

inaccurate data, and of deducing the vapor-pressure temperature function from meager data.

In conclusion, it may be stated that the theoretical bearing of the rule regarding the entropy of vaporization will be the subject of a future communication.

Summary.

The rule concerning the entropy of vaporization, previously published by the author, is shown to apply to all liquid metals for which the experimental data are trustworthy, giving a general vapor-pressure equation,

$$\log p = -3140a/T + 7.85 + \log a,$$

where a is a constant characteristic of each substance, and p is expressed in millimeters of mercury.

Values of a for metals for which we have but meager or unsatisfactory vapor-pressure data have been calculated.

These values of a permit the calculation of the heat of vaporization, and of the volatility of metals at any temperature.

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THE LAWS OF CHEMICAL EQUILIBRIUM.

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In discussing the relations which exist among the variables in chemical systems, the safest guide is the paper, now a classic, due to the genius of Willard Gibbs. Chemists in general have fought shy of it, owing to the extremely mathematical setting with which he surrounds his arguments and the result of this is that much ink has been spilled in proving, by roundabout methods, theorems which are either explicitly stated by Gibbs or are so readily deducible from his equations as to be implicit in his work. In the following pages we have attempted to popularize, insofar as such a term can be used in such a connection, the derivation of the fundamental equations and to deduce from them such extra formulas as are required for the derivation of the theorems bearing on the chemical side of equilibrium. The actual applications of the theorems will be discussed in later papers.

The greatest importance of this form of attack lies in the fact that the relations apply equally to concentrated and dilute solutions. The approximate formulas used at present for dilute solutions necessarily break down and are worse than useless as qualitative guides when examining the complicated systems which must be dealt with in geophysical problems. These approximate formulas can, however, be derived from the general ones by means of the necessary simplifying assumptions and such

a derivation has often the advantage of emphasizing the assumptions in a manner never equaled in other methods.

Our initial discussion of equilibrium conditions is frankly inadequate but it will serve for many purposes and for those who wish real mathematical exactness nothing can hope to equal the original treatment by Gibbs.

The conditions for equilibrium are deduced from the fact that any closed system tends to reach a condition in which as much of the energy as possible has been dissipated as heat, or to be more exact, the system approaches the condition of maximum entropy consistent with its energy.¹ We can derive as many kinds of particular conditions as the kinds of energy we are considering. For example, we may have (a) thermal conditions regulating the flow of heat, (b) mechanical conditions regulating the movement of matter without change of composition, (c) chemical conditions regulating the changes in composition of the phases present, (d) electrical conditions, and so on. Usually only a few of these are used at one time, as the general equations become cumbersome when too many variables are present.

Let us consider a system at equilibrium consisting of a number of phases—vapor, solid and liquid—of various components. We shall assume that it is shut off from outside action by a rigid non-conducting envelope. This means no loss of generality, as, if the system is already in equilibrium it will still be so if enclosed in such an envelope. The following results are obtained:

I. Thermal Conditions.—The temperature must be uniform; otherwise heat will flow from high to low temperature.

II. Mechanical Conditions.—If only ordinary hydrostatic pressure is considered it must be everywhere equal, but if gravity is taken account of or membranes are present this must be modified.

III. Chemical Conditions.—The variable which determines chemical equilibrium is not so familiar as temperature, pressure or electrical potential and a few words are therefor necessary in explanation of what is best called the "chemical potential" of a substance. Consider a particular substance present in two different phases and for a moment deal with these phases separately. Let a supply of the substance be available in a reference state and an infinitesimal amount of it pass from this state to one of the phases. Keep the volume and entropy of the phase constant by sub-

¹ Gibbs' statements are as follows:

I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of the entropy shall either vanish or be negative.

II. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variations of its energy shall either vanish or be positive.

tracting heat and changing the pressure. Let the energy required for the transfer be $\mu' dm$ in the case of the one phase and $\mu'' dm$ for the other, dm being the amount of substance transferred. Unless $\mu' dm$ be equal, to $\mu'' dm$, diminution of energy will take place if we let the amount dm pass in this way from the phase from which μdm is greater through the reference phase into the phase where it is less. Since this leaves the reference state unchanged, we may consider the change as merely the transfer of dm from one phase to the other. For equilibrium between the two phases, therefore, according to our hypothesis, μ' must be equal to μ'' . The variable μ which bears to the mass of a component the same relation that pressure bears to volume, temperature to entropy or electric potential to quantity of electricity is what we call the "chemical potential"¹ of a substance. For equilibrium, therefore, we must have equality of chemical potentials wherever a substance occurs in different phases.

These constitute the conditions for the variables usually considered, but we can find the conditions for other variables provided we know the form of the energy terms involved.

Development of Mathematical Relations.

Since for chemical purposes we need to deal mainly with μ and the changes in μ , some necessary relations containing this variable will first be deduced. Let a phase of variable composition be subjected to slight change by having work done on it, heat added to it and its composition changed. The total energy² change is given by $d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n$, where $td\eta$ is the heat added, pdv the work done, and the other terms are the amounts of energy gained or lost in the addition or subtraction of the small amounts of the various components.

This leads as usual to

$$d(\epsilon - t\eta + pv) = -\eta dt + v dp + \mu_1 dm_1 + \dots + \mu_n dm_n.$$

This gives us

$$n \text{ relations like } \left(\frac{\partial \mu_r}{\partial t}\right) = -\left(\frac{\partial \eta_r}{\partial m_r}\right) = \text{spec. entropy of component } r \text{ in the phase considered.} \quad (\text{A})$$

$$n \text{ relations like } \left(\frac{\partial \mu_r}{\partial p}\right) = \left(\frac{\partial v_r}{\partial m_r}\right) = \text{spec. vol. of comp. in this phase.} \quad (\text{B})$$

$$\frac{1}{2} n(n-1) \text{ relations like } \left(\frac{\partial \mu_r}{\partial m_q}\right) = \left(\frac{\partial \mu_q}{\partial m_r}\right). \quad (\text{C})$$

The subscripts are omitted as these are obviously in each case simply all the variables with the exception of the one in the denominator. These

¹ " μ " is one of the many quantities which has been called "Thermodynamic Potential" while G. N. Lewis uses the term "partial molal free energy" for it.

² We prefer to use Gibbs' notation for the sake of reference to his papers.

are all valuable relations among the partial differential coefficients¹ of the variable in question. We must remember that the partial differential coefficients with respect to mass are not independent as μ depends evidently on the composition of the phase (and hence on the ratio of the masses present), not on the amount present. This can be taken account of by observing that this means that the potentials are not changed by adding to the phase more of itself, for if we add dm , etc., we get n equations of the type

$$d\mu_1 = \left(\frac{\partial\mu_1}{\partial m_1}\right) dm_1 + \left(\frac{\partial\mu_1}{\partial m_2}\right) dm_2 + \text{etc.}$$

but if $dm_1 : dm_2 : dm_3$, etc., = $m_1 : m_2 : m_3$, etc., $d\mu_1$, $d\mu_2$ and the others must vanish.

$$\begin{aligned} \therefore 0 &= m_1 \left(\frac{\partial\mu_1}{\partial m_1}\right) + m_2 \left(\frac{\partial\mu_1}{\partial m_2}\right) + \dots + m_n \left(\frac{\partial\mu_1}{\partial m_n}\right). \\ 0 &= m_1 \left(\frac{\partial\mu_2}{\partial m_1}\right) + m_2 \left(\frac{\partial\mu_2}{\partial m_2}\right) + \dots + m_n \left(\frac{\partial\mu_2}{\partial m_n}\right). \end{aligned} \quad (D)$$

(n such relations.)

These relations are of great importance in the applications of our equations.

