Cours de chimie séparative M3/D1-D2 Master CSMP ED 459
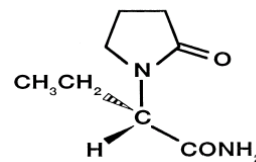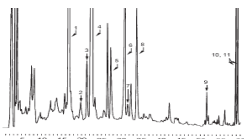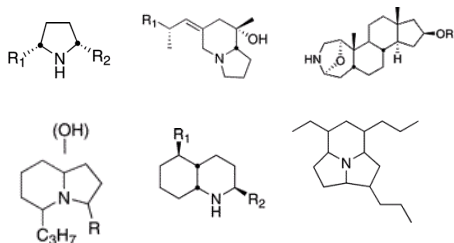
Session 2013-2014 :

Chemical isotopic separation :

The most difficult separation chemistry nowadays since chemical potentials involved are different when observed and when theoretically expected : a few elements for triggering new research

stephane.pellet-rostaing@cea.fr

7/12/2103

Purification of organic compounds

Enantioselective separation

Keppra (Levitiracetam)

Separation science

Catalyst recycling

$CH_3CH=CH_2 + CO + H_2$

phase organique

$CH_3CH_2CH_2CHO$

Interface

phase aqueuse

cycle catalytique $L_2Rh(CO)H$

NaO_3S $)_3P = L$

solubilité 1kg/ L H_2O

Ion separation

Mélange eutectique $AlCl_3/KCl$

$ZrCl_4$ enrichi en Hf
Zr/Hf= 75/25

1

6

$ZrCl_4$ déhafnié
Zr/Hf= 5/99,99/0,0

3

T= 500°C

N_2

8

$ZrCl_4$ (+ $HfCl_4$, $SiCl_4$, $TiCl_4$) + CO_2

Isotopic putity
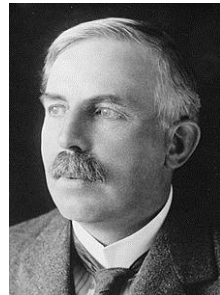
Un peu d'histoire

Frederick Soddy (1877 - 1956)

Nobel prize in chemistry (1921) : « chemistry of radioactive substances and nature of isotopes »

"Put colloquially, their atoms have identical outsides but different insides."

"... The same algebraic sum of positive and negative charges of the nucleus, when the arithmetical sum is different, gives what I call 'isotopes' or' isotopic elements" because they occupy the same place in the periodic table . They are chemically identical and except for some physical properties that depend directly on the atomic weight, are also physically identical... "

Nature **1913**, 92, 399

E. Rutherford (1871 – 1937)

Nobel prize in chemistry: 1908

"Disintegration of the chemical elements"
- Demonstration of the existence of the atomic nucleus.

Enrichment methods

electromagnetic separation

(magnetic field: differential deflection of species depending on the ratio electric charge / mass)

Thermal diffusion

(Heat Transfer: lighter atoms diffusion to warmer surfaces compared heavier atoms which tend to diffuse toward a cold surface)

Gaseous diffusion

(filtration through porous wall: kinetic transfer between different isotopes)

The ultracentrifugation

(centrifugal force: heavier atoms projected at the periphery , while the lighter migrate toward the middle of the centrifuge)

streamlined process

(nozzles or vortex separation: centrifuges " nonrotating " using carrier gas , separation via a pressure gradient due to differences in molecular weight)

chemical processes

(separation through flow contact: difference in the modes of interaction between the phases)

Laser separation

(selective excitation of atoms or molecules)

Enrichment types

2 types :

☞ Kinetic

☞ Chemical exchange

Example : uranium enrichment

Uranium = 3 isotopes

Uranium-234 : 0.006%

Uranium-235 : 0.718%

Uranium-238 : 99.276%

 Difference:

- atomic mass of the nuclei,

- by interaction with their electron distribution with the chemical environment or electromagnetic radiation

The possibility of separation of these atoms operate one or the other of these two types of differences.

In thermal equilibrium, all molecules have the same average kinetic energy:

$$E = 1/2 M v_m^2 \Rightarrow v_m = (2E/M)^{1/2}$$

$$\frac{V_{238}}{V_{235}} = \left(\frac{352}{349}\right)^{1/2} = 1{,}0043$$

theoretical ➡ $^{235}UF_6 = 349$
$^{238}UF_6 = 352$

Gaz diffusion

UF₆ $^{238}U : 99.274\%$
$^{235}U : 0.72\%$
$^{236}U : 0.006\%$

^{235}U (3.5%)

$(^{235}U/^{238}U = 1.002)$

1400 stages

^{235}U (3.5%)

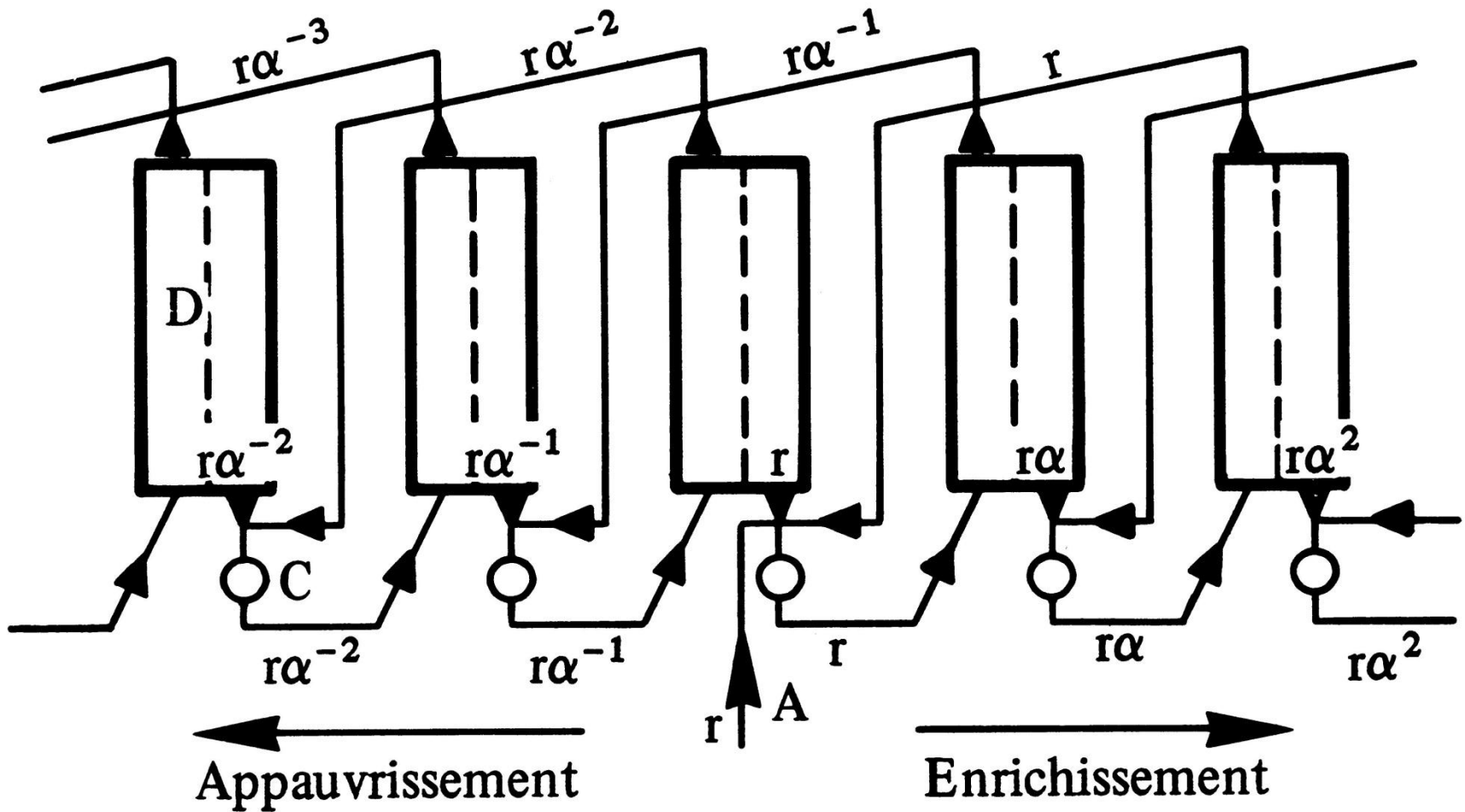*diffuseurs*

Enrichment is effected by rate difference of the molecular diffusion of UF6 gas through a barrier to very small pores (0.01 mm).

