*A General Treatment of the Solvent Extraction of Inorganic Compounds.**

By H. IRVING, F. J. C. ROSSOTTI, and R. J. P. WILLIAMS.

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A comprehensive treatment of partition equilibria in inorganic systems can be given by combining the concept of step-equilibrium with that of the Nernst partition isotherm. A general relation has been derived between the average composition of the species in each phase. Partial differentiation of this equation with respect to the concentration variables of the system provides a method for determining the relative degrees of association in each phase of metal ions with hydrogen ions and with ligand ions. Its applications in deriving values for the partition coefficients and stability constants of species present in simple " ideal " systems, and in deducing the probable nature of species present in more complicated systems, are outlined. It is shown how the species extracted into the organic phase may occur in the aqueous phase as an insignificant fraction of the total metal present there.

In " non-ideal " systems, changes in the mutual miscibility of aqueous and organic phases brought about by the addition of mineral acids or salts are shown to influence distribution ratios through changes in partition coefficients and stability constants, and to affect the percentage of extraction through these two factors as well as through changes in the ratio of the volumes of the two phases.

Retrograde extraction leading to a maximum in the percentage of extraction is explained, and factors influencing the relative efficiencies of different organic solvents as extracting agencies, and those influencing the relative extractability of different metallic compounds, are discussed.

THE solvent extraction of inorganic compounds embraces such diversified observations (cf. Irving, *Quart. Reviews*, 1951, **5**, 200, and refs. therein) that a generalised quantitative treatment might appear to be impossible. The types of compounds which undergo extraction into organic solvents may be classified broadly into four categories, *viz.*: (i) covalent compounds, such as the halogens, sulphur dioxide, osmium tetroxide (cf. Friedman, *J. Amer. Chem. Soc.*, 1954, **76**, 3294); (ii) inner complexes of metals with reagents such as dithizone, cupferron, 8-hydroxyquinoline, and acetylacetone; (iii) the mineral acids, their salts, and metal acido-complexes; and (iv) certain salts or ion-pairs which incorporate bulky anions or cations, *e.g.*, tetraphenylarsonium per-rhenate or pertechnetate, salts of cuprous bis-2 : 9-dimethyl-1 : 10-phenanthroline, or ferrous tris-1 : 10-phenanthroline in association with long-chain alkyl sulphates or sulphonates (Friedman and Haugen, *ibid.*, 1954, **76**, 2060; Powell and Taylor, *Chem. and Ind.*, 1954, 726).

Quantitative treatments of various degrees of elaboration have been applied to representative examples of each of these classes, but since systems allocated to one or other class seem superficially to have so few features in common, no general treatment has hitherto been considered. In the first part of this paper it is shown that existing ideas can be integrated by combing the concept of step-equilibrium (Bjerrum, " Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941) with the original treatment of partition equilibrium by Nernst (*Z. physikal. Chem.*, 1891, **8**, 110). In the second part certain additional complexities, especially in systems of type (iii), which arise from changes in partition coefficients and stability constants in consequence of modifications in phase compositions, are discussed in some detail. Further papers, published concurrently (see footnote,*) describe the application of these ideas to experimental studies of the solvent extraction of ferric chloride and indium halides.

To illustrate the mathematical approach, consider the partition of a solute X. By the

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* This is to be regarded as Part I of a group of related papers of which Part II (Chalkley and Williams), and Parts III, IV, and V (Irving and Rossotti) are the four following papers.

Nernst partition law $[X]_o = p[X]$, where the subscript o is used to distinguish a species in the organic phase. If X is polymerised (virtually completely) in the organic phase to a species X_n which is not itself partitioned, we have $[X_n]_o = K[X]_o^n$. Then since $[X_n]_o \gg [X]_o$, the distribution ratio is given by

$$q = \frac{[X]_o + n[X_n]_o}{[X]} = \frac{nK[X]_o^n}{[X]} = nKp[X]^{n-1}$$

whence $d \log q/d \log [X] = n - 1$. If, then, the gradient of the double logarithmic plot of experimental values of q and [X] is constant and integral, this will establish the validity of the simplifying assumptions and furnish the precise degree of polymerisation of X in the organic phase. However, with inorganic systems the species which undergoes partition may only be a minor component of a complex system in equilibrium; polymerisation may occur in either or both of the phases; and more than one substance may undergo partition simultaneously. Although the equations describing such behaviour (given below) must necessarily be more complicated, their resemblance to the foregoing will be apparent, and the behaviour of their (partial) derivatives will be shown to provide a great deal of detailed information concerning the species which take part in the complex equilibria.

We shall first examine the equilibria existing between the simple ions and all the complex species in a system of two relatively immiscible liquid phases. Such equilibria can be described quantitatively in terms of step-equilibria governing the relative concentrations of different species in the aqueous phase, and a series of partition coefficients referring to the relative concentrations of the species which are common to the two phases. Clearly, the proposed treatment does not exclude the possibility of step-equilibria between species in the organic phase. But it is impossible to infer from measurements of distribution ratios at equilibrium whether a particular species identified in the organic phase has crossed the phase boundary as such, or has been formed *in situ* by the interaction of two or more species in the organic phase which are in partition equilibrium with corresponding species in the aqueous phase.

General Treatment of Solvent Extraction in Ideal Systems.—Consider an aqueous solution saturated with organic solvent, S, containing metal ions, $M^{+\nu}$. hydrogen ions, H^+, and anions, $L^{-\lambda}$, in a medium of constant strength. Assuming the concentration of acid and anion to be such that hydrolysis of any kationic species can be neglected, all the (solvated) complex ions ML_n, the acido-species H_hML_n, and any polynuclear species such as M_2L_6 or $H_2M_3L_{12}$ which might exist in step-equilibria can be represented by a general term $H_hM_mL_n(H_2O)_wS_s$, and their concentrations related to those of the simplest ions by a series of overall stoicheiometric equilibrium constants defined as follows

$$\beta_{hmnws} = H_hM_mL_n(H_2O)_wS_s/[H]^h[M]^m[L]^n[H_2O]^w[S]^s \quad . \quad . \quad . \quad . \quad (1)$$

Here and subsequently charges on the various species will be omitted unless they are specially relevant to the discussion. For purposes of definition no distinction need be drawn between different types of complexes, *e.g.*, between normal or " robust " complexes (cf. Bjerrum, *op. cit.*, p. 81) and weaker ion-pair aggregates. Stoicheiometric partition coefficients for each possible species are defined by

$$p_{hmnws} = [H_hM_mL_n(H_2O)_wS_s]_o/[H_hM_mL_n(H_2O)_wS_s] \quad . \quad . \quad . \quad . \quad (2)$$

where the subscript o is used to distinguish the organic phase from the aqueous phase. We can now write a general expression for the distribution ratio

$$q = \frac{\text{total concn. of metal in the organic phase}}{\text{total concn. of metal in the aqueous phase}}$$

$$= \frac{\Sigma m[H_hM_mL_n(H_2O)_wS_s]_o}{\Sigma m[H_hM_mL_n(H_2O)_wS_s]} =$$

$$= \frac{\Sigma p_{hmnws}\, \beta_{hmnws}\, m\, [H]^h[M]^m[L]^n[H_2O]^w[S]^s}{\Sigma \beta_{hmnws}\, m\, [H]^h[M]^m[L]^n[H_2O]^w[S]^s} \quad . \quad . \quad . \quad . \quad (3)$$

