

If the number of heliostats, the trajectories of which are outside the permissible range, does not exceed the admissible percentage over the given time period, then group control is effective, and thus, desirable. Use of the group control principle permits a significant reduction in the mathematical complexity of the heliostat field control system.

The operational efficiency of the solar power station is determined to a significant degree by the quality of automatic equipment operation. Results of an economic analysis of construction of the 200-MW electrical station indicate that the cost of the heliostat field can reach 50% of the cost of the entire plant, while the automatic control systems are responsible for about 25% of the cost of the heliostat field. These data show the desirability of further development of economically efficient automation measures for the solar power station.

NOTATION

β , z , azimuthal and zenith angles of normal to heliostat mirror surface; t , time; δ , solar declination.

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METHODS FOR CALCULATION OF COMPRESSIBILITY AND CRITICAL CHARACTERISTICS OF NORMAL LIQUID MIXTURES

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Rules for the concentration dependence of compressibility and critical parameters of mixtures are established, and calculation algorithms are developed.

In [1, 2] analysis of empirical material by the thermodynamic similarity method established a relationship describing the dependence of isothermal compressibility of normal nonassociating liquids $\beta_T = -\frac{1}{v} \left(\frac{dv}{dp} \right)_T$ on temperature and pressure in terms of a function of one variable, the reduced volume $\varphi = V/V_C$. In [3, 4] the possibility of extending this principle to the case of mixtures was noted. We will consider this question in detail below, commencing from a new formula

$$P \equiv \frac{\beta_T RT}{V} = 120 \varphi^8, \quad (1)$$

which approximates the function in question for φ values from 0.28 to 0.44. A method of calculating mixture compressibility will be formulated on this basis. Data were analyzed for 10 systems from [5-10]. It developed that the V_C values for the mixtures, determined with Eq. (1) for various temperatures and pressures, were accurate to tenths of a percent. As an illustration, Table 1 presents values of V_C of the hexane-hexadecane system [6]. The mean-square scattering of the data in this example is 0.4%, which corresponds to 3% uncertainty in β_T . The V_C values determined in this manner will now tentatively be termed critical volumes. We cannot identify them with experimental values of critical volume, since the latter are known only with very high uncertainty. At the same time, it cannot be said that these values found characterize the true critical volume, and not some "pseudocritical" value. In fact, in Eq. (1) instead of φ some other reduced volume, such as V/V_0 ,

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TABLE 1. Values of V_C (cm³/mole) Found with Eq. (1) Using Data for Various States at Different Temperatures (°K) and Pressures (MPa)

x	T=303 K		T=413 K		Mean
	P=0,1 MPa	40 MPa	0,1 MPa	250 MPa	
0	985	989	977	978	982,4
0,2	855	855	850	856	853,6
0,4	727	729	723	724	725,9
0,6	601	602	596	598	598,8
0,8	478	478	476	474	476,6
1	360	362	364	366	362,5

TABLE 2. Parameters α and γ

No.	System	α	γ	No.	System	α	γ
1	C ₆ H ₆ -C ₁₁ H ₂₁	0,2	3	11	C ₆ H ₁₄ -C ₁₂ H ₂₆	0,26	3,8
2	C ₆ H ₆ -C ₁₂ H ₂₆	0,2	3,4	12	C ₆ H ₁₄ -C ₁₆ H ₃₄	0,26	3,8
3	C ₆ H ₆ -C ₁₃ H ₃₀	0,2	3,8	13	C ₆ H ₁₄ -C ₂₂ H ₄₆	0,27	3,8
4	C ₆ H ₆ -C ₁₆ H ₃₄	0,23	3,9	14	C ₆ H ₁₄ -C ₂₄ H ₅₀	0,28	3,8
5	C ₆ H ₁₄ -C ₁₀ H ₂₂	0,27	3,7	15	C ₇ H ₁₆ -C ₁₂ H ₂₆	0,26	3,8
6	C ₆ H ₁₄ -C ₁₆ H ₃₄	0,29	3,9	16	C ₇ H ₁₆ -C ₁₆ H ₃₄	0,25	3,8
7	C ₆ H ₁₄ - C ₅ H ₁₂ (neopentane)		3,8	17	C ₈ H ₁₈ -C ₁₆ H ₃₄	0,25	3,8
8	C ₅ H ₁₂ -C ₁₀ H ₂₂	0,27	3,8*	18	C ₈ H ₁₈ -C ₃₆ H ₇₄	0,29	3,8
9	C ₅ H ₁₂ -C ₁₆ H ₃₄	0,27	3,8	19	C ₉ H ₂₀ -C ₂₄ H ₅₀	0,28	3,8
10	C ₆ H ₁₄ -C ₁₀ H ₂₂	0,26	3,8				

