LIQUID–LIQUID EXTRACTION IN INORGANIC CHEMISTRY

By F. S. Martin and R. J. W. Holt
[United Kingdom Atomic Energy Authority, Development and
Engineering Group (R. & D. Branch), Springfields]

1. Introduction

Liquid–liquid extraction most frequently involves an aqueous phase, an immiscible organic liquid phase, and one or more solutes in a system which is commonly operated under prevailing atmospheric conditions. There are a few recent developments in which the immiscible phases are liquid metals; these represent a threshold of future work and expansion and as such they merit brief mention in this Review. The analytical implications of liquid–liquid extraction are extensive but since these have previously been comprehensively reviewed by Irving[1] in these Reviews, no more than cursory attention will be paid to them here.

2. Historical

In 1872, Berthelot[2] stated that when a third substance is present in a system of two immiscible liquids it distributes itself between them in a definite manner if it is soluble in both of them. If c_1 and c_2 are the concentrations of the solute in phases 1 and 2 at equilibrium at constant temperature, then

$$c_1/c_2 = \text{constant (the distribution or partition coefficient)} \quad . \quad (1)$$

This is the simplest form of the distribution or partition law. Equation (1) may be derived from the equality of the chemical potential (μ) of the solute in two phases at equilibrium, *i.e.*, $\mu_1 = \mu_2$.

Since $\mu = \mu^0 + RT \ln a$ (where μ^0 = const. and a = activity), then

$$a_1/a_2 = \text{const. (at constant } T) \quad . \; . \; . \; . \; . \; . \quad (2)$$

If the solutions obey Henry's or Raoult's law, activities can be replaced, in practice, by mole fractions, and then

$$x_1/x_2 = \text{const.} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

For dilute solutions the ratio of mole fractions approximates to that of concentrations (in molarities or molalities); consequently

$$c_1/c_2 = \text{constant } (\equiv \text{equation 1}).$$

Hence equation (1) will only be strictly true for ideal dilute solutions; however, many substances obey the law in this form, for example, iodine

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[1] Irving, *Quart. Rev.*, 1951, **5**, 200.
[2] Berthelot and Jungfleisch, *Ann. Chim. Phys.*, 1872, **26**, 396.

in the carbon tetrachloride–water pair, sulphur dioxide in water–chloroform, and mercuric chloride in water–benzene.

According to Nernst,[3] the distribution law applies only to those species common to both phases. If α represents the fraction of solute which undergoes association or dissociation in a phase, equation (1) becomes

$$c_1 (1 - \alpha_1) / c_2(1 - \alpha_2) = \text{constant} \quad . \ . \ . \ . \ . \ . \ . \quad (4)$$

The inexactitude of equation (4) is greater than that of (1) since dissociable or associable solutes depart from ideal behaviour. The use of activity coefficients in modern treatments[4] results in improved forms of the distribution expression.

In spite of the inexactitude of equation (4), it has formed the basis of several studies of association or dissociation, *e.g.*, the distribution of benzoic acid between water and benzene, a study of which has shown that in benzene benzoic acid is largely dimerised.[5] However, similar studies in other systems may lead to false conclusions. For instance, Anderson and Yost[6] showed that the distribution of osmium tetroxide between carbon tetrachloride and water was consistent with the hypothesis that the solute exists in the organic phase as the tetramer, $(OsO_4)_4$. Later studies[7] showed that a similar hypothesis was not tenable in the case of the very similar ruthenium tetroxide; Hildebrand and Scott[8] suggested that differences in internal pressure of solute and solvent were more likely to account for the experimental results than the existence of tetramers in this case.

Experimental details of studies of this type will be found in most text books of physical chemistry.

3. Classification of solvent extraction

(a) *Aqueous Phase.*—Of recent years, solvent extraction (this term is frequently used instead of liquid–liquid extraction for aqueous–organic pairs) has been used for a variety of studies and practical applications; these are based on various reactions between solute species or between solute and solvent (Table 1).

This classification is not rigid or exact. For example, uranyl nitrate may be extracted under different conditions as the dinitrato-complex $UO_2(NO_3)_2$, or the trinitrato-anionic one $H[UO_2(NO_3)_3]$; in neither case can the formation of these species be said to result solely from ion association [*e.g.*, $(UO_2^{++})(2NO_3^-)$] or solely from simple co-ordination.

The extraction of a species usually depends on its conversion into a

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[3] Nernst, *Z. phys. Chem.*, 1891, **8**, 110.
[4] McKay, *Chem. and Ind.*, 1954, 1549.
[5] Hendrixson, *Z. anorg. Chem.*, 1896, **13**, 73.
[6] Anderson and Yost, *J. Amer. Chem. Soc.*, 1938, **60**, 1822.
[7] Martin, *J.*, 1954, 2564.
[8] Hildebrand and Scott, "Solubility of Non-Electrolytes," Reinhold Publ. Corp. New York, 1950, p. 220.

compound capable of solution in the organic phase, *e.g.*, anionic ion-association complexes may form oxonium salts with ethereal solvents, or the metal may be associated with hydrophobic complexes as in many chelates. In a few cases the inorganic compound seems to dissolve as such in the organic phase, *e.g.*, ruthenium tetroxide in carbon tetrachloride; in these cases, the compound usually possesses a high degree of covalency. Some compounds may be extracted into an organic phase with the formation of "solvates" or mixed solvate hydrates, as exemplified by the extraction of several metal nitrates into ethers and ketones.

TABLE 1. *Types of extractable species involving inorganic solutes in aqueous phases.*

Reactions involved	*Example*
1. Ion association with the metal in either the cation or the anion	Cationic: Copper hexanoate Anionic: $H[UO_2(NO_3)_3]$
2. Simple co-ordination	Germanium tetrachloride
3. Chelating co-ordination	Zirconium thenoyltrifluoroacetonate

(b) *Types of Extraction.*—Table 2 summarises the main types of extraction; following this each will be dealt with in more detail.

TABLE 2. *Categories of solvent extraction*

Type	*Example*
1. Physical solution in organic phase without solvation	RuO_4 in CCl_4; 8-hydroxyquinolinates in $CHCl_3$, etc.
2. Physical solution accompanied by partial or complete solvation	$UO_2(NO_3)_2,2H_2O,2S$, where S = molecule of solvent (ether, ketone, ester, etc.)
3. Oxonium or other compound formation with the solvent, including ion exchange	Nitric acid in ether: $(Et_2OH^+)(NO_3^-)$: $FeCl_3$–HCl in ether: $(Et_2OH^+)(FeCl_4^-)$

Irving, Rossotti, and Williams[9] have developed a quantitative generalised treatment of partition equilibria in inorganic systems by combining the concept of step equilibrium with the partition law. In this, the partition equilibria are described quantitatively in terms of step equilibria governing

[9] Irving, Rossotti, and Williams, *J.*, 1955, 1906.

the relative concentrations of different species in the aqueous phase and of a series of partition coefficients referring to the species which are common to the two phases. Development of this theme enables the relative degrees of association in each phase of metal ion with hydrogen and ligand ions to be determined; partition coefficients and stability constants of species present in simple "ideal" systems may be derived and the probable nature of species present in more complicated systems may be deduced. Although the comprehensive treatment of Irving *et al.* should be read by all serious students of inorganic extraction, we consider it more appropriate here to give individual attention to the various classes of extraction.

(c) *Extraction of Covalent Compounds* (*into Inert Solvents*).—The extraction of such compounds is often described as being effected by "simple" physical solution in the organic phase. However, although direct solvation or co-ordination of solvent to solute molecules may not seem to be involved, there must nevertheless be some intermolecular interaction leading in many cases to departures from ideality. Examples of species which fall into this category include elements (*e.g.*, chlorine, bromine, iodine) and compounds (*e.g.*, sulphur dioxide, mercuric chloride, and the tetroxides of Group VIII); the organic solvents which will extract these from aqueous solutions are usually inert (hydrocarbon, halogenated hydrocarbon, etc.).

Accounts of studies of systems such as iodine in carbon tetrachloride–water will be familiar to many readers; the general principles involved are applicable to less familiar but equally interesting cases, *e.g.*, the tetroxides of Group VIII. For ruthenium tetroxide the distribution coefficient for the carbon tetrachloride–water system is constant over the twenty-fold concentration range 0·006—0·012M in the organic phase and has the value $D = 58{\cdot}4$;[7] *i.e.*, equation (1) is applicable and it may be deduced that the reactions represented by

$$\left.\begin{array}{ll}\text{(i)} & RuO_4 + H_2O \rightleftharpoons H_2RuO_5 \\ \text{(ii)} & H_2RuO_5 \rightleftharpoons HRuO_5^- + H^+ \\ \text{(iii)} & H_2RuO_5 \rightleftharpoons HRuO_4^+ + OH^-\end{array}\right\} \quad \text{(Aqueous phase)}$$

$$\text{(iv)} \quad xRuO_4 \rightleftharpoons (RuO_4)_x \qquad \text{(CCl}_4\text{ phase)}$$

do not occur appreciably. However, reactions (ii) and (iii) are obviously dependent upon pH, and by varying the latter their equilibrium constants may be obtained from partition experiments.

