Relative Intermolecular Energy Parameters for the Freons from Sound Velocity Data

RONALD A. AZIZ

Department of Physics, University of Waterloo, Waterloo, Ontario

The velocity of sound has previously been measured in liquids CCl_4 (Rowlinson, 1959) at constant pressure and in CF_4 (Aziz et al., 1967) and CCl_2F_2 (Poole and Aziz, 1972) under saturated vapor. To complete this series, measurements for the velocity of sound in liquid CCl_3F and $CClF_3$ under saturated vapor are presented in this paper. On the assumption that the principle of corresponding states is valid, we have determined relative values for the energy parameter of an effective potential of the type $\phi = \epsilon f(\sigma/r)$ required to force corresponding states. Data on the velocity of sound under saturated vapor are especially suitable in this regard for two reasons. Firstly, measurements can be made very accurately (accuracy of ± 0.1% or better is possible). Secondly, plots of reduced sound velocity under saturated vapor vs. reduced temperature involve only the energy parameter ϵ for reduction. Forcing corresponding states will yield unambiguous relative values of ϵ since the parameter σ does not enter the picture.

APPARATUS AND METHOD

The velocity of sound was measured in liquids $CClF_3$ and CCl_3F from near their triple points to 189K and 257K respectively by the resonance technique of Guptill et al. (1955) using a cylindrical barium titanate transducer. The details of this method and the experimental technique were given by Lim and Aziz (1967) and Aziz et al. (1967). The gases were supplied by Matheson of Canada Ltd. The quoted purity of CCl_3F is 99.9% and that of $CClF_3$ is 99.0% minimum. Temperatures expressed on the IPTS 1968 scale were measured with the use of a Tinsley platinum resistance thermometer calibrated at the National Physical Laboratory in England. The uncertainty in the data is about ± 0.1% or less arising mainly from an uncertainty in the transducer diameter and its temperature variation and to a lesser extent in the determination of the resonance frequency.

RESULTS

CCl_3F

The data were fitted by the method of least squares to the curve

$$V_\sigma = 1963.17 - 4.81430T + .00240859T^2 \qquad (1)$$

Standard estimate of error = 0.2_3 m/s

$CClF_3$

The data were fitted by the method of least squares to the curve

$$V_\sigma = 1775.43 - 5.75289T + .00129947T^2 \qquad (2)$$

Standard estimate of error = 0.4_8 m/s

ANALYSIS OF RESULTS

For classical liquids, whose effective intermolecular potential is a central and pair-wise additive one of the form

$$\phi(r) = \epsilon f \left[\frac{\sigma}{r}\right], \qquad (3)$$

the reduced velocity of sound V^* has the form

$$V^* = F_1(P^*, T^*, \gamma) \quad \text{(Hamann, 1960)} \qquad (4)$$

where

$$V^* = V/V_0; \quad P^* = P/P_0; \quad T^* = T/T_0$$

and

$$V_0 = \left[\frac{N_0 \epsilon}{M}\right]^{1/2}; \quad P_0 = \epsilon/\sigma^3; \quad T_0 = \epsilon/k$$

Since the liquids under consideration have very nearly the same value of the specific heat ratio γ, Equation (4) may be considered, to a good approximation, as a universal equation for all members of the series. Under saturated conditions, P^* is a function of T^* only. Hence

$$V^* = V_\sigma^* = F_2(T^*) \qquad (5)$$

For liquids satisfying corresponding states, plots of reduced velocity V^* vs. reduced temperature T^* should coincide provided the appropriate values of the energy parameter ϵ are used. Alternatively, we may determine a new set of relative values of ϵ which will produce coincidence of the reduced curves. As reported in a previous note (Poole and Aziz, 1972) the Lennard-Jones 12-6 values of ϵ/k proposed by Nierode et al. (1970) for CCl_2F_2 (ϵ/k = 264.98K) and for CF_4 (ϵ/k = 167.47K) bring the reduced curves $V_\sigma^*(T^*)$ for these two substances in the liquid phase into close coincidence. It was reported further that a value of ϵ/k = 377.1K for CCl_4 was necessary to bring its reduced curve into close coincidence with those of CF_4 and CCl_2F_2. We now find that the reduced sound velocity curves for CCl_3F and $CClF_3$ are brought into close coincidence with the other curves for values of ϵ/k of 318.8K and 213.2K, respectively. The reduced velocity curves are shown in Figure 1.

By forcing corresponding states we are essentially determining relative values of ϵ/k. Recommended values of ϵ/k relative to that of CF_4 are given in Table 1. To see that it is the relative value which is determined, consider Figure 2 in which we have schematically plotted $\log (V_\sigma^2 M/N_0 k) = \log V_\sigma^{*2} + \log (\epsilon/k)$ vs. $\log T = \log T^* + \log (\epsilon/k)$ for substances X and Y. Assume that the reduced curve V_σ^* vs. T^* is represented by the dotted line. The precise location of the reduced curve will depend on the specific model potential chosen with the form of Equation (3). The curves for X and Y may be brought into coincidence with the dotted one by mapping corresponding points along a 45° angle. For example, points A and B map into C and lengths ab and de, both equal to $\log \epsilon_Y/\epsilon_X$ give the relative value of the energy parameter regardless of the detailed form of the intermolecular potential provided only it has the general form of Equation (1). Thus, the determination of the relative value of ϵ can be made in an unambiguous way without any simultaneous adjustment of σ.

