

the separation of charge in the activated complex is not great. This is confirmed very nicely by studying the effect of adding small amounts of polar substances and of salts on the rates in a non-polar solvent. Such addition has a very great influence on the equilibrium constant for primary amines and virtually none for tertiary amines presumably because of interaction with the excess acidic protons in the former case.⁴

Table III shows a comparison of the increases in rate in benzene caused by small additions of ethanol, or tosylate salts, and the corresponding changes in the equilibrium constants for reaction 2. The much smaller changes in the rates show that the transition state while polar is not strongly so.

In view of this it is surprising that triethylamine does not show up as a stronger catalytic base in all of the solvents and, particularly the more basic ones. In these cases the relative weakness of tertiary amines, as judged by equilibrium studies, was attributed to solvation of the excess acidic protons of the primary and secondary ammonium ions. Such effects should be smaller in the rate studies as demonstrated above.

The additional complicating factor seems to be that of steric hindrance in the rate studies (of the F-strain type). The tosylate compound is much more blocked toward proton removal than nitroethane, for example. Thus in 50% dioxane-water trimethylamine reacts twice as rapidly with the tosylate compound as does triethylamine even

TABLE III
THE EFFECTS OF ADDING SMALL AMOUNTS OF ALCOHOL AND SALTS TO BENZENE AT 25° ON $B + \text{RHOTs} \xrightarrow{k} R + \text{BH}^+ \text{OTs}^-$

B	Mole % ethyl alcohol	$k(M^{-1} \text{ hr.}^{-1})$	K^a
n-Hexylamine	0.00	2.19	53 ^b
	4.20	8.08	1600 ^b
Triethylamine	0.00	3.18	2700 ^b
	4.20	3.11	2700 ^b
Added n-hexylammonium <i>p</i> -toluenesulfonate, <i>M</i>			
n-Hexylamine	0.00	2.19	50
	3.06×10^{-3}	8.80	2300
Added di-n-butylammonium <i>p</i> -toluenesulfonate, <i>M</i>			
Di-n-butylamine	0.00	4.64	950
	4.80×10^{-3}	7.62	4500
	7.04×10^{-3}	7.88	..

^a Ion-pair formation constants using 2,4-dinitrophenol as reference acid. ^b In chloroform solvent. Very similar results would be expected in benzene.

though the latter is a ten times stronger base in water.³ With nitroethane as a substrate, triethylamine reacts 1.5 times as rapidly as trimethylamine. By this argument all of the rates for triethylamine in Tables I and II are low by roughly a constant factor because of steric strain in the transition state.

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Solubility, Entropy and Partial Molal Volumes in Solutions of Gases in Non-polar Solvents

BY J. E. JOLLEY AND J. H. HILDEBRAND

RECEIVED AUGUST 13, 1957

A critical review of such gas solubilities as appear to be sufficiently reliable for our purposes reveals the following relations. (a) For a given gas at 1 atmosphere and 25° dissolving in a series of solvents, $\log x_2$ ($x_2 \equiv$ mole fraction of gas) decreases with increasing solubility parameter, δ_1 , of the solvent. (b) For different gases in the same solvent, $\log x_2$ increases linearly with increasing Lennard-Jones force constant, ϵ/k , of the gas. (c) The entropies of solution of different gases in the same solvent vary linearly with $R \ln x_2$, and extrapolate at $x_2 = 1$ to the entropy of condensing to pure liquid the vapor of the solvent from a hypotheticalal pressure of 1 atmosphere. The temperature coefficient of solubility may thus be obtained from its isothermal value. Solubility increases with temperature for common solvents when x_2 is less than about 10^{-3} , and *vice versa*. (d) The partial molal entropy of solution of any one gas from 1 atmosphere to the same mole fraction (here 10^{-4}) is nearly the same in all solvents except fluorocarbons, where it is a little greater. In any one solvent, it increases in going to gases with smaller force constant. This is attributed mainly to increase in freedom of motion of the adjacent molecules of the solvent rather than to change in the behavior of the gas molecule in a "cage." Partial molal volumes of hydrogen, deuterium and argon have been determined in a variety of solvents. The results accord with the above interpretation.