If: $K_w = [H^+][OH^-]$

$D = [RuO_4]_o/[RuO_4]_{aq.}$ (o = organic phase)

$D' = [RuO_4]_o/([RuO_4]_{aq.} + [HRuO_5^-])$ (at high pH)

$K_a = \dfrac{[HRuO_5^-]\,[H^+]}{[RuO_4]_{aq.}}$ = acid dissociation constant of RuO_4aq.

then $K_a = K_w(D - D')/[OH^-]D'$ . . . . (5)

Experimentally, K_a (from 5) was found to be constant when the hydroxyl ion concentration was varied over the tenfold range 0·001—0·01M, as would be expected if the simple partition theory is applicable.

Salting-out of extractable non-electrolytes. The solubility of non-electrolytes in water is affected by the presence of neutral, basic, and acidic salts ("Setchenow" salting-out);[10] hence the distribution of a non-electrolyte between organic and aqueous phases will also be affected by their presence. There is a marked difference between this type of salting-out and that caused by the common-ion effect which applies to the extraction of dissociable species. The latter plays a prominent part in many other systems and is discussed in the appropriate sections.

"Setchenow" salting-out is described qualitatively by:

$$\log S/S_0 = kc \quad \ldots\ldots\ldots \quad (6)$$

where S_0 = solubility of non-electrolyte in water; S = solubility of non-electrolyte in salt solution of concentration c; and k = constant (salting-out coefficient). For gases in water, the expression is found to hold up to surprisingly high values of c (*e.g.*, up to 3N).

For distribution experiments, expression (6) becomes

$$\log D_a - \log D = kc \quad \ldots\ldots\ldots \quad (7)$$

where D applies to water and D_a to salt solutions. D_a is proportional to the activity coefficient (γ) of the non-electrolyte in the aqueous phase; for dilute solutions in pure water, γ may be taken as unity. Hence we also have:

$$\log \gamma = kc \quad \ldots\ldots\ldots \quad (8)$$

where γ (= D_a/D) is the activity coefficient of the non-electrolyte in aqueous solutions of salt concentration c. As in the case of gases, the linearity of this expression is verified for ruthenium tetroxide up to quite high salt concentrations in water (Fig. 1).

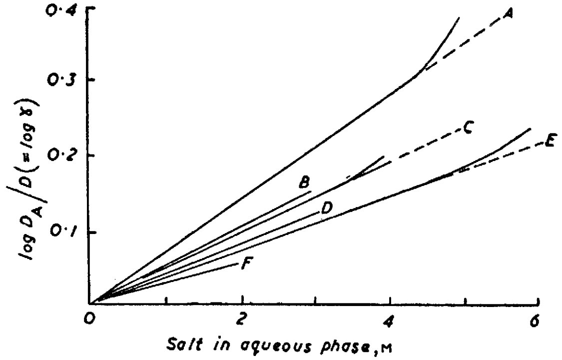

FIG. 1 *Effect of salting-out on the extraction of* RuO_4 *by carbon tetrachloride from water. A,* NaCl. *B,* $NaNO_3$. *C,* KCl. *D,* KNO_3. *E,* LiCl. *F,* $LiNO_3$.

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[10] McDevit and Long, *Chem. Rev.*, 1952, **51**, 119.

Setchenow salting-out results usually in a decrease in solubility of the non-electrolyte in the aqueous phase (and hence enhanced extraction into the second phase). However, k is sometimes negative ("salting-in"). Whilst salting-out can be tentatively described in terms of a lowering of water activity by the binding of water molecules into the hydration spheres of the added electrolyte species, such an explanation does not unambiguously apply to salting-in; a satisfactory explanation of Setchenow salting-out or -in is still lacking.

(d) *Extraction of Ion Association Complexes into Neutral Solvents.*—Since no classification of types of solvent extraction can be rigid, the term "neutral" here is relative and does not mean, for instance, that the solvent cannot form solvates with the solute; it does mean that it does not (in the present context) participate in any kind of ionic reaction. Some solvents, *e.g.*, diethyl ether, act by solvating an electrically neutral ion-association complex, and also by participating in ionic reactions as in oxonium-salt formation: examples of the two modes are:

$$\text{(i)}\quad UO_2^{++} + 2NO_3^- + xH_2O + (4-x)\,Et_2O \rightleftharpoons UO_2(NO_3)_2,(Et_2O)_{4-x}(H_2O)_x$$

$$\text{(ii)}\quad H^+ + NO_3^- + Et_2O \rightleftharpoons [Et_2OH]^+ + (NO_3)^-$$

where the left-hand and the right-hand side represent aqueous and organic phases, respectively.

Many solvents, *e.g.*, tributyl phosphate, are always neutral and act by solvation of electrically neutral species. A large amount of work has been carried out on the uranyl nitrate–tributyl phosphate (TBP) extraction system:

$$UO_2^{++}{}_{\text{aq.}} + 2NO_3^-{}_{\text{aq.}} + n\text{TBP}_{\text{org.}} \rightleftharpoons UO_2(NO_3)_2,\ n\text{TBP}_{\text{org.}}$$

$$\text{whence } D_U = \frac{[UO_2(NO_3)_2,\ n\text{TBP}_{\text{org.}}]}{[UO_2^{++}]_{\text{aq.}}[NO_3^-]_{\text{aq.}}[\text{TBP}]^n_{\text{org.}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

[Square brackets denote appropriate activities.]

Thus D_U depends upon the nth power of the concentration of tributyl phosphate. By using an inert diluent such as kerosene, the variation of D_U with ester concentration can be observed, and thus the value of n determined. For uranyl nitrate, D_U varies as the square of the phosphate concentration; consequently, it is concluded that the disolvate, $UO_2(NO_3)_2$, 2TBP, exists in the solvent phase.[11] Similarly, nitric acid is extracted from aqueous solutions by tributyl phosphate, and D_{NHO_3} varies directly as the solvent concentration (for dilute solutions); nitric acid therefore seems to extract as HNO_3,TBP.[12] Tributyl phosphate also extracts the nitrates of tervalent cations [*e.g.*, $La(NO_3)_3$,3TBP], and of quadrivalent cations [*e.g.*, Th $(NO_3)_4$,2TBP] as well as of other bivalent oxyions such as

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[11] Moore, 1951, USAEC Unclassified Document, AECD, 3196.

[12] Alcock, Grimley, Healey, Kennedy, and McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.

plutonyl and neptunyl. In this type of extraction the number of solvate molecules attached to the central atom of the extractable solute makes up the usual co-ordination number of that atom. When solvents like ethers, alcohols, and ketones act in their so-called neutral capacity, mixed solvate–hydrate conditions sometimes arise, *e.g.*, as in $UO_2(NO_3)_2$, $3H_2O$,Et_2O and $UO_2(NO_3)_2$,$2H_2O$,$2Et_2O$.[13,14]

(e) *Extraction of Ion-association Complexes into Inert Solvents.*—Some ion-association complexes, notably those containing bulky anions or cations, *e.g.*, tetraphenylarsonium per-rhenate, pertechnetate, or permanganate, are soluble in non-reactive solvents such as chloroform. The extractable complexes are usually formed *in situ* by reaction of the appropriate salt with, *e.g.*, tetraphenylarsonium chloride. Relatively simple equilibria are involved in these reactions; their treatment bears a formal resemblance to that of chelate extraction systems which are dealt with on page 337.

(f) *Thermodynamics of the Extraction of Ion-association Complexes.*—Uranyl nitrate again provides us with an example of the treatment of the extraction of ion-association complexes.[4,15] From equation (9), we have

$$y = D_U x(NO_3^-)^2 \gamma^3 T^2 \gamma_T^2 / \gamma_\theta \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

where x and y are the molar concentrations of uranyl nitrate in aqueous and organic phases respectively; γ_θ is the activity coefficient of the solvate in the organic phase; γ is the mean molar activity coefficient of uranyl nitrate in the aqueous phase (γ is related in the usual manner to γ_+ and γ_-); γ_T is the activity coefficient of solvent; and T is the concentration of free solvent in the organic phase.

If the sole source of nitrate is from dissociation of uranyl nitrate, $(NO_3^-) = 2x$, and

$$y = 4D_U x^3 \gamma^3 T^2 \gamma_T^2 / \gamma_\theta \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

Also T is equal to $T_0 - T_{\text{bound}}$ where T_0 is the original concentration, and T_{bound} is the quantity found in the solvate. In the present case $T_{\text{bound}} = 2y$; hence

$$T = T_0 - 2y = T_0(1 - \epsilon) \quad . \; . \; . \; . \; . \; . \; . \quad (12)$$

where $\epsilon = 2y/T_0$ = degree of binding of solvent = amount of saturation of solvent with solvate. ϵ is an important quantity in the consideration of the similtaneous extraction of two solutes.