Let this phase of variable composition be our reference phase and consider another phase in equilibrium with it. If this second phase is to remain in equilibrium it must undergo changes to keep the chemical potentials equal to those in the reference phase.

Therefore if $d\mu_1$, etc., be the changes in the reference phase and dm_1' , dm_2' , etc., be the necessary changes in the other phase to keep it in equilibrium, we must have

$$d\mu_1 = \left(\frac{\partial\mu_1'}{\partial m_1'}\right) dm_1' + \left(\frac{\partial\mu_1'}{\partial m_2'}\right) dm_2' + \dots + \left(\frac{\partial\mu_1'}{\partial m_n'}\right) dm_n' + \left(\frac{\partial\mu_1'}{\partial p}\right) dp + \left(\frac{\partial\mu_1'}{\partial t}\right) dt$$

where the right hand symbols refer entirely to the second phase.

$$\text{Similarly } d\mu_2 = \left(\frac{\partial\mu_2'}{\partial m_1'}\right) dm_1' + \left(\frac{\partial\mu_2'}{\partial m_2'}\right) dm_2' + \dots + \left(\frac{\partial\mu_2'}{\partial m_n'}\right) dm_n' + \left(\frac{\partial\mu_2'}{\partial p}\right) dp + \left(\frac{\partial\mu_2'}{\partial t}\right) dt.$$

¹ A number of these coefficients are necessarily positive. For instance all of the types A and B as all substances have positive volume and entropy. Also n of the others, namely $\left(\frac{\partial\mu_1}{\partial m_1}\right)$, $\left(\frac{\partial\mu_2}{\partial m_2}\right)$, ..., $\left(\frac{\partial\mu_n}{\partial m_n}\right)$ where the increase of chemical potential of a component in respect to increase of its own concentration is considered. Going back to the definition of the quantity the reader will see that this simply states that a sub-

$$d\mu_n = \left(\frac{\partial\mu_n}{\partial m_1'}\right) dm_1' + \dots + \left(\frac{\partial\mu_n}{\partial m_n'}\right) dm_n' + \left(\frac{\partial\mu_n}{\partial p}\right) dp + \left(\frac{\partial\mu_n}{\partial t}\right) dt.$$

Multiplying by m_1' , m_2' , etc., and adding, we get

$$m_1'd\mu_1 + m_2'd\mu_2 + \dots + m_n'd\mu_n = v'dp + \eta'dt, \quad (\text{E})$$

the right hand simplifying on account of relations A, B and D. This is equation number 97 in Gibbs' paper and is *one* of the convenient forms.

If the phase in equilibrium with the reference phase be a phase of fixed composition the derivation of the equation is modified slightly. Let its composition be α , β , γ , in the weight units used, etc., of the components, then

$$\mu_s dM_s = \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n,$$

where $dm_1 : dm_2 : dm_3$, etc., = $\alpha : \beta : \gamma$, etc., and $\Sigma dm_i = dM_s$.

This gives us

$$(\Sigma\alpha)\mu_s = \alpha\mu_1 + \beta\mu_2 + \text{etc.},$$

and since μ_s is a function of p and t and $(\partial\mu_s/\partial t)$ = specific volume while $-(\partial\mu_s/\partial p)$ = specific entropy by relations A and B only we get for a change in p , t and the composition of the reference phase

$$v'dp - \eta'dt = \alpha d\mu_1 + \beta d\mu_2 + \text{etc.},$$

which is of the same form as for the case of variable composition.

Condition for Non- and Meta-Stability.—If in the preceding case p and t are changed so that $\mu_s dM_s$ becomes greater than $\Sigma\mu_i dm_i$, then the phase in question will dissolve in the reference phase. On the other hand, if it becomes less, then the phase will separate from the reference phase. In this case if the phase is not already present supersaturation may result and we have a metastable condition. This condition, by

$$v'dp - \eta'dt < m_1'd\mu_1 + m_2'd\mu_2 + \dots + m_n'd\mu_n,$$

is useful in the study of the pressure-temperature relations.

