Deduction of a Rate Law for a Chemical Reaction Occurring *via* Several Steady-State Intermediates

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

A method of deducing rate equations has been devised for reaction mechanisms containing several rate determining elementary reactions coupled to each other. In the deduction an analogy is used between a diagram of the reaction mechanism and a corresponding diagram of an electrical circuit. The concept of kinetic potential, analogous to an electrical potential, has been introduced in such a way that the net rate in all reaction paths becomes analogous to a current in the electrical circuit. The method is convenient when elucidating a complicated reaction mechanism from kinetic data, since it is often possible to deduce the number of elementary reactions coupled in parallel and in series directly from the algebraic form of the experimental rate constant. The conditions for the use of the method are explicitly defined in the text.

The stoichiometric mechanism for a chemical reaction is generally elucidated by kinetic studies, from which primarily a rate constant, k_{obs}, is obtained. The number and the algebraic form of the terms used to describe k_{obs} give then a hint as to the number and the composition of the activated complexes in the process.[1]

If the reaction proceeds successivly *via* several activated complexes there must also exist several intermediates, which for many reactions are in a steady-state during most of the reaction time. The rate law for such a reaction is deduced, generally, by writing the time derivatives for the concentration of a reactant (or a product) and for all the intermediates. The steady-state means that those latter derivatives are all zero, which gives a number of equations from which the final nonintegrated rate

law can be deduced by elimination of all concentrations of intermediates. This is a rather tedious procedure if many intermediates are involved, and if many different combinations of elementary reactions must be tried. In the following, a method is described which makes it possible to write down a rate law directly for a given mechanism even if it contains a large number of intermediates.

DEDUCTION OF THE RATE LAW

It has been pointed out [1,2] that a diagram of a stoichiometric mechanism, which contains a number of elementary reactions, can be compared to an electrical circuit diagram, containing a number of rheostats coupled together in the same way as the elementary reactions are coupled in the stoichiometric mechanism (*cf.* also Ref. 3). In such a comparison each rheostat corresponds to the activated complex of an elementary reaction, each branching point in the electrical circuit diagram to an intermediate (or sometimes to the substrate or the product), and finally the electrical current through a rheostat to the net rate of reaction *via* the corresponding elementary reaction. Here and in the following the term net rate is used for the rate of increase of concentration of a species *via* this particular (reversible) elementary reaction (*cf.* Ref. 4). Such analogies have earlier been pointed out for some rather simple mechanisms, *vide e.g.* Refs. 1, 2, 3, but to our knowledge it has not been handled for a general case. Hence the conditions for the validity of the analogy have not been explicitly stated, nor has a generally valid method been

described for the calculation of the parameters in the rate equations. Since the analogy is very convenient when elucidating complicated reaction mechanisms, we have found it worthwhile to carry out a general deduction of this method and to define the conditions for its use. This is done as follows.

Equations are written which describe the net rate *via* each elementary reaction as a product of two factors. One such factor corresponds to the potential difference, U, and the other to the conductance, κ, in Ohm's law, $I = \kappa U$, where the current, I, corresponds to the net rate. The total reaction rate from substrate to product can then be deduced by combination of the kinetic analogues to the conductances, according to well-known rules for the corresponding electrical circuit. This can be shown as follows, where the analogy to Ohm's and Kirschoff's laws is immediately evident.

Let us look at a reaction from a substrate A to a product B, in which the i:th elementary reaction is

$$X + R_i \rightleftharpoons Y + P_i \qquad (1)$$
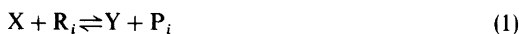
In this reaction the intermediate X is transformed to another intermediate Y by reaction with the species R_i, whereby the species P_i is also formed.

Reaction (1) is preceded by a number of other elementary reactions, by which the substrate A has been transformed to the intermediate X. These reactions can be summarized as

$$A + \Sigma R_j \rightleftharpoons X + \Sigma P_j \qquad (2)$$

The total reaction from A to B can then be written schematically:

(3)
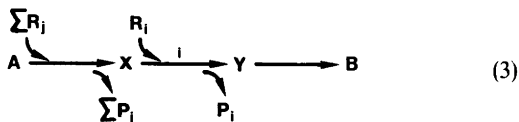
The net rate, v_i, in (1) is

$$v_i = k_i[X][R_i] - k_{-i}[Y][P_i] \qquad (4)$$

or

$$v_i = k_i[X][R_i]\left(1 - \frac{Q_i}{K_i}\right) \qquad (5)$$

where the symbol [ ] denotes time dependent concentrations, k_i and k_{-i} are rate constants and

$K_i = k_i/k_{-i}$ the equilibrium constant of reaction (1). Q_i is the time dependent concentration quotient corresponding to K_i.

