

The series of experiments performed also permitted determining the magnitude of the phase shift. As is evident from the oscillograms, as the wire passes the temperature equilibrium position, the wire length, and with it, the sag distance, are decreasing, which is a necessary condition for parametric pumping of pendulum oscillations [7].

#### NOTATION

$l$ , wire length;  $L$ , tube length;  $d$ , wire diameter;  $D$ , tube diameter;  $T$ , mean wire temperature over volume;  $T_0$ , temperature of surrounding medium.

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#### CALCULATION OF GAS-GAS PHASE EQUILIBRIUM FOR THE MIXTURE He-F12

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Equilibrium conditions are determined by use of the Redlich-Kwong equation of state and two different methods for numerical calculation of the mixture phase behavior.

By analyzing the geometric properties of the  $F-v-x$  surface with the aid of the theory of folds proposed by Korteveg, using his own approximate equation of state for the mixture, Van der Waals arrived at the conclusion [1] that the existence of a longitudinal (relative to the  $v$  axis) fold on this surface corresponds to the condition of equilibrium of two fluid phases at some fixed value of molar volume. This simple approach also permitted a qualitative description of all the experimentally observed variants of behavior of the critical curve of a binary system in  $P-T-x$  space. The calculation of phase behavior of a fluid mixture is usually refined by introducing a more complex equation of state and solving a quite cumbersome system of nonlinear equilibrium equations. It will be shown below that use of the Van der Waals approach (i.e., direct analysis of  $F$ ), together with refinement of the mixture equation of state, permits equilibrium calculations with results comparable in accuracy to traditional methods.

The Redlich-Kwong equation of state was used to describe the properties of the coexisting phases. This equation is one of the most useful variants of the semiempirical approach to construction of a unified equation of state for pure materials and mixtures. The specifics of the problem in question here require reliable determination of the mixture thermodynamic properties over a narrow temperature interval somewhat above  $T_{CF12}$ , at pressures above  $P_{CF12}$ . Accordingly, the constants  $a$  and  $b$  in the Redlich-Kwong equation of state

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$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \quad (1)$$

were defined for F12 with the aid of the critical properties

$$a = \frac{0.4278 R^2 T_{cF12}^{2.5}}{P_{cF12}}, \quad b = \frac{0.0867 RT_{cF12}}{P_{cF12}} \quad (2)$$

For He the pseudocritical values  $T_{cHe} = 12.2^\circ\text{K}$  and  $P_{cHe} = 7.8$  bar were taken, permitting an average accuracy with respect to  $z \approx 1\%$  in the temperature interval 150–500°K up to 500 bar [12].

The mixture coefficients were defined with the relationships

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad (3)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}. \quad (4)$$

For the cross coefficients  $a_{12}$  and  $b_{12}$  the expressions

$$a_{12} = (1 - k_{12}) \sqrt{a_1 a_2}, \quad (5)$$

$$b_{12} = (1 - l_{12}) \frac{1}{2} (b_1 + b_2) \quad (6)$$

were used.

The authors of [2-4] attempted to calculate gas-gas equilibrium using the Redlich-Kwong equation. Generally, a very approximate description of the phase content was obtained. In our opinion, this result can be explained almost completely by an incorrect choice of the value  $k_{12}$ . Moreover, only in [2] was the correction  $l_{12}$  (together with  $k_{12}$ ) included, the consideration of which is extremely important in helium systems, as we have established.