If the phase we are considering be of variable composition it is to be noted that we can only say that at least some of the components will disappear or appear, and not the whole phase, but this is generally immaterial.

Applications.—The form of equilibrium equation which we have deduced can be used to deduce the relation commonly known as the phase rule and is the most useful in tracing pressure and temperature relations in systems. Its use will be discussed at some length in the next paper on "Pressure-temperature curves in univariant systems."

For other purposes, however, it is useful to get an equation containing stance tends to dissolve in a less concentrated and crystallize from a more concentrated solution.

as variables the changes in composition, pressure and temperature. This could have been deduced primarily, or we can get it from Equation E by substituting for $d\mu_1$, etc.,

$$d\mu_1 = \left(\frac{\partial\mu_1}{\partial p}\right) dp + \left(\frac{\partial\mu_1}{\partial t}\right) dt + \Sigma \left(\frac{\partial\mu_1}{\partial m_1}\right) dm_1, \text{ and so on.}$$

Using our relations A and B this gives us

$$\begin{aligned} + \Delta V dp = & + \frac{\Delta H}{T} dt + \left[m_1' \left(\frac{\partial\mu_1}{\partial m_1}\right) + m_2' \left(\frac{\partial\mu_1}{\partial m_2}\right) + \text{etc.} \right] dm_1 \\ & + \left[m_1' \left(\frac{\partial\mu_2}{\partial m_1}\right) + m_2' \left(\frac{\partial\mu_2}{\partial m_2}\right) + \text{etc.} \right] dm_2 \\ & + \text{etc.,} \end{aligned} \quad (\text{E}')$$

where ΔV is the increase of volume and ΔH the heat taken in when $m_1' + m_2' + \text{etc.}$, weight units of the phase separate from a large amount of the reference phase. Referring back to the deduction of our relation D it will be seen that the coefficients of dm , etc., represent the change of the μ 's for the same reaction, so the equation can be written¹

$$+ \Delta V dp = \frac{\Delta H}{T} dt + \Sigma \Delta\mu_1 dm_1.$$

It is hardly necessary to point out that, in a one-component system where no change of composition is possible and therefore dm_1 , dm_2 , etc., are zero, Equation E' simplifies to

$$\Delta V dp = \frac{\Delta H}{T} dt$$

which is the ordinary Clausius-Clapeyron relation.

In a two-component system we are generally interested in what happens at constant temperature or at constant pressure, so a simple form of equation for these cases will be found.

Along an isobar

$$- \frac{\Delta H}{T} dt = dm_1 \left[\alpha \left(\frac{\partial\mu_1}{\partial m_1}\right) + \beta \left(\frac{\partial\mu_1}{\partial m_2}\right) \right] + dm_2 \left[\alpha \left(\frac{\partial\mu_2}{\partial m_1}\right) + \beta \left(\frac{\partial\mu_2}{\partial m_2}\right) \right]$$

We can combine this with

$$dm_1 + dm_2 = 0$$

since we need only consider the composition of the reference phase and can deal with a constant weight of it.

Also from relation D

$$m_1 \left(\frac{\partial\mu_1}{\partial m_1}\right) + m_2 \left(\frac{\partial\mu_1}{\partial m_2}\right) = 0.$$

¹ In dealing with three-component systems Schreinemakers uses an equation which is equivalent to this form, but he uses the ratio of the components instead of their actual amounts.

$$m_1 \left(\frac{\partial \mu_2}{\partial m_1} \right) + m_2 \left(\frac{\partial \mu_2}{\partial m_2} \right) = 0.$$

Simplification gives

$$- \frac{\Delta H}{T} dt = dm_1 \left(\alpha - \frac{m_1}{m_2} \beta \right) \left(1 + \frac{m_1}{m_2} \right) \left(\frac{\partial \mu_1}{\partial m_1} \right).$$

A well-known theorem may be immediately deduced from this.

