

On the basis of an analysis of familiar experimental and theoretical studies we have formulated the problem of the vapor-liquid state of helium II and the phase transition to this region, and we also offer a T-S diagram and an analysis for the transition from the standpoint of quantum physics.

It is the goal of the present study to draw attention to the contemporary states of work being done on the properties of helium II in the area of liquid-vapor mixtures and the T-S diagram of ^4He .

Our concepts of liquid helium have frequently been changed and refined in accordance with the appearance of new or revised earlier familiar data [1, 2]. A need has arisen for immediate improvements.

W. Nernst, M. Planck, A. Einstein, P. Kapitsa, and D. Landau demonstrated the groundlessness of classical thermodynamics to explain the fundamental physical properties and phase transitions of liquid helium II. These individuals have the honor of bringing quantum physics into play to explain the physical processes and phase transitions at the temperatures of liquid helium.

The usual phase state of helium is represented in P-T diagrams (Fig. 1). However, such a diagram is inconvenient and provides limited information, and moreover it is not sufficiently clear, since it contains none of the two-phase vapor-liquid state regions.

The region bounded by the $\lambda_{\text{III}}-\lambda_{\text{II}}-\lambda_{\text{I}}-\lambda_{00}$ lines is occupied by the superfluid liquid helium II. It exhibits quantum properties and is in contact with solid helium, liquid helium I, and vapor.

The phase transition of liquid helium II into liquid helium I along the $\lambda_{\text{II}}-\lambda_{\text{I}}$ line (Fig. 1) has been studied in considerable detail. This relates to the phase transitions of the second kind, which are accomplished without participation of latent heat, when the first Gibbs energy derivatives are noncontinuous ($\Delta V = 0$; $r = T\Delta S = 0$), and the second derivatives change in discontinuous fashion:

$$C_p = -T \left(\frac{\partial^2 \Phi}{\partial T^2} \right)_p; \quad \beta = -\frac{1}{v} \left(\frac{\partial^2 \Phi}{\partial P^2} \right)_T; \quad l = \frac{1}{v} \left(\frac{\partial^2 \Phi}{\partial T \partial P} \right);$$

The phase transitions of liquid He II into the solid state along the $\lambda_{\text{II}}-\lambda_{\text{III}}$ lines have also been studied in considerable detail, and these are phase transitions of the second kind [3, 4]. However, the phase transitions of superfluid helium II into the vapor-liquid region along the $\lambda_{\text{I}}-\lambda_{00}$ line has not been studied at all. Knowledge of the helium properties in this region is essential to the design of cryogenic systems, thermodynamic circuits, as well as for purposes of calculating the parameters of state for helium, as well as the thermal processes which occur in cryostats and heat exchangers intended for the production of helium II.

McLennan [5], followed by Kapitsa [6], were the first who demonstrated experimentally that subsequent to the cooling of liquid helium below 2.17 K the external form of the liquid changes markedly and boiling, i.e., the formation of vapor bubbles within the volume of the liquid, ceases instantaneously, while the "thermal conductivity" increases by a factor of a million.

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Usually, with a reduction in temperature the latent heat of vapor formation increases in liquids. However, it has been established [7, 8] that in the case of liquid helium there is a sharp reduction in the latent heat of vapor formation when the temperature drops below 3.1 K.

Let us take particular note of the fact that these important differences in the physical properties of liquid helium II from those of helium I (the absence of boiling, the sharp lowering of the heat of vapor formation in the case of $T < 3.1$ K, as well as the absence of latent heat in the phase transition of ${}^4\text{HeII}$ into ${}^4\text{HeI}$) are not currently reflected in contemporary diagrams of phase state.

The thermodynamic properties and phase transitions of helium are most clearly seen in the T-S diagram. However, existing T-S diagrams [9-12] show the vapor-liquid region of the helium only for temperatures in excess of 2.2 K, although T-S diagrams for temperatures below 2.17 K are essential.

The first entropy diagrams for the helium II region were constructed by Keesom [13, 14] on the basis of limited and rather precise experimental data [8]. The state of the liquid vapor in such diagrams is represented by a single line without a two-phase vapor-liquid region. Their form corresponds to the traditional thermodynamic P-v-T surface for ordinary materials and, in addition, they exhibited other shortcomings as well.

After Kapitsa drew attention to their inaccuracy [15], the publication of entropy diagrams for helium II was curtailed totally for many years, and all known T-S diagrams are constructed in traditional form only for helium I with a temperature higher than 2.2 K.