Progress toward a satisfactory theory of gas solubility has been difficult because of the inaccuracy of much of the published data and the failure to cover a range of temperature sufficient to yield figures for the entropy of solution. An outstanding exception has been the broad work of Horiuti,¹ published in 1931. The need for precise, comprehensive data has recently been partly met by Cook and Hanson² and by Cook, Hanson and Alder³ for

hydrogen and deuterium, and by Reeves and Hildebrand⁴ for argon. Clever, Battino, Saylor and Gross⁵ have kindly put at our disposal in advance of publication their results for helium, neon, argon and krypton. We can utilize, further, data by Lannung⁶ for helium, neon and argon in two sol-

(1) J. Horiuti, *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, No. 341, **17**, 125 (1931).

(2) M. W. Cook and D. N. Hanson, University of California Radiation Laboratory Report, UCRL 2459 (1954); *Rev. Sci. Instr.*, **28** (1957).

(3) M. W. Cook, D. N. Hanson and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957).

(4) L. W. Reeves and J. H. Hildebrand, *THIS JOURNAL*, **79**, 1313 (1957).

(5) H. L. Clever, R. Battino, J. H. Saylor and P. N. Gross, *J. Phys. Chem.*, **61**, 1078 (1957).

(6) A. Lannung, *THIS JOURNAL*, **52**, 68 (1930).

vents; by Gjaldbaek and Hildebrand for nitrogen⁷ and chlorine⁸; by Gjaldbaek for carbon monoxide,⁹ oxygen⁹ and carbon dioxide¹⁰; and by Taylor and Hildebrand for chlorine.¹¹

Table I gives the figures for solubility that we select, expressed as mole fraction of gas, x_2 , at 1 atmosphere and 25°. Table II gives figures for the entropy of solution under the same conditions, obtained from the slopes of the lines of $\log x_2$ vs. $\log T$, and the reasonable assumption that Henry's law holds for such dilute solutions because solute-solute interactions are negligible. Gaps in these tables emphasize the need for additional data.

Solubility and Solubility Parameter of Solvent.—Figure 1 shows the relation of the solubility of each gas, plotted as $\log x_2$, to the solubility

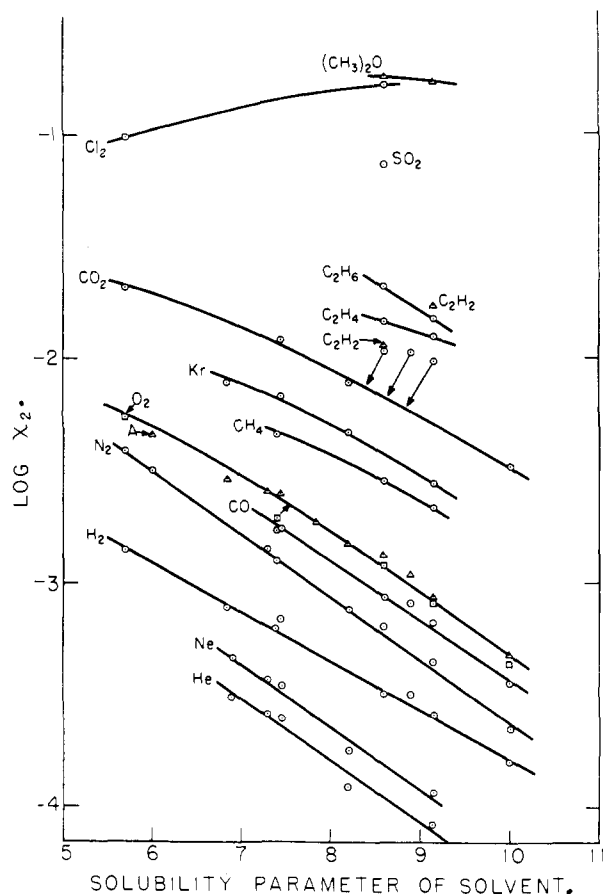


Fig. 1.

parameters of the solvents, δ_1 . We use mole fraction instead of concentration, as in an earlier paper,¹² for reasons that will later be apparent. This plot would permit a fairly good prediction of the solubility in a new solvent of any of the gases represented.

Such divergent points as the ones for C_2H_2 and CO_2 in C_6H_6 indicate chemical effects, acid-base

(7) J. C. Gjaldbaek and J. H. Hildebrand, *THIS JOURNAL*, **71**, 3147 (1949).

(8) J. C. Gjaldbaek and J. H. Hildebrand, *ibid.*, **72**, 609 (1950).

