On the Equilibrium of a System of three Components where two Liquid-Phases co-exist.

By

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The system of three components where two liquid-phases co-exist was studied by W. D. Bancroft[1] about twenty years ago. He pointed out that the Mass law could be applied to a case of equilibrium of such a system. In which case the exponential factors of the mathematical formula of mass law representing the equilibrium are neither necessarily nor usually integers.

" Let A and B be two non-miscible liquid, S the common solvent with which A and B are miscible in all proportions when taken singly, and let the amount of S remain constant, so that we are considering the amounts of A and B, namely x and y, which will dissolve simultaneously in a fixed amount of S. This, being a case of equilibrium, must come under the general equation of equiliblium,

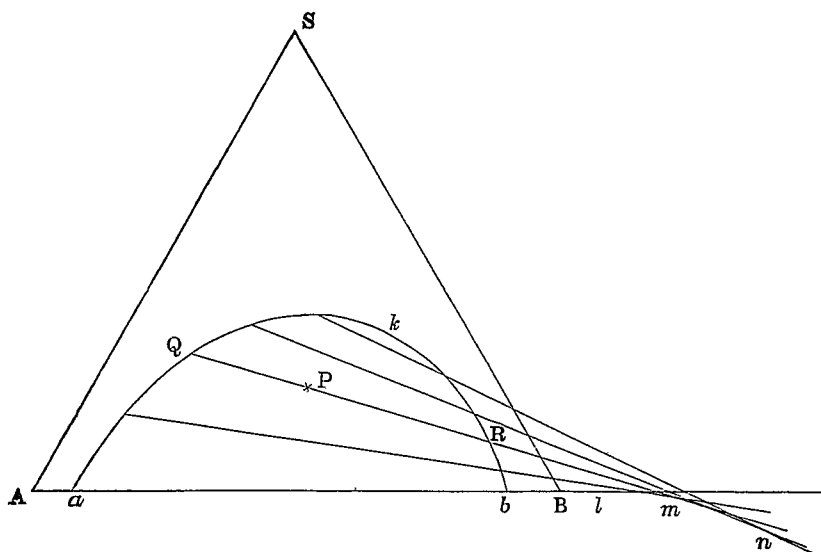$$\frac{\delta F(x, y)}{\delta x} dx + \frac{\delta F(x, y)}{\delta y} dy = 0 \qquad (1)$$

where dx and dy denote the changes in the concentrations of A and B respectively. If it is assumed, in accordance with the Mass law, that the change in solubility is a function of the amounts of A and B already present,

$$\frac{a}{x} dx + \frac{\beta}{y} dy = 0 \qquad (2)$$

or $\qquad a\, d\ln x + \beta\, d\ln y = 0$

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1 Physic. Rev., 3, 21, (1895); J. Chem. soc., Abst., 68, 157, (1995).

where α and β are proportionality factors. If these are constants, and $\alpha/\beta = n$, we get, after integration and clearing of logarithms,

$$x^n y = \text{Const.} \qquad (3)$$

"It is fouud, however, that in most cases the concentrations can not be given by one curve, but involve two, so that for one set of concentrations we have the relation

and for the other set
$$\left.\begin{array}{l} x^{n_1} y = C_1 \\ x^{n_2} y = C_2 \end{array}\right\} \qquad (4)$$

The two sets of saturated solutions correspond with different conditions. Thus, in the chloroform-water-alcohol series, the one set of solutions is saturated in respect to chloroform and not in respect to water; the other set is saturated in respect to water and not in respect to chloroform."

In the present paper a further theoretical study of the equilibrium of such a system of three components is given. If the triangular co-ordinates be taken to express the three components system as usual, the compositions of two sets of the saturated solutions will be repre-sented by the curve $a\,k\,b$ in the figure and ak is the saturated solu-tions of A with respect to B and $k\,b$ that of B with respect to A. Ac-

cording to Bancroft's consideration, if we take a definite amount of S, the above mentioned relation (4) must hold; but these relations can not be directly used in reference to the triangular co-ordinates here choosen, but must be transformed as follows:

$$\left.\begin{array}{l} \dfrac{x^{n_1}y}{z^{n_1+1}} = C_1(x+y+z)^{n_1+1} \\[3mm] \dfrac{x^{n_2}y}{z^{n_2+1}} = C_2(x+y+z)^{n_2+1} \end{array}\right\} \qquad (5)$$

where $x+y+z = 1$. These equations correspond to the curves ak and kb. They do not, however, express the condition of equilibrium between two liquid-phases which might co-exist. It is evident that this condition is most important to determine the equilibrium of the system. If we take such a mixture as is represented by P in the figure, it will be separated in equilibrium into two liquid phases of the compositions represented by Q and R; and these two points evidently must be on the curves of equations (5).

