ON THE CRITICAL STATE OF A ONE-COMPONENT SYSTEM

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It does not seem to be generally known that Gibbs, in his memoir on the energy surface,¹ has given in outline a very elegant theory of the critical state of a one-component system and of the continuity of the liquid and gaseous states. In particular, he has deduced four pairs of conditions which are satisfied at the critical point. One of these pairs of conditions when interpreted geometrically shows that the critical isotherm has a point of inflexion at the critical point. This theorem had previously been given by van der Waals² as a consequence of the equation of state to which he had been led by molecular considerations.

The conditions given by Gibbs in this first memoir do not readily lend themselves to further developments. But in the great memoir, published a few years later, Gibbs gives a general discussion of the critical state of a two-phase system from which he deduces the general conditions which must be satisfied by a critical phase.³ These conditions lend themselves more readily to analytical treatment than those first given.

In the present article we give a demonstration of the conditions which are satisfied by a one-component system in a critical state, and from them we deduce the most important of the theorems relating to the critical state. In particular, it will be found that most of the theorems which Duhem, in his very complete discussion of the critical state,⁴ has found it necessary

¹ A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. Transactions of the Connecticut Academy of Arts and Sciences, 2, (2) 382 (1873).

² Over de Continuïteit van den Gas-en Vloeistofoestand, p. 84. Leiden (1873).

³ On the Equilibrium of Heterogeneous Substances, p. 191.

⁴ Traité élémentaire de Mécanique chimique, 2, 147-157 (1898).

to assume as hypotheses, are consequences of the fundamental assumptions of Gibbs.

The assumption which lies at the basis of Gibbs' discussion is that, for a given substance, there exists a one-valued analytic function ϵ of the two variables η and v such that if η and v denote the entropy and the volume of the unit of mass of a homogeneous phase of the substance in equilibrium, ϵ is equal to the energy of the unit of mass of the homogeneous phase. This hypothesis is one form, and perhaps the simplest, of the so-called principle of continuity. If we measure η , v and ϵ along three rectangular axes in space, the surface determined by the simultaneous values of η , v and ϵ is Gibbs' energy surface.

From the definition of the function ϵ , it follows that, in passing from one point of the energy surface to an adjacent point on the surface, we have

$$d\epsilon = \frac{\partial \epsilon}{\partial \eta} d\eta + \frac{\partial \epsilon}{\partial v} dv. \quad (1)$$

If we compare this equation with the thermodynamic equation which applies to an infinitely small reversible change, viz. :

$$d\epsilon = Td\eta - \Pi dv, \quad (2)$$

in which T and Π denote the temperature and the pressure, it follows that when a homogeneous phase is in equilibrium

$$\begin{aligned} T &= \frac{\partial \epsilon}{\partial \eta}, \\ -\Pi &= \frac{\partial \epsilon}{\partial v}. \end{aligned} \quad (3)$$

The condition that the equilibrium be stable requires that, in any virtual change from a state of a stable equilibrium, we should have

$$\delta\epsilon > T\delta\eta - \Pi\delta v, \quad (4)$$

in which the variations are to be construed strictly. On the other hand, the definition of the function ϵ requires that, in passing from one point of the energy surface to an adjacent point of the surface, we should have

$$\delta\epsilon = \frac{\partial\epsilon}{\partial\eta}\delta\eta + \frac{\partial\epsilon}{\partial v}\delta v + \frac{1}{2} \left\{ \frac{\partial^2\epsilon}{\partial\eta^2}\delta\eta^2 + 2\frac{\partial^2\epsilon}{\partial\eta\partial v}\delta\eta\delta v + \frac{\partial^2\epsilon}{\partial v^2}\delta v^2 \right\} + \dots \quad (5)$$

From 3, 4 and 5 it follows without difficulty that when a homogeneous phase is in stable equilibrium, the quantity

$$\frac{\partial^2\epsilon}{\partial\eta^2}\delta\eta^2 + 2\frac{\partial^2\epsilon}{\partial\eta\partial v}\delta\eta\delta v + \frac{\partial^2\epsilon}{\partial v^2}\delta v^2$$

is positive for all values of $\delta\eta$ and δv . The well-known conditions that this be so, are that

$$\begin{vmatrix} \frac{\partial^2\epsilon}{\partial\eta^2} & \frac{\partial^2\epsilon}{\partial\eta\partial v} \\ \frac{\partial^2\epsilon}{\partial\eta\partial v} & \frac{\partial^2\epsilon}{\partial v^2} \end{vmatrix} > 0, \quad (6)$$

$$\frac{\partial^2\epsilon}{\partial\eta^2} > 0. \quad (7)$$

As a consequence of 6 and 7 we obtain without difficulty

$$\frac{\partial^2\epsilon}{\partial v^2} > 0. \quad (8)$$

Equations 3 may be called the conditions of equilibrium while inequalities 6, 7, 8 may be called the conditions of stability. If we suppose the ϵ -axis to be drawn upward, conditions 6 and 7 may be expressed geometrically by saying that at a point of the energy surface which corresponds to a homogeneous phase in stable equilibrium the surface is convex in every direction and this convexity is turned downward.

