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Translated by G. Volkoff

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SOVIET PHYSICS JETP

VOLUME 6 (33), NUMBER 4

APRIL, 1958

*THERMODYNAMICS OF THE He I — He II PHASE TRANSITION IN HELIUM ISOTOPE MIXTURES*

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Submitted to JETP editor April 19, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) 33, 936-944 (October, 1957)

A thermodynamic investigation of the phenomena associated with a phase transition of the second order in liquid mixtures is carried out. The results obtained are compared with the experimental data on liquid-vapor equilibrium in the He<sup>3</sup> — He<sup>4</sup> system.

IN pure He<sup>4</sup>, as is well-known, the He I — He II transition is a phase transition of the second order. The question of the nature of this transition in mixtures of the helium isotopes has been repeatedly submitted to theoretical investigation, as a result of which, in particular, it has been predicted<sup>1</sup> that the  $\lambda$ -transition in such mixtures will be a transition of the first order for sufficiently small concentrations and high temperatures.

Inasmuch as this problem is of fundamental significance, it appears desirable to carry out a detailed thermodynamic investigation of the phenomena associated with the He I — He II transition in helium isotope mixtures, and to compare the results thus obtained with the experimental data (cf. also references 2, 3).

It is necessary first of all to note that a conclusion regarding the nature of the He I — He II phase transition in helium isotope mixtures can be drawn from a study of the dependence of the vapor pressures of these mixtures upon their He<sup>3</sup> content. In the case of a first order phase transition, in fact, there should be observed a separation of the liquid phase into two mixtures of differing He<sup>3</sup> content, which would yield vapor pressures independent of the concentration of the light isotope in the region of separation.

Carefully-conducted experiments<sup>4-6</sup>, however, have shown that in the interval 1.35 — 3.0°K there is a marked dependence of the vapor pressure upon the He<sup>3</sup> content of the liquid phase, indicating that the hypothesis concerning the occurrence of a first order phase transition in this temperature interval is not borne out.

Thus, as in the case of pure He<sup>4</sup>, the He I — He II phase transition in helium isotope mixtures within the temperature range investigated is a phase transition of the second order.\*

Inasmuch as this is the only instance of the occurrence of a second order phase transition in liquid

\*It must be noted that Walters and Fairbank<sup>7</sup> have recently observed a separation of helium isotope mixtures into two phases below 0.8°K.

mixtures, the opportunity provided for investigating the special features arising therefrom is extremely interesting. In particular, it is possible on purely thermodynamic grounds to draw conclusions concerning the special features appearing on the  $P-T$  curves at the transition through the  $\lambda$ -point, and concerning the behavior of the heats of mixing and vaporization at the transition through the same temperature.

Use of the experimental data which have been obtained<sup>4-6</sup> relative to liquid-vapor equilibrium in the  $\text{He}^3-\text{He}^4$  system makes possible a direct comparison of the theoretical results with experiment.

### 1. FEATURES OF THE LIQUID-VAPOR DIAGRAM IN THE VICINITY OF THE $\lambda$ -POINT

Let us represent the thermodynamic potential for a mixture in the form  $\Phi = N\varphi$ , where  $\varphi$  is the thermodynamic potential per particle and  $N = N_3 + N_4$  is the total number of particles. Representing the concentration of the mixture by  $x_L = N_3/N$ , we find the chemical potentials  $\mu_3^m$  and  $\mu_4^m$  of the components in the mixture:

$$\mu_3^m = \varphi + (1 - x_L) \frac{\partial \varphi}{\partial x_L}, \quad \mu_4^m = \varphi - x_L \frac{\partial \varphi}{\partial x_L}. \quad (1)$$

Using the condition of equilibrium between the phases and the expressions for the chemical potentials of the constituents in the gaseous phase, we obtain, assuming ideality for the vapor:

$$kT \ln P_3 + \chi_3(T) = \varphi + (1 - x_L) \partial \varphi / \partial x_L, \quad kT \ln P_4 + \chi_4(T) = \varphi - x_L \partial \varphi / \partial x_L, \quad (2)$$

where  $P_3$  and  $P_4$  are the partial pressures.

