Institut Matériaux Microélectronique Nanosciences Provence

Diffusion dans les verres

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4ème atelier thermodynamique des verres 2019 du GDR TherMatHT- USTV

11 octobre 2019, Marcoule

References

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- **Review**
  - **Chakraborty, Diffusion in silicate melts, Rev. Mineral. Geochem. 1995**
  - **Faupel et al, Diffusion in Metallic Glasses and Supercooled Melts, Rev. Mod. Phys. 2003**
  - **Mehrer, Diffusion and Ion Conduction in Cation-Conducting Oxide Glasses, Diffus. Found. 2015**
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  - **H. Pablo, Diffusion chimique dans les verres borosilicates d’intérêt nucléaire, 2017.**
  - **C. Claireaux, Mobilité atomique dans les silicates vitreux et fondus, 2014.**

Diffusion dans les verres

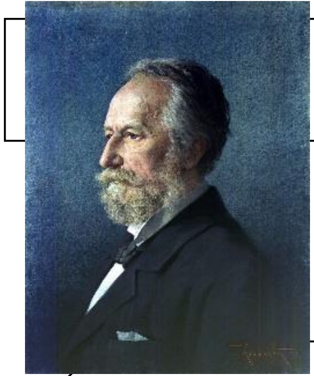
Rappel de diffusion

Diffusion dans les verres métalliques

Diffusion dans les verres d'oxydes

Diffusion chimique dans les verres d'oxydes.

Diffusion: a little bit of history



1 - **“ The law ”** - A. Fick - 1855

Salt in water (Phil. Mag. 10 (1855) 30)

“ It was quite natural to suppose that this law for the diffusion of salt in its solvent must be identical with that according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same which Ohm applied with such extraordinary success to the diffusion of electricity in a conductor ”

2 - **“ Solids diffuse in solids ”**

W. C. Roberts-Austen - 1889

Fe can be carburized by diamond in vacuum at low temp. (Nature 41 (1899) 14)

“ and I can measure it “

Au in Pb Phil. Trans. Roy. Soc. A187 (1896) 383

“ The following experiment constitutes so far as I am aware the first attempt to actually measure the diffusivity of one solid metal in another ”

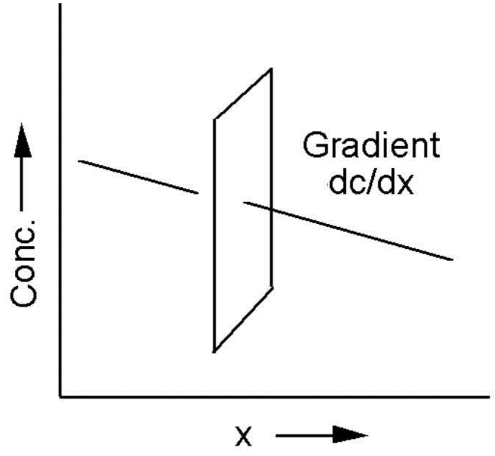
3 - **“Radioactive tracers ”** G. Hevesy - 1921

^{210}Pb in Pb J. Groh and G. v Hevesy Ann. Phys. 65 (1921) 216

Fick's first law of diffusion

- Fick proposed a relationship of diffusion of matter similar to Fourier's equation for heat. He proposed that the flux of particles is proportional to the gradient in concentration of particles. In one dimension this is written:

$$j = -D\frac{dc}{dx}$$



- The flux density *j* of particles has units e.g. #/(cm^{2}s) or mol/(cm^{2}s)

- The concentration is given in e.g. #/cm^3 or mol/cm^3

- The diffusion coefficient (or diffusion constant) then has units cm^2/s

- The minus sign states that the flux goes *down* the concentration gradient. The negative of the concentration gradient may be taken as the driving force.

Fick’s first law of diffusion - comments

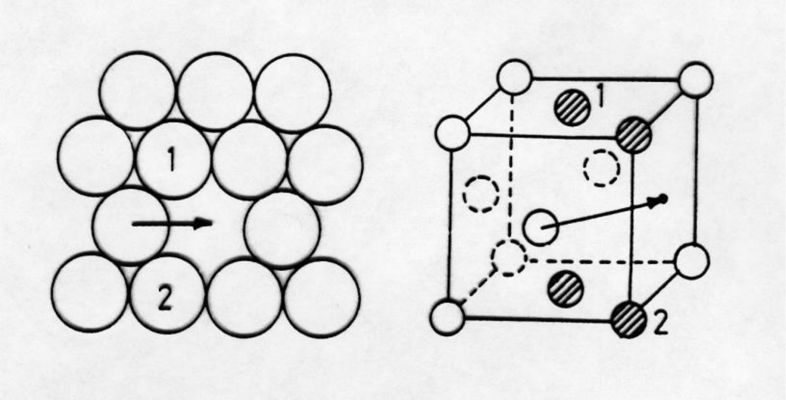
$$j = -D\frac{dc}{dx}$$

- Fick’s first law is a phenomenological – or empirical – expression; It describes a flux in terms of a concentration gradient and a proportionality coefficient – the diffusion constant, or diffusivity.
- However, Fick’s first law applies strictly only to neutral non-interacting particles. Examples comprise dilute solutions of interstitial atoms, e.g. atomic H in metals.
- For other situations, the coefficient in Fick’s first law is not a constant.
- *D* in Fick’s first law has not been given any physical meaning up to now. In the next, we will give it more content.
- Fick’s law is useful because, in experiments, it is easier to determine the composition

Diffusion: how atoms can move in a cristal ?

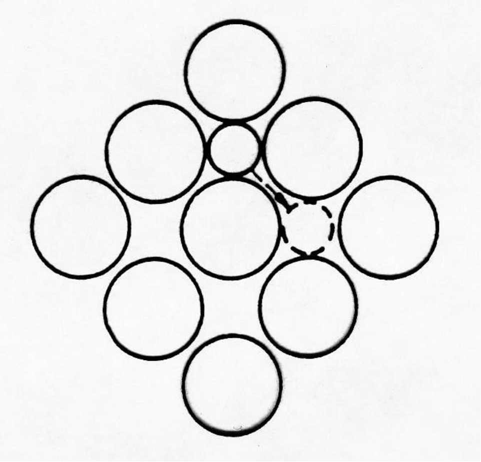
Because of point defects
(lattice perturbation with a size in the order of the atomic volume)

Atoms oscillate around a given lattice site of minimum energy (mean vibration energy ~ 3kT) but their movement is limited by their neighbors except if a vacant site exist in their vicinity



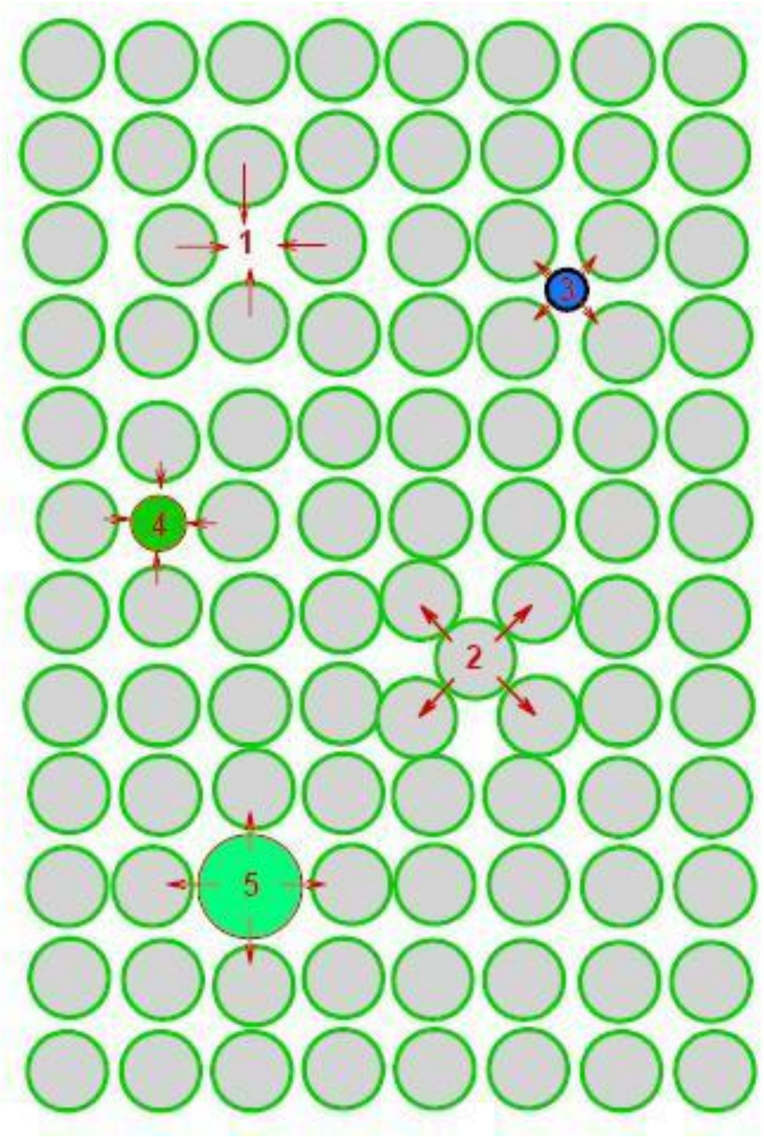
The diffusion rate depends on the jump frequency and the vacancy concentration

If the solute atoms are smaller than the atoms of the matrix, they can use interstitial sites



Diffusion rate depends only on the jump frequency

Point defects: examples



(1) Vacancy ⇒ V

(2) Self-interstitial ⇒ I

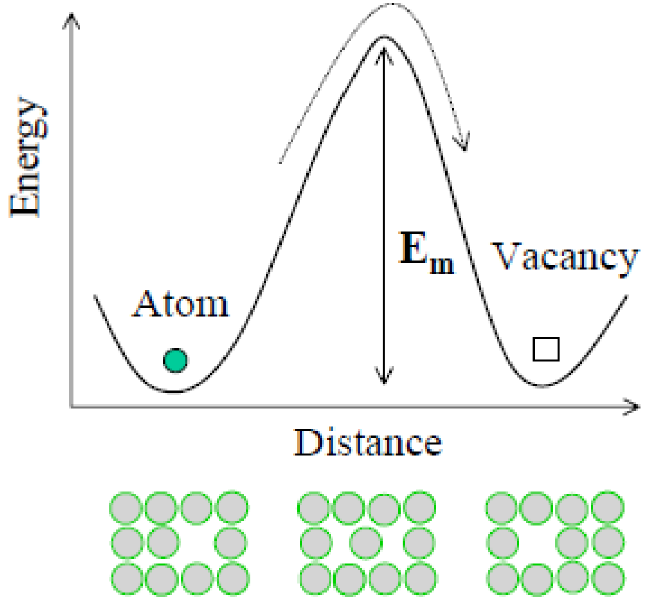
(3) Interstitial impurity ⇒ A_i

(4), (5) substitutional impurity ⇒ A_s

Arrows show the local stress introduced by the point defects

Diffusion – Thermally Activated Process (I)

In order for atom to jump into a vacancy site, it needs to posses enough energy (thermal energy) to to break the bonds and squeeze through its neighbors. The energy necessary for motion, E_m, is called **the activation energy** for vacancy motion.



Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy E_m has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.

$$D_d = \beta \, \Gamma a^2 = \beta a^2 \nu_0 \exp\left[-\frac{\Delta G_m}{kT}\right]$$

$$D_d = \beta a^2 \nu_0 \exp\left(\frac{\Delta S_m}{k}\right) \exp\left[-\frac{E_m}{kT}\right]$$

$$D_d = D_0 \exp\left[-\frac{E_m}{kT}\right]$$

β: geometrical factor
a: jump distance
ν_0: attempt frequency (~10^{13} s^{-1})
ΔG_m: free enthalpy of migration
E_m: migration energy

D_0 ~ 10^{-2} cm^2 s^{-1}

Diffusion assisted by defect

$$D = p_d D_d$$ p_d=probability of defect

$$p_d = \frac{n_d}{N} = C_d = \exp\left[-\frac{E_f}{kT}\right]$$

$$D = D_0 \exp\left[-\frac{E_f + E_m}{kT}\right]$$

Variation with temperature

$$\boxed{D = n_d \Gamma a^2}$$

$$n_d = p_d = c_d = c_0 \exp\left(-\frac{\Delta H_f}{kT}\right)$$

$$\Gamma = \nu_0 \exp\left(-\frac{\Delta H_m}{kT}\right)$$

$$D = D_0 \exp\left(-\frac{\Delta H}{kT}\right)$$

$\Delta H = \Delta H_f + \Delta H_m$ (= Q activation energy)

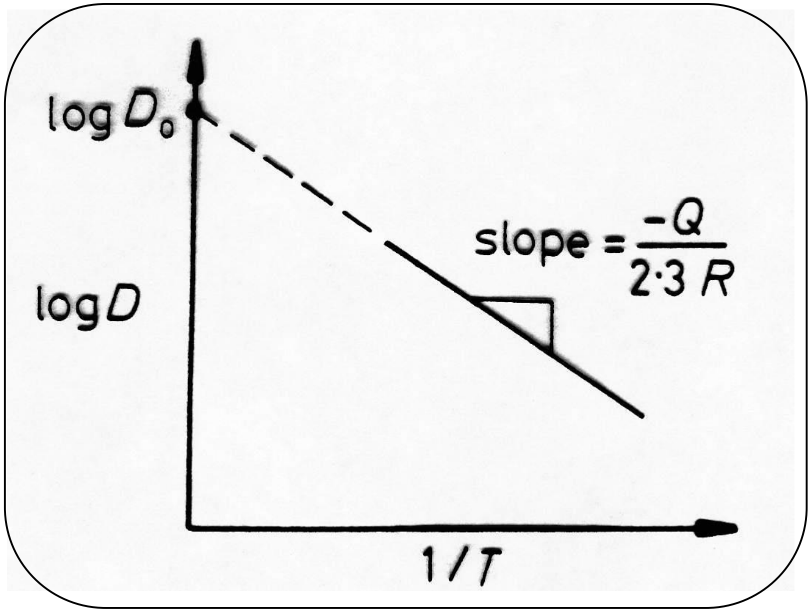
ΔH_f = enthalpy of formation of the defect

ΔH_m = enthalpy of migration of the defect

pure Interstitial: $\Delta H = \Delta H_m$

Vacancy: $\Delta H = \Delta H_m + \Delta H_f$

$\Delta G = \Delta H - T\Delta S$



Arrhenius plot

$D = C_d D_d = C_d D_{d\,0} \exp(-H_m/kT)$

D_d Diffusion coefficient of the defect

Correlation

Auto diffusion: $D = C_d D_d$

Tracer diffusion: $D^* = f\,D = f\,C_d\,D_d$

f = correlation factor

- f=1 for interstitial mechanism
- f<1 if diffusion vehicle: vacancy, divacancy, self-interstitiel
- f: complex function of T and C for alloys

→ Nastar et al , Phil. Mag. 2000

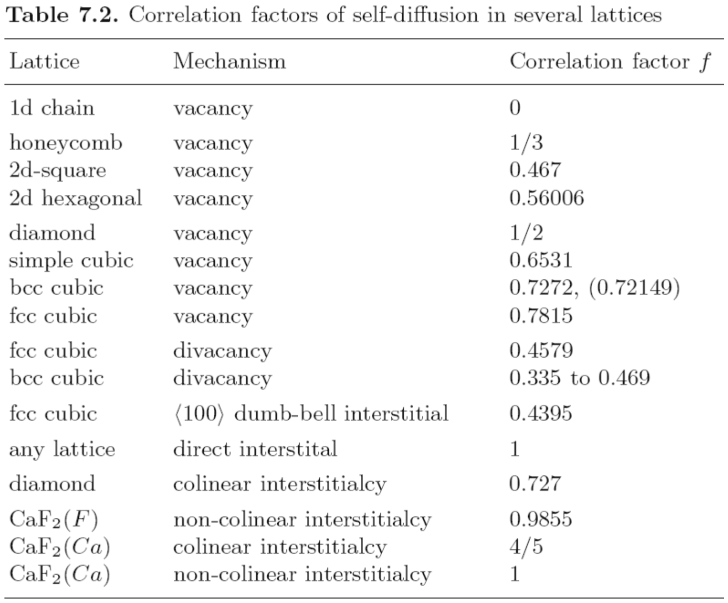


Table 7.2. Correlation factors of self-diffusion in several lattices

Lattice	Mechanism	Correlation factor *f*
1d chain	vacancy	0
honeycomb	vacancy	1/3
2d-square	vacancy	0.467
2d hexagonal	vacancy	0.56006
diamond	vacancy	1/2
simple cubic	vacancy	0.6531
bcc cubic	vacancy	0.7272, (0.72149)
fcc cubic	vacancy	0.7815
fcc cubic	divacancy	0.4579
bcc cubic	divacancy	0.335 to 0.469
fcc cubic	⟨100⟩ dumb-bell interstitial	0.4395
any lattice	direct interstital	1
diamond	colinear interstitialcy	0.727
$CaF_2(F)$	non-colinear interstitialcy	0.9855
$CaF_2(Ca)$	colinear interstitialcy	4/5
$CaF_2(Ca)$	non-colinear interstitialcy	1

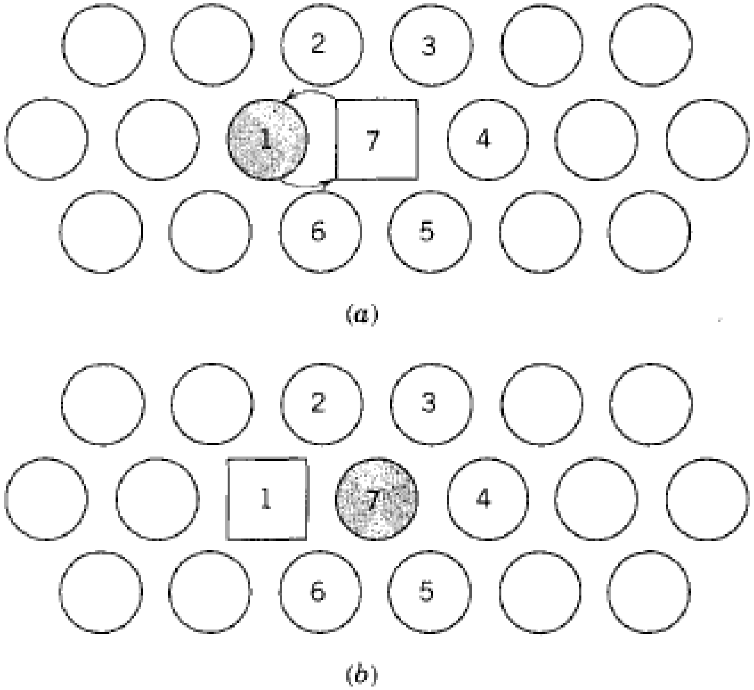


Fig. 3.7 Schematic depicting correlation effect for diffusion in a 2-D hexagonal lattice. After the atom at 1 exchanges with the vacancy at 7, there is a finite probability that the next jump will return the atom to its original position. If the atom is chemically indistinguishable from the host lattice atoms, as for a tracer atom, this probability is 1/6 in this lattice.

Diffusion: atomistic approach

$D = p_d \Gamma a^2$

a: jump distance

p: probability to find a defect

Γ: jump rate

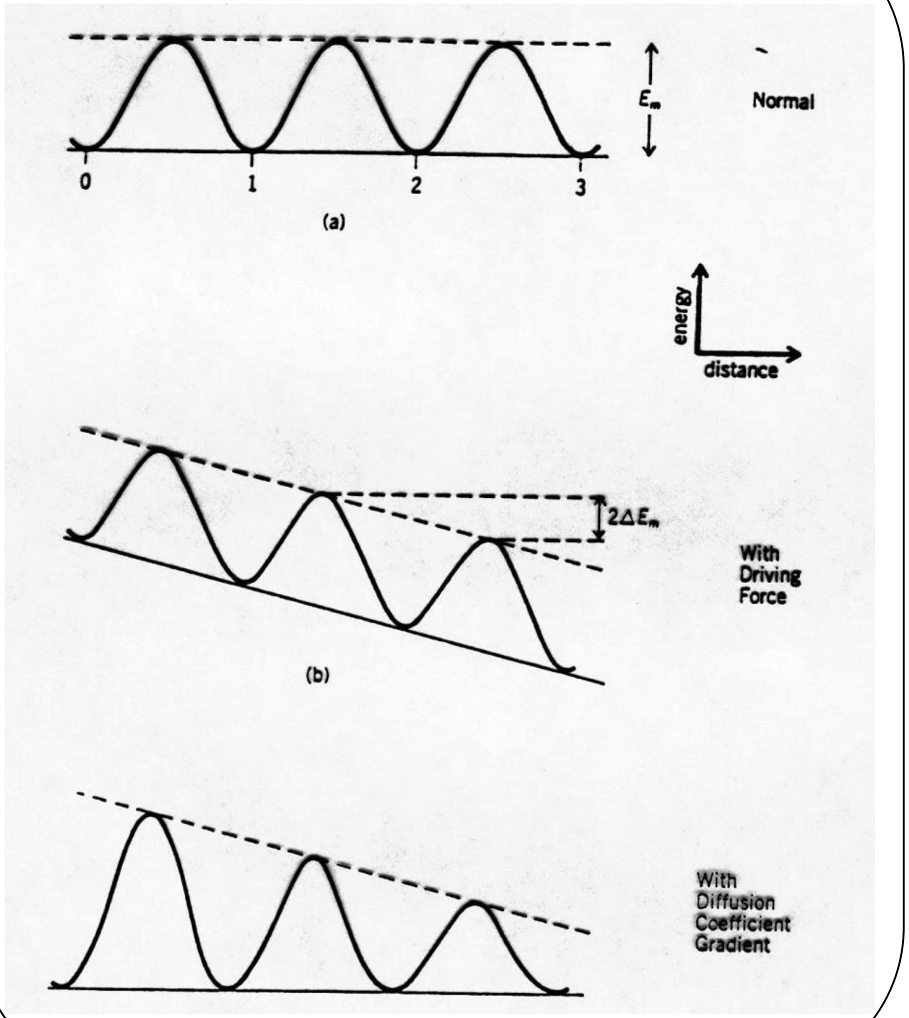
Everything which affects Γ and p will affect D

