SOLVENT EXTRACTION AND ITS APPLICATIONS TO INORGANIC ANALYSIS

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"If a dissolved substance distributes itself between two different liquids of small mutual solubility (*e.g.*, if iodine is shaken with water and carbon disulphide) the ratio of the concentrations of the solute in the two phases in a state of equilibrium at a given temperature is independent of its total amount: in other words, the solute must possess a constant partition coefficient, provided it has the same molecular weight in the two solvents."

First presented in this form in 1891, Nernst's partition law [1] gives quantitative expression to the facts of a phenomenon which has long been exploited in organic chemistry in the familiar technique of "extraction with ether". Yet although examples of the partition of inorganic materials between organic and inorganic phases have been reported from time to time, it is only comparatively recently that the techniques of *extraction for removal*, as they may be called,[2] have gained a similar prominence in inorganic chemistry.

During the solvent extraction of a mixture the constituents will partition independently to an extent determined by their distribution coefficients (p. 203), and if these are of similar magnitude, as in most mixtures of closely related substances, *e.g.*, compounds of the rare earths, members of an organic homologous series or of a group of alkaloids, "extraction for removal" will not give a pure product and a process of *extraction for fractionation* must be carried out. Whilst in the comparable process of fractional distillation for separating a mixture of liquids of similar boiling points a series of liquid–vapour equilibrations are carried out, a countercurrent effect being introduced through the device of a controlled amount of reflux, so a comparable "extraction for fractionation" can be effected through a series of liquid–liquid equilibrations in which the countercurrent procedure secures the advantages of retrograde extraction (p. 205) whilst the operation analogous to refluxing can readily be introduced by automatic recycling.[3] Just as fractional distillation will serve to test the homogeneity of a liquid and a boiling-point determination will help to identify it, so Craig [4] has shown that the way in which a solute is distributed in an apparatus devised for multiple extractions forms a characteristic pattern by which its purity can be tested and from which its partition ratio can be calculated, thus facilitating its identification.

The present activity in the field of liquid–liquid extraction parallels to

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[1] Nernst, *Z. physikal. Chem.*, 1891, **8**, 110.

[2] Craig, *Analyt. Chem.*, 1949, **21**, 85; 1950, **22**, 61; 1951, **23**, 41.

[3] Craig and Craig, in Weissberger, "Technique of Organic Chemistry", New York, 1950, Vol. III, pp. 171—311.

[4] *Analyt. Chem.*, 1950, **22**, 1346.

some extent that displayed in developing the techniques of ion-exchange and chromatography, for they have the common goal of effecting the separation of complex mixtures and in favourable circumstances combine a high degree of selectivity with the ability to concentrate minute amounts of material and to segregate minor from major constituents. They are, furthermore, adaptable to continuous-flow methods, and solvent extraction is particularly suited to handling large amounts of material whilst by its use the problems of co-precipitation—one of the most adverse features of separations involving the precipitation of a solid—are circumvented. As compared with such unit processes as precipitation, filtration, and the dissolution of solids, the mixing, equilibration, and transport of solutions are more readily adaptable to continuous as opposed to batch operations, and to operation by remote control—factors of importance when dealing with substances that are thermolabile or readily oxidisable, etc., and in minimising the hazards inherent in handling toxic or highly radioactive materials.

It is no exaggeration to state that, but for the separation techniques made available by the extended usage of solvent extraction, the recent spectacular advances in the chemistry of the heavier and transuranic elements,[5] in the cognate fields of nuclear physics and chemistry, in the large-scale production of certain radio-isotopes, and in the utilisation of atomic energy would have been seriously retarded. Certainly, the urgent demands of work in these fields have greatly stimulated the study of the solvent extraction of inorganic compounds, though on the grounds of security the results of much of this effort have not yet been made public.

The scope of the present Review will be confined largely to the liquid–liquid partition of inorganic substances of which no comprehensive survey so far exists : for details of actual analytical procedures standard text-books [6] and the original literature must of course be consulted. The theory and practice of solvent extraction in the organic field are already highly developed and well documented [3, 4, 7] and specific examples will only be quoted to illustrate points of analogy or procedure. The extraction of gases, and many important industrial separations, cannot be dealt with for reasons of space, but the annual reports by Elgin [8] and papers contributed to the 1950 Symposium on Absorption and Extraction [9] afford a valuable introduction to the subject, especially in so far as large-scale and chemical-engineering problems are concerned.

The Partition Isotherm.—For a solute A distributed between two immiscible phases *a* and *b* the Nernst partition law states that

$$[\mathrm{A}]_a/[\mathrm{A}]_b = p^\circ_\mathrm{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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[5] Lister, *Quart. Reviews*, 1950, **4**, 20.

[6] Sandell, " Colorimetric Determination of Traces of Metals ", 2nd edn., New York, 1950 ; and references therein.

[7] Frey and Scheibel in *Emil Barrel Jubilee Volume*, Basle, 1946, p. 446.

[8] *Ind. Eng. Chem.*, 1946, **38**, 26 ; 1947, **39**, 23 ; 1948, **40**, 53 ; 1949, **41**, 35 ; 1950, **42**, 47.

[9] *Ibid.*, pp. 1021—1230.

but the partition coefficient, p_A°, is seldom strictly constant in actual practice ; for, as Hildebrand and Scott point out,[10] if two liquids are practically immiscible the deviations from Raoult's law must be very large and the same must be true for any solute distributed between them, though the deviations may be quite different with respect to the two solvent phases : even if the solute obeys Raoult's law in the one, it will deviate markedly from it in the other. We can, however, rigidly define a thermodynamic partition constant p_A^T as the ratio of the activity $\{A\}$ of the solute in the two phases and relate it to p° as follows :

$$\begin{aligned} p_A^T = \{A\}_a/\{A\}_b &= [A]_a(f_A)_a/[A]_b(f_A)_b \\ &= p_A^\circ(f_A)_a/(f_A)_b \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

At infinite dilution the activity coefficients, $(f_A)_{a,b} = 1$, and over a small range of solute concentrations the ratio $(f_A)_a/(f_A)_b$ may be sufficiently close to unity for the observed (Nernst) partition coefficient, p_A°, to be effectively independent of concentration. Using radioactive gallium, Grahame and Seaborg [11] showed this to be the case for the partition coefficient of gallium trichloride between ether and 6N-hydrochloric acid, since it ranged only from 17·5 to 18·1 in 10^{-12}M- to 16·9 in 0·0016M-gallium trichloride. A similar result has been obtained for the distribution of ferric chloride between 5·6M-hydrochloric acid and *iso*propyl ether in concentrations up to 10^{-2}M.,[12, 13] whilst values for the distribution coefficient of $(NH_4)_2Co(SCN)_4$ between amyl alcohol and water ranged from 10·9 in 10^{-5}M- to 10·05 in 10^{-12}M-solutions.[11] On the other hand, the distribution coefficient (*q.v.*) of thenoyltrifluoroacetone (IX ; see p. 224) between benzene and 0·115M-hydrochloric acid falls from 58·7 to 43·6 as the concentration of the reagent decreases from 1·8M. to 0·1M. ; but since its concentration in the aqueous phase never exceeds 0·03 g.-mol./l., the activity coefficient there can be taken as unity and the experimental data then afford a means of calculating the activity of this important reagent in the benzene phase.[14]

For a substance of sufficiently low solubility, equation (1) should continue to apply with increasing total solute concentration until both phases are simultaneously saturated. At this point p_A° should equal the ratio of the molar solubilities of the solute in the two phases—a relationship confirmed experimentally by Jakowkin in the case of iodine and several solvents pairs.[10] However, in using this relationship to estimate the value of p° where a direct determination is difficult or experimentally inaccessible, many authors have underestimated the extent to which the mutual solubility of the two solvents will affect the result. Indeed, sometimes the inferences drawn from solubility measurements alone can be quite misleading.[15] A classical case is afforded by silver perchlorate, for though its solubility at 25° in water is

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[10] " The Solubility of Nonelectrolytes ", New York, 1950.

[11] *J. Amer. Chem. Soc.*, 1938, **60**, 2524 ; cf. ref. 64.

[12] Myers, Metzler, and Swift, *ibid.*, 1950, **72**, 3767.

[13] Nachtrieb and Conway, *ibid.*, 1948, **70**, 3547, 3552.

[14] King and Reas, AECD 2573 (references to MDDC or AECD numbers are to American atomic energy declassified reports).

[15] Garwin and Hixson, *Ind. Eng. Chem.*, 1949, **41**, 2298, 2303.

84·5% by weight and in toluene no less than 50·3%, the salt is said to be found after partition wholly in the aqueous phase : partition between water and aniline, however, exclusively favours the organic phase.[16]

Equations (1) and (2) apply only to a solute which has the same molecular weight in each phase. Should it associate or dissociate in one or both, the experimentally determined values for the ratio of concentrations (or activities) in the two phases will not be independent of total solute concentration. For example, the fraction of iron, gallium, and gold chlorides extracted from hydrochloric acid by an organic solvent increases as the concentration of metal increases (pp. 212—216), owing possibly to association in the organic phase. But the fraction of a phenol, carboxylic acid, thiol (*e.g.*, dithizone, IV ; p. 222), or diketone (*e.g.*, IX) extracted from an aqueous buffer decreases as the latter becomes more alkaline, in consequence of increasing ionisation (p. 204). But since in the practical applications of solvent extraction we are interested primarily in the fraction of the total solute in one or other phase—quite regardless of its mode of dissociation, association, or interaction with other dissolved species—it is expedient to distinguish this fraction as its *extractability*, *extraction coefficient*, or *distribution ratio* $E = (C_A)_a/(C_A)_b$, where the symbol C_A denotes the concentration of A in all its forms as determined analytically. Thus for the solvent extraction of aluminium with " oxine " (I, p. 207 ; HOx) in the presence of fluoride ions :

$$E_{\text{Al}} = (C_{\text{Al}})_o/(C_{\text{Al}})_w = [\text{AlOx}_3]_o/\{\sum_0^3 [\text{AlOx}_n^{-n+3}]_w + \sum_0^4 [\text{Al(OH)}_n^{-n+3}]_w + \sum_0^6 [\text{AlF}_n^{-n+3}]_w\}$$

where the subscripts w and o refer to the aqueous and the organic phase, respectively, and co-ordinated water or solvent molecules are omitted from the formulæ for the metallic complexes AlX_n for the sake of simplicity. For the distribution ratio of the reagent in the same system we should have to write :

$$\begin{aligned} E_{\text{HOx}} &= \Sigma\,(\text{oxine})_o/\Sigma\,(\text{oxine})_w \\ &= \{[\text{HOx}]_o + 3[\text{AlOx}_3]_o\}/\{\Sigma\, n[\text{AlOx}_n^{-n+3}]_w + [\text{H}_2\text{Ox}]_w^+ + [\text{HOx}]_w + [\text{Ox}]_w^-\} \end{aligned}$$

