The affine spin connection is characterized by expressions $\Gamma_{\mu k}{}^\nu$. These are defined by

$$\sigma^{k\lambda\mu}{}_{,s}+\left\{{k \atop r\ s}\right\}\sigma^{r\lambda\mu}+\Gamma_{\dot{\rho}s}{}^{\lambda}\sigma^{k\dot{\rho}\mu}+\Gamma_{\sigma s}{}^{\mu}\sigma^{k\lambda\sigma}=0, \tag{B41}$$

where $\left\{{k \atop r\ s}\right\}$ are the Christoffel symbols of the metric (B1). For a free electron, i.e., in the absence of an electromagnetic field, we also have

$$\Gamma_{\alpha s}{}^{\alpha}=\Gamma_{\dot{\alpha}s}{}^{\dot{\alpha}}. \tag{B42}$$

The relations (B41), (B42) suffice to determine the $\Gamma_{\mu k}{}^\nu$ uniquely. The only non-vanishing components are found to be

$$\Gamma_{12}{}^{1}=-\Gamma_{22}{}^{2}=\tfrac{1}{2}i\cos\rho,$$

$$\Gamma_{23}{}^{1}=-\Gamma_{13}{}^{\dot{2}}=\tfrac{1}{2}\cos\rho\sin\theta+\tfrac{1}{2}i\cos\theta. \tag{B43}$$

Dirac's equations are

$$2^{\frac{1}{2}}\sigma^{k}{}_{\lambda\mu}(\Psi^{\lambda}{}_{,k}+\Gamma_{\dot{\rho}k}{}^{\lambda}\Psi^{\dot{\rho}})=i\beta_{E}X_{\mu}, \tag{B51}$$

$$2^{\frac{1}{2}}\sigma^{k\dot{\mu}\lambda}(X_{\lambda,k}-\Gamma_{\lambda k}{}^{\rho}X_{\rho})=i\beta_{E}\Psi^{\dot{\mu}}, \tag{B52}$$

where β_E is the constant given by (15.15). Explicitly, these equations assume the form

$$\sin\rho[i\Psi^{1}{}_{,\tau}-i\Psi^{2}{}_{,\rho}-i\cot\rho\Psi^{2}+\beta_{E}X_{1}]=\Psi^{2}{}_{,\theta}+\tfrac{1}{2}\cot\theta\Psi^{2}+(i/\sin\theta)\Psi^{1}{}_{,\varphi}, \tag{B61}$$

$$\sin\rho[i\Psi^{2}{}_{,\tau}-i\Psi^{1}{}_{,\rho}-i\cot\rho\Psi^{1}+\beta_{E}X_{2}]=-\Psi^{1}{}_{,\theta}-\tfrac{1}{2}\cot\theta\Psi^{1}-(i/\sin\theta)\Psi^{2}{}_{,\varphi}, \tag{B62}$$

$$\sin\rho[iX_{1,\tau}+iX_{2,\rho}+i\cot\rho X_{2}+\beta_{E}\Psi^{1}]=-X_{2,\theta}-\tfrac{1}{2}\cot\theta X_{2}-(i/\sin\theta)X_{1,\varphi}, \tag{B63}$$

$$\sin\rho[iX_{2,\tau}+iX_{1,\rho}+i\cot\rho X_{1}+\beta_{E}\Psi^{2}]=X_{1,\theta}+\tfrac{1}{2}\cot\theta X_{1}+(i/\sin\theta)X_{2,\varphi}. \tag{B64}$$

