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The Rate of Extraction Under Kinetic Conditions (Reaction in the Bulk Phase)

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Under kinetic conditions the rate of extraction depends on the rate of one or two slow reactions in the aqueous phase with the ion A^- or the molecule HA and also on the rate of reaction in the aqueous phase not involving the extractant. This has been examined for the extraction of trace amounts of bivalent and tervalent elements from aqueous solutions of their salts by solutions of an acid HA in organic solvents. The rate of extraction varies in a complex manner both with the rate constants for the corresponding reactions and with the stability constants of the complex ions formed; for this reason, studies on the mechanism of the reactions determining the rate of extraction in which no account was taken of complex formation in general give erroneous results. The possibility of using the proposed methods to determine the mechanism of the extraction of macroamounts of a univalent element has been demonstrated.
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I. INTRODUCTION

The study of the rate of extraction has significant practical interest, since the efficiency or size of extraction apparatus depends on the rate. The rate of extraction is also of theoretical interest, since it makes it possible to establish the mechanism of extraction, which cannot be done by studying extraction equilibria alone.

The extraction of inorganic compounds is usually accompanied by chemical processes: the formation of salts in extraction by acids and amines and of solvates in extraction by neutral extractants[1]. Apart from the reactions with extractants, other reactions may occur, for example complex formation and hydrolysis in the aqueous phase, which determine the rate of extraction. We refer to such processes not involving the extractant as "side" reactions[2]. There is no doubt that the slow shift of equilibrium in hydrolysis accounts for the time variation of the partition coefficients in the extraction of zirconium from nitric acid solutions by solutions of dicresylphosphoric acid in organic solvents[3].

Since the reactions can occur both in the bulk phases and at the interface, heterophase and heterogeneous reactions are distinguished[4].

The wide-scale and increasing application of extraction in technology increases interest in the question of the rate of extraction, which has been noted, for example, in a review published in 1964.[5] The number of studies on this topic has now greatly increased. However, in most of the published work the authors confine themselves to characterising the dependence of the degree of extraction or the partition coefficient on time without establishing the mechanism of the process determining the rate of extraction.

Extraction is always associated with the transfer of a substance from one phase to another (mass transfer) and therefore its rate can be determined by the rate of the reaction occurring, the rate of mass transfer, or the rates of both processes.

If the rate of extraction depends only on the rate of the chemical reaction, the process is said to occur under kinetic conditions, when the rate of extraction depends only on the rate of mass transfer, it is said to occur under diffusion-dependent conditions, and, when the rate of extraction depends on the rate of both the reaction and of mass transfer, the process is said to take place under mixed conditions.

Under kinetic conditions, the rate of mass transfer is so high that at any instant an equilibrium distribution between the phases of the compound passing from one phase to the other is virtually attained[6,7]; however, in extraction this is valid only for the given compound and not for all the compounds of the element being extracted which exist in the system investigated.

For example, when in the extraction of iron from aqueous solutions of inorganic acids by acetylacetone solutions FeA_3 (A is the acetylacetonate anion) is formed slowly in the aqueous phase and only this compound passes to the organic phase, then, under kinetic conditions, equilibrium in its distribution between the phases is established very rapidly ("instantaneously"), but a long time is needed to establish the equilibrium in the determination of analytical concentrations of iron.

Under diffusion-dependent conditions, the rates of the chemical reactions in the given system are so high that equilibrium between the compounds present is virtually attained in every phase but there is no equilibrium between the phases.

The rate of mass transfer depends on the rate of stirring of the phases, which determines the rate of transfer of material from the bulk of the phase to its surface and from the surface to the bulk and also on the area of the interface. Under kinetic conditions, the rate of mass transfer is so high that a change in the area of the interface and in the rate of stirring hardly disturbs the equilibrium distribution of the compound extracted and the change in its concentration is due solely to the rate of the chemical reaction; for this reason, the rate of extraction in

this region is independent of both the area of the interface and of the rate of stirring of the phases.

Under diffusion-dependent and mixed conditions, the rate of extraction depends on the rate of mass transfer and hence on the rate of stirring and the area of the interface. Only after having demonstrated that this type of dependence exists can one assert that the process takes place under one of the above conditions.

However, if the extraction is accompanied by a reaction at the interface, then under kinetic conditions the rate of extraction is independent of the rate of stirring for a constant area of the interface but varies with the area for a constant rate of stirring. This is in fact why in the determination of the conditions under which the process takes place it is necessary to determine the dependence of the rate both on the rate of stirring for a constant area of the interface and on the area of the interface for a constant rate of stirring.

Under mixed conditions as well as under diffusion-dependent conditions, the rate of extraction varies with the rate of stirring and with the area of the interface, which makes it difficult to solve the problem of the process conditions, but, as will be shown below, there are methods whereby one can deduce whether one process (diffusion-dependent conditions) or two processes with comparable rates take place.

With increased rate of mixing of the phases, there is usually an increase of the degree of comminution and hence of the area of the interface and therefore the absence of a dependence of the rate of extraction on the rate of stirring is frequently regarded as evidence that the process occurs under kinetic conditions. However, it has been noted in the literature that a constant rate of dissolution of a solid can be maintained by increasing the rate of rotation of the stirrer[8].

Since only the absence of a dependence of the rate of extraction both on the rate of stirring and on the area of the interface is convincing evidence for a transition of the process to kinetic conditions with the reaction in the bulk of one or both phases, in order to establish the extraction mechanism it is necessary to determine at least the relative surface areas of the phases. A number of methods have been proposed for this, among which the most convenient for extraction (in the case of dispersed phases) are the light scattering and photographic methods. The methods have been described and examples of their applications in studies on the rate of mass transfer have been given, for example, in Refs. 9–18.

When light passes through an emulsion, the specific surface S/V (S is the area of the emulsion and V its volume) is determined from the equation

$$\frac{I_0}{I} = 1 + \beta \frac{S}{V} \quad , \qquad (1)$$

where I_0 is the intensity of the light which has passed through the continuous phase (without emulsion), I the intensity of the light which has passed through the emulsion, and β a coefficient which depends on the refractive indices of the phases. This equation makes it possible to find the ratio of the surface areas of the emulsion in two experiments with different rates of stirring without knowing β and hence one can solve the problem of whether or not the change in the surface area affects the rate of the process. We may note that, in order to determine the degree of light scattering, one can employ a nephelometer using its cell as an extraction vessel[19].

The dimensions of drops and hence their surface areas can be determined by the sedimentation method[20], but the method suffers from the disadvantage that the process has to be interrupted and the surface areas must be determined in independent experiments.

Under diffusion-dependent conditions in a system with constant partition and mass transfer coefficients, the change in the concentration in the receiving phase over a time t, when the concentration is initially zero, is given by the equation

$$\ln \frac{C_{2p} - C_2}{C_2} = - \frac{K_2(q+1)}{V} S t \quad , \qquad (2)$$

where V is the phase volume ($V_1 = V_2$), S the area of the interface, $q = C_{2p}/C_{1p}$ the partition coefficient, and K_2 the mass transfer coefficient referred to the receiving phase.

Then, in the first experiment (area S_1) we have $\ln 2 = K_2(q+1)S_1 t/V$ after a time interval such that, for example, $C_2 = 0.5C_{2p}$, where C_{2p} is the equilibrium concentration in the given system. In another experiment (area S_2) the change in concentration during the same time interval can be found from the equation $\ln (C_{2p} - C_2)/C_{2p} = - \ln (2S_1/S_2)$. If $S_1/S_2 = 2$, then

$$\ln \frac{C_{2p} - C_2}{C_{2p}} = - \ln 4 \text{ and } C_2 = 0.75 C_{2p} \quad .$$

Thus, for constant mass-transfer and partition coefficients, the change in area by a factor of two leads to a change in concentration in the receiving phase (during the same period) by a factor of 1.5, which can be readily detected. If the increase in area has occurred as a result of an increase of the rate of stirring, then, under diffusion-dependent conditions, there is an increase of the mass-transfer coefficient and the change in concentration is even greater.

In the study of the rate of mass transfer one frequently employs apparatus with a constant area of the interface, for example that proposed by Lewis[21]. In such apparatus the phases are separated by a horizontal partition with an annular aperture in which the level of the interface is established and each phase is agitated by its own stirrer. However, in this system the thickness of the ring has some importance, since the conditions governing the stirring of the liquids in the gap may differ from those in the bulk of the phases, which may affect the process conditions.

In the study of the rate of mass transfer one frequently employs cylindrical vessels with vertical partitions. Their purpose is to prevent the breakdown of the surface during the stirring of the phases, i.e. to prevent the formation of waves[22-24].

However, apparatus with a constant area of the interface has a small specific surface and hence the rate of mass transfer is also low, as a result of which many processes which occur under kinetic conditions when the phases are dispersed can occur under mixed or diffusion-dependent conditions in apparatus with a constant area of the interface[19].

The employment of apparatus of the Lewis type with a variable width of the annular aperture can be useful in testing the hypothesis that the process occurs under kinetic conditions with a surface reaction, since in such apparatus one can vary the area of the interface keeping constant the rate of stirring or one can vary the rate of stirring keeping constant the area of the interface.

In studies on diffusion accompanied by a chemical reaction and on mass transfer with chemical reaction[25,26] it has been shown that, for a fairly high rate of reaction (for this reason it takes place in the diffusion film), the rate of the process under the conditions of a constant area

of the interface is independent of the rate of stirring. Such conditions are referred to as fast reaction conditions[27]. They resemble the kinetic conditions with a surface reaction. An example of mass transfer with a rapid or surface reaction is the interaction of certain organic [sic!] formates and acetates with aqueous solutions of alkalis accompanied by the transfer of the acid to the aqueous phase and its neutralisation. These reactions are used to determine the dependence of the surface area of the emulsion on the rate of stirring and on the design of the stirrers[28-31]. They can be used to test the constancy of the area of the interface when the rate of stirring is varied in apparatus of the Lewis type and particularly in cylindrical vessels with partitions.

