MASKING AND PROMOTION OF REACTIONS IN QUANTITATIVE ANALYSIS

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The problems of the analyst have changed their character to a large extent in recent times. The demands on increased speed, accuracy, selectivity and sensitivity have made many of the old "classic" methods almost worthless. New methods are being developed continuously, and today there is such an abundance of methods that a choice between them may be a real problem. On the other hand, since new analytical problems constantly arise, there is also, in spite of the many existing methods, a great demand for new or improved methods of analysis.

As a rule, the analysis of a solution containing a single solute offers little difficulty. The problems arise when interfering species are present. Then the analyst cannot avoid asking how selective is the reaction, how sensitive is the method, and how small is the error. The answers depend on the chosen experimental conditions, and the modern analyst, for a successful solution of his problems, must master the relevant theories.

In order to simplify my presentation, I shall start with an example, the complexometric titration of a metal. Every analyst knows that modern chelating agents have led to a revolution in quantitative inorganic analysis during the last two decades. But he also knows the weakness of complexometric methods, their lack of specificity. Moreover, interfering side reactions are induced by buffer agents present, by hydrogen ions and by hydroxide ions.

A partly new approach that takes all interfering side reactions into consideration will be outlined below. However, the standard treatment of complexometric titrations will first be summarized. We denote a metal ion by M, plot $pM = - \log [M]$ as a function of the added volume of reagent and obtain a curve like that shown in *Figure 1*. Here a 10^{-3} M calcium salt solution is titrated with EDTA (ethylenediaminetetraacetate) at pH 11. pCa at the equivalence point can be calculated from equation (1).

$$pM_{eq} = \tfrac{1}{2}(\log K_{ML} - \log C_M) \qquad (1)$$

in which K_{ML} is the stability constant of the formed complex and C_M is the total concentration of metal in the solution. Hence

$$pCa_{eq} = \tfrac{1}{2}(10\cdot7 + 3) \approx 6\cdot8 \qquad (2)$$

The transition points of some indicators are inserted in the figure. The attainable accuracy depends on the distance between $pM_{end point}$ and pM_{eq}, and the percentage error can be simply read from the diagram of *Figure 2*,

in which the product of the stability constant and the total metal concentration is the abscissa and the percentage error the ordinate. The difference between pM_{end} and pM_{eq}, denoted by ΔpM, can easily be estimated.

If we titrate calcium with Eriochrome Black T, Calmagite or Murexide as indicator to the mixed colour, ΔpCa approximately equals -2 pCa units and the corresponding error is between -1 and -2 per cent as can be seen
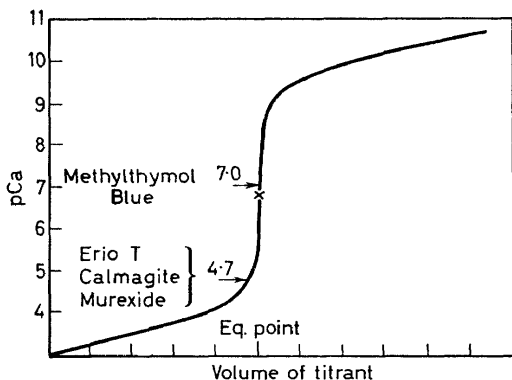

Figure 1. Titration of calcium in 10^{-3} M solution with EDTA
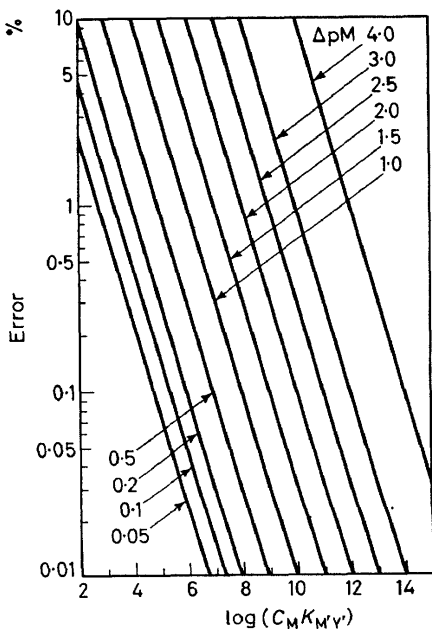

Figure 2. Titration error as a function of the total metal concentration and the conditional constant for different values of $\Delta pM = pM'_{end} - pM'_{eq}$

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from the diagram; if we titrate to full colour change, ΔpCa is approximately -1 unit and the error is -0.1 to -0.2 per cent; if we titrate with Methyl-thymol Blue, ΔpCa is about 0.2 pCa unit, and even if we assume the precision in detecting the end point to be ± 0.5, the error will be less than ± 0.1 per cent.
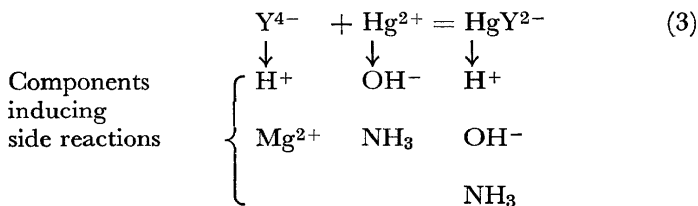
From this diagram the analyst can thus estimate the accuracy of a titration almost without any calculations. Only the values of three quantities are needed: the total concentration of the metal in the titrated solution, the stability constant of the formed complex, and the estimated value of ΔpM.

