The Adiabatic Compressibility of Liquids

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IN recent years a number of investigators have determined the adiabatic compressibility of liquids. Tyrer[1,2] has determined the adiabatic compressibility of a few liquids in the range 0 deg. to 80 deg. C, while Shiba has found the adiabatic compressibility of liquids at two temperatures, namely 30 deg. and 35 deg. C. Measurements on the velocity of sound in liquids also yield values of adiabatic compressibility. In general, these values compare well with those determined by direct methods with the piezometer.

A simple relation[3] between the velocity of sound v in liquids and its volecular volume V exists, viz.

$$v^{\frac{1}{3}}V = R, \qquad (1)$$

where R is a constant independent of temperature. It has also been shown[4] that the constant R is an additive function of the chemical composition as in the case of the parachor. R is further related[5] to the molecular critical volume V_c and critical temperature θ_c and molecular weight M by the relation $R = \alpha(\theta_c/M)^{1/6}V_c$ where α is a constant with a mean value of 2.68. The velocity of sound in a liquid is related to the adiabatic compressibility β_ϕ and density ρ of the liquid by the relation

$$v = 1/(\beta_\phi\rho)^{\frac{1}{2}}. \qquad (2)$$

Combining relation (1) with (2) it follows that

$$\beta_\phi^{1/7}\rho = \text{constant} \qquad (3)$$

independent of temperature for each liquid. In Table I values of β_ϕ and ρ are given at various temperatures and the last column gives the values of $\beta_\phi^{1/7}\rho$ computed in the case of benzene. The same result is found to hold good for other liquids like carbontetrachloride ether, toluene, chlorobenzene, chloroform, cyclohexane, bromobenzene, o-nitrotoluene, M-nitrotoluene, actophenone, carbondisulphide, cyclohexanone, and acetic acid.

As regards the temperature variation of the adiabatic compressibility, it is generally found that the value of β_ϕ increases with temperature, the increase becoming more

TABLE I

Liquid	Temp.	$\beta_\phi 10^6$	ρ density	$\beta_\phi^{1/7}\rho$
Benzene	0	56	0.9001	1.599
	10	61	0.8896	1.601
	20	66.32	0.8790	1.601
	30	72	0.8684	1.601
	40	78.26	0.8576	1.599
	50	85.12	0.8467	1.597
	60	92.99	0.8351	1.595
	70	101.91	0.8262	1.600
	80	111.50	0.8145	1.597

rapid as the temperature increases. With many liquids the adiabatic compressibility increases by about 60 percent for a rise of temperature 0 to 60 deg. C. A large part of the high initial compressibility of ordinary liquids is connected with the nearness of the critical point liquid-gas for compressibility in the gas phase which is high and which at the critical point itself, β_ϕ, is infinite. Hence the absolute value of the compressibility depends on how far the temperature is from the critical point.

For temperatures at which the saturation vapor density can be neglected in comparison with the liquid density the variation of liquid[6] density with temperature is represented by the relation

$$\rho = \rho_0\{1 - \theta/\theta_c\}^{3/10}. \qquad (4)$$

Combining (3) with (4) it follows that

$$\beta_\phi = \beta_{\phi 0}\{1 - \theta/\theta_c\}^{-2.1} \qquad (5)$$

where $\beta_{\phi 0}$ is independent of the temperature, θ is any temperature on the absolute scale. The critical temperatures calculated from the above relation are in good agreement with observed values of θ_c.

By starting from the general equation of state for the liquid and using Maxwell's thermodynamic relations, it can be shown that the compressibility in the case of liquids should be a function of the density only. Details about these will be published elsewhere.

[1] Tyrer, J. Chem. Soc. 105, 2334 (1914).
[2] For a review see Bridgman, Rev. Mod. Phys. 7 (1935).
[3] M. Rama Rao, Cur. Sci. 8, 510 (1939) and Ind. J. Phys. 14, 109 (1940).
[4] M. Rama Rao, J. Chem. Phys. 9, 682 (1941).
[5] M. Rama Rao, J. Mys. Uni. 12, 896 (1942).
[6] Sugden, J. Chem. Soc. 1700–1786 (1927); J. Chem. Soc. 1055 (1929).