

On Equilibria in Systems with Polynuclear Complex Formation

V. Some Useful Differential Expressions

LARS GUNNAR SILLÉN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

A general method is indicated for deriving the relationships that hold between the free and total concentrations of the reagents in an equilibrium mixture, regardless of the reactions taking place in it. Equations are given for calculating, from measurements (A , B , b) or (A , B , a), the average \bar{p} and \bar{q} for complexes A_pB_q formed by two reagents A and B. These equations have already been used repeatedly in this laboratory.

The appearance of a precipitate of constant or variable ratio $A/B = Z_s$ can be detected, and its composition determined, from diagrams $A(B)_s$. The equations derived for a solution hold also for an equilibrium mixture of solution and precipitate.

The extension to cases with several reagents, and to distribution equilibria with two phases are indicated.

Since the first papers in this series appeared^{1,2} some experience has accumulated in this laboratory how to study equilibria of polynuclear complexes experimentally, and how to treat the experimental data. We have found it advisable to apply as many independent experimental and mathematical-graphical methods as possible to reach our primary aim: to find the formulas of the predominant complexes and the equilibrium constants for their formation.

One of our methods is based on equations (19,21,22) below and allows one to calculate the average composition of the complexes, without any previous assumption except that the law of mass action is obeyed in its simple form (activity coefficients held constant by ionic medium).

This method was derived by the present author many years ago and has been applied, among other things, to equilibria of polyborate³, and polyvanadate⁴ ions. In these cases as in many others, the method has given valuable hints for the following treatment.

A general proof for the equations used — which can also be applied for deriving a number of other relationships — was given⁵ in my lectures at MIT

in the spring of 1957. The equations are founded on the simple law of mass action, there is nothing difficult or unusual about them, and equations related to some of them have been given earlier for instance by Hedström⁶, Byé⁷ and Lefebvre⁸.

The latter two workers, in the opinion of the present writer, may not use the most convenient variables and symbolism for treating these systems. The differences in our conclusions on specific systems may partly reflect a difference in the accuracy of our data. The French workers, besides the data, sometimes also use their chemical intuition for concluding on the formulas of the complexes.

It was hoped that it might help some chemists if a rather general approach were given, which could be applied to other situations as well. In the following, the main stress will be on the principles and it will in general be left to the reader to make those smaller transformations that will simplify the calculations, such as transforming natural to decadic logarithms.

TWO REAGENTS: ASSUMPTIONS AND DEFINITIONS

A solution contains two reagents, A and B, with the free concentrations
 $[A] = a$; $[B] = b$ (1)

A and B form one or more complexes, of the general formula A_pB_q , with p and q integral. In the equilibria we need not consider any other species than A, B, and the various A_pB_q . As usual, a formula like $[A_pB_q]$ stands for the total of all species containing pA , qB , and in addition an indefinite number of solvent and medium ions.

For brevity we shall write

$$[A_pB_q] = c_{pq} \quad (2)$$

The total concentrations of A and B we shall as usual denote by

$$A = a + \sum p c_{pq} ; \quad B = b + \sum q c_{pq} \quad (3a, b)$$

We shall find it useful to introduce the »complexity sum» S , which is the sum of the concentrations of all complexes:

$$S = \sum c_{pq} \quad (4)$$

The average composition of the complexes can be described using the average values \bar{p} and \bar{q} :

$$\bar{p} = \frac{\sum p c_{pq}}{\sum c_{pq}} = \frac{A-a}{S} ; \quad \bar{q} = \frac{\sum q c_{pq}}{\sum c_{pq}} = \frac{B-b}{S} \quad (5a, b)$$

Eqns. (1) through (5) are symmetrical in A and B. In the definitions (6–8) below, we shall arbitrarily denote one of the reagents, say B, as the »nucleus» or »central group» whereas A is the »ligand». All formulae deduced below will also be valid if the roles of the two reagents are interchanged.

