Solubility of Carbon Dioxide, Krypton, and Xenon in Aqueous Solution

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The solubility of carbon dioxide, krypton, and xenon has been measured at 1 Atm. total pressure and at temperatures of 25, 30, 37, and 45° in distilled water, 0.9 per cent sodium chloride, and .066 M phosphate buffer solution at pH 7.0. The solubility of the gases studied in aqueous solution decreased as the temperature increased. Heats and entropies of solution have been calculated according to Eley's equation (16). The relation between $\Delta S°$ and $\Delta H°$ at various temperatures is exactly linear in every case, and the slope is approximately equal to $1/T$.

THE SOLUBILITY of krypton and xenon in water has been measured by many investigators (1–5,9). However, the results reported in the literature are not in agreement. The present study was undertaken to obtain more precise solubility coefficient data needed for calculation of body fat in a living body from the equilibration of these gases in the body. The solubility of carbon dioxide in water and normal saline has also been measured in order to test the apparatus and technique employed.

EXPERIMENTAL

Materials.—Research grade carbon dioxide, krypton, and xenon were purchased from the Matheson Co. According to their specifications, carbon dioxide contained maximum possible impurities of 0.3% of nitrogen or carbon monoxide and oxygen; krypton contained maximum possible impurities of 0.04% nitrogen and oxygen; xenon contained maximum possible impurities of 0.02% nitrogen and 0.05% krypton. No further analysis for the purity of the gases was made. No correction was applied to the experimental data obtained for the impurity of the gases.

The water used was redistilled from glass apparatus.

Sodium chloride solution (0.9%) and .066 M sodium phosphate buffer solution at pH 7.0 were made by weighing a proper amount of analytical grade salt and dissolving it in distilled water. The pH of the phosphate buffer solution was adjusted by using a Beckman model GS pH meter.

Apparatus and Manipulation.—The solubility apparatus used was essentially the one previously described (6), except that the absorption flask (125 ml.) did not have a mercury sealing cup, and a few drops of water were added to the gas buret to saturate the gas with water vapor before an experiment was conducted.

Degassing of Solution.—The absorption flask was charged with about 100 ml. of freshly boiled solution assembled on the solubility apparatus, frozen in a low temperature bath, evacuated, then boiled in a warm water bath. This process was repeated three times. The saturation of the solution with the gas was done essentially by the procedure previously described (6). The weight of the solution was determined at the conclusion of the experiment.

The densities and vapor pressures of distilled water were found in the literature (7). The densities of sodium chloride and phosphate buffer solution were determined in the usual way, their vapor pressure data being taken from the literature (8) and extrapolated between the concentrations.

RESULTS AND DISCUSSION

The solubility of carbon dioxide, krypton, and xenon in distilled water, 0.9% sodium chloride solution, and .066 M phosphate buffer solution at pH 7.0 were measured at 1 Atm. total pressure and temperatures of 25, 30, 37, and 45°. Each solution was measured three or four times. The standard deviation of each measurement closely approximated ±1.0% from the values reported in Tables I, II, and III. Possible systematic errors of those measurements would be predominantly due to the barometric pressure reading, which was assumed to have ±0.2 mm. error, and the temperature, which was assumed to have ±0.05° error. Therefore, the volume of the absorption flask calibrated by filling with a known volume of air might have ±0.034-ml. difference. Also, if the densities of the solution had an error of 1×10^{-4}, there would be ±0.01-ml. difference in volume for a 100-ml. solution. In terms of Ostwald coefficient, it would make a difference of about ±0.0005. Therefore, for the large solubility of carbon dioxide and xenon in water, it would cause approximately an 0.2% deviation, and for the smaller solubility of krypton, it would cause a 1% deviation from other investigators' values.

