

Furthermore, the characteristic change in refraction for a conjugated system is expressed by a definite exaltation, in particular  $F^{\Sigma} \text{disp} \% = 145\%$  for the ketones  $-\text{CH}:\text{CH}:\text{CH}:\text{CO}:\text{R}$ , the structure of this group corresponding to homologues of series C. Comparing the contribution of conjugation to the retention volume with that of one double bond, we obtain from Fig. 1 for the actual compounds  $J_0-A$ ,  $J_0-B$ , and  $J_0-C$

$$\frac{\lg V_{g,I}(J_0-C) - \lg V_{g,I}(J_0-B)}{\lg V_{g,II}(J_0-B) - \lg V_{g,I}(J_0-A)} \cdot 100 = 145 (\pm 2\%),$$

i.e. complete agreement is obtained between the relative refraction and exaltation and the relative retention volumes of the same groups of compounds.

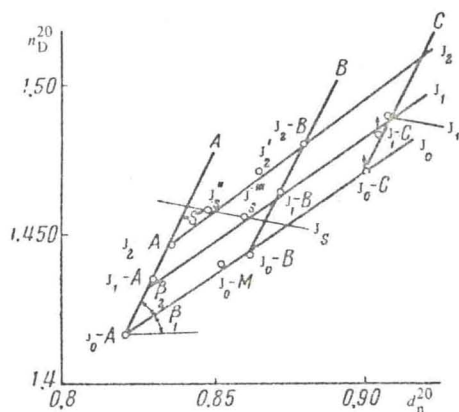
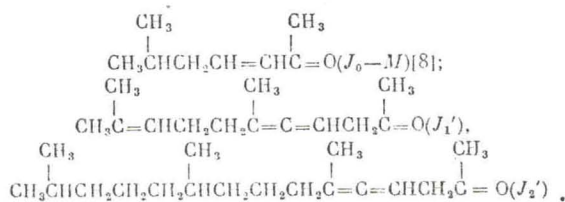
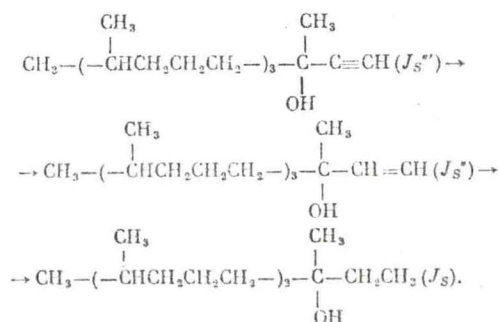


Figure 2. Dependence of refractive index  $n_D^{20}$  on density  $d_n^{20}$  for the same compounds as in Fig. 1.

The above relation extends to other compounds which, although not members of these homologous series, have common structural features (Figs. 1 and 2):



Analogous relations are obtained for another class of compounds, alcohols, distinguished by a monotonic variation in unsaturation:



The angle  $S$  on the plot of  $\lg V_{g,I}$  against  $\lg V_{g,II}$  (Fig. 1) and the angle  $S''$  on the  $n_D-d_n$  graph (Fig. 2) between the straight lines  $J_S$  and  $A$  ( $B$ ,  $C$ ) are equal.

Thus the investigations reported above confirm the existence of an analogy between the relations  $\lg V_{g,I} = f(\lg V_{g,II})$  and  $n_D = f(d_n)$  for compounds which differ in molecular weight and in degree of unsaturation. This principle justifies the previously assumed additivity of the retention volume. Hence group or atomic increments may exist (by analogy with refraction), from which the retention of any compound can be calculated.

