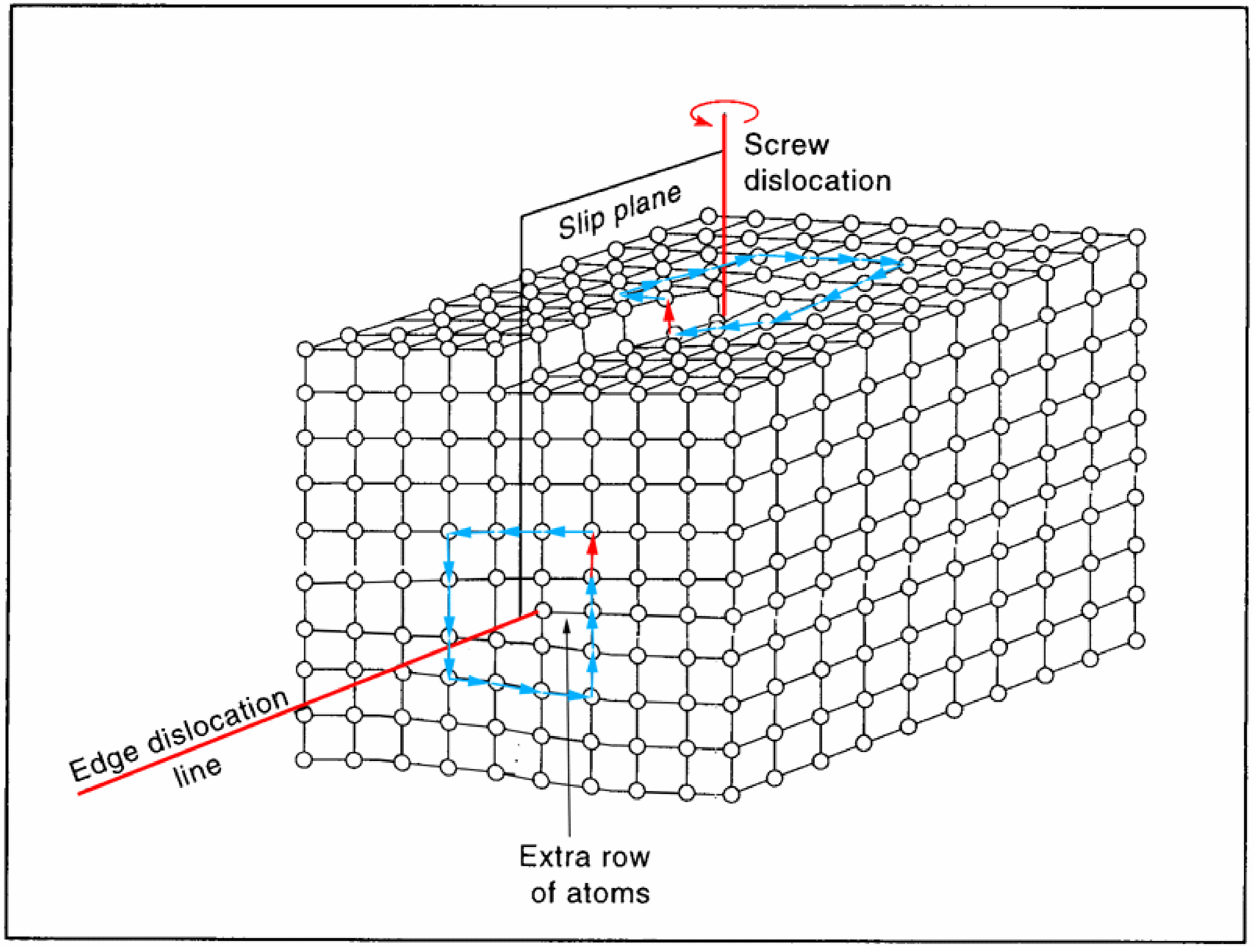
Burger's Vector ($\vec{b}$)

What is Burger's vector?

How do we find it?

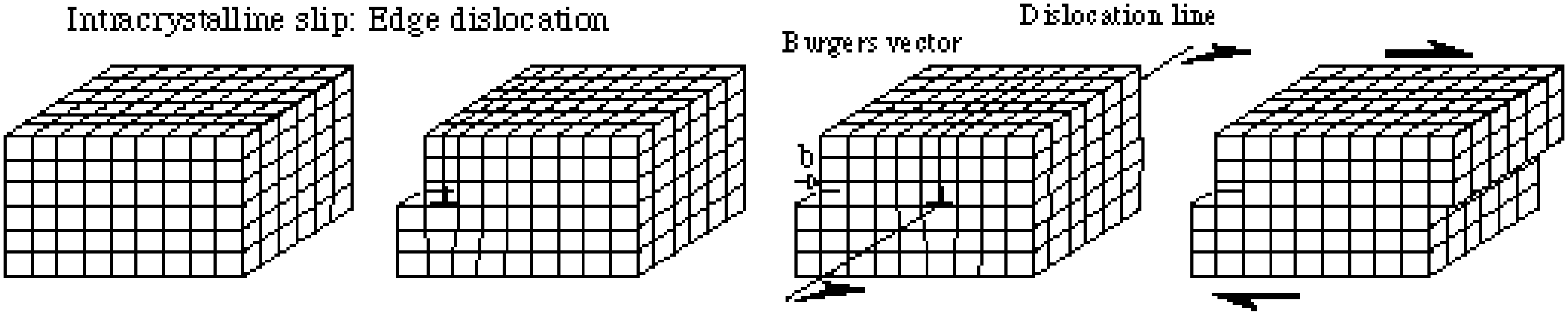
What does it tell us?

What is the relationship between Burger's vector and deformation of metals?



Dislocation Generation and Motion– Shear forces generates AND moves dislocations

How shear stress generate dislocaitons:



Under the action of applied shear stress, τ , the dislocation line movs parallel to its Burger's vector, $\vec{b}$.

During this process only bonds along the line of the dislocaiton have to be broken to move the disl^n.

For an edge dislocation, the Burger's vector is perpendicular to the dislocation line direction, and the half-plane.

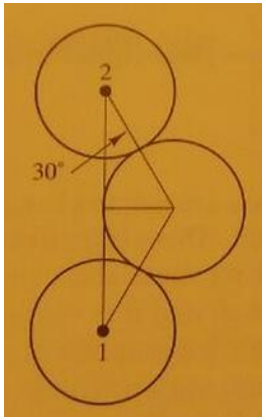
Example for Burger's Vector

Calculate the magnitude of the Burger's vector for alpha-Fe, Al, and Al_2O_3

$r_{Fe} = 0.124$ nm

$r_{Al} = 0.143$ nm

$r_{O2-} = 0.132$ nm



Energy of a Dislocation

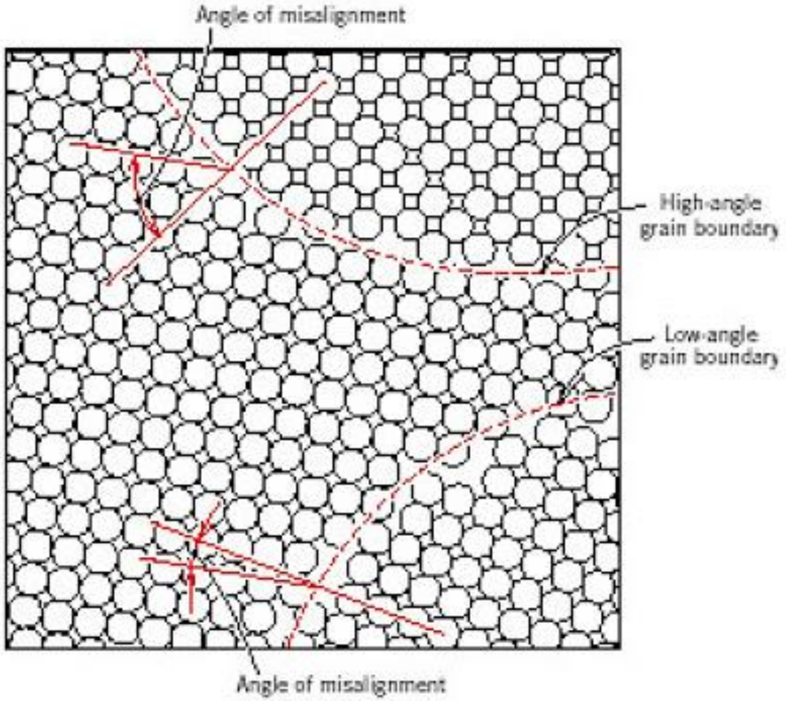
$$E_{\text{total}} \approx G \cdot b^2$$

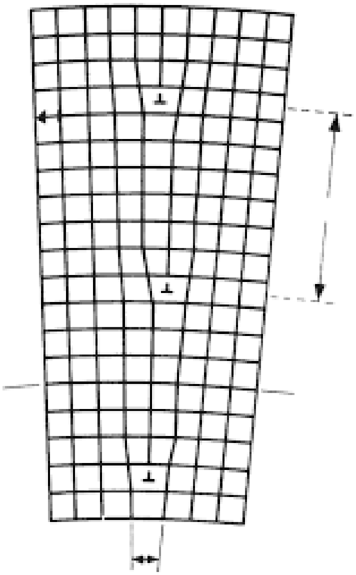
where E_{total} is the energy of a dislocation, G is the shear modulus, and b is the magnitude of the burgers vector.

The direction of a dislocation motion is highly dependent on the burgers vector on different directions.

2-D Defects : Grain Boundaries and Phase Boundaries

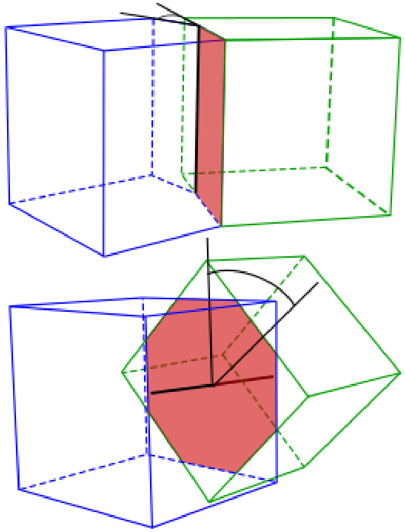
When crystals with different crystallographic orientations are joined, grain or phase boundaries form (if 2 surface energy is larger than 1 GB energy). (e.g. Solidification of a crystal)





For a small angle boundary, made up of a dislocaiton array, where dislocations are seperated by a distance L. For small angles,

$L = |\vec{b}|/\phi$



As with other imperfections, grain boundaries are the areas where the energy is higher than the perfect lattice. This leads GB as more reactive.

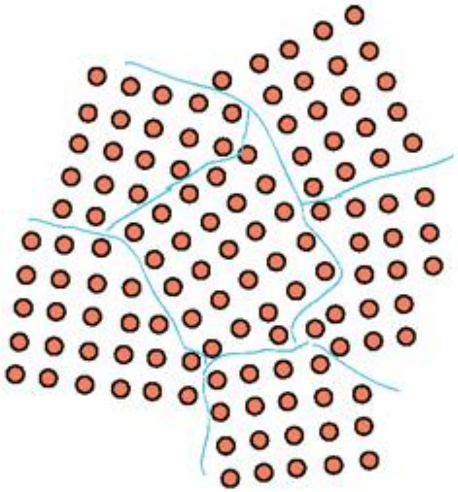
GB may move at high temperatures to decrease its total energy (γGB). This is the driving force behind the GB-migration and grain growth.

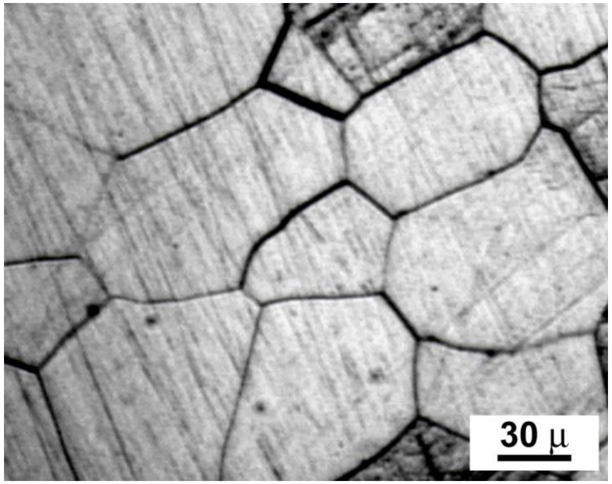
GBs are locations where many «accomodation» processes can take place, such as:

Dislocation source and sink

Segregation of misfit foreign atoms

Second phases, or films at GBs.