The results obtained from those measurements, in terms of Ostwald solubility coefficient, are presented in Tables I, II, and III. The literature values taken were reduced in terms of Ostwald solubility coefficient for uniform comparison. The data obtained from present studies agree well with the results of Morrison and Johnstone (4) and are considerably lower than those of Valentiner (2) and Antropoff (1). The solubility of carbon dioxide, krypton, and xenon in normal saline and in phosphate buffer solution at pH 7 was less than in pure water. The de-

TABLE I.—SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS

Soln.	Temp., °C.	Ostwald Solubility Coefficient	Lit. Value	$-\Delta H$ cal./mole	$-\Delta S$ cal./deg./mole
Distilled water	45	0.5453	0.558[a]	3912	20.0
	37	0.6282	0.638[a]	4310	21.3
	30	0.7264	0.738[a]	4657	22.4
	25	0.8129	0.828[a]	4906	23.2
0.9% NaCl	45	0.5100	...	3923	20.2
	37	0.5876	...	4322	21.2
	30	0.6800	...	4670	22.6
	25	0.7576	...	4919	23.4

[a] See *Reference 7*.

TABLE II.—SOLUBILITY OF KRYPTON IN AQUEOUS SOLUTION

Soln.	Temp., °C.	Ostwald Solubility Coefficient	Lit. Value	$-\Delta H$ cal./mole	$-\Delta S$ cal./deg./mole
Distilled water	45	0.0441	0.0441[b]	2337	20.0
	37	0.0481	0.0511[c]	3250	22.9
	30	0.0539	0.0540[b]	4037	25.5
			0.0566[a]		
	25	0.0581	0.0611[a]		
			0.0582[b]	4603	27.4
0.9% NaCl	45	0.0411	...	1957	19.0
	37	0.0444	...	3181	22.9
	30	0.0499	...	4252	26.4
	25	0.0542	...	5017	28.9
Phosphate	45	0.0417	...	2941	22.0
	37	0.0462	...	3369	23.4
	30	0.0516	...	3744	24.6
	25	0.0558	...	4012	25.5

[a] See *Reference 2*.   [b] See *Reference 3*.   [c] See *Reference 5*.

TABLE III.—SOLUBILITY OF XENON IN AQUEOUS SOLUTION

Soln.	Temp., °C.	Ostwald Solubility Coefficient	Lit. Value	$-\Delta H$ cal./mole	$-\Delta S$ cal./deg./mole
Distilled water	45	0.0737	...	2946	20.9
	37	0.0827	...	4045	24.4
	30	0.0958	0.0108[a]	5006	27.6
			0.0934[b]		
	25	0.1068	0.1195[a]	5692	29.9
0.9% NaCl	45	0.0680	...	3729	26.6
	37	0.0778	...	4158	24.9
	30	0.0895	...	4533	26.1
	25	0.0976	...	4801	27.0
Phosphate	45	0.0688	...	3585	23.1
	37	0.0782	...	3977	24.3
	30	0.0893	...	4320	25.4
	25	0.0990	...	4566	26.3

[a] See *Reference 2*.   [b] See *Reference 4*.

creased solubility of the gas in the sodium chloride and sodium phosphate solutions was essentially the same (8%). The decrease in the solubility of the gas in aqueous solution is due to the "salting out" effect of the electrolytes in the solution as reported by previous investigators (19).

Effect of Temperature on Solubility.—The solubility of carbon dioxide, krypton, and xenon in aqueous solution decreased as temperature was raised (Tables I, II, and III). The relation between the solubility and temperature fitted the equations of Valentiner (2), Horiuti (10), and Kobatake and Hildebrand (11) very well, but did not fit the Clapeyron equation, *i.e.*, linear relationship between logarithm β and $1/T$. Lanning (12), who measured the solubility of rare gases in water and organic solvents, found that the solubility of gas in organic solvents fitted the Clapeyron equation very well,

but not that of gas in water. Clever, *et al.* (18), also reported that the relation between temperature and the solubility of rare gases in organic solvents fitted the Clapeyron equation very well, and that their solubility increased as temperature increased. The decrease in gas solubility in an aqueous system as temperature is raised is due to modification of water structure as the gas atoms dissolve. The change is in the direction of greater crystallinity of water structure, as pointed out by Frank and Evans (13)—the water builds a microscopic "iceberg" around the gas atoms. As the temperature is raised, these "icebergs" melt, and the amount of gas trapped in the water is decreased. Similarly, Pauling stated that the nonhydrophilic molecules—krypton, xenon, etc., are trapped in clathrate structure, which he called krypton hydrate, xenon hydrate, etc. (14). The decrease of gas solu-

bility in normal saline and phosphate buffer is probably due to the effect of electrolytes which decrease in "icebergs" forming or clathrate tendencies.