(9) J. C. Gjaldbaek, *Acta Chem. Scand.*, **6**, 623 (1952).

(10) J. C. Gjaldbaek, *ibid.*, **8**, 1398 (1954).

(11) N. W. Taylor and J. H. Hildebrand, *THIS JOURNAL*, **45**, 682 (1923).

(12) J. H. Hildebrand, *J. Phys. Chem.*, **58**, 671 (1954).

interaction in these cases. The reversal of slope in going to the more soluble gases is in harmony with the fact that the molecular force field, of, say, chlorine, is nearer to that of carbon tetrachloride than to the field of a fluorocarbon.

Solubility and Force Constant of Gas.—In Fig. 2 are plotted values of $\log x_2$ for many cases in the three solvents for which we have the most data vs.

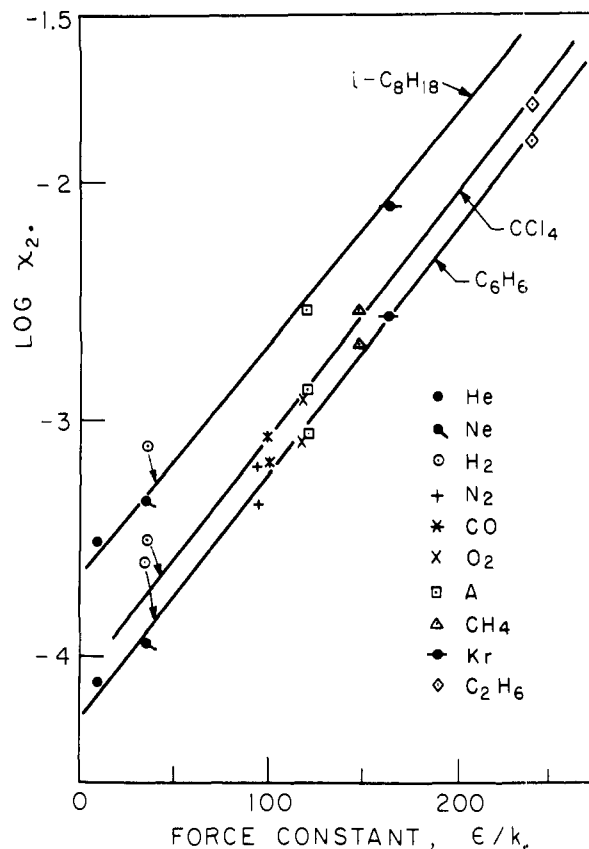


Fig. 2.

the Lennard-Jones force constants of the gases, ϵ/k , as given by Hirschfelder, Curtis and Bird.¹³ It will be seen that the correlation, except in the case of hydrogen, is excellent. It would appear possible to predict the solubility of another gas in any of these solvents with good approximation. The displacement of the lines corresponds to the solubility parameters of the solvents.

Solubility and Entropy of Solution.—Figure 3 is a plot of the entropy of solution, $\bar{S}_2 - s_2^g$, from gas at 1 atmosphere to solution at the equilibrium concentration, x_2 , against $R \ln x_2$. It shows a remarkably close correlation for different gases in the same solvent, except for the small displacement of the line for the hydrocarbon gases, and relates the solubility of a gas to its temperature coefficient in a particular solvent.

Descent along a line corresponds to changing to a gas more like the solvent in force constant, ending at $R \ln x_2 = 0$ for the solvent itself. The entropy of condensing carbon tetrachloride vapor at 25°

(13) J. O. Hirschfelder, C. F. Curtis and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York, N. Y., 1954, p. 1110.