Taking the total derivative with respect to temperature on both sides of Eqs. (2), we arrive at the expressions:

$$-S_3 + kT \frac{d}{dT} \ln P_3 = \frac{\partial \varphi}{\partial T} + (1 - x_L) \frac{\partial^2 \varphi}{\partial T \partial x_L}, \quad -S_4 + kT \frac{d}{dT} \ln P_4 = \frac{\partial \varphi}{\partial T} - x_L \frac{\partial^2 \varphi}{\partial T \partial x_L}, \quad (3)$$

where  $S_3$  and  $S_4$  are the partial entropies per particle. At the temperature  $T_\lambda$ , inasmuch as at a phase transition of the second order the first derivative of the thermodynamic potential suffers a break in slope, and the second derivative a discontinuity, we obtain:

$$kT_\lambda \Delta \frac{d \ln P_3}{dT} = (1 - x_L) \Delta \frac{\partial^2 \varphi}{\partial T \partial x_L}, \quad kT_\lambda \Delta \frac{d \ln P_4}{dT} = -x_L \Delta \frac{\partial^2 \varphi}{\partial T \partial x_L}, \quad (4)$$

where

$$\Delta f = f(T_\lambda - 0) - f(T_\lambda + 0).$$

From (2) and (4) it follows immediately that in this case at  $T_\lambda$  there should be observed breaks in the  $P_3-T$  and  $P_4-T$  curves, and discontinuities in the  $dP_3/dT-T$  and  $dP_4/dT-T$  curves.

Taking into account the fact that near the transition point<sup>8</sup>

$$\varphi_{II} = \varphi_I - (\Delta C_p / 2T_\lambda) (T - T_\lambda)^2, \quad (5)$$

where  $\varphi_{II}$  and  $\varphi_I$  are the values of the thermodynamic potential below and above the  $\lambda$ -point, respectively, and  $\Delta C_p$  is the discontinuity in the specific heat at  $T_\lambda$ , we obtain

$$\Delta (\partial^2 \varphi / \partial T \partial x_L) = (\Delta C_p / T_\lambda) \partial T_\lambda / \partial x_L, \quad (6)$$

and, in place of (4)

$$kT_\lambda \Delta \frac{d \ln P_3}{dT} = (1 - x_L) \frac{\Delta C_p}{T_\lambda} \frac{\partial T_\lambda}{\partial x_L}, \quad kT_\lambda \Delta \frac{d \ln P_4}{dT} = -x_L \frac{\Delta C_p}{T_\lambda} \frac{\partial T_\lambda}{\partial x_L}. \quad (7)$$

Using (7), it is possible to find a relation between the discontinuities in the derivatives of the partial pressures

$$x_L \Delta (d \ln P_3 / dT) + (1 - x_L) \Delta (d \ln P_4 / dT) = 0. \quad (8)$$

Setting

$$P_3 = x_V P; \quad P_4 = (1 - x_V) P, \tag{9}$$

where  $x_V$  is the concentration of  $\text{He}^3$  in the vapor, we obtain from (7) an expression for the discontinuity in the derivative of the total pressure with respect to temperature

$$kT_\lambda \Delta \frac{d \ln P}{dT} = (x_V - x_L) \frac{\Delta C_P}{T_\lambda} \frac{\partial T_\lambda}{\partial x_L}. \tag{10}$$

Since  $\partial T_\lambda / \partial x_L < 0$ ,<sup>3</sup>  $\Delta C_P > 0$ ,<sup>8</sup> and  $x_V > x_L$ ,  $\Delta(d \ln P/dT) < 0$ , which is found to be in agreement with experiment.<sup>3</sup>

Thus at a second order phase transition in mixtures the derivatives with respect to temperature of the partial and total pressures suffer discontinuities. It should be remarked, however, that magnitude of the discontinuity in the derivative of the total pressure is small, as is evident from (10); this is a consequence of the fact that the discontinuities in the derivatives of the partial pressures have opposite signs and the same order of magnitude [cf. Eqs. (4) and (8)]. As a result of this and also of the large value of  $dP/dT$ , the comparatively small discontinuity in this quantity at the  $\lambda$ -point will be scarcely discernible.

