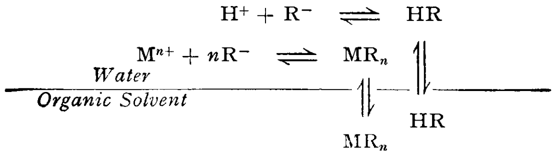
394. *Metal Complexes and Partition Equilibria.*

By H. Irving and R. J. P. Williams.

Many metals form inner complexes which can be extracted from aqueous solution on shaking with an immiscible organic solvent. The extractability is now shown to vary with the hydrogen-ion concentration of the aqueous phase and the concentration of excess reagent, and to depend upon the valency of the metal ion and the partition coefficients and dissociation constants of the various molecular species involved. An explicit relationship between the percentage of metal extracted and the pH of the aqueous phase is derived in terms of $\mathrm{pH}_{\frac{1}{2}}$, the hydrogen-ion exponent at which the extraction reaches 50% : this is itself a function of the excess of reagent present. The effect of a change of solvent on the rate of attaining partition equilibrium and on the percentage of metal then extracted, and the consequences of competitive complex formation in the aqueous phase, are discussed in relation to contemporary analytical procedures.

The interaction of an n-valent kation M^{n+} with an organic reagent HR often yields an inner complex MR_n which is sparingly soluble in water though relatively soluble in non-polar solvents. When therefore an aqueous solution of M^{n+} is shaken up with a solution of the reagent HR in a solvent immiscible with water, the equilibria depicted in Fig. 1 come into play and some of the complex formed in accordance with equation (1) will partition into the aqueous phase. Such partition equilibria are involved in many analytical procedures in constant use (*e.g.*, the extraction and absorptiometric determination of trace metals with dithizone and oxine, the fluorometric determination of gallium, etc.; cf. Sandell, " The Colorimetric Determination of Traces of Metals "). An appreciation of the difficulties in determining mercury with dithizone in the presence of copper (Irving, Andrew, and Risdon, this vol., p. 541) and a consideration of the principles underlying the valuable procedures of extractive titration, together with problems encountered in the separation of related kations (as metal complexes) by counter-current extraction or partition chromatography, emphasised the need for a generally applicable and quantitative treatment of such partition equilibria. The present paper contains a simple theoretical treatment by which it is possible to relate the percentage of a metal extracted to the concentration of reagent, the pH of the aqueous phase, and the dissociation constants and partition coefficients of the various molecular species involved. It is intended as a general introduction to a series of experimental studies of specific systems which will be published in due course.

Fig. 1.



$$M^{n+} + nHR \rightleftharpoons MR_n + nH^+ \qquad (1)$$

Quantitative Treatment of Partition Equilibria.—Consider first the case of a reagent HR which behaves as a monobasic acid throughout the range of pH studied. It is postulated that this reagent and its metal complex MR_n exist in both water and the organic solvent as unassociated molecules. Relevant equilibrium constants are defined as follows :

The instability constant of the complex,

$$K_c = [M^{n+}]_w[R^-]_w{}^n/[MR_n]_w \qquad (2)$$

The Brønsted dissociation constant of the reagent,

$$K_r = \{H^+\}_w[R^-]_w/[HR]_w \qquad (3)$$

Partition coefficients,

$$p_c = [MR_n]_w/[MR_n]_o \qquad (4)$$

and

$$p_r = [HR]_w/[HR]_o \qquad (5)$$

where the subscripts c and r refer to the complex and reagent, and the subscripts w and o refer to the aqueous and the organic phase respectively ; K_c is, of course, the reciprocal of the " gross " complexity constant of the complex MR_n as defined by Bjerrum (" Metal Ammine Formation in Aqueous Solution," Copenhagen, 1941, p. 54). The ratio of the amount of metal extracted as complex into the organic phase to that remaining in all forms in the aqueous phase is termed the (true) extractability, E_t, and is given by