This standard treatment is simple and rapid, but some authorities may object because usually several side reactions strongly interfere in practice, and their neglect will lead to erroneous results. Actually, if somebody were to ask me why I have taken this particular titration of calcium at pH 11 as an example, I must confess that my honest answer would be that this is almost the only EDTA titration I know of where the simple theory agrees with experiment. In all other cases there will be some kind of interference. With the exception of the alkaline earth metals, most metals form hydroxo complexes that greatly influence the final equilibrium; at pH values below 11 the quadrivalent EDTA anions take up hydrogen ions and form acid species $(HY^{3-}, H_2Y^{2-}, H_3Y^-, H_4Y$, if the free acid is denoted by $H_4Y)$; also buffer agents may induce side reactions, and most foreign metals present will strongly interfere. Finally, acid, basic or mixed metal–EDTA complexes may also be formed.

As there is no point in presenting a theoretical treatment that can be applied to only one exceptional case, I shall take a complementary example where several interfering side reactions proceed concurrently. My intention is to show that in such a case also it is possible to estimate the attainable accuracy without involved calculations.

Let us assume that an analyst wants to titrate with EDTA a dilute solution of a mercury salt containing an ammonium–ammonia buffer mixture. Moreover, let us assume that a second metal, magnesium, for instance, is present in the solution.

The main reaction occurs according to the scheme given in equation (3) where possible side reactions are also indicated.

$$Y^{4-} \; + \; Hg^{2+} \; = \; HgY^{2-} \qquad (3)$$

Components inducing side reactions	$\downarrow$ H^+	$\downarrow$ OH^-	$\downarrow$ H^+
	Mg^{2+}	NH_3	OH^-
			NH_3

The Y^{4-} ions may react with hydrogen ions to give possibly four acid species, or with magnesium ions; the mercury ions may react with hydroxide ions or with ammonia forming 4 species; finally, the complex HgY^{2-} may react with hydrogen or hydroxide ions, depending on the pH, or with ammonia to form mixed complexes. Actually, about a dozen products may be formed by these side reactions.

Consequently, there would be no sense at all in proceeding as in the first example, *i.e.* employing the stability constant of the mercury–EDTA complex, equal to about 10^{22}, when estimating the error from the error diagram of *Figure 2*. The side reactions cannot be neglected.

Schwarzenbach[3] has proposed a simple way of taking into account the side reactions between Y ions and hydrogen ions. Instead of [Y] he computes a primed concentration [Y'] which is equal to the sum of the concentrations of the anion Y and all the protonated species, *i.e.*

$$[Y'] = [Y] + [HY] + [H_2Y] + [H_3Y] + [H_4Y] \qquad (4)$$

(Charges of the ions are omitted here and in the following). The relationship between [Y] and [Y'] is expressed by $\alpha_Y = [Y']/[Y]$. The coefficient α_Y is called the side reaction coefficient. Its value can be calculated from equation (5)

$$\alpha_Y = \frac{[Y']}{[Y]} = 1 + [H]\beta_1 + [H]^2\beta_2 + [H]^3\beta_3 + [H]^4\beta_4 \qquad (5)$$

where the β values are the over-all stability constants of the acid ions.

Schwarzenbach took into account also the side reactions between metal ions and ammonia molecules in an analogous way, *i.e.*, by introducing a primed concentration equal to the sum of the concentrations of the free metal ion and all its ammine complexes. Hence, in the case of mercury, [Hg'] equals

$$[Hg'] = [Hg] + [HgNH_3] + [Hg(NH_3)_2] + \\ [Hg(NH_3)_2] + [Hg(NH_3)_4] \qquad (6)$$

$\alpha_{Hg} = [Hg']/[Hg]$ can be calculated from the stability constants of the mercury ammine complexes according to

$$\alpha_{Hg} = \frac{[Hg']}{[Hg]} = 1 + [Hg]\beta_1 + [Hg]^2\beta_2 + [Hg]^3\beta_3 + [Hg]^4\beta_4 \qquad (7)$$

The equilibrium constant expressing the relationship between such primed concentrations is denoted by $K_{Hg'Y'}$. The primes of the subscripts indicate that the side reactions of mercury as well as those of the Y ions have been taken into account. The relationship between this "constant" which Schwarzenbach named "apparent" and the commonly used constant K_{HgY} is given by

$$K_{Hg'Y'} = \frac{K_{HgY}}{\alpha_{Hg}\alpha_Y} \qquad (8)$$

It may now be asked what is the point of introducing an "apparent constant". The point is above all that the simple form of the equilibrium equation can be maintained. This apparent constant can be handled in quite the same way as an ordinary equilibrium constant. It is possible to draw titration curves, to calculate pM' at the equivalence point and to compute titration errors—for instance, using the diagram of *Figure 2*—without knowing the exact nature of all species contributing to [M'] and [Y']. A collection of tabulated values of required α coefficients facilitates the calculation of apparent constants.