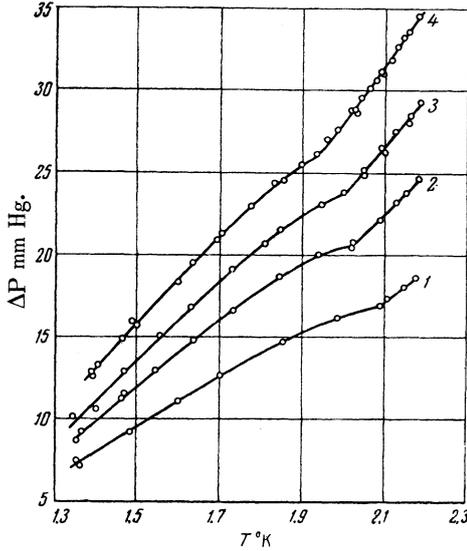


FIG. 1. Dependence of the difference between the mixture and  $\text{He}^4$  vapor pressures ( $\Delta P$ ) upon temperature: (1) 8.3%  $\text{He}^3$ ; (2) 11.1%  $\text{He}^3$ ; (3) 13.4%  $\text{He}^3$ ; (4) 16.7%  $\text{He}^3$ .

The dependence of  $\Delta P$  upon  $T$ , where  $\Delta P$  is the difference between the vapor pressures of the mixture and of pure  $\text{He}^4$ , has been investigated experimentally, and in this case breaks at  $T_\lambda$  are clearly visible. This is explained by the fact that the magnitude of  $d(\Delta P)/dT$  has now been considerably reduced, while the magnitude of the discontinuity has remained the same. The dependence of  $\Delta P$  upon  $T$ ,<sup>6</sup> is represented in Fig. 1 for mixtures of varying  $\text{He}^3$  content. On each curve a break is visible at  $T_\lambda$ . This confirms the conclusions we have drawn regarding the characteristics of the  $P - T$  curves, and provides a new possibility for determination of the displacement of  $T_\lambda$  with increasing  $\text{He}^3$  concentration in the mixture.<sup>3</sup>

It is essential to note that at the  $\lambda$ -point a discontinuity should be observed in the first derivative with respect to temperature of the  $\text{He}^3$  concentration in the gaseous phase ( $x_V$ ). Specifically, substituting the values for  $P_3$  and  $P_4$  from (9) into (3), we readily find

$$\Delta \frac{\partial x_V}{\partial T} = x_V(1 - x_V) \frac{\Delta C_P}{kT_\lambda^2} \frac{\partial T_\lambda}{\partial x_L}; \tag{11}$$

$$\Delta \frac{\partial}{\partial T} \left( \ln \frac{c_V}{c_L} \right) = \frac{\Delta C_P}{kT_\lambda^2} \frac{\partial T_\lambda}{\partial x_L}, \tag{12}$$

where

$$c_V = (N_3 / N_4)_V \quad c_L = (N_3 / N_4)_L$$

Thus there follows from Eq. (11) the presence of a discontinuity in the derivative of  $x_V$  with respect to temperature, and from Eq. (12), the existence of a discontinuity in the derivative of the distribution coefficient with respect to temperature.\*

The occurrence of breaks in the  $P - T$  and  $x_V - T$  curves at  $T_\lambda$  should lead to breaks in the two curves of the liquid-vapor equilibrium diagram. It should, however, be noted that these breaks do not appear in the published diagram,<sup>6</sup> as a consequence of the fact that the variation in these quantities at the  $\lambda$ -point is small, and also because the function  $x_V(T)$  was determined, not directly, but from the diagram.

The magnitude of the discontinuity in the derivative of the total pressure with respect to  $x_L$  at the

\*This expression was obtained by us in 1950.<sup>2</sup> More recently it has been obtained by de Boer and Gorter.<sup>9</sup>

transition temperature is

$$\Delta(\partial \ln P / \partial x_L) = (x_L - x_V)(\Delta C_P / kT_\lambda^2)(\partial T_\lambda / \partial x_L)^2. \quad (13)$$

It is evident from (13) that the discontinuity in the derivative of the pressure with respect to the concentration of the liquid phase is negative.