* Here and below 3.8 is taken as the value of γ .

TABLE 3. Values of Excess Isothermal Compressibility (calculations and experiment)

No.	System	$\beta E \cdot 10^{-4} \text{ TPa}^{-1}$		
		calc.	expt.	calc. [12]
1	C ₆ H ₁₄ -C ₁₆ H ₃₄	-8	-8	-7
2	C ₇ H ₁₆ -C ₁₆ H ₃₄	-5	-5	-4
3	C ₆ H ₁₂ -C ₆ H ₆	+1	+3	+1
4	C ₆ H ₆ -1,2 dibromoethane	0	-1	0
5	C ₆ H ₁₂ -1,2 dibromoethane	-1	0	-3
6	C ₆ H ₆ -1,2 dichloroethane	0	+1	0
7	SiCl ₄ -SnCl ₄	-5	-3	-3
8	CCl ₄ -SnCl ₄	+2	+2	0
9	C ₆ H ₁₂ -CCl ₄	+2	+1	0
10	CCl ₄ -SiCl ₄	-5	-0,5	-2

may be used, where V_0 is the volume extrapolated to the point $T=0$, whereupon the principles found below concerning V_C would relate to V_0 instead.

The concentration dependence of the V_C values is close to additive; deviations from additive V_C values, even for systems in which V_C of the components differ by a factor of 4, do not exceed 2-3%, but are of a systematic character. The best approximation is given by

$$V_C = V_{C1}x_1^2 + V_{C2}x_2^2 + 2V_{12}x_1x_2 \quad (2)$$

This equation can also be written in the form

$$V_C = V_C^{\text{ad}} - [V_{C1} + V_{C2} - 2V_{12}] x_1x_2 \quad (3)$$

We will use the form of Eq. (3):

$$V_C = V_C^{\text{ad}} - \frac{\alpha \delta^2}{V} x_1x_2 = V_C^{\text{ad}} - \Delta V_C \quad (4)$$

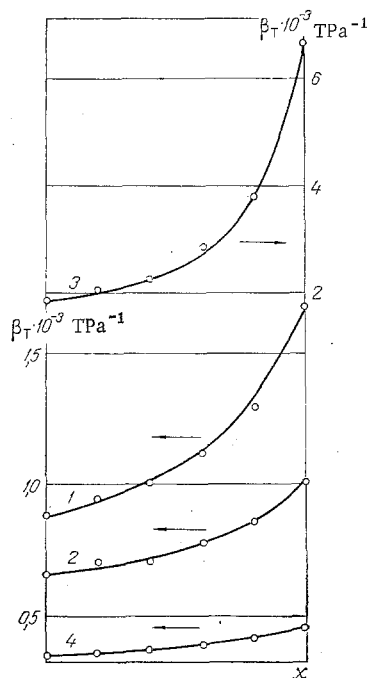


Fig. 1. Isothermal compressibility of the hexane-hexadecane mixture (curves, calculation; points, from [6]): 1) $T=303^{\circ}\text{K}$, $P=0.1$ MPa; 2) 303, 40; 3) 413, 0.1; 4) 413, 250.

where $\bar{V}=(V_{c1}+V_{c2})/2$; $\delta=(V_{c1}-V_{c2})/2$.