For pure, undiluted solvent and low concentrations of solute, equation (11) reduces to

$$y = 4D_U \, x^3 \gamma^3 / \gamma_\theta \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

Thus the plot of $y\gamma_\theta$ against $x^3\gamma^3$ should be linear, with slope $= 4D_U$. Values of γ are available from vapour-pressure studies of uranyl nitrate

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[13] Katzin and Sullivan, *J. Phys. Colloid. Chem.*, 1951, **55**, 346.

[14] Bachelet and Cheylan, *J. Chim. phys.*, 1947, **44**, 248.

[15] Rozen and Khorkhorina, *Zhur. neorg. Khim.*, 1957, **2**, 1956.

solutions; γ_θ may be taken to equal unity at low concentrations of solute. Having found D_U for low concentrations, we can use it to find γ at higher concentrations. The validity of this linear law has been demonstrated for uranyl nitrate over a concentration range of 10^2 for ethereal solvents.[16]

Equations (11) and (13) imply the complete immiscibility of the two phases. In practice, the solubility of the solvent in the aqueous phase can usually be neglected; however, in some cases dissolved water in the organic phase may appreciably affect the activity of the solvent. Some of this water may be associated as hydration of the solute (*e.g.*, the mixed hydrate–solvates already mentioned), a phenomenon more usually associated with ethereal, ketonic, and alcoholic solvents than with esters of the phosphate type. For uranyl nitrate, the solute activity in the organic phase appears to be a function of the fourth power of the water activity,[4] as a result of which, equation (13) becomes:

$$y = 4D_U\, x^3\gamma^3 a_w{}^4/\gamma_\theta{}^\circ \quad . \; . \; . \; . \; . \; . \; . \quad (14)$$

where $\gamma_\theta{}^\circ$ is the limiting value of γ_θ with pure water and a_w is the water activity (or water vapour pressure).

Salting-out. The addition of a second salt with a common ion (insoluble in the organic phase) to these systems results qualitatively in the formation of a higher proportion of neutral or ion-association solute molecules through the common-ion effect and hence in enhanced extraction. As an example, the addition of a bivalent metal nitrate to uranyl nitrate will be considered.

In the aqueous phase the activity of uranyl nitrate is given by

$$[UO_2{}^{++}]\,[NO_3{}^-]^2 = 4x(x + z)^2\gamma^3$$

where z is the concentration of the second nitrate. This leads to the partition equation[17]

$$y = 4D_U(x + z)^2\gamma^3 a_w{}^4/\gamma_\theta{}^\circ \quad . \; . \; . \; . \; . \; . \; . \quad (15)$$

where γ is now the activity coefficient of uranyl nitrate in the mixed nitrate system. If values of γ are available, partitions can be estimated; alternatively, if the partitions are determined, values of γ can be derived.

If the second nitrate is itself extracted into the solvent, account must be taken of altered activity coefficients in that phase and also of the factor ϵ (equation 12). If the second extractable nitrate is nitric acid, the main effect in the case of neutral phosphate solvents is on the value of ϵ and there is "competition" for solvent molecules between uranyl nitrate and nitric acid. This leads to the type of extraction curve shown in Fig. 2 where for small additions of nitric acid the salting-out effect is apparent, but for larger additions the competition effect becomes predominant and the extraction of solute falls. In the case of ethereal solvents, the "neutral"

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[16] Glueckauf, McKay, and Mathieson, *Trans. Faraday Soc.*, 1951, **47**, 437.
[17] Jenkins and McKay, *Trans. Faraday Soc.*, 1954, **50**, 107.

rôle is transformed into a reactive one in the presence of concentrations of strong acid, and the solvent may extract complex anions as oxonium salts (see below); the competition effect is therefore less marked and salting-out is effective over a wide range of concentrations.

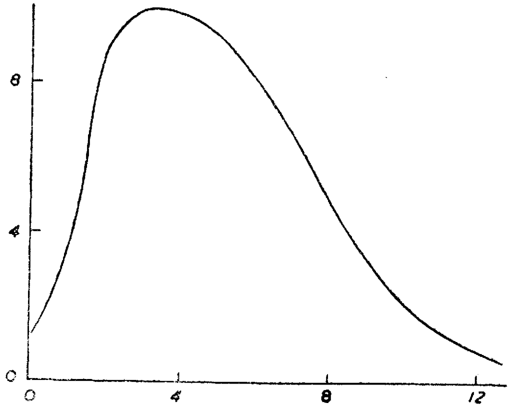

FIG. 2 *Typical curve for the extraction of an actinide nitrate from various concentrations of nitric acid into a neutral phosphate ester, such as tributyl phosphate (TBP), being a plot of partition coefficient of extractable nitrate (D, in arbitrary units) against the molarity of nitric acid in the aqueous phase* (M,HNO_3). *To the left of the peak salting-out predominates; to the right competition.*

(g) *Extraction into Reactive Solvents.*—Some solvents, particularly ethers, become reactive under conditions of high acidity by virtue of formation of oxonium-type salts; in this, a solvent molecule becomes co-ordinatively attached to a hydrogen ion, and electrical neutrality is maintained by ion association with an anion. Such solutions may have determinable (but low) electrical conductivities, whereas solutions of inorganic salts in neutral solvents such as tributyl phosphate will have negligible conductivities.

Nitric acid can be extracted from water by ether in the following way:

$$H^+_{aq.} + NO_3^-{}_{aq.} + Et_2O \rightleftharpoons [Et_2OH]^+ NO_3^-{}_{org.}$$

With another extractable nitrate such as uranyl nitrate the presence of nitric acid leads to the formation of acids having complex anions such as $H[UO_2(NO_3)_3]$ and this tri-nitrate acid species may be found in the solvent phase. Another example is the extraction of ferric chloride into di-isopropyl ether from hydrochloric acid, where one of the extractable species is $H[FeCl_4]$ and the oxonium salt $(Pr^i_2OH)^+$ $(FeCl_4)^-$ exists in the solvent phase.

(h) *Acidic Solvents.*—Whereas solvents like ethers, ketones, and alcohols are most useful in the extraction of nitrates (as a result of the ready formation of neutral or anionic nitrate complexes) some newer organophosphorus acidic solvents are of great interest in the extraction of metal compounds from aqueous sulphate, chloride, and phosphate solutions. Typical examples are monoheptadecylphosphoric acid (HDPA) (heptadecyl dihydrogen phosphate) and di-2-ethylhexylphosphoric acid (D2EHPA) [di-(2-ethylhexyl) hydrogen phosphate]. For viscosity reasons, these solvents are normally used in kerosene, xylene, or some other inert diluent. It has been shown that acid alkyl phosphates exist in these phases as dimers, and that uranium extraction varies as the square of the acid alkyl phosphate concentration and inversely as the square of the hydrogen-ion concentration in the aqueous phase.[18,19] It may be concluded that the extraction mechanism is:

$$UO_2{}^{++}{}_{aq.} + 2(HX)_2 \rightleftharpoons UO_2X_2{,}2HX_{org.} + 2H^+{}_{aq.} \quad . \quad (16)$$

where $(HX)_2$ represents the dimerised acid.

This is a type of cation exchange and explains the ability to extract uranium from solutions containing sulphate ions, etc., as well as from the nitrate solutions. Generally, the extracting power of dialkylphosphoric acids is three or four times greater than that of neutral alkyl phosphates.

Synergism. A remarkable feature exhibited by dialkyl hydrogen phosphates is their synergistic behaviour in the presence of small amounts of neutral alkyl phosphates or other organophosphorus compounds. Synergism here is the co-operative and cumulative action of separate extractants such that the total effect is greater than the sum of the individual effects. Di-(2-ethylhexyl) hydrogen phosphate (D2EHPA) forms synergistic mixtures with, *e.g.*, tributyl phosphate (TBP), dihexyl hexylphosphonate (DHHP), and trioctylphosphine oxide (TOPO).[20] Synergistic enhancement occurs in the extraction of uranyl, plutonyl, and quadrivalent plutonium solutions[21] but not of U(IV), V(IV), Al, or Mo.

Considering that diethylhexyl hydrogen phosphate (D2EHPA) extracts 3–4 times as strongly as tributyl phosphate, the effect of small additions of the latter is quite notable. The addition of as little as 0·05M-tributylphosphine oxide to the diethylhexyl ester in the extraction of uranium from 1·5M-sulphuric acid may increase the partition coefficient by a factor of fifty.

As a rule, as the concentration of neutral additive increases, the enhancement increases to a maximum and then decreases; an extraction curve of the general shape similar to that of Fig. 2 is obtained.

A tentative explanation[22] of the synergism implies that two moles of

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[18] Blake, Baes, Brown, Coleman, and White, UNICPUAE 1958, P/1550.*

[19] Baes, Zingaro, and Coleman, *J. Phys. Chem.*, 1958, **62**, 129.