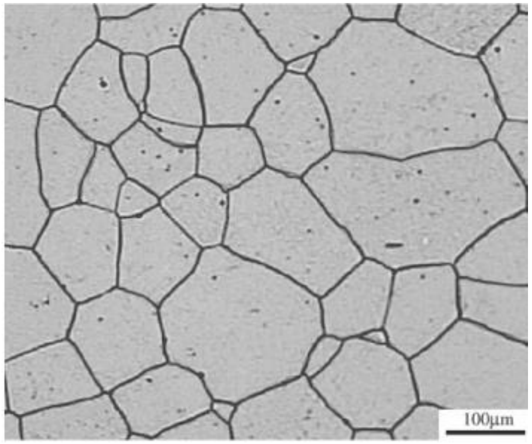
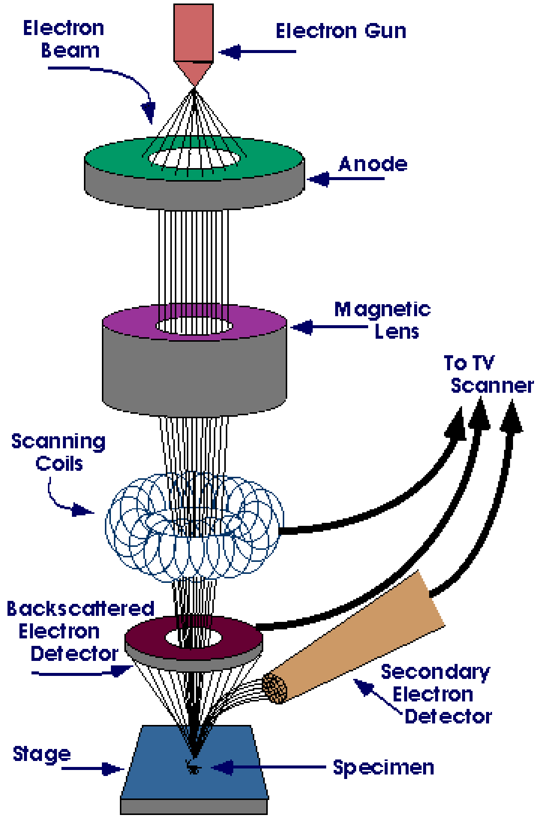
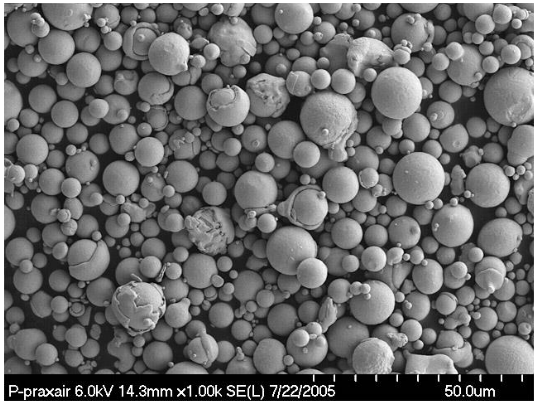


Figure 1. Typical microstructure of polycrystalline ZnO used in this work, after thermal etching at 1150 °C, for 1 h, in air.

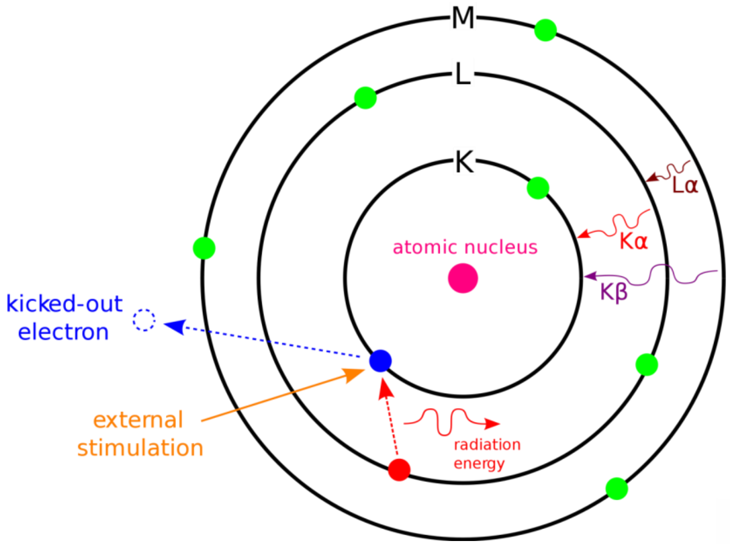
Microscopy

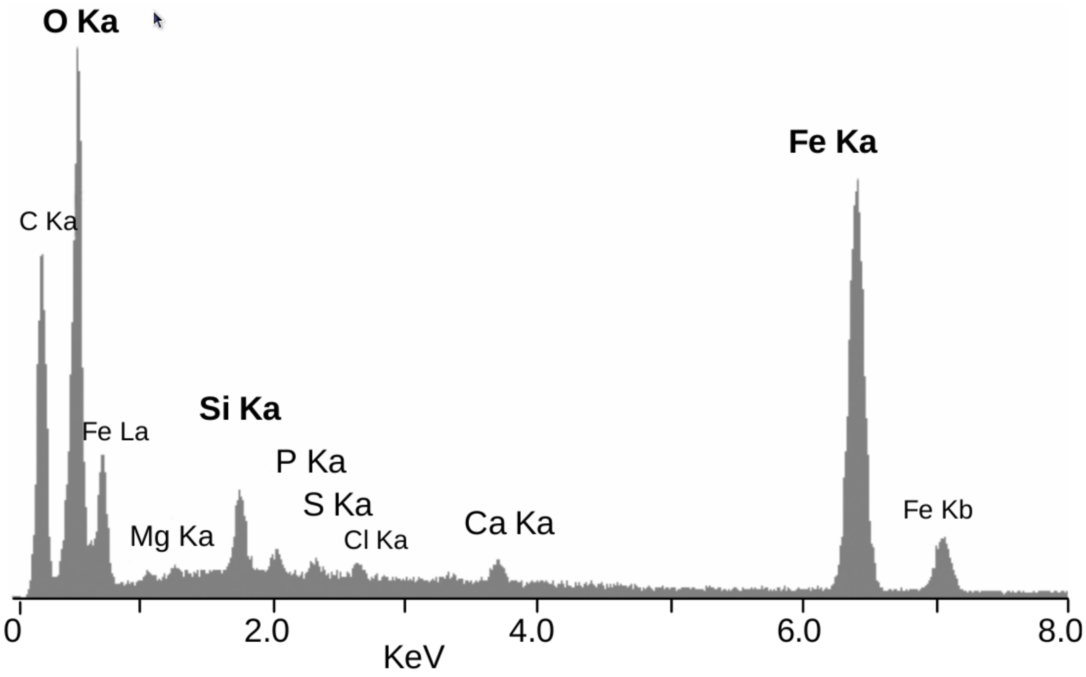

GEMINI
LEO
LEO 1550 VP


Electron Beam
Electron Gun
Anode
Magnetic Lens
To TV Scanner
Scanning Coils
Backscattered Electron Detector
Secondary Electron Detector
Stage
Specimen


P-praxair 6.0kV 14.3mm x1.00k SE(L) 7/22/2005
50.0um

Energy Dispersive X-Ray Spectroscopy, EDX





Kröger-Vink Notation

Since in ionic solids, there are species involved with charges, one has devised a notation to describe possible defect configuration: *Kroger-Vink Notation*
In this notation, defects are defined relative to "perfect" crystal.

Possible point defects are

-vacancies
-substitutional solutes
-interstitial solutes
-Misplaced atoms
-free electrons or holes
-associated defects
and their charges

The notation has three parts
Body: defines type of defect: vacancy or atom
Subscript: defines the location of the defect: normal atom site or interstitial site(*i*)
Superscript: defines the effective charge of the defect : Where dot (·), defines positive effective charge; apostrophe (') defines negative effective charge.

e.g. $Al^{\cdot}_{Mg}$: An Al^{+3} ion sitting in the site which is usually occupied by a Mg^{+2} ion. And the effective charge of the defect is +1.

e.g. $V^{```}_{Al}$: A vacant Al^{+3} ion site with an effective 3 negative charges relative to the perfect lattice.

Some fraction of electrons or holes, even in strongly ionic material may not me localized at a particullar site. They will be noted as e' or $h^{\cdot}$. In addition to single defects, some defects may associate with one another forming a defect cluster.
$(V_{Na}' \; V^{\cdot}_{Cl})$ a clustered sodium and chlorine vacancy pair which are electrically neutral (*).

Solid Solutions

Lowering of G resulting from an increase in S requires that there is at least a small solubility for foreign atoms in the structure. Factors that allow substitution are

Size factor:	$\Delta \varnothing < 15\ \%$ → substitutional solid solution $\Delta \varnothing > 15\ \%$ → $\mathrm{conc}_{\mathrm{subst.}} < 1\ \%$
Valency Factor:	If solute's valence is different that solvent's and there is a limited substitution.
Chemical Affinity:	The greater chemical reactivity of the solute with host, the smaller is the solid solubility. So there occurs a new phase.
Structure Type:	For complete solid solubility the end members must have the same crystal structure.

Solutes that differ in their valence from the host ion _that they are replacing (aliovalent substitution) _must be compensated by additional charged defects in order to maintain the charge neutrality.

$$\mathrm{CaO}\ (s) \xrightarrow{ZrO_2} \mathrm{Ca}_{\mathrm{Zr}}'' + \mathrm{O}^{*}_{\mathrm{O}} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot}$$

There may be several possible defect reactions. Especially if defect ion (solute) is of similar size like the host ion. For example introducing Al into MgO Al^{+3} and Mg^{+2} are of similar sizes in octahedral coordination.

→ Al^{+3} substitutes for Mg^{+2}

$$Al_2O_3 \xrightarrow{MgO} 2Al_{Mg}^{\cdot} + 3O^{*}_{O} \qquad \text{(mass balance)}$$

But stoichiometry (site) and charge balance are not yet satisfied.

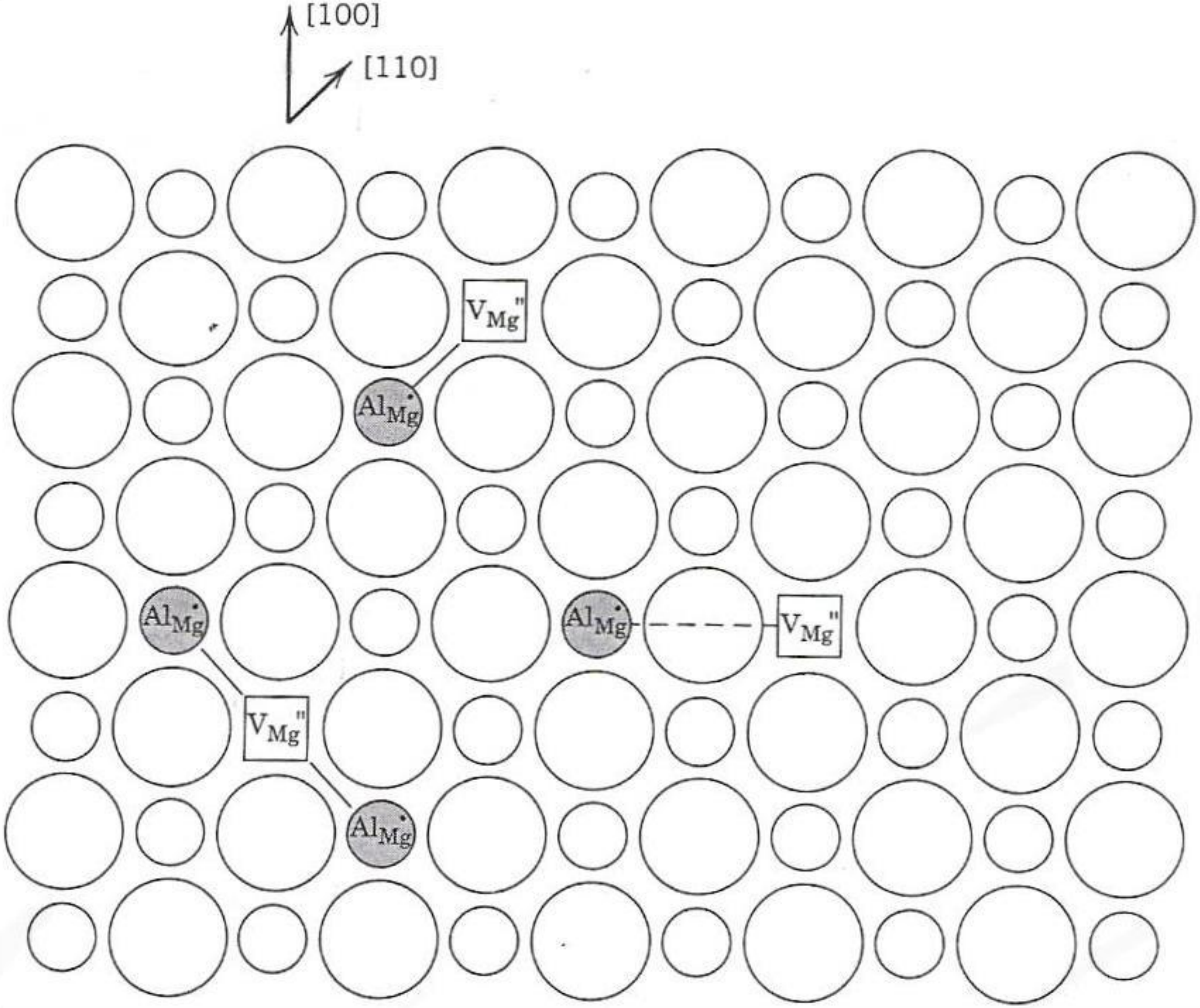
$$Al_2O_3 \xrightarrow{MgO} 2Al_{Mg}^{\cdot} + 3O^{x}_{O} + V_{Mg}''$$