#### REFERENCES

1. A. A. Zhukhovitskii, M. S. Selenkina, and N. M. Turkel'taub, *Khim. Tekhnol. Topliv Masel*, 57, No. 11 (1960).
2. M. Wurst, *Coll. Czech. Chem. Comm.*, 29, 1458 (1964).
3. J. Franc, *Coll. Czech. Chem. Comm.*, 26, 1579 (1961).
4. A. N. Vorob'ev, *Coll. Czech. Chem. Comm.*, 27, 1045 (1962).
5. M. E. Maurit, G. V. Smirnova, E. I. Parfenov, I. K. Sarycheva, and N. I. Preobrazhenskii, *Dokl. Akad. Nauk SSSR*, 140, 1330 (1961).
6. M. A. Miropol'skaya, N. I. Fedorova, A. Ya. Veinberg, M. Ts. Yanotovskii, and G. I. Samokhvalov, *Zhur. Obshch. Khim.*, 32, 2214 (1962).
7. E. I. Kozlov, M. Ts. Yanotovskii, and G. I. Samokhvalov, *Zhur. Obshch. Khim.*, 34, 2748 (1964).

All-Union Vitamins  
Scientific Research  
Institute, Moscow

Received 10th January 1969

U.D.C. 541.121/.123

## Equations of State of Liquids in the Temperature Range adjacent to the Triple Point

A. A. Glinskii

Equations of state, derived from the concept of condensed media as sets of oscillators, have been used to calculate the isotherms of liquids and also several of their thermodynamic properties. The calculations are compared with experiment up to a static pressure of 40000 atm, the highest yet achieved with liquids.

In the vicinity of the triple point a liquid is in a quasi-solid state<sup>1,2</sup>, and therefore its properties can be described by the caloric and thermal equations of state

$$U = u_1(T) + u; \quad p = p_1(T, V) - u'_v, \quad (1)$$

which derive from the concept of crystals and amorphous substances as systems of oscillators at sufficiently high temperatures<sup>1,3</sup>. Here  $u_1(T)$  is the sum of the mean kinetic and the mean potential energy of vibrational motion of the molecules, and  $p_1(T, V)$  is the thermal pressure. The mutual potential energy  $u$ , calculated on the assumption that the molecules are located at fixed equilibrium positions, about which they oscillate, should satisfy the condition<sup>1,4</sup>

$$u'_v = 0 \quad \text{when } V = V_0, \quad (2)$$

where  $V_0 = V_0(T)$  is the volume of the liquid on the equilibrium curve.

It follows from condition (2) that away from the equilibrium curve  $u = u(V, V_0)$ . For small deformations  $u$  will be a quadratic function of the difference  $V - V_0$ . To investigate the behaviour of liquids during non-linear deformations, we express the pair interaction energy of the molecules as a Mie potential, for which  $u$  can be calculated both for crystals and approximately also for liquids taking into account long-range interactions of the molecules<sup>5</sup>. Equation (1) with the condition (2) then becomes

$$U = u_1(T) - \frac{u(V_0)}{n-m} (mv^n - nv^m); \quad p = \frac{u(V_0)nm}{V_0(m-n)} (v^{n+1} - v^{m+1}), \quad (3)$$

where  $v = V_0/V$ ,  $n$  and  $m$  are parameters of the Mie potential, and  $u(V_0)$  is the value of  $u$  on the equilibrium curve.

The second equation (3) is based on the condition<sup>6</sup>  $p_1(T, V) \ll u'_V$ , that far from the critical point the vapour pressure is very small in comparison with the external pressure. It has been shown<sup>7</sup> that, in calculating derivatives from the second equation (1), we can neglect also derivatives with respect to  $p_1$  when the condition  $V_1 \geq 10^3 V$  is satisfied, where  $V_1$  is the volume of saturated vapour in equilibrium with the liquid. Thus Eqns. (3) are applicable between the triple point and the temperature at which this condition is satisfied. With most liquids this range constitutes about 30–50% of the range of existence of the liquid phase. From Eqns. (3) we find the isothermal modulus of elasticity  $K$ , the thermal coefficient of the pressure  $\beta$ , the heat capacity  $c_V$ , and the velocity of sound  $c$ :