The average number of A bound per B we shall call Z .

$$Z = \frac{A-a}{B} \quad (6)$$

For mononuclear complexes A_nB , Z is often denoted by \bar{n} , which is quite logical: it is the average value for n . For polynuclear complexes the notation \bar{n} would have no direct meaning. It is often advantageous to consider the number of moles of bound A per liter, from (3 a) and (6):

$$BZ = \Sigma p c_{pq} \quad (6a)$$

The total molar concentration of species containing B we shall denote by BR :

$$BR = b + \Sigma c_{pq} = b + S \quad (7)$$

The fraction of B that is present as free B we denote by α_0

$$[B] = b = \alpha_0 B \quad (8)$$

Equilibrium conditions

If the system is at equilibrium, and if the activity coefficients can be assumed to be kept constant (for instance by means of an ionic medium), the formation »constants» β_{pq} of the various complexes are really constant, and we have

$$c_{pq} = \beta_{pq} a^p b^q \quad (9)$$

Inserting (9) into (3a, 3b, 4, 6a) we find

$$A - a = BZ = \Sigma p \beta_{pq} a^p b^q; B - b = \Sigma q \beta_{pq} a^p b^q \quad (10a, 10b)$$

$$S = \Sigma \beta_{pq} a^p b^q \quad (11)$$

Differentiating (11) with respect to the variables a and b we easily find using (10 a) and (10 b)

$$dS = \Sigma p \beta_{pq} a^{p-1} b^q da + \Sigma q \beta_{pq} a^p b^{q-1} db = (A-a)d \ln a + (B-b)d \ln b \quad (12)$$

Differentiating (10a) and (10b), one will obtain similar equations where, however, the sums $\Sigma p^2 c_{pq}$, $\Sigma pq c_{pq}$ and $\Sigma q^2 c_{pq}$ appear. These equations could be used for finding more complicated averages.

We shall now center our attention on eqn. (12).

GENERAL METHOD: AUXILIARY EQUATIONS

Perhaps the simplest way of deriving the differential expressions we will need is by means of total differentials. Let us assume that F is a function of two independent variables x and y , and that its total differential can be expressed by

$$dF(x,y) = G(x,y) dx + H(x,y) dy \quad (13)$$

where the partial derivatives, G and H , are functions of x and y . The second partial derivative of F , $(\partial^2 F / \partial x \partial y)$ gives

$$\left(\frac{\partial G}{\partial y} \right)_x = \left(\frac{\partial H}{\partial x} \right)_y \quad (14)$$

From (13) we may derive the total differential for $(F-Hy)$, which is also a function of x and y :

$$d(F-Hy) = Gdx - ydH \quad (13a)$$

In the same way as (14) was derived from (13), we find from (13a)

$$\left(\frac{\partial G}{\partial H}\right)_x = -\left(\frac{\partial y}{\partial x}\right)_H \quad (14a)$$

From (14) and (14a) we find by integration, at constant x :

$$G = \text{const} + \int_{x \text{ const}} \left(\frac{\partial H}{\partial x}\right)_y dy = \text{const} - \int_{x \text{ const}} \left(\frac{\partial y}{\partial x}\right)_H dH \quad (15, 15a)$$

In the equilibrium case we are considering, we have used a and b as independent variables, but we could have chosen practically any pair out of $a, b, A, B, Z, R, S, \alpha_0$ or other convenient variables that can be defined by means of a, b and sums, $\Sigma p^r q^s c_{pq}(r, s = \text{integer})$.

We shall not bother about degenerate cases such as systems with no complexes, or with only mononuclear complexes: they are easily and joyfully recognized, and treated by simpler methods.