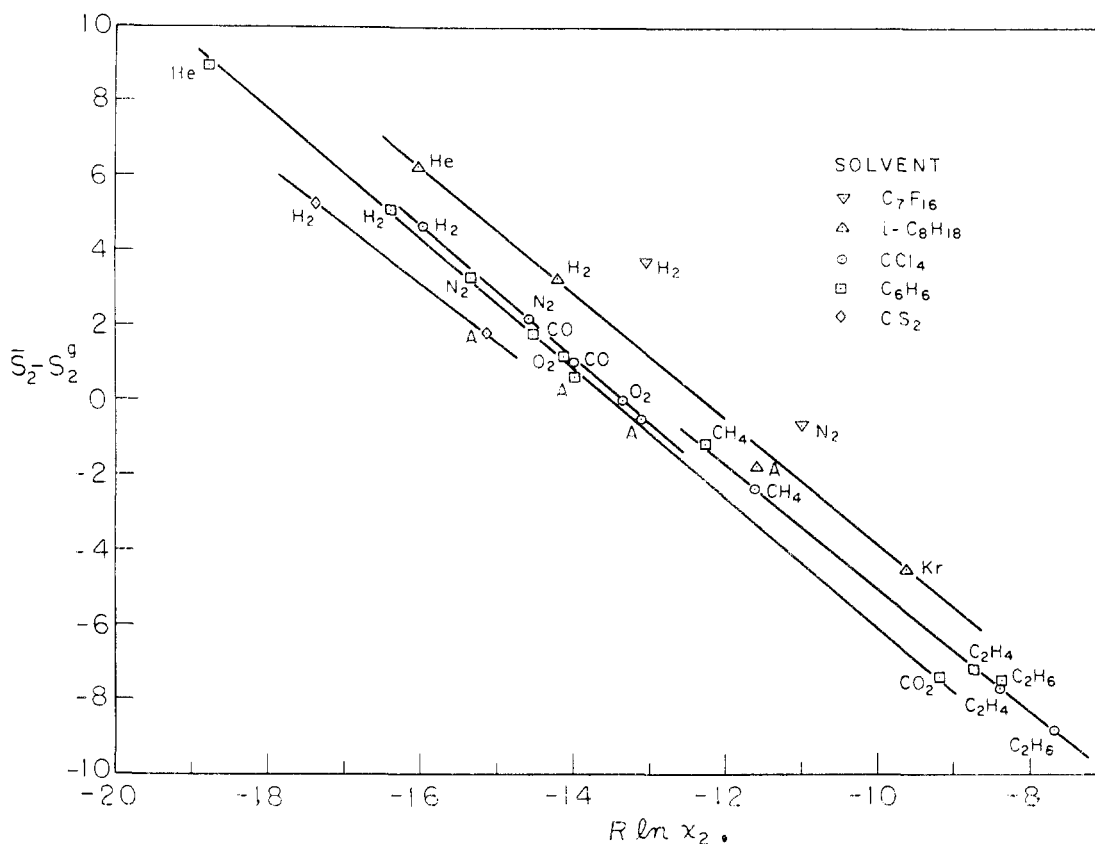


Fig. 3.

and 115.3 mm. is -26.3 e.u.; from hypothetical vapor at 1 atmosphere this would be -22.5 e.u., agreeing remarkably well, in view of the long extrapolation, with the intercept of the CCl_4 line at $R \ln x_2 = 0$, which is -24.1 e.u. The agreement is equally good for benzene.

The long-puzzling question of the temperature dependence of gas solubilities is answered by reference to Fig. 3. The entropy of solution in benzene, for example, is positive for any gas for which $x_2 < 8.9 \times 10^{-4}$; its solubility would therefore increase with temperature. The reverse is true when $x_2 > 8.9 \times 10^{-4}$.

Entropy of Transferring Gas at 1 Atmosphere into Solutions at Same Mole Fraction.—Reeves and Hildebrand⁴ pointed out that the greater entropy of solution of argon in a poorer solvent is mainly the result of the additional entropy of dilution, and that the differences largely disappear if argon at 1 atmosphere is transferred into different solvents at the same mole fraction, 10^{-4} . The entropy of dilution from x_2 for gas at 1 atmosphere to 10^{-4} is equal, according to Henry's law, to the entropy of expanding the gas from 1 atmosphere to $x_2/10^{-4}$ atmospheres, which is $R \ln 10^4 x_2$. Table III gives representative values calculated by adding this term to corresponding values given in Table II. The gases and solvents are arranged, as in Table I, in order of increasing force constants and solubility parameters, respectively. One sees that the figures for any one gas in different solvents do not differ significantly, except in the fluorocarbons, where they are distinctly larger, but that they fall off

horizontally from left to right for different gases in the same solvent, in accord with their rapidly increasing force constants. The significance of these relations is discussed below.

Partial Molal Volumes.—The obvious connection between entropy of solution and partial molal volumes¹⁴ made it desirable to have reliable values of the latter quantity for some of the solutions considered in our survey.

