

KINETIC METHODS IN THE INVESTIGATION OF COORDINATION COMPOUNDS

K. B. YATSIMIRSKII*

Ukrainian Academy of Sciences, Kiev, U.S.S.R.

To investigate the stability of coordination compounds in solutions it is necessary to determine the equilibrium concentrations of the reactants: the metal ion, ligands, and the coordination compounds being formed. There are many ways of measuring the equilibrium concentrations: potentiometric, optical, ion-exchange *etc.* It is also possible to determine the equilibrium concentration of many substances by measuring the rate of reactions in which these substances participate.

The determination of equilibrium concentrations of substances which act as catalysts in appropriate reactions is of great interest. We call the reactions chosen for measuring concentrations "the indicator reactions" by analogy with "the indicator electrode" in the potentiometric methods of measuring equilibrium concentrations. By using catalytic reactions it is possible to determine extremely minute concentrations of more than 30 elements in different oxidation states. Thus 10^{-6} mg/ml of cobalt may be detected by means of catalytic reactions¹. Ionic concentrations of the order of 10^{-6} – 10^{-8} mole/l. can usually be determined with sufficient accuracy.

At such concentrations polynuclear products are not, as a rule, formed and the original particles are of the simplest composition. At such concentrations very interesting coordination compounds can exist without settling out and without forming polynuclear products. For instance, we have investigated the formation of silver iodide in homogeneous solutions with the help of a reaction catalysed by iodide (the oxidation of arsenic (III) by cerium (IV)).

By means of kinetic methods it is possible to determine the equilibrium concentration of metal ions, ligand-anions or molecules, and coordination compounds. The first case (the determination of the concentration of metal ions) is the most usual.

It is reasonable to divide the reactions forming coordination compounds, and which are studied by kinetic methods, into three groups:

(i) Those in which the ligands participate in the indicator reactions, and form coordination compounds with metal ions whose concentrations are determined.

(ii) Those in which the ligands (or metal ions) do not participate in the indicator reaction, but react with metal ions (or anions) forming catalytically inactive coordination compounds.

(iii) Those in which the ligands form, with simple catalysts, new catalytically active compounds. The catalytic activity of these coordination compounds can be either greater or less than that of the simple ions.

* In the absence of the author, this paper was not read at the meeting.

K. B. YATSIMIRSKII

Let us consider an indicator reaction of the type:



This reaction can proceed in two stages:



The rate of the whole reaction may be expressed as:

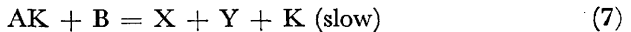
$$\frac{dx}{dt} = K[AB] \quad (4)$$

The concentration of the compound AB may be calculated by the equation:

$$[AB] = \frac{\beta[B]}{1 + \beta[B]} C_A^0 \quad (5)$$

where C_A^0 is the total concentration of the compound A, and β is the equilibrium constant of reaction (2) (stability constant).

When reaction (1) is catalytic it can proceed through several stages. This situation may be represented by the following scheme:



in which K represents the catalyst.

In this case the concentration of the compound KA may be expressed as follows:

$$[KA] = \frac{\beta[A]}{1 + \beta[A]} C_K^0 \quad (8)$$

where β is the equilibrium constant of reaction (6) (the stability constant of the complex KA), and C_K^0 is the total concentration of the catalyst.

The kinetic equation then has the form:

$$\frac{dx}{dt} = \kappa[KA][B] \quad (9)$$

or taking into account equation (8)

$$\frac{dx}{dt} = \kappa \frac{\beta[A]}{1 + \beta[A]} C_K^0 [B] \quad (10)$$

Equation (10) may be converted into a form convenient for the determination of the stability constant β :

$$\frac{1}{dx/dt} = \frac{1}{\kappa C_K^0 [B]} + \frac{1}{\kappa C_K^0 [B]} \cdot \frac{1}{\beta} \cdot \frac{1}{[A]} \quad (11)$$

This shows that the reciprocal of the rate of a chemical reaction is a linear function of $1/[A]$. The stability constant of the compound KA may be found from the slope of the straight line in the graph of $1/[A]$ against $1/(dx/dt)$.

