Point defects and diffusion

Crystal defects

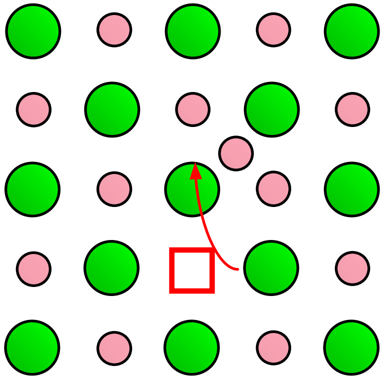
Crystalline solids have a very regular atomic structure: that is, the local positions of atoms with respect to each other are repeated at the atomic scale. These arrangements are called perfect crystal structures. However, above 0°C all crystalline materials are not perfect: the regular pattern of atomic arrangement is interrupted by crystal defects. The defect types are classified according to their dimension:

- Point defects
- Line defects
- Planar defects
- Bulk defects

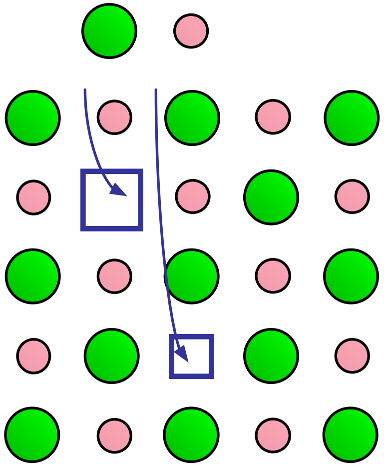
Importance of defects: Defects determine many properties of materials (those properties that we call "structure sensitive properties"). Even properties like the specific resistance of semiconductors, conductance in ionic crystals or diffusion properties in general which may appear as intrinsic properties of a material are defect dominated - in case of doubt by the intrinsic defects. Few properties - e.g. the melting point or the elastic modulus - are not, or only weakly influenced by defects.

Point defects in ionic solids I

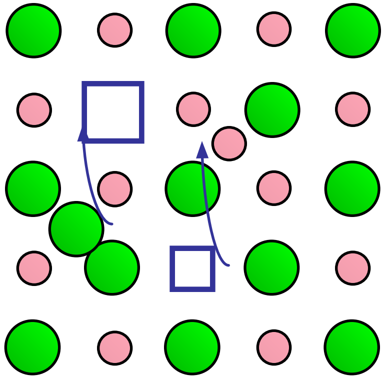
Missing atoms within a structure, atoms at "wrong" sites, "wrong" atoms (impurities) are considered 0-dimensional irregularities and are called point defects.



Frenkel defect: anion vacancy-interstitial cation pair.



Schottky defect: anion -cation vacancy pair.

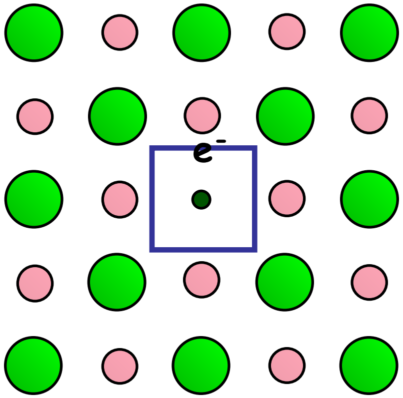


Anti-Schottky defect: anion-cation vacancy pair plus interstial pair.

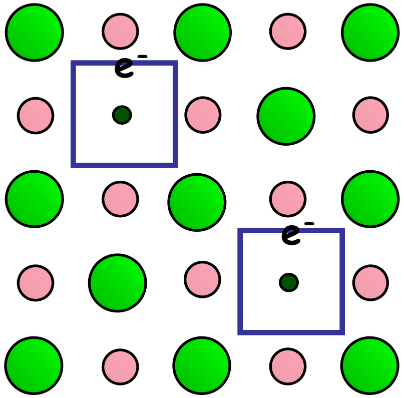
Yanagida et al.: p. **59**

http://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

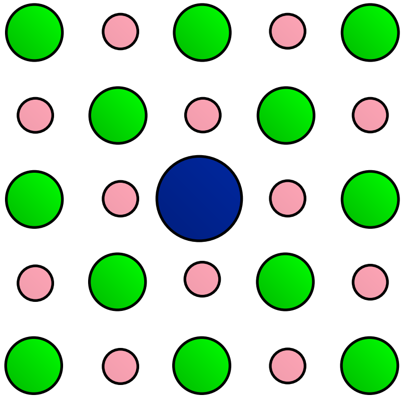
Point defects in ionic solids II



F-center: anion vacancy with excess electron replacing the missing anion



M-center: two anion vacancies with one excess electron each



Isovalent **substitute** atom

Kröger-Vink notation I

Point defects can be treated like chemical species. The Kröger-Vink notation is a set of conventions used to describe defect species e.g their electical charge and their lattice position.

General form: $$M_S^C$$

M corresonds to the species. These include:
atoms - e.g. Si, Ni, O, Cl,
vacancies - V
interstitials - i
electrons - e
holes - h (missing electrons)

S indicates the lattice site that the species occupies. For instance, Ni might occupy a Cu site. In this case, M in the general formula would be Ni and S would be replaced by Cu. Interstitial sites are also used here.

C corresponds to the electric charge of the species relative to site that it occupies. To continue the previous example, Ni often has the same valency as Cu, so the relative charge is zero. To indicate null charge, the sign "×" is used. A single "·" indicates a single positive charge, while two would represent two positive charges. Finally," ' "signifies a single negative charge, so two, would indicate a double negative charge.

Kröger-Vink notation II

Symbol	Description	eff. ch.
e’	extra electron in the conduction band	-1
h˙	lack of an electron in the conduction band	+1
V_M^x	vacancy in a metal (M=metal atom in this case)	0
V_M''	cation (M) vacancy	-2
$V_X^{\square\square}$	anion (X) vacancy	+2
$M_X^{\square\square}$	M (+1) at X site (-1)	+2
$M_i^{\square}$	M (+1) at an interstitial site	+1
M_M^x	M(+2) at a M site	0
$F_M^{\square}$	foreign atom F (+2) at a M(+1) site	+1
$\square V_M V_X \square^x$	associate of M and X vacancies at neighboring sites, Schottky defect	0
$\square F_X X_i \square^x$	associate of F at X site and X at an adjacent interstitial site	0

Examples

$Al_{Al}^{\times}$ = an aluminium ion sitting on an aluminium lattice site, with neutral charge.

$Ni_{Cu}^{\times}$ = a nickel ion sitting on a copper lattice site, with neutral charge.

$V_{Cl}^{\bullet}$ = a chlorine vacancy, with singular positive charge.

$Ca_i^{''}$ = a calcium interstitial ion, with double negative charge. = an electron. A

Defect chemical reaction

Reaction involving defects must be:

- mass balanced
- charge balanced: the effective charge must be balanced.
- site balanced: the ratio between anion and cation must remain constant

Example:

Formation of a Schottky defect in periclase:

$$Mg_{Mg}^{x} + O_{O}^{x} = V_{Mg}^{''} + V_{O}^{\square\square} + MgO\,(sf)$$

Thermodynamics of point defects I

- Free energy of a perfect crystal

$$G_{perf} = H_{perf} - TS_{perf} \qquad (1)$$

- The entropy has configurational, S_{conf}, and vibrational contributions S_{vib}

$$S_{perf} = S_{config} + S_{vib} \qquad (2)$$

- In a perfect crystal the configurational contribution is zero

- Free energy of a real crystal containing *n* Frenkel defect

$$G_{def} = G_{perf} + nh_{def} - nTs_{dvib} - TS_{conf} \qquad (3)$$

G_{perf}: free energy of the perfect crystal
h_{def}: enthalpy of formation of one defect
s_{dvib}: vibrational entropy of one defect
S_{conf}: configurational entropy due to the arrangement of *n* defects

$$g_{def} = h_{def} - Ts_{dvib} \qquad (4)$$

g_{def}: free energy of one defect

- Change of the free energy due to the formation of *n* defects:

$$\Delta G = G_{perf} - G_{def} = ng_{def} - TS_{conf} \qquad (5)$$

-Configurational entropy

$$S_{conf} = k \ln W \qquad (6)$$

Yanagida et al.: p. **60-61**

s. Exercice 2.1-4 in http://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

