U. D. C. 541.183.25

The Masking of Reactions

F.P.Sudakov

CONTENTS

I.	Introduction	142
II.	Classification of masking processes	143
III.	Methods for calculating the efficiency of masking	144
IV.	Masking and the selectivity of reactions	148
V.	The most common masking agents	149
VI.	Characteristic examples of the practical application of masking	153

I. INTRODUCTION

Any chemical reaction is characterised not only by stoichiometric conditions but also by thermodynamic and kinetic conditions. Changes in the last two conditions may increase the rate of a reaction or, on the other hand, decrease the rate of the reaction until the reaction is completely suppressed. In recent years the rapid development of science and technology has faced chemists with a number of problems associated with the suppression of undesirable chemical processes[1], and the attention of chemists is now drawn equally to problems of increasing reaction rates and problems of decreasing reaction rates.

One particular example of the retardation of chemical reactions is masking, which is of considerable importance in analytical chemistry. The term masking is used to describe the retardation or complete suppression of a reaction in the presence of substances capable of altering the rate or direction of the reaction as a result of their influence on its kinetic or thermodynamic conditions without the physical or chemical separation of the participants of the reaction into a new phase. The substances introduced into the reaction medium in order to retard or suppress the reaction are called masking agents. A classical example of the masking of a reaction is the non-precipitation of $Fe(OH)_3$ from an alkaline solution containing F^- ions; in this example, F^- prevents the formation of $Fe(OH)_3$, by combining with Fe^{3+} to form the soluble complex FeF_6^{3-} (that is, by bringing about another, thermodynamically more favourable reaction) and thus acts as a masking agent for the reaction of Fe^{3+} with OH^-.

Frequently, instead of the masking of a reaction, one speaks of the masking of the ions (or molecules) taking part in the reaction; usually it is not even emphasised which of the ions taking part in the reaction being masked are in fact masked directly, that is, which of the ions is responsible for the masking of the reaction as a whole. For example, in the masking of the formation of the yellow molybdophosphate complex in the presence of $C_2O_4^{2-}$ in the traditional use of this masking agent to eliminate the interfering influence of PO_4^{3-} in the photometric determination of Si, reference is made to the masking of the PO_4^{3-} ion, rather than to the masking of the MoO_4^{2-} ion, although it is the MoO_4^{2-} ion which is responsible for the masking of the reaction, since it reacts with $C_2O_4^{2-}$ to form a colourless soluble complex. In most instances when a knowledge of the mechanism of masking is not required, this replacement of concepts, with a correct understanding of the essential features of the process, is quite justified, but for greater accuracy and to avoid misunderstanding it is desirable even in these instances to indicate the reaction (or reagent) with respect to which a given ion is masked. The statement (without any additional information) that a given ion is masked should evidently be understood to mean that all the reactions which are possible for this ion in the given reaction medium (before the addition of the masking agent) are masked. Thus if one speaks of the masking of Fe^{3+} by tartrate in the determination of Ni by dimethylglyoxime, one means that the Fe^{3+} is masked with respect to all reactions possible for this ion under the conditions of the determination of Ni, including (and this is the most important) the formation of $Fe(OH)_3$.

Frequently, the masking of ions is erroneously identified with the separation of ions, and it is forgotten that the separation of ions, unlike masking, always involves the transfer of ions into a new phase, that is, their actual removal from the sphere of reaction. For example, the reaction of NH_4^+ with CH_2O with the formation of soluble hexamethylenetetramine $(CH_2)_6N_4$ is a typical example of masking of the NH_4^+ ion, but the decomposition of NH_4^+ by nitrite with the formation of the gaseous product N_2 cannot be regarded as masking of the NH_4^+ ion. According to the same principle, masking does not include examples where the interfering influence of ions is eliminated by precipitating them in the form of sparingly soluble compounds, even when the latter remain in the mother-liquor [for example, the precipitation of Mg^{2+} as $Mg(OH)_2$ in the complexometric titration of Ca^{2+}].

The incorrect view that masking is merely a method for eliminating the interfering influence of substances in qualitative and quantitative analysis is widely encountered. Masking is a process in which the ion or molecule being masked, under the influence of the masking agent, loses its ability to undergo certain reactions characteristic of the ion or molecule. Like any other process, masking may be either desirable or undesirable, that is, it may be useful or harmful. Thus the masking of many qualitative reactions of the cations of analytical groups II and III in the presence of PO_4^{3-} is undesirable and steps have to be taken to prevent it. On the other hand, the masking of accompanying ions in various analytical reactions is useful and desirable, and is used to eliminate the interfering influence of these ions.

Masking has two significant advantages over methods of separation as a method for eliminating the interfering influence of substances: maximal speed, since almost no time is required for the actual masking, and high efficiency due to the absence of the usual errors associated with phase separations. Because of these advantages, the masking of reactions and ions has now become an extremely widespread and powerful means of eliminating the interfering influence of the medium in chemical analysis. This

has been greatly facilitated by the work of Feigl[2,3], who first drew attention to the importance of the study of the masking of reactions and ions in analytical chemistry, and also by Ringbom[4-6], Reilley and Schmid[7], Suzuki[8,9], Tanaka[10,11], Chaberek and Martell[12], Cheng[13], Schwarzenbach[14], and Yatsimirskii[15,16], who have made important contributions to the theory of masking processes.

Although the study of problems in the theory and practical application of masking is not restricted to analytical chemistry, but is also of importance in, for example, biology, and various branches of industry[12], the present state of development of these problems is closely related to the development of general problems in analytical chemistry. The present paper therefore deals chiefly with analytical aspects of the masking of reactions and ions.

II. CLASSIFICATION OF MASKING PROCESSES

Two basic types of masking can be distinguished, according to their fundamental nature: (1) masking due to a change in the thermodynamic conditions for the reaction being masked; and (2) masking due to a change in the kinetic conditions for the reaction being masked.

In all examples of masking belonging to the first type, the essential feature of the masking action of the substances specially introduced (or the factors deliberately altered) is the change in the reaction system from the initial equilibrium state in the newly created conditions; a characteristic feature of this new equilibrium state is that the reaction being masked takes place to the minimal extent. This type of masking can be described as equilibrium (or thermodynamic) masking. In equilibrium masking, the masking action responsible for the change in the direction of the reaction being masked is described qualitatively by le Châtelier's principle, and quantitatively by the corresponding thermodynamic equations, in particular the equation for the law of mass action (when there is a change in the concentration of the substances taking part in the reaction being masked) and the isobar or isochore equations (when there is a change in temperature).

In specific instances, masking action of the first type is brought about by the most varied mechanisms: (a) mechanical introduction of additional quantities of the compound which is the product of the reaction being masked; (b) oxidation or reduction of one or more of the substances taking part in the reaction being masked; (c) the reaction of one or more of the participants in the reaction being masked to form soluble complexes (including chelate compounds); and (d) the reaction of one or more of the participants in the reaction being masked to form other types of soluble compound (molecular adducts, ion associates, covalent compounds, etc.). This list should also include the masking of reactions as a result of a change in temperature and pressure (without the introduction of special masking agents) and also as a result of a change in the composition of the reaction medium (the nature of the solvent, ionic strength, etc.). In the last instance, and also when the direction of the reaction being masked is changed as a result of the addition of an excess of the product of the reaction, the original form of the substances being masked remains unchanged.

The following are some examples: (a) in the cerimetric titration of Fe^{2+}, Sn^{2+}, or Sb^{3+}, the interfering reaction between AsO_2^- and Ce^{4+} can be reliably masked with a large excess of AsO_4^{3-}, which is the product of the reaction of AsO_2^- and Ce^{4+}; (b) in the hydrogen sulphide scheme of qualitative analysis, $Cr_2O_7^{2-}$ is masked by reduction to Cr^{3+} with ethanol; (c) the oxidising reactions of Fe^{3+} are completely masked in the presence of ethylenediaminetetraacetate (EDTA), which combines with Fe^{3+} to form a stable soluble complex; and (d) in the titrimetric analysis of mixtures of H_2SO_3 and HSO_3^-, the acid strengths of these substances are "moved apart" by masking the HSO_3^- with formaldehyde, which reacts with HSO_3^- to form a soluble adduct with stability constant $\sim 10^7$.

The basis of masking action of the second type is the kinetic effect: the masking agent introduced into the reaction medium decreases the rate of the reaction being masked, either directly or by removing one of the participants of the reaction being masked, in another, more rapid reaction. In this instance the masking is not associated with the attainment of stable thermodynamic equilibrium in the system; this distinguishes the second type of masking from the first type, and the second type of masking can be described briefly as non-equilibrium (or kinetic) masking. The masking action produced by the kinetic effect can in principle be described quantitatively by the appropriate kinetic equations.

Comparatively few examples of masking of the second type have been studied (and hence become familiar), although this does not mean that they are not widely encountered. The primary example is masking based on negative catalysis, when the presence of a masking agent (which in this instance plays the part of catalyst) excludes one of the reaction paths which is possible in its absence, leaving slower reaction paths unaffected. An example of catalytic masking is provided by the suppression of the oxidation of AsO_2^- by $Cr_2O_7^{2-}$ ions in the presence of Mn^{2+} in the dichromate titration of Fe^{2+} (Mn^{2+} acts as negative catalyst for the spontaneous reaction of AsO_2^- with $Cr_2O_7^{2-}$). The action of the catalyst masking agent on the reaction being masked involves its intermediate chemical reaction with the reacting substances with the restoration of the original forms of these substances after each cycle of the intermediate reactions; the substances being masked thus remain finally unchanged.

A form of masking which is very similar to catalytic masking is that involving the suppression of induced (conjugated) reactions. The mechanism of the masking action in this instance has its own characteristic features, associated with the differences between induced reactions and purely catalytic reactions, and it makes allowance for the stoichiometry of the induction and the irreversible chemical transformation of the inductor, but, as in the previous example, the substances being masked retain their original forms as a result of the masking. A familiar example of the masking of an induced reaction is the suppression of the oxidation of Cl^- in the permanganometric titration of Fe^{2+} in the presence of Mn^{2+}, which acts as masking agent for the Cl^- ion.

Finally, the second type includes masking based on the difference in the rates of the reaction being masked and the masking reaction with a common participant—the masking agent. This principle forms the basis, for example, of the complexometric titration of Fe^{3+} in the presence of Cr^{3+}, which, unlike Fe^{3+}, forms a soluble complex with EDTA only very slowly, although the stability constants of the complexonato-compounds of Fe^{III} and Cr^{III} are close to one another (10^{25} and 10^{23} respectively); in this example, EDTA acts simultaneously as complexometric titrant for Fe^{3+} and masking agent for Cr^{3+}.

The above general and fundamental classification of masking processes naturally provides for special classifications of importance in various particular instances.

Thus if the masking of ions is one of the stages in the analysis of complex mixtures, it is usually always followed by demasking of the ions; in these instances the selection of rational methods of demasking is facilitated by Suzuki's classification[8,9], based on the state of the ion after masking.

