

Thermodynamic Equilibria of Higher Order

E. F. LYPE

Institute of Gas Technology and Armour Research Foundation, Chicago, Illinois

(Received September 12, 1945)

A NUMBER of observations of the thermodynamic properties of unary systems* has brought about a discussion of the existence of equilibria of higher order in various papers and textbooks between 1933 and 1940. In the following paper, a formulation of the problem of these equilibria is derived from Epstein's suggestion to expand the Taylor series for the thermodynamic potential to terms of higher order. The thermodynamic relations following from this formulation are in agreement with experimental data even in cases where Ehrenfest's equation yields an error of 100 percent. In connection with the equilibrium of the fourth order, the problem of extending the vapor pressure curve beyond the critical point is analyzed, and it is shown that the points of inflexion of various thermodynamic functions in the overcritical region may be regarded as this extension, as was suggested by Eucken.

1. DEFINITION OF THE PHASE EQUILIBRIUM OF HIGHER ORDER

Two phases of the same substance are in

equilibrium with each other, if the thermodynamic potential $G = h - Ts$ has the same value in both phases. The equilibrium condition is then

$$G' = G'',$$

where the symbols (') and (") indicate the two phases.

The equilibrium curve is the locus of all points for which the above condition is satisfied. For a unary system where G depends only on the variables p and T , this curve is obtained in the following way: it is

$$G'(p, T) = G''(p, T). \quad (11)^1$$

For a point $(p + dp, T + dT)$ on the equilibrium curve, infinitely close to the former, is

$$G'(p + dp, T + dT) = G''(p + dp, T + dT). \quad (2)$$

In the neighborhood of (p, T) , either side of (2) can be expanded in a Taylor series as suggested by Epstein.² Therefore

$$\begin{aligned} G(p + dp, T + dT) = & G(p, T) + \frac{1}{1!} \left(\frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial p} dp \right) + \frac{1}{2!} \left(\frac{\partial^2 G}{\partial T^2} dT^2 + 2 \frac{\partial^2 G}{\partial T \partial p} dT dp + \frac{\partial^2 G}{\partial p^2} dp^2 \right) \\ & + \frac{1}{3!} \left(\frac{\partial^3 G}{\partial T^3} dT^3 + 3 \frac{\partial^3 G}{\partial T^2 \partial p} dT^2 dp + 3 \frac{\partial^3 G}{\partial T \partial p^2} dT dp^2 + \frac{\partial^3 G}{\partial p^3} dp^3 \right) \\ & + \frac{1}{4!} \left(\frac{\partial^4 G}{\partial T^4} dT^4 + 4 \frac{\partial^4 G}{\partial T^3 \partial p} dT^3 dp + 6 \frac{\partial^4 G}{\partial T^2 \partial p^2} dT^2 dp^2 + 4 \frac{\partial^4 G}{\partial T \partial p^3} dT dp^3 + \frac{\partial^4 G}{\partial p^4} dp^4 \right) + \dots \quad (3) \end{aligned}$$

This expansion can be discontinued after the first term containing derivatives of G which have a different value in each phase. All subsequent terms can be neglected as infinitely small of higher order.

It follows from the definition of a total differential that the terms in the series (3) represent

the total differentials of G . Therefore, (3) can be written

$$\begin{aligned} G(p + dp, T + dT) = & G(p, T) + dG \\ & + \frac{1}{2!} d^2 G + \frac{1}{3!} d^3 G + \frac{1}{4!} d^4 G + \dots \end{aligned}$$

* The term "unäres System" was introduced by W. Schottky in his book *Thermodynamik* (1929) to describe a system which consists of a single substance.

¹ Roman figures refer to the order of the equilibrium in which the respective equation occurs.

² P. S. Epstein, *Textbook of Thermodynamics* (1937), pp. 131-132.

while, simultaneously, two or more of the following conditions must be satisfied :

$$\frac{\partial^n G'}{\partial T^n} \neq \frac{\partial^n G''}{\partial T^n} \dots \dots \dots \frac{\partial^n G'}{\partial p^n} \neq \frac{\partial^n G''}{\partial p^n}. \quad (8n)$$

3. THE EQUILIBRIUM CURVE FOR EQUILIBRIA OF HIGHER ORDER

For an equilibrium of the first order, the equation of the equilibrium curve is obtained by evaluating (5I) according to (3) as

$$\frac{\partial G'}{\partial T} dT + \frac{\partial G'}{\partial p} dp = \frac{\partial G''}{\partial T} dT + \frac{\partial G''}{\partial p} dp$$

or

$$\frac{dp}{dT} = \frac{\partial G''/\partial T - \partial G'/\partial T}{\partial G''/\partial p - \partial G'/\partial p}.$$

Substituting the partial derivatives from (6I) yields

$$\frac{dp}{dT} = \frac{s'' - s'}{v'' - v'} \quad (9I)$$

which is the Clausius-Clapeyron equation. All quantities in (9I) refer to the state on the equilibrium curve. When *s* and *v* are known as functions of *p* and *T*, integration of (9I) gives the equation of the first-order equilibrium curve.

For equilibrium of the second order, taking *n* = 2 in Eq. (5n) gives

$$d^2 G'' = d^2 G' \quad (5II)$$

or

$$d^2(G'' - G') = 0.$$

This can be written

$$d\left(\frac{\partial(G'' - G')}{\partial T} dT + \frac{\partial(G'' - G')}{\partial p} dp\right) = 0.$$

Since, according to the rules of differentiation, for independent variables *T* and *p*

$$d^n(dT) = 0, \quad d^n(dp) = 0, \quad (10)$$

it follows

$$d\left(\frac{\partial(G'' - G')}{\partial T}\right) dT + d\left(\frac{\partial(G'' - G')}{\partial p}\right) dp = 0$$

or

$$\frac{dp}{dT} = -d\left(\frac{\partial(G'' - G')}{\partial T}\right) / d\left(\frac{\partial(G'' - G')}{\partial p}\right),$$

and, from (6I)

$$\frac{dp}{dT} = \frac{d(s'' - s')}{d(v'' - v')}.$$

If, on the equilibrium curve, *T* is considered as the independent variable, this can be written

$$\frac{dp}{dT} = \frac{ds''/dT - ds'/dT}{dv''/dT - dv'/dT}. \quad (9')$$

The total differential quotients in the numerator can be further transformed. The heat to be supplied during a reversible change of state along the equilibrium curve is

$$dQ = Tds = cdT. \quad (11I)$$

By means of this equation, *c* is defined as the specific heat for a change of state along the equilibrium curve. If the reversible change of state were carried out first at constant pressure from the initial temperature *T* to the temperature *T* + *dT*, and afterwards at constant temperature from the initial pressure *p* to the pressure *p* + *dp*, then the first law of thermodynamics gives for the heat to be supplied

$$dQ = dh - vdp, \\ = \frac{\partial h}{\partial T} dT + \left(\frac{\partial h}{\partial p} - v\right) dp.$$

But

$$\partial h/\partial T = c_p, \quad \partial h/\partial p = v - T(\partial v/\partial T)_p. \quad (12)$$

Therefore

$$dQ = c_p dT - T(\partial v/\partial T)_p dp. \quad (11II)$$

The heat *dQ* must be the same for any reversible change of state between the same points, independent of the path. Therefore (11I) and (11II) can be equated, whence

$$c = c_p - T\left(\frac{\partial v}{\partial T}\right)_p \frac{dp}{dT}. \quad (12I)$$