Now mass, charge, and anion to cation ratio (stoichiometry and site balance) are satisfied.
What happens if Mg impurity is introduced to Al_2O_3

If substitutional: $MgO \xrightarrow{Al_2O_3} 2Mg_{Al}' + 2O^{x}_{O} + V_{O}^{\cdot\cdot}$

If interstitial : $3MgO \xrightarrow{Al_2O_3} 3Mg_{i}^{\cdot\cdot} + 3O^{x}_{O} + 2V_{Al}'''$

Mixed or “self-compensating” $3MgO \xrightarrow{Al_2O_3} 2Mg_{Al}' + 3O^{x}_{O} + Mg_{i}^{\cdot\cdot}$



[100]
[110]
V_{Mg}''
$Al_{Mg}^{\cdot}$
$Al_{Mg}^{\cdot}$
$Al_{Mg}^{\cdot}$
V_{Mg}''
V_{Mg}''
$Al_{Mg}^{\cdot}$

4.9 Nonstoichiometric Solids

In elementary chemistry and in many analytical chemical techniques we rely on the idea that chemical compounds are formed with constant fixed proportions of constituents. From a consideration of structure vacancies and interstitial ions we have already seen that this is only a special case and that compounds without simple ratios of anions to cations, that is, nonstoichiometric compounds, are not uncommon. An example for which the stoichiometric ratio does not even exist is wüstite, having an approximate composition of $Fe_{0.95}O$. This material has the sodium chloride structure; samples of different compositions were studied by E. R. Jette and F. Foote,* with the results shown in Table 4.5. For samples of different composition, the unit-cell size and the crystal density were determined. The departure from stoichiometry might be accounted for either by oxygen ions in interstitial positions (to give $FeO_{1.05}$, for example) or by vacant cation sites. Since the density increases

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*E. R. Jette and F. Foote, *J. Chem. Phys.*, 1, 29 (1933).

Table 4.5. Composition and Structure of Wüstite[a]

Composition	Atom% Fe	Edge of Unit Cell (Å)	Density (g/cm^3)
$Fe_{0.91}O$	47.68	4.290	5.613
$Fe_{0.92}O$	47.85	4.293	5.624
$Fe_{0.93}O$	48.23	4.301	5.658
$Fe_{0.945}O$	48.65	4.310	5.728

Source. E. R. Jette and F. Foote, *J. Chem. Phys.*, 1, 29 (1933).

as the oxygen-to-iron ratio decreases, the changing structure must be due to cation vacancies. As more iron vacancies are created, the density decreases, as does the size of the unit cell.

To compensate for the smaller number of cations and consequent loss of positive charge, two Fe^{2+} ions must be transformed into Fe^{3+} ions for each vacancy formed. From a chemical point of view, we may consider this simply as a solid solution of Fe_2O_3 in FeO in which, in order to maintain electrical neutrality, three Fe^{2+} ions are replaced by two Fe^{3+} and a vacant lattice site, that is, $Fe_2^{3+}V_{Fe}O_3$ replaces Fe_3O_3, in which V_{Fe} represents a vacant cation site. To a first approximation the Fe^{2+} ions may be considered as distributed at random. Similar structures are observed for FeS and FeSe, in which ranges of stoichiometry occur corresponding to vacancies in the cation lattice. Other examples are $Co_{1-x}O$, $Cu_{2-x}O$, $Ni_{1-x}O$, γ-Al_2O_3, and γ-Fe_2O_3. Similarly, there are compounds with vacancies in the anion lattice such as ZrO_{2-x} and TiO_{2-x}. Also oxides occur in which there are interstitial cations such as $Zn_{1+x}O$, $Cr_{2+x}O_3$, and $Cd_{1+x}O$. Compounds with interstitial anions are less common, but UO_{2+x} is one.

For the reaction of TiO_2 to form TiO_{2-x} plus $\frac{x}{2}O_2(g)$

$$2Ti_{Ti} + O_O = 2Ti'_{Ti} + V_O^{\cdot\cdot} + \frac{1}{2}O_2(g) \tag{4.57}$$

is equivalent to

$$O_O = V_O^{\cdot\cdot} + \frac{1}{2}O_2(g) + 2e' \tag{4.58}$$

where e' is an added electron in the structure. Similarly, the absence of an electron normally present in the stoichiometric structure corresponds to an electron hole or a missing electron $h^{\cdot}$

$$2Fe_{Fe} + \frac{1}{2}O_2(g) = 2Fe^{\cdot}_{Fe} + O_O + V''_{Fe} \tag{4.59}$$

$$\frac{1}{2}O_2(g) = O_O + V''_{Fe} + 2h^{\cdot} \tag{4.60}$$

Oxides in general show a variation of composition with oxygen pressure, owing to the existence of a range of stoichiometry. Stable oxides having a cation with a preference for a single valence state (a high ionization potential) such as Al_2O_3 and MgO have very limited ranges of nonstoichiometry, and in these materials observed nonstoichiometric effects are very often related to impurity content. Oxides of cations having a low ionization potential can show extensive regions of nonstoichiometry. For reactions such as those illustrated in Eqs. 4.57 to 4.60 we can write mass-action expressions and equilibrium constants and relate the atmospheric pressure to the amount of nonstoichiometry observed.

SURFACES

Surface Atoms

"Everything you see is a surface"
Almost everything happens at surfaces too. Oxidation, corrosion, soldering, sintering, bonding, etc

Surface Energy

Surface tension

Surface tension as driving force

Atoms at surfaces are more energetic than the atoms deep in the interior of a solid. This is because the atoms in the surfaces are bound with fewer bonds. Energy of these atoms depends on the geometry of the surface

increasing reactivity of atoms:
on concave < planar < convex surfaces.

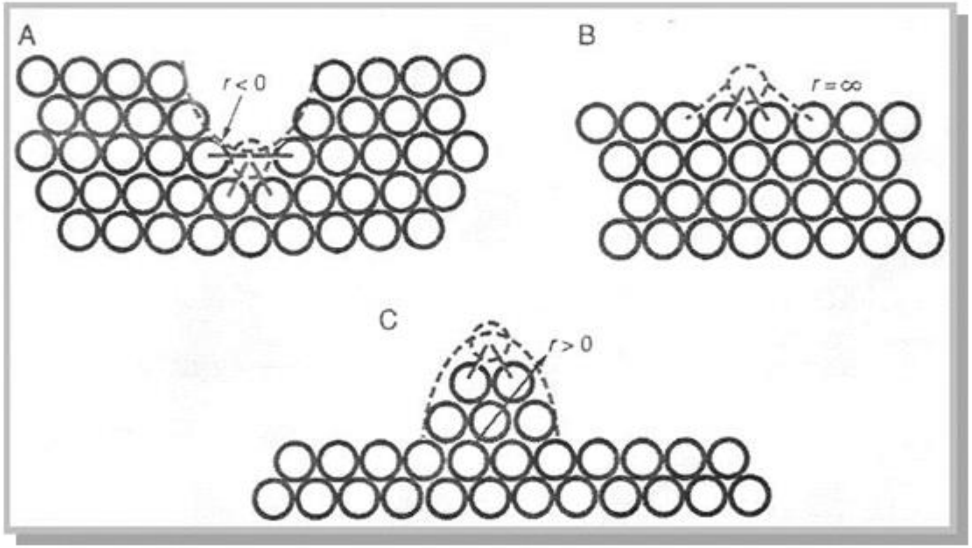


Figure 4.1 Atoms on (a) concave surface, (b) planar surface, (c) convex surface. On the convex surface atoms are most reactive: on the concave surface they are least reactive.

Surface free energy, γ: The difference in energy per unit area between atoms of a surface relative to the atoms embedded well below the surface (in the bulk)

Typically $0{,}1\ \mathrm{J/m^2} < \gamma < 1\ \mathrm{J/m^2}$

Surface energy for a material with spherical geometry, with radius, r

$$E_s = 4\pi r^2 . \gamma$$

$1\ \mathrm{J} = 6.24\ 10^{18}\ \mathrm{eV}$

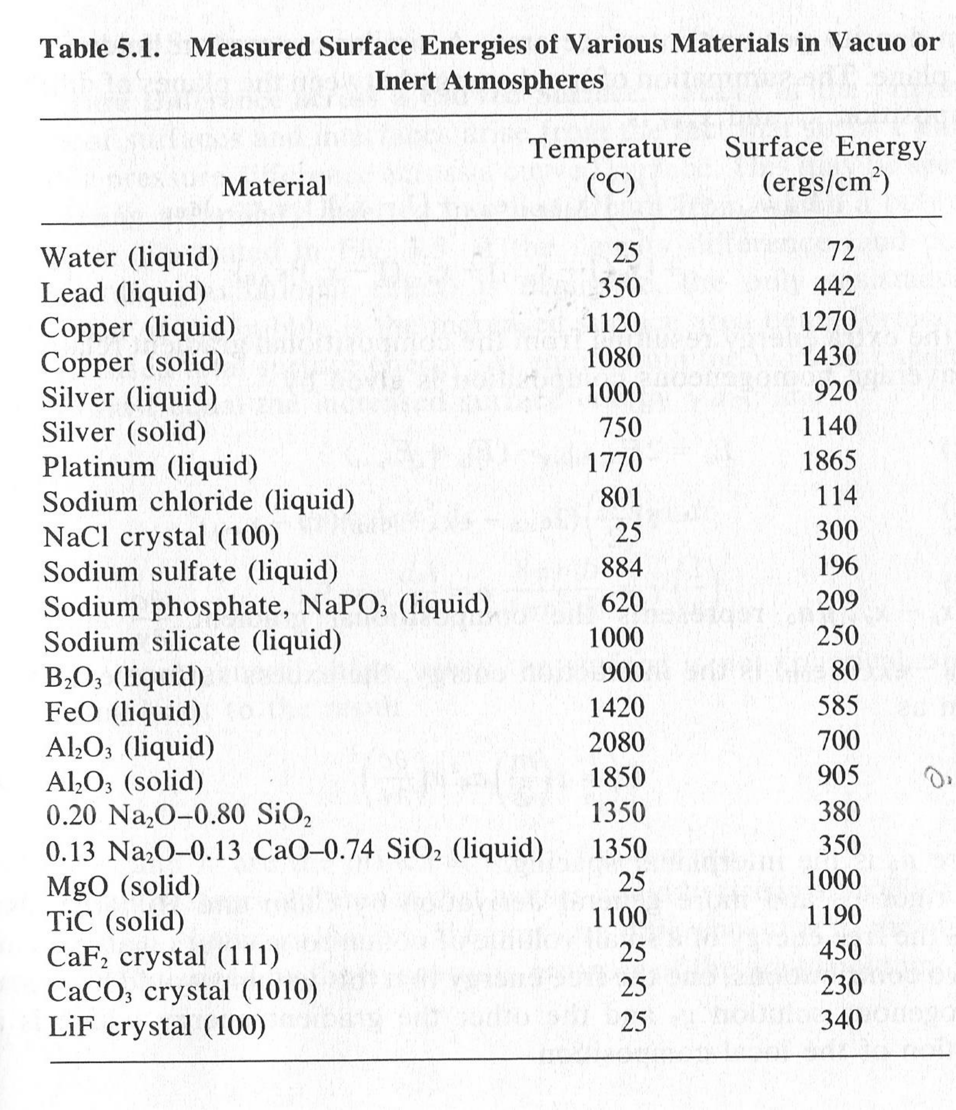


Table 5.1. Measured Surface Energies of Various Materials in Vacuo or Inert Atmospheres

Material	Temperature (°C)	Surface Energy (ergs/cm^2)
Water (liquid)	25	72
Lead (liquid)	350	442
Copper (liquid)	1120	1270
Copper (solid)	1080	1430
Silver (liquid)	1000	920
Silver (solid)	750	1140
Platinum (liquid)	1770	1865
Sodium chloride (liquid)	801	114
NaCl crystal (100)	25	300
Sodium sulfate (liquid)	884	196
Sodium phosphate, $NaPO_3$ (liquid)	620	209
Sodium silicate (liquid)	1000	250
B_2O_3 (liquid)	900	80
FeO (liquid)	1420	585
Al_2O_3 (liquid)	2080	700
Al_2O_3 (solid)	1850	905
0.20 Na_2O–0.80 SiO_2	1350	380
0.13 Na_2O–0.13 CaO–0.74 SiO_2 (liquid)	1350	350
MgO (solid)	25	1000
TiC (solid)	1100	1190
CaF_2 crystal (111)	25	450
$CaCO_3$ crystal (1010)	25	230
LiF crystal (100)	25	340

If the atomic volume is V, the total number of atoms (n) within the volume $4\pi r^3/3$ is $4\pi r^3/3V$.