A particular case of some importance is the partition of a monobasic acid, HR, between an aqueous buffer and an organic phase : it is assumed to dissociate ionically in the water and not to associate in the organic phase. Equation (3) shows that the distribution ratio, p_{HR}, is a function of the

$$p_{\text{HR}} = ([\text{HR}]_w + [\text{R}']_w)/[\text{HR}]_o = p^\circ_{\text{HR}}(1 + K^{\text{B}}_{\text{HR}}/\{\text{H}\}_w) \qquad (3)$$

hydrogen-ion concentration, and provided $p_{\text{HR}} \gg p^\circ_{\text{HR}}$ we can transform it into

$$\log_{10} p_{\text{HR}} = \log_{10} p^\circ_{\text{HR}} - \text{p}K^{\text{B}}_{\text{HR}} + \text{pH} \quad . \quad . \quad . \quad (4)$$

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[16] Hill, *J. Amer. Chem. Soc.*, 1921, **43**, 254 ; 1924, **46**, 1132 ; 1925, **47**, 2702.

where $K_{\mathrm{HR}}^{\mathrm{B}}$ is the Brønsted dissociation constant of the acid.[17] These equations have been shown to apply to the partition of the metal-complexing reagent "dithizone" (*q.v.*) and to a large number of phenols and other acidic substances.[18] Of great practical importance is the way in which y, the percentage of solute extracted into the aqueous phase, increases with rising pH at first slowly, then rapidly, and finally slowly once more as shown in the typical sigmoid curve *A* of Fig. 4, which is a plot of equation (5) for the case $\mathrm{pH}_{\frac{1}{2}} = 5{\cdot}22$, where $\mathrm{pH}_{\frac{1}{2}}$ is defined as the hydrogen-ion exponent of the aqueous phase when the distribution ratio is unity (50% extraction).

$$y = 100p/(1 + p) = 50\{1 - \tanh 1{\cdot}15(\mathrm{pH}_{\frac{1}{2}} - \mathrm{pH})\} \quad . \quad . \quad (5)$$

It follows from equations (4) and (5) that for any chosen organic solvent the value of $\mathrm{pH}_{\frac{1}{2}}$ may be used to characterise the solute ; in fact, for any one solute partitioned between water and a variety of organic solvents the prediction that $\mathrm{pH}_{\frac{1}{2}}$ should be proportional to the common logarithm of the solubility in the organic phase has been verified for dithizone and a very wide variety of solvents by Irving, Tilley, and Bell.[19] Data on the partition of some 200 organic substances between ether and water have enabled Collander [20] to draw some valuable conclusions regarding the structural factors which affect its magnitude, whilst Marvel and Richards,[21] who studied the extraction of mono- and poly-basic acids from unbuffered solutions, found that the order of increasing extractability was almost identical for each of twelve different solvents. Distribution ratios for (unbuffered) fatty acids between water and ether range from 2·8 (formic) to 0·2 (valeric acid), and although association is known to take place in the organic phase, the values are reasonably constant for solutions no stronger than 1%. The identification of a pure fatty acid should therefore be possible from a measurement of its distribution ratio,[22] whilst the analysis of a mixture of two acids follows from a measurement of the distribution ratio and a knowledge of the values for the pure components.[23] By using distribution data obtained from measurements at two different phase ratios, the composition of a mixture of three given acids can be calculated, and the procedure has been extended to the analysis of a five-component mixture [24] and adapted to the micro-scale.[25] Of course, if it is desired to separate the components of such a mixture, fractional extraction [21] or countercurrent extraction [4] must be resorted to.

Extraction for Removal.—It is sometimes possible to find conditions such that a particular constituent of a mixture is removed exclusively and essentially quantitatively in a single extraction. Where this is impossible a

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[17] Irving, Cooke, Woodger, and Williams, *J.*, 1949, 1847.

[18] Golumbic *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 2624, 2627, 4151 ; 1950, **72**, 1939, 4145.

[19] Irving, Tilley, and Bell, *J.*, 1951.

[20] *Acta Chim. Scand.*, 1949, **3**, 717—747.

[21] *Analyt. Chem.*, 1949, **21**, 1480.

[22] Dermer *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 1653 ; 1941, **63**, 3524.

[23] Werkman, *Ind. Eng. Chem. Anal.*, 1930, **2**, 302 ; 1936, **8**, 271 ; but cf. Tsai and Ying Fu, *Analyt. Chem.*, 1949, **21**, 818.

[24] Behrens, *Z. anal. Chem.*, 1926, **69**, 97.

[25] Spatt and Schneider, *Ind. Eng. Chem. Anal.*, 1944, **16**, 479.

succession of single extractions ("multiple extraction") will reduce the amount remaining to any desired level, for the fraction L_A of a substance A left after extracting a volume V_w of aqueous phase with n successive portions of organic solvent each of volume V_o is given by $L_A = \{V_w/(V_w + V_oE_A)\}^n$, which shows how desirable it is for E_A, the extraction coefficient, to be large for rapid and complete extraction. It is a special feature of systems employing metal inner complexes that the extraction coefficient can be made as large as desired by an appropriate increase in pH (p. 221). In the above expression it is assumed that the partition isotherm is linear, *i.e.*, that $[A]_o/[A]_w = E_A$ is constant for all values of [A]. Although this is approximately true for dilute solutions of common organic substances (and probably for most metal complexes of zero charge), yet it does not hold for highly concentrated solutions and for many inorganic substances (*q.v.*). Graphical methods have been elaborated for calculations with non-linear isotherms.[7] Multiple extractions can often be replaced in practice by continuous solvent extraction, and suitable apparatus has been devised for the cases where the organic phase is either denser or lighter than water.[26]

After an "extraction for removal" has been carried out, the solute can be recovered quantitatively from the organic phase by evaporating off the solvent or by back-extracting into an aqueous phase, a process which may be facilitated by change of pH or—especially when inorganic materials are concerned—by the addition of oxidising or reducing agents or specific complexing reagents.[27] Solvent extraction can thus be used for quantitative determinations if conditions can be specified under which the extraction is complete—or at least reproducible. The material recovered from the extract may be determined by standard analytical methods, though its concentration in the separated organic phase can in many cases be obtained more directly and more conveniently by measurement of its radioactivity, its absorbancy (optical density), or some other physical property.

Extraction for Fractionation.—If the solution contains two components A and B, it often happens that under the conditions favouring the complete extraction of A, some B is extracted as well. The effectiveness of separation increases with the magnitude of the separation coefficient β, which is related to the individual partition coefficients as follows :

$$\beta = \frac{[A]_o/[B]_o}{[A]_w/[B]_w} = \frac{[A]_o/[A]_w}{[B]_o/[B]_w} = \frac{E_A}{E_B} \quad . \quad . \quad . \quad (6)$$

Clearly, if $E_A = E_B$, $\beta = 1$, and no separation is possible.

Suppose $E_A = 10$ and $E_B = 0{\cdot}1$. A single extraction will remove 90·9% of A and 9·1% B (ratio 10 : 1). A second extraction of the same aqueous phase will bring the total amount of A extracted up 99·2% but increases that of B to 17·4% (ratio 5·7 : 1). More complete extraction of A thus involves an increased contamination by B. This can be minimised by the device of *retrograde extraction*. The initial organic extract containing 90·9% of A and 9·1% of B is equilibrated with fresh solvent which removes only

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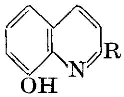
[26] Morrison, *Analyt. Chem.*, 1950, **22**, 1388.

[27] Irving, Risdon, and Andrew, *J.*, 1949, 537.

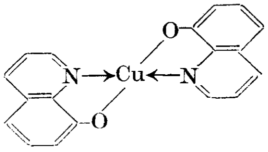
9·1% of A but 90·9% of B thus leaving 82·6% of total A and 0·8% of total B (ratio 100 : 1). But this reduced contamination of A is only achieved at the expense of the lower recovery (82·6%). It is clear that various combinations of multiple and retrograde extraction can be devised to meet specific needs,[3, 7, 21] and when the number of stages becomes impracticably large for manipulation with the conventional separating funnel or stoppered test-tube, apparatus specially designed for large numbers of simultaneous equilibrations and transfers must be constructed. The theory and use of such instruments has been fully described elsewhere. They have been employed with great success for the fractionation of complex mixtures of organic compounds and for purity studies [3, 4] but scarcely at all for inorganic separations where the non-linearity of the partition isotherm and the slowness with which equilibrium is sometimes reached introduce serious complications.

Factors favouring Solvent Extraction.—The maxim *similis similia solvuntur*—substances can best be got into solution by using similar substances as solvents—epitomises the familiar facts of experience, *viz.*, that hydrated inorganic salts tend to be more soluble in water than in organic solvents such as benzene, carbon disulphide, chloroform, etc., whereas organic substances tend to be more soluble in organic solvents than in water, unless they incorporate a sufficient number of hydroxyl, sulphonic, or other hydrophilic groupings. Now a solution of a salt in water is to be regarded as a collection of ions, each one more or less closely associated with a shell of water molecules to an extent determined on the one hand by its charge, radius, and electronic structure, and on the other by the concentration of all the other ions and dissolved substances present. Each ion is thus the centre of an ordered region of water molecules and forms a sort of ice-berg immersed in a solvent of high dielectric constant which serves to reduce the attractive forces between particles of unlike charge and so to discourage their association. The solubility of a salt in water may thus be attributed, in part at least, to the close similarity and compatibility between the water molecules of the solvent and those of the hydrated ions. Replacement of water completely by an organic solvent will affect this picture in several ways. First, the dielectric constant of the medium will be lowered—thus favouring the association of ions of opposite charge—and secondly, the solvation of the ions or ion-pairs will not take place to a significant extent unless the solvent molecules are dipolar or sufficiently polarisable. The solute aggregates then become less " water-like " and will thus be less water-soluble. Speaking very broadly, therefore, extraction into an organic phase will be favoured by conditions under which the ionic " ice-bergs " in an aqueous solution of a salt are replaced by aggregates of lower or zero net charge, and are modified in such a manner as to reduce their compatibility with water and to confer on them something of the character of an organic compound.