Also, from (11I)

$$ds/dT = c/T. \quad (13)$$

Substitution of (13) into (9') gives finally the equation of the second-order equilibrium curve:

$$\frac{dp}{dT} = \frac{c'' - c'}{T(dv''/dT - dv'/dT)}, \quad (9II)$$

where

$$\frac{dv}{dT} = \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial v}{\partial p}\right)_T \frac{dp}{dT}. \quad (14I)$$

The properties *c* and *dv/dT* in (9II) refer to a

change of state in the direction of the equilibrium curve. It follows from (12I) and (14I) that they have different values in both phases. This is caused by the fact that the contact between the surfaces $f'(G, p, T) = 0$ and $f''(G, p, T) = 0$ which represent the two phases has been treated as occurring in one point only, as suggested by Epstein.²

For equilibrium of the n th order, Eq. (5n) requires that

$$d^n(G'' - G') = 0$$

or

$$d^{n-1} \left(\frac{\partial(G'' - G')}{\partial T} dT + \frac{\partial(G'' - G')}{\partial p} dp \right) = 0.$$

In view of (10), this can be written

$$d^{n-1} \left(\frac{\partial(G'' - G')}{\partial T} \right) dT + d^{n-1} \left(\frac{\partial(G'' - G')}{\partial p} \right) dp = 0,$$

which yields

$$\frac{dp}{dT} = - \frac{\frac{d^{n-1}}{dT^{n-1}} \left(\frac{\partial(G'' - G')}{\partial T} \right)}{\frac{d^{n-1}}{dT^{n-1}} \left(\frac{\partial(G'' - G')}{\partial p} \right)}$$

and, from (6I) and (13),

$$\frac{dp}{dT} = \frac{d^{n-2}}{dT^{n-2}} \left(\frac{c''}{T} - \frac{c'}{T} \right) / \left(\frac{d^{n-1}v''}{dT^{n-1}} - \frac{d^{n-1}v'}{dT^{n-1}} \right). \quad (15)$$

The numerator can be evaluated by means of the mathematical relation

$$\frac{d^n}{dx^n} \left(\frac{y}{x} \right) = \frac{n!}{x} \sum_{r=0}^n \left(-\frac{1}{x} \right)^r \frac{y^{(n-r)}}{(n-r)!},$$

where $y^{(n-r)}$ is the differential quotient of y of the order $(n-r)$, and where $y^{(0)} = y$. When the term $r=0$ is taken out from under the summation sign, Eq. (15) can be written

$$\frac{dp}{dT} = \frac{[(c'')^{(n-2)} - (c')^{(n-2)}] + (n-2)! \sum_{r=1}^{n-2} \left(-\frac{1}{T} \right)^r \frac{(c'')^{(n-2-r)} - (c')^{(n-2-r)}}{(n-2-r)!}}{T \left(\frac{d^{n-1}v''}{dT^{n-1}} - \frac{d^{n-1}v'}{dT^{n-1}} \right)}. \quad (16)$$

The sum in the numerator is 0 as can be immediately seen from the calculation of the total differential quotients of c . From (12I), using (7), we obtain

$$\frac{dc}{dT} = \frac{\partial c_p}{\partial T} - \left(2T \frac{\partial^2 v}{\partial T^2} + \frac{\partial v}{\partial T} \right) \frac{dp}{dT} + T \frac{\partial^2 s}{\partial p^2} \left(\frac{dp}{dT} \right)^2 - T \frac{\partial v}{\partial T} \frac{d^2 p}{dT^2}, \quad (12II)$$

$$\begin{aligned} \frac{d^2 c}{dT^2} = & \frac{\partial^2 c_p}{\partial T^2} - \left(4 \frac{\partial^2 v}{\partial T^2} + 3T \frac{\partial^3 v}{\partial T^3} \right) \frac{dp}{dT} + \left(2 \frac{\partial^2 s}{\partial p^2} + 3 \frac{\partial^2 c_p}{\partial p^2} \right) \left(\frac{dp}{dT} \right)^2 + T \frac{\partial^3 s}{\partial p^3} \left(\frac{dp}{dT} \right)^3 \\ & - \left(3T \frac{\partial^2 v}{\partial T^2} + 2 \frac{\partial v}{\partial T} - 3T \frac{\partial^2 s}{\partial p^2} \frac{dp}{dT} \right) \frac{d^2 p}{dT^2} - T \frac{\partial v}{\partial T} \frac{d^3 p}{dT^3}, \quad (12III) \end{aligned}$$

and so forth. It is seen that the differential quotient of c of the order n comprises the partial derivatives of c_p up to the order n and the partial derivatives of s and v up to the order $(n+1)$. For equilibrium of the order n , the sum Σ comprises all differential quotients of c up to the order $(n-3)$, i.e., all partial derivatives of c_p up to the order $(n-3)$ and all partial derivatives of s and v up to the order $(n-2)$. Furthermore, Eqs. (1I) to (1n) must be satisfied. This means that all partial derivatives occurring in Σ have the same value

for both phases. Therefore,

$$\sum_{r=1}^{n-2} = 0$$

and the equilibrium curve for equilibrium of the n th order is given by the equation

$$\frac{dp}{dT} = \frac{\frac{d^{n-2}c''}{dT^{n-2}} - \frac{d^{n-2}c'}{dT^{n-2}}}{T \left(\frac{d^{n-1}v''}{dT^{n-1}} - \frac{d^{n-1}v'}{dT^{n-1}} \right)} \quad (9n)$$

All quantities in (9n) refer to a change of state in the direction of the equilibrium curve.

The differential quotients in the denominator are, with use of (7), obtained from (14I) as

$$\frac{d^2v}{dT^2} = \frac{\partial^2v}{\partial T^2} - 2 \frac{\partial^2s}{\partial p^2} \frac{dp}{dT} + \frac{\partial^2v}{\partial p^2} \left(\frac{dp}{dT} \right)^2 + \frac{\partial v}{\partial p} \frac{d^2p}{dT^2}, \quad (14II)$$

$$\begin{aligned} \frac{d^3v}{dT^3} = & \frac{\partial^3v}{\partial T^3} - \frac{3}{T} \frac{\partial^2c_p}{\partial p^2} \frac{dp}{dT} \\ & - 3 \frac{\partial^3s}{\partial p^3} \left(\frac{dp}{dT} \right)^2 + \frac{\partial^3v}{\partial p^3} \left(\frac{dp}{dT} \right)^3 \\ & - 3 \frac{\partial^2s}{\partial p^2} \frac{d^2p}{dT^2} + \frac{\partial v}{\partial p} \frac{d^3p}{dT^3} \\ & + 3 \frac{\partial^2v}{\partial p^2} \frac{dp}{dT} \frac{d^2p}{dT^2}, \quad (14III) \end{aligned}$$

and so forth. When the differences of the differential quotients in (9n) are calculated, then it follows from the equilibrium conditions (1III) to (1n) that all those terms in (12II), (12III), etc. and (14II), (14III), etc. which contain differential quotients of p of a higher order than the first cancel out.

4. DISCUSSION OF AVAILABLE EXPERIMENTAL RESULTS

a. Equilibrium of the Second Order

Observations of certain substances have shown a sudden change of at least two of the second derivatives of G , while both first derivatives remained constant. This would then indicate the existence of two phases which are with each other in equilibrium of the second order. For such an equilibrium state, Eq. (9II) must hold. If all quantities occurring in (9II) are known from experiments, this equation can be verified. This is possible for the transition between the two modifications of liquid helium and solid methane which have frequently been interpreted as equilibria of the second order.³⁻⁵ In both cases, the transition curve and the thermodynamic properties on this curve are known.