Let the total number of mols in P be N, and A, B and S be in ratios of x_0, y_0 and z_0. Again let the total number of mols in the solutions Q and Z be n_a and n_b respectively, and the ratios of the three components in them respectively be x_a, y_a, z_a and x_b, y_b, z_b. Then we get the following relations

$$n_a x_a + n_b x_b : n_a y_a + n_b y_b : n_a z_a + n_b z_b = x_0 : y_0 : z_0,$$

or $\quad \dfrac{n_a x_a + n_b x_b}{x_0} = \dfrac{n_a y_a + n_b y_b}{y_0} = \dfrac{n_a z_a + n_b z_b}{z_0} = \dfrac{n_a + n_b}{1} = N.$ (6)

Then $\qquad\left.\begin{array}{l} n_a x_a + n_b x_b = (n_a + n_b)\,x_0 \\[2mm] n_a y_a + n_b y_b = (n_a + n_b)\,y_0 \\[2mm] n_a y_a + n_b z_b = (n_a + n_b)\,z_0 \end{array}\right\} \qquad (7)$

or $\qquad\left.\begin{array}{l} x_0 = \dfrac{n_a x_a + n_b x_b}{n_a + n_b} \\[3mm] y_0 = \dfrac{n_a y_a + n_b y_b}{n_a + n_b} \\[3mm] z_0 = \dfrac{n_a z_a + n_b z_b}{n_a + n_b} \end{array}\right\} \qquad (8)$

And the equation of the straight line passing through the two ponits (x_a, y_a, z_a) and (x_b, y_b, z_b) is

$$\begin{vmatrix} x & y & z \\ x_a & y_a & z_a \\ x_b & y_b & z_b \end{vmatrix} = 0. \tag{9}$$

If we put the values of x_0, y_0 and z_0 in eq. (8) for x, y and z of the above equation, we have

$$\begin{vmatrix} n_a x_a + n_b x_b & n_a y_a + n_b y_b & n_a z_a + n_b z_b \\ x_a & y_a & z_a \\ x_b & y_b & z_b \end{vmatrix} = 0.$$

This equation holds evidently, therefore the point (x_0, y_0, z_0) is on the straight line passing through the two points $(x_a\, y_a\, z_a)$ and (x_b, y_b, z_b).

Now let the thermodynamical potential of the solution Q be $\varPhi_a$, and that of R be $\varPhi_b$, then the total potential of the whole system is

$$\varPhi = \varPhi_a + \varPhi_b.$$

When these two saturated solutions are in equilibrium, the change of the potential for the change dn_a and dn_b must be zero, viz.

$$d(\varPhi_a + \varPhi_b) = 0. \tag{10}$$

Taking this equation together with eq. (7) and solving this differential equation, we have

$$\left.\begin{aligned} x_a &= f_a\,(x_0, y_0, z_0) & x_b &= f_b\,(x_0, y_0, x_0) \\ y_a &= \varphi_a\,(x_0, y_0, z_0) & y_b &= \varphi_b\,(x_0, y_0, z_0) \\ z_a &= \chi_a\,(x_0, y_0, z_0) & z_b &= \chi_b\,(x_0, y_0, z_0) \end{aligned}\right\} \tag{11}$$

Eliminating x_0, y_0, z_0, we get

$$\left.\begin{aligned} g_a\,(x_a, y_a, z_a) &= 0 \\ g_b\,(x_b, y_b, z_b) &= 0 \end{aligned}\right\} \tag{12}$$

These equations must correspond to Bancroft's formula

$$\left.\begin{aligned} \frac{x^{n_1} y}{z^{n+1}} &= C_1 \\[1em] \frac{x^{n_2} y}{z^{n+1}} &= C_2 \end{aligned}\right\}$$

To determine the functional form of eq. (12), we must have knowledge of the functional form of eq. (10). Planck[1] gives the formula for the potential of any solution of solid or liquid state from the Nernst's heat theorem, as

$$\varPhi = \int_0^T \frac{C_p}{T} \, dT - R\Sigma n_1 \ln c_1 - \frac{W}{T} \tag{13}$$

where C_p is the heat capacity of the system, n_1 the number of molecules, c_1 the concentration, W the heat function represented by $W = U + pV$. Then we get the molecular potential of each component,

$$\frac{\partial \varPhi}{\partial n_1} = \int_0^T \frac{\partial w_1}{\partial T} \frac{dT}{T} - \frac{w}{T} - R \ln c_1 \tag{14}$$

because if we put $\dfrac{\partial W}{\partial n_1} = w_1, \dfrac{\partial W}{\partial n_2} = w_2, \ldots$ then

$$\frac{\partial C_p}{\partial n_1} = \frac{\partial w_1}{\partial T}, \quad \frac{\partial C_p}{\partial n_2} = \frac{\partial w_2}{\partial T}, \ldots$$

If these two liquid phases are in equilibrium, the molecular potentials of each components in both phases must be respectively equal, viz.

