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INVESTIGATION OF THE PROPERTIES OF SUBSTANCES ON THE BOUNDARY CURVES OF LIQUID–VAPOR PHASE TRANSITION

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A new approach to construction of generalized dependences for different properties of substances is proposed. A study is made of the changes in the difference in the properties of various substances on the boundary curves of liquid–vapor phase transition. Generalization results obtained in processing of experimental data on the thermodynamic and transport properties of substances on the boundary curves of liquid–vapor transition of monatomic and multiatomic gases, normal and polar organic and inorganic liquids, alkali metals, and mercury are discussed. An analogous approach may be used in studying solid body–liquid and solid body–gas phase transitions.

It is well known that certain physical effects determining the specific value of any property of a substance are equally inherent in both liquid and gaseous states. Therefore, in studying the difference in the values of the property under study on the boundary curves of liquid–vapor transition, the influence of these effects becomes much weaker or disappears. Such an approach enables one, for example, to exclude the influence of dipole–dipole interaction characterized by the dipole moment and the influence of acentricity represented by the criterion of L. P. Filippov (or Pittser).

When selection of the complexes of reduced values for the properties under study is correct, one may hope to obtain unique generalized nonparametric dependences for various groups of substances.

Certain difficulties are associated with selection of the reduction scales for both thermodynamic and transport properties. As far as the argument is concerned, one uses the recommendation of L. P. Filippov [1] on the universality of the reduced volume $V'/V_{cr}(\rho_{cr}/\rho')$. A confirmation of the correctness of selection of the argument ρ_{cr}/ρ' may be the fact that $\lambda \sim \rho$ [1] and $r \sim \rho^2$ [2].

It is proposed that the reduction scales for the difference in the properties of a liquid and a vapor on the boundary saturation curves be sought in the following manner. Based on the experimental temperature dependence of any property χ, we determine such a value of the temperature T^* for which the quantity $\Delta\chi = |\chi' - \chi''|$ will be equal to the numerical value of this property at the critical point, i.e.,

$$|\chi'(T^*) - \chi''(T^*)| = \chi(T_{cr}) . \tag{1}$$

It is noteworthy that T^* for which equality (1) holds can be found not for all the properties of the substance. Thus, for example, for r, ΔS, and σ, such a temperature has neither been found nor is existent at all. At the same time, this temperature is existent for the density of all substances. Noting the particular role of density in investigating the properties of substances, we determine T^* as a result of the processing of experimental data [3–9] for the density

$$(\rho' - \rho'')/\rho_{cr} = f_1(\rho_{cr}/\rho') \tag{2}$$

or

$$(\rho' - \rho'')/\rho_{cr} = f_2(\tau) . \tag{3}$$

The results of the processing of experimental data [3–9] in the form (2) led to a unified generalized dependence (Fig. 1).

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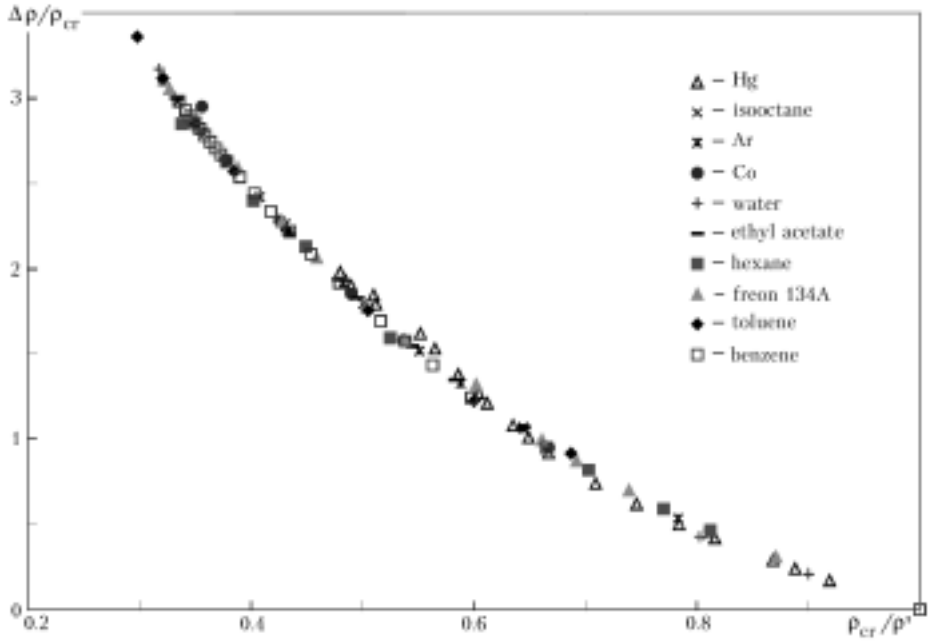