Now we can define chemical potential

$$\mu = \frac{\partial E_s}{\partial n} = \frac{\partial 4\pi r^2 \gamma}{\partial (4\pi r^3/3V)} = 2V\gamma/r$$

Small particles have large μ, so they are more reactive. Here comes **the nanotechnology**.

$$\mu = 2V\gamma/r$$

Implications:

- small particles are more reactive (high μ)
- Atoms on convex surfaces($r>0$) with large μ; atoms on concave surfaces ($r<0$) with small μ; for atoms on flat surfaces ($r = \infty$) μ is zero.
- For particles of different sizes in contact, larger particles would grow at the expense of the smaller one (i.e. grain growth).

Material with large surface energy will minimize it by minimizing surface area. Liquid mercury balls up to convert some energetic "surface atoms" to less energetic "bulk atoms" by reducing the surface area.

For materials (or phases) in contact, the system will try to minimize high surface energy interfaces.

In the three phase system below the surface (interface = a thin surface layer between two phases) energies are in equilibrium between solid, liquid and vapor (gas) from the balance of horizantal surface tension forces

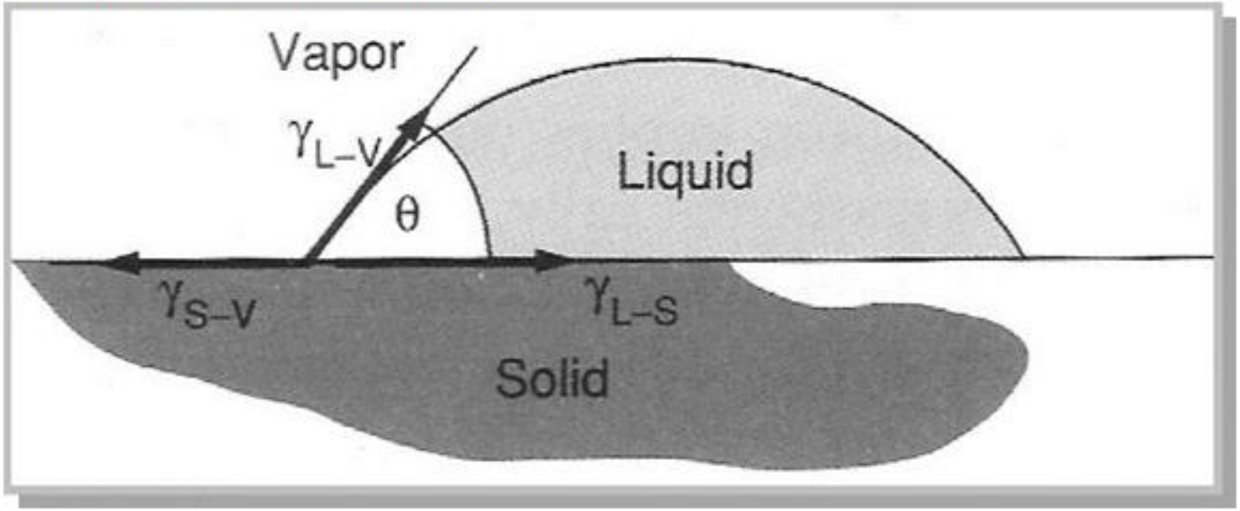
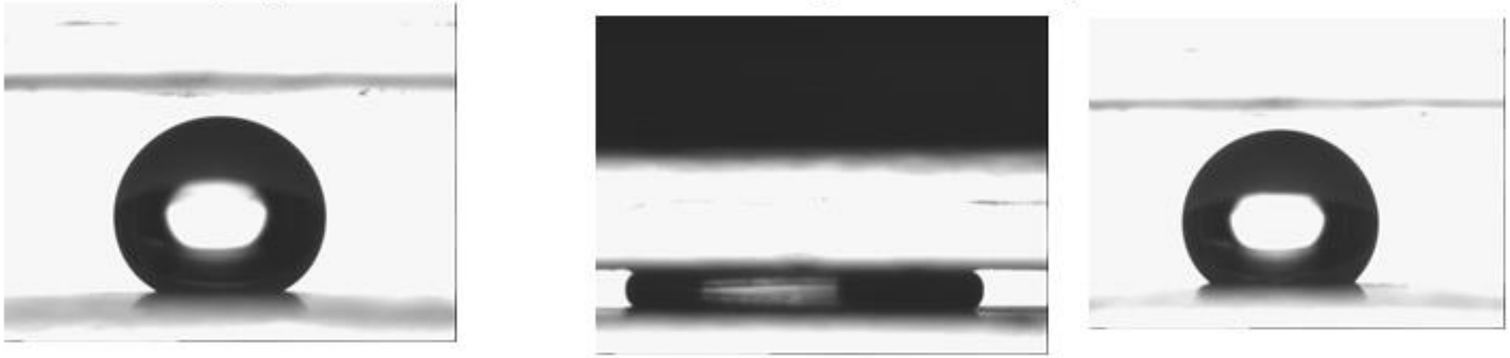


Figure 5.2 A liquid drop on a solid surface pulled by thr various interfacial tensions.

$$\gamma_{S\text{-}V} = \gamma_{L\text{-}S} + \gamma_{L\text{-}V} \, . \, \cos \O$$

Ø: wetting angle
Ø=0° → complete wetting
Ø=180° → complete dewetting
Enormously important in glaze and enamels, sealings and electrical ports.



Surface energy (and surface tension) causes a ΔP across a curved surface

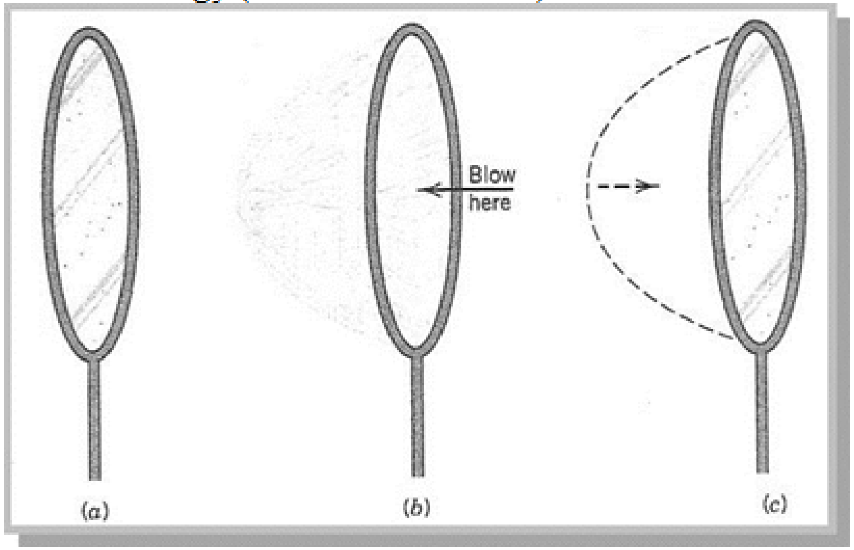


Figure 4.2 (a) a soap film held on a bubble-blowing film forms a flat sheet of minimum surface area. (b) steady, gentle blowing extends the film to become a hemisphere. (c) if we stop blowing, the half-bubble springs back towards its concave side. All curved surfaces tend to move towards their center of curvature in the absence of external forces.

When the expansion of the bubble occurs, that increases the surface area. With it an increase in total surface energy results.

$$\Delta P dv = \gamma . dA$$

Assuming a sphere $V = \frac{4}{3}\pi r^3$

$dv = 4\pi r^2\, dr$; $dA = 8\pi r dr$

$$\Delta P = \gamma . 2/r$$

for more general (non spherical)

$$\Delta P = \gamma . (\frac{1}{r_1} + \frac{1}{r_2})$$

r_1, r_2 are principal radii of curvature.

It is the same pressure difference that cause the liquid to raise in a thin straw: Capillarity; capillarity pressure

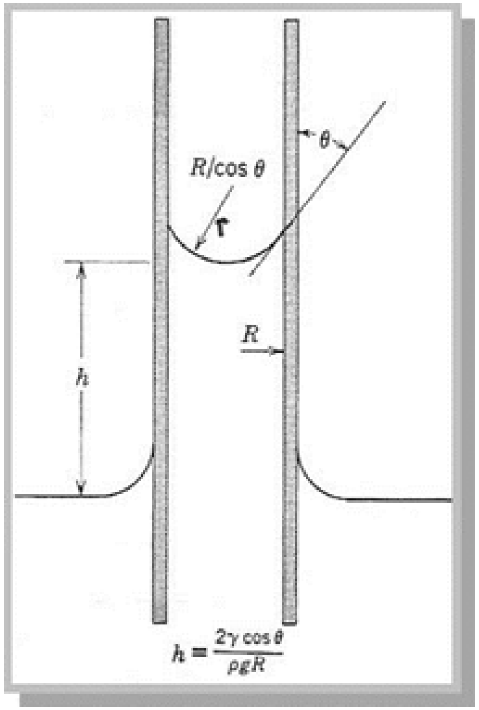


Figure 4.3 Liquid rise in a capillary. Radius curvature of liquid surface is R/cos Ø

$$\Delta P = \gamma.2/r = \gamma.\ 2\cos Ø/R = \rho g h \rightarrow \gamma = R\rho g h / 2\cos Ø$$

- The surface energy can be determined from the capillary rise if the contact angle θ is known!

Important consequences:

Pressure difference across curved surfaces causes increase in vapor pressure, solubility, chemical potential at points of high surface curvature.

The increase in the vapor pressure due to an applied external pressure ΔP is:

$$V\Delta P = RT\ ln(P/P_0) = V.\ \gamma.(\frac{1}{r_1} + \frac{1}{r_2})$$

Here V is the molar volume, P is the vapor pressure over curved surface, P_0 is the vapor pressure over flat surface.

$$ln(P/P_0) = \frac{V\gamma}{RT}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)= \frac{M\gamma}{\rho RT}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

where M is molecular weigth and ρ is the density.

The same relationship can also be derived by considering the transfer of one mole of material from a flat surface through the vapor phase to a spherical surface. The work done must be equal to the surface energy and the change in the surface area;

$$RT.ln(P/P_0) = \gamma dA = \gamma 8\pi r dr$$

Since the change in volume is $dv=4\pi r^2 dr$, the radius change for a one-mole transfer is $dr = V/4\pi r^2$, and

$$ln(P/P_0) = \frac{V\gamma}{RT}\left(\frac{2}{r}\right)$$

which is the same result as obtained previously.

The strong effect of particle size in these relations is one of the bases for the use of clay minerals in ceramic technology. Their fine particle size aids in fabrication processes, since it is a source of plasticity. In addition, this fine particle size produces surface-energy forces which cause densification during the firing process.