Appauvrissement ← → Enrichissement

1400 étages disposés en cascade
2000 tonnes d'uranium en permanence

Ce procédé est basé sur la différence de gradient de pressions partielles due à la force centrifuge créée par la rotation d'un bol à grande vitesse.
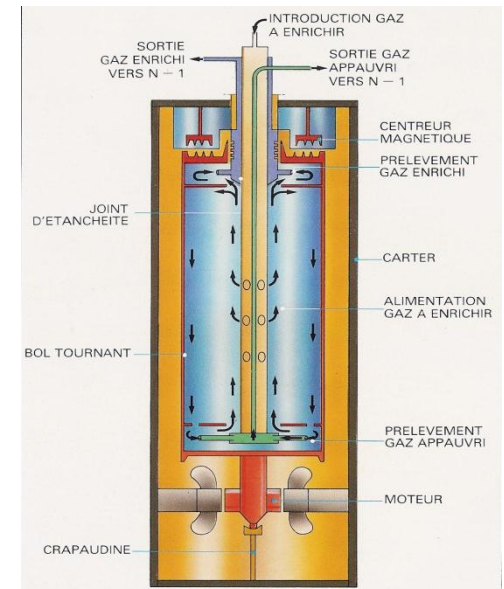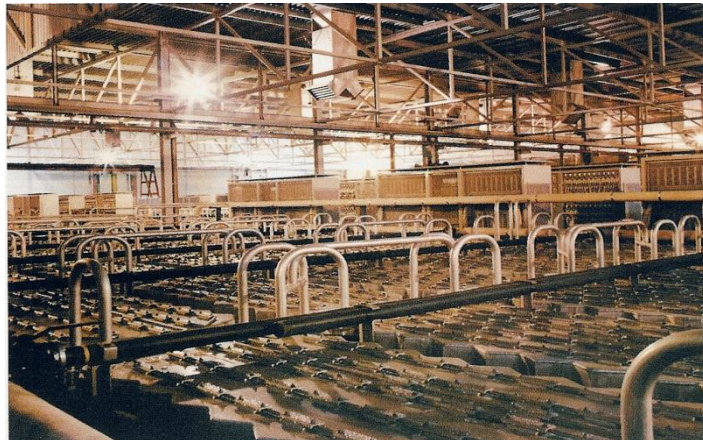
Le coefficient de séparation dépend de la vitesse de rotation du bol mais il est plus élevé que celui de la diffusion gazeuse :

$$\alpha_0 = \exp\left(\Delta m\,\omega^2 r^2 / 2\,k\,T\right)$$

$\varepsilon = 0{,}13$ pour une vitesse périphérique de 450 m/s
$\varepsilon = 0{,}48$ pour une vitesse périphérique de 800 m/s
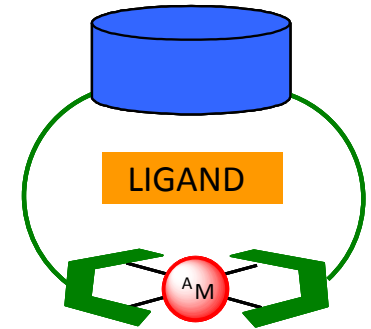
(à comparer à 0,0043 pour la diffusion gazeuse)

Ligands for isotope fractionation?

What drives ion selectively from a concentrated solution into an organic solvent?
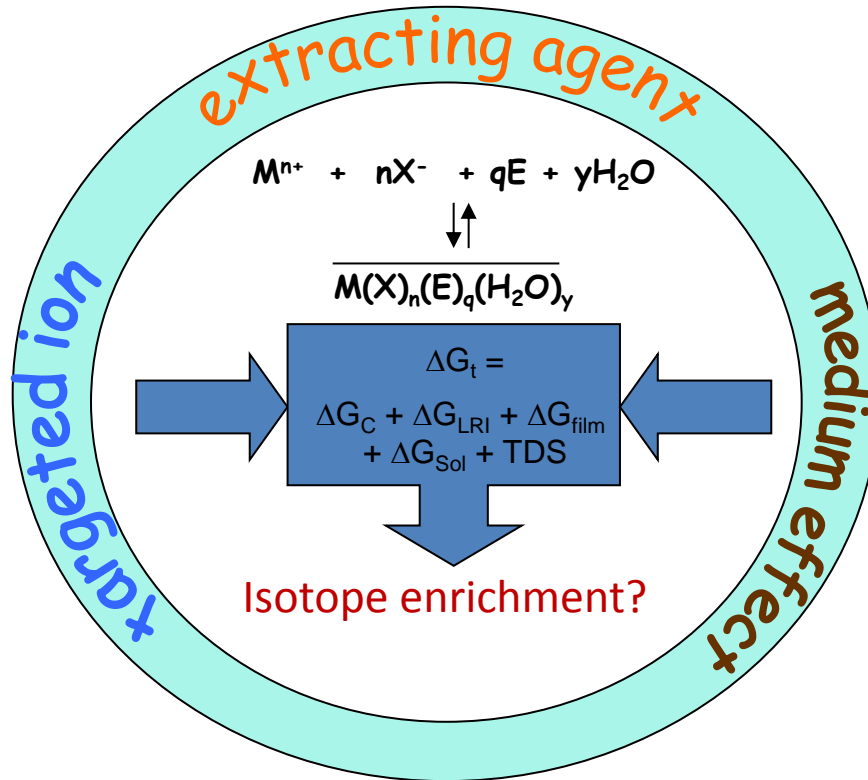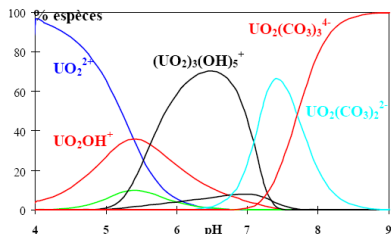
- **binding sites (hard/soft, solvating, ion exchange)**
- **Ligand/metal interactions (electrostatic...)**
- **Volume/steric hindrance**
- **Structure of the complex**

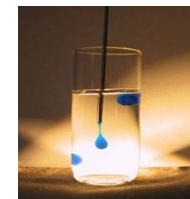But also : hydrophobic/hydrophylic (amphiphilic)

Solvating
Cation exchange
Anion exchange
chelating

LIGAND

^AM

extracting agent

$$M^{n+} + nX^- + qE + yH_2O$$

$$\overline{M(X)_n(E)_q(H_2O)_y}$$

$$\Delta G_t = \Delta G_C + \Delta G_{LRI} + \Delta G_{film} + \Delta G_{Sol} + TDS$$

Isotope enrichment?

targeted ion

- **Valency**
- **Oxidation state**
- **Size**
- **Hydration number**
- **Hard/Soft**
- **Counter ion**

medium effect

- **pH (neutral/acidic/basic)**
- **nature of the acid**
- **Ionic strenght**
- **Solvent/co-solvent**
- **Temperature**

% espèces — UO_2^{2+}, $(UO_2)_3(OH)_5^+$, $UO_2(CO_3)_3^+$, $UO_2(CO_3)_2^{2-}$, UO_2OH^+ — pH

Mass effect, field shift effect, magic number...

CHEMEX process

Oxydoreductive exchange between U(III) et U(IV) ions in two non miscible liquid phases (aqueous and organic).

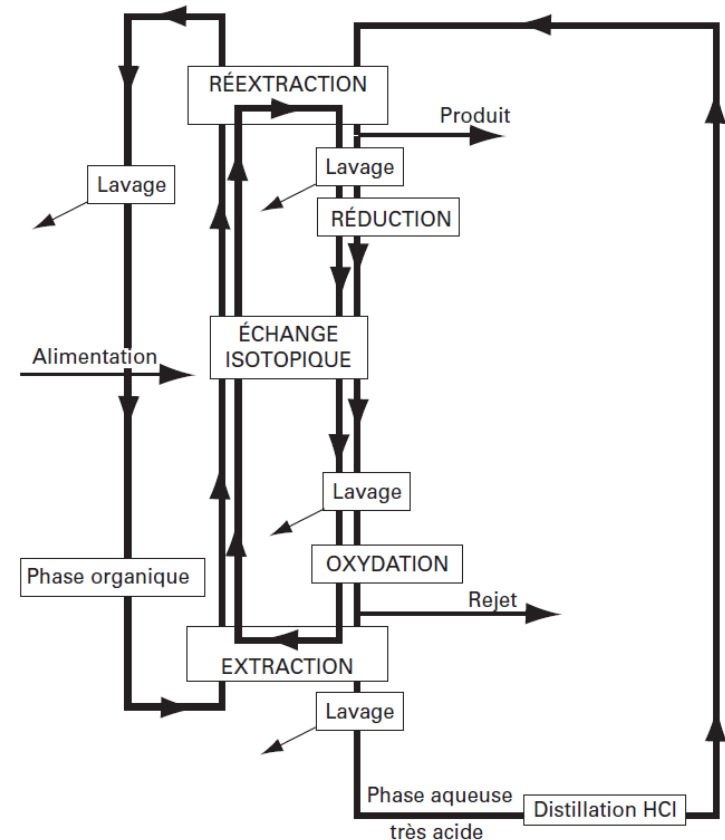$$^{235}U(III) + {}^{238}U(IV) \longleftrightarrow {}^{238}U(III) + {}^{235}U(IV)$$

all units of the isotope separation, the rich and poor at the end from which reflux allow recycling and converting the compound U (III) to the compound U (IV), and vice versa

^{238}U is concentrated in U (III) ions of a downward aqueous phase containing U (III) and U (IV)

^{235}U is concentrated in a bottom organic phase (tri-n-butyl-phosphate diluted / alkylated benzene) containing the U (IV) forms.