If it has been shown that at a certain rate of stirring, the process proceeds under kinetic conditions, then, by changing the rate of stirring, it is impossible to increase the rate of extraction, since the latter is determined by the rate of the chemical reaction. In this case the rate of extraction can be increased only by increasing the rate of reaction (by increasing the concentration or temperature). Under diffusion-dependent or mixed conditions, the rate of extraction can be raised by increasing the area of the interface and the rate of stirring as long as the process does not pass to kinetic conditions.

The extraction mechanism and the rate of the reactions taking place can be determined most simply under kinetic conditions. As will be shown below, even in this case the problem is more difficult than the determination of the mechanism and of the rates of reactions in a homogeneous system, but the difficulty becomes even more marked under mixed conditions.

An important complication in the study of extraction kinetics is associated with the measurement of concentration when one of the phases is dispersed. The main method, in which the stirring of the phases is stopped and the latter are allowed to separate before removing the samples, distorts the results, since the hydrodynamic conditions and the area of the interface change during this period. This type of method can be used only for fairly slow processes. The effect of the interruptions on the results of the measurement of the rate can be tested by carrying out two experiments under the same conditions. In one experiment samples are removed twice or more frequently and in the other only one sample is removed after stirring for a period equal in duration to the overall time of stirring in the first experiment. Comparison of the results will then reveal the effect of the interruption of stirring.

A method has been proposed[14] for the measurement of concentration in a continuous aqueous phase in the presence of an emulsion on the basis of conductivity. The application of this method is restricted to systems with one electrolyte in the aqueous phase and does not allow the employment of trace amounts of radioactive elements, the use of which frequently simplifies the interpretation of the experimental data, because the concentrations of the other components, reacting with the given element, can be regarded as constant. It is much easier to measure the concentration in apparatus with a constant level of the interface. In this case one can measure the conductivity in the aqueous and sometimes in the organic phases[32,33], the radioactivity of the phase can be determined (for example on the basis of γ-radiation) when radioactive isotopes are employed[34-37], and removal of samples for analysis is simplified (samples can be removed without stopping the stirrer).

A significant defect of many studies on extraction kinetics is that the authors did not establish the conditions under which the process occurred, introducing thereby an uncertainty into their results.

In a number of studies[38-45] the authors assumed that the extraction proceeds under kinetic conditions (with the reaction in the aqueous phase) and described the rate of extraction by an equation of the type

$$-\frac{d[M]_w}{dt} = \varkappa [M]^m \ [A]^n , \qquad (3)$$

where [M] is the analytical concentration of the element being extracted, [A] the concentration of the extractant anions in the aqueous phase when the extractant is an acid HA, and κ the rate constant for the reaction determining the rate of extraction. Under these conditions, one frequently employs trace amounts of the compound (element) being extracted and for this reason [A] in a given experiment at constant pH is itself constant. Then Eqn. (3) can be put in the form

$$-\frac{d[M]_w}{dt} = \varkappa' [M]_w^m , \qquad (4a)$$

where $\kappa' = \kappa[A]^n$ and $[A] = K_{HA}[HA]_0/q_{HA}[H^+]$, $[HA]_0$ being the concentration of the acid HA in the organic phase, q_{HA} is the partition coefficient, and K_{HA} the dissociation constant. If $m = 1$, integration of Eqn. (4a) yields

$$\ln \frac{[M]_w}{[M]_w^0} = -\varkappa' t , \qquad (4b)$$

where $[M]_w^0$ is the initial concentration of M in the aqueous phase. If $m > 1$, then integration gives

$$\frac{1}{[M]_w^{m-1}} - \frac{1}{([M]_w^0)^{m-1}} = (m-1)\ \varkappa' t . \qquad (4c)$$

These equations make it possible to find m and κ' for the given value of [A] by varying t. Assuming that m is constant and having determined κ' for different concentrations of the extractant [A], it is possible to find κ and n. For example, it was established in this way that in the extraction of zinc from aqueous solutions of its salt by dithizone solutions in organic solvents, $m = 1$ and $n = 1$ and therefore the authors[38] suggest that the rate of extraction is determined by the rate of the reaction $Zn^{2+} + A^- \rightleftharpoons ZnA^+$, while the reaction $ZnA^+ + A^- \rightleftharpoons ZnA_2$ and mass transfer are rapid. The extraction mechanisms have been determined similarly also in other investigations[39-46]. However Eqns. (4a), (4b), and (4c) do not reflect the essential property of extraction—its reversibility. It follows from these equations that, when t tends to infinity, $[M]_w$ tends to zero and the plot of $\ln\{[M]_w/[M]_0\}$ as a function of t will be linear up to infinity, although it is evident that, under the specified conditions, $\ln\{[M]_w/[M]_w^0\}$ will approach a limit equal to $\ln\{[M]_{w,e}/[M]_w^0\}$, where $[M]_{w,e}$ is the equilibrium concentration.

In addition, the equations quoted above include the analytical concentration of the element M in the aqueous phase, although the latter contains its various species, namely complex ions and molecules. Thus in the example quoted the ions and the species ZnA^+ and ZnA_2 exist in the aqueous phase, which follows from the hypothesis, adopted in the study quoted, that the processes take place in steps. In the extraction of acids and salts from solutions, complexes with the corresponding ions are formed in the aqueous phase and for this reason the concentration of the cations of M or of any compounds involved in the reaction determining the rate of extraction can differ significantly from the analytical concentration of the element M. For example, in a study[47] of the rate of extraction of beryllium

by thenoyltrifluoroacetone (TTA) from a mixture of hydrochloric and perchloric acids (with a constant overall concentration) the equation for the rate of extraction was put in the form $-d[Be^{2+}]/dt = K^*[Be]^a[HA]_o^b[H^+]^c[ClO_4^-]^d$, where $[HA]_o$ is the concentration of TTA in the organic phase, $K^* = \kappa K_A/D$, K_A the dissociation constant of TTA, D its partition coefficient, and κ the reaction rate constant. The concentration of ClO_4^- ions has been included in the equation, since it has been established that the rate of extraction increases with increase in the concentration of perchloric acid (and with the corresponding decrease in hydrochloric acid concentration). To account for this dependence, the authors suggest that beryllium perchlorate passes to the organic phase where it is very rapidly converted into the thenoyltrifluoroacetonate and perchloric acid is also rapidly re-extracted. However, beryllium chloride complexes are formed in the aqueous solution (the authors quote the stability constants) and therefore the analytical concentration is not equal, for example, to the concentration of Be^{2+} ions and the rate equation must include the concentration of those beryllium cations or complex ions directly involved in the reaction determining the rate of extraction and not the analytical concentration of beryllium. In particular, when TTA reacts with Be^{2+} ions, the concentration of the latter must increase with increase of the concentration of perchloric acid, since the concentrations of chloride ions and beryllium chloride complexes then decrease.

It has been noted in the literature that complex formation can decrease the rate of extraction[40]†. In particular it has been shown[48] that, in the extraction of zinc by dithizone, the introduction of chloride ions into the aqueous phase reduces the rate of extraction and increases the rate of re-extraction. However, the introduction of certain substances to the aqueous phase sometimes increases the rate of extraction. For example, the extraction of iron by thenoyltrifluoroacetone is slow, but the introduction of ammonium thiocyanate into the aqueous phase increases its rate[49]. In the extraction of chromium by TTA or hydroxyquinoline, sodium acetate[50], ammonium fluoride, and other compounds[51-53] have a similar effect. These examples show that the rate of extraction is not determined by the analytical concentration of the element being extracted and the expression for the rate of extraction in terms of the latter constitutes only an empirical description of the process and does not yield information about the mechanism of extraction.

Finally, in the investigations quoted no account is taken of the fact that each phase is an open system and therefore a change in the concentrations of certain compounds is caused not only by a chemical reaction but also by the transfer of compounds from one phase to another. Problems associated with the rate of reactions in open systems have been considered in the literature[4,54], but usually for processes in flow-type apparatus of different kinds and not for extraction.

In this connection, the mechanism of extraction under kinetic conditions with complex formation in the aqueous phase has been examined in greater detail, in particular for complex formation involving the extractant or its ions. An acid HA was employed as the extractant and it was assumed for simplicity that complex anions involving A^- are not formed in the aqueous phase (this does not alter the general approach to the problem, but reduces the number of parameters introduced into the corresponding equations) and in the organic phase there are no solvates formed by the extractant with the salt being extracted. We shall restrict the treatment to reactions in the bulk of the aqueous phase and in the first place to the extraction of trace amounts of the corresponding substance; also we shall disregard the use of isotope exchange for this purpose, which has been briefly described already[55].

Some results of such analysis have already been published[56,57]; this review gives a systematic description of the problem and a number of possible mechanisms, which were not analysed previously, are discussed.

II. ONE SLOW REACTION WITH THE EXTRACTANT (AN ACID HA) IN THE AQUEOUS PHASE

We shall consider the determination of the rate of extraction under kinetic conditions in the case of one slow reaction of the metal being extracted, forming the ions M^{3+} in the aqueous phase, with the extractant (an acid HA) under conditions such that the rate of reaction is determined by the concentrations of the reactants (the activity coefficients are virtually unity). The molecules MA_3 formed in the aqueous phase pass to the organic phase. In the general case the flux of the molecules MA_3 from the aqueous to the organic phase is

$$j = K_w([MA_3]_w - [MA_3]_w^*) \quad , \qquad (5)$$

where $[MA_3]_w$ is the concentration of these molecules in the aqueous phase and $[MA_3]_w^*$ the concentration which must occur in this phase at a given instant to ensure its equilibrium with the organic phase. Then $[MA_3]_w^* = [MA_3]_o/q_{MA_3}$, where q_{MA_3} is the partition coefficient of the compound MA_3, $[MA_3]_o$ the concentration of MA_3 in the organic phase, and K_w the mass transfer coefficient referred to the aqueous phase‡. We believe that the mass-transfer coefficient of a specific compound as well as its partition coefficient are independent of phase composition (concentrations of the components) over a fairly wide concentration range; for this reason, the driving force of the mass-transfer process can be expressed in terms of the concentrations as $[MA_3]_w - [MA_3]_w^*$. This is confirmed by the determinations of a number of mass transfer coefficients for compounds which remain unchanged in extraction[58,59]. However, under kinetic conditions there is virtually an equilibrium between the phases with respect to the compound MA_3, so that the driving force of the process is extremely small, but the mass transfer coefficient is very high (in the limit the driving force is zero and the mass transfer coefficient is infinite). The flux is a finite quantity determined by the rate of reaction.