Thermodynamics of point defects II

-Number of ways to arrange n_v vacancies within a crystal with N lattice sites and to distribute n_i interstitial sites :

$$\Omega_v = \frac{N!}{(N-n_v)!\,n_v!} \qquad \Omega_i = \frac{N!}{(N-n_i)!\,n_i!} \qquad \Omega = \Omega_v \Omega_i \tag{7}$$

$$N! \approx N \ln N - N$$ (8, Stirling approximation)

-Configurational entropy (assuming number of interstial sites = number of lattice sites):

$$S_{conf} = 2k\left[N \ln N - (N-n)\ln(N-n) - n \ln n\right] \tag{9}$$

-Change of the free energy due to the formation of n defects:

$$\Delta G = n g_{def} - \left[N \ln\left(\frac{N}{N-n}\right) + n \ln\left(\frac{N-n}{n}\right)\right] \tag{10}$$

- Concentration of defects at equilibrium

$$\frac{\partial \Delta G}{\partial n} = 0 \Rightarrow \frac{n}{N} = \exp\left(\frac{-g_{def}}{2kT}\right) \tag{11}$$

Yanagida et al.: p. **60-61**

s. Exercice 2.1-4 in http://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

Thermodynamics of point defects III

Entropy

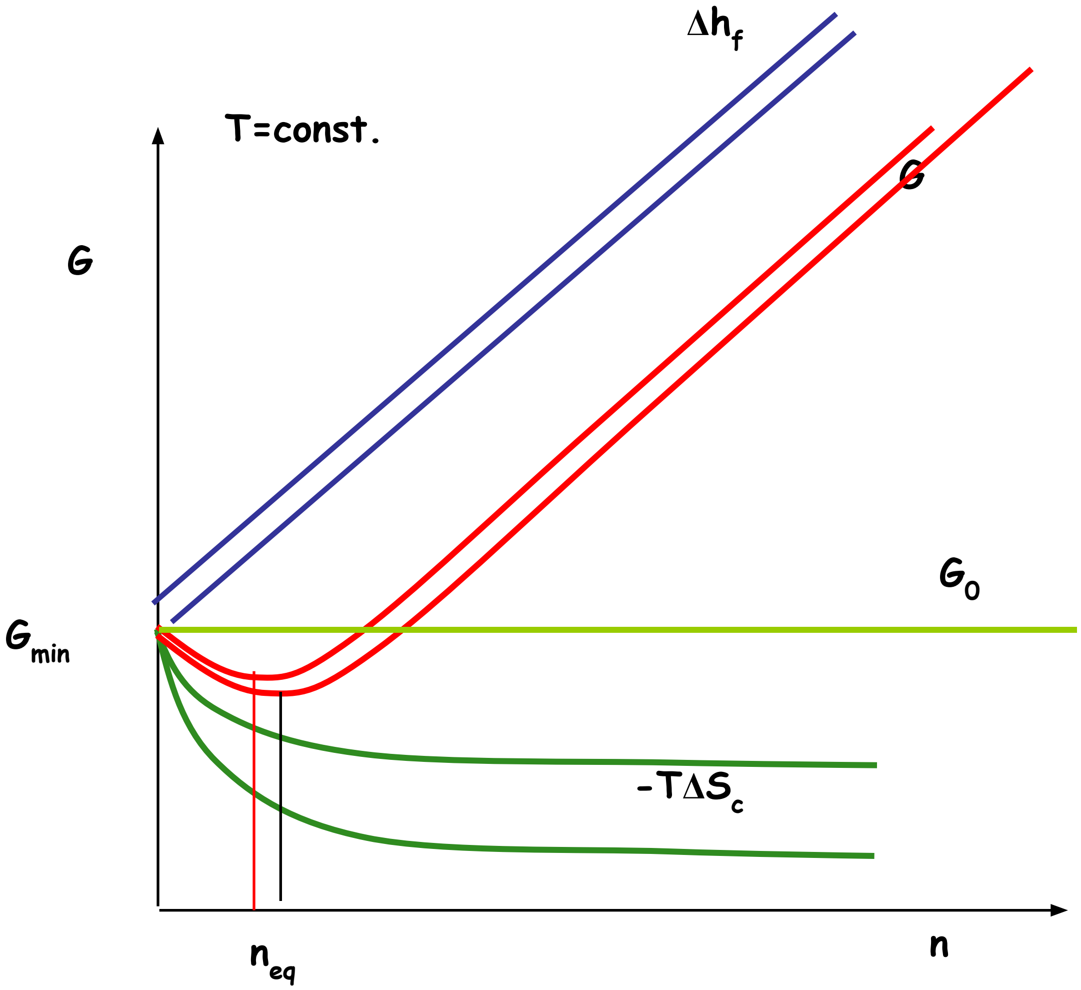
Configurational Entropy

Entropy originating from the many possibilities of arranging *many* vacancies

Formation ("vibrational") Entropy

It can be seen as the *additional* entropy or disorder added to the crystal with every additional vacancy. There is disorder associated with every single vacancy because the *vibration modes* of the atoms are disturbed by defects.Atoms with a vacancy as a neighbour tend to vibrate with lower frequencies because some bonds, acting as "springs", are missing. These atoms are therefore less well localized than the others and thus more "unorderly" than regular atoms.

Thermodynamics of point defects IV



The stippled lines are for a higher temperature than for the solid lines. The equilibrium defect concentration increases thus with increasing temperature.

Equilibrium Schottky defect concentration

- Formation of a Schottky defect pair in NaCl:

$$Na_{Na}^{x} + Cl_{Cl}^{x} \Leftrightarrow V_{Na}^{'} + V_{Cl}^{\bullet} + NaCl(sf) \quad \textbf{(1)}$$

$$\frac{X_{V,Na}\,X_{V,Cl}}{X_{Na,Na}\,X_{Cl,Cl}} = X_{V,Na}\,X_{V,Cl} = K_{eq} \quad \textbf{(2)}$$

- Number of Schottky pairs:

$$X_{V,Na}X_{V,Cl} = K_{eq} = \exp\left(\frac{-\Delta g_{def}}{2kT}\right) \quad \textbf{(3)}$$

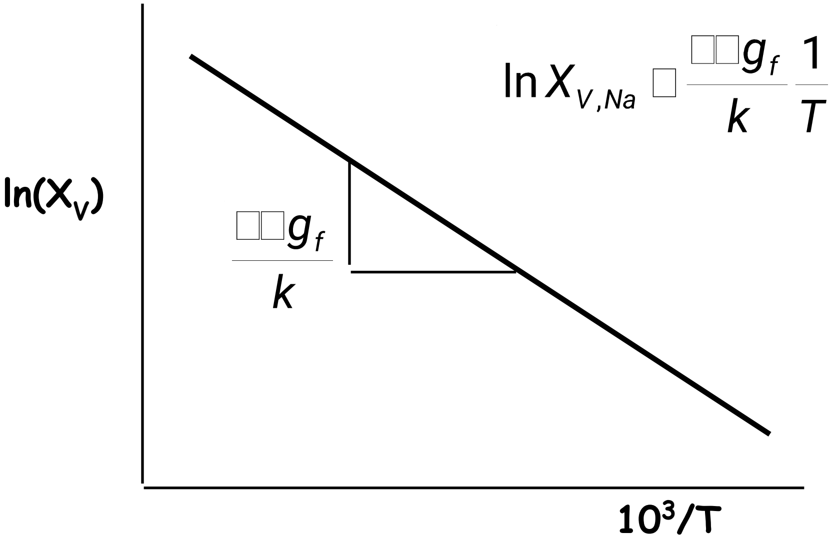
$$X_{V,Na} = X_{V,Cl} = \exp\left(\frac{-\Delta g_{def}}{kT}\right) \quad \textbf{(4)}$$

- Energetics of a Schottky pair in NaCl

$$\Delta h_{NaCl}^{Schottky} \approx 240 kJ/mol$$

$$\Delta S_{s,NaCl}^{Schottky} \approx 80 J/Kmol$$

- Arrhenius plot:



$$\ln X_{V,Na} = \frac{-\Delta g_f}{k}\frac{1}{T}$$

Yanagida et al.: p. **62--64**

Extrinsic defect concentration I

- Substitution of a divalent cation (Ca) for Na in NaCl and formation of extrinsic vacancies:

$$2\mathrm{Na}_{\mathrm{Na}}^{x} \square Ca \square \ Ca_{\mathrm{Na}}^{\square} + \mathrm{V}_{\mathrm{Na}}^{'} \square \mathrm{Na(sf)} \quad (1$$

$$X_{\mathrm{V,Na}} = X_{\mathrm{Ca,Na}} \quad (2)$$

- Formation of intrinsic vacancies:

$$\mathrm{Na}_{\mathrm{Na}}^{x} \square \mathrm{Cl}_{\mathrm{Cl}}^{x} \square \ \mathrm{V}_{\mathrm{Na}}^{'} + \mathrm{V}_{\mathrm{Cl}}^{\square} \square \mathrm{NaCl(sf)} \quad (3$$