## 2. THE HEAT OF MIXING AND ITS DEPENDENCE UPON TEMPERATURE AND CONCENTRATION

At the temperature of the He I — He II phase transition there should also be observed a discontinuity in the heat of mixing. The magnitude of this discontinuity can be computed using an expression<sup>8</sup> for the quantity of heat ( $q_3$ ) absorbed during the transfer of a single particle out of the pure liquid substance ( $\text{He}^3$ ) into the mixture:

$$q_3 = \frac{\partial W^m}{\partial N_3^m} - W_3^L = -kT^2 \frac{\partial}{\partial T} \ln \frac{P_3}{P_3^0}, \quad (14)$$

where  $\partial W^m / \partial N_3^m$  is the change in the heat function of the mixture as one atom of  $\text{He}^3$  is added to it, while  $W_3^L$  is the molecular heat function for pure liquid  $\text{He}^3$ .

At  $T_\lambda$

$$\Delta q_3 = \Delta(\partial W^m / \partial N_3^m),$$

since

$$\partial W^m / \partial N_3^m = \partial \Phi / \partial N_3^m - T \partial^2 \Phi / \partial T \partial N_3^m.$$

Therefore

$$\Delta q_3 = -T_\lambda \Delta(\partial^2 \Phi / \partial T \partial N_3^m).$$

Taking the fact that  $\Phi = N\phi$  and Eq. (6) into account, we obtain

$$\Delta q_3 = -(1 - x_L) \Delta C_P \partial T_\lambda / \partial x_L. \quad (15)$$

In the case of small concentrations, using the value  $\Delta C_P = 7$  cal/mole degree for  $\text{He}^4$ , from Ref. 10, and the value of  $\partial T / \partial x_L = -1.5^\circ$ , from Ref. 3, we obtain for the discontinuity in the heat of mixing at the He II — He I transition  $\Delta q_3 = 10.5$  cal/mole.

It should be noted that the indicated changes in the distribution coefficient and the heat of mixing at the  $\lambda$ -point can be related to the discontinuities in the derivatives of the partial and total pressures:

$$\Delta \frac{\partial}{\partial T} \left( \ln \frac{c_V}{c_L} \right) = \frac{1}{x_V - x_L} \Delta \frac{d \ln P}{dT}, \quad \Delta q_3 = -kT_\lambda^2 \frac{1 - x_L}{x_V - x_L} \Delta \frac{d \ln P}{dT} \quad (16)$$

Using the experimental data for the dependence of the vapor pressure upon temperature for mixtures of varying  $\text{He}^3$  content, it would be possible to compute both the one quantity and the other from (16). In view, however, of the great difficulty in determining sufficiently precisely the indicated discontinuities in the derivatives of the partial and total pressures with respect to temperature, it does not appear possible as yet to use this method to compute the quantities in (16).

The temperature dependence of  $q_3$  to either side of  $T_\lambda$  can be computed using Eq. (14). The results of such a calculation are presented in Fig. 2 for a mixture of 8.3%  $\text{He}^3$ . The error in the magnitude of the discontinuity  $\Delta q_3$  at the  $\lambda$ -point is naturally determined here by the error in determining the magnitude of the discontinuity in the derivative of  $P_3$  with respect to temperature.

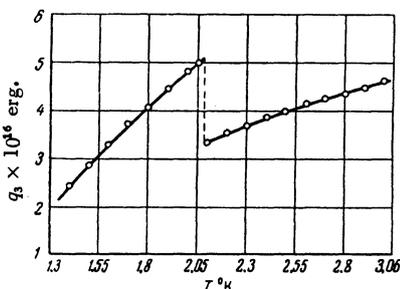


FIG. 2. Dependence of the heat of mixing ( $q_3$ ) upon temperature. Calculated data for a mixture with 8.3%  $\text{He}^3$ .

