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RELATION BETWEEN THE VAPORIZATION HEAT AND THE VIBRATIONAL FREQUENCIES FOR MONATOMIC AND DIATOMIC LIQUIDS

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ABSTRACT

Reassessing the previously found linear correlation between the latent heat of vaporization and the Raman spectra for hydrocarbons; it has been found that smooth connections exist also for diatomic and monatomic liquids. This finding permits:

First, to state that the dimensionless inequality set:

$$hc\nu/kT_B \lesseqgtr 1.0$$

introduces corresponding liquid groups, out of which the special case when $hc\nu/kT_B = 1.0$ defines a class of liquids for which the well-known Trouton's rule is valid.

Secondly, the presented findings have in more general manner confirmed the previously established thought that there is need to study the evaporation process in terms of the excited frequencies and the quantum theory of the intermolecular forces of the liquid.

Earlier work[1-5] has shown that a correlation exists between the Raman spectra and boiling points of normal and substituted hydrocarbons. Later, Lielmezs *et al.*[6] and Lielmezs[7] have established that direct linear relation exists between the reduced vaporization energy change $\delta(\Delta H_{vap})/RT_B$ of benzene[6] and its halogen substituted homologues (C_6H_5X, where X = F, Cl, Br and I) as well as of normal and substituted hydrocarbons[7] and the X-sensitive[6]; or in the case of paraffins, the skeletal deformation frequencies, $hc\nu/kT_B$, at their normal boiling point temperatures. Finally, Lielmezs[8] has shown that the latent heat of vaporization for hydrocarbons can be directly determined from the Raman spectra by means of the following equation set:

$$Y = 2.341-0.061\,X, \text{ valid for normal hydrocarbons} \tag{1a}$$

$$Y = 2.346-0.107\,X, \text{ valid for paraffins with one isopropyl group} \tag{1b}$$

$$Y = 2.337-0.112\,X, \text{ valid for paraffins with one tertiary butyl group} \tag{1c}$$

$$Y = 2.386-0.049\,X, \text{ valid for cyclanes} \tag{1d}$$

In each of the above Eqns. (1a, 1b, 1c, 1d):

$$Y = \ln \frac{\Delta H_{vap}}{RT_B} \quad \text{and} \quad X = \ln \frac{hc\nu}{kT_B} \text{ ; where}$$

ΔH_{vap} are the vaporization heat values of the given hydrocarbon at the normal boiling point, cal/g-mole; T_B is the normal boiling point value, °K; h is the Planck's constant; R is the universal gas constant; k is the Boltzmann's constant; and ν is the skeletal deformation frequency, $\nu_{\delta C-C}$ cm^{-1}.

These authors[1-8] have also pointed out that the existence of such correlations might assist in the formulation of quantum theory of vaporization process. That is, the presented evidence[1-8] implies that it may be possible to propose a mechanism of evaporation on the basis of the thermally excited vibrational state of molecule as differing from the mechanism of evaporation utilizing solely the kinetic theory of liquids (the postulate that the evaporation process is chiefly controlled by the molecular rotational partition function[9-11]).

The purpose of this communication is to reassess these previously established correlations[1-8] and to reconsider them for the case of monatomic and diatomic

TABLE I

SUMMARY OF DATA[a]

Compound	*Normal boiling point (°K)*	*Heat of vaporization at normal boiling point (cal/g-mole)*	*Frequency given as product $h\bar{\nu}$, first ionization potential or wave number*
		Monatomic liquids	*$h\nu \times 10^{11}$*
He	4.3	22.4	3.898
Ne	27.3	413.0	3.415
Ar	87.5	1500.0	2.496
Kr	121.4	2314.0	2.217
Xe	164.1	3210.0	1.921
			Ionization potential, eV
Na	1172	23675	5.12
K	1045	18975	4.32
Rb	934	16850	4.16
		Diatomic liquids	*Wave number, cm^{-1}*
H_2	20.39	218	4395
CO	81.61	1444	2170.2
N_2	77.32	1352	2359.6
O_2	90.2	1630	1580.3
Cl_2	239.5	4865	564.9
Br_2	331.8	7280	323.2
I_2	457.5	10120	214.57
HCl	189.0	3538	2989.74
HBr	205.5	4158	2649.67
HI	237.4	4948	2309.5

[a] All presented data taken from Refs. 12 and 13.

liquids. Using the published literature values for the latent heat of vaporization and the vibrational frequencies (Table I) and plotting the logarithm of the reduced latent heat of vaporization ($Y = \ln (\Delta H_{vap}/RT_B)$ *versus* the logarithm of the dimensionless frequency ($X = \ln (hcv/kT_B)$, we obtain Figs. 1 and 2.

