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The nuclear field shift effect in chemical exchange reactions

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ABSTRACT

Mass-independent isotope fractionations found in laboratory-scale chemical exchange experiments are reviewed. The classic theory of stable isotope fractionation in chemical exchange reactions has been established by Bigeleisen, Mayer, and Urey in 1947. In 1996, the conventional mass-dependent theory was expanded by Bigeleisen to include a mass-independent term named the nuclear field shift effect. The nuclear field shift is an isotope shift in orbital electrons, which results from the isotopic difference in nuclear size and shape. Since the revised theory was proposed, the mass-independent isotope fractionation of various elements, (*e.g.*, Ti, Cr, Zn, Sr, Mo, Ru, Cd, Sn, Te, Ba, Nd, Sm, Gd, Yb, and U), found in chemical exchange systems has been successfully explained as the nuclear field shift effect. In this review article, from both theoretical and experimental viewpoints, origins of mass-independent isotope effects are discussed.

1. Introduction

This article presents an overview of the mass-independent isotope fractionation found in laboratory scale chemical exchange experiments, whose origin is considered to be the nuclear field shift effect. The fundamental theory of the chemical isotope effect was established by Urey (1947) and Bigeleisen and Mayer (1947). From the theory, at a constant temperature, the isotope enrichment factor is proportional to the isotopic mass difference δm and inversely proportional to the product of masses m and m' of two isotopes. As long as four decades after the formulation of the mass-dependent theory, a failure of the isotope effect in chemical exchange equilibria to follow the theory has not been reported.

Mass-independent isotope fractionations were first observed for O and S (see a review by Thiemens, 2006). The difference in the symmetry and the densities of states of the activated isotopomers is a possible origin for these mass-independent isotope fractionations (Hathorn and Marcus, 1999). Alternative interpretations have been discussed in review articles (Weston, 1999; Thiemens, 2006). For heavy elements, an anomalous isotope effect in chemical exchange was found in an isotope enrichment of ^{235}U in a redox reaction (Fujii et al., 1989a,b). Isotope enrichment factors for even atomic mass isotopes, ^{234}U, ^{236}U, and ^{238}U, showed a mass-dependent line, while that of ^{235}U deviated from that line. After that observation, the anomalous isotope enrichment of odd atomic mass isotopes has been examined. In cation exchange chromatography, a similar property has been found in ^{157}Gd enrichment (Chen et al., 1992), while fractionations of Ca (Oi et al., 1993), Sr (Oi et al., 1992), and Ba (Kondoh et al., 1996) isotopes showed the conventional mass-dependent trends. Nishizawa et al. (1993, 1994) have found different fractionation properties between odd and even atomic mass isotopes of Zn (1993), Sr (1994), and Ba (1994) in a liquid–liquid extraction system with a macrocyclic polyether. The effect was named "odd/even isotope effect" (Nishizawa et al., 1994), but at that time, the origin of the odd/even isotope effect was not clear.

A further investigation on the odd/even isotope effect has been carried out for Sr isotopes (Nishizawa et al., 1995). In the study, a similarity between the odd/even isotope effect and the odd–even staggering found in atomic spectra was observed. In atomic spectra, lines of the odd isotopes do not lie midway between the adjacent even isotopes, but are shifted towards the isotope of lower atomic mass number. This effect, which is known as the odd–even staggering (Stacey, 1966; Kurn, 1969; Heilig and Steudel, 1978, King, 1984; Aufmuth et al., 1987), is attributable to their nuclear charge radii. Odd neutron number nuclei often appear to be smaller than that estimated from the adjacent even isotopes (see Fig. 3 in a review by Aufmuth et al., 1987).

In 1996, the Bigeleisen–Mayer equation was expanded by the original author (Bigeleisen, 1996a). The nuclear field shift effect, which is one of the terms added in the expansion, is recognized as the origin of the mass-independent isotope fractionation. The nuclear field shift is an isotope shift in orbital electrons (Kurn, 1969; Heilig and Steudel, 1978, King, 1984; Aufmuth et al., 1987). This results from the isotopic

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difference in nuclear size and shape. Different isotopes have the same number of protons, but they do not have the same distribution of protons in space. That is, the nuclear charge distribution is affected by the number of neutrons in the nucleus. The nuclear charge distribution gives an electric field, and its isotopic difference shifts the atomic energy levels (details will be explained in Section 4.1), also displacing the electronic molecular states. The nuclear field shift is not mass-dependent but is strongly related to neutron configuration of a nuclear structure. The nuclear field shift effect is therefore a mass-independent isotope effect. The new theory gave a sufficient explanation of the anomalous isotope enrichment of U. Nomura et al. (1996) have independently come to the same conclusion. At the current stage, the Bigeleisen 1996 theory is the most reliable theory for studying the mass-independent isotope fractionation found in chemical exchange reactions.

2. Chemical exchange reaction

The theory of chemical isotope effect has been derived for equilibrium reactions based upon the calculation of the isotopic reduced partition function (Urey, 1947; Bigeleisen and Mayer, 1947). The isotopic reduced partition function based on differences in vibrational frequencies of isotopically substituted molecules is an estimate of isotopic partitioning between a separated atom and the molecule.

