COMMUNICATIONS TO THE EDITOR

THERMAL PROPERTIES OF ISOPENTANE[1]

Sir:

Several years ago some work from the Cryogenic Laboratory of this School[2,3,4] reported hysteresis effects in the determination of the liquid heat capacities and vapor pressures of isopentane (2-methylbutane). This effect was attributed to a slow change with temperature of the rotational isomeric composition of the liquid. Guthrie and Huffman[5] did not observe such effects in their independent determination of the heat capacities of this hydrocarbon.

It was decided to postpone further work on the heat capacity until this compound was investigated as part of a contemplated study of rotational isomerism by means of Raman spectroscopy in the Department of Physics of this School. The Raman spectroscopic study of this compound over a range of temperatures has now been completed.[6] In the course of this work the relative intensity changes of two Raman lines, assumed to be caused by a change in the rotational isomeric composition of the liquid, were measured over the temperature range 310–120°K. If the above-mentioned hysteresis effects were real it would be expected that they might be observable in this experiment, *i. e.*, different results should be obtained for the relative concentration of the isomers, and therefore of the line–pair intensity ratio, at the lower temperature by slow and fast cooling of the sample. In order to investigate this point the line–pair ratio at low temperature was determined (a) after cooling from room temperature to the lower temperature in approximately ten minutes, and (b) after cooling gradually down to the low temperature over a period of five and a half hours. In both cases the line–pair ratio measured was identical within experimental error, *i. e.*, no hysteresis effects were observed.

Although the interpretation of the spectroscopic results with respect to rotational isomerism is not unequivocal,[5] the absence of any observable hysteresis suggests that the results and conclusions of Guthrie and Huffman are essentially correct.

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[1] This Research was supported by contract N6onr-269, Task V, of the Office of Naval Research.

[2] J. G. Aston and S. C. Schumann, This Journal, **64**, 1034 (1942).

[3] S. C. Schumann, J. G. Aston and M. L. Sagenkahn, *ibid.*, **64**, 1039 (1942).

[4] J. G. Aston, *ibid.*, **65**, 2041 (1943).

[5] A. B. Guthrie, Jr., and H. M. Huffman, *ibid.*, **65**, 1143 (1943).

[6] G. J. Szasz and N. Sheppard, *J. Chem. Phys.*, to be published.

WATER ACTIVITY CORRELATION IN THE HYDROCHLORIC ACID AZEOTROPIC SYSTEM

Sir:

In a recent paper[1] Stokes and Robinson attempted to extend the concepts of the Brunauer, Emmett and Teller adsorption theory to the case of ionic hydration in concentrated aqueous solution. They were able to show that the available data on water activity in several concentrated electrolytes were remarkably well fitted with reasonable values for the parameters in the following equation

$$\frac{m a_{\text{W}}}{55.51\,(1 - K a_{\text{W}})} = \frac{1}{cKr} + \frac{c - 1}{cr}\, a_{\text{W}}$$

where m is the molality of electrolyte; a_{W} is the activity of water; r, c and K are dimensionless parameters related to the number of water molecules in a monomolecular hydration layer when complete, the heat of adsorption of the first layer and of subsequent layers, respectively. In particular, the data from e. m. f. measurements on hydrochloric acid[2] in the range 0–50° were fitted with an average deviation of 0.0016 in a_{W} using the parameters $r = 4.00$, $RT \ln c = 1.57 \pm 0.01$ kcal.; $K = 0.825$ to 0.870.

It occurred to the present author that a further test of the validity of the theory would be afforded by data in a higher range of temperature, available in the form of accurate measurements of the azeotropic composition and total pressure of aqueous hydrochloric acid.[3]

The exact thermodynamic equation $a_{\text{W}} f^0_{(\text{l})} = N_{\text{W}} f^0_{(\text{g})}$, was applied to the calculation of water activity in the azeotropic mixtures. The use of fugacities (from Dorsey's data[4]) rather than the corresponding pressures introduced corrections of about 0.5%. The activities so calculated are believed to be correct within 0.0010 in a_{W}.

Table I

Water Activity in Azeotropic Hydrochloric Acid Systems

Temp., °C.	Mm.	N HCl	m HCl	a_{W}
90	366.7	0.11712	7.3633	0.617_8
100	548.3	.11692	7.1819	$.639_8$
110	799.8	.11088	6.9210	$.665_4$
120	1119	.10700	6.6514	$.675_2$

Choosing the parameters $r = 4.00$ and $RT \ln c = 1.57 \pm 0.01$ kcal., the present data were fitted (average deviations 0.0008 in a_{W}) by values of

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[1] R. H. Stokes and R. A. Robinson, This Journal, **70**, 1870 (1948).

[2] G. Akerlof and J. W. Teare, This Journal, **59**, 1855 (1937).

[3] W. D. Bonner and R. E. Wallace, *ibid.*, **52**, 1747 (1930).

[4] N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corporation, New York, N. Y., 1940, pp. 576, 596.