

## A Formula to Detect Association in Liquids

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where  $A$  and  $B$  do not depend upon the applied potential gradient.

If the load acts in a steady manner, it may be assumed as a first approximation that the force tending to break a bond increases directly with the number of bonds which have already been broken. Consequently,  $f = f_0 + cN$ , where  $f_0$  is the force tending to break the bond when the load is first applied. Substituting this relation into Eq. (2), integrating, and assuming that when fracture takes place the number of bonds broken is large, there results

$$f_0 = D \log \coth Et \quad (3)$$

as the relation between the initially applied stress,  $f_0$ , and the time to fracture,  $t$ ;  $D$  and  $E$  are constants which may be expressed in terms of  $A$ ,  $B$ , and  $c$ . Through  $A$  and  $B$  the temperature dependence of the process may be studied.

For long times, Eq. (3) may be written:

$$f_0 = 2De^{-2Et}. \quad (4)$$

For short breaking times, the effect of the rate of loading is predominant, and the additional stresses in the remaining bonds due to the breaking of bonds may be neglected. Assuming that the rate of loading is constant,  $f$  may be expressed in the form

$$f = rt. \quad (4)$$

Substituting this into Eq. (2) and integrating leads to

$$t = (1/Br) \cosh^{-1}[(BrN_B/A) + 1],$$

$N_B$  being the number of bonds broken to bring about fracture. If the rate of loading is high and the first term in the parentheses large, this becomes approximately

$$t = (0/Br) \log Fr, \quad (5)$$

where  $F$  is a constant. This is a relation between the time to fracture,  $t$ , and the rate of loading,  $r$ . It is interesting to note that Eq. (5) also implies the temperature dependency of the process through the constant  $B$  and through  $F$ , which in turn depends on  $A$  and  $B$ . In a paper which the author expects to publish soon, the details and a comparison with experimental data will be given.

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<sup>1</sup> E. S. Machlin and A. S. Nowick, N.A.C.A. Tech. Note No. 1126 (September, 1946).

<sup>2</sup> Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

## A Formula to Detect Association in Liquids

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July 28, 1947

THERE are various formulas in literature which distinguish a normal liquid from an abnormal or associated liquid. In the following we present another such theory.

For normal liquids

$$E\chi/V\alpha = T,$$

and for associated liquids,

$$E\chi/V\alpha > T,$$

in which  $E$  is cohesive energy in ergs per mole, expressed as the latent heat of vaporization minus  $RT$ , and written positive.

$\chi$  is the isothermal compressibility in absolute units (barye<sup>-1</sup>),

$V$  is the molar volume in ccms,

$\alpha$  is the coefficient of cubical expansion, and

$T$  is the absolute temperature.

As an example, we compute the formulas at 20°C = 293°A. (See Table I.) The data for the liquids were mainly taken

TABLE I.  $E\chi/V\alpha$  for liquids.

No.	Liquid	$\frac{E}{\times 10^{-7}}$ ergs	$\chi$ $\times 10^{12}$	$V$	$\alpha$	$\frac{E\chi}{V\alpha}$
Class I						
1	Pentane	27000	200	114.9	.001589	295
2	Iso-pentane	25920	225	117.0	.001533	325
3	Hexane	31390	150	130.3	.001445	250
4	Heptane	35000	134	146.3	.00115	279
5	Octane	37620	121	162.4	.001124	249
6	Decane	48280	102	194.3	.000988	256
7	Ether	27010	200	104	.001656	310
8	Acetone	32016	100	73.5	.001487	292
9	Cyclohexane	31080	109	105.4	.00114	282
10	Cyclohexanol	50000	55	105.5	.000804	324
11	Carbon tetrachloride	32953	105	96.5	.001206	297
12	Chloroform	30989	100	80.2	.001254	308
13	Carbon disulphide	28138	75	60.3	.0011823	296
14	Ethylene chloride	33810	80	78.9	.00112	308
15	Ethylene bromide	42255	60	86.1	.000942	312
16	Methyl iodide	39110	56	62.2	.001273	276
17	Methyl acetate	33670	90	79	.00136	281
18	Ethyl bromide	29403	105	74.6	.00141	293
19	Ethyl iodide	31980	95	80.8	.001179	310
20	Ethyl formate	35558	75	80.2	.001378	241
21	Ethyl acetate	34359	113	97.9	.001359	292
22	Ethyl propionate	40800	98	115.0	.001344	264
23	Ethyl <i>n</i> -butyrate	46440	95	132.2	.001156	289
24	<i>n</i> -Propyl acetate	42840	100	115.1	.001214	306
25	Benzene	33883	92	89	.00124	282
26	Aniline	31080	44	84	.000855	265
27	Nitrobenzene	43970	54.5	105	.0008263	276
28	Chlorobenzene	42750	75	101.7	.0009967	316
29	Bromobenzene	58090	50	105	.00091505	302
30	<i>O</i> -Xylene	39220	75	118	.000973	257
31	<i>m</i> -Xylene	38160	85	122	.001009	274
32	<i>p</i> -Xylene	37600	80	124	.001011	240
33	Toluene	35420	92	106.3	.001099	279
34	<i>p</i> -Toluidine	46200	50	112.2	.0008681	259
Class II						
1	Methyl alcohol	37440	95	140	.001229	735
2	Ethyl alcohol	41860	90	98	.000739	520
3	<i>n</i> -Propyl alcohol	42600	90	75	.000956	533
4	<i>i</i> -Propyl alcohol	41400	100	75	.001094	493
5	<i>n</i> -Butyl alcohol	46620	99	91.4	.000950	488
6	<i>i</i> -Butyl alcohol	45880	93	103.6	.0009	458
7	<i>n</i> -Amyl alcohol	47520	85	110	.000907	403
8	Allyl alcohol	40600	80	70	.0001241	500
9	Glycol	50840	34	56	.0006375	484
10	Glycerine	924000	22	73	.000505	552
11	Formic acid	28520	55	37.7	.000999	416
12	Acetic acid	27600	98	56	.001065	454
13	<i>n</i> -Valeric acid	54129	90	108.8	.0009886	453
14	Mercury	5897934	3.4	14.81	.00018169	745
15	Water	41706	45.5	18.06	.0002097	5010

