Heats of the Vaporization of Non-ionic Liquids

Dilip Kumar MAJUMDAR

Department of Chemistry, Faculty of Science, University of Kalyani, Kalyani, West Bengal, India

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In the significant liquid structure theory, as developed by Eyring and his co-workers,[1] the motion of solid-like molecules has been described by an Einstein oscillator. In this form the theory does not lead to an equation of state for rigid spheres. This defect can, however, be remedied if we replace the Einstein oscillator by the Lennard-Jones and Devonshire[2] cell model and then apply the usual restrictions on the intermolecular potential between two rigid-sphere molecules:

$$\phi(r) = 0, \quad r > \sigma$$

$$\phi(r) = \infty, \quad r < \sigma$$

(where σ is rigid sphere diameter).
We may obtain the following partition function following Henderson[3]:

$$Z = \left\{\left(\frac{2\pi m\boldsymbol{k}T}{\boldsymbol{h}^2}\right)^{3/2}\frac{eV}{\boldsymbol{N}}\right\}^N \left\{0.00967\left(8-11\frac{V}{V_0}\right)^{3/2(\boldsymbol{N}V_0/V)}\right\} \tag{1}$$

where $V_0 = N\sigma^3/\sqrt{2}$ is the closed packed volume; V is the volume at a given temperature, T, on the absolute scale; $\boldsymbol{k}$, the Boltzmann constant; $\boldsymbol{h}$, Planck's constant; m, the mass of a single molecule, and $\boldsymbol{N}$, Avogadro's number.

Henderson has employed this partition function for calculating the compressibility factor[3] and the excess entropy[3] for a system of rigid spheres; his results were found to compare favourably with the predictions of the cell model and the machine calculations of Alder and Wainwright.[4]

It is our purpose to apply the significant structure theory for a system of rigid spheres as developed by Henderson to calculating the standard heats of vaporization for non-ionic liquids. A similar approach using the scaled particle[5] theory has been made by Yosim and Owens,[6] who have shown that the scaled particle theory for a system of rigid spheres gives $\Delta H°_v$ values which are in remarkably good agreement with the experimental results.

We assume that the standard heat of vaporization should be equal to the isothermal work of compressing a mole of rigid spheres from the volume it occupies at one atmosphere, V_g, to the molar volume, V_1 of the liquid. Therefore, we may write:

$$\Delta H°_v = \int_{V_1}^{v_g} P\mathrm{d}V = \boldsymbol{R}T\ln\frac{V_g}{V_1} + \frac{3\,\boldsymbol{R}TV_0}{2}\left(\ln 0.00967\right)\left(\frac{1}{V_g}-\frac{1}{V_1}\right) + \frac{3\boldsymbol{R}T}{2}\left[\frac{1}{V_g}\ln\left(8-11\frac{V_0}{V_g}\right)-\frac{1}{V_1}\ln\left(8-11\frac{V_0}{V_1}\right)\right] \tag{2}$$

$$\text{and} \quad P = \boldsymbol{k}T\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

We have applied Eq. (2) to many non-ionic liquids. The molecular rigid sphere diameters were taken from Hirzchfelder, Curtiss and Bird.[7]

By way of comparison, we have also calculated the standard heats of vaporization for these compounds using two other theories for rigid spheres, namely, the cell[3] and tunnel[8] theories. The relevant equations we have used are:
Tunnel theory:

$$\Delta H°_v = \boldsymbol{R}T\ln\frac{V_g}{V_1} + 3\,\boldsymbol{R}T\left[\ln\frac{1-\left(\frac{3}{2}\right)^{1/6}\left(\frac{V_g}{V_0}\right)^{-1/3}}{1-\left(\frac{3}{2}\right)^{1/6}\left(\frac{V_1}{V_0}\right)^{-1/3}}\right]$$

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[2] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)*, **A163**, 53 (1937); **A165**, 1 (1938).

[3] D. Henderson, *J. Chem. Phys.*, **39**, 1857 (1963).

[4] B. J. Alder and T. E. Wainwright, *ibid.*, **27**, 1208 (1957).

[5] H. Reiss, H. L. Frisch and J. L. Lebowitz, *ibid.*, **31**, 369 (1959).

[6] S. J. Yosim and B. B. Owens, *ibid.*, **39**, 2222 (1963).

[7] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, New York (1954), p. 1110.

[8] J. A. Barker, *Australian J. Chem.*, **13**, 187(1960).

Cell theory:

$$\Delta H^\circ_v = 3\boldsymbol{R}T\ln\frac{V_g^{1/3} - V_0^{1/3}}{V_1^{1/3} - V_0^{1/3}}$$

These results, along with those calculated by Yosim and Owens,6) are included in Table 1.

