

**On Equilibria in Systems with Polynuclear Complex
Formation. II. Testing Simple Mechanisms which give
"Core + Links" Complexes of Composition $B(A_rB)_n$ ***

LARS GUNNAR SILLÉN

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

It was shown in Part I that very simple conditions are met with if all complexes that are formed by two reactants A and B can be written in the form $B(A_rB)_n$, where t is constant, and n variable. In this case, the curves giving $Z = (A - a)/B$ as a function of $\log a$ have the same shape for all values of the total concentration B and are parallel to each other.

As a matter of fact, parallel $Z(\log a)_B$ curves are often found experimentally. It was proved inversely (I, eq. 16—20) that this behavior requires a "core + links" mechanism: if b is negligible in the whole range studied, the general formula of the complexes must be $A_r(A_tB)_n$ (r and t constant, n variable) whereas if the curves are parallel in a range where b is not negligible we must have the additional condition $r = -t$ and thus the general formula $B(A_rB)_n$.

If the curves $\frac{b}{B}(\log a)_B$ and consequently $\log \frac{B}{b}(\log a)_B$ are found to be parallel, the only possible formula is $B(A_rB)_n$ (I, eq. 40—42).

It was indicated in Part I that, for further discussion of the mechanism, one may conveniently transform the coordinates so that all of the previously parallel curves coincide and the constants r and t disappear from the equations (I, eq. 25—26, 44). The experimental data are then reduced to a single curve which can be compared with a few families of theoretical curves, calculated under various simple assumptions.

In the present paper we shall only treat complexes of the general formula $B(A_rB)_n$. If the general formula of the complexes is $A_r(A_tB)_n$ and b is always negligible, one may consider the core to be $C = A_{r+t}B$ and the complexes as $C(A_{-t}B)_n$. It is then possible to use exactly the same equations and families of curves as will be derived below for $B(A_rB)_n$ (compare I, eq. 33, 34) so there is therefore no need for a separate treatment.

* Part I: *Acta Chem. Scand.* 8 (1954) 299.

List of symbols

- A* total concentration of A (I, 2).
a concentration of free A (I, 1).
B total concentration of B (I, 2).
b concentration of free B (I, 1).
c_n concentration of *n*:th complex (1).
f = *S/b*, function of *u* (3).
g = *S/b*, function of *v* (3a).
k equilibrium constant in (17), (19), or (28).
k_n equilibrium constant defined by (1).
l_n = *k_nk⁻ⁿ*, constant (6).
N number of links in singular complex (19).
n variable integer, number of links in "core + links" complex.
r number of A in core (if free from B).
S complexity sum (3, I 4).
t number of A per B in link.
u = *a^tb* (2).
v = *ka^tb* (6).
v₁ value of *v* for *y* = $\frac{1}{2}$, (33), (40), (44).
v₂ value of *v* that makes *B* = 2*b*, η = log 2 (70).
 \bar{X} = *x* + log 2 - *x₁* (10).
x = *t* log *a* + log *B* (9).
x₁ value of *x* for *y* = $\frac{1}{2}$ (10).
y = (*A* - *a*)/*Bt* = *Z/t* (8).
Z = (*A* - *a*)/*B*, average number of A bound per B (4).
 η = log $\frac{B}{b}$ (46).
 ξ = *x* + constant, chosen so as to make the asymptote of $\eta(\xi)$ go through the origin (51, 53); or (69, IIIc) to make all curves go through $\eta = \xi$ = log 2.

General equations

We shall assume as before that the activity factors are constant. The law of mass action gives for the formation of the complex $B(A_rB)_n$ from A and B (I, 21):

$$[B(A_rB)_n] = c_n = k_n b (a^t b)^n = k_n b u^n \quad (1)$$

Here, *a* and *b* are the free concentrations of the two reactants A and B, and the variable *u* is defined (I, 10) as:

$$u = a^t b \quad (2)$$

For the complexity sum *S* and the amounts of A and B bound in complexes (in mole/l) we find (I, 22):

$$S = \Sigma [B(A_rB)_n] = b \Sigma k_n u^n = b f(u) \quad (3)$$

$$A - a = a \left(\frac{\partial S}{\partial a} \right)_b = ab \frac{df}{du} \left(\frac{\partial u}{\partial a} \right)_b = bt u f'(u) = BZ \quad (4)$$

$$B - b = b \left(\frac{\partial S}{\partial b} \right)_a = b [f(u) + u f'(u)] \quad (5)$$

In the following it will prove advantageous to introduce a new variable $v=ku$ and a new set of constants l_n . Here k is a constant (at first unknown) related to the equilibrium constants k_n (see eq (19) and (28)).

$$v = ku = ka^i b; k_n = l_n k^n \quad (6)$$

$$S = \Sigma b l_n v^n = bg(v); g(v) = \Sigma l_n v^n \quad (3 \text{ a})$$

Here $g(v)$ is a function of v only. From (3), (3 a), and (6) we see that

$$f(u) = g(v) = Sb^{-1}; u f'(u) = v g'(v) \quad (7)$$

Equations (4–5) will then be transformed in the following way:

$$A-a = BZ = btvg'(v) \quad (4 \text{ a})$$

$$B-b = b[g(v) + vg'(v)]; B = b(1 + g + vg') \quad (5 \text{ a})$$

DATA (a , A , B)

Plotting of the data

Let us remember that t , the number of A per B in a link, can be obtained from the spacing of the $Z(\log a)_B$ curves using equation (I, 24).

In any experiment, A and B , the total concentrations of the reactants, should be known from the analytical data. If, in addition, the free concentration a is measured but not b , it is convenient to calculate and plot on a diagram the two quantities y and x from (I, 25 and 26). Using these equations together with (6) and (7) we find:

$$y = \frac{A-a}{Bt} \quad (8)$$

$$y = vg' (1 + g + vg')^{-1} \quad (8 \text{ a})$$

$$x = t \log a + \log B \quad (9)$$

$$x = \log v - \log k + \log (1 + g + vg') \quad (9 \text{ a})$$

The expressions for x and y in (8 a) and (9 a) contain only constants and functions of the variable v , and neither a nor b separately. Then y may be plotted as a function of x only and all points should fall on a single curve which is independent of B . Thus our problem reduces to the calculation of the shape of $y(x)$ under various assumptions and a comparison of the calculated curves (from 8 a and 9 a) with the experimental one (from 8 and 9).