³ P. Ehrenfest, Leiden Commun. Supp. 75 b (1933).

⁴ W. H. Keesom, Leiden Commun. Supp. 80 b (1936).

⁵ K. Clusius and A. Perlick, Zeits. f. physik. Chemie B24, 313 (1934).

For second-order equilibrium, Eq. (5II) yields²

$$\begin{aligned} \left(\frac{\partial^2 G''}{\partial T^2} - \frac{\partial^2 G'}{\partial T^2} \right) dT^2 + 2 \left(\frac{\partial^2 G''}{\partial T \partial p} - \frac{\partial^2 G'}{\partial T \partial p} \right) dT dp \\ + \left(\frac{\partial^2 G''}{\partial p^2} - \frac{\partial^2 G'}{\partial p^2} \right) dp^2 = 0. \end{aligned}$$

Substituting the derivatives from (6II) gives

$$\begin{aligned} \left(\frac{c_p''}{T} - \frac{c_p'}{T} \right) dT^2 - 2 \left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T} \right) dT dp \\ - \left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p} \right) dp^2 = 0. \quad (17) \end{aligned}$$

This equation can be written in either one of the following two forms:

$$\begin{aligned} \left(\frac{c_p''}{T} - \frac{c_p'}{T} \right) \left(\frac{dT}{dp} \right)^2 - 2 \left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T} \right) \frac{dT}{dp} \\ - \left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p} \right) = 0, \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p} \right) \left(\frac{dp}{dT} \right)^2 + 2 \left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T} \right) \frac{dp}{dT} \\ - \left(\frac{c_p''}{T} - \frac{c_p'}{T} \right) = 0. \end{aligned}$$

Solving for dT/dp and dp/dT , respectively, gives

$$\frac{dT}{dp} = \frac{\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}}{\frac{c_p''}{T} - \frac{c_p'}{T}} \pm \left[\left(\frac{\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}}{\frac{c_p''}{T} - \frac{c_p'}{T}} \right)^2 + \frac{\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}}{\frac{c_p''}{T} - \frac{c_p'}{T}} \right]^{1/2}, \quad (18a)$$

$$\frac{dp}{dT} = - \frac{\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}}{\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}} \pm \left[\left(\frac{\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}}{\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}} \right)^2 + \frac{\frac{c_p''}{T} - \frac{c_p'}{T}}{\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}} \right]^{1/2}. \quad (18b)$$

Equation (18b) is also obtained when (12I) and (14I) are substituted in (9II), and when the resulting equation is solved for dp/dT .

Because of the double sign of the square root in Eqs. (18), there are two possible equilibrium curves for an equilibrium of the second order.

It is compatible with the existence of a second-order equilibrium that one of the three second-

order derivatives of G has identical values in both phases. Thus, according to (6II), any one of the following relations may exist:

$$\partial v''/\partial p = \partial v'/\partial p, \quad (19a)$$

$$c_p'' = c_p', \quad (19b)$$

$$\partial v''/\partial T = \partial v'/\partial T. \quad (19c)$$

If Eqs. (19) are introduced alternately in (17), the equilibrium equation becomes, if the trivial solutions $dT \equiv 0$ or $dp \equiv 0$ are excluded,

for case (19a)

$$\left(\frac{c_p''}{T} - \frac{c_p'}{T}\right)dT - 2\left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}\right)dp = 0, \quad (17a)$$

for case (19b)

$$\left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}\right)dp + 2\left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}\right)dT = 0, \quad (17b)$$

for case (19c)

$$\left(\frac{c_p''}{T} - \frac{c_p'}{T}\right)dT^2 - \left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}\right)dp^2 = 0. \quad (17c)$$

The slope of the equilibrium curves is then, for these three cases,

$$\frac{dp}{dT} = \frac{1}{2} \frac{c_p'' - c_p'}{T(\partial v''/\partial T - \partial v'/\partial T)}, \quad (20a)$$

$$\frac{dp}{dT} = -2 \frac{\partial v''/\partial T - \partial v'/\partial T}{\partial v''/\partial p - \partial v'/\partial p}, \quad (20b)$$

$$\frac{dp}{dT} = \pm \left(\frac{c_p''/T - c_p'/T}{\partial v''/\partial p - \partial v'/\partial p} \right)^{\frac{1}{2}}. \quad (20c)$$

It is seen from Eqs. (20) that, if conditions (19a) or (19b) hold, only one equilibrium curve will be observed, while two equilibrium curves are possible for case (19c).

There is still the possibility that any one of Eqs. (19) may be satisfied only asymptotically, i.e., that as we proceed on the equilibrium curve the values in the two phases for one of the quantities in (19) approach each other. Then, the slope of the equilibrium curve (18) must asymptotically approach the value given by (20). This can only occur if, in case (19a), the plus sign is used in (18a), and if, in case (19b), the minus sign is used in (18b). For case (19c), either one of the two signs in (18) is valid. Our present knowl-

edge of the equilibrium of the second order is still incomplete. So far, of the three conditions (19), only (19a) has been observed as an asymptotic condition. In this case, only one equilibrium curve will be found with values dT/dp corresponding to those obtained from (18a) for the plus sign. The discriminant of the quadratic form (17) is

$$D = -\left(\frac{c_p''}{T} - \frac{c_p'}{T}\right)\left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}\right) - \left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}\right)^2.$$

This discriminant will, in general, be different from zero. Epstein² has pointed out that the restriction $D \equiv 0$ leads to Ehrenfest's theory of the second-order equilibrium.³ In this case, the square roots in (18) vanish, and it is

$$\text{from (18a)} \quad \left(\frac{c_p''}{T} - \frac{c_p'}{T}\right)dT - \left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}\right)dp = 0,$$

$$\text{from (18b)} \quad \left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}\right)dT + \left(\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}\right)dp = 0.$$

In view of (7), these equations can be written

$$d(s'' - s') = 0 \quad \text{and} \quad d(v'' - v') = 0.$$

These are the conditions which, according to Ehrenfest, should be satisfied on the second-order equilibrium curve. They represent Ehrenfest's formulation of the equilibrium curve of the second order and would make indeterminate the Eq. (9II) which was derived from (5II). The latter is Epstein's formulation of the second-order equilibrium curve on which the present study is based.

Ehrenfest's postulate $D \equiv 0$ implies that the surfaces $f'(G, p, T) = 0$ and $f''(G, p, T) = 0$ have contact along a finite part of the equilibrium curve. The slope of this curve is, from (18a) with $D \equiv 0$,

$$\frac{dp}{dT} = \frac{c_p'' - c_p'}{T(\partial v''/\partial T - \partial v'/\partial T)}, \quad (21)$$

which is twice as large as the value from (20a) for condition (19a). Therefore, for an equilibrium where (19a) is valid, the experiment can decide in favor of one theory or the other.

Equations (18a) and (20a) will now be checked against experimental results.