In this way Schwarzenbach took into consideration two types of interfering side reactions, but in the example under discussion also side reactions of other types occurred. The question arises: *Can we not take into account every interfering reaction by inserting a corresponding α coefficient?* My opinion is that this is the only rational way of treating complex equilibria in analytical chemistry and my aim in this paper is to prove the simplicity of this approach by means of appropriate examples.

The rule is briefly that the influence of all side reactions interfering in a reaction between a metal ion M and a complexing agent Y can be taken into account by introducing only three coefficients, α_M, α_Y and α_{MY} according to

$$K' = \frac{\alpha_{MY}}{\alpha_M \alpha_Y} K_{MY} \qquad (9)$$

The conditional constant is here denoted by K' in omitting the subscripts.

The α coefficients always exceed unity (or equal unity if side reactions can be neglected) and hence side reactions of MY, expressed by α_{MY}, effect a *favourable* shift in the equilibrium whereas side reactions of M and Y, expressed by α_M and α_Y, respectively, effect an *unfavourable* shift in the equilibrium.

Any of these three α coefficients may take into account more than one side reaction, and the coefficient to be used in such a case—we may call it the over-all α coefficient—approximately equals the sum of the individual coefficients as shown by equations (10), (11), and (12).

$$\alpha_{Hg} \approx \alpha_{Hg(OH)} + Hg(NH_3) \qquad (10)$$

$$\alpha_Y \approx \alpha_{Y(H)} + \alpha_{Y(Mg)} \qquad (11)$$

$$\alpha_{HgY} \approx \alpha_{HgY(H)} + \alpha_{HgY(OH)} + \alpha_{HgY(NH_3)} \qquad (12)$$

The interfering ion or molecule is inserted in parentheses in the subscript. The symbol for the over-all coefficient (left side of the equation) does not contain any parenthesis.

The equations (10), (11), and (12) are approximate. They can be made exact by including the term $(1 - p)$, where p is the number of terms on the right side of the equation (*cf.* ref. 2). However, this term can be neglected in most cases. As a rule, the orders of magnitude of the individual α coefficients differ, and hence one value predominates.

The term *conditional constant* has been introduced to denote an apparent constant extended in this way and will be used in the following. This term was suggested by Kolthoff who wished to stress that a conditional "constant" is not a real constant but depends on the experimental conditions. Conditional constants are in the following denoted either by K' or by K with primed subscripts.

We will now apply the proposed approach to the presented problem of titrating mercury with EDTA. We may assume that a 10^{-3} M mercury salt solution is titrated with EDTA at pH 9 in a buffer solution containing ammonia and ammonium ion in about 0·1 M total concentration. Moreover, magnesium is assumed present in about 10^{-3} M concentration. (To

avoid a transient precipitation of $Hg(OH)_2$ it may be advantageous to titrate in the opposite direction).

According to equation (9)

$$K' = \frac{\alpha_{HgY}}{\alpha_{Hg}\alpha_Y} K_{HgY} = \frac{10^{5\cdot4}}{10^{14\cdot6}\,10^{5\cdot7}}\,10^{21\cdot8} = 10^{6\cdot9} \qquad (13)$$

i.e., the conditional constant is obtained by multiplying or dividing K_{HgY} by three coefficients: α_{HgY}, which affects the equilibrium favourably, takes into account side reactions leading to basic or mixed complexes,

$$\alpha_{HgY} \approx \underset{10^{0\cdot3}}{\alpha_{HgY(OH)}} + \underset{10^{5\cdot4}}{\alpha_{HgY(NH_3)}} = 10^{5\cdot4} \qquad (14)$$

α_{Hg} takes into account the hydrolysis of the mercury ion and the side reactions of mercury with the buffer agent, *i.e.*, ammonia (equation (15)).

$$\alpha_{Hg} \approx \underset{10^{11\cdot9}}{\alpha_{Hg(OH)}} + \underset{10^{14\cdot6}}{\alpha_{Hg(NH_3)}} = 10^{14\cdot6} \qquad (15)$$

α_Y takes into account the formation of acid EDTA species and the formation of MgY (equation (16)).

$$\alpha_Y \approx \underset{10^{1\cdot4}}{\alpha_{Y(H)}} + \underset{10^{5\cdot7}}{\alpha_{Y(Mg)}} = 10^{5\cdot7} \qquad (16)$$

The calculation of $\alpha_{Y(H)}$ was already explained; as this coefficient is frequently needed in all complexometric titrations with EDTA, it is convenient to tabulate its values at various pH values. Also $\alpha_{Hg(NH_3)}$ can best be taken from a table or read from a curve. All the other coefficients can be obtained by a simple algebraic addition of only two numbers, as shown for the last coefficient $\alpha_{Y(Mg)}$ in equation (17):

$$\alpha_{Y(Mg)} = 1 + \underset{10^{-3}}{[Mg]}\,\underset{10^{8\cdot7}}{K_{MgY}} = 10^{5\cdot7} \qquad (17)$$

According to equation (13) the conditional constant K' has the value $10^{6\cdot9}$. Let us assume that the end point is detected potentiometrically with an accuracy of about ±6 millivolts, *i.e.*, about $\pm0\cdot2$ pHg unit. The logarithm of the product $K'C$ equals $6\cdot9 - 3 = 3\cdot9$, and according to *Figure 2* the error is about ±1 per cent. Without magnesium present the error would be less than $\pm0\cdot1$ per cent.