I. Let the two phases in equilibrium be a salt hydrate and solution and let dm_1 be the concentration of anhydrous salt. Consider the equilibrium curve near the point where the solution has the same composition as the hydrate. ΔH is negative, as we know of no substance which does not require heat to melt it, and the last two terms are positive. The sign of the slope of the curve therefore depends on the terms $(\alpha - m_1/m_2 \beta)$ which is positive or negative according as α/β is greater or less than m_1/m_2 , that is, whether the solution contains a greater or less proportion of water than the hydrate. Therefore the temperature increases with the concentration up to the point considered and then decreases. This can be illustrated by the solubility curves of most hydrates.

II. Let the two phases in question be a vapor and a liquid. Consider as before the point where the two phases have the same composition. The reasoning above applies except that ΔH is positive, as the vapor gives out heat in liquefying. It is impossible to say offhand whether we get a maximum or minimum temperature in this case.

Along an isotherm the equation reduces similarly to

$$\Delta V dp = dm_1 \left(\alpha - \frac{m_1}{m_2} \beta \right) \left(1 + \frac{m_1}{m_2} \right) \left(\frac{\partial \mu_1}{\partial m_1} \right).$$

From this we can make deductions like those above and in particular we may mention the two known as Konowalow's Laws.¹ (1) If $\alpha/\beta = m_1/m_2$ the system has a maximum vapor pressure at the temperature in question. (2) If one component is markedly more volatile than another so that α/β is never equal to m_1/m_2 , the vapor pressure increases steadily with the concentration of the more volatile component. For dilute solutions a sufficient approximation for $(\partial \mu_1/\partial m_1)$ is $[RT/(m_1 + m_2)] \times m_2/m_1$, based on the assumption of $(\partial \mu_1/\partial m_2) = -[RT/m_1 + m_2]$. This assumption is discussed by Gibbs in several places. Using this, we can get the usual forms of equations given in all text-books. However, while any one specific property such as the increase of solubility with temperature at constant pressure, or the lowering of the freezing point of a solution depends on $(\partial \mu_1/\partial m_1)$, the ratio of two will not, as the term will cancel out. This may be otherwise stated as follows: knowing the volume and heat changes involved and one relation between the concentration and another

¹ See van der Waals, "Lehrbuch der Thermodynamik."

variable, we can in a two-component system calculate the other relations among the variables.

Theorems Regarding the Shape of Isotherms.

There are two general theorems¹ regarding tangents to isotherms which we have occasionally found useful and which can be deduced from the relations already proved and one additional one, namely—

$$\alpha \left[\alpha \left(\frac{\partial \mu_1}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_1}{\partial m_2} \right) + \dots + \right] + \beta \left[\alpha \left(\frac{\partial \mu_2}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_2}{\partial m_2} \right) + \dots \right] + \text{etc.} > 0.$$

This can be proved as follows: Suppose we have a solid of composition α , β , etc., at a given temperature and pressure in contact with a liquid phase at the same temperature and pressure but that equilibrium is on the point of being attained so that an amount dM of the solid must yet dissolve so as to reach the proper equilibrium concentration. Let μ_1 , μ_2 , etc., be the equilibrium potentials. The potentials in the liquid will be

$$\mu_1 - \left(\frac{\partial \mu_1}{\partial m_1} \right) dm_1 - \left(\frac{\partial \mu_1}{\partial m_2} \right) dm_2 - \text{etc.}$$

$$\mu_2 - \left(\frac{\partial \mu_2}{\partial m_1} \right) dm_1 - \left(\frac{\partial \mu_2}{\partial m_2} \right) dm_2 - \text{etc.}$$

$$\mu_n - \left(\frac{\partial \mu_n}{\partial m_1} \right) dm_1 - \left(\frac{\partial \mu_n}{\partial m_2} \right) dm_2 - \text{etc.}$$

