

## SOLVENT EXTRACTION BY SELECTIVE ION SOLVATION

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*Abstract* - Extraction reactions are identified, in which the main step is the replacement of the water that hydrates the ions in the aqueous phase by a solvation shell provided by the water-immiscible solvent. The change in solvation is measured by the standard molar Gibbs free energy of transfer of the ion, which is related in a definite manner to certain properties of the solvent and of the ion and to the composition of the solvent, if it contains much water. Enthalpy or entropy changes may predominately control the transfer. These concepts are illustrated by the extraction of the halide anions into substituted phenols, of lithium, magnesium, and aluminium halides into (hydrated) 1-hexanol, and of dioxouranium (VI) and thorium or plutonium (IV) nitrates into neutral phosphoryl-group-containing solvents.

### INTRODUCTION

When ions are extracted from an aqueous solution into an immiscible organic solvent, the ions are generally removed from their immediate aqueous environment and provided by a new environment. The Gibbs free energy of hydration of the ions must therefore be invested first, to be regained by the Gibbs free energy of the new interactions that the ions undergo. The standard molar Gibbs free energy of hydration,  $\Delta G_i^\circ \text{ hyd}$ , may thus be considered as a barrier which must be surmounted for extraction to proceed. Table 1 presents the (absolute values of)  $\Delta G_i^\circ \text{ hyd}$  of some ions (Ref. 1 & 2).

TABLE 1. Absolute standard molar Gibbs free energies of hydration of some ions (in  $\text{kJ mol}^{-1}$  at 298.15 K)

Cation	$\Delta G_i^\circ \text{ hyd}$	Anion	$\Delta G_i^\circ \text{ hyd}$
$\text{H}^+$	-1056	$\text{F}^-$	-460
$\text{Li}^+$	-476	$\text{Cl}^-$	-338
$\text{Na}^+$	-377	$\text{Br}^-$	-324
$\text{K}^+$	-305	$\text{I}^-$	-309
$\text{Mg}^{2+}$	-1828	$\text{NO}_3^-$	-306
$\text{Ca}^{2+}$	-1525	$\text{SO}_4^{2-}$	-1090
$\text{UO}_2^{2+}$	-1329		
$\text{Al}^{3+}$	-4537		
$\text{Th}^{4+}$	-5823		

Several interactions may return the invested  $\Delta G_i^\circ \text{ hyd}$ , including ion association [e.g.,  $\text{UO}_2^{2+} + 2\text{NO}_3^-$  to give the species extracted with tri-*n*-butylphosphate (TBP),  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ ], the exchange of ions with others already in the organic phase (see below for examples), and solvation. This paper deals specifically with ions extractable selectively by solvation, but the other interactions, too, are often involved in these cases. In other cases solvation may

play only a minor role or no role at all. For example, when a metal ion  $M^{m+}$  is extracted with a chelating agent HX dissolved in carbon tetrachloride, the essential steps are the dehydration of  $M^{m+}$ , the displacement of  $H^+$  from HX by  $M^{m+}$ , which forms the chelate  $MX_m$ , and the hydration of the  $H^+$  ions returned to the aqueous phase. Another such example is the extraction of an anion  $X^-$  with the liquid anion exchanger (long-chain-substituted ammonium salt) RY dissolved in benzene. The essential steps here are the dehydration of  $X^-$ , the replacement of  $Y^-$  in the ion-pair with  $R^+$  by  $X^-$ , and the hydration of  $Y^-$  returned to the aqueous phase. Any solvation provided by carbon tetrachloride or benzene is generally only a second order effect (a so-called "inert solvent effect") on the extraction.

The change in the Gibbs free energy of an extraction reaction depends on the concentration not only via the concentration terms of the chemical potentials but also via the excess chemical potentials, which arise from interactions that are not explicitly shown in the extraction reaction proper. These include ion-ion interactions (expressed by activity coefficients) and any side reactions (ion association in the aqueous phase, adduct formation in the organic phase, etc.) that may occur in the system. In this paper attention is focused on the standard state of infinite dilution, where the excess chemical potentials vanish, and all side reactions are disregarded. The cations and anions act independently in this state, and the total effect is additive in the individual ionic contributions.