If it is desired to calculate one of the variables mentioned above from measurements of some other variables, one should try to transform (12) or some analogous differential equation into another expression of the form (13); to the left should stand a total differential, the unknown quantity searched for would be in the place of G , and H, x and y would be experimentally known quantities. Then, one easily derives the desired expressions for partial derivatives (14, 14a) and integrals (15, 15a)

DATA (A, B, α)

Let us assume that we know the total concentrations A and B and can measure the free concentration a , for instance by emf methods. It is then practical to eliminate A and use $BZ = A - a$ (6), so that (12) takes the form

$$dS = BZ d \ln a + (B-b) d \ln b$$

which we may transform using (7):

$$d(BR) \equiv d(S+b) = BZ d \ln a + B d \ln b \quad (16)$$

If we introduce the identity $d(BR) = BdR + RdB$, into (16), divide through B , and rearrange, we find

$$d(\ln b - R) = R d \ln B - Z d \ln a \quad (17)$$

Adding $d(Z \ln a)$ to both sides of (17) we can alternatively use

$$d(\ln b - R + Z \ln a) = R d \ln B + \ln a dZ \quad (17a)$$

Both (17) and (17a) are total differentials and analogous to equations (13) and (13a); in analogy to (14) and (14a) we obtain:

$$\left(\frac{\partial R}{\partial \ln a}\right)_B = -\left(\frac{\partial Z}{\partial \ln B}\right)_a; \left(\frac{\partial R}{\partial Z}\right)_B = \left(\frac{\partial \ln a}{\partial \ln B}\right)_Z = \left(\frac{\partial \log a}{\partial \log B}\right)_Z \quad (18a, 18)$$

(In the following, transformations from natural to decadic logarithms will be left to the reader).

We may, in passing, see from (18) or (18a) that if these expressions are = 0, thus $Z(a)$ is independent of B , for a single value for a , then R has a maximum or minimum there. If they are zero for all values for a , then R is independent of a ; which is possible in general only of the system is homonuclear.

Integration, by analogy with (15) and (15a) gives

$$R = \text{const} - \int_{B \text{ const}} \left(\frac{\partial Z}{\partial \ln B} \right)_a d \ln a = \text{const} + \int_{B \text{ const}} \left(\frac{\partial \log a}{\partial \log B} \right)_Z dZ \quad (19, 19a)$$

Usually the last formula, (19a), is more convenient for use: the partial derivative $(\partial \log a / \partial \log B)_Z$ is obtained directly as the inverted value of the slope of the curves $\log B (\log a)_Z$ in »projection maps»⁹, and in many systems it tends to be more constant and thus easier to interpolate than $(\partial Z / \partial \log B)_a$.

Finding the integration constant. In an integration at constant B according to (19) or (19a), one should start at a point with a known value for R , in order to obtain the integration constant.

Sometimes the data extend or can easily be extrapolated into a range with low A where free B predominates, so that $b \approx B$, and $R = 1$. For instance, the derivative in (19a) often behaves well on extrapolation.

In other cases, the extrapolation is uncertain, or at any rate, accuracy is gained by integrating only from some point where one can presume that only two species, say B and $A_p B_Q$, exist in appreciable amounts. In such case we have:

$$B = b + Qc_{PQ}; BR = b + c_{PQ}; BZ = Pc_{PQ} \quad (20)$$

By elimination of c_{PQ} and b in (20) we obtain

$$R = 1 - Z(Q - 1)P^{-1} \quad (20a)$$

From Z in the first experimental point that is to be used, R for that point can be calculated from (20a) and used as the integration constant in (19a). Usually, P and Q can be deduced from the shape of the experimental curves at low values for Z , but it is conceivable that in some cases alternative sets (P, Q) might be tried. A similar procedure can be used in any range where only two species can be presumed to predominate.

Eliminating c_{PQ} in (20) we may also deduce.

$$\alpha_0 = b/B = 1 - ZQP^{-1} \quad (20b)$$

Calculation of b or α_0 from data (A, B, a). One may integrate (17) directly at constant B , add $(-\ln B)$ to both sides and introduce it into the constant to the right; after rearranging one obtains

$$\ln \alpha_0 \equiv \ln b - \ln B = \text{const} + R - \int_{B \text{ const}} Z d \ln a \quad (21)$$

Inserting the expression for R from (19) we get

$$\ln \alpha_0 \equiv \ln b - \ln B = \text{const} - \int_{B \text{ const}} \left[Z + \left(\frac{\partial Z}{\partial \ln B} \right)_a \right] d \ln a \quad (21a)$$

Eqn. (21a) can also be deduced from (16) *via* the transformation

$$d(B \ln b - BR) = \ln b d B - BZ d \ln a$$

The integration constant in (21) or (21a) can be obtained either by extrapolation, or using (20b), if B and $A_p B_q$ predominate at one limit of integration.

