

## Estimation of Energies and Entropies of Vaporization

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of water as a radiolysis product lends support to the conception that the reaction mechanisms postulated by these latter authors for concentrated acetic acid solutions can be extrapolated to the case of glacial acetic acid. The proof of this conception will require additional data on other products in the liquid phase.

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## Estimation of Energies and Entropies of Vaporization

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IN a forthcoming publication,<sup>1</sup> Dr. McLachlan and I have discussed various methods of deriving Trouton's rule.<sup>2</sup> In the course of that work it became apparent that assuming a slightly different distribution law gives much more accurate entropies of vaporization, and permits the estimation of energies of vaporization from density and boiling point of any liquid.

This distribution law is, for one mole of the same molecules in each of the liquid and vapor phases,

$$V_f/V_v = \exp(-\Delta E_v/RT), \quad (1)$$

where  $V_f$  is the free volume in the liquid phase,  $\Delta E_v$  is the internal energy of vaporization, and  $V_v$  is the molar volume in the vapor phase, which is almost equivalent to the free volume. Substitution of the perfect gas law in (1) gives

$$\frac{V_f P}{RT} = \exp\left(-\frac{\Delta E_v}{RT}\right), \quad (2)$$

where  $P$  is the vapor pressure at temperature  $T$ . Various forms of the free volume expression have recently been

TABLE I. Energies and entropies of vaporization calculated from Eq. (6).

Substance	$\Delta E_v$ kcal/mole		$\Delta S_v$ cal/mole-deg	
	calc	obs	calc	obs
Perfect liquids				
A	1.32	1.38	17.1	17.9
Kr	1.82	1.91	17.1	18.0
Xe	2.63	2.69	17.9	18.3
Rn	3.34	3.50	17.8	18.6
N <sub>2</sub>	1.11	1.18	16.4	17.2
O <sub>2</sub>	1.37	1.45	17.2	18.1
CO	1.18	1.28	16.5	17.7
CH <sub>4</sub>	1.67	1.73	17.0	17.5
Imperfect liquids				
SiBr <sub>4</sub>	6.54	8.25	17.4	21.4
SnCl <sub>4</sub>	5.89	7.53	17.3	21.5
TiCl <sub>4</sub>	6.35	7.58	17.5	20.5
SiCl <sub>4</sub>	4.94	6.34	17.0	21.2
CCl <sub>4</sub>	5.44	6.47	17.5	20.5
CHCl <sub>3</sub>	5.30	6.35	17.9	21.0
CS <sub>2</sub>	5.23	5.76	18.4	20.0
CH <sub>3</sub> OH	5.88	7.75	19.4	25.0
Metals				
Ag	60.3	55.0	26.2	24.2
Na	23.9	21.1	22.7	20.2
Sn	57.5	65.0	25.3	28.3
Pb	45.3	38.7	24.5	21.2
Bi	40.7	37.4	24.2	22.4
Hg	13.25	13.3	23.0	23.2

reviewed by us.<sup>1</sup> One of these can be derived by writing the simple equation of state for liquids

$$P_{\text{int}} V_f = RT. \quad (3)$$

Scott<sup>3</sup> has evaluated the internal pressure  $P_{\text{int}}$  in the form

$$P_{\text{int}} = \left( \frac{-E}{V_l} \right) = \frac{\Delta E_v}{V_l}, \quad (4)$$

where  $V_l$  is the molar volume of the liquid ( $V_l = M/\rho$ ). Substitution of (3) and (4) in (2) results in

$$\frac{V_l P}{\Delta E_v} = \exp\left(-\frac{\Delta E_v}{RT}\right), \quad (5)$$

or

$$\Delta E_v = RT \ln \frac{\Delta E_v}{V_l P} = RT \ln \frac{\rho \Delta E_v}{MP}. \quad (6)$$

The energy of vaporization can thus be determined by iteration of (6) when one knows the density  $\rho$  and vapor pressure  $P$  at temperature  $T$ . The results of a number of such calculations are shown in Table I for a variety of substances taken from Hildebrand and Scott's tables.<sup>4</sup> A number of metals<sup>5</sup> have been included to show the range of Eq. (6). Having calculated the energy of vaporization, it is easy to obtain the entropy

of vaporization at the boiling point:

$$\Delta S_v = (\Delta E_v/T_B) + R. \quad (7)$$

Comparison of entropies thus calculated with observed entropies of vaporization is quite favorable in the case of perfect liquids, less so for imperfect liquids. This comparison is also included in Table I.