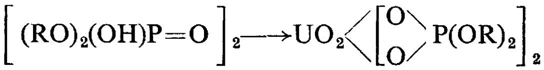
[20] Anon., *Reactor Fuel Processing*, 1959, **2**, (1), 12.

[21] Blake, Horner, and Schmitt, 1959, USAEC Unclassified Document, ORNL 2259.

[22] Kennedy, 1958, U.K.A.E.A., Document Number AERE C/M 369.

* Here and later UNICPUAE refers to the Geneva Conferences on the Peaceful Uses of Atomic Energy.

dimer normally (*i.e.*, in the absence of synergistic additives) depolymerise before forming the octaco-ordinated complex:



$$\Big[(RO)_2(OH)P{=}O\Big]_2 \longrightarrow UO_2\Big<\Big[\begin{matrix}O\\O\end{matrix}\Big> P(OR)_2\Big]_2$$

(*i.e.*, the extracted species according to equation 16).

In the presence of the neutral additive, two of the links in this complex could be replaced by links from the additive, it being assumed that the solvating (co-ordinating) properties of, *e.g.*, tributyl phosphate, would not differ much from those of the di-(2-ethylhexyl) ester. Thus the necessity of monomerising one of the two moles of dimer would be obviated with an estimated saving in free-energy change of about 8000 cal./mole. The diminished energy requirements could account for the enhanced extraction. The equation representing the synergistic extraction would then be of the form:

$$UO_2{}^{++}{}_{aq.} + (HX)_{2org.} + 2TBP \rightleftharpoons UO_2X_2{,}2TBP_{org.} + 2H^+{}_{aq.} \quad (17)$$

The decrease in enhancement at high neutral additive concentrations is accounted for by a type of competition effect due to interaction (hydrogen bonding) between the dialkyl hydrogen phosphate and the additive,[21] *e.g.*, $TBP + (HX)_2 \rightleftharpoons TBP(HX)_2$ and $TBP + \frac{1}{2}(HX)_2 \rightleftharpoons TBP(HX)$ thus effectively increasing the value of ϵ (equation 12).

(i) *Basic Extractants.*—Like the acidic organophosphorus reagents, the basic organonitrogen compounds are relative newcomers into the extraction field. These are amines (*e.g.*, tri-iso-octylamine) and they act esssentially as liquid anion-exchanger materials just as the acid phosphates are liquid cation-exchanger materials. They will extract simple and complex anions (*e.g.*, trinitratouranyl) from highly acid solutions, and the solute may be recovered by washing the solvent with dilute acid or complexing solutions. For example, quadrivalent neptunium and plutonium both form anionic nitrate complexes in 4—6M-nitric acid and may be extracted as such by a solution of tri-iso-octylamine in xylene,[23] whilst the same solvent will extract anionic uranium chloro-complexes from hydrochloric acid.[24]

(j) *Extraction of Chelate Compounds.*—Although extractable metal chelates (usually soluble in inert solvents such as benzene, chloroform, etc.) are essentially covalent compounds, they cannot be treated in quite the same simple way as the extractable covalent compounds described on pp. 330—332. The latter exist essentially in a single form in both phases, whereas the presence of the extractable chelates depends upon a number of equilibria (hydrolysis and association), as well as upon the presence of excess of chelating compound in the inert solvent.

[23] Sheppard, 1957, USAEC Unclassified Document HW 51958.

[24] Moore, 1957, USAEC Unclassified Document CR-57-1-61; *Analyt. Chem.*, 1951, **29**, 1661.

General treatment. The equilibria involved are:
Ionisation of chelating compound (assumed to be a weak acid, HA):

$$HA \rightleftharpoons H^+ + A^-;\ K_i = [H^+]\,[A^-]/[HA] \quad . \ . \ . \ . \ . \ . \ . \quad (18)$$

Stepwise formation of chelate with metal ions of valency *n*:

$$M^{n+} + A^- \rightleftharpoons MA^{(n-1)+}\ ;\ K_1 = [MA^{(n-1)+}]/[M^{n+}][A^-]$$
$$MA^{(n-1)+} = A^- \rightleftharpoons MA_2^{(n-2)+};\ K_2 = [MA_2^{(n-2)+}]/[MA^{(n-1)+}][A^-];$$

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$$MA^+_{n-1} + A^- \rightleftharpoons MA_n; \qquad K_n = [MA_n]/[MA^+_{n-1}][A^-] \quad . \ . \quad (19)$$

The overall formation constant $K_f = K_1.K_2.K_3 \ldots\ldots K_n$.
Hydrolysis:

$$M^{n+} + OH^- \rightleftharpoons M(OH)^{(n-1)+} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (20)$$

and so on.
Anion co-ordination (anion = X^-):

$$M^{n+} + X^- \rightleftharpoons MX^{(n-1)+} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (21)$$

and so on.
Distribution of chelating compound:

$$D_{HA} = [HA]_{org.}/[HA]_{aq.} \quad . \ . \ . \ . \ . \ . \ . \quad (22)$$

distribution of the metal chelate:

$$D_{MA_n} = [MA_n]_{org.}/[MA_n]_{aq.} \quad . \ . \ . \ . \ . \ . \ . \quad (23)$$

From these equilibria, an expression for the apparent partition coefficient, *D* (*i.e.*, the ratio of the total metal concentrations in the two phases), can be derived.

If we assume that M is present in the organic phase only as MA_n, it follows that

$$D = \frac{[MA_n]_{org.}}{[M^{n+}] + [MA^{(n-1)+}] + \ldots\ldots [MA^+_{n-1}] + \sum_i [M(OH)_i^{(n-i)+}] + \sum_j [MX_j^{(n-j)+}]} \quad . \ . \ . \ . \quad (24)$$

Substituting from expressions (19) and (23) after division of numerator and denominator by $[MA_n]_{aq.}$, we have

$$D = \frac{K_f\, D_{MA_n}\, [A^-]^n}{1 + K_1\,[A^-] + K_1K_2\,[A^-]^2 \ldots\ldots + K_f\,[A^-]^n\,(1 + x)} \quad . \ . \quad (25)$$

where $x = \left\{ \sum_i [\mathrm{M(OH)}^{n-i}] + \sum_j [\mathrm{MX}_j{}^{n-j}] \right\} \Big/ [\mathrm{MA}_n]_{\mathrm{aq.}}$

Substituting from (18) and (19), we have

$$D = \frac{K_f\, D_{\mathrm{MA}_n} K_i{}^n}{D_{\mathrm{HA}}{}^n} \left[\left\{ \frac{[\mathrm{H}^+]}{[\mathrm{HA}]_{\mathrm{org.}}} \right\}^n + \frac{K_1 K_i}{D_{\mathrm{HA}}} \left\{ \frac{[\mathrm{H}^+]}{[\mathrm{HA}]_{\mathrm{org.}}} \right\}^{n-1} \right.$$
$$\left. + \cdots \frac{K_1 K_2 \ldots\ldots K_{n-1} K_i{}^{n-1}}{D_{\mathrm{HA}}{}^{n-1}} \cdot \frac{[\mathrm{H}^+]}{[\mathrm{HA}]_{\mathrm{org.}}} + \frac{K_f K_i{}^n}{D_{\mathrm{HA}}{}^n} (1 + x) \right]^{-1} \quad . \quad (26)$$

This expression shows clearly the importance of the hydrogen-ion concentration, the stability of the chelate (reflected by K_f), and the relative solubility of the chelate (reflected by D_{MA_n}) in the organic phase in governing the extraction of the metal.

Equation (26) may be simplified by assuming that hydrolysis and anion co-ordination of the metal ion in the aqueous phase are negligible (*i.e.*, $x = 0$), that $[\mathrm{MA}_n]_{\mathrm{aq.}}$ is negligible

$\left(i.e., \left\{ \frac{[\mathrm{H}^+]}{[\mathrm{HA}]_{\mathrm{org.}}} \right\}^n \gg \frac{K_f K_i{}^n}{D_{\mathrm{HA}}{}^n} \right)$, and that negligible amounts of the intermediate chelate species are formed;[25]

$$D = \frac{K_f\, D_{\mathrm{MA}} K_i{}^n}{D_{\mathrm{HA}}{}^n} \left\{ \frac{[\mathrm{HA}]_{\mathrm{org.}}}{[\mathrm{H}^+]} \right\}^n = K' \left[\frac{[\mathrm{HA}]_{\mathrm{org.}}}{[\mathrm{H}^+]} \right]^n \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Thus if $[\mathrm{HA}]_{\mathrm{org.}}$ is constant, the extraction is a function of pH alone and curves of distribution versus pH are of great analytical significance.[26]

Treatment of hydrolysable species. In the case of the extraction of, *e.g.*, zirconium, by thenoyltrifluoracetone (TTA) where hydrolysis in aqueous solution cannot be neglected, Connick and McVey[27] derived by a rather similar mathematical route the expression:

$$\frac{\partial \ln D}{\partial \ln [\mathrm{HA}]} = 4f'_0 + 3f'_1 + 2f'_2 + f'_3 - (4f_0 + 3f_1 + 2f_2 + f_3) \quad . \quad (28)$$

where f' and f refer to aqueous and solvent (TTA in benzene) phases respectively and are equal to the fraction of total activity contributed by each zirconium species containing the indicated number of chelate groups.

