

## Thermodynamic Considerations on a New Kind of Transition Points

Otto Halpern

Citation: *J. Chem. Phys.* **1**, 880 (1933); doi: 10.1063/1.1749258

View online: <http://dx.doi.org/10.1063/1.1749258>

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## Thermodynamic Considerations on a New Kind of Transition Points

OTTO HALPERN, *Physics Department, New York University, University Heights*

(Received October 14, 1933)

According to previous experiments liquid helium shows a "transition point" with discontinuity in the values of its specific heat and expansion coefficient. It has not been possible, however, to observe the coexistence of the two "phases." This fact is here explained on a thermodynamic

basis. Coexistence of two phases at a transition point can only be anticipated if the two phases exhibit a discontinuity in energy. An analogy is made with similar cases like that of the "transition point of superconductivity."

EXPERIMENTS<sup>1</sup> have recently led to the surprising result that liquid helium shows a "transition point" at extremely low temperatures. This transition point distinguishes itself from those with which we are usually acquainted by the fact that the two phases of helium exhibit no discontinuity as far as energy content or specific volume is concerned. They distinguish themselves from each other essentially by a jump in the values of the expansion coefficient  $(\partial v/\partial T)_p$  and of the specific heat  $c_p$ . It has been found experimentally that this transition point also depends upon the pressure so that we should speak more strictly of a transition curve in the  $p$ - $T$  diagram. Furthermore, relations have been found to exist between the values for the discontinuity of the specific heat and the expansion coefficient. These empirical relations have been derived theoretically as a consequence of the second law by Keesom<sup>1</sup> and Ehrenfest.<sup>2</sup> We reproduce briefly the line of reasoning developed by Ehrenfest, since it will help to disclose the main theme of this short note more easily.

Let us denote by  $Z$  the thermodynamic potential of each helium phase;  $Z$  is a function of  $p$  and  $T$ . Ehrenfest considers the two modifications of helium as two different phases which when in equilibrium are characterized by the condition  $Z_1 = Z_2$ . If we differentiate  $Z$  with respect to  $p$  and  $T$ , we obtain,  $\partial Z/\partial p = v$  and  $\partial Z/\partial T = -\rho$ . Since there is no discontinuity in volume or energy (and therefore entropy) the

first differential coefficients of the thermodynamic potential are continuous at the transition point. This does not hold true for the second derivatives.

$$\partial^2 Z/\partial T^2 = -\partial/\partial T = -c_p/T,$$

$$\partial^2 Z/\partial T \partial p = \partial v/\partial T,$$

$$\partial^2 Z/\partial p^2 = \partial v/\partial p.$$

Since as mentioned above the values for the entropies do not show a discontinuity at any point of the transition curve, we may take the total differential of both sides of the equation  $S_1 = S_2$  provided the differentials  $dp$  and  $dT$  are so chosen that we always remain on the transition curve. These special values of  $dp$  and  $dT$  shall be denoted by  $Dp$  and  $DT$ , following Ehrenfest.

We thus obtain

$$-(\partial v_1/\partial T)_p Dp + (c_{p1}/T) DT$$

$$= -(\partial v_2/\partial T)_p Dp + (c_{p2}/T) DT$$

or

$$Dp/DT = (c_{p1} - c_{p2})/T(\partial v_1/\partial T - \partial v_2/\partial T),$$

a relation which has been established experimentally by Keesom. Several other similar relations can be derived which need not be discussed at present.

The question which has been raised by Ehrenfest, and which we shall try to answer is the following: Though we have treated liquid helium on both sides of the transition point as two different phases in a thermodynamical sense, and though the results derived from the equilibrium condition for the two phases are correct and in agreement with experiment, the observa-

<sup>1</sup> For references cf. W. H. Keesom, *Proc. Amsterdam Acad. Sci., Sect. A* **36**, 147 (1933).

<sup>2</sup> Ehrenfest, *Proc. Amsterdam Acad. Sci., Sect. A* **36**, 153 (1933).

tion of the coexistence of the two phases at the transition point as is usually possible at all other transition points has not been accomplished. What is the nature of the distinction between the helium transition point and the commonly observed transition points?

This question is readily answered if, for the sake of lucidity, we take as the independent variables of our thermodynamic system energy and volume instead of temperature and pressure. It then becomes obvious that a coexistence of two phases is only stable, i.e., observable, if these two phases show a *discontinuity in energy* (the *first* differential coefficient of the thermodynamic potential) and *not only in specific heat* (the *second* differential coefficient of the thermodynamic potential).

This will be clear from the following considerations. Let us plot, for example, the melting curve in the energy-volume diagram. Each point in this curve represents a certain equilibrium state with a definite ratio between the respective amounts of molten and solid substance present. To an infinitesimal variation of the energy there corresponds an infinitesimal displacement of the point on this curve or an infinitesimal change in this ratio. Temperature does not change unless

we have reached the terminals of the curve at which points the whole substance is either solid or molten.

In the case of the helium transition point the situation is essentially different. Here all ratios of the composition of helium I and II correspond to *one* value of the energy. An infinitesimal change in energy would immediately eliminate one phase, and raise the temperature of the substance. This would hold true for every point in the transition curve, and not merely for the terminals, since there is no energy difference between the two phases. The coexistence of the two phases therefore never would be stable with respect to infinitesimal fluctuations in energy. This explains why the two phases could not be observed simultaneously.

It has already been pointed out by Ehrenfest that the discontinuity in the specific heat of helium shows much similarity to the discontinuity which is observable at the temperature at which a metal exhibits superconductivity. Here too it has not been possible to observe the coexistence of the two "metal phases." We can infer from the preceding line of reasoning that, at the transition point of superconductivity, no appreciable energy change occurs.