$. The values in Table I yield $\bar{H}_2 = -140$ cal. in perfluoro-*n*-heptane and -260 cal. in perfluorodimethylcyclohexane. These values are small and obviously subject to considerable percentage error.

A few remarks may be added concerning the point mentioned above, that of stretching a theory based upon mixing liquids to cover the solubility of a gas above its critical temperature. First it would be quite possible to go back to an early step in the derivation of Eqn. 1 where the potential energy of a liquid mixture relative to its two gaseous components is expressed in terms of the liquid structure, and to subtract therefrom only the potential energy of the pure liquid solvent, which would give an expression for the partial molal energy of the solution of the gas. Its free energy of solution at the equilibrium pressure and composition is of course zero. If we had a satisfactory expression for the entropy of solution of the gaseous component, the problem would be solved, but unfortunately we have not been able to express the entropy of this process as satisfactorily as we have the entropy of mixing two liquids to form a regular solution.

Acknowledgment.—We express our gratitude to Dr. J. M. Tinker, Director of the Jackson Laboratory, E. I. du Pont de Nemours Co., for the substituted perfluoro-cyclohexanes used in this research, and to the Office of Naval Research for financial support.

Summary

1. Values for the solubility of nitrogen have been determined, expressed as Bunsen coefficient. In *n*-perfluoroheptane, 0°, 0.411; 25°, 0.385; 50°, 0.360; perfluoromethylcyclohexane, 25°, 0.375; perfluorodimethylcyclohexane, 25°, 0.328; 50°, 0.317; *n*-hexane, 25°, 0.239; cyclohexane, 25°, 0.156; benzene, 25°, 0.124; carbon disulfide, 25°, 0.0823.

The above data are tabulated with existing data for six other solvents and it is shown that the order of solubility, expressed as mole fraction, closely parallels the order of the "solubility parameters," defined as the square roots of their energies of vaporization per cc.

3. The solubility equation for regular solutions, with a semiempirical adjustment of its parameters, yields calculated values in fair agreement with the experimental ones, except in the case of the fluorocarbons, where the experimental values are larger. This discrepancy is attributed to the unusually large molal volumes of these solvents because it is considerably reduced by introducing a correction of the Flory–Huggins type.

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[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY, PITTSBURGH, PENNSYLVANIA]

Ultraviolet Absorption Study of the Ionization of Substituted Phenols in Ethanol

BY NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR.

It is well known that the ultraviolet absorption spectra for the anions or cations of many polar substituted aromatic materials are markedly different from the spectra obtained for the compounds themselves. The spectra of the ions generally exhibit a large bathochromic shift of the absorption ascribed to the phenyl ring chromophore. In addition the intensity of absorption is increased. Since the spectral shift is large, often of the order of 20 mμ or larger, it provides a method whereby dissociation constants may be determined. Ordinarily these cannot be calculated from the spectrophotometric data alone but depend also on separately determined values of *p*H or on previously determined equilibrium constants which are pertinent to the processes involved.

In this manner Stendstrom and co-workers[1,2] demonstrated that the shift of the phenol spectrum induced by the addition of sodium hydroxide is due to the creation of the phenolate ions. From their data they obtained a value of the dissociation constant for phenol. Using the same procedure, Flexser, Hammett and Dingwall[3] calculated the ionization constants for benzoic acid, 2,4-dinitrophenol and acetophenone. More recently Ewing and Steck[4] have utilized this phenomenon in studies of the acidic and basic properties of quinolinols and isoquinolinols. Similar studies were made of various 4-aminoquinolines by Irvin and Irvin.[5]

The present studies are of the substituted phenols. The substituted phenols may be divided into three classes according to their steric hindrance to inter-molecular hydrogen bonding.[6] Phenols with the ortho positions either unsubsti-

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[1] W. Stendstrom and M. Reinhard, *J. Phys. Chem.*, **29**, 1477 (1925).

[2] W. Stendstrom and N. Goldsmith, *ibid.*, **30**, 1683 (1926).

[3] L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2103 (1935).

[4] G. W. Ewing and E. A. Steck, *ibid.*, **68**, 2181 (1946).

[5] J. L. Irvin and E. M. Irvin, *ibid.*, **69**, 1091 (1947).

[6] N. D. Coggeshall, *ibid.*, **69**, 1620 (1947).