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CORRELATION BETWEEN THE VAPORIZATION HEAT AND THE RAMAN FREQUENCIES FOR NORMAL HYDROCARBONS

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ABSTRACT

It has been shown that a correlation can be established between the heat of vaporization and the Raman frequencies for normal hydrocarbons at equal pressures. The values predicted by the correlating equation compare well with the available experimental values and values obtained by using selected (Riedel, Giacalone, Riedel–Plank–Miller, Pitzer–Chen and Klein–Fishtine) estimating methods. Finally, possible relation between the latent heat of vaporization at the normal boiling point and the Raman frequencies for several classes of compounds, is discussed briefly.

INTRODUCTION

In a series of communications Lielmezs[1–3] and Lielmezs *et al.*[4] have shown that at the normal boiling point the latent heat of vaporization for hydrocarbons can be directly determined from the Raman spectra by means of a linear equation set:

$$Y = a - mX \tag{1}$$

In above eqn. (1)

$$Y = \ln\left(\frac{H_v}{RT_B}\right) \quad \text{and} \quad X = \ln\left(\frac{hc\nu}{kT_B}\right)$$

where H_v is 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 Planck's constant; R is the universal gas constant; k is the Boltzmann's constant; ν is the corresponding Raman frequency, cm^{-1}; while a and m are constants describing particular hydrocarbon classes.

This, as well as the finding that a connection between the vaporization heats and Raman spectra exists[1] also for monatomic and diatomic liquids, has in a more general way implied that it may be possible to consider the evaporation mechanism on the basis of the thermally excited vibrational state of a molecule as differing from the postulate that the evaporation process is chiefly governed by the molecular rotational partition function[5–7].

In this work, however, we consider whether previously obtained correlations are valid at other than normal boiling point conditions. To this end, these proposed relations were referred to the critical point of the substance thus defining a thermodynamic reference state (in accordance with the principle of corresponding states) and then generalized correlations in terms of reduced pressures, latent heats of vaporization and Raman frequencies (specifically C–C bond skeletal deformation frequency) were established.

PROPOSED CORRELATION

To establish the proposed correlations, first, the two dimensionless parameters, $Y = \ln(H_v/RT)$ and $X = \ln(hc\nu/kT)$, were calculated using frequency data from Mizushima and Simantouti[8], and vapour pressure–temperature data* from Zwolinski and Wilhoit[9] for nine *n*-paraffins at four reduced pressures (Table 1). The obtained data (Table 1), formed an orderly array of straight lines, satisfying general conditions as prescribed by eqn (1).

TABLE 1

CALCULATED VALUES OF $X = \ln(hc\nu/kT)$ AND $Y = \ln(H_v/RT)$ FOR NORMAL PARAFFINS AT FOUR REDUCED PRESSURES

Compound	*Parameter*	*Reduced pressure*			
		0.0407	*0.0815*	*0.203*	*0.407*
n-butane	*X*	0.7668	0.6929	0.5834	0.4890
	Y	2.2103	2.0672	1.8060	1.4294
n-pentane	*X*	0.6080	0.5368	0.4317	0.3415
	Y	2.2498	2.1107	1.8557	1.5455
n-hexane	*X*	0.4335	0.3642	0.2620	0.1742
	Y	2.2803	2.1424	1.8902	1.5839
n-heptane	*X*	0.1782	0.1110	0.0119	−0.0731
	Y	2.3118	2.1757	1.9264	1.6220
n-octane	*X*	0.0217	−0.0438	−0.1404	−0.2231
	Y	2.3388	2.2045	1.9589	1.6588
n-nonane	*X*	−0.1594	−0.2232	−0.3171	−0.3974
	Y	2.3678	2.2349	1.9916	1.6925
n-decane	*X*	−0.2814	−0.3436	−0.4352	−0.5133
	Y	2.3932	2.2621	2.0218	1.7257
n-dodecane	*X*	−0.5339	−0.5935	−0.6811	−0.7557
	Y	2.4379	2.3089	2.0721	1.7782
n-hexadecane	*X*	−0.9076	−0.9632	−1.0448	−1.1141
	Y	2.5131	2.3881	2.1606	1.8813

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*All latent heat data were predicted from the Antoine equation. The Antoine coefficients and the necessary pressure–temperature data came from Zwolinski and Wilhoit[9]. It is felt that the presented calculations are within the range of experimental accuracy (this statement was confirmed by cross-checking with selected heat of vaporization values obtained using available vapour pressure–temperature data from Jordan[10]), and so of sufficient validity for use in establishing a correlation—for more detailed discussion regarding this matter, refer to Zwolinski and Wilhoit[9].