$$\begin{aligned} K &= \frac{u_0 nm}{(n-m)V_0} [(n+1)v^{n+1} - (m+1)v^{m+1}], \\ \beta p &= \frac{nm}{V(n-m)} [u_0 \alpha_0 (nv^n - mv^m) + u'_{0T} (v^n - v^m)], \\ c_v &= c_{v0} + u'_{0T} + \frac{u_0 \alpha_0 nm}{n-m} (v^n - v^m) + \frac{u'_{0T}}{n-m} (mv^n - nv^m), \\ c^2 &= \frac{VK}{M} \left( 1 + \frac{TV\beta^2 p^2}{Kc_v} \right), \end{aligned} \quad (4)$$

where  $\alpha_0 = (1/V_0)(dV_0/dT)$ ,  $u_0 = -u(V_0)$ , and  $M$  is the molecular mass.

Putting  $v = 1$  in Eqns. (3) and (4), and denoting quantities on the equilibrium curve by the subscript 0, we obtain

$$\begin{aligned} U_0 &= u_1(T) - u_0; \quad p_0 = 0; \quad K_0 = \frac{u_0 nm}{V_0}; \quad (\beta p)_0 = \frac{nm u_0 \alpha_0}{V_0}; \quad c_0^2 = \\ &= \frac{nm u_0}{M} \left( 1 - \frac{T \alpha_0^2 n m u_0}{M c_{v0}} \right)^{-1}. \end{aligned} \quad (5)$$

From the thermodynamic identity  $p = T\beta p - (U'_V)_T$  applied to the equilibrium curve and the first, second, and fourth relations (5) we obtain the equation

$$u'_{0T} + T n m \alpha_0^2 u_0 = 0 \quad (6)$$

for computing  $u_0$ . If the exponent  $n$  is known, calculations by means of formulae (3)–(6) with  $m = 2$ , which has a theoretical basis, contain no adjustable parameters. The quantity  $u_0$ , which is required for the calculations, can be computed from experimental values of  $c_0$ ,  $\alpha_0$ , and  $c_{p0}$  from the last equation (5) or even by integrating Eqn. (6) using only one value of  $u_0$ , found from (5), as an integration constant.

Curve (a) in Fig. 1 illustrates the quantity  $\Delta V/V_0 = 1 - v^{-1}$ , calculated from Eqn. (2)<sup>3</sup> for liquid argon by a method of successive approximations with  $n = 3.5$ , found by approximate numerical quantum-mechanical calculations of the energy of repulsion based on a power law<sup>8</sup>. Values of  $n$  for a few substances, found from their properties in the condensed state, have been collected<sup>5</sup>. Curve (b) in Fig. 1

has been calculated for pentane with  $n = 5.5$ . The quantities (4) are computed from values of  $v(p)$ . Curve (a) in Fig. 2 has been calculated for the speed of sound in carbon disulphide with  $n = 3.9$ . For most liquids  $n$  is unknown, and we then have a one-parameter theory. In this case  $n$  is found from one experimental value of  $\beta$  with  $v \neq 1$  by application of the second equation (3) or even by substitution in the last equation (5) of the semi-empirical formula  $u_0 = 2\sigma V_0^{2/3} N^{1/3}$ , where  $\sigma$  is the surface tension and  $N$  is Avogadro's number<sup>10</sup>. Another method requires knowledge of experimental data solely on the equilibrium curve.

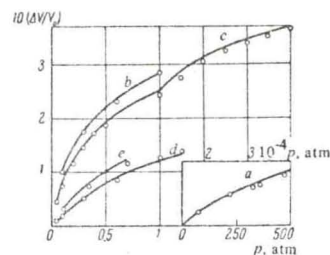


Figure 1. Points for different temperatures from various sources: a)  $-171.89^\circ\text{C}$ <sup>9</sup>; b)  $0^\circ\text{C}$ <sup>11</sup>; c)  $25^\circ\text{C}$ <sup>12</sup>; d)  $50^\circ\text{C}$ <sup>11</sup>; e)  $20^\circ\text{C}$ <sup>13</sup>.