As usual, it depends on the data which of the expressions (21) and (21a) is the most practical one to use.

Average composition of complexes

Now that R and b (or α_0) are known, one may calculate the average composition of the complexes (5a, 5b, 6, 7, 8): ,

$$\bar{p} = \frac{BZ}{S} = \frac{BZ}{BR-b} = \frac{Z}{R-\alpha_0}; \quad \bar{q} = \frac{B-b}{S} = \frac{B-b}{BR-b} = \frac{1-\alpha_0}{R-\alpha_0} \quad (22a, b)$$

Thus we can, in principle, determine the average composition of the complexes from data (A, B, a), without any more assumption about the system than that the law of mass action holds.

Elimination of mononuclear species. For special cases, a still more straightforward calculation may be devised. In several systems (such as for instance the borates³ and arsenates (III)), the mononuclear species predominate at low values for B , so that the functions pertaining to mononuclear species, $f_1(a)$ and $Z_1(a)$ in (23a, b), are accurately known. The polynuclear complexes are indicated by deviations at the higher values for B . One might use (19) and (21), but a higher accuracy may be obtained if one calculates directly B_1 , the total concentration of B in the form of mononuclear species. For the mononuclear species we have:

$$B_1 = b (1 + \sum \beta_{p1} a^p) = b f_1(a) \quad (23a)$$

$$B_1 Z_1 = b \sum p \beta_{p1} a^p = b d f_1(a) / d \ln a \quad (23b)$$

Thus we have

$$Z_1 = d \ln f_1 / d \ln a \quad (23c)$$

$$d \ln B_1 = d \ln b + d \ln f_1 = d \ln b + Z_1 d \ln a \quad (24)$$

We integrate (24) at constant B and introduce the expression for $\ln b$ from (21a):

$$\ln B_1 = \text{const} + \int \left[Z_1 - Z - \left(\frac{\partial Z}{\partial \ln B} \right)_a \right] d \ln a \quad (25)$$

In (25), Z_1 is known before as a function of a , whereas $Z(a, B)$ differs for each value of B chosen.

The integration constant is found in a way analogous to (20 a,b). If we may assume that at one integration limit, there is only one polynuclear complex of importance, say A_pB_q , we have

$$B = B_1 + Qc_{PQ}; BZ = B_1Z_1 + Pc_{PQ}; B_1 = B(P-QZ)(P-QZ_1)^{-1} \quad (26)$$

If the polynuclear complexes may be neglected at this limit, we have $B_1 = B$.

Having calculated B_1 from (25), we may then subtract from B , BZ and BR the contributions from the mononuclear species, which leaves the polynuclear terms:

$$B_{\text{poly}} = B - B_1; B_{\text{poly}} Z_{\text{poly}} = BZ - B_1Z_1; B_{\text{poly}} R_{\text{poly}} = BR - B_1 \quad (27)$$

For any experimental point we may then calculate the average composition of the polynuclear complexes (\bar{p} and \bar{q} in eqn. (22) include also the mononuclear complexes):

$$Z_{\text{poly}} = \frac{BZ - B_1Z_1}{B - B_1}; \bar{p}_{\text{poly}} = \frac{Z_{\text{poly}}}{R_{\text{poly}}} = \frac{BZ - B_1Z_1}{BR - B_1}; \bar{q}_{\text{poly}} = \frac{1}{R_{\text{poly}}} = \frac{B - B_1}{BR - B_1} \quad (28)$$

In (28), the average composition has been obtained from the data (A , B , a) without any other assumption than the validity of the law of mass action. B and Z are obtained from the experiments, Z_1 is known as a function of a , and B_1 calculated by means of (25).