The mass transport is characterized by the flux

Quantity of atoms which pass a surface unit in unit of time

Nernst Einstein relation:

$$J = \frac{CD}{kT} F$$



Diffusion flux, mobility, Onsager

J (at s^{-1}): particle flux = number of particles that are going through a surface unit (section) per time unit

$$J = CMF = LF$$

J proportional to the number of particles (C) and to their mobility (M) or J proportional to L (Onsager coefficient)

$$J = \frac{CD}{kT} F$$

C: particle concentration in the matrix, *F*: driving force

$$D = M k_B T$$

M: mobility of uncharged particles in a given matrix ,
1/*M*: friction coefficient, v=*M*×*F* = particles' velocity (m s^{-1})

$$D = \frac{L\, k_B T}{C}$$

D ($m^2\ s^{-1}$): diffusion coefficient

If several mechanisms and/or diffusion paths with different mobility:

$$J_i = \sum_k C_k M_k F_k$$

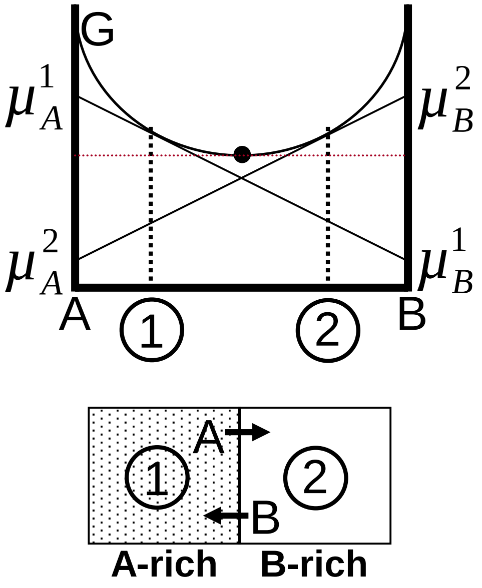
k: mechanisms, paths

If several components (elements, vacancy…), Onsager equations:

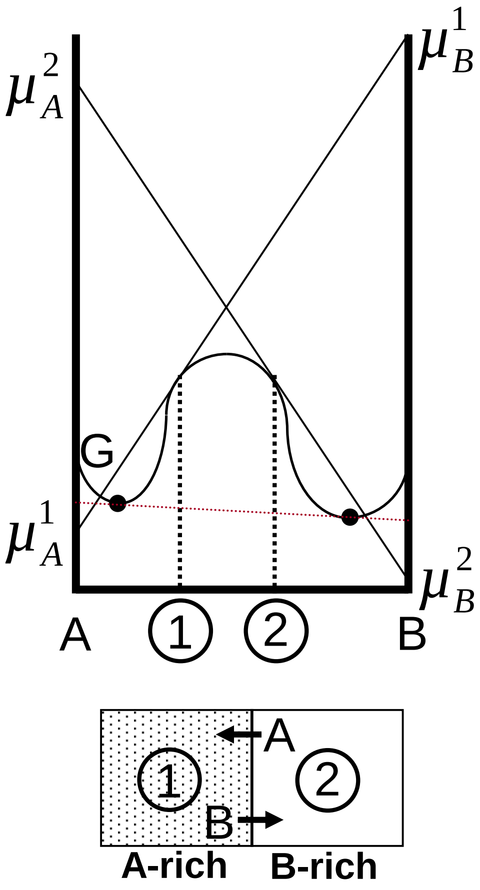
$$J_i = \sum_j L_{ij} F_j$$

j: components

Driving force: an example



Down hill “classical” diffusion



Up-hill diffusion
(spinodal decomposition)

Chemical diffusion in **binary system**

Driving force =
difference of chemical potential

$$F = -\frac{\partial \mu}{\partial x}$$

Nernst Einstein equation

$$J = -\frac{CD}{kT}\frac{\partial \mu}{\partial x}$$

Diffusion flux and diffusion equation

Driving force = minimum chemical potential $\Rightarrow$ $F = -\frac{d\mu}{dx}$

"–" $\Rightarrow$ atoms diffuse in the direction of decreasing chemical potential

$$J = -\frac{CD}{k_B T}\frac{d\mu}{dx}$$ Nernst-Einstein equation

$$J = -\frac{CD}{kT}\frac{\partial}{\partial x}\left(kT\ln(\gamma C)\right) = -D\left(\frac{\partial C}{\partial x}\left(1+\frac{\partial \ln\gamma}{\partial \ln C}\right)\right) = -\underset{\text{Kinetics}}{D}\overset{\text{Thermodynamics}}{\Phi}\frac{\partial C}{\partial x}$$

Φ is called the thermodynamic factor solution

$D_i = \Phi D$ is the intrinsic diffusion coefficient

Assuming *D* = constant and an ideal solution (or non-ideal diluted solution)
$\Rightarrow \gamma = 1$, $\mu = k_B T \ln(C)$

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

Fick's equation = random motion
diffusion depends only on concentration

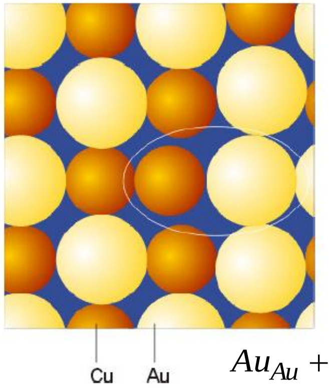
If the composition is constant $\Rightarrow \gamma = 1$, $\mu = k_B T \ln(C)$

Defects in oxides: Kröger-Vink notation

Schottky and Frenkel Defects:

Schottky defect : vacancies on both cation and anion sub-lattices. Because mass, site, and charge numbers remain balanced, these vacancies are always in stoichiometric ratio. Loss of ions within crystal lattice: density of the solid decreases.

Frenkel defect : vacancy on either cation or anion sub-lattice along with an interstitial site. Frenkel defect pairs maintain a balanced mass, site, and charge stoichiometric ratio. Since ions remain withinin the lattice, the density remains the same.



$$Au_{Au} + Cu_{Cu} = Au_{Cu} + Cu_{Au}$$

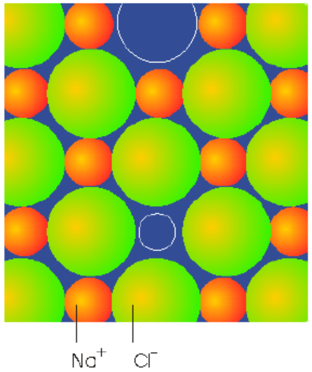
Anti-site in CuAu

Kröger-Vink Notation: M_S^C

M corresponds to the **species**, which can be ions (Na, Ag, O, Cl…), vacancies V, electrons e and electron holes h.

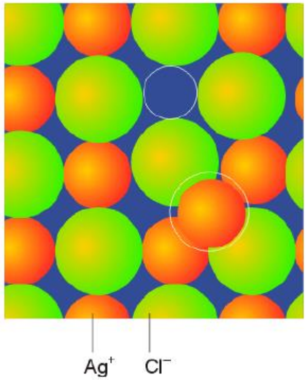
S indicates the lattice **site** that the species occupies. For instance, Au might occupy a Cu site. The site may also be a lattice interstice, in this case the symbol « ***i*** » is used.

C corresponds to the **charge** of the species relative to the occupied site. To indicate zero charge, **×** is sometimes used. **•** indicates a positive charge, while **′** signifies a negative charge.



$$nil = V_{Na}' + V_{Cl}^{\bullet}$$

Schottky disorder in NaCl



$$Ag_{Ag} = V_{Ag}' + Ag_i^{\bullet}$$

Frenkel disorder in AgCl

Defect reactions: imperative to keep mass, site, and charge balance in each reaction (mass conservation and electro-neutrality).

Nernst-Einstein equation for charged particules

General transport equation:
linear relation between flux *J* and driving force, gradient of electrochemical potential *η*,
both **chemical (μ) and electrical (ϕ) potentials can act as driving forces** (L: Onsager coefficient):

$$\boxed{J = -L\nabla\eta = -L\nabla\mu - LF_a\nabla\phi}$$

Uncharged species: only chemical potential term relevant, process reduced to pure diffusion:

$$J = -L\nabla\mu = -\frac{RTL}{c}\nabla c$$

Comparison with Fick's first law permits to identify:

$$\boxed{L = \frac{Dc}{RT}}$$

Conversely, if no noticeable chemical potential variation: electrical field remains only driving force.
Fulfilled for solids with high charge carrier concentrations:
metals, fast ion conductors, highly doped systems!

$$J = -LF_a\nabla\phi$$

Converting the particle flux into a current density:

$$i = FJ = -LF_a{}^2\nabla\phi$$

Ohm's law: $LF_a{}^2$ corresponds to electrical conductivity

$$\boxed{\sigma = LF_a{}^2 = F_a{}^2\frac{Dc}{RT}}$$

Electrical conductivity σ: F_a Faraday constant (96500 C/mol), *u* mobility, *c* concentration

$$\boxed{\sigma = F_a uc}$$

Nernst-Einstein equation between diffusion coefficient and mobility (in $cm^2.s^{-1}V^{-1}$):

$$\boxed{u = \frac{F_a D}{RT}}$$

Definition of various diffusion coefficients

1. Composition is constant

Self-diffusion coefficient: D_A

Tracer diffusion coefficient: D_A^*

$$D_A^* = f \cdot D_A$$

Correlation coefficient: f (Z: coordination number)

$$f \approx 1 - \frac{2}{Z}$$

Defect diffusion coefficient: D_d ([d]: molar fraction of defects)

$$D_A = \sum_d D_d [d]$$

2. Composition changes (chemical diffusion)

Intrinsic diffusion coefficient: $D_{A,AB}$

$$D_{A,AB} = D_A . \Phi$$

Chemical diffusion (interdiffusion) coefficient: $\check{D}$

Darken equation:

$$\check{D} = x_A . D_{B,AB} + x_B . D_{A,AB}$$

Integrated diffusion coefficient (Wagner, Van Loo)

$$\tilde{D}^{\beta}_{\text{int}} = \int_{N_B^{\beta 1}}^{N_B^{\beta 2}} \tilde{D} \, dN_B$$

3. Ionic systems (ceramics)

Ambipolar diffusion: transport limited by the slower component (electroneutrality)

In oxides with predominant electronic conduction (transference number: $t_{el} >>> t_A$):

$\check{D} = t_{el} . D_A . \Phi$

Diffusion dans les verres

Rappel de diffusion

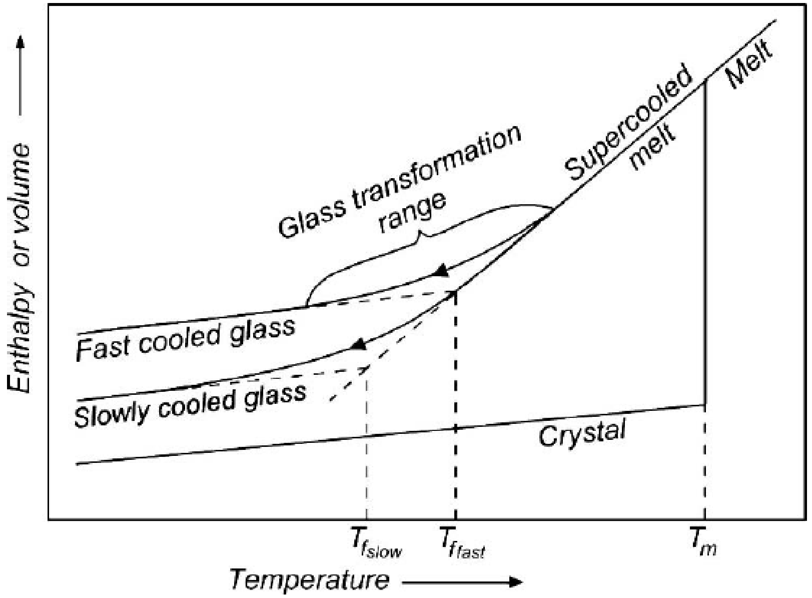
Diffusion dans les verres métalliques

Diffusion dans les verres d'oxydes

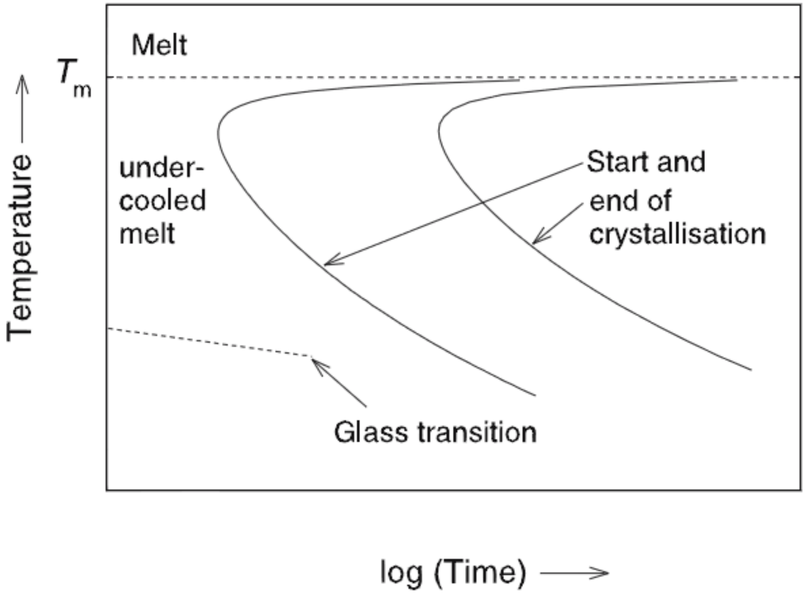
Diffusion chimique dans les verres d'oxydes.

Fabrication of a glass

Glass = metastable phase



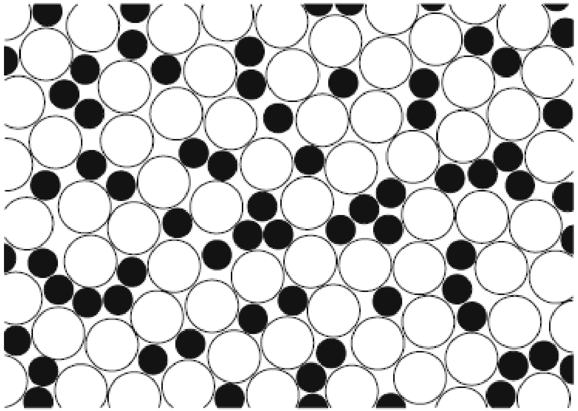
Volume (or enthalpy) versus temperature diagram of a glass-forming liquid



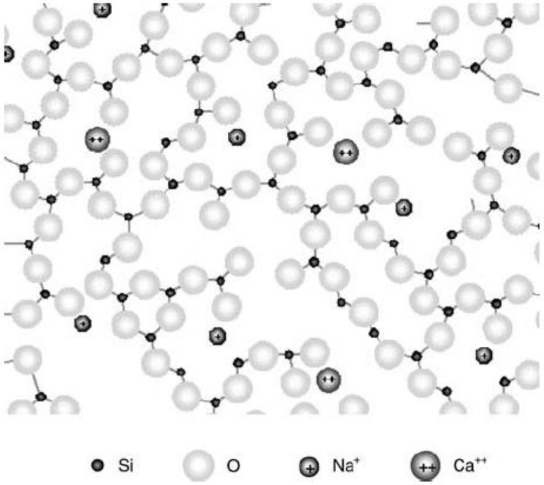
Schematic time-temperature-transformation diagram (TTT diagram) for the crystallisation of an undercooled melt

Different types of glasses [Mehrer 2007]

- **Vitreous silica (S** = SiO_2**)**
- **Soda-Lime Silicate Glasses (NCS** = Na_2O-CaO-SiO_2).
- **Borosilicate Glasses (BS** = SiO_2 - B_2O_3**-…)**
- **Lead Silicate Glasses** (PbO - SiO_2)
- **Aluminosilicate Glasses** (**AS** = SiO_2 - Al_2O_3)
- **Non-Silica-Based Glasses (**B_2O_3- and P_2O_5-)
- **Amorphous Semiconductors** (Si, Ge, P, As, tetrahedral glasses).
- **Metallic glasses (**$Pd_{80}Si_{20}$, $Ni_{80}P_{20}$, and $Fe_{40}Ni_{40}P_{14}B_6$)
- **Bulk metallic glasses (**Zr-Ti-Cu-Ni-Be, $Pd_{43}Cu_{27}Ni_{10}P_{20}$)
- **Bulk amorphous steels**
- **Organic Glasses**
- **Natural Glasses (**obsidian, **fulgarites, impactites)**



Structure of a binary metallic glass



Structure of a soda-lime silicate glass

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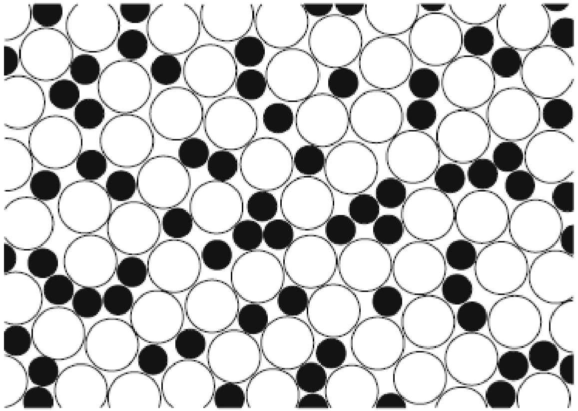

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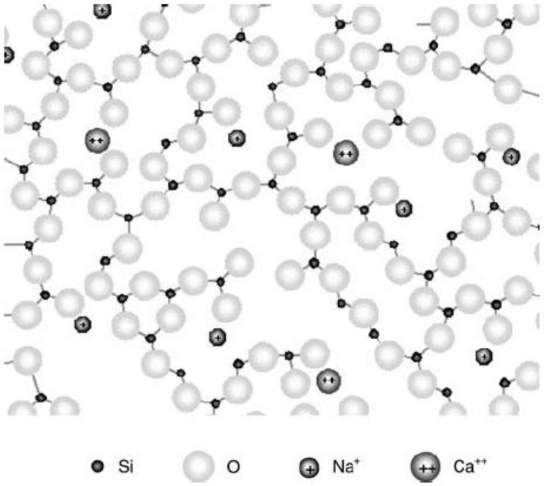
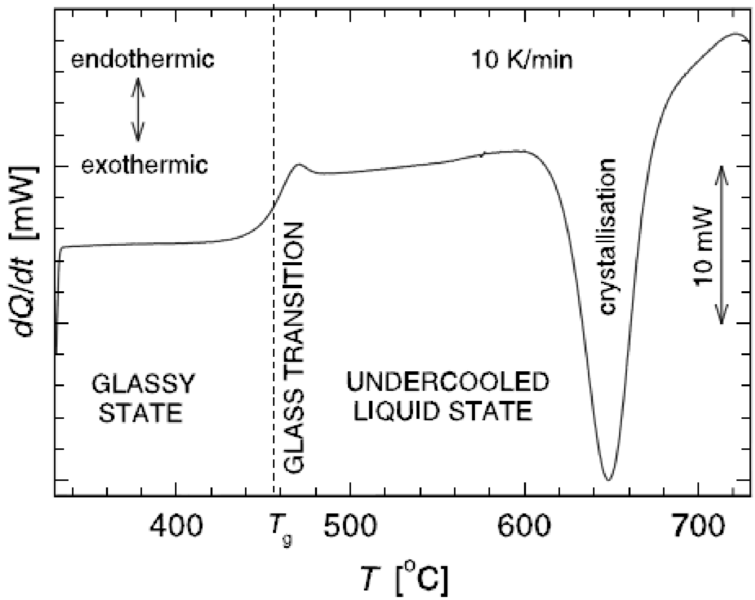


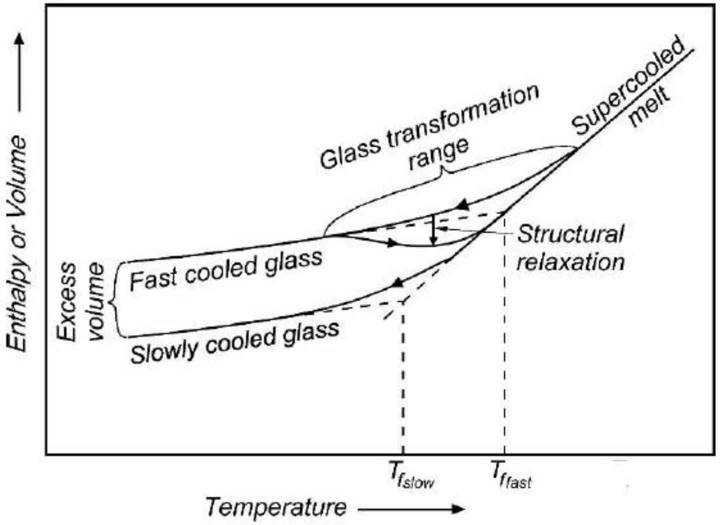
Structure of a soda-lime silicate glass

Stability of a glass

Diffusion experiment = heat treatment = evolution of glass



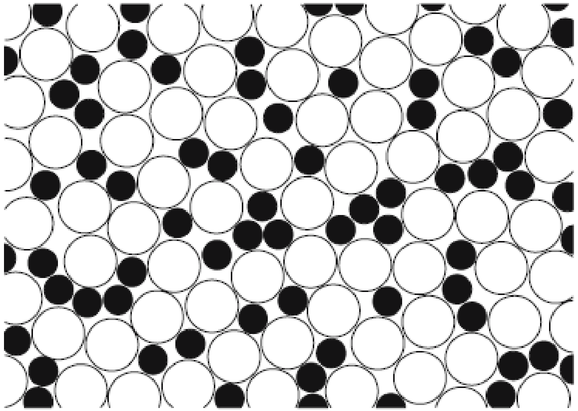
Differential Scanning Calorimetry (DSC) thermogram of a 0.2(0.8Na2O0.2Rb2O) 0.8B2O3 glass measured at a heating rate of 10K/min from [Imre et al 2002]. The glassy and undercooled liquid state are indicated.



Schematic illustration of structural relaxation in the V-T (or H-T) diagram of a glass-forming material

Questions about diffusion in glasses ?

