ON CERTAIN HEATS OF DILUTION

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The Potential of a Component

When the form of a Gibbsian 'fundamental equation' of a two-component system in a trivariant state, *i. e.*, in a one-phase state, is once found from experiment, the thermodynamic properties of the system in the state in question can be found by analytical means. The most convenient set of state variables to employ in the search for the form of a fundamental function of such a system is probably that composed of the pressure p , the absolute temperature θ , and the masses M_1 , M_2 , of the independently variable components of the system. These are the variables of which the thermodynamic potential H of the system is a function. The thermodynamic potential $H(p, \theta, M_1, M_2)$ can be found from the specific thermodynamic potential $h(p, \theta, m_1)$, where m_1 denotes the 'composition' of the phase,

$$m_1 = \frac{M_1}{M_1 + M_2};$$

and the specific thermodynamic potential, because of the general relation

$$h = m_1\mu_1 + (1 - m_1)\mu_2,$$

can be found from the 'potentials' of the components, $\mu_1(p, \theta, m_1)$, $\mu_2(p, \theta, m_1)$; so the determination of the form of any fundamental function of the system can be reduced to the determination of the forms of these two potentials.

To the end of finding expressions for these potentials, suppose the mass dM_j of the j -th component to be added, irreversibly, to the mixture of mass

$$M_1 + M_2,$$

under the conditions of constant pressure, temperature, and mass of the other component. Before the addition, the energy of both masses is

$$E + e_j dM_j,$$

where E is the energy $E(p, \theta, M_1, M_2)$, of unknown form, of the system, and $e_j(p, \theta)$ is the specific energy of the j -th component. After the addition, the energy of the system is

$$E + \left\{ e_j + \Delta_j - p \left(\frac{\partial V}{\partial M_j} - v_j \right) \right\} dM_j ;$$

where $V(p, \theta, M_1, M_2)$ is the volume of the mixture, v_j is the specific volume $v_j(p, \theta)$ of the j -th component, and Δ_j is the irreversible heat absorption accompanying the addition — *i. e.*, Δ_j is the 'heat of dilution' by the j -th component.

In the addition, then, the energy of the mixture has increased by the amount

$$(1) \quad \left\{ e_j + \Delta_j - p \left(\frac{\partial V}{\partial M_j} - v_j \right) \right\} dM_j = \frac{\partial E}{\partial M_j} dM_j ,$$

the rate of increase being equal to $\partial E / \partial M_j$, since it would have the same value were the addition in any way to be reversibly made. By changing variables in

$$dE = -p dV + \theta dH + \mu_1 dM_1 + \mu_2 dM_2,$$

where H is the entropy of the system, we obtain for $\partial E / \partial M_j$ the general equation

$$(2) \quad \frac{\partial E}{\partial M_j} = -p \frac{\partial V}{\partial M_j} + \theta \frac{\partial H}{\partial M_j} + \mu_j.$$

Elimination of $\partial E / \partial M_j$ between these two equations yields an expression for μ_j ,

$$(3) \quad \mu_j = e_j + p v_j + \left(\Delta_j - \theta \frac{\partial H}{\partial M_j} \right).$$

In these equations, e_j , v_j may be regarded as known functions of p , θ ; and Δ_j , $\partial V / \partial M_j$ as experimentally determinable functions of p , θ , m_1 ; but the function $\partial H / \partial M_1$ of the variables p , θ , M_1 , M_2 remains of unknown form. In order to obtain a formulation of this function, we must consider the addition of the mass aM_j along a reversible path.

The reversible addition may be imagined to be effected by

Fig. 1.

Before this reversible addition, the energy of the mass $M_1 + M_2 + dM_j$ is

$$E + e_j dM_j;$$

after the addition it is

$$E + \left\{ e_j - P_j \frac{\partial V}{\partial M_j} - p \left(\frac{\partial V}{\partial M_j} - v_j \right) + \theta \left(\frac{\partial H}{\partial M_j} - \eta_j \right) \right\} dM_j,$$

where η_j is the specific entropy of the j -th component. The rate of increase of the energy of the mixture has therefore been

$$(4) \quad e_j - P_j \frac{\partial V}{\partial M_j} - p \left(\frac{\partial V}{\partial M_j} - v_j \right) + \theta \left(\frac{\partial H}{\partial M_j} - \eta_j \right) = \frac{\partial E}{\partial M_j}.$$

We accordingly have:

In the irreversible addition,

$$\frac{\partial E}{\partial M_j} = e_j - p \left(\frac{\partial V}{\partial M_j} - v_j \right) + \Delta_j; \quad (a)$$

in the reversible addition,

$$\frac{\partial E}{\partial M_j} = e_j - p \left(\frac{\partial V}{\partial M_j} - v_j \right) + \theta \left(\frac{\partial H}{\partial M_j} - \eta_j \right) - P_j \frac{\partial V}{\partial M_j}; \quad (b)$$

the general relation,

$$\frac{\partial E}{\partial M_j} = \mu_j - p \frac{\partial V}{\partial M_j} + \theta \frac{\partial H}{\partial M_j}. \quad (\gamma)$$