Let us consider next the equilibrium of a system of two phases formed from a single component. To each phase in equilibrium there corresponds a point of the energy surface whose coordinates are respectively the specific energy, the specific entropy and the specific volume of the phase. If we denote quantities referring to these two points by the subscripts 1 and 2 respectively, it can be shown that when the system of two phases is in equilibrium, the following conditions are satisfied :

$$\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 = \left(\frac{\partial \epsilon}{\partial \eta}\right)_2, \quad (9)$$

$$\left(\frac{\partial \epsilon}{\partial v}\right)_1 = \left(\frac{\partial \epsilon}{\partial v}\right)_2, \quad (10)$$

$$\epsilon_1 - \eta_1 \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 - v_1 \left(\frac{\partial \epsilon}{\partial v}\right)_1 = \epsilon_2 - \eta_2 \left(\frac{\partial \epsilon}{\partial \eta}\right)_2 - v_2 \left(\frac{\partial \epsilon}{\partial v}\right)_2. \quad (11)$$

These conditions may be expressed geometrically by saying that the tangent planes at the points 1 and 2 of the energy surface coincide. To show this we observe that the equation of the tangent plane at the point 1 can be obtained by writing the subscript 1 after each of the quantities in equation 1 and then replacing $d\epsilon_1$, $d\eta_1$, dv_1 by $\epsilon - \epsilon_1$, $\eta - \eta_1$, $v - v_1$. The equation of the tangent plane at the point 1 is accordingly

$$\epsilon - \epsilon_1 = \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 (\eta - \eta_1) + \left(\frac{\partial \epsilon}{\partial v}\right)_1 (v - v_1) \quad (12)$$

or

$$\epsilon - \eta \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 - v \left(\frac{\partial \epsilon}{\partial v}\right)_1 = \epsilon_1 - \eta_1 \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 - v_1 \left(\frac{\partial \epsilon}{\partial v}\right)_1. \quad (13)$$

From equations 9, 10, 11 and 13 it follows at once that the tangent planes at the points 1 and 2 coincide.

If we denote by ϵ , η and v the specific energy, the specific entropy and the specific volume of the system, by M_1 and M_2 the masses of the two phases and by M the mass of the system, we have the following relations

$$M = M_1 + M_2,$$

$$M\epsilon = M_1\epsilon_1 + M_2\epsilon_2,$$

$$M\eta = M_1\eta_1 + M_2\eta_2,$$

$$Mv = M_1v_1 + M_2v_2,$$

from which we get

$$\epsilon = \frac{M_1\epsilon_1 + M_2\epsilon_2}{M_1 + M_2},$$

$$\eta = \frac{M_1\eta_1 + M_2\eta_2}{M_1 + M_2},$$

$$v = \frac{M_1v_1 + M_2v_2}{M_1 + M_2}.$$

From these equations it follows at once that the point which represents the specific energy, entropy and volume of the system of two phases lies on the straight line which joins the points 1 and 2 and divides this line into two segments which are to each other inversely as the masses of the two phases. From this it follows further that if the two-phase system is in equilibrium at a given temperature and under a given pressure, it admits of a continuous series of states of equilibrium at that temperature and under that pressure; throughout this series of states of equilibrium the specific entropy and the specific volume of each phase remains unchanged, while the masses of the phases, and the specific energy, entropy and volume of the system change.

Let us suppose that the system undergoes a reversible change such that the representative point moves from the point 1 to the point 2 along the straight line joining them. Throughout this change the temperature and the pressure remain constant; the thermodynamic equation 2 accordingly gives us

$$\epsilon_2 - \epsilon_1 = T(\eta_2 - \eta_1) - \Pi(v_2 - v_1). \quad (14)$$

Instead of moving from the point 1 to the point 2 along the straight line joining them let us move from one point to the other along some curve of the energy surface. Then, by equation 1 we have

$$\epsilon_2 - \epsilon_1 = \int_1^2 \left(\frac{\partial \epsilon}{\partial \eta} d\eta + \frac{\partial \epsilon}{\partial v} dv \right). \quad (15)$$

If, in particular, we move along a curve on the energy surface such that constantly

$$\frac{\partial \epsilon}{\partial \eta} = \left(\frac{\partial \epsilon}{\partial \eta} \right)_1 = \left(\frac{\partial \epsilon}{\partial \eta} \right)_2 = T, \quad (16)$$

