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SINGULARITIES IN THE EQUILIBRIUM DIAGRAM OF A He^3—He^4 *SOLUTION AT THE* λ*-POINT*

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The nature of the singularities arising at the λ-point on the equilibrium diagram of a He^3—He^4 solution is investigated.

THE phase transition He I—He II in a He^3—He^4 solution is the only existing case of a second-order phase transition in liquid solutions. It is therefore of interest to study in detail how the existence of the second-order phase transition influences the equilibrium diagrams of a solution. The form of the singularities occurring on the equilibrium diagrams at the point of their intersection with the λ-transition line must be determined by the singularity in the thermodynamic potential at the λ-transition.

The singularities arising on the equilibrium diagrams of a liquid-vapor system have been discussed by a number of authors [1-3] on the assumption that the singularity in the thermodynamic potential at the λ-point results in a finite discontinuity in its second derivatives. Our discussion will be applicable for the more general case of equilibrium of any two phases. We also consider the singularities arising on equilibrium diagrams in the case where the second derivatives of the thermodynamic potential have a logarithmic singularity.

1. If the singularity in the thermodynamic potential at the λ-point leads to a finite discontinuity of its second derivatives, then the thermodynamic potential of the solution will be of the following form near the λ-point:

$$\varphi_{II} = \varphi_I - [T - T_\lambda(x)]^2 \, \Delta C_p / 2T_\lambda, \qquad (1)$$

where φ_I and φ_{II} are the thermodynamic potentials per particle of the solution above and below the λ-point respectively, ΔC_p is the discontinuity in specific heat at the λ-point and $T_\lambda(x)$ is the temperature of the λ-point, which is concentration dependent.

The change in concentration with temperature along the equilibrium line of the phases is given by the well known equations:

$$\frac{dx'}{dT} = \frac{(\partial\varphi'/\partial T - \partial\varphi''/\partial T) + (x'' - x')\,\partial^2\varphi'/\partial x'\,\partial T}{(x' - x'')\,\partial^2\varphi'/\partial x'^2}, \qquad (2)$$

$$\frac{dx''}{dT} = \frac{(\partial\varphi''/\partial T - \partial\varphi'/\partial T) + (x' - x'')\,\partial^2\varphi''/dx''\,\partial T}{(x'' - x')\,\partial^2\varphi''/\partial x''^2}, \qquad (3)$$

where φ' is the thermodynamic potential per particle of the phase in which the second order phase transition takes place, x' is the concentration in this phase, φ'' and x'' are the thermodynamic potential and concentration in the second phase. It is easy to deduce from (2), bearing (1) in mind, that dx'/dT undergoes at the λ-point a jump, the value of which is

$$\Delta\left(\frac{dx'}{dT}\right) = -\Delta C_p \frac{1}{T_\lambda}\left(\frac{\partial T_\lambda}{\partial x'}\right)\left(1 - \frac{\partial T_\lambda}{\partial x'}\frac{dx'}{dT}\right) \Big/ \frac{\partial^2\varphi'}{\partial x'^2}\bigg|_\lambda, \qquad (4)$$

where the index λ on the derivatives means taking the average of the particular quantity below and above the λ-transition. As a consequence, there should be a break in the x'—T diagram in the given case and the λ-transition line should approach the phase equilibrium line at some angle (Fig. 1a). As can be seen from (3), the break should also be observed on the dx''/dT – T diagram.

2. The experimental data [4] show that the singularity in the thermodynamic potential of helium near the λ-point does not lead to a finite discontinuity of its second derivatives, but has a more complicated form:*

$$|T - T_\lambda(x)|^2 \ln|T - T_\lambda(x)| + \Delta\,|T - T_\lambda(x)|^2;$$
$$\Delta = 0 \text{ for } T - T_\lambda < 0, \qquad \Delta \neq 0 \text{ for } T - T_\lambda > 0. \qquad (5)$$

In this case, since the second derivatives of the thermodynamic potential tend to infinity at the λ-point, we obtain

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*We should point out that for a two-dimensional lattice (this is the only case for which the thermodynamic potential can be calculated exactly) the second derivatives of the thermodynamic potential at the λ-point also have a logarithmic singularity.[5]

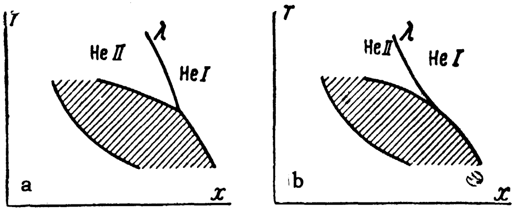

FIG. 1

$$\left(\frac{dT}{dx'}\right)_\lambda = -\lim_{T\to T_\lambda}\frac{\partial^2\varphi'/\partial x'^2}{\partial^2\varphi'/\partial x'\,\partial T} = \frac{\partial T_\lambda}{\partial x'}. \tag{6}$$

In the given case, therefore, the point at which the λ-transition line meets the phase equilibrium line is a point of tangency of these two curves, and no break should be observed on the first-order phase transition line (Fig. 1b).

Other equilibrium diagrams can also be considered in an analogous way, in particular the phase separation diagram of a He^3—He^4 solution.

The approach of the λ-transition line to the phase separation diagram of the solution is determined by the singularity in the thermodynamic potential at the λ-transition. If the singularity of the thermodynamic potential leads to a finite discontinuity of its second derivatives, then in such a case the λ-transition line approaches the separation curve at some angle, and a break in the separation curve will be observed at their point of intersection (Fig. 2a). If, however, the second derivatives of the thermodynamic potential have a logarithmic singularity for the He I—He II phase transition, then the point at which the λ-transition line meets the separation curve is a point of tangency of both these curves, and no break should be observed on the first order phase transition line (Fig. 2b).

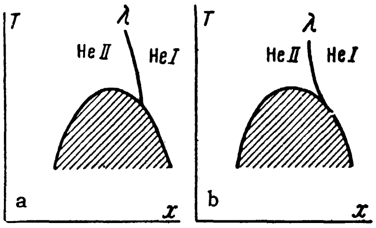

FIG. 2

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