

librium with solution under atmospheric pressure, the maximum temperature occurs when the solution has the same composition as the hydrate, *i. e.*, when we are at the melting point of the hydrate. If the system is under its own vapor pressure instead of a constant pressure greater than the vapor pressure this deduction fails.

In a condensed three-component system such as that discussed by Rankin,¹ the theorem shows that maximum temperature points occur when the liquidus points lie on the lines joining the two solid phases present. He uses the theorem as a guide, but following Bancroft attributes it to von Alkemade, whereas it was originally proved by Gibbs by a different method from that used in the present paper.

While discussing this matter of a linear relation among the composition of our phases it should be noted that if we are neither considering an isobar nor isotherm, we deduce by the same method

$$(a\Delta V_1 + b\Delta V_2 + \dots) dp = (a\Delta\eta_1 + b\Delta\eta_2 + \dots) dt,$$

and hence the slope of the p - t curves is determined by the reaction among the linearly related phases. This fact is amplified and made use of in the next paper.

Any further elaboration of the equations belongs to subsequent papers where specific applications will be made. We believe that it is only along the lines laid down by Gibbs that a fruitful attack can be made on any save the outskirts of involved systems. For a comprehensive and rigorous treatment of many points, with which we have dealt hurriedly, we must again refer to his masterly paper which, it is to be hoped, will in the future be still more of an inspiration to the chemists of this country than it ever has been.

Summary.

Using Willard Gibbs' methods as a basis, general equations are developed for equilibrium in chemical systems. Special forms for simple cases are evolved and a number of more or less well-known theorems deduced from these. The application of the general equations will be considered in later papers.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

PRESSURE-TEMPERATURE CURVES IN UNIVARIANT SYSTEMS.

BY GEORGE W. MOREY AND ERSKINE D. WILLIAMSON.

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At a constant temperature a salt has a definite solubility in water, and the vapor pressure of the solution is fixed. For example, at 25°, the solu-

¹ "Lime-Alumina-Silica," *Am. J. Sci.*, **39**, 1 (1915).

bility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in water is fixed, as is also the vapor pressure of the saturated solution. When the temperature is either raised or lowered, the solubility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and the vapor pressure of the saturated solution both change; the first change gives rise to the solubility curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the second to the pressure-temperature curve, or the P-T curve, of the saturated solution.

There are several other types of P-T curves. At the transition point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$,¹ the quadruple point $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - Na_2SO_4 -solution-vapor in the binary system H_2O - Na_2SO_4 , four P-T curves intersect. One of these is the P-T curve of the solutions saturated with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$,² a second, the P-T curve of solutions saturated with Na_2SO_4 , a third, the dissociation pressure curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and the fourth, the transition point curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the curve which gives the change in transition point with pressure in the condensed system. It is our intention to discuss P-T curves in general, first discussing the slopes of the P-T curves at or near the invariant points, then the change in slope as we move along the curves away from the invariant point. Our discussion will be based on Gibbs' classic paper "On the equilibrium of heterogeneous substances," and especially on Equation 97 in that paper,³

$$vdp = \eta dt + m_1 d\mu_1 + m_2 d\mu_2 + \dots + m_n d\mu_n, \quad (97)$$

the fundamental equation of the phase rule. In this equation the symbols v , p , η , t represent the volume, pressure, entropy and temperature, respectively. The symbols m_1 , m_2 , \dots , m_n , represent the masses of each of the n components, and μ_1 , μ_2 , \dots , μ_n the chemical potentials of these components, respectively.

We may generalize the above remarks in regard to the curves which intersect at the quadruple point $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - Na_2SO_4 -L-V, as follows: At an invariant point in a system of n components, $n + 2$ phases co-exist, and the temperature, pressure and the composition of the $n + 2$ phases are determined. Addition or subtraction of heat, or increase or decrease in volume will result in a reaction taking place between the phases without change in temperature or pressure until one of the phases has disappeared. We then have $n + 1$ co-existing phases, the system is univariant, and the pressure may be expressed as function of the temperature. In his chapter, "On co-existent phases of matter," Gibbs proceeds as follows to drive an expression for the relation between the variations in pressure and temperature in a univariant system, *i. e.*, in an equilibrium between $n + 1$ phases in a system of n components. In such a case

¹ This invariant point is discussed in some detail later. See Fig. 1.

² For an elementary discussion of these curves see Findlay's "The Phase Rule," pp. 138, *et seq.*

³ For a discussion of the derivation of this equation and an explanation of the terms used see the preceding paper (THIS JOURNAL, 40, 49-59 (1918)).

we have $n + 1$ equations of the type of (97) (one for each of the co-existent phases); since the phases are co-existent the quantities p , t , and the $n\mu$ 's¹ have the same value for each phase. Hence we may eliminate $d\mu_1, d\mu_2, \dots, d\mu_n$ from the $n + 1$ equations. We thus obtain Gibbs' Equation 129.²

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & \dots & \dots & m_n' \\ \eta'' & m_1'' & m_2'' & \dots & \dots & m_n'' \\ \eta''' & m_1''' & m_2''' & \dots & \dots & m_n''' \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \eta^{n+1} & m_1^{n+1} & m_2^{n+1} & \dots & \dots & m_n^{n+1} \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & \dots & \dots & m_n' \\ v'' & m_1'' & m_2'' & \dots & \dots & m_n'' \\ v''' & m_1''' & m_2''' & \dots & \dots & m_n''' \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ v^{n+1} & m_1^{n+1} & m_2^{n+1} & \dots & \dots & m_n^{n+1} \end{vmatrix}}$$

This equation gives us the relation between the variations in pressure and temperature in any univariant system.

A theorem in determinants states that whenever all the terms but one in any row or column are zero,³ the determinant reduces to the product of the term not zero and its minor. From the form of the above determinants it follows that whenever in an n -component system the composition of any phase can be expressed as a linear function of the composition of $n - 1$ or fewer phases, that is, whenever a phase reaction is possible between n or fewer phases,⁴ all the composition terms relating to that phase can be reduced to zero, and the numerator and denominator of 129 reduce, respectively, to an entropy or a volume term into the same composition determinant as minor. Since the latter term occurs in both

¹ That the pressure and temperature must be the same in co-existent phases, *e. g.*, ice, water and water vapor at the triple point, is obvious. For a discussion of the necessity that the chemical potential must be the same in each phase, see the preceding paper.

² This equation has been put in the form of a determinant because of the great convenience of that form of notation. For those not familiar with determinants we will say that this is merely a shorthand method of indicating the familiar operation of elimination by cross multiplication. Expansion of the above determinant and elimination of $d\mu_1, d\mu_2, d\mu_3, \dots, d\mu_n$ from the $n + 1$ equations by cross multiplication lead to the same result.

³ See any book on determinants; or, Mellor, "Higher Mathematics for Students of Physics and Chemistry," 2nd edition, p. 580.

⁴ In a 2-component system this means that 2 phases have the same composition, *e. g.*, ice and vapor at the cryohydrate point in the system $H_2O-Na_2SO_4$, or two allotropic forms. In a 3-component system it means either that two phases have the same composition or that three lie in a straight line in the composition diagram.

numerator and denominator, it cancels out, and the value of dp/dt reduces to an equation which contains only terms relating to the above reacting phases. Hence the slope of the P-T curve is independent of the presence of other phases. In other words, whenever a linear relation exists between the composition of n or fewer phases, the P-T curves of all univariant systems containing these phases coincide. When all the reacting phases have a constant composition, the curves will coincide throughout their course; when the composition of some or all of them are variable, and they only casually have such a composition that the above linear relation is possible, then the curves are tangent.¹

Let us prove this in detail for three phases lying on a straight line in a 3-component system. Consider the P-T curves of the univariant equilibria $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^V$, which proceed from the quintuple point $P' + P'' + P''' + P^{IV} + P^V$. The equation of the first of these is

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & m_3' \\ \eta'' & m_1'' & m_2'' & m_3'' \\ \eta''' & m_1''' & m_2''' & m_3''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & m_3' \\ v'' & m_1'' & m_2'' & m_3'' \\ v''' & m_1''' & m_2''' & m_3''' \\ v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}.$$

Now assume that P' , P'' , P''' lie on a straight line in the composition diagram.² We then have the relation

$$A'P' = A''P'' + A'''P'''$$

and hence also

$$A'm_1' = A''m_1'' + A'''m_1'''$$

$$A'm_2' = A''m_2'' + A'''m_2'''$$

and

$$A'm_3' = A''m_3'' + A'''m_3'''$$

By substituting these values of m_1' , m_2' , m_3' in the above determinants, and subtracting A'' times the second row and A''' times the third row from A' times the first row, we get

$$\frac{dp}{dt} = \frac{\begin{vmatrix} A'\eta' - A''\eta'' - A'''\eta''' & 0 & 0 & 0 \\ \eta'' & m_1'' & m_2'' & m_3'' \\ \eta''' & m_1''' & m_2''' & m_3''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} A'v' - A''v'' - A'''v''' & 0 & 0 & 0 \\ v'' & m_1'' & m_2'' & m_3'' \\ v''' & m_1''' & m_2''' & m_3''' \\ v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}$$

