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Discussion of Some Thermo-acoustical Relations for Simple Liquids

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Our present work is an attempt to contrast the degree of validity for some proposed relations between temperature coefficients of the volume and the ultrasonic velocity making use of experimental results compiled by us and calculated data using the significant structures theory. There is a fair correlation between the experimental and theoretical values, except in the neighbourhood of the triple point. We conclude that the theory is useful for prediction in the absence of experimental data.

1 INTRODUCTION AND THEORY

Among the various relations which link the expansion coefficient: $\alpha_v = (1/V)(\partial V/\partial T)_p$, and the temperature coefficient of the ultrasonic velocity: $\alpha_c = (1/c)(\partial c/\partial T)_p$, one can single out the Rao's formula^{1,2}:

$$\alpha_c = -K\alpha_v \quad (1.1)$$

where the parameter K is about 2 for simple liquids, about 3 for organic liquids and takes distinct values for molten metals.

Taking into account only the interactions of the nearest neighbours in a liquid system Schuyer³ has obtained:

$$\alpha_c = -\frac{m+n+1}{6}\alpha_v \quad (1.2)$$

where m and n are respectively the attractive and repulsive exponents in the $L - J$ potential. Kuczera⁴ has modified this expression in the form:

$$\alpha_c = -\frac{n}{6} \alpha_v \quad (1.3)$$

but has proposed that the coefficient n varies with the nature of the liquid. Finally, Hanzel and Krzak⁵ suggest the relation:

$$\alpha_c = -A(p, T)\alpha_v \quad (1.4)$$

where $A(p, T)$ is an unknown function which depends on both pressure and temperature.

Recently, Sharma⁶ has proposed a simple method for evaluating this quantity considering the critical state compressibility factor a , the number of nearest neighbours Z_c , the repulsive exponent n , the characteristic or hard core molar volume⁷ of liquids and the actual volume of liquid versus temperature.

2 RESULTS AND DISCUSSION

For the operative method we have fixed $n = 12$ and $Z_c = 4$, in agreement with other authors^{8,9} and the values of a and V^* were taken of the Ref. 6. The values of the volume versus temperature were taken from the literature.¹⁰⁻¹³ With these results, we have calculated the values of $A(p, T)$ as shown in Tables I-IV. One may see that A decreases slowly versus T in the same measure that the volume increases, in accord with Ref. 6.

We have compared these results with the ratio $-(\alpha_c/\alpha_v)$ experimental for Ar and Kr, and the ratio $-(\alpha_c/\alpha_v)$ theoretical for Ne, Ar, Kr and Xe, deduced from the significant structures theory using our previously published results.¹⁴ The results are also shown in Tables I-IV. The first conclusion is that the expressions of Rao, Kuczera and until Sharma's, are too simple to explain adequately the variation of the analyzed parameter.

TABLE I

Variation of the ratio between temperature coefficients for the ultrasonic velocity and volume versus temperature of liquid neon

$T(^{\circ}\text{K})$	$A(p, T)$	$(-\alpha_c/\alpha_v)$	$T(^{\circ}\text{K})$	$A(p, T)$	$(-\alpha_c/\alpha_v)$
24.55	1.81	1.09	30	1.67	2.04
26	1.77	1.81	34	1.54	1.91
27.09	1.76	1.72	40	1.25	1.34

TABLE II

Variation of the ratio between temperature coefficients for the ultrasonic velocity and volume versus temperature of liquid argon

$T(^{\circ}\text{K})$	$A(p, T)$	$-\alpha_c/\alpha_v$ theor.	$-\alpha_c/\alpha_v$ exp.	$T(^{\circ}\text{K})$	$A(p, T)$	$-\alpha_c/\alpha_v$ theor.	$-\alpha_c/\alpha_v$ exp.
83.81	1.83	0.80	1.94	97.76	1.70	2.01	1.96
85	1.82	1.12	1.97	110	1.59	2.05	1.94
86	1.81	1.21	1.98	122.39	1.46	2.13	2.06
87.30	1.79	1.38	1.96	130	1.37	1.87	1.61
92	1.75	1.83	1.97	140	1.21	1.13	1.25

TABLE III

Variation of the ratio between temperature coefficients for the ultrasonic velocity and volume versus temperature of liquid krypton

$T(^{\circ}\text{K})$	$A(p, T)$	$-\alpha_c/\alpha_v$ theor.	$-\alpha_c/\alpha_v$ exp.	$T(^{\circ}\text{K})$	$A(p, T)$	$-\alpha_c/\alpha_v$ theor.	$-\alpha_c/\alpha_v$ exp.
115.78	1.81	0.79	1.45	149.02	1.61	2.05	1.98
117.03	1.80	1.07	1.47	157.32	1.56	1.96	1.79
119.27	1.79	1.29	1.49	169.52	1.46	1.46	2.04
119.80	1.78	1.87	1.69	179.81	1.37	1.80	1.72
124.58	1.76	1.70	1.78	186.40	1.31	1.76	1.68
133.21	1.71	2.03	1.92	191.12	1.25	1.43	1.46
141.09	1.66	2.08	1.91	196.55	1.18	0.99	1.21