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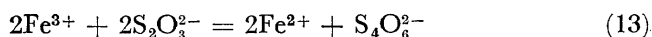
As examples of the use of the above method, the determination of the equilibrium constants in the formation of coordination compounds of vanadium (v), molybdenum (vi) and tungsten (vi) with hydrogen peroxide may be cited. Naryshkina in our laboratory showed that the rate of oxidation of thiosulphate to sulphate by hydrogen peroxide in the presence of catalysts consisting of compounds of vanadium (v), molybdenum (vi) and tungsten (vi) can be described by the equation

$$\frac{d[\text{SO}_4^{2-}]}{dt} = \kappa \frac{\beta[\text{H}_2\text{O}_2]}{1 + \beta[\text{H}_2\text{O}_2]} C_K^c [\text{S}_2\text{O}_3^{2-}] \quad (12)$$

The β values for the hydrogen peroxide complexes of molybdic and tungstic acids are 320 and 360 respectively, and for the vanadyl hydrogen peroxide complex $\beta = 20$ ($t = 22^\circ\text{C}$, $\mu = 0.1$).

An equation similar to equation (10) is well known in enzymology as the Michaelis equation, and is used for determining the equilibrium constants of reactions between enzymes and substrates involving the formation of coordination compounds. The values of $1/\beta$ have been determined for many compounds between enzymes and substrates in biological chemistry.

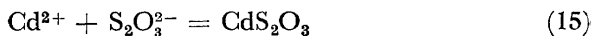
In the second class of reactions the concentrations of metal ions (or ligands) decrease as a result of the addition to the solution of substances which form inactive coordination compounds with metal ions or ligands. As an example, the reaction between Fe^{3+} and thiosulphate can be mentioned



The rate of this reaction may be expressed by the equation:

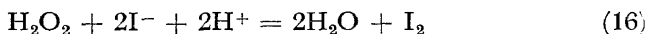
$$-\frac{d[\text{Fe}^{3+}]}{dt} = K[\text{Fe}^{3+}][\text{S}_2\text{O}_3^{2-}]^2 \quad (14)$$

From this equation it is possible to determine the equilibrium concentration of $\text{S}_2\text{O}_3^{2-}$. Cadmium salts are added to the solution, and the rate of reaction (13) is decreased because of the formation of CdS_2O_3 according to the equation:



The total concentrations of cadmium and thiosulphate are known, and, therefore, it is possible to calculate the equilibrium concentrations of all the particles participating in reaction (15).

Many catalysts lose their catalytic activity as a result of forming coordination compounds with different ligands (the catalyst K forms the compound KL_n). The disappearance of catalytic activity is connected with the screening of the metal ion by ligands so that the interaction of the particle A with the particle KL_n (according to equation 6) is impossible. Thus, for example, in oxidizing iodide by hydrogen peroxide in acid solution according to the equation:



the particles H_2MoO_4 , H_2WO_4 , ThOH^{3+} , ZrO^{2+} , Fe^{3+} , and some others,

are catalytically active. But the coordination compounds of these particles with PO_4^{3-} , F^- , $\text{C}_2\text{O}_4^{2-}$ and some others have no catalytic activity. From the rate of reaction (16) it is possible to determine the concentration of a free catalyst (C_K). The total concentration of a catalyst being known (C_K^0), it is possible by subtracting C_K to find the sum of the concentrations of the different coordination compounds (KL , KL_2 . . . KL_n), and with the help of the equation (17) to find out all the stability constants: β_1 , β_2 , . . . β_n :

$$\frac{C_K^0 - \bar{C}_K}{\bar{C}_K} = \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \dots + \beta_n[\text{L}]^n \quad (17)$$

The above method of determining equilibrium constants may be used in many cases. There is a wide variety of catalytic reactions which can be used. It is useful to divide the majority of catalytic reactions into eight groups as indicated in *Table 1*.