Separation factor α = 1,0027 very high
But energy consumption linked to the development of reflux

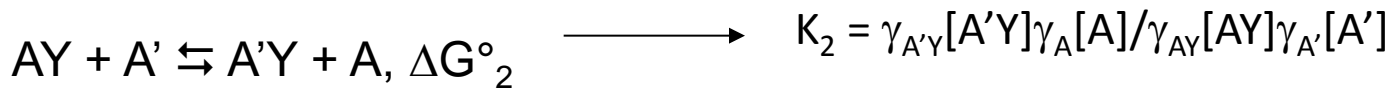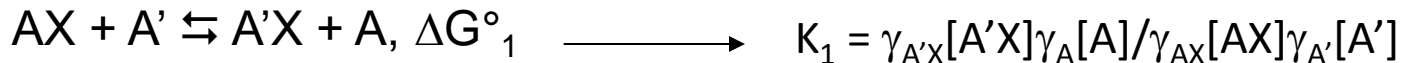The U (III) ion in the aqueous phase is stabilized by the addition of hydrochloric acid

A′Y + AX ⇆ A′X + AY

A and A 'represent the heavy and light isotopes of the same element and X and Y are the ligands

If the AX, AX' and AY, AY' couples are separated, it is possible to evaluate the isotope enrichment.

$AX + A' \leftrightarrows A'X + A, \Delta G°_1$ ⟶ $K_1 = \gamma_{A'X}[A'X]\gamma_A[A]/\gamma_{AX}[AX]\gamma_{A'}[A']$

$AY + A' \leftrightarrows A'Y + A, \Delta G°_2$ ⟶ $K_2 = \gamma_{A'Y}[A'Y]\gamma_A[A]/\gamma_{AY}[AY]\gamma_{A'}[A']$

$$K = \frac{K_1}{K_2} = \frac{\gamma_{A'X}[A'X]/\gamma_{AY}[AX]}{\gamma_{A'Y}[A'Y]/\gamma_{AY}[AY]}$$

and $\Delta G°_1 - \Delta G°_2 = -RT \ln K_1/K_2$

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

([A ']/[A])X and ([A']/[A])Y are the isotope compositions of the two phases at equilibrium:
- organic/aqueous
- resin/aqueous…

By convention, we express $\varepsilon = \alpha - 1$

Considering that the isotopic enrichment remains low

$$\alpha - 1 = \ln\alpha = \varepsilon$$

(for the chemist)

Isotope composition.
usually expressed in terms of deviations from a standard value

$$\delta = \frac{R_{\text{échantillon}}}{R_{\text{standard}}} - 1$$

Bigeleisen theory (1996)

for Z > 40

Bigeleisen theory :

(1996)

Mass difference $\longrightarrow$ Mass effect

Nuclear size and shape $\longrightarrow$ Field shift effect

Spin difference $\longrightarrow$ Nuclear spin effect

$$\varepsilon_{tot} = Ln\ \alpha = Ln\ \alpha_0 + Ln\ K_{anh} + ln\ K_{BOELE} + Ln\ K_{hfs} + Ln\ K_{fs}$$

Ln α_0 = **contribution of mass effect**
Ln K_{anh} = correction term for anharmonic vibration (neglectible)
Ln K_{BOELE} = correction term for the Born-Oppenheimer approximation (neglectible)
Ln K_{hfs} = **contribution of spin effect (zero for even isotope)**
Ln K_{fs} = **contribution of field shift effect**

$\longrightarrow$ $Ln\ \alpha = a(\Delta m/mm') + b\delta \langle r^2 \rangle + hf$ (at constant temperature)

m = mass isotope A
m' = mass isotope B
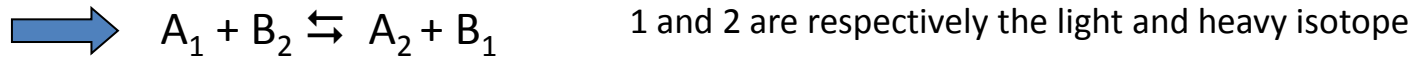Δm = mass difference

means square radius
difference

Term of spin displacement

Bigeleisen-Mayer theory (1947)

considering:
$$M'_{(phase\ 1)} + M_{(phase\ 2)} \leftrightarrows M'_{(phase\ 2)} + M_{(phase\ 1)}$$

$\Rightarrow \quad A_1 + B_2 \leftrightarrows A_2 + B_1$ 1 and 2 are respectively the light and heavy isotope

$$K = \frac{Z^{A2}/Z^{A1}}{Z^{B2}/Z^{B1}} = \frac{(Z_{trans}^{A2} Z_{rot}^{A2} Z_{vib}^{A2})/(Z_{trans}^{A1} Z_{rot}^{A1} Z_{vib}^{A1})}{(Z_{trans}^{B2} Z_{rot}^{B2} Z_{vib}^{B2})/(Z_{trans}^{B1} Z_{rot}^{B1} Z_{vib}^{B1})}$$

therefore

$$K = \frac{\prod_i \dfrac{\exp^{\frac{-u_i^{A2}}{2}}/(1-\exp^{-u_i^{A2}})}{\exp^{\frac{-u_i^{A1}}{2}}/(1-\exp^{-u_i^{A1}})}}{\prod_i \dfrac{\exp^{\frac{-u_i^{B2}}{2}}/(1-\exp^{-u_i^{B2}})}{\exp^{\frac{-u_i^{B1}}{2}}/(1-\exp^{-u_i^{B1}})}} \times \frac{(M^{A2}/M^{A1})^{3/2}}{(M^{B2}/M^{B1})^{3/2}} \times \frac{\left(\dfrac{I_1^{A2} I_2^{A2} I_3^{A2}}{I_1^{A1} I_2^{A1} I_3^{A1}}\right)^{1/2} \sigma_{A1}/\sigma_{A2}}{\left(\dfrac{I_1^{B2} I_2^{B2} I_3^{B2}}{I_1^{B1} I_2^{B1} I_3^{B1}}\right)^{1/2} \sigma_{A1}/\sigma_{A2}}$$

Bigeleisen-Mayer theory (1947)

$$\left(\frac{s}{s'}\, f\right) = 1 + \frac{1}{24}\left(\frac{h}{kT}\right)^2 \frac{\delta m}{mm'} < \nabla^2 U>$$

h = Plank cste (6,626 10^{-34} J.s)
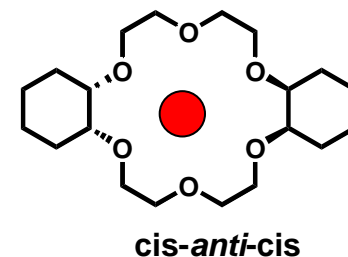k = Boltzmann cste (1,38 10^{-23} J.K^{-1})
T = temperature
m et m' = isotopes mass A et A'

$\dfrac{\delta m}{mm'}$ = reduced mass

$< \nabla^2 U>$ Means laplacian of intermolecular potential

Considering a molecule (or a complex) in which the central atom (ion) is surrounded by a number n of identical atoms (ligands) of mass M, then:

cis-*anti*-cis

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

ν = vibration frequency
M = mass of the ligand

Bigeleisen-Mayer theory (1947)

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

Then enrichment factor $\varepsilon = \alpha - 1 \approx \ln\alpha$ is:

$$\varepsilon = \ln\left(\frac{s}{s'}f\right)_Y - \ln\left(\frac{s}{s'}f\right)_X = \frac{1}{24}\left(\frac{h}{kT}\right)^2 \frac{\delta m}{mm'}(M_Y\nu_Y^2 n_Y - M_X\nu_X^2 n_X)$$