- **Different behaviours below and above Tg?**
- **Liquid or solid behaviour**?
- **Same behaviour for metallic glasses and oxide glasses ? For all glasses?**
- **Same behaviour for the different constituting elements?**
- **Arrhenius behaviour?**
- **Type of defects?**
- **…**



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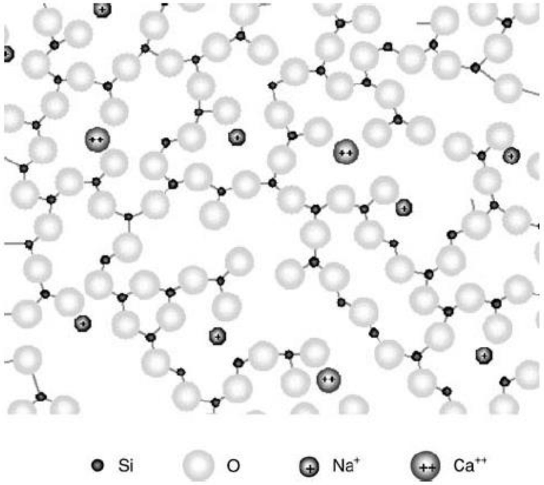
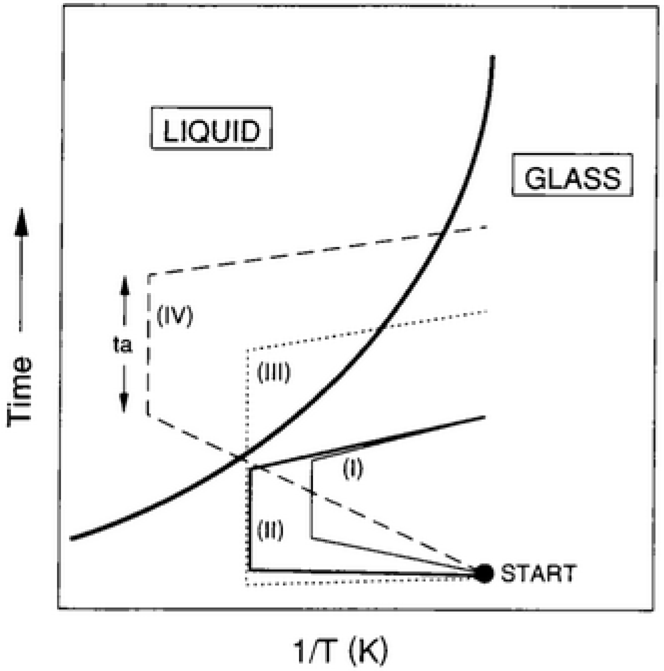


Structure of a soda-lime silicate glass

Difficulties in measuring diffusion

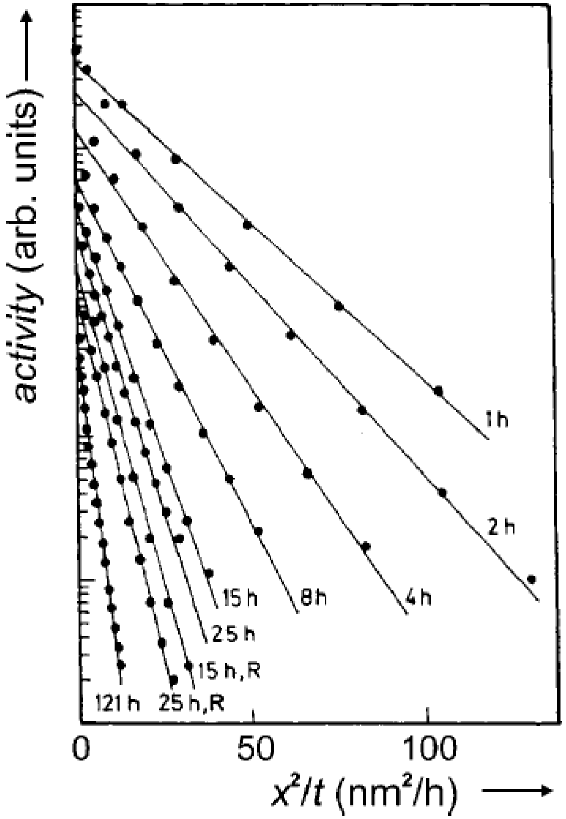
Difficulties [Chakraborty 1995, Pablo 2017, Claireaux 2014] :

- Sample preparation: bubles, shape, fragility…
- Handling
- Structural relaxation
- Convection
- …

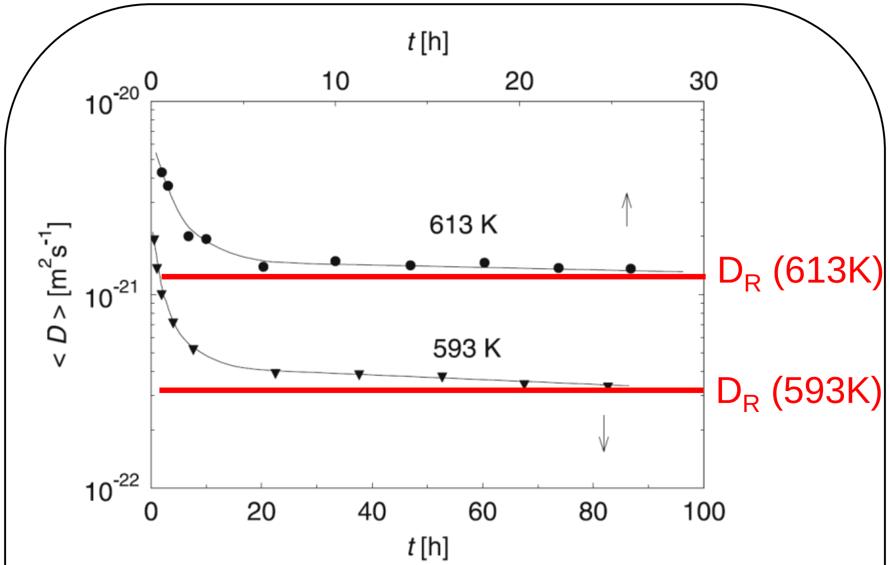


Relationship between thermal history and glass transition [Chakraborty 1995]

Diffusion in metallic glass : effect of relaxation



Diffusion profiles of 59Fe in as-quenched $Fe_{40}Ni_{40}B_{20}$ metallic glass measured after various annealing times at 593 K. (*R* = relaxation annealing before diffusion). [Horvath *et al* 1985]



Time-averaged diffusion coefficients of 59Fe in $Fe_{40}Ni_{40}B_{20}$ for various annealing times at 593 and 613 K. [Horvath *et al* 1985]

Time averaged diffusivity:

$$\overline{D}(t) = \frac{1}{t}\int_0^t D(t')dt'$$

Instantaneous diffusivity:

$$D(t) = \overline{D} + t\frac{d\overline{D}}{dt}$$

→ The diffusivity changes with time → $D_{relaxed}$ (D_R)

Arrhenius behavior in relaxed glasses

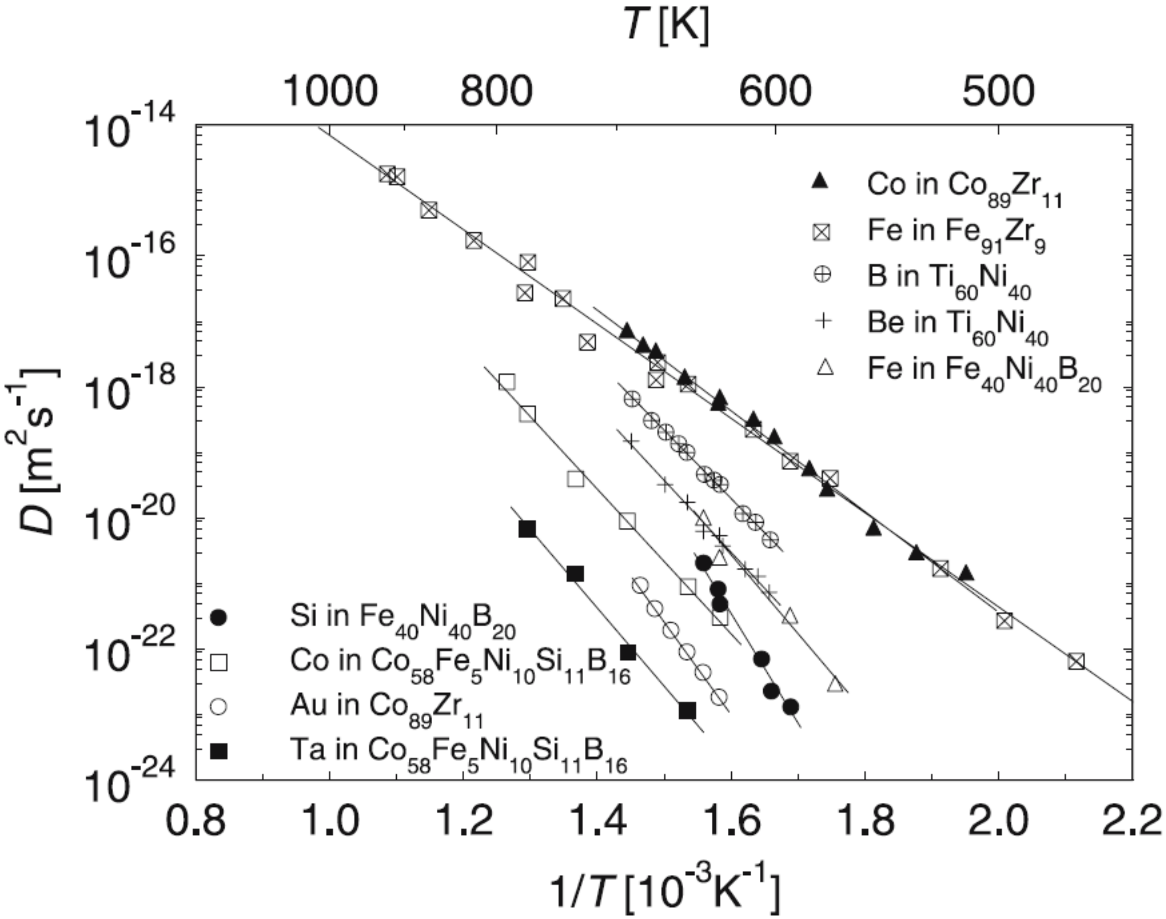
Arrhenius-type temperature dependence for structurally relaxed glassy state ?

$$D_R = D^0 exp\left(-\frac{\Delta H}{k_B T}\right)$$

- narrow height distribution of jump barriers in the disordered structure of an amorphous alloy?

- compensation effects between site and saddle-point disorder?

- Collectivity of the atom-transport mechanism leading to an averaging of disorder effects in the atomic migration process

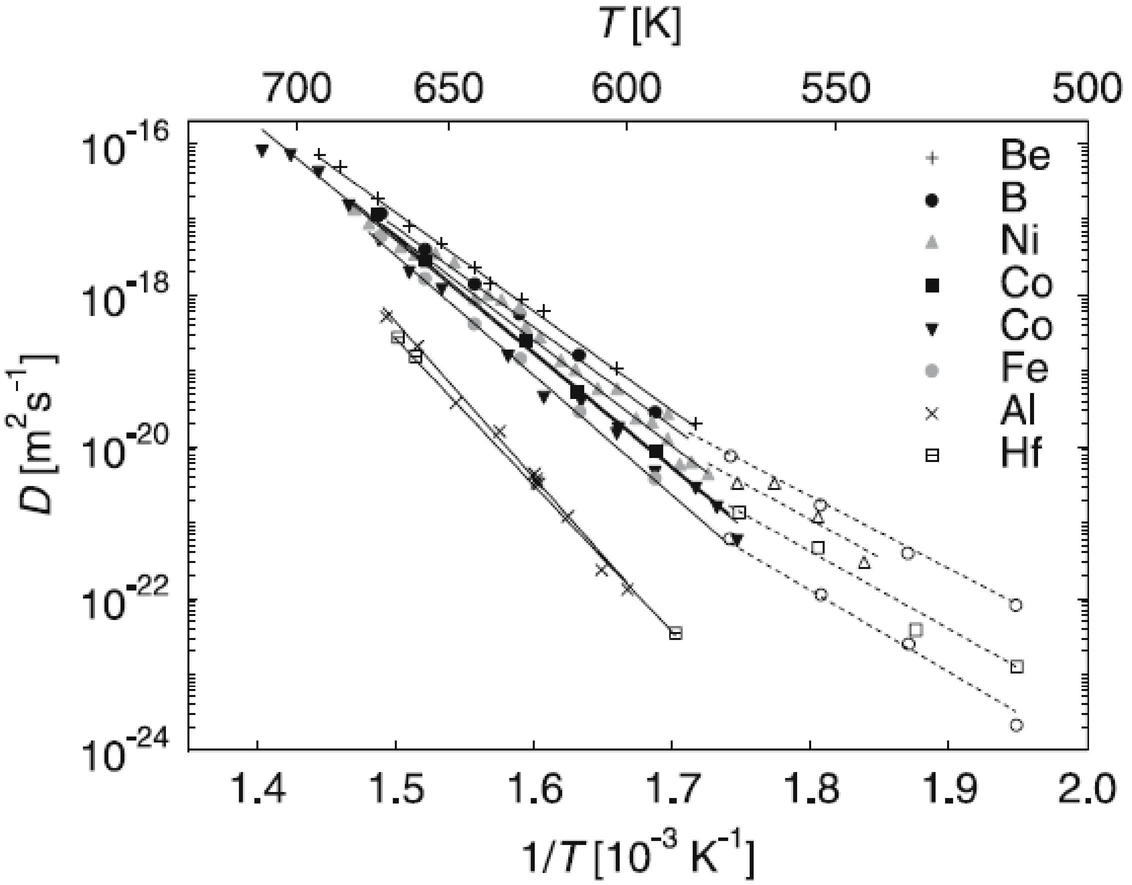


Arrhenius diagram of self- and impurity diffusion in relaxed metal-metalloid and metal-metal type conventional metallic glasses [Faupel et al. 2003]

→ Arrhenius behavior in most cases (up to 8 order of magnitude)

Diffusion in unrelaxed glasses

- Two different Arrhenius variation below and above a ‘kink temperature’.
- Higher activation enthalpies and pre-exponential factors in the supercooled liquid state than below the kink temperature.
- Higher kink temperatures separating the glassy and the supercooled region for faster diffusing elements in the amorphous state



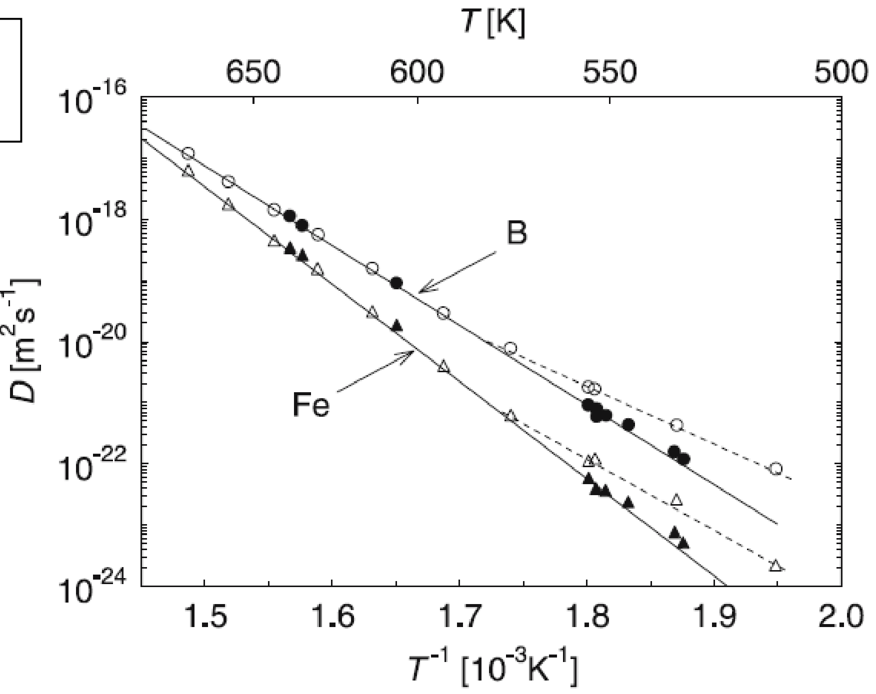
Arrhenius diagram of tracer diffusion of Be, B, Fe, Co, Ni, Hf in the bulk metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vitreloy4) [Faupel et al. 2003]

Relaxation and diffusion

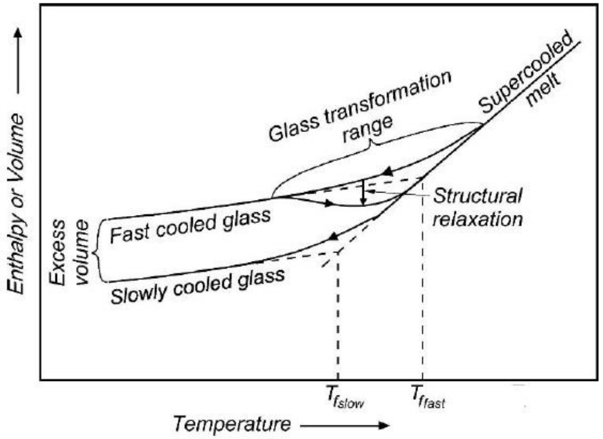
Difference between as cast and preannealed samples below Tg

- Sufficiently long annealing times → relaxation into the supercooled liquid state
- Below the calorimetric glass-transition temperature the diffusivities obtained after extended pre-annealing are smaller than those of the as-cast material
- In the high-temperature region the diffusivities of the as-cast and the pre-annealed material coincide.
- Furthermore, the diffusivities in the relaxed material can be described by one Arrhenius equation, which also fits the high-temperature data of the as-cast material.

→ the kink in the temperature dependence of the diffusivity is not related to a change in the diffusion mechanism but depends on the thermal history of the material. It is caused by incomplete relaxation to the state of the undercooled liquid.



Arrhenius diagram of tracer diffusion of B and Fe in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vitreloy4). Open symbols: as-cast material; filled symbols: pre-annealed material [Faupel et al. 2003]



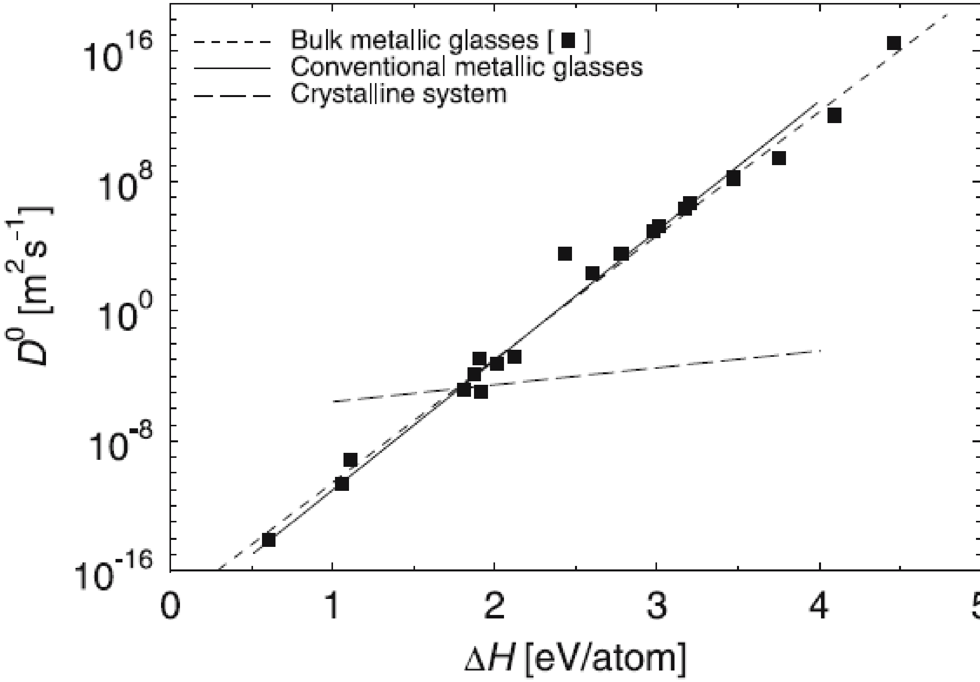
Schematic illustration of structural relaxation in the V-T (or H-T) diagram of a glass-forming material

Correlation between D_0 and ΔH

- The experimental values of D_0 and ΔH have been found to obey the following correlation “Meyer-Neldel rule”:

$$D_0 = A\ exp\left(\frac{\Delta H}{B}\right)$$

- Also valid for self- and impurity diffusion in crystalline metals and alloys involving both interstitial and substitutional diffusion
- Very different values for A and B for crystalline ($A \approx 10^{-7}$ $m^2\ s^{-1}$, $B \approx 0.41$ eV) and amorphous metals $A \approx 10^{-19}$ - 10^{-20} $m^2\ s^{-1}$, $B \approx 0.055$ eV.

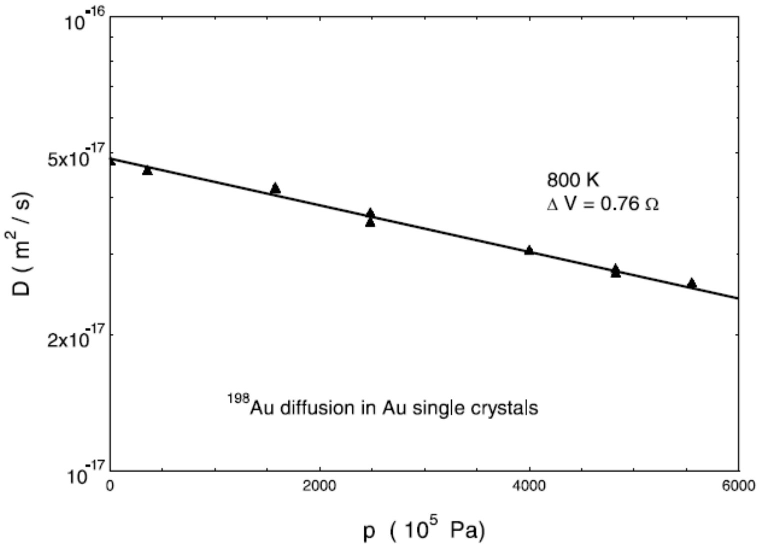


Correlation between D_0 and ΔH for amorphous and crystalline metals. Solid line=conventional metallic glasses; dotted line=bulk metallic glasses; dashed line=crystalline metals [Faupel et al. 2003]

→ different mechanism for metallic glasses and for the interstitial or vacancy mechanisms operating in crystals.