(a) **Materials.**—Argon gas was used directly from a cylinder of Linde "Standard Grade" Argon. A mass spectrographic analysis showed it to be 99.7% argon. The hydrogen and deuterium were 99.7 and 99.4% pure, respectively. Isooctane was a Phillips "pure" product, dried with anhydrous magnesium perchlorate and fractionated through a 15-plate column. J. T. Baker "purified" bromoform was dried over calcium chloride and distilled twice over argon. The remaining solvents were purified as described previously by Reeves and Hildebrand.⁴

(b) **Apparatus and Procedure.**—The apparatus was essentially that devised by Horiuti¹ and consisted of a gas buret connected by a loop of glass capillary tubing to the dilatometer immersed in a well-stirred thermostat, whose temperature was kept constant to within $\pm 0.001^\circ$. The dilatometer consisted of a bulb of approximately 140-ml. capacity entered at the lower end by two calibrated capillary side arms (about 2 cu. mm./cm.). One arm is connected to the gas buret and the other is led upward and left open to atmospheric pressure. Mercury in the bottom of the dilatometer serves to isolate the solvent in the bulb and also indicates its volume by the position of the mercury threads in the sidearms. Sealed into the bulb was a small glass enclosed piece of soft iron which could be agitated from outside by means of a magnet.

(14) Cf. J. H. Hildebrand and R. I. Scott, *J. Chem. Phys.*, **20**, 1520 (1952); J. H. Hildebrand and D. N. Glew, *J. Phys. Chem.*, **60**, 616 (1956); L. W. Reeves and J. H. Hildebrand, *ibid.*, **60**, 949 (1956).

TABLE I
 SOLUBILITY OF GASES, 10^4x_2 , AT 25° AND 1 ATM. PARTIAL PRESSURE

	δ_1	ϵ/k	He 10	Ne 35	H ₂ 37	N ₂ 95	CO 100	O ₂ 118	A 121	Kr ~165	CO ₂ ~200
<i>n</i> -C ₇ F ₁₆	6.0				14.01 ³	38.77	38.8 ⁹	55.3 ⁹			209 ¹⁰
<i>c</i> -C ₆ F ₁₁ CF ₃	6.1					32.77			46.0 ⁴		
<i>i</i> -C ₈ H ₁₈ ^a	6.85	3.10 ⁵	4.6 ⁵		7.82 ³				29.2 ⁵	78.8 ⁵	
<i>n</i> -C ₆ H ₁₄	7.3	2.60 ⁵	3.7 ⁵			14.07			25.3 ⁵		
(C ₂ H ₅) ₂ O	7.4				6.27 ¹	12.47 ¹	16.8 ¹	19.3 ¹			
<i>n</i> -C ₇ H ₁₆	7.45	2.49 ⁵	3.5 ⁵		6.88 ³		17.3 ⁹		25.0 ⁵	67.6 ⁵	121 ¹⁰
<i>c</i> -C ₆ H ₁₁ CH ₃	7.85								18.55 ⁴		
<i>c</i> -C ₆ H ₁₂ (Cyclohexane)	8.2	{ 1.21 ⁵ 1.22 ⁹	{ 1.80 ⁵ 1.81 ⁶			7.55 ⁷			14.9 ⁵ 14.8 ⁶	46.7 ⁵	77 ¹⁰
CCl ₄	8.6				3.19 ³	6.39 ¹	8.63 ¹	12.0 ¹	13.44 ⁴		107 ¹⁰
C ₆ H ₅ CH ₃	8.9				3.17 ³		8.15 ⁹		10.95 ⁴		105 ¹⁰
C ₆ H ₆	9.15	{ 0.78 ⁵ 0.77 ⁹	{ 1.1 ⁵ 1.15 ⁶		2.58 ³	4.42 ¹	6.63 ¹	8.15 ¹	8.77 ⁵	27.3 ⁵	97 ¹⁰
CS ₂	10.0				1.59 ³	2.23 ⁷	3.60 ⁹	4.42 ⁹	4.87 ⁴		33 ¹⁰
	ϵ/k	CH ₄ 148	C ₂ H ₆ 185	C ₃ H ₈ 200	C ₄ H ₁₀ 240	SO ₂ 252	Cl ₂ ~300 977 ⁸	(CH ₃) ₂ O			
<i>n</i> -C ₇ F ₁₆											
(C ₂ H ₅) ₂ O		45.3 ¹									
CCl ₄		28.4 ¹	115 ¹	145 ¹	208 ¹	727 ¹	1650 ¹¹	1790 ¹			
C ₆ H ₆		20.7 ¹	173 ¹	123 ¹	148 ¹			1707 ¹			

^a 2,2,4-Trimethylpentane.