This comparison is made easier if we shift the *calculated* curves along the abscissa so that they all go through a single point. We shall choose as abscissa for the calculated curves:

$$X = x + \log 2 - x_{\frac{1}{2}} \quad (10)$$

where $x_{\frac{1}{2}}$ is the value of x for $y = \frac{1}{2}$ (the "half-point"). Obviously all calculated curves $y(X)$ will then go through the point

$$X = \log 2, y = \frac{1}{2} \quad (11)$$

We may derive from (8 a) and (9 a)

$$x_{\frac{1}{2}} = \log 2 - \log k + \log(v^2g')_{y=\frac{1}{2}} \quad (12)$$

which gives with (9 a) and (10)

$$X = \log v + \log(1 + g + vg') - \log(v^2g')_{y=\frac{1}{2}} \quad (13)$$

One may prepare a transparent diagram with any calculated curve $y(X)$, place it over the diagram with the experimental curve $y(x)$, and move it parallel with the x axis. If a fit is obtained, one may use $x_{\frac{1}{2}}$ at the half-point and equation (12) to calculate the equilibrium constants.

Direct analysis

From (8a) we find $1 + g + vg' = (1 + g)/(1 - y)$. We insert this into (9a), differentiate and eliminate $d \ln v$ by using $d \ln v = (y^{-1} - 1) d \ln(1 + g)$, which may be found from (8a), observing that $vg' = d(1 + g)/d \ln v$. The result is

$$\log(1 + g) = \int_{-\infty}^x y dx + \log(1 - y) + y \log e \quad (14)$$

From (9a), inserting $1 + g + vg' = (1 + g)/(1 - y)$ (8a), $\log v - \log k = u$ (6), and (14)

$$\log u = x - y \log e - \int_{-\infty}^x y dx \quad (15)$$

With data (a, A, B) one might thus use the curve $y(x)$, (14), and (15) to calculate $g(v) = f(u)$ as a function of u , and then try to find the coefficients k_n (= the equilibrium constants) in the power series (3).

From data (a, b, A, B) one finds u directly. By integrating (5) one may find

$$1 + g = 1 + f(u) = \frac{1}{u} \int_0^u \frac{B}{b} du \quad (16)$$

This will also give $f(u)$ from the experimental data.

However, because of the limited accuracy of the data, these procedures seem impracticable at least with present techniques.

Choice of hypotheses

In the present paper we shall confine ourselves to studying a number of simple hypotheses, involving not more than two unknown constants to be determined with the aid of the experimental curves:

I) Our first hypothesis is that no soluble complexes are formed but that solid A_2B may precipitate. As usual, " $A_2B(s)$ " may also contain solvent molecules and inert ions from the ionic medium.

II) The next simple hypothesis is that out of all conceivable complexes $B(A_2B)_n$ only one, $B(A_2B)_N$, is formed, where N is constant and at first unknown.

III) The other extreme hypothesis is that complexes with all positive values for n are formed by a *repeated reaction* and we shall try three different equations (28a, b, c) for the variation of the equilibrium constants k_n with n .

Hypothesis I: No soluble complex; solid A_1B may precipitate

In all the mechanisms to be considered we shall find as one limiting case those curves that would be obtained if only solid A_1B and no soluble complexes were formed (hypothesis I). We shall now derive the equations of these curves.

If some A_1B has precipitated — ($B-b$) mole — we have:

$$A-a = t(B-b); u = a'b = k^{-1}; v = 1 \quad (17)$$

where k^{-1} is the solubility product of A_1B (including the terms from solvent molecules and medium ions). We then find from (8), (17), (9), and (10):

$$\left. \begin{aligned} y &= \frac{A-a}{Bt} = \frac{B-b}{B} = 1 - \frac{b}{B} \\ x &= \log a'B = -\log k - \log \frac{b}{B} = -\log k - \log (1-y) \\ x_{\frac{1}{2}} &= \log 2 - \log k; X = x + \log k = -\log (1-y) \end{aligned} \right\} \quad (17a)$$

If the product $u = a'b$ is less than k^{-1} , no precipitate occurs and we have $a = A$, $b = B$, $y = 0$ since there are no soluble complexes.

There will be a sharp break in the curve $y(X)$ at the point of precipitation:

$$\left. \begin{aligned} X &= -\log(1-y) & \text{for } X > 0 \\ y &= 0 & \text{for } X < 0 \end{aligned} \right\} \quad (18)$$

The curve $y(X)$ from (18) will be seen as limiting curve in fig. 1 (hypothesis II, $N \rightarrow \infty$) and fig. 2 (hypothesis III, $k_0 \rightarrow 0$).

Hypothesis II: Only one complex formed

Let us assume that the only complex formed is $B(A_1B)_N$ and that the equilibrium constant is k^N . We then have (cf 6 and 3a):

$$S = [B(A_1B)_N] = k^N b (a'b)^N = b v^N = b g \quad (19)$$

where

$$g(v) = v^N; v g'(v) = N v^N = N g \quad (20)$$

We may derive from (4a), (5a), and (20)

$$A-a = N t b g; B-b = (N+1) b g \quad (21)$$

The equations (21) may also be obtained immediately from (19) since the concentration of the complex is bg , the number of A bound per complex is Nt and the number of B bound per complex is $(N+1)$.