#### GIBBS FREE ENERGIES OF TRANSFER

The most direct measure of the energetics of solvation of ions is their standard molar Gibbs free energy of solvation, i.e., of transfer from the gas phase to the solvent. This quantity is generally unknown, and in the present context of extraction reactions is advantageously replaced by the standard molar Gibbs free energy of transfer of the ion X from water (W) to the solvent (S):

$$\Delta G_t^\circ(X, W \rightarrow S) = \mu_X^\circ(\text{in S}) - \mu_X^\circ(\text{in W}) = RT \ln {}_W Y_S(\text{of X}) \quad (1)$$

where  $\mu^\circ$  is the standard (infinite dilution) chemical potential and  ${}_W Y_S$  is the transfer activity coefficient. It has been shown by Ben-Naim (3) that this quantity expresses the difference in the interactions (work of coupling) of a solute particle with the two solvents, S and W, provided that the number density or molar ( $\text{mol dm}^{-3}$ ) concentration scale is used.

An extrathermodynamic assumption is necessary for obtaining  $\Delta G_t^\circ(X, W \rightarrow S)$  of individual ions from experimental data on electrolytes. The assumption that is most readily defensible (Ref. 4 & 5) is the tetraphenylarsonium tetraphenylborate one, i.e., that in general  $\Delta G_t^\circ[(C_6H_5)_4As^+, W \rightarrow S] = \Delta G_t^\circ[B(C_6H_5)_4^-, W \rightarrow S]$  for all solvents S. Values of  $\Delta G_t^\circ(X, W \rightarrow S)$  obtained on this basis have been compiled and critically evaluated by Marcus (4, 5 & 6).

Most solvents for which  $\Delta G_t^\circ$  data are available are water-miscible (exceptions are nitromethane, nitrobenzene, and the dichloroethane isomers). However the systematics of the dependence of  $\Delta G_t^\circ$  on the properties of these solvents (see below) permit estimates of this quantity also for the water-immiscible solvents of interest for ion extraction by solvation. These solvents are classified in Table 2.

TABLE 2. Classification of water-immiscible solvating solvents

Typical electron-pair donors (cation solvators)	Typical electron-pair acceptors (anion solvators)
<i>aprotic:</i>	
tertiary amines (e.g., quinoline)	nitro-compounds (e.g. nitrobenzene)
phosphine oxides (e.g., TOPO <sup>a</sup> )	nitriles (e.g., benzonitrile)
phosphates (e.g., TBP <sup>b</sup> )	sulfoxides (e.g. dioctylsulfoxide),
ethers (e.g., diethyl ether), etc.	etc.
<i>protic:</i>	
alcohols (e.g., 1-hexanol)	(hydrogen-bond donors) alcohols (e.g., 1-hexanol)
secondary amines (e.g., dioctylamine), etc.	phenols (e.g., <i>p</i> -nonylphenol) carboxylic acids (e.g. hexanoic acid) etc.
<sup>a</sup> Tri-n-octyl phosphine oxide;	<sup>b</sup> tri-n-butyl phosphate.

In a multiple regression statistical analysis by Glikberg and Marcus (6), in which the correlation of  $\Delta G_t^\circ$  data with many solvent properties was tested, significant correlation was found with the following set of properties. 1) The electron-pair acceptance index, as measured by the  $E_T$  of Dimroth and Reichardt (7). 2) The electron-pair donation index, as measured by the donor number  $DN$  of Gutmann (8). 3) The cooperative polarity, as measured by the reciprocal of the dielectric constant,  $1/\epsilon$ . 4) The work required for cavity formation, as measured by the cohesive energy density, i.e., the square of the solubility parameter,  $\delta^2$ . The same analysis (Ref. 6) also correlated  $\Delta G_t^\circ$  with the following set of properties of the ions, selected again from a much larger list on statistical grounds. 1) The charge, in the algebraic sense,  $z$ . 2) The size, as measured by the Pauling crystal radius or the thermochemical radius,  $r$ . 3) The capability of covalent bonding, as measured by the softness parameter  $\sigma$  of Marcus (9). The expression relating  $\Delta G_t^\circ$  to the properties of the solvents and of the ions is

$$\Delta G_t^\circ(X, W \rightarrow S) = \sum_i \sum_j A_j [P_i(X)] [P_j(S) - P_j(W)] \quad (2)$$

where  $P_j$  is the  $j$ -th property of the solvent or water, and the  $A_j$  are functions (for each of these properties) of the properties of the ions, as follows:

$$\begin{aligned} A(E_T) &= 0.105[z/(r+\Delta)]; \quad A(DN) = -0.0071 [z/(r+\Delta)^2] \exp(z-1); \\ A(\epsilon^{-1}) &= 226[z^2/(r+\Delta)] - 28.3 [z^2/(r+\Delta)^2]; \quad A(\delta^2) = -2.45 \times 10^{-4} [z/(r+\Delta)^2] + \\ &+ 0.0025\sigma; \quad \Delta = 0.06 \exp(z-1) \quad (r \text{ and } \Delta \text{ in nm, } E_T \text{ and } DN \text{ in kJ mol}^{-1}, \\ &\delta^2 \text{ in J cm}^{-3}, \text{ producing } \Delta G_t^\circ \text{ in kJ mol}^{-1}) \end{aligned} \quad (3)$$