where the summation includes all physically significant combinations of h, m, n, w, and s. Equation (3) can immediately be simplified by excluding terms from the numerator for which $p_{hmnws} = 0$. Moreover, considerations of electroneutrality exclude the partition of charged species and impose the condition $m\nu + h = n\lambda$. However complex, or however numerous, the different species in the aqueous phase may be, their average composition can be represented by a single symbol, *viz.*, $\mathrm{H}_{\bar{m}\bar{h}}\mathrm{M}_{\bar{m}}\mathrm{L}_{\bar{m}\bar{n}}(\mathrm{H_2O})_{\bar{m}\bar{w}}\mathrm{S}_{\bar{m}\bar{s}}$, where $\bar{m}$ represent the "polymerisation number," *i.e.*, the average number of metal atoms per molecular species, and $\bar{h}$ and $\bar{n}$ the average number of hydrogen and ligand atoms, and $\bar{w}$ and $\bar{s}$ the average number of molecules of water and of organic solvent attached per atom of metal. These definitions correspond exactly with the concept, originally introduced by Bjerrum (*op. cit.*), of the "degree of formation" (also termed the "ligand number" by other authors) of the simpler system of mononuclear complexes representable by the formula $\mathrm{ML}_n(n = 0, 1, \ldots . N)$. Equation (3) can now be rewritten in the form

$$q = \bar{\mathbf{m}}[\mathrm{H}_{\bar{\mathbf{m}}\bar{\mathbf{h}}}\mathrm{M}_{\bar{\mathbf{m}}}\mathrm{L}_{\bar{\mathbf{m}}\bar{\mathbf{n}}}(\mathrm{H_2O})_{\bar{\mathbf{m}}\bar{\mathbf{w}}}\mathrm{S}_{\bar{\mathbf{m}}\bar{\mathbf{s}}}]_o/\bar{m}[\mathrm{H}_{\bar{m}\bar{h}}\mathrm{M}_{\bar{m}}\mathrm{L}_{\bar{m}\bar{n}}(\mathrm{H_2O})_{\bar{m}\bar{w}}\mathrm{S}_{\bar{m}\bar{s}}]$$

$$= \frac{\bar{\mathbf{p}}\bar{\mathbf{m}}\bar{\boldsymbol{\beta}}[\mathrm{H}]^{\bar{\mathbf{m}}\bar{\mathbf{h}}}[\mathrm{M}]^{\bar{\mathbf{m}}}[\mathrm{L}]^{\bar{\mathbf{m}}\bar{\mathbf{n}}}[\mathrm{H_2O}]^{\bar{\mathbf{m}}\bar{\mathbf{w}}}[\mathrm{S}]^{\bar{\mathbf{m}}\bar{\mathbf{s}}}}{\bar{m}\bar{\beta}[\mathrm{H}]^{\bar{m}\bar{h}}[\mathrm{M}]^{\bar{m}}[\mathrm{L}]^{\bar{m}\bar{n}}[\mathrm{H_2O}]^{\bar{m}\bar{w}}[\mathrm{S}]^{\bar{m}\bar{s}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since the ligand numbers will not, in general, be identical in the two phases, those in the organic phase are distinguished by heavy (Clarendon) type, while italic subscripts refer to the aqueous phase. The partition coefficient and overall stability constant of the (average) species in the organic phase, $\mathrm{H}_{\bar{\mathbf{m}}\bar{\mathbf{h}}}\mathrm{M}_{\bar{\mathbf{m}}}\mathrm{L}_{\bar{\mathbf{m}}\bar{\mathbf{n}}}(\mathrm{H_2O})_{\bar{\mathbf{m}}\bar{\mathbf{w}}}\mathrm{S}_{\bar{\mathbf{m}}\bar{\mathbf{s}}}$, as defined by equations (2) and (1) are $\bar{\mathrm{p}}_{\bar{\mathbf{m}}\bar{\mathbf{h}},\bar{\mathbf{m}},\bar{\mathbf{m}}\bar{\mathbf{n}},\bar{\mathbf{m}}\bar{\mathbf{w}},\bar{\mathbf{m}}\bar{\mathbf{s}}}$ and $\bar{\beta}_{\bar{\mathbf{m}}\bar{\mathbf{h}},\bar{\mathbf{m}},\bar{\mathbf{m}}\bar{\mathbf{n}},\bar{\mathbf{m}}\bar{\mathbf{w}},\bar{\mathbf{m}}\bar{\mathbf{s}}}$, and are abbreviated to $\bar{\mathbf{p}}$ and $\bar{\boldsymbol{\beta}}$; the stability constant for the (average) species in the aqueous phase is $\bar{\beta}_{\bar{m}\bar{h},\bar{m},\bar{m}\bar{n},\bar{m}\bar{w},\bar{m}\bar{s}}$ and is abbreviated to $\bar{\beta}$. Taking logarithms, we have

$$\begin{aligned}\log q = {} & \log(\bar{\mathbf{p}}\bar{\boldsymbol{\beta}}/\bar{\beta}) + \log(\bar{\mathbf{m}}/\bar{m}) + (\bar{\mathbf{m}}\bar{\mathbf{h}} - \bar{m}\bar{h}) \log [\mathrm{H}] \\ & + (\bar{\mathbf{m}} - \bar{m}) \log [\mathrm{M}] + (\bar{\mathbf{m}}\bar{\mathbf{n}} - \bar{m}\bar{n}) \log [\mathrm{L}] \\ & + (\bar{\mathbf{m}}\bar{\mathbf{w}} - \bar{m}\bar{w}) \log [\mathrm{H_2O}] + (\bar{\mathbf{m}}\bar{\mathbf{s}} - \bar{m}\bar{s}) \log [\mathrm{S}] \quad . \quad . \quad . \quad (5)\end{aligned}$$

At this stage it will be convenient to develop the argument with reference to what may arbitrarily be distinguished as "ideal" and "non-ideal" systems. Systems are termed ideal if, over the whole range of conditions analytically accessible, there are no changes (*a*) in the solvent properties of the two phases, and (*b*) in the extent of solvation (by water and/or molecules of organic solvent) of any species in either phase. Under such conditions the stoicheiometric stability constants $\bar{\boldsymbol{\beta}}$ and $\bar{\beta}$, the partition coefficient $\bar{\mathbf{p}}$, and the ligand numbers $\bar{\mathbf{w}}$, $\bar{w}$, and $\bar{\mathbf{s}}$, $\bar{s}$ are constant. If the ionic strength is controlled and [S] and $[\mathrm{H_2O}]_o$ are constant, the last two terms in equation (5) may be assimilated into the first term, giving

$$\begin{aligned}\log q = {} & A + \log (\bar{\mathbf{m}}/\bar{m}) + (\bar{\mathbf{m}}\bar{\mathbf{h}} - \bar{m}\bar{h}) \log [\mathrm{H}] \\ & + (\bar{\mathbf{m}} - \bar{m}) \log [\mathrm{M}] + (\bar{\mathbf{m}}\bar{\mathbf{n}} - \bar{m}\bar{n}) \log [\mathrm{L}] \quad . \quad . \quad . \quad (5a)\end{aligned}$$

where the term A is independent of [H], [M], and [L] and can be eliminated by differentiation (see p. 1909). In non-ideal systems changes in one or other of the variables C_{H}, C_{M}, C_{L}, or C_{HL} (see p. 1915) bring about changes in the mutual miscibility of the phases. The various consequences of the concomitant changes in phase composition, stability constants, and partition coefficients are explored in the second section of this paper.

Solvent Extraction in Ideal Systems.—In principle, values of h, m, and n, for each complex species which exists in either phase, and the corresponding stability constants and partition coefficients can be calculated from a sufficiently large number of measurements of the distribution ratio, q, for known values of $[\mathrm{H}^+]$, [M], and [L]. The free hydrogen-ion concentration can often be obtained from measurements of pH, but in general only the total concentration of metal, C_{M}, and the total ligand concentration, C_{L}, can be determined analytically in the two phases. However, by using radioactive metal ions in tracer concentrations it is often possible to ensure that $C_{\mathrm{L}} \gg \Sigma n[\mathrm{H}_h\mathrm{M}_m\mathrm{L}_n]$ and that $C_{\mathrm{H}} \gg \Sigma h[\mathrm{H}_h\mathrm{M}_m\mathrm{L}_n]$ so that the approximations $[\mathrm{L}] \cong C_{\mathrm{L}}$ and $[\mathrm{H}^+] \cong C_{\mathrm{H}}$ are justified. Examples of this device appear in Parts III—V. So far no one has attempted to measure [M] or [L] directly in solvent extraction studies, doubtless owing to the uncertainties introduced by junction potentials. Having determined the distribution ratio, q, for known values of C_{H}, C_{M}, and C_{L}, covering as wide a range as possible, the results can best be evaluated by considering the partial derivatives of equation (5*a*).