The necessity to determine the rate from the variation of the analytical concentration of the element extracted in one or both phases constitutes a difficulty in the employment of trace amounts of the element. In the extraction of macroamounts it is possible to determine the concentrations of individual compounds by physical methods, for example by spectrophotometry, NMR, etc., but we have been unable to find examples of such studies in relation to the rate of extraction. Moreover, when the concentrations of individual compounds cannot be determined in the

† The same investigation quotes a number of references to other publications where the effect of complex formation on the rate of extraction is also noted.

‡ Eqn. (5) is also used in the form $j = K_o\{[MA_3]_o^* - [MA_3]_o\}$, where $K_o = K_w/q_{MA_3}$ is the mass transfer coefficient referred to the organic phase.

extraction of macroamounts, the number of variables increases, which, as shown below, makes it difficult to interpret the experimental results.

We examined previously[56,57] the effect of the rate of complex formation on the rate of extraction of trace amounts of an element M^{3+} by an acid HA under kinetic conditions when the reactions occur in the aqueous phase and the rate of extraction is determined by the rate of one of three reactions:

$$M^{3+} + A^- \underset{\varkappa_2}{\overset{\varkappa_1}{\rightleftarrows}} MA^{2+} , \quad (I)$$

$$MA^{2+} + A^- \underset{\varkappa_4}{\overset{\varkappa_3}{\rightleftarrows}} MA_2^+ , \quad (II)$$

$$MA_2^+ + A^- \underset{\varkappa_6}{\overset{\varkappa_5}{\rightleftarrows}} MA_3 . \quad (III)$$

The other two reactions and mass transfer are very rapid ("instantaneous"), so that they reach equilibrium at any instant. It is then assumed that the effect of the rate of mass transfer of the acid HA and of the rate of its dissociation is eliminated by the fact that the phases are equilibrated with respect to the macrocomponents, including the extractant, and the changes in their concentrations may be neglected when trace amounts of the element extracted are employed§.

The processes occurring in the system are described by the equations

$$-\frac{d[M^{3+}]}{dt} = \varkappa_1[M^{3+}][A^-] - \varkappa_2[MA^{2+}] , \quad (6a)$$

$$\frac{d[MA^{2+}]}{dt} = \varkappa_1[M^{3+}][A^-] - \varkappa_2[MA^{2+}] - \varkappa_3[MA^{2+}][A^-] + \varkappa_4[MA_2^+] , \quad (6b)$$

$$\frac{d[MA_2^+]}{dt} = \varkappa_3[MA^{2+}][A^-] - \varkappa_4[MA_2^+] - \varkappa_5[MA_2^+][A^-] + \varkappa_6[MA_3]_w , \quad (6c)$$

$$\frac{d[MA_3]_w}{dt} = \varkappa_5[MA_2^+][A^-] - \varkappa_6[MA_3]_w - \frac{V_o}{V_w}\cdot\frac{d[MA_3]_w}{dt} , \quad (6d)$$

where the last term on the right-hand side corresponds to the rapid transfer of part of MA_3 to the organic phase. We have

$$\frac{d[MA_3]_o}{dt} = q_{MA_3}\cdot\frac{d[MA_3]_w}{dt} , \quad (7)$$

where V_W and V_O are the volumes of the aqueous and organic phases.

Since only one reaction is slow and the others are rapid, equilibrium is established in the latter. For example, when reaction (I) is slow, there is at any instant equilibrium in the formation of MA_2^+ from MA^{2+} and A^- and of MA_3 from MA_2^+ and A^-. This makes it possible on the basis of Eqns. (6) and (7) to express the time dependence of the analytical concentration of M in one of the phases (for example the aqueous phase) in terms of the rate constant for the reaction which determines the rate of the process, the equilibrium constants for the complex formation reaction and the dissociation of the acid, and also the partition coefficients of the acid and MA_3.

Several different methods for the investigation of extraction kinetics are possible. For example, an element M can be introduced in microamounts into the aqueous phase of specified composition in equilibrium with the organic phase. In this case the aqueous phase does not initially contain the compound extracted (MA_3).

§ For this reason the concentration of the anions A^- is $[A^-] = K_{HA}[HA]_o/q_{HA}[H^+]$, where K_{HA} is the dissociation constant of the acid, q_{HA} its partition coefficient, and $[H^+]$ the concentration of hydrogen ions (constant in each experiment).

If, for example, reaction (II) is slow and reactions (I) and (III) as well as the partition of MA_3 between the phases are rapid, then at any instant

$$[MA^{2+}] = K_1[M^{3+}][A^-] , \quad (8a)$$

$$[MA_3]_w = K_3''[MA_2^+][A^-] , \quad (8b)$$

$$[MA_3]_o = q_{MA_3}[MA_3]_w = q_{MA_3}[MA_2^+][A^-]\ K_3'' , \quad (8c)$$

where K_1 and K_3'' are the stability constants of the MA^{2+} ions and MA_3 molecules. Having determined $d[MA_3]_w/dt$ and $d[MA_3]_o/dt$ from these equations, we find

$$\left(1 + K_3''[A^-] + \frac{V_o}{V_w}q_{MA_3}K_3''[A^-]\right)\frac{d[MA_2^+]}{dt} = \varkappa_3[MA^{2+}][A^-] - \varkappa_4[MA_2^+] , \quad (9)$$

since in the extraction of trace amounts of the element $[A^-]$ is constant.

The analytical concentration in the aqueous phase at any instant is

$$C_w = [M^{3+}] + [MA^{2+}] + [MA_2^+] + [MA_3]_w = \frac{[MA^{2+}]}{K_1[A^-]} + [MA_2^+] + [MA^{2+}] + K_3''[MA_2^+][A^-] . \quad (10)$$

This equation makes it possible to express the concentration $[MA^{2+}]$ in terms of C_W and $[MA_2^+]$ and since

$$[MA_2^+] = \frac{[MA_3]_w}{K_3''[A^-]} = \frac{[MA_3]_o}{q_{MA_3}K_3''[A^-]} = \frac{V_w(C_w^0 - C_w)}{V_o q_{MA_3}\cdot K_3''[A^-]} ,$$

where C_W^0 is the initial concentration of M^{3+} in the aqueous phase, it follows that, having determined $d[MA_2^+]$ from this equation and having substituted $[MA_2^+]$ and $d[MA_2^+]/dt$ in Eqn. (9), we find after appropriate rearrangements

$$-\frac{dC_w}{dt} = a_2C_w - b_2C_b^0 , \quad (11)$$

where

$$a_2 = \frac{\varkappa_3[A^-]\left\{\frac{V_o}{V_w}K_3''[A^-]\,q_{MA_3} + K_3''[A^-] + 1 + \frac{\varkappa_4}{\varkappa_3[A^-]}\left(1 + \frac{1}{K_1\cdot[A^-]}\right)\right\}}{\left(1 + \frac{1}{K_1[A^-]}\right)\left(1 + K_3''[A^-] + \frac{V_o}{V_w}q_{MA_3}K_3''[A^-]\right)} . \quad (12a)$$

since $\varkappa_4/\varkappa_3[A^-] = [MA^{2+}]_e/[MA_2^+]_e$, where the subscripts "e" denotes equilibrium concentrations, it follows that, having substituted this value in Eqn. (12a), having multiplied the numerator and denominator by $[MA_2^+]$, and having used Eqns. (8a), (8b), and (8c), we obtain

$$a_2 = \frac{\varkappa_3[A^-](V_o[MA_3]_{o,e} + V_w[MA_3]_{w,e} + V_w[MA_2^+]_e + V_w[MA^{2+}]_e + V_w[M^{3+}]_e}{\left(1 + \frac{1}{K_1[A]}\right)(V_w[MA_2^+]_e + V_w[MA_3]_{w,e} + V_o[MA_3]_{o,e})} = \frac{\varkappa_3K_1[A^-]^2\ C_w^0}{(K_1[A^-] + 1)\ (C_w^0 - [MA^{2+}]_e - [M^{3+}]_e)} . \quad (12b)$$

The quantity b can be found similarly, but it is determined more simply from the condition that at equilibrium $dC_W/dt = 0$, so that

$$b_2 = \frac{a_2\ C_{w,e}}{C_w^0} . \quad (13)$$

A similar derivation of the equations was made earlier[56,57] for a system with equal phase volumes. The same equation for the coefficient a was obtained when reaction (II) was slow. The rate of extraction is also described by Eqn. (11) when reaction (I) or (III) is slow, but the corresponding coefficients are

$$a_1 = \frac{\varkappa_1\ [A^-]\ C_w^0}{C_w^0 - [M^{3+}]_e} \quad (14)$$

for reaction (I) and

$$a_3 = \frac{\varkappa_3 K_2' K_2 [A^-]^3 C_w^0}{(K_2' + K_2[A^-] + K_2 K_2' [A^-]^2)(C_w^0 - [M^{3+}]_e - [MA^{2+}]_e - [MA_2^+]_e)} \quad (15)$$

for reaction (III).

In these equations

$$K_2 = \frac{[MA_2^+]}{[M^{3+}][A^-]}, \qquad K_2' = \frac{[MA_2^+]}{[MA^{2+}][A^-]} .$$

The volumes of the phases enter into equations in which the rate constant ratio has not been replaced by the ratio of the equilibrium concentrations [Eqn. (12a)]. In Eqns. (12b), (14), and (15) the change in phase volumes alters the equilibrium concentrations.

Integration of Eqn. (11) yields

$$\ln \frac{C_w - C_{w,e}}{C_w^0 - C_{w,e}} = -at , \quad (16)$$

where a is defined by one of the Eqns. (12b), (14), and (15) and $C_{w,e}$ is the analytical equilibrium concentration of M in the aqueous phase.