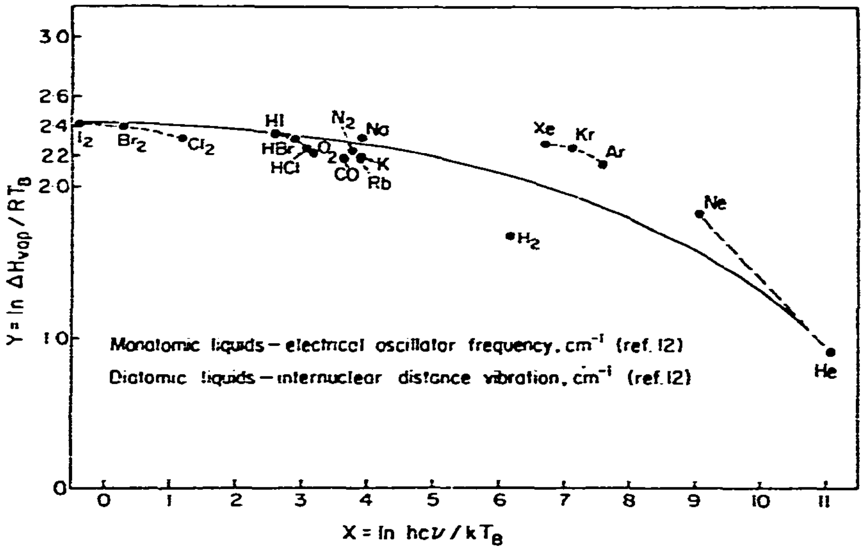

Fig. 1. Correlation between the dimensionless vaporization heat and the dimensionless frequency for monatomic and diatomic liquids.

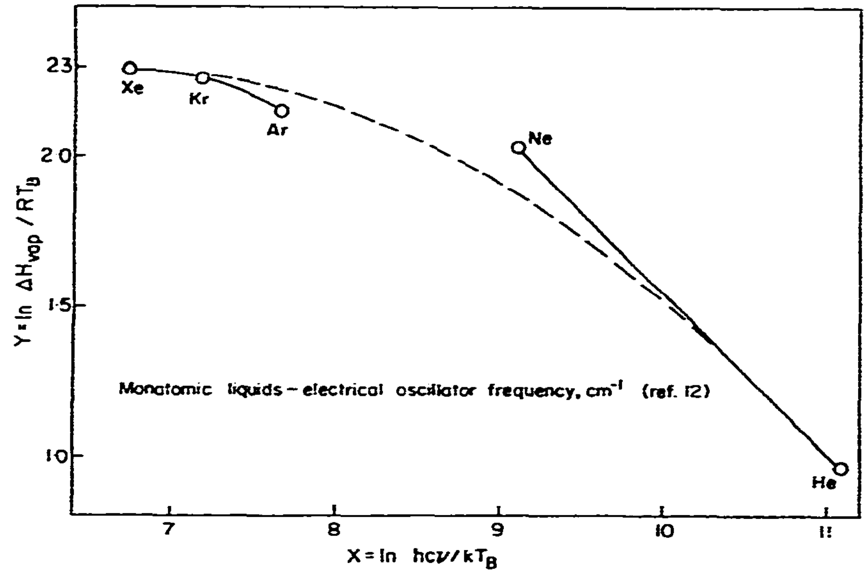

Fig. 2. Relation between the dimensionless vaporization heat and the dimensionless frequency for monatomic liquids only.