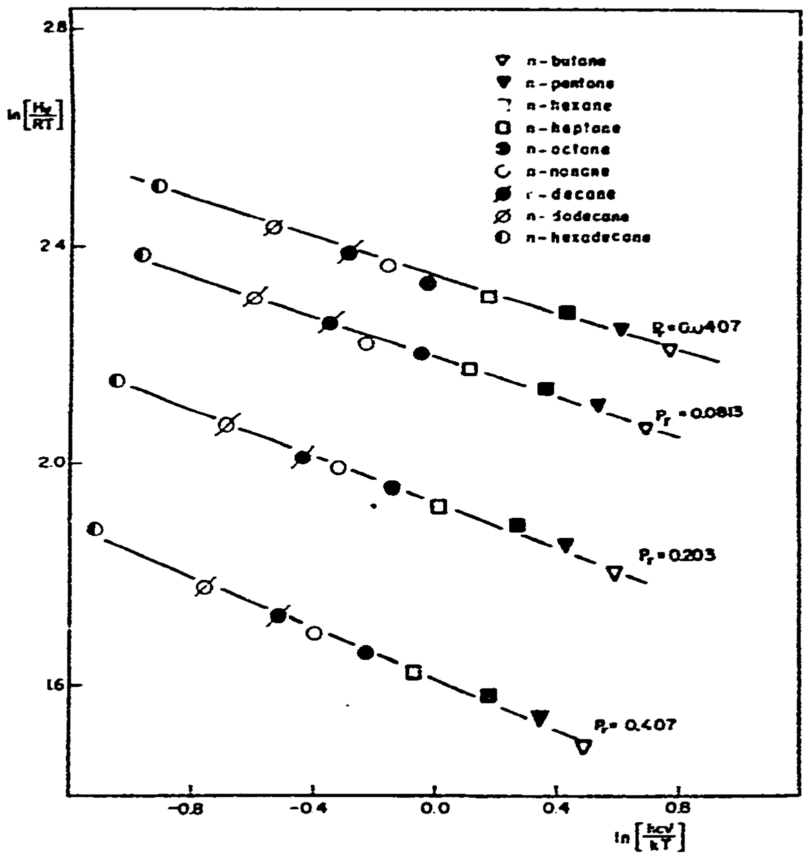

Fig. 1. Relationship between the latent heats of vaporization and the Raman frequency for n-paraffins at equal reduced pressures.

TABLE 2

SLOPE AND INTERCEPT VALUES CORRESPONDING TO THE LINES AT EQUAL REDUCED PRESSURE IN FIGURE 1

Reduced pressure	*Slope*	*Intercept*	*Correlation coefficient*[a]
0.0407	−0.1736	2.347	0.997
0.0813	−0.1877	2.200	0.997
0.203	−0.2095	1.933	0.997
0.407	−0.2303	1.611	0.997

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[a] The correlation coefficient is defined as

$$R^2 = \frac{1 - \Sigma Y^2 - A\Sigma Y - B\Sigma XY}{\Sigma Y^2 - 1/N\Sigma Y^2}$$

where: R = correlation coefficient
X, Y = data points of given correlation
N = the number of data points
A, B = constants of correlation satisfying relation of the form: $Y = A + BX$.

Using values from Table 1 and Fig. 1, and connections between straight line intercepts and slopes for each given reduced pressure (eqn (1); Fig. 1; Table 2); the following equation was established to express the heat of vaporization (H_v) for normal hydrocarbons by means of temperature (T); reduced pressure (P_r) and Raman frequency shift (ν):

$$H_v = 1.9872\,T \exp\left\{P_r^{\beta}\left[\alpha \ln\left(\frac{1.4404\,\nu}{T}\right) + \gamma\right] + \delta\right\} \tag{2}$$

where T = temperature (°K), P_r = reduced pressure referred to the critical point, ν = Raman frequency shift (cm^{-1}), and H_v = latent heat of vaporization (cal/g-mole): and constants $\alpha = -0.255945$, $\beta = 0.122373$, $\gamma = -3.318903$, and $\delta = 4.619987$. Equation (2) is valid, as derived, for the following reduced pressure range