It follows from Eqn. (16) that, when $C_{w,e} \ll C_w$ and particularly when $C_{w,e} \ll C_w^0$, it is converted into Eqn. (4b) but the coefficient a is not equal to κ_1'. In particular, a more complex dependence of the rate of extraction on the anions A^- will be observed than would follow from the expression for κ'. For example, when the rate of extraction is determined by the rate of reaction (II), then a_2 will be proportional to $[A^-]^2$ only when $K_1[A^-] \ll 1$ and $\{[MA^{2+}]_e + [M^{3+}]_e\} \ll C_w^0$. If $K_1[A^-] \gg 1$ but the second of the above conditions holds, then a_2 will be proportional to $[A^-]$ and therefore one can reach the erroneous conclusion that the rate is determined by reaction (I).

It follows from Eqn. (11) that $-dC_w/dt = C_w - C_{w,e}$ and therefore in the general case the rate of extraction cannot be of first order with respect to C_w, must be of first order with respect to $C_w - C_{w,e}$, and the first order with respect to C_w, established in the studies quoted here and in others[60], will be observed only when $C_w \gg C_{w,e}$. The observed first order with respect to C_w can be explained by the fact that the authors of many investigations restricted their treatment to the linear part of the time variation of $\ln(C_w/C_w^0)$, which is insufficient to deduce the extraction mechanism.

If the rate of extraction is determined by the rate of the reaction

$$M^{3+} + 2A^- \underset{\varkappa_6}{\overset{\varkappa_7}{\rightleftarrows}} MA_2^+ ,$$

it is also described by Eqn. (16), but in this case

$$a' = \frac{\varkappa_7 [A^-]^3 C_w^0}{C_w^0 - [M^{3+}]_e} \quad (17)$$

and therefore, when $[M^{3+}] \ll C_w^0$, the same variation with the concentration of the anions A^- (derived from the acid HA) will be observed as for reaction (II) when $K_1[A^-] \ll 1$ [Eqn. (12b)].

Thus the observation that the reaction is of second order with respect to the extractant, in accordance with Eqns. (12b) and (17), as was done, for example, by McClellan and Freiser[41] and Bodnya and Alimarin[61], does not allow one to decide whether the slow reaction is the addition of a second ligand (a bimolecular reaction) or whether the metal ion combines immediately with two anions (a trimolecular reaction).

In those cases where the system contains a complex-forming agent X and the equilibria in the reactions $MX_i + X = MX_{i+1}$ are established very rapidly (they do not affect the rate of extraction) and there are no mixed complex ions or molecules MX_iA_j, the following expressions hold for reactions (I)–(III) when the phase volumes are equal:

$$a_1 = \frac{\varkappa_1 [A^-] C_w^0}{(1 + f_o)\{C_w^0 - [M^{3+}]_e (1 + f_o)\}} , \quad (18a)$$

$$a_2 = \frac{\varkappa_3 K_1 [A^-]^2 C_w^0}{(\bar{K}_1 [A^-] + f_o + 1)\{C_w^0 - [M^{3+}]_e (1 + f_o) - [MA^{2+}]_e\}} , \quad (18b)$$

$$a_3 = \frac{\varkappa_5 \bar{K}_2' K_2 [A^-]^3}{(\bar{K}_2 [A^-] + \bar{K}_1 [A^-] + f_o + 1)\{C_w^0 - M^{3+}]_e (1 + f_o) - [MA^{2+}]_e - [MA_2^+]_w\}} , \quad (18c)$$

where $f_O = \sum_1^i \beta_i [X]^i$ and $\beta_i = [MX_i]/[M][X]^i$ are the stability constants of the complexes MX_i.

In the extraction by an acid HA of a bivalent metal, with formation of MA^+ and MA_2 in the aqueous phase, the rate of extraction corresponding to the partition of the molecules MA_2 is also characterised by Eqn. (16). If the slow reaction is M + A = MA and the phase volumes are equal, then

$$a_1 = \frac{\varkappa_1 [A^-] C_w^0}{C_w^0 - [M^{3+}]_e} , \quad (19a)$$

On the other hand, if the slow reaction is MA + A = MA_2, then

$$a_2 = \frac{\varkappa_3 K_1 [A^-]^2 C_w^0}{(K_1 [A^-] + 1)(C_w^0 - [MA^{2+}]_e - [M^{3+}]_e)} , \quad (19b)$$

where K_1 is the equilibrium constant for the reaction $M^{2+} + A^- = MA^+$. For a large partition coefficient, when $C_w^0 \gg C_{w,e}$ and $C_w^0 \ll [MA^+]_e + [M^{2+}]_e$ and especially $C_w^0 \gg [M^{2+}]_e$, the rate of extraction is in both cases described by the same equation $\ln(C_w/C_w^0) = -\kappa[A^-]$, where κ can be either κ_1 or κ_3, provided that the condition $K_1[A^-] \gg 1$ holds. Thus, in order to deduce the mechanism of the reaction determining the rate of extraction, it is necessary to know the composition of the compounds existing in each phase and also their stability constants. The knowledge of these constants is necessary also for the choice of conditions which allow one to distinguish the possible reactions. Thus, in the extraction of a bivalent metal under consideration, the determination of the nature of the reaction taking place requires a concentration of the anion A^- such that the condition $K_1[A^-] \ll 1$ hold but the concentration of the extractant greatly exceeds that of the element being extracted (to ensure the condition that only trace amounts of the latter are extracted). Such conditions in the extraction by an acid HA can be created by carrying out the extraction from a fairly acid solution, assuming that the concentration of the anions A^- is much higher than the analytical concentration of the element M or that the acid dissociates very rapidly.

Thus the conclusion[62] that extraction can serve as a method for the investigation of very rapid reactions is valid (a low concentration of the interacting components ensures a rate suitable for measurement), but the determination of the reaction mechanism from measurements of the rate of extraction is extremely difficult.

It follows from Eqn. (16) that, at a given concentration of HA in the case of a single slow reaction, the quantity $\ln[(C_w - C_{w,e})/(C_w^0 - C_{w,e})]$ is a linear function of time, as under diffusion-dependent conditions with constant partition and mass transfer coefficients. The difference between these processes is that a change in the rate of stirring and in the area of the interface does not alter the rate of extraction under kinetic conditions but does change it under diffusion-dependent or mixed conditions.

In the extraction of molybdenum in different valent states from a hydrochloric acid solution by solutions of oxine, acetylacetone, and other extractants in chloroform, the authors[63] assumed that it is possible to ignore the reversibility of the process and to characterise the rate of extraction by the degree reaction which they believe to be $F = q_t/q_p = 1 - e^{-\kappa_1' t}$, where $q_t = C_O/C_W$ is the ratio of the concentrations at any instant, q_p is the partition coefficient (the ratio of the equilibrium concentrations), and $\kappa_1' = \kappa_1[A^-]$, assuming that the rate of extraction is determined by the rate of formation of the ions MA^+. We believe that the degree of reaction must be characterised by the fraction of substance which has reacted relative to the overall amount which can react, for example by the quantity $F = C_O/C_{O,e} = (C_W^0 - C_W)/(C_W^0 - C_{W,e})$ (only then is the degree of reaction zero at the initial instant and unity at equilibrium). Indeed, it follows from Eqn. (16) that $F = 1 - e^{-at}$, but

$$F = \frac{C_o}{C_{o,e}} = \frac{q_t}{q_e} \cdot \frac{C_w}{C_{w,e}} \neq \frac{q_t}{q_e} \quad .$$

This can explain the authors' observation in a number of experiments of a discrepancy between the experimental results and the proposed equation.

In the study of the rate of extraction of trace amounts of the extractable compound the process can be achieved in another way: the phases must be equilibrated with the microcomponents, separated, and the aqueous phase must be brought into contact with the organic phase obtained in the same way but without the element to be extracted (extraction); the organic phase containing the extractable element is brought into contact with the aqueous phase without the compound (re-extraction). The same process can be carried out by equilibrating initially the phases without the extractable compound and separating them, after which, having introduced into the aqueous phase trace amounts of the element to be extracted without altering the composition of the phases with respect to the macrocomponents (a very small volume of the solution with the extractable element is employed), the phase is allowed to stand until equilibrium is reached, after which the phases are again brought into contact.

In contrast to the methods described previously, in this case all the compounds already exist in the aqueous phase at the instant of contact between the phases and are in equilibrium with the extractant. Therefore under kinetic conditions the quantity q_t will be non-zero at $t = 0$ and in the plot of its time variation will tend to a finite quantity when t tends to zero. A similar phenomenon was observed, for example, in a study[50] involving a "side" reaction in the course of the extraction of antimony from hydrochloric acid solutions by alcohols.

However, in certain investigations where the phases were initially equilibrated without the extractable element and the latter was then introduced into the aqueous phase[39,40], the authors state that the solution was adjusted to the required pH directly before extraction but they did not estimate the effect of the change in the hydrogen ion concentration on the partition coefficient of the extractant. When such an effect obtains, the concentration of the extractant can vary in the course of extraction, but this was disregarded in the experiments.

The introduction of the extractant, for example an acid HA, into the aqueous phase with subsequent extraction by the pure solvents constitutes a modification of the method described. Thus, it has been found[64] that in the extraction of indium by solutions of 1-(2-pyridylazo)-2-naphthol in chloroform, equilibrium is established in 45—50 min. When this extractant is added in the form of an alcoholic solution to the aqueous phase and the latter is then shaken with chloroform, a high initial degree of extraction is rapidly reached; however, it gradually diminishes and equilibrium is established in 30—35 min. In this case there is initially a partition of both the compound formed and of the extractant and the decrease of the concentration of the latter in the aqueous phase disturbs the equilibrium, which leads to the dissociation of the extractable compound in this phase and hence to its re-extraction from the organic phase. Such a process can be used to determine the rates of the reactions occurring, provided that it has been shown that kinetic conditions obtain.

In the case of extraction of a tervalent element by an acid HA in which the aqueous phase is equilibrated with the organic phase without the extractable element, the phases are separated, the extractable element is introduced into the aqueous phase, and the latter is allowed to stand until the attainment of equilibrium in it, the initial analytical concentration of the extractable element in the aqueous phase is

$$C_{w(init)} = [M^{3+}]_{int} + [MA^{2+}]_{int} + [MA_2^+]_{int} + [MA_3]_{int} \quad , \qquad (20)$$

where the subscript "init" shows that the concentrations refer to the initial aqueous solution in equilibrium with the organic phase used in the experiment with respect to the extractant (the acid HA).

