ON THE DISPLACEMENT OF THE EQUILIBRIUM OF UNIVARIANT AND OF BIVARIANT SYSTEMS

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If a chemical system be in equilibrium at a given temperature and under a given pressure, the change in the thermodynamic potential of the system due to a virtual change in which the masses of the phases vary while the temperature and the pressure remain constant will be equal to zero. If the thermodynamic potential of the system be denoted by Φ the condition of equilibrium may be written

$$\delta\Phi = 0. \quad (1)$$

The symbol δ is used to indicate differentiation with respect to the masses alone. Thus, if we denote the temperature by T , the pressure by Π and the mass of the j -th component which is present in the i -th phase by M_{ij} , we obtain $\delta\Phi$ by keeping T and Π constant and giving to the variables M_{ij} the increments δM_{ij} .

Let us consider two adjacent states of equilibrium of the system and let the temperature, the pressure and the masses in the first state be T , Π , M_{ij} , and in the second state $T + dT$, $\Pi + d\Pi$, $M_{ij} + dM_{ij}$. If the thermodynamic potential in the first state have the value Φ , in the second state it will have a value $\Phi + d\Phi$. If we apply the condition of equilibrium to each of these states we get, in addition to equation 1, the equation

$$\delta(\Phi + d\Phi) = 0. \quad (2)$$

From equations 1 and 2 we get at once the equation

$$\delta d\Phi = 0. \quad (3)$$

Just as equation 1 may be called the equation of equilibrium equation 3 may be called the equation of the displacement of equilibrium. From it we can find, in any particular case, the equations which connect the simultaneous changes in the temperature, the pressure, and the concentrations of the phases as the system passes from one state of equilibrium to an adjacent

state of equilibrium. In the present note we shall apply the general equation of displacement to the particular cases of univariant and of bivariant systems having any number of components. We shall thus obtain results which will include as special cases the formulae which van der Waals and Trevor have obtained for binary and for ternary systems.

Before applying equation 3 to univariant and to bivariant systems a few preliminaries are necessary. If we agree to use the symbol d_1 to indicate a change in which the masses M_{ij} alone vary and in which they receive increments dM_{ij} , we may write

$$d\Phi = d_1\Phi + \frac{\partial\Phi}{\partial\Pi} d\Pi + \frac{\partial\Phi}{\partial T} dT. \quad (4)$$

If we denote the volume and the entropy of the system by V and by H and if we make use of the relations

$$\frac{\partial\Phi}{\partial\Pi} = V, \quad \frac{\partial\Phi}{\partial T} = -H, \quad (5)$$

we get

$$d\Phi = d_1\Phi + Vd\Pi - HdT. \quad (6)$$

The equation of displacement 3 now takes the form

$$\delta d_1\Phi + \delta V.d\Pi - \delta H.dT = 0. \quad (7)$$

The thermodynamic potential of the system is the sum of the thermodynamic potentials of the phases. If there be r phases and if we denote the potential of the i -th phase by Φ_i we have

$$\Phi = \sum_{i=1}^r \Phi_i. \quad (8)$$

If there be n components the thermodynamic potential Φ_i is a homogeneous function of the first degree in the masses $M_{i1}, M_{i2}, \dots, M_{in}$. If then we write

$$F_{ij} = \frac{\partial\Phi_i}{\partial M_{ij}}, \quad (9)$$

we have

$$\Phi_i = \sum_{j=1}^n F_{ij} M_{ij}. \quad (10)$$

By differentiating this equation with respect to the masses M_{ij} and by making use of equation 9 we obtain the two equations