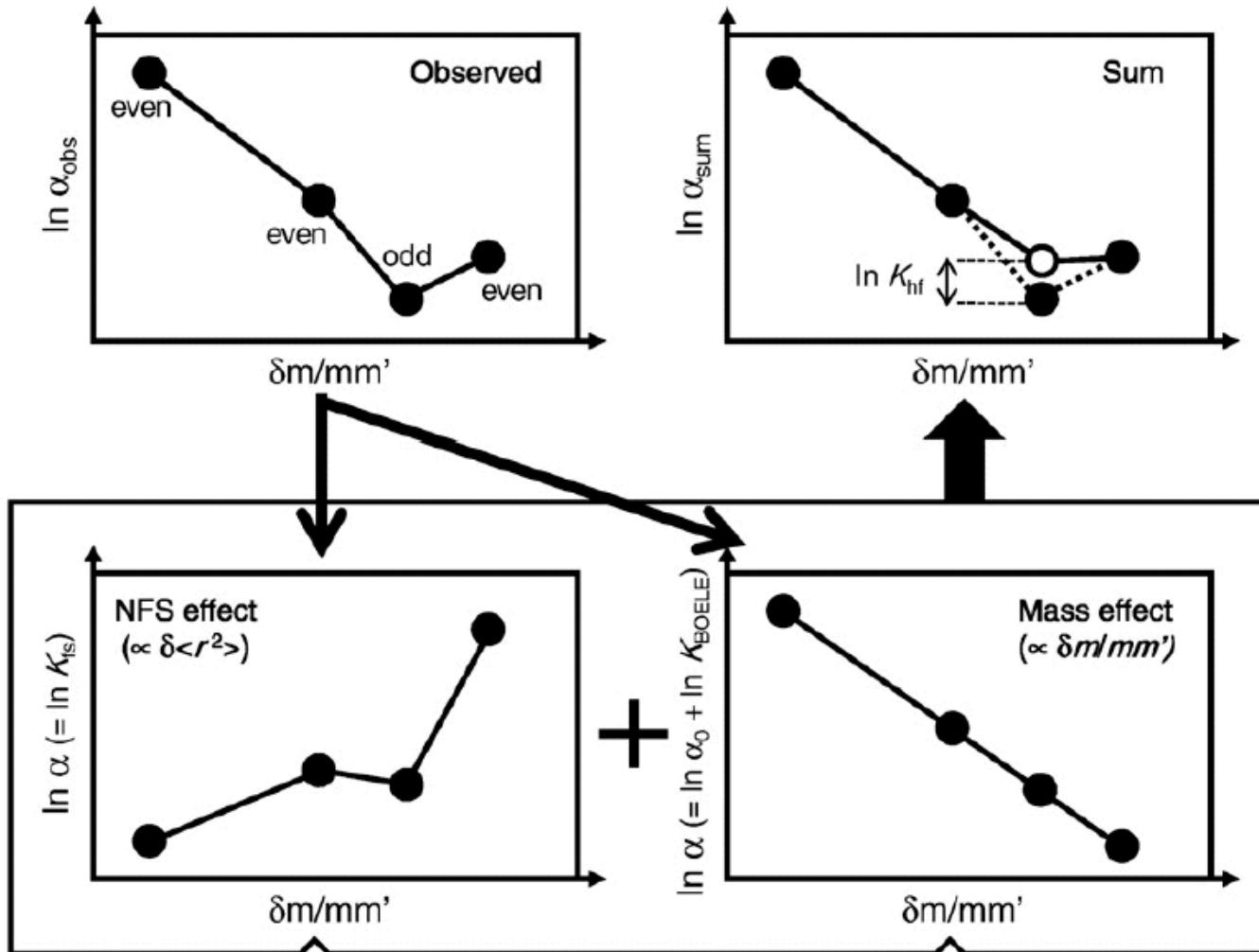Which is symplify as:

$$\varepsilon = a(\Delta m/mm')/T^2$$

a = scaling factor that determines the effects of mass and their contribution to the enrichment.

Checked for Z < 40

Link between theory and observation

Some examples

When $\delta\langle r^2\rangle$ does not vary linearly with $\delta m/mm'$
When ε does not vary linearly .

More easily explained by the field effects?
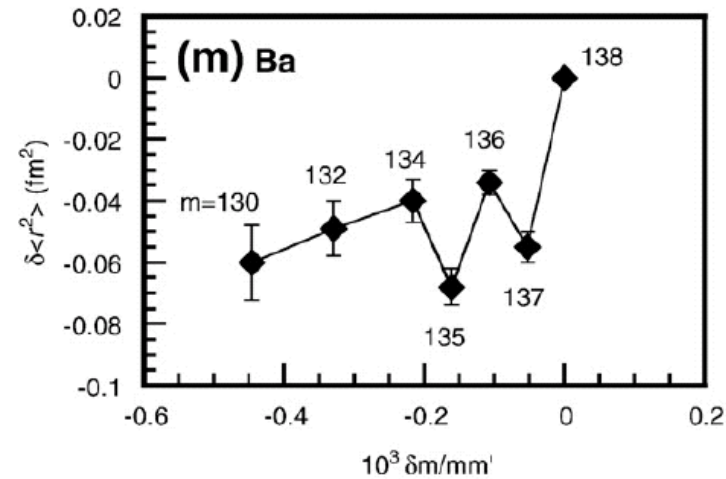

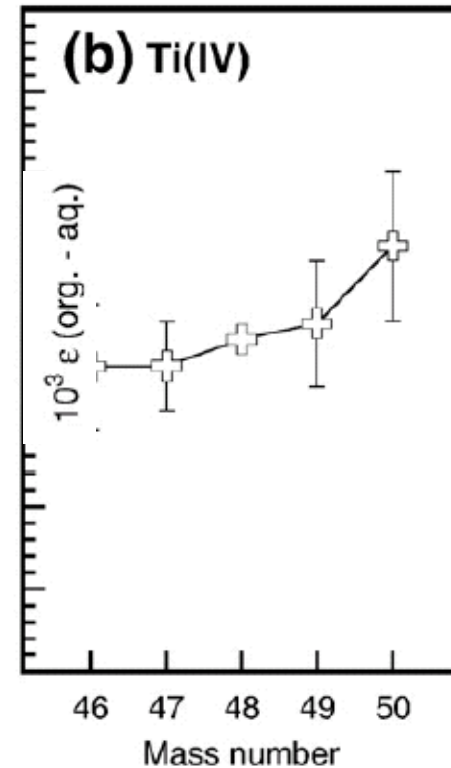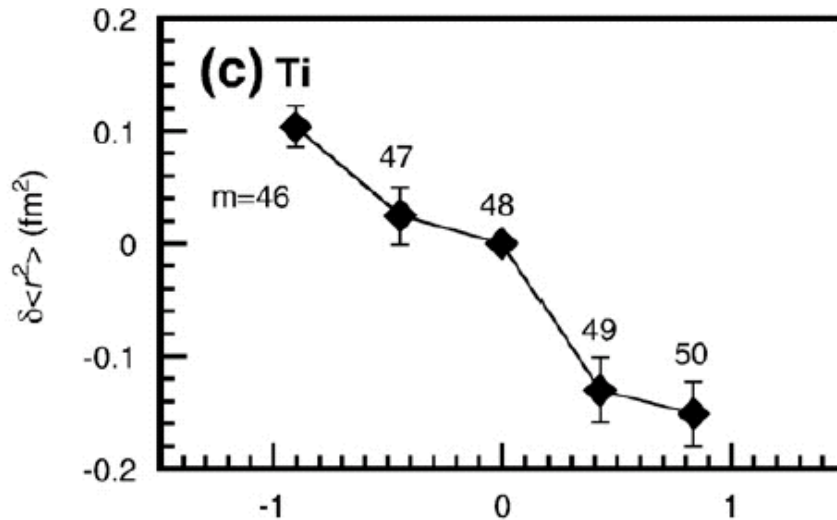*(Nishizawa 1994)*

chromatography

(Kondoh, 1996)

