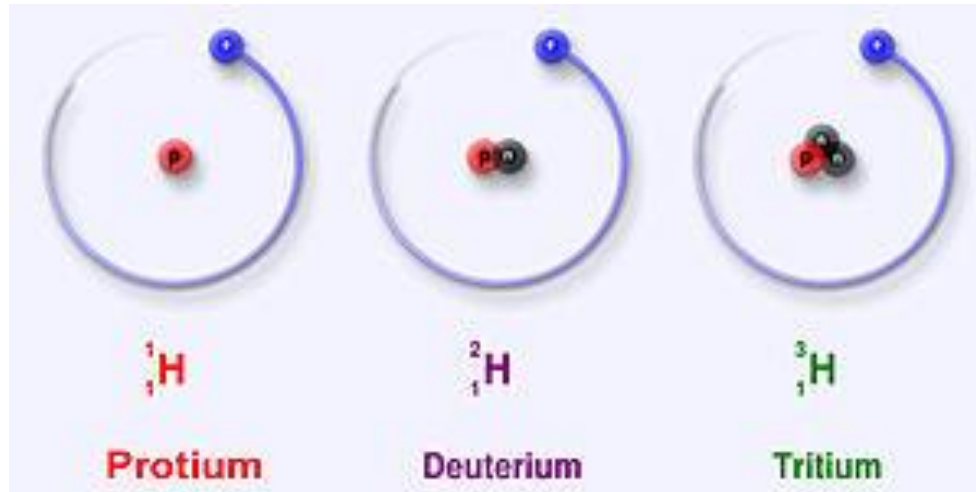**Jean-François Dufrêche**
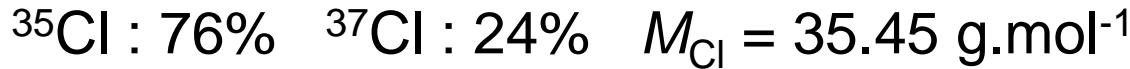
Isotopic effects
&
Separation Chemistry

What's the matter ?

Isotopes

- same proton number (atomic number Z)
- different neutron number (A-Z)

Exemple: isotopes of chlorine.

^{35}Cl : 76% ^{37}Cl : 24% M_{Cl} = 35.45 g.mol^{-1}

Lavoisier (1743-1794)

Chemistry is based on the concept of elements (first lists of elements)

In chemistry, Z matters, not A

Do isotopes have the same chemical properties ?

Noms nouveaux.	Noms anciens correspondans.
Lumière	Lumière.
Calorique	Chaleur.
	Principe de la chaleur.
	Fluide igné.
	Feu.
	Matière du feu & de la chaleur.
Oxygène	Air déphlogistiqué.
	Air empiréal.
	Air vital.
	Base de l'air vital.
Azote	Gaz phlogistiqué.
	Mofète.
	Base de la mofète.
Hydrogène	Gaz inflammable.
	Base du gaz inflammable.
Soufre	Soufre.
Phosphore	Phosphore.
Carbone	Charbon pur.
Radical muriatique .	Inconnu. = Cl
Radical fluorique . . .	Inconnu.
Radical boracique . .	Inconnu.
Antimoine	Antimoine.
Argent	Argent.
Arsenic	Arsenic.
Bismuth	Bismuth.
Cobalt	Cobalt.
Cuivre	Cuivre.
Etain	Etain.
Fer	Fer.
Manganèse	Manganèse.
Mercure	Mercure.
Molybdène	Molybdène.
Nickel	Nickel.
Or	Or.
Platine	Platine.
Plomb	Plomb.
Tungstène	Tungstène.
Zinc	Zinc.
Chaux	Terre calcaire, chaux.
Magnésie	Magnésie, base du sel d'epsom.
Baryte	Barote, terre pesante.
Alumine	Argile, terre de l'alun, base de l'alun.
Silice	Terre filiceuse, terre vitrifiable.

Lavoisier (1789)

Microscopic description of matter for chemistry
-Interactions between atoms are due to electromagnetic forces
-Quantum treatment is mandatory for electrons (not nuclei)
-Nuclei spin effects are small
☞ isotopic effects are small because they do not modify the forces between the atoms

General theorem in statistical thermodynamics
Within the three latest assumptions, if classical mechanics is used for nuclei, thermodynamical properties do not depend of the isotopes. Only quantum effects (of nuclei) can lead to isotopic effects in chemistry (for equilibrium properties)

Newton's law: F = ma
The difference of mass changes the atom trajectories
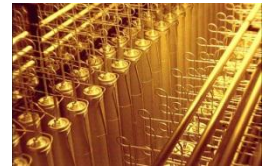☞ isotopic effects are presumably more important for transport properties