Fig. 1. Reduced difference in the densities on the boundary liquid–vapor saturation curves vs. reduced volume ρ_{cr}/ρ'.

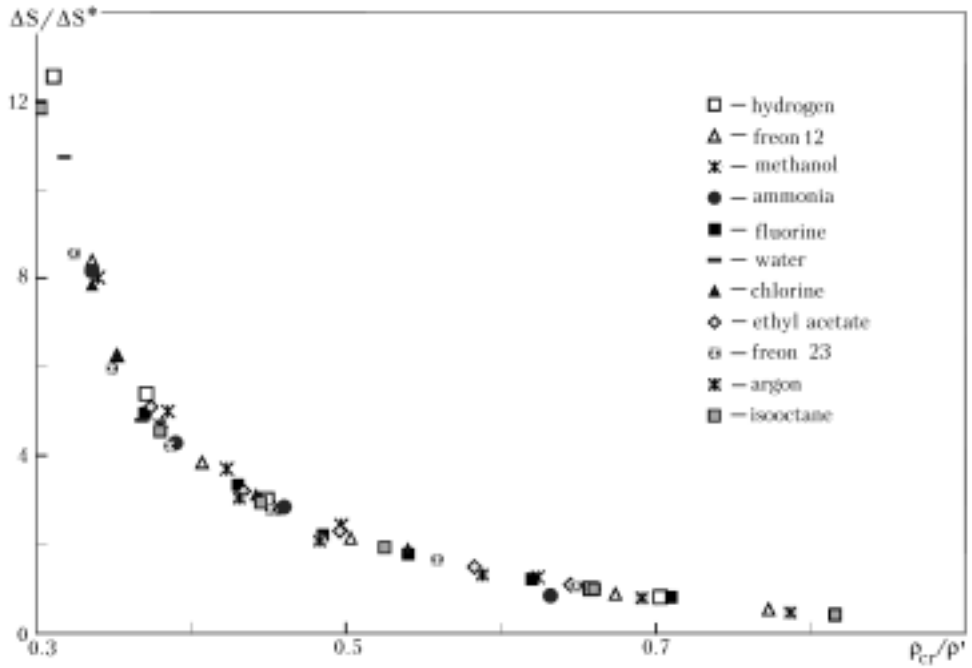

Fig. 2. Reduced excess entropy on the boundary liquid–vapor saturation curves vs. reduced volume ρ_{cr}/ρ'.

The value of $\rho' - \rho'' = \rho_{cr}$ in the coordinates $(\rho' - \rho'')/\rho_{cr} = f_2(\tau)$ corresponds to a reduced temperature $\tau^* = T^*/T_{cr}$ of 0.98 $\pm$ 0.005. The quantity $\Delta\rho/\rho_{cr}$ decreases from unity to zero (see Fig. 1) as τ changes from 0.98 to 1, i.e., only by 2%; the range of variation of ρ_{cr}/ρ' amounts to 34% (from 0.66 to 1).