Consequently, even if the main reaction is influenced by a dozen (or two dozen) side reactions, it is a simple matter to calculate the accuracy attainable in a titration. It may be mentioned that a comprehensive set of values of α coefficients is to be found in a recently published monograph on *Complexation in Analytical Chemistry*[2].

Analytical chemists who have become used to the suggested way of treating equilibria can usually decide in a moment, without using paper and pencil, how any change in the experimental conditions will affect the result. For instance, if the magnesium concentration in our example were ten times higher, *i.e.*, 10^{-2} M, a glance at equation (17) will show that the coefficient $\alpha_{Y(M)}$ would be one logarithmic unit higher and the conditional constant one

unit lower. The abscissa of the error diagram would be only 2·9, and the error corresponding to ± 6 mV would be ± 3 per cent.

The equations (11) and (17) for the calculation of α_Y can be used to determine the pH range where foreign metals present will interfere in a complexometric titration. The rule is simply: *If a metal* M_I *is titrated complexometrically in the presence of another metal* M_{II}, *the last mentioned metal will interfere only when* $\alpha_{Y(M_{II})} > \alpha_{Y(H)}$.

I will illustrate this rule by an example. If a metal, say zinc or aluminium, is to be titrated in acid solution, one may ask whether any calcium present will affect the result. Experimentally, it will be found that calcium has little effect at low concentrations but interferes strongly at high concentrations. The range of interference can be estimated from the $\alpha_{Y(H)}$ and $\alpha_{Y(Ca)}$ coefficients given in *Table 1*. It can be seen that calcium in 0·1 M concentration interferes at any pH above 3·5. If present in 10^{-3} M concentration, it

Table 1. Titration of a metal in acid solution with EDTA in the presence of calcium

pH	3	3·5	4	4·5	5	5·5	6	6·5	7
log $\alpha_{Y(H)}$	10·8	9·6	8·6	7·6	6·6	5·7	4·8	4·1	3·4
log $\alpha_{Y(Ca)}$ for [Ca] $= 10^{-1}$		↑ 9·7		↑	Ca interferes at pH $> 3·5$				
log $\alpha_{Y(Ca)}$ for [Ca] $= 10^{-3}$				7·7	Ca interferes at pH $> 4·5$				

interferes at any pH above 4·5. By subtracting log α_Y from log $K_{M_I Y}$ the conditional constant log $K_{M_I Y}'$ is obtained according to equation (9). The attainable accuracy at any pH and at any concentration of calcium can be directly read from the error diagram, *i.e.*, every interference can be expressed quantitatively.

It may be appropriate to illustrate, by means of a series of curves, the relationship between conditional constants and the commonly used stability constants, which, incidentally, are mostly concentration constants valid at an ionic strength of 0·1. (When using such constants, the analyst can usually omit activity corrections without a very bad conscience.) In *Figure 3* the conditional constants of several metal–EDTA complexes are given as functions of pH.

These constants are valid if no side reactions except those caused by hydrogen and hydroxide ions interfere. Buffering and masking agents capable of forming complexes with these metals may decrease these values. It is remarkable how much the maximum values in the figure differ from the values of the concentration stability constants. K_{HgY} equals $10^{21·8}$ but the conditional constant never exceeds the value 10^{12}. Although K_{FeY} ($= 10^{25·1}$) is more than six powers of ten larger than K_{CuY} ($= 10^{18·8}$) and K_{NiY} ($= 10^{18·6}$), the maximum value of the conditional constant for iron is considerably smaller than the maximum values of the conditional constants for copper and nickel. Very high values of stability constants may therefore be

misleading, because it is not possible in the majority of cases to prepare a solution in which all the metal is in the form of aquo ions and all the free EDTA in the form of Y ions. Only the alkaline earth metal complexes have conditional constants equal to K_{MY} at pH about 11, since then α_M and α_Y are both approximately unity.
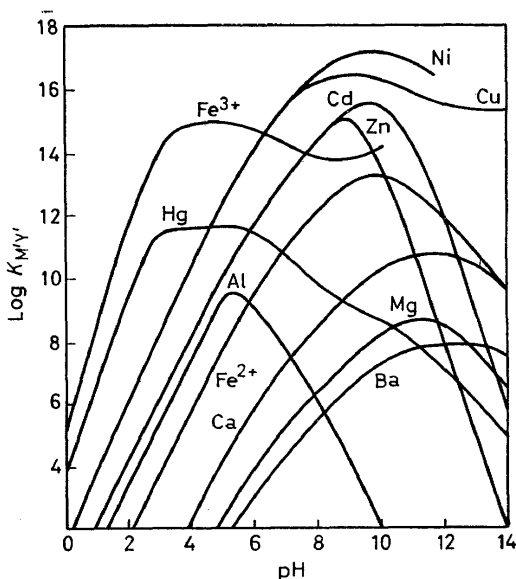

Figure 3. Conditional stability constants of various metal EDTA complexes as functions of pH

From Ringbom[2], by courtesy of John Wiley–Interscience, New York–London)

The concept of masking deserves some comments.