$$\begin{aligned} E_t &= [\mathrm{MR}_n]_\mathrm{o}/\{[\mathrm{MR}_n]_\mathrm{w} + [\mathrm{M}^{n+}]_\mathrm{w}\} \quad \ldots\ldots\ldots\ldots \quad (6) \\ &= 1/\{p_c + ([\mathrm{M}^{n+}]_\mathrm{w}/[\mathrm{MR}_n]_\mathrm{o})\} \\ &= 1/\{p_c + (p_c K_c\{\mathrm{H}^+\}_\mathrm{w}{}^n/p_r{}^n K_r{}^n[\mathrm{HR}]_\mathrm{o}{}^n)\} \\ &= 1/\{p_c + (\{\mathrm{H}^+\}_\mathrm{w}{}^n/K[\mathrm{HR}]_\mathrm{o}{}^n)\} \quad \ldots\ldots\ldots\ldots \quad (7) \end{aligned}$$

from equations (2), (3), (4), and (5), whereby

$$K = (K_r p_r)^n/K_c p_c \quad \ldots\ldots\ldots\ldots \quad (8)$$

If the partition coefficient p_c of the metal complex is negligible in comparison with the numerical value of the second term in the denominator of equation (7), this reduces to

$$E = K([\mathrm{HR}]_\mathrm{o}/\{\mathrm{H}\}_\mathrm{w})^n \quad \ldots\ldots\ldots\ldots \quad (9)$$

Kolthoff and Sandell (*J. Amer. Chem. Soc.*, 1941, **63**, 1906), discussing the extraction of zinc by dithizone, arrived at an expression of this form by assuming that the concentration of complex in the aqueous phase, $[\mathrm{MR}_n]_\mathrm{w}$, was always negligible when compared with that of the ion, $[\mathrm{M}^{n+}]_\mathrm{w}$; but this may not be justifiable in general when the extraction of metal is nearly completed. It follows from equations (7) and (9) that $E_t = E/(1 + p_c E)$, so the true extractability will always be less than that calculated by the approximate expression (9). Since, however, the partition coefficient of inner complexes is generally very small, the discrepancy is negligible so long as the extractability is not too large. The order of magnitude of the error for various values of p_c and E can be seen in Table I.

TABLE I.

Percentage of extraction is assumed to be :	E.	Actual percentage of extraction calculated for : $p_c = 0{\cdot}1$.	$p_c = 0{\cdot}01$.	$p_c = 0{\cdot}001$.
100	∞	90·9	99·0	99·9
99	99	90·1	98·0	98·9
90	9	82·6	89·2	89·9
50	1	47·6	49·75	49·8

Whilst equation (9) shows how a change in hydrogen-ion concentration would affect the relative amounts of metal in the two phases, an explicit relationship between the percentage of metal extracted and the pH of the aqueous phase would be of more immediate practical value. Writing equation (9) in the equivalent logarithmic form

$$\log_{10} E = \log_{10} K + n(\mathrm{pH} + \log_{10} [\mathrm{HR}]_\mathrm{o}) \quad \ldots\ldots\ldots \quad (10)$$

and defining $\mathrm{pH}_{\frac{1}{2}}$ as that value of the hydrogen-ion exponent when *for the same concentration of excess reagent* the extraction reaches 50% ($E = 1$), we have

$$0 = \log_{10} 1 = \log_{10} K + n(\mathrm{pH}_{\frac{1}{2}} + \log_{10} [\mathrm{HR}]_\mathrm{o}) \quad \ldots\ldots \quad (11)$$

Subtracting, we have

$$\begin{aligned} n\Delta\mathrm{pH} &= n(\mathrm{pH}_{\frac{1}{2}} - \mathrm{pH}) = -\log_{10} E \quad \ldots\ldots\ldots \quad (12) \\ &= \log_{10} (100 - x)/x \end{aligned}$$

where x is the percentage of metal extracted into the organic phase. Now equation (12) presents pH as a function of x, and we require the inverse function. By an obvious transformation the desired equation is

$$x = 50(1 - \tanh 1.1513\, n\Delta\mathrm{pH}) \quad \ldots\ldots\ldots \quad (13)$$