The thermodynamic properties of helium are published in contemporary literature in the form of tables. As is well known, such tables are prepared on the basis of averaged equations of state, compiled on the basis of experimental P-v-T data and caloric studies. At the present time, we can regard as most reliable the Soviet and American tables of thermophysical properties of helium-4 [9, 10, 16]. Unlike others, these have been calculated with rather high accuracy from single equations of state for gas and liquids.

Theoretical tables of thermodynamic properties of helium [9-12, 16-21] have appeared in recent times. Unfortunately, for a number of fundamental factors these do not completely describe the region below 2.2 K, differing in the inconsistency and contradictory nature of the data.

In this connection, a significant study is to be found in [22] where, on the basis of certain theoretical tables of properties, a T-S diagram has been constructed, and the two-phase vapor-liquid state of helium I and helium II is represented here by interpenetrating left and right boundary curves of equilibrium all the way to $T = 1$ K. And here also the λ line along which the phase transition of the second kind occurs is located by the authors within the vapor-liquid region in which, as is well known, only a transition of the first kind occurs. Thus the resulting concept of the λ line is rejected. Moreover, in the T-S diagram [22] the isobars ($P > 0.005$ MPa = const), extending out of the liquid helium I region, as temperatures drop, intersect the left equilibrium curve, enter the vapor-liquid region, touch the λ line, and then, intersecting each other, return again to the helium I region, remaining above the λ line. As a result, such a T-S diagram contradicts the physical concept of the λ transition, contradicts the existence of isobaric supercooled liquid helium II at temperatures below T_λ and pressures $P > P_{\lambda_1}$, failed to take into account the experimental facts relating to the cessation of liquid helium boiling at temperatures below the T_λ line and do not agree with the representation of the physical properties of helium I and helium II in the P-T diagrams.

Thus, some authors [17, 21, 22] hold that the two-phase vapor-liquid region spreads below the λ temperature, and that the latent heat of vapor formation increases with the drop in temperature; other authors [11, 12] operate under the assumption that the latent heat of vapor formation diminishes, and even at an absolute temperature of $T = 0$ K it remains equal to 59.62 J/mole. A third group of authors [18, 19, 23] offer no data relating to the existence of a latent heat of vapor formation in helium II and consequently, proceeding from the experiments of Kapitsa [6], McLennan [5], and others, assume that helium II exhibits no two-phase vapor-liquid region and they therefore take the extension of the left boundary curve of equilibrium out of the helium I region as the boundary separating the vapor and the liquid in helium II.

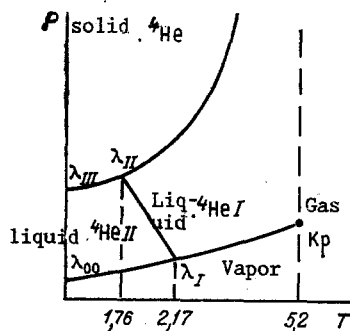


Fig. 1

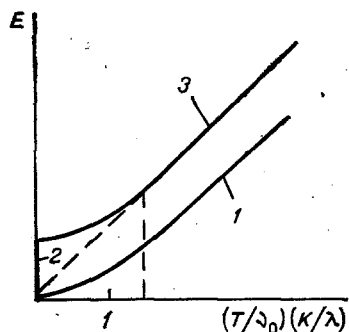


Fig. 2

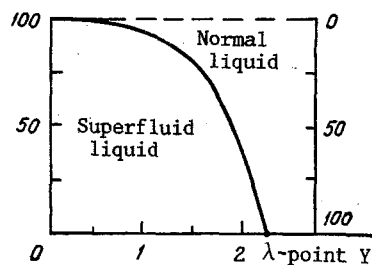


Fig. 3

Fig. 1. P-T diagram of state for helium-4. P, bar; T, K.

Fig. 2. Energy as a function of temperature: 1) kinetic (thermal) energy; 2) zero point quantum energy; 3) total energy.

Fig. 3. Diagram of two-liquid model of liquid⁴He, with the content of the superfluid and normal fluids plotted along the axes of ordinates, in %.