We shall now see what type of $y(x)$ plot one would obtain with this mechanism. We find from (8) and (21), or (8a) and (20)

$$y = N g [1 + (N+1)g]^{-1} \quad (22)$$

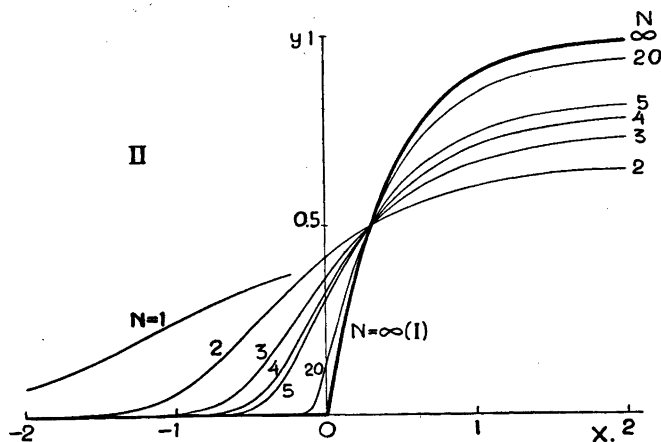


Fig. 1. Family of curves $y(X)_N$ for hypothesis II: only one complex $B(A_iB)_N$ is formed.

and from (9a) and (20)

$$x + \log k = N^{-1} \log g + \log [1 + (N + 1)g] \quad (23)$$

From (22) we find $y = \frac{1}{2}$ for $g = (N-1)^{-1}$ which gives with (23) and (10):

$$x_{\frac{1}{2}} = \log 2 - \log k + \log N - (1 + N^{-1}) \log (N-1) \quad (24)$$

$$X = x + \log 2 - x_{\frac{1}{2}} = N^{-1} \log g + \log [1 + (N + 1)g] - \log N + (1 + N^{-1}) \log (N-1) \quad (25)$$

The expressions for y and X in (22) and (25) contain only N and the single variable g . One may thus for each N draw a curve giving y as a function of X .

Fig. 1 gives a family of such curves $y(X)_N$ with various values for N : 1, 2, 3, 4, 5, 20 and ∞ . For the curve with $N = 1$, the abscissa was arbitrarily chosen as $x + \log k - 1$ since this curve approaches the value $y = \frac{1}{2}$ only asymptotically (see 24). All the other curves $y(X)_N$ intersect at the half-point (11) as they should.

The limiting curve for $N \rightarrow \infty$ is $X = -\log (1-y)$ as is seen from (22) and (25) if one lets $N \rightarrow \infty$ and $g \rightarrow 0$ in such a way that Ng has finite values. (For $N \rightarrow \infty$, $Ng = 0$ we find its linear continuation, $y = 0$, $X < 0$).

Now this is equation (18) derived assuming the precipitation of solid A_iB , which may be regarded as the limiting case of the formation of complexes $B(A_iB)_n$.

If the experimental data are given in the form of a curve $y(x)$, one may test the single-complex mechanism by trying to fit the curve family $y(X)$ of fig. 1. If a fit is found, the most likely value for N is found from the shape of the curve, especially from the upper limit (see 22):

$$y \rightarrow \frac{N}{N+1} \text{ for } x \rightarrow \infty \quad (26)$$

and from the slope at the half-point:

$$\left(\frac{dy}{dX}\right)_{y=\frac{1}{2}} = \left(\frac{dy}{dx}\right)_{y=\frac{1}{2}} = \frac{(N-1) \ln 10}{2(N+3)} \quad (27)$$

From $x_{\frac{1}{2}}$, the value for x at $y = \frac{1}{2}$, one can then obtain k from equation (24).

Hypothesis III: Repeated reaction

The other extreme assumption is that all positive integral values for n are represented by complexes $B(A_iB)_n$ in the solution. We shall try the following three working hypotheses on how k_n varies with n , where k_n is the equilibrium constant for the formation of the n :th complex from A and B (1, 6):

$$\text{IIIa: } k_n = k_0 k^n; \quad l_n = k_0; \quad k_{n+1} k_n^{-1} = k \quad (28a)$$

$$\text{IIIb: } k_n = k_0 n k^n; \quad l_n = k_0 n; \quad k_{n+1} k_n^{-1} = k(1 + n^{-1}) \quad (28b)$$

$$\text{IIIc: } k_n = \frac{k_0 k^n}{n}; \quad l_n = \frac{k_0}{n}; \quad k_{n+1} k_n^{-1} = k(n+1)^{-1} \quad (28c)$$

For all three hypotheses, the equilibrium constant for the formation of the first complex is given by $k_1 = k k_0$:

$$tA + 2B \rightleftharpoons BA_iB; \quad k_1 = [BA_iB] a^{-i} b^{-2} = c_1 a^{-i} b^{-2} = k k_0 \quad (29)$$

The equilibrium constant for the addition of a new link is:

$$B(A_iB)_n + tA + B \rightleftharpoons B(A_iB)_{n+1}; \quad k_{n+1} k_n^{-1} = c_{n+1} c_n^{-1} a^{-i} b^{-1} \quad (30)$$

and may vary with n . With IIIa, $k_{n+1} k_n^{-1}$ has always the same value, namely k ; if $k_0 = 1$, then also $k_1 = k$. With IIIb, $k_{n+1} k_n^{-1} = k(1 + n^{-1})$ tends to a constant value k , but the first few links are somewhat more easily added. With IIIc $k_{n+1} k_n^{-1} = k(n+1)^{-1}$ tends to zero with increasing n so that the formation of the higher complexes becomes increasingly difficult.

The first hypothesis is the simplest and has rendered good service for many systems. For this reason, IIIa will be treated more fully than the other two. It is also what one would expect, from statistical considerations, if the complexes are chain-like.

The two hypotheses IIIb and IIIc have been included because it seemed desirable to find out whether an equally good agreement with the experimental data could be obtained with widely different assumptions concerning the behavior of the constants, k_n . The assumptions (28b) and (28c) were not chosen on the basis of any statistical argument (which may have only a limited value in this case) but because they give an easy summation in (3) and (3a).