Pressure Dependence

- Pressure dependence of diffusion → activation volumes → diffusion mechanisms of crystalline solids.
- Intersitial diffusion : $V^{act} = V^{F} \approx 0.1\Omega$
- Defect-mediated diffusion
  - Activation volume = sum of the formation and migration volumes of the vacancy: $V^{act} = V^{F} + V^{M}$
  - Typical values of ΔV for vacancy between 0.5 Ω and 1 Ω (=atomic volume)



Pressure dependence of ^{198}Au diffusion in Au single crystals at constant temperature. Ω = atomic volume of Au [Mehrer 2007]

$$D = D^{0}\, exp\left(\frac{-\Delta G}{k_B T}\right)$$

ΔG = Gibbs energy of activation
D^0 = pre-factor without the entropy term.

$$\Delta G = \Delta H - T\Delta S = \Delta E + p\Delta V - T\Delta S$$

ΔH = activation enthalpy of diffusion,
ΔS =activation entropy,
ΔV =activation volume,
ΔE = activation energy.

$$\Delta V = \left(\frac{\partial \Delta H}{\partial p}\right)_T \qquad \Delta H = \Delta E + p\Delta V$$

$$D = D_0\, exp\left(\frac{-(\Delta E + p\Delta V\ )}{k_B T}\right)$$

$$D_0 = D^{0}\, exp(\Delta S / k_B)$$

For single-jump diffusion in a crystalline solid

$$V^{act} = \Delta V = -k_B T\left(\frac{\partial lnD}{\partial p}\right) + k_B T\left(\frac{\partial \ln(f g a^2 \nu_0)}{\partial p}\right)_T$$

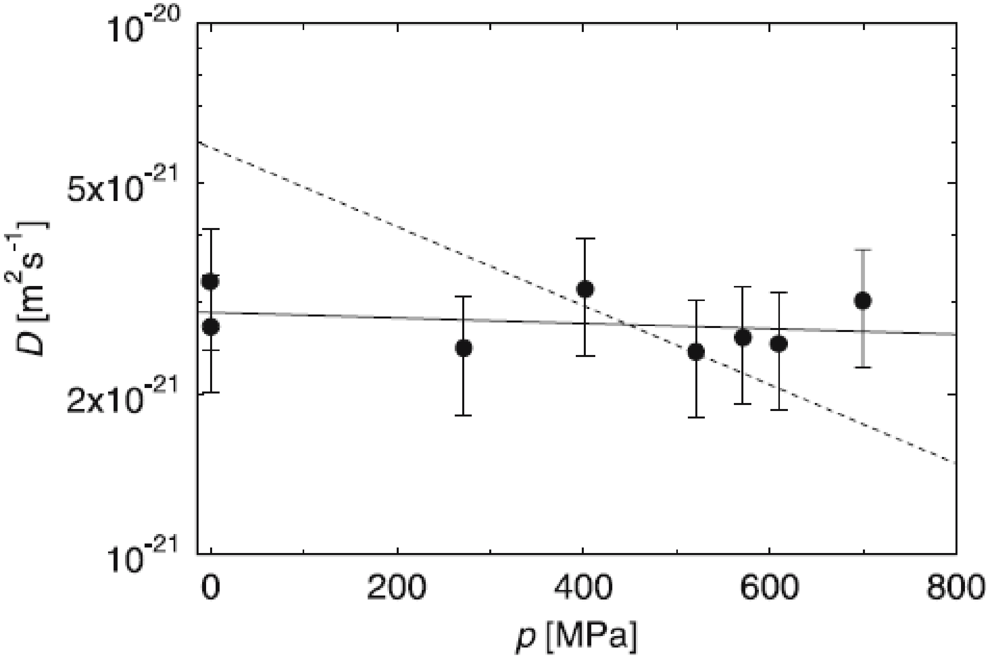
$$V^{act} \approx -k_B T\left(\frac{\partial lnD}{\partial p}\right)$$

Pressure Dependence in metallic glasses

Two categories for pressure dependence of diffusion in metallic glasses

- Systems with almost no pressure dependence: activation volumes close to zero
  - for metallic glasses, which mainly contain late transition elements and for tracers of similar size as the majority component.
  - No vacancy-mediated
  - diffusion mechanism without formation of a defect.
- Systems with significant pressure dependence: activation volumes comparable to those of vacancy-mediated diffusion in crystalline solids
  - for Zr-rich Co-Zr and Ni-Zr metallic glasses.
  - formation of diffusion mediating defects which are delocalized?
  - molecular dynamics simulations for Ni-Zr glasses = diffusion by thermally activated collective motion of chains of atoms

→ migration volume of chainlike motion with a significant activation volume?



Pressure dependence of Co diffusion in $Co_{81}Zr_{19}$ at 563K. The dashed line would corresponds to an activation volume of one atomic volume [Faupel et al. 2003]

Isotope effect

Isotope effect measurements → atomic mechanisms of diffusion in crystals

$$D_{i1}^* = A\omega_{i1} f_{i1} \qquad D_{i2}^* = A\omega_{i2} f_{i2} \qquad f_{i1}, f_{i2}: \text{correlation factors}$$

$$f_{i1} = \frac{u}{\omega_{i1} + u} \qquad f_{i2} = \frac{u}{\omega_{i2} + u} \qquad \rightarrow \qquad \frac{D_{i1}^* - D_{i2}^*}{D_{i2}^*} = f_{i1}\frac{\omega_{i1} - \omega_{i2}}{\omega_{i2}}$$

$$\omega_i = \nu_i^0 exp\left(\frac{-G_i^M}{k_B T}\right) \qquad G_{i1}^M = G_{i2}^M = G^M \qquad \frac{\omega_{i1}}{\omega_{i2}} = \frac{\nu_{i1}^0}{\nu_{i2}^0}$$

Einstein → $\frac{\nu_{i1}^0}{\nu_{i2}^0} \approx \sqrt{m_{i2}/m_{i1}}$ → $\frac{(D_{i1}^* - D_{i2}^*)/D_{i2}^*}{\sqrt{m_{i2}/m_{i1}} - 1} = f$

Classical statistical mechanics →

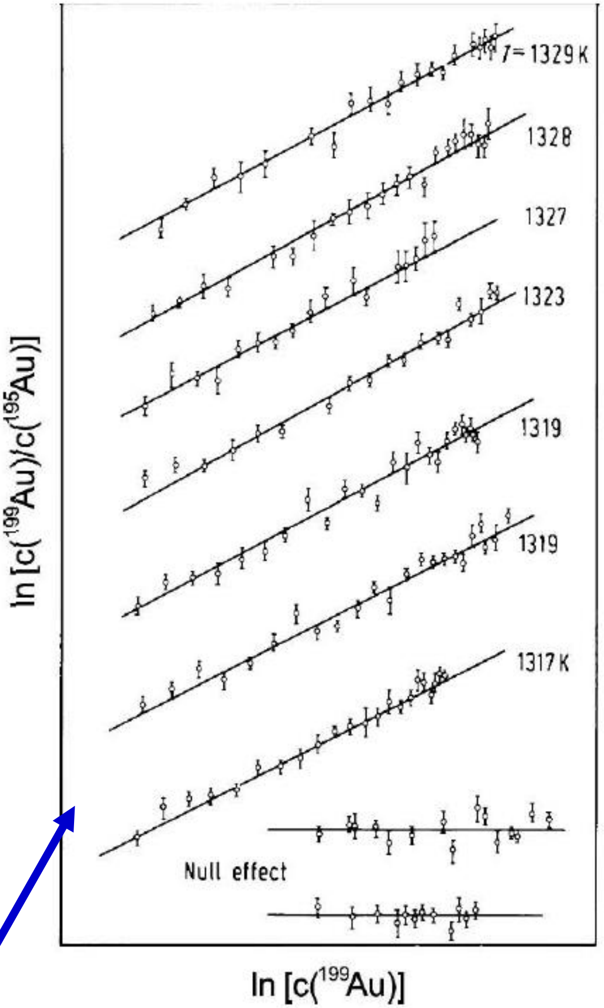
$$\frac{\omega_{i1} - \omega_{i2}}{\omega_{i2}} = \Delta K\left(\sqrt{m_{i2}/m_{i1}} - 1\right) \rightarrow \boxed{\frac{(D_{i1}^* - D_{i2}^*)/D_{i2}^*}{\sqrt{m_{i2}/m_{i1}} - 1} = f\Delta K = E}$$

$$\boxed{0 < E < 1}$$

Experiments → $C_i = C_i^0 exp\left(\frac{-x^2}{4D_i^* t}\right)$

$$\boxed{\ln\left(\frac{C_{i1}}{C_{i2}}\right) = const - \left(\frac{(D_{i1}^* - D_{i2}^*)}{D_{i2}^*}\right)\ln(C_{i1})}$$

$\boxed{E \approx 0.7 \approx f_{1V} = 0.78}$ → mono-vacancy



Simultaneous diffusion of the radioisotope pair ^{199}Au and ^{195}Au in monocrystalline Au [Mehrer 2007]

Isotope effect

Mechanism with n atoms moving collectively during one jump event

$$m_{i1} \rightarrow (n-1)m + m_{i1}$$

$$\frac{\nu_{i1}^{0}}{\nu_{i2}^{0}} \approx \sqrt{\frac{(n-1)m + m_{i2}}{(n-1)m + m_{i1}}}$$

$$E = \frac{(D_{i1}^{*} - D_{i2}^{*})/D_{i2}^{*}}{\sqrt{\left((n-1)m + m_{i2}\right)/\left((n-1)m + m_{i1}\right)} - 1}$$

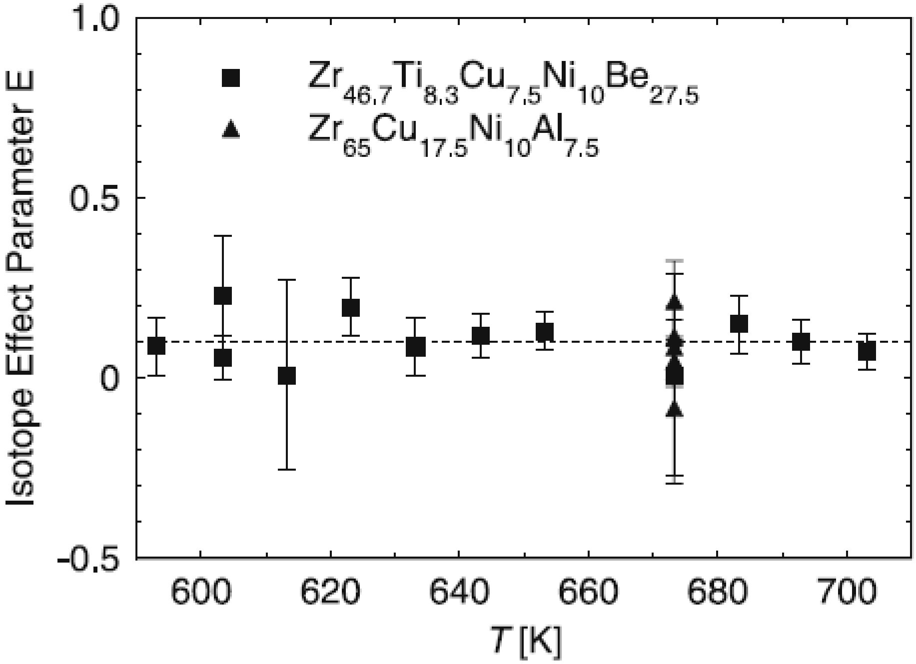
Almost vanishing isotope effects for Co diffusion in various relaxed, conventional metallic glasses.

→ Small isotope effects → strong dilution of the mass dependence of diffusion due to the participation of a large number of atoms in a collective diffusion process.

→ Small isotope effect also for the deeply undercooled liquid state of bulk metallic glasses.

→ Collective nature of diffusion processes in metallic glasses

→No change in diffusion mechanism at the calorimetric glass transition.



Isotope effect parameter as function of temperature for Co diffusion in bulk metallic glasses [Faupel et al. 2003]

E for as-cast metallic glasses ~ E for crystalline metals

→ excess volume quenched-in from the liquid state

→ quenched-in quasi-vacancies in unrelaxed glasses = diffusion vehicles during anneal

Atomic Mechanisms

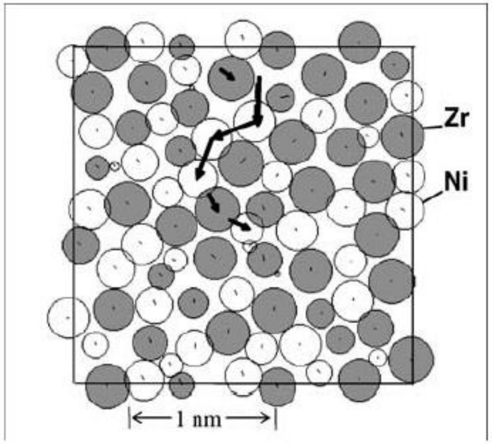
- Experiments and computer simulations → different diffusion mechanisms in metallic glasses and in crystals.

- **High temperature = liquid-like viscous flow via atomic collisions**
- **Low temperature= thermally activated transport characteristics of solids.**

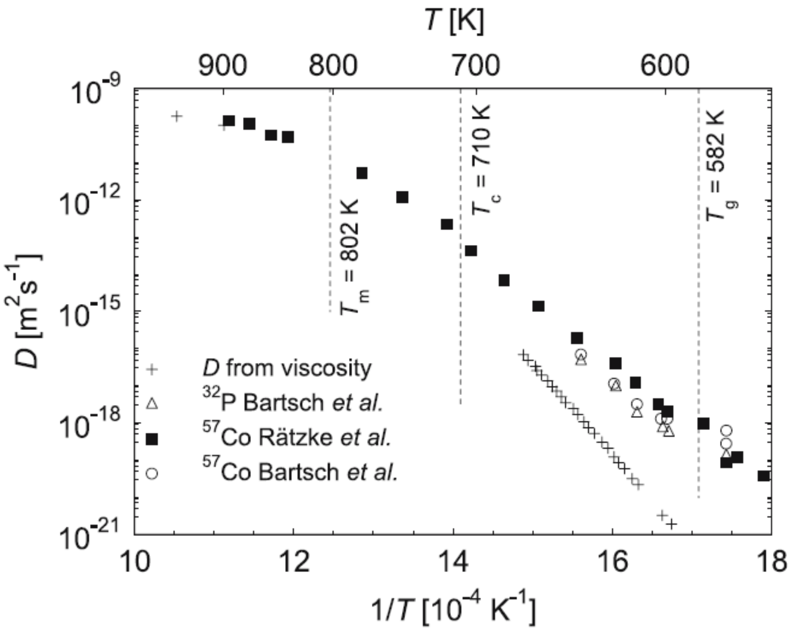
- Simulation and theory → change-over occurs at a critical temperature T_C.
  - Well above T_C:
    - collective motion of chains and rings of atoms.
    - Vogel-Fulcher-Tammann type temperature dependence (downward curvature):

      $$\eta = \eta_0 exp\left(\frac{B}{T-T_0}\right)$$
  - Below T_C, but well above Tg (calorimetric glass temperature):
    - linear Arrhenius behavior: limited temperature range of the experiment)... Mainly chain-like displacements of atoms have been observed in molecular dynamics simulations.

→ molecular dynamics simulations: Collective atomic motion in a chain-like manner leads to total displacements of the order of one nearest-neighbour distance displacement chains typically involve 10 to 20 atoms, where each atom moves only a small fraction of the nearest-neighbour distance



Chain-like collective motion of atoms in a Co-Zr metallic glass according to molecular dynamics simulations by Teichler [Faupel et al. 2003]



Tracer diffusion coefficients of P and Co in comparison with viscosity diffusion coefficients of the alloy $Pd_{43}Cu_{27}Ni_{10}P_{20}$ [Mehrer 2007]

Diffusion dans les verres

Rappel de diffusion

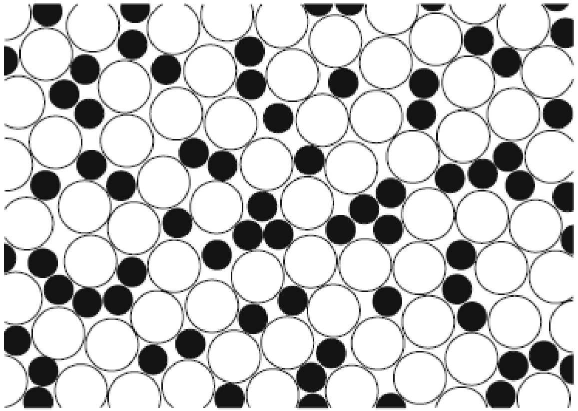
Diffusion dans les verres métalliques

Diffusion dans les verres d'oxydes

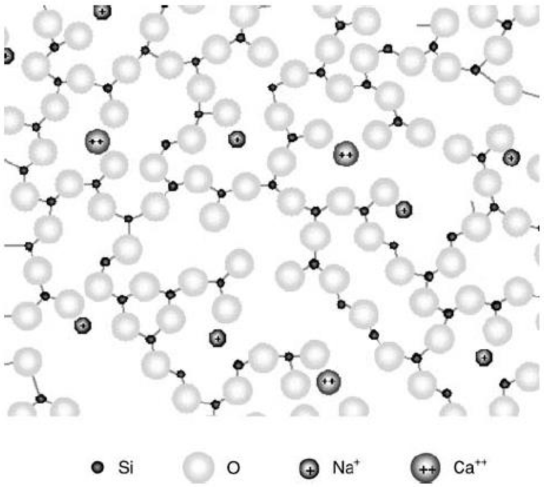
Diffusion chimique dans les verres d'oxydes.

Different types of glasses [Mehrer 2007]

- **Vitreous silica (S** = SiO_2**)**
- **Soda-Lime Silicate Glasses (NCS** = Na_2O-CaO-SiO_2).
- **Borosilicate Glasses (BS** = SiO_2 - B_2O_3**-…)**
- **Lead Silicate Glasses** (PbO - SiO_2)
- **Aluminosilicate Glasses** (**AS** = SiO_2 - Al_2O_3)
- **Non-Silica-Based Glasses (**B_2O_3- and P_2O_5-)
- **Amorphous Semiconductors** (Si, Ge, P, As, tetrahedral glasses).
- **Metallic glasses (**$Pd_{80}Si_{20}$, $Ni_{80}P_{20}$, and $Fe_{40}Ni_{40}P_{14}B_6$)
- **Bulk metallic glasses (**Zr-Ti-Cu-Ni-Be, $Pd_{43}Cu_{27}Ni_{10}P_{20}$)
- **Bulk amorphous steels**
- **Organic Glasses**
- **Natural Glasses (**obsidian, **fulgarites, impactites)**



Structure of a binary metallic glass

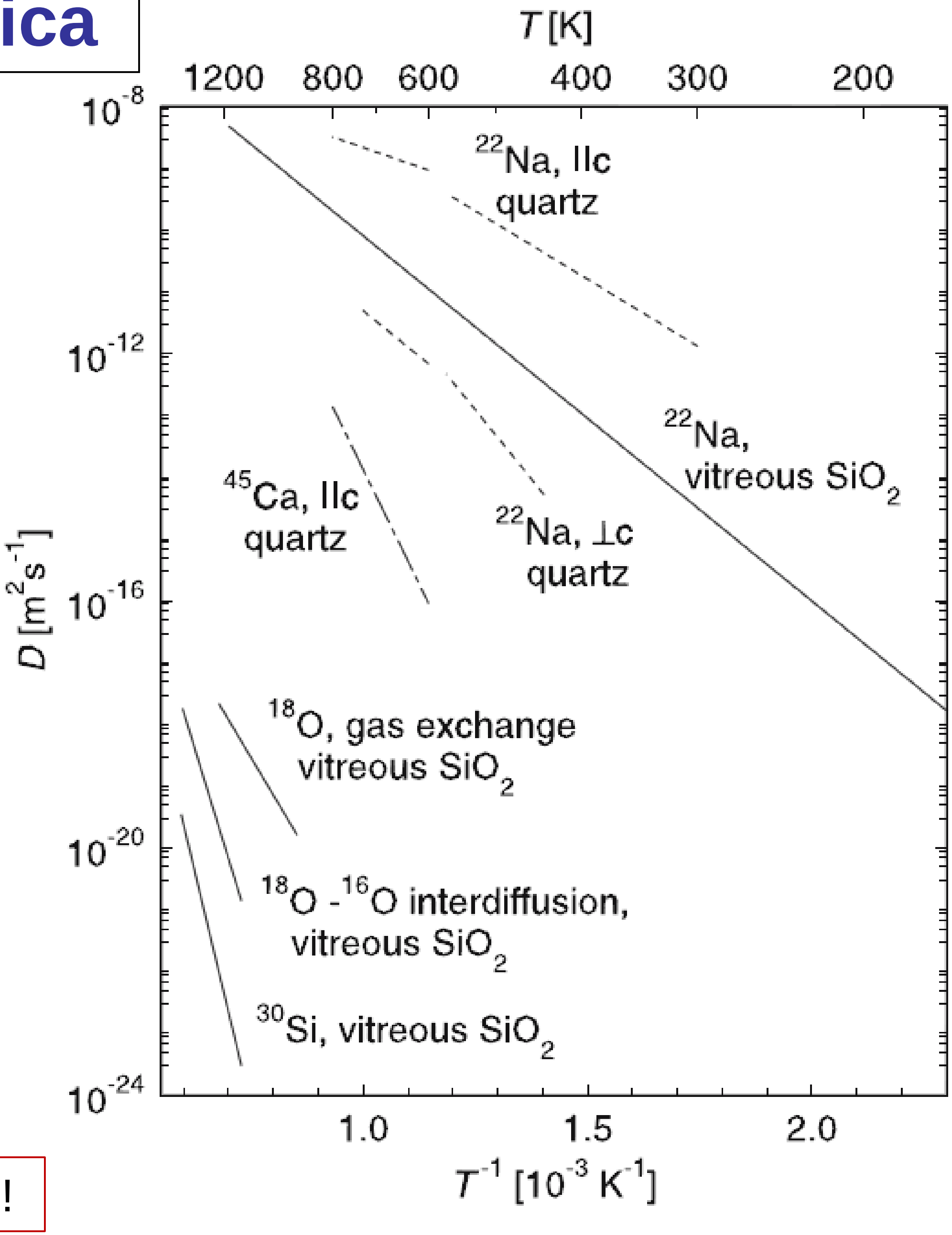


Structure of a soda-lime silicate glass

Diffusion in vitreous silica

- Experiments:
  - ^{22}Na (170 - 1200°C) by residual activity.
  - ^{30}Si (1110 to 1410°C) by SIMS.
  - ^{18}O by gas phase isotope exchange reaction
  - interdiffusion in $Si^{18}O_2$ – $Si^{16}O_2$ thin-film structure by SIMS
- Network former (Si):
  - Ea(Si) = 6 eV
  - = 4x1/2x 2.9 eV. (2.9 eV = energy of a Si-O bond)
- Network modifiers (Na):
  - Vitreous SiO_2 : different Na diffusivities parallel and perpendicular to the c axis of low- and high-quartz
  - Quartz: effect of the transition for Na diffusion between high- and low-quartz (575°C):
  - Quartz: lower activation enthalpy for hexagonal structure (high-quartz = higher symmetry) than the trigonal (low-quartz= lower symmetry)

→ 16 orders of magnitude !!!