A comprehensive description of the thermodynamic properties of liquid helium in the region of transition from HeI to HeII is given by

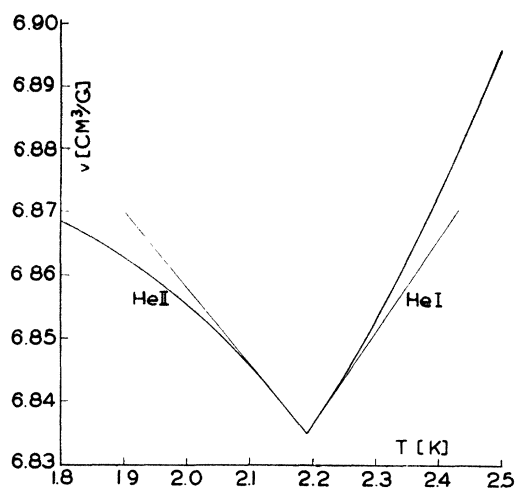


FIG. 1. Specific volume of liquid helium at saturation pressure, according to Kamerlingh Onnes and Boks.

Keesom.⁴ It can be seen from Keesom's Fig. 8 that the compressibilities of both phases become equal as the low pressure end of the transition curve is approached. For the lowest pressure, where both HeI and HeII are in equilibrium with saturated vapor, Eq. (19a) is satisfied. The transition curve is then given by (20a). Figure 1 of this paper shows the specific volume for liquid HeI and HeII in equilibrium with saturated vapor, according to experiments by Kamerlingh Onnes and Boks, as computed by Roberts.⁶ From this figure, the tangents in the transition point are

$$\begin{aligned} dv''/dT &= -0.1215 \text{ cm}^3/\text{g deg.}, \\ dv'/dT &= 0.1475 \text{ cm}^3/\text{g deg.} \end{aligned}$$

Since these quantities refer to a change of state along the vapor pressure curve, it is necessary to calculate the thermal expansion at constant pressure from the formula

$$(\partial v/\partial T)_p = [dv/dT]_{\text{sat}} - (\partial v/\partial p)_T [dp/dT]_{\text{sat}}. \quad (22)$$

The compressibility which, as already mentioned, is equal for both modifications is found from Keesom's Fig. 8 by a linear extrapolation of $(\partial/\partial p)(1/v')$ against $\log p$ as

$$(\partial v/\partial p)_T = -0.145 \times 10^{-3} \text{ cm}^5/\text{g}^2.$$

The quantity dp/dT is found from empirical

equations⁷ for the vapor pressure curve as follows:

$$\text{for HeII} \quad [dp/dT]_{\text{sat}} = 130.2 \text{ g/cm}^2 \text{ deg.},$$

$$\text{for HeI} \quad [dp/dT]_{\text{sat}} = 119.5 \text{ g/cm}^2 \text{ deg.}$$

Substituting these data in (22) gives

$$(\partial v''/\partial T)_p = -0.1404 \text{ cm}^3/\text{g deg.}$$

$$(\partial v'/\partial T)_p = 0.1302 \text{ cm}^3/\text{g deg.}$$

and

$$\partial v''/\partial T - \partial v'/\partial T = -0.2706 \text{ cm}^3/\text{g deg.}$$

Keesom's Fig. 11 gives, for both modifications in equilibrium with saturated vapor, values of c/R as function of temperature (not c directly). For the transition point is

$$c''/R = 5.84, \quad c'/R = 1.22.$$

These data would have to be converted to c_p according to (12I) and by using the above values for $(\partial v/\partial T)_p$ and $[dp/dT]_{\text{sat}}$. However, the effect of this conversion is negligible, so that the above values c'' and c' can be taken directly for c_p'' and c_p' , respectively. This gives

$$c_p'' = 2.902 \text{ cal./g deg.}, \quad c_p' = 0.606 \text{ cal./g deg.}$$

and

$$c_p'' - c_p' = 2.296 \text{ cal./g deg.} = 9.804 \times 10^4 \text{ cm/deg.}$$

The temperature of the transition point at saturation pressure is

$$T = 2.19^\circ \text{ K.}$$

From (20a) is now obtained

$$\begin{aligned} \frac{dp}{dT} &= -\frac{1}{2} \frac{9.804 \times 10^4}{2.19 \times 0.2706} = -8.27 \times 10^4 \text{ g/cm}^2 \text{ deg.} \\ &= -82.7 \text{ at./deg.} \end{aligned}$$

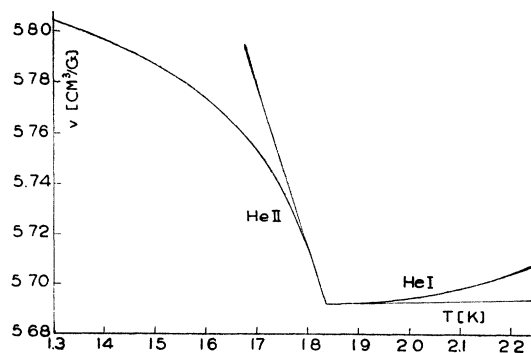


FIG. 2. Specific volume of liquid helium at 25 atmos. pressure, according to Keesom.

⁶ J. K. Roberts, *Heat and Thermodynamics* (1940), third edition, p. 328.

⁷ Landolt-Börnstein, *Phys.-Chem. Tab., Supp. II b*, p. 1291.

where 1 at.=1 kg/cm²=735.6 mm Hg. The observed value is, according to Keesom,

$$(dp/dT)_{obs} = -83.5 \text{ at./deg.}$$

The discrepancy is only 1 percent. Ehrenfest's Eq. (21) would give dp/dT twice as high as the observed value.

A rough check of the complete formula (18a) can be made for the He transition at 25 atmos. The specific gravity and the compressibility are given by Keesom for this pressure, but the specific heat is given for a pressure described as "about 25 atmos." Therefore, not too good an agreement between the data and Eq. (18a) may be expected.

From Keesom's Fig. 11

$$c_v''/R = 1.98, \quad c_v'/R = 0.84,$$

from which

$$c_v'' = 4.200 \times 10^4 \text{ cm/deg.},$$

$$c_v' = 1.782 \times 10^4 \text{ cm/deg.}$$

For HeI, the difference between c_v' and c_p' is negligible, such that c_v' can be taken for c_p' . For HeII, the difference is considerable, and correct evaluation of c_p'' is necessary. From Keesom's Fig. 8

$$\partial v''/\partial p = -0.3794 \times 10^{-4} \text{ cm}^5/\text{g}^2,$$

$$\partial v'/\partial p = -0.2508 \times 10^{-4} \text{ cm}^5/\text{g}^2,$$

$$\partial v''/\partial p - \partial v'/\partial p = -0.1286 \times 10^{-4} \text{ cm}^5/\text{g}^2.$$

Figure 2 of this paper shows the specific volume according to Keesom's Table I. From this figure, the tangents in the transition point are

$$\partial v''/\partial T = -0.6369 \text{ cm}^3/\text{g deg.},$$

$$\partial v'/\partial T = 0.0048 \text{ cm}^3/\text{g deg.},$$

$$\partial v''/\partial T - \partial v'/\partial T = -0.6417 \text{ cm}^3/\text{g deg.}$$

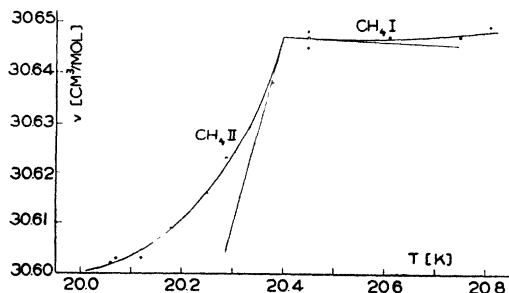


FIG. 3. Specific volume of solid methane, according to Heuse.