 TABLE II
 ENTROPY OF SOLUTION OF GASES AT 25° AND 1 ATM. PARTIAL PRESSURE

	He	Ne	H ₂	N ₂	CO	O ₂	A	Kr	CO ₂
<i>n</i> -C ₇ F ₁₆			3.7	-0.6					
<i>c</i> -C ₆ F ₁₁ CF ₃							-1.5		
<i>i</i> -C ₈ H ₁₈		3.7	3.3				-1.8	-4.5	
<i>n</i> -C ₆ H ₁₄	6.2						-1.8		
(C ₂ H ₅) ₂ O			3.9	1.2					
<i>n</i> -C ₇ H ₁₆	6.2	4.4	3.5				-1.0	-4.2	-7.9
<i>c</i> -C ₆ H ₁₁ CH ₃							-0.9		
<i>c</i> -C ₆ H ₁₂	8.1			2.1			- .6	-2.8	
CCl ₄			4.6	2.1	1.0	0.0	- .5		
C ₆ H ₅ CH ₃			4.2				.4		
C ₆ H ₆	8.9		5.1	3.3	1.8	1.2	.6	-1.6	-7.4
CS ₂			5.3				1.8		
		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	Cl ₂		
<i>n</i> -C ₇ F ₁₆							-11.5		
(C ₂ H ₅) ₂ O		-2.7							
CCl ₄		-2.4	- 7.8		-7.7	-8.8		-12.7	
C ₆ H ₆		-1.2	-10.3		-7.2	-7.5			

 TABLE III
 THE ENTROPY OF TRANSFER OF GASES FROM 1 ATMOSPHERE
 INTO SOLUTION AT $x_2 = 10^{-4}$ AND 25°

	He	H ₂	D ₂	N ₂	A	Cl ₂
C ₇ F ₁₆		8.9	8.8	6.6		2.2
<i>c</i> -C ₆ F ₁₁ CF ₃					6.1	
<i>c</i> -C ₆ H ₁₁ CH ₃					4.8	
<i>c</i> -C ₆ H ₁₂	8.6				4.8	
CCl ₄		6.9	6.8	5.8	4.7	2.0
C ₆ H ₅ CH ₃		6.5	6.4		5.2	
C ₆ H ₆	8.5	7.0	6.9	6.3	4.9	
CS ₂		6.2	5.9		5.0	

The solvent was thoroughly degassed by boiling for two hours, then sucked directly into the evacuated dilatometer. After being connected to the gas buret and allowed to come to equilibrium in the thermostat, the initial number of moles of gas in the gas buret was determined from six readings of its pressure and volume and simultaneously the heights of the mercury threads at different pressures read with a telescope. One or more doses of from 2 to 5 cc. of

gas were pushed over into the solvent bulb and dissolved rapidly upon gentle agitation with the magnetic stirrer, the readings being repeated after each absorption of gas. To eliminate errors due to changing atmospheric pressure and apparent compressibility of solvent, glass and mercury, the volume expansion of each system was plotted against the pressure acting on the solvent and interpolated at 760 mm.

(c) Results are given in Table IV. The numbers in parentheses represent the number of successive additions of gas in one run. In all but a few cases, which were rejected, the plots of volume of solution against moles of gas dissolved gave straight lines, whose slopes give values of the partial molal volume of the solute, \bar{v}_2 . The gas is so dilute in all these solutions that \bar{v}_2 is independent of x_2 . $\bar{v}_2 \cong kx_1^2$. Duplicate runs gave values differing in some cases as much as 2 cc. per mole; therefore, we give mean values rounded to two significant figures. We include two values for H₂ obtained by Horiuti, designated by (H).