Eqn. (5) can be brought in a form, (7), analogous to Ohm's law by introducing in it the equilibrium constant, K_X, of reaction (2) and its corresponding time dependent concentration quotient, Q_X,

$$Q_X = [X]\pi[P_j][A]^{-1}\pi[R_j]^{-1} \qquad (6)$$

Hence

$$v_i = k_i K_X[R_i]\pi[R_j]\pi[P_j]^{-1}[A]\left(\frac{Q_X}{K_X} - \frac{Q_X Q_i}{K_X K_i}\right) \qquad (7)$$

In eqn. (7) the terms Q_X/K_X and $Q_X Q_i/K_X K_i$ within the parenthesis may be regarded as kinetic potentials — in the points X and Y in (3) — whose difference corresponds to U in Ohm's law. The rest of the right-hand member of eqn. (7) corresponds to a conductance, κ, and finally v_i to an electric current.
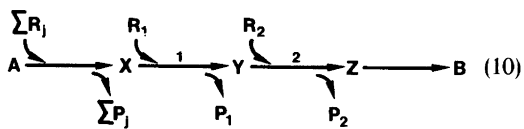
By introducing

$$f_i = k_i K_X[R_i]\pi[R_j]\pi[P_j]^{-1} \qquad (8)$$

eqn (7) is simplified to

$$v_i = f_i[A]\left(\frac{Q_X}{K_X} - \frac{Q_X Q_i}{K_X K_i}\right) \qquad (9)$$

Let us now regard two consecutive elementary reactions, 1 and 2 within a mechanism, which analogously to (3) can be represented as

(10)

Hence, as above

$$v_1 = f_1[A]\left(\frac{Q_X}{K_X} - \frac{Q_X Q_1}{K_X K_1}\right) \qquad (11)$$

$$v_2 = f_2[A]\left(\frac{Q_Y}{K_Y} - \frac{Q_Y Q_2}{K_Y K_2}\right) \qquad (12)$$

where

$$f_2 = k_2 K_Y[R_1][R_2]\pi[R_j]\pi[P_j]^{-1}[P_1]^{-1} \qquad (13)$$

and

$$Q_Y = Q_X Q_1, \; K_Y = K_X K_1 \qquad (14)$$

The last term within the parenthesis in eqn. (12) represents the kinetic potential, Q_Z/K_Z, in point Z in (10) − cf. eqn (14) − so eqns (11), (12) and (14) tell us immediately that the sum of the potential differences X to Y and Y to Z equals the potential difference between X and Z, as is required by the analogy to an electrical circuit diagram. Furthermore, if the intermediate Y exists in a steady-state, it follows that the two net rates v_1 and v_2 are equal, which is again the desired analogy to an electrical circuit. What remains is to find the combination of f_1 and f_2 to a quantity f_{XZ}, which makes it feasible to substitute formally the two successive elementary reactions with one single reaction of a net rate $v_{XZ} (= v_1 = v_2$, if the steady-state assumption is correct). The expression for v_{XZ} is

$$v_{XZ} = f_{XZ}[A]\left(\frac{Q_X}{K_X} - \frac{Q_Z}{K_Z}\right) \qquad (15)$$

and the eqns. (11), (12) and (15) together with the condition $v_1 = v_2 = v_{XZ}$ then give

$$f_{XZ}^{-1} = f_1^{-1} + f_2^{-1} \qquad (16)$$

which is just the expected analogy to the combined conductance, κ_{XZ}, of two rheostats of conductance κ_1 and κ_2 coupled in series in an electrical circuit, $\kappa_{XZ}^{-1} = \kappa_1^{-1} + \kappa_2^{-1}$. In any given reaction mechanism the quantities f_1 and f_2 are expressed by eqns. (8) and (13) so eqn. (16) enables the combination of two successive elementary reactions in any part of a complicated reaction mechanism.