We observed that the significant structure theory predicts ΔH°_v values for rare gases as closely as the scaled particle theory. In fact, one might discern a distinctly better agreement with the significant structure theory, even if it is very small. With regard to diatomic molecules, namely, fluorine, oxygen and bromine, the significant structure theory and scaled particle theory should be regarded as of equal value, though, of course, in these cases too, we find a distinctly better performance by the former theory.

The significant structure theory fails completely for chlorine and iodine. With the molecular diameters and densities of these liquids, given in Table 1, the $11\,V_0/V_1$ term becomes greater than 8 in Eq. (2). This is also the case when we try to calculate ΔH°_v values for more complex molecules, *e. g.*, carbon tetrachloride, chloroform, cyclohexane and sulphur dioxide. Such a situation does not arise with either the cell or scaled particle theory.

With the tunnel theory, the agreement is remarkable for alcohols, though for all other molecules the performance of this theory is the poorest. It is not clear why the tunnel theory apparently appears to be more suitable to an associated liquid like alcohol. In comparison, the low ΔH°_v values calculated from the significant structure and scaled particle theories are not unexpected, since the molecular diameter listed by Hirschfelder *et*

TABLE 1. HEATS OF VAPORIZATION*

Compound	Boiling point °K	Diameter σ(Å)	Density of liquid (g/cm³)	Heat of vaporization† (cal/mol)				
				ST	CT	TT	SPT	Obs.
He	4.22	2.556	0.1249	27.46	35.30	37.48	26.8	19.4
Ne	27.07	2.749	1.207	427.2	502.0	556.9	427	414
Ar	87.29	3.400	1.389	1587	1820	2043	1611	1558
Kr	119.8	3.597	2.413	2178	2473	2803	2188	2158
Xe	165.1	3.963	3.057	3235	3636	4128	3264	3020
H_2	20.39	2.87	0.07085	236.3	222.8	312.0	227.5	215.8
N_2	77.2	3.681	0.8091	1109	1624	1823	1434	1333
O_2	90.13	3.433	1.145	1734	1946	2215	1749	1628
F_2	85.20	3.65	1.108	1563	2203	2009	1581	1568
Cl_2	239.0	4.115	1.560	—	7835	—	5154	4878
Br_2	331.4	4.268	2.98	6813	7642	8640	6869	7170
I_2	456	4.982	3.744	—	12240	15340	12673	9970
NO	121.4	3.470	1.269	—	3105	2275	3139	3293
CO	81.61	3.59	0.799	1403	1626	1286	1409	1444
HCl	188.1	3.304	1.193	2502	2970	3301	3363	3860
HI	237.8	4.123	2.79	5079	5544	5493	5104	4724
CS_2	319.4	4.437	1.224	6285	7141	8019	6324	6400
N_2O	184.6	3.816	1.22	3977	4317	4994	3990	3958
SO_2	263.1	4.289	1.460	—	6890	9082	7086	5960
CH_4	111.7	3.796	0.415	2084	2358	2674	2098	1988
C_2H_4	169.4	4.232	0.566	2007	2507	2631	3499	3237
C_2H_6	184.5	3.954	0.546	3469	3597	4359	2987	3157
C_4H_{10}	272.7	4.971	0.601	4677	5470	6056	4676	5352
C_6H_6	353.2	5.270	0.8128	7281	7950	9194	7312	7353
C_6H_{12}	353.8	6.093	0.7199	—	9400	—	10430	7190
CH_3Cl	248.9	3.375	0.991	3713	4535	4768	3634	5150
$CHCl_3$	334.4	5.430	1.408	—	6544	13970	9539	7020
CCl_4	349.9	5.881	1.482	—	9500	—	10685	7170
CH_3OH	337.9	3.585	0.7484	6462	7557	8237	5923	8430
C_2H_5OH	351.7	4.455	0.7455	7114	7951	9040	7148	9220

* Boiling points, molecular diameter, density of liquid and observed heats of vaporization are taken from Yosim and Owens reference 6 and references cited therein.

† ST=Significat structure theory, CT=Cell theory, TT=Tunnel theory, SPT=Scaled particle theory.

al.[7] were calculated on the assumption that the intermolecular forces could be described solely by the Lennard-Jones potential.

For hydrocarbons, excepting ethylene, the predictions by the significant structure and scaled particle theories compare favourably with each other and with the experimental values.

With halogenated hydrocarbons, while the significant structure theory fails miserably, none of the other theories produces good results either. Again for carbon monoxide, nitric oxide, carbon disulphide, hydrogen chloride, iodide, and nitrous oxide, the agreement is good for these two theories.

Along with the scaled particle theory, it is our view that the significant structure theory may be used as a starting point for calculating other thermodyanamic properties of liquids, but only with caution, though in many cases, it gives exceedingly good results.