The justification for using a distribution law containing  $\Delta E_v$  rather than  $\Delta H_v$  must, for the moment at least, rest with the result given by Eq. (6). A model of the liquid state which would lead to this distribution law is a hypothetical state in which a molecule does no PV work in going from the liquid to the gaseous state.

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<sup>4</sup> J. Hildebrand and R. L. Scott, *The Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York, 1950).

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## Electron Spin Resonance Absorption Spectra of Some Organic Free Radicals

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THE hfs of organic free radicals containing a number of atoms  $j$  with nuclear moments can be described by the equation

$$E = \pm \{ \frac{1}{2} g_e \mu_B H + \sum a_j I_j \}, \quad (1)$$

in which  $I_j$  stands for the nuclear spin quantum number and  $a_j$  is the corresponding interaction parameter.

Usually it is assumed that  $a_j$  is proportional to the density of the unpaired electron at nucleus  $j$ ,<sup>1</sup> or to the density of the unpaired electron at the carbon atom to which  $j$  is bonded.<sup>2</sup>

In the case of triphenylmethyl (TPM), Eq. (1) must be written as

$$E = \pm \{ \frac{1}{2} g_e \mu_B H + a_o \sum I_o + a_m \sum I_m + a_p \sum I_p \}.$$

The subscripts  $O$ ,  $m$ ,  $p$  refer to the *ortho*-, *meta*-, and *para*-positions. For arbitrary values of  $a_o$ ,  $a_m$ , and  $a_p$  the spectrum contains 196 lines.<sup>3</sup> The experimental curve consists of a smaller number of lines with a complicated intensity pattern. Obviously a number of lines coincide.<sup>1</sup> The spectrum can be interpreted by assuming that  $a_o/a_m$  (or  $a_m/a_o$ )  $\cong 2$  and that  $a_p$  is much smaller than both  $a_o$  and  $a_m$ . This assumption leads to a spectrum of 19 lines with intensities of 1, 6, 21, 56, 120, 216, 336, 456, 546, 580 . . . (left part and central line). The outer lines, being so much smaller than the central one, are difficult to observe. The intensities of the central lines, however, are in good

agreement with our experimental curve, whereas other ratios of  $a_m$ ,  $a_o$ , and  $a_p$ , giving 16 to 22 lines, have quite different intensity distributions. We were unable to obtain the splitting of each line into four components, as observed by Jarrett and Sloan,<sup>3</sup> which can be ascribed to the  $p$  hydrogens thus indicating a very small value for  $a_p$ .

Another free radical that displays the same ratio of  $a_m$ ,  $a_o$ , and  $a_p$  seems to be diphenylnitricoxide (DPNO). For DPNO the energy levels are given by

$$E = \pm \{ \frac{1}{2} g_e \mu_B H + a_N \sum I_N + a_o \sum I_o + a_m \sum I_m + a_p \sum I_p \},$$

in which  $I_N$  represents the nitrogen nuclear spin quantum number. The protons give rise to 13 lines if  $a_o/a_m \cong 2$  (or  $a_m/a_o \cong 2$ ) and  $a_p \cong 0$ . Combined with the nitrogen triplet splitting this gives a spectrum of 39 lines. From the experimental curve<sup>4</sup> one may conclude that a few lines of the different parts of the triplet coincide, resulting in a spectrum of 35 lines. This can be explained by supposing that  $a_N = 11a_o$  (or  $a_N = 11a_m$ ). The calculated intensities then are 1, 4, 10, 20, 31, 40, 44, 40, 31, 20, 10, 5, 5, 10, 20, 31, 40, 44 . . . (left part and central line), in good agreement with Hoskins' results. For the moment it is difficult to decide which parameter,  $a_o$  or  $a_m$  has the highest value, because these coefficients appear symmetrically in the equations. For a decision it is necessary to investigate the *ortho*- or *meta*-substituted derivatives. If it is true that the interaction parameters  $a_o$ ,  $a_m$ , and  $a_p$  are proportional to the probability of finding the unpaired electron at the *ortho*-, *meta*-, and *para*-positions it is remarkable and at first sight at variance with MO calculations that  $a_p$  is so much smaller than both  $a_o$  and  $a_m$ .

The author is indebted to Professor L. J. Oosterhoff for many interesting discussions on the subject.

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## Thermodynamic Functions for Some Halogenated Methyl Cyanides

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RECENT investigations have shown the need for precise thermodynamic data for halogenated organic compounds. For some of the lower halocarbons, e.g., halomethanes and haloethanes, these functions have been reported.<sup>1-6</sup> The present communication reports the statistical thermodynamic functions for the