In contrast to previous studies which directly related the behavior of  $k_{12}$  [2, 4] and  $l_{12}$  [2] to an arbitrarily selected experimental point on the equilibrium curve, we employed the more justifiable approach of estimating these quantities with consideration of the general features of intermolecular interactions of the heliumless volatile component type. If we take a potential energy for the  $ij$ -pair of molecules equal to

$$\Phi(r) = \epsilon(\sigma/r)^n, \quad (7)$$

then for  $\epsilon_{12}$  and  $\sigma_{12}$  we may introduce relationships analogous to Eqs. (5), (6)

$$\epsilon_{12} = (1 - k'_{12}) \sqrt{\epsilon_1 \epsilon_2}, \quad (8)$$

$$\sigma_{12} = (1 - l'_{12}) \frac{1}{2} (\sigma_1 + \sigma_2). \quad (9)$$

Generalization of various empirical information on the different interactions in helium systems permitted establishment of these values for an He-F12 system:  $k'_{12} = 0.55$ ,  $l'_{12} = -0.19$ . The relationship between these quantities and the correction coefficients in Eqs. (5), (6) is easily obtained:

$$(1 - k_{12}) = (1 - k'_{12})^{3/2} \frac{\sigma_{12}^3}{\sigma_1^{3/2} \sigma_2^{3/2}}, \quad (10)$$

$$(1 - l_{12}) = (1 - l'_{12})^3 \frac{(\sigma_1 + \sigma_2)^3}{4(\sigma_1^3 + \sigma_2^3)}. \quad (11)$$

The values of  $\sigma_i$  and  $\epsilon_i$  were taken from data of [5]:  $\sigma_{He} = 2.556 \text{ \AA}$ ,  $\sigma_{F12} = 5.20 \text{ \AA}$ ,  $\epsilon/k_{He} = 10.22 \text{ K}$ ,  $\epsilon/k_{F12} = 289 \text{ K}$ . Substituting these values in Eqs. (10), (11) we obtain:  $l_{12} = -0.24$  and  $k_{12} = 0.385$ . Despite the approximate nature of these estimates the introduction of this method permitted reliable quantitative reproduction of the experimental measurements of [6] on gas-gas equilibrium in He-F12 systems.

To calculate the volatility of the  $k$ -th component of the mixture a formula obtained in [7] by sequential thermodynamic analysis was used:

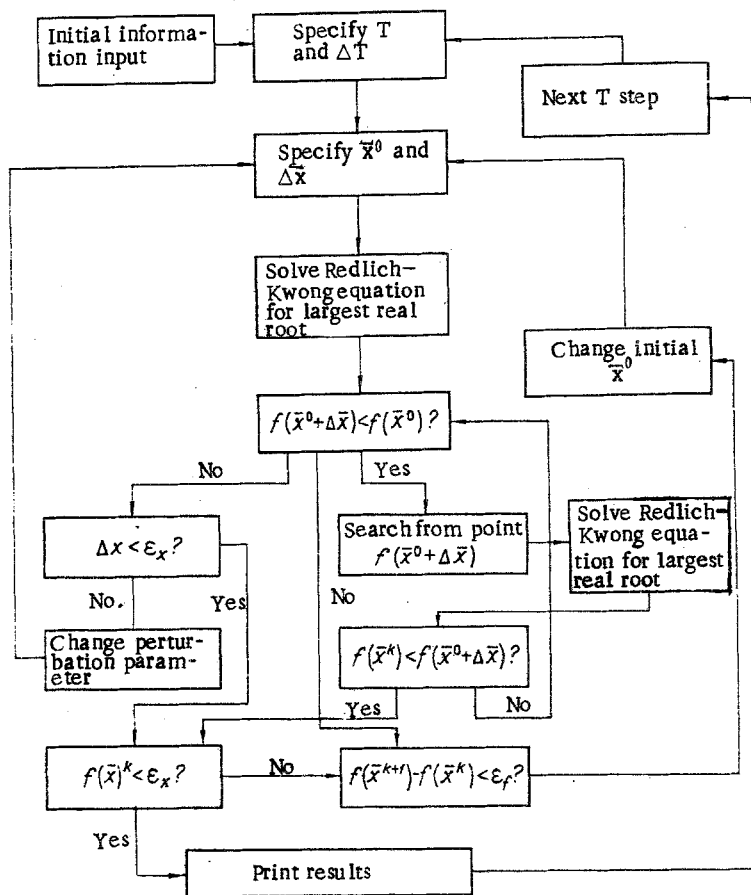


Fig. 1. Flow chart of gas-gas equilibrium calculation by direct grid search method.