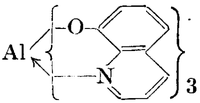
Those characteristic of an inorganic cation which contribute to its water solubility are most effectively masked by reaction with an organic reagent so constructed that through the formation of chelate rings it can both neutralise the positive charge completely and also occupy the maximum number of places in its co-ordination sphere. Thus, 8-hydroxyquinoline (I ; R = H) will react with a large number of metal ions to give uncharged metal " oxinates " of which the copper and the aluminium complex (II and III) are typical. Uncharged *inner complexes* of this kind are also formed by dithizone (IV), cupferron (V), dimethylglyoxime, diethylthiocarbamates, benzoin oxime, and a host of other organic reagents.[28]



(I.)



(II.)



(III.)

Unless the organic molecule contains a hydrophilic group (*e.g.*, the sulphonic group in " ferron ", 8-hydroxy-7-iodoquinoline-5-sulphonic acid) such inner complexes are very sparingly soluble in water but readily so in organic solvents, more especially in chloroform. Their special analytical importance is derived in part from the fact that the distribution coefficient of the metal in the system n-valent cation–organic reagent–water–organic solvent is a function of the nth power of the hydrogen-ion concentration (p. 220) ; by changing the pH by (say) x units it is thus possible to change the extractability by a factor of x^n and so to select those conditions favouring its complete partition into one or other phase, or the optimum conditions for its separation from other substances (p. 222).

A less pronounced masking of ionic character takes place when metal halides MX_n and halogen acids HX form association complexes H_mMX_{n+m} which in a solvated form are extractable into an organic solvent (pp. 212—216), and similar considerations may apply to the extraction of some metal nitrates (pp. 208—212) and thiocyanates (p. 217). As an extreme case may be cited the solubility in ether of $H_4Fe(CN)_6$ and analogous substances. The extraction of anions may likewise be enhanced by the addition of the appropriate cation, *e.g.*, phosphate extracts in the presence of ferric ions, and per-rhenates in the presence of tetraphenylarsonium(or phosphonium) ions.[29] It is well known that the hydrochlorides of some aromatic amines are more soluble in chloroform than in water, and use can be made of this for the extraction from water of even such strong acids as hydrochloric and sulphuric by a solution of a long-chain tertiary amine (*e.g.*, methyldioctylamine) in chloroform.[30] A comparable case illustrating the dramatic changes which can be effected in the magnitude of a distribution ratio by the presence of a suitable auxiliary substance is afforded by streptomycin. This is a basic sugar derivative and strongly hydrophilic : it can nevertheless be made to partition preferentially into an organic phase by the presence of

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[28] Welcher, " Organic Analytical Reagents ", 4 Vols., New York, 1947.

[29] Tribalat, *Anal. Chim. Acta*, 1949, **3**, 113 ; 1950, **4**, 228.

[30] Smith and Page, *J. Soc. Chem. Ind.*, 1948, **67**, 48.

certain fatty acids and alkyl- or aryl-sulphonic acids. Many similar cases of importance in biochemistry have been reported.[3]

Substances normally favouring the organic phase can be made to partition preferentially into an aqueous phase if a suitable water-soluble complex can be formed : [27, 32, 82] proteins are known to produce this effect in the case of carotene.[31] Anions capable of competitive complex formation will reduce the extent to which a metal can form an inner complex in the manner described above : indeed, a quantitative study of the effect of such ions upon the magnitude of the distribution ratio forms a particularly elegant and powerful method of determining the stability constants of the complexes they form with the metals concerned.[32] We now proceed to illustrate these general points by examples provided by the solvent extraction of various types of inorganic substances.

The Solvent Extraction of Nitrates.—The extractability by ether of uranyl nitrate, $UO_2(NO_3)_2$ (abbreviated to UN), has been known since 1842 when Péligot first employed it for separating and purifying uranium from pitchblende,[33] and the process has assumed great importance in recent years in connection with the analytical chemistry of uranium and problems incidental to atomic energy projects. The percentage of uranium extracted by ether is increased by the presence of nitric acid [34, 35] (Fig. 1) and by salting-out agents such as ammonium and other soluble nitrates [35, 36] diethyl ether may be replaced by a wide variety of other organic solvents notably other ethers, and ketones, alcohols, and esters, *i.e.*, solvents containing oxygen atoms capable of electron donation : [37] UN does not dissolve at all in solvents such as benzene and carbon tetrachloride.[38]

Now the formula $[UO_2(H_2O)_6](NO_3)_2$ for the hexahydrate suggests 8-fold co-ordination round the central uranium atom, and there is a marked tendency to preserve this even when organic solvent molecules replace one or more water molecules in the hydration shell. This is clearly shown in the compounds, generally of the formula $UN,3H_2O,S$ and $UN,2H_2O,2S$ ($S =$ solvent molecule), obtained by Mathieson,[40] and in the composition of the solid phases (in addition to $UN,6H_2O$) observed in the system $UN–H_2O–S$: [37]

Solvent.	Solid phases in order of appearance.			
Diethyl ether or ethylene glycol diethyl ether	$UN,3H_2O,S$;	$UN,2H_2O,S$		
Hexyl ether	$UN,3H_2O$;	$UN,2H_2O,2S$		
Acetone	$UN,4H_2O$;	$UN,3H_2O$;	$UN,2H_2O,S$;	UN,2S
*iso*Butyl methyl ketone	$UN,4H_2O(?)$;	$UN,2H_2O,S$;	UN,2S	
*iso*Butyl alcohol	$UN,3H_2O$;	$UN,2H_2O,S$;	UN,2S	
tert.-Butyl alcohol	$UN,3H_2O,3S$;	$UN,2H_2O,4S$;	UN,3S	

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[31] Dzialoszynski, Mystkowski, and Stewart, *Biochem. J.*, 1945, **39**, 63.

[32] Connick and McVey, *J. Amer. Chem. Soc.*, 1949, **71**, 3182.

[33] *Ann. Chim. Phys.*, 1842, **5**, 7, 42.

[34] Bock and Bock, *Z. anorg. Chem.*, 1950, **263**, 146.

[35] Norström and Sillen, *Svensk Kem. Tidskr.*, 1948, **60**, 227.

[36] Hecht and Grünwald, *Mikrochemie ver. Mikrochem. Acta*, 1943, **30**, 279 ; Rodden, *Analyt. Chem.*, 1949, **21**, 327.

[37] Katzin and Sullivan, AECD 2537.

[38] Gluekauf and McKay, *Nature*, 1950, **165**, 594.

[40] *J.*, 1949, S 294.

The solubility of water in ether is increased by the presence of UN, for as it partitions it carries water with it. Since the resulting solution is substantially undissociated, as shown by its low electrical conductivity, the predominant species may well be uncharged $[UO_2(NO_3)_2(H_2O)_4]^\circ$ associated by " secondary solvation " (hydrogen-bonding, etc.) with up to four organic solvent molecules.[38] The implied formation of covalent bonds between uranyl and nitrate ions is consistent with the existence of the ion $[UO_2(NO_3)_3]^-$ and the formation of the double nitrates $UO_2M(NO_3)_3$ (where M = K, NH_4, NMe_4, Rb, and Cs), $UO_2M_2(NO_3)_4$ (where M = K, NMe_4, NEt_4, Rb), and $(NH_4)_2UO_2(NO_3)_4,2H_2O$. Although UN is a strong electrolyte in dilute solution, changes in the visual absorption spectrum of the UO_2^{++} ion on the addition of nitrate ions [41] {from which the equilibrium constant $K = [UO_2(NO_3)^+]/[UO_2^{++}]\,[NO_3^-] = 0{\cdot}2$ ($\mu = 5{\cdot}4$) can be calculated} support this hypothesis of covalent bonding rather than that of ion-pair association, whilst measurements of the osmotic coefficients in saturated solutions of UN indicate that up to 20% of undissociated $[UO_2(NO_3)_2, aq.]^\circ$ may be present.[38]

It is noteworthy that neptunyl and plutonyl nitrates behave in the same way as UN.[38] Moreover, after removal of sulphate ions with barium ions and salting out with nitric acid and ammonium nitrate, all the americium in the yellow solution obtained by oxidising Am^{3+} with persulphate can be solvent-extracted,[42] thus indicating by analogy to uranium the existence of sexavalent americium and the AmO_2^{++} ion.

Although only hydrates of cobalt nitrate (denoted CN) with 6, 4, 3, and 2 molecules of water appear in the system CN–water–acetone, yet when *tert.*-butyl alcohol (B) replaces the acetone the solid phases are $CN,6H_2O$; $CN,4H_2O,2B$; $CN,3H_2O,3B$; and $CN,2H_2O,4B$.[43] Absorption spectra of the solutions suggest that there is competition between water, organic solvent molecules, and anions for the six co-ordination positions around the cobalt ion, and in the presence of a favourably high nitrate-ion concentration, solvated uncharged complexes $[Co(NO_3)_2X_4]$ (X = water or organic molecules) may result : any consequent decrease in water-solubility should be reflected in an increased tendency to partition into an organic phase. However, the distribution ratios of the formally bivalent nitrates of Mn^{++}, Co^{++}, Cu^{++}, and UO_2^{++} when measured under comparable conditions [38] are in the ratio $0{\cdot}1 : 1 : 2 : 10^7$ and the disproportionately large ether solubility of uranyl nitrate (and likewise neptunyl, plutonyl, and americyl nitrates) is clearly related to the high co-ordination number and valency of their central atoms and to their greater tendency to co-ordinate to water, to oxygen-containing molecules, and to the nitrate ion. They differ, too, in possessing *f*-shell orbitals which may be essential for the formation of six coplanar bonds to which the linear MO_2 group acts as an axis.[38]

Other elements which show a marked tendency to form nitrate complexes may be expected to resemble uranium to a greater or lesser degree, and

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[41] Betts and Michels, *J.*, 1949, S 286.