Link between theory and observation

When $\delta\langle r^2\rangle$ does not vary linearly with $\delta m/mm'$
When ε does not vary linearly.
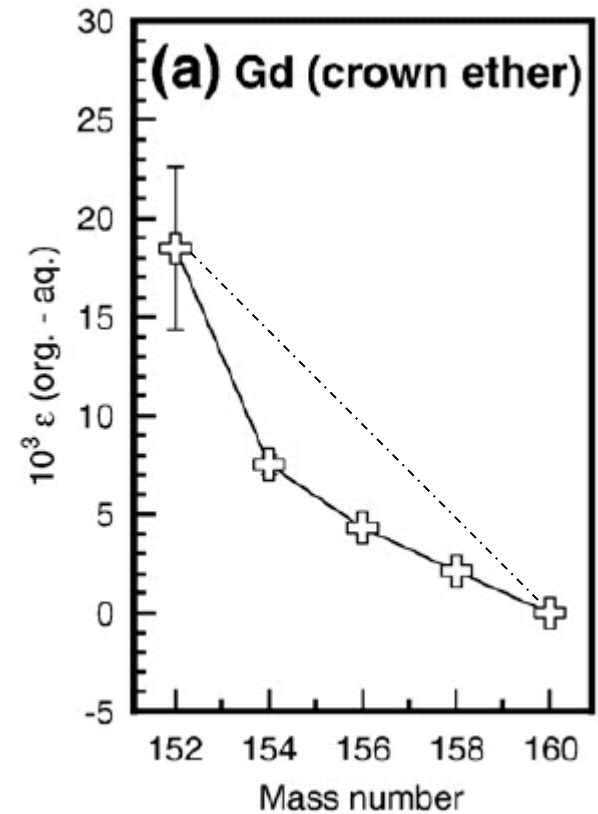
More easily explained by the field effects?
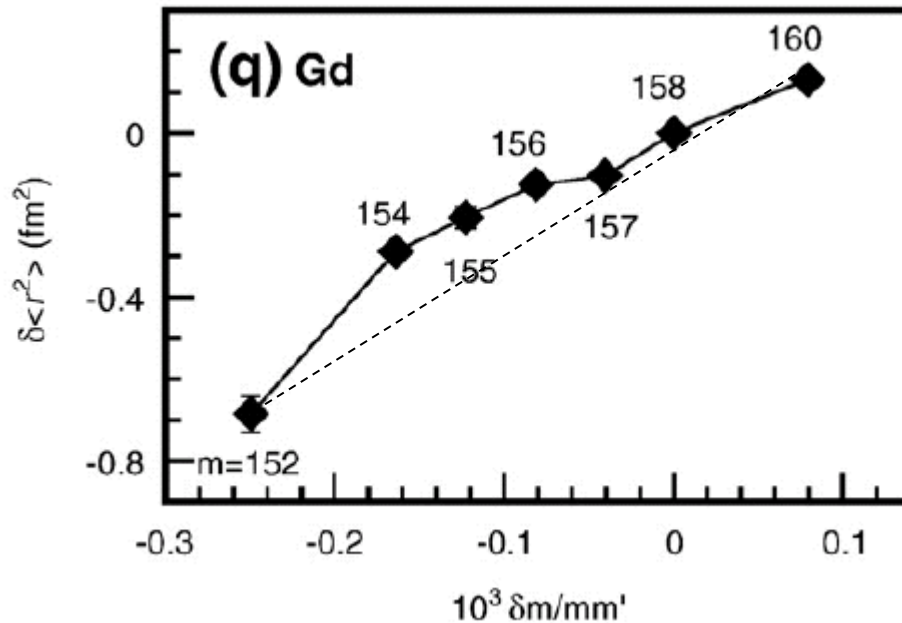
Link between theory and observation

When $\delta\langle r^2 \rangle$ varies linearly with $\delta m/mm'$
When ϵ does not vary linearly with $\delta m/mm'$
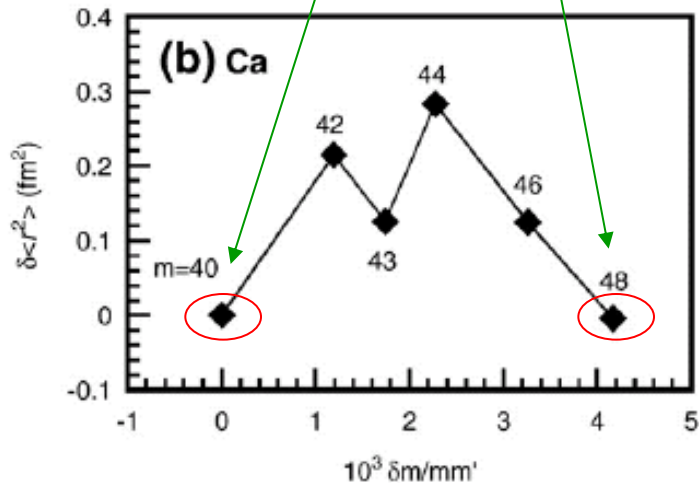
More easily explained by the field effects?

Link between theory and observation

When $\delta\langle r^2\rangle$ does not vary linearly with $\delta m/mm'$
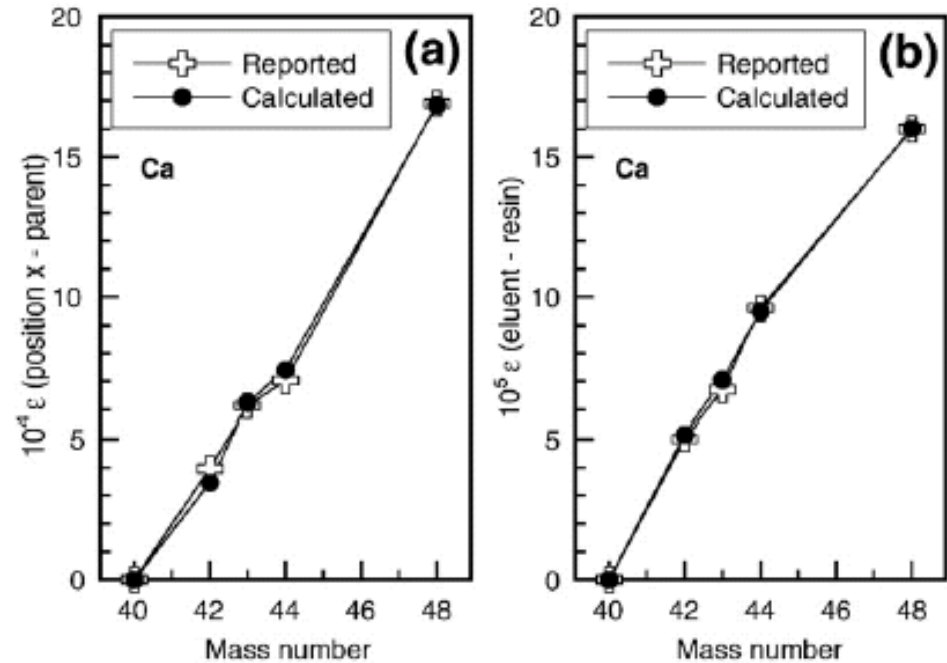When ε varies linearly

→ Field effects and effects of mass inseparable?

Isotope separation of calcium
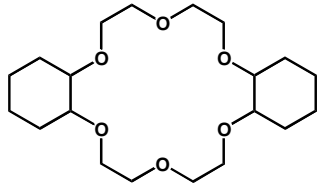
Doubly magic

(20 p, 20 n)   *(20 p, 28 n)*

a) Ca isotope enrichment by supported liquid membrane (Fujii et al. 1985)
b) Ca isotope enrichment by chromatography (Oi et al. 1993)

Isotope fractionation of calcium

18DCHC6

Isotope 48, 44, 43, 42, 40 (96,6%)

$$\alpha_{M\text{-}48} + ([^{M}Ca]/[^{48}Ca])_{org}/([^{M}Ca]/[^{48}Ca])_{aq}$$

$$\varepsilon_{M\text{-}48} = \alpha - 1$$

$$\varepsilon_{40\text{-}48} = a(\Delta M/MM')_{40\text{-}48} + b\delta<r^2>_{40\text{-}48}$$
$$\varepsilon_{44\text{-}48} = a(\Delta M/MM')_{44\text{-}48} + b\delta<r^2>_{40\text{-}48}$$
$$\varepsilon_{43\text{-}48} = a(\Delta M/MM')_{43\text{-}48} + b\delta<r^2>_{43\text{-}48} + (lnK_{hf})_{43}$$

Mass	$\delta<r^2>_{M\text{-}48}$	Relative value	Atomic mass	$\Delta M/MM'$ (x10^{-3})	Relative value
40	-0,0215	0,161	39,9626	-4,1694	1,72
44	-0,2907	2,173	43,9555	-1,8963	0,78
43	-0,1338	1	42,9588	-2,4241	1
48	0	0	47,9525	0	0

Isotope separation of calcium

	b$\delta< r^2 >$ / [a($\Delta M/MM'$)]	lnK_{hf}/[a($\Delta M/MM'$)]
^{40}Ca-^{48}Ca	0,02±0,48	-
^{44}Ca-^{48}Ca	0,62±1,31	-
^{43}Ca-^{48}Ca	0,22±0,88	0,64±1,35