These equations immediately reduce to Schrödinger's form, i.e., Eqs. (15.11) to (15.14), under the 4-dimensional transformation

$$\omega_{1}=\sin\rho\sin^{\frac{1}{2}}\theta[\Psi^{1}+\Psi^{2}+X_{1}+X_{2}], \tag{B71}$$

$$\omega_{2}=\sin\rho\sin^{\frac{1}{2}}\theta[-\Psi^{1}+\Psi^{2}-X_{1}+X_{2}], \tag{B72}$$

$$\omega_{3}=\sin\rho\sin^{\frac{1}{2}}\theta[\Psi^{1}+\Psi^{2}-X_{1}-X_{2}], \tag{B73}$$

$$\omega_{2}=\sin\rho\sin^{\frac{1}{2}}\theta[\Psi^{1}-\Psi^{2}-X_{1}+X_{2}]. \tag{B74}$$

On Higher Order Transitions

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IN the June 1–15, 1946 number of *The Physical Review*, E. F. Lype discusses thermodynamic equilibria of higher order from the point of view of an expansion of the thermodynamic potentials in Taylor's series, and obtains results which, when applied to transitions of the second order, differ from the well-known results of Ehrenfest by a factor of two. Application of the results to the experiments of Keesom on helium and of Clusius and Perlick on methane is held to valid-

ate the method of thermodynamic potential and Taylor's series.

The difference between the results of Ehrenfest and of Lype is not to be attributed to any failure of mathematical rigor on the part of Ehrenfest, but to two different conceptions of the nature of the physical phenomena, which are essentially incompatible with each other. To bring out the difference it will be sufficient to restrict ourselves for the present to transitions

of the second order. The mathematics as used by Lype demands that the equilibrium of the second order occur at a single isolated point, p_0, τ_0, in the p-τ plane. At this point the first-order derivatives of the potentials of the two phases are equal to each other and there is a discontinuity in the second derivatives. The difference of thermodynamic potential of the two phases in the neighborhood may be expanded in the form

$$\Delta G = A(p-p_0)^2 + B(p-p_0)(\tau-\tau_0) + C(\tau-\tau_0)^2.$$

By setting $\Delta G = 0$, the equation of two lines is obtained on which the two phases are in equilibrium. The point now is that everywhere except at p_0, τ_0 the first derivatives of the difference of thermodynamic potentials no longer vanish, that is, the first derivative becomes discontinuous, so that the transition reverts to a normal first-order transition except at p_0, τ_0. That is, the mathematics demands a second-order transition where two first-order transition lines between the same two phases cross each other. The p-τ plane is divided into four quadrants, in one opposite pair of which the one phase is stable and in the other the other, the transition being everywhere, except at one point, of the first order. This is obviously a highly exceptional state of affairs and there is no experimental evidence for its existence. According to Ehrenfest's picture, on the other hand, there is a single transition line, on the one side of which the one phase is stable and on the other the other. On this line the first derivatives are always continuous so that the transition remains of the second order over the extent of the line. Mathematically, Ehrenfest's case may be considered a degenerate case of the more general case in which two intersecting first-order transition lines have become coincident. The thermodynamic potential surface of the one phase everywhere lies above that of the other, the two surfaces being tangent along the bottom of a trough. This degenerate case involves the vanishing of a certain discriminant, which may be written in the form:

$$\Delta C_p = -\tau[\Delta(\partial v/\partial \tau)_p^2 / \Delta(\partial v/\partial p)_\tau], \quad (I)$$

a condition which was obtained by Ehrenfest. The experiments of Keesom from which Lype

takes numerical values to the disadvantage of Ehrenfest indicate that the volumes of HeI and HeII are continuous along a line running at least from the vapor pressure to 25 atmospheres, and that on this line the first volume derivatives (second potential derivatives) are discontinuous. That is, the physical system is that to which Ehrenfest's assumptions apply. Under these conditions the relation (I) is a mathematical identity, which can be used to check the internal consistency of the experimental results. Keesom's results, as extrapolated by Lype, do not satisfy the relation, which indicates either unsatisfactory accuracy in the experiment or an improper extrapolation. In any event, considering the failure of the basic assumptions, any apparent numerical check can be dismissed as coincidental. Furthermore, experimentally there is no evidence for the second of the two transition lines. In his solution, Lype disregarded as "trivial" the solution $d\tau = 0$. This is not trivial, but represents the second transition line as demanded by the assumed equality of the compressibility of the two phases. The check presented by Lype based on the data of Clusius and Perlick did not yield so definite an inferiority of Ehrenfest's result, and involved the assumption of equal compressibility for the two phases, an assumption which loses much of its plausibility if Ehrenfest's relation is recognized as an identity.