We may say that a metal ion or a complexation reaction is *masked* if the conditional constant is sufficiently decreased by the addition of some reagent. This is the only rule needed. By calculating conditional constants, the degree of masking can be expressed quantitatively, and masking agents can be objectively compared. In the previously given equation (9)

$$K' = \frac{\alpha_{MY}}{\alpha_M \alpha_Y} K_{MY} \qquad (9)$$

α_M and α_Y are direct measures of the masking ability of some agent. On the other hand, a value of α_{MY} greater than unity implies a promotion of the main reaction on which a titration is based.

The usefulness of the suggested way of treating masking problems will be illustrated by an example relating not to a complexometric titration, but to an extraction.

The curves of *Figure 4* refer to the extraction of zinc from an aqueous solution with dithizone dissolved in carbon tetrachloride. The α coefficients of several masking agents are plotted as functions of pH. A glance at the

figure is enough to decide the success of an extraction under widely differing conditions. The hatched area indicates complete masking, the dotted area complete extraction. In the unshaded area between these, the extraction is incomplete.

For instance, zinc is completely masked in the presence of oxalate in 0·1 M concentration (curve 3) at a pH below 3 but quantitatively extracted
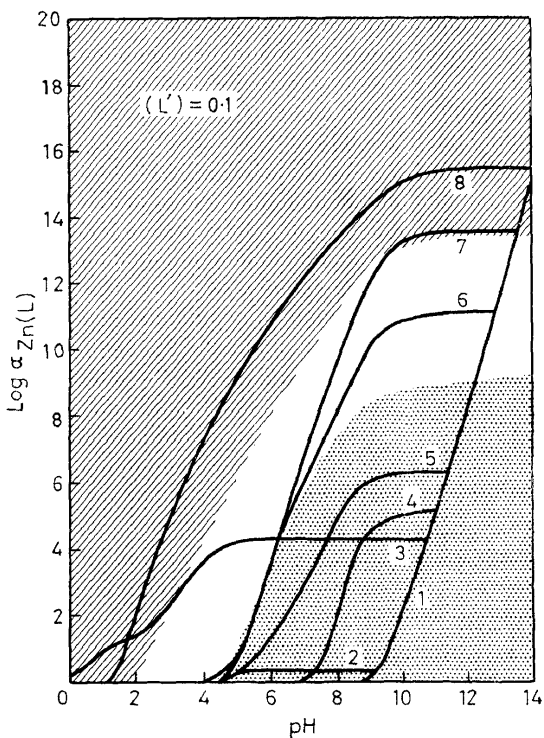

Figure 4. The curves plot log $\alpha_{Zn(L)}$ as a function of pH in the presence of complexing agents 2–8. Valid for a 0·1M concentration of complexing agent not bound to metal ([L'] = 0·1). 2: acetate; 3: oxalate; 4: ammonia; 5: acetylacetone; 6: trien; 7: tren; 8: EDTA. Curve 1 plots log $\alpha_{Zn(OH)}$
(From Ringbom and Still[4])

at a pH higher than 6·5. On the other hand, if the polyamine "tren" (triaminotriethylamine) is present (curve 7), complete extraction occurs at pH 5–6, but the masking is complete at pH 10. > Curve 8 shows that EDTA masks zinc at all pH values.

Any extraction process can be treated in an analogous way and the influence of various complexing agents can be calculated. The α values for plotting the curves are read from tables, and the boundaries of the fields can be calculated from the experimental conditions (*i.e.*, concentration of extracting reagent and volumes).

As acids and bases can be considered hydrogen or hydroxo *complexes*, the suggested treatment of complexometric titrations can also be applied to neutralization titrations. If an acid or a base is titrated in the presence of

other acids and bases, the use of conditional constants offers many advantages. For instance, it is possible to use the error diagram even when rather complicated mixtures of acids and bases are titrated. Incidentally, I may mention that if a dibasic acid is titrated to the first equivalence point, it can easily be shown that the abscissa of the error diagram, log $K'C$, is equal to $\Delta \log K$, *i.e.*, the difference between the logarithms of the two stability constants[2]. For instance, when carbonic acid (or the carbonate ion) is titrated to bicarbonate,

$$\log K'C = \Delta \log K = 10\cdot1 - 6\cdot3 = 3\cdot8 \qquad (18)$$

This value when taken as the abscissa of the diagram in *Figure 2* directly gives the percentage error. If ΔpH is assumed $\pm 0\cdot5$, the error is about $\pm 3\cdot5$ per cent independent of the concentration (within reasonable limits).

However, my purpose in including acid–base reactions in this presentation is not to illustrate error calculations but to show that many neutralization problems in aqueous solutions that at first sight appear difficult or impossible to solve, nevertheless can be solved by inducing *favourable* side reactions promoting the main reaction on which the titration is based.