Through elimination of common terms between these equations, we find :

From (α) and (β) ,

$$(5) \quad \Delta_j = \theta \left(\frac{\partial H}{\partial M_j} - \eta_j \right) - P_j \frac{\partial V}{\partial M_j};$$

From (α) and (γ) ,

$$(6) \quad \mu_j = e_j + p v_j + \left(\Delta_j - \theta \frac{\partial H}{\partial M_j} \right);$$

From (β) and (γ) ,

$$(7) \quad \mu_j = (e_j + p v_j - \theta \eta_j) - P_j \frac{\partial V}{\partial M_j}.$$

The first of these equations determines $\partial H / \partial M_j$, whereupon the second determines μ_j . The result of both together is given by (7). Since the parenthesized expression in (7) is the specific thermodynamic potential h_j of the j -th component, this expression may be written

$$(8) \quad \mu_j = h_j - P_j \frac{\partial V}{\partial M_j}, \quad (j = 1, 2)$$

which is the relation sought. It may be noted here that, when the mass of the other component vanishes, P_j becomes zero and the equation reduces to

$$\mu_j = h_j,$$

as it should.

Another Derivation

In place of successive reversible additions of the masses dM_1 , dM_2 to the mixture having the mass $M_1 + M_2$, let us

imagine the described osmotic apparatus to be utilized for the reversible addition of the mass M_1 to the mass M_2 , and for the addition of M_2 to M_1 . In either case, the energy of both masses before the addition of M_j is

$$e_1 M_1 + e_2 M_2 ;$$

and after the addition it is

$$e_1 M_1 + e_2 M_2 - \int_0^{M_j} P_j \frac{\partial V}{\partial M_j} dM_j - p(V - v_1 M_1 - v_2 M_2) + \theta(H - \eta_1 M_1 - \eta_2 M_2).$$

Equating the difference of these quantities with the change

$$E - e_1 M_1 - e_2 M_2$$

of the energy of the whole affair during the operation, and rearranging, we find

$$E + pV - \theta H = M_1(e_1 + pv_1 - \theta\eta_1) + M_2(e_2 + pv_2 - \theta\eta_2) - \int_0^{M_j} P_j \frac{\partial V}{\partial M_j} dM_j ;$$

which may be written

$$H = M_1 h_1 + M_2 h_2 - \int_0^{M_j} P_j \frac{\partial V}{\partial M_j} dM_j ;$$

whence, on differentiation with regard to M_j ,

$$\mu_j = h_j - P_j \frac{\partial V}{\partial M_j}, \quad (j = 1, 2)$$

as before.

The First Derivatives of the Thermodynamic Potential

From the general relation

$$V = (M_1 + M_2) \cdot v(p, \theta, m_1),$$

where v is the specific volume of the system, we find¹

$$(9a) \quad \frac{\partial V}{\partial M_1} = v + (1 - m_1) \frac{\partial v}{\partial m_1} = \phi_1,$$

$$(9b) \quad \frac{\partial V}{\partial M_2} = v - m_1 \frac{\partial v}{\partial m_1} = \phi_2.$$

Incidentally it may be noted that ϕ_1, ϕ_2 are obviously equal to $\partial\mu_1/\partial p$ and $\partial\mu_2/\partial p$, respectively. The equations (9a), (9b) convert the equations (8) for μ_1, μ_2 to

$$(10) \quad \mu_j = h_j - P_j \phi_j; \quad (j = 1, 2)$$

wherefore the general equation

$$H = M_1 \mu_1 + M_2 \mu_2$$

for the thermodynamic potential of the system in a trivariant state may be written

$$(11) \quad H = M_1(h_1 - P_1 \phi_1) + M_2(h_2 - P_2 \phi_2).$$

¹ If it should be desired to express ϕ_1, ϕ_2 by means of the specific volumes, or of the densities, of the components as they stand in the mixture, we should have

$$\phi_1 = (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1} \frac{v}{1 - m_1}$$