Table 1

	Type of reaction	Catalysts
(1)	$\text{H}_2\text{O}_2 + \text{reducing agent (acid medium)}$	Os^{8+} , Mo^{6+} , W^{6+} , V^{5+} , Nb^{5+} , Ta^{5+} , Zr^{4+} , Hf^{4+} , Th^{4+} , Fe^{3+}
(2)	$\text{H}_2\text{O}_2 + \text{reducing agent (alkaline medium)}$	Os , Co , Cu
(3)	$\text{XO}_n + \text{reducing agent (acid medium)}$	Os , Mo , W , V
(4)	$\text{R}^{n+} + \text{reducing agent (acid medium)}$	Os , I
(5)	$\text{Ox} + \text{R}^{n+} \text{ (acid medium)}$	Os , Re , W , Mo , V
(6)	$\text{H}_2\text{O}_2 + \text{(polarographic currents)}$	Mo^{6+} , W^{6+} , V^{5+}
(7)	Isotopic exchange	Fe , F^- , . . .
(8)	$\text{Fe}(\text{CN})_6^{4-} + n\text{A} = \text{FeA}_n + 6\text{CN}^-$	Ag , Au , Hg

It is interesting to note that for different oxidation reactions which take place in the acid medium the list of catalysts is very similar. They are the elements of the IV, V, VI, VII and VIII A groups of the periodic system, mainly of the fifth and sixth periods, which can accept electrons in *d*-orbitals. As a rule catalytic activity increases with increase of oxidation state. For example, catalytic activity for reaction (16) increases in the order $\text{Hf} < \text{Ta} < \text{W}$.

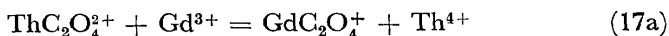
The concentration of the free catalyst can be determined by measuring different quantities, characterizing the reaction rates. The slope of the time-concentration curve is preferable for the most exact determination of the concentration of reactants. In some cases it is necessary to use a semilogarithmic graph (time-logarithm of concentration). Alternatively, for the determination of concentration, one can use the reciprocal time ($1/t$ for the reaction to proceed to a definite degree, or to a definite product concentration).

In the case of catalytic polarographic currents, the strength of the current is a measure of the catalytic reaction rate. There is a linear dependence between the reciprocal of the induction period (more accurately, the square of this quantity $1/t_i^2$ and the concentration of the free catalyst. When ligands are added to the solution, the induction period becomes longer.

All the above methods utilize the inhibiting action of ligands. In some

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cases indirect methods can be employed for the determination of stability constants. There are many ions which have no catalytic activity, but are capable of forming coordination compounds with ligands which are inhibitors for catalysts. The addition of such ions to the solution of catalyst compounds capable of coordinations increases the catalytic activity. As an example, we may consider (in reaction 16) the increase of catalytic activity of the solution containing thorium compounds with oxalate after gadolinium ions have been added. The gadolinium ions have no catalytic activity in this reaction, but they react with thorium oxalate compounds according to the equation:

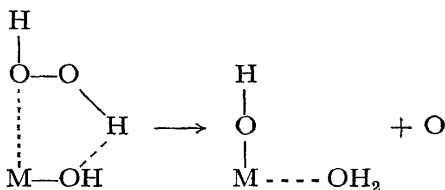


The resulting ions Th^{4+} (and, hence, ThOH^{3+}) are catalysts for reaction (16). The total concentrations of thorium, oxalate, and gadolinium are known. The equilibrium concentration of thorium may be determined from the rate of reaction (16). Then the equilibrium concentrations of all the participants of reactions (17a) may be calculated, and, thus, the equilibrium constant of reaction (17a) may be determined. This quantity is the ratio of the stability constants of GdC_2O_4 and $\text{ThC}_2\text{O}_4^{2+}$.

However, in many cases the coordination compound of the catalyst K with ligands L also has catalytic activity. The catalytic activity of the compound KL_n may be either more or less than that of the free catalyst K.

The decrease of catalytic activity of the particles of the KL_n type, as compared with the particle K, is connected with partial screening of the metal ion K by ligands and the resulting difficulty which the particle A experiences in combining with the particle KL_n (according to equation 6) to give an intermediate compound KL_nA instead of the compound KA.

An increase of catalytic activity due to complex formation can arise in various ways. In some cases, in our opinion, intermediate complexes must have a cyclic structure. Thus, for example, the oxidation of iodide by hydrogen peroxide is catalysed by particles of the type MO or MOH, but not by simple M^{n+} ions. It is likely in this case that an H_2O_2 cyclic complex is formed initially and afterwards gives off oxygen atoms:



The particle formed after splitting off water is reconverted into MO (or MOH) which can again form a cyclic compound with H_2O_2 .