$$0.0407 \leq P_r \leq 0.407 \tag{3}$$

and can be expressed as a three parameter (T, P_r, ν) relation:

$$H_v = \mathrm{f}(T, P_r, \nu) \tag{4}$$

Equation (4) indicates that at a known thermodynamic state (T, P_r given), the evaporation process, as already stated (compare with Lielmezs[1-3] and Kashaev[11]), may be described through the behavior of thermally excited vibrational degrees of freedom (in this case the deformation frequency of C–C bond, for data see Mizushima and Simantouti[8]) of molecules. Whether this mechanism of evaporation should be associated with a significant increase of repulsive force field between molecules (again compare with Kashaev[11] and Lielmezs[1-3]) in such a way that the repulsive forces exceed the attractive and the liquid structure is disrupted, is a matter of further study.

If a correlation is established between the Raman frequency and the number of carbon atoms in the normal paraffin chain, eqn (2) could be further generalized. Using Raman frequency data as recorded by Mizushima and Simantouti[8], we obtained Fig. 2 which graphically correlates Raman frequency to the carbon atom number "n" up to $n = 16$ in the given normal hydrocarbon chain. Figure 2 shows that when $n \leq 6$, the obtained Raman frequency-carbon number relation resembles a hyperbola. Assuming that there indeed exists a hyperbolic relation between Raman frequency shift ν, and n, the number of carbon atoms in an n-paraffin chain, we may propose a general hyperbolic equation:

$$\nu n = \text{constant} \tag{5}$$

Introducing curve fit factors with respect to $n = 4$, we can correspondingly determine the value of constant in eqn (5) and then write the relation between Raman frequency and the carbon number in n-paraffin chain as

$$\nu = \frac{2177}{n}\left[1.012^{n-7} - (1.0268^{n^3})^{-1}\right] \tag{6}$$

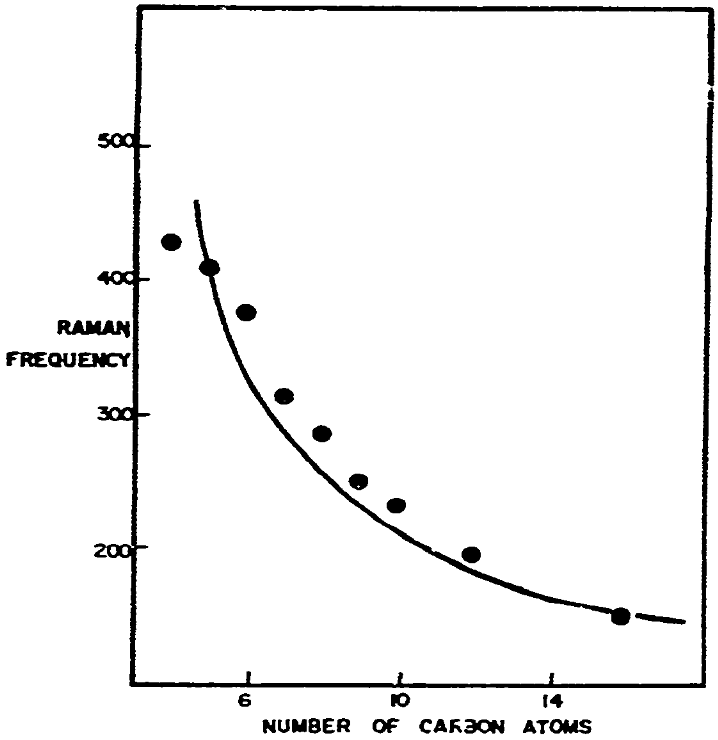

Fig. 2. Relation between Raman frequency (C–C bond skeletal deformation) and the carbon number "*n*" in the *n*-hydrocarbon chain. Data taken from Mizushima and Simantouti[9].

where ν = Raman frequency shift (in this case C–C bond deformation) characterizing the vaporization process, and n = number of carbon atoms in the given n-hydrocarbon.

Table 3 shows that eqn (6) predicts Raman frequencies within 4.3% of the literature values[8] for the normal paraffins ranging from n-butane to n-hexadecane. As derived, eqn (6) is valid up to $n = 85$. It is expected (compare with Fig. 2) that within this range of n (up to $n = 85$), the error in Raman frequency shift will remain within the range of 6%.