The dependence of Connick and McVey's experimental values of $\ln D$ on TTA activity fitted a line of slope 4, and it was concluded that the extraction reaction is:

$$\mathrm{Zr(OH)}_n{}^{(4-n)+} + 4\mathrm{HA} = \mathrm{ZrA}_4 + (4 - n)\mathrm{H}^+ + n\mathrm{H_2O}$$

By studying the dependence of the extraction on the hydrogen-ion activity in the aqueous phase, Connick and McVey were able to determine

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[25] Kolthoff and Sandell, *J. Amer. Chem. Soc.*, 1941, **63**, 1906.

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

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

the average degree of hydrolysis of the zirconium species in the system by using the expression:

$$\partial \ln D/\partial \ln [\mathrm{H}^+] = -4 + f_1 + 2f_2 + 3f_3 + \ldots \quad (29)$$

where each f = fraction of total zirconium in the aqueous phase having the number of OH groups per zirconium indicated by the subscript. For very dilute solutions of zirconium in 2M-perchloric acid the average species has between 0 and 1 hydroxyl groups attached to it, *i.e.*, it lies between Zr^{4+} and $\mathrm{Zr(OH)}^{3+}$.

For the study of general anion (chloride, nitrate, sulphate, fluoride) complex formation of zirconium, the expression:

$$\partial \ln D/\partial \ln [\mathrm{HX}] = -f_1 - 2f_2 - 3f_3 \text{ (where X = anion)}$$

was used and the degree of complex-ion formation was determined.

4. Solvent extraction in practice

(a) *Practical Calculations.*—The simple distribution equation (equation 1) applies only occasionally, the value of D often varying with solute concentration. If this variation is known it is possible to calculate the separation and extraction of different solutes.

It is often convenient to plot extraction systems graphically by using x and y co-ordinates for aqueous and solvent concentration. The mass balance for a single equilibration of a volume V_{a1} of aqueous phase containing concentration x_0 of a solute with volume V_{s1} of pure solvent is:

$$V_a x_0 = V_{a1} x_1 + V_{s1} y_1 \quad (30)$$

By substituting $y_1/x_1 = D_1$ and $V_{s1}/V_{a1} = R_1$, we have $x_0 = x_1(1+R_1D_1)$. If the two phases are separated after equilibration, and a volume V_{s2} of pure solvent is equilibrated with the aqueous phase from the first operation, then

$$x_1 = x_2(1 + R_2D_2) \text{ and } x_0 = x_2(1 + R_2D_2)(1 + R_1D_1) \quad (31)$$

In the ideal case (D = constant), if R is constant for all stages then

$$x_0 = x_n(1 + RD)^n \quad (32)$$

The distribution diagram (Fig. 3A) refers to a three-stage batch extraction process. The point A ($x = x_0$, $y = 0$) represents the composition of the starting phases before mixing; the point B, where the line through A of slope $-1/R$ cuts the line $y/x = D$, gives the equilibrium concentrations y_1 and x_1. If the equilibrium had not been fully attained, the concentrations would still be on the line AB but the solvent concentration would be less than y_1. The second stage of the extraction starts at C, the point $(x_1, 0)$, and after equilibrium is reattained gives x_2, y_2 as the appropriate concentrations.

As "batch" extraction this is familiar in the form of extraction of, *e.g.*, fatty acids with ether in organic chemistry, and of ferric chloride with ether in inorganic analysis. Batch extraction is a poor method for separating materials with similar D values. The ease of separation of two solutes is indicated by the magnitude of the "separation factor", *i.e.*, the ratio of the two D values. As the separation factor approaches unity, so the difficulty of separation increases. Separation even in more or less difficult cases, can, however, be accomplished by countercurrent liquid extraction where the effective number of stages is large. It is convenient to consider first the mass balance and the distribution diagram (Fig. 3B) for a batch extraction in which both phases initially contain solute, *i.e.*,

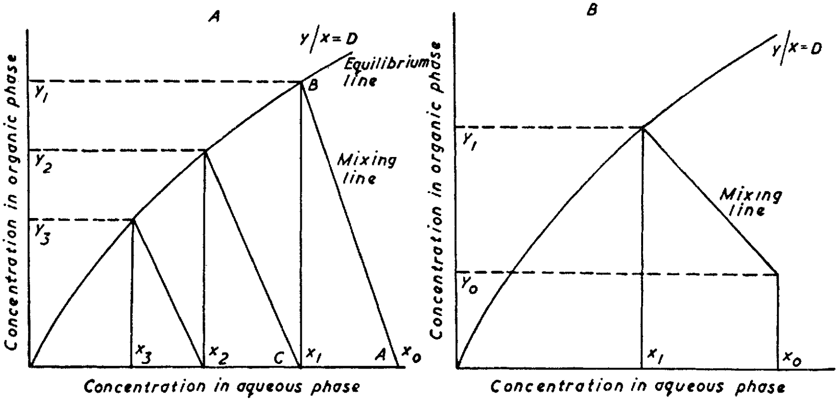

FIG. 3 *Distribution diagrams for batch extractions.*

$$(x_0 - x_1) = R(y_1 - y_0) \text{ and } y_1/x_1 = D_1 \quad \ldots\ldots \quad (33)$$

Fig. 4A shows the flow diagram for countercurrent extraction for a hypothetical three-stage process. Each stage can be regarded as a batch extraction whose products are the feeds to adjacent stages; this leads to the following mass balances:

$$\left.\begin{array}{ll} \text{Stage 1: } (x_0 - x_1) = R(y_1 - y_2) & \text{and } y_1/x_1 = D_1 \\ \text{Stage 2: } (x_1 - x_2) = R(y_2 - y_3) & \text{and } y_2/x_2 = D_2 \\ \text{Stage 3: } (x_2 - x_3) = R(y_3) & \text{and } y_3/x_3 = D_3 \end{array}\right\} \quad \ldots \quad (34)$$

These are shown in the form of a distribution diagram in Fig. 4B, whilst a simplification is shown in Fig. 4C.

This type of diagram (due to Varteressian and Fenske[28]) is based on the fact that in the rectangle representing stages in Fig. 4B the diagonals opposite the mixing lines all fall on a straight line of slope $1/R$; this line

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[28] Varteressian and Fenske, *Ind. Eng. Chem.*, 1936, **28**, 928, 1353.

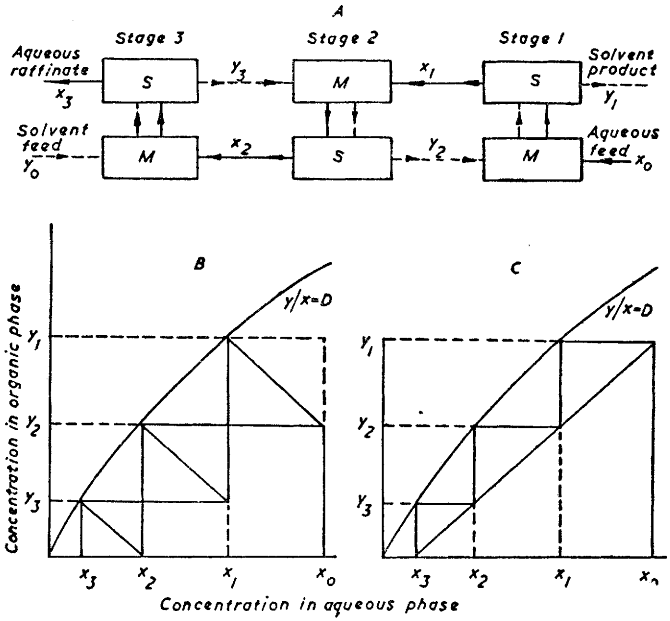

FIG. 4 *Flow diagram* (A), *distribution diagram* (B), and *Varteressian and Fenske diagram* (C) *for three-stage countercurrent system.* S = *Settler;* M = *Mixer.*

is the "operating line" and each stage is represented by a step between the operating and the equilibrium lines.

Ideally (*i.e.*, D = constant) the mass balances reduce to

$$\left.\begin{aligned}&\text{Stage 1: } (x_0 - x_1) = RD(x_1 - x_2)\\&\text{Stage 2: } (x_1 - x_2) = RD(x_2 - x_3)\\&\text{Stage 3: } (x_2 - x_3) = RD(x_3)\end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (35)$$

which combine to give the geometric progression

$$\frac{x_0 - x_1}{x_1 - x_2} = \frac{x_1 - x_2}{x_2 - x_3} = \frac{x_2 - x_3}{x_3} = RD \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (36)$$

whose summation in the general case for n stages is

$$x_0 = x_n \frac{(RD)^{n+1} - 1}{RD - 1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (37)$$

More efficient separations and purifications are obtained if the solvent product from such countercurrent extraction is "stripped" in further countercurrent stages. In this operation a solute-free aqueous phase washes part of the solute from the solvent together with the bulk of any impurities which may have been extracted with a low partition coefficient.