It is seen from Fig. 1 that a general smooth curve connects the dimensionless latent heat of vaporization with the dimensionless frequency for a series of monatomic and diatomic liquids. It should be noted that the general curve tends to a constant value:

$$Y = \ln(\Delta H_{vap}/RT_B) \simeq 2.42 \text{ when } X = \ln(hc\nu/kT_B) = 0.$$

Also note that similar liquid groups such as: Ar, Kr, Xe; HCl, HBr, HI; I_2, Br_2, Cl_2, form separate family curves; none of them however, exceeding the limiting constant value $\simeq 2.42$ when $hc\nu/kT_B \rightarrow 1.0$. Fig. 2 shows the same type correlation for monatomic liquids (He, Ne, Ar, Kr, Xe) only. In this case the limiting constant value could be seen to be:

$$\ln(\Delta H_{vap}/RT_B) \simeq 2.29, \text{ when } hc\nu/kT_B \rightarrow 1.0.$$

Again note that so called "ideal" fluids Ar, Kr, Xe form a separate smooth curve; with the quantum fluids He, Ne showing an apparent deviation from the general behavior (Fig. 1; as well as Fig. 2). If we compare the obtained intercept constant values (when $hc\nu/kT_B \rightarrow 1.0$; Figs. 1, 2) with those as given by the linear equation set (1a, 1b, 1c, 1d); we see that these intercepts are approximately the same (2.341 from Eqn. 1a; 2.346 from Eqn. 1b; 2.337 from Eqn. 1c; 2.386 from Eqn. 1d). If we select the following limiting constant values: 2.42 (the largest); 2.29 (the smallest); 2.35 (arithmetic mean of all presented 6 constant values — from Eqns. 1a, 1b, 1c, 1d and Figs. 1 and 2); and if we rewrite $\ln(\Delta H_{vap}/RT_B) \rightarrow$ constant value (axial intercept) when $\ln(hc\nu/kT_B) \rightarrow 0$; then using these three selected constants, we obtain the following values for the entropy of vaporization at the normal boiling point:

$$S_{vap} = \frac{H_{vap}}{T} = 22.35 \text{ e. u. (largest value);}$$

$$S_{vap} = \frac{H_{vap}}{T} = 19.61 \text{ e. u. (smallest value);}$$

$$S_{vap} = \frac{H_{vap}}{T} = 20.90 \text{ e. u. (arithmetic mean of all 6 presented values).}$$

These obtained (axial intercept) entropy values compare reasonably well with the conventional Trouton constant[14];

$$S_{vap} = 19.5 \pm 2.1 \text{ e.u.} \tag{2}$$

It appears that the ratio of radiation ($hc\nu$) to thermal (kT_B) energy taken at the normal boiling point may present a useful criterion for the discussion of the nature of liquids by the following inequalities:

$$hc\nu/kT_B \gtreqless 1.0 \tag{3}$$

For instance, if $hc\nu/kT \rightarrow 1.0$; we have a group of liquids for which we may assume that Trouton's rule is valid. How this criterion (both coordinates, $\Delta H_{vap}/RT_B$ and $hc\nu/kT_B$, together) is related to the principle of corresponding states, is a question worthy of further investigation. However, the presented reassessment (Figs. 1 and 2;

as well as Eqns. 1a, 1b, 1c, 1d) has in a more general manner confirmed the previously established thought[1–8] for the need to study the evaporation process in terms of the excited frequencies and the quantum theory of the intermolecular forces of the liquid.

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REFERENCES

1 S.-Kh. G. Kashaev, B. Le and M. Z. Zinyatov, *Dokl. Akad. Nauk, S. S. S. R.*, 156 (1964) 1458.
2 S.-Kh. G. Kashaev, *Opt. Spektrosk.*, 21 (1966) 308.
3 J. Lielmezs, *Nature*, 211 (1966) 742.
4 J. Lielmezs, *Ind. Eng. Chem. Fundam.*, 7 (1968) 315.
5 N. K. Sanyal, A. N. Pandey and H. S. Singh, *J. Quant. Spectrosc. Radiat. Transfer*, 9 (1969) 465.
6 J. Lielmezs, J. B. Butler, H. C. Henry and R. G. Orr, *Theor. Chim. Acta*, 17 (1970) 81.
7 J. Lielmezs, unpublished manuscript.
8 J. Lielmezs, unpublished manuscript.
9 E. M. Mortensen and H. Eyring, *J. Phys. Chem.*, 64 (1960) 846.
10 G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand, 1945.
11 J. Frenkel, *Kinetic Theory of Liquids*, Dover, New York, 1955.
12 E. A. Moelwyn-Hughes, *Physical Chemistry*, Pergamon Press, London, 1957.
13 E. R. Cohen and J. W. M. Du Mond, *Rev. Mod. Phys.*, 37 (1965) 537.
14 D. H. Everett, *Chem. Soc.*, 519 (1960) 2566.

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