(such a curve is called an isothermal curve), equation 15 becomes

$$\epsilon_2 - \epsilon_1 = T(\eta_2 - \eta_1) + \int_1^2 \frac{\partial \epsilon}{\partial v} dv. \quad (17)$$

If, on the other hand, we move along a curve on the energy surface such that constantly

$$\frac{\partial \epsilon}{\partial v} = \left(\frac{\partial \epsilon}{\partial v} \right)_1 = \left(\frac{\partial \epsilon}{\partial v} \right)_2 = -\Pi, \quad (18)$$

(such a curve is called an isopiestic curve), equation 15 becomes

$$\epsilon_2 - \epsilon_1 = \int_1^2 \frac{\partial \epsilon}{\partial \eta} d\eta - \Pi(v_2 - v_1). \quad (19)$$

Comparing equations 14, 17 and 19, we obtain the following equations

$$\Pi(v_2 - v_1) = - \int_1^2 \frac{\partial \epsilon}{\partial v} dv, \quad (20)$$

$$T(\eta_2 - \eta_1) = \int_1^2 \frac{\partial \epsilon}{\partial \eta} d\eta. \quad (21)$$

Equations 20 and 21 admit of a simple geometrical interpretation. Let us take in a plane a pair of rectangular axes along which we shall measure the specific volume and the pressure of a one-component system. If the system is kept at the constant temperature T the representative point in the pressure-volume plane describes a curve which may be called the actual isotherm corresponding to the temperature T . If, on the other hand, we construct in the same plane the curve whose equation is obtained by eliminating η between the equations

$$-\Pi = \frac{\partial \epsilon}{\partial v},$$

$$T = \frac{\partial \epsilon}{\partial \eta},$$

in which T is supposed to be constant, we obtain a curve which may be called the theoretical isotherm corresponding to the temperature T . Equation 20 then gives us Maxwell's theorem:¹ If we agree that areas lying on opposite sides of a curve shall be given opposite signs, then the area included between the actual isotherm and the theoretical isotherm is equal to zero. Equation 21 yields in like manner the following theorem analogous to Maxwell's: The area included between the actual isopiestic and the theoretical isopiestic is equal to zero.

¹ Maxwell. *Nature*, 11, 358 (1875). Clausius. *Wied. Ann.* 9, 337 (1880). Planck. *Gleichgewichtszustände isotroper Körper*, p. 39 (1880).

Let us now return to the consideration of the conditions of equilibrium 9, 10 and 11. If we remember that ϵ_1 is a function of η_1 and v_1 and that ϵ_2 is a function of η_2 and v_2 , it follows that equations 9, 10 and 11 furnish three relations between the four quantities η_1, v_1, η_2, v_2 ; one of the four being chosen arbitrarily the others are accordingly determinate. Thus the point 1 must lie on a certain curve of the energy surface and the point 2 must lie on a certain other curve of the surface; moreover to each point of either of these curves there corresponds one and only one point of the other. These two curves together constitute the so-called connodal curve, the locus of the points of contact of a doubly tangent plane.

Since the temperature and the pressure of the two-phase system in equilibrium are determined by the position of the tangent plane at the points 1 and 2, it follows that for a two-phase system in equilibrium the temperature and pressure cannot both be chosen arbitrarily; they are functions one of the other. We can go further and determine the relation that exists between the simultaneous increments in the temperature and equilibrium pressure. For this purpose let us consider equations 9, 10 and 11. As we pass from a pair of corresponding points 1 and 2 to an adjacent pair, the following relations, obtained by differentiating equations 9, 10 and 11, must hold :

$$d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 = d\left(\frac{\partial \epsilon}{\partial \eta}\right)_2, \quad (22)$$

$$d\left(\frac{\partial \epsilon}{\partial v}\right)_1 = d\left(\frac{\partial \epsilon}{\partial v}\right)_2, \quad (23)$$

$$\begin{aligned} d\epsilon_1 - \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 d\eta_1 - \left(\frac{\partial \epsilon}{\partial v}\right)_1 dv_1 - \eta_1 d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 - v_1 d\left(\frac{\partial \epsilon}{\partial v}\right)_1 \\ = d\epsilon_2 - \left(\frac{\partial \epsilon}{\partial \eta}\right)_2 d\eta_2 - \left(\frac{\partial \epsilon}{\partial v}\right)_2 dv_2 - \eta_2 d\left(\frac{\partial \epsilon}{\partial \eta}\right)_2 - v_2 d\left(\frac{\partial \epsilon}{\partial v}\right)_2. \end{aligned} \quad (24)$$