Consequences:
The smaller the particle, the higher is the vapor pressure. And also the higher is the solubility and reactivity. Looking at the chemical potential point of view, μ

$$\Delta\mu = RT\,(\ln P - \ln P_0) = RT\ln C - RT\ln C_0$$

P, C and P_0, C_0 are vapor pressure and solubility over curved and flat surfaces.
If the work is done reversibly, it is equal to exchange in surface energy $\gamma.dA$.

$$RT\ln(C/C_0) = RT\ln(P/P_0) = \gamma.dA = \gamma.8\pi r dr$$

Radius change per mole $dr = V_m / 4\pi r^2$ where V_m is molar volume

$$C = C_0.\exp\left[\frac{\gamma.V_m}{RT}.\frac{2}{r}\right]$$ This is Thompson-Freundlich Equation

for non spherical

$$C = C_0.\exp\left[\frac{\gamma.V_m}{RT}.\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right]$$

Fine particles => high surface energy => better densification during sintering.
Fine particles are also more reactive and have high solubility.

In order to minimize free energy, *pure* system will take a geometric configuration to minimize surface energy. That is spherical shape.

In systems with *more than one component*, the system will distribute components to minimize surface energy. Low surface tension component goes to the surface. Even a small concentration will concentrate at surfaces. That lowers the free energy of the surface drastically. In the meanwhile, high surface tension component will mostly stay in the bulk. It will be less concentrated in the surface layer. Even if high surface tension component exists in high amounts, it affects the surface energy only slightly. So, the surface energy does not change linearly with composition

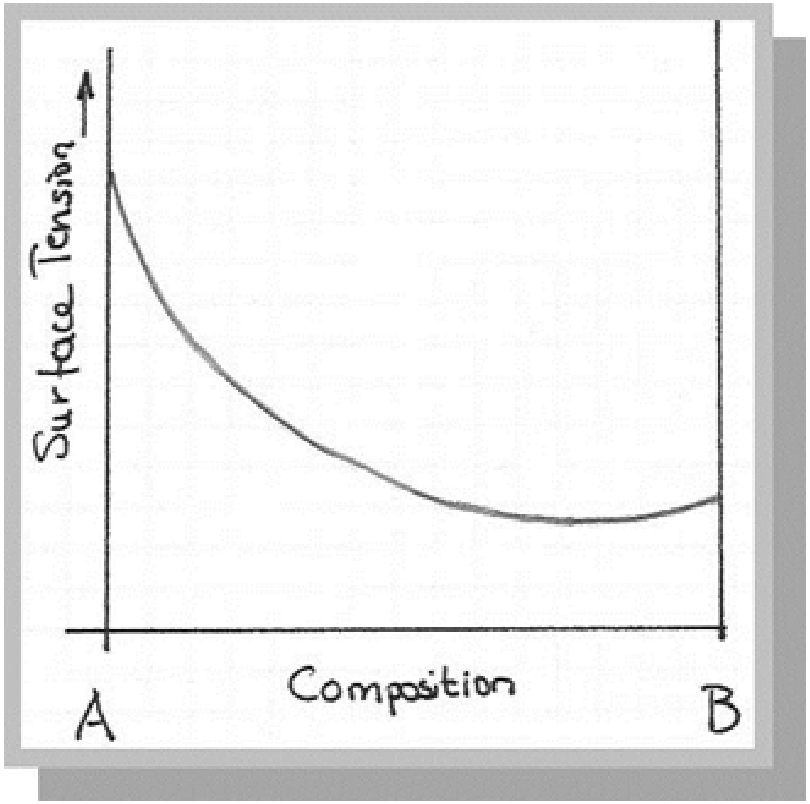


Figure 4.4 Altering of surface tension according to composition. B is the low surface tension component.

Drastic effects of surface tension (energy) in polycrystalline ceramic processing and microstructure

Wetting versus non-wetting versus spreading

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$$

wetting angle, θ

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

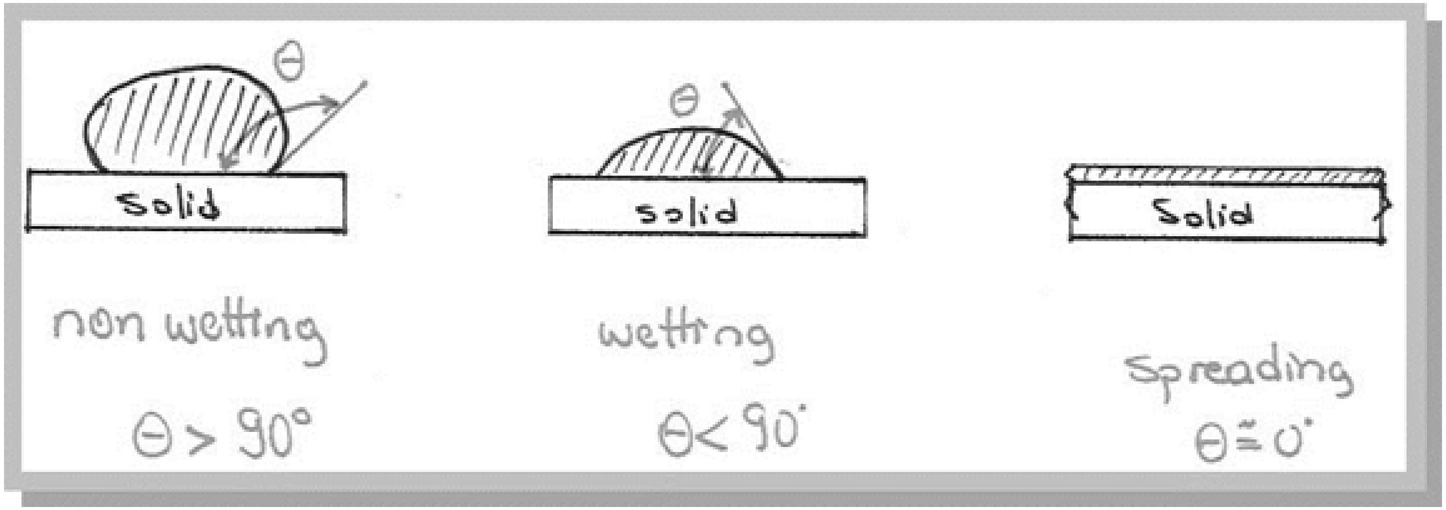


Figure 4.7 wetting angle in nonwetting, wetting, spreading

Similar behavior is observed at interface in polycrystalline materials between the matrix grains and the second phase (liquid, solid, or vapor phase)

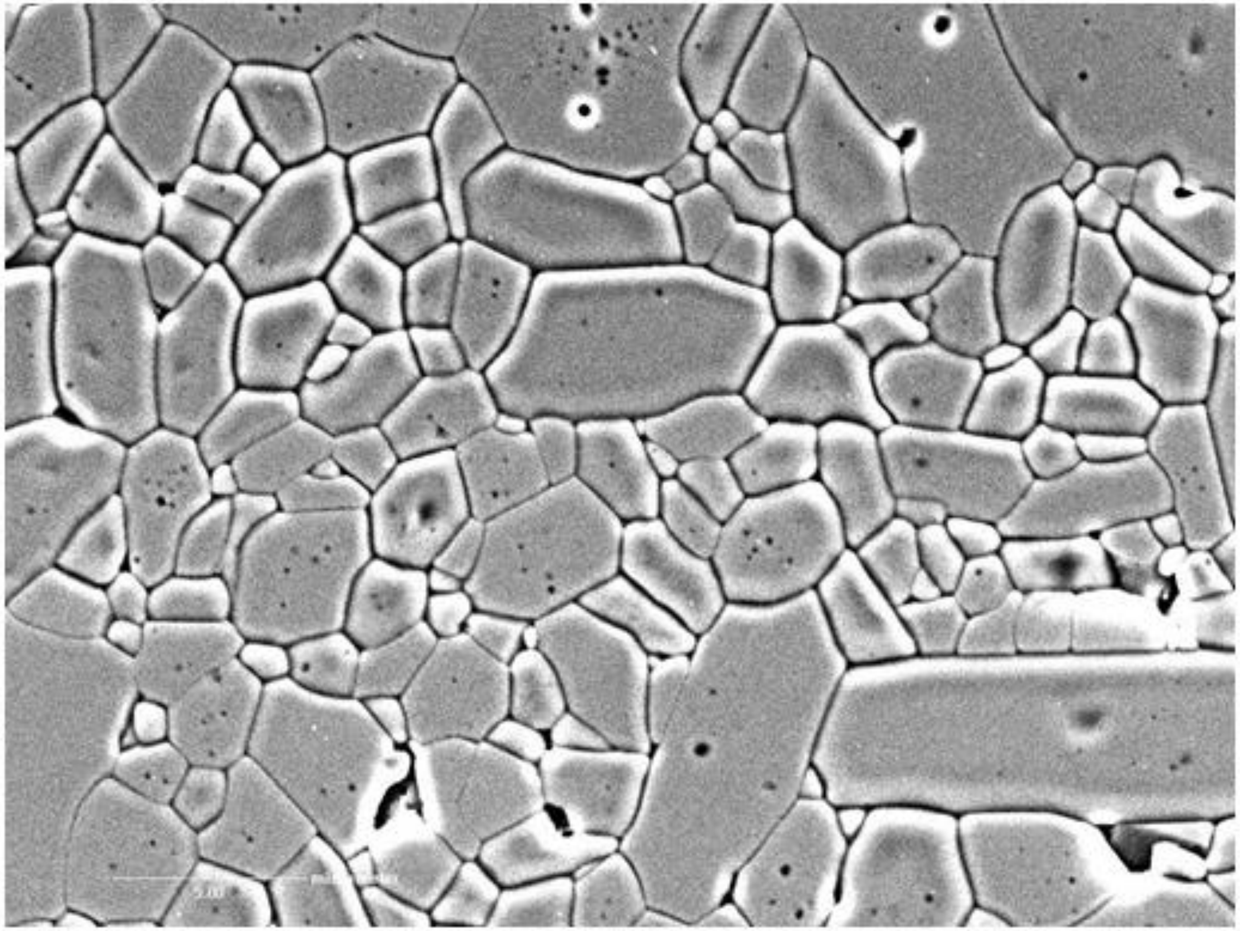
TEM

CA_2 film @ 1300°C, 1h

CA_2 film @ 1400°C, 1h

$CaO.2Al_2O_3 = CA_2$

Polycrystal immersed in a liquid or vapor phase grooves form where grain boundary intersects surfaces.



The angle of etching is called *Dihedral Angle*.
Dihedral angle = F (grain boundary energy / surface–liquid or surface–vapor interface energy)

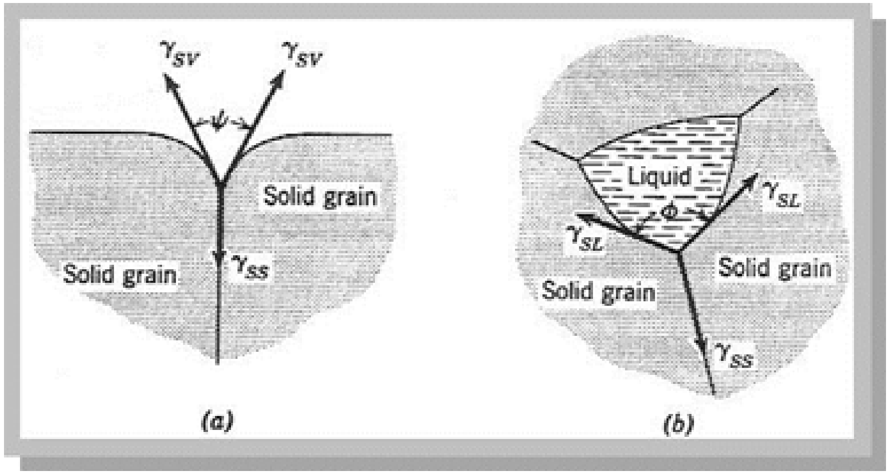


Figure 4.8 Dihedral angle at equilibrium where the grain boundary meets a surface.

Remember surface energies in crystalline solid are anisotropic where:

Grain boundary energy = f (grain misorientation)

AND

Adsorption of even dilute impurities can alter grain boundary energy. Adsorption on different surfaces is also anisotropic.

As with vapor and liquid phases, solid second phase particles make angle according to their relative surface energies.