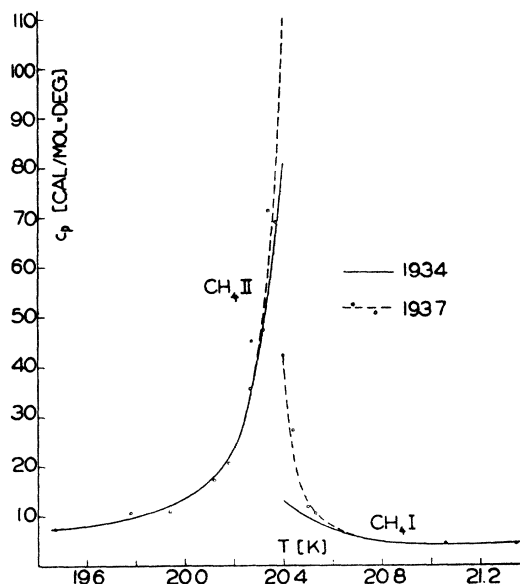


FIG. 4. Specific heat of solid methane. Solid line, according to Clusius and Perlick, 1934. Broken line, according to Frank and Clusius, 1937.

The temperature of transition at 25 atmos. is $T = 1.835^\circ\text{K}$.

For the specific heat at constant pressure follows

$$c_p' = 1.782 \times 10^4 \text{ cm/deg.},$$

$$c_p'' = c_v'' - T \frac{(\partial v''/\partial T)^2}{\partial v''/\partial p}$$

$$= 4.200 \times 10^4 + 1.835 \frac{0.6369^2}{0.3794} 10^4$$

$$= 6.162 \times 10^4 \text{ cm/deg.},$$

$$c_p'' - c_p' = 4.380 \times 10^4 \text{ cm/deg.}$$

In view of the asymptotic condition (19a), the observed equilibrium curve will correspond to the plus sign in (18a). Using the positive square root in (18a) yields

$$dT/dp = -10^{-4}(0.2688 - (0.07227 - 0.05388)^{\frac{1}{2}}) \\ = -0.1332 \times 10^{-4} \text{ cm}^2 \text{ deg./g}$$

or

$$dp/dT = -7.50 \times 10^4 \text{ g/cm}^2 \text{ deg.} = -75.0 \text{ at./deg.}$$

The observed value is, according to Keesom,

$$(dp/dT)_{obs} = -63.2 \text{ at./deg.}$$

while Ehrenfest's Eq. (21) would give dp/dT

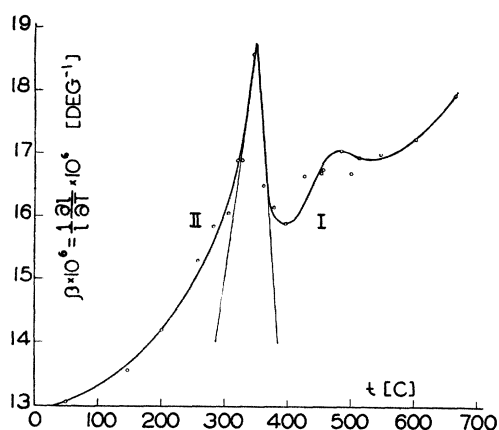


FIG. 5. Coefficient of linear expansion of nickel, according to Eucken and Dannöhl.

$= -37.2$ at./deg. which is an error of 41 percent. The value from (18a) is 19 percent too large, probably because of the fact, that the specific heats are not measured at exactly the same pressure as the other properties.

Clusius and Perlick⁵ have described the thermodynamic properties of solid methane in the region of the transition point at atmospheric pressure where the transition temperature is 20.4°K . Observations of the compressibility are not available, but it is reasonable to assume that, in the solid state, the difference in the compressibilities of both modifications is negligible; then, condition (19a) is satisfied, and the equilibrium Eq. (20a) can be applied. Figure 3 shows the molecular volume of both modifications in the neighborhood of this transition point based on the experimental data by Heuse⁸ as interpreted by Clusius and Perlick. From this figure, the tangents are

$$\begin{aligned} (\partial v''/\partial T)_p &= 0.376 \text{ cm}^3/\text{mole deg.}, \\ (\partial v'/\partial T)_p &= -0.005 \text{ cm}^3/\text{mole deg.}, \end{aligned}$$

and

$$\begin{aligned} \partial v''/\partial T - \partial v'/\partial T &= 0.381 \text{ cm}^3/\text{mole deg.} \\ &= 0.0238 \text{ cm}^3/\text{g deg.} \end{aligned}$$

The molecular heat as given by these authors is represented by the solid curve in Fig. 4. They found c_p' and c_p'' by linear extrapolation from the highest value observed to 20.4°K as

$$c_p'' = 81 \text{ cal./mole deg.}, \quad c_p' = 13 \text{ cal./mole deg.}$$

⁸ W. Heuse, *Zeits. f. physik. Chemie* **A147**, 270 (1930).

whence

$$c_p'' - c_p' = 68 \text{ cal./mole deg.} = 18.15 \times 10^4 \text{ cm/deg.}$$

Substituting these data in (20a) yields

$$\frac{dp}{dT} = \frac{1}{2} \frac{18.15 \times 10^4}{20.4 \times 0.0238} = 18.7 \times 10^4 \text{ g/cm}^2 \text{ deg.}$$

$$= 187 \text{ at./deg.}$$

This is identical with the observed value, as obtained by differentiation from the empirical equation of the transition curve given by Clusius and Perlick. Ehrenfest's Eq. (21) would again give dp/dT twice as large as the observed value.

More recently, Frank and Clusius⁹ reported on a new set of experimental data of the c_p 's obtained by Perlick. He observed $c_p' = 42.5$ cal./mole deg. In order to restore the agreement between (20a) and these new data, the value of $c_p'' - c_p'$ has to be preserved as 68 cal./mole deg. This would then require to extrapolate c_p'' (which was not observed) to as high a value as 110.5 cal./mole deg. This is done by the broken curve in Fig. 4. It can be seen that this extrapolation is compatible with the observed data. It may be noted, however, that these c_p data give for the entropy change from 20°K to 21°K a value which exceeds slightly the value derived theoretically by Frank and Clusius.

b. Equilibrium of the Third Order

Observations of certain transformations in metals have shown a discontinuity of two of the third derivatives of G , namely the quantities $\partial c_p/\partial T$ and $\partial^2 v/\partial T^2$, while all first and second derivatives of G remained unchanged. This would then indicate the existence of an equilibrium of the third order for these two modifications. One of these transformations is the transition from the ferromagnetic to the paramagnetic state in the Curie point. Another is the transition between two different crystal lattices, as observed for Cobalt at 450°C . That the Curie point represents a point of equilibrium of the third order has first been stated by Clusius and Perlick⁵ and Eucken.¹⁰ The equation of the

⁹ A. Frank and K. Clusius, *Zeits. f. physik. Chemie* **B36**, 291 (1937).