If we make use of equations 1, 22 and 23, equation 24 reduces to

$$(\eta_2 - \eta_1)d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 + (v_2 - v_1)d\left(\frac{\partial \epsilon}{\partial v}\right)_1 = 0, \quad (25)$$

or

$$\frac{\eta_2 - \eta_1}{v_2 - v_1} = - \frac{d\left(\frac{\partial \epsilon}{\partial v}\right)_1}{d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1} = - \frac{d\left(\frac{\partial \epsilon}{\partial v}\right)_2}{d\left(\frac{\partial \epsilon}{\partial \eta}\right)_2}; \quad (26)$$

and if we remember that when a homogeneous phase is in equilibrium equations 3 are satisfied, we obtain Clapeyron's equation

$$\frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{d\Pi}{dT}. \quad (27)$$

The straight lines which join pairs of corresponding points of the connodal curve form a ruled surface, the various points of which represent the specific energy, entropy and volume of the various states of equilibrium of the two-phase system. We shall show that this ruled surface is a developable surface and that it is the envelope of the doubly tangent plane. To show this we observe that the equation of the tangent plane at the point 1 can be written in either of the forms

$$\epsilon - \epsilon_1 = \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 (\eta - \eta_1) + \left(\frac{\partial \epsilon}{\partial v}\right)_1 (v - v_1) \quad (28)$$

or

$$\epsilon - \eta \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 - v \left(\frac{\partial \epsilon}{\partial v}\right)_1 = \epsilon_1 - \eta_1 \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 - v_1 \left(\frac{\partial \epsilon}{\partial v}\right)_1. \quad (29)$$

In virtue of conditions 9, 10, and 11 this tangent plane is also tangent to the surface at the point 2. Moreover, in virtue of the same conditions, the coefficients in equation 29 are, as we have already shown, functions of a single arbitrary parameter. Consequently, the doubly tangent plane, in its motion, remains tangent to a developable surface. To find the characteristic of this surface, that is to say to find the intersection of two consecutive doubly tangent planes, we must differentiate equation 28 with reference to the arbitrary parameter. We thus obtain

$$-d\epsilon_1 = - \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 d\eta_1 - \left(\frac{\partial \epsilon}{\partial v}\right)_1 dv_1 + (\eta - \eta_1) d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 + (v - v_1) d\left(\frac{\partial \epsilon}{\partial v}\right)_1$$

or

$$(\eta - \eta_1)d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 + (v - v_1)d\left(\frac{\partial \epsilon}{\partial v}\right)_1 = 0. \quad (30)$$

Equations 28 and 30 are the equations of the characteristic. The plane 30 passes through the point 1 as is at once evident by substituting η_1 and v_1 for η and v . Moreover, it passes through the point 2 for, replacing η and v by η_2 and v_2 , we obtain

$$(\eta_2 - \eta_1)d\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 + (v_2 - v_1)d\left(\frac{\partial \epsilon}{\partial v}\right)_1 = 0. \quad (31)$$

Equation 25 shows that when the points 1 and 2 are on the connodal curve the condition 31 is satisfied. Thus the line joining the points 1 and 2 is the characteristic of the developable surface to which the doubly tangent plane remains tangent. This developable surface is therefore the same as the ruled surface formed by joining corresponding points of the connodal curve.

To complete the discussion of the equilibrium of the two-phase system it is necessary to add that it can be shown that the conditions of stability require that at each of the points 1 and 2 we should have

$$\begin{vmatrix} \frac{\partial^2 \epsilon}{\partial \eta^2} & \frac{\partial^2 \epsilon}{\partial \eta \partial v} \\ \frac{\partial^2 \epsilon}{\partial \eta \partial v} & \frac{\partial^2 \epsilon}{\partial v^2} \end{vmatrix} > 0, \quad (32)$$

$$\frac{\partial^2 \epsilon}{\partial \eta^2} > 0, \quad \frac{\partial^2 \epsilon}{\partial v^2} > 0.$$

To simplify we shall represent the determinant written above by the symbol Δ , so that, by definition,

$$\Delta \equiv \begin{vmatrix} \frac{\partial^2 \epsilon}{\partial \eta^2} & \frac{\partial^2 \epsilon}{\partial \eta \partial v} \\ \frac{\partial^2 \epsilon}{\partial \eta \partial v} & \frac{\partial^2 \epsilon}{\partial v^2} \end{vmatrix}. \quad (33)$$

We shall next deduce the conditions which are satisfied when a pair of corresponding points of the connodal curve coincide. Such a point of the energy surface is called a plait point

and the corresponding state of the one-component system is called a critical state of the system.