It would appear therefore that although Ehrefest's method of treatment may be so presented as to be a degenerate case from the point of view of pure mathematics, nevertheless from the point of view of physics it is the generalized mathematical treatment that involves a highly specialized physical state of affairs, namely a higher order transition existing at only a single point, with the plane about this point separated by transition lines into sectors in which the equilibrium of the two phases alternates.

Since the whole question of higher order transitions has evoked considerable discussion without any notable agreement, I take this opportunity to add a couple of general comments. In the first place, in view of the degenerate nature of the mathematics, a simplified method of mathematical treatment is to be preferred to the general method by Taylor's expansion. All the thermodynamic relations can be deduced from a

simple geometrical relation involving discontinuities in derivatives. Given z a function of two variables x and y. In Fig. 1 z is shown as a function of x at two constant values of y differing by dy. z is continuous, but its derivatives are discontinuous, as shown. The subscript (1) will be used to denote z on one side of the discontinuity, and (2) on the other. Then the following relation is demanded by simple geometrical considerations along the line connecting the points of discontinuity:

$$\frac{dx}{dy} = -\left(\frac{\partial z_1}{\partial y} - \frac{\partial z_2}{\partial y}\right) \Big/ \left(\frac{\partial z_1}{\partial x} - \frac{\partial z_2}{\partial x}\right)$$

$$\equiv -\Delta\frac{\partial z}{\partial y} \Big/ \Delta\frac{\partial z}{\partial x}. \quad \text{(II)}$$

The proof is straightforward and elementary and need not be given here. The assumptions evidently correspond to the conditions assumed by Ehrenfest, namely the discontinuity is propagated along a line and is not confined to a point.

By specializing the variables, many thermodynamic relations may be obtained. A transition of the first kind is characterized by discontinuities in entropy and volume. A transition of the second kind has continuous entropy and volume but discontinuous derivatives. Identify x with p, y with τ, and z successively with S and v. This gives, for a transition line of the second order:

$$\frac{dp}{d\tau} = \frac{1}{\tau}\left[\Delta C_p \Big/ \Delta\left(\frac{\partial v}{\partial \tau}\right)_p\right],$$

and

$$\frac{dp}{d\tau} = -\Delta\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ \Delta\left(\frac{\partial v}{\partial p}\right)_\tau.$$
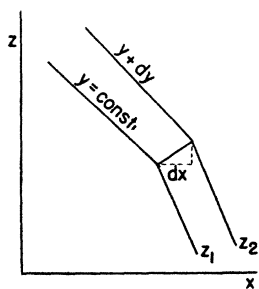

FIG. 1.

On equating these, Ehrenfest's identity is obtained.

Similarly, on a transition line of the first order, the thermodynamic potential G is continuous and its derivatives discontinuous. Identifying z with G gives:

$$\frac{dp}{d\tau} = -\Delta\left(\frac{\partial G}{\partial \tau}\right)_p \Big/ \Delta\left(\frac{\partial G}{\partial p}\right)_\tau = -\frac{\Delta S}{\Delta v},$$

which is Clapeyron's equation.