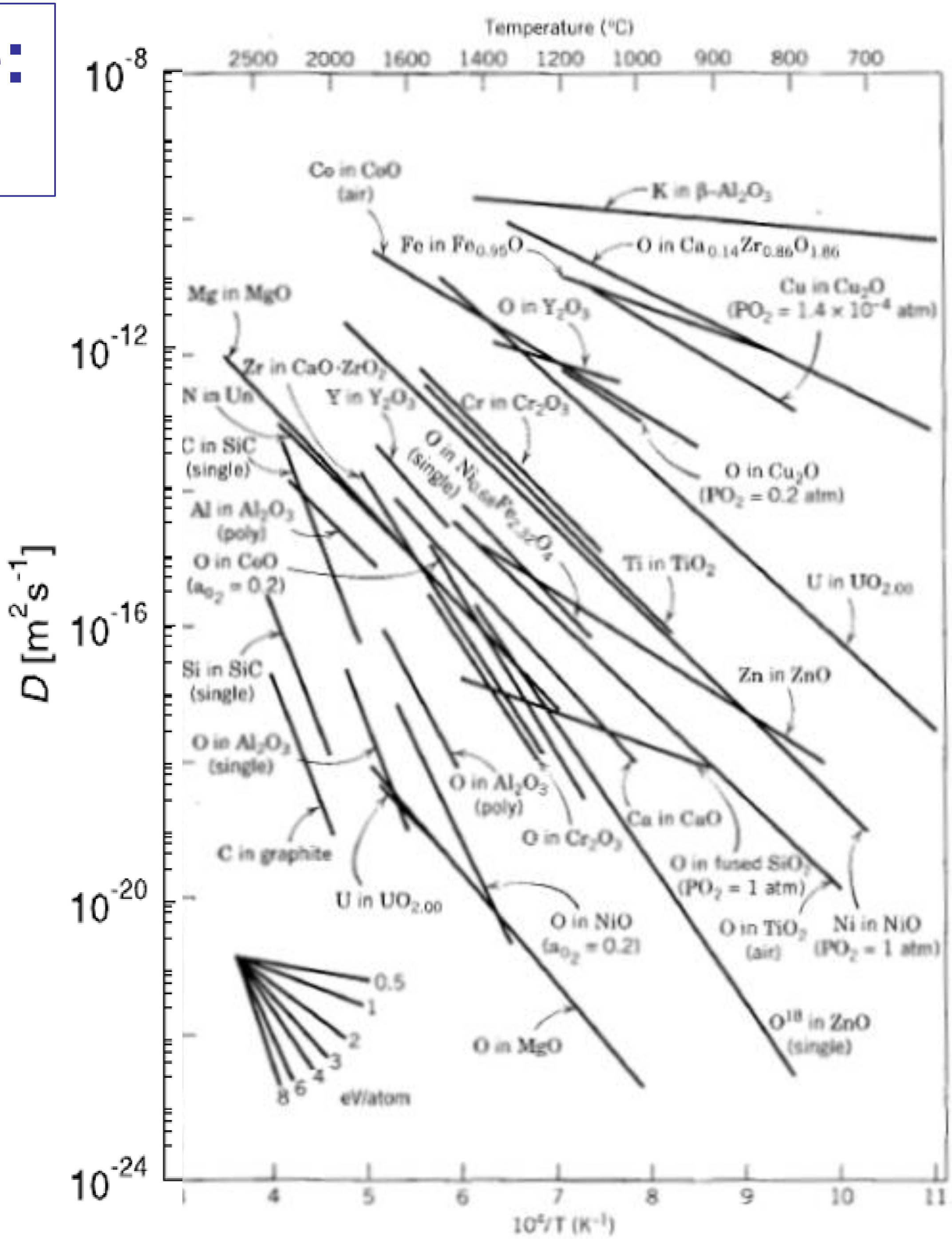
Diffusion in vitreous silica and in quartz [Mehrer 2007]

Diffusion in oxyde: overview

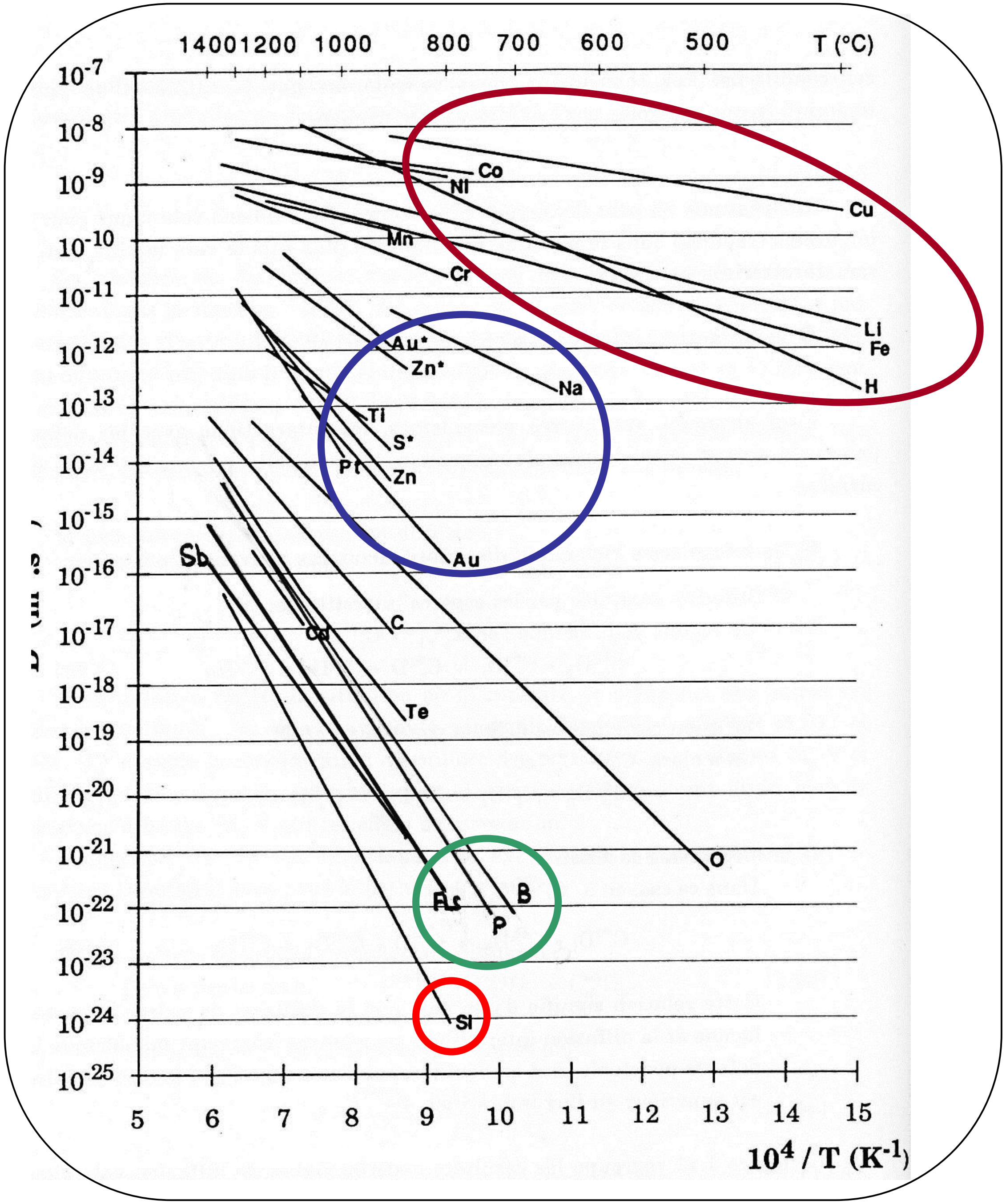
Diffusion coefficients:
13 orders of magnitude

Activation energy:
0.5-8 eV

Different structures,
Different defects,
different mechanisms



Diffusion of various elements in Si



Large variations
16 orders of magnitude

Fast elements
Ni, Co, Cu, Fe, H

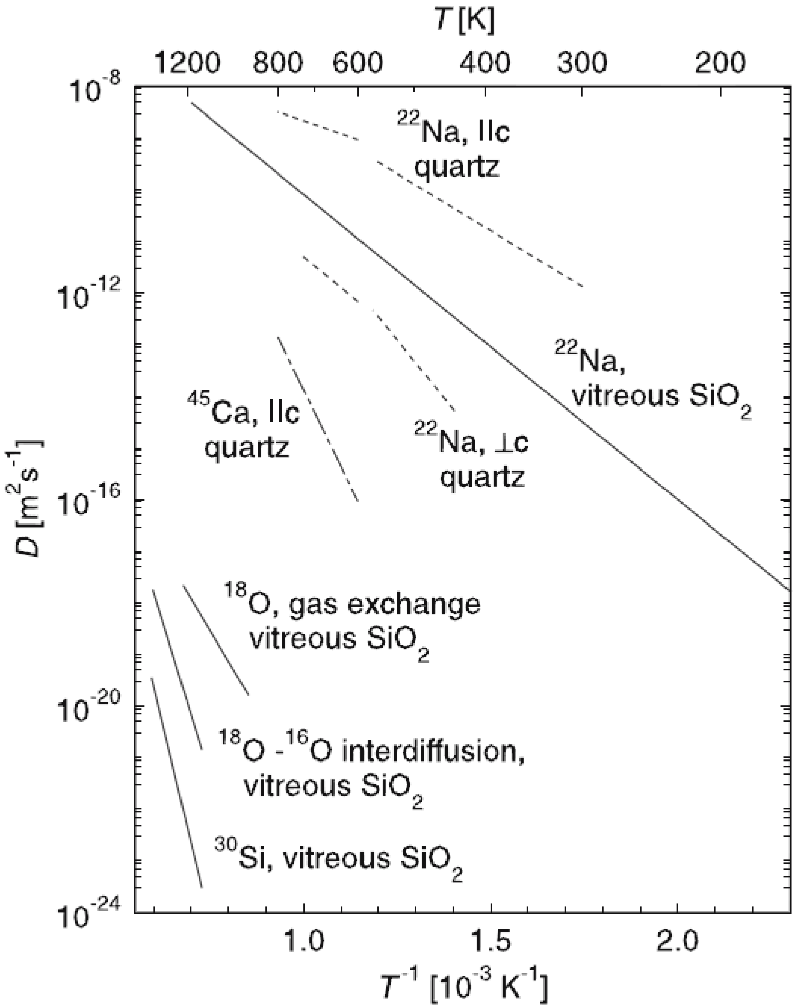
Intermediate elements
Au, Pt, Zn

Dopant elements
B, P, As, Sb
Close to Si

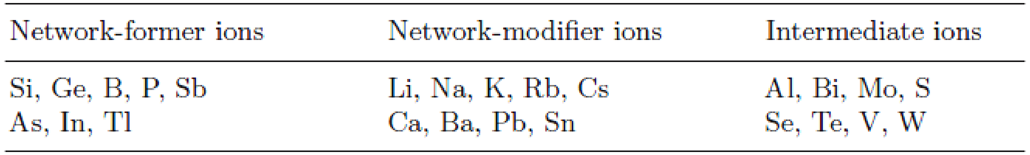
Diffusion in oxide glasses

Five behaviors [Chakraborty 1995]:

- Alkali ions
  - Fastest diffusion
  - Simplest behavior.
  - Weak dependence on composition at high T.
  - Mixed alkali effect → decrease of D for intermediate composition of alkali
- Network modifiers other than alkalies :
  - D similar for different cations
  - D decreases with increasing silica content
  - Mixed cation effect
- Network forming cations (Si):
  - Slowest diffusion
  - Scale with viscosity
  - Strong effect of impurities
- Anions (O):
  - Bridging oxygen, non-bridging oxygen, dissolved molecular oxygen → different behavior
- Chemical diffusion :
  - Uphill diffusion (~~effective binary D~~)
  - depend on composition (more strongly than tracers)
  - Modification of network → D of network former



Diffusion in vitreous silica and in quartz [Mehrer 2007]



Network-former ions	Network-modifier ions	Intermediate ions
Si, Ge, B, P, Sb As, In, Tl	Li, Na, K, Rb, Cs Ca, Ba, Pb, Sn	Al, Bi, Mo, S Se, Te, V, W

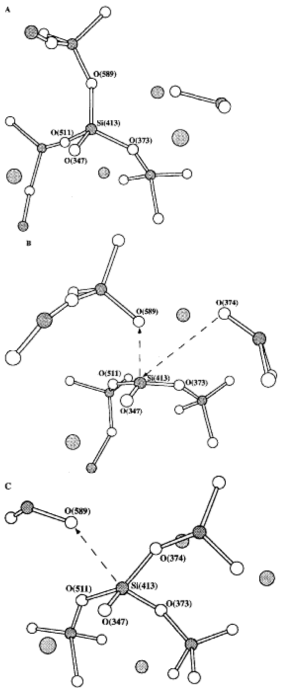
Diffusion of network former and viscosity

- Relation between viscosity and diffusion
- Eyring model

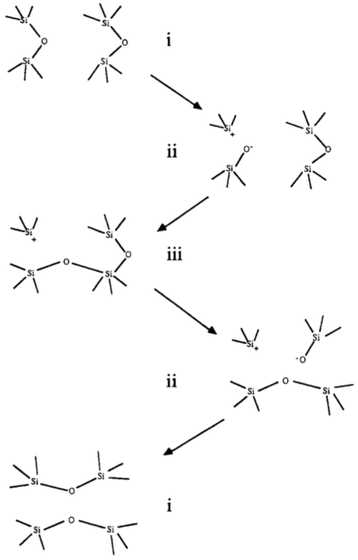
$$D_\eta = \frac{k_B T}{\eta \lambda}$$

$$D_\eta = \frac{k_B T}{\eta \lambda}$$

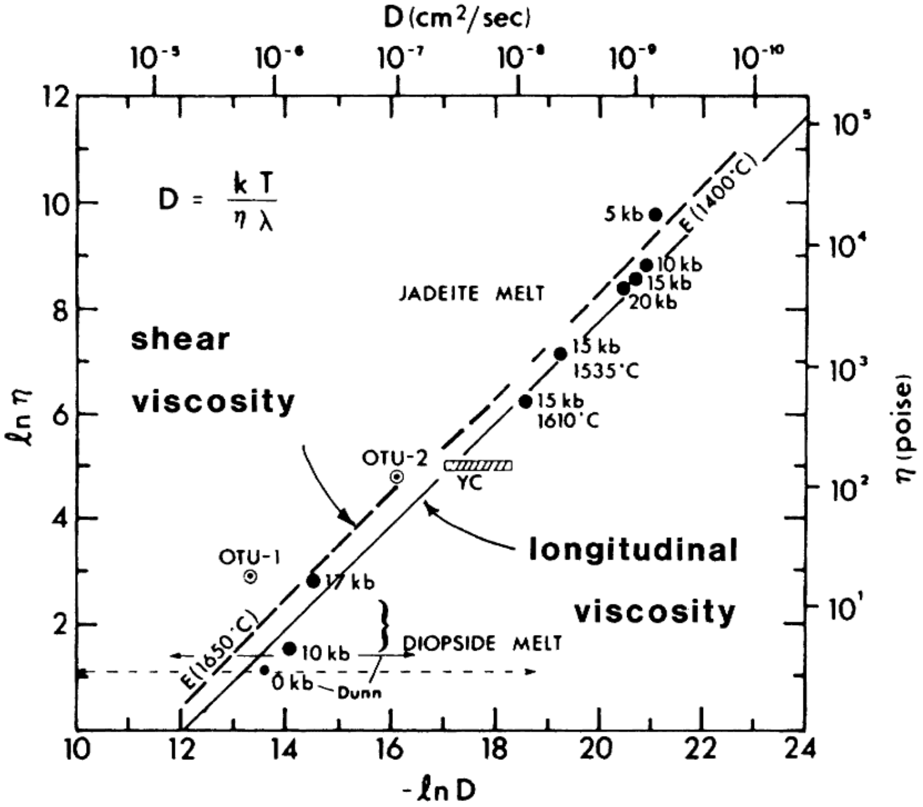
  - η = viscosity
  - λ = distance between two O or two Si



MD simulation of Si diffusion [Kubicki et al 1993]



Diffusion of O in silicates [Charkraborty 1995]



The Eyring relationship for silicate melts: The inverse correlation of viscosity (n) and oxygen dilfusivity (D) for the jadeite and diopside melts. The dashed line E is the relationship predicted by the Eyring equation with h = 2.8 A (diameter of oxygen ion). [Shimizu & Kushiro, 1984]

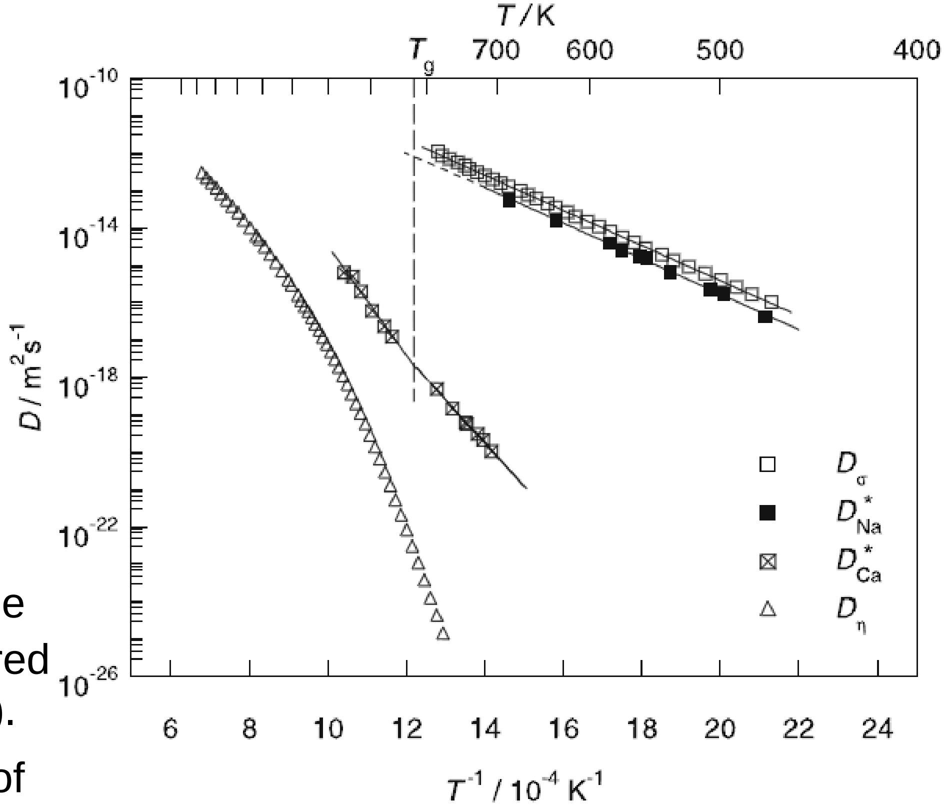
Mobility of network formers controls the viscosity

Ionic conduction

- The dc conductivity σ_{DC} is related to the diffusivity of charged particles (also called charge diffusion coefficient or charge diffusivity), D_σ, via the Nernst-Einstein relation:

$$D_\sigma = \frac{\sigma_{DC} k_B T}{N_{ion} q^2} \propto \sigma_{DC} T$$

  - N_{ion} = number density of mobile ions,
  - q = charge of ions



Viscosity diffusion coefficient, D_η, tracer diffusivities,D^*_{Na}, D^*_{Ca}, and charge diffusion coefficient D_σ, of soda-lime silicate glass [Mehrer 2007]

- D_η from the Stokes-Einstein relation using the ionic radius of Si (0.042 nm) and the measured viscosity (Vogel-Fulcher-Tammann behavior).
- At Tg, Ca diffusion < 6 orders of magnitude of Na diffusion → divalent Ca ions = much stronger linkage to the network than Na ions.
- Same activation enthalpy for conductivity diffusion and Na tracer diffusion

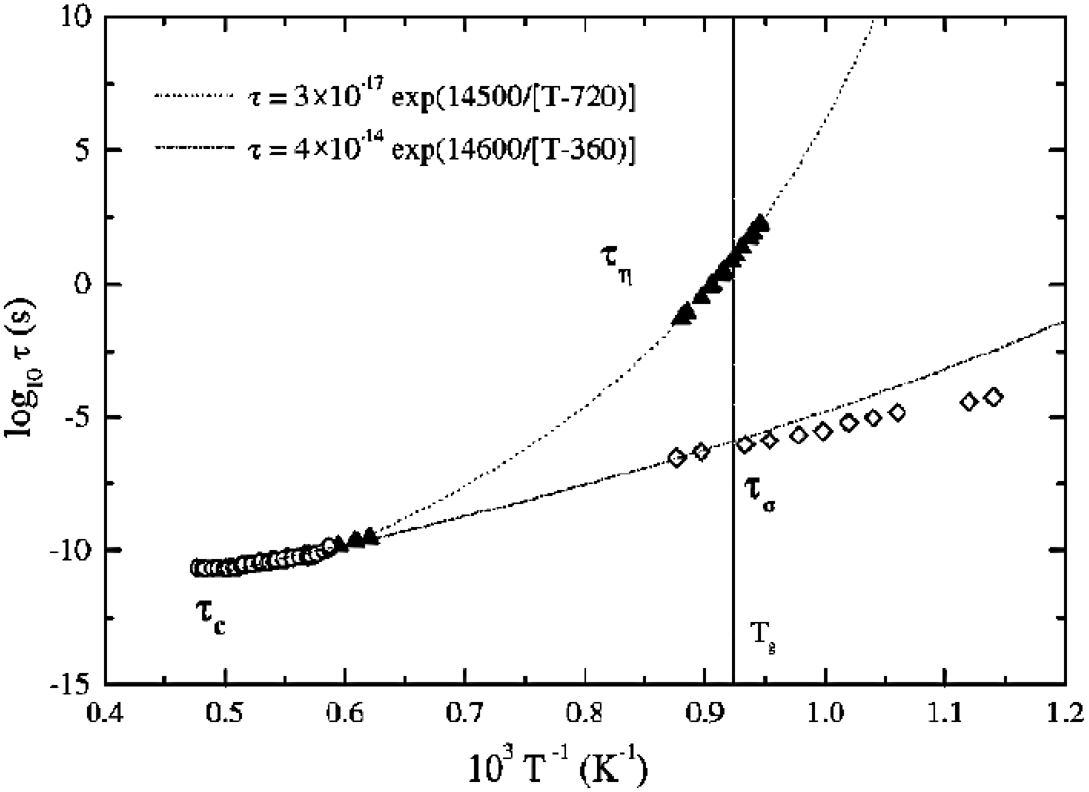
→ the electrical conductivity of soda-lime silicate (NCS) glasses is due to the motion of Na ions.

Conduction and viscosity

- In the supercooled liquid field: difference in the elementary transport mechanisms involved by the viscous and ionic fluxes. The mobility of sodium is poorly coupled to the viscous flow.

- In the liquid, the relaxation times of the ionic conductivity and the viscosity tend towards a single value, which tends to show that **at very high temperatures all the mechanisms adopt the same kinetics.**

More details → Chakraborty 1995, Pablo 2017…



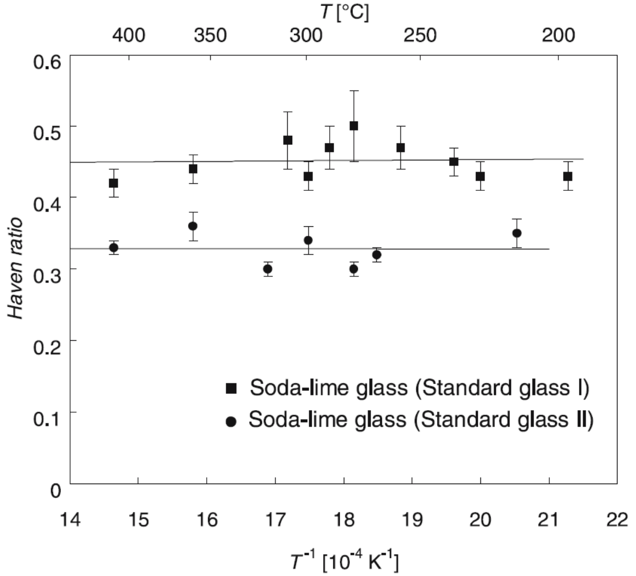
Evolution of relaxation times of viscosity (τ_η), conductivity (τ_σ) and NMR (τ_c) with temperature. [Pablo 2017]

Haven ratio

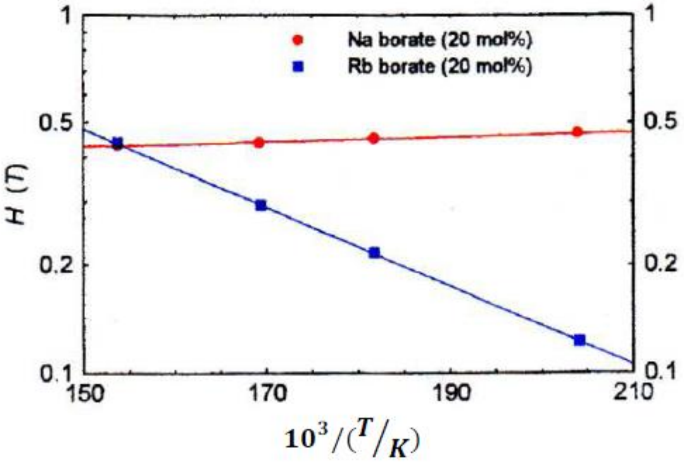
- Haven ratio based on the assumption that only Na ions are mobile:

$$H_R = \frac{D^*_{Na}}{D_\sigma}$$

- Haven ratios (H_R = 0.45 and 0.33) for the two soda-lime glasses are temperature-independent → the mechanism of Na diffusion does not change with temperature.
- Haven ratio < 1 <=> mobility of sodium is correlated with the ones of the other elements
- Decrease of the Haven ratio with temperature of Rubidium borate glass = increase of the number of ions that participate in the collective jump events of ionic motion.