If we expand by Taylor's theorem the expressions which appear on the right-hand side of equations 9 and 10, we obtain

$$\left(\frac{\partial \epsilon}{\partial \eta}\right)_1 = \left(\frac{\partial \epsilon}{\partial \eta}\right)_1 + \left(\frac{\partial^2 \epsilon}{\partial \eta^2}\right)_1 (\eta_2 - \eta_1) + \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 (v_2 - v_1) + \dots, \quad (34)$$

$$\left(\frac{\partial \epsilon}{\partial v}\right)_1 = \left(\frac{\partial \epsilon}{\partial v}\right)_1 + \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 (\eta_2 - \eta_1) + \left(\frac{\partial^2 \epsilon}{\partial v^2}\right)_1 (v_2 - v_1) + \dots, \quad (35)$$

the terms which are omitted being of the second and higher degrees in the differences $\eta_2 - \eta_1$, $v_2 - v_1$. If we suppose that $\eta_2 - \eta_1$, $v_2 - v_1$ are very small, that is to say, if we consider a pair of corresponding points very near the plait point, we may write the following equations which are approximately correct

$$(\eta_2 - \eta_1) \left(\frac{\partial^2 \epsilon}{\partial \eta^2}\right)_1 + (v_2 - v_1) \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 = 0, \quad (36)$$

$$(\eta_2 - \eta_1) \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v}\right)_1 + (v_2 - v_1) \left(\frac{\partial^2 \epsilon}{\partial v^2}\right)_1 = 0. \quad (37)$$

Thus at the plait point we have

$$\lim_{\substack{\eta_2 \rightarrow \eta_1 \\ v_2 \rightarrow v_1}} \frac{\eta_2 - \eta_1}{v_2 - v_1} = - \frac{\frac{\partial^2 \epsilon}{\partial \eta \partial v}}{\frac{\partial^2 \epsilon}{\partial \eta^2}} = - \frac{\frac{\partial^2 \epsilon}{\partial \eta \partial v}}{\frac{\partial^2 \epsilon}{\partial v^2}}. \quad (38)$$

From equations 38 it follows that at the plait point

$$\Delta = 0. \quad (39)$$

The plait point is accordingly a point on the spinodal curve, that is to say, on the curve which divides the portions of the surface which are convex in all directions from those which are concavo-convex. For, as is well-known, equation 39 is the equation of the spinodal curve.

We shall assume that the line joining corresponding points of the connodal curve becomes in the limit the tangent to the connodal curve at the plait point. From this assumption and from equations 38 it follows that the direction of the tangent to the connodal line at the plait point is given by either of the equations

$$\frac{\partial^2 \epsilon}{\partial \eta^2} d\eta + \frac{\partial^2 \epsilon}{\partial \eta \partial v} dv = 0, \quad (40)$$

$$\frac{\partial^2 \epsilon}{\partial \eta \partial v} d\eta + \frac{\partial^2 \epsilon}{\partial v^2} dv = 0. \quad (41)$$

Furthermore, at the plait point the connodal curve is tangent to the spinodal curve. For, in the first place, the plait point is on the spinodal curve and, in the second place, two corresponding points of the connodal curve adjacent to the plait point lie on the portion of the surface which is convex in every direction and for which therefore

$$\Delta > 0.$$

It follows that the spinodal curve does not cut the connodal curve at the plait point, and the simplest assumption that we can make is that the two curves are tangent at the plait point. The equation of the spinodal curve being

$$\Delta = 0,$$

it follows that the direction of the tangent at any point of the spinodal curve is given by the equation

$$\frac{\partial \Delta}{\partial \eta} d\eta + \frac{\partial \Delta}{\partial v} dv = 0. \quad (42)$$

At the plait point this equation must give the same value for the fraction $d\eta/dv$ as equations 40 and 41. Accordingly, at the plait point the three determinants of the second order which can be formed from the matrix

$$\begin{array}{cc} \frac{\partial^2 \epsilon}{\partial \eta^2}, & \frac{\partial^2 \epsilon}{\partial \eta \partial v} \\ \frac{\partial^2 \epsilon}{\partial \eta \partial v}, & \frac{\partial^2 \epsilon}{\partial v^2} \\ \frac{\partial \Delta}{\partial \eta}, & \frac{\partial \Delta}{\partial v} \end{array} \quad (43)$$

are equal to zero. Moreover, the limiting position of the line joining corresponding points of the connodal curve and the direction of the common tangent to the connodal and spinodal curves at the plait point are given by the equations

$$\lim_{v_2 \rightarrow v_1} \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{d\eta}{dv} = - \frac{\frac{\partial^2 \epsilon}{\partial \eta \partial v}}{\frac{\partial^2 \epsilon}{\partial \eta^2}} = - \frac{\frac{\partial^2 \epsilon}{\partial v^2}}{\frac{\partial^2 \epsilon}{\partial \eta^2}} = - \frac{\frac{\partial \Delta}{\partial v}}{\frac{\partial \Delta}{\partial \eta}}. \quad (44)$$

Conditions 43 and 44 suffice to establish the principal properties of the critical state of a one-component system. As the only case in which a critical state of a one-component system has been realized is when the coexistent phases are liquid and vapor, we shall, in what follows, suppose that the phases denoted by the subscripts 1 and 2 are respectively liquid and vapor.