$$d_1 \Phi_i = \sum_{j=1}^n F_{ij} dM_{ij}, \quad (11)$$

$$0 = \sum_{j=1}^n M_{ij} d_1 F_{ij}. \quad (12)$$

We then obtain from 11

$$\delta d_1 \Phi_i = \sum_{j=1}^n \delta F_{ij} dM_{ij}. \quad (13)$$

Moreover, since

$$\sum_{j=1}^n \delta F_{ij} dM_{ij} = \sum_{k=1}^n \sum_{j=1}^n \frac{\partial^2 \Phi_i}{\partial M_{ij} \partial M_{ik}} \delta M_{ik} dM_{ij} = \sum_{j=1}^n d_1 F_{ij} \delta M_{ij}, \quad (14)$$

it follows that we may also write

$$\delta d_1 \Phi_i = \sum_{j=1}^n d_1 F_{ij} \delta M_{ij}. \quad (15)$$

Since Φ_i is homogeneous and of the first degree in the masses M_{ij} , it follows that F_{ij} must be homogeneous and of the degree zero in the same variables. In other words, if m_{ij} be the mass of the j -th component which is present in the unit of mass of the i -th phase, we may say that F_{ij} is a function of the concentrations $m_{i1}, m_{i2}, \dots, m_{in}$. Accordingly, if the virtual change to which δ refers be one in which the concentrations of the i -th phase remain constant, it follows that δF_{ij} will be equal to zero; equation 13 shows that $\delta d_1 \Phi_i$ will also be equal to zero.

If we denote the thermodynamic potential of the unit of mass of the i -th phase by ϕ_i , equations 10, 11 and 12 enable us to write

$$\phi_i = \sum_{j=1}^n F_{ij} m_{ij}, \quad (16)$$

$$d_1\phi_i = \sum_{j=1}^n F_{ij} dm_{ij}, \quad (17)$$

$$0 = \sum_{j=1}^n m_{ij} d_1 F_{ij}. \quad (18)$$

By definition

$$\sum_{j=1}^n m_{ij} = 1, \quad (19)$$

so that

$$\sum_{j=1}^n dm_{ij} = 0. \quad (20)$$

Making use of equation 20 to eliminate dm_{in} from equation 17 we get

$$d_1\phi_i = \sum_{j=1}^{n-1} (F_{ij} - F_{in}) dm_{ij}. \quad (21)$$

If we imagine that ϕ_i has been expressed as a function of the $n-1$ concentrations $m_{i1}, m_{i2}, \dots, m_{i,n-1}$, equation 21 allows us to write

$$F_{ij} - F_{in} = \frac{\partial \phi_i}{\partial m_{ij}}. \quad (22)$$

The volume of the system is equal to the sum of the volumes of the phases. If we denote the mass of the i -th phase by M_i and the volume of the unit of mass of this phase by v_i we may accordingly write

$$V = \sum_{i=1}^r M_i v_i. \quad (23)$$

In like manner if η_i denote the entropy of the unit of mass of the i -th phase we have

$$H = \sum_{i=1}^r M_i \eta_i. \quad (24)$$

v_i and η_i are functions of the concentrations of the phase and it will be convenient to think of them as having been expressed in terms of the $n - 1$ concentrations $m_{i1}, m_{i2}, \dots, m_{i, n-1}$.

Let us now consider a univariant system consisting of $n + 1$ phases formed by means of n components. We shall begin by considering a virtual change in which the masses of the second and third phases vary while their concentrations remain constant and in which, moreover, the mass of the first phase remains constant while its concentrations vary; the remaining phases are not varied in any way. This virtual change may be described as consisting in the addition of a small mass of the second phase to the first and in the simultaneous removal from the first phase of a mass equal in magnitude to the added mass but having the composition of the third phase. The virtual change in question is defined by the equations

$$\delta M_1 = 0, \quad \delta M_2 + \delta M_3 = 0 \quad (25)$$

$$-\delta M_{1j} = m_{2j} \delta M_2 + m_{3j} \delta M_3 = (m_{2j} - m_{3j}) \delta M_2, \quad (26)$$

$$\delta M_{4j} = \delta M_{5j} = \dots = \delta M_{n+1j} = 0. \quad (27)$$

Since the concentrations of all the phases except the first remain constant, the first term in the equation of displacement 7 reduces to $\delta \mathcal{A}_1 \Phi_1$. In virtue of equations 15 and 26 we have

$$\delta \mathcal{A}_1 \Phi_1 = \sum_{j=1}^n d_1 F_{1j} \delta M_{1j} = -\delta M_2 \sum_{j=1}^n (m_{2j} - m_{3j}) d_1 F_{1j}. \quad (28)$$