The aqueous product from this stripping operation is re-cycled with the aqueous feed solution to the extraction stages. Fig. 5A shows the flow arrangement for a countercurrent extraction system with three extraction

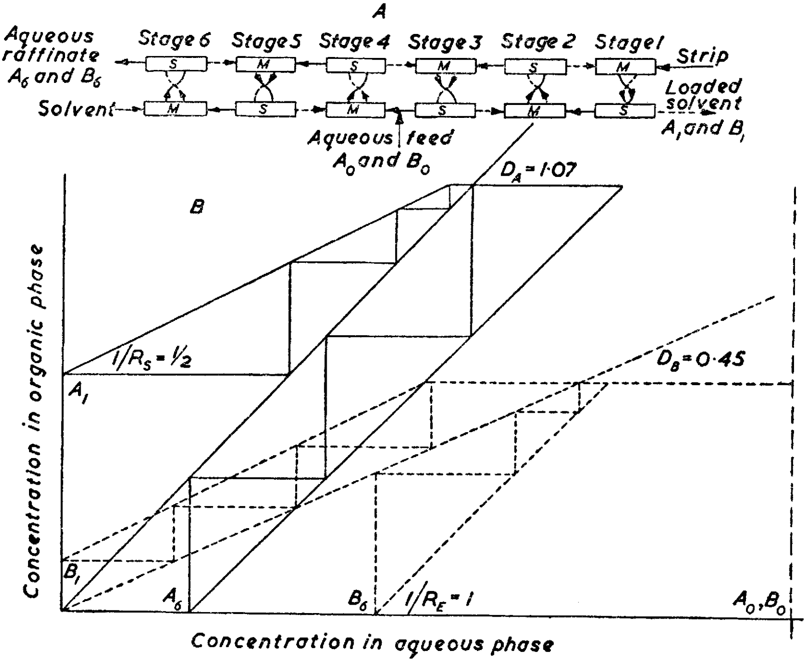

FIG. 5 *Flow diagram* (A) *and Varteressian and Fenske diagram* (B) *for a system having three strip and three extraction stages. Two solutes are considered. The relative flow rates are: strip* 1*; solvent,* 2*; aqueous feed,* 1.

and three stripping stages. The Varteressian and Fenske diagram (Fig. 5B) shows the stage-to-stage concentration changes for two solutes whose *D* values differ only slightly. The values of *D* chosen in the illustration approximate to those for praseodymium and neodymium nitrates in the nitric acid (13·8M)–tributyl phosphate system.[29] Fig. 5B shows that the use of six stages brings about a considerable separation between praseodymium and neodymium; since countercurrent extraction can readily be made a continuous process with numerous stages, the technique is obviously a powerful tool for difficult separations and for preparing high-purity materials either in small quantity in the laboratory, or in bulk industrially.

In most cases, complications in treatment are caused by the dependency of *D* on concentration and on the presence of other solutes in both phases (page 334).

(b) *Equipment*.—Continuous countercurrent solvent extraction is usually

[29] Hesford, Jackson, and McKay, *J. Inorg. Nucl. Chem.*, 1959, **9**, 279.

carried out either in a vertical column or in a mixer–settler cascade. The scale of operations can vary between a small analytical apparatus handling less than one ml. of liquids per minute up to large industrial plants processing 2000 l. or more per minute. A comprehensive review of equipment cannot be given here but a brief description of some simple columns and mixer–settlers is desirable.

(i) *Columns.* In columns, one phase is dispersed in, and is made to flow under gravity through, a continuous column of the other. The light phase is introduced at the bottom of the column and taken off at the top; the denser phase is admitted at the top and flows downwards. In order to improve solute transfer rates across the solvent–aqueous interface, and so to reduce the height of column equivalent to a theoretical stage (HETS), various packing systems and/or mechanical agitation are used.

(ii) *Mixer–settlers.* The many varieties of this type mostly fall into two classes: first, those in which the mixer lifts the mixed phases into a settler from which the separated phases can flow over weirs to the next mixers, and secondly, those in which the mixers perform virtually no lifting. In the first class, the position of the interface in the settler is controlled by the relative position of the weirs and is therefore independent of the neighbouring stages. This makes possible a very flexible unit; additionally, the contents of a settler can be sampled for analysis.

The other class of mixer–settler is used mostly for large-scale work but may also be used in the laboratory. They suffer on the small scale from instability in operation as a result of surface-tension effects interfering with inter-stage flows. For a fuller discussion of laboratory-scale mixer–settlers the review by Jamrack *et al.*[30] should be consulted; large-scale equipment has been reviewed by Pratt.[31]

(c) *Applications.*—Solvent extraction is of increasing importance in general extraction metallurgy and in other fields where difficult separations are to be made or high-purity products are required. It is used extensively in analysis[1] and as a laboratory technique in such fields as the study of lanthanide and actinide chemistry[29] and of complex formation as described in earlier sections.

Analytical aspects have been reviewed by Irving;[1] the review by Fletcher[32] of the potential uses of solvent extraction for purification in extraction metallurgy should be consulted for the broader aspects in that field.

(i) *Nuclear energy field.* Much work on solvent extraction has been initiated by the special needs of the atomic energy industries. It is frequently necessary to attain high levels of purity in materials in order to remove trace amounts of contaminants having undesirable nuclear

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[30] Jamrack, Logsdail, and Short, "*Progress in Nuclear Energy*," Series III, 1958, Vol. 2 (Process Chemistry), Pergamon Press, London, p. 332.

[31] Pratt, UNICPUAE, 1958, **8**, 520.

[32] Fletcher, "Extraction and Refining of the Rarer Metals," Institute of Mining and Metallurgy, 1957, London, p. 15.

properties, *e.g.*, nuclides with high capture cross sections for thermal neutrons.

The important nuclear fuels are the fissile isotopes uranium-233, uranium-235, and plutonium-239; ^{233}U and ^{239}Pu are obtained by neutron irradiation of the natural fertile materials ^{232}Th and ^{238}U.

Solvent-extraction procedures have been devised to separate these from irradiated fertile fuels in high states of purity (usually as their nitrates). Similar procedures may also be used to obtain other very pure materials for nuclear reactor use, *e.g.*, zirconium for the protection of bare uranium fuel or structural use.

(ii) *Uranium.* Naturally occurring uranium is the most important source of fissile and fertile materials; its separation from ores and subsequent purification have been the subject of much research in which solvent extraction studies have played a large part.

Uranium is usually extracted from solutions as an ion association nitrate complex by ethers (as solvate or oxonium salts) or by tributyl phosphate (as a solvate). An early British process[33] used batch extraction of molten uranyl nitrate hexahydrate by diethyl ether. Present processes[34] use continuous countercurrent extraction of uranyl nitrate from filtered acidic ore leach liquor into tributyl phosphate diluted with kerosene. The purified uranyl nitrate is washed back from the loaded solvent by water. In this system the uranyl nitrate partition coefficient decreases with increasing temperature; the wash-back section is therefore operated at a high temperature to obtain more efficient solute recovery. Processes based on tributyl phosphate are also used extensively in the U.S.A. and in France for uranium purification.

Complexing anions in the crude aqueous solution, *e.g.*, PO_4^{3-}, SO_4^{2-}, F^-, etc., reduce the partition coefficient of uranyl nitrate into most solvents including tributyl phosphate.[35] However, recently developed processes[36] for the extraction of uranium from sulphate, phosphate, and chloride liquors use liquid-ion exchange solvents of the type described on p. 335 and the quaternary ammonium anion-exchange solvents, for example, are sufficiently strong bases to be able to extract anionic uranyl carbonate from alkaline sodium uranyl carbonate solution. The values of the partition coefficients for uranium obtainable with these ion-exchange solvents can be as high as several thousand; it is thus possible to extract uranium efficiently from dilute solutions and to recover it in a more concentrated form.

(iii) *Thorium.* Thorium, being a fertile nuclear material, must be freed very thoroughly from rare-earth metals with high neutron cross sections and from uranium in order to avoid dilution of "bred" ^{233}U by the

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[33] Grainger, UNICPUAE, 1958, **8**, 149.

[34] Hamilton, *Nature*, 1959, **183**, 789.

[35] Quoted in ref. 36.

[36] Brown, Coleman, Crouse, Blake, and Ryan, UNICPUAE, 1958, **3**, 472; see also refs. 18 and 32.