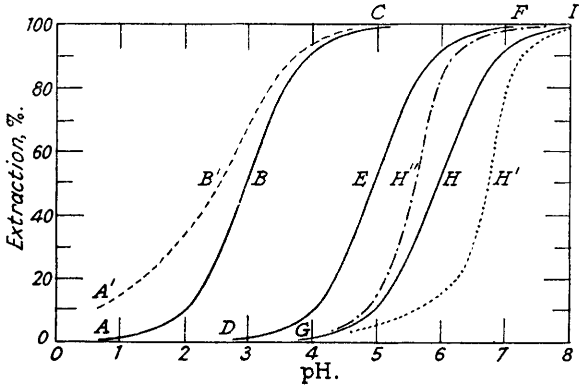
which is shown plotted in Fig. 2 (curve *ABC*) for the particular case of a bivalent metal ($n = 2$) where $\mathrm{pH}_{\frac{1}{2}} = 3{\cdot}0$. Values of 0% and 100% extraction are approached asymptotically, whilst the whole curve is centrosymmetric with respect to B ($\mathrm{pH}_{\frac{1}{2}}$, 50%), it being assumed that p_c for this system is negligible (see above). From equation (9), and assuming that the concentration of excess reagent amounted to 10^{-5} g.-mol./l., we calculate the value of the extractability constant K for this particular metal–reagent–solvent system to be 10^4. Curves *DEF* and *GHI* are plotted for the same system for values of $\mathrm{pH}_{\frac{1}{2}}$ equal to 5·0 and 6·0, corresponding to concentrations of excess reagent of 10^{-7} and 10^{-8} respectively. It will be noted that they are identical in form and that they could be obtained from *ABC* by a simple lateral translation equal to the change in $\mathrm{pH}_{\frac{1}{2}}$ value.

The Effect of Changes in Hydrogen-ion and Reagent Concentration.—From Fig. 2, or more directly from equation (10) whence by differentiation

$$(\partial \log E/\partial \mathrm{pH})_{[\mathrm{HR}]_0} = (\partial \log E/\partial \log [\mathrm{HR}]_0)_{\mathrm{pH}}$$

it is clear that a change in extractability due to an increase (or decrease) of one unit in pH can be exactly offset only by a ten-fold decrease (or increase) in the concentration of excess reagent in the organic phase. Now purely practical considerations often limit the permissible variations in the magnitude of the latter parameter. The upper limit is set by the solubility of the reagent—and this is often quite small—whilst in cases where the metal complex is to be determined absorptiometrically a large excess of reagent would be undesirable if it had an appreciable extinction coefficient at the wave-length used for measurements. It is precisely this feature which complicates the use of dithizone in such procedures. On the other hand, where more than one extractable complex can be formed from a metal and an organic reagent (a specific example is provided by copper and dithizone) an adequate excess of reagent is imperative to ensure the stoicheiometric or constant composition of the material extracted. Furthermore, the amount of reagent naturally plays a significant rôle in the kinetics of complex formation (see p. 1845), and its concentration must not be diminished too greatly if complex formation and partition equilibrium are to be effected in a reasonable time. Since such varied factors can and must restrict the possible variations in the term $[\mathrm{HR}]_0$, it is clear that changes in hydrogen-ion concentration (which may readily be varied by a factor of 10^{14}) are of overwhelming importance in the practical applications of partition equilibria.

FIG. 2.



It should be emphasised that the term $[\mathrm{HR}]_0$ refers explicitly to the *excess* of reagent present in the organic phase at equilibrium. This may differ but little from the total amount of reagent employed if the amount of metal to be extracted is relatively small, or where the pH of the aqueous phase is such that the percentage extracted is negligible; but even in circumstances where the amount of complex formation is strictly limited, the term $[\mathrm{HR}]_0$ may comprise but a small fraction of the total concentration of reagent should the pH of the aqueous phase and the value p_r of the partition coefficient of the reagent be such as to cause a large proportion of it to be extracted into the aqueous phase. The extent to which this can take place in the case of a typical organic reagent, dithizone, is described in the following paper and its consequences in analytical procedures are discussed elsewhere (Irving, Risdon, and Andrew, this vol., p. 537). The difficulty of determining the actual value of $[\mathrm{HR}]_0$ is perhaps the greatest single obstacle in testing the applicability of the foregoing equations to specific systems.

The Influence of the Valency of the Metal Ion.—By differentiating equation (13), the slope of the extraction curve is found to be given by

$$\mathrm{d}x/\mathrm{d}\,\mathrm{pH} = 57{\cdot}57n(1 - \tanh^2 1{\cdot}1513n\Delta\mathrm{pH})$$

which is a function of n, the number of protons liberated when the metal complex is formed. At its mid-point ($x = 50\%$, $\Delta\mathrm{pH} = 0$) its numerical value is $57{\cdot}57n\%$ per pH unit, a prediction which has been verified in the case of zinc and dithizone (Irving and Williams, unpublished). It follows from equation (9) that an increase of one unit in the pH will increase the extractability ten-fold in the case of a univalent metal, but 100-fold and 1000-fold in the case of bi- and tervalent metals respectively. The position of the extraction curve with respect to the origin will likewise be subject to greater displacement owing to a change in the amount of uncombined reagent as the valency of the metal ion increases. An appreciation of such factors is obviously of great importance when studying the extraction of mixtures of metals of different valency, *e.g.*, the determination by dithizone of lead and bismuth in admixtures.