Discussion.—It is to be seen that the partial molal volumes given in Table IV, like the entropies of solution to $x_2 = 10^{-4}$, are practically the same for each gas in all these solvents except the fluorocar-

TABLE IV
PARTIAL MOLAL VOLUMES, CC. MOLE⁻¹, 25°

	H ₂	D ₂	A
<i>n</i> -C ₇ F ₁₆	54(3)	54(4)	
<i>c</i> -C ₈ F ₁₁ CF ₃			51(5)
<i>i</i> -C ₈ H ₁₈			50(5)
<i>c</i> -C ₉ H ₁₁ CH ₃			44(5)
CCl ₄	38(H)		44(5)(2)
C ₆ H ₅ CH ₃	36(4)(2)	35(3)	45(5)(3)(2)(3)
C ₆ H ₆	35(4)	34(3)	
	36(H)		
CS ₂			45(6)(6)
CHBr ₃			44(4)

bons and *i*-C₈H₁₈. The increase is strikingly large in the case of H₂. It is evident, therefore, that the entropy of solution is mainly determined by the dilution, in terms of *mole fraction*, not *volume fraction*, necessary to balance the enthalpy. This confirms our recent findings for iodine dissolved in solvents of widely different molal volumes.¹⁵

We interpret the differences in volume and entropy between different gases and solvents as follows. We reiterate, first, a point all too easily forgotten, namely, that what we commonly designate as a partial molal quantity of the *solute* is in reality what takes place in the *system* when a differential amount of solute is added. In the case of solutions so dilute as those here considered, these changes represent what happens in the immediate neighborhood of the solute gas molecules. These have low attractive fields and small volumes but possess the same kinetic energy as the molecules of solvent, hence the latter gain added volume and freedom of motion, the greater the smaller their force fields, such as they would gain at the surface of a bubble. Although \bar{V}_2 is a little larger for argon than for hydrogen in CCl₄, this must be attributed mainly to its greater molecular size. Its volume per mole

(15) K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **61**, 789 (1957).

from its second virial coefficient is 49 cc., whereas that of hydrogen is 32 cc.¹³ The solvent around a molecule of hydrogen approaches more nearly to the state of a bubble than that around a molecule of argon.

The force constants of the gases represented in Tables III and IV are much greater than the range in the solubility parameters of the solvents, hence the changes in entropy going horizontally in Table II, from one gas to another, are much larger than those going vertically, from solvent to solvent. The values of \bar{V}_2 for H₂ and D₂ in Table IV are so nearly the same as to fall within the experimental uncertainty, but they differ in the right direction to accord with the slight excess of entropy in the case of H₂.

This contribution to the entropy of solution accords also with the fact that, in going from gases with larger to those with smaller force constants, the entropy increases faster than ideal as given by $-R \ln \alpha_2$. The lines in Fig. 3 have slopes of about -1.6 instead of -1.0.

We believe that these findings support an opinion often expressed by the senior author¹⁶ that lattice models are not strictly appropriate for liquid solutions. A gas molecule is not oscillating in a cage with a definite frequency and then jumping to a new lattice site, but is rather participating with its solvent neighbors in a "random walk" with infinitesimal steps.

The relations revealed in the foregoing survey invite detailed theoretical study and reconciliation with our treatment of liquid-liquid solutions, but they are of such practical use and so suggestive as to model for theoretical treatment that we content ourselves provisionally with this presentation.

We express our gratitude to Dr. Berni J. Alder for helpful discussions during the course of this investigation, and to the Atomic Energy Commission for its support.

(16) J. H. Hildebrand, *Disc. Faraday Soc.*, **15**, 9 (1953).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Infrared Spectrum, Vibrational Assignment and Spectroscopic Entropy of Carbonyl Chloride¹

BY EDWARD CATALANO AND KENNETH S. PITZER

RECEIVED SEPTEMBER 16, 1957

It had been believed, from correlation with fluorine and sulfur substituted analogs of carbonyl chloride, that the lowest frequency fundamental lay in the 220-240 cm.⁻¹ region. A search in the far infrared has failed to reveal the existence of this band. It is shown, by means of the "Matrix Isolation" method, that the gas phase 575 cm.⁻¹ band consists of two almost accidentally degenerate vibrational modes of different symmetry species. This leads to a new vibrational assignment with a calculated spectroscopic entropy which is almost in agreement with the calorimetric entropy, thus removing what has hitherto been regarded as a major third law discrepancy.

Introduction

The infrared and Raman spectra of phosgene have been investigated by a number of workers,²⁻⁴

of which the Nielsen⁴ work is the most recent and complete. In these investigations, only five of the six fundamentals were observed. These are at

(1) This research was assisted by the American Petroleum Institute through Research Project 50.

(2) R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **5A**, 285 (1937).

(3) C. R. Bailey and J. B. Hale, *Phil. Mag.*, **25**, 98 (1938).

(4) A. H. Nielsen, T. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952).