As we move along the connodal curve towards the plait point the quantities ϵ_1 and ϵ_2 , η_1 and η_2 , v_1 and v_2 approach limits which we may call the specific energy, entropy and volume of the critical state. The temperature and the pressure also approach limits which we may call the critical temperature and the critical pressure. It follows that the change in volume during the vaporization of unit mass, $v_2 - v_1$, the corresponding change in entropy, $\eta_2 - \eta_1$, the external work during vaporization, $\Pi(v_2 - v_1)$, and the heat of vaporization, $T(\eta_2 - \eta_1)$, all approach zero as the system approaches the critical state.

Although $\eta_2 - \eta_1$ and $v_2 - v_1$ approach zero as a limit, the ratio of these two quantities, in general, will approach a finite limit. This follows from the fact that there is nothing in equations 44 which obliges us to assume that the limit in question is either zero or infinity. Equation 27 taken in connection with the result just obtained shows that as we approach the critical state the slope of the temperature-pressure curve of the two-phase system approaches a finite limit.

We have stated above that the system under consideration is supposed to consist of the two phases liquid and vapor. This assumption is expressed analytically by the inequalities

$$\eta_2 > \eta_1, \quad v_2 > v_1. \quad (45)$$

It follows from these inequalities that the limit of the ratio $(\eta_2 - \eta_1)/(v_2 - v_1)$ is positive, from which it follows at once that at the critical point the slope of the temperature-pressure curve of the two-phase system is positive. Moreover, since the plait

point is an ordinary point on the connodal curve it follows that the specific entropy and volume of the critical state lie respectively between the specific entropies and the specific volumes of the two phases in equilibrium in the immediate neighborhood of the critical state.

Since, by conditions 45, the different fractions in equations 44 are positive and since, by conditions 32,

$$\frac{\partial^2 \epsilon}{\partial \eta^2} > 0, \quad \frac{\partial^2 \epsilon}{\partial v^2} > 0, \quad (46)$$

it follows that, at the plait point,

$$\frac{\partial^2 \epsilon}{\partial \eta \partial v} < 0. \quad (47)$$

Equations 3, 9 and 10 give the temperature and the pressure of the two-phase system in equilibrium. As we move along the connodal curve the changes in temperature and pressure are accordingly given by the equations

$$dT = \left(\frac{\partial^2 \epsilon}{\partial \eta^2} \right)_1 d\eta_1 + \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v} \right)_1 dv_1 = \left(\frac{\partial^2 \epsilon}{\partial \eta^2} \right)_2 d\eta_2 + \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v} \right)_2 dv_2, \quad (48)$$

$$-d\Pi = \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v} \right)_1 d\eta_1 + \left(\frac{\partial^2 \epsilon}{\partial v^2} \right)_1 dv_1 = \left(\frac{\partial^2 \epsilon}{\partial \eta \partial v} \right)_2 d\eta_2 + \left(\frac{\partial^2 \epsilon}{\partial v^2} \right)_2 dv_2. \quad (49)$$

From equations 44 it follows that at the plait point the right-hand members of equations 48 and 49 are equal to zero. We have accordingly at that point

$$\frac{dT}{d\eta_1} = 0, \quad \frac{dT}{d\eta_2} = 0; \quad (50)$$

$$\frac{dT}{dv_1} = 0, \quad \frac{dT}{dv_2} = 0; \quad (51)$$

$$\frac{d\Pi}{d\eta_1} = 0, \quad \frac{d\Pi}{d\eta_2} = 0; \quad (52)$$

$$\frac{d\Pi}{dv_1} = 0, \quad \frac{d\Pi}{dv_2} = 0. \quad (53)$$

Let us consider equations 50. These equations show that if in the temperature-entropy plane we draw the two curves which show the relation between the temperature and the specific

entropies of the two phases in equilibrium, these two curves meet at the point corresponding to the critical state and have at that point a common tangent parallel to the entropy axis. Moreover, since the specific entropy of the critical state is intermediate between η_1 and η_2 , it follows that the critical temperature is a maximum or a minimum of the temperatures at which the two-phase system can exist in equilibrium. If we assume that the critical temperature is a maximum, and if we remember that η_1 is less than η_2 it follows that in the neighborhood of the critical state

$$\frac{dT}{d\eta_1} > 0, \quad \frac{dT}{d\eta_2} < 0. \quad (54)$$

Similar reasoning enables us to deduce the following pairs of inequalities which correspond respectively to equations 51, 52 and 53.