¹⁰ A. Eucken and W. Dannöhl, *Zeits. f. Elektrochemie* **40**, 814 (1934).

transition curve is obtained from (5n) by taking $n = 3$ as

$$\begin{aligned} &\left(\frac{\partial^3 G''}{\partial T^3} - \frac{\partial^3 G'}{\partial T^3}\right) dT^3 + 3\left(\frac{\partial^3 G''}{\partial T^2 \partial p} - \frac{\partial^3 G'}{\partial T^2 \partial p}\right) dT^2 dp \\ &+ 3\left(\frac{\partial^3 G''}{\partial T \partial p^2} - \frac{\partial^3 G'}{\partial T \partial p^2}\right) dT dp^2 \\ &+ \left(\frac{\partial^3 G''}{\partial p^3} - \frac{\partial^3 G'}{\partial p^3}\right) dp^3 = 0. \end{aligned}$$

Substituting the derivatives from (6III) gives

$$\begin{aligned} &-\frac{1}{T} \left(\frac{\partial c_p''}{\partial T} - \frac{\partial c_p'}{\partial T}\right) dT^3 + 3\left(\frac{\partial^2 v''}{\partial T^2} - \frac{\partial^2 v'}{\partial T^2}\right) dT^2 dp \\ &- 3\left(\frac{\partial^2 s''}{\partial p^2} - \frac{\partial^2 s'}{\partial p^2}\right) dT dp^2 \\ &+ \left(\frac{\partial^2 v''}{\partial p^2} - \frac{\partial^2 v'}{\partial p^2}\right) dp^3 = 0. \quad (23) \end{aligned}$$

Since this is a cubic equation, there can be three transition curves of the third order. For transitions in the solid state, the assumption may be made that the derivatives with respect to pressure are equal for both modifications in equilibrium with each other. Then, the following conditions are satisfied simultaneously:

$$\frac{\partial^2 v''}{\partial p^2} = \frac{\partial^2 v'}{\partial p^2}, \quad \frac{\partial^2 s''}{\partial p^2} = \frac{\partial^2 s'}{\partial p^2}. \quad (24)$$

If (24) is introduced in (23), only one equation for the third-order transition curve is obtained:

$$\frac{dp}{dT} = \frac{1}{3T} \frac{\partial c_p''/\partial T - \partial c_p'/\partial T}{\partial^2 v''/\partial T^2 - \partial^2 v'/\partial T^2}. \quad (25)$$

This equation can be used to calculate the variation of the transition temperature with pressure from the tangents of observed functions c_p and $\partial v/\partial T$. Reliable data on these properties are available in the neighborhood of the Curie point of nickel to which (25) shall now be applied. Eucken's and Dannöhl's¹⁰ data of the coefficient of linear expansion of Ni,

$$\beta = (1/l)(\partial l/\partial T)$$

are shown in Fig. 5, together with a curve representing the average data and the tangents to this curve in the Curie point. For a regularly crystallizing element, such as Ni, the coefficient

of cubic expansion

$$\alpha = (1/v)(\partial v/\partial T)$$

is three times as great: $\alpha = 3\beta$. Because of the extremely small variation of v , the quantity $\partial v/\partial T$ can be obtained by multiplying α by an average volume v_0 . The values of $\partial v/\partial T$ obtained in this manner with $v_0 = 0.114 \text{ cm}^3/\text{g}$ are given in Fig. 6 for a 100-deg. range, together with the same curve and tangents as in Fig. 5.

The specific heat of Ni has been measured by Ahrens.¹¹ His data for a 99.4 percent pure Ni are likewise given in Fig. 6. For the tangents is now obtained from Fig. 6:

$$\begin{aligned} \frac{\partial^2 v''}{\partial T^2} &= 2.51 \times 10^{-8} \text{ cm}^3/\text{g deg.}^2, \\ \frac{\partial^2 v'}{\partial T^2} &= -4.76 \times 10^{-8} \text{ cm}^3/\text{g deg.}^2, \\ \frac{\partial c_p''}{\partial T} &= 0.59 \times 10^{-3} \text{ cal./g deg.}^2, \\ \frac{\partial c_p'}{\partial T} &= -5.46 \times 10^{-3} \text{ cal./g deg.}^2, \end{aligned}$$

which yields

$$\begin{aligned} \frac{\partial^2 v''}{\partial T^2} - \frac{\partial^2 v'}{\partial T^2} &= 7.27 \times 10^{-8} \text{ cm}^3/\text{g deg.}^2, \\ \frac{\partial c_p''}{\partial T} - \frac{\partial c_p'}{\partial T} &= 6.05 \times 10^{-3} \text{ cal./g deg.}^2 \\ &= 258 \text{ cm/deg.}^2. \end{aligned}$$

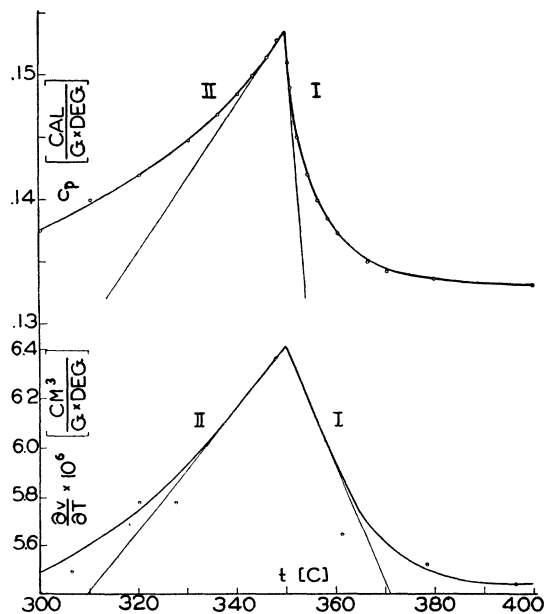


FIG. 6. Specific heat of nickel, according to Ahrens, and thermal expansion of nickel, calculated from the data in Fig. 5.

¹¹ E. Ahrens, Ann. d. Physik 21, 169 (1934).

The Curie temperature of Ni is $t=350^\circ\text{C}$ or $T=623^\circ\text{K}$. Substituting these data in (25) gives

$$\frac{dp}{dT} = \frac{1}{3} \frac{258 \times 10^8}{623 \times 7.27} = 1.9 \times 10^6 \text{ g/cm}^2 \text{ deg.} \\ = 1900 \text{ at./deg.}$$

A pressure of 1900 at. would raise the Curie temperature of Ni by 1 deg. C.

This result is in good agreement with $dp/dT = 2000$ at./deg. as obtained by Englert¹² from experiments under two pressures only, but this effect was already of the same order of magnitude as the accuracy of his experiments. It must also be kept in mind that the data of the thermal expansion in Fig. 5 scatter considerably, such that some margin was available in plotting the curve and its tangents. There is, furthermore, extreme disagreement in the experimental data obtained by various authors, ranging from 80 at./deg. to 20,000 at./deg. This discrepancy arises from differences both in the experimental methods and in the interpretation of the data obtained. Others did not observe any effect of pressure on the Curie temperature, not even in experiments¹³ which were supposed to show any displacement under 100,000 at./deg. Rutgers' and Wouthuysen's¹⁴ method of calculating equilibria of higher order by substituting a fictitious first-order equilibrium yields, when applied to the Curie point of Ni alloys,^{15,16} $dp/dT \approx 20,000$ at./deg. However, this method is not accurate; for the second-order equilibrium of liquid He in the saturation state, $dp/dT = -136$ is obtained,¹⁴ instead of -83.5 . It must be expected that the inaccuracy inherent in this method increases the higher the order of the equilibrium is.