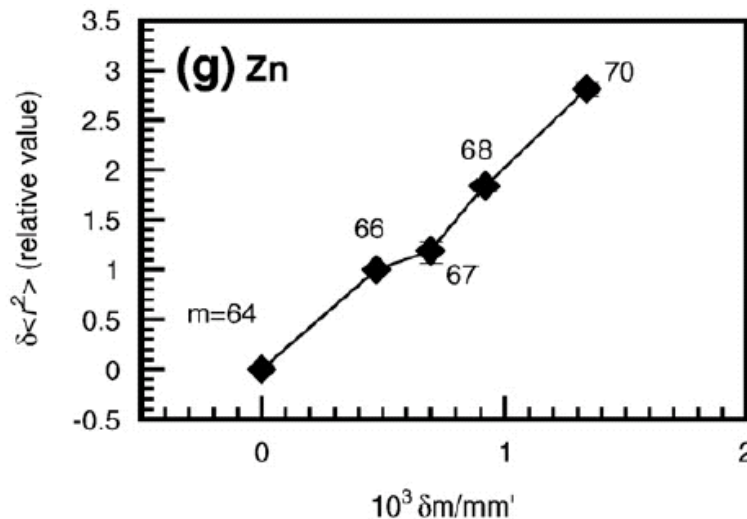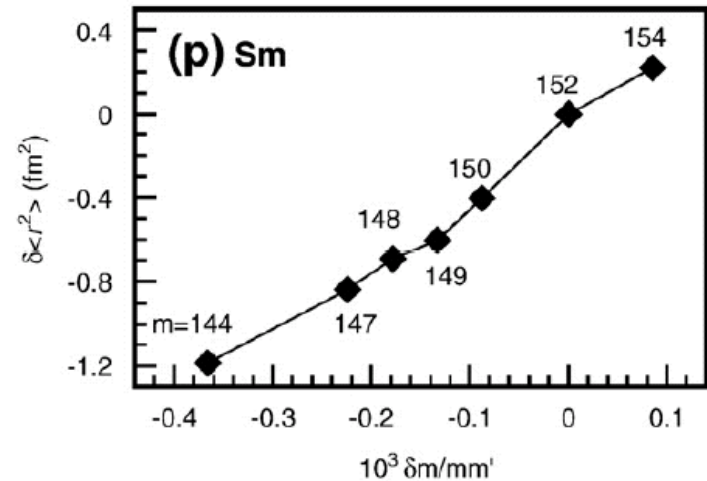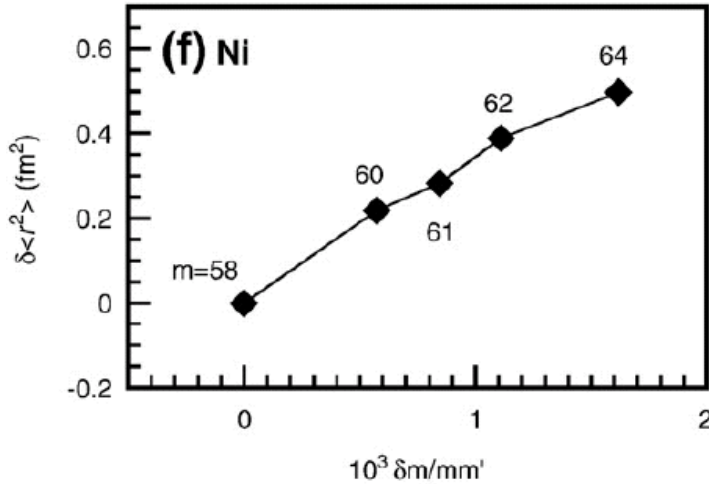$\delta< r^2 >$ theoretical

Observed enrichment

Expected mass effect

when $\delta\langle r^2\rangle$ varies linearly with $\delta m/mm'$
When ε varies linearly with $\delta m/mm'$

Mass and field effects inseparable?

The difference between the experimental values and the prediction for the odd isotopes is due to the effect of nuclear spin
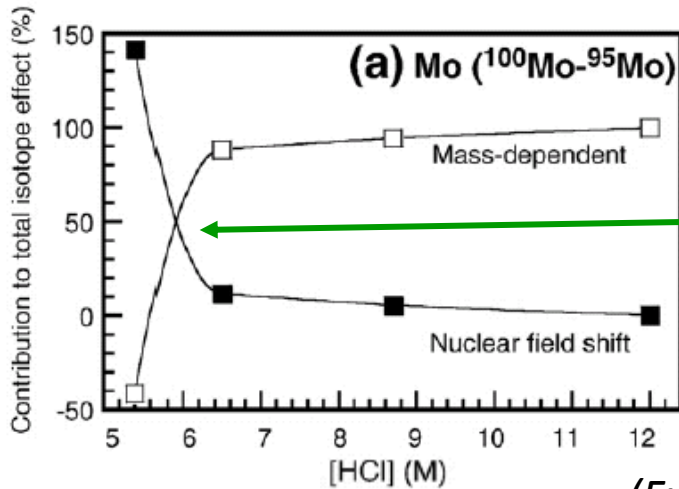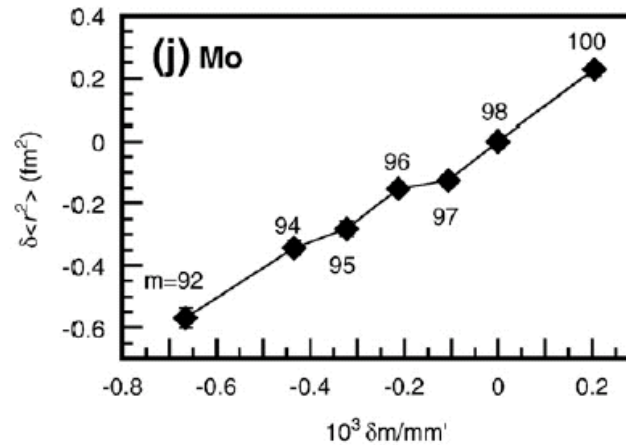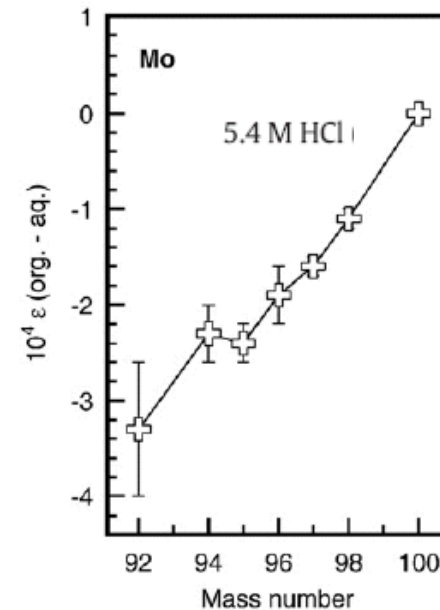
Link between theory and observation

When $\delta\langle r^2 \rangle$ varies linearly with $\delta m/mm'$

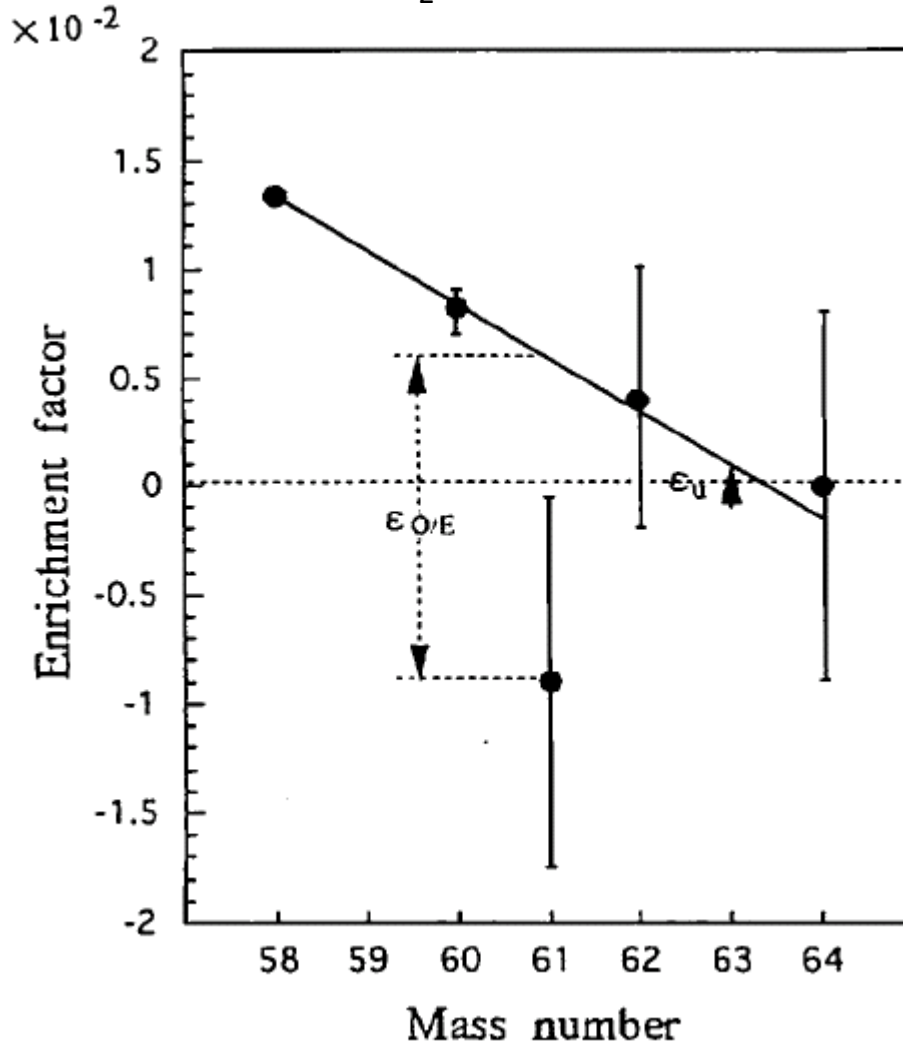Field and mass effects inseparable?