¹ Schreinemakers (*Proc. Acad. Sci. Amsterdam*, 19, 514-27, and subsequent papers

which reduces to

$$\frac{dp}{dt} = \frac{A'\eta' - A''\eta'' - A'''\eta'''}{\begin{vmatrix} m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \\ m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}} \cdot \frac{\begin{vmatrix} m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \\ m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{A'v' - A''v'' - A'''v'''}$$

Similarly, the relation between the variations of P and T in the second of the above univariant equilibria $P' + P'' + P''' + P^V$, reduces to the same expression. It will be observed that, since the coefficients A' , A'' , A''' are those which occur in the reaction equation¹

$$A'P' = A''P'' + A'''P'''$$

the numerator in the expression

$$\frac{dp}{dt} = \frac{A'\eta' - A''\eta'' - A'''\eta'''}{A'v' - A''v'' - A'''v'''} = \frac{\Delta\eta}{\Delta v},$$

is the entropy change² taking place in the reaction, the denominator, the volume change. Hence we see that whenever three phases lie on a straight line in the composition diagram the P-T curves of all ternary equilibria containing these three phases coincide with each other and with the P-T curve of the univariant binary equilibrium between the three phases alone.

As will be explained later, from this theorem alone we are able from a knowledge of the composition of the phases at an invariant point, but without any knowledge of the volume or entropy changes, to deduce the order of the slopes³ of the $n + 2$ P-T curves which proceed from an invariant point. These curves will extend on both directions from the invariant point; in one direction the equilibrium under consideration will be stable, in the other direction, metastable. To tell the actual position of any curve, or to distinguish between the stable and metastable portions of any one curve, a knowledge of the volume and entropy changes is necessary. However, it will be shown that two adjoining curves, *i. e.*, in the same Journal) mentions some special cases of this general theorem.

² An example of this is found in Fig. 3, there the phases being $K_2Si_2O_5 \cdot H_2O$, $K_2Si_2O_5$ and vapor, the vapor phase containing only H_2O , and its composition being represented by the apex of the component triangle.

¹ The actual values of these coefficients are deduced and discussed below, in the discussion of the change in slope with change in composition of a phase of variable composition.

² It will be remembered that the entropy η is defined by the $d\eta = dQ/T$, where Q is the heat change taking place at the absolute temperature T. Hence for η we may substitute Q/T or L/T , where L is the change in latent heat.

³ By "the order of the slopes of the P-T curves" is meant the sequence in which we will cut the curves as we circle around the invariant point; reversing the direction of rotation reverses the sequence but does not affect the order.

curves which are not separated by either the stable or metastable portions of other curves, *e. g.*, the P-T curves of the univariant ternary equilibria $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^V$, will coincide in their stable portions, that is, are stable in the same direction from the invariant point, when the phases P^{IV} and P^V lie on opposite sides of the straight line $P'P''$, and *vice versa*. Examples of this are discussed later. Similar relations are found in systems containing any other number of components. In a 2-component system the univariant equilibrium consists of three phases. When the phases P' and P'' in the univariant equilibria $P' + P'' + P'''$ and $P' + P'' + P^{IV}$ have the same composition, the P-T curves of these equilibria are stable in the opposite direction when the phases P''' and P^{IV} lie on the same side of the point $P'P''$. An example of this is found in the cryohydrate point ice- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ -L-V in the binary system H_2O - Na_2SO_4 . Here the vapor phase consists of H_2O only; ice and vapor have the same composition. In the concentration diagram, the phases $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and solution lie on the same side of the point representing the composition of both ice and vapor, hence the curves ice + vapor + $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and ice + vapor + solution will coincide, stable to metastable. That such is the case is well known.¹ Also in a system of four components when the phases P' , P'' , P''' and P^{IV} lie on a plane the curves $P' + P'' + P''' + P^{IV} + P^V$ and $P' + P'' + P''' + P^{IV} + P^{VI}$ are stable in the same direction when the phases P^V and P^{VI} lie on opposite sides of the plane $P'P''P'''P^{IV}$. The same principle may be extended to systems of any number of components. We will now prove the general theorem.

In the preceding paper² it was shown that equality of the chemical potential μ is a necessary condition for chemical equilibrium, and that if the chemical potential of a substance in one given phase is greater than the chemical potential of the same substance in another phase, the two phases are not in equilibrium in regard to that substance, which will tend to pass from the phase in which its chemical potential is the greater into the phase in which its chemical potential is the lesser. At the triple point ice-water-steam in the one-component system H_2O , the chemical potential of H_2O in all three phases is the same. If we simultaneously change the pressure and temperature so as to proceed along any one of the three P-T curves which intersect at the triple point, one of the phases will disappear. By giving these changes we have given greater increments to the chemical potential of the phase which disappears than to the chemical potentials of the other two phases; the chemical potential of water remains equal in these two phases since we, by

¹ See Findlay's "The Phase Rule," p. 128.

² THIS JOURNAL, 40, 49-50 (1918).

hypothesis, have given such changes of pressure and temperature as to proceed along the P-T curve of stable coincidence of these phases.

The fundamental equations of the form of (97) for the three phases which co-exist at the triple point are

$$\begin{aligned} v^v dp &= \eta^v dt + m^v d\mu^v \\ v^l dp &= \eta^l dt + m^l d\mu^l \\ v^s dp &= \eta^s dt + m^s d\mu^s \end{aligned}$$

in which the exponents v, l, s refer to the vapor, liquid and solid phases. Each of these equations may be divided by the mass m of the phase; in the resulting equations

$$\begin{aligned} v^v dp &= \eta^v dt + d\mu^v \\ v^l dp &= \eta^l dt + d\mu^l \\ v^s dp &= \eta^s dt + d\mu^s \end{aligned}$$

the volume and entropy terms refer to the specific volume and entropy of each phase.

Now if, as stated above, we proceed along the P-T curve of the condensed system ice + liquid, one of the P-T curves which intersect at the triple point, we can obtain a value for $d\mu$, the change in the chemical potential, from the two equations of the type of (97) referring to the liquid and solid phases by solving the two equations for dt in terms of dp , which will give us

$$dt = \frac{v^l - v^s}{\eta^l - \eta^s} dp,$$

and substituting this value of dt in one of the original equations. Substituting in the equation referring to the liquid phase, we get

$$d\mu = v^l - \mu^l \frac{v^l - v^s}{\eta^l - \eta^s} dp.$$

Similarly, the value of $d\mu^v$ for the same increments, *i. e.*, along the same curve, is given by

$$d\mu^v = v^v - \eta^v \frac{v^l - v^s}{\eta^l - \eta^s} dp.$$

Now, since we have, by hypothesis, proceeded along the stable portion of the curve ice + liquid,

$$d\mu^v > d\mu.$$

Hence

$$dp \left[\left(v^v - \eta^v \frac{v^l - v^s}{\eta^l - \eta^s} \right) - \left(v^l - \eta^l \frac{v^l - v^s}{\eta^l - \eta^s} \right) \right] > 0,$$

which reduces to

$$\frac{d\phi[(v^v - v^l)(\eta^l - \eta^s) - (v^l - v^s)(\eta^v - \eta^l)]}{\eta^l - \eta^s} > 0,$$

one form of the condition for stability of the equilibrium solid + liquid.

When we consider the actual magnitude of the various terms in this equation we see that the coefficient of $d\phi$ in the numerator is necessarily positive. All the individual terms $(v^v - v^l)$, $(\eta^v - \eta^l)$, $(\eta^v - \eta^l)$ and $(v^l - v^s)$ are of necessity positive except the last one, the volume change of melting of ice, which is negative. But the last term is affected by the negative sign, hence the term as a whole is positive, and the coefficient of $d\phi$ has a positive sign.¹ The equilibrium in question will then be stable as the pressure is increased from the invariant point when the denominator is positive; $(\eta^l - \eta^s)$ is of necessity positive, hence the equilibrium ice + liquid is stable with increasing pressure from the invariant point; on decreasing the pressure we pass on to the metastable portion of the curve, into a region where vapor is stable.

By solving for $d\phi$ in the above equations of the type of (97) referring to the solid and liquid phases, we get an exactly similar inequality,

$$\frac{dt[(v^v - v^l)(\eta^l - \eta^s) - (v^l - v^s)(\eta^v - \eta^l)]}{v^l - v^s} > 0$$

which gives the condition for stability with change in temperature. It will be observed that the condition for temperature stability differs from the condition for pressure stability in having dt in place of $d\phi$ in the numerator, and in having the volume change $(v^l - v^s)$ in place of the entropy change. Since the coefficient in the numerator is unchanged, it is always positive; the equilibrium solid + liquid is stable with increasing temperature when the denominator is positive, and is stable with decreasing temperature when the denominator is negative. In the exceptional case of H_2O , this volume change is negative, hence the equilibrium ice + liquid is stable with decreasing temperature from the triple point; on increasing the temperature we pass on to the metastable portion of the curve, into a region in which vapor is stable.