DATA (A , B , b)

From (12) we obtain by easy transformations:

$$d(A \ln a + B \ln b - S - a - b) = \ln a \, dA + \ln b \, dB \quad (29)$$

$$d(A \ln a - S - a - b) = \ln a \, dA - B \, d \ln b \quad (29a)$$

The two differentials in (29) and (29a) give

$$\left(\frac{\partial \ln a}{\partial B}\right)_A = \left(\frac{\partial \ln b}{\partial A}\right)_B \text{ or } \left(\frac{\partial \ln(aA^{-1})}{\partial B}\right)_A = \left(\frac{\partial \ln(bB^{-1})}{\partial A}\right)_B \quad (30)$$

$$\left(\frac{\partial \ln a}{\partial \ln b}\right)_A = -\left(\frac{\partial B}{\partial A}\right)_b \quad (30a)$$

Integrals for practical evaluation can be written in several forms, for instance

$$\ln \left(\frac{a}{A}\right) = \text{const} + A^{-1} \int_{A \text{ const}} \left(\frac{\partial \ln(b/B)}{\partial \ln A}\right)_B \, dB \quad (31)$$

$$\ln a = \text{const} - \int_{A \text{ const}} \left(\frac{\partial B}{\partial A}\right)_b \, d \ln b \quad (31a)$$

Eqns. (30) and (30a) have been derived in other ways by Hedström⁶ and McKay¹⁰.

DATA (a , B , b)

In some systems, both b and a can be measured, but the difference ($A - a$) is too small for an accurate treatment. Such cases are for instance the hydrolysis of metal ions in very acidic solutions, where the metal ion activity can be measured by means of amalgam electrodes.

By transformation of (16) we obtain using (8)

$$d(S+b-B) = BZ d \ln a + B d \ln \alpha_0 \quad (32)$$

$$d(S+b-B-B \ln \alpha_0) = BZ d \ln a - \ln \alpha_0 d B \quad (32a)$$

From the total differentials (32) and (32a) we find

$$\left(\frac{\partial(BZ)}{\partial \ln \alpha_0}\right)_a = \left(\frac{\partial B}{\partial \ln a}\right)_{\alpha_0}; \left(\frac{\partial(BZ)}{\partial B}\right)_a = -\left(\frac{\partial \ln \alpha_0}{\partial \ln a}\right)_B \quad (33, 33a)$$

$$BZ = \text{const} + \int_{a \text{ const}} \left(\frac{\partial B}{\partial \ln a}\right)_{\alpha_0} d \ln \alpha_0 = \text{const} - \int_{a \text{ const}} \left(\frac{\partial \ln \alpha_0}{\partial \ln a}\right)_B d B \quad (34, 34a)$$

Thus we can obtain Z ; S and R are obtained directly from (32) which gives us, for a constant a :

$$BR - B = S + b - B = \text{const} + \int_{a \text{ const}} B d \ln \alpha_0 \quad (35)$$

Eqns. (34) and (35) can be transformed in various ways for convenience in calculations. The integration constant can usually be found by starting in a region where only two species predominate.

SPECIAL EQUATIONS FOR HYDROLYSIS

An important case of polynuclear complex formation is the hydrolysis of metal cations B . The ligand A may be considered to be OH^- , but since one measures

$$h = [\text{H}^+] \quad (36)$$

it is often practical^{10a} to describe the ligand, instead, as $(-\text{H}^+)$. Eqn. (9) is replaced by

$$c_{pq} = [\text{H}_{-p}\text{B}_q] = \beta_{pq} h^{-p} b^q \quad (37)$$

Instead of A we must introduce the total analytical excess of H^+ , H , and then find, instead of (3a) and (6a)

$$BZ = h - H = \Sigma p c_{pq} \quad (38)$$

Eqns. (3b) and (4) are valid as before:

$$B - b = \Sigma q c_{pq}; S = \Sigma c_{pq} \quad (3b, 3c)$$

Differentiation gives

$$dS = (B-b) d \ln b - (h - H) d \ln h \quad (39)$$

Introducing (38) into (39) we find

$$d(S+b) = B d \ln b - BZ d \ln h \quad (40)$$

This is equivalent to eqn. (16). If we have data (H, B, h) , to apply eqns. (18) — (22) we need only replace a by h^{-1} , or $\ln a$ by $-\ln h$.