When we are dealing with the masking of individual ions (and not reactions), it is sometimes convenient to distinguish various forms (or techniques) of masking, for example, direct and indirect, single-stage and multi-stage, etc. The suppression of the reaction between PO_4^{2-} and MoO_4^{2-} in the presence of $C_2O_4^{2-}$ is an example of direct masking for MoO_4^{2-} and of indirect masking for PO_4^{3-} (most examples of equilibrium masking can be regarded in this way). The masking of the Cu^{2+} ion by glycerol (which forms a soluble complex with Cu^{2+}) in the qualitative analysis of the cations of analytical group IV is an example of single-stage masking, whereas the masking of the same Cu^{2+} ion by cyanide is an example of double (two-stage) masking, since in this example the Cu^{2+} is first reduced by the cyanide to Cu^{+}, after which it reacts with cyanide to form the soluble complex $Cu(CN)_4^{3-}$, that is, it is masked twice.

Special attention must be made of self-masking and buffer masking. The self-masking of a reaction is masking brought about by the reaction being masked; in this instance the addition of a special masking agent is not required, since its part is played by one of the reacting substances or reaction products (an example in the suppression of the formation of sparingly soluble HgI_2 at high I^- concentrations as a result of the formation of the soluble complex HgI_4^{2-}). Buffer masking differs from ordinary masking in that the substance added to the reaction medium is not the free masking agent but its complex with a given ion; the absence of a large quantity of free masking agent from the reaction medium leads to the strictly selective masking of only that reaction which is capable of being influenced by the very small quantities of masking agent produced by dissociation of the added complex. An example of buffer masking is the masking of Sr^{2+} by a mixture of EDTA and Mg^{2+} in the precipitation of Ba^{2+} as $BaCrO_4$ (the comparatively unstable complex of Mg^{2+} with EDTA formed in this instance does not prevent the quantitative precipitation of $BaCrO_4$, but is capable of creating conditions leading to the complete conversion of Sr^{2+} into a soluble complexonate).

III. METHODS FOR CALCULATING THE EFFICIENCY OF MASKING

1. The Masking of Reactions and Their Conditional Constants

For equilibrium (thermodynamic) masking, that is, for most examples of masking known at present, all the information on the masking process could in principle be obtained by solving the thermodynamic equations for the masked and masking reactions in the given system, containing the ions being masked and the masking agent. For systems of any complexity, however, this involves practically unsurmountable difficulties, since the necessary equilibrium constants are not known. This makes it necessary to examine the masking of reactions using approximate methods of calculation, and in some instances using semi-quantitative and qualitative-descriptive methods.

In analytical chemistry at present, ordinary (thermodynamic) equilibrium constants are being widely replaced by so-called "conditional constants", which were introduced by Ringbom[4,5] and which make allowance for the influence, on the main reaction, of all side-reactions possible in the given system (the reactions of the participants in the main reaction with hydrogen and hydroxide ions, buffer and masking agents, competing ions, etc.).

For a reaction of the type

$$M + A \rightleftarrows MA$$

the conditional constant is defined by the expression

$$K_{M'A'} = \frac{[MA]}{[M'][A']}, \quad (1)$$

where [M'] denotes the concentration of not only the free participant in the reaction M, but also all the M in solution which has not reacted with A. Similarly [A'] denotes the concentration of not only free A but also all the A which has not reacted with M.

The conditional constant for the reaction $K_{M'A'}$ is related to the ordinary equilibrium constant for this reaction K_{MA} by the simple relationship

$$K_{M'A'} = \frac{K_{MA}}{\alpha_M \alpha_A}, \quad (2)$$

where α_M and α_A are the so-called "α-coefficients" or "side reaction coefficients" proposed by Schwarzenbach[14]. For the reaction being considered, the α-coefficients are defined as follows:

$$\alpha_M = \frac{[M']}{[M]} \quad (3) \text{ and } \alpha_A = \frac{[A']}{[A]} \quad (4)$$

where [M] and [A] are the concentrations of free (not combined with one another or with other substances) participants in the reaction M and A respectively.

The α-coefficients α_M and α_A are functions of the equilibrium constants of the corresponding side-reactions. If, for example, one of the participants in the main reaction M (a metal ion) takes part in a side-reaction with a ligand L with the formation of a series of mononuclear complexes, we have

$$\alpha_{M(L)} = \frac{[M']}{[M]} = \frac{[M] + [ML] + [ML_2] + \ldots + [ML_n]}{[M]}, \quad (5)$$

or

$$\alpha_{M(L)} = 1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n, \quad (6)$$

where $\beta_1, \beta_2, \ldots \beta_n$ are the cumulative stability constants of the complexes of M with L. Similarly, if the second participant in the main reaction A (an anion) reacts with another cation N to form a series of complexes, we have

$$\alpha_{A(N)} = \frac{[A']}{[A]} = \frac{[A] + [NA] + [N_2A] + \ldots + [N_mA]}{[A]}, \quad (7)$$

or

$$\alpha_{A(N)} = 1 + \beta_1[N] + \beta_2[N]^2 + \ldots + \beta_m[N]^m, \quad (8)$$

where $\beta_1, \beta_2, \ldots \beta_m$ are the cumulative stability constants of the complexes of A with N.

In the above particular cases, when the side-reactions involve complex formation, the function giving the α-coefficients in terms of the equilibrium constants of the side-reactions is often called the degree of complex formation, following Yatsimirskii's suggestion[17].

Thus the α-coefficients essentially provide a quantitative measure of the extent to which side-reactions take place in the given system: in the absence of side-reactions, when M reacts only with A, $\alpha_M = 1$ and $\alpha_A = 1$; if, however, M and A take part in side-reactions with L and N respectively, $\alpha_{M(L)} > 1$ and $\alpha_{A(N)} > 1$.

The values of the α-coefficients for any ion can be calculated from the equilibrium constants of the corresponding side-reactions using equations of type (6) and (8), or determined experimentally by potentiometric, polarographic, or spectrophotometric methods, without using the equilibrium constants. The possibility of direct experimental determination of the α-coefficients, combined with the possibility of using the conditional constants in the same way as ordinary equilibrium constants, makes the principle of conditional constants of practical importance in the examination of various analytical problems, in particular the problems of masking action.

The principle of conditional constants is used in all known methods for calculating the efficiency of masking reactions, of which the most commonly encountered are the method which is referred to as the method of conditional constants, and the chelate buffer method.

2. Method of Conditional Constants

In the method of conditional constants, developed by Ringbom[4-6], the masking reactions are regarded as side-reactions with respect to the reaction being masked, so that the latter is taken as the main reaction in the given system. Accordingly, the masking of the reaction can be defined as a process (or technique) leading to a decrease in the conditional constant of this reaction.

Eqn. (2), which can be written in the more general form

$$K_{M'_mA'_n} = \frac{K_{M_mA_n}}{\alpha_M^m \alpha_A^n}, \qquad (9)$$

is the fundamental equation for the quantitative characterisation of masking action in various examples of equilibrium masking. The α-coefficients, which appear in this equation, provide a quantitative measure of the extent to which the masking reactions take place in the given system: in the absence of masking reactions, $\alpha_M = 1$ and $\alpha_A = 1$, but if M and A take part in masking reactions with the masking agents L and N, we have $\alpha_{M(L)} > 1$ and $\alpha_{A(N)} > 1$. In other words, the α-coefficients characterise the ability of ions to be masked by given masking agents (or the ability of the masking agents to mask the given ions), and the conditional constant defines the actual degree of masking of the reaction between these ions in the presence of the corresponding masking agents.

The problem of the value to which the conditional constant of a reaction must be reduced for the reaction to be regarded as masked is of practical importance; this value depends on the concentration conditions and on the degree of masking required. In complexometry, for example, the following limits are acceptable in most instances for the conditional constants of the reactions being masked: for $K_{M'A'} < 10^2$ the interfering reaction is almost completely masked, for $K_{M'A'} > 10^7$ there is almost no masking, and for intermediate values of $K_{M'A'}$ masking is incomplete.

The no less important problem of selecting a suitable masking agent is related to the calculation or determination of the α-coefficients. Eqn. (6) for the calculation of $\alpha_{M(L)}$, in addition to the cumulative stability constants of the complexes of M with L, contains the concentration of free masking agent [L]. If the analytical (total) concentration of L in the solution is much greater than the analytical concentration of the free metal ion M (that is, if $C_L \gg C_M$ and the dissociation of the complex ML is slight), masking of the reactions is observed in practice in most instances, and if L is the anion of a strong acid or of a weak acid which is completely dissociated at the given pH, we have

$$[L] = [L'] \simeq C_L - C_M \text{ (or even) } [L] \simeq C_L) \qquad (10)$$

If, however, L is a weak acid [L] in the general case is given by the equation

$$[L] = \frac{[L']}{\alpha_{L(H)}} = \frac{C_L - C_M}{1 + \frac{[H^+]}{K_m} + \frac{[H^+]^2}{K_m K_{m-1}} + \ldots \frac{[H^+]^m}{K_m K_{m-1} \ldots K_2 K_1}}, \qquad (11)$$

where $\alpha_{L(H)}$ is the coefficient of the side-reaction of L with H^+, and $K_1, K_2, \ldots K_m$ the consecutive dissociation constants of the product of this reaction H_mL. In some instances, particularly for the ions of multivalent metals in strongly alkaline solutions, it is also necessary, in the calculation of the α-coefficients, to make allowance for the possibility of the reaction of M with OH^- with the formation of hydroxo-complexes; this can be done by introducing an additional side-reaction coefficient $\alpha_{M(OH)}$.

The calculation of the α-coefficients using Eqns. (6) and (8) is in general fairly tedious; it is therefore simpler and more convenient to use available α-coefficient values, which are usually provided in the form of graphs and tables. A collection of the values of the α-coefficients for a large number of ligands and metal ions is given in Ringbom's monograph[5]. Table 1 gives as an example the values of

Table 1. Logarithmic values of α_M (EDTA) (concentration of metal ion and EDTA 0.1 M; ionic strength $I = 0.5$).