(a) *Variations in metal concentration.* By partial differentiation of equation (5*a*) with respect to the concentration of free metal ions we have

$$(\partial \log q/\partial \log [\mathrm{M}])_{[\mathrm{H}],[\mathrm{L}]} = (\bar{\mathbf{m}} - \bar{m}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus when the extent of polymerisation of the metal complexes is the same in each phase, the value of this derivative is zero. In the limiting case, as the concentration of free metal ions, [M], tends to zero, $\bar{m}$ tends to unity, so that a zero value of the derivative at low metal concentrations signifies that all the species are mononuclear. Positive values of $\partial \log q/\partial \log [\mathrm{M}]$ indicate that the degree of polymerisation is greater in the organic phase ($\bar{\mathbf{m}} > \bar{m}$), while negative values indicate that it is greater in the aqueous phase ($\bar{\mathbf{m}} < \bar{m}$). Although the value of the derivative $\partial \log q/\partial \log [\mathrm{M}]$ at a particular concentration of free hydrogen ion and free ligand ion provides a useful index of the relative association of metal in the two phases, it clearly affords no further information concerning the nature of the species in the organic phase, or, indeed, of the nature of the species which may be polymerising. However, if the composition of the species extracted into the organic phase is already known, deductions concerning the polymerised species may be made by investigating the way in which the value of the derivative (6) depends on the parameters [H] and [L]. A particular illustration of this type of treatment appears in Part IV of this series. If it is impossible to neglect hydroxy-complexes in setting up a general equation of type (3), an obvious extension provides a method of studying polynuclear hydrolysis products (cf. Connick and Reas, *J. Amer. Chem. Soc.*, 1951, **73**, 1171). Indeed any type of competitive complex formation can be studied.

Examples of every type of behaviour predicted by equation (6) have been realised in practice. In the extraction of most inner complexes with organic reagents, mononuclear species appear to predominate in both phases. Association in the organic layer has been postulated in the extraction of ferric, gallium, and auric chlorides from hydrochloric acid (Nachtrieb and Conway, *ibid.*, 1948, **70**, 3547; Nachtrieb and Fryxell, *ibid.*, 1949, **71**, 4035; Haas, Thesis, Chicago, 1950), and the formation of a dinuclear species in the aqueous phase (which undergoes partition to a negligible extent) appears to be the reason for the decreasing extraction of indium from hydrobromic acid into *iso*butyl methyl ketone as the metal concentration increases (Irving and Rossotti, Part IV).

A plot of experimental values of log q against log C_{M} gives values of the partial derivative $(\partial \log q/\partial \log C_{\mathrm{M}})_{[\mathrm{H}],[\mathrm{L}]}$ which can readily be shown to be identical with those of the partial derivative $\partial \log q/\partial \log [\mathrm{M}]$ for the case where $\bar{\mathbf{m}} = \bar{m}$. But in the general case, and where the phases at equilibrium have the same volume,

$$\partial \log q/\partial \log C_{\mathrm{M}} = (\bar{\mathbf{m}} - \bar{m})(1 + q)/(\bar{\mathbf{m}} + \bar{m}q) \quad . \quad . \quad . \quad (6a)$$

Introducing the identity, E (percentage extraction) $= 100q/(1 + q)$, valid for equal phase volumes, we obtain an equivalent expression

$$\partial \log E/\partial \log C_{\mathrm{M}} = (\bar{\mathbf{m}} - \bar{m})/(\bar{\mathbf{m}} + \bar{m}q) \quad . \quad . \quad . \quad . \quad . \quad (6b)$$

(b) *Variations in free ligand concentration.* At constant metal and hydrogen-ion concentration we have

$$(\partial \log q/\partial \log [\mathrm{L}])_{[\mathrm{H}],[\mathrm{M}]} = \bar{\mathbf{m}}\bar{\mathbf{n}} - \overline{mn} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The condition [M] = constant is difficult to realise where polynuclear species contribute appreciably to the equilibria, and the potentialities of metal buffers for studies of solvent extraction have not yet been exploited.

In the most favourable case, where only mononuclear species are present in either phase and a single complex of composition $\mathrm{H}_h\mathrm{ML}_n$ is extracted into the organic phase, $\bar{\mathbf{m}} = \bar{m} = 1$, and $\bar{n}$ is simply the customary "degree of formation" of the aqueous system of complexes. Equation (7) now reduces to the form

$$\partial \log q/\partial \log [\mathrm{L}] = \bar{\mathbf{n}} - \bar{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

A particular case of this equation, in the form $\bar{n} = 4 + \mathrm{d}(\log q)/\mathrm{d}(\mathrm{pAa})$, was derived by Rydberg in 1950 (*Acta Chem. Scand.*, 1950, **4**, 1503) and shown to apply to the extraction of the neutral thorium complex $\mathrm{ThAa_4}$ from solutions of $\mathrm{Th^{4+}}$ and acetylacetone, HAa.

From the plot of $\log q$ against $\mathrm{pL} = -\log_{10} [\mathrm{L}]$, a series of values of $\bar{n}$ can be calculated by equation (7*a*) if the value of $\bar{\mathbf{n}}$ is known or assumed. From the derived formation curve (the plot of $\bar{n}$ against pL) it is possible to calculate values for the individual stability constants, K_1, K_2, ... K_n defining the metal–ligand equilibria (Irving and Rossotti, *J.*, 1954, 2904, and refs. therein) though the accuracy of the data derived from partition measurements only justifies the evaluation of all the constants in favourable cases (cf. Rydberg, *loc. cit.*). A two-parameter equation developed by Dyrssen and Sillén (*Acta Chem. Scand.*, 1953, **7**, 663) facilitates the calculation of a series of equilibrium constants which satisfy the quite arbitrary condition $K_n/K_{n+1} =$ constant; the calculations are, however, exact when $n = 1$ or 2. It should be emphasised that all these approximate conditions assume implicitly that $\bar{\mathbf{n}}$ is known and constant, and that $\bar{\mathbf{m}} = \bar{m} = 1$. In the general case only the difference between the ligand numbers $\overline{\mathbf{mn}}$ and $\overline{mn}$ can be determined experimentally from equation (7).

(c) *Variations in hydrogen-ion concentration.* By partial differentiation of equation (5) we have

$$(\partial \log q/\partial \log [\mathrm{H}])_{[\mathrm{M}],[\mathrm{L}]} = (\overline{\mathbf{mh}} - \overline{mh}) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that if the values of $\bar{\mathbf{m}}$ and $\bar{m}$ are known, the relative extent of association of hydrogen to metal in each case can be determined. Where $\bar{\mathbf{m}} = \bar{m} = 1$, the partial derivative of (8) can be replaced by the more conveniently measurable $(\partial \log q/\partial \log [\mathrm{H}])_{C_{\mathrm{M}}[\mathrm{L}]}$. The more general case is approached from a different angle on p. 1913. If a non-acidic species, ML_n, represents the composition of the organic phase, values of equation (8) will be zero provided $\bar{h} = 0$ as well; this condition is usually met for solutions of mineral salts in moderate concentrations of mineral acids. Positive values of the derivative (8) will then correspond to the extraction of acido-species. However, negative values are also feasible at high acidities if, *e.g.*, a non-acidic species were to partition, while $\bar{h} > 0$ owing to the presence in the aqueous phase of an acido-species of low or negligible partition coefficient.