Now since

$$\sum_{j=1}^n m_{2j} = 1 = \sum_{j=1}^n m_{3j}, \quad (29)$$

it follows that

$$m_{2n} - m_{3n} = - \sum_{j=1}^{n-1} (m_{2j} - m_{3j}). \quad (30)$$

If we make use of this result to eliminate $m_{2n} - m_{3n}$ from equation 28 we get

$$\begin{aligned}
 \delta d_1 \Phi_1 &= -\delta M_2 \sum_{j=1}^{n-1} (m_{2j} - m_{3j}) (d_1 F_{1j} - d_1 F_{1n}) \\
 &= -\delta M_2 \sum_{j=1}^{n-1} (m_{2j} - m_{3j}) d_1 (F_{1j} - F_{1n}). \quad (31)
 \end{aligned}$$

Finally, if we make use of equation 22, we get

$$\delta d_1 \Phi_1 = -\delta M_2 \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} (m_{2j} - m_{3j}) \frac{\partial^2 \phi_1}{\partial m_{1j} \partial m_{1k}} dm_{1k}. \quad (32)$$

Moreover, since

$$V = \sum_{i=1}^{n-1} M_i v_i$$

we have for the virtual change considered

$$\begin{aligned}
 \delta V &= M_1 \delta v_1 + v_2 \delta M_2 + v_3 \delta M_3 \\
 &= M_1 \sum_{j=1}^{n-1} \frac{\partial v_1}{\partial m_{1j}} \delta m_{1j} + (v_2 - v_3) \delta M_2. \quad (33)
 \end{aligned}$$

But since

$$M_1 m_{1j} = M_{1j} \quad (34)$$

we have

$$M_1 \delta m_{1j} = \delta M_{1j}. \quad (35)$$

Making use of equation 26 we get

$$M_1 \delta m_{1j} = -(m_{2j} - m_{3j}) \delta M_2. \quad (36)$$

We thus obtain

$$\delta V = \left[v_2 - v_3 - \sum_{j=1}^{n-1} \frac{\partial v_1}{\partial m_{1j}} (m_{2j} - m_{3j}) \right] \delta M_2. \quad (37)$$

In like manner

$$\delta H = \left[\eta_2 - \eta_3 - \sum_{j=1}^{n-1} \frac{\partial \eta_1}{\partial m_{1j}} (m_{2j} - m_{3j}) \right] \delta M_2. \quad (38)$$

If we substitute in equation 7 the values of $\delta d_1 \Phi_1$, δV and

δH given by equations 32, 37 and 38 we obtain at once the equation

$$\begin{aligned} \left[v_2 - v_3 - \sum_{j=1}^{n-1} (m_{2j} - m_{3j}) \frac{\partial v_1}{\partial m_{1j}} \right] d\Pi - \\ \left[\eta_2 - \eta_3 - \sum_{j=1}^{n-1} (m_{2j} - m_{3j}) \frac{\partial \eta_1}{\partial m_{1j}} \right] dT \\ - \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} (m_{2j} - m_{3j}) \frac{\partial^2 \phi_1}{\partial m_{1j} \partial m_{1k}} dm_{1k} = 0. \end{aligned} \quad (I)$$

We next consider a virtual change which differs from the one already used only in this respect: that the part previously played by the phase 3 is now played by the phase 4. This will lead to an equation in all respects similar to equation I; to obtain it, it is sufficient to replace the subscript 3 in equation I by the subscript 4. We may in like manner replace the subscript 3 by each of the subscripts 5, 6, ..., $n + 1$. The resulting equations form with equation I a set of $n - 1$ equations connecting the changes of the $n - 1$ concentrations of the phase 1 with the changes in temperature and pressure. If the changes in temperature and pressure be given these $n - 1$ equations determine the corresponding changes in the $n - 1$ concentrations of the phase 1.