As a result of the "instantaneous" distribution of the molecules MA_3 between the phases, in the initial instant of the extraction their concentration in the organic phase is $[MA_3]_O^0 = q_{MA_3}[MA_3]_W^0$, and for equal phase volumes we have

$$[MA_3]_{int} = [MA_3]_o^0 + [MA_3]_w^0 = [MA_3]_w^0(q_{MA_3} + 1) = \frac{[MA_3]_o^0(q_{MA_3} + 1)}{q_{MA_3}} \cdot \qquad (21)$$

Under these conditions, the rate of extraction is also characterised by Eqn. (11) but $C_{W(init)}$ enters into the coefficient a instead of C_W^0. The derivation of the equation for the rate of extraction in the system under consideration is similar to that quoted above.

Thus the linear time variation of $\ln[(C_W - C_{W,e})/(C_W^0 - C_{W,e})]$ under kinetic conditions and the experimental conditions adopted shows that the rate of extraction may be determined by one slow reaction (below it will be shown that, for two reactions at comparable rates, the corresponding relation is not linear). The coefficient a can be found from the slope of the resulting straight line, but, in order to deduce the mechanism of the reaction determining the rate of extraction and to determine its rate constant, it is necessary to know the stability constants of the compounds existing in the given system, which may make the solution of the problem significantly more difficult. For example, in the extraction of iron from perchloric acid solutions with acetylacetone, it is essential to know the stability constants of the complex ions and molecules FeA^{2+}, FeA_2^+, and FeA_3. However, the data published in different studies for these constants differ appreciably. Thus, according to Badoz-Lambling[65], at zero ionic strength the dissociation constants of these ions are $K_1 = 3 \times 10^{-12}$, $K_2 = 8 \times 10^{-23}$, and $K_3 = 2 \times 10^{-27}$; according to Izatz et al.[66], $K_1 = 1.6 \times 10^{-10}$, $K_2 = 1.6 \times 10^{-19}$, and $K_3 = 6.4 \times 10^{-27}$. Bearing in mind that the dissociation constant of acetylacetone is 1.12×10^{-9} litre mole^{-1}, the difference between the complex formation constants will lead to a considerable difference between the equilibrium concentrations entering into the equations

for a, which hinders the choice of the appropriate mechanism.

However, when the slow stage determining the rate of extraction is the formation of the extractable compound (MA_3 in the extraction of a tervalent element or MA_2 in the extraction of a bivalent element), the coefficient a can be calculated from the experimental equilibrium data without knowing the constants. Then

$$C^0_w - [M^{3+}]_e - [MA^{2+}]_e - [MA_2^+] = C^0_w - (C_{w,e} - [MA_3]_{w,e}) = C_{o,e} + \frac{C_{o,e}}{q_{MA_3}} = \frac{C_{o,e}(q_{MA_3}+1)}{q_{MA_3}}$$

$$K_3' K_2 [A^-]^3 + K_2 [A^-] + K_2^+ \left(K_2 [A^-]^2 + \frac{K_2 [A^-]}{K_2'} + 1 \right) =$$

$$= K_2' \left(\frac{[MA_2^+]_e}{[M^{3+}]_e} + \frac{[MA^{2+}]_e}{[M^{3+}]_e} + 1 \right) = \frac{K_2'}{[M^{3+}]_e} ([MA_2^+]_e + [MA^{2+}]_e + [M^{3+}]_e) =$$

$$= \frac{K_3'}{[M^{3+}]_e} (C_{w,e} - [MA_3]_{w,e}) = \frac{K_2'}{[M^{3+}]_e} \left(C_{w,e} - \frac{C_{o,e}}{q_{MA_3}} \right) = \frac{K_2' \cdot C_{w,e}}{[M^{3+}]_e} \left(1 - \frac{q_p}{q_{MA_3}} \right),$$

where $q_p = C_{o,e}/C_{w,e}$ is the partition coefficient and $C_{o,e}$ and $C_{w,e}$ are the analytical equilibrium concentrations.

On substituting these values in Eqn. (15) and on replacing C^0_w by $C_{w,e}(q_p + 1)$, we obtain after rearrangement

$$a_3 = \frac{\varkappa_3 K_2 (q_p + 1)}{K_3 (q_{MA_3} + 1) \left(1 - \frac{q_p}{q_{MA_3}} \right)}, \qquad (22)$$

where

$$K_3 = \frac{[MA_3]_{w,e}}{[M^{3+}]_e [A^-]^3} = \frac{C_{o,e}}{q_{MA_3} [M^{3+}]_e [A^-]^3}. \qquad (23)$$

Assuming that the rate constants and the stability constants of the complex ions are constant, it is possible to find the ratio of the coefficients a_3 in two experiments at different concentrations of the acid HA. It follows from Eqn. (22) that this ratio is

$$\frac{a_3'}{a_3''} = \frac{(q_p' + 1)(1 - q_p''/q_{MA_3})}{(q_p'' + 1)(1 - q_p'/q_{MA_3})}. \qquad (23a)$$

Thus, when the partition coefficient of MA_3 molecules is known and the partition coefficient q_p has been found experimentally, it is possible to test whether the ratio of the coefficients a_3 is consistent with Eqn. (23a) and whether reaction (III) determines the rate of extraction. When the experiments are performed at a low concentration of the acid HA or at a fairly high acidity, $q_p \ll q_{MA_3}$ so that Eqn. (23a) assumes the form

$$\frac{a_3'}{a_3''} = \frac{q_p' + 1}{q_p'' + 1}. \qquad (23b)$$

For the extraction of a bivalent metal, we obtain similarly

$$a_2 = \frac{\varkappa_2 K_1}{K_2} \frac{(q_p + 1)}{(q_{MA_2} + 1)(1 - q_p/q_{MA_2})}, \qquad (24)$$

where K_1 is the stability constant of the ion MA^+ and K_2 is the overall stability constant of MA_2 molecules (dissociation into simple ions).

If reaction (I) or (II) is slow in the extraction of a tervalent metal or the former is slow in the extraction of a bivalent metal, it is necessary to know the stability constants of the compounds formed in order to deduce the mechanism.

The concentrations of the anions A^-, which are determined under the specified conditions (specified microconcentrations of the extractable element) from the equation $[A^-] = K_{HA}[HA]_o/[H^+]q_{HA}$, where $[HA]_o$ is the concentration of the acid in the organic phase, enter into the above equations for the coefficient a. The equation for $[A^-]$ can be used to determine the variation of the rate of extraction with hydrogen ion concentration for a constant value of $[HA]_o$. If the ionic strength hardly changes with hydrogen ion concentration and the degree of dissociation of the acid in the aqueous phase is very low, then its dissociation constant and the partition coefficient will not vary. Evidently, when there are no reactions in the system involving H^+ of OH^- ions (for example hydrolysis reactions), then, on applying Eqn. (4a), the rate constant κ_1 will include the hydrogen ion concentration raised to the power n, where n is the number of molecules of the acid HA or the ions A^- involved in the corresponding reaction. However, when Eqns. (12b), (14), and (15) are applied, the coefficients a will vary in a more complex manner with hydrogen ion concentration, since the latter determines not only the concentration of the anions A^- but also the equilibrium concentrations $[M^{3+}]_e$, $[MA^{2+}]_e$, etc.

A significant difference between the reaction orders with respect to the extractant and hydrogen ions has been noted, for example, in the extraction of nickel and cobalt by dithizone derivatives. It has been found[41] that, when Eqn. (4a) is employed, the order is 1.35 and 1.53 with respect to the extractant and 0.73 and 0.75 with respect to hydrogen. On the other hand, the corresponding values for zinc are 1.91 and 1.71.

The variation of the rate of extraction with hydrogen ion concentration is regarded[67] as evidence that the reaction determining the rate of extraction proceeds in the aqueous phase. This is true if the partition coefficient of the acid is independent of hydrogen ion concentration.

In the above scheme of reactions (I)—(III) occurring in extraction it was assumed that there is interaction with the anions of the acid HA, but one can also postulate the interaction with its molecules. For example, whereas it has been assumed in some studies[49,64,68,70] that in the interaction of Fe^{3+} ions with thenoyltrifluoroacetone there is a slow reaction of these ions with enolate ions, in the analogous reaction with acetylacetone the interaction with the molecules in the keto-form[71], and in another investigation[72] with both forms, was postulated.

Thus, in order to deduce the extraction mechanism, it is necessary to consider the possibility of, for example, the following reactions:

$$M^{3+} + HA \underset{\varkappa_2'}{\overset{\varkappa_1'}{\rightleftarrows}} MA^{2+} + H^+ \text{ (V)}, \quad MA^{2+} + HA \underset{\varkappa_4'}{\overset{\varkappa_3'}{\rightleftarrows}} MA_2^+, \qquad \text{(VI)}$$

$$MA_2^+ + HA \underset{\varkappa_6'}{\overset{\varkappa_5'}{\rightleftarrows}} MA_3 + H^+ \text{ (VII)}, \quad MA_{3_w} \rightleftarrows MA_{3_o}. \qquad \text{(VIII)}$$

Having expressed the equilibrium constants for the reactions in the form

$$K_1^* = \frac{[MA^{2+}][H^+]}{[M^{3+}][HA]_w}; \quad K_2^* = \frac{[MA_2^+][H^+]}{[MA^{2+}][HA]_w}; \quad K_3^* = \frac{[MA_2^+][H^+]^3}{[M^{3+}][HA]_w^3} \qquad \text{(25c)}$$

it is possible to show that the rate of extraction is also characterised by Eqn. (11), but the corresponding coefficients are given by

$$a_1^* = \frac{\varkappa_1'[HA]_w^0}{C_w^0 - [M^{3+}]_e} , \quad (26a)$$

$$a_2^* = \frac{\varkappa_2' K_1^* [HA]_w^2 C_w^0}{(K_1^*[HA]_w + [H^+])(C_w^0 - [M^{3+}]_e - [MA^{2+}]_e)} , \quad (26b)$$

$$a_3^* = \frac{\varkappa_3' K_2'^* K_2^* [HA]_w^3 C_w^0}{(K_2'^*[H^+]^2 + K_2''[H^+][HA]_w + K_2'^* K_2^*[HA]_w^2)(C_w^0 - [M^{3+}]_e - [MA^{2+}]_e - [MA_2^+]_e)} . \quad (26c)$$

If $C_w^0 \gg [M^{3+}]_e$, which is possible when the partition coefficients and the equilibrium constants for the corresponding reactions are high, it follows from Eqns. (14) and (26a) that

$$a_1 = \frac{\varkappa_1 K_{HA}[HA]_o}{q_{HA}[H^+]} ; \quad (27a)$$

$$a_1^* = \frac{\varkappa_1'[HA]_o}{q_{HA}} . \quad (27b)$$

Consequently, at a constant concentration of the acid HA in the organic phase, the quantity a_1 will be inversely proportional to the hydrogen ion concentration. This type of relation has been observed in certain experiments when Eqn. (4a) was used; a_1^* is independent of this concentration if q_{HA} is independent of the composition of the solution. Thus, there is a possibility of distinguishing reactions (I) and (V). However, in reactions involving HA molecules, for example with acetylacetone, there arises the problem of determining the reactive species (the enol or keto-form). There is a significant difference (depending on the hydrogen ion concentration) between the coefficients a_2 and a_2^*, but it is more difficult to analyse.