3. THE HEAT OF TRANSITION AND ITS DEPENDENCE UPON He<sup>3</sup> CONTENT AND TEMPERATURE

Using the liquid-vapor diagram of state which has already been obtained,<sup>6</sup> it is possible to determine the temperature and concentration dependences of the heat of the transition from mixture to vapor. For the case of mixtures, however, the determination of the heat of transition itself, as is well known, requires some elucidation.

The fact is that the relative quantities of liquid and vapor are in this case related by the lever rule

$$N_V/N_L = (x_L - c)/(c - x_V), \quad (17)$$

where

$$c = (N_V^{(3)} + N_L^{(3)})/(N_V + N_L)$$

is the mean concentration of the He<sup>3</sup> isotope in the system. Therefore the transfer of a molecule from the liquid to the vapor (or vice versa) by an equilibrium process (in accordance with the state diagram) cannot take place without variation of the pressure or the temperature. Such a situation does not arise in a single-component system, in which the transfer takes place at a point (for constant P and T).

Thus in determining the heat of transition it is necessary to specify the process by which the transition takes place. It is natural to investigate two processes: a) the transition takes place at constant temperature (T = const.), b) the transition takes place at constant pressure (P = const.).

Inasmuch as the heat of transition from gas to liquid for a single particle is

$$\lambda = T\delta S/\delta N_V, \quad (18)$$

it is necessary, in order to determine this, to compute the change in entropy  $\delta S$  accompanying the transfer of  $\delta N_V$  particles from the gas to the liquid. In doing this it is necessary to remember that the variation of all the parameters of the system proceeds in accordance with the diagram of state.

If it is assumed that T = const. [case (a)], then, taking into account the constancy of the number of particles of each sort in the system, and the fact that P and  $x_V$  are in this case functions of  $x_L$ , we readily obtain

$$\delta S/\delta N_V = S_V - S_L + \frac{x_L - x_V}{1 + \frac{x_L - c}{c - x_V} \frac{\partial x_V}{\partial x_L}} \left\{ \frac{\partial S_L}{\partial P} \frac{\partial P}{\partial x_L} + \frac{\partial S_L}{\partial x_L} + \frac{x_L - c}{c - x_V} \left( \frac{\partial S_V}{\partial P} \frac{\partial P}{\partial x_L} + \frac{\partial S_V}{\partial x_V} \frac{\partial x_V}{\partial x_L} \right) \right\}. \quad (19)$$

Here  $S_V$  and  $S_L$  are the entropies per particle of the gas and the liquid. In deriving Eq. (19) the lever rule (17) was employed.

If  $x_L = c$  (Fig. 3; a large quantity of liquid and virtually no gas in the system), then

$$\frac{\delta S}{\delta N_V} = (S_V - S_L) + (x_L - x_V) \left( \frac{\partial S_L}{\partial P} \frac{\partial P}{\partial x_L} + \frac{\partial S_L}{\partial x_L} \right). \quad (20)$$

If  $x_V = c$  (Fig. 4; a large quantity of gas and virtually no liquid in the system), then

$$\frac{\delta S}{\delta N_V} = (S_V - S_L) + (x_L - x_V) \left( \frac{\partial S_V}{\partial P} \frac{\partial P}{\partial x_V} + \frac{\partial S_V}{\partial x_V} \right). \quad (21)$$

Making use of the fact that

$$S_V = x_V S_V^{(3)} + (1 - x_V) S_V^{(4)}, \quad S_L = x_L S_L^{(3)} + (1 - x_L) S_L^{(4)}, \quad (22)$$

as well as of the equality of the chemical potentials of each component in the gas and the liquid, we find from (20), (21), and (18), assuming the gas to be ideal: for  $x_L = c$ :

$$\lambda_{T, x_L} = kT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{x_L} + (x_L - x_V) T \frac{\partial S_L}{\partial P} \left( \frac{\partial P}{\partial x_L} \right)_T; \quad (23)$$

for  $x_V = c$ :

$$\lambda_{T, x_V} = kT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{x_V} + (x_L - x_V) T \frac{\partial S_V}{\partial P} \left( \frac{\partial P}{\partial x_V} \right)_T. \quad (24)$$