Transitions of higher order may be similarly treated. Thus for a transition of the third order $\partial v/\partial \tau$ may be taken as continuous, but its derivatives discontinuous. The slope of the third-order transition line is then given by:

$$\frac{dp}{d\tau} = -\Delta\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p \Big/ \Delta\frac{\partial^2 v}{\partial p\partial \tau}.$$

Finally, comment is required on the nature of the physical system to which Ehrenfest's analysis applies. We have seen that for second-order transitions the thermodynamic potential surfaces of the two modifications are tangent along a trough, one surface everywhere lying higher than the other except on the line of contact. If we now apply the universal condition which has not hitherto been mentioned, namely that that phase is stable with respect to the other whose thermodynamic potential is less, it would appear that everywhere over the entire p-τ plane the one phase is stable with respect to the second, except on a single line where the second phase becomes capable of stable coexistence. This state of affairs has led to the expressed opinion that phase equilibria of even orders are physically impossible. Nevertheless, experimentally second-order transitions appear to exist. The explanation lies in other considerations than those connected with the thermodynamic potentials alone. If for some reason the phase represented by one of the potential surfaces should become incapable of physical realization to one side of the transition line, then the other phase must exist on that side of the line, whether or not its potential surface is lower. A very similar situation arose in connection with Planck's discussion of the fundamental triangle on the E-v plane. The thermodynamic potential surface

of the three-phase system is mathematically a plane overlying the entire E-v plane, but it corresponds to a physically realizable system only within the fundamental triangle, because outside of this triangle the mathematics makes the physically impossible demand of a negative mass for one or the other of the three phases. An analogous sort of thing may arise in connection with transitions of even orders. An example might be the gold-copper alloys, which below a critical temperature crystallize in a regular arrangement, with the gold and copper atoms each occupying definite well-ordered positions in the lattice, while above the critical temperature, disorder begins to appear in the location of the gold and copper atoms. The simplest assumption, which seems to correspond to the facts, and which was obtained, for example, in the analysis of Bragg, is that the amount of disorder is a linear function of the excess of temperature above the critical temperature. If now we identify the one phase with the completely ordered arrangement and the other with that of partial disorder, we see that although it makes sense mathematically to talk about the potential of the disordered phase below the critical temperature, physically it is meaningless because below this temperature the fraction of the total mass existing in the disordered condition would be *negative*. Under these conditions the physical system will pass from the one thermodynamic potential surface to the other on crossing the transition line, in spite of the fact that the mathematical surface for the disordered phase lies everywhere lower. This sort of thing would seem in general to allow the possibility of transitions of even as well as of odd orders. Obviously odd ordered transition lines are compatible with the same sort of physical situation. If, for example, the amount of disorder varies as the square of the temperature excess above a critical

temperature we would have a transition line of the third order.

Finally, the possibility brought out by Lype's analysis that there may be singular points at which first-order transition lines cross and where the transition degenerates, is of interest, and an outlook should be kept for the experimental realization. I have observed what may be part of this phenomenon.[1] At atmospheric pressure NH_4Br has what is usually considered a second-order transition at approximately $-35°C$. The temperature of transition is depressed with increasing pressure. I have measured the transition at $-72°$, where it was so sharpened that it was indistinguishable from a normal first-order transition, running at a pressure of 1600 kg/cm^2. But, in these experiments no trace was found of any other transition line on the isothermals at $0°$ and $75°$ up to 12,000 kg/cm^2. NH_4Cl also has a second-order transition at approximately $-35°$. The temperature of this rises with increasing pressure, but the transition becomes more blurred instead of sharpening. At $75°$ a new small anomoly made its appearance in the neighborhood of 5000 kg/cm^2. It is tempting to interpret this as the appearance of the second transition line demanded by the mathematics, but the fact that the transition did not sharpen into an obviously first-order transition is unfavorable. On the other hand, the impossibility of rigorously establishing any sort of true mathematical discontinuity by direct experiment must be considered—any discontinuity assumed on the basis of experiment must remain to a certain extent a matter of convenience of interpretation. In any event, in the case of NH_4Br and NH_4Cl further examination, preferably including x-ray analysis of the crystal structure under pressure, would be necessary to settle the matter.

[1] P. W. Bridgman, Phys. Rev. **38**, 182 (1931).