In the treatment of data (H, B, b) we can rewrite (39) to the form

$$dS = (H-h) d \ln h + (B-b) d \ln b \quad (39a)$$

which is obviously analogous to (12). In using (31) and corresponding equations, we need then only replace A by H and a by h .

SOLID PHASE PRESENT

An important and challenging task for the future seems to be the study of micellar systems by the methods of equilibrium analysis. Perhaps the micelles of various long-chain ions can be described as a sort of solid solution, thus a separate phase¹¹, perhaps they are better described as very large complexes, of definite or variable composition. Previous experience^{2,12} has shown that it is rather hard, without a high accuracy of measurement, to distinguish between large complexes and a solid phase (infinite complexes).

Let us assume that for each liter of solution, A_s mole A and B_s mole B are present as bound in a solid phase so that

$$A_s = B_s Z_s \quad (41)$$

The ratio Z_s may be a constant, but we shall consider the general case where Z_s is a function of a ; because of the equilibrium condition, b will also be a function of a in the presence of a solid phase.

Equations (3a, 3b, 4) are now replaced by

$$A = a + \Sigma p c_{pq} + A_s; B = b + \Sigma q c_{pq} + B_s; S = \Sigma c_{pq} \quad (42a, b, c)$$

In the presence of a solid phase, b and Z_s , and hence $(A - A_s)$ and $(B - B_s)$ are functions of a (cf. 42 a and b). It follows immediately that

$$\left(\frac{\partial A}{\partial B}\right)_a = \left(\frac{\partial A_s}{\partial B_s}\right)_a = Z_s \quad (43)$$

A plot $A(B)_a$, thus of $A(B)$ for a constant a -value, should thus give a straight line, of slope Z_s , when a solid is present; this may be used to find out whether a new phase is separated. In equilibria with only homonuclear complexes, and no solid, $A(B)_a$ is also a straight line since Z is a function of a only. There should be no difficulty distinguishing this case from that of precipitation.

We shall now apply the Gibbs-Duhem law to the new phase: $n_A d\mu_A + n_B d\mu_B = 0$. Inserting $n_A = A_s$, $n_B = B_s$, $\mu_A = \text{const} + RT \ln a$, $\mu_B = \text{const} + RT \ln b$, and dividing by RT , we obtain

$$A_s d \ln a + B_s d \ln b = 0, \quad (44)$$

$$\text{or using (41) } Z_s d \ln a + d \ln b = 0 \quad (44a)$$

Differentiation of (42 c) and insertion of (42 a, b), gives:

$$dS = \sum p c_{pq} d \ln a + \sum q c_{pq} d \ln b = (A - a - A_s) d \ln a + (B - b - B_s) d \ln b$$

Inserting (44) we find

$$dS = (A - a) d \ln a + (B - b) d \ln b \quad (12)$$

Thus, eqn. (12) is also valid if a solid phase exists in equilibrium with the solution, and eqns. (19), (21) *etc.* can be applied. One must, however, remember (42 a, b, c) that S is valid for the solution, whereas A and B also contain terms for the solid phase. So, $R = (S + b)/B$ for the mixture of solution and solid will come out lower than what corresponds to the solution only.

It is true that b is a function of a , so that (a, b) are not independent. The system is determined instead by, say (a, B) or (Z, B) which are really independent.

One might proceed to derive a number of equations, which could be used to determine the various equilibrium constants involved. However, in a real case it will not be hard to derive the equations one needs. The most important task is to obtain reliable experimental data over a broad concentration range.