Metal ion	pH														
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ag^+					0.1	0.5	1.5	2.6	3.7	4.7	5.5	5.9	6.0	6.0	6.0
Al^{3+}			1.8	4.1	6.2	8.2	10.3	12.5	14.5	16.5	18.3	21.3	25.3	29.3	33.3
Ba^{2+}							1.8	3.2	4.2	5.2	6.0	6.2	6.3	6.3	6.3
Be^{2+}					0.1	1.6	3.3	4.7	5.7	6.7	7.5	7.7	7.8	7.8	7.8
Ca^{2+}				0.1	1.1	3.2	4.7	6.1	7.1	8.1	8.9	9.1	9.2	9.2	9.2
Cd^{2+}		0.3	2.7	4.8	6.8	8.8	10.5	11.9	12.9	13.9	14.7	14.9	15.0	15.0	15.0
Co^{2+}		0.2	2.6	4.7	6.6	8.6	10.3	11.7	12.7	13.7	14.5	14.7	14.8	14.8	14.8
Cu^{2+}		1.9	4.6	6.8	8.7	10.7	12.5	13.9	15.0	16.0	16.8	17.3	18.0	18.9	19.9
Fe^{2+}			0.6	2.6	4.6	6.6	8.3	9.7	10.7	11.7	12.5	12.7	12.8	12.8	12.8
Fe^{3+}	3.8	7.0	10.3	13.0	15.2	13.2	18.9	20.4	22.0	24.0	26.4	28.5	30.6	32.6	34.6
Hg^{2+}	2.4	5.4	8.1	10.2	12.1	14.1	15.8	17.2	18.2	19.5	21.0	22.2	23.3	24.3	25.3
La^{3+}			0.8	3.5	5.7	7.7	9.4	10.8	11.8	12.8	13.6	13.8	13.9	13.9	13.9
Mg^{2+}						0.7	2.4	3.8	4.9	5.8	6.7	7.1	7.2	7.2	7.2
Mn^{2+}			0.5	2.4	4.3	6.3	8.0	9.4	10.4	11.4	12.2	12.4	12.4	12.4	12.4
Ni^{2+}	0.1	2.4	5.1	7.1	2.0	10.9	12.6	14.0	15.0	16.0	16.8	17.0	17.1	117.1	17.1
Pb^{2+}		1.4	4.2	6.3	8.2	10.2	12.0	12.4	14.4	15.4	16.2	16.4	16.5	116.5	16.5
Sr^{2+}					0.1	1.0	2.6	4.0	5.0	6.0	6.8	7.0	7.1	7.1	7.1
Th^{4+}	0.5	4.3	8.0	10.8	13.0	15.0	16.7	18.5	20.2	22.2	24.0	25.2	26.3	27.3	28.3
Zn^{2+}		0.3	2.8	4.9	6.8	8.8	10.5	11.9	12.9	13.9	14.7	14.9	15.0	15.0	15.6

the α-coefficients, taken from this monograph, for the most widely encountered masking agent EDTA, relative to the ions of various metals at various pH, and Table 2 gives the α-coefficients for the complexing anions most frequently used as masking agents, at various pH.

3. The Chelate Buffer Method

The chelate buffer method, developed by Chaberek and Martell[12] and Tanaka[10,11], is based on the recognition that a buffer action is produced in solutions containing a metal ion and ligand; when the system contains an excess of ligand, the metal ion is buffered (pM buffer), and in an excess of metal ion the ligand is buffered (pL buffer).

For the simplest system consisting of a metal ion M with total concentration C_M and an excess of ligand L with total concentration C_L, in which one chelate compound ML with stability constant K_{ML} is formed at $a = C_L/C_M > 1$, the concentration of free metal ion in the solution is given by the equation:

$$[M] = \frac{C_M}{1 + (a-1) K_{ML} C_M} . \quad (12)$$

If K_{ML} is sufficiently large, we have

$$[M] = \frac{1}{(a-1) K_{ML}} . \quad (13)$$

For a system consisting of a ligand L with total concentration C_L and an excess of a metal ion N with total concentration C_N, in which one chelate compound NL with stability constant K_{NL} is formed at $b = C_L/C_N > 1$, the concentration of free ligand in the solution is given by the equation:

$$[L] = \frac{1}{(b-1) K_{NL}} . \quad (14)$$

It follows from Eqns. (13) and (14) that in solutions containing a metal ion M and an excess of ligand L ($a = C_L/C_M > 1$) or a ligand L and an excess of a metal ion N ($b = C_N/C_L > 1$), the concentration of the metal ion [M] or [L] respectively depends only on the ratio of the total concentrations of the metal ion (C_M or C_N) and ligand C_L, but is independent of their absolute values, that is, these solutions exhibit buffer properties.

The example involving the buffering of a metal ion M in an excess of a masking ligand L (pM buffer) is of greatest importance in the solution of various problems of masking.

Let us examine the behaviour of a pM buffer in the presence of an ion A which reacts with the metal ion M to form, for example, a sparingly soluble compound MA. In the system we have competition between two reactions: the masking reaction:

$$M + L \rightleftarrows ML$$

and the reaction being masked:

$$M + A \rightleftarrows MA$$

and the effect of the competition is described quantitatively by the equation

$$\lg \frac{[L]}{[ML]} = \lg \frac{f}{K_{ML} K_{sp}} + \lg [A] . \quad (15)$$

It can be seen from Eqn. (15) that the ratio [L]/[ML] should be constant at constant concentration of the excess of precipitant ion [A]. The addition of ML to this system necessarily leads to the dissociation of ML and the precipitation of the liberated M as MA, and the addition of free masking agent L leads to the dissolution of part of the MA precipitate and reaction of the liberated metal ion to form the chelate compound ML until the original value of [L]/[ML] in the solution is restored. The ratio [L]/[ML] in the solution will again control [M] only after the disappearance of the solid phase as a result of the gradual addition of L.

The expression $1/K_{ML}K_{sp}$, in Eqn. (15), called the "precipitation constant" and denoted by K_p, provides a quantitative measure of the tendency for the metal ion to be precipitated from the chelate buffer solution: the greater K_p, the greater the quantity of masking agent required to mask the precipitation. Table 3 gives as an example the values of the precipitation constants for the precipitation of the oxalates of various metals in the presence of various masking agents.

If the masking ligand L is a weak acid, pM also depends on pH; for this example, Eqn. (15) becomes

$$\lg \frac{[L]}{[ML]} = \lg \frac{K_m K_{m-1} \cdots K_2 K_1}{K_{ML} \cdot K_{sp}} + \lg [H_m L] + mp\mathrm{H} , \quad (16)$$

where $K_1, K_2, \ldots, K_{m-1}, K_m$ are the consecutive dissociation constants of H_mL.

Table 2. Logarithmic values of $\alpha_{L(H)}$ for various masking agents*.

pH	TEA	en	den	tren	trien	tetren	penten	EDTA	NTA	DCTA	EGTA	CN^-	F^-	PO_4^{3-}	$P_2O_7^{2-}$	$C_2O_4^{2-}$	$C_4H_4O_6^{2-}$	$HC_6H_4O_7^{3-}$
0	7.8	17.4	23.7	28.7	29.4	34.1	37.9	21.4	14.4	24.1	23.3	9.2	3.05	20.7	18.1	5.1	7.0	13.5
1	6.8	15.4	20.7	25.7	25.4	29.1	33.9	17.4	11.4	20.1	19.3	8.2	2.05	17.7	14.4	3.35	5.0	10.5
2	5.8	13.4	17.7	22.7	21.5	24.1	29.9	13.7	8.7	16.2	15.6	7.2	1.1	15.0	11.3	2.05	3.05	7.5
3	4.8	9.4	14.7	19.7	17.8	19.6	25.9	10.8	7.0	12.8	12.7	6.2	0.3	12.6	8.7	1.05	1.4	4.8
4	3.8	6.2	11.8	16.7	14.1	15.5	21.9	8.6	5.8	10.1	10.5	5.2	0.05	10.6	6.6	0.3	0.4	2.7
5	2.8	5.1	9.3	13.7	11.0	11.9	17.9	6.6	4.8	8.0	8.5	4.2		8.6	4.6	0.05	0.05	1.2
6	1.8	4.1	7.2	10.7	8.1	8.7	13.9	4.8	3.8	6.2	6.5	3.2		6.6	2.9			0.25
7	0.9	3.1	5.2	7.7	5.5	5.7	9.9	3.4	2.8	4.9	4.5	2.2		5.0	1.6			0.05
8	0.2	2.1	3.3	4.8	3.3	3.0	6.0	2.3	1.8	3.8	2.5	1.2		3.7	0.6			
9		1.1	1.5	2.3	1.5	1.0	2.6	1.4	0.9	2.8	0,9	0.4		2.7	0.1			
10		0.4	0.4	0.7	0,3	0.1	0.6	0.5	0.2	1.8	0,1	0.1		1.7				
11		0.1		0.1				0.1		0.9				0.8				
12										0.2				0.2				

* en represents ethylenediamine, den diethylenetriamine, trien triethylenetetramine, tetren tetraethylenepentamine, penten pentaethylenehexamine, TEA triethanolamine, tren triaminotriethylamine, EDTA ethylenediaminetetra-acetic acid, NTA nitrilotriacetic acid, DCTA 1,2-diaminocyclohexanetetra-acetic acid, and EGTA ethylene glycol bis-(2-aminoethyl ether)tetra-acetic acid [presumably 2,2'-ethylenedioxybis(ethyliminodiacetic acid) (Ed. of Translation)].

To calculate the concentration of free metal ion [M] in the pM buffer (that is, in a solution containing the metal ion M and an excess of masking agent L), it is more convenient to use the equation derived in terms of the analytical (total) concentrations of the metal ion C_M and the masking ligand C_L:

$$[M] = \frac{C_M}{1 + K_{ML}(C_L - C_M)}. \quad (17)$$

In the general case, when the masking agent L is a weak acid, it is necessary to use Eqn. (11), which is equivalent

Table 3. Precipitation constants for metal oxalates in the presence of various masking agents [12]*.

M	pK_{sp}	EDTA		NTA		HIDA		DHEG	
		$\lg K_{ML}$	K_p	$\lg K_{ML}$	K_p	$\lg K_{ML}$	K_p	$\lg K_{ML}$	K_p
Cu	7.5	18.3	$1.6\cdot10^{-11}$	12.7	$6.3\cdot10^{-6}$	10	—	8.2	$2.0\cdot10^{-1}$
Pb	10.6	18.2	$1.6\cdot10^{-8}$	11.8	$2.0\cdot10^{-1}$	9.4	13	—	—
Zn	8.8	16.1	$5.0\cdot10^{-8}$	10.4	$2.5\cdot10^{-2}$	8.6	1.6	5.4	2500
Cd	7.8	16.4	$2.5\cdot10^{-9}$	9.8	10^{-2}	7.1	5.0	4.8	1000
Ca	8.7	10.6	$1.3\cdot10^{-2}$	6.4	200	4.8	7900	—	—
Mg	4.1	8.7	$2.5\cdot10^{-3}$	5.4	$2.0\cdot10^{-2}$	3.5	4.0	1.2	795

* EDTA represents ethylenediaminetetra-acetic acid, NTA nitrilotriacetic acid, HIDA *N*-hydroxyethyliminodiacetic acid, and DHEG dihydroxyethylglycine.

to the replacement of the ordinary constant K_{ML} by the conditional constant $K_{ML'}$:

$$[M] = \frac{C_M}{1 + K_{ML'}(C_L - C_M)}. \quad (18)$$

$K_{ML'} = K_{ML}/\alpha_{L(H)}$ and $\alpha_{L(H)} = (C_L - C_M)/[L]$.