[42] Asprey, Stephanou, and Penneman, *J. Amer. Chem. Soc.*, 1950, **72**, 1425.

[43] Katzin *et al.*, *ibid.*, pp. 5451, 5455.

Table I shows that gold, cerium, and thorium are outstanding in this respect.[34] Their distribution coefficients are, however, very dependent upon nitric acid concentration [34, 35] as shown in Fig. 1, whilst temperature

TABLE I

The percentage of metals extracted by ether from solutions in 8N-nitric acid at room temperature [34]

					H (HNO_3) 42%									
Be 1·4	B										B	C	N	O
Mg	Al 0·1										Al 0·1	Si	P 20·4[g]	S
Ca	Sc 0·1	Ti ⩽0·5	V^V 2[a]	Cr^{VI} >15[b]	Mn^{VII} <0·2[c,d]	Fe^{III} 0·1	Co 0·2	Ni 0·1	Cu^{II} 0·5	Zn 0·1	Ga <0·2	Ge 2·2[e]	As^V 14·4[f]	Se
Sr	Y 0·1	Zr ~8	Nb	Mo 0·6[h]	Tc	Ru	Rh	Pd	Ag 2·4	Cd 0·3	In 0·1	Sn	Sb^V <1	Te
Ba	La 0·1	Hf	Ta	W	Re	Os	Ir	Pt	Au^{III} 97	Hg^{II} 4·7	Tl^{III} 7·7[i]	Pb 0·5	Bi^{III} 6·8	Po
Ra	Ac	Ce^{IV}, 96·8	Pr,	Nd, and rare earths										
		Th^{IV}, 34·6	Pa, j	U^{VI} 65										

Notes : *a*, as NH_4VO_3 ; *b*, $K_2Cr_2O_7$ (decomp.) ; *c*, $KMnO_4$ (decomp.) ; *d*, Mn^{II} 0·2% ; *e*, GeO_2 ; *f*, Na_2HAsO_4 ; *g*, $(NH_4)_2HPO_4$; *h*, NH_4 molybdate ; *i*, Tl^I <0·5% ; *j*, cf. Refs. (52), (66).

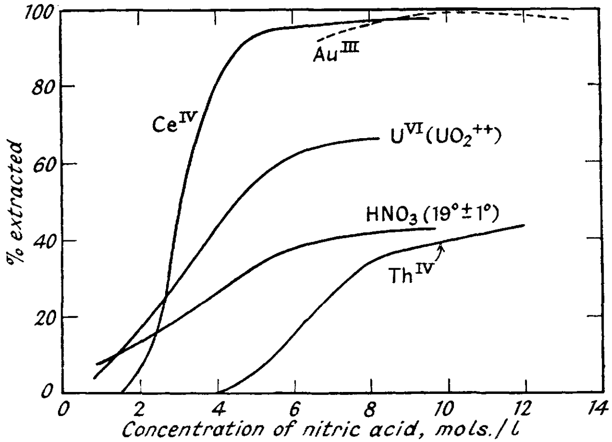

FIG. 1

The effect of concentration on the extractability of nitrates by diethyl ether.[34]

and salting-out agents may produce the most striking effects. For instance, scandium nitrate is extracted from 8N-nitric acid to the extent of 0·1% only ; but 14% is extractable even from 1M-nitric acid after saturation with lithium nitrate at 20°, and no less than 83% after saturation at 35°. Lithium nitrate (but not ammonium nitrate) facilitates the extraction of thorium ; ammonium nitrate increases that of UN but scarcely affects that of cerium ; whilst addition of lithium nitrate enhances the extractability of scandium but not that of beryllium. The almost specific effect of certain salting-out agents on the extractability of thorium nitrate is shown in Table II, and the difficulties attaching to any logically grounded choice of solvent may be seen from the following data : [34]

TABLE II [34]

Percentage of thorium extracted by ether from 0·1M-Th^{IV} *in* M-*nitric acid saturated with various nitrates,* $M^{n+}(NO_3^-)_n$

M^{n+}	Li^+	Na^+	K^+	NH_4^+	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}	Zn^{++}	Al^{3+}	Fe^{3+}
Percentage extracted . .	56·5	0·67	0·15	0·36	43·8	56·9	0·18	0·08	80·9	54·1	73·6

Solvent.	Percentage extracted.		Separation factor.
	Th.	La.	
Diethyl ether	56·5	0·014	9,300
Di*iso*propyl ether	1·2		
Dichlorodiethyl ether	2·1		
Ethyl acetate	98·2	4·81	1,100
Amyl alcohol	82·8	2·7	1,700
Amyl acetate	52·2	0·16	680
Methyl *n*-propyl ketone . . .	98·7	25·9	220
*iso*Butyl methyl ketone . . .	98·8	0·71	12,000
Diethyl ketone	98·9	0·65	13,000
Di-*n*-propyl ketone	78·4	0·17	2,100

Although such complexes as solvated $H_2Ce(NO_3)_6$, $HAu(NO_3)_4$, and $H_2Th(NO_3)_6$ may plausibly be postulated as the species extracted, yet definite evidence is lacking ; and indeed there is no certainty that the species extracted remains the same even in a particular metal nitrate–solvent–water system, save over quite limited ranges of composition.

Templeton and his co-workers [44] have made extensive studies of the partition of thorium nitrate between water and a variety of alcohols and methyl ketones. They showed [45] that the extractability of rare-earth nitrates by *n*-hexyl alcohol increased in the order Ce $<$ La $<$ Pr $<$ Nd $<$ and $<$ Sm and demonstrated [46] practically the feasibility of separating neodymium and lanthanum by solvent extraction.[46] Asselin and Comings [9] have shown that thorium nitrate is extracted preferentially by *n*-amyl alcohol from an aqueous solution of neodymium nitrate (representative of the rare-earth group) in the presence of ammonium thiocyanate which acts as a " separating agent ".

The efficient extraction of ceric nitrate needs high concentrations of nitric acid (Fig. 1), and the solvent readily takes part in an exothermic

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[44] *J. Phys. Colloid Chem.*, 1947, **51**, 1441 ; 1948, **52**, 1006 ; 1949, **53**, 838.

[45] *J. Amer. Chem. Soc.*, 1949, **71**, 2187.

[46] *Ibid.*, 1948, **70**, 3967.

reaction with concurrent reduction of the metal to a state in which it is no longer extractable.[47] Searching for non-oxidisable solvents, Warf [47] tried nitromethane and tri-*n*-butyl phosphate, of which the latter proved to have quite exceptional solvent properties for the nitrates of cerium, thorium, and uranium and as has been found since for a number of other substances. Ce^{IV} can be extracted completely from 8—10M-nitric acid containing 3M-sodium nitrate if sodium bromate is added to reoxidise any metal reduced by the solvent during the extraction, though this is less than 1% during 2 hours. Back-extraction with water or dilute nitric acid is slow, and although ammonium nitrate proves useful on account of its complexing powers, the most effective procedure is to shake the organic phase with a solution of hydrogen peroxide, hydroxylamine, or other reducing agent whereby the metal is transferred quantitatively to the aqueous phase as Ce^{III}.

Among typical procedures which make use of the solvent extraction of nitrates may be noted the preparation of pure thorium, cerium, and uranium ; [34] the determination of uranium in ores and minerals [36, 48] where solvent extraction may be used in conjunction with a column of absorbent cellulose ; [48] the isolation and determination of uranium on the microgram scale by paper chromatography ; [49] the removal of the bulk of uranium from a specimen prior to spectrographic determination of rare earths,[50] or in the preparation of carrier-free U-X_1 ; [51] the isolation of traces of protactinium after the deuteron bombardment of a 10-gram thorium target,[52] by using dibutoxytetraethylene glycol to remove the bulk of the thorium as nitrate and subsequently di*iso*propyl ketone to extract protactinium and uranium before purification stages involving TTA (*q.v.*) ; and the historical separation of the first 20-μg. sample of plutonium from 90 kg. of neutron-irradiated UN hexahydrate.[53]

The Solvent Extraction of Chlorides.—In contrast to the limited number of extractable metal nitrates, the number of chlorides known to be solvent extractable is already considerable, as shown in Table III. Needless to say, the figures quoted refer only to the actual conditions specified, for here again the addition of salting-out agents and variations in acid concentration (Fig. 2) can produce striking changes. Especially noteworthy are the curious and analytically important alternations in extractability in passing down Group IIIB, *viz.*, aluminium (0%), gallium (97%), indium (trace), and thallium (90—95%)—figures which should be contrasted with those quoted later (p. 216) for the corresponding bromides. Oxidation also produces great changes, decreasing the extractability of arsenic and tin whilst increasing that of iron, antimony, and thallium.

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[47] *J. Amer. Chem. Soc.*, 1949, **71**, 3257.

[48] " Handbook of Chemical Methods for the Determination of Uranium in Minerals and Ores ", H.M. Stationery Office, 1950.

[49] Arden, Burstall, and Linstead, *J.*, 1949, S 311.

[50] Hirt and Nachtrieb, MDDC 903.

[51] Erbacher, Herr, and Wiedemann, *Z. anorg. Chem.*, 1944, **252**, 282.

[52] " Chemical Procedures used at Berkeley ", AECD 2738.

[53] Cunningham and Werner, *J. Amer. Chem. Soc.*, 1949, **71**, 1521.

