

polar broadening; a large enough magnetic moment and isotopic abundance to give observable absorption; at least a moderate atomic number so there are measurable changes in magnetic shielding with compound; and, finally, chemical properties such that enough compounds are available for a more or less empirical analysis. Nuclei meeting these requirements are F^{19} , P^{31} and H^1 , in decreasing order on a rough, over-all basis. On the other hand, of the nuclei unsuitable for magnetic shielding measurements because they have spins greater than $1/2$, several have electric quadrupole moments of a convenient size for determining quadrupole coupling constants.² These include the other halogens and nitrogen, with the latter of particular interest in connection with electron distribution in double

bonds. So either the nuclear magnetic or quadrupole radiofrequency spectrum can be observed for a considerable number of nuclei, and thereby a wide variety of problems in molecular electronic distribution can be investigated.

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[CONTRIBUTION FROM ILLINOIS STATE WATER SURVEY]

Solubilities and Structures in Aqueous Aliphatic Hydrocarbon Solutions

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A microcombustion method was developed for detecting hydrocarbons in water. This method was utilized for determining solubilities of methane, ethane, propane and *n*-butane. Calculated heats of solution are interpreted in terms of the hypothesis of iceberg formation around the solute hydrocarbon molecule. The pentagonal dodecahedron and pentagonal-hexagonal 14- and 16-hedra are considered as models for the solution icebergs of methane, ethane and propane, respectively.

The solubilities of methane and ethane in water had been first reported by Bunsen² and by Schickendantz³ and later with greater precision by Winkler.⁴ The method of solubility determination was a physical one, in which a volume of gas was measured, a sample of water was saturated with this gas and finally the amount of gas which did not dissolve was measured. Single solubility determinations of propane and *n*-butane at 17° are reported.^{5,6} In this investigation a chemical method of solubility determination is described, which consists in removing the dissolved hydrocarbon with oxygen, burning and weighing the resultant carbon dioxide.

The purpose of this investigation was first to develop this microcombustion method of solubility determination, then to check some of the values in the literature and to determine some unreported solubilities, and finally to interpret these data in regard to solution structure. It seemed especially important to check some of the earlier solubility data, using another method than originally employed, because these data occupied such a pivotal position in the theoretical deductions concerning water solutions.⁷ The reported temperature coefficients of solubility indicated that methane and ethane dissolve in water with a liberation of heat; further, the entropies of solution in water calculated from these heats of solution are much more negative than in corresponding non-aqueous solutions.

Frank and Evans have postulated an ice formation which surrounds the dissolved hydrocarbon molecules in order to explain the existing thermal data. Some of these same gases which exhibit such anomalous effects in solution also form a new and once-puzzling type of hydrate, puzzling because little attractive force is known to exist between these gas molecules and water.^{8,9} After the solubility work of this paper was completed, the structures of these inert gas hydrates were proposed by Claussen.¹⁰ The character of these structures has proven¹¹ to be as suspected, that the water molecules in these hydrates are in an arrangement energetically almost equivalent to that found in ordinary ice, while, in addition, the arrangement in the hydrate contains some void spaces, much larger than those in ordinary ice, in which spaces are entrapped the inert molecules. The suggestion that these water structures surrounding the voids in the hydrates are the same water structures which constitute the icebergs in the inert gas solutions is made in this paper.

Experimental Details.¹²—The procedure of hydrocarbon solubility determination involved a modified microcombustion technique. The main components of the micro train and technique, as described by Niederl and Niederl,¹³ were

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(13) J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 101-137.

(1) Corning Glass Works, Corning, New York.

(2) R. Bunsen, *Ann.*, **93**, 1 (1855).

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(4) L. W. Winkler, *Ber.*, **34**, 1408 (1901).

(5) M. P. Lebeau, *Bull. soc. chim. France*, [3] **33**, 1139 (1905).

(6) M. P. Lebeau, *Chem. Zentr.*, **79**, II, 292 (1908).

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used. The chief modification involved the aeration of the water solution sample with prepurified oxygen and passing this gas directly into the combustion zone. The train was composed of the following elements, in order: oxygen tank, pressure regulators, mercury manometer, preheater, absorption U-tube containing ascarite and anhydrous, aerator (Fig. 1, B), combustion tube containing copper oxide at 700°, weighing tubes containing ascarite and anhydrous, and finally, the Mariotte flask. Some minor changes from the standard micro train included the following: using a mercury manometer to measure oxygen pressures up to about 10 cm., the pressure usually required to pass the oxygen through the sintered glass disc in the aerator; weighing only the CO tube; omitting the heating mortar containing lead peroxide, since no nitrogen compounds were used with the train; passing about 250 cc. of oxygen through the solution, this being well over the experimentally determined minimum of 150 cc. for the quantitative removal of methane by aeration. Preparation of the saturated solution involved bubbling the hydrocarbon gas through doubly-distilled water for about two hours, fine bubbles of about 1 mm. diameter being produced by a sintered glass filter (Fig. 1, A).