We might, in like manner, consider a virtual change involving the phases 1, 3, 4, in which the phases 3 and 4 should play the parts previously played by the phases 2 and 3. If the resulting equation be written down it will be found without difficulty that it is the result of subtracting from the equation that corresponds to the combination of phases 1, 2, 3 the equation that corresponds to the combination 1, 2, 4. In general, the equation corresponding to the combination 1, l , m , is a consequence of the equations corresponding to the combinations 1, 2, l , and 1, 2, m . It is thus evident that it is sufficient to consider only the $n - 1$ combinations (1, 2, 3), (1, 2, 4), (1, 2, 5), ..., (1, 2, $n - 1$).

We should next have to consider a set of $n - 1$ virtual changes in which the phase 2 should play the part previously played by the phase 1. We should thus obtain a set of $n - 1$ equations connecting the changes in the $n - 1$ concentrations of the phase 2 with the changes in temperature and pressure. There will be a similar set of $n - 1$ equations for each of the remaining phases. We thus obtain $n + 1$ sets of $n - 1$ equations; all of these equations are of the same form as equation 1.

The $n - 1$ equations in one set determine the changes in the concentrations of the corresponding phase due to given changes in temperature and pressure. In a univariant system, however, the changes in temperature and pressure are not independent but are connected by the well-known Clapeyron-Clausius equation. This equation also can be derived without difficulty from equation 7. To obtain it, it is sufficient to consider a virtual change in which all the phases participate and in which the concentrations of each phase remain constant. The first term in Equation 7 vanishes and there results at once the Clapeyron-Clausius equation:

$$\frac{d\Pi}{dT} = \frac{\delta H}{\delta V}.$$

Thus the Clapeyron-Clausius equation and the $(n + 1)(n - 1)$ equations of the type I completely describe the displacement of the equilibrium of a univariant system.

In the preceding discussion the concentrations of all of the phases have been variable. If, however, the composition of any given phase be invariable, the $n - 1$ equations corresponding to that phase will disappear, for the virtual changes which enabled us to deduce these equations now become impossible.

For binary systems the equations of type I are due to Trevor.¹

Let us next consider a bivariant system consisting of n phases formed by means of n components. We shall begin by considering a virtual change which consists in adding to the first phase a small mass of the second phase; the remaining

¹ Jour. Phys. Chem., 10, 99 (1906).

phases are not varied in any way. This virtual change is defined by the equation

$$\delta M_{1j} = -m_{2j} \delta M_2. \quad (39)$$

Since the concentrations of all the phases except the first remain constant, the first term in the equation of displacement 7 reduces to $\delta d_1 \Phi_1$. In virtue of equations 15 and 39 we have

$$\delta d_1 \Phi_1 = \sum_{j=1}^n d_1 F_{1j} \delta M_{1j} = -\delta M_2 \sum_{j=1}^n m_{2j} d_1 F_{1j}. \quad (40)$$

From equation 18 we have

$$0 = \sum_{j=1}^n m_{1j} d_1 F_{1j}. \quad (41)$$

Multiplying this equation by δM_2 and adding to equation 40 we get

$$\delta d_1 \Phi_1 = -\delta M_2 \sum_{j=1}^n (m_{2j} - m_{1j}) d_1 F_{1j}. \quad (42)$$