The next step is to deduce a combination corresponding to eqn. (16) for two parallel elementary reactions. This can be done by starting from diagram (17)

(17)
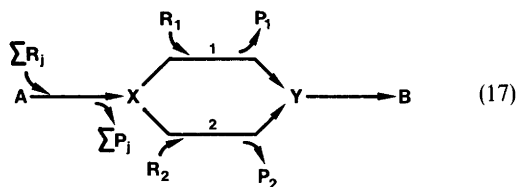
where the notations correspond to those in diagrams (3) and (10). Hence, as before

$$v_1 = k_1 K_X[R_1]\pi[R_j]\pi[P_j]^{-1}[A]\left(\frac{Q_X}{K_X} - \frac{Q_X Q_1}{K_X K_1}\right) \qquad (18)$$

$$v_2 = k_2 K_X[R_2]\pi[R_j]\pi[P_j]^{-1}[A]\left(\frac{Q_X}{K_X} - \frac{Q_X Q_2}{K_X K_2}\right) \qquad (19)$$

The difference within parenthesis in eqn. (18) equals that in eqn. (19) if

$$Q_1/K_1 = Q_2/K_2 \qquad (20)$$

Eqn. (20) is true if the reaction $R_1 + P_2 \rightleftharpoons P_1 + R_2$ is a rapid equilibrium. The total net rate, v_{XY}, from X to Y via the two paths in diagram (17) then equals the sum of v_1 and v_2, and it also follows that

$$f_{XY} = f_1 + f_2 \qquad (21)$$

where f_1 and f_2 are the products preceding the factor [A] in the right-hand members of eqns. (18) and (19). Eqn. (21) is again a direct analogy to the conductances in an electrical circuit, this time for two branches coupled in parallel.

Eqns. (16) and (21) make it feasible to successively combine two consecutive or two parallel elementary reactions in a reaction mechanism, until one arrives at the rate equation for the total reaction mechanism from the substrate to the product (cf. the example, mechanism (23), below). As pointed out in the deduction the following conditions must be fulfilled:

(i) All reactions between reactants and products interfering with the substrate and the intermediates by side reactions are rapid.

(ii) All intermediates are in steady-states.

The procedure to write the rate law for a given mechanism of the reaction from A to B then runs as follows:

(i) Write the expression for f_i, eqn. (8), for each elementary reaction of the mechanism.

(ii) Combine the quantities f_i according to the rules valid for conductances in an analogous electrical circuit diagram. The obtained combination of f_i values is denoted $f_k(t)$. It contains among other quantities the rate constants of the elementary reactions but also time dependent factors.

(iii) The rate law is

$$-d[A]/dt = f_k(t)[A](1 - Q/K) \qquad (22)$$

where K is the equilibrium constant of the total reaction and Q the corresponding time dependent concentration quotient. (Since the equation describes a reaction, which starts at point A in our mechanism schedule, the first term within the parenthesis is 1 and not a Q/K quantity, *cf.* eqn. (5)). The kinetic experiments can often be arranged in such a way that $f_k(t)$ is kept practically constant during each run and $Q/K \ll 1$, *i.e.* eqn. (22) takes the form of a rate equation for a pseudo first-order reaction (*vide infra*).

In order to exemplify the procedure we choose a mechanism described by the following diagram

$$(23)$$
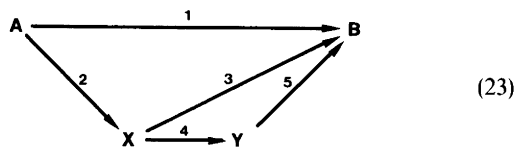
where X and Y are steady-state intermediates in one of the reaction paths (2, 4, 5) between A and B. There is also a direct reaction, 1, from A to B, and a direct path, 3, from X to B. In each elementary reaction i, $(i = 1,...,5)$, there is a reactant R_i and a product P_i taking part besides the species marked in the diagram. All existing reactions between R_i and P_i are rapid, compared to the rate-determining elementary reactions marked by arrows in the diagram. The equilibrium constant and rate constant for each elementary reaction are K_i and k_i.