If x denotes the fraction of the metal ion M remaining in solution in the presence of the precipitant ion A, Eqn. (18) becomes

$$[M] = \frac{C_M x}{1 + K_{ML'}(C_L - C_M x)}. \quad (19)$$

Making use of the relationship $[M] = K_{sp}/[A]$, we obtain

$$x = \frac{1 + K_{ML'}C_L}{\left(K_{ML'} + \frac{[A]}{K_{sp}}\right)C_M}. \quad (20)$$

Since $K_{ML'}C_L \gg 1$, we obtain finally:

$$x = \frac{C_L}{\left(1 + \frac{[A]}{K_{ML'}K_{sp}}\right)C_M}. \quad (21)$$

For the formation of a metal hydroxide $M(OH)_n$, Eqn. (21) becomes

$$x = \frac{C_L}{\left(1 + \frac{K_w^n}{K_{ML'}K_{sp}[H^+]^n}\right)C_M}. \quad (22)$$

Let us now consider the pL buffer, which is also of importance in the theory of masking by virtue of its use as masking agent (instead of free ligand) in buffer masking.

In the pL buffer, consisting of a masking ligand L and an excess of an indifferent metal ion N ($K_{NL} < K_{ML}$), the concentration [L] is buffered when its value is low (at a low level) and is determined by Eqn. (14).

When the pL buffer is introduced into a solution containing the metal ion M to be masked, the formation of the chelate compound NL in the pL buffer can be regarded, like the formation of the proton complexes H_mL, as a side-reaction with respect to the reaction being masked (between M and L), so that the conditional constant $K_{ML'}$ in Eqn. (18) is given by

$$K_{ML'} = \frac{K_{ML}}{\alpha_{L(H,N)}}, \quad (23)$$

where $\alpha_{L(H,N)} = \alpha_{L(H)} + \alpha_{L(N)}$.

In the presence of the precipitant ion A the value of b in Eqn. (14) depends on the value of x in Eqn. (21)—that is, $b = C_N/(C_L - C_M x)$—so that Eqn. (14) becomes

$$[L] = \frac{1}{K_{NL}\left(\frac{C_N}{C_L - C_M x} - 1\right)}. \quad (24)$$

Eqn. (18) can be used to construct graphs giving the pH dependence of pM, and Eqn. (21) can be used to construct graphs giving the pH dependence of $\lg x$. These graphs, called pM–pH diagrams, provide a convenient means of predicting the efficiency of the masking of various reactions in the presence of free or complexed ligands as masking agents. Fig. 1 gives as an example the pM–pH diagrams for the masking of the formation of $Fe(OH)_3$ in the presence of EDTA, and also in the presence of Ca–EDTA.

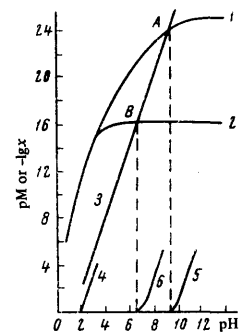


Figure 1. pM–pH and $\lg x$–pH diagrams [10].

Curve *1* gives the pH dependence of pFe in the presence of an excess of EDTA, curve *2* gives the pH dependence of pFe in the presence of a pL buffer consisting of EDTA and an excess of Ca, curve *3* gives the pH dependence of pFe in the absence of masking agent; and curves *4*, *5*, and *6* give the pH dependence of the negative logarithm of the fraction of Fe remaining in solution under the conditions corresponding to curves *1*, *2*, and *3*. The points of intersection of curves *1* and *2* with curve *3* (*A* and *B*) correspond to the start of the precipitation of $Fe(OH)_3$.

4. Other Methods

In addition to the two general methods of calculating the efficiency of masking, described above, various particular methods have been proposed, in which attempts are made to obtain a clearer and simpler description of the equilibrium state in systems containing masking agents and ions being masked, by the introduction of various formally specific masking criteria. Two of these methods deserve mention: Cheng's selectivity ratio method [13], and Hulanicki's masking coefficient method [18].

The first method introduces the concept of "selectivity ratio", defined as

$$\text{S.R.} = \frac{(pM_p)^a}{pM_m}, \qquad (25)$$

where pM_p and pM_m are the negative logarithms of the concentrations of the metal ion resulting from the dissociation of the compound of the metal with the analytical reagent (the product of the reaction being masked) and the complex of the same metal with the masking agent (the product of the masking reaction) respectively.

Calculation of the selectivity ratio, from the pM values determined experimentally or calculated from the thermodynamic or conditional equilibrium constants, makes it possible to predict which of the reactions—the reaction being masked or the masking reaction—predominates in the given system. If the value of the S.R. is less than 7, the masking reaction takes place preferentially in the system (the metal ion is masked), but if the S.R. is greater than 7, masking does not take place and the reaction to be masked takes place normally. Table 4 gives as an example the results of the calculation of the S.R. for the masking action of EDTA on various reactions of the Ag^+ ion.

Table 4. Reactions of the silver ion in the presence of EDTA [13] (concentration of complexes 1 M; pH 10; $K_{Ag\text{-}EDTA} = 2 \times 10^7$; $pM_m = 3.6$).

Reaction	K_{sp} or K_{MA}	pAg^+ (pM_p)	$\frac{(pM_p)^2}{pM_m}$
$2Ag^+ + 2OH^- \rightleftarrows Ag_2O + H_2O$	$2.0 \cdot 10^{-8}$	3.8	4.0
$2Ag^+ + CrO_4^{2-} \rightleftarrows Ag_2CrO_4$	$1.9 \cdot 10^{-12}$	3.6	3.6
$Ag^+ + IO_3^- \rightleftarrows AgIO_3$	$2.0 \cdot 10^{-8}$	3.8	4.0
$Ag^+ + Cl^- \rightleftarrows AgCl$	$1.0 \cdot 10^{-10}$	5.0	7.0
$Ag^+ + Br^- \rightleftarrows AgBr$	$5.0 \cdot 10^{-13}$	6.1	10.3
$Ag^+ + I^- \rightleftarrows AgI$	$8.5 \cdot 10^{-17}$	8.0	17.8
$2Ag^+ + C_2O_4^{2-} \rightleftarrows Ag_2C_2O_4$	$5.0 \cdot 10^{-12}$	3.5	3.4
$Ag^+ + SCN^- \rightleftarrows AgSCN$	$1.0 \cdot 10^{-12}$	6.0	10.0
$2Ag^+ + S^{2-} \rightleftarrows Ag_2S$	$1.0 \cdot 10^{-50}$	16.3	73.8
$Ag^+ + 2S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)^{3-}$	$1.7 \cdot 10^{-13}$	4.6	5.9
$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^-$	$5.6 \cdot 10^{18}$	6.4	11.4

In the second method, use is made of the concept of "masking coefficient", which gives the total concentration of the metal M present in the solution in equilibrium with an equivalent concentration of the analytical reagent, for example, the precipitant ion A for the masking of a precipitation of the type

$$mM + nA \rightleftarrows M_mA_n.$$

For this reaction the masking coefficient is given by

$$pM' = \frac{1}{m+n}\left(pK_{sp} - n \lg \frac{m}{n}\right) - \frac{m}{m+n} \lg \alpha_M - \frac{n}{m+n} \lg \alpha_A, \qquad (26)$$

where pM′ is the negative logarithm of the total concentration of the metal ion M in the solution [M′], pK_{sp} the negative logarithm of the solubility product of M_mA_n, and α_M and α_A the α-coefficients—see Eqns. (6) and (8). Eqn. (26) is derived by expansion of the expression for the conditional constant for the solubility product of M_mA_n.

The value of pM′ calculated from Eqn. (26) can be used to predict which reaction—the masking reaction or the reaction being masked—takes place in a given system under given conditions. Since in the usual analytical procedures the metal ion concentrations lie in the range 10^{-3}–10^{-5} M, complete masking of the reaction takes place when pM′ < 3, and complete demasking takes place when pM′ > 5. As an example let us consider the masking of the formation of $Ag_2C_2O_4$ ($pK_{sp} = 10.46$) in the presence of 0.1 M EDTA at pH 5. We find from Tables 1 and 2 that $\lg \alpha_{Ag(EDTA)} = 0.5$ and $\lg \alpha_{C_2O_4(H)} = 0.05$, so that pM′ = (1/3) − (10.46 − 0.30) − (2/3)(0.5) − (1/3)(0.05) = 3.36, − 0.34 − 0.02 = 3.00, that is, under the given conditions the formation of $Ag_2C_2O_4$ is masked completely.

IV. MASKING AND THE SELECTIVITY OF REACTIONS

To characterise quantitatively the increase in the selectivity of reactions due to masking, let us consider a solution containing one analytical reagent A and two metal ions M_I and M_{II}, which react with A to form products with different stabilities ($K_{M_IA} > K_{M_{II}A}$). By applying the principles of conditional constants [4,5], that is, by assuming that the reaction

$$A + M_{II} \rightleftarrows M_{II}A$$

is a side-reaction with respect to the reaction

$$M_I + A \rightleftarrows M_IA$$

we find that

$$K_{M_IA'} = \frac{K_{M_IA}}{\alpha_{A(M_{II})}} \qquad (27)$$

and

$$\alpha_{A(M_{II})} = \frac{[A] + [M_{II}A]}{[A]} = 1 + [M_{II}]K_{M_{II}A} \simeq K_{M_{II}A}[M_{II}]. \qquad (28)$$

Substituting the value of $\alpha_{A(M_{II})}$ from (28) in (27) and taking logarithms, we obtain

$$\lg K_{M_IA'} = \Delta \lg K + pM_{II}, \qquad (29)$$

where $\Delta \lg K = \lg K_{M_IA} - \lg K_{M_{II}A}$.

When a masking agent L is introduced into this solution, the metal ions M_I and M_{II} react with L in masking reactions, which, in accordance with the method of conditional constants, can be regarded as side-reactions with respect to the corresponding reactions involving the formation of M_IA and $M_{II}A$. Eqn. (29) then becomes

$$\lg K_{M_IA''} = \Delta \lg K' + pM_{II} \qquad (30)$$

where

$$\Delta \lg K' = \lg K_{M_IA} - \lg K_{M_{II}A}.$$

Thus if M_{II} is not to interfere in the analytical reaction of M_I with A in the presence of L (that is, if M_{II} is to be masked quantitatively), the conditional constant $K_{M'_{II}A}$ should be sufficiently small. For example, in the complexometric titration of M_I, which requires that $\lg K_{M'_IA''} > 7$, M_{II} is masked completely when $K_{M'_{II}A}$ becomes so small that

$$\lg K_{M_IA} - \lg K_{M_{II}A} + pM_{II} > 7.$$

As an example, Fig. 2 gives graphs showing the conditional constants for the reactions of various metals with EDTA in the presence and absence of tren (2,2′,2″-triaminotriethylamine) as masking agent. It can be seen from Fig. 2, for example, that in the titration of Ca with EDTA in the presence of 0.1 M tren at pH 10, Cu and Ni are masked almost completely, Fe is partly masked, and Mn is not masked at all.