TABLE IV

Variation of the ratio between temperature coefficients for the ultrasonic velocity and volume versus temperature of liquid xenon

$T(^{\circ}\text{K})$	$A(p, T)$	$-\alpha_c/\alpha_v$ theor.	$T(^{\circ}\text{K})$	$A(p, T)$	$-\alpha_c/\alpha_v$ theor.
161.36	1.87	0.74	190	1.68	2.03
163	1.84	0.96	230	1.49	1.88
166.04	1.80	1.04	270	1.19	1.17

The second conclusion is the theoretical values, deduced from this work, and experimental values are well correlated, except in a short range of temperatures near the triple point, with a small dispersion, which decreases noticeably near the maximum (see Figures 1 and 2). Therefore we suggest that, in the absence of experimental results, our theoretical values can predict the variation of the parameters studied here with useful accuracy if we omit the above mentioned range near the triple point.

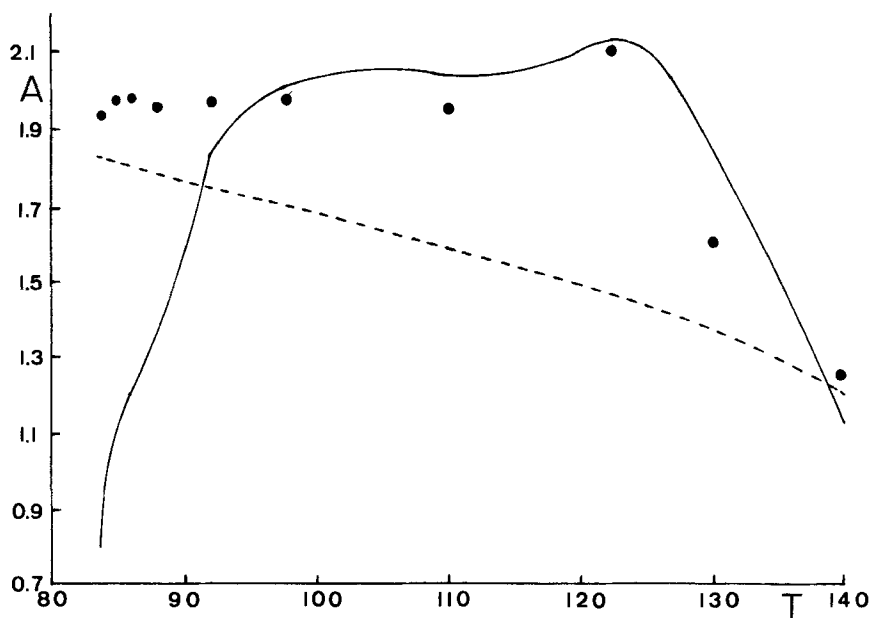


FIGURE 1 Variation of the ratio A between temperature coefficients for the ultrasonic velocity and volume versus temperature of liquid argon. Dashed curve is the variation deduced from the Rao's method. Continuous curve is the variation deduced from significant structures theory. Points are experimental data.

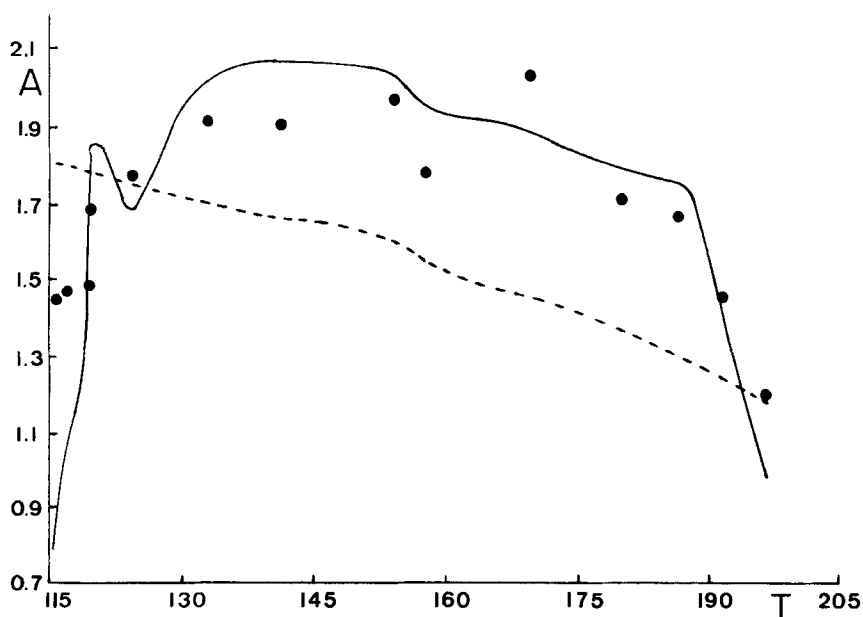


FIGURE 2 Variation of the ratio A between temperature coefficients for the ultrasonic velocity and volume versus temperature of liquid krypton. The curves and points have the same meaning as in Figure 1.

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