TABLE III[6]

The percentage of various metal chlorides extracted by ether from 6N-*hydrochloric acid* (t. denotes a trace only). [Metals reacting with dithizone (*q.v.*) are enclosed by the black lines]

Be 0	B										B 0	C	N	O
Mg 0	Al 0										Al 0	Si	P	S
Ca 0	Sc 0	Ti 0	V t.	Cr 0	Mn 0	Fe^{II} 0 Fe^{III} 99	Co 0	Ni 0	Cu 0·05	Zn 0·2	Ga 97	Ge 40—60	As^{III} 68 As^{V} 2—4	Se t.
Sr	Yt	Zr 0	Nb t.	Mo^{VI} 80—90	Tc	Ru	Rh 0	Pd 0	Ag t.	Cd 0	In t.	Sn^{II} 15—30 Sn^{IV} 17	Sb^{III} 66 Sb^{V} 81	Te 34
Ba	La	Hf	Ta	W 0	Re	Os 0	Ir 5	Pt^{IV} t.	Au^{III} 95	Hg^{II} 0·2	Tl^{I} 0 Tl^{III} 90—95	Pb^{II} 0	Bi 0	Po
Ra	Ac													
		Ce	Pr	Nd	and other rare earths :				0 or t.					
		Th	Pa t.	U	Pu	Am	Cm	Bk	Cf					

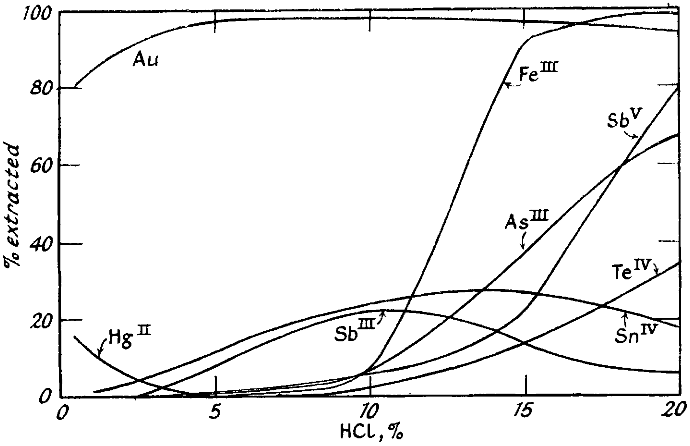

FIG. 2

The influence of hydrochloric acid concentration upon the extractability of chlorides.

Edwards and Voigt[54] found that the distribution coefficient of Sb^{V} between *iso*propyl ether and 6·5—8·5N-hydrochloric acid was greater than 200, whereas that of Sb^{III} was only 0·016, a result of great value in studying the kinetics of exchange between the two ions when using radio-tracer techniques.[56] Tl^{III} can be extracted from hydrochloric acid so dilute that very little iron or gallium accompanies it and the principal contaminant is Hg^{II}: under reducing conditions Tl^{I} is transferred to the aqueous phase, thus affording a facile separation from almost every other element.[55]

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[54] *Analyt. Chem.*, 1949, **21,** 1204.

[55] Irving *et al.*, unpublished observations.

[56] Bonner, *J. Amer. Chem. Soc.*, 1949, **71,** 3909.

The extraction of ferric chloride from hydrochloric acid with ether, first proposed as an analytical procedure by Rothe in 1892, has received very careful attention.[6] The amount of metal extracted depends on the concentration of acid and passes through a maximum. Extraction with di*iso*propyl ether is more nearly quantitative and, at its maximum, less sensitive to acid concentration. With use of 2 : 2′-dichlorodiethyl ether (which now forms the lower layer) quantitative extraction is only reached in 9—11N-hydrochloric acid. Thus :

Ether used.	Percentage of 250 mg. of iron extracted from hydrochloric acid of normality :								
	2.	3.	4.	5.	6.	7.	8.	8.5.	9.
Diethyl [57] . . .	1	17·8	81·5	<96	<99	97·8	87	~ 73	~ 45
Di*iso*propyl [12, 13] .	0	0·4	12·1	80·9	98·1	99·5	99·8	99·6	94
Dichlorodiethyl [58] .	0	~ 2	6	25	61	~ 88	97	98	99

Although excellently suited to the removal of large quantities of iron,[6] an adverse feature of such procedures is that the percentage of metal extracted falls off fairly rapidly with decreasing iron content, as shown in Fig. 3 and by the following data : [57]

Iron taken originally, mg. . .	500	243	203	102	41	22
Percentage extracted by *iso*propyl ether from 5M-HCl	90·2	82·4	79·5	67·5	39	36

Several theories have been advanced to account for this behaviour. It appears that ferric chloride partitions into *iso*propyl and dichlorodiethyl ethers with one equivalent of hydrochloric acid, presumably as solvated $HFeCl_4$,[12, 13, 58] and although the ratio HCl : $FeCl_3$ rises above unity when ether is used with a solution of high acidity, the absorption spectrum of the ethereal layer does not change, suggesting that the additional acid is but loosely associated with the $HFeCl_4$ complex.[13] Some 5 molecules of water accompany the complex into *iso*propyl ether,[12] and in certain circumstances *two* ethereal layers are formed in addition to the aqueous phase. Such additional complications to a system in which the components are present at high concentration and where the process of partition is accompanied by substantial changes in the phase volumes add greatly to the problems of interpretation. There appears, however, to be only one extractable species, since the absorption spectra of the two ether layers are identical, though different from that of ferric chloride in water, in ether, and in hydrochloric acid.[59] Swift *et al.*[12] report that a constant distribution coefficient $K_{25^\circ} = [\mathrm{Fe}]_{\mathrm{ether}}/[\mathrm{Fe}]_{\mathrm{aq.}} = 0{\cdot}3$, is maintained in 5·6M-hydrochloric acid up to a total iron concentration of $\sim 0{\cdot}001$M., and this is confirmed by other workers.[13] Following on the observations that the presence

[57] Dodson, Forney, and Swift, *J. Amer. Chem. Soc.*, 1936, **58,** 2573.
[58] Axelrod and Swift, *ibid.*, 1940, **62,** 33.
[59] Myers and Metzler, *ibid.*, 1950, **72,** 3772, 3767.

of aluminium chloride increased the efficiency of extraction of ferric chloride at low iron concentrations,* Nachtrieb and Conway [13] suggest that if it does so by increasing the activity of Fe^{3+}, a high concentration of ferric chloride should produce a similar increase in activity which would naturally decrease as the total concentration of iron decreases, with a concurrent falling-off of extraction efficiency. Other workers interpret the data in terms of a polymerised ferric complex in the organic phase, a hypothesis which also explains the variations in the number of water molecules co-extracted.[12, 59] It is interesting that the iron in the extracted complex has the same paramagnetic susceptibility ($\mu = 5{\cdot}96$) as in aqueous acid solutions.[59]

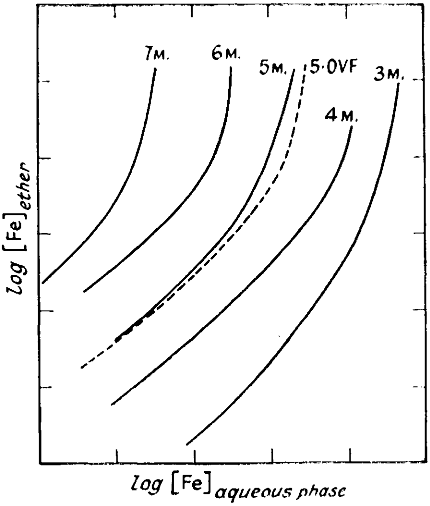

FIG. 3

The effect of total iron concentration upon the distribution of ferric chloride between diisopropyl ether and hydrochloric acid of various strengths. Data by Nachtrieb and Conway [13] *for* 20° ——, *data by Swift* et al.[12] *for* 25° - - - -.

Conditions operating during the extraction of ferric chloride in a liquid-liquid spray tower 1·45 in. in diameter and 2·57 ft. long have recently been examined in some detail.[60] Ether, or preferably amyl acetate, being used, iron can be extracted from 1·1N-hydrochloric acid without significant co-extraction of beryllium,[61] and some ketones appear to be still better as solvents.[62]

The extraction of gallium trichloride with ether,[63] or better with *iso*propyl

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[60] Geankoplis and Hixson, *Ind. Eng. Chem.*, 1950, **42,** 1141.

[61] Young, *J. Chem. Educ.*, 1949, **26,** 357 ; cf. Wells and Hunter, *Analyst,* 1948, **73,** 671.

[62] Kuznetsov, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17,** 175.

[63] Swift, *J. Amer. Chem. Soc.*, 1924, **46,** 2375.

* Further data on salting-out effects in the extraction of iron and molybdenum are given by Morrison [26] and refs. therein.

ether,[64] affords an important method for concentrating this element and separating it from likely impurities. The species extracted is (solvated) $HGaCl_4$, and the phenomenon of the coexistence of three liquid phases is again encountered. Radioactive gallium being used,[11] the distribution coefficient has been shown to be constant from 10^{-12} to 10^{-3}M., and Nachtrieb and Fryxell [64] found this to hold up to at least 0·01M., though at the optimum acidity (7·2M-hydrochloric acid) the extraction coefficient then increased steeply to a maximum of 2500 for 0·1—0·4M-gallium trichloride and then decreased again. That the 7½-hour activity produced along with the known gallium isotopes of half-life 68 m. and 83 h. by bombarding zinc with deuterons was in fact a new gallium isotope and not due to some impurity in the target was proved ingeniously by showing that it had the same distribution coefficient as ordinary gallium.[11]

$HAuCl_4,3H_2O$ is readily extracted even from quite dilute hydrochloric acid, though the extractability increases up to a concentration of about 10%. Among many organic solvents examined by Lenher,[65] ethyl acetate and other aliphatic esters were the most effective, but as in other systems [38] the introduction of chlorine atoms into the oxygenated solvent impaired extraction. The same solvents serve for the extraction of platinum from the red solutions in hydrochloric acid produced by reduction with stannous chloride and probably containing H_2PtCl_4.[6, 52] Selective behaviour is shown in the extraction of protactinium, and as much as 90% can be removed by dichlorodiethyl ether from 6N-hydrochloric acid made 8M. with respect to magnesium chloride, conditions under which less than 2% of uranium, manganese, zirconium, or titanium are co-extracted.[52, 66] Polonium can be separated from lead and bismuth by extraction from 6N-hydrochloric acid with 20% tributyl phosphate dissolved in dibutyl ether.[52]

Anhydrous cobalt chloride has been found to be soluble in aliphatic alcohols, esters, ketones, and acids, relatively insoluble in aromatic aldehydes and ketones, and almost insoluble ($<$ 0·05%) in aliphatic or aromatic hydrocarbons (whether unsubstituted or containing chloro or nitro groups): unlike UN it is insoluble in ether. Yet although the solubilities of anhydrous cobalt and nickel chloride in commercial 2-octanol (capryl alcohol) were 21·3% and 0·26%, respectively, no separation, and indeed no extraction from aqueous solution, could be effected at all. However, separation factors (p. 205) of 40—90 and 10—17 were obtainable in the presence of high concentrations of hydrochloric acid and calcium chloride, respectively, indicating the potentialities of large-scale separation by solvent extraction.[15]

The Extraction of Bromides and Fluorides.—Relatively little has as yet been published on the extraction of halides other than chlorides, but what information is available suggests that the differences in behaviour may well be large and analytically useful. From Table IV it will be seen that the efficiency of extraction of iron is reduced by replacing hydrochloric by hydrobromic acid, and the acidity for maximum extraction is also lowered.