$$\ln \varphi_h = \ln \frac{v}{v-b} - \frac{b - 2 \sum_i b_{ih} x_i}{v-b} - \frac{2 \sum_i a_{ih} x_i}{RT^{3/2} b}$$

$$\times \ln \frac{v+b}{v} + \frac{2a \sum_i b_{ih} x_i}{RT^{3/2} b^2} \ln \frac{v+b}{v} + \frac{a(b - 2 \sum_i b_{ih} x_i)}{RT^{3/2} b(v+b)} + \left(1 - \frac{1}{z}\right) \left\{ z - \left(b - 2 \sum_i b_{ih} x_i\right) \right.$$

$$\times \left[ \frac{v}{(v-b)^2} + \frac{a}{RT^{3/2} (v+b)^2} \right] + \frac{2(a - \sum_i a_{ih} x_i)}{RT^{3/2} (v+b)} \left. \right\} - \ln z. \quad (12)$$

Equation (12) differs from the formulas employed in [2-4] and is more strict. The phases in equilibrium with each other obey the equations

$$f'_1 = f''_1, \quad (13)$$

$$f'_2 = f''_2, \quad (14)$$

where the indices (') and (") denote the volatility of the components in the phases with higher and lower F12 content, respectively.

The solution of the system formed by Eqs. (13), (14) is essentially a problem of non-linear programming in the presence of restrictions. The requirements for a numerical method of finding the extremum of a function of  $n$  variables can be formulated in the following manner: minimize the target function  $f(\bar{x})$  (where  $\bar{x}$  is an  $n$ -dimensional Euclidean space) with limitations upon  $c(\bar{x})$ . By a minimum of the target function we understand satisfaction of the system of Eqs. (13), (14) to a prespecified accuracy. The basic criterion for completion of the iteration process is satisfaction of the inequality

$$f(\bar{x}^k) < \varepsilon_f. \quad (15)$$

The effective value of the quantity  $\varepsilon_f$  corresponding to the calculation accuracy chosen for the solution  $\varepsilon_x = 10^{-3}$  is  $\varepsilon_f = 10^{-4}$  bar. The limitations on the  $c(\bar{x})$  problem are the conditions relating the molar fractions of the components in each phase:

$$\sum_i x_i = 1. \quad (16)$$

The number of variables subject to variation can easily be reduced to a minimum by considering Eq. (16):

$$x_2' = 1 - x_1'; \quad x_2'' = 1 - x_1'', \quad (17)$$

and as limitations there appear only the admissible intervals of solution variables

$$0 < x_2' < x_2'' < 1. \quad (18)$$

We recall that the procedure for calculation of the target function in each step includes solution of the cubic Redlich-Kwong equation of state for  $v$ .

A widespread approach to the solution of a system of nonlinear equations of phase equilibrium is the use of numerical methods related to finding the first and second derivatives to the target function  $f(\bar{x})$ . Despite the undoubted effectiveness of such algorithms, they do require significant preparatory work (analytical differentiation or estimation of the derivatives by finite-difference methods) and may prove quite inaccurate near the  $f(\bar{x})$  extrema. To solve the conditional optimization problem formulated above, in the present study a direct grid search procedure [8] was used, which is free of the above shortcomings, since it does not require regularity of the target function or presence of its derivatives. In those cases where  $f(\bar{x})$  does not include cross products of the solution variables (of the type  $x_1^2 x_2^2$ ) the direct search methods' operation is completely reliable [9].