Finally, a fourth group of authors [16, 20, 24, 25] also proceed from the absence of a two-phase vapor-liquid mixture region in helium II, and take the extension of the right-hand boundary equilibrium curve as the line separating the vapor and the liquid. We can see from the tables listing the theoretical McCarty data [16, 20] that with a drop in temperature from 2.2 to 2.17 K, i.e., in the transition of helium I to helium II, the enthalpy of the liquid ($h_{2.2}' = 3276$) and the enthalpy of the vapor ($h_{2.2}'' = 25,510$ J/kg) become identical: $h_{2.17}' = h_{2.17}'' = 25,410$ J/kg. There are changes also in the entropy, in the heat capacity, and in other parameters of the helium. Let us note in particular that McCarty [16, 20], as well as the authors of [24, 25], report nothing about the existence of a latent heat of vapor formation and surface tension in helium II. Moreover, they demonstrate that these are absent in helium II.

All of these contradictory concepts relating to the two-phase vapor-liquid region of helium II give evidence of the fact that its properties have not been adequately studied in the vapor-liquid region, and moreover they point to the fact that at the present time no consistent opinion exists as to the form of the thermodynamic P-v-T surface for helium II, as well as to the fact that the initial positions of the authors have been based on classical thermodynamics which fail, to a considerable extent, to make provision for the quantum nature of helium II and are not based on contemporary quantum theory.

Einstein assumed that at temperatures below 2.17 K the behavior of liquid helium differs significantly from its behavior at normal temperature, since here the quantization of energy becomes perceptible.

According to Nernst's third law, with approach to absolute zero temperature, it is not energy but rather entropy that tends toward zero. With a reduction in temperature, beginning from $T = 2.17$ K, the total energy of the liquid helium $E = E_1 + E_2$ is reduced as a conse-

quence of the gradual disappearance of the thermal energy (Fig. 2), i.e., the kinetic (thermal) motion of the atoms ceases, $E_1 \sim mV^2/2 \sim kT \rightarrow 0$. According to quantum theory, at temperatures below 1 K "no" thermal energy and, consequently, no "latent heat" can possibly exist in actuality in liquid helium II. We are left only with the quantum component E_2 of total energy, governed by the energy of the zero oscillations within the atoms. According to the Nernst theorem, at low temperature in liquid helium II the zero oscillations are the dominant component of the total energy. The energy of zero oscillations is always inherent in matter and does not diminish even when $T = 0$ K [26]. As we know [27], this serves as an obstacle to the hardening of liquid helium II as its temperature is reduced at low pressures. The energy of the zero oscillations cannot take part in the exchange of energy [2, p. 119].

When the liquid helium is cooled below 2.17 K, not only is there a reduction in the kinetic (thermal) energy of atomic interaction, but the level of statistical ordering and particle motion increases, i.e., the entropy of the liquid helium II diminishes [2] and the percentage content of the superfluid component increases, while the content of the normal component declines (Fig. 3).

Quantum theory thus confirmed (Figs. 2 and 3) that at temperatures below $T_\lambda \rightarrow 0$ K in liquid helium II there is no thermal (kinetic) energy, no latent heat of vapor formation, and there should be no regions of a vapor-liquid mixture. The researchers therefore observed no vapor bubbles within the volume of the liquid helium II.

The above-mentioned tables for the properties of helium II [11, 12, 17, 21], based on the classical shape of the thermodynamic surface and providing for the existence of a two-phase vapor-liquid region and latent heat in the superfluid liquid helium II at temperatures below the λ line, turn out to contradict the experiments of Kammerling-Onnes [7], as well as those of McLennan [5], Kapitsa [6], as well as the numerous experiments of other researchers who demonstrated that liquid helium II does not boil and does not exhibit any regions of two-phase vapor-liquid mixture. As regards the finite magnitude of the latent heat for the case in which $T = 0$ K, this also contradicts Nernst's third law of thermodynamics, as well as the quantum nature of liquid helium II and quantum theory.

The absence of a two-phase vapor-liquid region in helium II and the absence of its boiling [5-7] has not been given adequate attention until now, although even Keesom [28], Kammerling-Onnes [7], and Mendelson [1] took note of the fact that at the λ temperature both branches of the vapor and liquid saturation curves in the T-S diagram merge into a single curve. This means that the latent heat of phase transition and the actual phase transition of the first kind at this temperature totally disappear. Keesom [28] and Mendelson [1] note that the "effect (the determination of the latent heat of helium II) falls outside of the measurement accuracy." It is therefore not surprising that these various authors offer contradictory data regarding the parameters and properties of helium II in the two-phase vapor-liquid region.

All of this speaks to the necessity of refining our theoretical concepts with regard to helium II and forces us to coordinate these ideas with the thoroughly tested experimental studies and contemporary quantum theory with regard to helium.