The basic values of ρ_{cr}/ρ' and τ found correspond to the states on the boundary liquid–vapor saturation curves, beginning from which the rate of change in the properties increases. This is demonstrated by the ρ–T phase diagram of any substance. As far as the density difference is concerned, the rate of its change is doubled as compared

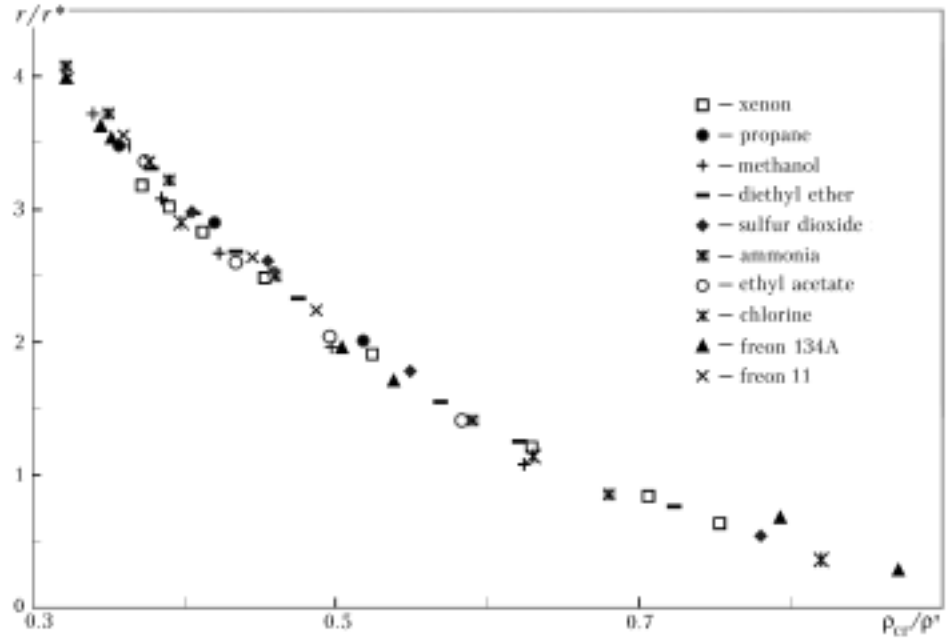

Fig. 3. Reduced heat of evaporation vs. reduced volume ρ_{cr}/ρ'.

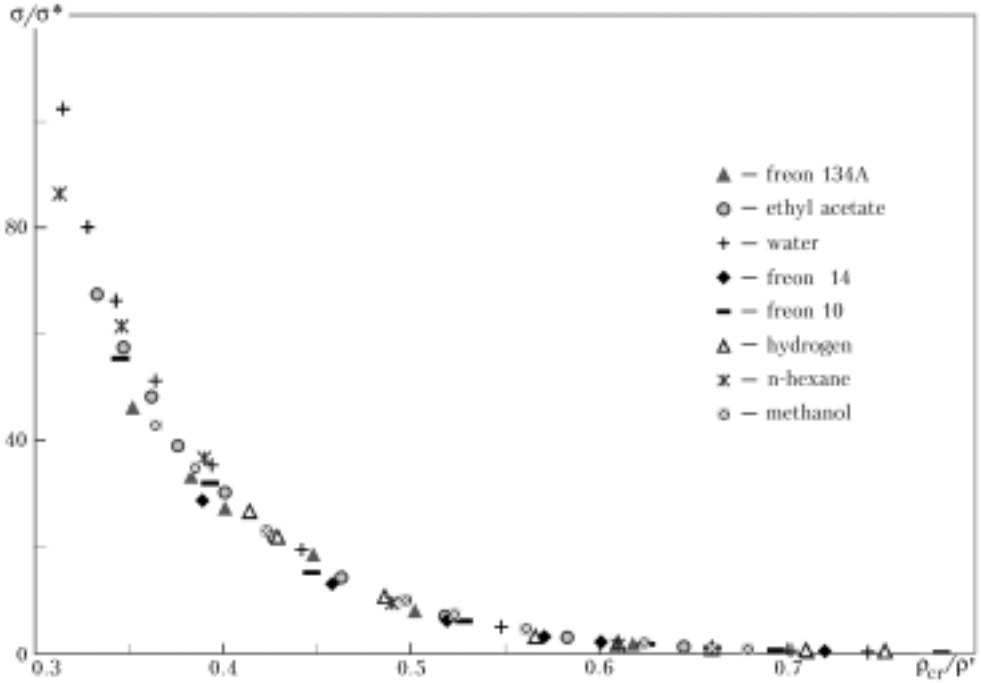

Fig. 4. Reduced surface tension vs. reduced volume ρ_{cr}/ρ'.