$$\frac{dT}{dv_1} > 0, \quad \frac{dT}{dv_2} < 0; \quad (55)$$

$$\frac{d\Pi}{d\eta_1} > 0, \quad \frac{d\Pi}{d\eta_2} < 0; \quad (56)$$

$$\frac{d\Pi}{dv_1} > 0, \quad \frac{d\Pi}{dv_2} < 0. \quad (57)$$

Corresponding to each of the three sets of conditions 51 and 55, 52 and 56, 53 and 57, there is a theorem analogous to the theorem stated above for conditions 50 and 54. Of these theorems the best known are those corresponding to conditions 51 and 55, 53 and 57.

Let us denote by L the heat of vaporization. We have

$$L = T(\eta_2 - \eta_1). \quad (58)$$

As we pass along the connodal curve the change in the heat of vaporization is given by the equation

$$dL = (\eta_2 - \eta_1)dT + T(d\eta_2 - d\eta_1)$$

or by

$$\frac{dL}{dT} = \eta_2 - \eta_1 + T\left(\frac{d\eta_2}{dT} - \frac{d\eta_1}{dT}\right). \quad (59)$$

If we make use of conditions 50 and 54 we find that as we ap-

proach the critical state dL/dT approaches negative infinity. From equation 59 it can also be shown that $dL/d\Pi$ also approaches negative infinity.

In like manner if we denote by W the external work during vaporization, we have

$$W = \Pi(v_2 - v_1), \quad (60)$$

and it can be shown without difficulty that $dW/d\Pi$ and dW/dT approach negative infinity as we approach the critical state.

Let us suppose that T and Π are always defined by equations 3, remembering, however, that only those points of the energy surface for which conditions 6, 7 and 8 are satisfied correspond to stable states of equilibrium. As we move from one point of the energy surface to an adjacent point, we have, from equations 3

$$dT = \frac{\partial^2 \epsilon}{\partial \eta^2} d\eta + \frac{\partial^2 \epsilon}{\partial \eta \partial v} dv, \quad (61)$$

$$-d\Pi = \frac{\partial^2 \epsilon}{\partial \eta \partial v} d\eta + \frac{\partial^2 \epsilon}{\partial v^2} dv. \quad (62)$$

By solving these equations for $d\eta$ and dv we obtain

$$\Delta d\eta = \begin{vmatrix} dT, & \frac{\partial^2 \epsilon}{\partial \eta \partial v} \\ -d\Pi, & \frac{\partial^2 \epsilon}{\partial v^2} \end{vmatrix}, \quad (63)$$

$$\Delta dv = \begin{vmatrix} \frac{\partial^2 \epsilon}{\partial \eta^2}, & dT \\ \frac{\partial^2 \epsilon}{\partial \eta \partial v}, & -d\Pi \end{vmatrix}. \quad (64)$$

If we suppose the point to move on the energy surface along an isopiestic curve we must have constantly

$$d\Pi = 0.$$

We thus obtain from equations 63 and 64

$$\left(\frac{dT}{d\eta} \right)_{\Pi} = \frac{\Delta}{\frac{\partial^2 \epsilon}{\partial \eta^2}}, \quad (65)$$

$$\left(\frac{dT}{dv}\right)_{\Pi} = - \frac{\Delta}{\frac{\partial^2 \epsilon}{\partial \eta \partial v}}. \quad (66)$$

The subscript Π in the left-hand members of these equations denotes that Π is supposed to remain constant during the change considered.

If we suppose the point on the energy surface to move along an isothermal curve we must have constantly

$$dT = 0.$$

Equations 63 and 64 then give us

$$\left(\frac{d\Pi}{d\eta}\right)_T = \frac{\Delta}{\frac{\partial^2 \epsilon}{\partial \eta \partial v}},$$

$$\left(\frac{d\Pi}{dv}\right)_T = - \frac{\Delta}{\frac{\partial \eta^2}{\partial \eta^2}}.$$

At the plait point of the energy surface Δ is equal to zero. Accordingly for the critical state of a one-component system the following conditions hold

$$\left(\frac{dT}{d\eta}\right)_{\Pi} = 0, \quad \left(\frac{dT}{dv}\right)_{\Pi} = 0, \quad \left(\frac{d\Pi}{d\eta}\right)_T = 0, \quad \left(\frac{d\Pi}{dv}\right)_T = 0. \quad (69)$$