$$\phi_2 = - m_1^2 \cdot \frac{\partial}{\partial m_1} \frac{v}{m_1},$$

or

$$\phi_1 = - v^2 \cdot \frac{\partial}{\partial m_1} \frac{1 - m_1}{v}$$

$$\phi_2 = + v^2 \cdot \frac{\partial}{\partial m_1} \frac{m_1}{v}.$$

Differentiating this equation,

$$\begin{aligned}
 (12) \quad dH = & \left\{ M_1 \left(v_1 - \frac{\partial(P_1\phi_1)}{\partial p} \right) + M_2 \left(v_2 - \frac{\partial(P_2\phi_2)}{\partial p} \right) \right\} dp \\
 & - \left\{ M_1 \left(\eta_1 + \frac{\partial(P_1\phi_1)}{\partial \theta} \right) + M_2 \left(\eta_2 + \frac{\partial(P_2\phi_2)}{\partial \theta} \right) \right\} d\theta \\
 & + \left\{ h_1 - P_1\phi_1 - M_1 \frac{\partial(P_1\phi_1)}{\partial m_1} \frac{\partial m_1}{\partial M_1} - M_2 \frac{\partial(P_2\phi_2)}{\partial m_1} \frac{\partial m_1}{\partial M_1} \right\} dM_1 \\
 & + \left\{ h_2 - P_2\phi_2 - M_2 \frac{\partial(P_2\phi_2)}{\partial m_1} \frac{\partial m_1}{\partial M_2} - M_1 \frac{\partial(P_1\phi_1)}{\partial m_1} \frac{\partial m_1}{\partial M_2} \right\} dM_2;
 \end{aligned}$$

whence we deduce

$$(13) \quad \begin{cases} V = M_1 \left(v_1 - \frac{\partial(P_1\phi_1)}{\partial p} \right) + M_2 \left(v_2 - \frac{\partial(P_2\phi_2)}{\partial p} \right) \\ H = M_1 \left(\eta_1 + \frac{\partial(P_1\phi_1)}{\partial \theta} \right) + M_2 \left(\eta_2 + \frac{\partial(P_2\phi_2)}{\partial \theta} \right); \end{cases}$$

or, dividing through by $M_1 + M_2$,

$$(13a) \quad \begin{cases} v = m_1 \left(v_1 - \frac{\partial(P_1\phi_1)}{\partial p} \right) + (1 - m_1) \left(v_2 - \frac{\partial(P_2\phi_2)}{\partial p} \right) \\ \eta = m_1 \left(\eta_1 + \frac{\partial(P_1\phi_1)}{\partial \theta} \right) + (1 - m_1) \left(\eta_2 + \frac{\partial(P_2\phi_2)}{\partial \theta} \right), \end{cases}$$

where η is the specific entropy of the system.

Rearranging these equations (13a), and appending an equation obtained by comparing the equations $\mu_j = \partial H / \partial M_j$ with the initial equations for μ_j , we find

$$(14) \quad \begin{cases} m_1 \frac{\partial(P_1\phi_1)}{\partial p} + (1 - m_1) \frac{\partial(P_2\phi_2)}{\partial p} = + m_1 v_1 + (1 - m_1) v_2 - v \\ m_1 \frac{\partial(P_1\phi_1)}{\partial \theta} + (1 - m_1) \frac{\partial(P_2\phi_2)}{\partial \theta} = - m_1 \eta_1 - (1 - m_1) \eta_2 + \eta \\ m_1 \frac{\partial(P_1\phi_1)}{\partial m_1} + (1 - m_1) \frac{\partial(P_2\phi_2)}{\partial m_1} = 0. \end{cases}$$

These three equations may be regarded as expressing the relations between the slopes of the two osmotic pressure curves in the P, p , in the P, θ , and in the P, m_1 -diagram, at any assigned p, θ, m_1 . The second members of the first two of the

equations are, respectively, the decrease of the specific volume and the increase of the specific entropy in the formation of the phase-mixture from its components. Denoting these changes of volume and entropy by $-\Delta v$ and $+\Delta\eta$, multiplying each equation through by the corresponding dp , $d\theta$, or dm_1 , and adding, we find

$$(15) \quad m_1.d(P_1\phi_1) + (1 - m_1).d(P_2\phi_2) = -\Delta v.dp + \Delta\eta.d\theta.$$

The first member of this equation is a portion of the differential of the increase Δh of the thermodynamic potential in the formation of the phase-mixture from its components. We have, equation (11),

$$H = M_1(h_1 - P_1\phi_1) + M_2(h_2 - P_2\phi_2);$$

whence, dividing through by $M_1 + M_2$,

$$\begin{aligned} h &= m_1(h_1 - P_1\phi_1) + (1 - m_1)(h_2 - P_2\phi_2) \\ &= \{m_1h_1 + (1 - m_1)h_2\} - \{m_1P_1\phi_1 + (1 - m_1)P_2\phi_2\}; \end{aligned}$$

whence

$$\begin{aligned} \Delta h &= -m_1P_1\phi_1 - (1 - m_1)P_2\phi_2, \\ -d\Delta h &= m_1d(P_1\phi_1) + (1 - m_1)d(P_2\phi_2) + (P_1\phi_1 - P_2\phi_2)dm_1; \end{aligned}$$

wherefore, on comparison with (15),

$$(16) \quad -d\Delta h = -\Delta v.dp + \Delta\eta.d\theta + (P_1\phi_1 - P_2\phi_2).dm_1.$$