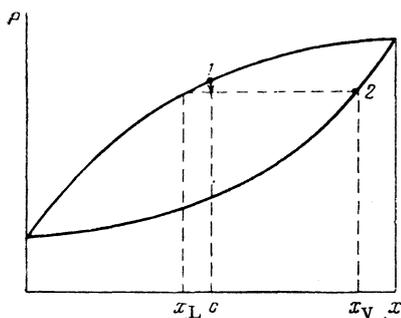


FIG. 3. For calculation of the heat of transition in the case  $T = \text{const.}$  and  $c = x_L$ : (1) state of the system before the transition; (2) concentration in the gaseous phase formed as a result of the transition; the arrow indicates the motion of the system due to the transition.

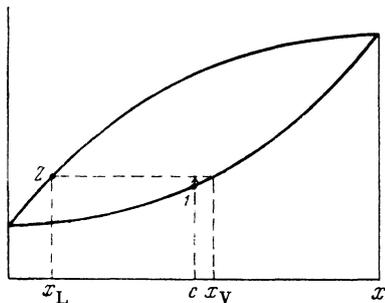


FIG. 4. For calculation of the heat of transition in the case  $T = \text{const.}$  and  $c = x_V$ : (1) state of the system before the transition; (2) concentration in the liquid phase formed as a result of the transition; the arrow indicates the motion of the system due to the transition.

If we take into account the fact that the entropy of the liquid is practically independent of the pressure, and if in calculating the second term in (24) we assume that the gas is ideal, we obtain:

$$\lambda_{T, x_L} = kT^2 (\partial \ln P / \partial T)_{x_L}, \quad (25)$$

$$\lambda_{T, x_V} = kT^2 \left( \frac{\partial \ln P}{\partial T} \right)_{x_V} + kT (x_V - x_L) \left( \frac{\partial \ln P}{\partial x_V} \right)_T. \quad (26)$$

In calculating the second term in Eq. (26) it is convenient to make use of the expression<sup>8</sup>

$$(\partial \ln P / \partial x_V)_T = (x_V - x_L) / x_V (1 - x_V). \quad (27)$$

Then

$$\lambda_{T, x_V} = kT^2 (\partial \ln P / \partial T)_{x_V} + kT (x_V - x_L)^2 / x_V (1 - x_V). \quad (28)$$

In precisely the same way it is possible to calculate the corresponding heats for the case  $P = \text{const.}$ :

$$\lambda_{P, x_L} = kT^2 (\partial \ln P / \partial T)_{x_L} + (x_L - x_V) C_P^L (\partial T / \partial x_L)_P; \quad (29)$$

$$\lambda_{P, x_V} = kT^2 (\partial \ln P / \partial T)_{x_V} + (x_L - x_V) C_P^V (\partial T / \partial x_V)_P, \quad (30)$$

where  $C_P^L$  and  $C_P^V$  are the specific heats per particle of the liquid and the vapor.

Analysis of the expressions thus obtained shows that for each of the cases investigated [Eqs. (25), (28) – (30)] the heat of transition is composed of two terms,\* the first representing the heat entering directly into the transfer of the particle from one phase into the other, and the second representing the heat associated with the change in entropy of the system due to this transfer. We note that in a real experiment (under the corresponding equilibrium conditions) the heats measured will be just those calculated here. The possibility of separating each of the heats into two components, each having a definite physical significance, arises from the fact that the first component may be obtained directly, from the quantity of heat absorbed during the transfer from the solution into the vapor of a single particle of the first constituent ( $\lambda_3$ ), and from the corresponding quantity for the second constituent ( $\lambda_4$ ). In actuality, when one mole of the mixture passes from the liquid, of concentration  $x_L$ , into the gaseous phase, its concentration will be  $x_V$ ; in consequence  $x_V \lambda_3 + (1 - x_V) \lambda_4$  calories (as calculated for a single particle) will be absorbed in the process. In accordance with reference 8, however, this quantity will be equal to the first term

$$x_V \lambda_3 + (1 - x_V) \lambda_4 = kT^2 (\partial \ln P / \partial T)_{x_L}. \quad (31)$$