Many analytical chemists are familiar with the way of titrating boric acid, an acid too weak to be titrated directly. An excess of mannitol is added to increase the apparent strength of boric acid. Mannitol (Ma) reacts with the borate ion (B^-), and the influence of this side reaction can be calculated in the usual way by means of an alpha coefficient, $\alpha_{B(Ma)}$. Hence,

$$K_{base} = \frac{[B^-]}{[HB]\,[OH^-]} \qquad (19)$$

$$\alpha_{B(Ma)} = 1 + [Ma]\,K_{BMa} + [Ma]^2\,K_{BMa_2} \qquad (20)$$

$$\log K'_{base} = \log K_{base} + \log \alpha_{B(Ma)} \qquad (21)$$

The conditional stability constant of the borate ion can be calculated from equation (21), and it is obvious that also pH at the equivalence point and the accuracy attainable in the titration will be determined by the obtained value.

The same principle of inducing a favourable side reaction can be applied to the titration of several very weak acids. One way is to add some metal ion M capable of forming complexes with the base B (*i.e.* the anion or the molecule formed by neutralization). Qualitatively, the reaction can be expressed by

$$HB + M = MB + H^+ \qquad (22)$$

quantitatively, the equilibrium can be treated as in complexometric titrations by introducing various α coefficients. In *Table 2* it is shown how a number of titrations is made possible by the addition of an appropriate reagent, mostly a metal salt. If we consider the first three acids in the table, glycine, α-alanine, and acetylacetone, they are all so weak that a satisfactory determination by direct titration is hardly possible. By the addition of metal ions, the conditional constants of the formed corresponding bases can be increased one to three powers of ten. This greatly improves the accuracy,

Table 2. Titration of weak acids after the addition of agents promoting the determination

	log K		Added ion	log K' log $K \pm$ log α_L	
	Acid	*Corr. base*		*Acid*	*Corr. base*
Glycine	9·7	4·3	Mg²⁺	8·6	5·4
α-Alanine	9·8	4·2	Cu²⁺	8·3	6·7
Acetylacetore	8·9	5·1	Cu²⁺	6·9	7·1
Ammonium	9·4	4·6	Ag⁺	8·2	5·8
,, } Sadek	9·4	4·6	HgY²⁻ (EDTA)	7·9	6·1
,, } Reilley	9·4	4·6	HgZ²⁻ (DCTA)	7·4	6·6
DTPA (5th stage)	10·5	3·5	Ca²⁺	1·9	12·1
Citric acid (4th stage)	16	—2	Cu²⁺	7·8	6·2

as will be found by entering these values in the error diagram. Also the ammonium ion is too weak an acid to be accurately determined by neutralization. Silver ions have a greater tendency to bind ammonia than hydroxide ions and improve the accuracy somewhat. Sadek and Reilley[5] have shown that a good accuracy is obtained also if the mercury complex of EDTA or DCTA (diaminocyclohexanetetraacetic acid) is added. The reason is that these compounds form mixed ammonia complexes, and the conditional constants given in the table are obtained by correcting the common acid-base constants with the α coefficients calculated according to

$$\alpha_{NH_3(HgX)} = 1 + [HgX] \, K_{HgX \cdot NH_3} \qquad (23)$$

On adding the mercury–DCTA complex, the apparent acid strength of the ammonium ion will increase two logarithmic units and fairly accurate results can be expected. Details of the calculations are given in the previously cited monograph[2].

DTPA (diethylenetriaminepentaacetic acid), after the addition of calcium chloride, will behave almost as a strong acid, also in its fifth stage, and the titration error in neutralization will be very small. The same is, of course, the case with most polyaminocarbonic acids, a fact that can be and has been utilized in analysis.

Particularly interesting is the behaviour of citric acid. Citric acid is usually considered a tribasic acid, but in addition to the three carboxylic groups it contains one hydroxyl group. A fourth stage of dissociation is thus theoretically possible, but the logarithmic stability constant has been estimated to be about 16, a value much too high for a direct titration. Nevertheless, citric acid can be titrated as a tetrabasic acid in the presence of copper ions, since the quadrivalent citrate ion forms a very stable complex with copper (log $K \approx 18$). From *Table 2* it can be seen that at a copper ion concentration of 0·01 the theoretical logarithmic conditional constant of citric acid in its fourth stage equals 7·8. Of course, a titration of such a weak acid is less accurate than the usual titration of citric acid as a tribasic acid, but in the analysis of various mixtures the possibility of titrating citric acid as a tetrabasic acid is very welcome. Let us assume that we want to analyse a mixture of some strong acid and citric acid. A direct titration does not allow any differentiation of the many neutralization stages. However, a determination

is possible if the sum of the two acids is titrated first to pH 9, and the hydrogen ions liberated from citric acid when copper ions are added are then titrated.

All the values given in *Table 2* were calculated theoretically taking into consideration also the possible formation of metal hydroxo complexes. In the calculation of some of the conditional constants, three α coefficients were needed. The error diagram immediately gives the probable accuracy.

The experimental results were in fair agreement with the theory when magnesium, calcium, or the mercury complexes promoted the main reaction. However, when the copper ion was used as complexing agent, the experimental accuracy (and the conditional constant of the formed base complex) was somewhat lower than the calculated. The discrepancy is probably due to the fact that the tendency of copper ions to form polynuclear hydroxo complexes interferes in a narrow pH range near the equivalence point (pH 5–6). This tendency was not taken into account in the calculations.