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[64] Nachtrieb and Fryxell, *J. Amer. Chem. Soc.*, 1949, **71**, 4035.

[65] *Ibid.*, 1913, **35**, 546; Lenher and Kao, *J. Physical Chem.*, 1926, **30**, 126.

[66] Maddock and Miles, *J.*, 1949, S 248, 253.

On the other hand, indium, which is extracted with difficulty from hydrochloric acid, can be removed completely from hydrobromic acid : the extraction of copper [55] and thallic thallium is also facilitated.

TABLE IV

The extractability of metal bromides.[67]. Percentage of metal extracted from 20 ml. of aqueous phase by 30 ml. of diethyl ether pre-saturated with hydrogen bromide. Comparative data for chlorides *ex* hydrochloric acid in parentheses)

Metal.	Normality of hydrobromic acid :							
	0·1.	0·5.	1·0.	2·0.	3·0.	4·0.	5·0.	6·0.
Tl^{III} . .	99	99·0	99·2	99·7	99·7	99·8	99·6	92 (92—95)
Fe^{III} . .	—	0	0	2	9·5	69·5	72·5	60·4
				(1)	(17·8)	(81·5)	(96)	(99)
Ga . . .	—	0	0	0	0·3	3·6	50	57 (40—60)
In . . .	—	1	3·2	19·2	89·3	99	—	99 (trace)
Au . . .	—	99	99	—	—	99	—	73 (95)
Te . . .	—	0·3	2	3	—	3	—	3 (34)
Hg^{II} . .	—	3	1	0·2	—	0·3	—	0·3 (0·2)

The solvent extraction of gold as bromoauric acid has been thoroughly studied by McBryde and Yoe.[68] Not only is it more satisfactory than the extraction from hydrochloric acid, but the method lends itself to a convenient absorptiometric determination of the element. If the acidity is kept low (2·5—3M.) relatively little iron, and of the platinum metals only osmium (43% as tetroxide), is extracted when *iso*propyl ether is used. Hexone, however, extracts 54% of iron, 56% of osmium, 21% of palladium, and 13·5% of platinum from 2·9M-hydrobromic acid. It is not yet known to what extent the distribution ratios in such systems are dependent on solute concentration.

Solvent extraction with ethyl methyl ketone containing some hydrogen fluoride has been used in conjunction with a column of activated cellulose for the determination of tantalum and niobium in minerals and ores, to separate these elements from titanium, zirconium, iron, and tin.[69]

The Extraction of Thiocyanates.—The red colour due to $FeCNS^{++}$ has long been employed for the colorimetric estimation of Fe^{III} and, in the presence of excess of thiocyanate, iron can be extracted as a stable red complex into alcohols, ethers, and esters.[6] Extractable yellow complexes suitable for absorptiometry [6] are similarly formed by U^{VI}, bismuth, and rhenium (all yellow), whilst Co^{II} forms the blue complex familiar also in qualitative analysis. In the presence of reducing agents and thiocyanates tungsten and molybdenum are also solvent-extractable,[6] possibly as

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[67] Wada and Ishii, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 264.

[68] *Analyt. Chem.*, 1948, **20**, 1094.

[69] Work at the Chemical Research Laboratory, D.S.I.R., Teddington ; *Chemistry Research*, 1949, 46 ; 1950, in the press.

(WO)CNS (purple) and $Mo(CNS)_5$ (amber to red). Cobalt, nickel, and copper in the presence of pyridine give complexes insoluble in water which dissolve in chloroform to give pink, blue, and green solutions of which the last, containing $Cu\,py_2(SCN)_2$, has been used in absorptiometry.[70] Similar complexes are formed by zinc, cadmium, and many other metals and may serve for their solvent extraction.

The most extensive studies on the extractability of thiocyanates have been reported by Fischer and Bock,[71] and some of their results are given in Table V. The unexpectedly high extractability of scandium enabled them to devise a procedure for separating this element completely from magnesium, calcium, manganese, yttrium, rare earths, and thorium, and for reducing contamination by titanium, zirconium, hafnium, uranium, and ferrous iron; the separation from beryllium, aluminium (and probably gallium), cobalt, ferric iron, molybdenum, and rhenium was less satisfactory. Some years later Chalybaeus and Zumbusch joined Fischer [72] in a very thorough study of the separation of zirconium and hafnium and showed that solvent extraction from an acidified thiocyanate medium compared very favourably with fractional crystallisation, precipitation, and volatilization methods. This conclusion is of considerable significance in view of the current interest in the commercial production of pure zirconium. Appleton and Selwood [73] have studied the extraction of mixed lanthanum and neodymium thiocyanates by *n*-butyl alcohol and report a separation factor of 1·06.

TABLE V

Metals dissolved in 0·5N-*hydrochloric acid containing* 530 *g./l. of ammonium thiocyanate and extracted with an equal volume of ether*

Metal	Be	Al	Fe^{III}	In	Sc	U^{VI}
Percentage extracted . .	>50	49	52	59	94	4·6

The extraction of Mg, Ca, Σ Y (mixture containing 70% Y_2O_3), La, and Zr was < 0·1%; of Th and Mn < 0·2%; of Ti^{IV} (0·3—1·0N-HCl) 2·4%.

The Solvent Extraction of Miscellaneous Inorganic Compounds.—The conditions under which nitric acid can be partitioned into ether were studied by Tanret [74] as long ago as 1897, and although the solvent extraction of phosphoric acid in the form of phosphomolybdic acid forms the basis of a familiar absorptiometric estimation of phosphorus,[75] it has only recently been demonstrated, by using radioactive ^{32}P, that the phosphate content of, *e.g.*, a mineral can be reduced to 0·02% of its original amount by treatment with concentrated sulphuric acid followed by two extractions with ether.[69] This discovery will surely find wide applications in analysis. Both acetic and hydrochloric acids can be extracted from water by tributyl

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[70] Moeller and Zogg, *Analyt. Chem.*, 1950, **22,** 612.

[71] *Z. anorg. Chem.*, 1942, **249,** 146—197.

[72] *Ibid.*, 1947, **255,** 79; 1948, **255,** 277.

[73] *J. Amer. Chem. Soc.*, 1941, **63,** 2029.

[74] *Bull. Soc. chim.*, 1897, **17,** 497.

[75] Berenblum and Chain, *Biochem. J.*, 1938, **32,** 286, 295.

phosphate,[76] but the latter acid can be held in the aqueous phase by raising the pH to 1—2. Blue peroxychromic acid is soluble in ether and forms the basis of a familiar qualitative test : it serves also for the solvent extraction of chromium.[52]

Rhodium and iridium form complexes which extract into pyridine,[52] and the remarkable result that MnO_4' is " essentially quantitatively " extracted into pyridine from 4M-potassium hydroxide whilst MnO_4'' is extracted only to a negligible extent has been used in recent studies of electron transfer.[77] The solvent extraction of tetraphenylarsonium per-rhenate into chloroform permits the separation of this element from molybdenum.[29]

Among the halogens, the partition of iodine has been most frequently studied, largely for its physicochemical interest : [10] it is exploited in Andrews's iodate titrations.[78] Like bromine and iodine, the newly discovered halogen astatine (At) is solvent-extractable : working with solutions no stronger than 10^{-11} to 10^{-15}M., Johnson, Leininger, and Segré [79] examined the effects of various reagents on its partition between carbon tetrachloride and 0·01M-nitric acid and were able to establish the existence of a zero-valency state (? At_2) reducible by sulphur dioxide to At^- (which is co-precipitated with silver iodide), oxidisable to At^{n+} by cold concentrated nitric acid, and disproportionating at pH 13.

The Solvent Extraction of Inner Complexes.—The foregoing account of the extraction of inorganic substances will have illustrated something of the difficulties and complexities—and one could fairly say perplexities—of this field. So many, and often such specific factors are involved that no simple and universally applicable theory of such extractions can be expected. One obviously relevant factor—the varying tendency of different ions and molecules to form aggregates—is surely the most fundamental problem of inorganic chemistry itself, whilst the far-reaching effects of changes in the nature of the solvents in the two phases and in the immediate neighbourhood of the solute aggregates, as well as the fact that the solutions must necessarily be non-ideal and are often very concentrated or even saturated, renders any quantitative treatment of their physical chemistry a matter of the greatest difficulty.

On the other hand, the solvent extraction of a metallic inner complex, MR_n, formed according to equation (7) is susceptible to a comparatively

$$M^{n+} + nHR \rightleftharpoons MR_n + nH^+ \qquad . \quad . \quad (7)$$

simple and general treatment. In the first place, the reagent and the metal complex exist as simple unassociated molecules in both phases ; secondly, solvation plays no significant part in the process of extraction ; finally, the solutes are uncharged molecules and their concentrations are generally so low that the behaviour of their solutions departs so little from ideality that their physical chemistry is relatively simple. When V_w ml. of an aqueous

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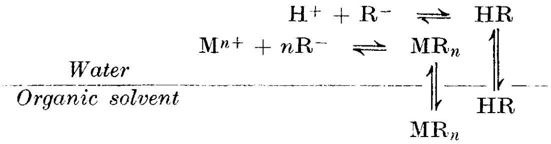
[76] Paget, Toren, and McLafferty, *Analyt. Chem.*, 1949, **21**, 1150.