The heat of transition for the case of a process taking place at  $T = \text{const.}$  can be calculated for the cases  $x_L = c$  and  $x_V = c$  from (25) and (28), using the data obtained from investigation of liquid-vapor equilibrium in the  $\text{He}^3 - \text{He}^4$  system. The results of these calculations are presented in Fig. 5 ( $x_L = c$ ), which shows the dependence of  $\lambda_{T, x_L}$  upon the concentration of the phase being formed ( $x_V$ ). It should be mentioned that in calculating  $\lambda_{T, x_L}$  the non-ideality of the vapor was taken into account by determining the molar volume using the second virial coefficient.<sup>11</sup> The values of  $\lambda$  for pure  $\text{He}^4$  and  $\text{He}^3$  were taken from Refs. 12 and 13. The solid curves in Fig. 5 refer to various temperatures. The dashed lines

\*The absence of a second term from Eq. (25) is of course due to the fact that we have ignored the variation of the liquid phase entropy with pressure.

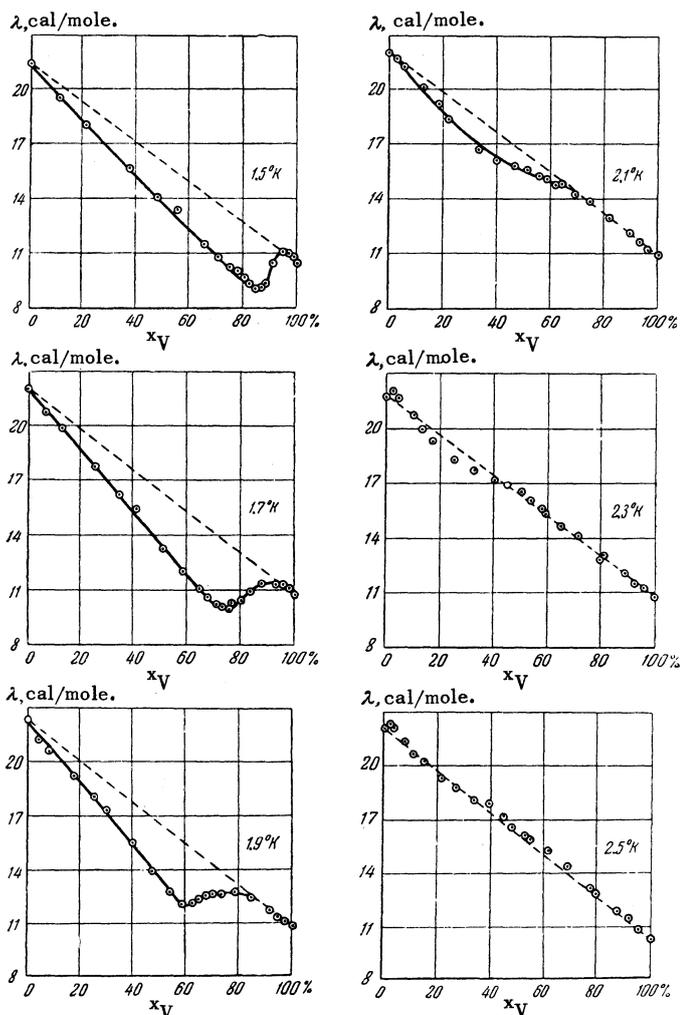


FIG. 5. Dependence of the heat of transition  $\lambda_{T,x_L}$  upon the concentration of the phase being formed ( $x_V$ ).

It is clearly evident that these heats differ fundamentally from one another, both in magnitude in the nature of their dependence upon the concentration.

It should be noted that at the transition through the  $\lambda$ -point the heat of transition suffers a discontinuity, as is evident from Eqs. (25), (28), (29), and (30). Due to the small magnitude of the change in  $dP/dT$ , such a discontinuity is not clearly displayed in the calculated heats. It can be supposed, however, that the considerable change in the heat of transition near the  $\lambda$ -point which is evident in Fig. 5 is connected with this circumstance.