Figure 1 presents a flow chart of the calculation of gas-gas equilibrium. The following unique features of this algorithm should be noted. The specification of the initial approximation of the solution variables  $\bar{x}^0$  has a significant effect on optimization speed and the possibility of successfully completing the search procedure. This is true because in the case of calculating the existence curve, with an inappropriate choice of  $\bar{x}^0$  we often obtained a trivial solution in which the iteration process was interrupted at the point  $x_1^1 = x_2^1$ . Practical operation of the program revealed this undesirable phenomenon could be avoided by specifying a broader interval for the first approximations of the independent variables (so that in the first steps the solution variables approached each other). The effective value of the perturbation parameter is directly related to choice of the initial approximation of the problem. It was established that use of a successive increment equal to twice the value of  $\Delta x$  in the previous step for a successful  $k$ -th search step (and decrease of  $\Delta x$  by a factor of two for an unsuccessful previous step) was the optimum approach to solution of the problem.

The strategy of direct grid search includes two basic stages: 1) study of the change in the target function in the first step to determine the direction of the search; 2) a series of accelerating steps along this vector until the function  $f(\bar{x})$  decreases. In the case of a successful sequential step, a new value is taken for the target function. At the end of the second stage, a search is always made for a possible new optimization direction, from which it is clear that the return to the first stage procedure is of a recursive nature. In those cases where the initial specified approximation of  $\bar{x}^0$  does not permit determination of a direction in which  $f(\bar{x})$  decreases, the program provides for division of the increment  $\Delta \bar{x}$  until the inequality

$$\Delta \bar{x} < \varepsilon_x \quad (19)$$

is satisfied. To avoid unproductive machine time expenditure when the target function falls into a "plateau" area (the change in  $f(\bar{x})$  is a sequential step becomes smaller than  $\varepsilon_f$ ) the system returns to the initial state and the iteration process is repeated with a changed vector  $\bar{x}^0$ .

The algorithm was realized in an ALGOL program for a medium-class computer (BESM-4, M-20), and the results of a gas-gas equilibrium calculation for the mixture He-F12 are shown in Fig. 3. The good ( $\delta x \approx 3\%$ ) agreement of our data and the experimental measurements of [6] for  $P \geq 80 \cdot 10^5$  Pa should be noted.

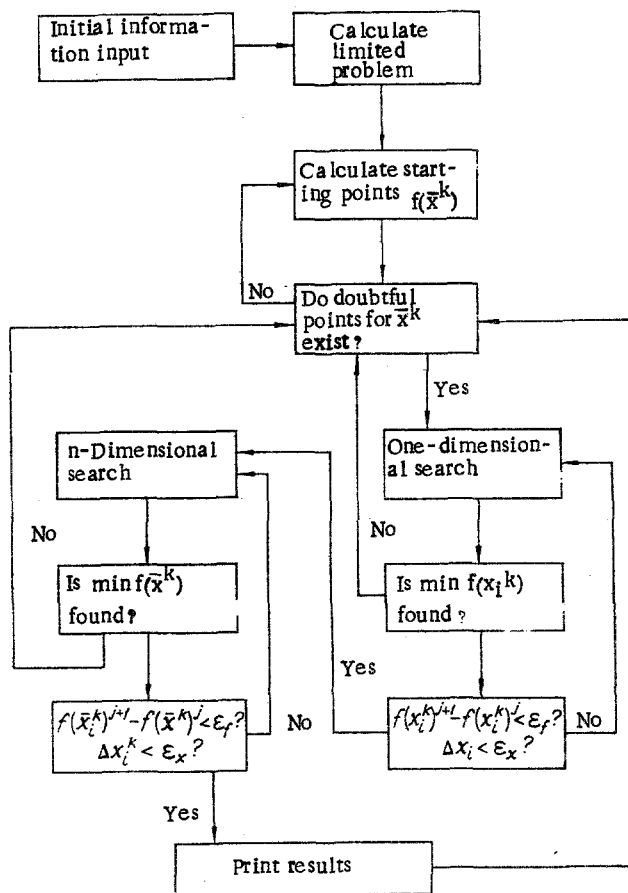


Fig. 2. Flow chart of gas-gas equilibrium calculation by F-minimization method.