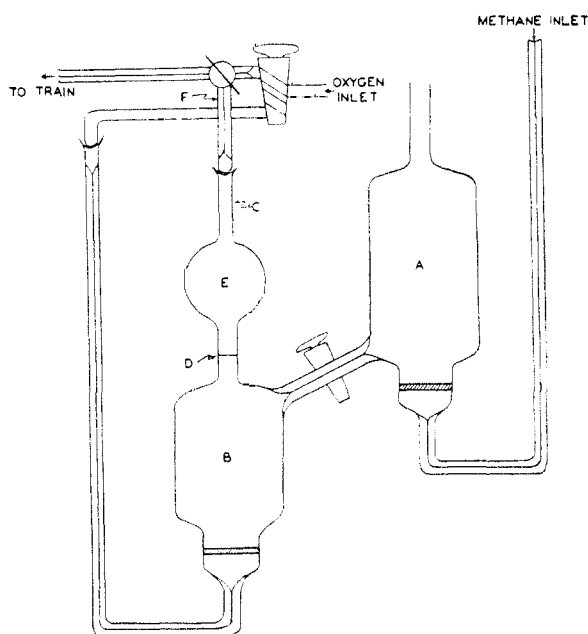


Fig. 1.—Saturator-aerator.

The transfer of the saturated solution was made into the calibrated volume B, filling being made to level D. Bulb E (25 cc.) was supplied to provide adequate mixing of excess oxygen and hydrocarbon. After aeration, this volume E was displaced into train with hydrocarbon-free water from A.

The hydrocarbons used in this work were as follows: methane, 99.7% with nitrogen the greatest impurity by mass spectrometer, from Phillips Petroleum Co.; ethane, 99.9%, with no detectable impurity by infrared, from Phillips; propane and *n*-butane, 99%, from Ohio Chemical Company.

The solubility data obtained on the four hydrocarbons in water are given in Table I. The methane and ethane data check those of Winkler⁴ quite closely. Propane and *n*-butane solubility data differ markedly from the single values reported by Lebeau.^{5,6} Detailed data on each run indicate a reproducibility within at least 1%. These data were not corrected for the slight impurities in the gas or for the saturating bubble size.

The partial molal heats of solution at 25°, given in Table II, were calculated by the formula

$$\log_{10} \frac{\alpha_2}{\alpha_1} = \frac{\Delta \bar{H}_{sol}}{2.3R} (1/T_1 - 1/T_2)$$

where α is the solubility and T is the absolute temperature. Plots of $\log \alpha$ versus $1/T$ (not shown here) for methane and ethane form slightly curved loci of points, this curvature indicating that the heat of solution is not strictly a constant

TABLE I

SOLUBILITIES (α) OF HYDROCARBONS IN WATER

α is the vol. of gas at 0° and 760 mm. dissolved in one vol. water at 760 mm. hydrocarbon pressure and temp. given in table.

Temp. °C.	α (Winkler)	α (this work, av.)	α (individual values)		
Methane					
1.6	0.05307	0.0547	0.0552,	0.0542	
2.0	.05244	.0538	.0542,	.0538,	0.0532
10.5	.04124	.0428	.0425,	.0429,	.0428
			.04316,	.04251	
19.8	.03322	.0351	.03488,	.03521,	.03509
30.4	.02753	.0289	.02886,	.02897	
39.6	.02383	.0255	.02542,	.02563	
Ethane					
1.5	0.09284	0.0937	0.0931,	0.0946,	0.0934
10.5	.06444	.0655	.0655,	.0657,	.0652
17.5	.05081	.0527	.0527		
19.8	.04751	.0496	.0490,	.0499,	.0499
29.8	.03641	.0375	.0374,	.0374,	.0375
			.0376		
39.7	.02934	.0307	.0306,	.0307,	.0308
Propane					
19.8	.065 (17°) ^b	0.0394	0.0395,	0.0395,	0.0397,
			.0392,	.0394,	.0393
29.80288	.0288,	.0289	
<i>n</i> -Butane					
19.8	.15 (17°) ^b	0.0327	0.0321,	0.0333,	0.0330
			.0326,	.0325	
29.80233	.0230,	.0236,	.0233,
			.0234,	.0230	

TABLE II

HEATS AND ENTROPIES OF SOLUTION

Standard states are taken the same as by Frank⁷: liquid, mole fraction of solute = 1; gas, $p = 760$ mm.