to the rate of change in $\rho'(T)$ and $\rho''(T)$ separately along the boundary curves of liquid–vapor phase transition. An analysis of the results of the theory of critical phenomena [10] shows that, at the vicinity of the critical point, the quantities $\rho' - \rho_{cr}$ and $\rho_{cr} - \rho''$ for low $(T_{cr} - T)$ are in proportion to $(T_{cr} - T)^{\beta}$ with the same proportionality factor. It is easily shown that the dependence of $\Delta\rho = \rho' - \rho''$ on $T_{cr} - T$ will be described by the power function with the same exponent but a proportionality factor twice as large: $\rho' - \rho'' \sim 2(T_{cr} - T)^{\beta}$.

The results presented in Fig. 1 enable us to check the legitimacy of the rectilinear-diameter rule. We recall: this rule states that $(\rho' + \rho'')/2$ is a linear function of the temperature [11]

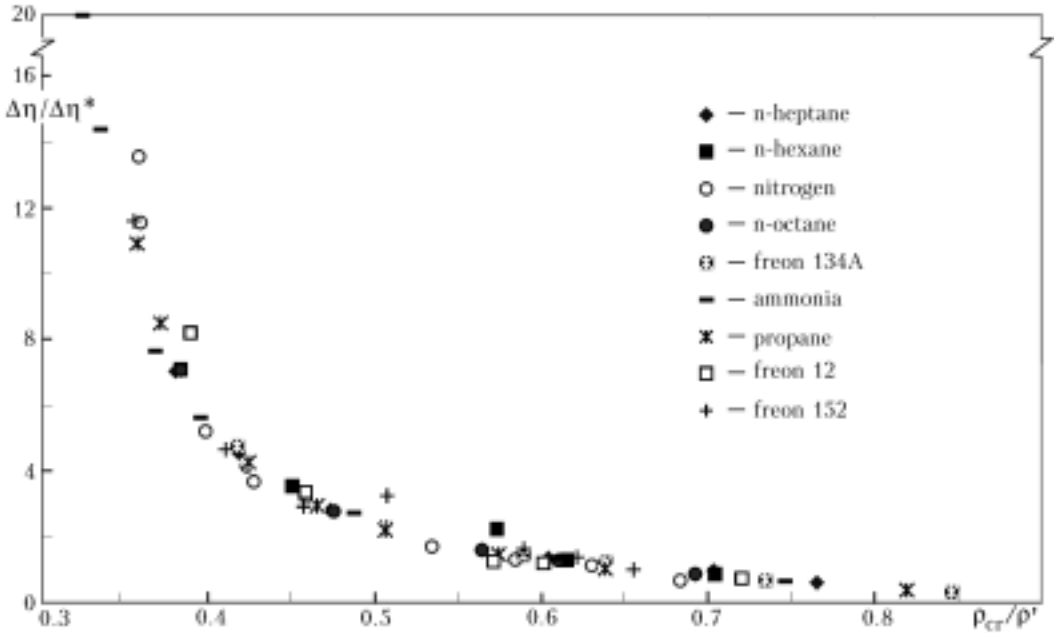

Fig. 5. Reduced difference of the dynamic viscosity on the boundary liquid–vapor saturation curves vs. reduced volume ρ_{cr}/ρ'.

$$\rho_{av} = (\rho' + \rho'')/2 = A - BT\,, \tag{4}$$

where A and B are the constants for a given substance. The straight line corresponding to Eq. (4) goes through the critical point.

An analysis of the results presented in Fig. 1 shows that if we have $\rho_{cr}/\rho' = 0.666...$ for $\Delta\rho/\rho_{cr} = 1$, then we obtain $(\rho' + \rho'')/2 = \rho_{cr}$. Furthermore, at $T = T_{cr}$, we have $\rho' = \rho'' = \rho_{cr}$ ($\Delta\rho = 0$) and $\rho_{av} = \rho_{cr}$. What this means is that at least two points at which we have $(\rho' + \rho'')/2 = \rho_{cr}$ must be found on the curve of the function $\rho_{av}(T)$.