(Fujii, 2006)

Isotope fractionation of Nickel

Nickel isotopes: 58 (68,27%), 60 (26,10%), 61 (1,13%), 62 (3,59%), 64 (0,91%)

$$Ni^{2+}(6H_2O) + 2Cl^- + L \rightleftharpoons Ni^{2+}LCl_2 + 6H_2O$$

Enrichment factor corresponding to the mass number and schematic illustration of unit mass enrichment factor (ε_u and odd/even isotope effect ($\varepsilon_{O/E}$). The straight line is drawn by joining the observed enrichment factors of mass numbers 58 and 60. These enrichment factors shown in solid circles are observed at 4.0 M $NiCl_2$ aqueous phase.

$$\varepsilon_u = \varepsilon/(A_{64} - A_L)$$

A_{64} et A_L = mass number of 64 and L isotopes

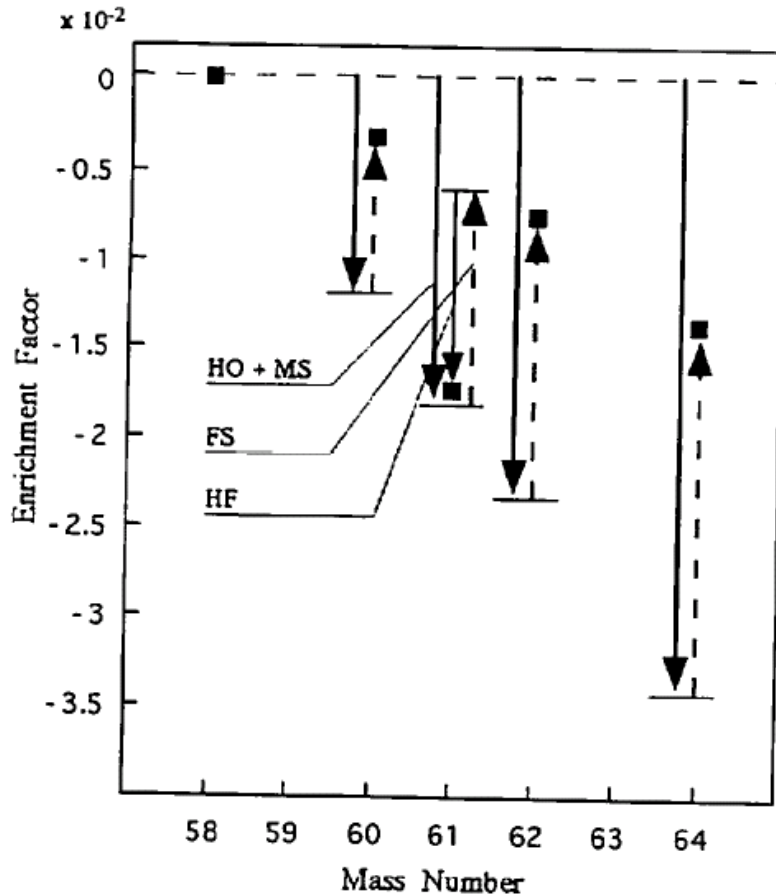**Table 3.** Enrichment Factors (ε), Field Shifts in $3d^8 4s 4p$–$3d^8 4s^2$ Transition, and Relative $\Delta m / mm'$

	Isotope pair			
	58–60	60–62	62–64	60–61
$\varepsilon \times 10^{-2}$	−0.29	−0.44	−0.62	−1.43
Field shift ($\times 10^{-3}$ cm^{-1})	−7.2	−5.5	−3.5	−2.1
Relative $\Delta m / mm'$	1.00	0.94	0.88	0.48

Enrichment factors and contributions of vibrational frequency, isotope shift and hyperfine structure shift. The observed enrichment factors are shown in solid square. These data are of 4.0 M $NiCl_2$ and 2.0 M HCl aqueous phase. The contribution of vibrational energy including mass shift shown in solid line is opposite to that of field shift shown in dashed line. The contribution of hyperfine structure shift is illustrated in thin straight line, which exists in the odd atomic mass isotope, ^{61}Ni.
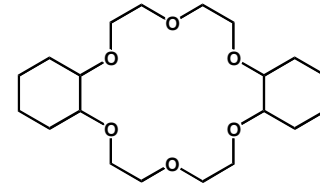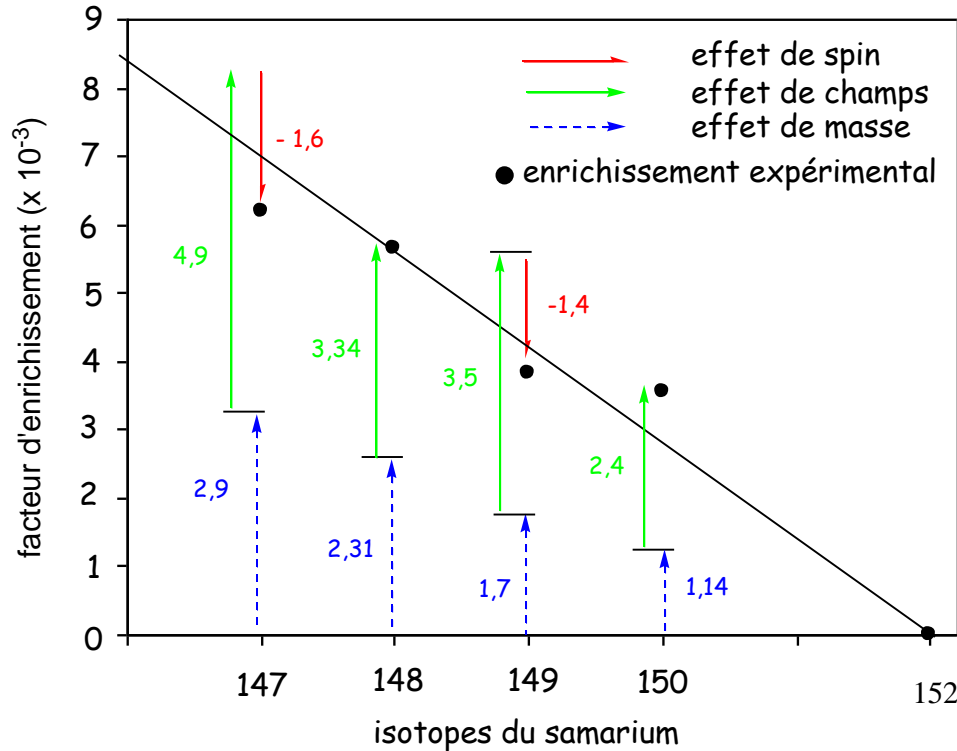
$$(ho+ms) = -5.9 \times 10^{-3}$$

$$fs = 2.7 \times 10^{-3}$$

$$hf = -1.11 \times 10^{-2}$$

Influence of mass effects, fields and spin on the isotopic enrichment of Samarium in a liquid:liquid process (1.3 SmCl3 in 1M HCl)