In the extraction of inner complexes, the chelating agent $\mathrm{H}_\lambda\mathrm{L}$ is usually a weak acid. If monobasic, then $[\mathrm{HL}]/[\mathrm{H^+}][\mathrm{L^-}] = \beta_{101}$, and $[\mathrm{HL}]_o/[\mathrm{HL}] = p_{101}$ from equations (1) and (2). Where only mononuclear complexes containing no additional hydrogen atoms are concerned $\bar{\mathbf{m}} = \bar{m} = 1$, and $\bar{\mathbf{h}} = \bar{h} = 0$. Eliminating [L] from equation (5*a*), we have

$$\log q = A + (\bar{\mathbf{n}} - \bar{n})\{\log [\mathrm{HL}]_o + \mathrm{pH} - \log \beta_{101}p_{101}\} \quad . \quad . \quad . \quad (9)$$

If a single uncharged complex of composition ML_n is extracted, the gradient of the plot of experimental values of $\log q$ against pH (the concentration of reagent in the organic phase being kept constant), or against $\log [\mathrm{HL}]_o$ (measured at constant pH), should be $(\bar{\mathbf{n}} - \bar{n})$, where $\bar{n}$, as before, is the degree of formation of the system of complexes in the aqueous phase. The limiting value of equation (9) as $\bar{n}$ tends to zero is given by

$$\log q = \log K + \bar{\mathbf{n}}\,(\log [\mathrm{HL}]_o + \mathrm{pH}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

which was derived earlier by different reasoning by several authors (Kolthoff and Sandell, *J. Amer. Chem. Soc.*, 1941, **63**, 1906; Irving and Williams, *J.*, 1949, 1841). The slope of the plot of $\log q$ against pH ($[\mathrm{HL}]_o$ being constant) yields an integral value for $\bar{\mathbf{n}}$ in some cases (see, *e.g.*, Connick and McVey, *J. Amer. Chem. Soc.*, 1949, **71**, 3182; Suttle, *ibid.*, 1954, **76**, 2184; Cornish, A.E.R.E. C/R 891; Dyrssen and Dahlberg, *Acta Chem. Scand.*, 1953, **7**, 1186); this indicates that appreciable extraction can occur in spite of a low value of $\bar{n}$ owing to a favourable combination of values of the partition coefficient and stability constants. However, in other cases non-integral values for the slope $(\bar{\mathbf{n}} - \bar{n})$ will be found (see, *e.g.*, Irving, Bell, and Williams, *J.*, 1952, 356; Rydberg, *Acta Chem. Scand.*, 1950, **4**, 1503; *Arkiv Kemi, Min., Geol.*, 1953, **5**, 413; Dyrssen, *Svensk Kem. Tidskr.*, 1953, **65**, 43; 1954, **66**, 234).

(d) *Extraction from strong acids.* If HL is a strong acid and the only source of the ions H^+ and L^-, then provided $C_M \ll C_{HL}$, we have $[H^+] = [L^-] = C_{HL}$. Substituting into equation (5*a*) and differentiating, we have

$$(\partial \log q/\partial \log C_{HL})_{[M]} = \bar{\mathbf{m}}(\bar{\mathbf{h}} + \bar{\mathbf{n}}) - \bar{m}(\bar{h} + \bar{n})$$
$$= (\bar{\mathbf{h}} - \bar{h}) + (\bar{\mathbf{n}} - \bar{n}) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

for mononuclear species. This is a particularly useful result since the readily measurable variations in q with the total acid concentration, C_{HL}, provide a useful check upon deductions made from the values of the partial derivatives $(\partial \log q/\partial \log [H])_{[M],[L]}$ and $(\partial \log q/\partial \log [L])_{[M],[H]}$. Thus, if ML_3 undergoes partition, values of the latter derivative and of $(\partial \log q/\partial \log C_{HL})_{[M]}$ would be $(3 - \bar{n})$ in either case. But if, *e.g.*, an acido-complex of formula HML_4 was the species in the organic phase and was almost completely dissociated into H^+ and ML_4^- in the aqueous phase, $\bar{\mathbf{h}} = 1$, $\bar{h} = 0$, and $\bar{\mathbf{n}} = 4$, so that the values of these derivatives would be $(5 - \bar{n})$ and $(4 - \bar{n})$, respectively. A decision between these two alternatives can then be made (cf. Irving and Rossotti, Part III). If, however, the acido-complex were appreciably associated in the aqueous phase, or dissociated in the organic phase, it might be impossible to distinguish unambiguously between its extraction and that of a hydrogen-free complex from considerations of partition equilibria and the valency, ν, of the metal alone. Independent determinations of $\bar{n}$, or supplementary studies of, *e.g.*, the conductivity of the organic phase might be necessary.

(e) *Step-equilibria in the aqueous phase.* The concentration of any non-acidic, mononuclear species, ML_n, in a system of complexes in step equilibrium in a monophase is simply related to its degree of formation, α_n, the total metal concentration, C_M, and the concentration of free ligand, [L], by the expressions

$$ML_n = \alpha_n C_M = \beta_n[L]^n/\sum_0^n \beta_n[L]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

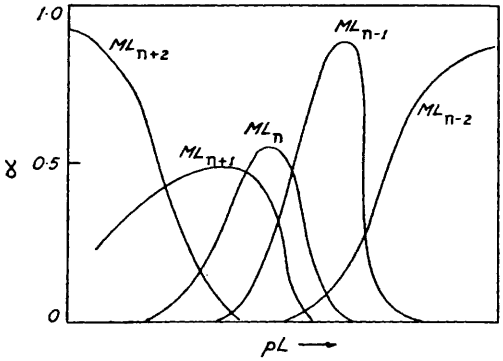
If $p_{\bar{n}}$ is the partition coefficient of this species, and C is the total concentration of metal in the aqueous phase we have

$$q = [ML_n]_o/C = p_n \alpha_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Equations (11) and (12) emphasise the close dependence of the distribution ratio [and thence the percentage of extraction $E = 100q/(1 + q)$ for equal phase volumes] upon the values of the partition coefficient of the extracted species, the stability constants governing equilibria in the aqueous phase, and the free ligand concentration in the aqueous phase. Fig. 1 represents a typical set of curves for the degree of formation of each of a system of complexes of general formula ML_n, expressed as a function of the free ligand exponent, pL. The distribution ratio will follow α_n of equation (12) and if ML_n were the (uncharged) species extracted (cf. Fig. 1), q would pass through a maximum as the free ligand concentration is increased. But if ML_{n-2} (or ML_{n+2}) were the uncharged species extracted, Fig. 1 shows that q would steadily decrease (or increase) with [L]. The extraction of thorium or uranyl oxine complexes (Dyrssen, *locc. cit.*) and of ferric thiocyanate (Mitchell and MacDonald, *J.*, 1951, 1310) illustrates such behaviour. If the domain of ML_n were more extensive than that shown in Fig. 1, the maximum value of q would be maintained over a wide range of pL values, *e.g.*, between pL = 4 and 8 in the case of thorium and 8-hydroxyquinoline. If the species which undergoes partition is the highest complex that is formed in the system, q will not fall off from its maximum value $(\sim p_n)$ with increasing free ligand concentration (cf. the case of $ThAa_4$, Rydberg, *loc. cit.*). But if the domain of ML_n is very restricted, q may never become large even when the partition coefficient, p_n, is very large. An extreme case is provided by the mercury halides. The stability constants (Sillén, *Acta Chem. Scand.*, 1949, **3**, 539) are such that if the dihalide is dissolved in water the predominant species is HgX_2. The 1 : 3 complexes, HgX_3^-, have an extremely limited range of existence so that the addition of very small concentrations of free halide ions to a solution of the dihalide in water abruptly decreases the concentration of HgX_2 in favour of HgX_4^{2-}. Accordingly, the distribution of HgX_2 into ether decreases continuously and rapidly with increasing halogen acid concentration (Hantzsch, *Z. physikal. Chem.*, 1899, **30**, 258; Mylius and Huttner, *Ber.*, 1911, **44**, 1315).

Depending then on values of β_n and p_n for particular systems, the widest variations in behaviour can be expected. Dyrssen and Sillén (*loc. cit.*) have discussed many possible types, but in extending the treatment of the solvent extraction of metal complexes in step-equilibria from the particular case of inner complexes to the wider field of inorganic salts and acido-complexes, particular interest attaches to systems of low stability.