Since the quantities  $E_T$ ,  $DN$ ,  $\epsilon^{-1}$ , and  $\delta^2$ , and  $z$ ,  $r$ , and  $\sigma$  are known or can be estimated for many more solvents and ions (13 and 17, respectively) than form the data-base for the correlation, equations (2) and (3) can be used for the prediction of yet unknown  $\Delta G_t^\circ$  values.

For the transfer of ions into mixed solvents, especially mixed aqueous-organic solvents, the quasi-lattice quasi-chemical theory (Ref. 10 & 11) has recently been shown by Marcus (4 & 12) to apply. The resulting expression is

$$\begin{aligned} \Delta G_t^\circ(X, W \rightarrow W + S) &= \phi \Delta G_t^\circ(X, W \rightarrow S) - \Delta G_{W,S}^E(\phi) \\ &- 4\phi(1-\phi)ZRT \ln \cosh[\Delta G_t^\circ(X, W \rightarrow S)/2ZRT] \end{aligned} \quad (4)$$

where  $\phi$  is the volume fraction of  $S$  in the mixed solvent,  $\Delta G_{W,S}^E(\phi)$  is the excess molar Gibbs free energy of mixing of water,  $W$ , with the solvent  $S$  of the volume fraction  $\phi$ .  $Z$  is the total number of water and solvent molecules surrounding the ion in the first coordination shell. This number is a free parameter (possibly a function of  $\phi$ ), but has been found to be  $5 \pm 2$  for many systems, and not to affect the results strongly, even if it varies with the composition.

#### ENTHALPY OR ENTROPY CONTROL

When  $\Delta G_t^\circ$  for the transfer of an ion into a water-immiscible organic solvent or a mixed aqueous-organic solvent is known, the standard Gibbs free energy change for the extraction process  $\Delta G_{\text{extr}}^\circ$  can be estimated, provided the solvation of the ions is the predominant energetic effect. However, in order to obtain more insight into the energetics of the reaction, and particularly in order to see what steps are the major contributors - so that they may be optimized by a proper choice of the variables - it is necessary to ascertain the enthalpic and entropic components of the Gibbs free energy change. If these are known, questions such as: how large is the distribution ratio  $D$ , how does  $D$  depend on the temperature, how can the system be made more selective, how does  $D$  depend on the solvent/diluent, etc., can be answered. However, no statistical evaluation has so far been performed on the available  $\Delta H_t^\circ$  and  $\Delta S_t^\circ$  data (which are less abundant than  $\Delta G_t^\circ$  data) comparable to that sketched above, which relates  $\Delta G_t^\circ$  to the properties of the solvents and of the ions.

In view of the lack of general predictive expressions for  $\Delta H_t^\circ$  and  $\Delta S_t^\circ$ , they must be obtained from the experimental data for suitable extraction reactions. These data are the calorimetrically obtained  $\Delta H_{\text{extr}}^\circ$ , with the necessary corrections for heats of dilution, of mixing, etc., applied, and the distribution equilibrium constants  $K_{\text{extr}} \approx K_t$ , leading to  $\Delta G_{\text{extr}}^\circ = -RT \ln K_{\text{extr}}$  and to  $T\Delta S_{\text{extr}}^\circ = \Delta H_{\text{extr}}^\circ - \Delta G_{\text{extr}}^\circ$ . Less preferred for the estimation of  $\Delta H_{\text{extr}}^\circ$  are values of  $RT^2 d \ln K_{\text{extr}}/dT$ , since although the equilibrium quotient  $Q_{\text{extr}}$ , often used in lieu of  $K_{\text{extr}}$ , gives an acceptable approximation of  $\Delta G_{\text{extr}}^\circ$ , its temperature dependence is generally too different from that of  $K_{\text{extr}}$  to permit a reliable evaluation of

$\Delta H_{\text{extr}}^{\circ}$ . Whatever their source, however, the extraction reactions dominated by dehydration and resolution of ions,  $\Delta H_{\text{extr}}^{\circ}$  and  $\Delta S_{\text{extr}}^{\circ}$  will for the present serve instead of  $\Delta H_{\text{t}}^{\circ}$  and  $\Delta S_{\text{t}}^{\circ}$ .