The procedure of determination of the reduction scales was carried out in the following manner. From the basic function $\Delta\rho = \rho' - \rho'' = f(T)$ approximated in the form of a polynomial, we determined the temperature T^* at which we have $\Delta\rho = \rho_{cr}(\Delta\rho/\rho_{cr} = 1)$. The temperature found at the basic point was used to determine the reduction scales for other properties: the dependences $\Delta S(T)$, $r(T)$, $\sigma(T)$, $\Delta\eta(T)$, and $\Delta\lambda(T)$ were approximated in an analogous manner to find the values ΔS^*, r^*, σ^*, $\Delta\eta^*$, and $\Delta\lambda^*$.

The subsequent procedure of construction of generalized dependences for a specific property was reduced to processing of experimental data in the form:

for the density difference

$$(\rho' - \rho'')/(\rho' - \rho'')^* = \Delta\rho/\rho_{cr} = f_\rho\,(\rho_{cr}/\rho')\,, \tag{5}$$

for the entropy difference

$$(S'' - S')/(S'' - S')^* = \Delta S/\Delta S^* = f_S\,(\rho_{cr}/\rho')\,, \tag{6}$$

for the heat of evaporation

$$r/r^* = (i'' - i')/(i'' - i')^* = f_r\,(\rho_{cr}/\rho')\,, \tag{7}$$

for the surface tension

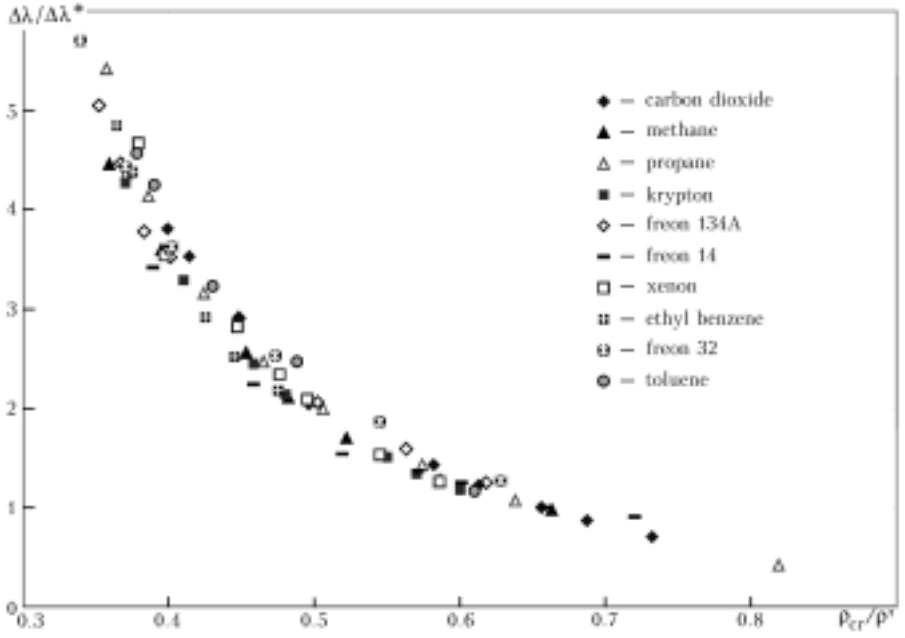

Fig. 6. Reduced difference of the thermal conductivity on the boundary liquid–vapor saturation curves vs. reduced volume ρ_{cr}/ρ'.