FIG. 1.



(f) *The partition of several species in equilibrium.* The concentration of the acido-complex, HML_{n+1}, in the organic phase is given by $p_aK_a[H^+][ML_{n+1}^-]$, where p_a is the appropriate partition coefficient, and $K_a = [HML_{n+1}]/[H^+][ML_{n+1}^-]$, so that if both uncharged ML_n and the acido-complex HML_{n+1} are extracted simultaneously

$$q = \alpha_n p_n + \alpha_{n+1} p_a K_a [H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and it will be obvious that values of $(\partial \log q/\partial \log [L])_{[H],[M]}$ will lie between those for which α_n and $\alpha_{n+1} = 0$. Specifically the limiting value of $\partial \log q/\partial \log [L]$ as the free ligand concentration tends to zero will be $(n - \bar{n})$; and as [L] tends to infinity, $(1 + n - \bar{n})$. At intermediate values of [L], the magnitude of the derivative of equation (13) will depend on the constants of the system. Thus

$$(\partial \log q/\partial \log [L])_{[H],[M]} = (n - \bar{n}) + c[L]/(1 + c[L]) \quad . \quad . \quad . \quad (14)$$

where $c = p_aK_aK_n[H^+]/p_n$, and K_n is the equilibrium constant for the reaction $ML_{n-1} + L \rightleftharpoons ML_n$. Hence if the value of $p_aK_a[H^+] \ll p_n/K_n$, the value of equation (14) will approximate to $(n - \bar{n})$; but if $p_aK_a[H^+] \gg p_n/K_n$, it will approximate to $(1 + n - \bar{n})$.

When several species are co-extracted we can write

$$q = \sum_0^n \alpha_i p_i + \alpha_{n+1} p_a K_a [H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Individual values of α_i can be calculated from the magnitude of [L] and the stability constants of the system, where these are known, so that, in favourable cases, individual values of p_i and p_aK_a can be calculated from a sufficient number of simultaneous equations of the form (15). This has been attempted in analysing data from experiments in which $InBr_3$ and $HInBr_4$ are co-extracted (Irving and Rossotti, Paper III). A further complication sometimes encountered, *viz.*, that alkali-metal salts or ion-pairs of the type AML_{n+1} can also be co-extracted under certain conditions (*loc. cit.*), can be treated quantitatively by an obvious extension of equation (15). Since q depends upon the product of terms α_i and p_i it will be obvious that the species which predominates in the organic phase may only contribute to a relatively insignificant extent to the total metal concentration of the aqueous phase.

(g) *The solvent extraction of salts of type* (iv). In the previous cases the ligand, L, has been a base conjugate to an acid HL. But when dealing with complexes of the type M_mL_n it is formally immaterial whether L should be regarded as the ligand attached to M, or *vice versa*. If, then, we consider, *e.g.*, the per-rhenate ion, ReO_4^- as the central group, M, and the tetraphenylarsonium ion, Ph_4As^+, as the ligand L (derived in this instance from the salt $Ph_4As^+Cl^-$), the foregoing mathematical treatment leads immediately to equations for the solvent extraction of $[Ph_4As^+][ReO_4^-]$ and similar compounds which are more general and exact than those used by Tribalat (*Analyt. Chim. Acta*, 1949, **3**, 113; 1950, **4**, 228). Considerations of electroneutrality impose the conditions $\nu = n\lambda$ as in the extraction into *o*-dichlorobenzene of, *e.g.*, $[SbI_4^-][L^-]$, $[Cu(CNS)_4^{2-}][L^+]_2$, $[Co(CNS)_4^{2-}][L^+]_2$, and $[Fe(CNS)_6^{3-}][L^+]_3$ ($L^+ = Ph_3MeAs^+$; Gibson, *Rev. Pure Appl. Chem., Roy. Austral. Chem. Inst.*, 1954, **4**, 101, and refs. therein). The equations are further simplified by the fact that only mononuclear complexes can be formed since the species, M, is already co-ordinatively fully saturated.

(h) *The solvent extraction of acids.* Polybasic acids may conveniently and logically be treated as resulting from the successive attachment of the ligand H^+ to a central anionic core X^{-h}. Equation (5*a*) may then be applied to the solvent extraction of acids of general composition H_hX_x by setting $M = X$, $m = x$, and putting $n = 0$. Thence

$$\log q = A' + \log(\bar{\mathbf{h}}\bar{\mathbf{x}}/\bar{h}\bar{x}) + (\bar{\mathbf{h}}\bar{\mathbf{x}} - \bar{h}\bar{x})\log[H^+] + (\bar{\mathbf{x}} - \bar{x})\log[X] \quad . \quad (15)$$

under the limiting conditions outlined above for ideal systems, *i.e.*, at low total acidities. A' is a function of stability constants and partition coefficients and may be eliminated by differentiation. For a strong monobasic acid, HL, we have $\partial \log q/\partial \log C_{\text{HL}} = (\bar{\mathbf{h}} - \bar{h})$, so that the gradient of the double logarithmic plot of the distribution ratio against total acid concentration can be used to determine differences between the ligand numbers of hydrogen in the two phases. If it is assumed that $\bar{h} = 0$ at low total acid concentrations, *i.e.*, that there is complete dissociation in the aqueous phase, the degree of association of the acid in the organic phase follows immediately.

Archibald (*J. Amer. Chem. Soc.*, 1932, **54**, 3178) and Crittenden and Hixson (*Ind. Eng. Chem.*, 1954, **46**, 265) have approached a similar problem by considering plots of log $[\text{acid}]_o$ against log $[\text{acid}]_{\text{aq.}}$ from which it appears that hydrochloric and nitric acids are appreciably associated in the lower alcohols and ketones, and still more so in ethers and higher homologues of alcohols, ethers, and ketones. Measurements of the extraction of hydrochloric acid and hydrobromic acid into diethyl and di*iso*propyl ether (Chalkley and Williams, Part II) confirm that association is appreciable even at moderate acidities. By an E.M.F. method (Everett and Rasmussen, *J.*, 1954, 2812) hydrogen chloride has been shown to be a weak acid in acetone with a dissociation constant of about 10^{-8}.

A modified treatment when [M] *cannot be held constant.* When the condition $[M] \ll C_M$ is no longer valid, some progress can still be made in interpreting partition data. Using the same notation as before, we define a new function, $\bar{n}_T$, *viz.*, the overall formation function of the system (*i.e.*, the average number of ligands bound per atom of metal in the two phases considered together), by the equation

$$\bar{n}_T = \frac{\bar{\mathbf{m}}\bar{\mathbf{n}}\ p_{\bar{\mathbf{h}}\bar{\mathbf{m}}\bar{\mathbf{n}}}\beta_{\bar{\mathbf{h}}\bar{\mathbf{m}}\bar{\mathbf{n}}}[H]^{\bar{\mathbf{h}}\bar{\mathbf{m}}}[M]^{\bar{\mathbf{m}}}[L]^{\bar{\mathbf{m}}\bar{\mathbf{n}}} + \bar{m}\bar{n}\beta_{\bar{h}\bar{m}\bar{n}}[H]^{\bar{h}\bar{m}}[M]^{\bar{m}}[L]^{\bar{m}\bar{n}}}{(C)_o + (C)_{\text{aq.}}} \quad . \quad . \quad (16)$$

