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by the proper molecular weight. The V and α values are comparatively more accurate to the figure described, because density-temperature relations of most of the liquids mentioned are given in the I.C. Tables.

It will be seen that despite the approximations used in computing the data, the liquids bifurcate neatly into two classes. From the variation of $E\chi/V\alpha$ for associated liquids, it can be seen that its magnitude depends not upon the strength of associations (carboxylic acids have much greater strength of association than water), but upon the amount of abnormal behavior of a liquid. It has already been shown that the abnormal behavior of an associated liquid depends not upon the strength of an association, but rather upon its weakness and extensiveness.

Mercury turns out to be an 'associated liquid,' but as it is a metallic liquid it cannot be discussed in the same class as the other organic molecular liquids.

The formula has more than passing interest, and its theoretical implications will be discussed in another paper.

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Microwave Spectrum and Structure of Isothiocyanic Acid*

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TO aid in the analysis of the complicated microwave spectrum of methyl isothiocyanate[1] a search for transitions of the simpler molecules HSCN and HNCS was made in the region from 19,000 to 30,000 mc/sec. Stark modulation apparatus[2,3] was used with a 10-foot wave guide absorption path of the acid vapor. Table I gives the absorption lines found for HNCS and its artificially enriched isotopic forms.

TABLE I. The absorption spectrum of isothiocyanic acid molecules.

Molecule	νmc/sec.
$HNC^{12}S^{32}$	23,464
$DNC^{12}S^{32}$	21,897
$HNC^{13}S^{32}$	23,389
$DNC^{13}S^{32}$	21,839
$HNC^{12}S^{34}$	22,915

The acid was prepared by gentle warming of a mixture of KSCN with H_3PO_4. The $HNC^{13}S$ was prepared from $KSC^{13}N$ obtained by fusing sulfur and $KC^{13}N$ containing 17 percent of C^{13}. The deuterium isotopes were made by the same processes, merely substituting D_3PO_4 for H_3PO_4.

In the preliminary analysis of the spectrum the assumption was made that the NCS group was linear and that, while the HNC angle differed from 180°, the molecule was very nearly a symmetric top. The symmetric Stark pattern

of two components gives strong support to this assumption and indicates that the observed spectral lines correspond to transitions from $J=1$ to $J=2$. Using the symmetric top approximation that ν cm$^{-1}=2C(J+1)$, four of the frequencies of the lines of the isotopic molecules enable one to solve for approximate values of the three interatomic distances and the $H-N-C$ angle, neglecting for the moment the effect of the zero-point vibrational energy on these parameters.

The solution for the structure HSCN results in quite unreasonable values of the bond distances and angle. The solution for the structure HNCS, however, yielded: $HN=1.2\pm0.1A$, $NC=1.21\pm0.01A$, $CS=1.57\pm0.01A$, and the angle $HNC=112°\pm10°$.

The NC and CS distances are intermediate between the values for double and triple bonds. The probable resonating structures are $H-N=C=S$, $H-N^+\equiv C-S^-$, and $H-N^--C\equiv S^+$. The CS distance is the same as in COS and CS_2. The NCS distances for HNCS compare well with those obtained by Goubeau and Gott[4] from Raman spectra of $NC=1.21A$ and $CS=1.575A$. The HNC angle of 112° compares with that of 111° obtained for the HNN angle of N_3H by Eyster.[5] The HN distance is larger than the 1.01A value in N_3H and NH_3 which may indicate partial ionic character of this bond.

The spectral analysis indicated that the vapor is principally isothiocyanic acid; HSCN if it exists in the vapor could not be present by more than 5 percent. Gallais and Voigt,[6] by measuring molecular magnetic rotations, conclude that the acid is isothiocyanic. Goubeau and Gott[4] also conclude that HNCS is the predominant form. The position and intensity of the very weak line at 22,915 mc indicate that it may be the HNCS^{34} line due to the natural 4 percent abundance of S^{34}.

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Measurement of Na$^+$ Ion Diffusion by Means of Radiosodium

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AN interesting application of the radioactive tracer technique is to the measurement of the diffusion of ions in solution. This approach was first made by Jehle,[1] who used Na^{24} and Cl^{38} to obtain ionic-diffusion constants in NaCl solutions. Similar work has been done by Schubert and others[2] on the Plutonium Project, and some preliminary studies have been described recently by Robinson

and Drew.[3] Such investigations are potentially of considerable fundamental importance since they constitute one of the few means of studying individual ion behavior.