Combining eqn (6) with eqn (2) and correcting the resulting[*] equation by means of an error weighing function; the following equation for calculating the heats of vaporization in terms of temperature T (°K), reduced pressure P_r, and n, the number of carbon atoms in n-paraffin chain, may be presented:

$$H_v = \frac{1.9872\,T}{\left(\dfrac{13.3}{n}\right)^{0.0645}} \left\{ \exp P_r^{\beta} \left[\alpha \ln \left(\frac{3135.75}{nT} \left[(1.012)^{n-7} - \frac{1}{(1.0268)^{n^3}} \right] \right) + \gamma \right] + \delta \right\} \tag{7}$$

---

[*] It can be shown that in this resulting equation the percent deviation is a function of carbon number n, and may be written as:

$$g(n)_{\text{error \%-deviation}} = \left(\frac{13.3}{n}\right)^{0.0645}$$

TABLE 3

RAMAN FREQUENCIES PREDICTED BY EQUATION (6) AND COMPARED TO VALUES GIVEN BY MIZUSHIMA AND SIMANTOUTI[8]

Compound	*Number of carbon atoms*	*ν (cm^{-1})*		*Deviation*[a]
		predicted	*literature*	
n-butane	4	425	425	0.00%
n-pentane	5	409	406	0.74%
n-hexane	6	357	373	−4.29%
n-heptane	7	311	311	0.00%
n-octane	8	275	283	−2.83%
n-nonane	9	248	249	−0.40%
n-decane	10	226	231	−2.16%
n-dodecane	12	193	194	−0.51%
n-hexadecane	16	151	150	+0.67%

[a] The % deviation was calculated by the formula:

$$\% \text{ deviation} = \frac{\text{predicted value} - \text{literature value}}{\text{literature value}} \times 100$$

It should be recalled that the derivation of eqn (7) is based on the following restraints:

$$0.0407 \leqq P_r \leqq 0.407 \tag{8a}$$

$$4 \leqq n \leqq 85 \tag{8b}$$

The constants α, β, γ and δ, however, retain the same values as given with eqn (2).

If heat of vaporization values as obtained by eqn (7) are compared with the literature values (all literature data taken from Zwolinski and Wilhoit[9] at one atmosphere pressure ($0.027 \leqq P_r \leqq 0.091$) within the range of $4 \leqq n \leqq 20$, it is found that the maximum deviation* from literature value is −1.68% for n-pentane (Table 4). This comparison indicates that the proposed eqn (7) may well be used within the range of given restraints (eqn 8a); *i.e.* at least within the reduced pressure range of $0.020 \leqq P_r \leqq 0.500$.

On the other hand, using the same conditions as utilized in preparing Table 4 ($0.027 \leqq P_r \leqq 0.091$; $4 \leqq n \leqq 20$), the values of the heat of vaporization predicted by eqn (7) are compared with those as estimated from Riedel, Giacalone, Riedel–Plank–Miller, Pitzer–Chen and Klein–Fishtine correlations (for a description of these correlations refer to the book by Reid and Sherwood[12]). Table 5 shows that values of the heats of vaporization which have been obtained using eqn (7) compare quite well with those obtained from the above-mentioned correlations.

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*See Table 3, footnote [a] for definition of % deviation.

TABLE 4

COMPARISON OF THE LATENT HEAT VALUES PREDICTED BY EQUATION (7) WITH VALUES CALCULATED USING DATA FROM ZWOLINSKI AND WILHOIT[9]