If liquid helium II is a quantum liquid, then along all of the boundaries of the thermodynamic surface the change in its aggregate state must come about as a phase transition of the second kind. And indeed: at the boundary between liquid and solid the liquid ${}^4\text{He}$ II and solid ${}^4\text{He}$ I and at the liquid boundary between liquid ${}^4\text{He}$ II and liquid ${}^4\text{He}$ I the change in state is a phase transition of the second kind. But in this case the change in the aggregate state at the boundary between the liquid ${}^4\text{He}$ II and vapor ${}^4\text{He}$ must also be a phase transition of the second kind. Therefore, the liquid ${}^4\text{He}$ II does not boil in these experiments, i.e., indeed no vapor bubbles form within it as it is heated. This means that the T-S diagram must reflect this as well.

Analysis of the above-cited tabulated properties of helium II and the diagrams of the phase state [9-12, 16-20, 23-25], as well as the experiments on the "boiling" of helium II [5-7] and the experiments themselves we can propose a hypothetical T-S phase-state diagram of the helium (Fig. 4). These show the following phase regions: gas, normal liquid helium I, vapor, the two-phase vapor-liquid region, solid helium, and superfluid liquid helium II.

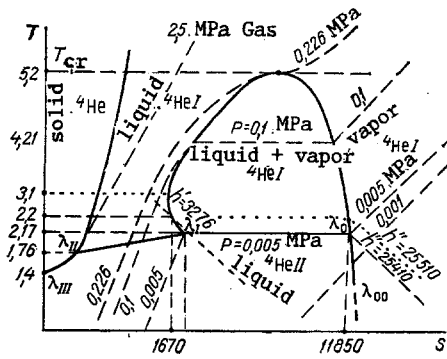


Fig. 4. T-S phase-state diagram for ${}^4\text{He I}$ - ${}^4\text{He II}$ with the vapor-liquid region. S, J/(kg·K).

TABLE 1. Thermophysical Properties of Helium at the ${}^4\text{He I}$ - ${}^4\text{He II}$

Temp., K	Enthalpy, J/kg		Entropy, J/(kg·K)		Heat capacity, J/(kg·K)		Thermal conductivity, 10^3 W/(m·K)		Viscosity, 10 Pa·sec		Surface tension, $\sigma \cdot 10^3$, N/m	Latent heat r , J/kg
	h'	h''	S'	S''	C_p'	C_p''	λ'	λ''	η'	η''		
2,2	3276	25510	1670	11850	3150	5630	1,48	0,453	36,1	5,46	0,306	22,23
2,17	25410	25410	11920	11920	5610	5610	0,447	0,447	5,38	5,38	—	—

We see from Fig. 4 that when $T = 2.17$ K the left-hand boundary equilibrium curve splits into two branches: $\lambda_I - \lambda_{II}$ and $\lambda_I - \lambda_0$; one of these ($\lambda_I - \lambda_{II}$) is deflected in the direction of the ordinate, separating the liquid into a region of normal liquid ${}^4\text{He I}$ and the superfluid liquid helium II, and at a temperature of $T_{\lambda_{II}} = 1.76$ K it combines with the hardening line; the other branch ($\lambda_I - \lambda_0$) links with the right-hand equilibrium curve at the point λ_0 . As a result, the region of the two-phase vapor-liquid mixture is characteristic only of helium I.

Mendeleev [33] referred to the critical temperature T_{cr} as the "temperature of absolute boiling." In analogy to the T_{cr} temperature, limiting the upper portion of the vapor-liquid region of the helium, we can refer to the uppermost temperature of absolute boiling, and we can refer to the temperature T_{λ_I} as the lowest boiling temperature for the helium. Only in the region between these temperatures and the isobars $P_{cr} = 2.26 - P_{\lambda_I} = 0.05$ bar can the helium boil and exhibit a two-phase vapor-liquid state.

We can see from Fig. 4 that when $T \approx 3.1$ K the latent heat of vapor formation for liquid He I assumes its maximum value [7, 8, 10, 24, 25], subsequent to which it diminishes, and with T_{λ_I} disappears entirely, while liquid helium I changes to the state of helium II.

Such a form for the T-S diagram of the phase state rather fully reflects the experimentally established properties of helium-4, clearly outlining the helium II phase region with quantum properties, and it eliminates the disagreement between the various researchers.