Figure 5 illustrates the courses of titrations of acetylacetone before and after adding metal salts. In case 3 copper hydroxide precipitated immediately after the equivalence point.
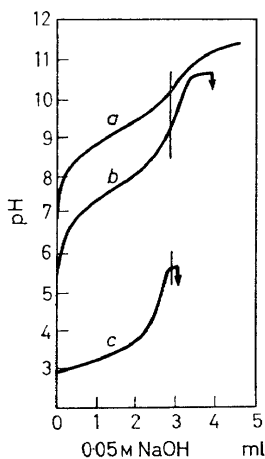
Figure 5. Titration of 0·006 M acetylacetone with 0·05 M NaOH (*a*) without additions; (*b*) MgSO$_4$ added in 0·01 M excess; (*c*) CuSO$_4$ added in 0·01 M excess
(From Eklund and Ringbom[6])

A few words may be added about the titration of *bases* too weak to be determined by direct neutralization. Such titrations are often performed in non-aqueous solvents, and the possibilities of inducing favourable side reactions in aqueous solutions are limited. However, they exist. As one example we may take the titration of a sodium benzoate solution. The benzoate ion is too weak a base for a satisfactory direct titration; the formed benzoic acid has a stability constant of $10^{4·2}$. It is, however, possible to promote the main reaction by extracting the liberated benzoic acid with ether, *i.e.*, by vigorously shaking the aqueous solution with ether during the titration. The conditional constant can be calculated in considering the

extraction into ether a side reaction that can be taken into account by a coefficient, $\alpha_{HB(ether)}$, which can be calculated from the equation

$$\alpha_{HB(ether)} = 1 + \frac{V_{org}}{V_{aq}} D_{HB} \qquad (24)$$

D_{HB} is the distribution coefficient of benzoic acid between ether and water. If the volumes of the two phases are equal, $\alpha_{HB} \approx D_{HB} = 10^{2 \cdot 1}$. The conditional constant of the benzoic acid is then simply

$$\log K'_{HB} = \log K_{HB} + \log D_{HB} = 4 \cdot 2 + 2 \cdot 1 = 6 \cdot 3 \qquad (25)$$

If a solution of about 10^{-2} M is titrated, the pH at the equivalence point equals $4 \cdot 15$ (equation (1)), and Bromphenol Blue is a suitable indicator[2]. The error diagram gives the accuracy under different experimental conditions.

Masking can be useful also in neutralizations. If we have to titrate a mixture of acids or bases about equal in strength, the pH jumps will coincide and no determination will be possible. However, one of the components can often be masked. Let us assume that free ammonia in a sodium citrate solution is to be titrated. A direct titration is not possible since no pH jump will occur at the equivalence point, but by adding an excess of calcium chloride the citrate ion will be complexed, *i.e.*, masked. The conditional stability constants of the hydrogen complexes of citric acid will decrease, and hence citrate ions will react with hydrogen ions *after* the ammonium ions are formed. The accuracy and the pH at the equivalence point for the masked solution are readily calculated.

If an ampholyte reacts with a neutral reagent, its acid properties as well as its base properties will be weakened. For instance, if formaldehyde is added to a solution containing bisulphite ions, an addition compound with a stability constant of about 10^7 will be formed. When formaldehyde in an about $0 \cdot 01$ M excess is used ([form] $\approx 0 \cdot 01$), the α coefficient equals

$$\alpha_{HSO_3(form)} = 1 + [form] \, 10^7 = 10^5 \qquad (26)$$

and the conditional acidity constants of sulphurous acid will change as follows:

$$\log K'_{H_2SO_3} = \log K_{H_2SO_3} - \log \alpha_{HSO_3} = 1 \cdot 9 - 5 = -3 \cdot 1 \qquad (27)$$

$$\log K'_{HSO_3} = \log K_{HSO_3} + \log \alpha_{HSO_3} = 7 \cdot 0 + 5 = 12 \qquad (28)$$

Sulphurous acid in its first dissociation stage will be an apparently *very strong acid* as the logarithmic conditional constant shifts from $1 \cdot 9$ to a negative value (equation 27), but in its second stage it will be a *very weak acid* since the logarithmic conditional constant shifts from 7 to 12 (equation 28). This fact makes it possible to determine sulphurous acid and sulphites in many complex mixtures. The difference between the results of two titrations, one in the absence of formaldehyde, and the other in the presence of formaldehyde gives the amount of bisulphite.