The enthalpic and entropic components of the standard Gibbs free energy change of an extraction reaction are generally of unequal importance. One or the other may be mainly responsible for the success or failure of the extraction reaction. Thus if

$$|\Delta H_{\text{extr}}^{\circ}| > |T\Delta S_{\text{extr}}^{\circ}| \quad \text{enthalpy control} \quad (5a)$$

and if

$$|T\Delta S_{\text{extr}}^{\circ}| > |\Delta H_{\text{extr}}^{\circ}| \quad \text{entropy control} \quad (5b)$$

of the reaction occur. The "control" expressed in eq. (5) may be favorable for the extraction, but it may also constitute the barrier which must be surmounted for effective extraction to occur (Ref. 13).

#### EXAMPLE 1. EXTRACTION OF THE HALIDE ANIONS WITH PHENOLS

Anions are generally extracted by liquid anion exchangers, and then solvation plays only a very minor role. It has been found, however, that they can be efficiently and selectively extracted with the solvating solvents, provided suitable large cations are present (Ref. 14) or that small cations are taken care of by other solvating agents (Ref. 15). The latter case is discussed here in detail: the potassium halides are extracted from their aqueous solutions by a mixture of dibenzo-18-crown-6 and *m*-cresol. An ion pair is formed in the organic phase, the potassium cation being located in the center of the plane of the crown ether, being solvated by it. The halide anion is in contact with the cation in a line perpendicular to this plane, and is solvated in turn by an average of two molecules of the *m*-cresol on the far side from the cation. The selectivity of the extraction of the halide anions can be expressed by means of the extraction equilibrium quotients given by Asher and Marcus (15):

$$F^{-}, Q_{\text{extr}} = 915; \quad Cl^{-}, Q_{\text{extr}} = 223; \quad Br^{-}, Q_{\text{extr}} = 246; \quad I^{-}, Q_{\text{extr}} = 376$$

(the units of  $Q_{\text{extr}}$  are  $\text{mol}^2 \text{dm}^{-6}$ ). The change in  $Q_{\text{extr}}$  (and in the corresponding  $\Delta G_{\text{extr}}^{\circ}$ ) is not monotonous with  $\Delta G_{\text{hyd}}^{\circ}$ , as should have been expected. The strong solvation of fluoride ions by the substituted phenol (by hydrogen bond formation) overcompensates the strong hydration of this anion, and makes it the most, rather than the least, extractable of halides. For the larger halides hydration has the upper hand over the solvation, and the normal order prevails.

This explanation is confirmed by independent data, as far as they are available: by the  $\Delta G_{\text{t}}^{\circ}$  (halides,  $\text{H}_2\text{O} \rightarrow \text{CH}_2\text{Cl}_2$ ), obtained from eq. (2) and (3), the solvation of the halides in  $\text{CH}_2\text{Cl}_2$  solution with phenol (Ref. 16), and the ion pairing of the phenol-solvated halides with potassium ions in  $\text{CH}_2\text{Cl}_2$  solvent (by calculation from the Bjerrum equation). The same pattern of the final  $\Delta G^{\circ}$  values is obtained as in the extraction, see Fig. 1.

No enthalpy data are available for this system, so that further analysis of this extraction system cannot be made.

#### EXAMPLE 2. EXTRACTION OF LITHIUM, MAGNESIUM AND ALUMINIUM CHLORIDES WITH 1-HEXANOL

Extraction from aqueous solutions into 1-hexanol is characterized by the fact that the organic phase contains a very appreciable amount of water (4.55 mol/kg 1-hexanol, mole fraction 0.313, at 298.15 K). The results from this fact are discussed further below. Lithium, magnesium and aluminium chlorides have been extracted from their aqueous solutions into 1-hexanol. The distribution data of Nakashima and Marcus (17) have been analyzed in terms of the equilibrium constants  $K_{\text{extr}}$ , leading to  $\Delta G_{\text{extr}}^{\circ}$  values, see Table 3.