The above reasoning may be generalized as follows: At an invariant point, if we give the variables increments satisfying the $(n + 1)$ equations of the type of (97) for the univariant equilibrium, $P' + \dots + P'' + P^{IV} + \dots + P^{n+1} + P^{n+2}$ (in which phase P^n is missing), we will move

¹ The case that $(v^l - v^s)$ is negative is, of course, exceptional. But in any case, the coefficient of $d\phi$ is positive, since the two entropy changes are of the same order of magnitude, while the volume change on evaporation is many times larger than the volume change on melting.

along the P-T curve of this equilibrium. In one direction from the invariant point the missing phase P'' will be stable, in the other direction phase P'' will be unstable. In the first case, we will be on the metastable prolongation of the P-T curve, in the second case, we will be on the stable portion of the P-T curve.

In the preceding paper the condition that a given phase is unstable, the condition that in the one-component system discussed above was given by its chemical potential becoming greater than the chemical potential of the stable co-existing set of phases, is given by the inequality

$$vdp - \eta dt > m_1 d\mu_1 + m_2 d\mu_2 + \dots + m_n d\mu_n.$$

The condition that the equilibrium

$$P' + \dots + P'' + P^{IV} + \dots + P^{n+1} + P^{n+2}$$

is stable is that the missing phase P'' is unstable. By solving the (n + 1) equations of the type of (97) referring to the (n + 1) co-existing phases of this equilibrium for $d\mu_1, d\mu_3, d\mu_4,$ and dt in terms of dp and substituting in the above inequality (the quantities $v, \eta, m_1, m_3, \dots, m_n$ referring to phase P'') the condition for stability takes the following form:

dp	η'	v'	m_1'	m_2'	m_3'	\dots	\dots	m_n'
	η''	v''	m_1''	m_2''	m_3''	\dots	\dots	m_n''
	η'''	v'''	m_1'''	m_2'''	m_3'''	\dots	\dots	m_n'''
	η^{IV}	v^{IV}	m_1^{IV}	m_2^{IV}	m_3^{IV}	\dots	\dots	m_n^{IV}
	\dots	\dots	\dots	\dots	\dots	\dots	\dots	\dots
	\dots	\dots	\dots	\dots	\dots	\dots	\dots	\dots
	η^{n+1}	v^{n+1}	m_1^{n+1}	m_2^{n+1}	m_3^{n+1}	\dots	\dots	m_n^{n+1}
	η^{n+2}	v^{n+2}	m_1^{n+2}	m_2^{n+2}	m_3^{n+2}	\dots	\dots	m_n^{n+2}
	η'	m_1'	m_2'	m_3'	\dots	\dots	m_n'	
	η''	m_1''	m_2''	m_3''	\dots	\dots	m_n''	
η^{IV}	m_1^{IV}	m_2^{IV}	m_3^{IV}	\dots	\dots	m_n^{IV}		
\dots	\dots	\dots	\dots	\dots	\dots	\dots		
\dots	\dots	\dots	\dots	\dots	\dots	\dots		
η^{n+1}	m_1^{n+1}	m_2^{n+1}	m_3^{n+1}	\dots	\dots	m_n^{n+1}		
η^{n+2}	m_1^{n+2}	m_2^{n+2}	m_3^{n+2}	\dots	\dots	m_n^{n+2}		

$< 0^1 \text{ (I)}$

The equilibrium $P' + \dots + P'' + P^{IV} + \dots + P^{n+1} + P^{n+2}$ will be stable if this expression is negative, and *vice versa*. Also the univariant equilibrium $P'' + P''' + \dots + P^{n+1} + P^{n+2}$ is stable when the expression

¹This inequality applies to pressure changes; the expression referring to temperature changes is exactly similar, and the subsequent reasoning applies to either.

$$\begin{array}{c}
 \left. \begin{array}{l}
 \eta' \\
 \eta'' \\
 \eta''' \\
 \eta^{IV} \\
 \dots \\
 \eta^{n+1} \\
 \eta^{n+2}
 \end{array} \right\} d\rho \quad \left| \begin{array}{ccccccc}
 v' & m_1' & m_2' & m_3' & \dots & \dots & m_n' \\
 v'' & m_1'' & m_2'' & m_3'' & \dots & \dots & m_n'' \\
 v''' & m_1''' & m_2''' & m_3''' & \dots & \dots & m_n''' \\
 v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \dots & \dots & m_n^{IV} \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 v^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & m_n^{n+1} \\
 v^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & m_n^{n+2}
 \end{array} \right. < 0 \quad (2)
 \end{array}$$

is negative. It will be observed that this latter quantity is affected by a negative sign.

The numerators of the two expressions given above are identical. When a linear relation exists between the phases P'' , P^{IV} , ... P^{n+1} , P^{n+2} , the denominators reduce to

$$\Delta\eta \quad \left| \begin{array}{ccccccc}
 m_1' & m_2' & m_3' & \dots & \dots & \dots & m_n' \\
 m_1''' & m_2''' & m_3''' & \dots & \dots & \dots & m_n''' \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & \dots & m_n^{n+1} \\
 m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & \dots & m_n^{n+2}
 \end{array} \right. \quad (3)$$

and

$$\Delta\eta \quad \left| \begin{array}{ccccccc}
 m_1'' & m_2'' & m_3'' & \dots & \dots & \dots & m_n'' \\
 m_1''' & m_2''' & m_3''' & \dots & \dots & \dots & m_n''' \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & \dots & m_n^{n+1} \\
 m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & \dots & m_n^{n+2}
 \end{array} \right. \quad (4)$$

in which $\Delta\eta$ denotes the entropy change which takes place when these n phases, P_3 , P_4 , ... P^{n+1} , P^{n+2} , react.

It will be observed that these two expressions are identical except for the first row of the determinants, which in (3) contains the composition terms of phase P' , and in (4) contains the composition terms of phase P'' . Hence it is evident that the numerical values of expressions 1 and 2 will be the same, *i. e.*, the two curves will be stable in the same direction from the invariant point, when (3) and (4) have opposite signs

(since (1) and (2) have opposite signs). But (3) and (4) will have opposite signs only when phases P' and P'' lie on opposite sides of the onefold P''' , P^{IV} ,, P^{n+1} , P^{n+2} . In a 2-component system this onefold is a point; in a 3-component system, a line; in a 4-component system, a plane, etc.

The above may be summarized as follows: When two adjoining P-T curves, which represent the relation between the variations in pressure and temperature in two different univariant equilibria between $n + 1$ phases in a system of n components, coincide, due to a linear relation being possible between the compositions of the n phases common to both equilibria, *i. e.*, to these n phases lying on the onefold n , whose position is determined by the above linear relation, these equilibria are stable in the same direction from the invariant point, *i. e.*, their stable portions coincide, when the other two phases lie on opposite sides of the onefold n . By "the other two phases" is meant the phases, one in each of the univariant equilibria, which do not lie on the onefold n . In a 2-component system, the onefold n is a point; in a 3-component system, a line; in a 4-component system, a plane, etc.

The above has been proved for the case that a linear relation exists between the compositions of n of the $n + 2$ phases which co-exist at the invariant point. The cases that a linear relation exists between the composition of $n - 1$, $n - 2$, $n - a$, phases may be regarded as a special case of the above.

The actual number of coincidences possible is an interesting question. If among the $(n + 2)$ phases at an invariant point a phase reaction is possible between $(n - a)$ phases, then there are $(a + 2)$ phases which play no part in the reaction. The following P-T curves will then coincide: (1) the P-T curve of the univariant equilibrium between the $(n - a)$ phases in the system of $[(n - a) - 1]$ components; (2) the P-T curves of the various univariant equilibria containing the $(n - a)$ phases, together with each of the $(a + 2)$ other phases in the various systems of $(n - a)$ components; (3) the P-T curves of the various univariant equilibria containing the $(n - a)$ phases, together with every possible pair of the $(a + 2)$ other phases in the various systems of $[(n - a) + 1]$ components; (4) the P-T curves of the various univariant equilibria containing the $(n - a)$ phases together with every possible triplet of the $(a + 2)$ other phases in the various systems of $[(n - a) + 2]$ components, etc., until the system of n components is reached. The coincidences will be stable or metastable according to whether the number of phases on each side of the onefold $n - a$ are both odd or even, or are odd on one side, even on the other.

As an example of the above, consider the P-T curves which intersect at the cryohydrate point in a system of four-components, H_2O and the 3 non-volatile salts S_1 , S_2 and S_3 , which do not form hydrates. Here the two

phases ice and vapor have the same composition; $a = 2$ and $(n - a) = 2$ phases have the same composition; the other $(a + 2) = 4$ phases have different compositions, and play no part in the reaction. The following curves will coincide:

(1) The P-T curve of the equilibrium between the $(n - a) = 2$ phases ice + V in the system of $(n - a) - 1 = 1$ component. One curve, the curve ice + V.