^{238}U originally associated with the thorium. The values of the partition coefficients under one set of conditions for uranium and thorium nitrates into 40% tributyl phosphate in xylene are respectively 20 and 0·5, whereas they are 6 and 0·04 into 5% phosphate in xylene. Thus an initial extraction with the dilute solvent will remove the uranium and a second operation with the more concentrated solvent will recover the thorium. This principle forms the basis of a process[37] described by Audsley, and Table 3 shows the power of the solvent extraction method in effecting the necessary separations.

TABLE 3. *Weight of impurity per* 1 *kg. of contained thorium* (after Audsley[37]).

Feed solution		*Final product solution (overall Th recovery = 99·7%)*
CeO_2	830 g.	1·1 mg.
RE_2O_3*	780 g.	3·5 mg.
U	48 mg.	0·08 mg.

* RE = Rare earths

Residual phosphate (derived from the monazite) in the feed solution to the solvent extraction may be complexed by adding an equivalent amount of ferric nitrate[38] in order to prevent its interfering with extraction efficiency through the formation of inextractable thorium phosphate complexes.

Methods for the separation of uranium-233 from irradiated thorium[39] depend upon first extracting both uranium and thorium, leaving the bulk of the fission products in the aqueous phase; the thorium is then preferentially washed back. Some of these processes use tributyl phosphate with aluminium nitrate as salting-out agent in an acid-deficient aqueous phase. These conditions, together with saturation by thorium nitrate of the solvent in part of the system, *i.e.*, the value of ϵ (p. 333) is high, give good decontamination from rare-earth fission products and protactinium which otherwise tend to follow the thorium.

(iv) *Plutonium.* Plutonium is found in irradiated fuel elements in association with a large bulk of "unburned" uranium and with fission products of low bulk but high specific radioactivity. The approximate composition of natural uranium after an irradiation corresponding to an energy release of 1000 megawatt-days per ton is: U 99·8%, Pu 0·08%,

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[37] Audsley, Lind, and England, ref. 32, p. 351.

[38] Menzies, *J. Appl. Chem.*, 1959, 9, 249.

[39] Greskey, UNICPUAE, 1955, 9, 505; Bruce, Shank, Brooksbank, Parrott, and Sadowski, *ibid.*, 1958, **17**, 49; Buller, *ibid.*, 1955, 9, 464.

fission products 0·08%.[40] From this mixture it is required to separate the uranium and plutonium and to purify each of them from highly radioactive fission products. Many chemical processes for accomplishing this have been described, the most successful of which are based on solvent extraction.[41]

Older separation processes use ketonic or ethereal solvents like "butex" (diethylene glycol dibutyl ether), diethyl ether, isobutyl methyl ketone (hexone), and triglycol dichloride. These are oxonium-type extractants, and they accordingly extract solutes more efficiently under highly acid or salting-out conditions.

In a process as used at Windscale (U.K. Atomic Energy Authority), irradiated uranium is converted into a solution of uranyl, Pu(IV), and plutonyl and fission product nitrates in excess of free nitric acid (3M). Both uranyl and plutonium nitrates are extracted into "butex", leaving the bulk of the fission products in the aqueous raffinate. The solvent from this extractor is partially neutralised with aqueous ammonia and is treated with ferrous sulphamate to reduce the extractable PuO_2^{++} and Pu(IV) to the inextractable Pu(III). This behaviour reflects the greater tendency of the higher-valency states to form nitrate complexes.

The plutonium is re-extracted into an aqueous phase containing 8M-ammonium nitrate; the uranium remains in the solvent under the influence of the salting-out agent and is subsequently recovered in a third column by washing the organic phase with dilute nitric acid (0·05N). The plutonium and uranium solutions require further purification by extraction and wash-back cycles.

Tributyl phosphate is used in most of the more recent plutonium separation processes[41] to carry out the primary separation of plutonium, uranium, and fission products. This solvent acts by solvation and highly acid conditions are less necessary than in the case of ethereal or ketonic solvents. Neptunium and americium may also be separated pure from irradiated fuel-element solutions by solvent-extraction.[42]

(v) *Niobium and tantalum.* In Nature, these two metals are always associated, and separation from each other by classical methods is very difficult.[43] Solvent extraction, however, provides a satisfactory process,[44] either a hydrochloric acid aqueous phase and methyldioctylamine in xylene[45] being used as the extractant, or fluoride solutions (containing free hydrofluoric acid) with either ketones[46] or tributyl phosphate[47] as extractants. In fluoride extractions tantalum has the higher partition coefficient; either it is preferentially extracted, leaving niobium in the aqueous phase,

[40] Howells, Hughes, Mackey, and Saddington, UNICPUAE, 1958, **17**, 3.
[41] See UNICPUAE, 1955, **8**, and 1958, **17**, for a selection of papers.
[42] McKay, UNICPUAE, 1955, **9**, 314.
[43] Miller, *Ind. Chemist*, 1959, 175.
[44] Foos and Wilhelm, 1954, USAEC Unclassified Document ISC 694.
[45] Ledlicotte and Moore, *J. Amer. Chem. Soc.*, 1952, **74**, 1618.
[46] Werning, Highie, Grace, Speece, and Gilbert, *Ind. Eng. Chem.*, 1954, **46**, 644.
[47] Morris. Wain, and Fletcher, *Bull. Inst. Min. Met.*, 1956, No. 497, 487.

or both metals can be extracted, leaving other impurities in the aqueous raffinate; the niobium is then selectively washed back from the solvent by suitably adjusting the composition of the wash-back solution.

(vi) *Zirconium and hafnium.* Zirconium occurs in Nature associated with hafnium, a powerful neutron absorber. For use in atomic energy processes efficient removal of hafnium is essential. Various methods are available; solvent extraction is used on the large scale in the U.S.A.,[48] France,[49] and Britain.[50] In the American process, isobutyl methyl ketone preferentially extracts hafnium thiocyanate from a hydrochloric acid solution. In the French and British processes, tributyl phosphate preferentially extracts zirconium from a nitrate solution, leaving the hafnium and other impurities in the aqueous raffinate. The French use an aliphatic diluent for the phosphate, and the ready formation of an organic third phase owing to the limited solubility of the zirconium solvate in the diluent limits the zirconium concentration in the feed solution to about 30 g./l.; if xylene is used as a diluent the concentration can be increased to about 80 g./l.[50]

(vii) *Rare-earth metals.* The separation of the rare-earth metals is a difficult problem which has recently been eased by the use of ion-exchange techniques, but the amounts of material handled are small compared with the size of equipment used. Solvent extraction offers a possible method; a partial separation has been reported[51] by extraction with tributyl phosphates of rare-earth nitrates in aqueous nitric acid. Several papers[52] have reported the behaviour of the rare earths in tributyl phosphate–nitrate systems. Useful separation factors have been obtained and some interesting differences between rare earths of odd and even atomic numbers have been discovered as a result of this work.

(viii) *Miscellaneous separations.* Many other metals have been the subject of solvent-extraction studies for general chemical purposes, as well as for their separation or purification and even for isotope separation. Table 4 lists a few metals for which solvent-extraction studies are reported.

Some interesting processes have been reported for the recovery of acids from aqueous solutions. Moore reports a general study of the use of the anion-exchange solvents (long-chain amines) for the extraction of various acids, including hydrofluoric, nitric, sulphuric, and phosphoric, as well as various complex acids containing the metals Po, Pu, Zr, and Pa.[53] The extraction of phosphoric acid into n-butyl or isopentyl alcohols has been operated on a pilot-plant scale for the production of phosphoric acid from phosphate rock treated with hydrochloric acid.[54]

[48] Shelton, Dilling, and McClain, UNICPUAE, 1955, **8**, 505.
[49] Hure and Saint James, *ibid.*, p. 551.
[50] Hudswell and Hutcheon, *ibid.*, p. 563.
[51] Foos and Wilhelm, USAEC Unclassified Report ISC 695.
[52] Hesford, Jackson, and McKay, *J. Inorg. Nucl. Chem.*, 1959, **9**, 279.
[53] Moore, *Analyt. Chem.*, 1957, **29**, 1660.
[54] Daniel, Blumberg, and Alon, *Brit. Chem. Engineer*, April, 1959, 223.

TABLE 4. *Miscellaneous extraction studies* (those discussed in the text are excluded).

Metal	*Aqueous phase*	*Solvent phase*	*Purpose of investigation*	*Ref.*
Polonium	HCl or H_2SO_4	20% TBP	Separation from Bi, Ra*E*, Radio-Pb	55
Actinium	HCl; controlled pH	TTA in benzene	Separation from Ra, Th, Po, Pb, Bi	56
Gallium	6M-HCl	Diethyl ether	Separation from Ge process wastes	57
Scandium	Thiocyanate	Ether	Separations from rare earths	57
Thallium	HCl or other chloride	Ethers	General chemical study	58
Lithium	Thiocyanate	40% TBP	Attempted isotope separation	59
Strontium, Cæsium	Nitrate; controlled pH	Ion-exchange solvents	Separation	60
Cobalt	Thiocyanate and perchlorate	Ketones and alcohols	General chemical study	61
Indium	HCl and chlorides	Various	General chemical study	62
Iron	$BeSO_4$ and NH_4CNS	10% TBP	Removal of Fe from Be	63

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[55] Bagnall, "Chemistry of the Rare Radioelements," Butterworths Scientific Publications, London, 1957.