Enrichment methods

electromagnetic separation
(magnetic field: differential deflection s 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 etween 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 interaction modes between the phases)
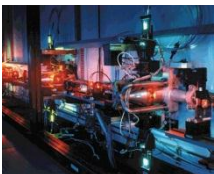
Laser separation
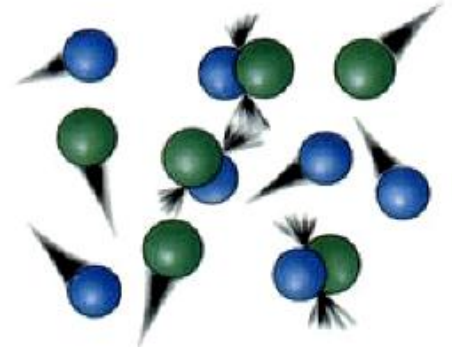(selective excitation of atoms or molecules)

Courtesy of S.Pellet-Rostaing

General idea (Maxwell)

Velocity is connected to temperature

$$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_{\mathrm{B}}T \;\triangleright\; \frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{1+\frac{(m_2-m_1)}{m_1}}$$

Hence

$$\frac{v_1}{v_2} \approx 1 + \frac{(m_2-m_1)}{2m_1} \approx 1 + \frac{\Delta m}{2m}$$

Application for $^{235}UF_6$ and $^{238}UF_6$: $v_1/v_2 = 1.004 \rightarrow 0.4\%$

Application for diffusion
Boltzmann's equation for gas implies: $D = \dfrac{3}{8\sqrt{p}}\sqrt{\dfrac{k_{\mathrm{B}}T}{m}}\dfrac{1}{s^2 r}$

☞ same mass dependency

True for ultracentrifugation velocities as well…

For a gas, dynamical isotopic effects read

$$\frac{X_1}{X_2} = \sqrt{\frac{m_2}{m_1}} \approx 1 + \frac{\Delta m}{2m}$$

X = dynamical quantity (*D*, mobility, *etc.)*

Dynamical effects for liquids

Isotopes are in a liquid (condensed phase)

Now, the mass dependence is different:
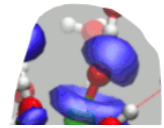
$$\frac{D_1}{D_2} \neq \sqrt{\frac{m_2}{m_1}}$$

Typically $D_i \propto m^a$ with $a \approx 0.1$

If the solute size is similar to the solvent. For a dynamical quantity:

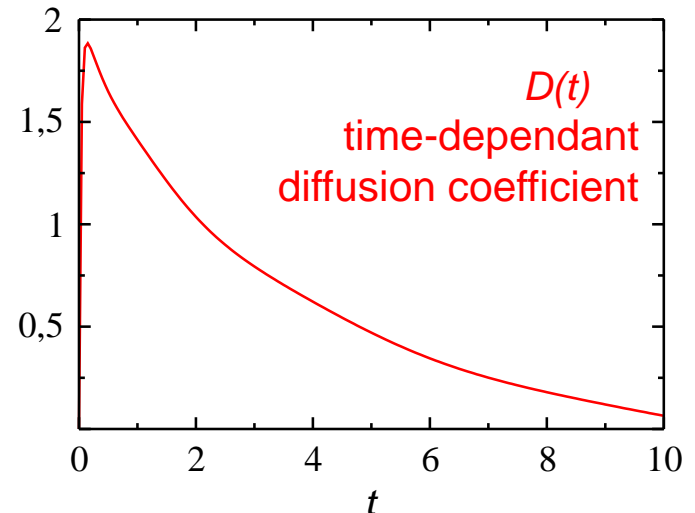$$\frac{X_1}{X_2} = \left(\frac{m_2}{m_1}\right)^a \approx 1 + a\frac{\Delta m}{m}$$

In case of uranium for example ($^{238}UO_2^{2+}$ and $^{235}UO_2^{2+}$ in water)

$$\Delta D \approx 0.1\ \% \rightarrow \text{very lo}$$

Why isotopic effects are **much lower** in **liquid** than in gas

- at short times, collisions → similar to gas → depends on the mass

- at long time, hydrodynamics streami → does not depend on the mass (Sto Einstein $D \approx k_B T/6\pi\eta R$ → no mass)

D(t) time-dependant diffusion coefficient

t

Heavy water and Normal water

D$_2$O and H$_2$O

How are they different ?

Very similar structure, both for the fluid and the molecule.

Similar equilibrium properties

Different transport properties

Role of rotational dynamics

Isotopic effects are important for internal degrees of freedom (rotation, vibration, etc.)