This equation (16) corresponds to the general thermodynamic equation

$$dh = vdp - \eta d\theta + (\mu_1 - \mu_2)dm_1.$$

The quantity Δh is, of course, always negative. The equations

$$\frac{\partial \Delta h}{\partial p} = \Delta v, \quad \frac{\partial \Delta h}{\partial \theta} = -\Delta\eta, \quad \frac{\partial \Delta h}{\partial m_1} = P_2\phi_2 - P_1\phi_1,$$

are identical with the equations (14), and so are equivalent to the 'derived relations'

$$\frac{\partial H}{\partial p} = V, \quad \frac{\partial H}{\partial \theta} = -H, \quad \frac{\partial H}{\partial m_j} = \mu_j. \quad (j = 1, 2)$$

Osmotic Pressures and Heats of Dilution

The 'heats of dilution' Δ_1 , Δ_2 of irreversible dilution of the

phase-mixture are given by (5) and (6) as

$$(17) \quad \Delta_j = -P_j \frac{\partial V}{\partial M_j} + \theta \left(\frac{\partial H}{\partial M_j} - \eta_j \right)$$

$$\Delta_j = \mu_j - e_j - p v_j + \theta \frac{\partial H}{\partial M_j}.$$

If Δ_j be expressed with the aid of the osmotic pressures and the specific volume, the second of these formulations yields the same result as the first. We shall, therefore, employ the simpler of the two equations—the first.

As a preliminary, it is necessary to express $\partial H / \partial M_j$ with the aid of the osmotic pressures and the specific volume. We have, equation (13),

$$H = M_1 \left(\eta_1 + \frac{\partial(P_1 \phi_1)}{\partial \theta} \right) + M_2 \left(\eta_2 + \frac{\partial(P_2 \phi_2)}{\partial \theta} \right);$$

whence

$$\frac{\partial H}{\partial M_1} = \eta_1 + \frac{\partial(P_1 \phi_1)}{\partial \theta} + M_1 \frac{\partial^2(P_1 \phi_1)}{\partial \theta \partial m_1} \frac{\partial m_1}{\partial M_1} + M_2 \frac{\partial^2(P_2 \phi_2)}{\partial \theta \partial m_1} \frac{\partial m_1}{\partial M_1}$$

$$(18a) = \eta_1 + \frac{\partial(P_1 \phi_1)}{\partial \theta} + m_1 (1 - m_1) \frac{\partial^2(P_1 \phi_1)}{\partial \theta \partial m_1} + (1 - m_1)^2 \frac{\partial^2(P_2 \phi_2)}{\partial \theta \partial m_1}$$

$$\frac{\partial H}{\partial M_2} = \eta_2 + \frac{\partial(P_2 \phi_2)}{\partial \theta} + M_2 \frac{\partial^2(P_2 \phi_2)}{\partial \theta \partial m_1} \frac{\partial m_1}{\partial M_2} + M_1 \frac{\partial^2(P_1 \phi_1)}{\partial \theta \partial m_1} \frac{\partial m_1}{\partial M_2}$$

$$(18b) = \eta_2 + \frac{\partial(P_2 \phi_2)}{\partial \theta} - m_1 (1 - m_1) \frac{\partial^2(P_2 \phi_2)}{\partial \theta \partial m_1} - m_1^2 \frac{\partial^2(P_1 \phi_1)}{\partial \theta \partial m_1}.$$

The last of equations (14) convert (18a) and (18b) to

$$(19) \quad \begin{cases} \frac{\partial H}{\partial M_1} = \eta_1 + \frac{\partial(P_1 \phi_1)}{\partial \theta} \\ \frac{\partial H}{\partial M_2} = \eta_2 + \frac{\partial(P_2 \phi_2)}{\partial \theta} \end{cases};$$

which convert (17) to

$$(20a) \quad \Delta_1 = \theta \frac{\partial(P_1 \phi_1)}{\partial \theta} - P_1 \phi_1$$

$$(20b) \quad \Delta_2 = \theta \frac{\partial(P_2 \phi_2)}{\partial \theta} - P_2 \phi_2;$$

which equations may be written,

$$(21a) \quad \Delta_1 = \theta^2 \cdot \frac{\partial P_1 \phi_1}{\partial \theta}, \quad \Delta_2 = \theta^2 \cdot \frac{\partial P_2 \phi_2}{\partial \theta}. \quad (21b)$$

It may be noted also that, because of equations (20), the two heats of dilution are connected by the relation

$$\Delta_2 - \Delta_1 = \theta \cdot \frac{\partial}{\partial \theta} (P_2 \phi_2 - P_1 \phi_1) - (P_2 \phi_2 - P_1 \phi_1),$$

which, since

$$P_2 \phi_2 - P_1 \phi_1 = \frac{\partial \Delta h}{\partial m_1},$$

may be written

$$(22) \quad \begin{aligned} \Delta_2 - \Delta_1 &= \frac{\partial}{\partial m_1} \left(\theta \frac{\partial \Delta h}{\partial \theta} - \Delta h \right) \\ &= \theta^2 \cdot \frac{\partial}{\partial \theta \partial m_1} \frac{\Delta h}{\theta}, \end{aligned}$$

a relation of simple and rather curious form.