(2) The P-T curves of the equilibria between the $(n - a) = 2$ phases, ice + V, together with each, separately, of the $(a + 2) = 4$ other phases in the system of $(n - a) = 2$ components. Four curves: ice + V + L, ice + V + S₁, ice + V + S₂, ice + V + S₃. The last three of these will coincide stably with each other, metastably with the first, and all will coincide with the curve (ice + V).

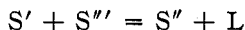
(3) The P-T curves of the equilibria between the $(n - a) = 2$ phases, ice + V, together with every possible pair of the $(a + 2) = 4$ other phases in the various systems of $[(n - a) + 1] = 3$ components. Six curves: ice + V + L + S₁, ice + V + L + S₂, ice + V + L + S₃, ice + V + S₁ + S₂, ice + V + S₁ + S₃, ice + V + S₂ + S₃. The first three curves will coincide stably with each other, metastably with the last three.

(4) The P-T curves of the equilibria between the $(n - a) = 2$ phases ice + V, together with every possible triplet of the $(a + 2) = 4$ other phases in the systems of $[(n - a) + 2] = 4$ components. Four curves: ice + V + L + S₁ + S₂, ice + V + L + S₁ + S₃, ice + V + L + S₂ + S₃, ice + V + S₁ + S₂ + S₃. The first three curves will coincide stably with each other, metastably with the fourth. There are a total of 15 curves which coincide, representing one unary, four binary, six ternary, and four quaternary univariant equilibria.

Before illustrating the application of the above principles to actual cases, we will point out certain generalizations which may be made concerning the P-T curves from the state of aggregation of the phases. The actual value of dp/dt for any univariant equilibrium is given by Equation 129, which, as will be shown later, is equivalent to

$$\frac{dp}{dt} = \frac{\Delta\eta}{\Delta v}$$

in which $\Delta\eta$ is the entropy change, Δv the volume change of the reaction in question. Whenever we have a reaction in which the vapor does not take part, *e. g.*, the reaction



the slope of the P-T curve is always very great, because of the small value of Δv . In other words, the P-T curves of all condensed systems are almost vertical, and go from the invariant point to regions of higher pressure,

and in almost all cases, higher temperature. When the reaction is one between solid phases and vapor, *e. g.*, the dissociation pressure curve of S' ,

$$S' = S'' + v.$$

The P-T curve always goes from the invariant point to regions of lower temperature and pressure; since Δv is large (except under high pressure), the slope of the curve is comparatively small. In reactions of the type,



in which both liquid and vapor take part, dp/dt may be large or small, positive or negative. We will consider this case in detail later.

We will now consider the application of the above principles to the determination of the sequence of P-T curves around an invariant point.¹ The method used is based on the fact that the order of the slopes dp/dt of the various curves is determined by the masses of the phases which take part in the various univariant reactions. This is evident from Gibbs' Equation 129, or from the expanded form of 129 given below. The method of application of this criterion is by considering what curves will coincide when we vary the composition of different phases. If by varying the composition of one phase in a certain direction n phases get on the one-fold (n), then, as proved above, the P-T curves of the two univariant equilibria formed by these n phases with each of the other two phases will coincide; these two curves must be adjoining curves, and no other curves can be between them. By repeating this reasoning, assuming the composition of the same phase to change in other directions, or assuming the composition of another phase to change, the relative positions of the P-T curves, the order in which they succeed one another around the invariant point, can be deduced. The stable and metastable portions can be distinguished by means of the theorems previously given.

First consider a simple case, the curves at the quadruple point $\text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O-Na}_2\text{SO}_4\text{-L-V}$ in the binary system $\text{H}_2\text{O-Na}_2\text{SO}_4$. The Na_2SO_4 content of these phases increases in the order $V < L < \text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O} < \text{Na}_2\text{SO}_4$; this is indicated in Fig. 1. The P-T curve of the condensed system $L + \text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$ is practically vertical, going to regions of higher pressure; the dissociation-pressure curve, the curve $V + \text{Na}_2\text{SO}_4\text{-}10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$, goes to lower temperatures and lower pressures. They are so drawn in Fig. 1. Now, if the two solid phases were to coincide in composition, these two curves would coincide, metastably, since the phases V and L lie on the same side of the two solid phases. Hence there

¹ The question of the sequence of P-T curves around an invariant point has been discussed by Smits (*Proc. Acad. Sci. Amsterdam*, 18, 800-804 (1916)), and by Schreinemakers, "Die Heterogenen Gleichgewicht," 1, and, in more detail, in the series of papers in "In-, mono-, and divariant equilibria" in *Proc. Acad. Sci. Amsterdam*, beginning with 18, 116-26 (1916). The treatment in this paper is from a totally different point of view.

can be no other curves in between these two. Now, if the liquid were to have the same composition as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the curves $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{L} + \text{V}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{L}$ would coincide, stable to stable. But, since there can be no curve between the two curves $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{L}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{V}$, the curve $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{L} + \text{V}$ must lie between the curves $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{L}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{V}$; otherwise it could not coincide with the former curves. Also, if V and L were to have the same composition, the curves $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{L} + \text{V}$ and $\text{Na}_2\text{SO}_4 + \text{L} + \text{V}$ would coincide, stable to metastable. Hence the metastable portion of curve $\text{Na}_2\text{SO}_4 + \text{L} + \text{V}$ must lie between the curve $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{L} + \text{V}$ and either the curve $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{V}$ or the curve $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{L}$. But it cannot be in the former position, because, as we have just seen, no curves may lie between the curves $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{L} + \text{V}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{L}$. Hence the metastable portion of curve $\text{Na}_2\text{SO}_4 + \text{L} + \text{V}$ must lie between the stable portions of curves $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{L} + \text{V}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{V}$, as drawn in Fig. 1.

Fig. 1.—The sequence of P-T curves at the quadruple point V-L- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - Na_2SO_4 .

Now consider a three-component system, and assume that the phases

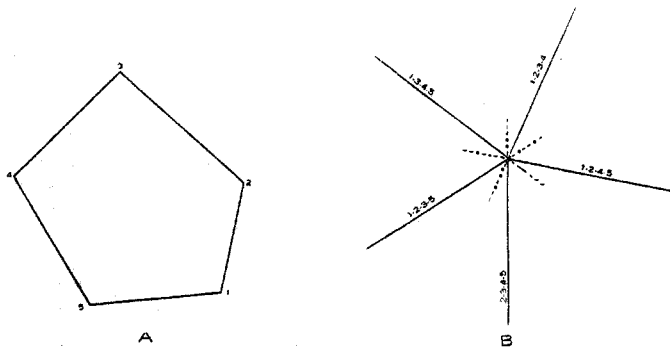


Fig. 2.—The sequence of P-T curves around a quintuple point. The compositions of the five phases are shown in Fig. 2A; the sequence of P-T curves in Fig. 2B.

have the compositions shown in Fig. 2A. If the composition of phase P'' were to change so that phases P' , P'' and P''' lay on a straight line, then the curves $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^V$ would coincide; stable to metastable, since phases P^{IV} and P^V are on the same side of the line $P'P''P'''$. Draw them in any arbitrary position, as shown in Fig. 2B. Now, if phase P''' were to change in composition so that phases P'' , P''' and P^{IV} lay on a straight line, curves $P' + P'' + P''' + P^{IV}$ and $P'' + P''' + P^{IV} + P^V$ would coincide, stable to metastable. Hence these curves must lie as drawn in Fig. 2B; no curve may lie between these two curves. If phase P^{IV} were to get on the line $P''P^V$, curves $P' + P'' + P^{IV} + P^V$ and $P'' + P''' + P^{IV} + P^V$ would coincide metastably; curve $P' + P'' + P^{IV} + P^V$ must lie as shown, and no curve may lie between these two curves. Similarly, curve $P' + P'' + P^{IV} + P^V$ must lie between the metastable portions of curves $P' + P'' + P''' + P^V$ and $P' + P''' + P^{IV} + P^V$.

Let us see under what conditions the stable parts of curves $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P^{IV} + P^V$ can coincide. For such a coincidence to take place, phase P'' would have to change its composition until it lay on the line $P'P^{IV}$. Before it could do this, it would just get on, then cross, the line $P'P'''$ (Fig. 2A); this would cause curves $P'P''P'''P^{IV}$ and $P'P''P'''P^V$ to coincide, metastably, then change places. There then would be no curves between the stable portions of $P' + P'' + P^{IV} + P^V$ and $P' + P''' + P^{IV} + P^V$; as phase P'' approached the line $P'P^V$, these two curves would get closer to each other, and would coincide in their stable portions when phase P'' got on the line $P'P^{IV}$.

The same method may be extended to systems of more components. In the case of quaternary systems, as stated before, the onefold n is a plane, etc.