Property	D$_2$O	H$_2$O
Bond length / Angstrom	0.98	0.99
Angle	106°	106°
Dipole moment / D	1.87	1.86
Molar volume / mL.mol^{-1}	18.1	18.0
Isothermal compressibility / GPa^{-1}	0.476	0.460
Dielectric constant	78.3	78.4
pH	7.43	7.00
Surface tension / mN.m^{-1}	71.87	71.98
Heat of fusion / kJ.mol^{-1}	6.132	6.007
Heat of vaporisation / id.	41.52	40.66
Melting point / ^{o}C	3.82	0.0
Boiling point / ^{o}C	101.4	100.0
Diffusion coefficient / 10^{-9} m^2.s^{-1}	2.11	2.30
Dynamic viscosity / mPa.s	1.10	0.891
Moment of inertia / 10^{-40} g.cm^2	1.84	1.02
D (H$^+$) or D(D$^+$) / 10^{-9} m^2.s^{-1}	6.5	9.3

at 25 ^{o}C and 1 bar if not specified
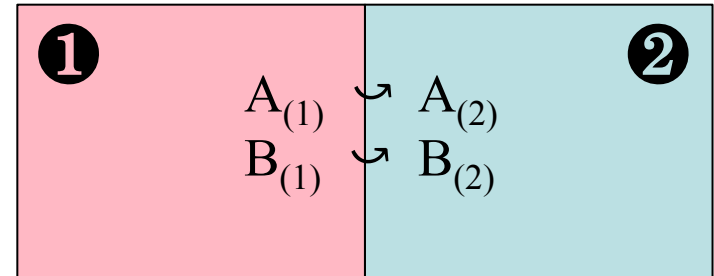
Chemical equilibrium

Two isotopes A and B
Two "media" (solvent (extraction),
Ligand (complexation), etc.) 1 and 2

$$A_{(1)} \searrow A_{(2)}$$
$$B_{(1)} \searrow B_{(2)}$$

❶ **❷**

Two equilibria:

$$A_{(1)} = A_{(2)} \quad K^0_A$$
$$B_{(1)} = B_{(2)} \quad K^0_B$$

If the isotope are dilute:

$$K^0_A = \frac{\left[A_{(2)}\right]}{\left[A_{(1)}\right]}, \quad K^0_B = \frac{\left[B_{(2)}\right]}{\left[B_{(1)}\right]}$$

$(K^0_A$ close to $K^0_B)$
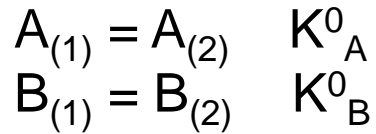
Enrichment factor

$$a = \frac{\left[A_{(2)}\right]/\left[A_{(1)}\right]}{\left[B_{(2)}\right]/\left[B_{(1)}\right]} = \frac{K^0_A}{K^0_B}$$

close to 1

Generally, results expressed in terms of:

$$e = a - 1$$

Chemical equilibrium

In terms of free enthalpy:

$$a = \frac{K_A^0}{K_B^0} = e^{\left(-D_r G_A^0 + D_r G_B^0\right)/k_B T}$$

Thus:

$$e = a - 1 \approx \ln a = \frac{D_r G_B^0 - D_r G_A^0}{k_B T}$$

It can be expressed in terms of standard chemical potentials:

$$e = \frac{m_{B2}^0 - m_{B1}^0 - m_{A2}^0 + m_{A1}^0}{k_B T} = \frac{1}{k_B T}\left[\left(m_{B2}^0 - m_{A2}^0\right) - \left(m_{B1}^0 - m_{A1}^0\right)\right]$$

The enrichment factor is nothing but ΔΔG⁰ in $k_B T$ unit:

$$e = \frac{DDG^0}{k_B T} \qquad \left(= \frac{\left[\left(m_{B2}^0 - m_{A2}^0\right) - \left(m_{B1}^0 - m_{A1}^0\right)\right]}{k_B T}\right)$$
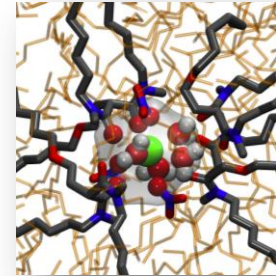
The separation factor is the difference of the difference in free enthalpy in the two media.