The equations

$$P_1 = P_1(p, \theta, m_1), \quad P_2 = P_2(p, \theta, m_1),$$

for the two osmotic pressures of the phase-mixture are found from equations (21)

$$\frac{\partial P_1 \phi_1}{\partial \theta} \frac{1}{\theta} = \frac{\Delta_1}{\theta^2}, \quad \frac{\partial P_2 \phi_2}{\partial \theta} \frac{1}{\theta} = \frac{\Delta_2}{\theta^2},$$

by integration with regard to θ ; which yields

$$(23a) \quad P_1 \phi_1 = \theta \int \frac{\Delta_1}{\theta^2} d\theta, \quad P_2 \phi_2 = \theta \int \frac{\Delta_2}{\theta^2} d\theta.$$

Substituting for ϕ_1 , ϕ_2 their values, as expressed by equations (9), we find

$$(23b) \quad \begin{cases} P_1 \left(v + (1 - m_1) \frac{\partial v}{\partial m_1} \right) = \theta \int \frac{\Delta_1}{\theta^2} d\theta \\ P_2 \left(v - m_1 \frac{\partial v}{\partial m_1} \right) = \theta \int \frac{\Delta_2}{\theta^2} d\theta. \end{cases}$$

Evaluation of the second members of these equations depends upon the formulation, from experiment, of the functions $\Delta_j(p, \theta, m_i)$.

When the equations (23a),

$$\begin{aligned} P_j \phi_j &= \theta \int \frac{\Delta_j}{\theta^2} d\theta \\ &= \theta \cdot D_1(p, \theta, m_i), \end{aligned}$$

representing the osmotic pressures by means of the heats of dilution, are combined with the equations (10) for the component potentials,

$$\mu_j = h_j - P_j \phi_j,$$

and the resulting expressions for the potentials are substituted in the equation

$$H = M_1 \mu_1 + M_2 \mu_2,$$

for the thermodynamic potential of the phase-mixture, we obtain

$$(24) \quad H = M_1(h_1 - \theta D_1) + M_2(h_2 - \theta D_2).$$

From this equation it appears that appeal to experiment for the forms of the two functions Δ_j suffices for determination of the forms of the fundamental functions of a two-component phase-mixture, when the fundamental functions of the separate components are known. This is a very interesting general result.

Let us now return to consideration of the equations for the two osmotic pressures P_j . If throughout any region of p, θ, m_i -values it may be assumed that $\Delta_1 = 0$, or that $\Delta_2 = 0$, the equations (21) become

$$(25) \quad \frac{\partial P_1 \phi_1}{\partial \theta} = 0, \quad \frac{\partial P_2 \phi_2}{\partial \theta} = 0,$$

whence

$$(26) \quad P_1 \phi_1 = r_1(p, m_1) \cdot \theta. \quad P_2 \phi_2 = r_2(p, m_2) \cdot \theta.$$

It thus appears that, when $\Delta_j = 0$,

$$\int \frac{\Delta_j}{\theta^2} d\theta = r_j.$$

When the phase-mixture is a 'dilute solution,' m_1 is small in comparison with unity, and $\partial v/\partial m_1$ is small in comparison with v , wherefore the first of equations (26) sensibly reduces to the van't Hoff equation,

$$P_1 v = r_1 \theta,$$

in which the function r_1 , as was discovered by van 't Hoff from experimental evidence, is approximately equal to the ideal-gas constant r . The *general* form of the relation is, of course, that of the first equation (23*b*). Van 't Hoff's theory omits all consideration of the simultaneous value of the complementary osmotic pressure P_2 .

If the assumption of a vanishing heat of dilution may be replaced by the assumption that, in any region of p, θ, m_1 -values, Δ_1 or Δ_2 is independent of θ , how will the osmotic pressures in this region depend upon the temperature? From the equations (20),

$$\Delta_j = \theta \frac{\partial(P_j \phi_j)}{\partial \theta} - P_j \phi_j,$$

the rates of change of the heats of dilution with changing temperature are found to be

$$\frac{\partial \Delta_j}{\partial \theta} = \theta \frac{\partial^2(P_j \phi_j)}{\partial \theta^2};$$

wherefore, in the region in question,

$$\frac{\partial^2(P_j \phi_j)}{\partial \theta^2} = 0,$$

$$\frac{\partial(P_j \phi_j)}{\partial \theta} = f_j,$$

$$(27) \quad P_j \phi_j = f_j \theta + g_j, \quad (j = 1, 2)$$

where the f 's and g 's are independent of θ . These equations differ in form from the equations (26) by an additive term.

The Locus $P_1 = P_2$

Let the plane diagram of Fig. 2 represent the osmotic pressures P_1, P_2 of a phase-mixture, in their dependence on the com-

position m_1 at any assigned values of p, θ . Since both curves rise from zero values, they will intersect at a point a . The equation $P_1 = P_2$ is the locus $R(p, \theta, m_1) = 0$ of the points a .