Values of  $n$  which are almost independent of temperature, and agree satisfactorily among themselves and with the above and other independent values, are obtained in such ways. Thus in Fig. 1 curve (c) has been calculated for oct-1-ene ( $n = 5.81$ ), curve (d) for glycerol (7.92), and curve (e) for ethylene glycol (6.17), and in Fig. 2 curve (b) has been calculated for n-butanol (6.16).

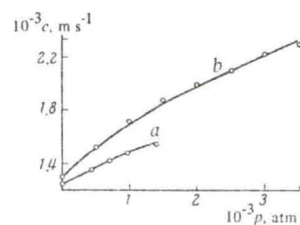


Figure 2. Points for different temperatures: a)  $0^\circ\text{C}$ <sup>15</sup>; b)  $20^\circ\text{C}$ <sup>16</sup>.

The isotherms of about eighty liquids have now been studied experimentally and will be found in Refs. 9 and 11–13 and in certain other works. Calculations were made for sixteen liquids up to 40 000 atm<sup>12</sup> and for seven-teen liquids up to 10 000–12 000 atm<sup>11</sup>. Data on the equilibrium curve could not be found for other liquids. All calculations agree satisfactorily with experiment, even if the liquid crystallised under the influence of external pressure<sup>12</sup>, when the change in  $\Delta V/V_0$  on crystallisation is small. Considerable divergence is found only with

four sub-  
exceed  
immedi

The  
sures,  
theory  
highest  
liquids  
~40%  
empiri  
of 1000  
pressed  
Refs. 15  
been m  
lated m  
 $\alpha = \beta p$   
torily w  
Equatio  
the ent  
curves  
which a  
curves

If th  
tions,  
first eq  
since th  
interna  
in gene  
been ta

Equi  
tension  
availab  
suitabl  
equilib  
of the l  
ment.  
ticity b

Apply  
equatic  
K on th

$$K_0 = \frac{u_0 nm}{V_0}$$

Num  
temper  
the vic  
tetrach  
ergs m  
deg<sup>-1</sup>  
find th  
-5.0 x  
values  
Calcul  
1.04 x  
0.97 x  
contai  
for the  
~10<sup>3</sup>  
tion an  
tion in  
and ca  
intera

The  
stem



four substances having a low crystallisation pressure (not exceeding 600 atm) and a large change  $\Delta V/V_0$ <sup>12</sup> 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<sup>12,14</sup>, 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 atm<sup>8</sup>. 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  $\beta$  up to 200 atm<sup>17</sup>, and isolated measurements of the coefficient of thermal expansion  $\alpha = \beta p K^{-1}$  up to 3000 atm<sup>11</sup>. They all agree satisfactorily with those calculated by means of the formulae (4).<sup>7</sup> 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 curves<sup>18</sup>.

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  $(S''_{VV})_T = p''_{VT}$  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  $\alpha_0$  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<sup>-1</sup>. From the experimental values  $\alpha_0 = 0.00121$  deg<sup>-1</sup> and  $\alpha_0' T \approx 2.0 \times 10^{-6}$  deg<sup>-2</sup> together with Eqn. (6) we find that  $u_0' T = -4.33 \times 10^8$  ergs mole<sup>-1</sup> deg<sup>-1</sup> and  $u_0'' T T = -5.0 \times 10^5$  ergs mole<sup>-1</sup> deg<sup>-2</sup>. On substituting these values in Eqn. (8) we obtain  $K_0 = 1.11 \times 10^{10}$  dyn cm<sup>-2</sup>. Calculation by means of the third equation (5) gives  $K_0 = 1.04 \times 10^{10}$  dyn cm<sup>-2</sup>, and the experimental value is  $K_0 = 0.97 \times 10^{10}$  dyn cm<sup>-2</sup>.<sup>11</sup> 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) bodies<sup>19</sup>.

## 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.

Krupskaya Moscow  
Regional Pedagogic  
Institute

Received 13th January 1969