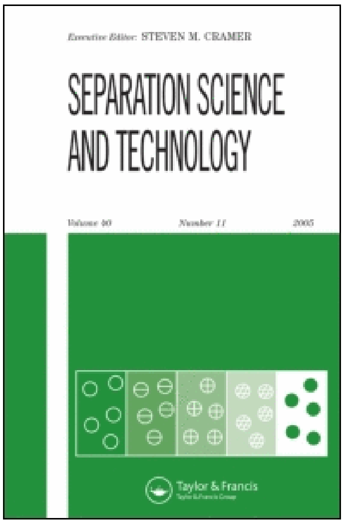

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Betts, Robert H. and Bron, Jan(1977) 'A Discussion of Partial Isotope Separation by Means of Solvent Extraction', Separation Science and Technology, 12: 6, 635 — 639

To link to this Article: DOI: 10.1080/00372367708057076

URL: http://dx.doi.org/10.1080/00372367708057076

SEPARATION SCIENCE, 12(6), pp. 635–639, 1977

A Discussion of Partial Isotope Separation by Means of Solvent Extraction

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Abstract

An analysis of the problem of isotope enrichment in species dissolved in aqueous and organic phases is presented. Two examples are given and discussed.

Two compounds of a different chemical nature can be separated by solvent extraction. Separation of two species, differing only in isotopic substitution, can also in principle be achieved by the same method. However, separation of isotopic molecules is more difficult, since the difference of the distribution coefficients is usually much smaller than for the nonisotopic species.

Separation of isotopes is of great practical importance and, hence, it is worthwhile to explore the possibility of isotope separation by means of the simple method of solvent extraction. The theoretical aspects of solvent extraction will be discussed first in a general way, after which two examples will be given as illustrations. The main aim of this discussion is to investigate the feasibility of the separation of the isotopes of the heavier elements (heavy atom isotope effects).

Let us assume that partitioning of isotopic molecules takes place between an aqueous (aq) and an organic phase (org). Although the nature of the organic solvent may be of great practical importance, it is of no consequence in this general theoretical discussion. Isotope partitioning between the two phases can be written as an equilibrium:

$$\mathrm{A(aq)} + \mathrm{B'(org)} \rightleftarrows \mathrm{A'(aq)} + \mathrm{B(org)} \tag{1}$$

The equilibrium constant of this exchange reaction is K and the prime refers to the *heavier* isotope. The magnitude of K will determine the ease and feasibility of isotope separation. It should be noted that the molecules A and B are not necessarily chemically very similar.

The equilibrium constant, K, is in terms of partition functions

$$K = [q(\mathrm{A'})/q(\mathrm{A})]/[q(\mathrm{B'})/q(\mathrm{B})] \tag{2}$$

By means of the first quantum correction (*1*) and Wilson's F, G matrix elements (*2*), K can be written as

$$K = 1 + \kappa T^{-2}[\Sigma_i \Sigma_j (G_{ij}{}^{(\mathrm{A})} - G'^{(\mathrm{A})}_{ij}) F_{ij}{}^{(\mathrm{A})} - \Sigma_k \Sigma_l (G_{kl}{}^{(\mathrm{B})} - G'^{(\mathrm{B})}_{kl}) F_{kl}{}^{(\mathrm{B})}] \tag{3}$$

The constant κ is equal to $(h/2\pi k)^2/24$. Equation (3) is particularly useful for qualitative purposes (*1*), while its quantitative applications are limited to heavy atom isotope effects and high temperatures. Symmetry numbers have been ignored in Eq. (3) and elsewhere in this paper.

From Eq. (3) a lot of information about K can be obtained. At very high temperatures or at the classical limit, K is equal to unity (no isotope enrichment). Also, K is a linear function of the force constants $F_{ij}{}^{(\mathrm{A})}$ and $F_{kl}{}^{(\mathrm{B})}$ and K depends on temperature according to T^{-2}. It will be obvious that K can be smaller, equal, or larger than unity, depending upon the relative values of the sums in Eq. (3).

It is intuitively reasonable that isotope separation becomes easier when the differences in the masses of the isotopes, for a given mass increase, and more difficult when the masses of the isotopes increase. This can be derived from Eq. (3) and the additional matrix equations (*2*, *3*)

$$\mathbf{G} = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^t; \qquad \mathbf{S} = \mathbf{B}\mathbf{X} \tag{4}$$

In Eq. (4), **B** defines the transformation from Cartesian coordinates (**X**) to internal coordinates (**S**). The diagonal matrix, **M**, lists the masses of the atoms in the molecule; each atomic mass is repeated three times along the diagonal. Substitution of Eq. (4) into Eq. (3) gives

$$K = 1 + \kappa T^{-2}[\{\Sigma_i \Sigma_j F_{ij} \Sigma_r (\mu_r - \mu'_r) \Sigma_\alpha B_{ir}{}^{(\alpha)} B_{jr}{}^{(\alpha)}\}_A - \{\Sigma_k \Sigma_l F_{kl} \Sigma_s (\mu_s - \mu'_s) \Sigma_\alpha B_{ks}{}^{(\alpha)} B_{ls}{}^{(\alpha)}\}_B] \tag{5}$$