Fig. 2

If the variables p, θ, m_1 be represented by rectangular co-ordinates in space, to every point of the space in which the variables have possible values will correspond a pair of values of P_1, P_2 ; and the equation $R = 0$ will represent a surface that is the locus of the points at which P_1, P_2 are equal. Let us seek to connect the common value P_0 of the osmotic pressures at this locus with the specific thermodynamic potential $h(p, \theta, m_1)$ of the system.

A general thermodynamic relation that will be of service in this task is

$$\begin{aligned} \frac{\partial V}{\partial M_j} &= \frac{\partial}{\partial p} \mu_j(p, \theta, M_1, M_2), \\ (a) \qquad \qquad &= \frac{\partial}{\partial p} \mu_j(p, \theta, m_1), \end{aligned}$$

which is one of the conditions of integrability of the differential of the thermodynamic potential H ,

$$Vdp - Hd\theta + \mu_1 dM_1 + \mu_2 dM_2.$$

Further requisite general relations are obtained from

$$H = (M_1 + M_2) \cdot h,$$

whence follows

$$\frac{\partial H}{\partial M_j} = h + (M_1 + M_2) \frac{\partial h}{\partial m_1} \frac{\partial m_1}{\partial M_j},$$

wherefore

$$(b) \quad \begin{cases} \mu_1 = h + (1 - m_1) \frac{\partial h}{\partial m_1}, \\ \mu_2 = h - m_1 \frac{\partial h}{\partial m_1}, \end{cases}$$

which are the equations in question.

Now, from the equations (8)

$$P_j = \frac{h_j - \mu_j}{\frac{\partial V}{\partial M_j}},$$

the equation $P_1 = P_2$ of the locus may be written

$$(h_1 - \mu_1) \frac{\partial V}{\partial M_2} = (h_2 - \mu_2) \frac{\partial V}{\partial M_1},$$

which is converted by (a) and (b) to

$$\left(h_2 - h_1 + \frac{\partial h}{\partial m_1} \right) \frac{\partial h}{\partial p} = \left(h - m_1 h_1 - (1 - m_1) h_2 \right) \frac{\partial^2 h}{\partial p \partial m_1},$$

which, because of

$$h - m_1 h_1 - (1 - m_1) h_2 = \Delta h,$$

becomes

$$(28) \quad \begin{vmatrix} \Delta h & \frac{\partial h}{\partial p} \\ \frac{\partial \Delta h}{\partial m_1} & \frac{\partial^2 h}{\partial p \partial m_1} \end{vmatrix} = 0,$$

which is the equation of the locus. The vanishing of this Wronskian of Δh and $\partial h / \partial p$ requires that these functions shall be connected by a linear relation

$$-\Delta h = z(p, \theta) \cdot \frac{\partial h}{\partial p}.$$

We shall shortly see that the coefficient z of this relation is equal to the common value P_0 of the two osmotic pressures.

Let us now seek to express P_o . From (16) we have

$$\frac{\partial \Delta h}{\partial m_1} = P_2 \phi_2 - P_1 \phi_1,$$

which equation connecting P_1 , P_2 becomes, for $P_1 = P_2 = P_o$,

$$P_o (\phi_2 - \phi_1) = \frac{\partial \Delta h}{\partial m_1}.$$

Now, by (a) and (b),

$$\begin{aligned}\phi_2 &= \frac{\partial V}{\partial M_2} = \frac{\partial \mu_2}{\partial p} = \frac{\partial h}{\partial p} - m_1 \frac{\partial^2 h}{\partial p \partial m_1}, \\ \phi_1 &= \frac{\partial V}{\partial M_1} = \frac{\partial \mu_1}{\partial p} = \frac{\partial h}{\partial p} + (1 - m_1) \frac{\partial^2 h}{\partial p \partial m_1},\end{aligned}$$

whence

$$\phi_2 - \phi_1 = - \frac{\partial^2 h}{\partial p \partial m_1},$$

which converts the above equation for P_o to

$$(29) \quad P_o = - \frac{\partial \Delta h}{\partial m_1} : \frac{\partial^2 h}{\partial p \partial m_1},$$

the equation for the osmotic pressure at the locus. Elimination of

$$\frac{\partial \Delta h}{\partial m_1} : \frac{\partial^2 h}{\partial p \partial m_1}$$

between (28) and (29) yields a second equation for P_o ,

$$(30) \quad -P_o = \Delta h : \frac{\partial h}{\partial p}.$$

Starting with the equation (29) for P_o , we can obtain a succession of expressions for the locus $P_1 = P_2$, and also for the osmotic pressure there. Since the second member of this equation must be a function of p , θ only, we have, equating its m_1 -derivative to zero,

$$\left(\frac{\partial^2 h}{\partial p \partial m_1} \frac{\partial^2 \Delta h}{\partial m_1^2} - \frac{\partial \Delta h}{\partial m_1} \frac{\partial^3 h}{\partial p \partial m_1^2} \right) : \left(\frac{\partial^2 h}{\partial p \partial m_1} \right)^2 = 0.$$