Chemical exchange is known as a potential method for separating isotopes (London, 1961). A chemical exchange reaction can be represented as two half-reactions,

$$AX + Y \rightleftarrows AY + X, \Delta G_1^\circ \tag{1}$$

or

$$A'X + Y \rightleftarrows A'Y + X, \Delta G_2^\circ \tag{2}$$

where A and A' are the heavy and light isotopes of the element A, and X and Y represent ligands. ΔG_1° and ΔG_2° are the standard free energies of the reactions. The difference between reactions (1) and (2) corresponds to an isotopic exchange reaction between AX and AY,

$$A'Y + AX \rightleftarrows A'X + AY, \Delta G^\circ = \Delta G_1^\circ - \Delta G_2^\circ \tag{3}$$

For example, isotopes of light elements, C (Hutchison et al., 1940), N (Urey et al., 1937), and S (Stewart and Cohen, 1940), were successfully separated by chemical exchange in Urey's pioneering work. Even for heavy elements like U, isotope enrichment by chemical exchange is feasible (see a review by Bigeleisen, 1992).

The equilibrium constants of reactions (1) and (2) are,

$$K_1 = \frac{\gamma_{AY}[AY]\,\gamma_X[X]}{\gamma_{AX}[AX]\,\gamma_Y[Y]} \tag{4}$$

and,

$$K_2 = \frac{\gamma_{A'Y}[A'Y]\,\gamma_X[X]}{\gamma_{A'X}[A'X]\,\gamma_Y[Y]} \tag{5}$$

where γ means the activity coefficient. K_1/K_2 can be calculated as,

$$\frac{K_1}{K_2} = \frac{(\gamma_{AY}[AY])\,/\,(\gamma_{A'Y}[A'Y])}{(\gamma_{AX}[AX])\,/\,(\gamma_{A'X}[A'X])} \tag{6}$$

This is identical with the equilibrium constant K of the isotopic exchange reaction (3). From the general thermodynamic relation $\Delta G^\circ = -RT \ln K$, a relation $\Delta G_1^\circ - \Delta G_2^\circ = -RT \ln K_1 - (-RT \ln K_2) = -RT \ln (K_1/K_2)$ can be obtained. Hence, the relation $K = K_1/K_2$ is thermochemically consistent.

Under the equilibrium of reaction (3), if the chemical species AX and $A'X$ are separated from AY and $A'Y$, isotope fractionation can be evaluated. In the case, the equilibrium isotope separation factor α is defined as,

$$\alpha = \frac{([A]\,/\,[A'])_Y}{([A]\,/\,[A'])_X} \tag{7}$$

where $([A]/[A'])_X$ means the isotopic composition corresponding to AX and $A'X$, while $([A]/[A'])_Y$ corresponds to AY and $A'Y$. $([A]/[A'])_X$ and $([A]/[A'])_Y$ may be the isotopic compositions of two different equilibrated phases, *e.g.*, an aqueous phase and an organic phase in solvent extraction, a resin phase and a liquid phase in chromatography, and so on. Under an assumption that the activity coefficient is isotope-independent, that is, $\gamma_{AX} = \gamma_{A'X}$ and $\gamma_{AY} = \gamma_{A'Y}$ (see Eq. (6)), the isotope separation factor α is equal to the equilibrium constant K of reaction (3).

The isotope enrichment factor ε is defined as,

$$\varepsilon = \alpha - 1 \tag{8}$$

Considering the magnitude of chemical isotope fractionation, an approximation, $\alpha - 1 \approx \ln \alpha$ (or $\varepsilon \approx \ln(1+\varepsilon)$), can be applied. Here α and ε have been defined for a single stage reaction. Since chromatography is a multistage process, α and ε values are usually extracted from measurements by using equations proposed by Spedding et al. (1955), Glueckauf (1955), or Kakihana and Kanzaki (1969). It should be noted that ε here is different from that usually used in geochemistry (the use of ε to indicate a fractionation factor is not uncommon in environmental geochemistry). ε in Eq. (8) is as defined and used for engineered isotope enrichment. One can see that $10^3\,\varepsilon$ is similar to the delta unit used in geochemistry.

3. Bigeleisen and Mayer's (1947) theory of mass-dependent fractionation

Isotope effects in chemical exchange (reaction (3)) caused by intermolecular vibration has been clearly explained by Bigeleisen and Mayer (1947). A review prepared by Ishida (2002) is helpful for understanding it. The equilibrium constant K in the isotope exchange reaction (3) is,

$$K = \frac{\left(\frac{s}{s'}f\right)_Y}{\left(\frac{s}{s'}f\right)_X} \tag{9}$$

where s is the number of identical configurations obtained by fundamental geometric operations on each molecule such as symmetry or rotation (*e.g.*, $s = 1$ for HCl, 2 for O_2, 12 for CH_4), and X and Y represent ligands. The number $(s/s')f$ is called the "reduced partition function ratio." $(s/s')f$ is generally expressed as follows via the Bigeleisen–Mayer second-order approximation,

$$\frac{s}{s'}f = 1 + \frac{1}{24}\left(\frac{\hbar}{kT}\right)^2 \frac{\delta m}{mm'}\langle \nabla^2 U \rangle \tag{10}$$

where $\hbar$, k, and T are the Plank constant, the Boltzmann constant, and temperature, respectively. m and m' are masses of two isotopes A and A'. $\delta m/mm'$ represents $(1/m' - 1/m)$. $\langle \nabla^2 U \rangle$ is the averaged Laplacian of the intermolecular potential. This approximation is only valid at relatively high temperature (Bigeleisen and Mayer, 1947; Ishida, 2002). Consider a molecule, in which the central atom of mass m or m' is symmetrically surrounded by n identical atoms (ligands) of mass M. Eq. (10) can be simply rewritten as,

$$\frac{s}{s'}f = 1 + \frac{1}{24}\left(\frac{\hbar}{kT}\right)^2 \frac{\delta m}{mm'} M \nu^2 n \tag{11}$$