Hypothesis IIIa: All consecutive constants equal

For hypothesis IIIa we find, using (28a) and (3a):

$$g(v) = \sum_1^{\infty} l_n v^n = k_0 v(1-v)^{-1}; \quad v g'(v) = k_0 v(1-v)^{-2} \quad (31)$$

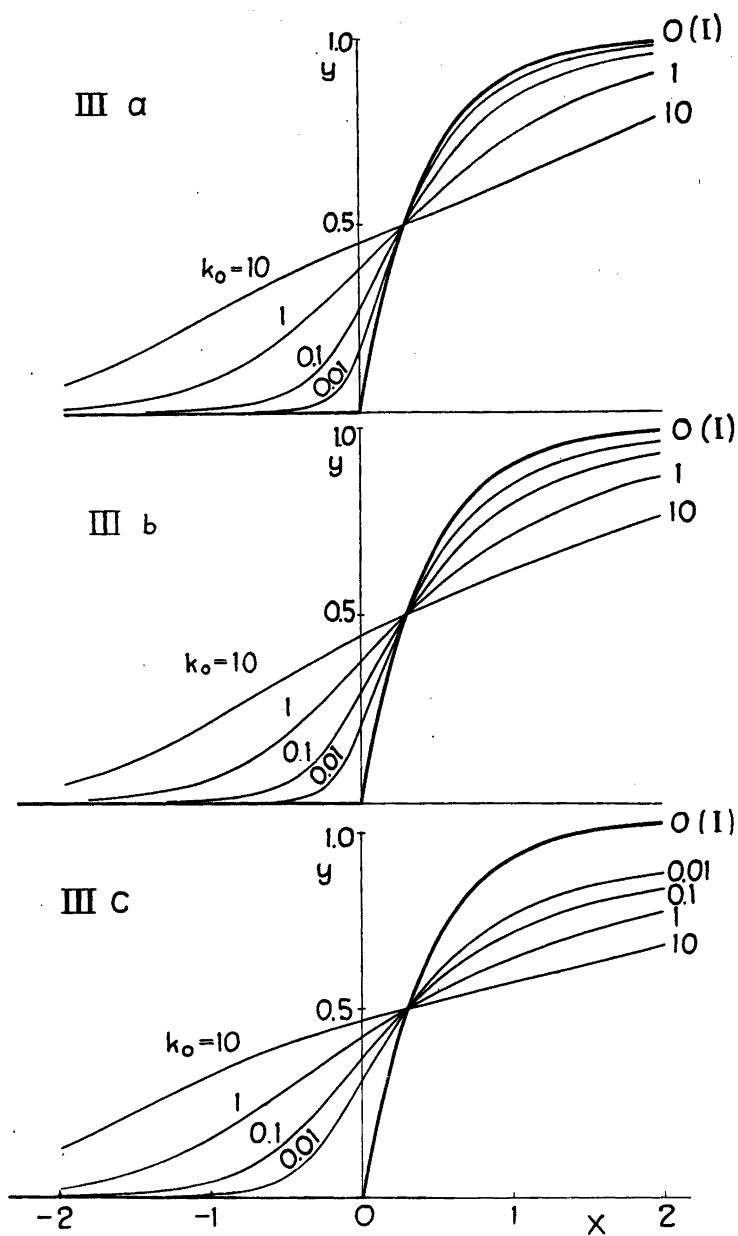


Fig. 2a-c. Families of curves $y(x)_{k_0}$ for repeated reaction, hypotheses IIIa, IIIb, and IIIc (eq 28 a-c).

Introducing (31) into (8a) we find

$$y = k_0 v [(1-v)^2 + k_0 v (2-v)]^{-1} \quad (32)$$

and from (32) and (12) with (31)

$$v_{\frac{1}{2}} = (1 + \sqrt{k_0})^{-1}; \quad x_{\frac{1}{2}} = \log 2 - \log k \quad (33)$$

Finally from (10) and (33) with (9a) and (31):

$$X = x + \log k = \log v + \log [1 + k_0((1-v)^{-2} - 1)] \quad (34)$$

With the aid of equations (32) and (34) we may construct a family of curves, giving y as a function of $X = x + \log k$ for various values of k_0 . Some of these curves are given in Fig. 2a. All the curves intersect at the half-point (11) as they should.

The limiting curve for the family $y(X)_{k_0}$ is that for $k_0 = 0$, its equation being (18), $X = -\log(1-y)$. This may be demonstrated by letting $k_0 \rightarrow 0$ and $v \rightarrow 1$ in equations (32) and (34) in such a way that $k_0(1-v)^{-2}$ has a finite value. It may be seen intuitively that $k_0 \rightarrow 0$, $k = \text{constant}$ means that the first complex is formed with greater and greater difficulty whereas the addition of new links is as easy as before. When v is increased towards the value 1, the formation of complexes starts suddenly and at once leads to very large complexes, which is equivalent to precipitation.

If $k_0 = 1$ all links are added with the same equilibrium constant. The equations (32) and (34) then take the simple forms:

$$y = v \quad (32a)$$

$$X = x + \log k = \log y - 2 \log(1-y) \quad (34a)$$

If the experimental data are seen to fit in with the family of curves in fig. 2a, one may obtain k from $x_{\frac{1}{2}}$, the x coordinate at the point $y = \frac{1}{2}$, using (33). To find k_0 one may either use the slope of the curve $y(x)$ at the half-point:

$$\left(\frac{dy}{dX}\right)_{y=\frac{1}{2}} = \left(\frac{dy}{dx}\right)_{y=\frac{1}{2}} = \frac{1}{2} \ln 10 \cdot (1 + 2\sqrt{k_0})^{-1} \quad (35)$$

as may be proved from (32) and (34). One may also, for a number of y values, measure x , calculate 10^X using (cf 10):

$$10^X = 2 \cdot 10^{(x-x_{\frac{1}{2}})} \quad (36)$$

and apply the equation

$$k_0 = y [1 - 10^X(1-y)]^2 [10^X(1-2y)^2]^{-1} \quad (37)$$

Equation (37) may be proved as follows. From (32) and (34), $y \cdot 10^X = k_0 v^2 (1-v)^{-2}$. If this expression is used for eliminating v from (32), (37) results after rearrangement.