Since a complexation reaction often alters the charge of a metal ion, *ion-exchange reactions* can be either masked or promoted effectively by complexing agents. The influence of complexations on ion-exchange equilibria

has frequently been discussed in the literature. In our terms we would say that if a complexation reaction changes the sign of charge of an exchanging ion, the *conditional* exchange constant, or equilibrium quotient, will change, and for the exchange of M^{n+} with H^+ the following expression is valid:

$$K'_{\text{exchange}} = \frac{[M]_r[H]^n}{[M][H]_r^n \, \alpha_M} = \frac{K_{\text{exch}}}{\alpha_M} \tag{29}$$

Concentrations in the resin phase are indicated by the subscript r. The distribution coefficient is given by

$$D^{M'} = \frac{[M]_r}{[M']} = \frac{[H]_r^n \, K_{\text{exch}}}{[H]^n \, \alpha_M} \tag{30}$$

Consequently, the distribution coefficient can be calculated if approximate concentrations of the counter ion in the solution and resin phases and the value of the coefficient α_M are known. The values of these coefficients as well as ion-exchange constants are tabulated in the literature[2]. It may be emphasized that if complexation reactions determine the equilibria, a knowledge of only the orders of magnitude of the various distribution coefficients is quite sufficient for many important conclusions. The distribution coefficients of two metals with almost identical exchange properties when present as aquo ions can be radically changed by the addition of a suitable complexing agent. The ratio of the two distribution coefficients is often altered by several powers of ten, and hence separations can be performed using batch methods or very short columns.

The inclusion of ion-exchange processes in this lecture was due to the fact that there exist interesting possibilities of separating various metals by combining *several* complexing agents, and conditional constants offer a simple way of treating the equilibria of the rather complex systems. As an example I will take the separation of copper and lead from a solution containing two rather strongly complexing agents, EDTA and "tetren", *i.e.*, tetraethylenepentamine, a polyamine with five basic nitrogen atoms.

The stability constants of the complexes of these two metals are

	$\log K_{\text{CuL}}$	$\log K_{\text{PbL}}$
EDTA	18·8	18·0
Tetren	22·9	10·5

The two EDTA complexes are about equal in stability, but copper forms with tetren a complex that is far more stable than the lead complex. Hence it should be possible to prepare such a solution that copper exists predominantly as positive copper–tetren ions and lead as negative PbY^{2-} ions. The problem can be conveniently treated by calculating conditional constants of the two metal–EDTA complexes in the presence of a known excess of tetren. Details of the calculations will not be repeated here. Assuming about 0·01 M excess of tetren the conditional stability constants of the two EDTA complexes will be $\log K_{\text{Cu'Y'}} = -2\cdot2$ and $\log K_{\text{Pb'Y'}} = 9\cdot4$ (pH $\approx$ 11). Using a resin loaded with sodium and assuming a sodium concentra-

tion equal to 0·05 M in the solution, the conditional distribution coefficients calculated from

$$D^{M'} = \frac{[Na]_r^2 \, K_{exch}}{[Na]^2 \, \alpha_M} \tag{31}$$

are $D^{Cu'} = 10^{3·9}$ and $D^{Pb'} = 10^{-2·7}$. These coefficients differ by several powers of ten. A separation is thus possible using a short resin column or even a batch method.

In the example presented the adsorption of copper is *promoted* by the addition of tetren, since copper–tetren cations are actually more strongly adsorbed than the aquo ions, but the adsorption of lead is prevented—*i.e.*, lead is *masked*—by the addition of EDTA. A study of some collection of equilibrium constants reveals the possibilities of carrying out numerous similar separations, and their theoretical treatment is rather simple if it is based on the concept of conditional constant.

The problem of choosing suitable experimental conditions for an ion-exchange separation in the presence of some complexing agent is often one of choosing the right pH. For instance, the theoretical possibilities of separating copper and calcium from a solution containing HEDTA (hydroxy-substituted EDTA) are shown in *Figure 6*.
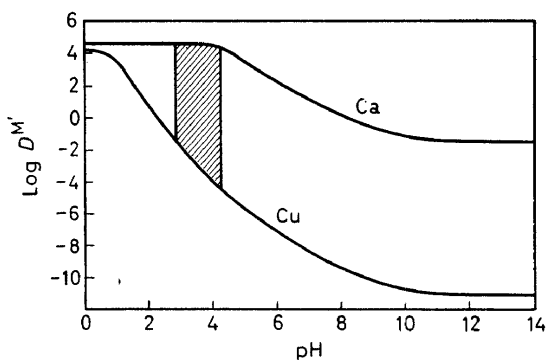
Figure 6. Ion-exchange distribution coefficients $D^{Cu'}$ and $D^{Ca'}$ as functions of pH for solutions 0·01 M in HEDTA

(From Ringbom[2], by courtesy of John Wiley–Interscience, New York–London)

The curves of this figure can be immediately calculated with the aid of α coefficients. In the lined field, *i.e.*, in the pH range from 2·9 to 4·2, a separation by means of a batch method is possible. This range refers to a resin loaded with sodium ions and a sodium ion concentration in the solution equal to 0·05 M.

Analytical chemists often complain that the theoretical treatment of various analytical problems is awkward and, worse still, far from reliable. They sometimes assert that simple theories are not correct and correct theories are too involved. I would be happy if the preceding discussion has revealed that although analytical problems are often complicated in the sense that a great number of side reactions may influence an equilibrium, a rather simple, yet nevertheless sufficiently correct mathematical treatment

is possible. Such treatment will help the analyst to make a critical choice from among all the many methods that nowadays threaten to overwhelm him and to develop new methods that hardly would be found by purely empirical experiments.

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