It is seen that the  $\Delta G_{\text{extr}}^{\circ}$  are positive for all three salts, i.e., that extraction is not favored, but that lithium chloride is the more readily extractable salt (at low concentrations). This is also predicted from a consideration of the energy that has to be invested in the dehydration of the ions, when they are removed from the aqueous phase,  $\Sigma \Delta G_{\text{hyd}}^{\circ}$ . However, the  $\Delta G_{\text{extr}}^{\circ}$  values bear no quantitative relationship to the  $\Sigma \Delta G_{\text{hyd}}^{\circ}$  values. This can be explained by assuming that the cations transfer together with their hydration shells, i.e.,  $\Delta G_{\text{t}}^{\circ} (M^{z+}, W \rightarrow 1\text{-hexanol}) = 0$ , and that only the chloride anions are dehydrated, and solvated by hydrogen bonding to 1-hexanol. Indeed  $\Delta G_{\text{t}}^{\circ} (Cl^{-}, W \rightarrow 1\text{-hexanol})$  accounts nearly quantitatively for  $\Delta G_{\text{extr}}^{\circ}$ , as seen in Table 3.

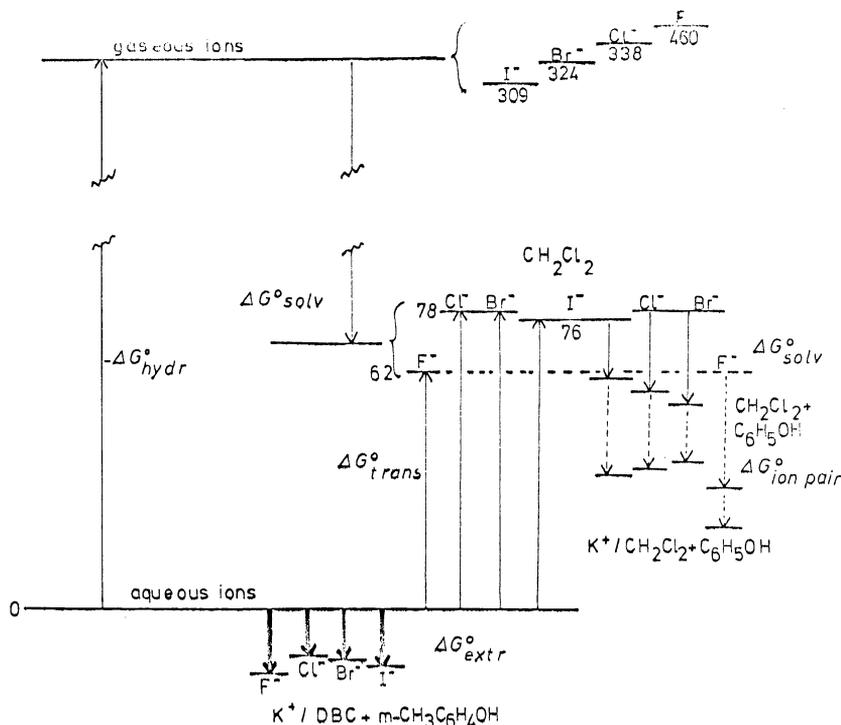


Fig. 1. Schematics of the  $\Delta G^\circ$  for the extraction of the halides with  $K^+$ /dibenzo-18-crown-6/*m*-cresol, and for their dehydration, solvation by  $CH_2Cl_2$ , by  $C_6H_5OH$  in  $CH_2Cl_2$ , and their ion-pairing in this mixture with  $K^+$ .

TABLE 3. Gibbs free energies (in  $\text{kJ mol}^{-1}$ ) for the extraction of chloride salts into 1-hexanol at 298.15 K

Salt	$\Sigma \Delta G^\circ_{\text{hyd}}$ $M^{+i} + i \text{Cl}^-$	$i \Delta G^\circ_t(\text{Cl}^-)$ $i \text{Cl}^-$	$\Delta G^\circ_{\text{extr}}$ $M^{+i} + i \text{Cl}^-$	Difference
$\text{LiCl}$	-814	+32	-30	-2
$\text{MgCl}_2$	-2504	+64	+65	+1
$\text{AlCl}_3$	-5551	+96	+109	+13

It must be realized, of course, that only the near hydration of the cations is exactly compensated by the water available in the organic phase (or transferred with the cations), since in 1-hexanol the water does not have the tetrahedral structure it has in bulk water, and is also bound to some extent by the alcohol. This fact may account for the small differences remaining between  $\Delta G^\circ_{\text{extr}}$  and  $i \Delta G^\circ_t(\text{Cl}^-)$ , especially in the case of aluminium, which has in aqueous solutions a considerable amount of secondary hydration.