- Total number of cation vacancies:

$$X_{\mathrm{V,Na}}^{\mathrm{tot}} = X_{\mathrm{V,Cl}} + X_{\mathrm{Ca,Na}} \quad (4)$$

- Number of anion vacancies:

$$X_{V,Na}^{tot} X_{V,Cl} \square K_{eq} \quad (5)$$

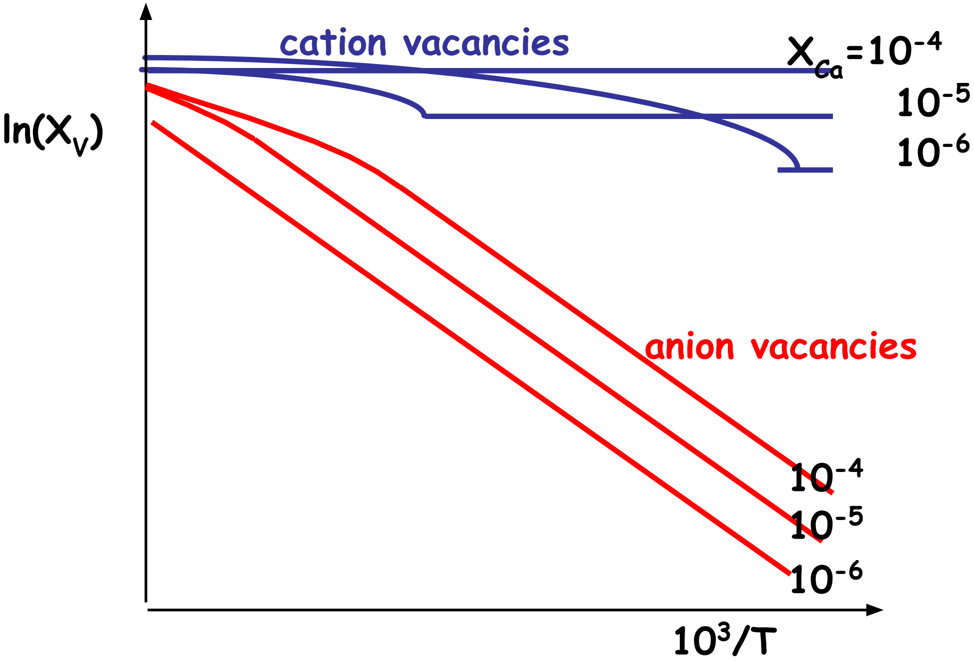
$$\square X_{V,Cl} \square X_{Ca,Na} \square X_{V,Cl} \square K_{eq} \quad (6)$$

$$\square X_{V,Cl} \square^{2} \square X_{V,Cl} X_{Ca,Na} \square K_{eq} \square 0 \quad (7)$$

$$X_{V,Cl} \square \frac{\square X_{Ca,Na} \square \sqrt{\square X_{Ca,Na} \square^{2} \square 4K_{eq}}}{2K_{eq}} \quad (8)$$

Extrinsic defect concentration II

- Temperature and impurity content dependence of vacancy concentrations in NaCl.



Nonstoichiometric defects

In nonstoichiometric defect reactions the composition of the cystal changes as a result of the reaction. One of the more common nonstoichiometric reactions that occurs at low oxygen partial pressure is

$$O_O^x = \frac{1}{2}O_2 + V_O^{\square\square} + 2e^-$$

The two electrons remain localized at the vacant site to guarantee charge neutrality.

At higher oxigen partial pressure addition of oxygen may lead to nonstoichiometry:

$$\frac{1}{2}O_2 = O_i^{\square\square} + 2h^{\square}$$

The label h means "electron hole" e.g. the oxygen atom "steels" the electrons from a cation leaving holes behind. The above reaction in the case of iron would be written

$$\frac{1}{2}O_2 = O_O^x + V_{Fe}^{\square\square} + 2h^{\square}$$

$$2Fe^{2+} + 2h^{\square} = 2Fe^{3\square}$$

The vacancy in the left side of the first reaction is necessary to maintain site neutrality. The overall reaction for the oxidation of magnetite is given by

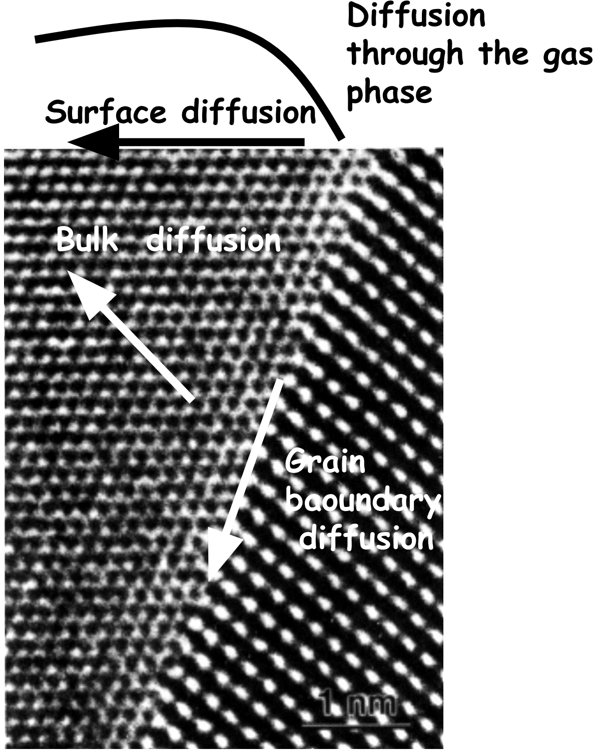
$$\frac{1}{2}O_2 + 2Fe^{2+} = O_O^x + 2Fe^{3\square} + V_{Fe}^{\square\square}$$

Diffusion

Atomic diffusion is a process whereby the random thermally-activated hopping of atoms in a solid results in the net transport of atoms. For example, helium atoms inside a balloon can diffuse through the wall of the balloon and escape, resulting in the balloon slowly deflating. Other air molecules (e.g. oxygen, nitrogen) have lower mobilities and thus diffuse more slowly through the balloon wall. There is a concentration gradient in the balloon wall, because the balloon was initially filled with helium, and thus there is plenty of helium on the inside, but there is relatively little helium on the outside (helium is not a major component of air).

Type of diffusion

Diffusion paths:



HRTEM image of an interface between an aluminum (left) and a germanium grain. The black dots correspond to atom columns.

In general: $D_{gp} > D_{sd} > D_{gb} >> D_b$ for high temperatures and short diffusion times