Thus the presence of appropriate quantities of suitable masking agents produces the required difference in the conditional constants of the analytical reaction and the reaction being masked, so that the analysis becomes selective; a given masking agent is effective, however, only under definite conditions, in particular at definite pH values. The behaviour of a masking agent under different conditions can be predicted on the basis of a theoretical examination

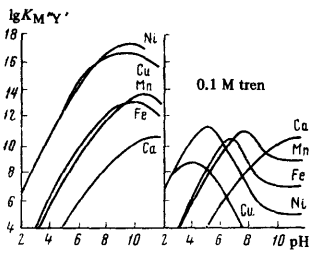


Figure 2. pH dependence of the conditional constants of the complexes of Cu, Ni, Fe, Mn, and Ca with EDTA in the absence and in the presence of an excess of triaminotriethylamine (tren).[5] ($K_{M''Y'} = K_{MY}/\alpha_{M(tren)}\alpha_{Y(H)}$).

of the equilibria established under these conditions. This theoretical approach is greatly facilitated, and the results obtained become extremely clear, if the systems being studied are described by means of diagrams of the type given in Fig. 2 or by means of pA–pH diagrams (pY–pH diagrams for the particular case of complexometry)[7].

V. THE MOST COMMON MASKING AGENTS

A large number of extremely varied inorganic and organic masking agents are now used for the masking of ions and reactions. Table 5 gives common masking agents for the most widely encountered ions of various elements.

Despite the large number and great variety of masking

Table 5. Masking agents for the ions of various elements*.

Element or ion	Masking agent
Ag	CN^-, NH_3, $S_2O_3^{2-}$, SCN^-, TGA, thiourea
Al	F^-, $C_2O_4^{2-}$, CH_3COO^-, OH^-, citrate, tartrate, EDTA, DMP. TEA, Tiron, salicylate, sulphosalicylate, acetylacetonate, malonate, gluconate
As	S_2^{2-}, OH^-, DMP
Au	CN^-, Br^-, $S_2O_3^{2-}$
B	F^-, hydroxy-acids, glycols
Ba	EDTA, citrate, tartrate, NTA, DHEG
Be	F^-, citrate, tartrate, sulphosalicylate
Bi	Citrate, tartrate, EDTA, I^-, Cl^-, NTA, DHEG, thiourea, TEA, DMP, TGA, $Na_5P_3O_{10}$, dithizone
Br	phenols
CN^-	CH_2O, Hg^{2+}, transition metal ions
Ca	EDTA, citrate, tartrate, $P_2O_7^{4-}$, NTA, DHEG
Cd	EDTA, CN^-, $S_2O_3^{2-}$, SCN^-, I^-, citrate, tartrate, NTA, DHEG, DMP, TGA, unithiol, malonate, dithizone
Ce	NTA, EDTA, DHEG, citrate, tartrate, Tiron

Table 5. (con'd).

Element or ion	Masking agent
Cl^-	Hg^{2+}
Co	NH_3, NO_2^-, SCN^-, CN^-, H_2O_2, $S_2O_3^{2-}$, NTA, EDTA, DHEG, citrate, tartrate, ethylenediamine, DMP, tren, penten, F^-, $Na_5P_3O_{10}$, malonate, dimethylglyoxime
Cr	EDTA, NTA, DHEG, citrate, tartrate, TEA, ascorbic acid, CH_3COO^-, F^-, NaOH + H_2O_2, $Na_5P_3O_{10}$, Tiron, sulphosalicylate
Cu	NH_3, I^-, SCN^-, CN^-, $S_2O_3^{2-}$, thiourea, EDTA, NTA, DHEG, S^{2-}, DMP, TGA, citrate, tartrate, TEA, tren, penten, NaH_2PO_2, NO_2^-, cysteine
F^-	H_3BO_3, Al^{3+}, Be^{2+}, Fe^{3+}, Zr^{4+}, Ti^{4+}, Th^{4+}, Nb, Ta
Fe	F^-, PO_4^{3-}, $P_2O_7^{4-}$, NTA, EDTA, DHEG, citrate, tartrate, DMP, SCN^-, $S_2O_3^{2-}$, $C_2O_4^{2-}$, CN^-, Tiron, ascorbic acid, thiourea, 1,10-phenanthroline, TGA, TEA, malonate, gluconate, sulphosalicylate, $NH_2OH.HCl$, 2,2′-bipyridyl
Ge	$C_2O_4^{2-}$, F^-
Hf	F^-, H_2O_2, SO_4^{2-}, DHEG, citrate, tartrate, NTA, EDTA, TEA, $P_2O_7^{4-}$, PO_4^{3-}, $C_2O_4^{2-}$
Hg	I^-, SO_3^{2-}, CN^-, NTA, EDTA, DHEG, DMP, Cl^-, citrate, tartrate, TEA, tren, penten, unithiol, thiosemicarbazide, cysteine, TGA
In	TGA
Ir	SCN^-, citrate, tartrate, thiourea
I	Hg^{2+}
Mg	NTA, DHEG, EDTA, $C_2O_4^{2-}$, citrate, tartrate, $P_2O_7^{4-}$, F^-, glycols, TEA
Mn	F^-, $C_2O_4^{2-}$, $P_2O_7^{4-}$, NTA, EDTA, DHEG, citrate, tartrate, DMP, TEA, CN^-, Tiron, sulphosalicylate, oxidising agents
Mo	SCN^-, $C_2O_4^{2-}$, F^-, H_2O_2, citrate, tartrate, EDTA, NTA, DHEG, Tiron, ascorbic acid, $Na_5P_3O_{10}$, $NH_2OH.HCl$
NH_4^+	CH_2O
Nb	F^-, OH^-, citrate, tartrate, $C_2O_4^{2-}$, H_2O_2, Tiron
Ni	CN^-, SCN^-, NTA, EDTA, DHEG, NH_3, citrate, tartrate, tren, F^-, penten, malonate, sulphosalicylate, $Na_5P_3O_{10}$
NO_2^-	sulphanilic acid
Os	CN^-, SCN^-, thiourea
Pb	I^-, CH_3COO^-, $S_2O_3^{2-}$, citrate, tartrate, NTA, EDTA, DHEG, SO_4^{2-}, unithiol, DMP, TGA, $Na_5P_3O_{10}$
Pd	CN^-, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{2-}$, NTA, EDTA, DHEG, citrate, tartrate, TEA, acetylacetone
Pt	NH_3, I^-, CN^-, NO_2^-, SCN^-, $S_2O_3^{2-}$, NTA, EDTA, DHEG, citrate, tartrate
Rh	thiourea, citrate, tartrate
Ru	thiourea
S	CN^-, S^{2-}, SO_3^{2-}
S^{2-}	S
SO_3^{2-}	Hg^{2+}, CH_2O
Sb	citrate, tartrate, DMP, I^-, S^{2-}, OH^-, F^-, S_2^{2-}, $S_2O_3^{2-}$, EDTA
Sc	tartrate
Se	S^{2-}, SO_3^{2-}, tartrate, citrate, I^-, F^-, reducing agents
Sn	citrate, tartrate, DMP, F^-, I^-, $C_2O_4^{2-}$, OH^-, TEA, TGA, PO_4^{3-}
Sr	NTA, EDTA, DHEG, citrate, tartrate
Ta	F^-, OH^-, citrate, tartrate, H_2O_2
Te	I^-, F^-, tartrate, citrate, S^{2-}, SO_3^{2-}, reducing agents
Th	F^-, NTA, EDTA, DHEG, citrate, tartrate, TEA, CH_3COO^-, SO_4^{2-}
Ti	SO_4^{2-}, OH^-, H_2O_2, F^-, NTA, EDTA, DHEG, citrate, tartrate, Tiron, TEA, gluconate, sulphosalicylate, ascorbic acid, $Na_5P_3O_{10}$
Tl	Cl^-, CN^-, NTA, EDTA, DHEG, citrate, tartrate, TEA, TGA, $NH_2OH.HCl$
U	F^-, CO_3^{2-}, $C_2O_4^{2-}$, H_2O_2, citrate, tartrate
V	CN^-, H_2O_2, F^-, EDTA, tiron, TEA, ascorbic acid, $NH_2OH.HCl$
W	Tiron, F^-, SCN^-, H_2O_2, tartrate, $Na_5P_3O_{10}$, $NH_2OH.HCl$
Zn	CN^-, NTA, EDTA, DHEG, citrate, tartrate, SCN^-, DMP, OH^-, NH_3, glycols, tren, penten, unithiol, TGA, F^-, $Na_5P_3O_{10}$, dithizone
Zr	F^-, SO_4^{2-}, citrate, tartrate, NTA, EDTA, DHEG, H_2O_2, $P_2O_7^{4-}$, PO_4^{3-}, $C_2O_4^{2-}$, TEA

* DMP represents dimercaptopropanol, and TGA thioglycollic acid; see Tables 2 and 3 for the other abbreviations.

agents, they can be grouped into several classes, of which the most important are the aminopolycarboxylic acids, the polyamines, the hydroxy-acids, and the polyphosphates.

The aminopolycarboxylic acids (complexones)[8,9,12-16,19-30] have molecules containing chelating amino- and carboxyl groups, and form stable water-soluble chelate compounds with a large number of metal ions, including the ions of the alkali and alkaline earth metals. They have a number of advantages over other chelating reagents as masking agents: (1) the high efficiency of masking, due to the high stability of the metal-chelates formed by the complexones; (2) the universal nature of the masking, resulting from the ability of the complexones to form comparatively stable chelate compounds with almost all known metals; (3) the wide pH range of masking, related to the high stability of the metal-chelates formed by the complexones and the comparatively low stability of their proton complexes; (4) the possibility of masking at relatively high temperatures, due to the thermal stability of the complexones and their metal-chelates in aqueous solutions; (5) the compatability of the complexones with the other components of usual analytical systems, related to their ability to function in many other capacities (as titrants, pH regulators, photometric reagents, etc.).

The complexone with the most useful properties and widest application is ethylenediaminetetra-acetic acid (EDTA). It reacts with metal ions usually as a sexidentate ligand by coordination through the two nitrogen atoms of the two amino-groups and four oxygen atoms of the four carboxyl groups. The resulting chelates have an octahedral structure with little steric distortion, stabilised by the presence of several five-membered rings and showing a stereochemistry favourable for most common metal ions. In EDTA the common tendency of the carboxyl group to form complexes is strengthened by the chelating effect, resulting in an increase in the stability of the chelate compounds compared with the corresponding complexes formed from the unidentate complexes without ring closure. As a result, EDTA exhibits chelating properties with respect to the ions of almost all metals; this makes it a universal masking agent, but it is not specific.

The selectivity of the masking action of EDTA can be increased slightly, however, by controlling the pH of the solutions. Masking by EDTA is most effective in weakly acidic and alkaline solutions.