Here the equilibrium phase volumes are assumed to be equal and the total concentration of metal in the organic phase, $(C)_o = \bar{\mathbf{m}}\ p_{\bar{\mathbf{h}}\bar{\mathbf{m}}\bar{\mathbf{n}}}\beta_{\bar{\mathbf{h}}\bar{\mathbf{m}}\bar{\mathbf{n}}}[H]^{\bar{\mathbf{m}}\bar{\mathbf{h}}}[M]^{\bar{\mathbf{m}}}[L]^{\bar{\mathbf{m}}\bar{\mathbf{n}}}$, and the total concentration of metal in the aqueous phase, $(C)_{\text{aq.}} = \bar{m}\ \beta_{\bar{h}\bar{m}\bar{n}}[H]^{\bar{h}\bar{m}}[M]^{\bar{m}}[L]^{\bar{m}\bar{n}}$. Since $q = (C)_o/(C)_{\text{aq.}}$, equation (16) reduces to

$$(C_L - [L]_T)/C_M = \bar{n}_T = (\bar{n} + \bar{\mathbf{n}}q)/(1 + q) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $[L]_T$ is the total concentration of free ligand. Differentiating, we have

$$\partial q/\partial\,(C_L - [L]_T) = (1 + q)^2/C_M(\bar{\mathbf{n}} - \bar{n}) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which can be transformed into an equivalent form

$$\partial(C_L - [L]_T)/\partial E = 100C_M(\bar{\mathbf{n}} - \bar{n}) \quad . \; . \; . \; . \; . \; . \; . \quad (17a)$$

by introducing the relation $E = 100q/(1 + q)$. By an entirely similar procedure we obtain

$$(C_H - [H]_T)/C_M = (\bar{n} + \bar{\mathbf{h}}q)/(1 + q) \quad . \; . \; . \; . \; . \; . \; . \quad (19)$$

whence

$$\partial q/\partial(C_H - [H]_T) = (1 + q)^2/C_M(\bar{\mathbf{h}} - \bar{h}) \quad . \; . \; . \; . \; . \quad (20)$$

and

$$\partial(C_H - [H]_T)/\partial E = 100C_M(\bar{\mathbf{h}} - \bar{h}) \quad . \; . \; . \; . \; . \; . \; . \quad (20a)$$

If it is possible to measure $[L]_T$, the difference between the average ligand numbers of the complex species in the two phases can be determined from the plot of q against $(C_L - [L]_T)$ by using equation (18). That in the aqueous phase, $\bar{n}$, may be calculable from a knowledge of the relevant stability constants, so that $\bar{\mathbf{n}}$ may be computed. Alternatively, the ligand number in the organic phase may be known from other sources so that $\bar{n}$ may be calculated, and thence from a sufficient number of pairs of values of $\bar{n}$ and [L], the stability constants, β_n, may be obtained. A similar treatment of equation (20) leads to the differences between the ligand numbers of hydrogen in the two phases which can be further discussed on the lines outlined above.

Summarising Discussion of Ideal Systems.—The extraction of undissociated compounds of type (i) is readily described in terms of the Nernst partition isotherm and needs no elaboration here (cf. Friedman, *locc. cit.*). There are, however, a number of interrelated reasons for the apparent differences between the behaviour of inner complexes of type (ii) and inorganic salts of type (iii).

When the acid HL is weak, and the complex ML_n is strong and unsolvated [as is usually the case with type (ii) solutes], the primary stage in extraction—considered in terms of equilibrium rather than mechanistically—is the formation of this complex from constituent ions at such a low free-ligand concentration that the solvent characteristics of the aqueous phase are not appreciably modified. The inner complexes are stable, stoicheiometric, monomeric compounds which can usually be isolated in the solid state. They are very sparingly soluble in water, but are usually extracted readily into chloroform, carbon tetrachloride, benzene, and hexone (*iso*butyl methyl ketone), but poorly into ethers and alcohols. The organic reagent, HL, from which they are derived is a comparatively weak acid and more soluble in organic solvents than in water. Changes in the solvent, and extensive variations in the composition of the aqueous phase due to the addition of other ions, do not affect the composition of the extracted species. The extraction of an (unsolvated) inner complex does not introduce water into the organic phase, and changes in the mutual solubility of the two phases are very small even when the free ligand concentration is varied sufficiently to change the extractability over a wide range of distribution ratios. Since changes in the mutual solubility of the phases are negligible, the constancy of (stoicheiometric) partition coefficients and stability constants may be assumed if the ionic strength of the aqueous phase is held constant. Such systems may usually be described quantitatively by equations of the form (5*a*) and it is possible to compute from experimental data the partition coefficient of the single extracted species and also one or more of the stability constants which refer, it should be noted, to an aqueous solution saturated with organic solvent. If the extraction of an inner complex into a number of solvents is " ideal " in each case, then plots of log q against pL will be parallel for the different solvents. This will no longer be the case if the complex is solvated to different extents by the various organic solvents, for the simplification of equation (5) to (5*a*) will no longer be valid.

Weak complexes are involved in the extraction of complexes of type (ii), so that a much higher ratio of ligand to metal concentration is required. The species extracted can rarely be isolated, and often even its composition is in doubt : there is reason to suppose that it varies in many cases with the experimental conditions. Extraction is highest into ketones, ethers, alcohols, and similar donor solvents, but is generally negligible into chloroform or hydrocarbons. The acid from which the anion of the salt is derived is strong and usually undergoes partition appreciably into the organic phase only at the highest concentrations. When changes in the concentration of anion are brought about by changing the concentration of the corresponding mineral acid (and this is usually the case) there may be gross changes in the volumes of the two phases, their direction and magnitude depending specifically on the organic solvent and acid employed. Hence under the conditions of experimentation, both the partitition coefficients and the stability constants are variables which change with phase composition, so that most systems deviate more or less from the behaviour predictable for ideal systems. However, by selecting mineral acid and organic solvent such that changes in mutual solubility are negligible over a sufficiently wide range of values of q, it appears that the extraction of salts of type (iii) (*e.g.*, the extraction of indium bromide from hydrobromic acid into *iso*butyl methyl ketone; Irving and Rossotti, Parts III and IV) can be treated on the lines developed for ideal systems.

It is impossible, at present, to control the ionic strength of an organic phase in solvent extraction, for although lithium perchlorate can be used for controlling the ionic strength of an anhydrous ethereal solution (Berglund and Sillén, *Acta Chem. Scand.*, 1948, **2**, 116) this expedient cannot be employed in a two-phase system. But when formally uncharged inner complexes are extracted and at low concentration, we shall expect comparatively small changes in their activity coefficients over the range of experimental conditions, though such cannot be the case when inorganic salts and acido-complexes are extracted. This provides another reason why the extraction of inner complexes should be easier to interpret quantitatively than that of type (iii).

The addition of neutral salts to the aqueous phase in attempts to control the ionic strength may either increase or decrease the extraction of inorganic salts in highly specific ways (Jenkins and McKay, *Trans. Faraday Soc.*, 1954, **50**, 107; Bock and Bock, *Z. anorg. Chem.*, 1950, **263**, 146) and it is noteworthy that, although the distribution generally remains substantially independent of metal concentration when inner complexes are extracted, yet it may remain constant, increase, or decrease with increasing metal concentration where inorganic salts of type (iii) are concerned. The solvent extraction of salts of type (iv) shows features of type (ii) in the main, though few systems have been examined quantitatively in any detail.

Solvent Extraction in Non-ideal Systems.—Glueckauf, McKay, and Mathieson (*Trans. Faraday Soc.*, 1951, **47**, 437) have indicated the lines on which the Gibbs–Duhem equation can be applied to the study of partition in what we have termed non-ideal systems. However, qualitative information about possible variations in behaviour in such systems can be obtained more readily by considering selected phase-diagrams.

If V_o', V' are volumes of an organic solvent and an aqueous solution, and V_o, V the corresponding volumes after equilibration, we have in practice the result that $V_o \neq V_o'$, and $V \neq V'$. The extent of mutual miscibility is determined by the nature of the organic solvent, the initial composition of the aqueous phase, the extent to which different species present are distributed between the two phases, and the actual composition of these solutes. If, in dealing with the extraction of an inorganic salt from hydrochloric acid the restriction $C_{\mathrm{M}} \ll C_{\mathrm{HCl}}$ is applied (*e.g.*, by using tracer or microgram quantities of metal) the behaviour of the system as a whole will not differ significantly from that of the simpler two-phase condensed system of three components, *viz.*, water–organic solvent–hydrogen chloride. Since the behaviour of this basic system—at least so far as changes in phase ratio and solvent composition are concerned—will serve as a common pattern for the extraction of any metal chloride, outstanding differences must be interpreted as due to specific properties, *e.g.*, stabilities or partition coefficients of the metal–chloride ion–proton system already discussed under the heading of ideal systems.