Let us apply the above considerations to the quintuple points in the ternary system $H_2O-K_2SiO_3-SiO_2$, and pay particular attention to the question of the sequence of the P-T curves around the invariant (quintuple) point. For the purpose of this discussion, we will combine the above theorems in regard to the conditions under which P-T curves coincide and in regard to the factors which determine whether the curves coincide stable to stable or stable to metastable in the following rule: Whenever in a ternary system three phases lie on a straight line, the P-T curves of all the ternary univariant equilibria containing these three phases coincide with each other and with the P-T curve of the univariant binary equilibrium between the three phases alone. When the other two phases at the quintuple point lie on the same side of the line on which lie the compositions of the three reacting phases, the curves coincide stable to metastable; when the other two phases lie on opposite sides of the line

on which lie the composition of the three reacting phases, the curves coincide stable to stable.

The composition of all the phases which are met with in the ternary system $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3-\text{SiO}_2$ are shown in Fig. 3.¹ The points indicating the composition of the solid phases are indicated. In treating this system we will assume that the vapor phase contains H_2O only. The presence of K_2O in the vapor has been detected,² but the amount was very small. The boundary curves show the change in composition of the liquid phase

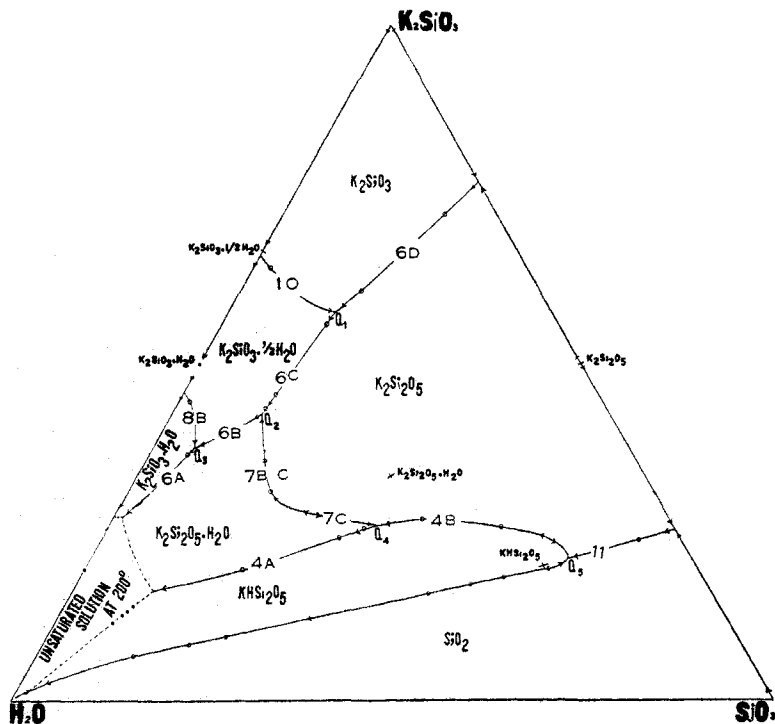


Fig. 3.—The boundary curves in the ternary system $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3-\text{SiO}_2$. The compound stable in contact with liquid and vapor in each field is shown by the large letters; the point representing the composition of the compound, by the small letters. Arrows show the direction of falling temperature. The broken line is the isotherm at 200° . For explanation of the numbers on the curves, see the legend to Fig. 5.

in the univariant equilibria $S' + S'' + L + V$ as we pass from quintuple point to quintuple point or from quintuple point to quadruple point in the limiting binary systems. The composition of the liquid phase at each quintuple point is given by the point of intersection of three boundary curves; these points are designated by the letters Q_1, Q_2 , etc. The P-T

¹ For a detailed account of the experimental study of this system, see Morey and Fenner, *THIS JOURNAL*, **39**, 1173-1229 (1917). Figs. 3 and 4 are copied from there.

² Consult the discussion of this point on p. 1210 of the above paper.

curves experimentally determined are shown in Fig. 4. Fig. 5 is a diagrammatic representation of the P-T curves, which is easier to follow.

At quintuple point Q_1 we have the 3 solid phases K_2SiO_3 , $K_2SiO_3 \cdot 0.5H_2O$ and $K_2Si_2O_5$, the liquid phase whose composition is given by the point Q_1 , and the vapor phase, whose composition is given by the H_2O apex of the component triangle (Fig. 3). Since K_2SiO_3 , $K_2SiO_3 \cdot 0.5H_2O$ and V lie on a straight line, the curves $K_2Si_2O_5 + K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + V$ (curve 10a)¹ and $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ (curve 10b) will coincide; metastably, since the phases $K_2Si_2O_5$ and L lie on the same side of the line V- K_2SiO_3 . These two curves also coincide with the dissociation-pressure curve of $K_2SiO_3 \cdot 0.5H_2O$ in the binary system $H_2O-K_2SiO_3$ (curve 10a + 10b), Fig. 5, hence their position is as shown.

If the composition of the phases were such that V, L, and $K_2Si_2O_5$ lay on a straight line, the P-T curves of the univariant equilibrium $K_2SiO_3 + K_2Si_2O_5 + L + V$ (curve 6d) would coincide, metastably, with the P-T curve $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$ (curve 6c); if the phases V, L, K_2SiO_3 lay on a straight line, the curve $K_2SiO_3 + K_2Si_2O_5 + L + V$ (curve 6d) would coincide, stably, with the curve $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O$

¹ The curves are numbered as in Figs. 3, 4 and 5. In Fig. 3 only curves of the type $S' + S'' + L + V$ are shown. In Fig. 5 the P-T curves of the condensed systems are not numbered; their position is obvious.

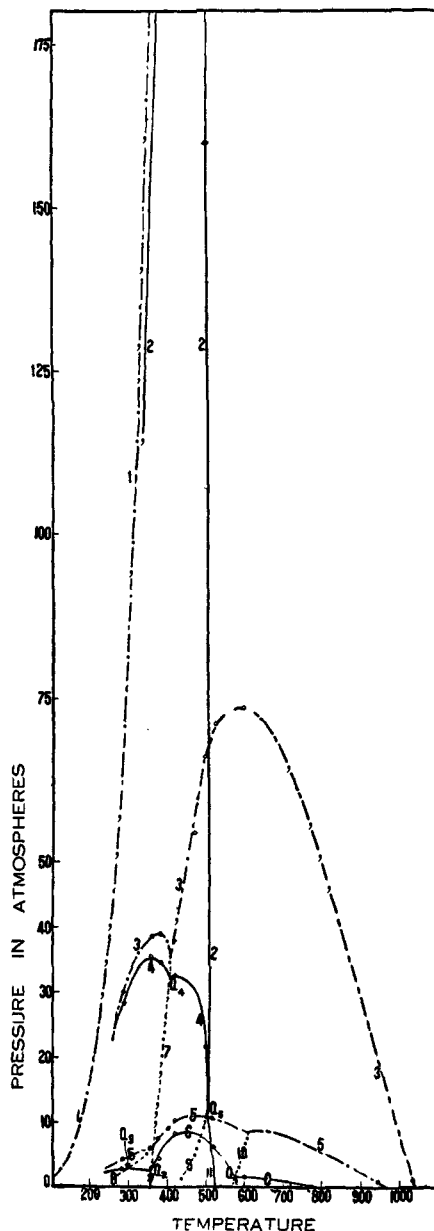


Fig. 4.—The P-T curves for the various univariant systems. The dot-dash curves represent binary systems; the full curves, the ternary univariant systems 2 solids-L-V; the dotted curves, the dissociation-pressure curves, the equilibria 3 solids-V. For explanation of the numbers on the curves, see the legend to Fig. 5.