Under optimal conditions of acidity, EDTA reacts with most metal ions to form complexes with a cation: ligand molar ratio of 1 : 1. Protonated complexes may be formed in strongly acidic solutions, and mixed hydroxo-complexes may be formed in strongly alkaline solutions. The formation of chelate compounds with molar ratio 1 : 2 is observed only for quadrivalent metals.

Attempts to modify the structure of EDTA in order to improve its coordinating properties have not in general given satisfactory results. Exhaustive data on the results of these studies, which are of undoubted theoretical importance, are given in a review by Dyatlova and Lastovskii[30], so that we shall mention only a few features which are of interest for increasing the efficiency and selectivity of masking. The closure of the alicyclic ring in *trans*-1,2-diaminocyclohexanetetra-acetic acid (DCTA), accompanied by a decrease in the freedom of rotation of the amino-groups in the ligand and the formation of an additional ring in the structure, leads to a marked increase in the stability of the chelate compounds formed with all metals and to a decrease in the rate of chelation; replacement of the cyclohexane ring by cyclopentane or cycloheptane rings gives complexones whose stabilities are respectively greater or less than the stability of DCTA, but greater than the stability of EDTA. Increase in the denticity of the ligand by the introduction of additional iminoacetate groups into the EDTA molecule (diethylenetriaminepenta-acetic, triethylenetetraminehexa-acetic, and tetraethylenepentaminehepta-acetic acids) brings about a selective increase in the stability of the chelate compounds for highly-charged metal ions. Replacement of the hydrogen atoms attached to the carbon atoms of the methylene groups by methyl groups (1,2-diaminopropanetetra-acetic and 2,3-diaminobutanetetra-acetic acids) leads to greater solubility of the complexones and to higher stability in the chelate compounds of various metals. The tetra-acetic acids of amino-ethers (ethyl etherdiaminetetra-acetic and glycol etherdiaminetetra-acetic acids†) combine more readily with the ions of the heavy alkaline earth metals (Ca^{2+}, Sr^{2+}, and Ba^{2+}) than with magnesium ions.

To conclude the list, it can be stated in general that special reconstruction of the complexone molecule by the introduction of hetero-atoms and functional groups, by changing the distance between the iminodiacetate groups or between the nitrogen and the carboxyl group, by replacing the methylcarboxyl groups by hydroxyethyl and methylphosphinic groups, by increasing the rigidity of the entire system, and by breaking down the electron density of individual units, produces chiefly selective reagents, but does not always lead to an increase in the stability of the complexes formed.

Of the known complexones, the most important masking agents are EDTA, DCTA, and nitrilotriacetic acid. These are widely used in qualitative analysis[19-22,25,30], gravimetric analysis[4,5,8,9,12,13,15,19,20,22,26-29], complexometric titration[4-9,12-15,19,20,22-30], photometry[4,5,8,9,15,19,20,22,27-30], polarography[8,9,12,15,19,20,22,27-30], ion-exchange chromatography[12,15,19,20,22,27-30], and a number of other analytical procedures.

Polyamines[12-14], like aminopolycarboxylic acids, contain several donor nitrogen atoms and are multidentate ligands. Thus complex formation with these compounds also involves simple stoichiometry (the chelate compounds formed with metal ions usually have cation: ligand molar ratio equal to 1 : 1) and a chelating effect (leading to the production of chelate compounds with five- or six-membered rings, which are more stable than the complexes with simple ammonia molecules).

The selectivity of polyamines in complex formation with metal ions is greater than that of the complexones, since the strength of the ligand field for amine ligands is greater than that for carboxylic acid ligands. With metal ions which react more readily with donor nitrogen than with oxygen (Cu, Ni, Co, Zn, Cd, and Hg), they form water-soluble chelate compounds with stability constants which differ fairly sharply (Table 6), whereas they undergo almost no reaction with alkaline earth metal ions.

The data in Table 6 first of all illustrate the chelating effect, that is, the effect of combining the donor groups into a single common molecule. For example, comparison of $\lg\beta_1$(Cu-En) (10.55) with $\lg\beta_2$ (Cu-2NH_3) (7.61) shows that the formation of one five-membered chelate ring in the ethylenediamine complex of copper increases the stability of the latter by a factor of ~ 1000 relative to the stability of the copper ammine formed by the coordination of

† Possibly 2,2′-oxybis(ethyliminodiacetic acid) and ethylenedioxybis-(methyliminodiacetic acid) are intended (Ed. of Translation).

Table 6. Stability constants of complexes of metals with amines (temperature 20°C, ionic strength $I = 0.1$).

Ion	NH_3				en			dien		trien	tetren	penten	tren	EDTA
	$lg\beta_1$	$lg\beta_2$	$lg\beta_3$	$lg\beta_4$	$lg\beta_1$	$lg\beta_2$	$lg\beta_3$	$lg\beta_1$	$lg\beta_2$	$lg\beta_1$	$lg\beta_2$	$lg\beta_1$	$lg\beta$	$lg\beta_1$
Ag^+	3.40	7.40	—	—	4.7	4.7	—	6.01	—	7.7	—	—	7.8	7.3
Cd^{2+}	2.60	4.65	6.04	6.92	5.47	10.02	12.09	8.45	13.85	10.75	14.0	16.8	12.3	16.5
Co^{2+}	2.05	3.62	4.61	5.31	5.89	10.72	13.82	8.1	14.1	11.0	15.1	15.75	12.8	16.3
Cu^{2+}	4.13	7.61	10.48	12.59	10.55	19.60	—	16.0	21.3	20.4	24.3	22.44	18.8	18.8
Fe^{2+}	1.4	2.2	—	3.7	4.28	7.53	9.52	6.23	10.36	7.8	11.4	11.20	8.8	14.3
Hg^{2+}	8.80	17.50	18.5	19.4	—	23.42	—	21.8	25.06	25.26	27.7	29.59	22.8	21.8
Mn^{2+}	0.8	1.3	—	—	2.73	4.79	5.67	3.99	6.82	4.9	7.62	9.37	5.8	14.0
Ni^{2+}	2.75	4.95	6.64	7.79	7.66	14.06	18.59	10.7	18.9	14.0	17.6	19.30	14.8	18.6
Zn^{2+}	2.27	4.61	7.01	9.06	5.71	10.37	12.08	8.9	14.5	12.1	15.4	16.24	14.65	16 5

two unidentate NH_3 ligands to Cu^{2+}. Table 6 also shows that the increase in the number of chelating rings in the 1 : 1 complexes for a given metal on going from ethylenediamine to penten (that is, with increase in the multidenticity of the ligand) leads to a progressive increase in the stability constants of the chelate compounds and to a gradual decrease in the tendency for the metal ion to combine with a second molecule of the ligand.

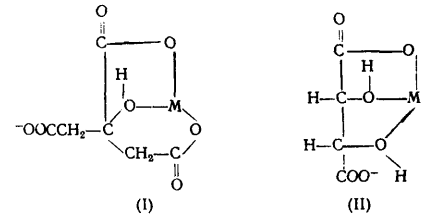
Of the above polyamines, tren, trien, tetren, and penten are most widely used as masking agents. A disadvantage of the polyamines as masking agents is their extreme sensitivity to inorganic acids, resulting from their ability to combine with several protons. Moreover, commercial polyamine specimens are always contaminated with lower amines and are difficult to purify, and this hinders their study and practical application.

Hydroxy-acids[12,13,31] have molecules containing chelating hydroxyl and carboxyl groups and act as multidentate ligands which are much weaker than the nitrogen-containing multidentate ligands (aminopolycarboxylic acids and polyamines). Moreover, they have a greater tendency, compared with the polyamines, to react with metal ions by a stepwise mechanism with the formation of chelate compounds with cation : ligand molar ratios of 1 : 1, 1 : 2, etc.; mixed complexes and polynuclear complexes may also be formed.

Table 7. The stability constants of the tartrato- and citrato-complexes of various metals in acid medium (1 : 1 type) (temperature 20°C, ionic strength $I = 0.5$).

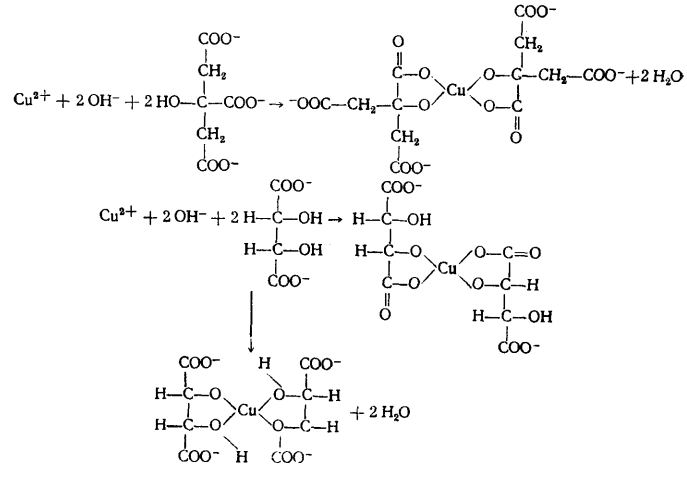
Ligand	lgβ								
	Ba	Ca	Cd	Co	Cu	Mg	Pb	Sr	Zn
Tartrate $(CHOHCOO)_2^{2-}$	1.5	1.7	2.8	2.1	3.2	1.2	3.8	1.4	2,4
Citrate $C_4H_4OH\ (COO)_3^{2-}$	2.4	3.5	4.0	4.4	6.1	2.8	5.2	2.8	4,5

The properties and stabilities of the chelate compounds formed depend on the number and mutual arrangement of the carboxyl and hydroxyl groups in the hydroxy-acid molecule, and also on the ability of these groups to give up hydrogen ions; this in turn is related to the pH of the solution. Comparison of the stabilities of the citrato- and tartrato-chelates of various metals formed in acid medium (Table 7) shows that the citrato-chelates are more stable than the tartrato-compounds. This is due to the fact that the coordination of the citrate ion to the metal ion leads to the formation of two stable rings including two strongly bonding carboxyl groups and one hydroxyl group (I), whereas the coordination of the tartrate ion is accompanied by the formation of two rings containing two weakly bonding hydroxyl groups and one carboxyl group (II); moreoever, the stabilities of these chelate compounds are also influenced by the magnitude of the charge on the ion (−3 for citrate and −2 for tartrate).



(I) (II)

Because of the comparatively low stability of their chelate compounds, the hydroxy-acids have a low efficiency as masking agents in acid medium, particularly for alkaline earth metal ions. Their masking power increases considerably, however, in alkaline medium (at pH > 10), in which they react with metal ions to form extremely stable chelate compounds, probably with the participation of alkoxy-groups:



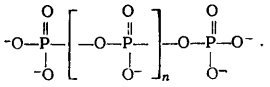
The formation of chelate compounds containing alkoxy-bonds may take place not only in strongly alkaline solutions, in which optimal conditions are created for the formation of alkoxide ions, but also in acidic solutions, if the

metal ion has a sufficiently high polarising power. For example, the Fe^{3+} ion brings about "induced dissociation" of the hydroxyl proton of the hydroxy-acid and forms stable chelate compounds with hydroxy-acids even in acidic solutions.