Assuming that V_{12} is expressed in terms of the component critical volumes as

$$V_{12} = \left(\frac{V_{c1}^{1/n} + V_{c2}^{1/n}}{2} \right)^n, \quad (5)$$

the value of the parameter α must be constant and equal to

$$\alpha \approx \frac{n-1}{n}. \quad (6)$$

Values of α for systems in which the difference in critical volumes is sufficiently large so that α can be determined are shown in Table 2.

Another fact established by analysis of the concentration dependence of compressibility on the basis of Eq. (1) is the relative smallness of deviations from additiveness of the reduced density φ and the possibility of describing the function $\varphi(x)$ with a single formula for a wide class of mixtures

$$\varphi = \varphi^{\text{ad}} - \gamma \frac{(\varphi_1 - \varphi_2)^2}{(\varphi_1 + \varphi_2)/2} x_1 x_2 = \varphi^{\text{ad}} - \Delta\varphi, \quad (7)$$

analogous in structure to Eq. (4). The parameter γ in this equation proves to be close in value for various systems (see Table 2).

Simultaneous examination of Eqs. (4) and (7) permits us to obtain a relationship relating the excess volume V^E , ΔV_c , and $\Delta\varphi$:

$$\frac{V^E}{V^{\text{ad}}} + \frac{\Delta V_c}{V_c^{\text{ad}}} + \frac{\Delta\varphi}{\varphi^{\text{ad}}} = \frac{\varphi^{\text{ad}} V_c^{\text{ad}}}{V^{\text{ad}}} - 1. \quad (8)$$

Equation (8) establishes the relationship between the parameters α and γ . Table 2 shows the results of α determination by Eq. (8) for a constant value of $\gamma=3.8$ for normal alkane mixtures (data on V^E taken from [11]).

The close similarity of the α values for the alkane mixtures (Nos. 6-19 in Table 2) is quite remarkable. At the same time, similar calculations for mixtures with benzol and cyclohexane lead to negative α values, on the order of magnitude of 1-2 (one can see the same tendency to lower α values in systems No. 1-4 of Table 2). Positive deviations from additiveness for these mixtures can be explained by the "noncompactness" of the molecules of these materials. When the packed molecules interact with each other in the pure materials, a greater density is achieved due to parallel orientation of the molecules with respect to each other. The same factor manifests itself in the excess volumes of the mixtures V^E . For alkane mixtures negative V^E volumes are characteristic ("compression"), while for mixtures with benzol and cyclohexane the values are, as a rule, positive. It is obvious that a more detailed study of the parameter α at the molecular level is called for.

The quite general equation (7) can be taken as a base for a method of calculating isothermal compressibility of mixtures with the use of Eq. (1). Calculations can then be performed knowing only the properties of the components, since the V value of the left side of Eq. (1) can be approximated well by the additive value. Calculations by this method provide completely satisfactory agreement with experiment. Thus, for the hexane-hexadecane system the mean-square deviation comprises 5% for the temperature range 303-412°K at pressures to 250 MPa. The results of calculation reproduce such "fine" detail of the compressibility concentration dependence as the ~-shaped character of deviations from additiveness for the benzol-hexadecane system.

Even better agreement with experiment can be obtained by using a formula refined with respect to Eq. (7) by considering asymmetry of deviations from additiveness:

$$\varphi = \varphi^{ad} - \frac{19}{5} \frac{(\varphi_1 - \varphi_2)^2}{(\varphi_1 + \varphi_2)/2} x_1 x_2 \left[1 + \frac{19}{3} (\varphi_1 - \varphi_2)(x_1 - x_2) \right]. \quad (7')$$

Results of compressibility calculations for the hexane-hexadecane system using Eq. (7') are shown in Fig. 1. The calculation results differ from experiment by 2%. Figure 2 shows the results of calculations for a benzol-hexadecane mixture; here the nonmonotonic character of the β_T deviation from additiveness can be clearly seen.