where $dm_1 = \frac{\alpha}{\alpha + \beta + \text{etc.}} dM$

$$dm_2 = \frac{\beta}{\alpha + \beta + \text{etc.}} dM, \text{ etc.}$$

But the chemical potential of the solid must be greater as it is still dissolving, and, therefore,

$$\left(\frac{\alpha}{\Sigma \alpha} \mu_1 + \frac{\beta}{\Sigma \alpha} \mu_2 + \text{etc.} \right) dM > \left[\mu_1 - \left(\frac{\partial \mu_1}{\partial m_1} \right) dm_1 - \text{etc.} \right] \frac{\alpha}{\Sigma \alpha} dM + \text{etc.}$$

$$\text{or } 0 > \alpha \left[- \left(\frac{\partial \mu_1}{\partial m_1} \right) dm_1 - \left(\frac{\partial \mu_1}{\partial m_2} \right) dm_2 - \text{etc.} \right] + \text{etc.}$$

and substituting the values of dm_1 , etc., we get

$$\alpha \left[\alpha \left(\frac{\partial \mu_1}{\partial m} \right) + \beta \left(\frac{\partial \mu_1}{\partial m_2} \right) + \text{etc.} \right] + \beta \left[\alpha \left(\frac{\partial \mu_2}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_2}{\partial m_2} \right) + \text{etc.} \right] + \text{etc.} > 0.$$

The first theorem is that if we have a solid in a three-component system in contact with a liquid phase at constant temperature and pressure the

¹ These theorems are deduced in an entirely different manner by Schreinemakers.

variation of the composition gives us a curve which tends to surround the point representing the composition of the solid. The equation representing the equilibrium is

$$0 = dm_1 \left[\alpha \left(\frac{\partial \mu_1}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_1}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_1}{\partial m_3} \right) \right] + dm_2 \left[\alpha \left(\frac{\partial \mu_2}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_2}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_2}{\partial m_3} \right) \right] + dm_3 \left[\alpha \left(\frac{\partial \mu_3}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_3}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_3}{\partial m_3} \right) \right]$$

If the tangent to the curve were to pass through the point representing the solid then

$$dm_1 dm_2 dm_3 = (m_1 - \alpha) (m_2 - \beta) (m_3 - \gamma),$$

hence we could have

$$0 = (m_1 - \alpha) \left[\alpha \left(\frac{\partial \mu_1}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_1}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_1}{\partial m_3} \right) \right] + (m_2 - \beta) \left[\alpha \left(\frac{\partial \mu_2}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_2}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_2}{\partial m_3} \right) \right] + (m_3 - \gamma) \left[\alpha \left(\frac{\partial \mu_3}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_3}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_3}{\partial m_3} \right) \right].$$

Part of this vanishes by the relation D and the rest cannot vanish on account of the relation just proved. Hence the tangent to the curve cannot pass through the solid point and the theorem is proved.

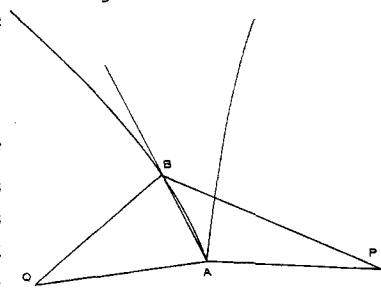
The second theorem shows that when two curves, of the kind just considered, meet, both the tangents at the points of intersection pass between the solid points or neither does. Let the two curves meet at A in the figure and let B, a point on one of the curves, be chosen at a distance, dm_1, dm_2, dm_3 from A. Whether the points P(α, β, γ) and Q(α', β', γ') lie on the same or different sides of the curve depends on whether the ratio

$$\left| \begin{array}{ccc} \alpha & \beta & \gamma \\ m_1 & m_2 & m_3 \\ dm_1 & dm_2 & dm_3 \end{array} \right| \Bigg/ \left| \begin{array}{ccc} \alpha' & \beta' & \gamma' \\ m_1 & m_2 & m_3 \\ dm_1 & dm_2 & dm_3 \end{array} \right|$$

is positive or negative.