Consider the isotherm for the system diethyl ether–water–hydrogen chloride which is illustrated (not to scale) in Fig. 2. After equilibration, a mixture of equal volumes of water and ether of composition represented by the point C will separate into an ether-rich phase A and a water-rich phase B. The partition coefficient of any solute will depend on the solvent properties of the two phases and is given approximately by the ratio of its solubility in them. On addition of hydrogen chloride to a mixture of composition C (or on equilibrating equal volumes of ether and hydrochloric acid), the total composition moves along the line $CC'C''H$. The volume of the ether phase decreases relative to that of the aqueous phase (cf. Fig. 3) and becomes zero at H, the boundary of the binodal curve AHB. For all mixtures of ether and hydrochloric acid with total compositions corresponding to points along a tie-line (*e.g.*, $A'C'B'$) the relative volumes of the two phases will vary according to the position of C', but their compositions are determined solely by the positions of the points A' and B'. Hence, the partition coefficient for each solute species which is distributed between the phases will be constant for all ether–hydrochloric acid compositions represented by points along the line $A'B'$; the same will be true for the stability constants in each phase for all species in equilibrium. Hence, values of q will be constant along any one tie-line, irrespective of the number of species partitioned (cf. equations 13 and 15). On the other hand, since the percentage extracted is given by

$$E = \frac{100C_oV_o}{(CV + C_oV_o)} = \frac{100qR}{(1 + qR)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where $R = V_o/V$ is the ratio of the phase volumes after equilibration, the percentage of extraction will vary along a tie-line according to the position of C', decreasing as C' approaches A'. Since for successive mixtures of composition C, C', C'', ... the composition of the organic phases A, A', A'', . . . and that of the corresponding aqueous phase B, B', B'', ... becomes progressively more alike, the partition coefficient will decrease as the point of complete miscibility, H, is approached: but it may retain a value $\gg 1$ even at this point. A common practice in studying extraction is to equilibrate equal volumes of organic solvent and aqueous phases of different composition. Only a limited range of phase compositions (and partition coefficients) can be explored by following such a path as $CC'C''H$, since complete miscibility is reached at the point H where the phase compositions at the extremes of the tie-line may still be very dissimilar. A fuller study would be achieved by choosing compositions along a line joining the plait-point, P, to a point on the base line such that the phase ratios after equilibration are always the same. The organic and the aqueous phase become indistinguishable at the point P, so that for two phases coexisting at a point immediately within the heterogeneous region, the partition coefficient, p, is equal to unity for all species, and equilibrium constants for any given process will be identical in the two phases.

FIG. 2. *The phase isotherm for water–ether–hydrogen chloride.* (Not to scale.)

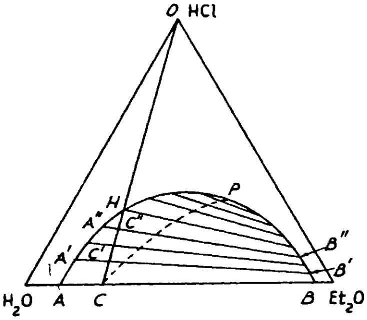
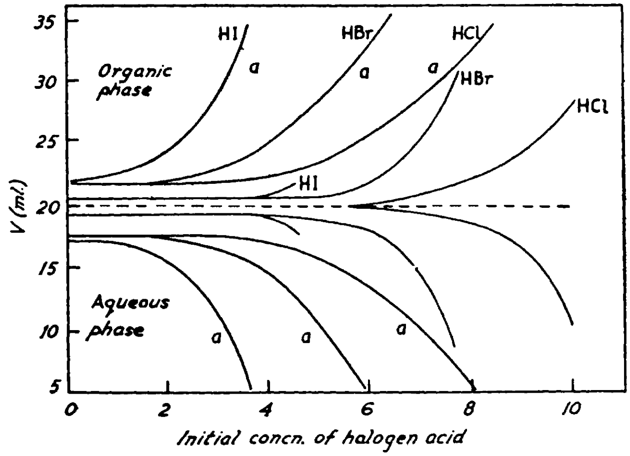


FIG. 3. *Volume changes on equilibration of* 20 *ml. of an ether with* 20 *ml. of halogen acid.*



Curves labelled *a* refer to diethyl ether, unlabelled curves to di*iso*propyl ether, and the broken line to 2 : 2′-dichloroethyl ether.

As P is approached, the increasing similarity of phase composition will make the physical separation of phases more and more difficult. Though this presents an increasingly serious practical disadvantage in batch or counter-current extraction, the objection is of little weight in partition chromatography (Irving and Williams, *Sci. Progress*, 1953, **41**, 418).

If the plait-point lay on the other side of *H*, equilibration of mixtures of composition lying along *CC'C''H* would give organic phases increasing in volume and water content, while the aqueous phases would be less modified by increasing acidity. Such a system is found with *iso*pentyl alcohol–water–hydrochloric acid. Volume changes which occur in a large number of other systems are reported elsewhere (Irving and Rossotti, Part V), and Fig. 3 shows some typical results for the volume changes which occur on equilibrating initially equal volumes of halogen acids and three different ethers. The decrease in the volume of the organic phase at the expense of the aqueous phase is more pronounced when hydrochloric acid is replaced by hydrobromic acid, and complete miscibility is reached at a lower acidity: similar effects are observed when hydrobromic acid is replaced by hydriodic acid. These changes are not due to the greater partition of hydrobromic (or hydriodic) acid as compared with hydrochloric acid, and there is no striking difference in the concentration of water in the organic layer. For any one acid the effects become less pronounced in ascending a homologous series of organic solvents. With *iso*pentyl alcohol, however, the volume of the organic phase increases at the expense of the aqueous phase, the effects increasing in the order HBr $<$ HCl $<$ HI. The partial inversion of order possibly reflects anomalies in the solvation of the halogen acids similar to those noted for the solvation of uranyl nitrate (McKay, *Trans. Faraday Soc.*, 1952, **48**, 1103) and cobalt chloride (Katzin and Ferraro, *J. Amer. Chem. Soc.*, 1953, **75**, 3821) in the presence of alcohols. At high acidities the behaviour of *iso*pentyl acetate is similar because the formation of the parent alcohol becomes appreciable even during the short period required for the equilibration. In contrast to the effects of halogen acids, the equilibration of diethyl ether with nitric acid leads to increases in the volume of the organic phase relative to the aqueous phase.

The Extraction of Metal Salts under Non-ideal Conditions.—Information of the above nature derived from studies of the equilibration of an organic solvent and mineral acids of different concentrations should be immediately applicable to the partition of metallic salts in such mixtures, provided the total concentration of metal is sufficiently low as not to modify the phase isotherms. But since there is abundant evidence that metal acido-complexes are hydrated in the organic phase, the extraction of macro-concentrations of an inorganic salt in this form will entail the transport of appreciable quantities of water into the organic phase, so that a full investigation would demand the investigation of a four-component system. Some progress can be made by comparing the concentration of water in the organic phase, measured after equilibration with an extractable salt, with that which obtains when the salt is omitted from the aqueous phase or, better, replaced by an equivalent concentration of a non-extractable salt of similar type (cf. Katzin and Sullivan, *J. Phys. Colloid Chem.*, 1951, **55**, 346; Yates, Laran, Williams, and Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 2212). In the absence of extractable metallic salt we find the concentration of water in diethyl ether to be about twice as high as in *iso*propyl ether equilibrated at the same acid concentration. For both solvents the concentration of water decreases with initial acidity and passes through a flat minimum at $N' \sim 5\text{M}$ (cf. Campbell, Laurenne, and Clarke, *ibid.*, 1952, **74**, 6193). Despite individual differences of this nature we have observed certain regularities even in cases of non-ideal extraction which are described below.