The Extraction of Different Metals with the Same Reagent.—We are now in a position to discuss problems arising out of the extraction of a series of metals by a solution of the same organic reagent in a given solvent. In considering the probable values of the individual extractability constants, K, for such systems we note that, of the various factors into which such constants can be resolved by equation (8), K_r and p_r refer to the reagent–solvent system and do not vary, whilst the magnitudes of the partition coefficients p_c, p_c', p_c'' . . . for the various metal complexes are likely to be of much the same order. Most of the variation is to be expected in the values of K_c, K_c', K_c'' . . ., the instability constants of the respective metal complexes. These constants are related by equation (11) to the $pH_{\frac{1}{2}}$ values which serve to characterise the partition equilibria. The more stable the complex, the more acid will be the medium from which it can be completely extracted. That such variations in K_c are of decisive importance is confirmed at least for compounds of the bivalent ions of the transition metals with dithizone by the fact that the sequence of $pH_{\frac{1}{2}}$ values is identical with their " natural " order of stabilities which has been shown to be independent of the nature of the ligand—whether ammonia, ethylene- or propylene-diamine, salicylaldehyde, glycine, quinaldinic acid, etc. (Irving and Williams, *Nature*, 1948, **162**, 746).

The curves *ABC*, *DEF*, and *GHI* of Fig. 2 were drawn to represent a system with $K = 10^4$ and $[HR]_0 = 10^{-5}$, 10^{-7}, and 10^{-8}, respectively. They could equally well represent systems with $K = 10^6$, 10^2, and 1, respectively, for the extraction of three different (bivalent) metals by a constant concentration (10^{-6} g.-mol./l.) of the same reagent. Clearly, a knowledge of the mutual disposition of such curves (or of the necessary parameters $pH_{\frac{1}{2}}$ or K, and $[HR]_0$ which would permit of their construction) would be an invaluable prerequisite to any reasoned attempt at separation. This was first pointed out by Wichman (*Ind. Eng. Chem. Anal.*, 1939, **11**, 66), who sketched the probable relative disposition of the extraction curves for various metal–dithizone systems from the many qualitative and semi-quantitative observations reported in the literature. He did not take into account the displacements which would be caused by variations in the amount of dithizone used in the different experiments. Many subsequent workers have published series of curves relating the percentage of metal extracted to the pH of the aqueous phase for partition systems involving metals and oxine, dithizone, and other reagents. They need not be specified here as they are unacceptable for quantitative treatment for one or both of two reasons. In the first place, the amount of excess reagent is seldom specified. Indeed, it is not often a constant amount for any given curve, for it is common practice to obtain such curves by measuring the percentage of extraction obtained when a solution of organic reagent of constant initial concentration is shaken with a fixed amount of metal dissolved in aqueous buffers of varying pH. Clearly, as the percentage of metal extracted is diminished by reducing the pH below that required for complete extraction, the excess of reagent in the organic layer must increase. There results a distorted curve (*e.g.*, *A'B'C* of Fig. 2) which lies to the left of the theoretical curve *ABC* and approximates to it the more closely the higher the pH. The second reason for rejecting most published data is that they do not represent systems at equilibrium.