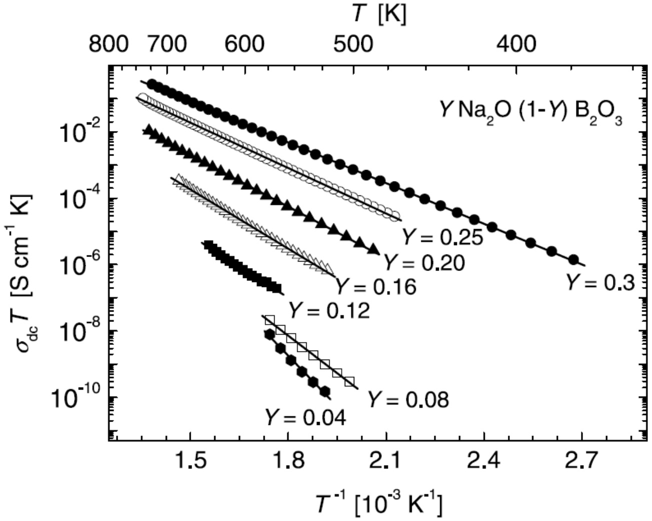
Haven ratios of soda-lime silicate glasses [Mehrer 2007]



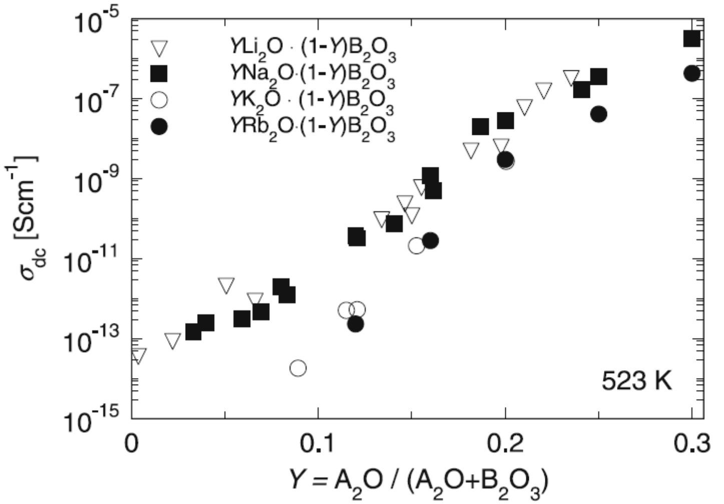
Haven ratios for $0.2Na_2O\ 0.8B_2O_3$ (upper line) and $0.2Rb_2O\ 0.8B_2O_3$ (lower line) glasses as functions of reciprocal temperature [Mehrer et al 2016]

Conductivity and concentration

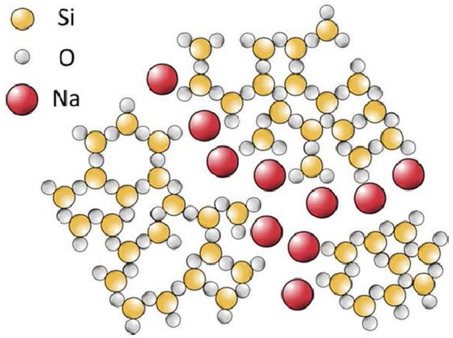
- DC conductivity of sodium borate glasses ($YNa_2O(1-Y)B_2O_3$ = $\mathbf{N_Y B_{1-Y}}$) increase with Na concentration:
  - Arrhenius behavior
  - Increase of several orders of magnitude for increasing alkali content
  - conductivity determined by the number density of mobile ions and by their mobility.
  - At 523K, conductivity increases 5 to 6 orders of magnitude for alkali content between 0 and 0.3 → large increase in mobility (supported by Na tracer diffusion studies).
- The smallest alkali ion = the highest conductivity: decrease of conductivity in the order of increasing ionic radii: Li > Na > K > Rb.



Arrhenius diagram of the dc conductivity (times temperature) for Y $\mathbf{N_Y B_{1-Y}}$ glasses [Mehrer 2007]



Electrical dc conductivity of Li, Na, K, and Rb borate glasses [Mehrer 2007]

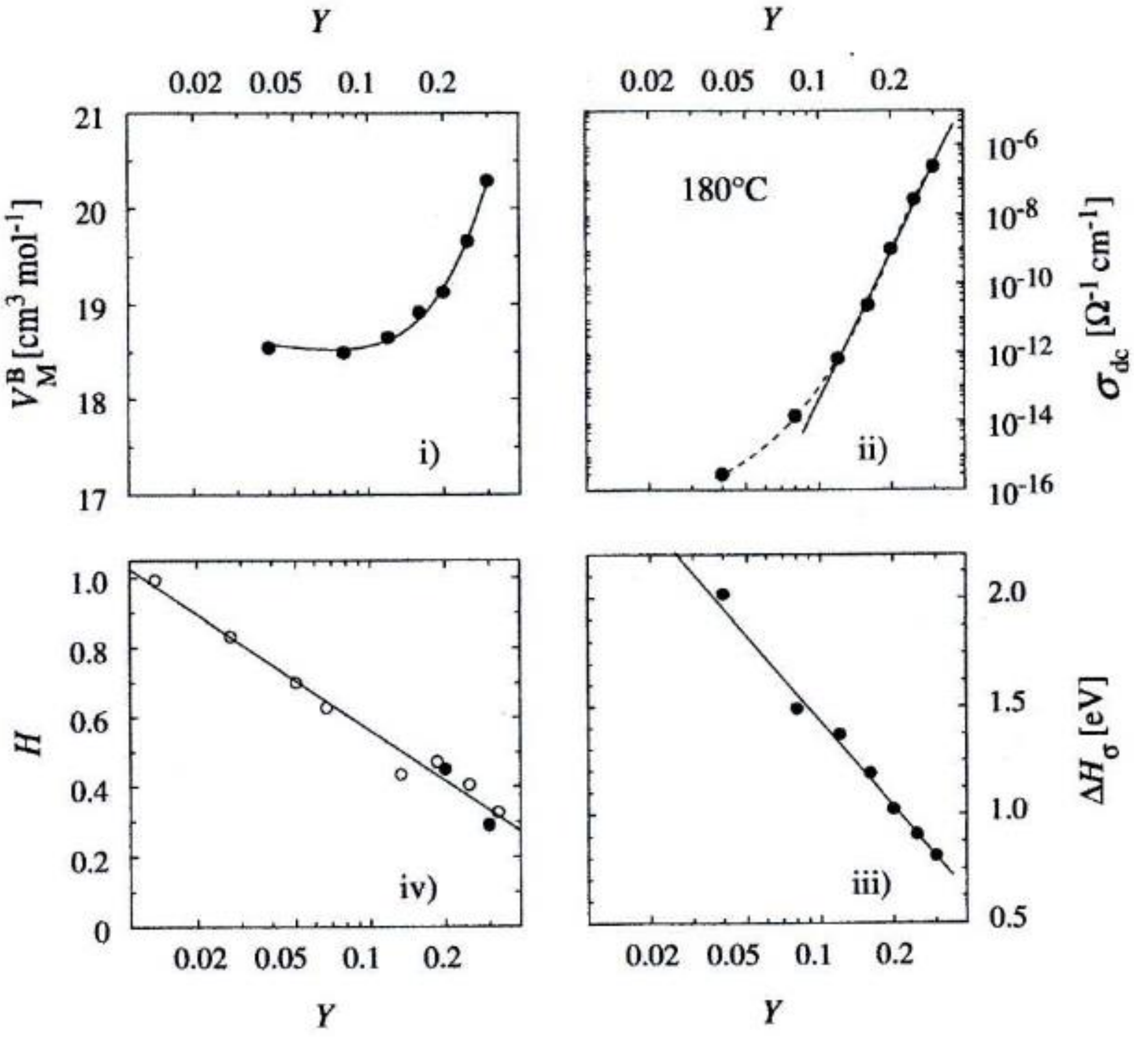


2D modified random network showing the modifiers channel [Claireaux 2014]

Properties

Properties of sodium borate glasses ($YNa_2O(1-Y)B_2O_3 = N_YB_{1-Y}$):

- The molar volume, normalized to the B content, passes through a shallow minimum and then increases with increasing Na content. The changes small and do not exceed 10%.
- In contrast, the ambient pressure dc conductivity increases by nine orders of magnitude with increasing Na content (0.02-0.24) → increase of the mobility of Na ions.
- The activation enthalpy of charge diffusion, ΔH, decreases linearly with the increasing logarithm of the Na content.
- The Haven ratio of Na in Na borate glass decreases from unity at low Na content to about 0.35 with increasing Na content



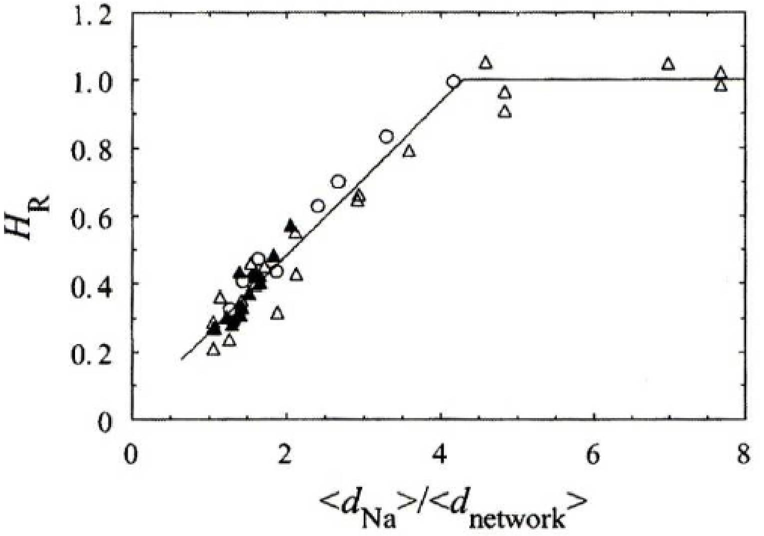
Properties of $YNa_2O(1-Y)B_2O_3$ glasses: i): molar volume normalized to the B content. ii): dc conductivity . iii): activation enthalpy of charge diffusion. iv): Haven ratio H (open circles) [Mehrer et al 2016]

Haven ratio and mechanisms of diffusion

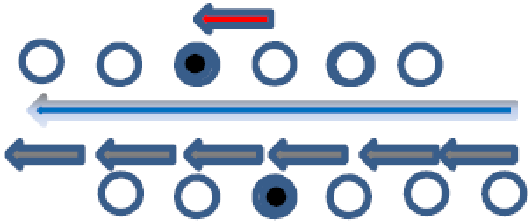
- Haven ratio depends on the separation parameter (= ratio between average Na-Na distance and average network distance) atoms

$$\frac{\langle d_{ion} \rangle}{\langle d_{network} \rangle} = \left(\frac{1 - Y}{Y} \right)^{1/3}$$

- $H_R \sim 1$ at low alkali concentrations → interstitial-like diffusion similar to interstitial diffusion in crystals.
- Higher alkali contents collective → chain-like motions of several ions prevail → decrease of the Haven ratio.
- Stronger pressure dependence for tracer diffusivities than for ionic conductivity → pressure-dependent Haven ratio → increasing degree of collectivity of the ionic jump process with increasing pressure.
- Monte Carlo simulations [Voss *et al*. 2005] : number of ions which participate in collective jump events increases with increasing ion content – i.e. with decreasing average ion-ion distance. For the highest alkali contents up to four ions can be involved in collective motion.
- Similar to diffusion in glassy metals



Haven ratios as a function of the ratio between the average Na-Na distance and the average network distance (separation parameter) for various Na oxide glasses [Mehrer et al 2016]



Schematic illustration of a collective jump event in a chain of six ions. The dark ion represents the tracer, which in a radiotracer experiment is tagged by its radioactivity. In the lower row of ions a collective movement of six ions is indicated. In the upper row the result of a collective jump is illustrated: the tracer moves just one interionic distance, whereas the charge moves six interionic distances [Mehrer et al 2016]

Diffusion dans les verres

Rappel de diffusion

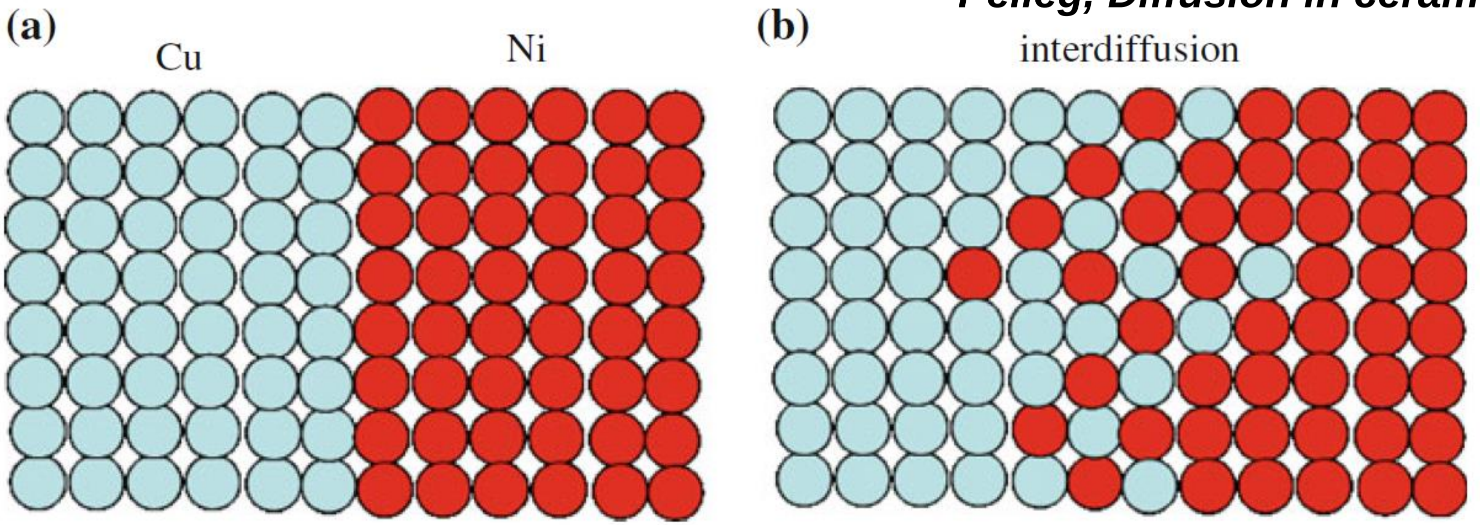
Diffusion dans les verres métalliques

Diffusion dans les verres d’oxydes

Diffusion chimique dans les verres d’oxydes.

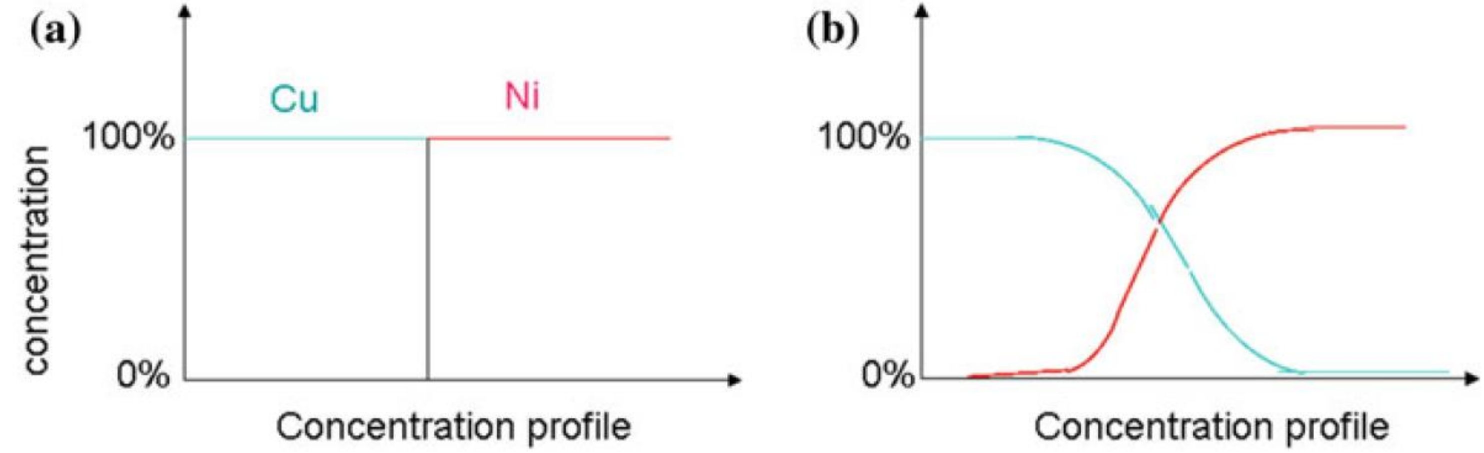
Diffusion in alloy: Interdiffusion

Pelleg, Diffusion in ceramics, 2016



$\eta \equiv$

Fig. 6.1 A schematic illustration of an intermixing Cu–Ni diffusion couple: **a** before diffusion; **b** after diffusion



a binary

$-2\eta\frac{\mathrm{d}}{\mathrm{d}}$

Fig. 6.2 Schematic illustration of a concentration profile: **a** before diffusion; **b** the intermixing of the components after diffusion

Interdiffusion in metallic alloy

Intrinsic flux (crystal lattice frame):

$$j_A = -D_A^I \frac{\partial C_A}{\partial x}, \quad j_B = -D_B^I \frac{\partial C_B}{\partial x}$$

$$v_K = -(\tilde{V}_A j_A + \tilde{V}_B j_B)$$

$$v_K = \tilde{V}_B (D_B^I - D_A^I) \frac{\partial C_B}{\partial x}$$

$$J = -D_i^I \frac{\partial C_i}{\partial x} \pm v_K C_i \quad i = A, B$$

$$\tilde{D} = C_B \tilde{V}_B D_A^I + C_A \tilde{V}_A D_B^I$$

$$j_i = -B_i C_i \frac{\partial \mu_i}{\partial x} \qquad D_i^* = B_i RT$$

$$\tilde{D}_{Darken} = (N_A D_B^* + N_B D_A^*)\, \Phi$$

$$\Phi = \frac{N_A N_B}{RT} \frac{\mathrm{d}^2 G}{\mathrm{d}N_i^2} = \frac{\partial \ln a_i}{\partial \ln N_i} = 1 + \frac{\partial \ln \gamma_i}{\partial \ln N_i}$$

$$\boxed{\tilde{D} = (N_A D_B^* + N_B D_A^*)\, \Phi S = \tilde{D}_{Darken} S}$$

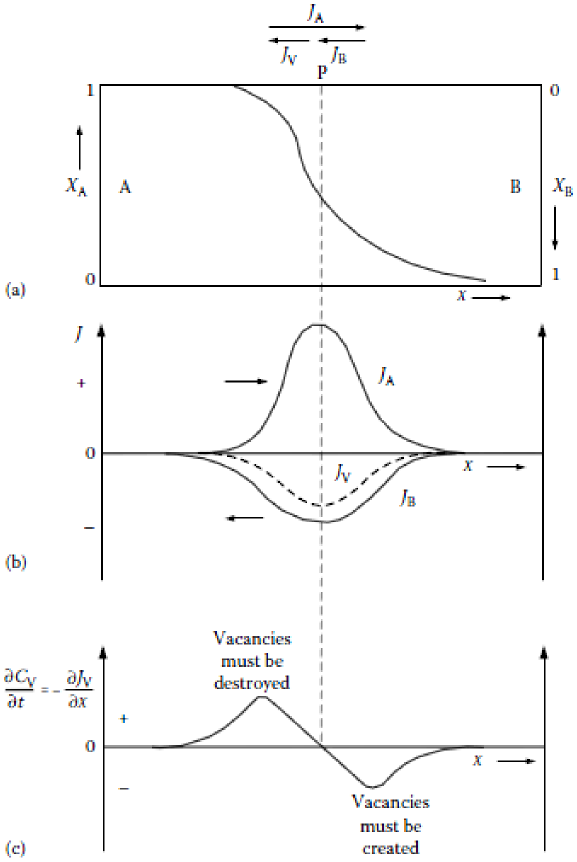


FIGURE 2.15
Interdiffusion and vacancy flow. (a) Composition profile after interdiffusion of A and B. (b) The corresponding fluxes of atoms and vacancies as a function of position x. (c) The rate at which the vacancy concentration would increase or decrease if vacancies were not created or destroyed by dislocation climb.

Porter and Easterling, Phase transformation in metals and alloys, 1992

Interdiffusion in metallic alloy

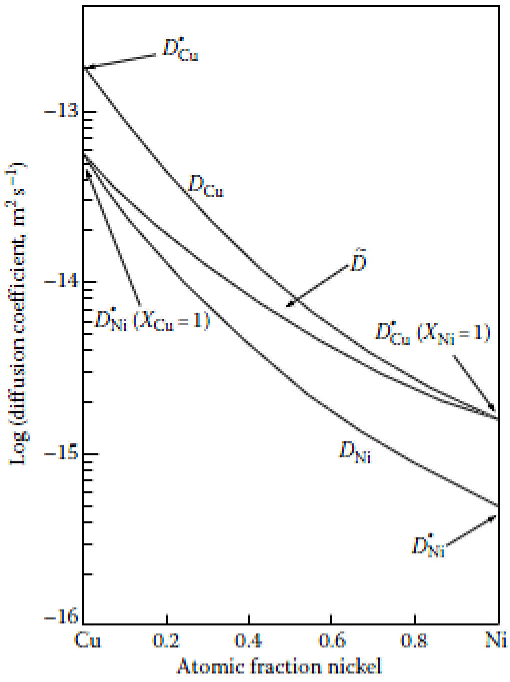


FIGURE 2.21
The relationship between the various diffusion coefficients in the Cu-Ni system at 1000°C (After A.G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1971.)