CONCLUSION

By forcing corresponding states as applied to sound velocity in the liquid freons, we have obtained accurate relative values of the energy parameter of an effective intermolecular potential of form of Equation (3) in an unambiguous way. These relative values of ϵ/k may be useful in removing the indeterminacy of potential parameters in the regression of other data.

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NOTATION

k = Boltzmann constant
K = kelvins
M = molecular weight
N_0 = Avogadro's number
P = pressure
P^* = reduced pressure, $P^* = [P/(\epsilon/\sigma^3)]$
r = separation between molecules
T = thermodynamic temperature
T^* = reduced thermodynamic temperature, $T^* = [T/(\epsilon/k)]$

TABLE 1. RELATIVE VALUES OF ENERGY PARAMETER ϵ OF AN EFFECTIVE POTENTIAL OF FORM $\phi = \epsilon f(\sigma/r)$ (Reference ϵ for CF_4)

System	Scaling factor
CCl_4	2.2517
CCl_3F	1.9036
CCl_2F_2	1.5823
$CClF_3$	1.2732
CF_4	1.0000

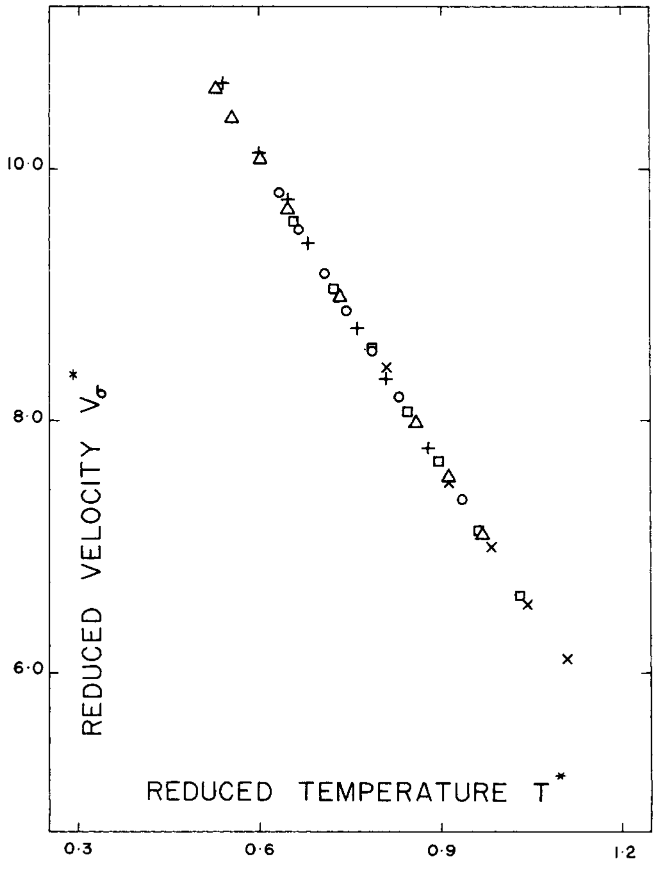

Fig. 1. Reduced velocity of sound vs. reduced temperature CCl_4(X: $\epsilon/k = 341.5K$), CCl_3F(○: $\epsilon/k = 288.7K$), CCl_2F_2(+: $\epsilon/k = 240.0K$), $CClF_3$(△: $\epsilon/k = 193.1K$), CF_4(□: $\epsilon/k = 151.67K$).

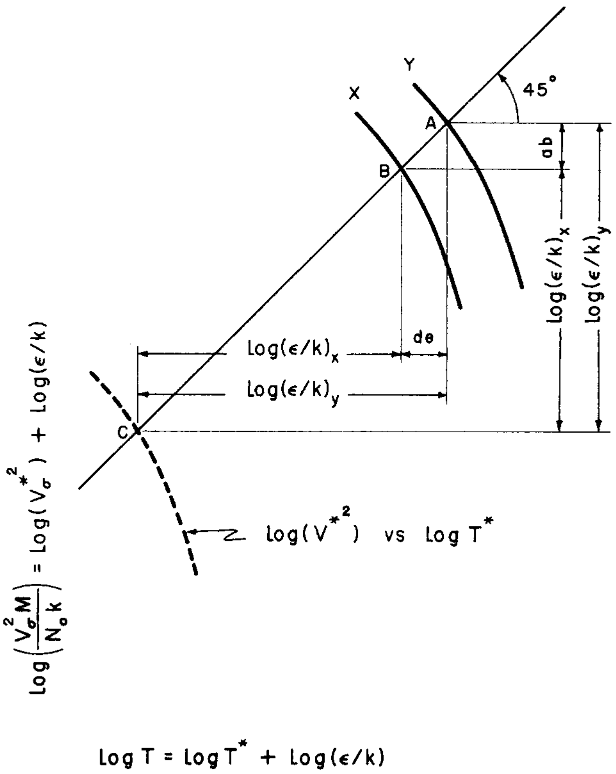

Fig. 2. Forcing of corresponding states as applied to sound velocity under saturated vapor determines relative values of ϵ/k.

V = velocity of sound
V_0 = reduction constant for velocity of sound, $V_0 = (N_0\,\epsilon/M)^{1/2}$
V^* = reduced velocity of sound, $V^* = [V/V_0]$
V_σ = velocity of sound under saturated conditions
V_σ^* = reduced velocity of sound under saturated conditions

Greek Letters

ϵ, σ = intermolecular potential parameters
ϕ = intermolecular potential
ρ = density
γ = specific heat ratio

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