Now since

$$\sum_{j=1}^n m_{2j} = 1 = \sum_{j=1}^n m_{1j} \quad (43)$$

it follows that

$$m_{2n} - m_{1n} = -\sum_{j=1}^{n-1} (m_{2j} - m_{1j}). \quad (44)$$

If now we eliminate $m_{2n} - m_{1n}$ from equation 42 we get

$$\begin{aligned} \delta d_1 \Phi_1 &= -\delta M_2 \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) (d_1 F_{1j} - d_1 F_{1n}) \\ &= -\delta M_2 \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) d_1 (F_{1j} - F_{1n}). \end{aligned} \quad (45)$$

Finally equation 22 enables us to write

$$\delta d_1 \Phi_1 = -\delta M_2 \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial^2 \phi_1}{\partial m_{1j} \partial m_{1k}} dm_{1k}. \quad (46)$$

Moreover since

$$V = \sum_{i=1}^n M_i v_i,$$

we have for the virtual change under consideration

$$\begin{aligned} \delta V &= M_1 \delta v_1 + v_1 \delta M_1 + v_2 \delta M_2 \\ &= M_1 \sum_{j=1}^{n-1} \frac{\partial v_1}{\partial m_{1j}} \delta m_{1j} + (v_2 - v_1) \delta M_2. \end{aligned} \quad (47)$$

Now since

$$M_i m_{1j} = M_{1j},$$

it follows that

$$\begin{aligned} M_1 \delta m_{1j} &= \delta M_{1j} - m_{1j} \delta M_1 \\ &= -m_{2j} \delta M_2 + m_{1j} \delta M_2 \\ &= -(m_{2j} - m_{1j}) \delta M_2. \end{aligned} \quad (48)$$

Thus

$$\delta V = \delta M_2 \left[v_2 - v_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial v_1}{\partial m_{1j}} \right]. \quad (49)$$

In like manner

$$\delta H = \delta M_2 \left[\eta_2 - \eta_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial \eta_1}{\partial m_{1j}} \right]. \quad (50)$$

If we substitute in equation 7 the values of $\delta \mathcal{A}_1 \Phi_1$, δV and δH given by equations 46, 49 and 50 we obtain at once the equation

$$\begin{aligned} &\left[v_2 - v_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial v_1}{\partial m_{1j}} \right] d\Pi - \\ &\quad \left[\eta_2 - \eta_1 - \sum_{j=1}^{n-1} (m_{2j} - m_{1j}) \frac{\partial \eta_1}{\partial m_{1j}} \right] dT \\ &- \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} (m_{1j} - m_{1k}) \frac{\partial^2 \phi_1}{\partial m_{1j} \partial m_{1k}} dm_{1k} = 0. \end{aligned} \quad (II)$$

We next consider a virtual change in which a small mass of the phase 3 is added to the phase 1. This yields an equation analogous to II; it can be obtained by replacing the subscript 2 in equation II by the subscript 3. In like manner we may replace the subscript 2 by 4, 5, . . . , n . The resulting equations form with II a set of $n - 1$ equations from which the changes in the $n - 1$ concentrations of the phase 1 can be determined when the changes in temperature and pressure are given.

We can, in like manner, consider a set of $n - 1$ virtual changes in which the phase 2 plays the part previously played by the phase 1. This yields a set of $n - 1$ equations from which the changes in the $n - 1$ concentrations of the phase 2 can be determined when the changes in temperature and pressure are given. Treating the remaining phases in the same way we obtain finally n sets of $n - 1$ equations of the type II. These equations determine the changes in the concentrations of the system due to given changes in temperature and pressure. Since, in a bivariant system, the temperature and the pressure can be varied arbitrarily, it follows that these equations completely describe the displacement of the equilibrium of a bivariant system.

If a given phase be of invariable composition the $n - 1$ equations corresponding to it will disappear, for the virtual changes which enabled us to get these equations now become impossible.

For binary and for ternary systems the equations of the type II are due to van der Waals.¹

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¹ Archives néerlandaises, 24, 15 (1890); 30, 267 (1896); (2) 2, 74 (1898). Die Continuität des gasförmigen und flüssigen Zustandes, 2, 13, 108, 112, 179 (1900).