from International Critical Tables and tables of Landolt-Bornstein. Generally, a direct value of  $E$  and  $\chi$  at 20°C and one atmospheric pressure was not available, and a rough reduction was made simply by guessing. The absence of round figures in most of the  $E$  values does not indicate the order of accuracy attained, but that the reduction was made for a value per g and then the value was multiplied

by the proper molecular weight. The  $V$  and  $\alpha$  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  $E_X/V\alpha$  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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<sup>1</sup> R. Parshad, *J. Chem. Phys.* **14**, 348 (1946).

## Microwave Spectrum and Structure of Isothiocyanic Acid\*

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September 12, 1947

TO aid in the analysis of the complicated microwave spectrum of methyl isothiocyanate<sup>1</sup> 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<sup>2,3</sup> was used with a 10-foot wave guide absorption path of the acid vapor. Table I gives the ab-

TABLE I. The absorption spectrum of isothiocyanic acid molecules.

Molecule	$\nu$ mc/sec.
HNC <sup>13</sup> S <sup>32</sup>	23,464
DNC <sup>13</sup> S <sup>32</sup>	21,897
HNC <sup>13</sup> S <sup>34</sup>	23,389
DNC <sup>13</sup> S <sup>32</sup>	21,839
HNC <sup>13</sup> S <sup>34</sup>	22,915

sorption lines found for HNCS and its artificially enriched isotopic forms.

The acid was prepared by gentle warming of a mixture of KSCN with H<sub>3</sub>PO<sub>4</sub>. The HNC<sup>13</sup>S was prepared from KSC<sup>13</sup>N obtained by fusing sulfur and KC<sup>13</sup>N containing 17 percent of C<sup>13</sup>. The deuterium isotopes were made by the same processes, merely substituting D<sub>3</sub>PO<sub>4</sub> for H<sub>3</sub>PO<sub>4</sub>.

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  $\nu$  cm<sup>-1</sup> =  $2C(J+1)$ , 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 =  $1.2 \pm 0.1$  Å, NC =  $1.21 \pm 0.01$  Å, CS =  $1.57 \pm 0.01$  Å, and the angle HNC =  $112^\circ \pm 10^\circ$ .

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<sup>+</sup>≡C-S<sup>-</sup>, and H-N<sup>-</sup>-C≡S<sup>+</sup>. The CS distance is the same as in COS and CS<sub>2</sub>. The NCS distances for HNCS compare well with those obtained by Goubeau and Gott<sup>4</sup> from Raman spectra of NC = 1.21 Å and CS = 1.575 Å. The HNC angle of  $112^\circ$  compares with that of  $111^\circ$  obtained for the HNN angle of N<sub>3</sub>H by Eyster.<sup>5</sup> The HN distance is larger than the 1.01 Å value in N<sub>3</sub>H and NH<sub>3</sub> 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,<sup>6</sup> by measuring molecular magnetic rotations, conclude that the acid is isothiocyanic. Goubeau and Gott<sup>4</sup> 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<sup>34</sup> line due to the natural 4 percent abundance of S<sup>34</sup>.

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<sup>1</sup> C. I. Beard and B. P. Dailey, paper presented at the Am. Chem. Soc. meeting in New York, September 15, 1947.

<sup>2</sup> R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.* **71**, 562 (1947).

<sup>3</sup> B. P. Dailey, *Phys. Rev.* **72**, 84 (1947).

<sup>4</sup> J. Goubeau and O. Gott, *Ber.* **73B**, 127 (1940).

<sup>5</sup> E. Eyster, *J. Chem. Phys.* **8**, 135 (1940).

<sup>6</sup> F. Gallais and D. Voigt, *Comptes Rendus* **210**, 104 (1940).

## Measurement of Na<sup>+</sup> Ion Diffusion by Means of Radiosodium

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July 29, 1947*

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,<sup>1</sup> who used Na<sup>24</sup> and Cl<sup>38</sup> to obtain ionic-diffusion constants in NaCl solutions. Similar work has been done by Schubert and others<sup>2</sup> on the Plutonium Project, and some preliminary studies have been described recently by Robinson