Hypothesis IIIb

For hypothesis IIIb we find from (3a) and (28b)

$$g(v) = \sum_1^{\infty} l_n v^n = k_0 \sum_1^{\infty} n v^n = k_0 v(1-v)^{-2}; \quad vg'(v) = k_0 v(1+v)(1-v)^{-3} \quad (38)$$

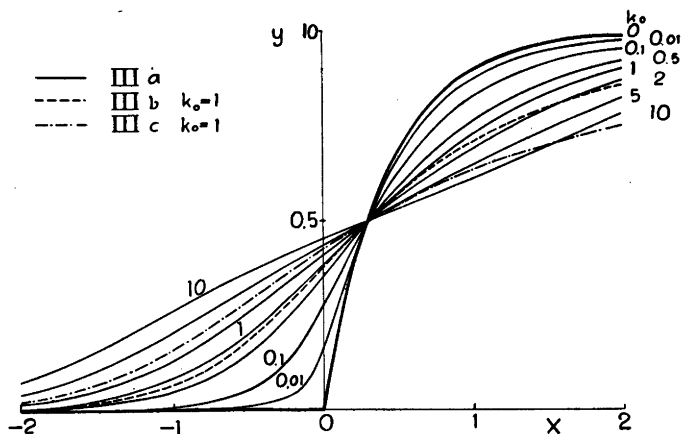


Fig. 3. Position of curves for $k_0 = 1$ with hypotheses IIIb and IIIc in the family of curves $y(X)_{k_0}$ for IIIa.

If the expressions for g and vg' from (38) are inserted into (8a) we find

$$y = k_0 v(1+v)[(1-v)^3 + 2k_0 v]^{-1} \quad (39)$$

For $y = \frac{1}{2}$ we find from (39), and from (12) and (38)

$$2k_0 v_{\frac{1}{2}}^2 = (1-v_{\frac{1}{2}})^3; \quad x_{\frac{1}{2}} + \log k = \log(1+v_{\frac{1}{2}}) \quad (40)$$

Thus $v_{\frac{1}{2}}$ is the solution of the third-degree equation in (40) which may be solved for any k_0 value. Finally with (10) and (40), (9a) and (38):

$$X - \log 2 + \log(1+v_{\frac{1}{2}}) = x + \log k = \log v + \log[1 + 2k_0 v(1-v)^3] \quad (41)$$

Fig. 2b gives $y(X)_{k_0}$ as calculated from (39–41). The limiting curve for $k_0 \rightarrow 0$ is (18): $X = -\log(1-y)$. — Fig. 3 shows the curve for $k_0 = 1$ with hypothesis IIIb together with the curve family for IIIa.

Hypothesis IIIc

For hypothesis IIIc we find from (3a) and (28c):

$$g(v) = \sum_1^{\infty} l_n v^n = k_0 \sum_1^{\infty} \frac{v^n}{n} = k_0(e^v - 1); \quad vg'(v) = k_0 v e^v \quad (42)$$

Inserting (42) into (8a) we find:

$$y = k_0 v e^v [1 + k_0(v e^v + e^v - 1)]^{-1} \quad (43)$$

From (43), and from (12) and (42):

$$e^{v_{\frac{1}{2}}}(v_{\frac{1}{2}} - 1) = k_0^{-1} - 1; \quad x_{\frac{1}{2}} = \log 2 - \log k + \log k_0 v_{\frac{1}{2}}^2 e^{v_{\frac{1}{2}}} \quad (44)$$

From (10) and (44), (9a) and (42):

$$X + \log k_0 v_{\frac{1}{2}}^2 e^{v_{\frac{1}{2}}} = x + \log k = \log v + \log[1 + k_0(v e^v + e^v - 1)] \quad (45)$$

Fig. 2c gives $y(X)_k$ as calculated from (43 to 45). Even in this case, the shape of the curve approaches that of (18) as $k_0 \rightarrow 0$. In fig. 3 the curve for $k_0 = 1$ with III c is shown together with the family $y(X)_k$ for IIIa.

For the special case $k_0 = 1$ we have $v_{\frac{1}{2}} = 1$ and the somewhat simpler expressions:

$$y = v(1 + v)^{-1} \quad (43a)$$

$$\begin{aligned} X + \log e = x + \log k = \log v + v \log e + \log (1 + v) = \\ = y(1-y)^{-1} \cdot \log e + \log y - 2 \log (1-y) \end{aligned} \quad (45a)$$

DATA (a , b , A , B)

Plotting of experimental data

We shall now see how the hypotheses discussed above can be tested if one can measure both a and b , *i. e.* the free concentrations of A and B. One convenient way of plotting the experimental data is then to give

$$\eta = \log \frac{B}{b} \quad (46)$$

as a function of $\log a$ with one curve for each value for B , the total concentration of B.

It has been observed in at least two systems that, within the limits of experimental error, the curves $\eta(\log a)_B$ are parallel and possess the same shape for all values for B , with a spacing $\Delta \log a$ proportional to $\Delta \log B$. If this is exactly true, then all complexes must have, as proved in part I (eq 40—43), a "core + links" formula $B(A)_n$ in which n is variable and t is a constant which can be calculated from the spacing of the curves using (I, 43).

Just as for data (a , A , B) it is convenient to transform the coordinates so that the experimental points fall on a single curve. As ordinate we shall take η ; as abscissa we may choose either (cf 2)

$$\log u = t \log a + \log b \quad (47)$$

or (cf 9 and 46)

$$x = t \log a + \log B (= \log u + \eta) \quad (48)$$

The curve $\eta(\log u)$ is somewhat more compact than $\eta(x)$. With $\eta(x)$, on the other hand, the experimental uncertainties in $\log a$ and $\log b$ come out separately, one on each coordinate axis. Thus the $\eta(x)$ diagram is more suitable for discussing the experimental errors and for successive approximations.