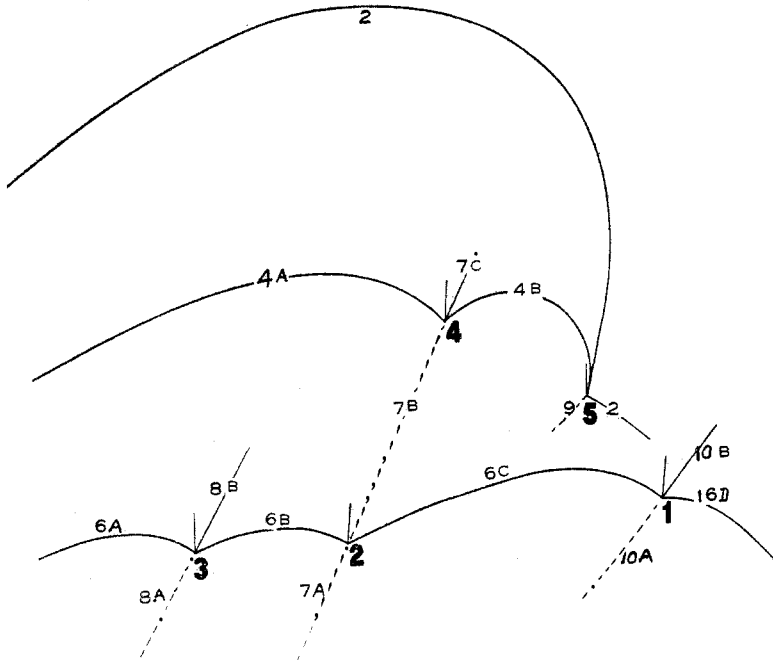


Fig. 5.—A diagrammatic representation of the ternary univariant equilibria shown in Fig. 4. Similar curves in Figs. 3, 4, and 5 are numbered the same. Following is a list of the phases stable along each curve:

- Curve 2 $\text{KHSi}_2\text{O}_5 + \text{SiO}_2 + \text{L} + \text{V}$.
 " 4a $\text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{KHSi}_2\text{O}_5 + \text{L} + \text{V}$.
 " 4b $\text{K}_2\text{Si}_2\text{O}_6 + \text{KHSi}_2\text{O}_5 + \text{L} + \text{V}$.
 " 6a $\text{K}_2\text{SiO}_3 \cdot \text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{L} + \text{V}$.
 " 6b $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{L} + \text{V}$.
 " 6c $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 + \text{L} + \text{V}$.
 " 6d $\text{K}_2\text{SiO}_3 + \text{K}_2\text{Si}_2\text{O}_6 + \text{L} + \text{V}$.
 " 7a $\text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 + \text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{V}$.
 " 7a + 7b $\text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 + \text{KHSi}_2\text{O}_5 + \text{L} + \text{V}$.
 " 7b + 7c $\text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 + \text{L} + \text{V}$.
 (7b + 7c together, Curves Q_2Q_4 , from Q_2 to the quadruple point $\text{K}_2\text{Si}_2\text{O}_6 + \text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{L} + \text{V}$ in binary system (Fig. 3); Curve 7c alone, Curve Q_2Q_4 from quadruple point to Q_4 .)
 " 7a + 7b + 7c $\text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 + \text{V}$ (binary system $\text{H}_2\text{O}-\text{K}_2\text{Si}_2\text{O}_6$).
 " 8a $\text{K}_2\text{SiO}_3 \cdot \text{H}_2\text{O} + \text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{K}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{V}$.
 " 8b $\text{K}_2\text{SiO}_3 \cdot \text{H}_2\text{O} + \text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{L} + \text{V}$.
 " 8a + 8b $\text{K}_2\text{SiO}_3 \cdot \text{H}_2\text{O} + \text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{V}$ (binary system $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3$).
 " 9 $\text{KHSi}_2\text{O}_5 + \text{K}_2\text{Si}_2\text{O}_6 + \text{SiO}_2 + \text{V}$.
 " 10a $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{K}_2\text{SiO}_3 + \text{K}_2\text{Si}_2\text{O}_6 + \text{V}$.
 " 10b $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{K}_2\text{SiO}_3 + \text{L} + \text{V}$.
 " 10a + 10b $\text{K}_2\text{SiO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} + \text{K}_2\text{SiO}_3 + \text{V}$ (binary system $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3$).
 " 11 $\text{K}_2\text{Si}_2\text{O}_6 + \text{SiO}_2 + \text{L} + \text{V}$.

+ L + V (curve 1ob). Hence curve $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6d) must lie between the metastable prolongation of curve $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$ (6c) and the stable portion of $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ (1ob). The position of the latter curve being fixed, the position of the curves $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6d) and $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$ (6c) must either be as shown at Q_1 , Fig. 5, or the position of these curves in regard to the curves $K_2Si_2O_5 + K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + V$ (10a) and $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ (1ob) must be reversed. That the latter arrangement cannot be correct is shown by the fact that if $K_2SiO_3 \cdot 0.5H_2O - L - K_2Si_2O_5$ were on a straight line, the curve $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$ (6c) would coincide with the curve $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L$, the P-T curve of the condensed system. But such a coincidence is possible only with the arrangement shown in Fig. 3; the reversed arrangement cannot be the correct one.

In order to show further the relation between the composition diagram and the P-T diagram, let us consider under what conditions the curves $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L$ (the P-T curves of the condensed system) and $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6d) will coincide stably. For this coincidence to take place, it is necessary that the phases L, K_2SiO_3 and $K_2Si_2O_5$ lie on a straight line in the composition diagram (Fig. 3), which intersects internally the line V- $K_2SiO_3 \cdot 0.5H_2O$. On reference to Fig. 3 we see that before the phases can take on the position mentioned above, it will be necessary for the phases K_2SiO_3 , $K_2SiO_3 \cdot 0.5H_2O$ and $K_2Si_2O_5$, then the phases V, L and K_2SiO_3 , to fall on straight lines. But in the P-T diagram, the first of these will result in the curves $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L$ and $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + V$ (10a) approaching each other, coinciding, then again diverging, having changed places. Similarly, as a result of the second triplet of phases getting on a straight line, the curves $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6d) and $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ (10a) will change places. The curves $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L$ and $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6d) now lie next to each other, their stable portions adjoining, and when the phases L, K_2SiO_3 and $K_2Si_2O_5$ fall on a straight line these two curves will coincide in their stable portions.

The quintuple point Q_3 is exactly similar to Q_1 ; instead of $K_2SiO_3 \cdot 0.5H_2O$, K_2SiO_3 and $K_2Si_2O_5$ we have $K_2SiO_3 \cdot H_2O$, $K_2SiO_3 \cdot 0.5H_2O$ and $K_2Si_2O_5 \cdot H_2O$, respectively. Making these substitutions, the discussion of Q_1 will apply to Q_3 .

Quintuple points Q_2 and Q_4 also are similar to each other. Both contain the same three phases V, $K_2Si_2O_5 \cdot H_2O$ and $K_2Si_2O_5$. At Q_2 we also have the liquid represented by the point Q_2 and the solid phase $K_2SiO_3 \cdot$

0.5H₂O; at Q₄ we have the liquid represented by the point Q₄ and the solid phase KHSi₂O₅. Since in both systems the phases V, K₂Si₂O₅.H₂O and K₂Si₂O₅ lie on a straight line, the curve V + K₂Si₂O₅.H₂O + K₂Si₂O₅ + K₂SiO₃.0.5H₂O (7a), which proceeds from Q₂ to lower temperatures and pressures, and the curve V + K₂Si₂O₅.H₂O + K₂Si₂O₅ + KHSi₂O₅ (7b + 7a), which proceeds from Q₄ to lower temperature and pressure, and the curve V + L + K₂Si₂O₅.H₂O + K₂Si₂O₅ (7b + 7c), which proceeds from both Q₂ and Q₄ to higher temperatures and pressures, coincide with each other and with the dissociation-pressure curve of K₂Si₂O₅.H₂O in the binary system H₂O-K₂Si₂O₅ (curve 7a + 7b + 7c). The position of the other curves which proceed from Q₂ and Q₄ are easily found by the same mode of reasoning as that applied to the curves at Q₁.

The quintuple point Q₅ differs from the others in the system in the fact that the liquid phase Q₅ lies inside the triangle K₂Si₂O₅-SiO₂-KHSi₂O₅, and hence is a eutectic point, while all the others are transition points. The exact position of Q₅ is uncertain, and it has been assumed that it lies on the line H₂O-KHSi₂O₅. Hence the curves V + L + KHSi₂O₅ + SiO₂ (curve 2) and V + L + KHSi₂O₅ + K₂Si₂O₅ (curve 4b) will coincide stably with each other and with the melting point curve of KHSi₂O₅ (a condensed system). If the phases KHSi₂O₅, L, and SiO₂ were to lie on a straight line, the curves V + L + KHSi₂O₅ + SiO₂ (curve 2) and L + K₂Si₂O₅ + KHSi₂O₅ + SiO₂ (the condensed system) would coincide stably; if the phases V, KHSi₂O₅, and SiO₂ were to lie on a straight line, the curves V + L + KHSi₂O₅ + SiO₂ (curve 2) and V + K₂Si₂O₅ + KHSi₂O₅ + SiO₂ (curve 9) would coincide metastably. Hence the curve V + L + KHSi₂O₅ + SiO₂ (curve 2) (and also V + L + KHSi₂O₅ + K₂Si₂O₅ (curve 4b), since the two coincide at the invariant point) must lie between the stable portion of curve L + K₂Si₂O₅ + KHSi₂O₅ + SiO₂, the P-T curve of the condensed system, and the metastable portion of the curve V + K₂Si₂O₅ + KHSi₂O₅ + SiO₂ (curve 9), the dissociation pressure curve. Similar reasoning shows that curve K₂Si₂O₅ + SiO₂ + L + V (curve 11) must lie between the metastable portions of the P-T curve of the condensed system and the dissociation-pressure curve.

We have seen that from a knowledge of the composition of the phases we are able to fix the sequence of the P-T curves around a quintuple point. Also, knowing that the P-T curves of condensed systems go from the invariant point to regions of higher pressure and, in almost all cases, higher temperature, and that dissociation pressure curves go from the invariant point to regions of lower temperature and pressure, we are able to fix the position of the P-T curves within fairly narrow limits. Let us now consider the slopes of these P-T curves in more detail, and pay especial attention to the change in slope as we move along a curve.