The denominator of the fraction here, which is equal to $(\partial v / \partial m_1)^2$, presumably does not vanish ; so we have

$$(31) \quad \begin{vmatrix} \frac{\partial \Delta h}{\partial m_1} & \frac{\partial^2 h}{\partial p \partial m_1} \\ \frac{\partial^2 \Delta h}{\partial m_1^2} & \frac{\partial^3 h}{\partial p \partial m_1^2} \end{vmatrix} = 0.$$

Eliminating

$$\frac{\partial \Delta h}{\partial m_1} : \frac{\partial^2 h}{\partial p \partial m_1}$$

between (31) and (29), and noting that $\partial^2 \Delta h / \partial m_1^2 = \partial^2 h / \partial m_1^2$, we find a corresponding third expression for the osmotic pressure at the locus,

$$(32) \quad P_o = - \frac{\partial^2 h}{\partial m_1^2} : \frac{\partial^3 h}{\partial p \partial m_1^2}.$$

The second member of (32) is, in its turn, a function of p , θ ; wherefore we can proceed as above, obtaining another pair of equations analogous to (31) and (32), and continue the process *ad infinitum*.

We thus have, collecting the equations (28) to (32), the successive equations

$$(33) \quad P_o = - \frac{\Delta h}{\partial p} = - \frac{\frac{\partial \Delta h}{\partial m_1}}{\frac{\partial^2 h}{\partial p \partial m_1}} = - \frac{\frac{\partial^2 h}{\partial m_1^2}}{\frac{\partial^3 h}{\partial p \partial m_1^2}} = \dots,$$

and the zero Wronskian matrix

$$(34) \quad \begin{vmatrix} \Delta h & \frac{\partial h}{\partial p} \\ \frac{\partial \Delta h}{\partial m_1} & \frac{\partial^2 h}{\partial p \partial m_1} \\ \frac{\partial^2 h}{\partial m_1^2} & \frac{\partial^3 h}{\partial p \partial m_1^2} \\ \dots & \dots \end{vmatrix} = 0.$$

The vanishing of this matrix, being the condition that the functions constituting each of its rows shall be connected by a linear relation whose coefficient is independent of m_1 , is the condition for the existence of the equations (33). When the first column is replaced by the values derived from the first of equations (33)

$$\Delta h = -P_o \frac{\partial h}{\partial p},$$

the matrix becomes

$$\begin{vmatrix} -P_o \frac{\partial h}{\partial p} & \frac{\partial h}{\partial p} \\ -P_o \frac{\partial^2 h}{\partial p \partial m_1} & \frac{\partial^2 h}{\partial p \partial m_1} \\ -P_o \frac{\partial^3 h}{\partial p \partial m_1^2} & \frac{\partial^3 h}{\partial p \partial m_1^2} \\ \dots & \dots \end{vmatrix} = 0,$$

which is obviously identically satisfied. It is, finally, not without interest to note that the equations (33) may be given the forms

$$-\Delta h = P_o v, \quad -\frac{\partial \Delta h}{\partial m_1} = P_o \frac{\partial v}{\partial m_1}, \quad \text{etc.}$$

From this equation we may obtain some curious information concerning the form of the thermodynamic potential, and the forms of the component-potentials, of the phase-mixture. From the equation

$$\Delta h = h - m_1 h_1 - (1 - m_1) h_2,$$

we find

$$h = \Delta h + (h_1 - h_2)m_1 + h_2;$$

whence, from (33), at the locus,*

$$(35) \quad h = -P_o \frac{\partial h}{\partial p} + (h_1 - h_2)m_1 + h_2.$$

* Note that this equation is

$$h = -P_o v + (h_1 - h_2)m_1 + h_2.$$

Further, from the general equations (b),

$$\mu_1 = h + (1 - m_1) \frac{\partial h}{\partial m_1},$$

$$\mu_2 = h - m_1 \frac{\partial h}{\partial m_1},$$

substituting for h from (35)

$$\mu_1 = -P_o \left(\frac{\partial h}{\partial p} + (1 - m_1) \frac{\partial^2 h}{\partial p \partial m_1} \right) + h_1,$$

$$\mu_2 = -P_o \left(\frac{\partial h}{\partial p} - m_1 \frac{\partial^2 h}{\partial p \partial m_1} \right) + h_2,$$

and replacing $\partial h / \partial p$ by the specific volume v of the mixture, we find that, at the locus,

$$(36) \quad \mu_1 - h_1 = P_o v^2 \cdot \frac{\partial}{\partial m_1} \frac{1 - m_1}{v}$$

$$\mu_2 - h_2 = -P_o v^2 \cdot \frac{\partial}{\partial m_1} \frac{m_1}{v}.$$

The quantities whose composition-derivatives appear in these equations are successively the densities, in the mixture, of the first and of the second components.