Maxima in Curves of Percentage Extraction: Retrograde Extraction.—Consider the extraction of iron from hydrochloric acid into ether in the form of $FeCl_3$ or $HFeCl_4$ (Part II). The distribution ratio, q, depends on the product of a partition coefficient, p_i, and the degree of formation, α_i, of the corresponding partitionable species (cf. equation 13). For phase compositions represented by a tie-line on or near the base line of Fig. 2, p may be large and favourable to extraction. However, at low acidities (and hence low free ligand concentrations) the degree of formation of $FeCl_3$ and $HFeCl_4$ is so low that the distribution ratio, q, is very small. In 4—5M-hydrochloric acid, the degree of formation of the complex species has increased considerably (Gamlen and Jordan, *J.*, 1953, 1435) and q has become large enough for the percentage of extraction to be quite high. Up to this stage changes in phase miscibility due to the presence of acid are comparatively small and the treatment corresponds approximately to that of ideal extraction already discussed. Now increase of the acidity still further to 7M or above certainly ought to increase the degree of formation of $FeCl_3$ and $HFeCl_4$ still further, for there is no evidence of the formation of higher complexes. But if the increased miscibility produces concomitant decreases in the partition coefficient of the extracted species, q may pass through a maximum.

If q passes through a maximum, there will normally be a maximum in the value of E, the percentage of extraction [cf. equation (21)]. But the falling-off in extraction after a maximum has been reached—" retrograde extraction " as it may be termed—may be due to a combination of effects whose relative importance will vary from system to system. In " ideal " systems in which the phase ratio, R, of equation (21) and all stability constants and partition coefficients are effectively constant, a maximum in q (and in E) is adequately explained by considerations of sequential equilibria (p. 1911) if the degree of formation α_i of the extracted species passes through a maximum with increase in free ligand concentration. While this may still be one of the factors operating in non-ideal systems the added feature here is the possibility of decreases in partition coefficients due to changes in phase composition. It follows from equation (13*a*) that the sign and magnitude of the derivative $\partial q/\partial \mathrm{pL}$ will depend on those of the partial derivatives $\partial \alpha_i/\partial \mathrm{pL}$ and $\partial p_i/\partial \mathrm{pL}$. Where, in the absence of changes in solvent character, α_i would pass through a maximum, concomitant decreases in p_i will bring about retrograde extraction at still lower values of pL. But where α_i is a monotonic increasing function of pL, retrograde extraction is still possible provided concomitant decreases in p_i are large enough. When such is the case, the onset of retrograde extraction may well be primarily a function of solvent composition and largely independent of the substances extracted. Thus for the chlorides of Fe^{3+}, Ga^{3+}, and Tl^{3+}, maximum extraction into ether occurs from hydrochloric acid of concentration ~7M, while for the bromides of Ga^{3+}, In^{3+}, Tl^{3+}, Fe^{3+}, and Tl^{+} the acid concentration is about 4·5M, and for iodides of Tl^{+}, Tl^{3+}, and In^{3+} it is about 2M (Irving and Rossotti, *Analyst*, 1952, **77**, 801).

Changes in phase ratio must be taken into account in considering percentage extraction [cf. equation (21)]. In " ideal " systems these are negligible. In " non-ideal " systems they may increase more or less rapidly (cf. Fig. 3) with changes in initial acidity and will tend to exaggerate the maximum in the curve of percentage extraction against acidity (or ligand concentration). But in some systems, *e.g.*, extraction from nitric acid into ether, R actually increases with acid concentration; q does not pass through a maximum and retrograde extraction is not normally observed over the range of acid concentrations accessible to experiment.

Extraction by Different Solvents.—Where it is possible to use the approximate expression

$$p = \frac{\text{solubility of a species in the organic solvent}}{\text{solubility of the same species in water}} = S_o/S$$

the relation $\log p = (\log S_o + \text{constant})$ should hold for a number of organic solvents. This has been confirmed for the partition of the weak monobasic acid dithizone between water and a wide range of organic solvents decreasing in efficiency in the order chloroform, *o*-dichlorobenzene, chlorobenzene, benzene, toluene, carbon tetrachloride, *cyclo*hexane, and *n*-hexane (Irving and Tilley, unpublished work). Discrepancies occur when solvents of greater miscibility with water are employed. Substantially the same order might be expected for inner complexes. But where both water and organic solvent are capable of strong intermolecular attraction with each other and with dissolved species, as will be the case when the extraction of inorganic complexes into donor molecules such as ketones, alcohols, and ethers is under consideration, no such order may hold. For predominantly covalent inorganic complexes which can be expected to have a low polarity, *e.g.*, HgI_2, intermediate behaviour would be expected. It seems unlikely, therefore, that any generally applicable " order of solvent efficiency " could be given.

One great practical difficulty in attempting to draw up such an order may be illustrated by the observations that iron is extracted more completely by diethyl ether than by di*iso*propyl ether from 4M-hydrochloric acid, but that the order of efficiency is reversed with 9M-acid. On the other hand, it would be of great value to the analyst if some sort of prediction could be made. It has frequently been observed that the lower members of a homologous series extract inorganic complexes more effectively than higher members, and it appears to be a rough guide that the more miscible the phases in the absence of acid, the more effective the extraction. This is consistent with the order ethyl methyl ketone > methyl *iso*propyl ketone > ethyl acetate > ethyl ether > . . . . . benzene, often noted. For the extraction of similar substances, *e.g.*, indium as the acido-complex $HInX_4$,aq., from hydrochloric, hydrobromic, and hydriodic acids, the order methyl propyl ketone > methyl *iso*propyl ketone > *iso*butyl methyl ketone > furfuraldehyde > ethyl acetate > diethyl ether > *iso*pentyl alcohol > *iso*pentyl acetate > 2 : 2′-dichlorodiethyl ether > di*iso*propyl ether > hydrocarbons is generally valid. Much the same order holds for the extraction of other acido-complexes, *e.g.*, of gold, gallium, or iron, from halogen acids, and for a number of nitrates from nitric acid (Part V, and refs. therein).

Discrete changes in partition coefficient are effected when one solvent is replaced by another. The behaviour of mixtures of solvents has not been widely studied although many empirical observations have been recorded. Changes in the partition of hydrochloric acid, of water, and of ferric chloride brought about by adding methanol progressively to ether–hydrochloric acid mixtures are reported elsewhere (Chalkley and Williams, Part II). The percentage of indium extracted from hydrobromic acid by a mixture of two solvents is found to agree with that calculated from the mixture law in certain cases (Irving and Rossotti, unpublished work), but in the extraction of rare-earth nitrates from tributyl phosphate mixtures no such simple treatment is adequate (Peppard, Faris, Gray, and Mason, *J. Phys. Chem.*, 1953, **57**, 294).

The Order of Extractability of Different Metals.—A series of tris-complexes of, *e.g.*, 8-hydroxyquinoline and tervalent metals should be strikingly alike and consist of a comparatively large organic matrix with an inner core of metal occupying a comparatively small fraction of the total molecular volume and completely shielded from the solvent. Solvation by water or organic solvent may well be small and should at least be constant from one metal complex to the next. There should not, therefore, be significant differences in their partition coefficients, and differences in extractability ought to be determined primarily by considerations of sequential equilibria; any order of increasing extractability for different metals ought thus to be independent of the extracting solvent used. When, however, the extent of solvation by water and organic solvent changes from one metal complex to another, the order of extraction will depend more or less specifically on the solvents and complexes concerned. Since any change in acidity in the aqueous phase modifies the relative activity of these two solvents, the relative extractability of two metals into a given solvent may become a function of acidity even when considerations of hydrolysis can be dismissed (cf. Peppard *et al.*, *loc. cit.*). Several of the more general points raised in this paper will be discussed in the following Parts II—V in relation to specific systems.

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THE INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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