When all the phases have a fixed composition, as is the case in a dissociation-pressure curve when only one of the components is volatile, or when the composition of a variable phase changes but little with pressure, as is the case in the equilibrium between several solids and liquid, the P-T curve of a condensed system, the slope of the P-T curve changes but slowly. But when we have a phase whose composition changes materially as we move along the P-T curve, the slope of the curve may become radically different. In the first two cases mentioned, the value of $\Delta\eta/\Delta v$ changes but little; in the third case it may change materially in magnitude, and may even change sign. Let us examine this case in detail. To prevent our equations from becoming too cumbersome, we will restrict our discussion to systems of three components; all the equations developed can readily be extended to any other case by putting in the requisite number of composition terms in the determinantal coefficients.

We have seen that the relation between the variations in pressure and temperature in any univariant equilibrium is given by Gibbs' Equation 129, which for a 3-component system reduces to

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & m_3' \\ \eta'' & m_1'' & m_2'' & m_3'' \\ \eta''' & m_1''' & m_2''' & m_3''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & m_3' \\ v'' & m_1'' & m_2'' & m_3'' \\ v''' & m_1''' & m_2''' & m_3''' \\ v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}$$

In this the composition of the phases is represented by the actual masses of the components m_1, m_2, m_3 . By setting $m_1 + m_2 + m_3 = 1$;

$$\frac{m_2}{m_1 + m_2 + m_3} = m_2 = x; \quad \frac{m_3}{m_1 + m_2 + m_3} = m_3 = y, \quad \text{and substituting,}$$

adding the third and fourth columns to the second, we get

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & 1 & x' & y' \\ \eta'' & 1 & x'' & y'' \\ \eta''' & 1 & x''' & y''' \\ \eta^{IV} & 1 & x^{IV} & y^{IV} \end{vmatrix}}{\begin{vmatrix} v' & 1 & x' & y' \\ v'' & 1 & x'' & y'' \\ v''' & 1 & x''' & y''' \\ v^{IV} & 1 & x^{IV} & y^{IV} \end{vmatrix}}$$

in which the composition of the phases is represented by the mol fractions x and y of 2 of the components. Expansion of this gives

$$\frac{dp}{dt} = \frac{\eta' \begin{vmatrix} I & x'' & y'' \\ I & x''' & y''' \\ I & x^{IV} & y^{IV} \end{vmatrix} - \eta'' \begin{vmatrix} I & x' & y' \\ I & x''' & y''' \\ I & x^{IV} & y^{IV} \end{vmatrix} + \eta''' \begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x^{IV} & y^{IV} \end{vmatrix} - \eta^{IV} \begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x''' & y''' \end{vmatrix}}{v' \begin{vmatrix} I & x'' & y'' \\ I & x''' & y''' \\ I & x^{IV} & y^{IV} \end{vmatrix} - v'' \begin{vmatrix} I & x' & y' \\ I & x''' & y''' \\ I & x^{IV} & y^{IV} \end{vmatrix} + v''' \begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x^{IV} & y^{IV} \end{vmatrix} - v^{IV} \begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x''' & y''' \end{vmatrix}}$$

Now the coefficients of η' , v' , η'' , v'' , etc., represent the areas of the triangles $P''P'''P^{IV}$, $P'P''P'''$, $P'P''P^{IV}$ and $P'P''P'''$, respectively.¹ It is important to bear in mind the direction in which a given triangle is circumscribed, since, if the area of the triangle $P'P''P'''$ is positive, the area of the triangle $P''P'P'''$ is negative.

Since the above coefficients represent areas, we will denote determinant by the letter A, followed by subscripts indicating which triangle is meant, and the direction in which it is to be circumscribed is given by the order of the subscripts. Thus A_{123} represents the determinant

$$\begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x''' & y''' \end{vmatrix}$$

the area of the triangle $P'P''P_1'''$. Our equation becomes

$$\frac{dp}{dt} = \frac{A_{234}\eta' - A_{134}\eta'' + A_{124}\eta''' - A_{123}\eta^{IV}}{A_{234}v' - A_{134}v'' + A_{124}v''' - A_{123}v^{IV}}$$

Now it is easy to show that

$$\begin{vmatrix} I & x'' & y'' \\ I & x''' & y''' \\ I & x^{IV} & y^{IV} \end{vmatrix} + \begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x^{IV} & y^{IV} \end{vmatrix} = \begin{vmatrix} I & x' & y' \\ I & x''' & y''' \\ I & x^{IV} & y^{IV} \end{vmatrix} + \begin{vmatrix} I & x' & y' \\ I & x'' & y'' \\ I & x''' & y''' \end{vmatrix}$$

or, expressed in areas, that

$$A_{234} + A_{124} = A_{134} + A_{123}.$$

Hence we can eliminate any one of the above coefficients,² and cast our equation into the form

$$\frac{dp}{dt} = \frac{(\eta''' - \eta^{IV}) + \frac{A_{234}}{A_{123}}(\eta' - \eta'') - \frac{A_{134}}{A_{123}}(\eta'' - \eta''')}{(v''' - v^{IV}) + \frac{A_{234}}{A_{123}}(v' - v'') - \frac{A_{134}}{A_{123}}(v'' - v''')}$$

We will now apply this equation to the ternary equilibrium $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$ (curve 6c), the curve which proceeds from the quintuple point Q_2 to quintuple point Q_1 (Fig. 3). Calling $K_2SiO_3 \cdot 0.5H_2O$, S' , and $K_2Si_2O_5$, S'' , our equation becomes

¹ In a 2-component system, the determinantal coefficient represents the lengths of lines; in a 4-component system, volumes of solids; in an n -component system the volume of an n -dimensional solid.

² A similar elimination can of course be made in the general case.

$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \frac{A_{2lv}}{A_{12l}} (\eta' - \eta^h) - \frac{A_{1lv}}{A_{12l}} (\eta'' - \eta^h)}{(v^l - v^v) + \frac{A_{2lv}}{A_{12l}} (v' - v^h) - \frac{A_{1lv}}{A_{12l}} (v'' - v^h)}$$

At Q_2 , the terms $(\eta^l - \eta^v)$ and $(v^l - v^v)$, both of which are negative and much larger than the other terms, preponderate; dp/dt is positive. As with increasing temperature the liquid traces the curve Q_2Q_1 , the triangle A_{12l} becomes smaller, while the triangles A_{2lv} and A_{1lv} become larger. The values of the coefficients of $(\eta' - \eta^h)$ and $(\eta'' - \eta^h)$ in the numerator and $(v' - v^h)$ and $(v'' - v^h)$ in the denominator thus increase rapidly. Since the value of $(v^l - v^v)$ is comparatively large, this increase in the coefficients at first affects materially the value of the numerator only. As the liquid follows the curve Q_2Q_1 the value of the last two terms of the numerator soon becomes equal to the value of the first term. The numerator then becomes zero, dp/dt becomes zero, and the curve has a horizontal tangent. It will be observed that such a point of maximum pressure is found on many of the P-T curves representing univariant equilibrium between two solids, liquid and vapor in the system. It is most pronounced in the univariant equilibrium $KHSi_2O_5 + SiO_2 + L + V$.

On further increase in temperature the numerator becomes positive, the denominator remains negative, hence dp/dt is negative. This continues until, in the case we are considering, the phase K_2SiO_3 makes its appearance at the quintuple point Q_1 . Let us consider the metastable continuation of the curve $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$ (Curve 6c).

Beyond Q_1 , on further increase in temperature the triangle A_{12l} approaches zero, the coefficients of $(v' - v^h)$ and $(v'' - v^h)$ in the denominator increase rapidly, reaching such a value that the sum of the last two terms in the denominator become numerically equal to the first, in spite of the large value of $(v^l - v^v)$. The denominator then becomes zero, dp/dt becomes infinite, and the P-T curve has a vertical tangent. Beyond this point dp/dt again becomes positive. An illustration of this case is found in the P-T curves of the monovariant systems $K_2Si_2O_5 + KHSi_2O_5 + L + V$ (curve 4b) and $SiO_2 + KHSi_2O_5 + L + V$ (curve 2), which proceed from Q_5 to higher temperature and pressure.

On further increase in temperature the liquid will lie on the line $K_2SiO_3 \cdot 0.5H_2O - K_2Si_2O_5$; the area A_{12l} now is zero, and our equation becomes

$$\frac{dp}{dt} = \frac{A_{2lv} (\eta' - \eta^h) - A_{1lv} (\eta'' - \eta^h)}{A_{2lv} (v' - v^h) - A_{1lv} (v'' - v^h)}$$

In harmony with our previous considerations, we see that at this point the curve has the same slope as the common melting-point curve of $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5$. This is an illustration of the case that the phases only casually have such a composition that a linear relation is possible;

the curves are tangent. In the usual case which we are assuming throughout, dp/dt is positive.