If reaction (VII) is slow, then, as in the preceding case, it is possible to show that, subject to the conditions $q_{MA_3} \gg q_p$, we have, for two experiments at the same value of $[HA]_O$,

$$\frac{a_3^{*'}}{a_3^{*''}} = \frac{[H^+]'}{[H^+]''} \cdot \frac{(q_p' + 1)}{(q_p'' + 1)} , \quad (28)$$

which makes it possible to choose one of the reactions [(III) or (VII)].

The examples quoted naturally by no means exhaust completely all the possible reactions in extraction under kinetic conditions. Thus even reaction (V) can proceed in two stages

$$M(H_2O)_x^{3+} + HA \rightleftarrows M(H_2O)_{x-i} \cdot HA^{3+} + i H_2O;$$

$$M(H_2O)_{x-i}HA^{3+} \rightleftarrows M(H_2O)_j A^{2+} + H^+ H_2O + (x - i - j - 1) H_2O$$

It has been noted in a number of studies that the rate of reactions in the aqueous phase can be determined by the rate of loss of water molecules[73,74]. In particular, in a study of the rate of formation of nickel complexes of malonic and succinic acids (in the case of a homogeneous reaction) it was established[74] that the rate of the forward reaction is determined by the rate of loss of water molecules and therefore the rate constants for this reaction are independent of the nature of the ligand, while the rate constants for the reverse reaction differ appreciably.

It has also been suggested for the reactions of zinc with dithizone quoted previously[62] that the rate depends only on the rate of elimination of water from the hydration shell. However, here the rate constant for the elimination of water is a factor of ten higher than the constant found from extraction experiments. The conclusion that the rate of reaction is determined by the rate of loss of water must be based on a comparison of the rates of the given reaction and of the exchange of water, for example on the basis of Eigen's data[73]. Such a comparison and the absence of a dependence of the rate of reaction on the nature of the ligand are probably the only means of proving that the rate is determined by the rate of loss of water.

Thus, studies on the mechanism of extraction under kinetic conditions are difficult even in the case of one slow reaction. The investigation of the corresponding reactions in a homogeneous system using physical methods permitting the determination of the concentrations of the individual compounds is important for such studies. However, if it has been shown that the process occurs under kinetic conditions and is determined by the rate of one reaction, the use of Eqn. (16) and of the empirical dependence of the coefficients a on the extraction conditions can facilitate the choice of the optimal conditions for the extraction process.

III. TWO SLOW REACTIONS WITH THE EXTRACTANT IN THE AQUEOUS PHASE

If two consecutive reactions occur at comparable rates under kinetic conditions in the aqueous phase of the given system, for example in the extraction of a bivalent metal by an acid HA,

$$M_w^{2+} + A^- \underset{\varkappa_2}{\overset{\varkappa_1}{\rightleftarrows}} MA_w^+; \quad MA^+ + A^- \underset{\varkappa_4}{\overset{\varkappa_3}{\rightleftarrows}} MA_2 ,$$

then, as shown before[75], the concentration in the aqueous phase for equal phase volumes is given by the equation

$$C_w = C_1 e^{z_1 t} + C_2 e^{z_2 t} + \frac{a_3}{a_2} , \quad (29)$$

where z_1 and z_2 are the roots of the characteristic equation $z^2 + a_1 z + a_2 = 0$;

$$a_1 = \varkappa_1[A^-]_w + \varkappa_2 + \varkappa_3 + [A^-]_w + \frac{\varkappa_4}{q_{MA_2} + 1} , \quad (30a)$$

$$a_2 = (q_{MA_2} \varkappa_1\varkappa_3[A^-]_w^2 + \varkappa_1\varkappa_3[A^-]_w^2 + \varkappa_1\varkappa_4[A^-]_w + \varkappa_2\varkappa_4)/(q_{MA_2} + 1) , \quad (30b)$$

$$a_3 = -(\varkappa_1\varkappa_3[A^-]_w^2 + \varkappa_1\varkappa_4[A^-]_w + \varkappa_2\varkappa_4) C_w^0/(q_{MA_2} + 1) , \quad (30c)$$

$$\frac{a_3}{a_2} = C_{w,e} , \quad (30d)$$

C_1 and C_2 are integration constants which, as required by Eqn. (29) satisfy the condition

$$C_w^0 = C_1 + C_2 + C_{w,e} . \quad (30e)$$

It follows from Eqns. (29) and (30d) that

$$\frac{C_w - C_{w,e}}{C_w^0 - C_{w,e}} = \frac{C_1 e^{z_1 t}}{C_w^0 - C_{w,e}} \left[1 - \frac{C_2}{C_1} e^{(z_2 - z_1)t}\right] , \quad (31)$$

and for this reason $\ln[(C_w - C_{w,e})/(C_w^0 - C_{w,e})]$ is not a linear function of time. We shall assume that $z_2 < z_1$, whereupon we have, for fairly high values of t when $(C_2/C_1)e^{(z_2 - z_1)t} \ll 1$,

$$\ln \frac{C_w - C_{w,e}}{C_w^0 - C_{w,e}} \approx z_1 t + A , \quad (32)$$

where $A = C_1(C_w^0 - C_{w,e})$. It is seen from Eqn. (32) that for high values of t the logarithmic term on the left-hand side is a linear function of time. For low values of t, the equation represents a curve whose slope diminishes with increase of t until a constant value is reached.

Thus the initial section of the relation between $\ln[(C_w - C_{w,e})/(C_w^0 - C_{w,e})]$ and time (t is small) shows whether one or more than one reaction determine the rate

of extraction in the given system under kinetic conditions.

From the linear part of the plot of $\ln[(C_W - C_{W,e})/(C_W^0 - C_{W,e})]$ as a function of t, it is possible to determine z and C_1. Knowing C_1, one can find C_2 from Eqn. (30e) and then z_2 from the curved part of the plot. The same quantities can be calculated with the aid of the coordinates of two points on the curved part of the plot by solving the resulting system of two equations.

Since $a_1 = -(z_1 + z_2)$, $a_2 = z_1 z_2$, and $a_3 = a_2 C_{W,e}$, it follows that, knowing the partition coefficient of MA_2 (q_{MA_2}) and the stability constants of the ions MA^+ and molecules MA_2,

$$K_1 = \frac{[MA^+]}{[M^{2+}][A^-]} = \frac{\varkappa_1}{\varkappa_2} \tag{33a}$$

and

$$K_2' = \frac{[MA_2]}{[MA^+][A^-]} = \frac{\varkappa_3}{\varkappa_4} , \tag{33b}$$

it is possible to find from the above equations all the rate constants (κ_1, κ_2, κ_3 and κ_4) by carrying out a series of experiments with different concentrations of the acid $[A^-]$. Since there are five equations relating the rate and equilibrium constants [Eqns. (30a), (30b), (30c), (33a), and (33b)], it is possible to determine one of the equilibrium constants (when it is unknown) from kinetic data.

Since $\ln[(C_W - C_{W,e})/(C_W^0 - C_{W,e})]$ is also a nonlinear function of time under mixed conditions, the conclusion that the deviation from linearity is due to two reactions with comparable rates requires evidence that in the given case kinetic conditions obtain.

This type of relation probably also obtains for a large number of consecutive reactions but analysis of the relevant cases is fairly difficult. A deviation from linearity will probably be observed for parallel reactions, for example for slow reactions with the extractant and a complex-forming agent present in the aqueous phase.

The rate of extraction under mixed conditions for a reaction in the bulk of one of the phases, for example the receiving phase[76], can be described similarly.

It has been found[60] for the extraction of chromium(III) from 1 N perchloric acid by acetylacetone solutions that $\ln(C_W/C_W^0)$ is a linear function of time if the latter is longer than 90 min at pH 4 and longer than 5 min at pH 7. This can be caused either by the occurrence of two reactions with the extractant (if the equilibrium concentration of chromium is much lower than its concentration at any instant whereupon the equation describes the corresponding process) or by a side reaction and a reaction with the extractant, since the specified pH was established by adding alkali directly before extraction whereby equilibrium might have been only slowly established, for example in a hydrolysis reaction. Evidently in this case the determination of the reaction order by the van't Hoff method with the aid of Eqn. (4a) employed by the authors is doubtful.

IV. EXTRACTION WITH A SIDE REACTION

The determination of the rate of extraction in the presence of a slow side reaction has been examined[77]. The following scheme was analysed: a slow reaction

$$A_W + D_W = AB_W + E_W \tag{IX}$$

takes place in the aqueous phase and only the compound A passes very rapidly to the organic phase, where it either does not change or a very rapid reaction takes place.