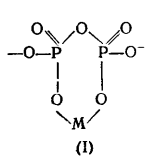
The participation of alkoxide groups in chelate formation probably explains the fact that in alkaline solutions the tartrato-complexes are more stable than the citrato-complexes. It is also of interest to relate the increased stability of the complexes formed by hydroxy-acids in alkaline solutions with the possibility of formation, under these conditions, of mixed dinuclear complexes containing both hydroxide ions and hydroxy-acid anions as ligands[27].

The hydroxy-acids most frequently used as masking agents are tartaric and citric acids, mentioned above, and also malonic, gluconic, and salicylic acids. Tartaric and citric acids are in most instances interchangeable, but there are instances in which the use of one or the other is to be preferred, apparently due to differences in the stabilities of their chelate compounds at different pH values.

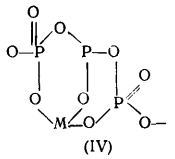
Polyphosphates[12,33], which are used as masking agents, are inorganic linear polymers whose chain structure contains four oxygen atoms arranged tetrahedrally around each phosphorus atom



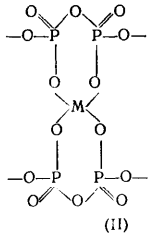
They react with many metal ions, particularly the alkaline earth metal ions, to form water-soluble polymeric complexes with a six-membered chelate structure, in which the metal ion is joined to two or more negatively charged oxygen atoms attached to neighbouring phosphorus atoms (I–III):



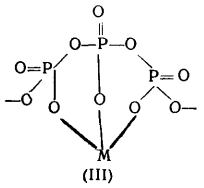
(I)



(IV)



(II)



(III)

Because of the complexity of the structures of the polyphosphates, it is difficult to characterise quantitatively their reactions with metal ions. The published formation constants for the chelates of various polyphosphates (Table 8) indicate, however, that the stabilities of their chelates increase with increase in the length of the polyphosphate chain (that is, with increase in the multidenticity of the ligands).

A serious disadvantage of the polyphosphates as masking agents is their tendency to undergo hydrolysis with the formation of orthophosphate ion, which is able in turn to precipitate the ions of many metals. The rate of hydrolysis depends on many factors (pH, temperature, degree of dehydration of the polyphosphate, etc.), including the length of the polyphosphate chain (the degree of hydrolysis increases rapidly with increase in chain length). The hydrolysis of polyphosphates is catalysed by hydrogen ions, and also by the ions of various metals, the catalytic effect of the latter being directly proportional to their Lewis acid strength ($Cu^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+}$).

Table 8. Formation constants of chelates for various polyphosphates (temperature 20°C, ionic strength $I = 0.1$).[12]

Polyphosphate	Chain length n	lgβ		
		BaL	CaL	MgL
Sodium pyrophosphate $Na_4P_2O_7$	2	4.5	–	–
Sodium tripolyphosphate $Na_5P_3O_{10}$	3	4.5	–	–
Sodium tetrapolyphosphate $Na_6P_4O_{13}$	4	5.5	–	–
Vitreous sodium polyphosphate	7.5	6.0	–	–
Vitreous sodium polyphosphate	8.5	6.5	–	–
Adenosine monophosphate	0	–	1.41	1.69
Adenosine diphosphate	1	–	2.78	3.11
Adenosine triphosphate	2	–	3.60	4.00

The masking action of polyphosphates with respect to alkaline earth metal ions is widely used in technology for water softening. Organic polyphosphates are of considerable interest in biology; in particular, adenosine triphosphate apparently acts as a universal accumulator and distributor of the chemical energy of nutrients and as the chief energy donor in all fundamental reactions of biosynthesis in the organism, and also in such important physiological processes as muscle contraction and higher nervous activity.

In analysis, the polyphosphates most widely used for masking are sodium pyrophosphate $Na_4P_2O_7$, sodium triphosphate $Na_5P_3O_{10}$, and sodium hexaphosphate $Na_6P_6O_{18}$. Sodium triphosphate in neutral and alkaline media forms water-soluble complexes with the ions of a large number of metals, including Li, Be, Mg, Ca, Sr, Ba, Zn, Cd, Fe^{II}, Fe^{III}, Co, Ni, Mn, Cu, Pb, V, Al, Y, In, La, Ce^{III}, Pr, Nd, Ag, Hg^{I}, Ti, Zr, Bi, Sn^{II}, Sn^{IV}, Th, and U^{VI}.

The following compounds are not precipitated in the presence of $Na_5P_3O_{10}$: the hydroxides, phosphates, carbonates, and borates of all the above elements; calcium fluoride, oxalate, tartrate, and citrate; and lead fluoride, chromate, and sulphate; similarly, iron(III) sulphosalicylate and sulphide are not formed. $Na_5P_3O_{10}$ does not prevent the precipitation of zinc, mercury, lead, and copper sulphides, however.

Of the other known masking agents, extensive use in chemical analysis is made of cyanide, fluoride, and triethanolamine[13]. Cyanide is a very effective masking agent for the elements of Groups IB, IIB, and VIII of the Periodic Table, since extremely stable soluble complexes are formed; cyanide is used chiefly in alkaline or neutral solutions—its use in acid solutions is undesirable because of the formation of toxic hydrogen cyanide. Fluoride forms stable soluble complexes with Be, Al, Fe, Si, Ge, B, Sm, Sb, Ti, Zr, Hf, the rare-earth elements, etc., and is often used to mask these elements. Triethanolamine (2,2,2-nitrilotriethanol) is an effective masking agent for Al, Fe, Mn, and various other highly-charged ions; it prevents the hydrolysis of tervalent and quadrivalent metals at high pH.

VI. CHARACTERISTIC EXAMPLES OF THE PRACTICAL APPLICATION OF MASKING

Any type of chemical reaction—precipitation, oxidation–reduction, complex formation, etc.—can be subjected to masking under various circumstances. Thus masking may be used in all chemical and physicochemical methods of analysis in which a chemical reaction takes part in any form. It can confidently be stated that most papers now published on chemical analysis deal to some extent with the masking of reactions and ions; in a number of instances masking is an essential step in the analytical methods or procedures recommended or described in these papers. It is therefore understandable that a short review cannot give exhaustive data on the practical application of the masking of reactions and ions in chemical analysis. In the present review, therefore, we shall merely refer to published reviews on the use of masking in qualitative analysis [2,3,20-22,25], gravimetric analysis [3,8,9,12,13,20,22,26], complexometric titration [14,20,22,23,27,28], photometry [3,8,9,20,22], polarography [8,9,12,15], and ion-exchange chromatography [12,15,20], and examine some characteristic examples of application of masking.

In most instances the masking of the reaction of a given ion is required when it is necessary to eliminate the interfering influence of this ion when carrying out the analogous reaction of another ion with the same reagent. In equilibrium masking this is achieved by decreasing the concentration of the interfering ion or reagent, and in most instances the mechanism of masking is based on the formation of soluble complexes of the interfering ion or reagent with the masking agent. The necessary decrease in the concentration of the interfering ion naturally depends on the method of analysis employed; in spectrophotometry, for example, the concentration of the interfering ion should be very low, whereas in complexometric titration the conditions of masking are much less severe.

The masked form of the interfering ion must often satisfy additional special requirements in addition to the main requirement of stability, ensuring the necessary decrease in the concentration of the interfering ion. The nature of these additional requirements depends on the analytical method: in gravimetric analysis the masked form should not be coprecipitated with the analytical form, in spectrophotometry the masked and analytical forms should absorb light in different ranges of the spectrum, in redox titrations they should have different redox potentials, in ion exchange they should have different affinities for the ion exchanger, etc.

The satisfactory fulfillment of the main and additional requirements by the masked forms of various ions creates the prerequisite for another widely encountered example of the use of masking, namely for the determination of these ions when present together, or for their separation. The efficiency of the simultaneous determination and separation of ions using masking is particularly high when the abilities of these ions to be masked by given masking agents and to take part in analytical reactions with a given reagent change in the opposite sense.

A large number of examples of the use of masking to eliminate the interfering influence of accompanying ions, to determine various ions when present together, and to separate these ions, that is, examples of the use of masking to increase the selectivity of analysis, are given in the reviews cited above; we shall give only two examples as illustration: (1) the increase in the selectivity of the polarographic analysis of the ions of various metals in the presence of DCTA (Table 9) [34], and (2) the increase in the selectivity of the colour reaction of rare-earth metal ions with Methylthymol Blue in the presence of EDTA (Table 10) [35].

The masking of reactions is often used for the direct detection and determination of ions. In addition to the familiar use of the masking of the formation of the zirconium–Alizarin lake in the presence of F^- for the detection and photometric determination of F^-, mention may also be made of the photometric determination of Te from the decrease in the light absorption of a solution of molybdosilicic acid as a result of the partial masking of the formation of the molybdosilicate in the presence of Te^{4+}. [36]

Table 9. Values of $E_{1/2}$ for metal ions in the presence and absence of 1,2-diaminocyclohexanetetra-acetic acid (DCTA).

Metal ion	pH 2.7, 0.4 M CH_3COOH		pH 4.6, 0.4 M CH_3COOH + 0.4 M CH_3COONa		pH 9.5, 0.1 M NH_4OH + 0.1 M NH_4Cl	
	$E_{1/2}$(M)	$E_{1/2}$(M-DCTA)	$E_{1/2}$(M)	$E_{1/2}$(M-DCTA)	$E_{1/2}$(M)	$E_{1/2}$(M-DCTA)
Cu^{2+}	+0.02	−0.16	−0.02	−0.40	−0.29	−0.62
Pb^{2+}	−0.38	−0.85	−0.43	i.a.	—	i.a.
Cd^{2+}	−0.60	−1.04	−0.61	i.a.	—	i.a.
Zn^{2+}	−1.01	i.a.*	−1.03	i.a.	−1.14	i.a.
Bi^{3+}	0.00	−0.47	−0.14	−0.66	—	−0.70
Fe^{3+}	—	−0.11	—	−0.11	—	−0.11
Sn^{2+}	−0.02	−0.14	−0.17	−0.17	—	—
Tl^{1+}	−0.42	−0.42	−0.42	−0.42	0.42	−0.16

* i.a. indicates chelate polarographically inactive.

Table 10. Colours of complexes formed by r.e.e.-EDTA with Methylthymol Blue.