Paraffin	*Number of carbon atoms*	*H_v (kcal/g-mole)*		*Deviation*	*Pressure (atm)*	*Temperature (°K)*	*Reduced pressure*
		predicted	*literature*				
n-butane	4	5.296	5.352	−1.05%	1.00	272.7	0.027
n-pentane	5	6.057	6.160	−1.68%	1.00	309.2	0.030
n-hexane	6	6.843	6.898	−0.768%	1.00	341.9	0.033
n-heptane	7	7.584	7.576	0.107%	1.00	371.6	0.037
n-octane	8	8.272	8.225	0.574%	1.00	398.8	0.041
n-nonane	9	8.902	8.823	0.891%	1.00	424.0	0.044
n-decane	10	9.497	9.388	1.15%	1.00	447.3	0.048
n-unadecane	11	10.03	9.92	1.15%	1.00	469.1	0.052
n-dodecane	12	10.55	10.43	1.15%	1.00	489.5	0.056
n-tridecane	13	11.08	10.91	1.52%	1.00	508.6	0.059
n-tetradecane	14	11.54	11.38	1.39%	1.00	526.7	0.063
n-pentadecane	15	11.95	11.82	1.11%	1.00	543.8	0.067
n-hexadecane	16	12.31	12.24	0.591%	1.00	560.0	0.071
n-heptadecane	17	12.62	12.64	−0.185%	1.00	575.2	0.077
n-octadecane	18	13.15	13.02	0.083%	1.00	589.5	0.077
n-nonadecane	19	13.37	13.39	−0.154%	1.00	603.1	0.083
n-eicosane	20	13.56	13.74	−1.32%	1.00	617.0	0.091

TABLE 5

COMPARISON BETWEEN THE ACCURACY OF EQUATION (7) OF THIS WORK AND SEVERAL OTHER CORRELATIONS DISCUSSED BY REID AND SHERWOOD[12] IN PREDICTING THE LATENT HEATS OF VAPORIZATION FOR NORMAL PARAFFINS AT THEIR NORMAL BOILING POINT

Correlation used	*Maximum deviation from experimental values for the normal paraffins from butane to decane*
Riedel	2.3% (for n-decane)
Giacalone	4.2% (for n-decane)
Riedel–Plank–Miller	0.9% (for n-decane)
Pitzer–Chen	0.3% (for n-butane)
Klein–Fishtine	1.7% (for n-decane)
Equation (7) of this work	−1.7% (for n-pentane)

POSSIBLE EXTENSION OF RELATION BETWEEN HEAT OF VAPORIZATION AND VIBRATIONAL FREQUENCY AT EQUAL REDUCED PRESSURE FOR OTHER CLASSES OF COMPOUNDS

Lielmezs[1] has already shown that a correlation exists between the vibrational frequency and the heat of vaporization at the normal boiling point for several classes of compounds including normal hydrocarbons. This finding has been confirmed and enlarged (Table 6, Fig. 3 in this work) by including additional compound groups.

TABLE 6

CALCULATED VALUES OF $\ln(hcv/kT)$ AND $\ln(H_v/RT)$ FOR NUMEROUS COMPOUNDS AT THEIR NORMAL BOILING POINTS

Experimental data references are in Appendix.

Compound	$\ln(hcv/kT)$	$\ln(H_v/RT)$
n-butane	0.8088	2.284
n-pentane	0.6373	2.302
n-hexane	0.4520	2.314
n-heptane	0.1869	2.328
n-octane	−0.02184	2.339
n-nonane	−0.1673	2.352
n-decane	−0.5605	2.382
n-dodecane	−0.2959	2.364
n-hexadecane	−0.9524	2.414
iodine	−0.3155	2.562
bromine	0.3206	2.359
chlorine	1.231	2.336
sodium chloride	−1.125	2.425
rubidium chloride	−1.617	2.429
rubidium iodide	−1.808	2.469
rubidium bromide	−2.203	2.510
xenon	9.047	1.401
krypton	9.484	1.338
argon	9.970	1.327
2-methyl-butane	0.5659	2.289
2-methyl-pentane	0.3391	2.305
2-methyl-hexane	0.2098	2.318
2-methyl-heptane	0.6315	2.342
2-methyl-octane	−0.1203	2.361
2-2-dimethyl butane	0.4765	2.282
2-2-dimethyl pentane	0.3291	2.298
2-2-dimethyl hexane	0.1366	2.324
2-2-dimethyl heptane	0.6110	2.334
cyclopentane	1.379	2.321
cyclohexane	1.183	2.325
cycloheptane	0.9918	2.339
hydrogen	5.738	1.683
carbon monoxide	3.646	2.186
nitrogen	3.783	2.175
oxygen	3.228	2.208
hydrogen chloride	3.126	2.243
hydrogen bromide	2.922	2.321
hydrogen iodide	2.640	2.350

Clearly as seen from Fig. 3 and previous work[1–3], all compounds forming this correlation fall into family groups which in turn align in a unique curve.