[56] Farr, Giorgi, Bowman, and Money, 1953, USAEC Unclassified Report LA 1545.

[57] Powell, reported in Ref. 32.

[58] Foos and Wilhelm, USAEC Unclassified Report ISC 694.

[59] Dury, USAEC Unclassified Report Y 785.

[60] Anon., "*Reactor Fuel Processing*," 1959, **2** (1), 13.

[61] Brubaker and Johnson, *J. Inorg. Nucl. Chem.*, 1959, **9**, 184.

[62] Diamond, *J. Aner. Chem. Soc.*, 1959, **63**, 659.

[63] Byersmith, Pomelee, and Birmbaum, USAEC Unclassified Report NYO 1116.

5. Molten metal systems

Liquid–liquid extraction using immiscible or partially miscible metal is still very much in its infancy although the origins of one application (the Parkes process for the desilverisation of lead) go back more than 100 years. Even more so than for immiscible aqueous–organic systems, the recent progress in molten–metal extraction systems is derived from the impact of nuclear energy. Briefly, this arises from the consideration that metallic nuclear fuel may conceivably be reprocessed in the metallic state by processes which are inherently cheaper and simpler than those which involve chemical destruction of the metal followed by purification and reconversion into metal, albeit the processes would be less efficient.

(a) *Principles.*—Little fundamental work has been done on liquid-metal extraction systems, but it is clear that the basic extraction law is similar to that of aqueous–organic systems and equation (1) applies ideally. For the system silver distributed between immiscible molten lead and zinc phases (*i.e.*, the basis of the Parkes process), Mellor[64] quotes results showing that the partition coefficient for silver is about 300 (in favour of the zinc phase) and is reasonably constant for all silver concentrations up to 6% in lead.

To describe systems exactly, appropriate activities should be used, but data are scanty and there is scope for much investigation. Just as aqueous–organic systems have been used to study complex formation, ionic effects, solvation, etc., so liquid–liquid metal systems may be used to study intermetallic compound formation, "salting-out" (the effect of adding a second metallic solute), and heats of solutions, etc.

(b) *Theoretical Predictions.*—Within limits one can forecast whether certain pairs of molten metals are miscible, and hence the qualitative behaviour of systems containing three liquid metals. MacKenzie[65] used an expression due to Hildebrand and Scott[8] to predict miscibilities and to deduce that in a system of uranium, plutonium, and silver, the plutonium should be extractable into the silver phase (which is immiscible with the uranium phase). Direct prediction may be made from phase diagrams when available.

Hildebrand and Scott[8] deduced as a criterion for the complete miscibility of two molten metals the expression

$$\tfrac{1}{2}(V_1 + V_2)(\delta_1 - \delta_2)^2 < 2\boldsymbol{R}T \quad . \; . \; . \; . \; . \; . \; . \quad (38)$$

where V_1 and V_2 are the atomic volumes of metals 1 and 2, δ_1 and δ_2 are their solubility parameters, $\boldsymbol{R}$ is the gas constant, and T is the absolute temperature. The solubility parameter $\delta = (\Delta E_v/V)^{\frac{1}{2}}$, where ΔE_v is the energy of vaporisation of the metal.

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[64] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 313, Longmans, Green & Co., 1952.

[65] MacKenzie, *Canad. J. Chem.*, **34**, 749, 1956.

The same criterion has been used to predict whether plutonium and some metallic fission products might be extracted from uranium by molten calcium, the last two metals forming an immiscible pair. The determined partition coefficients of a number of fission-product elements showed that qualitative predictions based on miscibility considerations were largely substantiated. In addition, in accordance with equation (1), the distribution coefficient for plutonium ($D_{\text{Pu}} = 0{\cdot}0073$) was reasonably constant over the concentration range 0·01% to 20·4% of plutonium in uranium, and the one for cerium ($D_{\text{Ce}} = 9{\cdot}4$) did not vary significantly over the range 0·04% to 0·46% of cerium in uranium.[66]

(c) *Applications of Liquid–Liquid Metal Extraction.*—So far, the main developments in this field have been made with the aim of removing plutonium and/or fission products from irradiated uranium, or in some cases of removing uranium-233 from irradiated thorium. Silver,[65] rare-earth metals,[67] and magnesium[68] have been used to extract plutonium from molten uranium in addition to the use of calcium for removing some fission products. For magnesium, the applicability of equation (1) has been demonstrated. Experiments involving both magnesium and uranium would normally be carried out in pressurised systems since magnesium has a vapour pressure of > 760 mm. at the m.p. of uranium (1135°C). Feder[68] overcame this difficulty by alloying the uranium phase with 5% of chromium and thereby lowering its m.p. to 950°C. In a similar manner a molten uranium–chromium eutectic phase may be used to extract protactinium from molten magnesium–thorium eutectic,[69] and calcium–magnesium eutectic may be used to extract certain metallic fission products from molten plutonium–cobalt and plutonium–iron alloys.[70]

(d) *Fundamental Studies.*—(i) *Analogy of salting-out or complex formation.* The distribution of plutonium in the uranium–silver system is dependent on the plutonium concentration;[65] it is known from vapour-pressure measurements[71] that plutonium forms ideal (dilute) solutions in uranium. Consequently, in the uranium–silver system, the variation of D_{Pu} with plutonium concentration must reflect on some non-ideal behaviour of plutonium in the silver phase. Insufficient data exist as yet to enable this effect to be assessed quantitatively.

The addition of small amounts of gold to the uranium–silver system has an interesting effect on plutonium distribution (Fig. 6). Whilst the distribution of gold itself is virtually independent of concentration, the extraction of plutonium into the silver phase is increased by a factor of over 2 as the gold concentration increases from zero to about 3·5 wt. % in the

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[66] Martin, Jenkins, and Keen, UNICPUAE, 1958, **17**, 352.
[67] Voigt, *ibid.*, 1955, **9**, 591.
[68] Feder, Greenberg, Nathans, and Nutthall, Paper presented at Amer. Chem. Soc. Meeting, April 7—12th 8957.
[69] Chiotti and Voigt UNICPUAE, 1958, **17**, 368.
[70] Anon., "*Reactor Fuel Processing*," 1958, **1** (2),
[71] McKenzie, *Canad. J. Chem.*, 1956, **34**, 515.

uranium; beyond this point, the plutonium extraction suddenly decreases. Qualitatively, and terms being used analogous to those found in the sections on aqueous–organic systems, this behaviour may be described as initial "salting-out", followed by "competition" of gold atoms with plutonium atoms for interaction with silver atoms as the gold concentration increases. It appears that the gold atoms "compete" successfully, thereby indicating the greater stability of gold–silver "complexes" than of those of plutonium–silver.

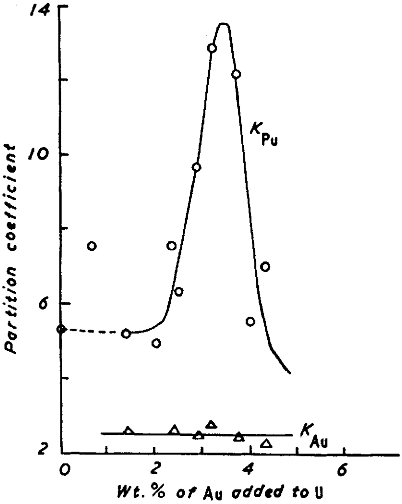

FIG. 6 *Variation of* K_{Pu} *in silver–uranium with addition of gold (reprinted with permission from McKenzie,* Canad. J. Chem., 1956, **34**, 749).

(ii) *Determination of thermodynamic properties.* By measuring the variation with temperature of D_{Pu} in the system uranium–silver, the limiting heat of solution of plutonium in silver has been determined. The distribution data[65] were found to fit the equation $\log D_{Pu} = 2{\cdot}21 - 2{\cdot}74 \times 10^3/T$. From the slope of this, a value of ΔH (= 12·5 kcal.) is obtained, where ΔH represents the heat of transfer of one g.-atom of plutonium from liquid uranium to liquid silver. On the basis of the ideal behaviour of plutonium in uranium, and recognising that the experiments were carried out at low plutonium concentrations (about 0·05 atom % in silver), this value of ΔH may be equated with $\bar{L}_{0,Pu}$, the limiting partial molal heat content, relative to liquid plutonium, of plutonium in liquid silver. Similarly, the limiting heat of solution of plutonium in some rare-earth metals has been estimated[72] by determining the variation of its distribution with temperature in the systems uranium–cerium, –neodymium, and –mischmetall.

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[72] McKenzie, *Canad. J. Chem.*, 1956, **34**, 1176.