Element	$lg\beta$	4 M NH_3 solution
Y	18.09	pale blue
La	15.50	intense blue
Ce	15.98	ditto
Pr	16.40	»
Nd	16.61	»
Sm	17.14	»
Eu	17.35	»
Gd	17.37	pale blue
Tb	17.93	ditto
Dy	18.30	»
Ho	18.74	none
Er	18.85	»
Tu	19.32	»
Yb	19.51	»
Lu	19.83	pale pink

Mention may also be made of the mechanism of the masking action of masking agents, in particular F^-. The decolorisation of the zirconium–Alizarin lake in the presence of F^- is usually attributed to the formation of colourless ZrF_6^{2-}, and an analogous explanation was previously put forward for all other examples of the determination of F^- based on the decolorisation of the coloured chelate compounds formed by metals with various dyes. It was found, however, that in a number of instances, for example in the photometric determination of F^- from the decrease in the light absorption of a Zr–Xylenol Orange mixture, the decrease in the light absorption is due to the formation of a colourless Zr–F–Xylenol Orange ternary complex [37], that is, the determination of F^- in this instance cannot be regarded as indirect. These examples deserve careful attention in the theoretical examination of the masking of reactions.

In some instances the masking of reactions provides a very convenient and simple method for establishing the stoichiometric composition and determining the stability constants of complexes in aqueous solutions. Thus the decrease in the light absorption of a solution of molybdosilicic acid as a result of the partial masking of the formation of molybdosilicate in the presence of various complexing agents (oxalate, tartrate, or tellurite) can be used to determine the compositions and stabilities of the complexes formed by molybdenum with these complexing agents [38].

The possibilities provided by the use of the masking of reactions and ions for various purposes are not exhausted by the above examples—the number of examples could be greatly extended. In conclusion, mention must be made of another promising application of masking—for the production of an "ideal" blank specimen. The usual method of preparing a blank specimen suffers from one major disadvantage: because of the need to exclude some component of the analytical reaction from the blank specimen, the chemical composition of the latter is not completely identical with that of the specimen being analysed. Masking makes it possible to eliminate this disadvantage in the preparation of a blank specimen. If an additional reagent (the masking agent) is introduced into a blank specimen containing the substance being analysed and all the necessary reagents in the same quantities as in the specimen being analysed, the analytical reaction is frozen (masked) from the beginning; the additional reagent is added to the specimen being analysed only after the analytical reaction is complete. Thus the blank specimen finally has a chemical composition which is completely identical with that of the specimen being analysed, and differs only in the absence of the analytical effect being measured, that is, it is an ideal blank specimen. The value of this new method of preparing a blank specimen has been illustrated, for example, in the photometric determination of silicon [39] and phosphorus [40] as their molybdenum heteropolycomplexes.

---o0o---

The two types of masking examined at the start of the present paper, namely: (1) equilibrium masking due to a change in the thermodynamic conditions of the reaction being masked, and (2) non-equilibrium masking due to a change in the kinetic conditions of the reaction being masked, cover all examples of the masking of reactions known in practice. The opposite is also true, namely, that almost all chemical reactions can be masked by appropriate means: if a given reaction cannot be masked by influencing its thermodynamic conditions, it can be masked through kinetics and catalysis.

These two forms of masking—equilibrium and non-equilibrium—naturally require different approaches to their theoretical examination. The material given above deals chiefly with the problems of equilibrium masking. This is due to the fact that the techniques of equilibrium masking have been used to a much greater extent up to the present, and the associated problems have undergone corresponding development. Even the few observations and examples which have been published, however, indicate the promising possibilities provided by the use of non-equilibrium (kinetic) masking in addition to equilibrium (thermodynamic) masking.

Non-equilibrium masking is a useful supplement to equilibrium masking, since it is applicable to those systems for which equilibrium masking is unsuitable. An important feature of non-equilibrium masking is the possibility of controlling it by means of the temperature factor.

The kinetics of analytical reactions with particular reference to masking have not been specially studied. It is therefore not yet possible to reach any general conclusions. Recently, however, the importance of a detailed study of the kinetics of analytical reactions, particularly reactions involving complex formation, has been pointed out by a number of authors [5,30,41], particularly Reilley [42], who in addition to other problems discusses the kinetics of the formation and dissociation of metal complexonates, and considers that these problems are the most important at the present stage of the study of complexonates.

REFERENCES

1. K.C.Bailey, "Retardation of Chemical Reactions" (Translated into Russian), Goskhimizdat, Moscow–Leningrad, 1940.
2. F.Feigl, "Qualitative Analyse mit Hilfe von Tupfelreaktionen" (Translated into Russian), Goskhimizdat, Moscow, 1937, p.56.
3. F.Feigl, "Chemistry of Specific, Selective and Sensitive Reactions", Academic Press, New York, 1949, p.67.
4. A.Ringbom, in "Treatise on Analytical Chemistry" (Edited by I.M.Kolthoff, P.J.Elving, and E.B.Sandell), Interscience, New York, 1959, Part I, Vol.1, p.616.
5. A.Ringbom, "Complexation in Analytical Chemistry", Interscience, New York, London, 1963, p.61.
6. A.Ringbom, Pure Appl.Chem., **7**, 473 (1963).
7. C.N.Reilley and R.W.Schmid, Analyt.Chem., **31**, 887 (1959).
8. S.Suzuki, Saishin no Bunseki Kagaku, No.9, 41 (1958).
9. S.Suzuki, Proc.Sci.Inst.Kinki Univ., No.1, 21 (1959).
10. M.Tanaka, Analyt.Chim.Acta, **29**, 193 (1963).
11. M.Tanaka, Japan Analyst, **12**, 773 (1963).
12. S.C.Chaberek and A.E.Martell, "Organic Sequestering Agents: A Discussion of the Chemical Behaviour and Application of Metal Chelate Compounds in Aqueous Systems" Wiley, New York, 1959.
13. K.L.Cheng, Analyt.Chem., **33**, 783 (1961).
14. G.Schwarzenbach, "Die komplexometrische Titration" (Translated into Russian), Goskhimizdat, Moscow, 1958, p.5.
15. K.B.Yatsimirskii, Zavod.Lab., **21**, 1149, 1275 (1955).
16. K.B.Yatsimirskii, Zhur.Anal.Khim., **10**, 94 (1955).
17. K.B.Yatsimirskii, Zhur.Neorg.Khim., **1**, 412 (1956).
18. A.Hulanicki, Talanta, **9**, 549 (1962).
19. F.J.Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid", Van Nostrand Co., Princeton, 1958.
20. R.Přibil, "Komplexometrie" (Translated into Russian), Inostr.Lit., Moscow, 1960.
21. R.Přibil, Chem.Listy, **45**, 57 (1951).
22. H.A.Flaschka, Angew.Chem., **69**, 707 (1957).
23. H.A.Flaschka and A.J.Barnard, in "Comprehensive Analytical Chemistry" (Edited by C.L.Wilson and D.W.Wilson), Elsevier, Amsterdam, 1960, Vol.1B, p.288.
24. T.S.West, Analyt.Chim.Acta, **25**, 301 (1961).
25. W.Hoyle, J.P.Sanderson, and T.S.West, Analyt.Chim. Acta, **26**, 290 (1962).
26. R.Přibil, Experientia, **20**, 65 (1964).
27. P.J.Hol, Chem.Tech.(Amsterdam), **18**, 556 (1963).
28. P.J.Hol, Chem.Tech.(Amsterdam), **20**, 549 (1965).
29. R.P.Lastovskii, N.M.Dyatlova, I.D.Kolpakova, and V.Ya.Temkina, Zhur.Vses.Khim.Obshch. im.Mendeleeva, **9**, 138 (1964).
30. N.M.Dyatlova and R.P.Lastovskii, Uspekhi Khim., 34, 1153 (1965) [Russ.Chem.Rev., 481 (1965)].

31. I.V.Pyatnitskii, Uspekhi Khim., **32**, 93 (1963) [Russ.Chem. Rev., 44 (1963)].
32. K.L.Malyarov and F.P.Sudakov, Zhur.Neorg.Khim., **6**, 1559 (1961) [Russ.J.Inorg.Chem., 800 (1961)].
33. J.R. van Wazer, "Phosphorus and Its Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1962, p.462.
34. K.Přibil and Z.Zabransky, Coll.Czech.Chem.Comm., **16**, 554 (1951).
35. R.Přibil and V.Vesely, Chemist-Analyst, **54**, 100 (1965).
36. Ku Than Long, F.P.Sudakov, and E.F.Shakhova, Zhur. Anal.Khim., **19**, 734 (1964).
37. R.Valach, Talanta, **11**, 973 (1964).
38. Z.F.Shakhova, Ku Than Long, and F.P.Sudakov, Vestnik Moskov.Gos.Univ., Khimiya, No.2, 69 (1966).
39. G.E.Shaffer and G.W.Scheider, U.S.P. 3 015 544. Chem. Abs., 56, 6676 (1962).
40. F.P.Sudakov, V.I.Klitina, and N.T.Maslova, Zhur.Anal. Khim., **21**, 1089 (1966).
41. F.Basolo and R.G.Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1958.
42. C.N.Reilley, Analyt.Chem., **37**, 1298 (1965).

Analytical Chemistry Department
Chemistry Faculty, Moscow State University

U. D. C. 543.422.4 : 547.921

Infrared Spectra of Steroids

Yu.N.Levchuk

CONTENTS

I. Features of the chemical structure of steroids 155
II. Correlation of the infrared spectra of steroids with their structure 156
III. Use of infrared spectroscopy in steroid chemistry 164
1. Sterols 164
2. Unsaturated steroids 165
3. Steroidal ketones 165
4. Epoxysteroids and lactones 165
5. Methyl- and methylene-steroids. Steroidal acetates 165
6. Halogenosteroids 166
7. Nitrogen-containing steroids 166
8. Conversions of steroids 166
9. Some particular structural problems 166

Valuable information about chemical structure obtained in the study of infrared spectra of individual compounds produces a natural increase in the interest of chemists in molecular spectroscopy.

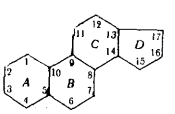
In the Russian literature there are hardly any papers dealing with the infrared spectra of steroids. Furthermore there is not one review on the infrared spectra of the steroids.

This review considers work on the infrared spectra of the steroids during the period from its inception (1939) to 1966.

I. FEATURES OF THE CHEMICAL STRUCTURE OF THE STEROIDS

The main features of the chemical structure of the steroids have now been explained quite definitely. The general principles are reliable, although there are still a greater number of compounds of the steroid series details of whose structure are either unknown or require proof.

The structure of the steroids is based on a complex polycyclic system consisting of three cyclohexane rings and one cyclopentane ring. Such a system is 10,13-dimethylcyclopentanoperhydrophenanthrene, with the accepted numbering of the atoms of the carbon skeleton (I):



(I)

The rings are denoted by the letters A, B, C, and D in accordance with the increasing numbering of the carbon atoms.

There are six asymmetric carbon atoms, so theoretically such a compound can have $2^6 = 64$ stereoisomers but only some of the steroisomeric forms are encountered in natural compounds. From this it follows that the steroid molecules have rigidly fixed spatial conformations, unlike the mobile conformations of cyclohexane.

Sometimes the ring of the steroidal skeleton (ergosterol, 7-dehydrocholesterol, ring B; oestrogen, ring A) contains a C=C double bond. This fixes still more rigidly a definite conformation of the molecule. Despite the non-planar structure of the cyclohexane rings, their combination in a