Diffusion mechanisms

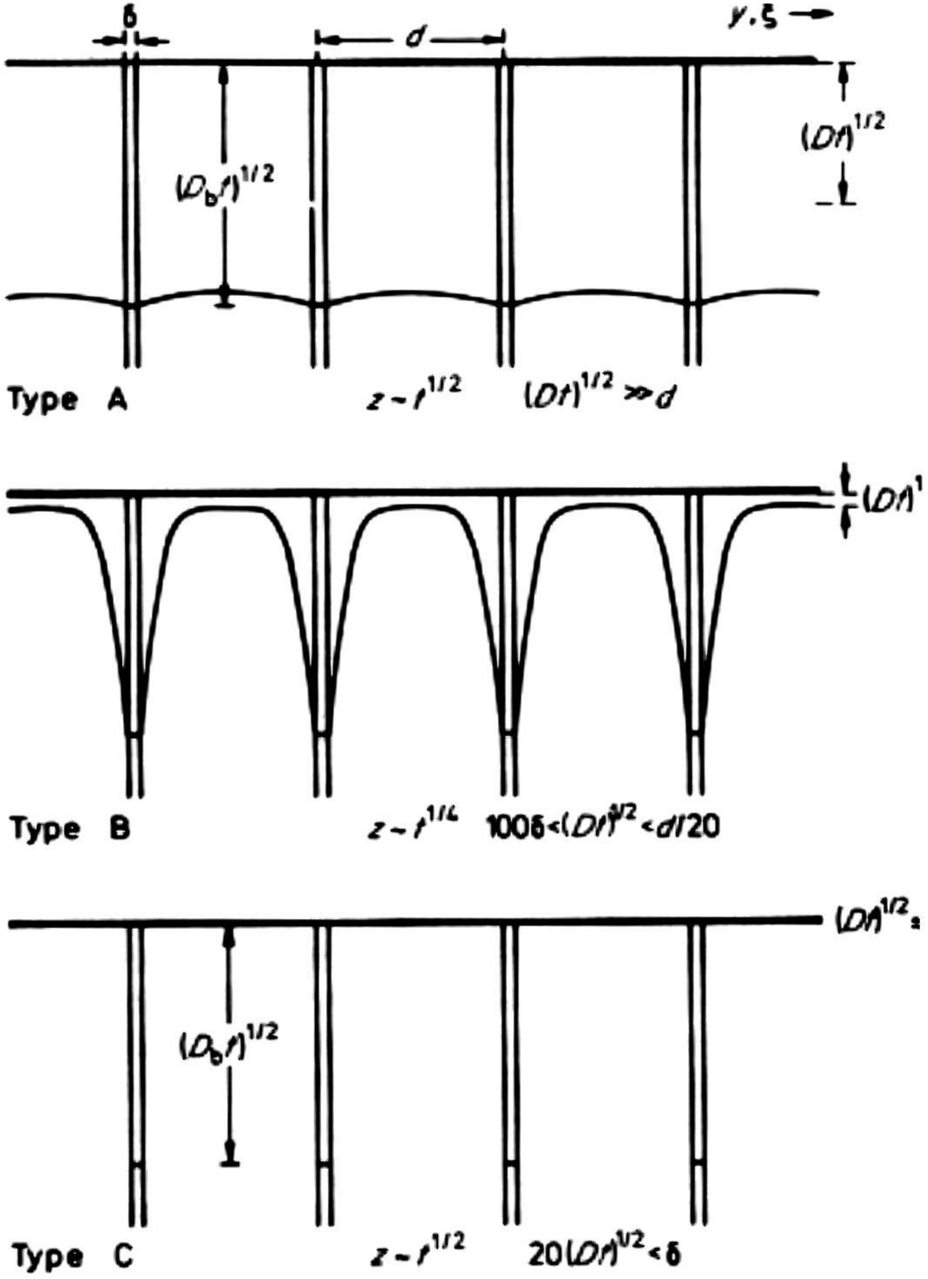
Self diffusion:
Motion of host lattice atoms. The diffusion coefficient for self diffusion depends on the diffusion mechanism:

Vacancy mechanism: $D_{self} = [C_{vac}]\, D_{vac}$

Interstitial mechanism: $D_{self} = [C_{int}]\, D_{int}$

Inter diffusion, multicomponent diffusion:
Motion of host and foreign species. The fluxes and diffusion coefficient are correlated

Diffusion regimes



Types of diffusion kinetics: 3 regimes A, B and C are usually distinguished. They are represented using a parallel boundary model:

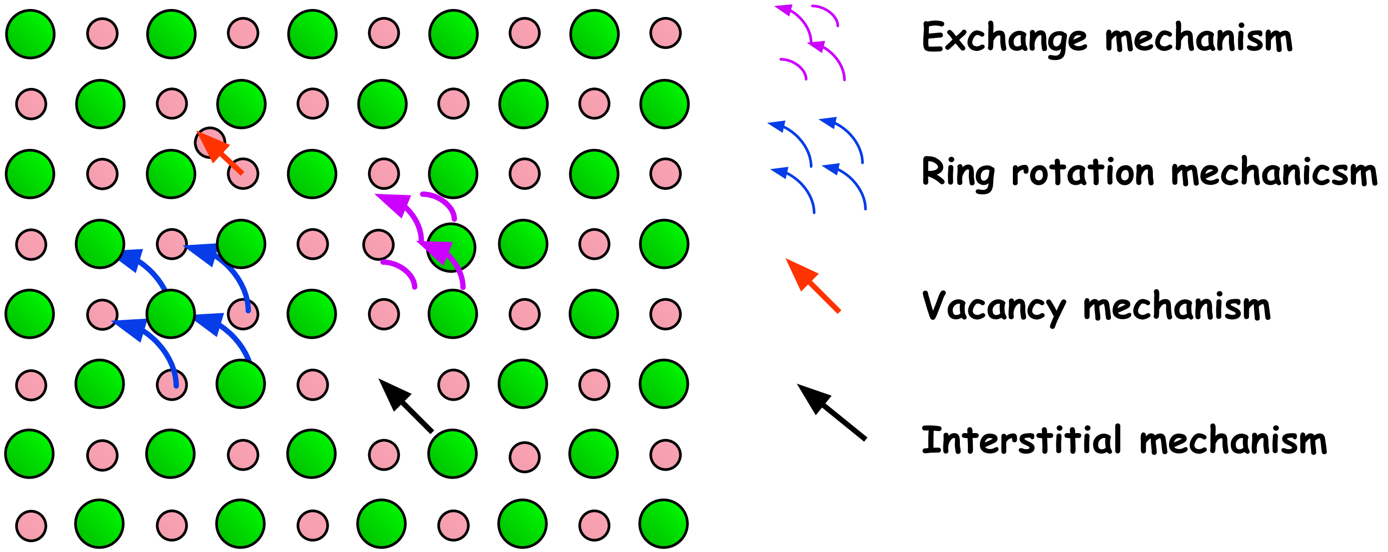
Type A: The diffusion front in the bulk and in the boundary advance ± with the same speed
valid for: - long annealing times
- small grain sizes
-volume diffusion coefficient D_b ≈ interface diffusion coefficient D

Type B: The diffusion in the *grain boundary* is considerably faster than in the bulk, but a certainamount of diffusant is lost to the bulk grains.

Type C: The diffusion in the bulk is negligible, the diffusant is transported only through the grainboundaries.
valid for: - short annealing times
(- large grain sizes)
-volume diffusion coefficient << interface diffusion coefficient

General diffusion law $z \sim Dt^{1/n}$

Atomistic diffusion mechanisms



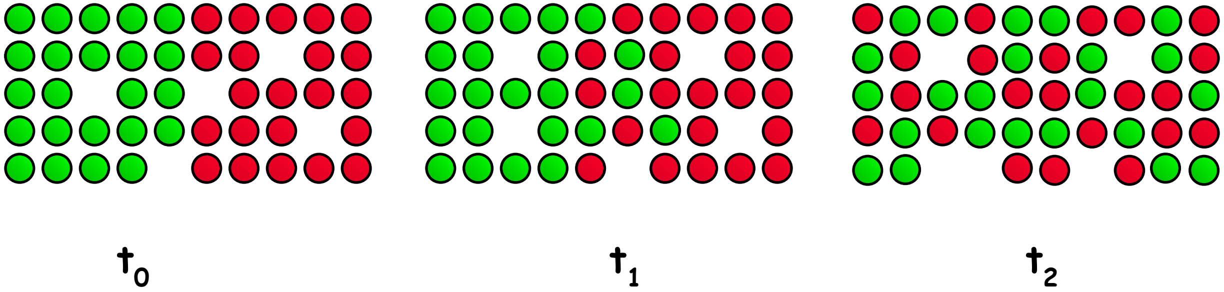
Exchange mechanism

Ring rotation mechanicsm

Vacancy mechanism

Interstitial mechanism

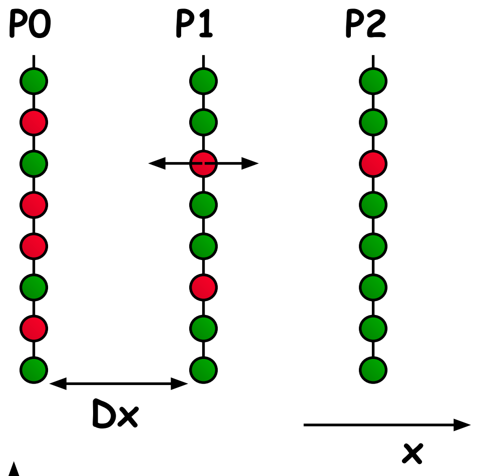
Diffusion couple

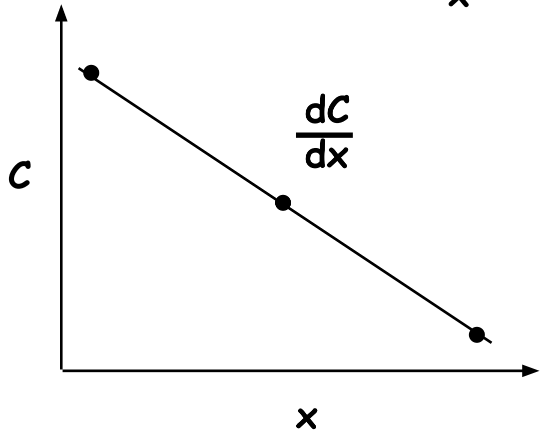


A diffusion couple is an assembly of two materials in such intimate contact that the atoms of each material can diffuse into the other.

