

four substances having a low crystallisation pressure (not exceeding 600 atm) and a large change $\Delta V/V_0$ ¹² in the immediate vicinity of the crystallisation point.

The theory can probably be extended to higher pressures, since no considerable discrepancies between theory and experiment are observed near 40 000 atm, the highest static pressure which has yet been achieved with liquids^{12,14}, at which the compression deformation is ~ 40% (curve (c) in Fig. 1). The applicability of Tait's empirical isotherms has been assessed up to pressures of 1000 atm⁸. Besides the velocity of sound in compressed liquids, which has been quite well studied in Refs. 15 and 16 and elsewhere, direct measurements have been made of the coefficient β up to 200 atm¹⁷, and isolated measurements of the coefficient of thermal expansion $\alpha = \beta p K^{-1}$ up to 3000 atm¹¹. They all agree satisfactorily with those calculated by means of the formulae (4).⁷ Equations (3) also enable an expression to be obtained for the entropy of compressed liquids, from which adiabatic curves for the liquids are found by a numerical method, which agree satisfactorily with Tait's empirical adiabatic curves¹⁸.

If the second equation (3) is used in the above calculations, only V_0 need be known experimentally; and if the first equation (3) is still used, c_{p0} must also be known, since the term $u_1(T)$ contains the vibrational energy of the internal degrees of freedom of the molecules, which is not in general known. For the calculations these data have been taken mainly from Ref. 17.

Equations (3) enable the properties of liquids under tension to be calculated, but no experimental data are available for comparison. The method of calculation is suitable also for computing the properties of liquids on the equilibrium curve. Values of $c_0(T)$ calculated by means of the last formula (5) agree satisfactorily with experiment. Let us compute the isothermal modulus of elasticity by means of the well known relation

$$K = V[(\partial^2 U / \partial V^2)_T - T(\partial^2 S / \partial V^2)_T]. \quad (7)$$

Applying the relation $(S''_{VV})_T = p''_{VV}$ and using the second equation (3) and the first equation (5), we hence obtain for K on the equilibrium curve

$$K_0 = \frac{u_0 T}{V_0 \alpha_0} \left(1 + \frac{\alpha_0 T}{\alpha_0^2} - \frac{u_0 T T}{\alpha_0 u_0 T} \right) + \frac{T n m}{V_0} \left[\frac{n(n+1) - m(m+1)}{n-m} \times \right. \\ \left. \times u_0 \alpha_0 + u_0 T \right]. \quad (8)$$

Numerical integration of Eqn. (6) taking into account the temperature dependence of α_0 with the initial condition in the vicinity of the solidification point yields for carbon tetrachloride ($n = 4.9$) at 20°C the value $u_0 = 1.03 \times 10^{11}$ ergs mole⁻¹. From the experimental values $\alpha_0 = 0.00121$ deg⁻¹ and $\alpha_0' T \approx 2.0 \times 10^{-6}$ deg⁻² together with Eqn. (6) we find that $u_0' T = -4.33 \times 10^8$ ergs mole⁻¹ deg⁻¹ and $u_0'' T T = -5.0 \times 10^5$ ergs mole⁻¹ deg⁻². On substituting these values in Eqn. (8) we obtain $K_0 = 1.11 \times 10^{10}$ dyn cm⁻². Calculation by means of the third equation (5) gives $K_0 = 1.04 \times 10^{10}$ dyn cm⁻², and the experimental value is $K_0 = 0.97 \times 10^{10}$ dyn cm⁻².¹¹ In view of the fact that Eqn. (8) contains six terms differing in sign, and existing methods for the direct measurement of K_0 have an accuracy of ~ 10%, the agreement among the two methods of calculation and experiment is satisfactory. The latter calculation indicates that Eqns. (3) and (5) represent the energy and entropy portions of K correctly, and that the theory is internally consistent.

The precomputer potentialities of Eqns. (3) evidently stem from their taking into account long-range molecular

interactions. This fact, as well as the dependence of u on V_0 and the presence of the term $u_1(T)$, is not usually taken into account when equations of this type are used to calculate the properties of condensed (solid) bodies¹⁹.

REFERENCES

1. Ya. I. Frenkel', "Kineticheskaya Teoriya Zhidkosti" (Kinetic Theory of Liquids), Izd. Akad. Nauk SSSR, Moscow, 1959, pp. 159, 175, 191.
2. J. D. Bernal, in "Rost Kristallov" (Growth of Crystals), Nauka, Moscow, 1965, Vol. 5, p. 149.
3. L. D. Landau and E. M. Lifshits, "Statisticheskaya Fizika" (Statistical Physics), Nauka, Moscow, 1964, p. 211.
4. I. Prigogine and R. Defay, "Chemical Thermodynamics" (Translated into Russian), Nauka, Novosibirsk, 1966, p. 171.
5. E. A. Moelwyn-Hughes, "Physical Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1962, Vol. 1, p. 284.
6. K. P. Stanyukovich, "Neustanovivshiesya Dvizheniya Sploshnoi Sredy" (Unsteady Movements of a Continuous Medium), Gostekhizdat, Moscow, 1955, p. 15.
7. A. A. Glinskii, in "Primenenie Ul'traakustiki k Issledovaniyu Veshchestva" (Application of Ultrasonics to the Investigation of Matter), Izd. MOPI, Moscow, 1967, No. 23, p. 95.
8. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "The Molecular Theory of Gases and Liquids" (Translated into Russian), Inostr. Lit., 1961, pp. 218, 819.
9. W. van Witenburg and J. C. Stryland, Canad. J. Phys., 46, 811 (1968).
10. A. A. Glinskii, Izv. Vys. Ucheb. Zaved., Fiz., No. 2, 185 (1964).
11. Landolt-Börnstein, "Physikalisch-chemische Tabellen", I, II, 1923, I, 1935.
12. P. W. Bridgman, Proc. Amer. Acad. Arts Sci., 77, 129 (1949).
13. Yu. A. Atanov, V. A. Borzunov, and V. N. Razumikhin, Trudy Inst. Gos. Komiteta Standartov, Mer i Izmeritel'nykh Priborov SSSR, No. 75 (135), 143 (1964).
14. C. A. Swenson, "Physics of High Pressures" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 124.
15. J. F. Mifsud and A. W. Nolle, J. Acoust. Soc. America, 28, 469 (1956).
16. L. F. Vereshchagin and N. A. Yuzefovich, Zhur. Fiz. Khim., 36, 969 (1962) [Russ. J. Phys. Chem., No. 5 (1962)].
17. N. B. Vargaftik, "Spravochnik po Teplofizicheskim Svoistvam Gazov i Zhidkosti" (Handbook of the Thermophysical Properties of Gases and Liquids), Fizmatgiz, Moscow, 1963.
18. A. A. Glinskii, Zhur. Fiz. Khim., 43, 752 (1969) [Russ. J. Phys. Chem., No. 3 (1969)].
19. G. A. Ostroumov, "Osnovy Nelineinoy Akustiki" (Foundations of Non-linear Acoustics), Izd. Leningrad. Univ., 1968, p. 30.

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