When the superfluid helium II is heated, for example, from a temperature of $T = 0.5$ K to T_λ and $P > 0.05$ bar, the incoming heat is expended on elevating the temperature of the liquid in the isobaric process, on the transformation of the superfluid component of the liquid into the normal component, due to the ordering of the mutually oriented atoms of the liquid, and to increasing their relative motion. As a result, we have an increase in the quantity of the normal component due to a reduction in the superfluid portion. The forming normal component in this case leads to an increase in the "superconductivity of heat" due to phonon convection within the volume of the liquid [26], rather than to the conduction of the liquid, as had earlier been assumed [26]. The superfluid liquid helium II does not boil in this case, i.e., it forms no vapor bubbles within the volume of the liquid. Therefore, at temperatures below those of the lambda line $\lambda_{II} - \lambda_I - \lambda_0$, the transformation of the superfluid component into a normal component proceeds as a phase transition of the second kind, without boiling, and without participation of latent heat.

Let us take note of two unique features, i.e., two various cases of phase transition of the second kind in liquid helium II: transition through the $\lambda_0 - \lambda_{00}$ line and through the $\lambda_I - \lambda_{II}$ line. In the first case, as a result of the phase transition vapor is formed, while in the second case we have liquid helium I. The reason for this is that in the first

case the transition occurs at very low pressures, that is, at pressures below $P < 0.05$ bar (0.5 KPa). Under the condition of such low pressure the direct transition of the liquid helium II into vapor through the λ_0 - λ_{00} line requires no reserve of kinetic (thermal) energy in the form of "latent heat of vapor formation." With such low pressures and low densities, when the atoms are situated at "great" mutual distances, the transition of the liquid helium II into vapor is accomplished easily and "spontaneously," without latent heat, i.e., as a phase transition of the second kind. In this case, the phase transition of the liquid into vapor necessarily occurs only at the free surface (on the mirror surface) of the liquid, where because of the absence of hydrodynamic pressure the energy conditions for the transition into vapor are better than within the depth of the liquid layer. Therefore, liquid helium II never boils in the depth of the liquid and the phase transition of the second kind does not take place during transition into vapor.

In the second case, through the λ_I - λ_{III} line, the phase transition takes place at elevated (0.005-0.226 MPa) or even higher pressures ($P > 0.226$ MPa). Here the incoming heat is also spent on raising the temperature and on disordering the state of the liquid particles, and on restructuring the superfluid liquid components into a normal component. This process of phase transition is also achieved without participation of latent heat, but unlike the transition at low temperatures along the λ_0 - λ_{00} line, here, as a result of the transition, we always have only normal liquid helium I rather than vapor. Through this we see the influence of the elevated pressure. At higher pressures (above 26 bar along the λ_{II} - λ_{III} line) the influence of the pressure leads even to the hardening of the liquid helium II, even without participation of the latent heat.

Let us draw our attention to the phase transition in the heating of liquid ^4He II at a pressure of 0.005-0.226 MPa. Here the parts of the λ_I - λ_{III} line of helium II are initially converted into normal liquid helium I, which subsequently, with later isobaric heating only at these pressures, reaches the left-hand boundary equilibrium curve and only such liquid helium I begins to boil, i.e., it forms a two-phase vapor-liquid region (mixture), and only in such a liquid helium is there a phase transition of the first kind with participation of the latent heat of vapor formation.

Let us also take note of the fact that only in helium I with such pressure and at temperatures of T_{λ_I} - T_{cr} can there exist binodals and spinodals, promoting metastable existence [29]. At temperatures below T_{λ_I} the spinodals degenerate and the metastable state in helium II therefore does not exist [29].

Since the transition of liquid helium II into liquid helium I and into solid helium along the λ_I - λ_{II} - λ_{III} lines is accomplished as a phase transition of the second kind, there arises the natural logical assumption that on the other edge, along the λ_0 - λ_{00} , the phase transition of the liquid helium II must also come about as a phase transition of the second kind without participation of the latent heat and without the formation of an intermediate region of a two-phase vapor-liquid mixture.

In the process of the continual heating of the liquid helium I with high pressure ($P > 0.226$ MPa), for example when $P = 1$ MPa, it will not boil, but its temperature will rise to $T_{cr} = 5.25$ K, subsequent to which the liquid changes to the state of a supercritical gas. In this case the transition undergoes no discontinuities in density, internal energy, etc. [27, 30-32]. The phase transition of the helium through the T_{cr} line has not been studied in detail and, probably, pertains to a transition of the second kind. The transition along this line has been recently assumed practical significance (for example, for tokamaks).

Experiments [5-7 and others] and the physical explanations given above, based on quantum theory, confirm and prove that in the T-S diagram the boundaries of the phase state for helium II must be represented in the manner shown in Fig. 4.

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