Chemical equilibrium

Calculation of μ^0_{A1} standard free enthalpy of isotope A in the environment 1. We have:

$$m^0_{A1} = G^A_{\text{aggregate}} + C$$

$G^a_{\text{aggregate}}$ is the free enthalpy of the aggregate around A in the media (calculation similar to a solvation term).
C is a gas phase reference term which can be omitted because the terms cancel out for the global enrichment factor

Isotopic effects directly comes from the free energy of the aggregates in the two media ($F \approx G$ in a condensed phase)

In the canonical ensemble:

$$G^A_{\text{aggregate}} = F^A_{\text{aggregate}} = -k_B T \ln Z = -k_B T \ln \sum_i \exp(-E_i / k_B T)$$

i represents the various states of the aggregate with energy E_i

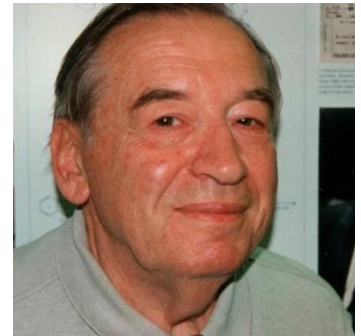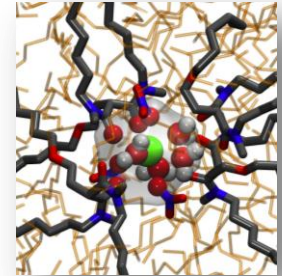Free energy of the aggregate around the isotope

The total energy of the aggregate is the sum of several
Contributions:

$$E = \underbrace{E_{rot} + E_{vib}}_{\text{nuclei energy}} + \underbrace{E_{coupling}}_{\text{electron energy}}$$

E_{rot}: rotational energy of the agregate
E_{vib}: vibrational energy of the agregate
$E_{coupling}$: represent the change of energy levels of electrons
because of the interactions with the nuclei

J. Bigeleisen (1919-2010)

Typically, there are two effects for $E_{coupling}$
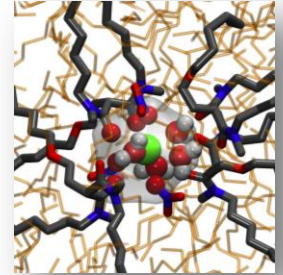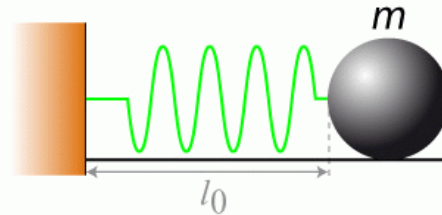- Change of the shape of the nuclei (which translates the level of
energy in the atom)
- Change of the spin of the nuclei (which modifies the hyperfine
structure of the atoms)

The three effects result in three terms in the enrichment factor.

Oscillator model (1947)

$$E = \frac{1}{2}kx^2 + \frac{p^2}{2m}$$

It is typically a mass effect.

Around equilibrium, the contribution for the free energy reads

$$e = \frac{1}{24}\left(\frac{h}{k_B T}\right)^2 \frac{\mathrm{D}m}{m_{ave}^2} k$$

k is the rigidity of the vibration force. At first order approximation, it is related to the second derivative of the interaction potential:

$$k = \langle \mathrm{D}U \rangle$$

More precisely it is the Laplacian of the intermolecular potential

Note the fact that h is in the formula → quantum effect in fact

Fine model (1996)

1 Change of the shape of the nuclei

The charge distribution is not spherical for any nucleus. So it modifies the electron/nucleus energy by a constant factor (shift In the energy) which depends on the charge distribution in the nucleus
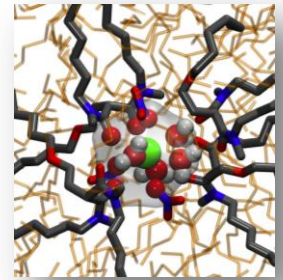
$$E' = E + \Delta E \Rightarrow G' = G + Cte$$

Thus for the contribution to the enrichment factor is

$$e = \frac{\Delta\Delta G^0}{k_B T} = \frac{B}{k_B T}$$

To first order appoximation, B is proportionnal to the square of the average raidus of charge in the nuclei δr^2

2 Change of the spin of the nuclei
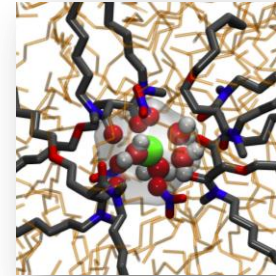
The nuclei spin changes the hyperfine structure of the energy levels. Difficult to predict. Perturbation term c_{hfs}
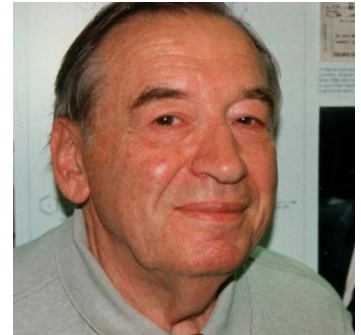
Free energy of the aggregate around the isotope

The three contributions can be added
(perturbation method).

So:

$$e = a\frac{Dm}{m_{ave}^2}\frac{1}{T^2} + b\frac{dr^2}{T} + c_{hfs}\frac{1}{T}$$

Conclusion: not that complicated !

J. Bigeleisen (1919-2010)