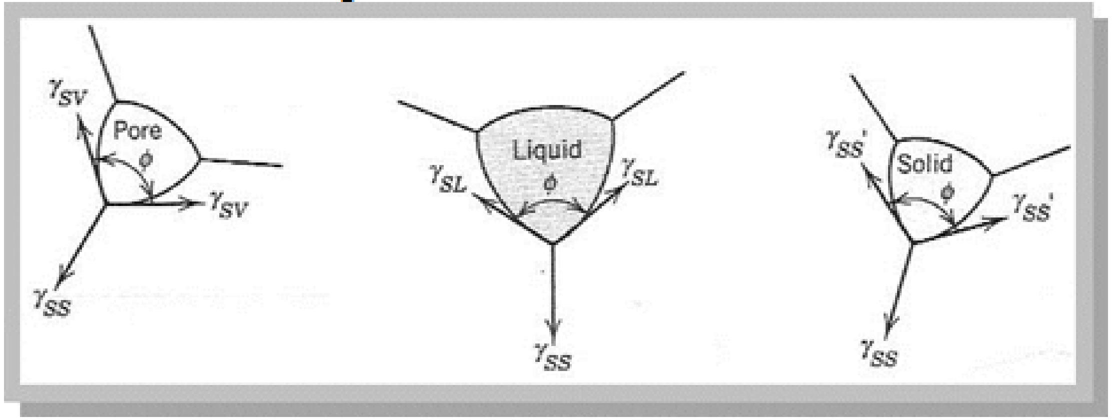


Figure 4.9 dihedral angles at inclusions within a polycrystal

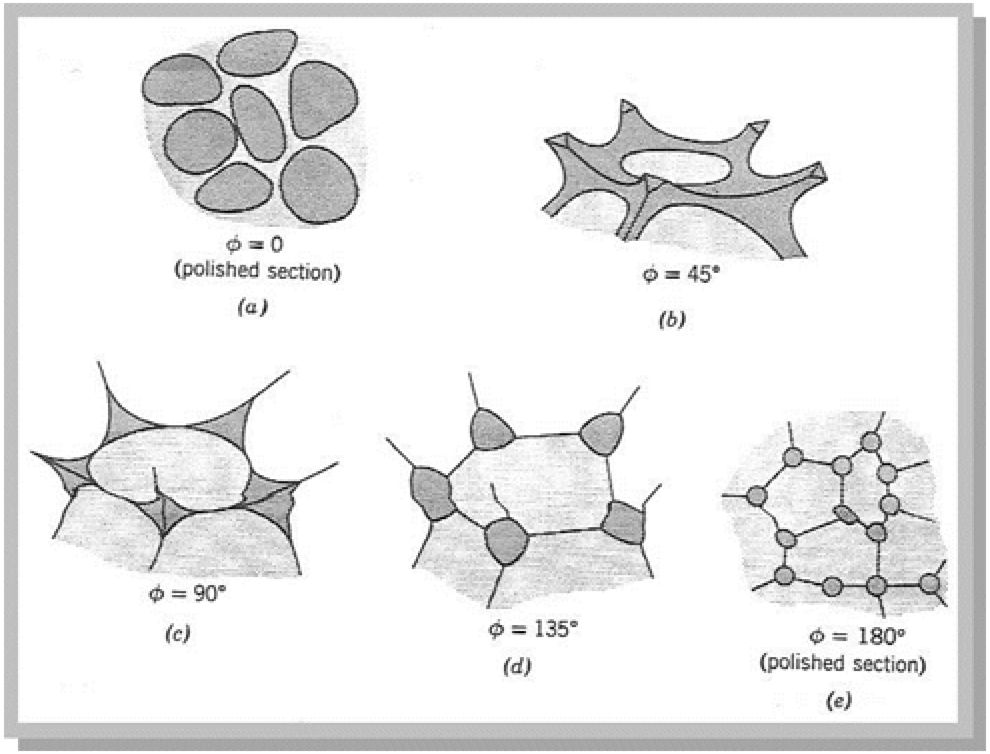

$\phi = 0$ (polished section) (a)
$\phi = 45°$ (b)
$\phi = 90°$ (c)
$\phi = 135°$ (d)
$\phi = 180°$ (polished section) (e)

Figure 4.10 Second phase distribution for different values of dihedral angle.

In solids, microscopic faceting of surfaces may render measurements of dihedral angle extremely difficult.

The distribution of small amount of second phase strongly dependent on dihedral angle (i.e relative surface energies)

- For $\gamma_{SS}/\gamma_{SL} \geq 2$, second phase penetrates and becomes interconnected (reactive liquid sintering)
- For $\sqrt{3} \prec \gamma_{SS}/\gamma_{SL} \prec 2$ or 60°>Ø>0°, Triangular prism pipes along three grain junctions still continuous network of second phase.
- For $1 \prec \gamma_{SS}/\gamma_{SL} \prec \sqrt{3}$ or 120°>Ø>60°, triple point pocket phases no longer continuous.
- For $\gamma_{SS}/\gamma_{SL} < 1$, spheroidized second phase particles

Grain Boundary mobility and grain growth

Normal versus abnormal grain growth

In normal grain growth grain size shifts to larger grain size.

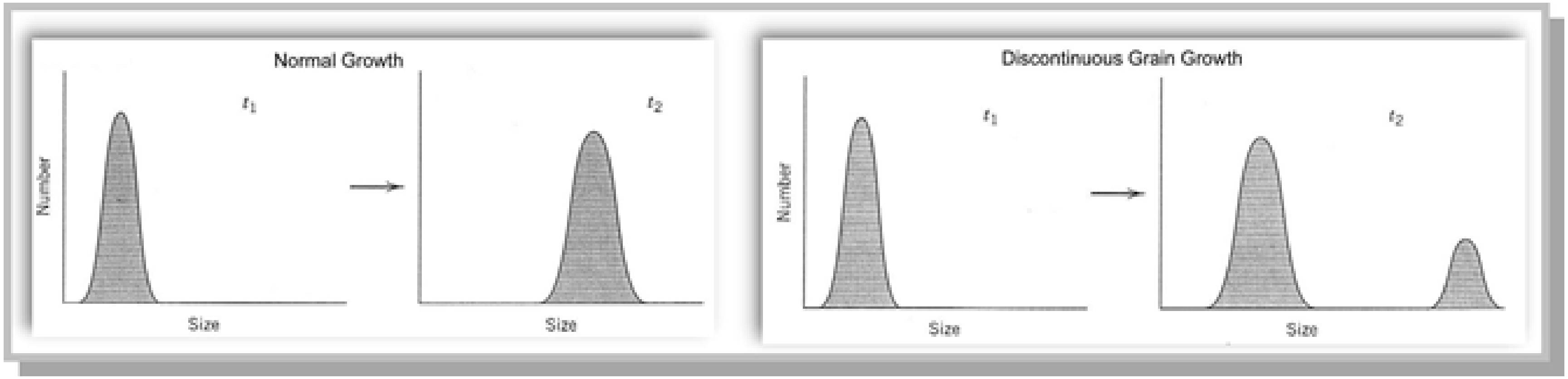


Figure 4.12 Beginning with a single modal distribution of grain sizes, normal grain growth is characterized by an increase in average size while retaining similar size distribution, while discontinuous growth results in a broadened or bimodal distribution with some grains growing much faster than the average

In abnormal grain growth, few large grains grow faster in small grain matrix. That results with coarsening or Ostwald ripening.
Grain growth occurs to reduce grain boundaries area. That is to reduce total grain boundary energy. To reduce the chemical potential of atoms across curved boundary, boundary moves towards its center of curvature.

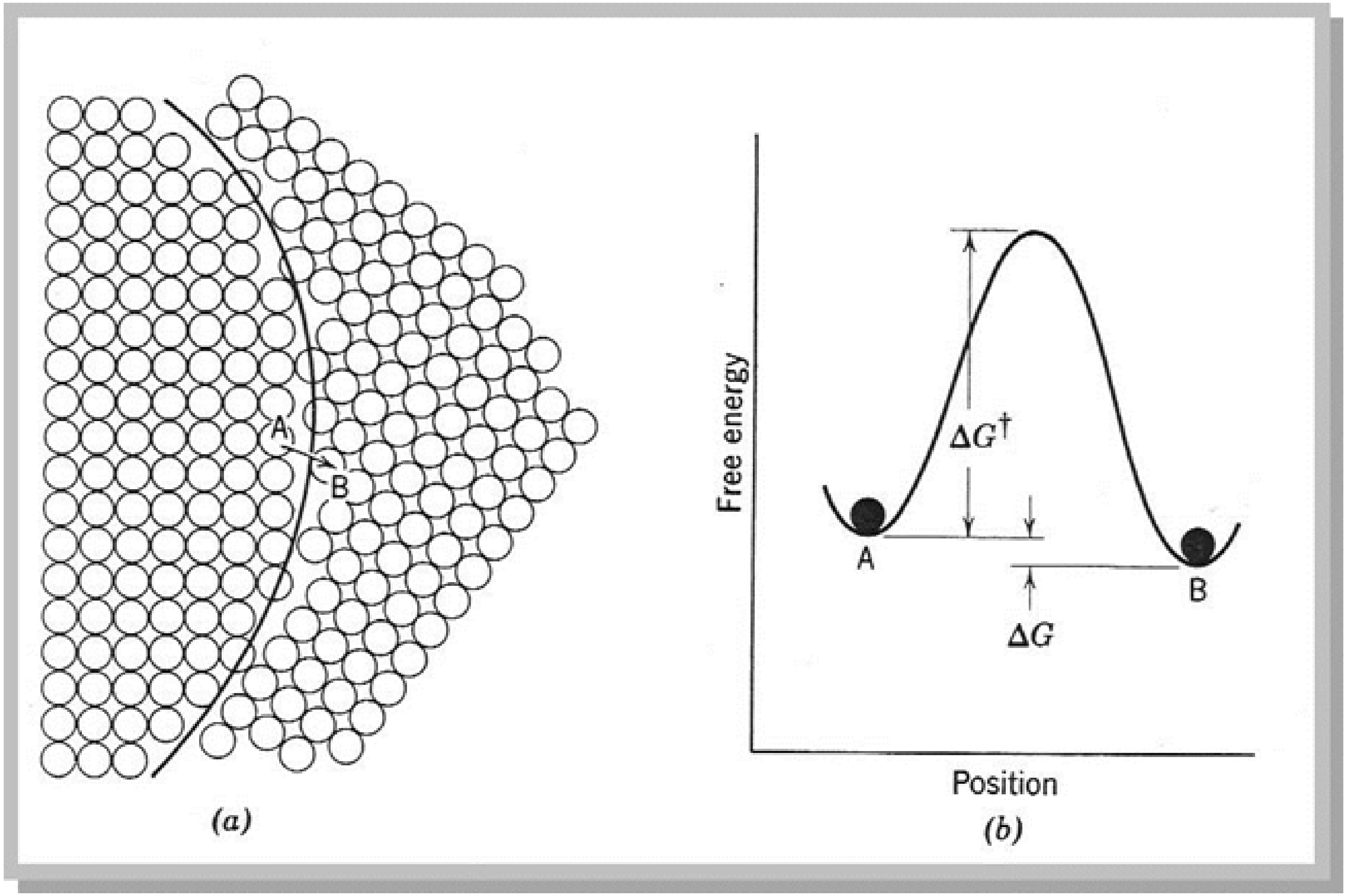


Figure 4.14 (a) structure of boundary and (b) energy change for atomic jump

When grain boundaries with equal energy meet at three grain junctions, it forms 120°angles with flat grain boundaries.

In three dimension, this will be 12 grains surrounding one grain. In two dimension model, 6 equal sized grains will be surrouning one grain (if space fills). These six-sided cell will have flat boundaries. In these bundaries, as the center of the curvature is near infinity, there is no driving force to move.

Grains with fewer sides will shrink while grains with more sides will grow.