Free Energy, Heats, and Entropies of Solution.— Lange and Watzel (15), Eley (16), and Bulter (17), using the gas-solubility data of Valentiner, have calculated the heats and entropies for the solution of rare gases in water. Eley plotted both the values of $\Delta H°$ and $T\Delta S°$ against T giving straight lines of slope $R(B-1)$. Lange and Watzel have derived values of $\Delta H°$ and $\Delta S°$ similar to Eley's and observed their strong dependence on temperature. Bulter calculated the values of $\Delta S°$ and $\Delta H°$ at 25° and found that there is a linear relation between the heats and entropies of solution. The $\Delta H°$ and $\Delta S°$ values presented in Tables I, II, and III were calculated according to the equations derived by Eley (16). Plotting the values of $\Delta H°$ and $T\Delta S°$ against T gave straight lines of slope $R(B-1)$. Plotting $\Delta S°$ against $\Delta H°$ also gave straight lines of slope approximately equal to $1/T$ (3.3 × 10⁻³). Those plots showed that the data fitted the following equation well:

$$T\left(\frac{\partial \Delta S}{\partial T}\right)_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p$$

Although ΔC_p can be calculated from the straight lines plot of either $\Delta H°$ or $T\Delta S°$ against T, this method is a very insensitive one.

SUMMARY

The solubility of carbon dioxide, krypton, and xenon has been measured at 1 Atm. total pressure and at temperatures of 25, 30, 37, and 45° in distilled water, 0.9% sodium chloride, and .066 M phosphate buffer solution at pH 7.0.

The solubility of the gases studied in aqueous solution decreased as the temperature increased.

Heats and entropies of solution of carbon dioxide, krypton, and xenon have been calculated. The relation between $\Delta S°$ and $\Delta H°$ at various temperatures is exactly linear in every case, and the slope is approximately equal to $1/T$.

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Synthesis of N-Methyl-1,3-dimethylbutylamine

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A procedure has been described for the preparation of N-methyl-1,3-dimethylbutylamine from methyl isobutyl ketone and methylamine. The method involves low pressure hydrogenation of ketimine in the presence of platinum catalyst.

RELATIVELY low molecular weight organic compounds with one or more electronegative atoms—such as nitrogen or oxygen—can dissolve salt-free water without losing their identity to a separate phase. The solvent then releases the purified water during a slight temperature increase. In view of the interesting physical properties of N-ethyl-n-butylamine and N-methyl-n-amylamine (1, 2), similar secondary amines seem worthy of study. This paper describes the synthesis of N-methyl-1,3-dimethylbutylamine.

EXPERIMENTAL

N-Methyl-1,3-dimethylbutylamine.—Methylamine (31 Gm., 1 mole) was dissolved in 385 Gm. absolute ethanol; the solution was chilled in ice. Methyl isobutyl ketone (300 Gm., 3 moles) was added dropwise, and the resulting solution slowly generated heat which was removed by additional cooling. This was divided into approximately four equal quantities. These were reduced catalytically over 8 Gm. of 10% platinum-on-charcoal at a maximum pressure of 60 p.s.i. The total amount of hydrogen absorbed corresponded to 99.5% of the theoretical quantity. After removing the catalyst by filtration, the filtrate was added to an excess of dilute hydrochloric acid at a temperature below 20°. The acidic solution was then concentrated to a small volume to remove ethanol, methyl isobutyl ketone, and any other volatile product. After making the acidic solution basic with an excess of aqueous sodium hydroxide, the water insoluble layer was removed, and the water layer was extracted four times with ether. The combined water-insoluble layers were dried over potassium hydroxide pellets and finally over calcium hydride. The ether solution was distilled carefully through a 28 × 1-in. metal helices-packed column from a small quantity of calcium hydride to yield 78.9 Gm. (69% on the basis of methyl amine employed) of N-methyl-1,3-dimethyl-butylamine, b.p. 122 to 122.5°, n_D^{20} 1.4131, d_4^{20} 0.7458, MR_D (calcd.) 38.53, MR_D (obs.) 38.13.

Anal.—Calcd. for $C_7H_{17}N$: C, 72.97; H, 14.87; N, 12.16. Found: C, 72.95; H, 15.01; N, 12.19.

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