[77] Hornig, Zimmerman, and Libby, *J. Amer. Chem. Soc.*, 1950, **72**, 3808.

[78] Oesper, " Newer Methods of Volumetric Chemical Analysis ", New York, 1938, p. 72.

[79] *J. Chem. Physics*, 1949, **17**, 1.

solution of an n-valent cation, M^{n+}, are shaken with V_0 ml. of a solution of the organic reagent HR in a solvent immiscible with water, the equilibria depicted below will come into play :



If K_c^T, K_r^T are the thermodynamic dissociation constants for the complex MR_n and reagent HR, and p_c^T, p_r^T their respective thermodynamic partition coefficients (p. 202) between water and organic solvent, it can be shown (subject to certain reasonable simplifying assumptions [80] based upon a knowledge of the relative magnitudes of these constants) that the extractability constant is given by

$$E = \frac{(K_r^T p_r^T)^n}{K_c^T p_c^T} \cdot \frac{(f_{HR})_o^n (f_{M^{n+}})_w}{(f_{MR_n})_o} \cdot \frac{V_w}{V_o} \cdot \left(\frac{[HR]_o}{\{H\}_w}\right)^n$$

where $[HR]_0$ is the concentration in the organic phase of the excess of reagent over and above the amount used in complex formation, and $(f_X)_a$ is the activity coefficient of the species X in the phase a. For the case where the activity coefficients are unity (or maintained constant) and $V_0 = V_w$ we can write

$$E = K([HR]_0/\{H\})^n \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

and

$$\log_{10} E = \log_{10} K + n\log_{10} [HR]_0 + n\text{pH} \quad . \quad . \quad . \quad (8b)$$

where $K = (K_r^T p_r^T)^n/(K_c^T p_c^T)$ is the *extractability constant.* Equation (8*b*; $n = 1$) shows a close formal similarity to equation (4) developed for the partition of a monobasic acid, and indeed, the percentage, x, of metal extracted as complex into an organic phase is represented by an expression very similar to equation (5), *viz.*

$$x = 50[1 - \tanh 1{\cdot}1513n(\text{pH}_{\frac{1}{2}} - \text{pH})] \quad . \quad . \quad . \quad (9)$$

where $\text{pH}_{\frac{1}{2}}$ is the hydrogen-ion exponent when extraction reaches 50% ($E = 1$) for the particular concentration of reagent under consideration.[80]

It is clear from equations (8) and (9) that the graph representing the extraction of a bivalent metal with $K = 10^{-6}$ and $[HR]_0 = 10^{-4}$ must be identical with that for the case $K = 10^{-8}$ and $[HR]_0 = 10^{-3}$, or $K = 10^{-10}$ and $[HR]_0 = 10^{-2}$, and so on. Curves D, C, and B of Fig. 4 have been drawn to represent the extraction of one and the same inner complex of a bivalent metal of $K = 10^{-6}$ from solutions in which $[HR]_0$ was 10^{-4}, $10^{-3{\cdot}25}$, and 10^{-1}, respectively. The effect of gradually increasing the concentration of excess of reagent is seen to be simply a lateral shift of the extraction curve to regions of higher acidity. But from equation (8) it is clear that a ten-fold change in reagent concentration is exactly offset by a ten-fold change in hydrogen-ion concentration, *i.e.*, by a change of a single unit of

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[80] Irving and Williams, *J.*, 1949, 1841.

pH, and such a change is much easier to effect in practice.[80] Now, since equation (8) applies to the extraction of *any* metal, complexed with *any* monobasic organic reagent, we can equally well envisage curves B, C, and D as referring to bivalent metals of extraction constants $K = 10^{-2}, 3{\cdot}2 \times 10^{-3}$, and 10^{-4}, respectively, which, with a univalent metal with $K = 0{\cdot}6$ (curve A) and a quadrivalent metal with $K = 10^{-8}$ (curve E) are in partition equilibrium with the same excess of reagent of concentration, $[HR]_0 = 10^{-5}$M. The effect of valency change is shown by the varying steepness of the curves, the slope at the mid-point being $57{\cdot}57n\%$ per pH unit.[80] The range between 1% and 99% extraction is completely covered by $4/n$ units of pH, and whilst this may facilitate sharp separations of ions of high valency, the adjustment of pH will necessarily prove more critical.

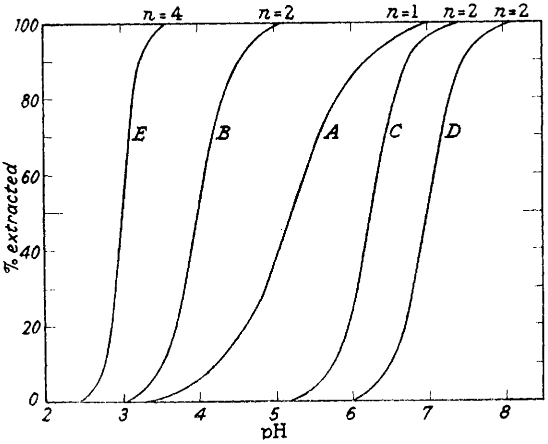


Fig. 4

It is not easy to prove experimentally that equations (8) and (9) do really represent the behaviour of metal–reagent systems, but where it has been possible to maintain $[HR]_0$ constant irrespective of the amount of metal partitioned (by using, *e.g.*, radio-isotopes of high activity), the linearity of the plot of log E against pH confirms the basic theory, whilst the integral value of the slope n establishes the formula of the complex.[81, 55] Deviations may be caused by the formation of water-soluble complexes or by the existence of species in equilibrium not envisaged in the derivation of the simple equations given above.[32, 82] Measurements of the effect on E of changing the reagent concentration at constant pH are also consistent with the basic theory,[32, 81, 82, 83, 84] which has been very thoroughly tested for the systems zinc and dithizone in chloroform and carbon tetrachloride by using stable isotopes.[85]

[81] Suttle, AECD 2800.

[82] McBride, AECU 399.

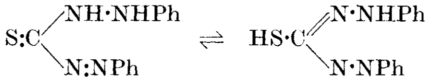
[83] Huffman and Beaufait, *J. Amer. Chem. Soc.*, 1949, **71**, 3179.

[84] Schultz and Larsen, *ibid.*, 1950, **72**, 3610.

[85] Irving, Bell, and Williams, *J.*, 1951, in the press.

Extraction curves obtained in practice may differ considerably from those depicted in Fig. 4, either because the *total* amount of reagent has been kept constant throughout (so that the magnitude of $[HR]_0$ has varied with the percentage of metal extracted) or because they do not represent systems at true equilibrium.[80] However, failure to reach partition equilibrium simultaneously for all the components of a mixture may be turned to good account in certain analytical procedures.[86] In any case a knowledge of the relative disposition of extraction curves for various metals in a chosen reagent–solvent system is a prerequisite to any reasoned attempt to develop a logical analytical procedure aimed at separating one particular component.[87] Such curves must be obtained under the conditions envisaged for the actual separation, for so many factors (pH, reagent concentration, salt-effects, competitive complexing, solvent and kinetic effects) may affect their position.[6, 27, 80] Had those of Fig. 4 been obtained experimentally, the feasibility of separating M^{4+} (curve *E*) from the two bivalent metals giving curves *C* and *D* would be assured, but on extraction at pH 3·5 appreciable quantities of B and some A would be expected to co-extract with it, and retrograde extraction would be necessary to reduce the contamination.

The Extraction of " Dithizonates " and " Oxinates ".—Turning to specific reagents, diphenylthiocarbazone (IV ; " dithizone ") demands pride of place on account of its great versatility and the extent to which it has



(IV.)

$C_6H_5{\cdot}N(NO){\cdot}ONH_4$

(V.)

been studied. The reagent is a weak monobasic acid [17, 88] of dissociation constant $\sim 10^{-5}$: its partition coefficient between carbon tetrachloride and water is $\sim 10^4$. Its intense green colour in organic solvents ($\lambda_{\text{max.}} \sim 620$ mμ., $\varepsilon \sim 30{,}000$) and the fact that its metal complexes are strongly coloured red, orange, brown, or violet make it well suited for the absorptiometric determination of microgram quantities. There is, however, as yet no certainty as to which of the hydrogen atoms of the reagent are involved in complex formation, and the structures of the metal complexes merit examination. Dithizone reacts with a comparatively small number of elements in the middle of the periodic table (cf. Table III) as well as with polonium.[89] Quantitative separations can readily be effected in most cases and details are to be found in the standard text-books.[6] Di-β-naphthylthiocarbazone has certain advantages over dithizone, but owing to difficulties connected with its preparation and purification it has not come into general use.

As compared with dithizone, oxine (I) is much less selective and will

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[86] Irving, Andrew, and Risdon, *J.*, 1949, 541.

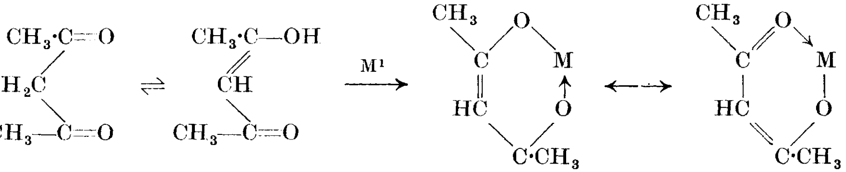
[87] Hagemann, *J. Amer. Chem. Soc.*, 1950, **72**, 768.

[88] Sandell, *ibid.*, p. 4660.