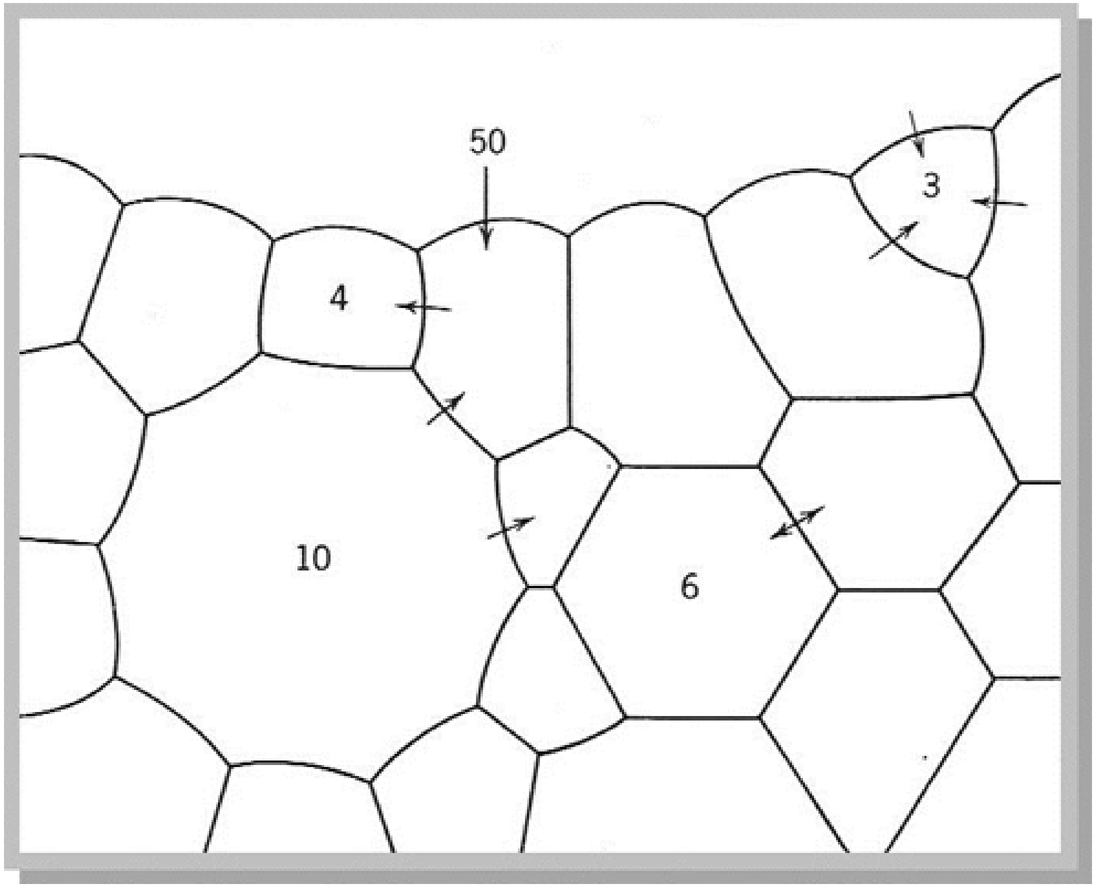


Figure 4.15 Schematic drawing of two dimensional polycrystalline specimen. If all boundaries meet at 120°, the sign of curvature of the boundaries changes as the number of sides increases from less than six to more than six. The radius of curvature becomes less, the more the number of sides deviates from six. Arrows indicate the directions in which boundaries migrate.

DIFFUSION

Atom movements will happen under the influence of

- chemical potential difference (generally concentration difference)

- applied stress or applied fields such as electrical and magnetic

There is also always random atomic movements without applied field.

Even in pure materials, there is self-diffusion

Diffusion - Mass transport by atomic motion

Mechanisms

Gases & Liquids – random (Brownian) motion
Solids – vacancy diffusion or interstitial diffusion

Why Study Diffusion?

Diffusion plays a crucial role in;

Alloying metals => bronze (Cu-Sn), silver, gold
Strengthening and heat treatment processes
Hardening the surfaces of steel
High temperature mechanical behavior
Phase transformations
Mass transport during FCC to BCC
Environmental degradation
Corrosion, etc.

Why do atoms move in Solids?

Diffusion, simply, is atoms moving from one lattice site to another in a stepwise manner. Transport of material by moving atoms

-Two conditions are to be met:

+An empty adjacent site (VACANCY)

+Enough energy to break bonds and cause lattice distortions during displacement

-What is the energy source ?

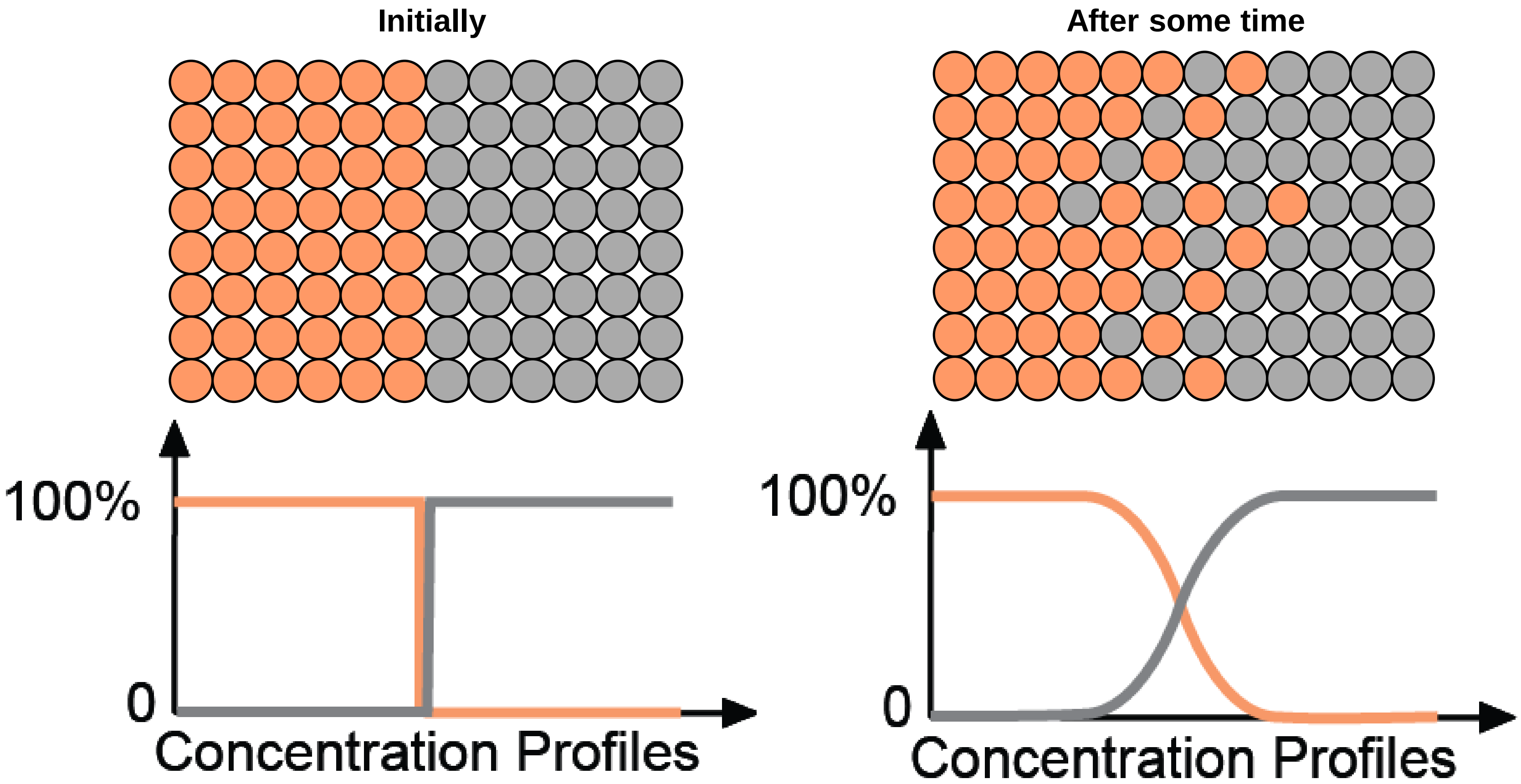
+HEAT !

-What else ?

+<u>Concentration gradient !</u>

Diffusion Types (i) interdiffusion

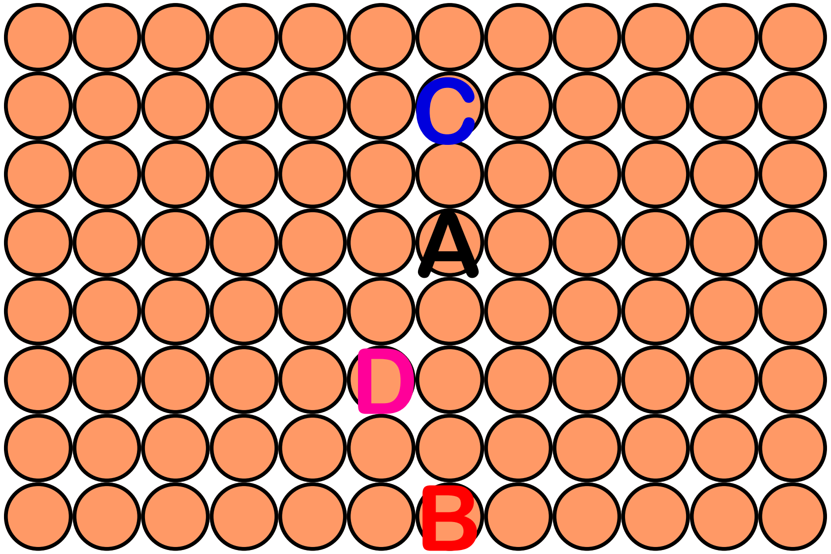
In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration



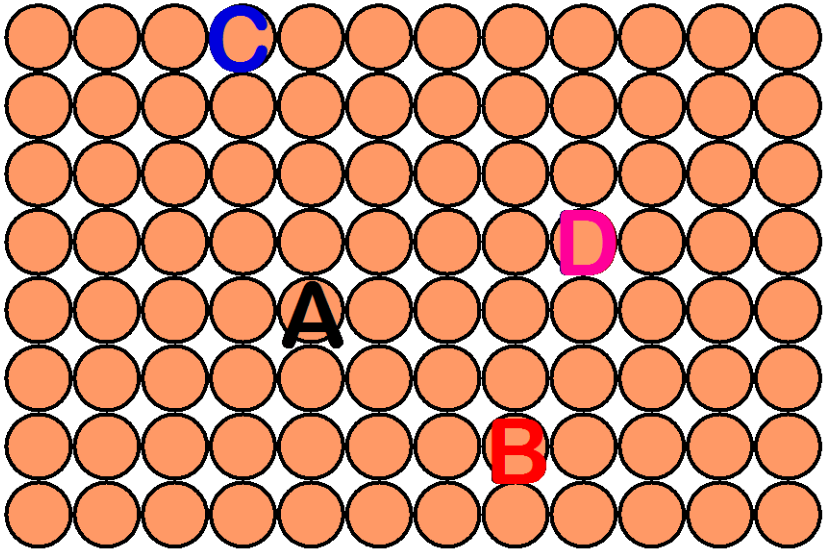
Diffusion Types (ii) self-diffusion

In an elemental solid, atoms also migrate.