Moreover, if we consider a point on the energy surface in the immediate neighborhood of the plait point, conditions 46 and 47 are satisfied. If, in addition, we suppose that for the point considered Δ is positive, we obtain from equations 65, 66, 67 and 68 the following inequalities:

$$\left(\frac{dT}{d\eta}\right)_{\Pi} > 0, \quad \left(\frac{dT}{dv}\right)_{\Pi} > 0, \quad \left(\frac{d\Pi}{d\eta}\right)_T < 0, \quad \left(\frac{d\Pi}{dv}\right)_T < 0. \quad (70)$$

These inequalities apply to a one-component system consisting of a single homogeneous phase in stable equilibrium in the immediate neighborhood of the critical state. Since the quantities on the right-hand sides of equations 65 and 68 are positive for any homogeneous phase in stable equilibrium it follows that the first and fourth of inequalities 70 are verified for

any homogeneous phase in stable equilibrium. But we are not justified in asserting that the second and third of these inequalities are verified elsewhere than in the immediate neighborhood of the critical state.

We shall next calculate the value of

$$\left(\frac{d^2T}{d\eta^2}\right)_{\Pi}$$

at the plait point. From equation 65 we get

$$\left(\frac{d^2T}{d\eta^2}\right)_{\Pi} = \frac{\frac{\partial\Delta}{\partial\eta}d\eta + \frac{\partial\Delta}{\partial v}dv}{\frac{\partial^2\epsilon}{\partial\eta^2}} - \frac{\Delta \cdot d \frac{\partial^2\epsilon}{\partial\eta^2}}{\left(\frac{\partial^2\epsilon}{\partial\eta^2}\right)^2}. \quad (71)$$

if Δ is equal to zero and the right-hand member of equation 65 reduces to its first term. Since Π is to remain constant, equation 62 gives us

$$0 = \frac{\partial^2\epsilon}{\partial\eta\partial v}d\eta + \frac{\partial^2\epsilon}{\partial v^2}dv. \quad (72)$$

Substitute dv between equation 72 and the simplified form of equation 71, we obtain

$$\left(\frac{d^2T}{d\eta^2}\right)_{\Pi} = \frac{\begin{vmatrix} \frac{\partial\Delta}{\partial\eta} & \frac{\partial\Delta}{\partial v} \\ \frac{\partial^2\epsilon}{\partial\eta\partial v} & \frac{\partial^2\epsilon}{\partial v^2} \end{vmatrix}}{\frac{\partial^2\epsilon}{\partial\eta^2} \cdot \frac{\partial^2\epsilon}{\partial v^2}}. \quad (73)$$

From conditions 43 we know that the determinant which appears in this equation is equal to zero at the plait point. We thus obtain the first of the following equations:

$$\left(\frac{d^2T}{d\eta^2}\right)_{\Pi} = 0, \quad \left(\frac{d^2T}{dv^2}\right)_{\Pi} = 0, \quad \left(\frac{d^2\Pi}{d\eta^2}\right)_{\Gamma} = 0, \quad \left(\frac{d^2\Pi}{dv^2}\right)_{\Gamma} = 0. \quad (74)$$

The others can be established in the same manner.

The corresponding relations in 69, 70 and 74 give us four theorems. For the sake of brevity we shall state only the last

of these:¹ If in the pressure volume plane, we construct the isothermal corresponding to the critical temperature, this curve will have a point of inflexion at the critical point. The tangent at the point of inflexion is parallel to the volume axis; at any other point of the curve the tangent makes an obtuse angle with the volume axis.

Equations 69 and 74 were given by Gibbs in his memoir on the energy surface.² Conditions 43, which we have taken as the starting point of our discussion, were given a few years later in the great memoir "On the Equilibrium of Heterogeneous Substances."³

It is hoped that the foregoing discussion will help to draw attention to the fact that Gibbs' memoir on the energy surface contains a general theory of the critical state of a one-component system and of the continuity of the liquid and gaseous states which is not only extremely simple but which, at the same time, is entirely independent of molecular hypotheses.

The memoir in question is important in the history of thermodynamics for another reason. In it Gibbs shows that the condition that a system be in stable equilibrium at a given temperature and under a given pressure is that the thermodynamic potential, $\epsilon - T\eta + \Pi v$, be a minimum.⁴ A few months previously Horstman had stated the condition of equilibrium in terms of the entropy.⁵

New York, June 30, 1902.

¹ van der Waals. *Over de Continuïteit*, p. 84.

² p. 396.

³ p. 191.

⁴ p. 393.

⁵ *Liebig's Annalen*, 170, 197 (1873).