Yanagida et al.: p. 58 - 68

Fick's 1. law





$$J_x = \frac{1}{2}(n_x - n_{x+\Delta x})\Gamma \qquad (1)$$

Γ: jump frequency

n: number of atoms

$$C_x = \frac{n_x}{\Delta x A} \qquad C_{x+\Delta x} = \frac{n_{x+\Delta x}}{\Delta x A} \qquad (2)$$

C_x: concentration on plane x

A: unit surface

$$J_x = \frac{1}{2}\Delta x\left(C_x - C_{x+\Delta x}\right)\Gamma \qquad (3)$$

$$J_x = \frac{1}{2}\Delta x^2\Gamma\frac{\partial C}{\partial x} \qquad (4)$$

$$J_x = -D\frac{\partial C}{\partial x} \qquad (5)$$

D: diffusion coefficient

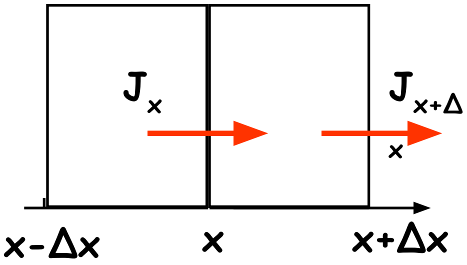
The flux J in direction x of the red atoms is proportional to the concentration gradient along x. It is obvious that the diffusion of the red atoms is coupled to the diffusion of the green atoms in the -x direction!

Coupling of fluxes:

$$D_{red}C_{red} = D_{green}C_{green}$$

Yanagida et al.: p. 122-132

Fick's 2. law



$$\Delta n = \frac{1}{2}\Gamma\left(n_{x-\Delta x} + n_{x+\Delta x} - 2n_x\right)\Delta t \quad (1)$$

$$\Delta n = \left(J_x - J_{x+\Delta x}\right)\Delta t \quad (2)$$

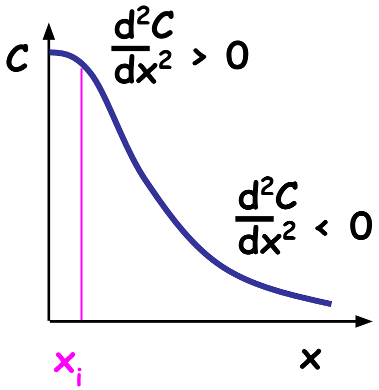
$$\frac{\Delta n}{\Delta t\,\Delta x} = \left(\frac{J_x - J_{x+\Delta x}}{\Delta x}\right) \quad (3)$$

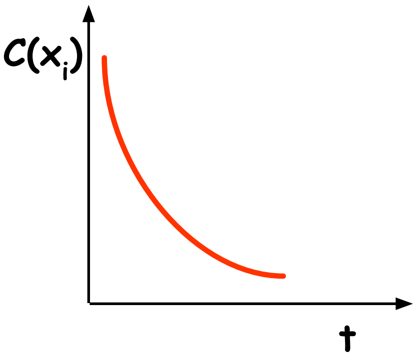
$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \quad (4)$$

$$\frac{\partial C}{\partial t} = \frac{\partial J}{\partial x} \quad (5)$$

with $J_x = -D\frac{\partial C}{\partial x}$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad (6)$$



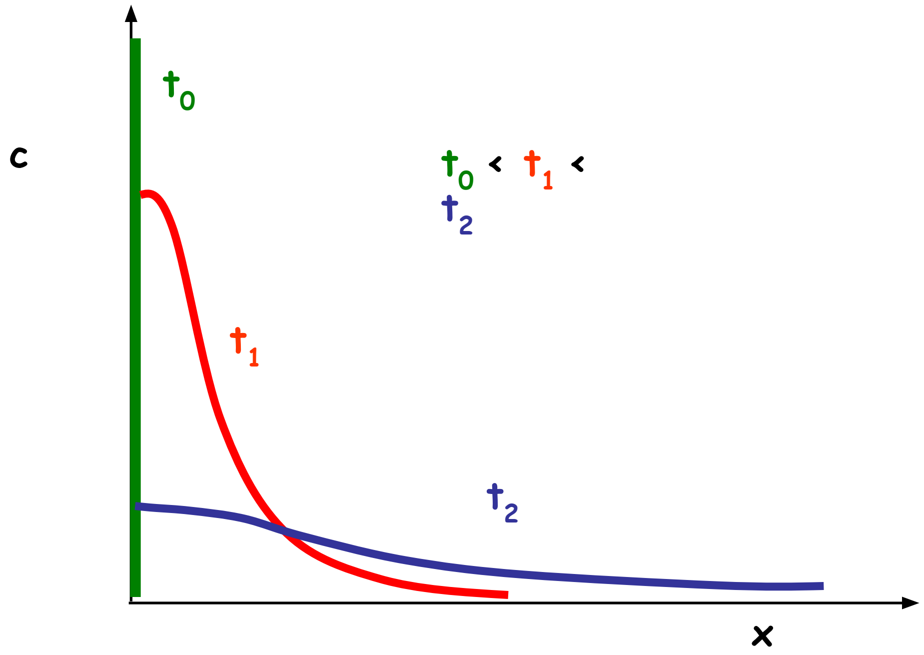


In regions where the concentration gradient is convex, the flux (and the concentration) will decrease with time, for concave gradients it will increase.

Solutions to Fick's 2. law I

-Finite thin film source, one-dimensional diffusion into semi-infinite solid:

$c(x \neq 0, t=0)$: 0

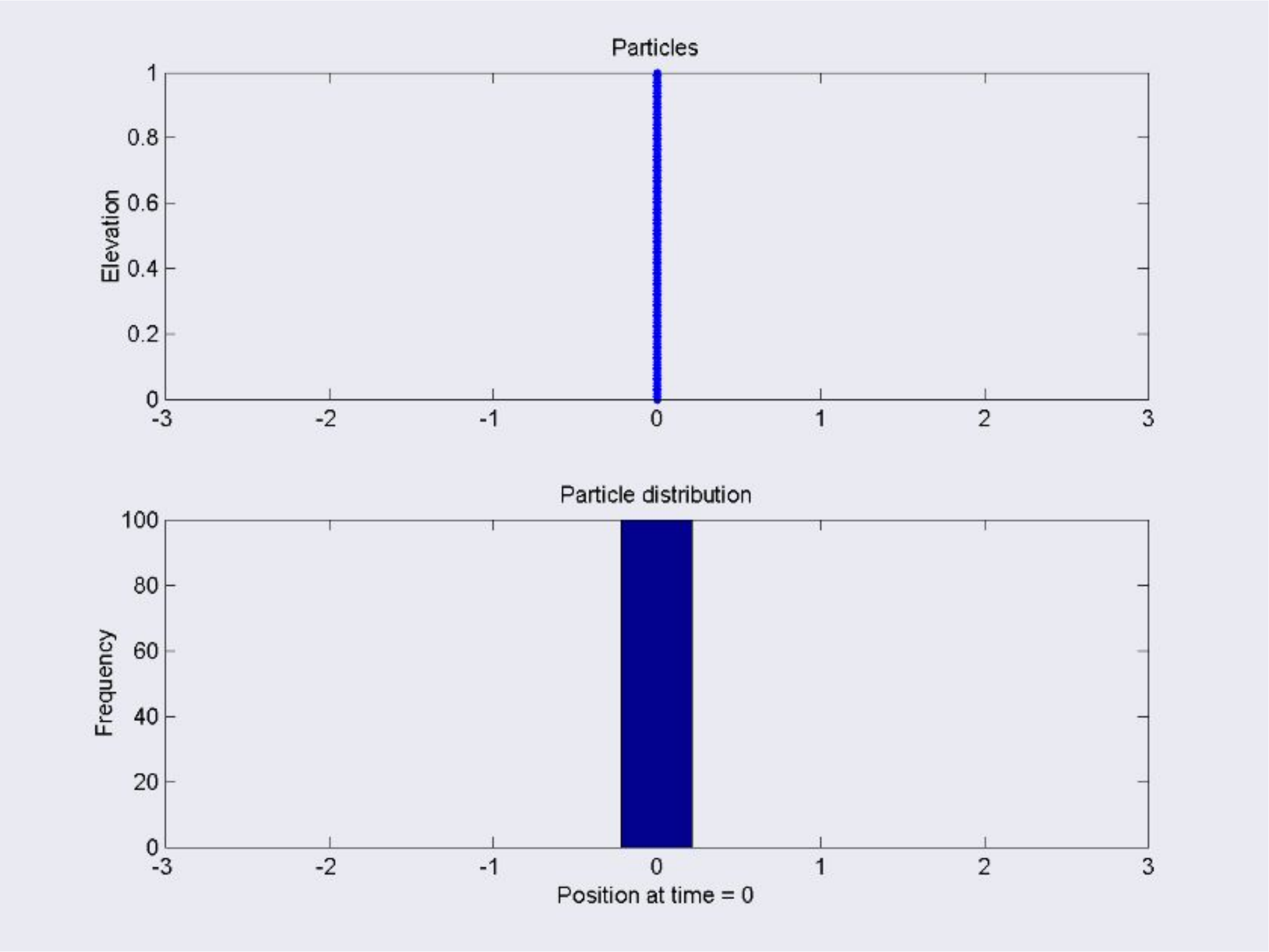


$t_0 < t_1 < t_2$

$$c(x,t) = \frac{s}{2\sqrt{\pi D t}} \exp^{\frac{-x^2}{4Dt}}$$

s: initial amount of diffusive species.

1-D diffusion

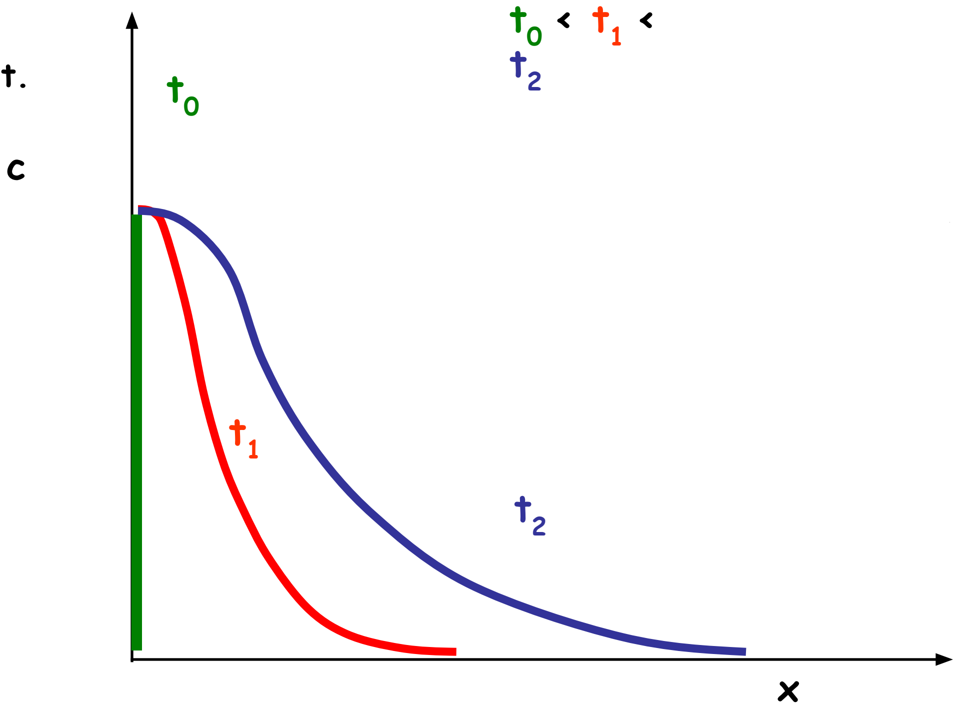


1-D diffusion from a finite point source

Solutions to Fick's 2. law II

-Finite thin film source of constant concentration, one-dimensional diffusion into semi-infinite solid:

$c(x\neq0, t=0)$: 0
$c(x=0, t)$: const.