The method of direct minimization of  $F$  is distinguished from other search procedures using the equation of state  $P = P(v, T, x)$  by the lack of need to determine  $v$  in the intermediate operations. The authors modified the  $F$  minimization program proposed in [10] to calculate gas-gas equilibrium. Figure 2 presents a flow chart of the procedure for calculating phase composition.

For the target function the free Helmholtz energy corresponding to Eq. (1) was chosen:

$$f(\bar{x}) \equiv F = F_0 - RT \ln(v - b) - \frac{a}{bT^{1/2}} \ln \left( 1 + \frac{b}{v} \right) + RT \sum_i x_i \ln x_i. \quad (20)$$

The direct grid search method used previously is not very useful here for two reasons:  $f(\bar{x})$  includes cross products of the solution variables, and moreover, it proves to be insensitive to change in the quantities varied near the minimum. In this and other cases Hook-Jeeves type algorithms [8] are not effective. To solve the problem a specific combination of one-dimensional and mixed (n-dimensional) searches was employed.

The number of degrees of freedom of a two-phase, two-component mixture is equal to 2. Consideration of the basic limitation of the phase equilibrium problem, Eq. (6), leads to appearance of one additional solution variable. Using as the mathematical model of the real system a vessel of constant volume  $V_0$  (we chose  $V_0 = 0.1 \text{ m}^3$ ) containing  $m_1$  and  $m_2$  moles of the components, it will be convenient to consider the following set of solution variables:  $\rho_1''$ ,  $\rho_2''$ , and  $\rho'$ . It is easily seen that the given quantities completely define the binary system:

$$v'' = \frac{V_0 \rho' - m_1 - m_2}{\rho' - \rho_1'' - \rho_2''}, \quad m_1'' = \rho_1'' v'', \quad x_1'' = \frac{\rho_1''}{\rho_1'' + \rho_2''}, \quad m_1' = m_1 - m_1''. \quad (21)$$

The following limitations  $c(\bar{x})$  are imposed on the solution variables:

$$\rho_{\min} < \rho_1'' < \frac{m_1}{V_0}, \quad \rho_{\min} < \rho_2'' < \frac{m_2}{V_0}, \quad \frac{m_1 + m_2}{V_0} < \rho' < \rho_{\max}. \quad (22)$$

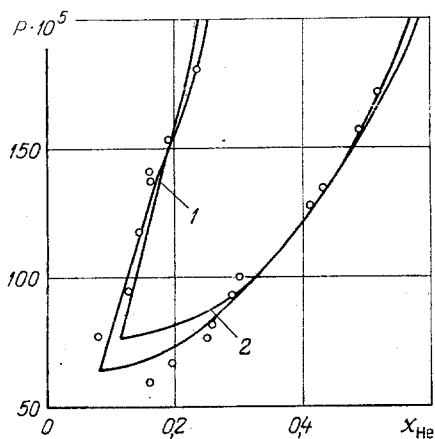


Fig. 3. Numerical determination of pressure-composition relationship for gas-gas equilibrium in mixture He-F12 at  $T = 388^\circ\text{K}$ : P, Pa: 1) F-minimization method; 2) direct grid search method; points) experimental data of [6].

We note that specification of upper and lower limits for the variables to be varied,  $\rho_{\min}$  and  $\rho_{\max}$ , determines the search intervals, and thus affects the rate at which the minimization process converges to the solution. Due to the similarity of the molar volumes of the respective phases in the case of gas-gas equilibrium, with the aid of  $\rho_{\min}$  the region of low densities for  $\rho_1''$  and  $\rho_2''$  was eliminated.

The first stage of minimization consists of dividing the intervals of each variable to choose a series of search starting points. The number of divisions is determined by the practical considerations of the concrete form of phase equilibrium. Thus, for gas-liquid equilibrium, 5-10 sections are sufficient, while to find the parameters of gas-gas equilibrium, usually up to 30 starting points are required. Further minimization is achieved by successive one-dimensional and n-dimensional analysis of the F-surface. The value of the step for the case of search of a local n-dimensional minimum is automatically reduced, which eliminates jumps into regions of other minima, and also prevents oscillations about the minimum point. For the one-dimensional search the gold section method [9] was used, which is quite effective when there are few variables and only a short time is needed for calculation of the target function.