We will now consider the application of our equation to a different type of equilibrium between two solids, liquid and vapor. Consider the equilibrium $K_2Si_2O_5 \cdot H_2O + K_2Si_2O_5 + L + V$ (curve $7b + 7c$). In the concentration diagram the course of this equilibrium is the curve Q_2Q_4 , the boundary curve between the $K_2Si_2O_5$ and $K_2Si_2O_5 \cdot H_2O$ fields. Since the two solid phases and vapor lie on a straight line our equation is

$$\frac{dp}{dt} = \frac{A_{234} (\eta' - \eta^v) - A_{134} (\eta'' - \eta^v)}{A_{234} (v' - v^v) - A_{134} (v'' - v^v)},$$

the equation of the dissociation pressure curve of $K_2Si_2O_5 \cdot H_2O$. Hence, as we saw before, the P-T curves of the equilibrium $K_2Si_2O_5 \cdot H_2O + K_2Si_2O_5 + L + V$ coincide with the dissociation-pressure curve of $K_2Si_2O_5 \cdot H_2O$. The slope of this curve will remain positive as we go along the boundary curve $K_2Si_2O_5 - K_2Si_2O_5 \cdot H_2O$, and will not show anything special until the liquid phase falls on the line $V - K_2Si_2O_5$. Here the two triangles A_{234} and A_{134} become zero at the same time, and our equation becomes intermediate. This point corresponds to the termination of the curve at the quadruple point $K_2Si_2O_5 + K_2Si_2O_5 \cdot H_2O + L + V$ in the binary system $H_2O - K_2Si_2O_5$. When the liquid has crossed the line $H_2O - K_2Si_2O_5$ the areas of all the triangles change sign, hence dp/dt remains positive, and with decreasing temperature we retrace the same P-T curve to the quintuple point Q_4 . This portion of the curve also corresponds to the equilibrium $KHSi_2O_5 + K_2Si_2O_5 + K_2Si_2O_5 \cdot H_2O + V$.

In the first equilibrium we considered, the univariant equilibrium $K_2SiO_3 \cdot 0.5H_2O + K_2Si_2O_5 + L + V$, our assumption that the vapor phase is pure H_2O was practically without influence; the vapor phase might contain appreciable quantities of either K_2O or SiO_2 or both without appreciably affecting the course of the P-T curve. The only effect would be a slight diminution of the areas A_{1lv} and A_{2lv} , the coefficients of $(\eta'' - \eta^l)$ and $(v'' - v^l)$, and $(\eta' - \eta^l)$ and $(v' - v^l)$, respectively. In the second case, however, the assumption is of importance; only in the improbable case that the ratio of SiO_2/K_2O in the vapor is the same as in the solid, *i. e.*, $2/1$, would it still be true that equilibrium $K_2Si_2O_5 + K_2Si_2O_5 \cdot H_2O + L + V$ coincides with the equilibria $K_2Si_2O_5 + K_2Si_2O_5 \cdot H_2O + K_2SiO_3 \cdot 0.5H_2O + V$ and $K_2Si_2O_5 + K_2Si_2O_5 \cdot H_2O + KHSi_2O_5 + V$, and with the dissociation-pressure curve of $K_2Si_2O_5 \cdot H_2O$. In case the vapor contained a small amount of K_2O , the curve $K_2Si_2O_5 + K_2Si_2O_5 \cdot H_2O + L + V$ would consist of 2 parts, one on one side of, the other on the other side of, the dissociation-pressure curve, and the two parts would join at the top in a smooth curve, whose point of maximum temperature would be found at the point where the entropy change in the reaction passes

through zero, hence on the K_2O side of the line $K_2Si_2O_5 - K_2Si_2O_5 \cdot H_2O$. But unless the K_2O content of the vapor is large, which is improbable, the effect will be small; the area $K_2Si_2O_5 - K_2Si_2O_5 \cdot H_2O - V$, instead of being zero, will be a very small quantity, which will have but a slight influence on the above relations; the curves would, instead of coinciding, lie very close to each other.

All the P-T curves so far discussed have had their end points inside the component triangle; all of them have gone from one quintuple point to another. Let us now consider one which goes from a quintuple point to a quadruple point in one of the limiting binary systems, *e. g.*, the curve $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ (curve 10*b*), which goes from quintuple point Q_1 to the quadruple point $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ in the binary system $H_2O - K_2SiO_3$. Since the phases V , $K_2SiO_3 \cdot 0.5H_2O$, and K_2SiO_3 lie on a straight line, the area of the triangle $V - K_2SiO_3 \cdot 0.5H_2O - K_2SiO_3$ is zero, and the equation on the P-T curve reduces to

$$\frac{dp}{dt} = \frac{A_{2vl} (\eta' - \eta^v) - A_{1vl} (\eta_1' - \eta^v)}{A_{2vl} (v' - v^v) - A_{1vl} (v_1' - v^v)}$$

in which the exponents (') and (") refer to the solid phases K_2SiO_3 and $K_2SiO_3 \cdot 0.5H_2O$, respectively. This is evidently the dissociation-pressure curve of $K_2SiO_3 \cdot 0.5H_2O$; in harmony with our previous conclusions, the slope of the curve $K_2SiO_3 + K_2SiO_3 \cdot 0.5H_2O + L + V$ (10*b*) is the same as that of the dissociation-pressure curve of $K_2SiO_3 \cdot 0.5H_2O$ (10*a* + 10*b*). At the quintuple point it is evident that both numerator and denominator are negative, dp/dt therefore positive. Also, the denominator being much larger than the numerator, the numerical value of dp/dt is less than unity. As the liquid approaches the side of the component triangle along the boundary curve, both the triangles A_{2vl} and A_{1vl} diminish the size in about the same proportion, and the value of dp/dt will not change materially. When the liquid gets on the line $H_2O - K_2SiO_3$, both triangles become zero simultaneously, and the equation becomes indeterminate; the curve is at its end point at the quadruple point in the binary system.

It is evident that when the phases have the composition indicated above, no maximum is possible in the P-T curve of the univariant equilibrium. However, if the vapor phase, instead of being pure H_2O , contained a small amount of SiO_2 , the curve would have a horizontal tangent before the phases L , $K_2SiO_3 \cdot 0.5H_2O$, and K_2SiO_3 fell on a straight line, as can be readily seen from the equation of the curve.

In the preceding paper the theorem that along a boundary curve in a condensed system the temperature is a maximum at the point where the boundary curve crosses the line joining the composition of the two solid phases is derived. It is interesting to compare the condition for maximum temperature under the vapor pressure of the system. An example

is the curve $K_2Si_2O_5 + KHSi_2O_5 + L + V$ (curve 4*b*), which goes from Q_4 to Q_5 . The equation of this curve is

$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \frac{A_{1lv}}{A_{12l}} (\eta' - \eta^l) - \frac{A_{1lv}}{A_{12l}} (\eta'' - \eta^l)}{(v^l - v^s) + \frac{A_{2lv}}{A_{12l}} (v' - v^l) - \frac{A_{1lv}}{A_{12l}} (v'' - v^l)},$$

in which the exponents (*l*) and (*v*) refer to the phases $K_2Si_2O_5$ and $KHSi_2O_5$, respectively. The condition for a temperature maximum is that the denominator of this expression shall become zero; dp/dt become infinite. Since the volume difference between vapor and liquid is far greater than that between solid and liquid, the denominator will become zero only when the coefficients of the last two volume differences become very large, hence when the area of the triangle $K_2Si_2O_5 - KHSi_2O_5 - L$ becomes very small. This point will be reached slightly before the liquid phase lies on the line $K_2Si_2O_5 - KHSi_2O_5$, hence the point of maximum temperature has been displaced slightly in the direction of the volatile component.

Summary.

In this paper the curves which represent the relation between the variations in pressure and temperature in monvariant systems, the P-T curves, are discussed on the basis of equations deduced by Gibbs. Theorems are developed showing under what conditions different P-T curves coincide, when the curves coincide throughout their course and when they are tangent, and whether they coincide in their stable or metastable portions. On the basis of the above theorems a method is developed for determining the order of succession of the P-T curves which intersect at an invariant in a system of any number of components. This application is illustrated by applying it to the P-T curves proceeding from the quintuple points in the ternary system $H_2O - K_2SiO_3 - SiO_2$. In addition, Gibbs' general equation for the slope of a P-T curve is discussed, and a method given for casting it into a form convenient for practical use. The application of this equation to the change in slope of a P-T curve with change in composition of a variable phase is illustrated by discussing various curves in the above-mentioned ternary system.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY.]

A LEAD STANDARD CELL AND A DETERMINATION OF THE POTENTIAL OF THE LEAD ELECTRODE.

By W. E. HENDERSON AND GEBHARD STEGEMAN.

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While engaged in a study of the transition temperature of some hydrated salts, a galvanic cell came under our observation which exhibited