On this view it is possible to explain the unusual behaviour of thorium, hafnium and zirconium compounds in reaction (16). The catalytic activity of these elements increases with increase of pH, passes through a maximum and then decreases with further increase of pH. We suppose that in all

these cases only one hydrolytic form has noticeable catalytic activity; for instance, that only ThOH^{3+} possesses a marked catalytic activity and that neither Th^{4+} nor $\text{Th}(\text{OH})_2^{2+}$ have any noticeable catalytic activity.

In other cases, the orientation of electronic orbitals in definite directions is necessary. For instance, in the planar coordination compounds the axis of the d_{z^2} orbital is directed perpendicularly to the tetragonal plane formed by the tetragonally oriented atoms of ligands. The electrons in these orbits are easily withdrawn from the catalyst by an oxidant and transferred to the reacting substance. It is possible that in some cases the compound formed by coordination of the reactant and the catalyst acts as a powerful oxidant. As an example one may mention that all catalytically active coordination compounds in oxidation reactions by oxygen have a planar structure. The coordination compounds with four nitrogen atoms firmly located at the corner of the square (porphyrin, phthalocyanin, and other similar compounds) have exceptional catalytic activity. The catalytic activity of Cu^{2+} in solutions increases after addition of different amines, but only to a certain limit. If coordination compounds with coordination number five or more are formed, the catalytic activity decreases or disappears³.

It is probable that in some cases neutral ligands, combining with metal ions, considerably decrease their hydration and facilitate the formation of intermediate complexes.

The dependence of the reaction rate on the ligand concentrations in solution in the case of catalytically active coordination compounds is rather complicated. The rate of reaction (1) may be expressed as:

$$\frac{dx}{dt} = \bar{\kappa} C_K^2 I_C \quad (18)$$

where C_K^2 is the total concentration of a catalyst, and I_C is a function of the concentrations of the compounds A and B. During the investigation of coordination compounds formed by the catalyst and ligands L, the initial concentrations of the catalyst (K), and the compounds A and B, remain constant and only the ligand L concentration is changed in a given series of experiments. Thus quantity $\bar{\kappa}$ changes with the change of the concentration L, and this dependence may be expressed by the equation:

$$\bar{\kappa} = \frac{\kappa_0 + \kappa_1 \beta_1 [\text{L}] + \kappa_2 \beta_2 [\text{L}]^2 + \dots}{1 + \beta_1 [\text{L}] + \beta_2 [\text{L}]^2 + \dots} \quad (19)$$

where $\beta_1, \beta_2, \beta_3 \dots$ are the stability constants of $\text{KL}, \text{KL}_2, \text{KL}_3 \dots$ respectively and $\kappa_0, \kappa_1, \kappa_2 \dots$ are the rate constants for reaction (1) without ligands and for the hypothetical cases in which only one form of coordination compound (for instance KL or KL_2 etc.) is present. From the experimental data the series of $\bar{\kappa}$ values may be determined, and the dependence of these values on the ligand concentration may be established. By equation (19) the series of values $\kappa_1(\kappa_0, \kappa_1, \kappa_2 \dots)$ and the series of values $\beta_1(\beta_1, \beta_2, \beta_3 \dots)$ may be calculated.

Instead of $\bar{\kappa}$ and κ_1 it is possible to use other values which characterize the rate of chemical reactions. For instance, for the catalytic polarographic currents it is possible to use i (the measured current strength) and $i_0, i_1,$

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i_2 . . . *etc.* that is, the strength of current which would exist if only K or KL or KL_2 *etc.* were present. It is also possible to use the reaction rate measured under definite conditions, the reciprocal time, *etc.*

We have considered the investigation of the composition and the stability of coordination compounds with the help of kinetic methods. Kinetic methods are of great interest from the theoretical point of view because they provide an opportunity of determining the true mechanism of the catalytic action of different particles in solutions (especially enzyme-like substances), and the mechanisms by which inhibitors and activators act. The influence of different ligands on the catalytic action of different substances is also a question of a considerable interest.

From the practical point of view, kinetic methods indicate ways of using coordination compounds of catalysts in analytical chemistry: analyses utilizing the inhibiting effect, the masking of catalysts, the rise of sensitivity and the specificity of some reactions.

References

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