The equation for the self-diffusion of an ion can be derived from the basic relationship: $\mathfrak{D} = -nw\partial\mu/\partial n$, where n is the moles per cc, w the mobility, and μ the chemical potential of the ion. On expressing mobility in terms of equivalent conductance and introducing the activity coefficient, it follows that for a monovalent ion

$$\mathfrak{D}(cm^2/sec.) = 8.97 \times 10^{-10}\lambda_+T(1+c\partial\ln\gamma_+/\partial c). \quad (1)$$

Using the limiting-law expression, $\log\gamma_+ = 0.508(c)^{\frac{1}{2}}$ (1) becomes:

$$\mathfrak{D}(cm^2/day) = 0.0231\lambda_+[1-0.583(c)^{\frac{1}{2}}] \text{ at } 25°C. \quad (2)$$

Equation (2) applies to the diffusion of a tracer in an otherwise uniform solution, and hence is much simpler than that of Onsager and Fuoss.[4] For example, it is not necessary to relate the net movement of the trace ions to that of the oppositely charged ions by the requirement of electro-neutrality, necessary when a bulk concentration gradient exists. Thus, under these circumstances, the differential diffusion coefficient for the ion is obtained, rather than the mean coefficient for the salt.

Another feature of tracer studies is that the measurements may be extended to smaller concentrations than has otherwise been possible (ca. 10^{-5}M).

Preliminary investigations have been carried out in this laboratory on the diffusion of Na$^+$ ion in NaI solutions at 25°C, using Na^{22} (3 yr.) as tracer.[5] The data were obtained by means of McBain-Northrup[6] type, sintered-glass diaphram cells which were calibrated by allowing 0.20 N HCl to diffuse into water. The mean diffusion constant for the HCl was taken to be 2.52 cm^2/day, from the data of James and Gordon.[7] Separate tests showed that the tracer sodium was in the same chemical state as the bulk Na$^+$. For the self-diffusion measurements, both compartments of the cell were filled with NaI solutions, identical except for tracer in the upper cell. The diffusion constant at each bulk NaI concentration was obtained from the amount of tracer present in the lower compartment after a given time. Radio-chemical analyses were made by evaporating aliquots on 1-in. watch glasses and counting by means of a mica-window tube and a scaling circuit.[8]

The results are shown in Fig. 1, where $\mathfrak{D}$ is plotted against $(c)^{\frac{1}{2}}$, and can be represented up to $c = 0.01$M by the equation:

$$\mathfrak{D} = \mathfrak{D}_0(1-1.40(c)^{\frac{1}{2}}), \quad \mathfrak{D}_0 = 1.24 \text{ cm}^2/day. \quad (3)$$

Where duplicate runs were made, the average deviation was about 1 percent, close to the practical limit set by the various counting errors.

To compare these results with (2), λ_+ must be evaluated as a function of concentration. This was done using the Onsager equation[9] for a 1:1 electrolyte at 25°C.

$$\lambda_+ = \lambda_+^0 - [0.221\lambda^0 + 29.9(c)^{\frac{1}{2}}],$$
$$\lambda_+ = 50.1[1-0.825(c)^{\frac{1}{2}}] \text{ for NaI.} \quad (4)$$
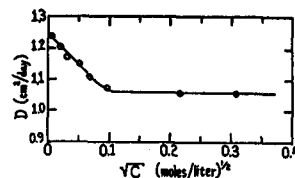
On combining Eqs. (2) and (4), the approximate relation-

FIG. 1. Diffusion coefficient of Na$^+$ in NaI solutions at 25°C.

ship is obtained:

$$\mathfrak{D}(cm^2/day) = 1.16[1-1.41(c)^{\frac{1}{2}}]. \quad (5)$$

The observed dependence on concentration is in satisfactory agreement with Eq. (5), but $\mathfrak{D}_0$ is about 7 percent greater than the theoretical value. A similar effect is apparent in Jehle's data.

It is planned to present results on I$^-$ diffusion rates in a later paper, together with a more complete discussion.

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A New Type of Micelle: Soap with Alcohol, Amine, or Other Polar-Nonpolar Molecules*

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A MEASURE of the thickness of the micelle of a colloidal electrolyte is the spacing d_M' derived from a newly recognized, x-ray diffraction M-band.[1] The unmodified Bragg spacing d_M for potassium caprate (10°C) is 31.7, for the laurate (12°C) 35.3, and for the myristate (14°C) 40.3A. For the corrected micelle thickness these Bragg spacings should be increased by perhaps 10 to 15 percent, but this modification is omitted here for simplicity. An aqueous solution of soap or colloidal electrolyte, when saturated with a hydrocarbon such as benzene, ethyl benzene, or n-heptane, shows a micelle thickness increased by as much as 12A (Table IA), which is presumably the thickness Δd_M of the oil layer. There is no evidence that the oil molecules *penetrate between* the hydrocarbon chains of the soap molecules in the double monolayer, since the area per soap molecule remains at 27A^2. Thus, hydrocarbons are apparently solubilized in the middle of the micelle between the ends of the hydrocarbon chains of the soap molecules.

The attraction between a hydrocarbon and water is increased if a terminal hydrogen atom is replaced by a hydroxyl group. For example, the energy of adhesion at 20°C between n-heptane and water is 41 ergs/cm^2 and the