The quantities f_i are, *cf.* eqn. (8),

$$f_1 = k_1[R_1]$$
$$f_2 = k_2[R_2]$$
$$f_3 = k_3K_2[R_2][R_3][P_2]^{-1}$$
$$f_4 = k_4K_2[R_2][R_4][P_2]^{-1}$$
$$f_5 = k_5K_2K_4[R_2][R_4][R_5][P_2]^{-1}[P_4]^{-1}$$

These f_i values are combined to $f_k(t) = f_{AB}$ by the following steps

$$f_{AB} = f_1 + f_{AXB} \qquad \text{, two parallel reactions}$$
$$f_{AXB} = (f_2^{-1} + f_{XB}^{-1})^{-1} \qquad \text{, two consecutive reactions}$$
$$f_{XB} = f_3 + f_{XYB} \qquad \text{, two parallel reactions}$$
$$f_{XYB} = (f_4^{-1} + f_5^{-1})^{-1} \qquad \text{, two consecutive reactions}$$

which gives

$$f_k(t) = f_1 + \{f_2^{-1} + [f_3 + (f_4^{-1} + f_5^{-1})^{-1}]^{-1}\}^{-1}$$

with the values of f_i given above.

Hence, all the quantities in the rate eqn. (22) are known. The simplest expression for K and Q in eqn. (22), valid for mechanism (23), are $K = K_1$ and $Q = [B][P_1][A]^{-1}[R]^{-1}$. Another possibility could be, *e.g.*, $K = K_2K_4K_5$ and
$$Q = [B][P_2][P_4][P_5][A]^{-1}[R_2]^{-1}[R_4]^{-1}[R_5]^{-1}.$$

Other examples where the method is used can be found in Refs. 5, 6, 7, 8.

We wish to point out that the rate eqn. (22) can be directly written down for the given mechanism (23), simply by keeping in mind which elementary reactions in the diagram are coupled in parallel or in series. It is not necessary to carry out the deduction above, since the result follows immediately from the analogy to an electrical circuit (*vide* Ref. 5, pp. 45–48).

In practice when a mechanism shall be deduced from an experimentally determined rate constant, k_{obs}, it is an easy task to try a number of diagrams like (23) and compare the algebraic form of the rate equation corresponding to each such diagram to the experimental rate equation. Such a procedure is considerably quicker than deducing the rate equation for each tried mechanism by solving a number of equations, each containing a great number of terms, as is done in the standard method mentioned in the introduction. The present authors feel that there are several examples in the literature where wrong mechanisms have been proposed, for the reason that one has found it too time consuming to try a sufficient number of possible mechanisms because of the lengthy deduction for each such trial.

INTEGRATION OF THE RATE LAW

The rate law in eqn. (22) is valid for the reaction,

$$A + \sum R_j \rightleftharpoons B + \sum P_j \qquad (24)$$

In order to carry out an integration of eqn. (22) as simply as possible we introduce the equilibrium concentration of all species, which in the following are denoted with low case letters. Hence, the equilibrium constant of reaction (24), K, is

$$K = b \pi p_j a^{-1} \pi r_j^{-1} \qquad (25)$$

As before

$$Q = [B]\pi[P_j][A]^{-1}\pi[R_j]^{-1} \qquad (26)$$

Each time-dependent concentration is written as the sum of its equilibrium concentration and a time-dependent Δ term representing the distance to the equilibrium value. Hence

$$[A] = a + \Delta_A, \ [R_j] = r_j + \Delta_{Rj}, \ [B] = b + \Delta_B,$$
$$[P_j] = p + \Delta_{Pj} \tag{27}$$

Combination of eqns. (22), (25), (26) and (27) gives an expression for the net rate, which as a first approximation — essentially obtained by neglecting products of Δ quantities — can be written

$$-\frac{d\Delta_A}{dt} = \Delta_A f_k \{1 + a[\sum(r_j^{-1}\Delta_{Rj}\Delta_A^{-1}) -$$
$$b^{-1}\Delta_B\Delta_A^{-1} - \sum(p^{-1}\Delta_{Pj}\Delta_A^{-1})]\} \tag{28}$$

Here f_k is a time-independent function of the same form as $f_k(t)$ in eqn. (22) but with all time dependent concentrations in $f_k(t)$ substituted by the corresponding equilibrium concentrations.

If the species in the total reaction (24) are not taking part in any side reactions, all the Δ quotients within the parenthesis in eqn. (28) are simple rational numbers, determined by the stoichiometry of the total reaction. If this condition is true for our reaction (24), it follows that $\Delta_{Rj}\Delta_A^{-1} = 1$ and $\Delta_B\Delta_A^{-1} = \Delta_{Pj}\Delta_A^{-1} = -1$. So eqn. (28) takes the form (29) of a pseudo first-order reaction, if the approximations are valid

$$-\frac{d\Delta_A}{dt} = \Delta_A f_k [1 + a(\sum r_j^{-1} + b^{-1} + \sum p_j^{-1})] \tag{29}$$

The deduction of a suitable form of eqn. (28), when rapid side reactions are coupled to the main paths of the reaction now remains. Then two complications arise:

(i) The substrate (and/or the product) may exist in several forms in rapid equilibrium.