The case of the analogous extractions of lithium bromide into 2-ethoxyethanol has been studied in greater detail (Ref. 13). It has been found that the extraction reaction is entropy-controlled, in the sense of eq. (5), and, since  $\Delta G^\circ_{\text{extr}}$  is positive, it is  $\Delta S^\circ_{\text{extr}}$  that provides the main barrier to the extraction. The schematics of the entropy changes involved are shown in Fig. 2.

One of the major contributions to the entropy barrier to the extraction arises from the structure-breaking effect of bromide ions in the aqueous phase. This barrier practically vanishes when the transfer occurs between saturated solutions rather than between solutions

at infinite dilution, because in the saturated solution of lithium bromide in water there remains essentially no tetrahedral water structure to be broken.

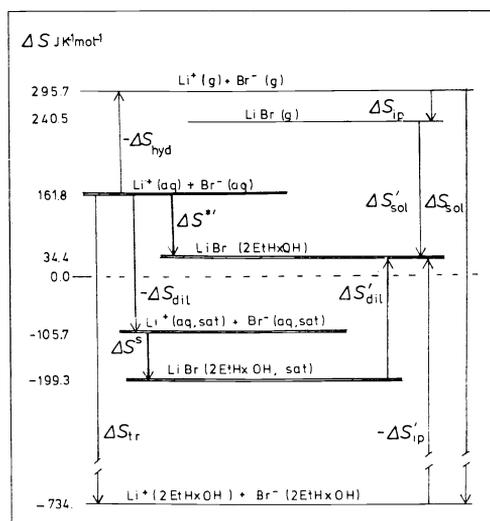


Fig. 2. Entropy level diagram for the extraction of LiBr into 2-ethylhexanol, based on the infinite dilution and on the saturated solution standard states.  $\Delta S_{ip}$  refers to ion-pairing.

#### EXAMPLE 3. EXTRACTION OF URANYL AND THORIUM OR PLUTONIUM(IV) NITRATES WITH PHOSPHORYL COMPOUNDS

As a last example, the extraction of dioxouranium (VI) (uranyl) nitrate and of thorium nitrate with neutral phosphoryl-group-containing compounds will be dealt with. The extracting solvents are of the type  $(RO)_nR_{3-n}PO$ , and are generally diluted with an inert diluent (e.g.,  $CCl_4$  or dodecane), which need be of only marginal concern for the present purposes. The extraction equilibrium quotients have been reported (Ref. 18) for the extraction of uranyl nitrate and plutonium (IV) nitrate, rather than thorium nitrate, under comparable conditions. It is expected that these two tetravalent ions have similar properties, in view of their similar crystal ionic radii, 0.099 and 0.093 nm for  $Th^{4+}$  and  $Pu^{4+}$ , respectively, although the former is "harder",  $\sigma = -0.55$ , than the latter,  $\sigma = -0.21$  (Ref. 9). Approximate values of  $\Delta G_{extr}^\circ$  have therefore been calculated for the two salts for three extractants, having  $R = C_4H_9$  and  $n = 0, 2$ , and 3 (no data have been found for butyl dibutylphosphinate,  $n = 1$ ). On the other hand, no value for the "extraction" of the plutonium salt into the gas phase, i.e., for  $\Delta G_{hyd}^\circ$  of  $Pu^{4+}$ , has been reported, and the value for  $Th^{4+}$  is used instead. Table 4 summarizes these data. As in the last example, Table 4 shows that no apparent

TABLE 4. Standard molar Gibbs free energies (in  $kJ\ mol^{-1}$ ) for the extraction of nitrates<sup>a</sup>

Extractant	$\Delta G_{extr}^\circ$ for $UO_2^{2+}$	$\Delta G_{extr}^\circ$ for $Pu^{4+}$
Gas phase (i.e., $-\Delta G_{hyd}^\circ$ )	+1329	-5823 ( $Th^{4+}$ )
$(C_4H_9)_3PO$	-34	-45
$(C_4H_9)(C_4H_9O)_2PO$	-19	-29
$(C_4H_9O)_3PO$ (TBP)	-10	-18

<sup>a</sup> Extraction from  $\leq 0.5\ mol\ dm^{-3}\ HNO_3$  into  $0.5\ mol\ dm^{-3}$  extractant in  $CCl_4$  at 298.15 K, with formation of the disolvate.