To avoid premature terminations of the minimization process on sharp dropoffs and flat regions of the F-surface, the criterion for completion of the problem used was the simultaneous fulfillment of the inequalities

$$f(\bar{x}_i^h)^{j+1} - f(\bar{x}_i^h)^j < \varepsilon_f, \quad (23)$$

$$\Delta \bar{x}_i^h < \varepsilon_x. \quad (24)$$

We note that good scaling of the solution variables  $\rho_1''$ ,  $\rho_2''$ , and  $\rho'$ , which produce comparable contributions to the target function F. Thus there is no need for supplementary normalization of the quantities to be varied. However, due to the great sensitivity of the pressure to change in the densities of the respective phases in the gas-gas equilibrium region, the equilibrium pressure values found sometimes differ by  $\approx 3$  bar. We find such a result to be satisfactory, and did not introduce higher requirements for  $\varepsilon_x$  and  $\varepsilon_f$ , specifying them as  $\varepsilon_x = 10^{-5}$  and  $\varepsilon_f = 10^{-7}$ , respectively.

Practical use of the technique revealed the presence of 3-4 local n-dimensional minima in the F-surface in the gas-gas equilibrium region. The global minimum was determined by choosing the smallest of the local minima, which is perfectly acceptable in minimization problems of low dimensionality [9].

Comparison of the two methods shows the similar accuracy of the techniques evident in Fig. 3. This then indicates that use of the simpler direct F-minimization technique is preferable.

A serious shortcoming of the Redlich-Kwong equation is the unrealistic value of the critical volume ( $z_c = 0.333$ ), which leads to a distorted description of the parameter region close to the critical point. But in this regard the following must also be noted. Since our main problem is the determination of the conditions for equal volatility of the components in the constituent phases, and not calculation of the intrinsic volume and volatility values, it can be assumed that this shortcoming of the Redlich-Kwong equation will not have such a significant effect on the position of the layering curve as would appear at first glance.

Calculations performed have confirmed this fact. In those cases where it is necessary to reliably determine the volumes of the component phases, the Redlich-Ngo equation [11] should be used in preference to Eq. (1) to describe the region directly adjacent to the critical point of the less volatile component.

#### NOTATION

F, free Helmholtz energy; v, molar volume; x, molar fraction of component; P, pressure; T, temperature;  $a_{ii}$ ,  $b_{ii}$ , constants in the Redlich-Kwong equation of state for identical ( $i = i$ ) and differing ( $i \neq i$ ) types of interaction; R, universal gas constant;  $k_{12}$ ,  $l_{12}$ , parameters correcting the usual constant combination rules in the Redlich-Kwong equation;  $\epsilon_{ii}$ ,  $\sigma_{ii}$ , parameters characterizing the various types of interaction potentials ( $\phi$ ) of the binary mixture;  $k'_{12}$ ,  $l''_{12}$ , parameters correcting usual combination rules for  $\epsilon_{12}$  and  $\sigma_{12}$ ;  $\phi_k$ , volatility coefficient of k-th component in mixture; z, compressibility coefficient;  $f_i$ , partial molar volatility of mixture component;  $f(\bar{x})$ , target function for minimization procedure;  $\bar{x}$ , vector in n-dimensional space;  $c(\bar{x})$ , limitations of minimization process;  $\epsilon_x$ , required accuracy in argument;  $\epsilon_f$ , required accuracy in function;  $V_0$ , volume of system model;  $m_1$ ,  $m_2$ , number of moles of components present;  $\rho_1'$ ,  $\rho_2''$ ,  $\rho'$ , solution variables chosen for respective phases;  $\rho_{\min}$ ,  $\rho_{\max}$ , boundaries for variables to be varied.

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