In accordance with the above, we shall formulate a calculation method using the procedure of [2]. To be determined is the concentration dependence of isothermal compressibility $\beta_T(x)$ of a mixture of normal liquids. Data available are the values of β_T and V of the components. The calculation method is based on Eqs. (1), (7). Equation (1) is used to find the values of the component reduced volumes φ , and Eq. (7) is then used to calculate the reduced volume of the mixture. The value of V for the mixture is determined by additive calculation, and the isothermal compressibility β_T of the mixture is calculated with Eq. (1).

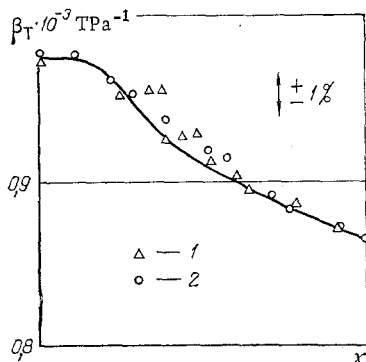


Fig. 2

Fig. 2. Isothermal compressibility of benzol-hexadecane mixture at $T=298^\circ\text{K}$: curve, calculation; 1) from [7]; 2) [8].

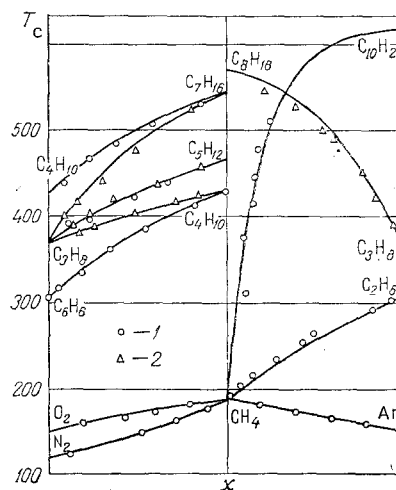


Fig. 3

Fig. 3. Mixture critical temperature: curves, calculation; 1) [14]; 2) [15]; T , °K.

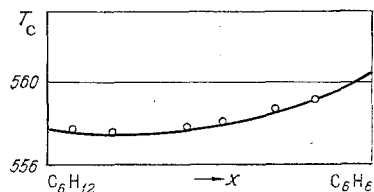


Fig. 4. Critical temperature of the benzol-cyclohexane system: curve, calculation; points, from [14]; T , °K.

Since calculations by this method can be performed at different temperatures and pressures, they provide knowledge of the isotherms of the dense liquid over the entire concentration range. A somewhat different approach to the same question is connected with the so-called excess compressibility β^E :

$$\beta^E \equiv \beta_T - \beta_{T_1} \psi_1 - \beta_{T_2} \psi_2, \quad (9)$$

where $\psi_i = (V_i/V)x_i$ are volume fractions. This particular definition of excess compressibility is used because β^E is then simply related to the pressure derivative of the excess volume:

$$V\beta^E = -\frac{\partial V^E}{\partial p}. \quad (10)$$

Commencing from Eq. (1), we obtain for β^E

$$\beta^E = \frac{120}{RTV} \left[V^2 \varphi - \frac{V_1^2 \varphi_1^8 + V_2^2 \varphi_2^8}{2} \right]. \quad (11)$$

Using Eq. (7) for φ , we have the ability to determine β^E . We will formulate the calculation algorithm. To be determined is the value of the excess compressibility of the mixture (or the pressure derivative of the excess volume). The data available are the compressibility and density of the components and the excess density of the mixture V^E . The calculation method uses Eqs. (1), (7). The values of β_T and V of the components together with Eq. (1) are used to determine the reduced volume φ_i of the components. The mixture density is determined additively with correction of V^E . Calculation of φ for the mixture is performed with Eq. (7), and values of β^E are found with Eq. (11).

Results of β^E calculations for equimolar mixtures are presented in Table 3. Data from [12] were used in the calculations. Also shown are β^E calculations by the method used in [12].