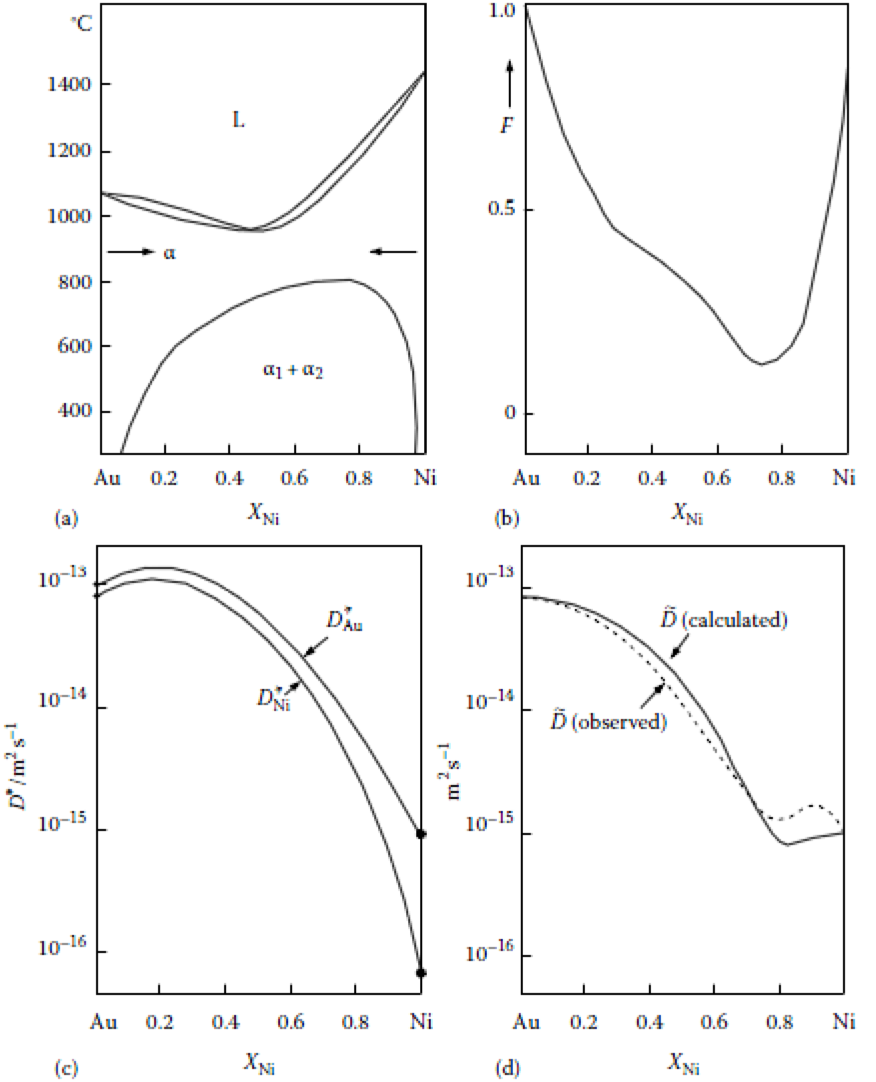


FIGURE 2.22
Interdiffusion in Au-Ni alloys at 900°C (a) Au-Ni phase diagram, (b) the thermodynamic factor, *F*, at 900°C, (c) experimentally measured tracer diffusivities at 900°C, (d) experimentally measured interdiffusion coefficients compared with values calculated from (b) and (c). (From J.E. Reynolds, B.L. Averbach and Morris Cohen, *Acta Metallurgical* **5** (1957) 29.)

Porter and Easterling, Phase transformation in metals and alloys, 1992

Ambipolar diffusion

Ambipolar diffusion = two diffusing species of different signs

$$j_A = -D_A^* \frac{\partial C_A}{\partial x} + \frac{q C_A D_A^*}{k_\mathrm{B} T} E$$

$$j_B = -D_B^* \frac{\partial C_B}{\partial x} + \frac{q C_B D_B^*}{k_\mathrm{B} T} E$$

Electrical neutrality $j_A + j_B = 0$

$$E = \frac{k_\mathrm{B} T}{q} \frac{D_A^* - D_B^*}{C_A D_A^* + C_B D_B^*} \frac{\partial C_A}{\partial x}$$

$$j_A = -D_A^I \frac{\partial C_A}{\partial x} \quad \text{and} \quad j_B = -D_B^I \frac{\partial C_A}{\partial x}$$

$$D_A^I = D_B^I = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*}$$

Non ideal solution

$$\boxed{D_A^I = D_B^I = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*} \Phi \equiv \tilde{D}_{Nernst-Planck}}$$

→ Diffusion controls by the slower species

Diffusion in multicomponent system

Flux of species in multicomponent system (1st law of Fick): $J_i = -\sum_{j=1}^{n} D_{i,j}\, \nabla C_j$

Mass conservation : $\sum_{j=1}^{n} C_j = 1 \Longrightarrow \sum_{j=1}^{n} \nabla C_j = 0 \;\; \Rightarrow \nabla C_N = -\sum_{j=1}^{n-1} \nabla C_j$

Flux of : $J_i = -\sum_{j=1}^{n-1} \left(D_{i,j} - D_{i,N}\right) \nabla C_j = -\sum_{j=1}^{n-1} D_{i,j}^{N}\, \nabla C_j$ with $D_{i,j}^{n} = D_{i,j} - D_{i,n}$

Matrix notation (1st and 2nd laws of Fick): $\boldsymbol{J} = -\boldsymbol{D}^{\boldsymbol{N}} \frac{\partial \boldsymbol{C}}{\partial x}$ *and* $\frac{\partial \boldsymbol{C}}{\partial t} = \boldsymbol{D}^{\boldsymbol{N}} \frac{\partial^2 \boldsymbol{C}}{\partial x^2}$

$$\boldsymbol{D}^{\boldsymbol{N}} = \begin{bmatrix} D_{1,1}^{N} & \cdots & D_{1,n-1}^{N} \\ \vdots & \ddots & \vdots \\ D_{n-1,1}^{N} & \cdots & D_{n-1,n-1}^{N} \end{bmatrix}$$

Onsager relationship for flux in multicomponent system: $J_i = -\sum_{k=1}^{n-1} L_{i,k}^{N} \frac{\partial(\mu_k - \mu_n)}{\partial x}$

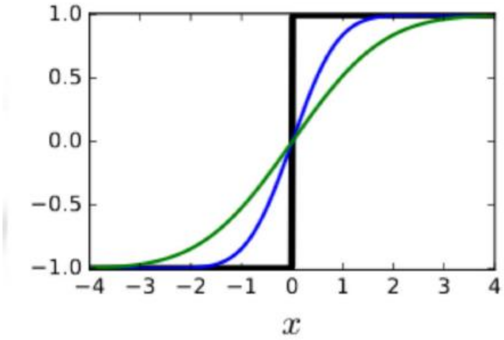
Matrix notation for Onsager : $\boldsymbol{J} = -\boldsymbol{L} \frac{\partial \boldsymbol{\mu}^{N}}{\partial x}$ *and* $\boldsymbol{G} \frac{\partial \boldsymbol{C}}{\partial x} = \frac{\partial \boldsymbol{\mu}^{N}}{\partial x} \;\; \Rightarrow \boxed{\boldsymbol{D} = \boldsymbol{L}\boldsymbol{G}}$

Kinetics *Thermodynamics*

Diffusion in multicomponent system

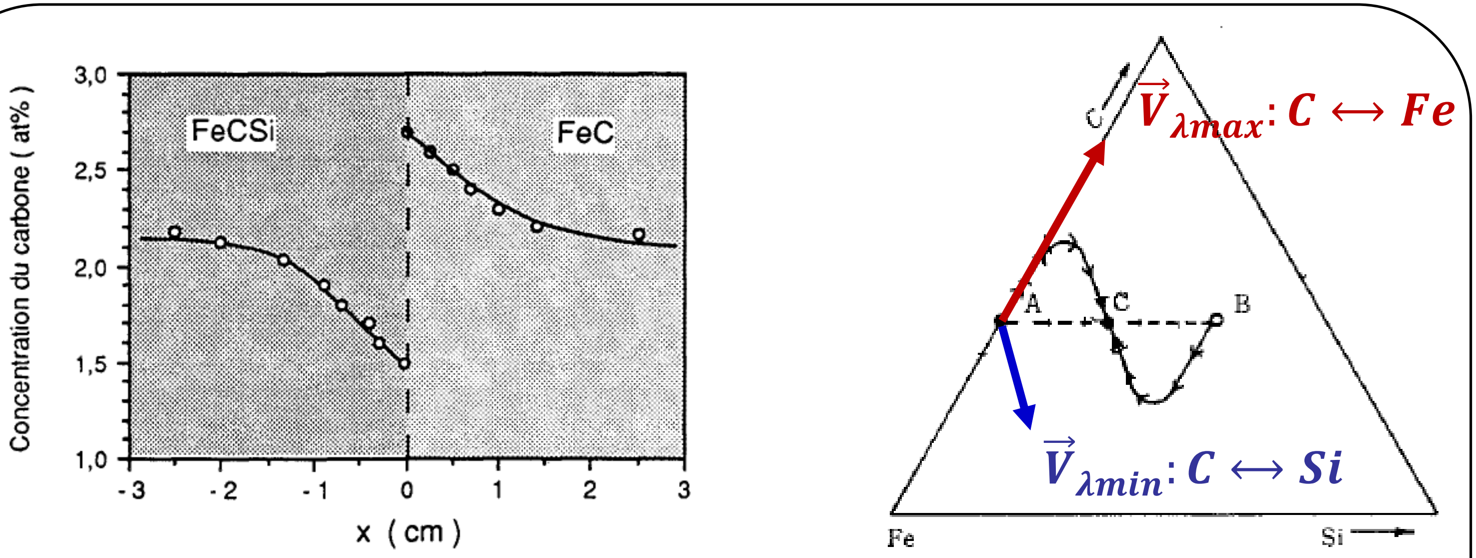
Diagonalization of the D matrix : $\boldsymbol{D} = \boldsymbol{P\Lambda P^{-1}}$

$$\boldsymbol{\Lambda} = \begin{bmatrix} \boldsymbol{\lambda_1} & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \boldsymbol{\lambda_{n-1}} \end{bmatrix}$$



With $\widetilde{\boldsymbol{C}} = \boldsymbol{P^{-1}C}$ and $\boldsymbol{\Delta\widetilde{C}} = \boldsymbol{P^{-1}\Delta C}$ $\quad \Rightarrow \dfrac{\partial \widetilde{\boldsymbol{C}}}{\partial t} = \boldsymbol{\Lambda} \dfrac{\partial^2 \widetilde{\boldsymbol{C}}}{\partial x^2}$

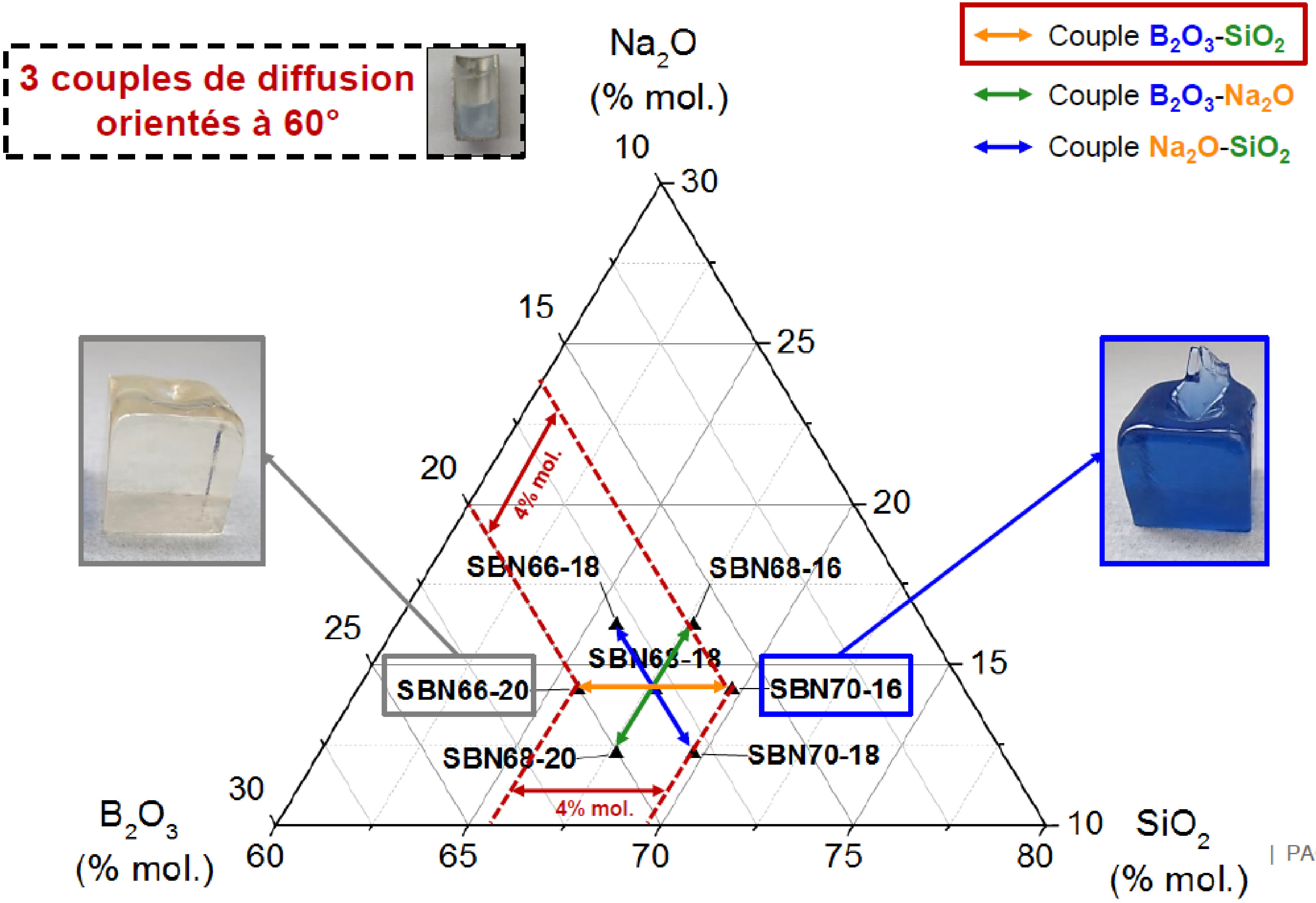
$$\Rightarrow \tilde{C}_i(x,t) = \tilde{C}_i^0 erf\left(\frac{x}{\sqrt{2\lambda_i t \partial x^2}}\right)$$



Darken's experiment: (a) redistribution of C in a FeC/FeSiC diffusion couple after 13 days at 1050°C "uphill diffusion" (b) diffusion path

Hélène PABLO « Diffusion chimique dans les verres borosilicates d'intérêt nucléaire », 2017

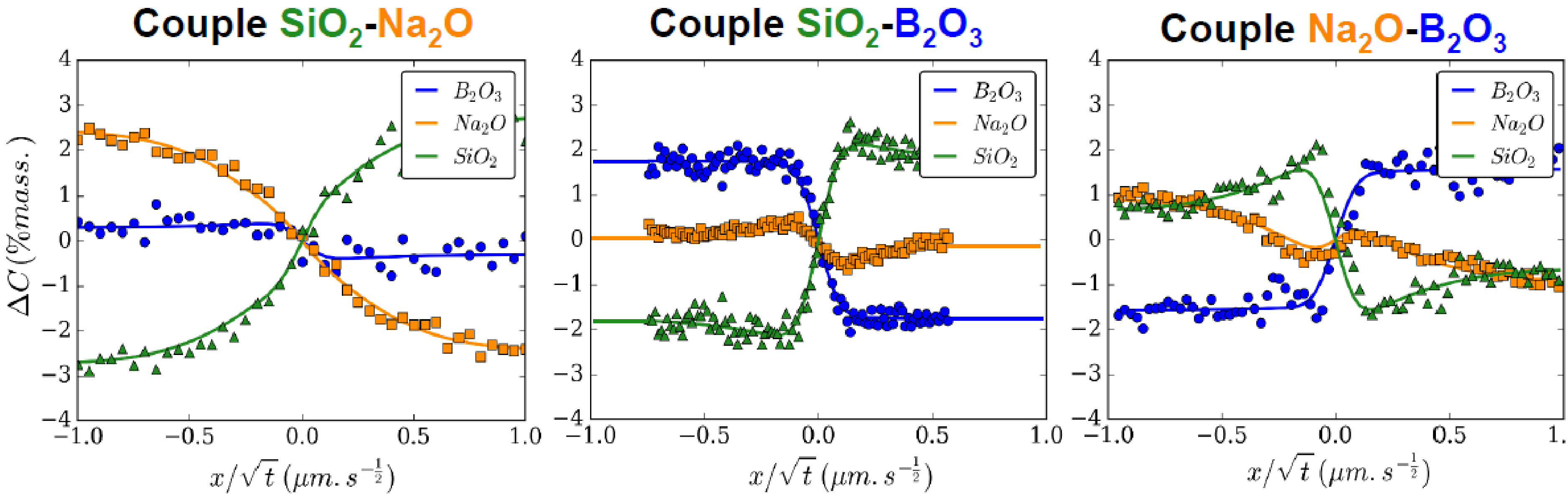
Verres des couples de diffusion



3 couples de diffusion orientés à 60°

Hélène PABLO « Diffusion chimique dans les verres borosilicates d'intérêt nucléaire », 2017

Profils de concentration à 800 °C (1,5 h)


Couple SiO_2-Na_2O

Couple SiO_2-B_2O_3

Couple Na_2O-B_2O_3

Quelles sont les informations à extraire des profils de diffusion?

1) Les **épaisseurs de diffusion** donnent une information sur la cinétique des **échanges diffusifs**.

- ➢ **Valeurs propres (λ)**

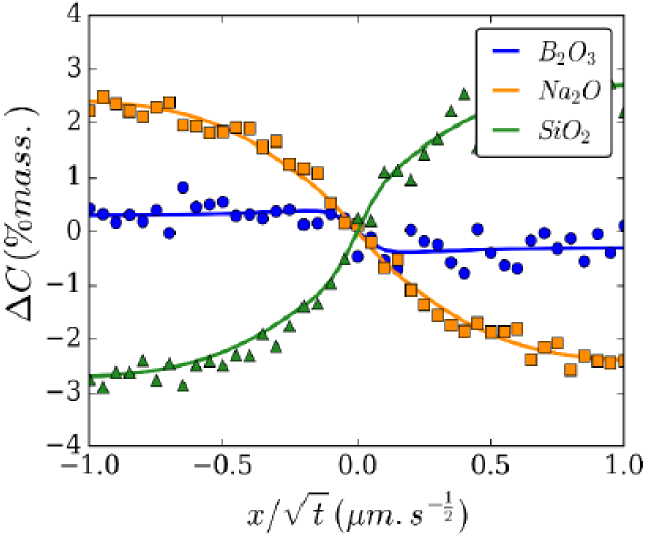
2) La **forme** des profils de concentration permet de déterminer les couplages diffusifs et contiennent des informations sur les **mécanismes de diffusion**.

- ➢ **Vecteurs propres ($\vec{V}$)**

Hélène PABLO « Diffusion chimique dans les verres borosilicates d’intérêt nucléaire », 2017

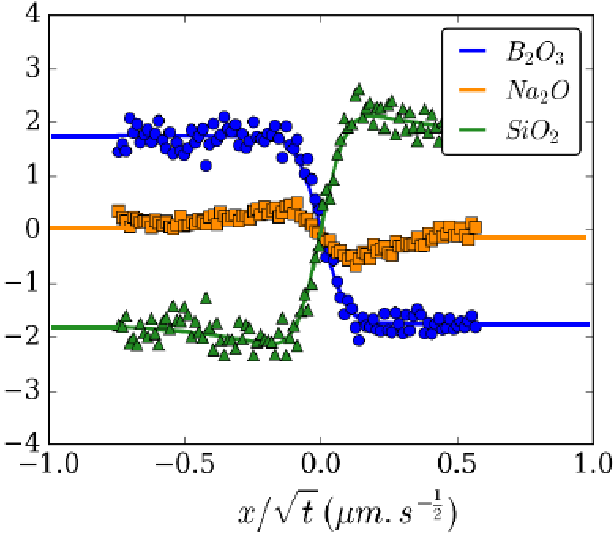
Profils de concentration à 800 °C (1,5 h)

Couple SiO_2-Na_2O



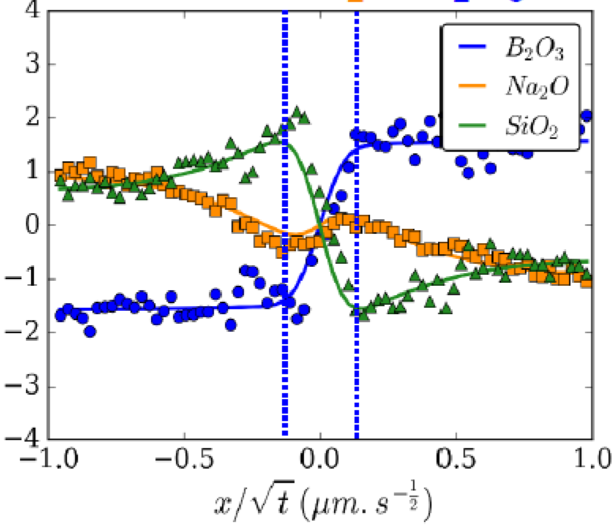
- Pas de *uphill*
- SiO_2 diffuse aussi vite que Na_2O

Couple SiO_2-B_2O_3



- *Uphill* de SiO_2
- *Uphill* de Na_2O

Couple Na_2O-B_2O_3



- *Uphill* de SiO_2
- *Uphill* de Na_2O

- ➢ **SiO_2 accéléré en présence d’un gradient de concentration en Na_2O**
- ➢ **Couplages SiO_2/Na_2O et SiO_2/B_2O_3**

Comment quantifier ces couplages?