quantitative relationship exists between  $\Delta G_{hyd}^\circ$  and the  $\Delta G_{extr}^\circ$  values. The solvating properties of the phosphoryl-group-containing extractants have been well documented, and the

frequency shifts in the vibration of the P-O bond indicate strong electron-pair donation from this oxygen to the uranyl (or the tetravalent) cation (Ref. 19 & 20). It might have been expected, therefore, that a large compensation of the invested  $-\Delta G_{\text{hyd}}^{\circ}$  would have arisen from  $\Delta G_{\text{Solv}}^{\circ}$  by the extractants. This seems, however, not to be the case.

A detailed analysis has been made of the uranyl nitrate - tri-n-butyl phosphate (TBP) in dodecane system (Ref. 13 & 21). It has been shown that the extraction reaction is enthalpy controlled in the sense of eq. (5). The schematics of the  $\Delta H^{\circ}$  values involved in the various hypothetical steps leading to the extraction is shown in Fig. 3.

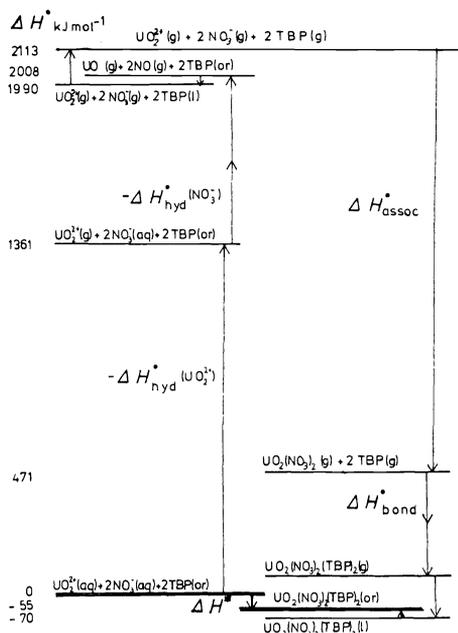


Fig. 3

Fig. 3. Enthalpy level diagram for the extraction of uranyl nitrate with TBP in dodecane.

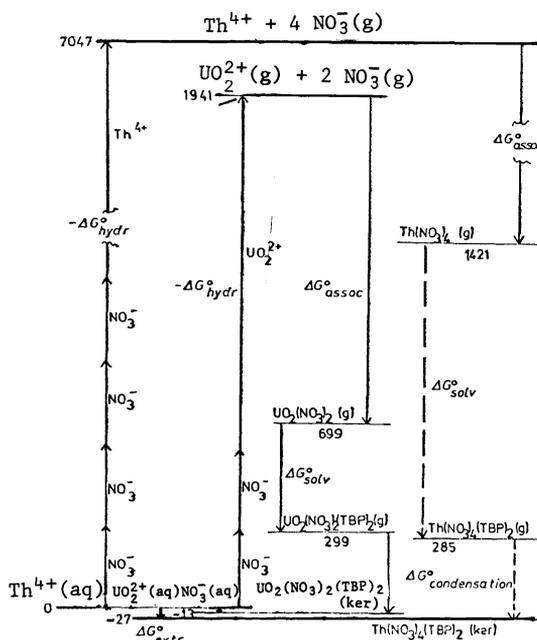


Fig. 4

Fig. 4. Gibbs free energy level diagram for the extraction of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  nitrates into TBP in kerosene ( $\approx$  dodecane).

The invested enthalpy for the dehydration of the ions is  $-\Sigma\Delta H_{\text{hyd}}^{\circ} = 1367$  (for  $\text{UO}_2^{2+}$ ) +  $2 \times 329$  (for  $2 \times \text{NO}_3^-$ ) =  $2025 \text{ kJ mol}^{-1}$ . The compensation does not come primarily from solvation, however, but from the association of the uranyl and nitrate ions. The electrostatic work for this association in the gas phase is  $-1642 \text{ kJ mol}^{-1}$ . The enthalpy changes for the (hypothetical) evaporation of TBP from the dodecane and for the (hypothetical) condensation of the adduct into dodecane, when taken into account, yield the small amount  $+17 \text{ kJ mol}^{-1}$  to account for the diluent effect (the  $\Delta\Delta G^{\circ}$  is larger,  $-340 \text{ kJ mol}^{-1}$ , because of large entropy gains). The balance,  $-400 \text{ kJ mol}^{-1}$ , is the  $\Delta H_{\text{Solv}}^{\circ}$  of  $\text{UO}_2(\text{NO}_3)_2(\text{g})$  with 2 TBP(g).