[89] Smales, private communication, 1948 ; cf. Bouissières and Ferradini, *Anal. Chim. Acta*, 1950, **4**, 611.

form extractable complexes with a very large number of elements, including plutonium and its congeners. With few exceptions the complexes are yellow and permit of absorptiometric measurements for which many procedures have been described.[6] In a few cases (indium, gallium, and aluminium) the strong fluorescence in chloroform solution affords another analytical possibility. 5 : 7-Dichloro(and dibromo)-8-hydroxyquinoline are sometimes to be preferred to the parent reagent, notably in the extraction of gallium, indium, and thallium [55, 90] or the rare earths.[90] It is noteworthy that 8-hydroxy-2-methylquinoline (I ; R = CH_3), which differs from oxine itself in giving no precipitate with aluminium,[91] facilitates the solvent extraction and estimation of indium and gallium in the presence of this element.[55] Lacroix [92] and others [55] have made a start in treating the quantitative aspects of partition equilibria in metal–oxine systems, but the difficulties are considerable owing to the amphoteric character of the reagent,[93] the slowness with which equilibrium is reached with certain metals, *e.g.*, aluminium, and the occurrence of basic and water-soluble complexes.[55, 90]

Inner Complexes with 1 : 3-Diketones and Their Solvent Extraction.—A very important class of inner complexes is formed by 1 :3-diketones, of which acetylacetone (VI ; acac) is the simplest representative. In its enolic form (VII) it possesses a hydrogen atom replaceable by a metal, the ketonic oxygen then completing a chelate ring (VIII). The metal " acetylacetonates " are typical non-electrolytes, low-melting [*e.g.*, $Al(acac)_3$, m.p. 192° ; $Be(acac)_2$, b.p. 270°], practically insoluble in water, but readily soluble in benzene, and thus lend themselves to solvent extraction. For instance, during the irradiation of cobalt in a nuclear reactor, the process $^{59}Co(n\,;p)^{59}Fe$ is accompanied by $^{59}Co(n\,;\gamma)^{60}Co$, and the resulting cobalt activity is more than 3000 times that of the iron : nevertheless, solvent extraction of ferric acetylacetonate by xylene at pH 4—7 gives carrier-free iron with complete separation from cobalt.[94]



(VI.) (VII.) (VIII.)

After a fundamental study of complex formation between the cupric ion and a number of substituted acetylacetonates,[95] Reid and Calvin [96] selected

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[90] Moeller *et al.*, *Analyt. Chem.*, 1950, **22**, 1393, and refs. therein.

[91] Irving, Butler, and Ring, *J.*, 1949, 1489.

[92] Lacroix, *Anal. Chim. Acta*, 1947, **1**, 260.

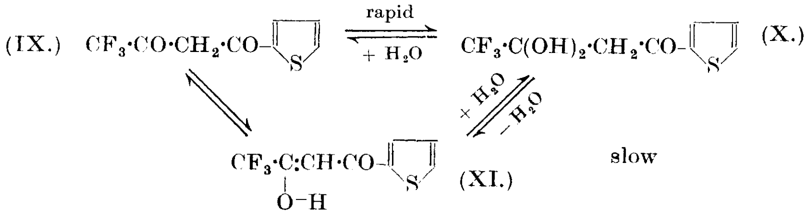
[93] Irving, Ewart, and Wilson, *J.*, 1949, 2672.

[94] Kenny, Morton, and Spragg, *Nature*, 1950, **165**, 483.

[95] Calvin and Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003.

[96] *Ibid.*, 1950, **72**, 2948.

α-thenoyltrifluoroacetone (IX; denoted TTA) as combining the most desirable characteristics of solvent stability, enhanced acidity, and stability towards oxidising, reducing and hydrolytic conditions.



The effect of replacing the methyl group of (VI) by trifluoromethyl is to increase the acid strength of the enol form (XI) and TTA is an acid ($K_{\mathrm{TTA}} = 5 \times 10^{-5}$ at 25°) which can be titrated with alkali. It reacts rapidly with water to give a hydrate (X), which is dehydrated rather slowly into the enol (XI). However, the partition coefficient $[\mathrm{enol}]_{benzene}/[\mathrm{enol}]_{water}$ is very large ($\gg 3000$) and as the reagent concentration changes from 0·1 to 1·8M the value of $\Sigma[\mathrm{TTA}]_{\mathrm{b}}/\Sigma[\mathrm{TTA}]_{0{\cdot}115\mathrm{M}\text{-}\mathrm{HCl}}$, the overall distribution ratio, varies only from 40 to 60. The tautomeric equilibrium ratio $K = [\mathrm{enol}]/[\mathrm{keto}]$ is 17 in benzene, but only 0·015 in water, so that after partition equilibrium has been attained the amount of enol in the aqueous phase is ~ 0·3% of the total, and in the benzene phase ~ 90% of the total, the rest consisting of the hydrate (X) in both cases.[14, 96]

Equilibrium constants for a number of metal–TTA–benzene systems have been measured (Table VI) or can be estimated roughly from published data. Though very restricted in scope the data indicate a decrease in stability of the complexes as the valency of the ion decreases, and as the atomic number increases down any vertical periodic group. B-Sub-group elements appear to form stronger complexes than A-sub-group elements of similar ion radius. The great range of magnitude of the extractability

TABLE VI

Extractability constants for metal–TTA–benzene systems. (Literature references cited)

Univalent ions.		Bivalent ions.		Tervalent ions.		Quadrivalent ions.	
		Be $6{\cdot}3 \times 10^{-4}$	97	Al 6×10^{-6}	97		
		Ca 10^{-12}	98	Sc 0·9	98		
		Sr 9×10^{-10}	97	Y 10^{-7}	97	Zr $9{\cdot}4 \times 10^{7}$	83
		—		La 2×10^{-10}	81	Hf $4{\cdot}6 \times 10^{6}$	83
		Ra v. low	87	Ac 8×10^{-12}	87	Th 5	87
		Cu $4{\cdot}8 \times 10^{-2}$	97	Fe $\gg 1$	97		
$\mathrm{Tl^{I}}$ $6{\cdot}3 \times 10^{-6}$	87	Pb 8×10^{-6}	87	Bi $2{\cdot}5 \times 10^{-4}$	87	Po 4×10^{-2}	87
				$\mathrm{Tl^{III}}$ 2×10^{-6}	87		
				$\mathrm{Am^{III}}$ 3×10^{-7}	99		

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[97] Bolomy and Wish, *J. Amer. Chem. Soc.*, 1950, **72**, 4483.
[98] Broido, AECD 2616.

constants is especially noteworthy as indicating the possibility of excellent separations by an appropriate adjustment of pH. Thus Werner [99] used TTA in purifying ^{241}Am from lanthanum before its neutron irradiation for the synthesis of ^{242}Cm, and it proved invaluable for the preparation of tracer-free ^{45}Ca and the purification of scandium,[98] and the preparation of pure tracer-free beryllium from the products of the cyclotron reaction $^{7}_{3}\mathrm{Li}(d\,;2n)^{7}_{4}\mathrm{Be}$ where Cu, Fe, Al, Sr, Yt, Ca, and Zn are possible contaminants.[97] Other separations include that of bismuth from ^{228}Pa and daughter elements, traces of actinium from $\sim$ 25 g. of thorium, and thorium from protactinium, uranium, and actinium.[52] It has been used to study the complexes of thorium [100] and hafnium [82] and the aqueous chemistry of zirconium,[32] and a very promising separation of zirconium and hafnium can be achieved by solvent extraction with this reagent [83] or less efficiently with trifluoroacetylacetone.[84] The isolation of $\sim$ 1·27 μg. of $> 95\%$ pure actinium from one gram of radium after irradiation in a nuclear reactor, fully described by Hagemann,[87] affords a striking example of its potentialities. The problem of separating this small amount of actinium from its daughter elements and from radium and its daughters thorium, polonium, lead, bismuth and thallium and other impurities was solved by a process involving a series of extraction cycles based on the facts that at pH 6 all the elements save radium were freely extractable by TTA, that at pH $\sim$ 1(N/10-HCl) all the thorium and a trace of polonium were extractable, whilst all the elements could be taken out of the organic phase on shaking with 6N-hydrochloric acid.

Solvent Extraction of "Cupferrates" and Other Metal Complexes.—Cupferron (V) is well known as an important selective precipitant for metals. Its use in extraction analysis has been very thoroughly reviewed by Furman, Mason, and Pekola,[101] who develop a theory for the partition of metal cupferrates on the same lines as that given above (p. 220). It has been tested by Sandell and Cummings for the extraction of ferric cupferrate by chloroform.[102] Cupferron extraction has proved to be particularly useful for the purification of protactinium from mineral concentrates.[66]

No more than a passing reference can be given to the use of dimethylglyoxime, benzoin oxime, 1 : 2-dimercapto-4-methylbenzene (" dithiol "), 3 : 5 : 7 : 2′ : 4′-pentahydroxyflavone (" morin "), nitroso-phenols and -naphthols, and dialkylthiocarbamates, all of which give metal complexes soluble to a greater or less extent in organic solvents ; for though they have been used in specific procedures,[6] no detailed study of extractions using these or a host of other organic reagents [28] has yet been made.

Concluding Remarks.—Our knowledge of the extraction of inorganic substances (as opposed to inner complexes) is largely based on empirical observations, and until recently few attempts have been made to interpret the data on any rational theoretical basis. Though some of the older work awaits a critical reinvestigation, there is still much new territory to explore,

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[99] AECD 2729.

[100] Day and Stoughton, *J. Amer. Chem. Soc.*, 1950, **72**, 5662.

[101] *Analyt. Chem.*, 1949, **21**, 1325.

[102] *Ibid.*, p. 1356.

and we may confidently expect to discover further peculiarities which will in due course be exploited in analysis. Studies over a wider range of temperature, and of solvent extraction from non-aqueous solutions will certainly prove valuable. So far as inner complexes are concerned, the quantitative study of many systems has yet to be undertaken and there must clearly be a move towards the development of more selective and even specific reagents.[91] Much remains to be known of the factors controlling the rate of attaining partition equilibrium,[3, 80,] whether we wish to reach this rapidly—as when performing a continuous counter-current separation—or deliberately to work under non-equilibrium conditions to achieve some specific analytical purpose.[86] Though developed primarily by the analyst and radio-chemist concerned in trace determinations and the separation of complex mixtures, the principles and practice of solvent extraction are of no less interest and importance to the manufacturer of fine chemicals, whilst their aid in solving particular problems and the knowledge which must accrue from attempts to interpret the peculiarly specific features they so often present, cannot fail to exert a profound influence on the development of inorganic chemistry itself.

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