

ULTRASONIC VELOCITY AND  
MOLECULAR VOLUME

It was shown by Rao<sup>1</sup> that the thermal coefficient of velocity of sound  $v$  in organic liquids is about three times the thermal coefficient of density  $\rho$ . The relation can be written

$$v^{\frac{3}{2}} V = R \tag{1}$$

Here  $R$  is a constant independent of temperature and  $V$  is the molecular volume  $M/\rho$ .  $R$  was found to compare favourably with the parachor as far as its additive properties were concerned. It was shown that plot of  $R$  against  $M$  resulted in a series of straight lines for each homologous series represented by the equation

$$R = \alpha M + \beta \tag{2}$$

$\alpha$  was shown to have the same value (14) and  $\beta$  was found to be different for different homologous series. Parthasarathy<sup>2</sup> found that by plotting  $v^{\frac{3}{2}}/\rho$  against  $1/M$  a family of straight lines is obtained, satisfying the equation

$$v^{\frac{3}{2}}/\rho = A + B/M \tag{3}$$

where  $A$  is 13.56 which is the same for all series and  $B$  varies from series to series. Equations 2 and 3 are algebraically the same.

The proof of the constancy of  $\alpha$  in (2) and  $A$  in (3) is simple. If  $R_1, R_2$  are the values of  $R$  for two successive members of homologous series, then the difference in the value of  $R$  divided by 14, the molecular weight of  $\text{CH}_2$  gives the value of  $\alpha$  or  $A$  which according to Rao is 14 and 13.535 according to Lagemann, McMillan and Wolsey,<sup>3</sup> and 13.56 according to Parthasarathy. Rao took the average value of  $R = 195$  for a number of series including alcohols. It would therefore appear that more measurements of the velocity of sound on a larger number of series are needed to check up the value of the difference in the value of  $R$  for two successive members. It is very easy to extend this result to the case of parachor on similar grounds. The constancy of  $A$  or  $\alpha$  when  $v^{\frac{3}{2}}/\rho$  is plotted against  $\eta$  is to be traced to the same cause, namely, that  $R$  is additive. But the fact remains that such a relation holds only for one temperature, as  $\eta$  varies considerably with temperature.

The quantity  $R$  is an additive function as the parachor is. It is known that the molecular critical volumes are additive. Since  $R$  is independent of temperature and has the property of being additive, one naturally thinks of comparing  $R$  with  $V_c$ . It was shown by Rao<sup>4</sup> that the ratio of  $R$  to  $V$  is a constant for most substances. We will be then comparing quantities

which are not dimensionally the same. Instead of expressing  $R$  in terms of length, mass and time, if we build up a dimensional equation in terms of energy, length and mass then  $R$  could be expressed as  $(\text{energy})^{\frac{1}{2}} (\text{length})^{\frac{3}{2}}$  and  $(\text{Mass})^{-\frac{1}{2}}$ . Since  $R$  is nearly proportional to  $V_c$  any departure from the constancy of the ratio is to be attributed to other factors not taken into consideration. Since we are considering the molecular critical volume, the other corresponding quantities will be the critical temperature, and critical pressure. Either of these could be used to build up the equation. Since energy is directly proportional to the temperature we replace the energy term by  $\theta_c$ . Thus  $R$  can be expressed

$$R = R' \left( \frac{\theta_c}{M} \right)^{\frac{1}{2}} V_c \tag{4}$$

The constancy of  $R'$  is very much better than the constancy of the ratio  $R/V_c$  as found from an examination of 30 substances. From the known values of  $\theta_c, V_c$  for any liquid and from the mean value of  $R'$ , the  $R$  value for any liquid could be found and hence the velocity of sound in the liquid at any temperature knowing its density at that temperature. In the intermolecular potential used by Lennard Jones and his collaborators the quantities  $\phi$  and  $r_0$  which are constants of energy and length characteristic of the molecule are found proportional respectively to  $\theta_c$  and  $V_c^{\frac{1}{3}}$ . We may, therefore, write equation (4) as follows:

$$R = R'' \left( \frac{\phi_0}{M} \right)^{\frac{1}{2}} V_c \tag{12}$$

where  $R''$  is a temperature-independent constant, the same for all substances. From the interpretation of  $r_0^3$  as a collision volume we would expect  $R$  to be additive when more complicated molecules are built up as the contribution of the term  $(\phi_0/M)^{\frac{1}{2}}$  is indeed small. The utility of the function  $R$  in studying molecular association has been pointed out by Lagemann<sup>5</sup> and his collaborators. The additive property could be extended to solution as was first pointed by Rao in 1940.<sup>1</sup> Starting from the equation of state of the type

$$Pv + f(v) = \frac{\gamma_m E}{\lambda} \tag{5}$$

after Van Laar,<sup>6</sup> we can show by a little calculation that the adiabatic compressibility  $\beta_\phi$  can be put as

$$\beta_\phi = 1 / \left[ P \left( 1 + \frac{\gamma_m}{\lambda} \right) + \frac{\gamma_m}{\lambda} \frac{f(v)}{v} + f'(v) \right] \tag{6}$$

If we neglect  $P$  the external pressure with reference to the internal pressure