c. Equilibrium of the Fourth Order

The equilibrium of the fourth order is of particular interest as a possible extension of the vapor pressure curve beyond the critical point, though its existence has not yet been observed. If the assumption is made that the vapor

pressure curve is not abruptly terminated at the critical point but that an extension of this curve for values p and T greater than the critical values can be defined, then a fundamental requirement of such an extension must be that, at the critical point, the extension and the vapor pressure curve have a common tangent. The tangent of the latter is given by (9I) which yields at the critical point, where condition (III) is satisfied, the indeterminate form 0/0. The actual value is obtained from de l'Hôpital's rule as

$$\lim_{T \rightarrow T_k} \frac{dp}{dT} = \lim_{T \rightarrow T_k} \frac{\frac{d}{dT}(s'' - s')}{\frac{d}{dT}(v'' - v')} = \frac{\frac{c''}{T} - \frac{c'}{T}}{\frac{dv''}{dT} - \frac{dv'}{dT}}$$

in view of (13). If the first lim operation still yields an indeterminate form, this procedure has to be repeated until this is no longer the case. If $n-1$ lim operations are necessary to determine the tangent at the critical point, it is obtained

$$\lim_{T \rightarrow T_k} \frac{dp}{dT} = \frac{\frac{d^{n-2}}{dT^{n-2}} \left(\frac{c''}{T} - \frac{c'}{T} \right)}{\frac{d^{n-1}}{dT^{n-1}} (v'' - v')}$$

The evaluation of this equation is given by (16). The sum in the numerator comprises the differences in vapor and liquid phase of the differential quotients of c from the order 0 to the order $n-3$. However, the vanishing of each of these differences is the reason why the preceding lim operations yielded indeterminate forms, and why these operations had to be continued $n-1$ times. Therefore, the entire sum is zero, and the tangent at the critical point is

$$\left[\frac{dp}{dT} \right]_k = \frac{d^{n-2}c''/dT^{n-2} - d^{n-2}c'/dT^{n-2}}{T(d^{n-1}v''/dT^{n-1} - d^{n-1}v'/dT^{n-1})} \quad (26)$$

It is now seen, that the $(n-1)$ st lim of the tangent of the vapor pressure curve is of the same form as the tangent of the equilibrium curve of the n th order, Eq. (9n). This leads to the following conclusion:

If the curve of n th order equilibrium as defined by (9n) extends from the critical point into a region of values p and T greater than the critical values, and if the differential quotients in (9n) can be represented by the same functions

¹² E. Englert, Zeits. f. Physik **97**, 94 (1935).

¹³ H. Ebert and A. Kussmann, Physik. Zeits. **39**, 598 (1938).

¹⁴ A. J. Rutgers and S. A. Wouthuysen, Physica **4**, 235, 515 (1937).

¹⁵ A. Michels, *et al.*, Physica **4**, 1007 (1937).

¹⁶ J. C. Slater, Phys. Rev. **58**, 54 (1940).

as the differential quotients in (26), and if these functions are continuous at the critical point, then the curve of n th order equilibrium has at the critical point the same slope as the vapor pressure curve. In this case, the extension of the vapor pressure curve beyond the critical point is represented by a curve of equilibrium of higher order.

A study of d^2p/dT^2 shows that the value of this quantity for the equilibrium curve of higher order is not the same as for the vapor pressure curve at the critical point. Therefore, the curvature has a discontinuity at the critical point, if the liquid-vapor equilibrium is extended beyond the critical point by an equilibrium of higher order.

The thermodynamic properties in the region above the critical point are well known for many vapors. Nowhere has a discontinuity of the second or third derivatives of G been observed. An equilibrium of the second- or third-order can, therefore not be the extension of the vapor pressure curve. The lowest order equilibrium representing such an extension would then be an equilibrium of the fourth order. The equilibrium curve is obtained from (9n) for $n=4$ as

$$\frac{dp}{dT} = \frac{d^2c''/dT^2 - d^2c'/dT^2}{T(d^3v''/dT^3 - d^3v'/dT^3)}. \quad (27)$$

Substituting (12III) and (14III) with consideration of (1III) and (1IV), and collecting equal derivatives of G , yields

$$\begin{aligned} & \left(\frac{\partial^2 c_p''}{\partial T^2} - \frac{\partial^2 c_p'}{\partial T^2} \right) - 4T \left(\frac{\partial^3 v''}{\partial T^3} - \frac{\partial^3 v'}{\partial T^3} \right) \frac{dp}{dT} \\ & + 6 \left(\frac{\partial^2 c_p''}{\partial p^2} - \frac{\partial^2 c_p'}{\partial p^2} \right) \left(\frac{dp}{dT} \right)^2 \\ & + 4T \left(\frac{\partial^3 s''}{\partial p^3} - \frac{\partial^3 s'}{\partial p^3} \right) \left(\frac{dp}{dT} \right)^3 \\ & - T \left(\frac{\partial^3 v''}{\partial p^3} - \frac{\partial^3 v'}{\partial p^3} \right) \left(\frac{dp}{dT} \right)^4 = 0. \quad (27I) \end{aligned}$$

Any curve which makes (27I) an identity is an equilibrium curve of the fourth order and as such an extension of the vapor pressure curve. As shown by (6IV), the fourth derivatives of G which would have to be different for the two phases in equilibrium correspond to the third derivatives of the directly observed properties h and v . There is little chance that the third

derivatives will ever be known with sufficient accuracy to discover whether there are states where two or more of them have discontinuities in exactly such a manner as would satisfy (27I). For this reason, the question whether the equilibrium of the fourth order is an extension of the vapor pressure curve will remain undecided.

There is, however, still another possibility of making (27I) an identity, not along its entire length, but at least in the immediate neighborhood of the critical point. The curves of those states or sets of states which accomplish this will still be extensions of the vapor pressure curve though they may no longer represent an equilibrium of the fourth order.

An experimental investigation of the thermodynamic properties in the region above the critical point shows the following characteristics very distinctly:

- (1) the $v(p)$ isothermals have a point of inflexion;
- (2) the $s(p)$ isothermals have a point of inflexion;
- (3) the $v(T)$ isobares have a point of inflexion;
- (4) the $h(T)$ isobares have a point of inflexion.

All these characteristics are also obtained from the van der Waals equation of state. Eucken¹⁷ has defined the extension of the vapor pressure curve as the curves by which any or all of the conditions 1 to 4 are satisfied. This can only be so if conditions 1 to 4 make Eq. (27I) an identity, at least near the critical point. This will now be examined.

The four conditions can be expressed as follows:

$$(\partial^2 v / \partial p^2)_T = 0, \quad (28I)$$

$$(\partial^2 s / \partial p^2)_T = 0; \quad (28II)$$

$$(\partial^2 v / \partial T^2)_p = 0, \quad (29I)$$

$$(\partial^2 h / \partial T^2)_p = 0. \quad (29II)$$

On account of (7) and (12), Eq. (29) can be written

$$(\partial c_p / \partial p)_T = 0, \quad (28III)$$

$$(\partial c_p / \partial T)_p = 0. \quad (28IV)$$

Applying (7) to (28II), the four conditions (28) can be interpreted as the minima of $\partial v / \partial p$ and the maxima of c_p . The latter ones are a particularly prominent characteristic for the region

¹⁷ A. Eucken, Physik. Zeits. **35**, 711 (1934).

under discussion.¹⁸ The loci of these extrema, i.e., the curves on which conditions (28) are satisfied can be regarded as transition curves between two different modifications of higher order and are obtained in the same way as (51) was derived from (11). On each of these four curves, one of the conditions (28) must hold at an arbitrary point (p, T) as well as at the infinitely close point $(p+dp, T+dT)$. A Taylor expansion discontinued after the second term yields the four equations

$$d(\partial^2 v / \partial p^2) = 0, \quad (30I)$$

$$d(\partial^2 s / \partial p^2) = 0, \quad (30II)$$

$$d(\partial c_p / \partial p) = 0, \quad (30III)$$

$$d(\partial c_p / \partial T) = 0, \quad (30IV)$$

where

$$d(\quad) = \frac{\partial(\quad)}{\partial T} dT + \frac{\partial(\quad)}{\partial p} dp.$$