The corresponding entropy change can be estimated, yielding  $T\Delta S_{\text{Solv}}^{\circ} = -32 \text{ kJ mol}^{-1}$  for 2 TBP molecules, hence  $\Delta G_{\text{Solv}}^{\circ}$  of uranyl nitrate comes out to be  $-184 \text{ kJ mol}^{-1}$  per mole of TBP. The condensation and evaporation Gibbs free energy changes for the other extractants listed in Table 4 are expected not to differ much from those for TBP. Hence the values of  $\Delta G_{\text{Solv}}^{\circ}$  can be estimated as  $-184$ ,  $-189$ , and  $-201 \text{ kJ mol}^{-1}$  per molecule of TBP,  $(\text{C}_4\text{H}_9)_3\text{C}_4\text{H}_9\text{O}_2\text{PO}$ , and  $(\text{C}_4\text{H}_9)_3\text{PO}$ , respectively, solvating the hypothetical species  $\text{UO}_2(\text{NO}_3)_2$  in the gas phase, from the data in Table 4. That the solvation capabilities of these extractants vary only over a range of  $\pm 5\%$  from the mean is in line with the small differences in the frequency shifts in the vibration of the P-O bond noted for these extractants by Nikolaev (20). This is contrary to the impression that may be gained from the tabulated  $\Delta G_{\text{extr}}^{\circ}$  values (Table 4), the extraction equilibrium constants (Ref. 18), or statements in the literature concerning the effectiveness of these solvating extractants.

If this analysis is repeated for thorium [or plutonium (IV)] and TBP, a picture similar in its gross lines to the previous one is obtained, see Fig. 4. Again, the major fraction of  $-\Sigma\Delta G_{\text{hyd}}^{\circ} = 5823 + 4 \times 306 = 7047 \text{ kJ mol}^{-1}$  is regained from the electrostatic work of the ion association in the gas phase,  $-5626 \text{ kJ mol}^{-1}$ . If the difference in the Gibbs free energy of the condensation of the adduct into the inert diluent and the evaporation of the TBP is equated with the amount found in the previous case ( $\sim -340 \text{ kJ mol}^{-1}$ ), since the same number

of bulky TBP molecules is involved, the value of  $\Delta G_{\text{solv}}^{\circ}$  of  $\text{Th}(\text{NO}_3)_4$  with TBP in the gas phase comes out to be  $-540 \text{ kJ mol}^{-1}$  per TBP molecule. This is 46% larger (in the absolute sense) than for the solvation of  $\text{UO}_2(\text{NO}_3)_2$ , a fact that reflects the higher charge density on the directly solvated atom,  $\text{Th}^{4+}$  compared with the dioxo- $\text{U}^{\text{VI}}$  in  $\text{UO}_2^{2+}$ . The final result is that the average value of  $\Delta G_{\text{extr}}^{\circ}$  for the extraction of  $\text{Pu}^{4+}$  is larger (in the absolute sense) than that of  $\text{UO}_2^{2+}$  by 42%, see Table 4. The resemblance of this figure with the difference in  $\Delta G_{\text{solv}}^{\circ}$  noted above for  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$ , the stand-in for  $\text{Pu}^{4+}$ , is however purely coincidental, in view of the many other steps involved in this extraction.

#### CONCLUSIONS

The main point that has been made in this paper is that in many extraction reactions changes of solvation of the ions from water to an organic solvent predominate, or at least are important components of, the standard molar Gibbs free energy of extraction,  $\Delta G_{\text{extr}}^{\circ}$ . The distribution ratio  $D$  in practical systems depends strongly on excess chemical potential terms, not dealt with here. The relative abilities of solvents to solvate ions, however, which determines the relative values of  $D$  for given aqueous phases, are determined primarily by the standard molar Gibbs free energies of transfer of the ions. These, in turn, have been related to the properties of the solvents, the properties of the ions, and the water content of a mixed aqueous organic solvent by means of eqs. (2), (3), and (4), for a certain set of solvents, and by implication also to many more, water immiscible, solvents useful for extraction. Thus the approach advocated in this paper should permit the prediction of the distribution ratios  $D$  in dilute solutions of ions (or whole electrolytes) extracted mainly by solvation.

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