CONCLUSIONS

1. A thermodynamic study of the phenomena associated with the He I – He II transition in mixtures of the helium isotopes has been carried out. It is shown that in the interval 1.35 – 3.0°K this transition is a phase transition of the second order.

2. It is shown that at the temperature of a second order phase transition in helium isotope mixtures there should be observed discontinuities in the derivatives of the partial and total pressures with respect to temperature. This effect is confirmed experimentally.

3. It is established that at  $T_\lambda$  there should be observed a discontinuity in the derivative of the distribution coefficient with respect to temperature.

show the heat of transition which would obtain in the additive case.

From these diagrams it follows that the heat of transition as calculated by the method indicated passes through a minimum, the position of which moves in the direction of smaller  $x_V$  as the temperature is raised. In the region of high  $x_V$  the points lie on the dashed line corresponding to the additive case, while the concentration region over which this is true increases as the temperature rises. Above 2.2°K  $\lambda_{T,x_L}$  has a practically linear dependence upon  $x_V$ .

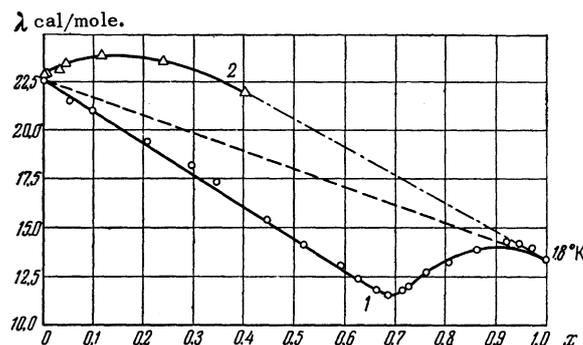


FIG. 6. Dependence of the heats of transition  $\lambda_{T,x_L}$  (curve 1) and  $\lambda_{T,x_V}$  (curve 2) upon the concentration of the phase being formed.

Fig. 6 shows for a temperature of 1.8°K the dependence of the heats of transition  $\lambda_{T,x_L}$  (curve 1) and  $\lambda_{T,x_V}$  (curve 2) upon the concentration of the phase being formed ( $x_V$  in the first case and  $x_L$  in the second), as calculated from Eqs. (25) and (28).

4. It is shown that at  $T_\lambda$  there should be observed a discontinuity in the heat of mixing and a discontinuity in the heat of vaporization. A numerical value for the magnitude of the discontinuity in the heat of mixing has been obtained for weak mixtures. For one of these mixtures the temperature dependence of the heat of mixing has been calculated. The dependence of the heat of transition upon the concentration of the phase being formed has been calculated for various temperatures.

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Translated by S. D. Elliott

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SOVIET PHYSICS JETP

VOLUME 6 (33), NUMBER 4

APRIL, 1958

## ON THE EQUATIONS OF THE OSCILLATIONS OF THE MOLECULAR GENERATOR

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Submitted to JETP editor April 20, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) 33, 945-947 (October, 1957)

By use of a density matrix in the proper approximation, equations are derived that describe both stationary and nonstationary operating conditions of the molecular generator.

THE theoretical problems connected with the molecular generator have been discussed by several authors.<sup>1-3</sup> In these articles, however, only stationary or nearly stationary operating conditions are described. It is of interest to derive equations of the molecular generator that are valid for arbitrary operating conditions.

Upon replacing the resonant cavity by an equivalent circuit it is not difficult to derive the following equation, which describes the oscillations in the circuit:

$$\ddot{E} + 4\pi\dot{P} + (\omega_0/Q)(\dot{E} + 4\pi\dot{P}) + \omega_0^2 E = 0. \quad (1)$$

Here  $E$  is the electric field intensity,  $P$  is the polarization of the medium in the resonant cavity,  $Q$  is the figure of merit of the circuit, and  $\omega_0$  is the natural frequency of the circuit. Equation (1) is still