Equilibrium Conditions.—When describing the routine details of the extraction stage preliminary to specific absorptiometric determinations, analysts have—with few exceptions—been at pains to specify carefully the minimum time (or minimum " number of shakes ") needed to ensure complete extraction at that optimum pH where it had been found that this was effectively quantitative. The assumption commonly made that equilibrium is attained within the same period of time when plotting the course of the extraction curve at lower pH values is quite unjustifiable. Indeed, measurements on the copper–dithizone system by Barnes (*J. Marine Biol. Assoc.*, 1946, **26**, 303; *Analyst*, 1947, **72**, 469) and by Irving, Andrew, and Risdon (*loc. cit.*), and data on other metal–dithizone and metal–oxine systems (Irving *et al.*, to be published) clearly demonstrate that the rate at which the metal complex is formed and extracted into the organic phase decreases rapidly as the pH is reduced below that value appropriate to 100% extraction. Failure to reach true equilibrium will give false extraction curves (*e.g.*, *GH'I* in Fig. 2) lying below the true equilibrium curves plotted for a constant amount of reagent. Furthermore, whilst *CB'A'* may represent true equilibrium conditions in a system with a gradually increasing excess of reagent, a curve closely resembling *CBA* may result if the same system is studied under conditions where true equilibrium is not reached. The literature provides numerous examples of extraction curves which appear superficially to follow the course predicted by equation (**13**); but where the excess of reagent may have varied and no true guarantee of equilibrium is provided, such data are useless for the present purpose.

The simple test for the attainment of equilibrium—the approach to a common value from either side—has not apparently been applied to metal–complex partition problems. This is quite understandable, since the analysts who have studied them in greatest detail have been more interested in defining conditions essential to the extraction of a single species or favouring the predominant extraction of one constituent of a mixture. Indeed, failure to reach equilibrium within a given time may be of great practical value. Thus the fact that mercury (but not copper) is rapidly extracted at low pH values by a solution of dithizone in chloroform has been exploited by Barnes and by Irving *et al.* (*locc. cit.*) in methods for the determination of mercury in the presence of copper.

However, in 1942 Walkley (*Proc. Austral. Chem. Inst.*, **9**, 29) observed that the organic phase resulting from shaking a solution of zinc " dithizonate " in chloroform with acid contained a greater percentage of zinc than was obtained by extracting the same quantity of zinc from aqueous solution at the same pH and for the same length of time. The implications of this discovery do not appear to have been generally realised. We have confirmed them and observed similar behaviour in other metal–reagent systems. Whenever a solution of a metal complex in an organic solvent is shaken with an aqueous buffer, reaction with hydrogen ions will cause some decomposition in the sense of equation (1) right to left, and more or less metal ion will pass into the aqueous phase whilst the concentration of reagent in the organic phase will increase until new equilibrium conditions governed by equation (9) are set up. The rate of attaining equilibrium is found to depend on hydrogen-ion concentration and to increase rapidly as the pH is lowered. At sufficiently low acidities (*e.g.*, point *G* of Fig. 2) equilibrium is attained so rapidly that correct values for the percentage of metal extracted at equilibrium are obtained after even a brief period of shaking. At higher pH values (*e.g.*, point *I* of Fig. 2), where the extraction is virtually complete, no significant error will appear in the measured extraction even though the rate of attaining true equilibrium may be very low. At intermediate values of pH, false equilibrium curves (*i.e.*, curves based on measurements in which the time of shaking, though constant, is not adequate for the attainment of true equilibrium at all acidities) will follow a course such as *GH''I*, the greatest errors occurring in the region where the extraction approaches 100%. False equilibrium curves may thus form a sort of hysteresis loop *GH''IH'G* enveloping the true equilibrium curve *GHI*.

The Rôle of the Solvent and Kinetic Aspects of Partition Equilibria.—In considering the effect of changing the solvent on the extraction of a particular metal by a given reagent, two effects must be distinguished. The first concerns the new position of extraction equilibrium; the second involves the kinetics of the equilibration process.

Consider the partition of a metal as governed by equations (9) and (8). Changing the solvent will not alter K_c or K_r but will involve new values p_c' and p_r' for the partition coefficients of the complex and reagent respectively in the new solvent. If [H] and [H]' are the hydrogen-ion concentrations at which the same extractability E is attained in either case with the same excess reagent, it can easily be shown that

$$[\mathrm{H}]/[\mathrm{H}]' = (p_r/p_r')^n/(p_c/p_c') \qquad \ldots \ldots \ldots \quad (14)$$