In Eq. (5), α is equal to x, y, or z. In case only one atom in A (and B) is involved in isotopic substitution, Eq. (5) reduces to a simple form. At a given temperature, K can then be written as

$$\begin{aligned} K &= 1 + \kappa T^{-2}(\mu - \mu')[(\Sigma_i \Sigma_j F_{ij} \Sigma_\alpha B_{ir}{}^{(\alpha)} B_{jr}{}^{(\alpha)})_A - (\Sigma_k \Sigma_l F_{kl} \Sigma_\alpha B_{ks}{}^{(\alpha)} B_{ls}{}^{(\alpha)})_B] \\ &= 1 + \left(\frac{m' - m}{mm'}\right) \times \text{constant} \end{aligned} \tag{6}$$

The masses of the heavier and lighter isotopes are m' and m, respectively. From Eq. (6) it can be deduced that at a given temperature and for a given reaction the isotope effect, $K - 1$, is directly proportional to the difference in the masses of the isotopes and inversely proportional to the product of these masses. It is implied in Eqs. (5) and (6) that B is independent of isotopic substitution, which is always true when the atomic coordinates in the frame of reference are taken to be invariant with respect to isotopic substitution (*3*).

Let us now discuss isotope enrichment by means of solvent extraction in a more concrete way. Suppose that A and B are metal complexes differing only in the nature of the ligands. Let A and B have the same coordination number p. The metal ion may be M^{n+}; A and B are then $ML_p{}^{(A)}$ and $ML_p{}^{(B)}$ respectively. Only the isotope effect with respect to M will be considered. Since the charge of the complex is of no significance in this discussion, it will be omitted. The ligands are $L^{(A)}$ and $L^{(B)}$. Isotope effects can be estimated by using an "abbreviated" version (*4*) of the actual molecule or ion, or, stated differently, only the atoms in the immediate neighborhood of the center of isotopic substitution are important. Therefore, only those atoms directly bonded to the (central) metal ion, the seat of isotopic substitution, need be considered.

It has been shown recently, that, because of smallness of magnitude, off-diagonal **G** and **F** matrix elements contribute very little to isotope effects (*5*). If these off-diagonal elements are ignored, Eq. (3) becomes

$$K = 1 + \kappa T^{-2}[\Sigma_i \Delta G_{ii}{}^{(A)} \cdot F_{ii}{}^{(A)} - \Sigma_j \Delta G_{jj}{}^{(B)} \cdot F_{jj}{}^{(B)}] \tag{7}$$

In Eq. (7), ΔG_{ii} is equal to $G_{ii} - G'_{ii}$. If ΔG_{ii} is defined by a bond stretching internal coordinate, it is simply equal to (*2*) $(m' - m)/mm'$. When applied to the complexes $ML_p^{(A)}$ and $ML_p^{(B)}$, Eq. (7) leads to a simple expression for K:

$$K = 1 + p\kappa T^{-2}\Delta F(m' - m)/mm' \tag{8}$$

In Eq. (8) it has been implied that the main contribution (*6*) to the isotope effect, $K - 1$, comes from the matrix elements G_{ii} and F_{ii} defined by the stretching coordinates corresponding to metal-ligand bond. The quantity ΔF is the difference in force constants of the metal-ligand bonds in the aqueous and organic phases. From Eq. (8) it can be concluded that the value of K and the feasibility of (partial) isotope separation, in the case of the metal complexes $ML_p^{(A)}$ and $ML_p^{(B)}$, are mainly determined by $|\Delta F|$. It is of great practical importance to choose the ligands $L^{(A)}$ and $L^{(B)}$ in such a way as to make $|\Delta F|$ as large as possible. It is interesting to note that the form of Eq. (8) suggests that the chemical identity of the atom in the ligand bonded to M is not so important, since m' and m refer to M^{n+} only.

While realizing its limitations, Eq. (8) may be used for quantitative purposes. Let M^{n+} be Fe^{3+} and the isotopes ^{59}Fe and ^{56}Fe. The coordination number, p, in the case of Fe^{3+} is most likely to be six. If the atoms bonded to Fe in the aqueous species belong to element X and the atoms bonded to Fe in the organic phase to element Y, then the abbreviated versions of $ML_p^{(A)}$ and $ML_p^{(B)}$ are FeX_6(aq) and FeY_6(org), and Reaction (1) becomes

$$^{56}FeX_6(aq) + {}^{59}FeY_6(org) \rightleftarrows {}^{59}FeX_6(aq) + {}^{56}FeY_6(org) \tag{9}$$

Equation (8) for the exchange Equilibrium (9) can be written at 300°K as

$$K(^{59,56}Fe^{3+}) = 1 + 0.009\Delta F \tag{10}$$

An estimate of K can be obtained from Eq. (10), if force constant data exist. The units of ΔF in Eq. (9) are md/Å. An equation similar to Eq. (10) can be given for U^{4+}. If p is equal to 8 in both phases, then (300°K)

$$K(^{238,235}U^{4+}) = 1 + 0.0007\Delta F \tag{11}$$

As expected for identical values of ΔF, $K(^{238,235}U^{4+})$ is much smaller than $K(^{59,56}Fe^{3+})$. In order to achieve maximum isotope partitioning, K should be as large or small as possible. This can be achieved by a choice of ligands which will maximize $|\Delta F|$.

With the aid of the above discussion and examples, the theory presented in this paper may be applied to other systems where unequal isotope distribution between two phases is of interest.

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Received by editor January 24, 1977