Calculated curves

If $g(v)$ is the function (3a) that follows from a special hypothesis we want to test, we have from (5a) and (46)

$$\eta = \log (1 + g + vg') \quad (49)$$

and from (9a)

$$x + \log k = \log v + \log (1 + g + vg') \quad (50)$$

$$x + \log k = \log v + \eta \quad (50a)$$

On the right hand side of (50) and (49) we have functions of v only. Thus as k is constant, η should be a function of x .

If there is a maximum value for n , n_{\max} , the complex with $n = n_{\max}$ predominates at high values for v , and $g = l_{n_{\max}} v^{n_{\max}}$ in (3a). One may then prove from (50) and (49) that the maximum slope for $\eta(x)$ is $(1 + n_{\max}^{-1})^{-1}$ and that $\eta(x)$ has a linear asymptote of this slope.

For comparison it is convenient to shift the calculated curves laterally so that their asymptotes always go through the origin. We shall do this by choosing the abscissa

$$\xi = x + \log k + n_{\max}^{-1} [\log (n_{\max} + 1) + \log l_{n_{\max}}] \quad (51)$$

$$\xi = \log v + \log (1 + g + vg') + n_{\max}^{-1} [\log (n_{\max} + 1) + \log l_{n_{\max}}] \quad (51a)$$

For high v values, $\eta(\xi)$ approaches the asymptote:

$$\eta = \xi (1 + n_{\max}^{-1})^{-1} \quad (52)$$

For low v , $g \rightarrow 0$, and we have another linear asymptote

$$\eta = 0 \quad (52a)$$

If n is unbounded, we may take

$$\xi = x + \log k + \lim_{n \rightarrow \infty} (n^{-1} \log l_n) \quad (53)$$

$$\xi = \log v + \eta + \lim_{n \rightarrow \infty} (n^{-1} \log l_n) \quad (53a)$$

If the limit is finite, v has a maximum value, and for high ξ (53a) approaches asymptotically the line

$$\eta = \xi \quad (54)$$

In our three "unbounded" mechanisms, the limit expression becomes zero for IIIa and IIIb and infinite for IIIc.

The calculated curves $\eta(\xi)$ may be drawn on transparent paper and moved parallel with the abscissa axis across the experimental $\eta(x)$. If a fit is found, then (51) may be used for finding the equilibrium constants.

If the experimental data have been plotted as $\eta(\log u)$, one may test them with calculated curves giving η as a function of $(\xi - \eta)$: from (48) and (51)

$$\xi - \eta = \log u + \log k + n_{\max}^{-1} [\log (n_{\max} + 1) + \log l_{n_{\max}}] \quad (55)$$

and from (49) and (51a)

$$\xi - \eta = \log v + n_{\max}^{-1} [\log (n_{\max} + 1) + \log l_{n_{\max}}] \quad (55a)$$

Equation (55a), with the parameter v , may be used together with (49) for calculating $\eta(\xi - \eta)$ under various assumptions whereas (55) may be used for finding the equilibrium constants once a fit has been found between the experimental $\eta(\log u)$ and a calculated $\eta(\xi - \eta)$ curve.

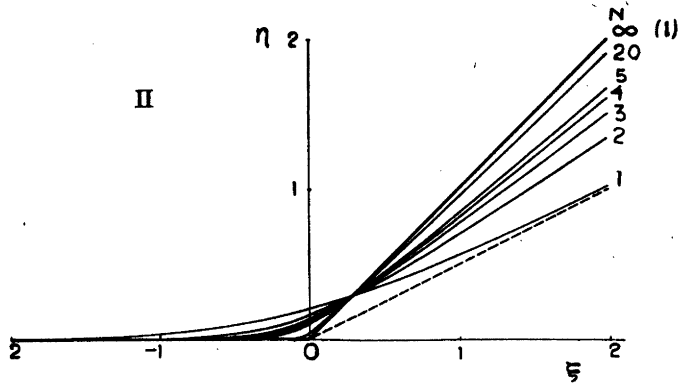


Fig. 4. Family of curves $\eta(\xi)_N$ for hypothesis II: only one complex, $B(A_i B)_N$, is formed. The dotted line is the asymptote $\eta = \frac{1}{2}\xi$ for $N = 1$.

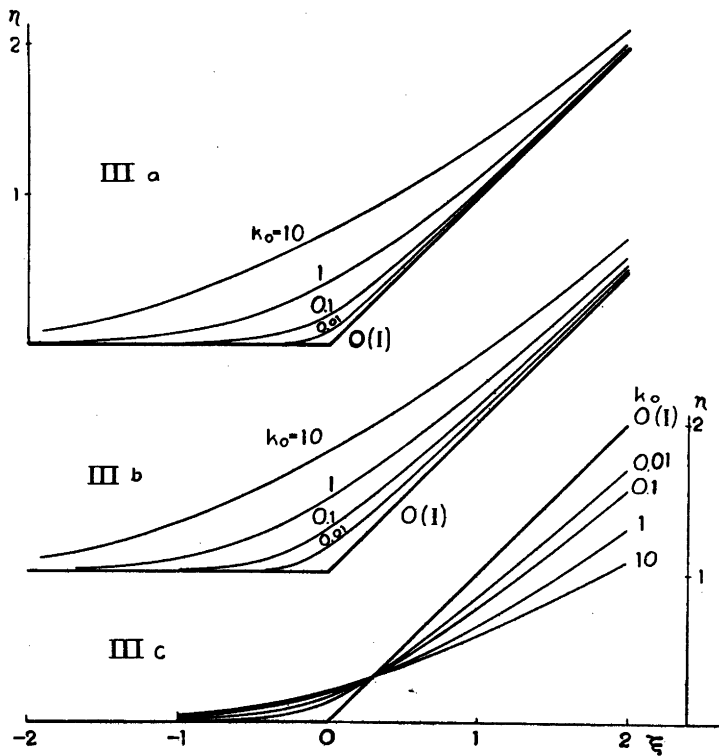


Fig. 5a-c. Families of curves $\eta(\xi)_{k_0}$ for repeated reaction, hypotheses IIIa, IIIb, and IIIc (28a-c).