Microconcentrations of A are employed, while the concentrations of D and E are high and hardly change. For example, A = $HSbCl_6$, D = H_2O, AB = $HSb(OH)Cl_4$, E = HCl, the compound A being extracted by alcohols[78]. In this case the variation of the concentrations of A in the aqueous and organic phases, subject to the condition that the phase volumes are equal, is described by the equations

$$\frac{d[A^-]_W}{dt} = -\varkappa_1'[A]_W + \varkappa_2'[AB]_W - K'[A]_W + K'[A]_O , \tag{34a}$$

$$\frac{d[A]_O}{dt} = K'[A]_W - K''[A]_O , \tag{34b}$$

where $\kappa_1' = \kappa_1[D]_W$, $\kappa_2' = \kappa_2[E]_W$, κ_1 and κ_2 are the rate constants for the forward and reverse reactions, $K' = K_W S/V_W$, and S is the area of the interface.

Therefore $d[A]_W/dt + d[A]_O/dt = -\kappa_1'[A]_W + \kappa_2'[AB]_W$ and under kinetic conditions we have at any instant $[A]_O = q_A[A]_W$, where q_A is the partition coefficient of the compound A assumed to be constant.

It follows from the above equations that

$$\left(1 + \frac{1}{q_A}\right)\frac{d[A]_O}{dt} = -\varkappa_1'\frac{[A]_O}{q_A} + \varkappa_2'\left(C_W - \frac{[A]_O}{q_A}\right) , \tag{35a}$$

where $C_W = [A]_W + [AB]_W$ is the analytical concentration of A in the aqueous phase at any instant.

Since $C_W = C_{W(init)} - [A]_O$, where $[A]_O$ is the concentration of A in the organic phase, Eqn. (34a) can be put in the form

$$-\frac{dC_W}{dt} = aC_W - b , \tag{35b}$$

where

$$a = \frac{\varkappa_1' + (q_A + 1)\varkappa_2'}{q_A + 1} , \tag{36a}$$

$$b = \frac{(\varkappa_1' + \varkappa_2')C_{W(init)}}{q_A + 1} = aC_{W,e} . \tag{36b}$$

After integrating Eqn. (35b) and assuming that $C_W = C_W^0$ when $t = 0$, we obtain

$$\ln\frac{C_W - C_{W,e}}{C_W^0 - C_{W,e}} = -at . \tag{37}$$

However, under kinetic conditions when there is an equilibrium in the initial aqueous phase, $C_W^0 \neq C_{W(init)}$, where $C_{W(init)}$ is the initial concentration in the aqueous phase (concentration before contact between the phases)¶, since under these conditions part of A is very rapidly ("instantaneously") transferred to the organic phase when the phases come into contact. For this reason, in the initial instant of extraction the following condition holds: $C_{W(init)} = C_W^0 + [A]_O^0$, where $[A]_O^0$ is the concentration of A in the organic phase in the initial instant of the extraction process (at $t = 0$). Hence, when t tends to zero, $[A]_O$ does not tend to zero but to a value $[A]_O^0$.

C_W^0 and $[A]_O^0$ can be found from the conditions for equilibrium in the initial aqueous solution and for equilibrium in the partition of A at the starting point. Indeed at equilibrium in the initial aqueous solution $C_{W(init)} = [A]_{W(init)} + [AB]_{W(init)} = (1 + \tilde{K}')[A]_{W(init)}$, where $\tilde{K}' = \tilde{K}[D]_W/[E]_W$ and $\tilde{K}$ is the equilibrium constant for reaction

¶ In the paper by one of the present authors[77] $C_{W(init)}$ is designated by C_W^0 and the concentration at $t = 0$ (after the instantaneous distribution of the extractable species) by $C_{W(t=0)}$.

(IX) under consideration. When A is distributed between the phases, we have at the starting point

$$[A]_{w(init)} = [A]^0_w + [A]^0_o = \frac{[A]^0_o}{q_A} + [A]^0_o = \left(\frac{1}{q_A} + 1\right)[A]^0_o .$$

Therefore

$$[A]^0_o = \frac{[A]_{w(init)}}{\left(\frac{1}{q_A}+1\right)} = \frac{C_{w(init)}}{(1+\tilde{K}_1)\left(\frac{1}{q_A}+1\right)}\ ;\ C^0_w = C_{w(init)} - [A]^0_o = \frac{\left(\frac{1}{q_A} + \frac{\tilde{K}'}{q_A} + \tilde{K}'\right)C_{w(init)}}{\left(\frac{1}{q_A}+1\right)(1+\tilde{K}')} .$$

The analytical partition coefficient $q_p = [A]_{o,e}/C_{w,e}$, where $C_{w,e}$ is the analytical concentration of A in the equilibrium aqueous phase but $C_{w,e} = [AB]_{w,e} + [A]_{w,e} = (\tilde{K}' + 1)[A]_{w,e}$, so that

$$q_p = \frac{[A]_{o,e}}{(\tilde{K}'+1)[A]_{w,e}} = \frac{q_A}{\tilde{K}'+1},\ \text{a}\ C^0_w = \left(\tilde{K}' + \frac{1}{q_p}\right)q_p\ \ C_{w,e} = \left(\tilde{K}' + \frac{1}{q_p}\right)[A]_{o,e} .$$

One must bear in mind that C^0_w can be found from experimental data (even if $\tilde{K}'$ and q_p are unknown) by extrapolating C_w or C_o as a function of t to $t = 0$. Knowing C^0_w and the equilibrium concentrations, it is possible to find K' and q_p.

In the given case the rate of extraction is characterised by the variation of the concentration in the aqueous phase, but it is not difficult to obtain the corresponding equation for the rate in terms of the variation of the concentration in the organic phase. Since for the reaction under consideration $C_w = C_{w(init)} - [A]_o$, $C^0_w = C_{w(init)} - [A]^0_o$, and $C_{w,e} = C_{w(init)} - [A]_{o,e}$, substitution of these values in Eqn. (31) yields $\ln\dfrac{[A]_{o,e} - [A]_o}{[A]_{o,e} - [A]^0_o} = -at$. Putting the last equation in the form $[A]_{o,e} - [A]_o = \{[A]_{o,e} - [A]^0_o\}e^{-at}$, we obtain $[A]_o = [A]_{o,e} - \{[A]_{o,e} - [A]^0_o\}e^{-at}$. It follows from this equation that

$$q_t = \frac{[A]_o}{C_w} = \frac{[A]_{o,e} - ([A]_{o,e} - [A]^0_o)e^{-at}}{C_{w(init)} - [A]_o} = \frac{[A]_{o,e} - ([A]_{o,e} - [A]^0_o)e^{-at}}{C_{w(init)} - [A]_{o,e} + ([A]_{o,e} - [A]^0_o)e^{-at}} = \frac{[A]_{o,e} - ([A]_{o,e} - [A]^0_o)e^{-at}}{C_{w,e} + ([A]_{o,e} - [A]^0_o)e^{-at}} .$$

When $t = 0$, we have $q_t = q_o = [A]^0_o/\{C_{w(init)} - [A]^0_o\}$ whence $[A]^0_o = C_{w(init)}/(1 + 1/q_o)$. Bearing in mind that $\tilde{K}' = \kappa'_1/\kappa'_2$, the equation for the coefficient a can be put in the form $a = \kappa'_1[1/(q_A + 1) + 1/\tilde{K}']$. If q_A and $\tilde{K}'$ are fairly large and κ'_1 is small because the corresponding reaction is slow, the case $a \ll 1$ is possible and therefore $e^{-at} \simeq 1 - at$. Only in this case will the equation for q_t not contain an exponential term.

Hydrolysis or dehydrolysis in the extraction of antimony chloride complexes from hydrochloric acid solutions by oxygen-containing solvents (for example alcohols), which has been investigated by Iofa[78], can serve as an example of side reactions of this kind. Iofa found that q_t expressed as a function of extraction time does indeed have a finite value at $t = 0$.

V. DETERMINATION OF THE PHASE IN WHICH THE REACTION TAKES PLACE

If it has been established that the extraction proceeds under kinetic conditions with the reaction in one of the bulk phases, the determination of the phase in which the reaction occurs is of significant interest. In the extraction of electrolytes from aqueous solutions by organic extractants dissolved in non-polar solvents under the conditions where the extractant (in the given case an acid HA) is fairly soluble in the aqueous phase and the initial salt is completely dissociated in the aqueous phase and therefore has extremely low solubility in the organic phase, one can suggest with a great deal of confidence that the reaction takes place in the aqueous phase. The hypothesis put forward by Sekine et al.[47] that in the extraction of beryllium from aqueous solutions containing hydrochloric and perchloric acids beryllium perchlorate passes to the organic phase is therefore unlikely. However, when the extractant exists in several forms in the organic phase, for example the enolic and keto-forms of acetylacetone or thenoyltrifluoroacetone, which reach equilibrium slowly, and the extractable element reacts rapidly with one of these forms, the rate of extraction of macroamounts of the element M can be determined by the rate of the keto–enol transformation.

Thus the low rate of extraction of the lanthanides by thenoyltrifluoroacetone observed by Healy[79] is accounted for by the low rate of the keto–enol transformation, since according to the author these elements react only with the enol form.

In a qualitative study[80] of the rate of extraction of zirconium by benzoylacetone and thenoyltrifluoroacetone in various solvents, it was concluded, from the dependence of the relative amount of the enol form on the polarity of the diluent and the solubility of the ketone in water, that the enol forms of the ketones react. In the extraction of trace amounts in the presence of a high concentration of the extractant the transformation of one form into another does not limit the rate of the process, provided that equilibrium in the distribution of the extractant has been attained (the phases have been "equilibrated" without the extractable element).

When the dissociation of the extractable salt in the aqueous phase is incomplete (complex formation with the anion of the initial salt), the molecular form (undissociated molecules), whose partition coefficient is possibly insignificant, may pass to the organic phase also when the solubility of the extractant in water is low and the rate of extraction is then determined by the rate of reaction in the organic phase. For example, the partition coefficient of $AuCl_4$ between xylene and 2 M HCl is 0.005, but increases significantly following the addition of tributyl phosphate (TBP) to the organic phase[81]. If the given reaction is not a surface process, then, bearing in mind the low solubility of TBP in water, one can suggest with some confidence that the formation of a solvate, which increases the partition coefficient, takes place in the organic phase, although this should of course be tested experimentally.