When the differentiations in (30) are carried out it is, with the aid of (7),

$$\frac{\partial^3 v}{\partial p^3} \frac{dp}{dT} = \frac{\partial^3 s}{\partial p^3}, \quad (31I)$$

$$\frac{\partial^3 s}{\partial p^3} \frac{dp}{dT} = -\frac{1}{T} \frac{\partial^2 c_p}{\partial p^2}, \quad (31II)$$

$$\frac{\partial^2 c_p}{\partial p^2} \frac{dp}{dT} = T \frac{\partial^3 v}{\partial T^3} + \frac{\partial^2 v}{\partial T^2}, \quad (31III)$$

$$\left(T \frac{\partial^3 v}{\partial T^3} + \frac{\partial^2 v}{\partial T^2} \right) \frac{dp}{dT} = \frac{\partial^2 c_p}{\partial T^2}. \quad (31IV)$$

Equations (31) represent the curves on which conditions 1 to 4 are satisfied. Obviously, none of them alone could reduce (27I) to an identity, but all four equations combined could do this. Before substituting them in (27I), it must be examined whether the dp/dT is the same quantity in all four equations, i.e., whether the four curves represented by these equations coincide in the p, T plane. For this purpose, the Eqs. (28) may be expressed by Planck's *Characteristic Function*

$$\Phi(p, T) = -G/T = s - (h/T).$$

Differentiation yields

$$d\Phi = (h/T^2)dT - (v/T)dp,$$

¹⁸ J. H. Keenan and F. G. Keyes, *Thermodynamic Properties of Steam*, Fig. 7.

whence

$$h = T^2(\partial\Phi/\partial T), \quad v = -T(\partial\Phi/\partial p).$$

From the Eqs. (28) we now obtain, with the aid of (7),

$$\frac{\partial^3 \Phi}{\partial p^3} = 0, \quad (32I)$$

$$\frac{\partial^2 \Phi}{\partial p^2} + T \frac{\partial^3 \Phi}{\partial T \partial p^2} = 0, \quad (32II)$$

$$2 \frac{\partial^2 \Phi}{\partial T \partial p} + T \frac{\partial^3 \Phi}{\partial T^2 \partial p} = 0, \quad (32III)$$

$$2 \frac{\partial \Phi}{\partial T} + 4T \frac{\partial^2 \Phi}{\partial T^2} + T^2 \frac{\partial^3 \Phi}{\partial T^3} = 0. \quad (32IV)$$

It is apparent, that none of Eqs. (32) can be derived from any of the others. Therefore, all four conditions (28) are independent, and the points where they hold will not coincide but will be located on four different curves. They all originate in the critical point where all four conditions (28) are satisfied. Since this point is simultaneously a point of the equilibrium curve of the fourth order, the derivatives in (31) will have discontinuities there. If in the immediate neighborhood of the critical point these four curves approach each other, then the (dp/dT) 's in all four Eqs. (31) will be approximately equal. In this region, these four curves will also be infinitely close to the actual fourth-order equilibrium curve (27I) with its discontinuities of the five derivatives. Then, in this particular region, Eqs. (31) may be substituted for both phases in (27I). Substitution of (31I) in (27I) gives

$$\begin{aligned} & \left(\frac{\partial^2 c_p''}{\partial T^2} - \frac{\partial^2 c_p'}{\partial T^2} \right) - 4T \left(\frac{\partial^3 v''}{\partial T^3} - \frac{\partial^3 v'}{\partial T^3} \right) \frac{dp}{dT} \\ & + 6 \left(\frac{\partial^2 c_p''}{\partial p^2} - \frac{\partial^2 c_p'}{\partial p^2} \right) \left(\frac{dp}{dT} \right)^2 \\ & + 3T \left(\frac{\partial^3 s''}{\partial p^3} - \frac{\partial^3 s'}{\partial p^3} \right) \left(\frac{dp}{dT} \right)^3 = 0. \quad (27II) \end{aligned}$$

Substitution of (31II) in (27II) gives

$$\begin{aligned} & \left(\frac{\partial^2 c_p''}{\partial T^2} - \frac{\partial^2 c_p'}{\partial T^2} \right) - 4T \left(\frac{\partial^3 v''}{\partial T^3} - \frac{\partial^3 v'}{\partial T^3} \right) \frac{dp}{dT} \\ & + 3 \left(\frac{\partial^2 c_p''}{\partial p^2} - \frac{\partial^2 c_p'}{\partial p^2} \right) \left(\frac{dp}{dT} \right)^2 = 0. \quad (27III) \end{aligned}$$

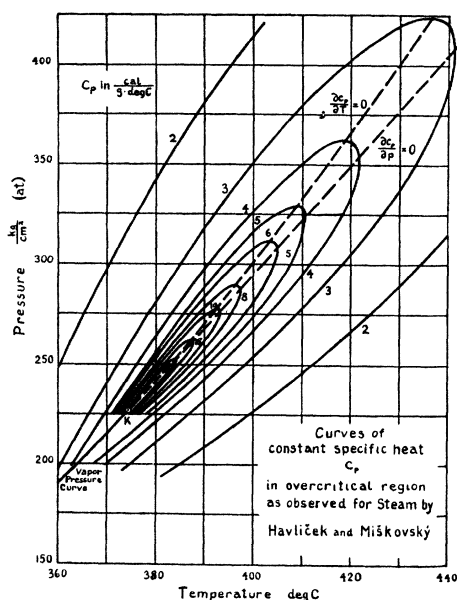


FIG. 7. Curves of constant specific heat of high pressure steam, according to Havlicek and Miskovsky.

Substitution of (31III) in (27III) gives, in view of (1IV)

$$\left(\frac{\partial^2 c_p''}{\partial T^2} - \frac{\partial^2 c_p'}{\partial T^2}\right) - T \left(\frac{\partial^3 v''}{\partial T^3} - \frac{\partial^3 v'}{\partial T^3}\right) \frac{dp}{dT} = 0. \quad (27IV)$$

Substitution of (31IV) in (27IV) gives, in view

of (1IV)

$$0 = 0.$$

Equations (31) reduce (27I) to an identity and, for this reason, the four curves where conditions (28) hold are apparent extensions of the vapor pressure curve.

This is shown in Fig. 7 for the conditions (28III) and (28IV). The specific heat of steam in the overcritical region has been measured with great accuracy by Havlicek and Miskovsky.¹⁹ Figure 7 is redrawn from these authors' Fig. 17 and shows the curves $c_p = \text{const.}$ in a p, T diagram. It is seen from the relation

$$\left(\frac{\partial p}{\partial T}\right)_{c_p} = - \frac{(\partial c_p / \partial T)_p}{(\partial c_p / \partial p)_T}$$

that (28III) corresponds to those points where the c_p curves have vertical tangents, while (28IV) corresponds to the points with horizontal tangents. The two curves $\partial c_p / \partial p = 0$ and $\partial c_p / \partial T = 0$ approach each other in the neighborhood of the critical point K , and both curves are extensions of the vapor pressure curve. There are not sufficient data available to show the same phenomenon for conditions (28I) and (28II).

¹⁹ J. Havlicek and L. Miskovsky, *Helv. phys. acta* **9**, 161 (1936).