HCl 1M
$SmCl_3 = 1,3M$

m	147	148	149	150	152
ε_{exp} ($\times 10^{-3}$)	6,19	5,65	3,83	3,54	0
$\Delta m/152m$ ($\times 10^{-4}$)	2,24	1,78	1,32	0,88	0
$\delta \langle r^2 \rangle$ (fm^2)	-0,878	-0,726	-0,634	-0,432	0

$$^{152-m}\varepsilon = a[(152 - m)/152m] + b(^{152-m}\langle r^2 \rangle) + hf$$

avec $a = 13$ et $b = -0,0055$

$$\sum fs / \sum \varepsilon_0 = 1,94$$

$$Ln\, \alpha = a(\Delta m/mm') + b\delta \langle r^2 \rangle + hf$$

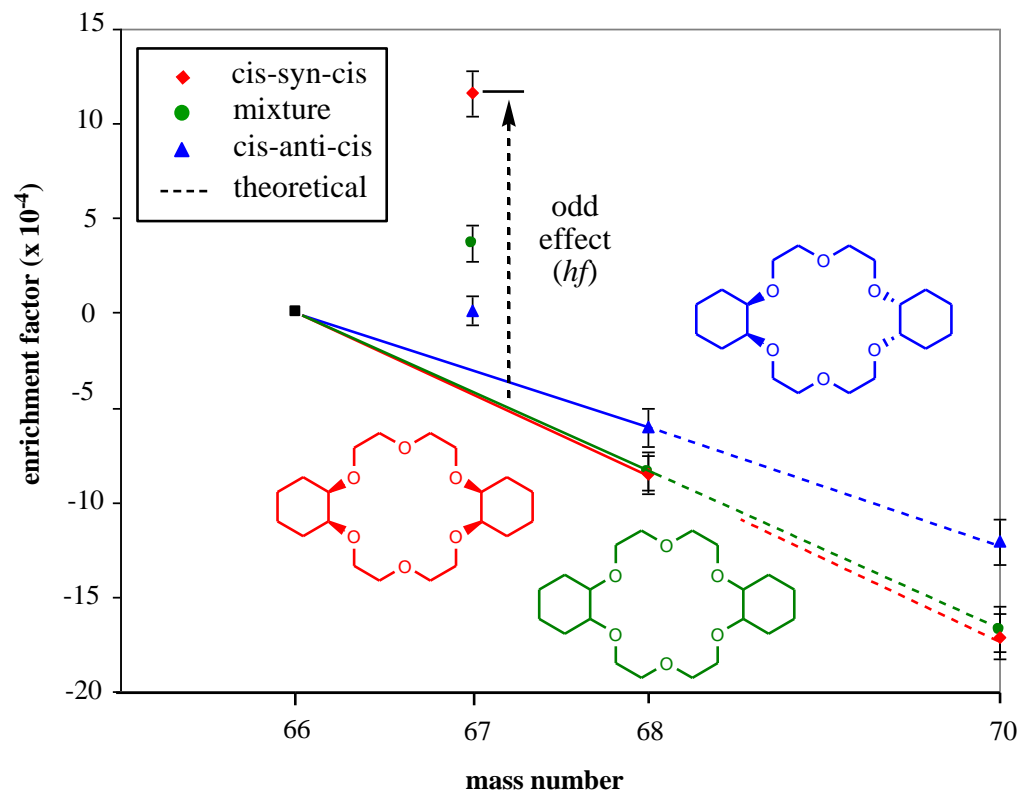$$\varepsilon_0 \qquad \varepsilon_{fs}$$

Contribution of the field shift effect = 2 x mass effect

T. Fujii, T. Yamamoto, K. Nishizawa, J. Inagawa, K. Gunji, K. Watanabe *Solv. Extract. Ion Exch.* **1998**, *16*, 985

Isotope fractionation of zinc isotopes

[ZnCl$_2$]	0,7M		
	$\varepsilon_{67/66}$	$\varepsilon_{68/66}$	$\varepsilon_{70/66}{}^{a}$
Cis-*syn*-cis	11.60	-8.55	-17.08
Mélange 63/37	3.68	-8.36	-16.73
Cis-*anti*-cis	0.14	-6.18	-12.72

Couple of isotope	66,67	66,68	66,70
(δm/mm')/10^{-4}	2.21	4.456	8.658
(δm/mm')$_{rel}$	0.5074	1	1.9430
Field shift/GHz	-0.140	-0.620	-1.332
(δ<r^2>)$_{rel}$	0.2262	1	2.1548

Some example

Contribution of mass and field shift effects

$$^{m,66}\varepsilon = a((m-66)/66m) + b\delta\langle r^2\rangle + hf$$

Mass effect   Field shift effect   Spin effect
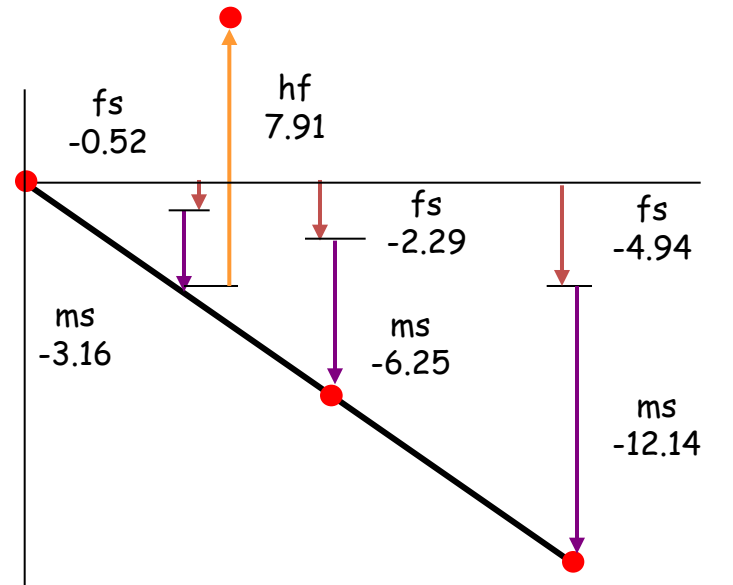
(cis-*syn*-cis) / 10^{-4}

$$\varepsilon^{68/66} = \quad (1)a \quad + \quad (1)b$$

$$\varepsilon^{70/66} = \quad (1,943)a \quad + \quad (2,1548)b$$

$$\varepsilon^{67/66} = \quad (0,5074)a \quad + \quad (0,2262)b \quad + \quad hf$$

$$a = -6,247$$
$$b = -2,293$$
$$hf = 7,916$$

$$\frac{\Sigma\,\varepsilon_0}{\Sigma\,\varepsilon_{fs}} = \frac{\Sigma\,[-6,25(m_i-66)/66m_i]}{\Sigma\,-2,29\,\delta\langle r_i^2\rangle]} = 2.73$$

The influence of the mass effect is about 3 times greater on the zinc isotope enrichment.

fs -0.52   hf 7.91   fs -2.29   fs -4.94

ms -3.16   ms -6.25   ms -12.14

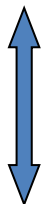## Réflexions personnelles

Physique nucléaire : connaissance des noyaux et maîtrise des effets isotopiques

Effet de masse, effet de champs, angles magiques, déformation de la charge nucléaire…

Chimistes organiciens, physico-chimistes… : conception des ligands, formulations, mécanismes d'extraction, effets de milieu…
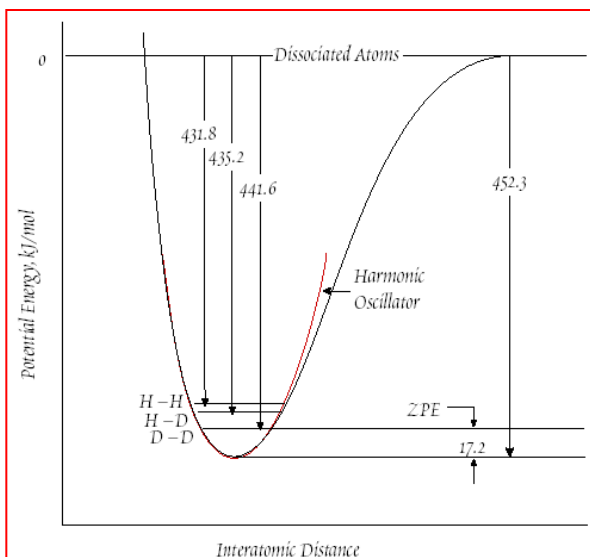

Figure 9.1. Energy-level diagram for the hydrogen molecule. Fundamental vibration frequencies are 4405 cm^{-1} for H$_2$, 3817 cm^{-1} for HD, and 3119 cm^{-1} for D$_2$. The zero-point energy of H$_2$ is greater than that of HD which is greater than that of D$_2$. Arrows show the energy, in kJ/mol, required to dissociate the 3 species. After O'Niel (1986).