Let the curve considered be represented by the equation in the previous proof.

We can simplify the required ratio by multiplying the columns by the coefficients of dm_1 , etc., and adding across. After canceling out common factors we get



$$\frac{\alpha \left[\alpha \left(\frac{\partial \mu_1}{\partial m_1} \right) dm_1 + \beta \left(\frac{\partial \mu_1}{\partial m_2} \right) dm_2 + \gamma \left(\frac{\partial \mu_1}{\partial m_3} \right) dm_3 \right] + \beta \left[\alpha \left(\frac{\partial \mu_2}{\partial m_1} \right) \right.}{\alpha' \left[\alpha \left(\frac{\partial \mu_1}{\partial m_1} \right) dm_1 + \beta \left(\frac{\partial \mu_1}{\partial m_2} \right) dm_2 + \gamma \left(\frac{\partial \mu_1}{\partial m_3} \right) dm_3 \right] + \beta' \left[\alpha \left(\frac{\partial \mu_2}{\partial m_1} \right) \right.} \\ \left. + \beta \left(\frac{\partial \mu_2}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_2}{\partial m_3} \right) \right] + \gamma \left[\alpha \left(\frac{\partial \mu_3}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_3}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_3}{\partial m_3} \right) \right]}{\left. + \beta \left(\frac{\partial \mu_2}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_2}{\partial m_3} \right) \right] + \gamma \left[\alpha \left(\frac{\partial \mu_3}{\partial m_1} \right) + \beta \left(\frac{\partial \mu_3}{\partial m_2} \right) + \gamma \left(\frac{\partial \mu_3}{\partial m_3} \right) \right]}$$

The other curve yields a similar condition with the α and α' reversed. But we have just proved that the numerators are positive and the denominators, while they may have either sign, are by relation C equal, therefore the two ratios have the same sign and the theorem follows.

General Conditions for Maxima or Minima of Temperature and Pressure.

The conditions for points of maximum or minimum temperature along isobars or maximum or minimum pressure along isotherms which have already been discussed in two-component systems may be derived quite generally. If we have a system of n components we may have altogether n phases present on such a curve and therefore have $(n - 1)$ equations representing the equilibrium of each of the others with the reference phase. Let those for an isotherm be

$$\Delta V_1 dp = dm_1 \left[m_1' \left(\frac{\partial \mu_1}{\partial m_1} \right) + m_2' \left(\frac{\partial \mu_1}{\partial m_2} \right) + \text{etc.} \right] + \text{etc.}$$

$$\Delta V_{n-1} dp = dm_1 \left[m_1^{n-1} \left(\frac{\partial \mu_1}{\partial m_1} \right) + m_2^{n-1} \left(\frac{\partial \mu_1}{\partial m_2} \right) + \text{etc.} \right] + \text{etc.}$$

Suppose a linear relation exists such that

$$m_1 = am_1' + bm_1'' + cm_1''' + \dots$$

$$m_2 = am_2' + bm_2'' + \dots$$

$$m_n = am_n' + bm_n'' + \dots$$

Multiplying the equations in order by a , b , c , etc., and adding, we get, remembering that by relation D $\sum m_i (\partial \mu_i / \partial m_1) = 0$.

$$(a\Delta V_1 + b\Delta V_2 + \dots) dp = 0. \\ dp = 0.$$

That is, we have a point of maximum or minimum pressure.

In exactly the same manner we can prove for an isobar that the same condition gives us $dt = 0$, which is the condition for a maximum or minimum of temperature.

Special cases of this are as follows:

In a two-component system the condition leads us to identity in composition of two phases. For example, if we consider a salt hydrate in equi-

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.

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PRESSURE-TEMPERATURE CURVES IN UNIVARIANT SYSTEMS.

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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).