(ii) The Δ quotients are, generally, no longer simple rational numbers.

If (i) is true the kinetic experiments measure the change with time of the sum, C_A, of the concentrations of all the substrate forms, which disappear, however, by the rate of the form A directly reacting via the main path. To handle this case we substitute eqn. (28) by

$$-\frac{d(\Delta C_A)}{dt} = \Delta C_A f_k$$
$$\cdot \frac{1 + a[\sum(r_j^{-1}\Delta_{Rj}\Delta_A^{-1}) - b^{-1}\Delta_B\Delta_A^{-1} - \sum(p_j^{-1}\Delta_{Pj}\Delta_A^{-1})]}{\Delta C_A \Delta_A^{-1}} \tag{30}$$

which may be shortened to

$$-\frac{d(\Delta C_A)}{dt} = \Delta C_A k_{obs} \tag{31}$$

where $k_{obs} = f_k f_c$ \qquad (32)

with

$$f_c =$$
$$\frac{1 + a[\sum(r_j^{-1}\Delta_{Rj}\Delta_A^{-1}) - b^{-1}\Delta_B\Delta_A^{-1} - \sum(p_j^{-1}\Delta_{Pj}\Delta_A^{-1})]}{\Delta C_A \Delta_A^{-1}} \tag{33}$$

As mentioned in point (ii) above, the difference quotients in the parenthesis of eqn. (30) are no longer simple rational numbers. When the reaction is far from equilibrium they are not even necessarily constant. In relaxation experiments, however, they can be regarded as constants and substituted by the corresponding derivatives, which can be calculated in the following way.

In the reaction mixture there are a number of components. One of these contains among other species the substrate A and the product B. Other components contain species denoted as R_j and P_j in the diagrams, e.g. (3) and (17), of the reaction mechanism. Finally a number of components might be present, e.g. as buffers or indicators. The difference quotients in eqn. (30) can be calculated from the derivatives of the total concentration of each component, eqn. (34). These total concentrations, C_i, can be written as sums of the concentrations of all species belonging to this component. Each term in this sum can be substituted by a product of a stoichiometric integer, an equilibrium constant and pseudo equilibrium concentrations (in dignities corresponding to the equilibrium equation chosen for each species). This can be carried out by choosing one suitable representative, D_j, for each component. For the components taking part in the side reactions mentioned above the representatives are chosen among the species R_j and P_j.

The total concentrations, C_i, can then be written as functions

$$C_i = F_i([A], [B], [D_j]) \tag{34}$$

which contain a number of equilibrium constants as parameters. Derivation of this function gives

$$0 = \frac{\partial F_i}{\partial [A]} + \frac{\partial F_i}{\partial [B]} \frac{d[B]}{d[A]} + \sum_j \left(\frac{\partial F_i}{\partial [D_j]} \frac{d[D_j]}{d[A]} \right) \tag{35}$$

where all the partial derivatives are known, if the equilibrium constants and hence also the pseudo equilibrum concentrations are known. There is one such equation for each component, so from this set of equations all the derivatives $d[B]/d[A]$ and $d[D_j]/d[A]$ can be calculated and substituted for the corresponding difference quotients Δ_B/Δ_A, Δ_{Rj}/Δ_A and so on in eqn. (30) for all R_j and P_j which have been chosen as representatives, D_j, for their respective components. (If there are also some R_j or P_j in eqn. (30) which have not been chosen as D_j the difference quotients can still be easily calculated from the corresponding $d[D_j]/d[A]$ and a suitable equilibrium equation).

This calculation of the difference quotients in eqn. (30) demands that the two conditions given after eqn. (21) are fulfilled. From condition (i) it follows that the equilibrium equations can be used for all species when writing the total concentrations, C_i, in the form (34). This is true because the reactions between A (and B) species with P_j are rapid, so there is in practice equilibration between, e.g., [A] and all species in the side reactions, even though [A] itself might be far from its final equilibrium value. Obviously equilibrium expressions which contain both A and B species cannot be used in this connection, since the corresponding reactions are not equilibrated during the kinetic run. This is the reason why A and B have been marked in eqn. (34), as if they belonged to two different components. Condition (ii) means that the concentrations of all species containing some intermediate are so small that they can be neglected in eqns. (30) and (34).