Data on the effect of a change of solvent on the value of partition coefficients are meagre and the theoretical treatment is too involved to be of value here. At best one can infer from measurements on the solubilities of non-polar substances in a range of organic solvents (cf. Hildebrand, " Solubility," New York, 1936, p. 165) and from relevant partition data that if, for one substance, r, $p_r/p_r' = a > 1$ on change of solvent, the partition coefficient of another non-polar material, c, not too unlike the first, will be changed in the same sense and to much the same extent, *i.e.*, $p_c/p_c' = b > 1$, and $a \sim b$. At least for multivalent metals ($n > 1$), the probable effect of a change to a solvent in which the reagent and its metal complexes are more soluble will be to shift the extraction curves towards regions of higher pH. It is well known that metal " dithizonates " are more soluble in chloroform than in carbon tetrachloride; the same is true of the reagent dithizone itself (see following paper), and in the case of every metal–dithizone extraction curve we have examined that in chloroform lies in a more alkaline region than that in carbon tetrachloride. An additional effect, of some analytical importance, is that extraction curves for a given pair of elements are better separated in the former solvent; but the data need extending to other solvents and other metal–reagent systems.

The rate at which a metal complex appears in the organic phase during the process of extraction depends upon the rates of two separate processes, *viz.*, the formation of metal complex (which may reasonably be expected to take place in the aqueous phase) followed by its (partial) transfer into the organic phase. Partition equilibria of such reagents as oxine and dithizone between water and organic solvents are established very rapidly—certainly within a minute's shaking (cf. following paper) and under optimum conditions extraction equilibrium between metal ions and an organic solution of a reagent is attained equally rapidly, which proves that the partition of the inner-complex is not significantly slower The rate-determining stage in the attainment of extraction equilibrium is thus that of forming the metal complex in the aqueous phase. Since this is strongly influenced (retarded) by hydrogen ions, it can scarcely be due wholly to reactions between metal ions and undissociated reagent. If the rate is a simple function of the activities of the reacting species we can write

$$\text{rate } (r) = k\{\mathrm{M}^{n+}\}\{\mathrm{R}^-\}^n = k\{\mathrm{M}^{n+}\}(p_rK_rf_\mathrm{R} - [\mathrm{HR}]_\mathrm{o}/\{\mathrm{H}\}_\mathrm{w})^n \quad . \quad . \quad . \quad . \quad (15)$$

from equations (3) and (5). The rate of attaining equilibrium should thus depend upon the product p_rK_r, which is a characteristic of the reagent–water–solvent system. It will be proved in the following paper that $-\log_{10} p_rK_r = \mathrm{pH}_{\frac{1}{2}}$, the hydrogen-ion exponent at which the reagent is equally partitioned between water and the organic phase.

If r' is the rate of reaction when another solvent is used, the pH and ionic strength of the aqueous buffer, and the concentration of metal and excess reagent, remaining the same,

$$r/r' = (p_rK_r/p_r'K_r')^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

For dithizone the values of p_rK_r are $1{\cdot}26 \times 10^{-9}$ and $2{\cdot}75 \times 10^{-11}$ in carbon tetrachloride and chloroform respectively, whence we deduce that the rate of attaining equilibrium in a metal–dithizone system should be about 46^n times slower in the latter solvent. Preliminary experiments gave a factor of 30 in the case of zinc extraction which suggests that the rate-determining stage may involve only one dithizonate ion. Theory predicts that the rate factor due to a change of solvent should be independent of pH and the nature of the metal involved. Experimental confirmation will be reported elsewhere.

Competitive Complex Formation.—Putting $n = 1$ in equation (13) gives the equation to the curve which describes extraction in any univalent metal–reagent–solvent system, its position along the pH axis being determined by the appropriate values of $\mathrm{pH}_{\frac{1}{2}}$ and $[\mathrm{HR}]_\mathrm{o}$. Regarding the hydrogen ion merely as a particular example of a univalent kation, the same equation describes how the percentage of hydrogen bound as complex (*i.e.*, as the undissociated acid HR) and extracted into the organic phase will increase as the pH rises. At first sight this would appear to contradict experience, for as the aqueous phase becomes more alkaline, more and more reagent acid passes into it as the anion R^-. The paradox arises from the unequal rates of diminution of the terms $[\mathrm{HR}]_\mathrm{o}$ and $[\mathrm{H}^+]$ as shown in Table II for the reagent dithizone at a total concentration of 10^{-5}M. Here $p_c \equiv p_r$ and $K_c \equiv K_r$, so the extractability constant, K, of equation (8) is unity; similarly, from equation (11), $\mathrm{pH}_{\frac{1}{2}} = -\log_{10} [\mathrm{HR}]_\mathrm{o}$.