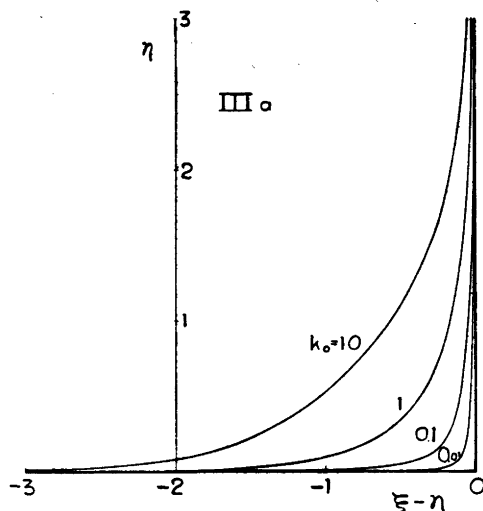


Fig. 6. Family of curves $\eta(\xi-\eta)k_0$ for IIIa. Thick lines = limiting curve for $k_0 = 0$.

The asymptotes for $\eta(\xi-\eta)$ will be (cf 52a and 52)

$$\left. \begin{aligned} \eta &= 0 \\ \eta &= n_{\max} (\xi-\eta) \end{aligned} \right\} \quad (56)$$

If n is unbounded, the second asymptote (if it exists) will be

$$\xi-\eta = 0 \text{ (vertical line)} \quad (56a)$$

We shall now give equations for calculating the $\eta(\xi)$ and $\eta(\xi-\eta)$ curves for each of the hypotheses discussed above. Since it is generally hard to give explicit equations, we shall express η and ξ in terms of a parameter, v or g , just as we did with y and X .

Hypothesis I: No soluble complex; solid A_2B may precipitate

If some $A_2B(s)$ has precipitated, we have from (17)

$$\log u + \log k = 0$$

and with (48)

$$x = \log a^2B = \log u + \eta = \eta - \log k$$

We shall put

$$\xi = x + \log k$$

so that $\eta(\xi)$ becomes a line, $\eta = \xi$, passing through the origin.

If the product a^2b is less than k^{-1} , we have no precipitate and no complex formation, and thus $b = B$ and $\eta = 0$. Each of the curves $\eta(\xi)$ and $\eta(\xi-\eta)$ will consist of two lines intersecting at the point of precipitation:

$$\eta = \xi, \quad \xi > 0, \text{ precipitate} \quad (57)$$

$$\eta = 0, \quad \xi < 0, \text{ no precipitate}$$

$$\eta > 0, \quad \xi - \eta = 0 \text{ (vertical line), precipitate} \quad (57a)$$

$$\eta = 0, \quad \xi - \eta < 0 \text{ (horizontal line), no precipitate}$$

The two straight lines (57) or (57a) are seen as the limiting cases of the curves $\eta_k^I(\xi)$ or $\eta(\xi - \eta)$ in fig. 4 (hypothesis II, $N \rightarrow \infty$) and fig. 5 and 6 (III, $k_0 \rightarrow 0$).

Hypothesis II: Only one complex formed, $B(A, B)_N$

From (21), or (49) and (20), we find

$$\eta = \log \frac{B}{b} = \log [1 + (N + 1)g] \quad (58)$$

From (51) and (51a) since $n_{\max} = N$, $l_{n_{\max}} = 1$, cf (3a) and (20)

$$\xi = x + \log k + N^{-1} \log (N + 1) \quad (59)$$

$$\xi = N^{-1} \log g + \log [1 + (N + 1)g] + N^{-1} \log (N + 1) \quad (59a)$$

Since the right-hand members in (58) and (59a) contain only the constant N and the variable g one should get a single curve for each N by plotting η as a function of either ξ or $(\xi - \eta)$. These calculated curves can then be compared with the experimental curves $\eta(x)$ or $\eta(\log u)$.

A family of curves $\eta(\xi)_N$ is given in fig. 4. All curves $\eta(\xi)$ intersect at the point

$$\eta = \xi = \log 2 \quad (60)$$

The asymptotes of any curve are the lines (cf 52 and 52a)

$$\left. \begin{array}{l} \eta = 0 \\ \eta = \xi (1 + N^{-1})^{-1} \end{array} \right\} \quad (61)$$

When N tends toward infinity, the family of curves approaches a limiting curve, consisting of the two straight lines (57).

Repeated reaction, hypothesis IIIa

From (49) and (31)

$$\eta = \log [1 + k_0((1-v)^{-2} - 1)] \quad (62)$$

Using (28a) we find $n^{-1} \log l_n \rightarrow 0$ for $n \rightarrow \infty$, whence with (53), (53a) and (62)

$$\xi = x + \log k = \log v + \log [1 + k_0((1-v)^{-2} - 1)] \quad (63)$$

$$\xi - \eta = \log u + \log k = \log v \quad (64)$$

Fig. 5 a gives $\eta(\xi)_{k_0}$ and fig. 6 $\eta(\xi - \eta)_{k_0}$ for the same k_0 values as in fig. 2c, calculated by means of equations (62 to 64). The curves in a family do not intersect. For $k_0 \rightarrow 0$, the curves tend to the limiting curves (57) and (57a),

each consisting of two straight lines, these lines being also the asymptotes for any curve.

The curves may be used for fitting the experimental data $\eta(x)$ and $\eta(\log u)$. Depending on the accuracy of the data, several methods for finding k_0 may be invented.