Hélène PABLO « Diffusion chimique dans les verres borosilicates d'intérêt nucléaire », 2017

Résultats des ajustements à 800 °C

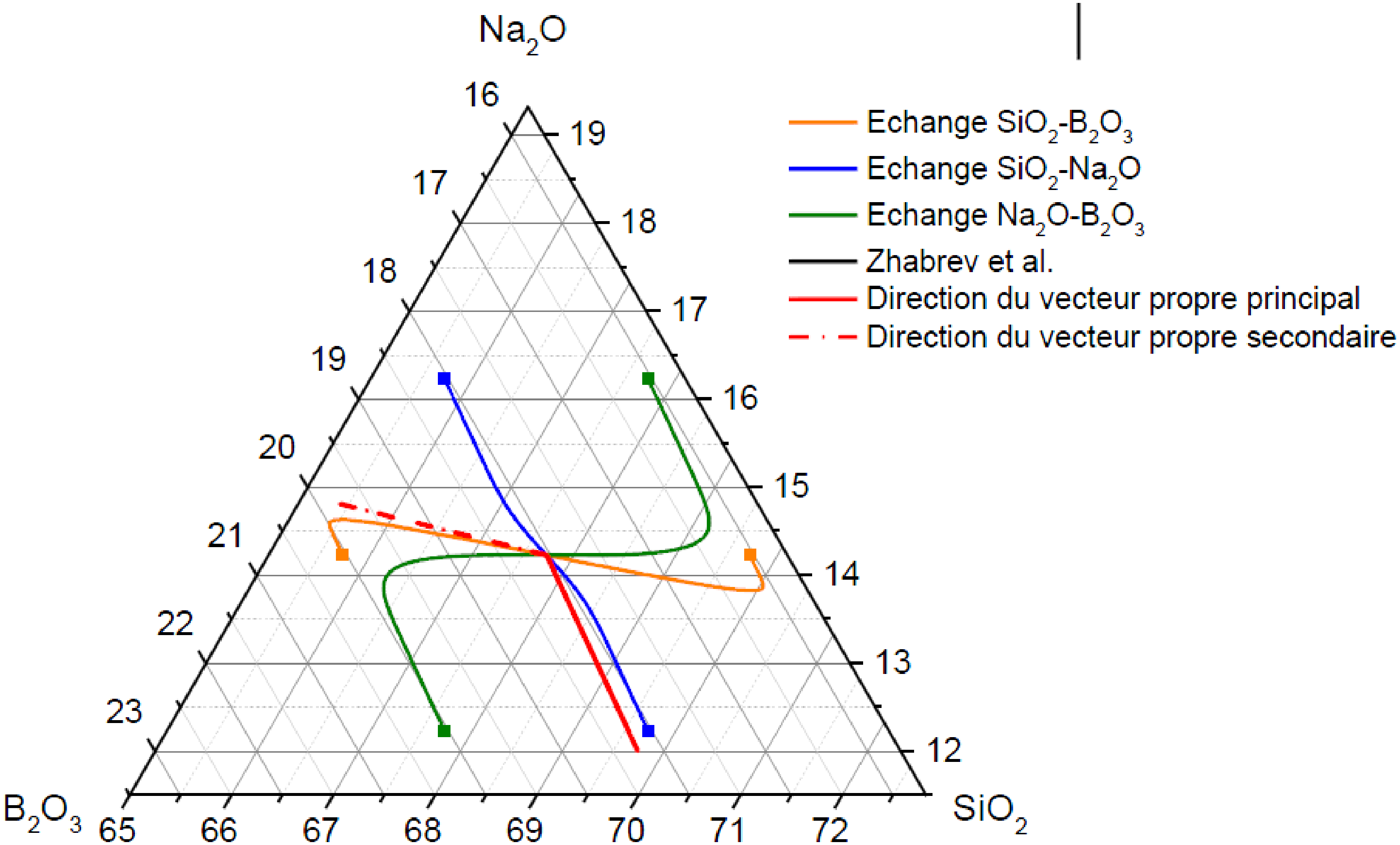
	Mécanisme diffusif principal	Mécanisme diffusif secondaire
Vecteurs propres (mol) $\vec{V}\begin{bmatrix}B_2O_3\\Na_2O\\SiO_2\end{bmatrix}$	$\overrightarrow{V_{max}}\begin{bmatrix}0{,}10\\-1{,}00\\0{,}90\end{bmatrix}$	$\overrightarrow{V_{min}}\begin{bmatrix}0{,}75\\0{,}25\\-1{,}00\end{bmatrix}$
Echanges diffusifs	$0,10\ B_2O_3 + 0,90\ SiO_2 \leftrightarrow 1\ Na_2O$ Couplages forts entre SiO_2 et Na_2O	$0,75\ B_2O_3 + 0,25\ Na_2O \leftrightarrow 1\ SiO_2$ Couplages forts entre SiO_2 et B_2O_3

	Cinétique échange diffusif principal	Cinétique échange diffusif secondaire
Valeurs propres (x10^{-11} cm^2/s)	$\lambda_{max} = 85,7\ (\pm\ 25,8)$	$\lambda_{min} = 2,60\ (\pm\ 0,28)$

Les deux échanges diffusifs représentent les mécanismes à l'origine de l'homogénéisation du bain de verre en l'absence de convection.

Comment ces deux échanges se produisent-ils?

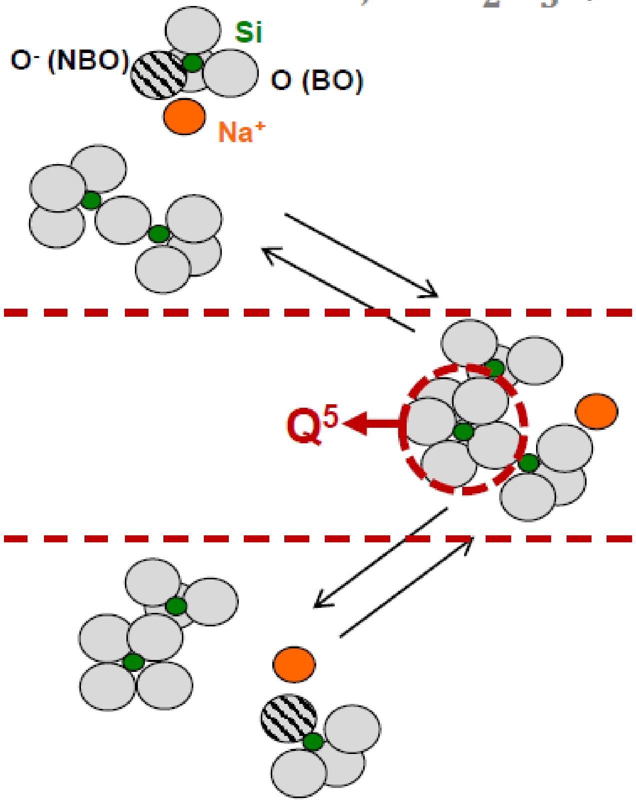
Hélène PABLO « Diffusion chimique dans les verres borosilicates d'intérêt nucléaire », 2017



Hélène PABLO « Diffusion chimique dans les verres borosilicates d'intérêt nucléaire », 2017

Mécanismes de diffusion : Echange diffusif principal

$$0,10\ B_2O_3 + 0,90\ SiO_2 \leftrightarrow 1\ Na_2O$$



1 tétraèdre Q^3
+
2 tétraèdres Q^4

1 tétraèdres Q^5
+
2 tétraèdres Q^4

2 tétraèdres Q^4
+
1 tétraèdre Q^3

Formation hypothétique de silicium en coordinence 5 dans un état intermédiaire

I. Farnan and J.F. Stebbins, The nature of the glass-transition in a silica rich oxide melt, Science (1994)
H. Pablo et al., Multicomponent diffusion in sodium borosilicate glasses, JNCS (2017)

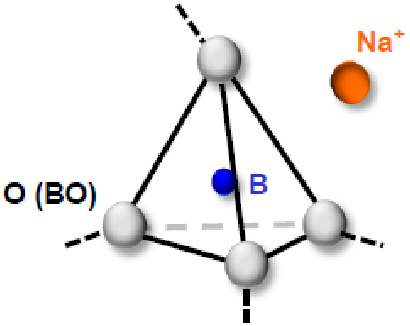
Mécanismes de diffusion : Echange diffusif secondaire

$$0,75\,B_2O_3 + 0,25\,Na_2O \leftrightarrow 1\,SiO_2$$

$$\Big\downarrow \; \times 2 + 1\,Na_2O$$

$$1,5\,B_2O_3 + 1,5\,Na_2O \leftrightarrow 2\,SiO_2 + 1\,Na_2O$$

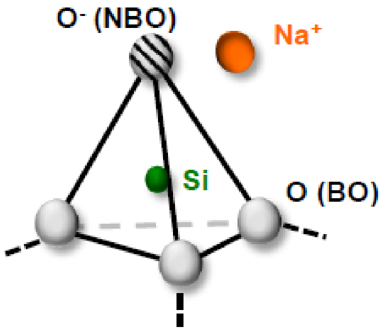
$$\Big\downarrow$$



$$3\underbrace{(B^{3+} + Na^{+})}_{BO_4^-} \leftrightarrow 2\underbrace{(Si^{4+} + Na^{+})}_{Q^{N-1}}$$

$$\xrightarrow{\hspace{6em}}$$

Dépolymérisation



Changement de rôle du sodium
(compensateur de charge → modificateur de réseau)

H. Pablo et al., Multicomponent diffusion in sodium borosilicate glasses, JNCS (2017)

Hélène PABLO « Diffusion chimique dans les verres borosilicates d'intérêt nucléaire », 2017

Comportement des valeurs propres proche de celui de la viscosité et découplé de celui de la conductivité ionique

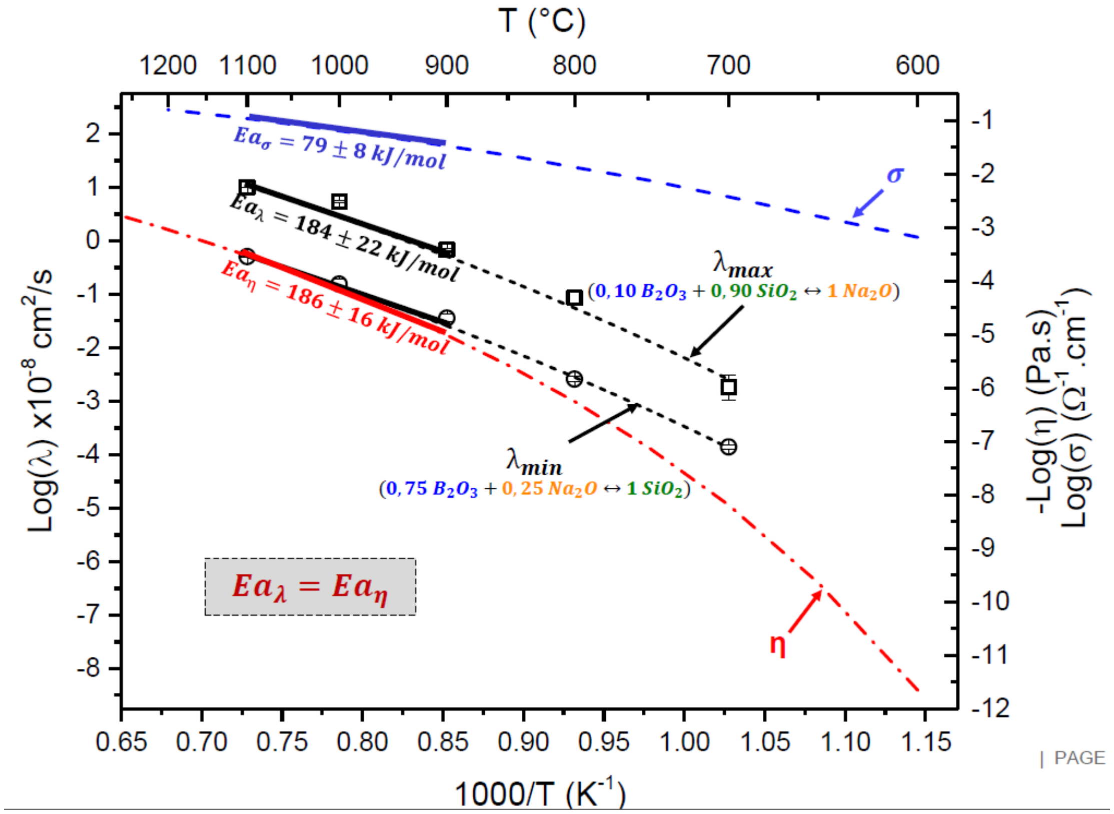
- ➢ Diffusion chimique et viscosité pilotées par la fréquence de rupture des liaisons Si-O-Si et Si-O-B
- ➢ Conductivité ionique à rapprocher de l'autodiffusion du sodium

Couplages diffusifs :

- ➢ Entre le silicium et le sodium : $\mathbf{0{,}10 B_2O_3+0{,}90 SiO_2 \leftrightarrow 1 Na_2O}$
- ➢ Entre le bore et le silicium : $\mathbf{0{,}75 B_2O_3+0{,}25 Na_2O \leftrightarrow 1 SiO_2}$

Pas d'évolution des vecteurs propres entre 700 °C et 1100 °C

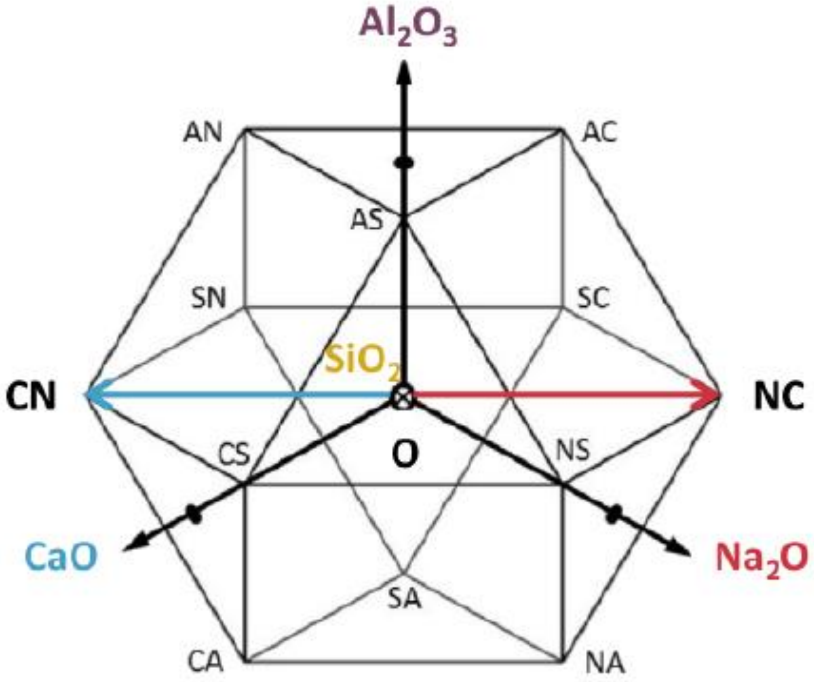
- ➢ Unicité des mécanismes de diffusion

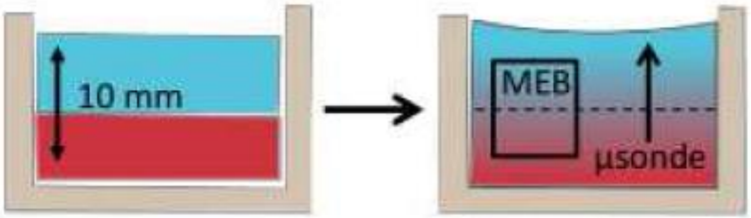


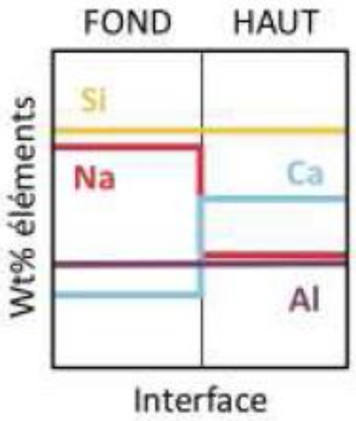
C. Claireaux, E Gouillard et al

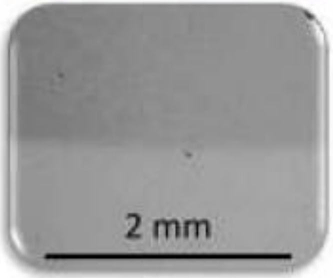
[Claireaux et al., 2016] : quaternary system $CaO-Na_2O-Al_2O_3-SiO_2$

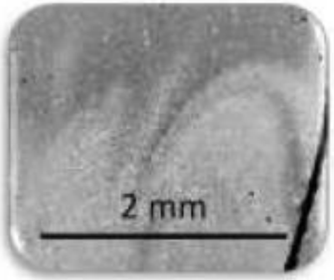
Diffusion couples centered on $64.5\%SiO_2, 13.3\%Na_2O, 10.8\%CaO, 11.33\%Al_2O_3$









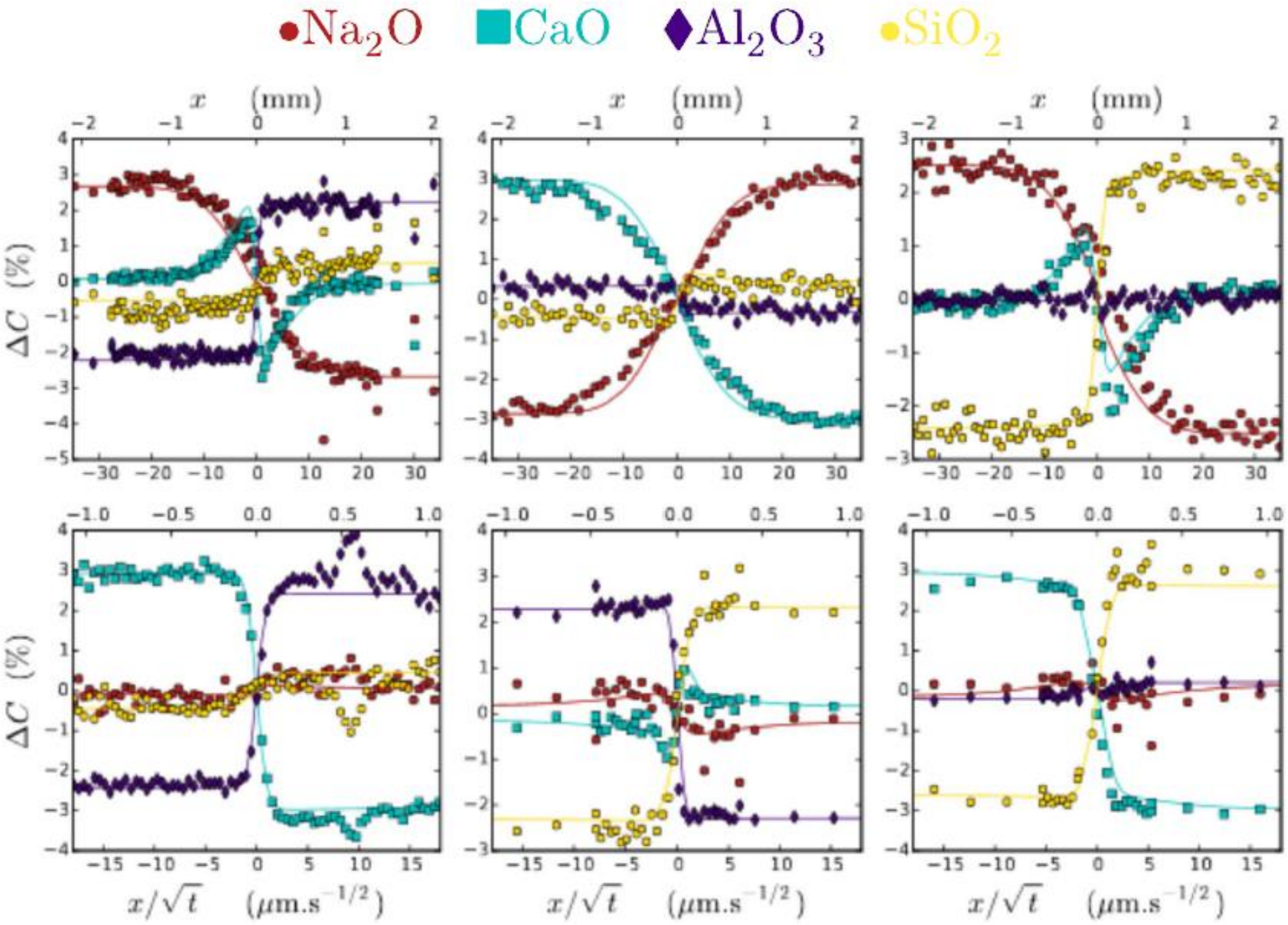


12 different compositions

$\Delta \pm 2.5\%$

A lot of diffusion experiments !

C. Claireaux, E Gouillard et al



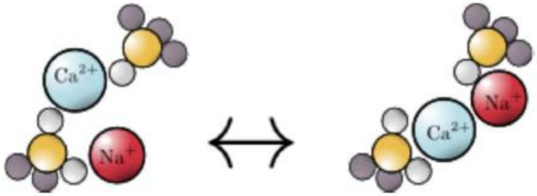
[Claireaux et al., 2016] GCA, Claireaux JNCS 2018

Python package to fit and simulate diffusion profiles : `multidiff`.

C. Claireaux, E Gouillard et al

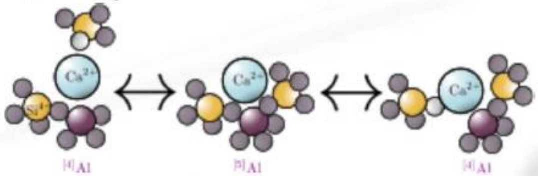
Dominant eigenvector, $\lambda_1 \simeq 30.10^{-12} \mathrm{m}^2.\mathrm{s}^{-1}$

$$\frac{1}{2}\mathrm{Ca}^{2+} \leftrightarrow \mathrm{Na}^{+}$$



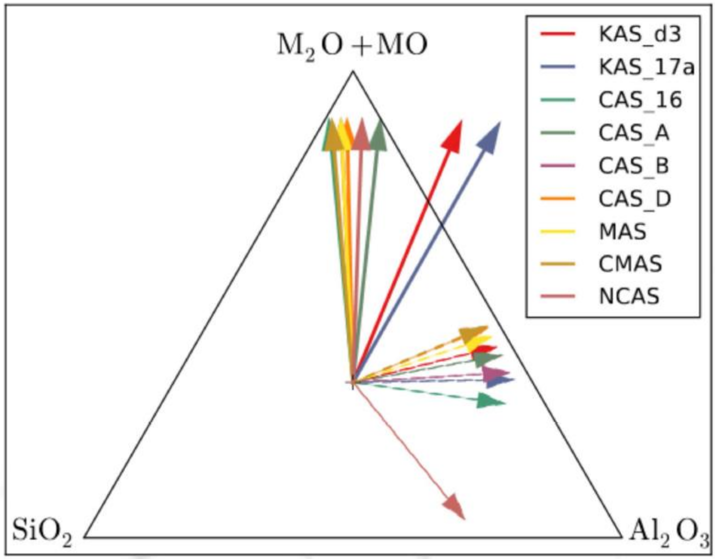
Second eigenvector (52x less frequent)

$$\mathrm{Ca}^{2+} \leftrightarrow 0.5\mathrm{Al}^{3+} + 0.5\mathrm{Si}^{4+}$$



Third eigenvector (155x less frequent)

$$\mathrm{Al}^{3+} \leftrightarrow 0.5\mathrm{Ca}^{2+} + 0.5\mathrm{Si}^{4+}$$



→ **The dominant eigenvector involves the fast diffusing species (Na)**

Diffusion in glasses: conclusions and questions

Complex materials = complex diffusion

Role of collective mechanisms?

Thermodynamics / kinetics? $\boldsymbol{D = LG}$

Precipitation

→ 2nd école "Diffusion dans les solides" Marseille 2019

Benoît Appolaire
ONERA: LEM

Hartmut Bracht
U. Munster

Yves Brechet
SIMAP

Chun Chun Fu
CEA: SRMP

Sergiy Divinski
U. Munster

Lijun Zhang
Central South U.

Ecole de diffusion dans les solides

2020, Marseille

Philippe Knauth
AMU/CNRS: Madirel

Thomas Schuler
CEA: SRMP

Eugen Rabkin
Technion

Alain Portavoce
CNRS/AMU: IM2NP

Maylise Nastar
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