The result of the discussion in the previous paragraph is important in cases where there are small deviations in the kinetic run from a pseudo first order reaction, since the difference quotients in eqn. (30) can be calculated at any reaction time from eqn. (34), e.g. at time zero or close to equilibrium. The value of f_c, calculated from eqn. (33) can then be combined with k_{obs} $(t=0)$ or k_{obs} $(t=\infty)$ in order to determine the corresponding value of f_k from eqn. (32). Finally the reaction mechanism is deduced from the algebraic form of f_k. This method to obtain

f_k has been used e.g. in Refs. 5 (pp. 39 and 94) and 8.

Deviations from a pseudo first-order reaction can also arise because the approximations made to calculate a constant value of f_k are not good enough during the whole time range of the kinetic run. Also in this case it is often practical to determine, e.g., k_{obs} $(t=\infty)$ and to obtain a corresponding value of f_k $(t=\infty)$ from eqn. (31). This is often the easiest approach to determine the relevant rate constants in a proposed mechanism, even when it is possible to carry out an explicit integration of the unapproximated (non first-order) rate equation. Such an example has been demonstrated in Ref. 6.

The approximations discussed above can in practice be made acceptable in the following two cases

(i) The concentration of the substrate is chosen much lower than all r_j and p_j. This can easily be carried out in experiments started by mixing two solutions. In most cases it is also possible to arrange the experiments so that the final equilibrium concentration, a, of the substrate is so small that f_c in eqn. (33) equals $\Delta_A/\Delta C_A$ (which can − in general − be kept at a sufficiently constant value and equals 1 if the substrate does not take part in any side reactions).

(ii) The measurements are carried out as relaxations. Since the concentrations of all participating species must, generally, be of the same order of magnitude in such experiments, the sum of the terms in the numerator of the right-hand member of eqn. (33) is about equal to the number of reactants and products. In this case, however, the approximations described above to calculate the terms in f_c are always accurate enough.

SUMMARY

A method has been described, by which a rate equation can be deduced for a reaction mechanism containing several steady-state intermediates. The observed rate constant is written as a product of two factors, f_k and f_c.

The factor f_k in eqn. (32) contains among other quantities the rate constants of all the rate-determining steps of the mechanism and also a number of equilibrium constants. These rate and equilibrium constants are often arranged so that their products, similar to f_i in eqn. (8), represent the experimentally determinable formal rate con-

stants for the various elementary reactions of the mechanism (cf., e.g., Ref. 6).

The form of the function f_k can be easily deduced for any given mechanism by comparing a diagram of the reaction mechanism to an analogous electric current diagram. This analogy gives a simple method to directly write down expressions for f_k for several different reaction mechanisms – even for rather complicated ones – in order to compare them with the experiments. It is often directly evident from the form of the experimentally obtained f_k that the mechanism must contain a certain (minimum) number of paths coupled in parallel and in series.

The factor f_c is often a minor correction factor and is — in principle — a function of the equilibrium concentrations of the reactants and products, but does not contain any rate constants.

The use of the method has been examplified in the paper, and references are also given to examples in the literature, where the method has been used.

REFERENCES

1. Newton, T. W. and Baker, F. B. *Adv. Chem. Ser.* *71* (1967) 268.
2. Birk, J. P. *J. Chem. Educ.* 47 (1970) 805.
3. Christiansen, J. A. In Schwab, G.-M., Ed., *Handbuch der Katalyse I*, Wien 1941, p. 260; Fronaeus, S. and Östman, C. O. *Acta Chem. Scand. 10* (1956) 769.
4. McGlashan, M. L. *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, Butterworths, IUPAC, London 1970, pp. 14, 35, 36.
5. Ekström, C.-G. *Kinetisk undersökning av lantanoidernas dipikolinatkomplex*, Diss., Lund University, Lund 1978.
6. Persson, H. and Ekström, C.-G. *Acta Chem. Scand. A 30* (1976) 31.
7. Persson, H. *Acta Chem. Scand. A 30* (1976) 39.
8. Ekström, C.-G., Nilsson, L., Duncan, I. A. and Grenthe, I. *Inorg. Chem. 18* (1979). *In press.*