Hydrocarbon	$\Delta \bar{H}_{sol}, 25^\circ$	$\Delta \bar{S}^\circ, 25^\circ$
Methane	-3052	-31.2
Ethane	-3983	-33.6
Propane	-5700	-40.0
<i>n</i> -Butane	-6000	-41.4

over the temperature range from 0–40°. The partial molal entropies of solution, also given in Table II, were calculated by the equation

$$\Delta \bar{S}^\circ = \frac{\Delta \bar{H}_{sol}}{298^\circ \text{K.}} + 2.3R \log_{10} N_2$$

where N_2 is the mole fraction of the hydrocarbon solute in the water solution.

Discussion of Results.—The large negative entropies of solution of the gases in water are in agreement with those previously found. The interpretation in terms of ice formation, in which the water molecules which enter into the solute complex are in a more ordered state than those in the bulk of the liquid, appears to be the only plausible explanation. The discoveries of the structures of the inert gas hydrates enables one to suggest similar, plausible structures for the solution icebergs, since both the solution and the hydrate phases exhibit ice-like thermal effects on formation. On the basis of the hydrate structural work,¹⁰ the assignment of the iceberg structures, given in Table III, were made. In these structures, the

water molecules occupy the corners of the polyhedra and the inert hydrocarbons occupy the void space inside. The angle formed by any three water molecules attached by hydrogen bonds is always close to the tetrahedral angle found between the water molecules in ordinary ice: the structures are thus considered to be in a fairly stable configuration, the central hydrocarbon molecule preventing the structure from collapse into a liquid water structure. The highly ordered state of these icebergs could account for the large negative entropies of solution.

TABLE III

Note: The justification for assigning the iceberg structures below is at present only by analogy, since no X-ray data are yet available on the structures of any of these hydrates. The molecules, corresponding in size to methane, ethane and propane, whose hydrates have been studied and found to conform to the above iceberg description, are hydrogen sulfide, methyl chloride and chloroform, respectively.

Dissolved hydrocarbon	Polyhedral structure ¹⁰ of iceberg	Description of polyhedral faces
Methane	Dodecahedron	12 Pentagons
Ethane	14-Hedron	12 Pentagons + 2 hexagons
Propane	16-Hedron	12 Pentagons + 4 hexagons

n-Butane cannot fit into this simple iceberg picture so easily, because no hydrate of butane appears possible,⁹ though it does aid in the formation of other hydrocarbon hydrates. It can be assumed that *n*-butane is too big to remain comfortably in the largest of the voids, the 16-hedron. The iceberg structure surrounding *n*-butane may be the 16-hedron part of the time and still another unknown structure for the remaining time.

The solubility data for methane and ethane were fitted to an equation of the type

$$\log_{10}\alpha - \frac{\Delta C_p}{R} (\log_{10}T) = - \frac{\Delta \bar{H}_0}{2.3R} (1/T) + \text{constant}$$

where ΔC_p is a constant in the equation

$$\Delta \bar{H}_T = \Delta \bar{H}_0 + T\Delta C_p$$

$\Delta \bar{H}_T$ is the partial heat of solution at $T^\circ\text{K}$. and $\Delta \bar{H}_0$ is a constant of integration. The term ΔC_p , as usually defined, is the difference between the heat capacities of the products of a reaction (solution) and the heat capacities of the reactants (pure water and hydrocarbon gas). The values of ΔC_p as calculated are 51.5 and 65.1 cal./mole. deg. for methane and ethane, respectively. The unusual fact about these values is that they are higher than the absolute heat capacities of either pure reactant. A possible explanation of this experimental fact is that the ice shell surrounding the hydrocarbon molecule is stretched or blown up as a balloon as the temperature is raised, and this work of stretching the hydrogen bonds of the structure is the main contribution to the high ΔC_p . This explanation, which has been summarily called melting,⁷ is especially interesting in view of the high heat capacity of liquid water, which phenomenon has also been attributed to a continuation of the melting process and to the breaking of hydrogen bonds. In the case of liquid water, infrared absorption data in the 3μ region indicate that as the temperature is raised, a gradual, not an abrupt, transition takes place,¹⁴ in which the behavior of the liquid molecules approaches that of the vapor molecules, there being no complete rupture of a few hydrogen bonds which would give the free OH 2.76 μ absorption. Thus, the high heat capacity of water may also be accounted for by the work of stretching and deforming the hydrogen bonds.

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