SEVERAL REAGENTS

The treatment may be extended to equilibria with several reagents. We shall arbitrarily denote one of them as the »central group» B , whereas the others are »ligands» $A_1, A_2, \dots, A_n, \dots$. Denoting, as before, total concentrations by capital letters and free concentrations by lower case letters, we have for any complex

$$c_i = [(A_1)_{p_1} (A_2)_{p_2} \dots B_q] = \beta_i a_1^{p_1} a_2^{p_2} \dots b^q \quad (45)$$

and, with easily understood symbols

$$S = \sum c_i \quad (46)$$

$$A_n - a_n = \sum p_n c_i = \bar{p}_n S; B - b = \sum q c_i = \bar{q} S \quad (46a, 46b)$$

Differentiation of (46) gives, introducing (46a, 46b):

$$dS = \sum (A_n - a_n) d \ln a_n + (B - b) d \ln b \quad (47)$$

$$\text{or } d \ln S = \sum \bar{p}_n d \ln a_n + \bar{q} d \ln b \quad (48)$$

$$d(S + b + \sum a_n - \sum A_n \ln a_n) = B d \ln b - \sum \ln a_n d A_n \quad (49)$$

Keeping all A_n constant except A' we find from (49)

$$d(S + b + \sum a_n - \sum A_n \ln a_n + A' \ln a') = B d \ln b + A' d \ln a' \quad (49a)$$

Eqns. (47) — (49) can be used as a basis for deriving useful relationships between the variables, if satisfactory data are available.

In differentiating eqn. (46 b), weighed averages \tilde{p}_n and \tilde{q} occur (Rossotti¹³), defined by

$$B\tilde{p}_n = \Sigma p_n q c_i; B\tilde{q} = b + \Sigma q^2 c_i \quad (50a, 50b)$$

Differentiating (46 b) we find

$$dB = B d \ln B = \Sigma \Sigma p_n q c_i d \ln a_n + (b + \Sigma q^2 c_i) d \ln b$$

or, after transformation using (50a, 50b)

$$d \ln B = \Sigma \tilde{p}_n d \ln a_n + \tilde{q} d \ln b \quad (51)$$

DISTRIBUTION EQUILIBRIA

Let us assume that there are two solution phases at equilibrium, say one aqueous (no subscript) and one organic (subscript "o"). There will then be two sets of equations, one for each phase. For instance, the counterpart to (51) is (51_o):

$$d \ln B_o = \Sigma \tilde{p}_{no} d \ln a_{no} + \tilde{q}_o d \ln b_o \quad (51_o)$$

The equilibrium between the phases requires that for each reagent the distribution ratio, a_n/a_{no} or b/b_o , remains constant so that

$$d \ln a_{no} = d \ln a_n; d \ln b_o = d \ln b \quad (52)$$

The distribution ratio for B, Q, is defined by

$$B_o = BQ, \text{ thus } d \ln B_o = d \ln Q + d \ln B \quad (53)$$

Eliminating $d \ln b$ and $d \ln B_o$ from (51), (51_o) and (53), using (52), we find

$$d \ln Q = \tilde{q}_o (\tilde{q}^{-1} - \tilde{q}_o^{-1}) d \ln B + \Sigma \tilde{q}_o (\tilde{p}_{no} \tilde{q}_o^{-1} - \tilde{p}_n \tilde{q}^{-1}) d \ln a_n \quad (54)$$

In special cases we may set

$$a_n \approx A_n \quad (55)$$

for instance when B is present in small or tracer amounts. From (54) and (55) we then find

$$\left(\frac{\partial \ln Q}{\partial \ln B} \right)_{\text{all } A_n} \approx \tilde{q}_o \left(\frac{1}{\tilde{q}} - \frac{1}{\tilde{q}_o} \right); \left(\frac{\partial \ln Q}{\partial \ln A'} \right)_{B, \text{ all other } A_n} \approx \tilde{q}_o \left(\frac{\tilde{p}_{no}}{\tilde{q}_o} - \frac{\tilde{p}_n}{\tilde{q}} \right) \quad (55a, 55b)$$

These equations are essentially the same as those given by Rossotti¹³. They can be simplified if \tilde{q}_o and \tilde{q} can be treated as constant, or even as equal.

We shall not further develop the cases of many ligands, or distribution equilibria. It is not hard to deduce a number of differential and integral expressions. The real difficulty is to get data over a broad range of concentrations for each reagent, data that are sufficiently reliable to allow valid conclusions to be drawn from such calculations.

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