

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.

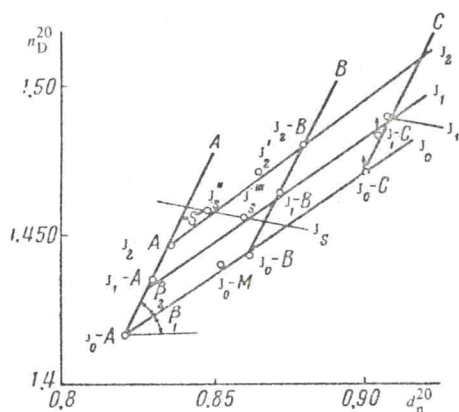
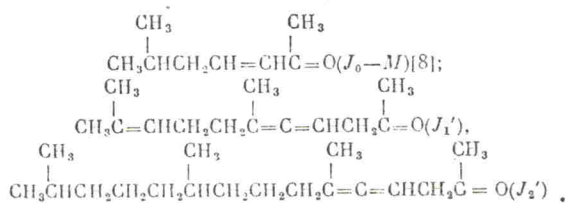
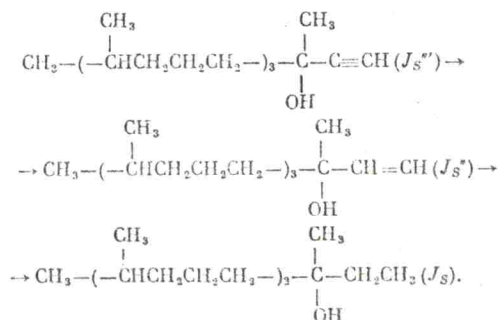


Figure 2. Dependence of refractive index  $n_D^{20}$  on density  $d_n^{20}$  for the same compounds as in Fig. 1.

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.

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Received 10th January 1969

U.D.C. 541.121/.123

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

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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>

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

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