TABLE II.

pH.	4.	5.	6.	7.	8.	9.	10.	11.
$p = [\mathrm{R}^-]_\mathrm{w}/[\mathrm{HR}]_\mathrm{o}$ * …………	$0{\cdot}0_63$	$0{\cdot}0_53$	$0{\cdot}0_43$	$0{\cdot}0_33$	0·003	0·03	0·275	2·75
$[\mathrm{R}^-]_\mathrm{w} \times 10^7$ …………………	$0{\cdot}0_43$	$0{\cdot}0_33$	$0{\cdot}0_23$	0·03	0·27	2·68	21·6	73·3
$[\mathrm{HR}]_\mathrm{o} \times 10^7$ …………………	~100	~100	~100	99·97	97·73	97·32	78·4	36·7
$[\mathrm{H}^+]_\mathrm{w}$ …………………………	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}
Percentage of hydrogen bound as the complex $[\mathrm{HR}]_\mathrm{o}$………	9·1	50	90·9	99·0	99·9	99·99	≈100	

* Partition coefficients calculated for the partition of dithizone between chloroform and water assuming that p_0 is negligible (cf. following paper)

Although this unconventional aspect of the partition of an acidic reagent is of less practical use than that developed in the following paper, it serves to emphasise the universal validity of equations (9) and (13) and the fact that no essential distinction need be drawn between the partition equilibrium of an acidic reagent and its metal complexes. Indeed, if the effect of an acid in decomposing a metal complex may be regarded as a competition between hydrogen ions and metal ions for the anions of the reagent (equation 1), Fig. 1 may equally be taken as representing the simultaneous partition of two complexes in equilibrium with each other through the common anion R^- in the aqueous phase. No new equations are thus required when considering the extraction of admixtures of complexes KR_j, LR_k, MR_l . . . of the same reagent, and little extra complication is introduced when two reagents HR and HS compete for a common kation (and hydrogen ions).

Now, in deriving the foregoing equations it was postulated that the total concentration of metal in each system could be expressed as the sum of three terms $[M^{n+}]_w$, $[MR_n]_o$, and $[MR_n]_w$, of which the third could generally be neglected. But should the metal ion form a complex soluble in water but insoluble in an organic solvent an extra term must be introduced into the denominator of (6). If the hydrophilic complex is of sufficient stability, the concentration of free metal ions will be so reduced that even under the most favourable conditions of extraction the amount held in the organic phase may be negligible. Good use is made of this effect in reversion procedures (Irving, Andrew, and Risdon, *Nature*, 1948, **161**, 805; this vol., p. 537) and when it is desired to extract one substituent in the presence of others which can be retained selectively in the aqueous phase as stabler complexes. The decreased extraction often noted in the case of amphoteric metals when the pH of extraction exceeds the optimum for 100% extraction is due to the removal of metal ions as complex anions of comparable or greater stability.

When determining traces of metals by extractive techniques, the concentration of salts in the buffer mixtures used to adjust the pH of the aqueous phase to its optimum value is relatively so large that conditions especially favourable to competitive complex formation are set up. Citrates, tartrates, and cyanides in the buffers are particularly effective, but the high concentration ratio of buffer to trace-metal ions may give significance even to relatively unstable complexes with ions such as acetate and borate which are often present. Even when the metal–reagent complex is of great stability, the tendency of the buffer constituents to form competitive hydrophilic complexes is often reflected in the displacement of the extraction curve towards regions of higher pH. Changes in the composition of the aqueous phase may thus alter the amount of metal extracted at equilibrium even when the pH and amount of excess reagent are kept the same (cf. Biefeld and Patrick, *Ind. Eng. Chem. Anal.*, 1942, **14**, 275, for a discussion of lead–dithizone curves). Large changes in ionic strength and specific salt effects will also influence the rate of attaining equilibrium [cf. equation (15)].

In view of the many factors which complicate the study of metal–reagent–water–organic solvent systems in true partition equilibrium, it is scarcely surprising that the data found in the literature, though self-consistent and reproducible under carefully defined conditions and of great value in elaborating arbitrary analytical procedures, must nevertheless be considered of insufficient accuracy for testing the conclusions arrived at above. The omissions will be rectified in subsequent papers.

THE INORGANIC CHEMISTRY LABORATORIES,
SOUTH PARKS ROAD, OXFORD.

[*Received, February* 15*th*, 1949.]