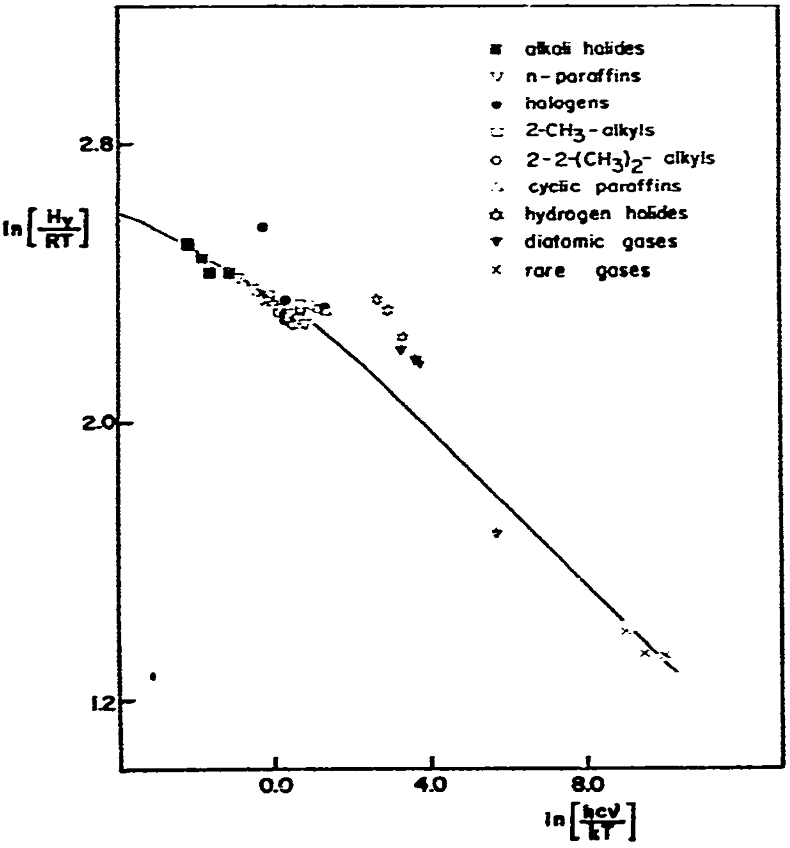

Fig. 3. Relationship between the latent heat of vaporization and the Raman frequency for numerous compounds at their normal boiling points.

Encouraged by all this as well as the observed regular behavior of n-hydrocarbons (Fig. 1, this work), it seems reasonable to generalize that all compound groups obeying the principle of corresponding states would fall for each given reduced pressure (compare with n-hydrocarbons, Fig. 1) on a separate unique curve. The required calculations were performed (for used data and extrapolation methods see Appendix), the results being presented in Table 7 and Fig. 4. While Fig. 4 reveals a distinct compound group alignment, there is seen an overlapping shift between various groups at each reduced pressure and so the hoped for unique curve encompassing all compound classes has not been properly established. Consequently, the proposed eqn (7) is presently limited to the use for n-hydrocarbons. However, in view of the inherent uncertainty of used data (see Appendix), it appears that the most likely reason for the shift of various data groups (Fig. 4) is caused by the inaccuracy of the data used rather than the differences in the physical properties of compounds. Hence, if more reliable vaporization heat values become available, it is entirely feasible to

TABLE 7

CALCULATED VALUES OF $X = \ln(hc\nu/kT)$ AND $Y = \ln(H_v/RT)$ FOR SEVERAL CLASSES OF COMPOUNDS AT FOUR REDUCED PRESSURES

Experimental data references are in Appendix.

Compound	*Parameter*	*Reduced pressure*			
		0.0407	*0.0813*	*0.203*	*0.407*
iodine	X	−0.4134	−0.4564	−0.5167	−0.5644
	Y	2.415	2.347	2.246	2.160
bromine	X	0.2189	0.1625	0.0912	0.0284
	Y	2.197	2.099	1.964	1.829
chlorine	X	1.114	1.035	0.9147	0.8155
	Y	2.151	2.011	1.761	1.484
sodium chloride	X	−1.344	−1.422	−1.534	−1.629
	Y	2.159	2.060	1.909	1.744
rubidium iodide	X	−1.917	−1.984	−2.080	−2.161
	Y	2.331	2.242	2.108	1.989
rubidium chloride	X	−1.772	−1.845	−1.950	−2.038
	Y	2.234	2.138	1.992	1.860
rubidium bromide	X	−2.342	−2.414	−2.518	−2.605
	Y	2.335	2.239	2.093	1.962
xenon	X	8.951	8.870	8.752	8.650
	Y	1.263	1.121	0.8462	0.4808
krypton	X	9.395	9.310	9.180	9.078
	Y	1.212	1.073	0.8164	0.5114
argon	X	9.891	9.795	9.673	9.561
	Y	1.210	1.055	0.7736	0.4180

begin to visualize that points at various reduced pressures might align in a more orderly pattern.