Formulation of Heats of Dilution

In conclusion, let us now formulate the heats of dilution Δ_1 , Δ_2 , of irreversible dilution of a two-component phase-mixture, by means of the specific thermodynamic potential of the mixture. For these heats of dilution we have the equations (20),

$$\Delta_1 = \theta \frac{\partial (P_1 \phi_1)}{\partial \theta} - P_1 \phi_1, \quad \Delta_2 = \theta \frac{\partial (P_2 \phi_2)}{\partial \theta} - P_2 \phi_2.$$

By equations (10) and (b) we have, respectively,

$$P_1 \phi_1 = h_1 - \mu_1,$$

$$P_2 \phi_2 = h_2 - \mu_2,$$

$$\mu_1 = h + (1 - m_1) \frac{\partial h}{\partial m_1},$$

$$\mu_2 = h - m_1 \frac{\partial h}{\partial m_1},$$

wherefore

$$P_1 \phi_1 = h_1 - h - (1 - m_1) \frac{\partial h}{\partial m_1}; \quad P_2 \phi_2 = h_2 - h + m_1 \frac{\partial h}{\partial m_1};$$

which values serve to convert the above equations for Δ_1, Δ_2 to

$$(37a) \quad \Delta_1 = - \left(h_1 - \theta \frac{\partial h_1}{\partial \theta} \right) + \left(h - \theta \frac{\partial h}{\partial \theta} \right) + \\ (1 - m_1) \cdot \frac{\partial}{\partial m_1} \left(h - \theta \frac{\partial h}{\partial \theta} \right)$$

$$(37b) \quad \Delta_2 = - \left(h_2 - \theta \frac{\partial h_2}{\partial \theta} \right) + \left(h - \theta \frac{\partial h}{\partial \theta} \right) - m_1 \cdot \frac{\partial}{\partial m_1} \left(h - \theta \frac{\partial h}{\partial \theta} \right).$$

The expression $h - \theta \partial h / \partial \theta$ is the specific Gibbsian heat-function, defined by the equation

$$g = e + pv;$$

wherefore the equations (37) may be expressed in the compact form

$$(38a) \quad \Delta_1 = (g - g_1) + (1 - m_1) \frac{\partial g}{\partial m_1}$$

$$(38b) \quad \Delta_2 = (g - g_2) - m_1 \frac{\partial g}{\partial m_1}.$$

Expressing the second member of each of these equations by means of a derivative of a single function, we find

$$(39a) \quad \Delta_1 = (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1} \frac{g - g_1}{1 - m_1}$$

$$(39b) \quad \Delta_2 = - m_1^2 \cdot \frac{\partial}{\partial m_1} \frac{g - g_2}{m_1}.$$

Finally, by subtraction, the equations (38) yield

$$\Delta_1 - \Delta_2 = g_2 - g_1 + \frac{\partial g}{\partial m_1} \\ (40) \quad = \frac{\partial \Delta g}{\partial m_1},$$

when Δg is written for the increase

$$g - m_1 g_1 - (1 - m_1) g_2$$

of the heat-function in the formation of unit mass of the phase-mixture from its components.

If the formulas for the heats of dilution be assembled, for comparison, we shall have :

$$\begin{aligned} (21a) \quad & \left\{ \begin{aligned} \Delta_1 &= \theta^2 \cdot \frac{\partial}{\partial \theta} \frac{P_1 \phi_1}{\theta} \\ (21b) \quad & \Delta_2 = \theta^2 \cdot \frac{\partial}{\partial \theta} \frac{P_2 \phi_2}{\theta} \\ & \Delta_1 - \Delta_2 = \theta^2 \cdot \frac{\partial}{\partial \theta} \frac{P_1 \phi_1 - P_2 \phi_2}{\theta} \end{aligned} \right. \end{aligned}$$

$$(37a) \quad \Delta_1 = (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1} \frac{\left(h - \theta \frac{\partial h}{\partial \theta} \right) - \left(h_1 - \theta \frac{\partial h_1}{\partial \theta} \right)}{1 - m_1}$$

$$(37b) \quad \Delta_2 = -m_1^2 \cdot \frac{\partial}{\partial m_1} \frac{\left(h - \theta \frac{\partial h}{\partial \theta} \right) - \left(h_2 - \theta \frac{\partial h_2}{\partial \theta} \right)}{m_1}$$

$$(22) \quad \Delta_1 - \Delta_2 = -\theta^2 \cdot \frac{\partial^2}{\partial \theta \partial m_1} \frac{\Delta h}{\theta}$$

$$(39a) \quad \Delta_1 = (1 - m_1)^2 \cdot \frac{\partial}{\partial m_1} \frac{g - g_1}{1 - m_1}$$

$$(39b) \quad \Delta_2 = -m_1^2 \cdot \frac{\partial}{\partial m_1} \frac{g - g_2}{m_1}$$

$$(40) \quad \Delta_1 - \Delta_2 = \frac{\partial \Delta g}{\partial m_1}$$

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