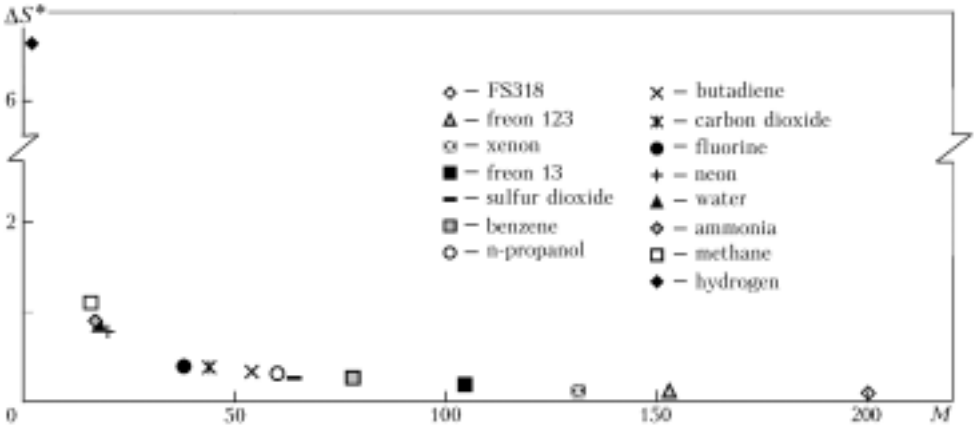

Fig. 7. Entropy difference for $\rho' - \rho'' = \rho_{cr}$ vs. molecular weight.

$$\sigma/\sigma^* = f_\sigma(\rho_{cr}/\rho'), \tag{8}$$

for the dynamic-viscosity difference

$$(\eta' - \eta'')/(\eta' - \eta'')^* = \Delta\eta/\Delta\eta^* = f_\eta(\rho_{cr}/\rho'), \tag{9}$$

for the thermal-conductivity difference

$$(\lambda' - \lambda'')/(\lambda' - \lambda'')^* = \Delta\lambda/\Delta\lambda^* = f_\lambda(\rho_{cr}/\rho'). \tag{10}$$

According to formulas (5)–(10), we processed the experimental data available at present for mon-, di-, and multiatomic gases, water, ammonia, hydrocarbons, alcohols, ethers, acids, freons, alkali metals, mercury, and inorganic liquids (chlorides, bromides, and iodides) of the elements of the IIIrd and IVth groups of the periodic table [3–9].

The obtained results presented in Figs. 1–6 show the correctness of the assumptions made in constructing the method. As is clear from the figures, there is a satisfactory convergence of the experimental data presented on the thermodynamic and transport properties of various substances in the form (5)–(10).

While on the subject of the advantages of dependences (5)–(10) over the existing generalization methods, where the parameters of a critical point are used as the scales, we should note the following ones:

(a) the state corresponding to the basic temperature lies several degrees below T_{cr}, which substantially simplifies experimental determination of the reduction scales;

(b) for the thermodynamic functions r, ΔS, and σ, we have found the reduction scales (they are equal to zero at the critical point);

(c) processing of the data on enthalpy and entropy in the method proposed is free of selection of the origins of i and s;

(d) the range of variation of the argument has substantially been extended in the vicinity of the critical region: 34% of the scale in the case of using ρ_{cr}/ρ' and only 2% of the scale for τ.

Of interest is the single-valued relation of ΔS^* to the molecular weight of a substance, which has been obtained based on processing of the data for 38 substances. Figure 7 gives ΔS^* values only for some of them.

NOTATION

i, enthalpy, J/kg; M, molecular weight, kg/kmole; r, heat of evaporation, J/kg; S, entropy, J/(kg·K); T, temperature, K; V, specific volume, m^3/kg; $V'/V_{cr} = \rho_{cr}/\rho'$, reduced volume; β, critical parameter (according to the theory of critical phenomena, $\beta = 0.34$); Δ, difference in the corresponding parameters on the boundary equilibrium curves; η, dynamic viscosity, Pa·sec; λ, thermal conductivity, W/(m·K); ρ, density, kg/m^3; σ, surface tension, N/m; $\tau = T/T_{cr}$, reduced temperature; χ, arbitrary property of the substance. Subscripts and superscripts: $'$, parameters on the line of a boiling liquid; $''$, parameters on the line of a dry saturated vapor; cr, critical state; *, basic value of the difference in the properties of substances in transition from the state of a boiling liquid to the state of a dry saturated vapor when $\rho' - \rho'' = \rho_{cr}$; av, average value of the corresponding quantity.

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