Repeated reaction, hypothesis IIIb

From (49) and (38)

$$\eta = \log [1 + 2 k_0 v(1-v)^{-3}] \quad (65)$$

From (28 b) we find $n^{-1} \log l_n \rightarrow 0$ for $n \rightarrow \infty$, whence with (53), (53a), and (65)

$$\xi = x + \log k = \log v + \log [1 + 2 k_0 v(1-v)^{-3}] \quad (66)$$

Fig. 5b gives the family $\eta(\xi)_{k_0}$. As with IIIa the limiting curve for $k_0 \rightarrow 0$ consists of the two lines (57) which are also asymptotes for each curve. The curves do not intersect.

Repeated reaction, hypothesis IIIc

From (49) and (42)

$$\eta = \log [1 + k_0(v e^v + e^v - 1)] \quad (67)$$

As before, it follows from our definitions that

$$x + \log k = \log v + \eta \quad (50a)$$

In (53), $n^{-1} \log l_n \rightarrow -\infty$ for $n \rightarrow \infty$ (28 c), and hence (53) cannot be used. The curves $\eta(x + \log k)_{k_0}$ do not intersect. They do approach the slope + 1 but have no asymptote for increasing η . To aid the comparison with the experimental data we shall, instead of (53), make a shift in the abscissa so that all curves intersect in the point

$$\eta = \log 2 = \xi \quad (68)$$

This is achieved by using the abscissa (cf. 50a)

$$\xi = x + \log k - \log v_2 = \log v + \eta - \log v_2 \quad (69)$$

where v_2 is the value for v when $\eta = \log 2$. This value is the solution of

$$e^{v_2} (v_2 + 1) = 1 + k_0^{-1} \quad (70)$$

Fig. 5c gives the family of curves $\eta(\xi)_{k_0}$ calculated from (67) and (69). As $k_0 \rightarrow 0$ the curve $\eta(\xi)$ is seen to approach the two lines (57) like in all other cases discussed.

More complicated assumptions

It may occur that the experimental data clearly indicate, using the criteria given in Part I, that the main products are complexes of the type $B(A_n B)_n$, but that the curves $y(x)$ or $\eta(x)$ do not fit in with any of the mechanisms proposed in this paper. Then one may go to more complicated assumptions.

As a complication of hypothesis II one may assume that two or three separate complexes are formed but no others. This explanation should be resorted to only if there are strong additional arguments for these two or three complexes being preferred to others.

In a repeated reaction, one may try other formulas for the dependence of k_n of n than those given in (28). For instance, there may be a certain minimum size $n = N$ for the complex, so that $k_n = 0$ for $n < N$ and $k_n = k_0 k^n$ for $n \geq N$.

Since the available experimental data on polynuclear reactions may be fairly well explained by the simple mechanisms II or IIIa given here, it has not been thought worth while at present to give detailed calculations for such more complicated cases. The formulas are however not difficult to derive. It is felt that unless the accuracy is extremely good, one should avoid introducing more than two arbitrary constants to be determined from the experiments.

Let us suppose that the data for a certain process can be well accounted for by, say, hypothesis IIIa. Of course this fact is not a proof that (28a) is exactly followed, and that all consecutive link-addition reactions have the same equilibrium constant k . However, it would indicate that this approximation is useful for calculations and that it also gives an approximate picture of the process.

Distribution of complexes

The chief aim of this paper has been to demonstrate how the experimental data may be used for distinguishing between various possible mechanisms and for finding the equilibrium constants involved. Once these are known one may calculate the concentration of each complex in a given solution (cf 1 and 6).

$$c_n = [B(A_t B)_n] = l_n b v^n \quad (71)$$

Furthermore one may calculate the fraction of all B groups present in the n :th complex (cf 71 and 5a)

$$\frac{(n+1)c_n}{B} = \frac{(n+1)l_n v^n}{1+g+vg'} \quad (72)$$

and the average number of links per complex (cf 3a)

$$\frac{\sum n c_n}{\sum c_n} = \frac{vg'}{g} = \frac{d \ln g}{d \ln v} \quad (73)$$

by inserting the expression for g for the mechanism in question.

The quantities in (72) and (73) are functions of v only.

SUMMARY

The paper deals with the mathematical analysis of data for a system in which the main products of the reaction between A and B are known (by methods given in part I) to be complexes $B(A_t B)_n$ with t constant and n variable.

The experimental data are suitably treated by plotting one t :th of the average number of A bound per B, $y = (A-a)/Bt$, as a function of $x =$

$t \log a + \log B$. If measurements of b are available, one may also plot $\eta = \log \frac{B}{b}$ as a function of x . In both cases, all experimental points should fall on a single curve independent of B .

These experimental curves $y(x)$ and $\eta(x)$ can then be compared with families of curves $y(X)$ and $\eta(\xi)$, calculated for various mechanisms. Here, X and ξ differ only by a constant (containing the equilibrium constants) from x , so one can move the calculated curves parallel with the horizontal axis in search for a fit.

Equations and curves are given for the following hypotheses: I) No soluble complex; solid A_iB precipitates. II) Only one complex, $B(A_iB)_N$ is formed. III) An infinite series of complexes is formed, by repeated reaction, with all positive values for n . Three equations are tried for the variation of k_n with n : IIIa: $k_n = k_0 k^n$, IIIb: $k_n = k_0 n k^n$ and IIIc: $k_n = k_0 k^n / n$. Here k_n is the equilibrium constant for the formation of the n :th complex from A and B .

The curves for precipitation of solid A_iB (hyp. I) are found as the limiting case of a single complex (hyp. II, $N \rightarrow \infty$) and of repeated reaction (hyp. III, $k_0 \rightarrow 0$).

By transformations described in Part I, eq. 30—34, the same families of curves may also be used to treat other "core + links" mechanisms, of general formula $A_r(A_iB)_n$.

This work is part of a program financially supported by *Atomkommittén* (Swedish Atomic Committee) and *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council).

The author is indebted to Dr. Georg Lundgren and to Miss Sirkka Hietanen, fil.mag., for many valuable discussions and for assistance with the numerical calculations.

Received November 28, 1953.