A value of 1.59 at 301° is obtained by averaging the separation factors and temperatures in the higher temperature range. This is a little lower than 1.67, the value obtained by extrapolating the data of Suess[9] to this temperature. Since the steam formed near the exit of the reaction tube remained in contact with the iron only a very short time, complete equilibrium would be unlikely.

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KNOXVILLE, TENNESSEE

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

The Solubility and Entropy of Solution of Argon in Five Selected Non-polar Solvents

BY L. W. REEVES AND J. H. HILDEBRAND

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The solubility of argon in five non-polar solvents with different solubility parameters has been measured over a sufficient temperature range to yield reliable values of the entropy of solution. The results for solubility in mole % and entropy of solution at 1 atm. and 25° are as follows: $C_6F_{11}CF_3$, 0.4600, −1.5; $C_6H_{11}CH_3$, 0.1855, −0.9; CCl_4, 0.134, −0.5; $C_6H_5CH_3$, 0.1095, +0.4; CS_2, 0.0487, +1.8. For the entropy of dissolving argon at 1 atm. and 25° into its solutions at the same mole %, 0.0100, the respective figures are 6.1, 4.8, 4.7, 5.15 and 5.0. They vary much more widely when calculated to equal volume concentration. The variation of solubility with temperature depends mainly upon the dilution necessary to balance the effects of intermolecular forces.

It is becoming increasingly evident that the considerable success of regular solution theory in accounting for equilibrium relationships in non-electrolyte solutions results from the fact that discrepancies between the actual entropy of solution and our expressions for it are more or less balanced by corresponding discrepancies for the enthalpy of solution. Our predictions of isothermal solubility are therefore much more reliable than those of its temperature dependence. The solubility of bromine in f-heptane, that we reported recently,[1] serves as a striking example. It is evident that there is still much to be learned about entropy of solution, and the work hereinafter described is directed to that end. We select solutions of gases in liquids instead of liquids in liquids because mixing liquids is equivalent to vaporizing one pure component, expanding the vapor and then condensing into the solution, where unknown factors involved in the first and third steps may partly cancel and thus escape attention. An additional advantage is that one may work with very dilute solutions, where solute–solute interaction is practically absent, and Henry's law is closely obeyed.

We have used solvents with a wide range of intermolecular forces, and we plan to extend the project to include the gases hydrogen, nitrogen, argon, carbon tetrafluoride and sulfur hexafluoride, in order to cover a range of molecular mass and size. Data from these laboratories for hydrogen and deuterium[2] are in press. We are also obtaining figures for partial molal volumes of the solute gases.

Materials.—Linde "Standard Grade" argon was found by spectroscopic analysis to be 99.9% pure. Since the main impurity was air, whose solubility is not very different from that of argon, it seemed unnecessary to try to correct for its presence. The f-methylcyclohexane was from the stock purified by Glew and Reeves.[3] "Spectro-grade" methylcyclohexane was passed through silica gel dried for several days at 250°. "Reagent Grade" carbon disulfide and carbon tetrachloride were shaken with mercury after standing over P_2O_5. All solvents were distilled in a vacuum-jacketed 15-plate column at a reflux ratio of 15:1. The densities at 25° and boiling points of the treated solvents were as follows: toluene, 0.8623, 110.60 ± 0.01°; carbon tetrachloride, 1.5845, 76.52 ± 0.05°; methylcyclohexane, 0 76505, 100.9 ± 0.05°; carbon disulfide, 1.2558, 46.41 ± 0.05°; f-methylcyclohexane, 1.7878, 76.14°.

Procedure.—The apparatus was that of Cook and Hanson,[4] with a few modifications. The gas is measured repeatedly at various pressures in a 20-cc. buret, and then admitted to the thoroughly degassed solvent, confined over mercury. The whole apparatus is then rocked by a motor-driven cam. After shaking for about 5 minutes, the residual gas is admitted to a secondary buret of about 1-cc. capacity with a calibrated capillary, where its volume and pressure are measured. The process is repeated until the amount of residual gas does not change. Changes in barometric pressure often occur more rapidly than the equilibrium can follow, therefore a manostat was used, consisting of a 12-liter bulb mounted in a thermostat controlled to 0.001°.

The temperature control of the original apparatus was replaced by a contact thermometer and relay box. The gas handling system of Cook and Hanson was replaced by a conventional all glass system.

Results.—The results are given in Table I, expressed as mole fraction of gas, x_2 in the solution at 1 atm. and a series of temperatures.

The data in Table I are plotted in Fig. 1 as log x_2 *vs.* log T. The slopes of these (slightly curved) lines at 298.15°K. plotted on large scale, multiplied by the gas constant, R, give the entropies of solution shown in Table II together with the smoothed out values of x_2 at 25°. The figures for CCl_4 at 25° are extrapolated. They are to be directly determined later.

Lannung[5] measured the solubility of argon in two non-polar solvents, cyclohexane and in benzene. His values recalculated as mole fraction are included in Table II for 25°, and plotted over his range of temperature in Fig. 1. The scatter of the points is such as to prevent calculation of the entropy of solution with the desired accuracy.

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(1) L. W. Reeves and J. H. Hildebrand, *J. Phys. Chem.*, **60**, 949 (1956).

(2) M. W. Cook, D. N. Hanson and B. J. Alder, *ibid.*, in press.

(3) D. N. Glew and L. W. Reeves, THIS JOURNAL, **60**, 615 (1956).

(4) (a) M. W. Cook and D. N. Hanson, *Rev. Sci. Instr.*, in press; (b) University of California Radiation Laboratory—2459 report (1954).