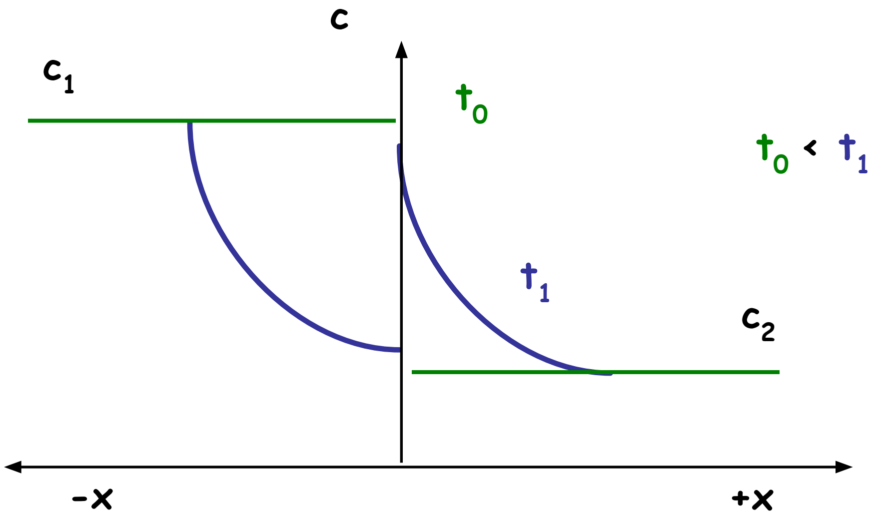


$$c(x,t) = c_0\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

c_0: initial concentration
erf: error function

Diffusion couple

$c(x < 0, t=0)$: c_1
$c(x > 0, t=0)$: c_2

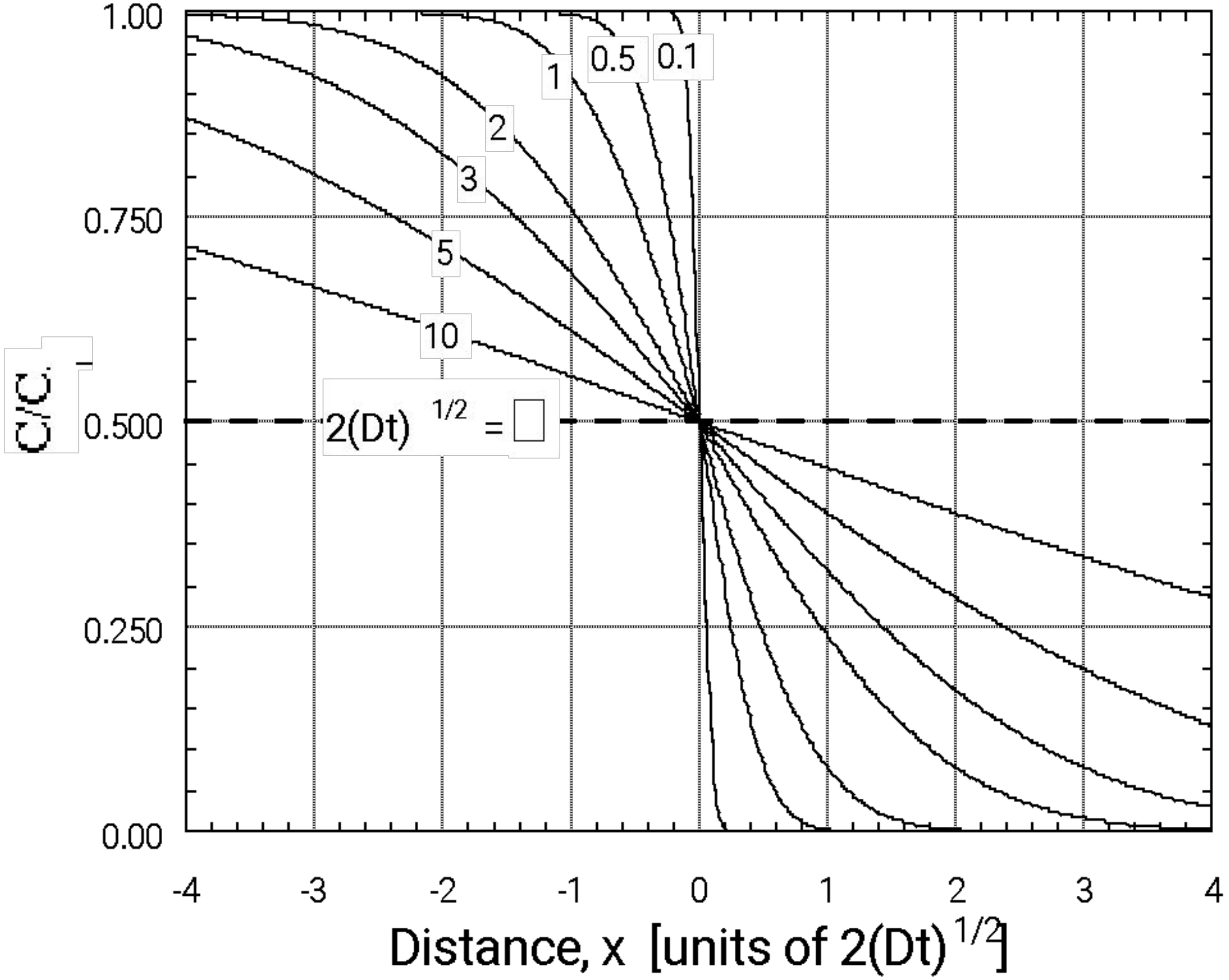


$$c(x,t) = \left(\frac{c_1 + c_2}{2} - \frac{c_1 - c_2}{2}\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

for $c_1 = c_i$ and $c_2 = 0$ $\quad c(x,t) = \frac{c_i}{2}\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right)$

$\frac{x}{2\sqrt{Dt}}$: = value of variable "x" in the error function table

1-D diffusion couple



Diffusion profiles for 1-D diffusion couple for different diffusion times

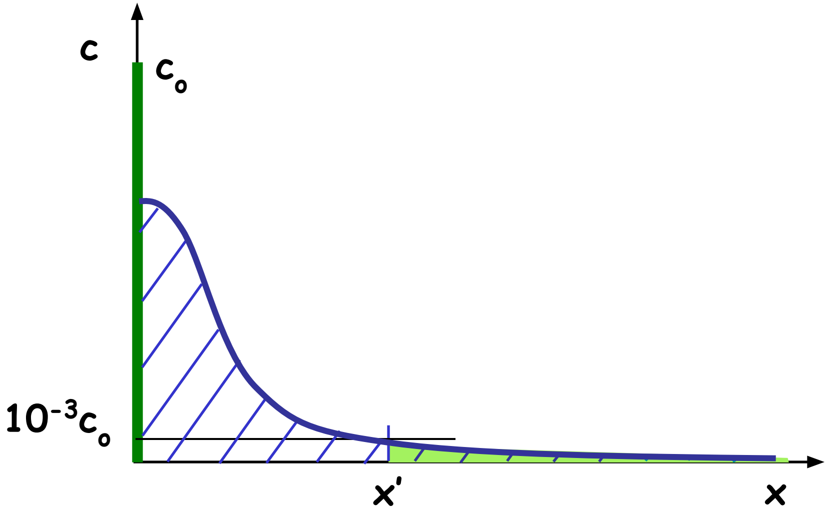
Error Function Table

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt$$

	Hundredths digit of x									
x	0	1	2	3	4	5	6	7	8	9
0.0	0.00000	0.01128	0.02256	0.03384	0.04511	0.05637	0.06762	0.07886	0.09008	0.10128
0.1	0.11246	0.12362	0.13476	0.14587	0.15695	0.16800	0.17901	0.18999	0.20094	0.21184
0.2	0.22270	0.23352	0.24430	0.25502	0.26570	0.27633	0.28690	0.29742	0.30788	0.31828
0.3	0.32863	0.33891	0.34913	0.35928	0.36936	0.37938	0.38933	0.39921	0.40901	0.41874
0.4	0.42839	0.43797	0.44747	0.45689	0.46623	0.47548	0.48466	0.49375	0.50275	0.51167
0.5	0.52050	0.52924	0.53790	0.54646	0.55494	0.56332	0.57162	0.57982	0.58792	0.59594
0.6	0.60386	0.61168	0.61941	0.62705	0.63459	0.64203	0.64938	0.65663	0.66378	0.67084
0.7	0.67780	0.68467	0.69143	0.69810	0.70468	0.71116	0.71754	0.72382	0.73001	0.73610
0.8	0.74210	0.74800	0.75381	0.75952	0.76514	0.77067	0.77610	0.78144	0.78669	0.79184
0.9	0.79691	0.80188	0.80677	0.81156	0.81627	0.82089	0.82542	0.82987	0.83423	0.83851
1.0	0.84270	0.84681	0.85084	0.85478	0.85865	0.86244	0.86614	0.86977	0.87333	0.87680
1.1	0.88021	0.88353	0.88679	0.88997	0.89308	0.89612	0.89910	0.90200	0.90484	0.90761
1.2	0.91031	0.91296	0.91553	0.91805	0.92051	0.92290	0.92524	0.92751	0.92973	0.93190
1.3	0.93401	0.93606	0.93807	0.94002	0.94191	0.94376	0.94556	0.94731	0.94902	0.95067
1.4	0.95229	0.95385	0.95538	0.95686	0.95830	0.95970	0.96105	0.96237	0.96365	0.96490
1.5	0.96611	0.96728	0.96841	0.96952	0.97059	0.97162	0.97263	0.97360	0.97455	0.97546
1.6	0.97635	0.97721	0.97804	0.97884	0.97962	0.98038	0.98110	0.98181	0.98249	0.98315
1.7	0.98379	0.98441	0.98500	0.98558	0.98613	0.98667	0.98719	0.98769	0.98817	0.98864
1.8	0.98909	0.98952	0.98994	0.99035	0.99074	0.99111	0.99147	0.99182	0.99216	0.99248
1.9	0.99279	0.99309	0.99338	0.99366	0.99392	0.99418	0.99443	0.99466	0.99489	0.99511
2.0	0.99532	0.99552	0.99572	0.99591	0.99609	0.99626	0.99642	0.99658	0.99673	0.99688
2.1	0.99702	0.99715	0.99728	0.99741	0.99753	0.99764	0.99775	0.99785	0.99795	0.99805
2.2	0.99814	0.99822	0.99831	0.99839	0.99846	0.99854	0.99861	0.99867	0.99874	0.99880
2.3	0.99886	0.99891	0.99897	0.99902	0.99906	0.99911	0.99915	0.99920	0.99924	0.99928
2.4	0.99931	0.99935	0.99938	0.99941	0.99944	0.99947	0.99950	0.99952	0.99955	0.99957
2.5	0.99959	0.99961	0.99963	0.99965	0.99967	0.99969	0.99971	0.99972	0.99974	0.99975
2.6	0.99976	0.99978	0.99979	0.99980	0.99981	0.99982	0.99983	0.99984	0.99985	0.99986
2.7	0.99987	0.99987	0.99988	0.99989	0.99989	0.99990	0.99991	0.99991	0.99992	0.99992
2.8	0.99992	0.99993	0.99993	0.99994	0.99994	0.99994	0.99995	0.99995	0.99995	0.99996
2.9	0.99996	0.99996	0.99996	0.99997	0.99997	0.99997	0.99997	0.99997	0.99997	0.99998
3.0	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998	0.99999	0.99999	0.99999
3.1	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999
3.2	0.99999	0.99999	0.99999	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000

Diffusion front

- Distance x’ from a source with finite concentration where a certain small amount of the initial concentration has passed f.ex. < $10^{-3}\,c_0$:



Diffusion profile after time t:

▨ $$c_0 \square \int_0^{\infty} \exp^{-x^2/4Dt}\,dt$$

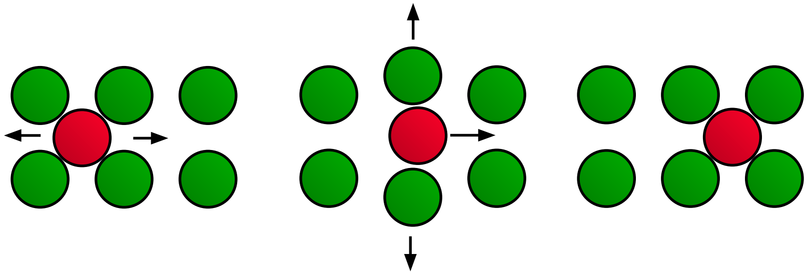
Material that diffused beyond the point x' at which the concentration is $10^{-3}\,c_0$:

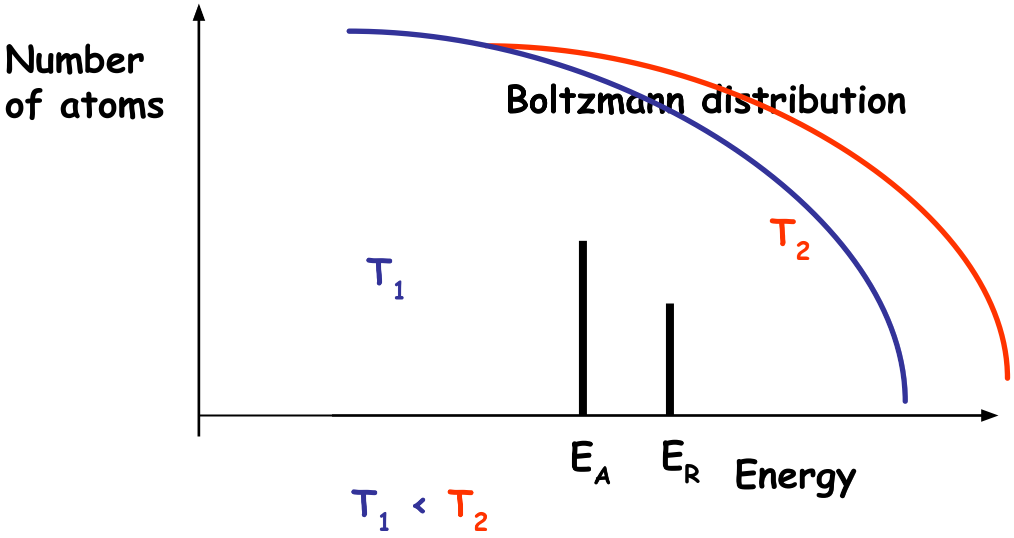
🟩 $$10^{-3} c_0 \square \int_{x'}^{\infty} \exp^{-x^2/4Dt}\,dt$$

$$10^{-3} \square \frac{\int_{x'}^{\infty} \exp^{-x^2/4Dt}\,dt}{\int_0^{\infty} \exp^{-x^2/4Dt}\,dt}$$

solving for x’: $x' \square 4\sqrt{Dt} \square \sqrt{Dt}$

Diffusion: A thermally activated process I





Energy of red atom= E_R

Minimum energy for jump = E_A

Probability that an atom has an energy $>E_A$:

$$P_{E_N > E_A} \propto \exp\left(-\frac{E_A}{kT}\right)$$

Diffusion coefficient

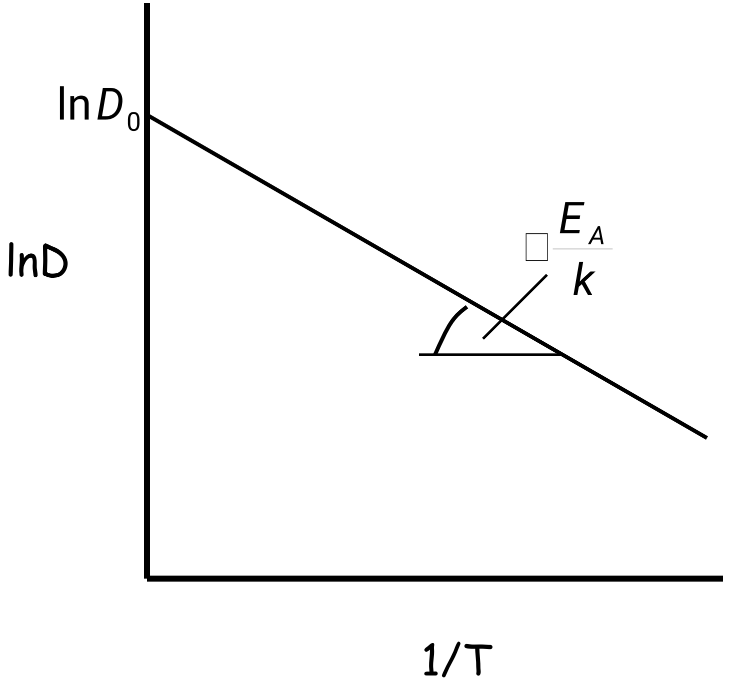
$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

D_0: Preexponential factor, a constant which is a function of jump frequency, jump distance and coordination number of vacancies

$$D_0 \;\square\; \square\square\;\square^2$$

Diffusion: A thermally activated process II

The preexponential factor and the activation energy for a diffusion process can be determined from diffuson experiments done at different temperatures. The result are presented in an Arrhenius diagram.



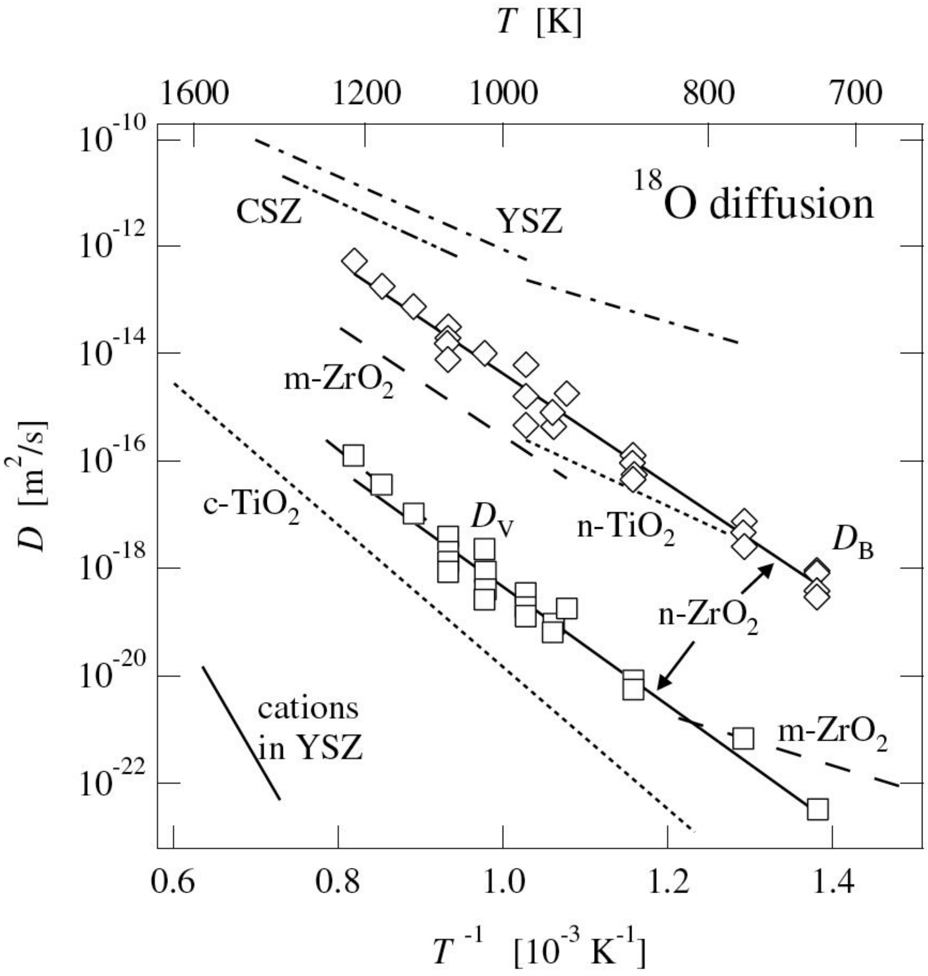
$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

$$\ln D = \ln D_0 - \frac{E_A}{k}\frac{1}{T}$$

In the Arrhenius diagram the slope is proportional to the activation energy and the intercept gives the preexponential factor.

Diffusion coefficients I

Tracer diffusion coefficients of ^{18}O determined by SIMS profiling for various micro- and nanocrystalline oxides: coarse grained titania c-TiO2 (- - - -), nanocrystalline titania n-TiO2 (- - - -), microcrystalline zirconia m-ZrO2 (- - -), zirconia doped with yttrium or calcium (YSZ —· · —, CSZ — · —), bulk diffusion DV ( ) and interface diffusion DB (♦) in nanocrystalline ZrO2 (——), after Brossmann et al. 1999.



Diffusion coefficients II

Self diffusion coefficient for cations and oxygen in corundum, hematite and eskolaite. Despite having the same structure, the diffusion coefficient differ by several orders of magnitude.