Above it was already noted that in the extraction by an acid HA the dependence of the rate of extraction on hydrogen ion concentration has been regarded as evidence that the reaction determining the rate of extraction occurs in the aqueous phase. However, this is true only under

certain conditions, in particular when the partition coefficient is independent of the acid on hydrogen ion concentration, which occurs, for example, in the partition of acetylacetone.

Comparison of the rates of extraction by solutions of a single extractant in different diluents, enabled a number of investigators[82,83] to find that the rate of extraction is higher the higher the concentration of the extractant in the aqueous phase for an equal concentration in the organic phase {the lower the partition coefficient $q = [HA]_o/[HA]_w$}. Hence it was concluded that the reaction determining the rate of extraction takes place in the aqueous phase. This conclusion would be correct if the rates of reactions were determined by the concentrations and not the activities. However, the different concentrations of the extractant in the aqueous phase for the same concentration in different organic phases imply that the activities of the extractant in the organic phases are different (they are higher the higher the solubility in the aqueous phase). The increase of activity may be caused, in particular, by a decrease in the degree of interaction with the diluent, an increase in the degree of dissociation of the polymer when the latter is formed in the organic phase, and other factors, let alone the change in the activity coefficient as a result of a change in the relative molecular dimensions and intermolecular interactions. Evidently an increase of the activity of the extractant in the organic phase would increase the rate of reaction in this phase if it occurred. When the concentration of the extractant in the same diluent is varied, its activity coefficients can change much less than on varying the diluent and therefore in a certain concentration range they may be regarded as constant and the kinetics may be interpreted on the basis of the concentrations. This yields "effective" rate constants and equilibrium constants, which include these constant activity coefficients. For this reason, the change in the rate constants when the concentration is altered appreciably may be related to a change in the activity coefficients and not in the reaction mechanism.

In a study[6] of heterophase processes under kinetic conditions accompanied by the reaction A + B = AB with known partition coefficients of all the substances, an equation was obtained for the amount of substance which has reacted (for example the amount of AB formed), whereby one can determine the phase in which the reaction takes place. The possibility of applying this type of equation to our systems is complicated by the existence of a number of compounds in the aqueous phase and the necessity to distinguish the analytical partition coefficient and the partition coefficient of the extractable compound. It is therefore necessary to analyse this equation and compare it with the equations for the rate of extraction determined by the rate of the reaction in the organic phase.

When different diluents and the same extractant are employed, the determination of the reaction rate constants is of significant interest, since this might constitute more reliable evidence for the occurrence of the reaction in one phase than a qualitative comparison of the rates.

VI. THE RATE OF EXTRACTION UNDER KINETIC CONDITIONS FOR MACROCONCENTRATIONS OF THE COMPONENTS

The extraction of microamounts of the extractable substance (element) for which the concentration of the extractant remains almost constant was examined previously. With a suitable preparation of the solutions for the experiment (equilibration of the phases with respect to the macrocomponents), this ruled out the influence of the rate of transformation of one form of the extractant into another when the extractant can exist in different forms. Equations for the rate of extraction under the conditions of comparable concentrations of the extractant and the extractable compound are derived in the present section for the extraction of a univalent element by an acid HA having only one form. In this case, assuming that the rate of extraction is determined solely by the rate of the reaction $M^+ + A^- = MA$ occurring in the aqueous phase, we have at any instant

$$[HA]_w = q_{HA}[HA]_w \quad , \tag{38a}$$

$$[MA]_o = q_{MA}\,[MA]_w \quad , \tag{38b}$$

$$[HA]_w = K_{HA}[H^+][A^-] \quad , \tag{39a}$$

$$[A^-] = \frac{[HA]_w}{K_{HA}[H^+]} = \frac{[HA]_o}{q_{HA}\ K_{HA}\ [H^+]} \quad . \tag{39b}$$

For equal phase volumes, we obtain, as in a system with microconcentrations of the extractable element,

$$\frac{d\,[MA]_w}{dt} + \frac{d\,[MA]_o}{dt} = \varkappa_1 [M^+]_w[A^-]_w - \varkappa_2 [MA]_w \quad . \tag{40}$$

Since the analytical concentration of M in the aqueous phase is $C_W = [M^+]_W + [MA]_W$, and in the organic phase $C_O = [MA]_O$, it follows that

$$[M^+]_w = C_w - [MA]_w = C_w^0 - C_o - \frac{C_o}{q_{MA}} = C_w^0 - \left(1 + \frac{1}{q_{MA}}\right) C_o \quad , \tag{41}$$

where C_W^0 is the concentration of M^+ in the initial aqueous solution.

We have from Eqns. (38b), (40), and (41)

$$\left(1 + \frac{1}{q_{MA}}\right)\frac{dC_o}{dt} = \varkappa_1 [A^-]\left\{C_w^0 - \left(1 + \frac{1}{q_{MA}}\right) C_o\right\} - \frac{\varkappa_2\ C_o}{q_{MA}} \quad . \tag{42}$$

[A] is determined using the material balance equations

$$[HA]_o = [HA]_o^0 - [HA]_w - [A^-]_w - [MA]_o - [MA]_w \quad , \tag{43a}$$

$$[H^+]_w = [H^+]_w^0 + [A^-]_w + MA]_w + [MA]_o \quad , \tag{43b}$$

where $[HA]_O^0$ and $[H^+]^0$ are the initial concentrations of the acid HA in the organic phase and of hydrogen ions in the aqueous phase. Then

$$[A^-] = \frac{[HA]_w}{q_{HA}\ K_{HA}\left\{[H^+]_w^0 + [HA]_o^0 - [HA]\left(1 + \frac{1}{q_{HA}}\right)\right\}} \quad , \tag{44a}$$

$$[HA]_o = [HA]_o^0 - [HA]_w - \frac{[HA]_o}{q_{HA}\ K_{HA}\left\{[H^+]_w^0 + [HA]_o^0 - [HA]_o\left(1 + \frac{1}{q_{HA}}\right)\right\}} - [MA]_w - [MA]_o \quad . \tag{44b}$$

On replacing $[HA]_W$ by $[HA]_O/q_{HA}$, it is possible to find $[HA]_O$ from Eqn. (44b). When $[HA]_O^0$, $[H^+]_W^0$, C_O, and $[HA]_O$ are known, it is easy to determine $[H^+]$ and $[A^-]$. Evidently, under these conditions Eqn. (42) is converted into a complex expression. However, if the degree of dissociation of the acid is low and $[A^-]$ can be neglected in Eqns. (43a) and (43b), it follows from the latter that

$$[HA] = \frac{[HA]_o^0 + \left(1 + \frac{1}{q_{MA}}\right) C_o}{1 + \frac{1}{q_{HA}}} \quad , \tag{45a}$$

$$[H^+]_w = [H^+]_w^0 - \left(1 + \frac{1}{q_{MA}}\right) C_o \quad . \tag{45b}$$

Putting, for brevity, $1 + 1/q_{MA} = a$ and $1 + 1/q_{HA} = b$, we have

$$[HA]_o = \frac{[HA]_o^0 - aC_o}{b} \quad , \tag{46a}$$

$$[H^+]_w = [H^+]_w^0 + aC_o \quad , \tag{46b}$$

$$[A^-] = \frac{[HA]_w^0 - aC_o}{q_{HA} K_{HA} b ([HA]_o^0 + aC_o)} \quad . \tag{46c}$$

Having substituted the value of $[A^-]$ from Eqn. (46c) in Eqn. (42), we obtain after appropriate rearrangements

$$f \frac{dC_o}{dt} = \frac{(a' - C_o)(C' - C_o)}{b' - C_o} + gC_o \quad . \tag{47}$$

In this equation $f = bq_{HA}K_{HA}/\kappa_1$, $a' = [HA]_o^0/a$, $b' = [H^+]_w^0/a$, $C' = C_w^0/a$, and $g = \frac{\kappa_2 q_{HA} K_{HA} h}{a\kappa_1 q_{MA}} = \frac{K_{HA}(q_{HA}+1)}{K_{MA}(q_{MA}+1)}$.

After adjusting Eqn. (47) to a common denominator and rearrangement, we obtain

$$\frac{(b' - C_o)\, dC_o}{C_o^2 - p C_o + r} = \frac{1+g}{r} dt \, , \tag{48}$$

where

$$p = \frac{a' + b'g + C'}{1 - g} \quad .$$

Integration of this equation subject to the condition $C_O = 0$ when $t = 0$ leads to the expression

$$(b' - x_1) \lg \frac{x_1 - C_o}{x_1} - (b' - x_2) \lg \frac{x_2 - C_o}{x_2} = \frac{(1-g)(x_1 - x_2)}{2.303 f} t, \tag{49}$$

where x_1 and x_2 are the roots of the equation $C_O^2 - pC_O + r = 0$.

The condition $C_O^2 - pC_O + r = 0$ corresponds to equilibrium and therefore one of the roots, for example x_2, is equal to $C_{O,e}$—the equilibrium concentration in the organic phase, which can be determined experimentally. In this case $x_1 = r/x_2 = r/C_{O,e}$. If q_{HA}, q_{MA}, K_{HA}, K_{MA}, a', b', C', and g are known, then there is only one unknown in Eqn. (44), namely f, which includes the rate constant κ_1. Thus, having determined experimentally C_O at a time t, it is possible to find f, and, knowing the equilibrium constant K_{MA} for the given reaction, κ_2 can be determined.

The above equations show that the determination of the rate constant for a comparatively simple reaction in extraction requires the knowledge of the stability constant of the compound formed and of its partition coefficient and the corresponding calculations involve a considerable error, since the equations include coefficients which are complex functions of the initial concentrations, the equilibrium constants, and partition coefficients.

Evidently, in extraction whose rate is determined by the rate of a chemical reaction accompanied by the formation of several compounds of the extractable element, the corresponding equations will be still more complex.

When the concentrations of the components are altered appreciably, there is a possibility of a considerable change in their activity coefficients, which complicates still further the study of the extraction mechanism. For this reason, the use of radioactive traces is extremely desirable in the study of the extraction mechanism.

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