As a consequence of this, we feel that one should further investigate the presented relations and try to clarify how the coordinates $\ln(H_v/RT)$ and $\ln(hc\nu/kT)$ are related to the principle of corresponding states. Additionally, the given relations (eqns 1, 2, 4 and 7, Figs. 1, 3 and 4) have stressed the need for continued study of the vaporization process in terms of excited vibrational frequencies and the quantum theories of the intermolecular force fields of the liquid.

ACKNOWLEDGMENT

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APPENDIX

The following correlations were used to calculate heats of vaporization, H_v, at equal reduced pressures for several compound classes.

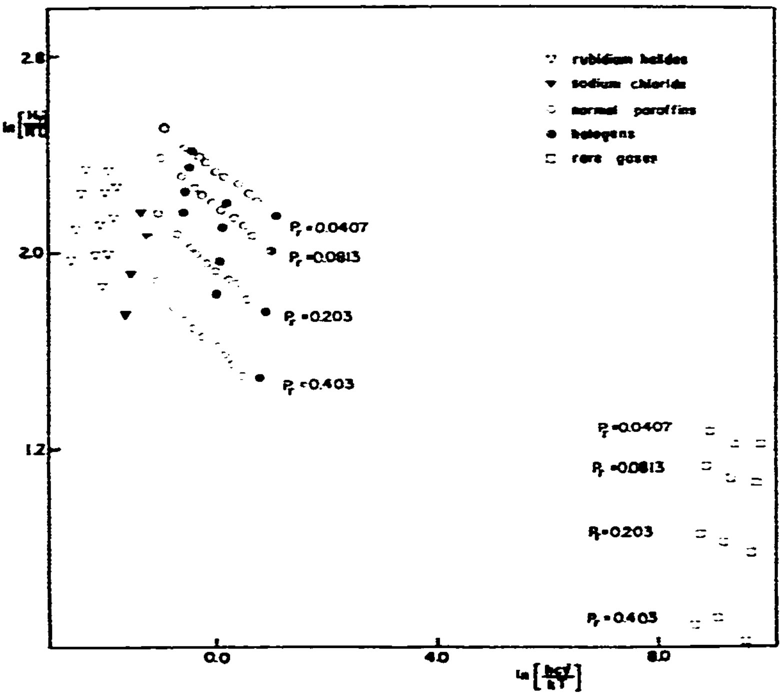

Fig. 4. Relationship between the latent heat of vaporization and the Raman frequency for several classes of compounds at constant reduced pressure P_r.

n-paraffins

The latent heat data were predicted, as already indicated, by the Antoine equation. The coefficients for this equation and all the necessary pressure–temperature data were obtained from Zwolinski and Wilhoit[9]. Lielmezs[1–3] gives other used data.

Xenon, argon and krypton

The heat of vaporization values were calculated from the Clapeyron equation:

$$H_v = \frac{-P\Delta V\,\mathrm{d}(\ln P)}{T\mathrm{d}(1/T)}$$

where ΔV is the volume change associated with the evaporation process. The phase transformation volume change, ΔV, was obtained through the use of Haggenmacher equation[13]. The necessary pressure and temperature data were taken from Codegone[14], while Lielmezs[1–3] refers to other data used.

Chlorine

Heat of vaporization values as given by Hampel[15] were used. For other data used refer to Lielmezs[1–3] work.

Bromine, iodine, NaCl, RbCl, RbI and RbBr

The Watson correlation[12] was used to predict the heat of vaporization values. The data used in conjunction with the Watson correlation are given by Mellor[16], and Wartenberg and Schulz[17]. The Raman spectra data were taken from Hampel[15], while the critical point thermodynamic parameter values from Landolt–Bornstein[18].

Other compounds

All other data were taken from references as given by Lielmezs[1–3].

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