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

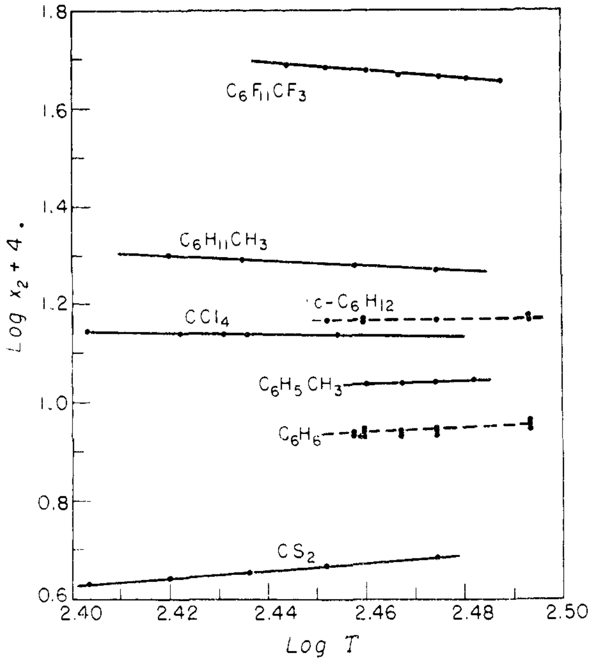

Fig. 1.—Solubility of argon.

Discussion.—The entropy of solution of argon increases rapidly in the solvents in Table II from top to bottom, but this is mainly the effect of increasing dilution. In the last column of the table we give the entropy of transferring argon at 1 atm. to solution at a dilution of $x_2 = 10^{-4}$, computed from the change in gas pressure required to reduce the solubility to $x_2 = 10^{-4}$. One sees that the values, except for $C_6F_{11}CF_3$, are close to 5 e.u. at equal mole fractions. This is not true if compared at equal molal concentrations. It is evident that the slopes of the curves in Fig. 1 are determined mainly by the degree of dilution necessary for equilibrium; the poorer the solvent, the larger the entropy of solution and the greater the temperature coefficient of solubility. There are also, however, additional contributions to the entropy of solution such as the one connected with the different partial molal volumes of the gas, to be reported in a forthcoming paper, and the properties of different gases, as we shall show by comparing the entropy of solution of argon, nitrogen and hydrogen.

TABLE I

SOLUBILITY OF ARGON AT 1 ATM. AND T°K. IN MOLE FRACTION × 10^{-4}

T, °K.	10^4x_2	Run	T, °K.	10^4x_2	T, °K.	10^4x_2
$C_6H_5CH_3$			$C_6F_{11}\cdot CF_3$		$C_6H_{11}\cdot CH_3$	
288.23	10.882	a	278.09	48.709	262.90	19.888
288.22	10.875	b			272.53	19.433
			283.06	47.999	286.75	18.872
293.04	10.918	b	283.10	47.965	298.14	18.543
293.03	10.921	a				
			288.36	47.234	CS_2	
297.87	10.963	a			253.13	4.272
297.87	10.949	b	293.08	46.625	262.76	4.391
297.86	10.943	b	293.17	46.634	273.22	4.513
297.88	10.955	a	293.18	46.689	283.14	4.654
298.20	10.950	b	293.19	46.623	298.14	4.866
303.31	10.982	b	298.48	45.962	CCl_4	
303.31	10.995	a			252.98	13.976
			303.16	45.470	264.18	13.809
			307.86	44.978	269.83	13.736
					272.65	13.697
					284.29	13.669

TABLE II

MOLE FRACTION, x_2 AND ENTROPY OF SOLUTION OF ARGON FROM GAS AT 1 ATM. AND 25° (a) TO x_2, MEASURED; (b) TO $x_2 = 10^{-4}$

Solvent	δ_1	10^4x_2	$\bar{S}_2 - S_2{}^g$ (a)	(b)
$C_6F_{11}CF_3$	6.0	46.00	−1.50	6.1
$C_6H_{11}CH_3$	7.85	18.55	−0.9	4.8
$c\text{-}C_6H_{12}$	8.2	14.8[a]	0	~5
CCl_4	8.6	13.4	−0.5	4.7
$C_6H_5CH_3$	8.9	10.95	+0.4	5.15
C_6H_6	9.15	8.85[a]	~1	~4.8
CS_2	10.0	4.87	1.8	5.0

[a] A. Lannung.

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BERKELEY, CAL.

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

Kinetics of the Pyrolysis of Ethyl Bromide[1]

BY ARTHUR EDWARD GOLDBERG AND FARRINGTON DANIELS

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The kinetics of the reaction $C_2H_5Br(g) \rightarrow C_2H_4 + HBr$ has been investigated between 310 and 476°, by determining the HBr formed by chemical analysis. The effects of surface and added gases have been studied. The primary step gives C_2H_4 and HBr directly with an activation energy of about 52 kcal. mole^{-1}, but the hydrogen bromide reacts at the surface with ethyl bromide producing a steady state of bromine atoms which give a faster reaction. The over-all reaction is first order and is given by the expression $k = 6 \times 10^{11} e^{46,400/RT}$ sec.$^{-1}$ but it is not a simple unimolecular reaction. Rate equations and a mechanism are given.

The decomposition of ethyl bromide $C_2H_5Br \rightarrow C_2H_4 + HBr$ at elevated temperatures was originally chosen as a first-order, gas-phase reaction, suitable for the study of chemical kinetics. As suc-