

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 ΔH° and $T\Delta S^\circ$ against T giving straight lines of slope $R(B-1)$. Lange and Watzel have derived values of ΔH° and ΔS° similar to Eley's and observed their strong dependence on temperature. Bulter calculated the values of ΔS° and ΔH° at 25° and found that there is a linear relation between the heats and entropies of solution. The ΔH° and ΔS° values presented in Tables I, II, and III were calculated according to the equations derived by Eley (16). Plotting the values of ΔH° and $T\Delta S^\circ$ against T gave straight lines of slope $R(B-1)$. Plotting ΔS° against ΔH° 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 ΔH° or $T\Delta S^\circ$ 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 dis-

tilled 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 ΔS° and ΔH° 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 the methyl amine employed) of *N*-methyl-1,3-dimethylbutylamine, 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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