$$\phi_A^{(a)} = \phi_A^{(b)}, \qquad \phi_B^{(a)} = \phi_B^{(b)}, \qquad \phi_S^{(a)} = \phi_S^{(b)}$$

where $\phi_A^{(a)}$ is the molecular potential of A in the first phase and $\phi_A^{(b)}$ is that of the second phase and so on. Representing every quantity in both phases similarly, we get from eq. (14)

$$\int_0^T \frac{\partial w_A^{(a)}}{\partial T} \frac{dT}{T} - \frac{w_A^{(a)}}{T} - R \ln c_A^{(a)}$$

$$= \int_0^T \frac{\partial w_A^{(b)}}{\partial T} \frac{dT}{T} - \frac{w_A^{(b)}}{T} - R \ln c_A^{(b)}. \tag{15}$$

In dilute solution w is a function of T and p only and in the any iosthermal change under a constant pressure, the expression $\int_0^T \dfrac{\partial w}{\partial T} \dfrac{dT}{T} - \dfrac{w}{T}$ remains constant; but in our case w is a function not only of p and T, but also of c. If the variation of concentration, however, be very small, we may take w to be independent of c and write eq. (15) as follows :

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[1] See Planck, Thermodynamik, 3 Aufl. § 291 and § 293.

$$\int_0^T \frac{\partial w_A^{(a)}}{\partial T} \frac{dT}{T} - \int_0^T \frac{\partial w_A^{(b)}}{\partial T} \frac{dT}{T} - \frac{w_A^{(a)}}{T} + \frac{w_A^{(b)}}{T} = R \ln \frac{c_A^{(a)}}{c_A^{(b)}} = K_A.$$

Since $c_A^{(a)} = x_a$, $c_A^{(b)} = x_b$, it follows

$$K_A = R \ln \frac{x_a}{x_b}$$

or $\qquad\qquad e^{\frac{K_a}{R}} = \frac{x_a}{x_b}$. $\qquad\qquad$ (16)

Eliminating x_b by means of (7)

$$e^{\frac{K_A}{R}} \frac{n_a + n_b}{n_b} x_0 = x_a \left(1 + \frac{n_a}{n_b} e^{\frac{K_A}{R}} \right).$$

In an analogous way, concerning the components A and B we have

$$e^{\frac{K_B}{R}} \frac{n_a + n_b}{n_b} y_0 = y_a \left(1 + \frac{n_a}{n_b} e^{\frac{K_B}{R}} \right),$$

$$e^{\frac{K_S}{R}} \frac{n_a + n_b}{n_b} z_0 = z_a \left(1 + \frac{n_a}{n_b} e^{\frac{K_S}{R}} \right).$$

Consequently, by combining above relations with $x_0 + y_0 + z_0 = 1$, it follows :

$$\frac{x_a}{e^{\frac{K_A}{R}}} + \frac{y_a}{e^{\frac{K_B}{R}}} + \frac{z_a}{e^{\frac{K_S}{R}}} = 1 .$$ $\qquad$ (17)

Similarly we have

$$\frac{x_b}{e^{\frac{K_A}{R}}} + \frac{y_b}{e^{\frac{K_B}{R}}} + \frac{z_b}{e^{\frac{K_S}{R}}} = 1 .$$ $\qquad$ (17$_1$)

Equations (17) and (17$_1$) are the relations corresponding to eq. (12) ; but it is a limiting case when the curves (5) or (12) may be seen as straight lines ; in relating K_A, K_B, K_S are functions of x_a, y_a, z_a, x_b, y_b, z_b and envelopes of the straight lines (17) and (17$_1$) are the real solutions.

The point of intersection of the curves ak and kb or the critical saturated point k is a point where K_A, K_B, and K_S are all equal to zero.

Moreover, to establish the relation between conjugate points P and Q, or the compositions of two liquid phases in equilibrium, the following operation is appreciable.

Put the values of x_a, y_a, z_a, x_b, y_b, z_b in (11) to eq, (9) and eliminate two in x_0, y_0, z_0 for example y_0 and z_0, with the relation (7), then we have a relation

$$h\,(x, y, z, x_0) = 0. \qquad (18)$$

This is a relation having one parameter; and, differentiating with x_0, we get an envelope of straight line QR, viz.,

$$\left.\begin{array}{l} h\,(x, y, z, x_0) = 0 \\[2mm] \dfrac{\partial h}{\partial x_0} = 0 \end{array}\right\} \qquad (19)$$

This is represented in the figure by the curve *lmn*. When we know the functions (12) and (19), the problem of the equilibrium of the three components system, where two liquid phases co-exist, is completely solved for a definite temperature and pressure. The curve *akb* or eq. (12) must be called an "equilibrium curve": and the envelope *lmn* or eq. (19) a "conjugate curve." To know the eqilibrium condition of any mixture of these three components, draw a tangent to the envelope from the point P representing the total mixture, then two intersecting points Q and R of the tangent with the curves of equilibrium are the points of the equilibrium.

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