The quality of the calculations by the proposed method and the Liebermann method are about the same; however, the latter requires knowledge of the component expansion coefficients.

We will now consider the question of mixture critical temperature further. The basic principle which can be established here is the additiveness of the quantities:

$$V\overline{T_c}V_c = V\overline{T_{c1}}V_{c1}x_1 + V\overline{T_{c2}}V_{c2}x_2. \quad (12)$$

The meaning of Eq. (12) can be understood from the following considerations. The quantity $T_c V_c^2$ has the dimensions of the dispersion Van der Waals constant C in the expression defining the attractive force potential:

$$u = -C/r^6. \quad (13)$$

Moreover, for such substances these quantities will be proportional to each other

$$T_c V_c^2 \sim f^2 C. \quad (14)$$

For the class of normal liquids the quantity f^2 is a universal function of one parameter, the thermodynamic similarity number A [2]. Thus,

$$V\overline{T_c}V_c = f(A)C. \quad (15)$$

The function $f(A)$ is approximated well by

$$f(A) = 0.709 - 0.3583 \lg A. \quad (16)$$

As was shown in [13], the quantity \sqrt{C} can with good accuracy be represented in the form of the sum of the moments $\sqrt{C_i}$ describing interaction of atoms of the i -th sort with each other:

$$V\bar{C} = \sum_i V\bar{c}_i n_i, \quad (17)$$

where n_i is the number of atoms of the i -th sort in the molecule. The existence of such a simple relationship is in turn the result of very good satisfaction of the combination rule

$$c_{ik} = c_i^{1/2} c_k^{1/2}, \quad (18)$$

where c_{ik} is a constant characterizing interaction of atoms of the i -th and k -th sort.

Application of the same considerations to mixtures leads to a formula analogous to Eq. (17):

$$V\bar{C} = V\bar{C}_1 x_1 + V\bar{C}_2 x_2. \quad (19)$$

Combination of Eqs. (19), (16), (15) leads to Eq. (12), if for the concentration dependence of A we have

$$\lg A = \frac{V\bar{C}_1 x_1 \lg A_1 + V\bar{C}_2 x_2 \lg A_2}{V\bar{C}_1 x_1 + V\bar{C}_2 x_2}. \quad (20)$$

Equation (12) permits calculation of mixture critical temperatures. This is done most simply for mixtures of alkane type hydrocarbons, for which Eq. (4) can be used with an identical coefficient $\alpha = 0.268$. Results of such calculations are shown in Fig. 3, and compared with experimental data of [14, 15]. Good results are obtained even with mixtures whose atoms have low atomic numbers. Calculations by this method show the main characteristic peculiarities of the function $T_C(x)$, e.g., the almost linear behavior of the function for the N_2 - CH_4 system, and the intense deviations from additiveness for CH_4 - $C_{10}H_{22}$.

In the general case, to calculate critical temperatures the parameter α can be determined on the basis of Eq. (8) as was described above. The benzol-cyclohexane system can serve as an example ($\alpha = -1.8$) (Fig. 4). The calculations here reproduce the characteristic minimum in $T_C(x)$ to the accuracy of a fraction of a degree (experimental data from [16]).

In accordance with the above we will formulate the calculation method. To be determined is the concentration dependence of critical temperature and volume of the mixture. Data available are the values of component critical temperatures and volumes (these, in turn, can be determined from more accessible data by the methods of [2]) and excess mixture volume V^E at one point (for the mixtures of alkane series hydrocarbons and their mixtures with low atomic number gases this information is not necessary). The method of calculation is based on Eqs. (12) and (4). The method proceeds as follows. Equations (8), (7) are used to determine the value of ΔV_C , which in turn is used to determine α from Eq. (4) (for alkane mixtures we may take $\alpha = 0.268$). The critical volume is calculated with Eq. (4). Critical temperatures are found from Eq. (12).

NOTATION

R, ideal gas constant; T, absolute temperature; V, molar volume; V_C , critical volume; T_C , critical temperature.

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