Label some atoms (use isotopes)



After some time

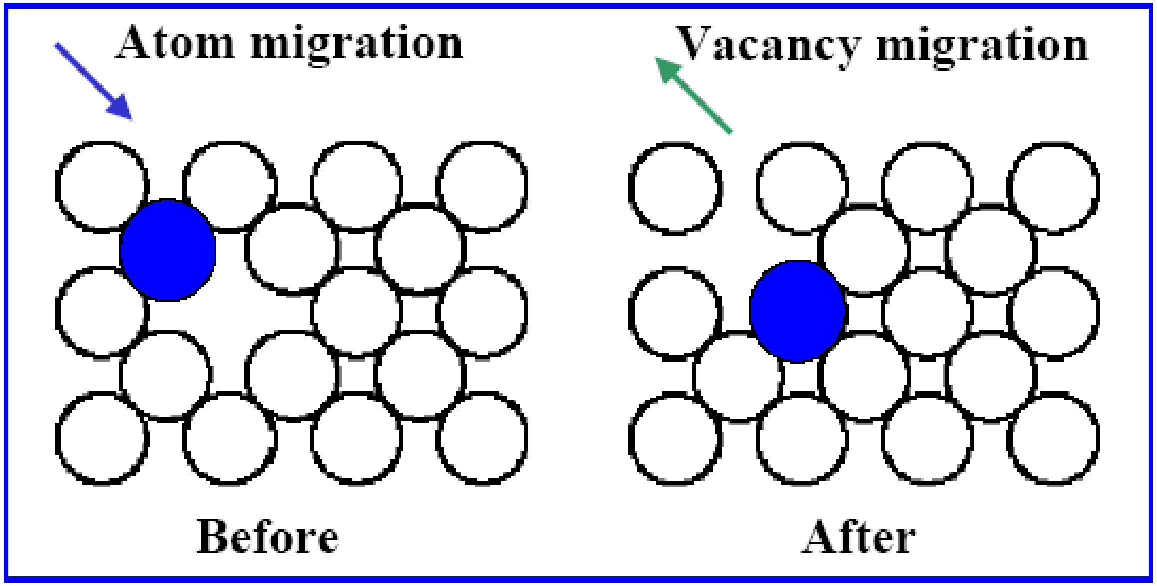


Diffusion Types (iii) vacancy diffusion

Energy is needed to generate a vacancy, break bonds, cause distortions. Provided by HEAT

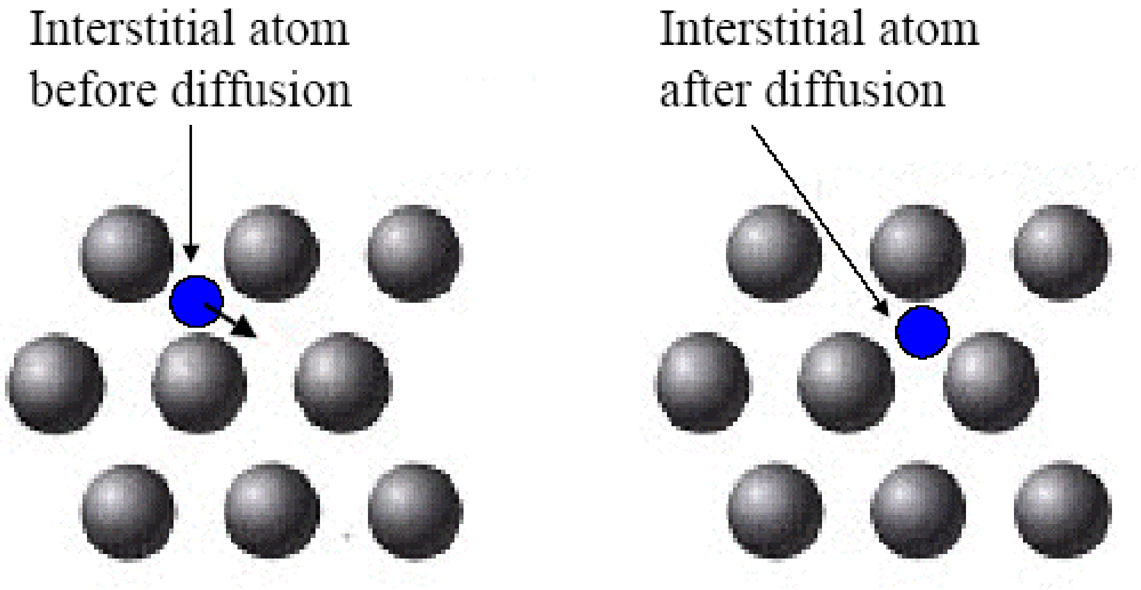
Atom moves in the opposite direction of the vacancy !

Vacancy diffusion



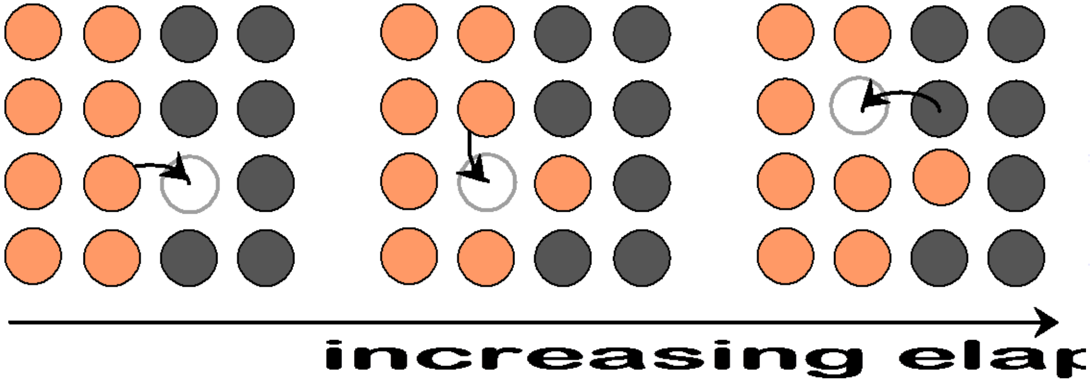
Diffusion Types (iv) interstitial diffusion

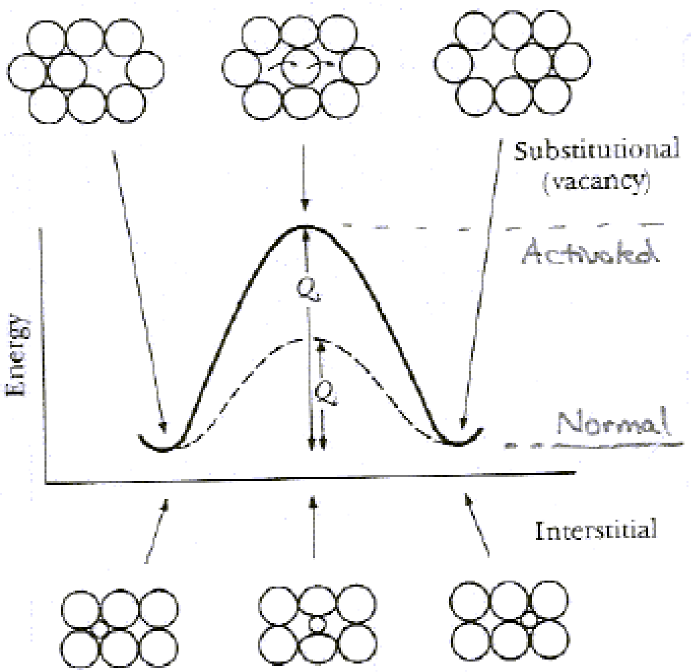
Much faster than vacancy diffusion, why ? Smaller atoms like B, C, H, O. Weaker interaction with the larger atoms. More vacant sites, no need to create a vacancy !



Diffusion Types (v) substitutional diffusion

- applies to substitutional impurities
- atoms exchange with vacancies
- rate depends on:
  - --number of vacancies
  - --activation energy to exchange.





Diffusion → jumps in one direction → mass transfer towards one direction to reach equilibrium.

→ jump frequency & succesful jump probability play important roles

→ governed by similar expressions that describe thermodynamic probability, P

$$P = \exp(\frac{-\Delta G}{RT})$$

ΔG is free energy difference between normal and activated states → activation energy
R (kN_A)– gas constant, T – temperature in Kelvin

when ΔG decreases → P increases
when T increases → P increases for atomic motion.

Diffusion coefficient has a similar form with P

$$D = D_0 \exp(\frac{-\Delta G}{RT})$$

D_0 – pre-exponential factor, depends on jump frequency ν, (~10^{13}, debye freq.), geometry of the crystal(available jump sites and jump distances)

Some rule of thumb: activation energy usually lower for

- *diffusion through open crystal structures*
- *lower melting point materials*

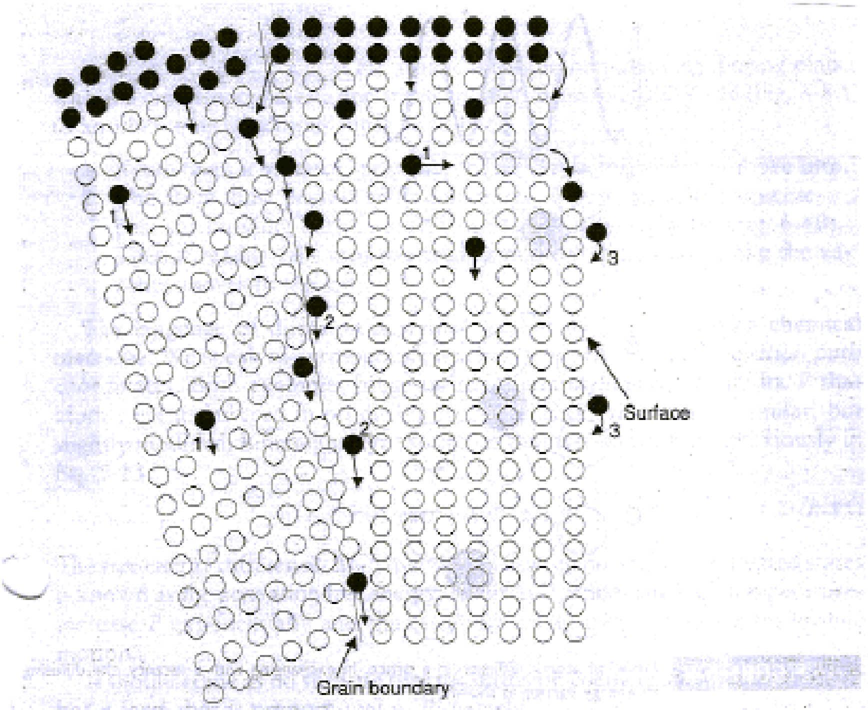
There are several different paths for a diffusing atom. Different paths will have different activation energies like;

- lattice
- dislocation cores
- grain boundaries
- free surfaces

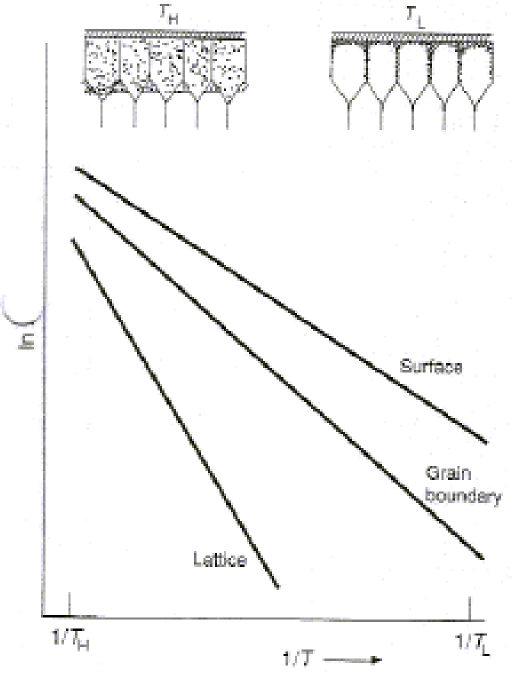
For different paths, different ΔG’s, i.e. different rates of mass transfer are valid.

Available diffusion paths are important! However, as temperature increases, the differences between ΔG loose its importance

@low T → fast diffusion paths dominate
@high T → the most # diffusion paths dominate



9 Atomic transport mechanisms in crystalline solids. Illustrated are (1) bulk diffusion due to vacancy–atom exchange, (2) grain boundary diffusion, and (3) surface diffusion.



12 Schematic dependence of lattice, grain boundary, and surface diffusion on temperature. For operative lattice and grain boundary diffusion mechanisms, diffusional penetration is primarily through the bulk of the grains at high temperature (T_H). At low temperature (T_L), diffusional penetration of grain boundaries is dominant as shown in the above structural model.

Arrhenius Type Plot

$$lnD = lnD_0 - \frac{Q}{R}\left(\frac{1}{T}\right)$$

Q-activation energy

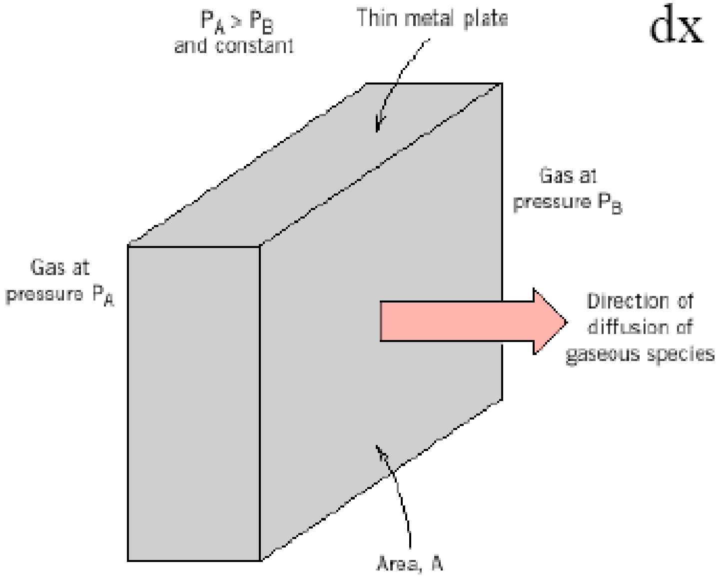
How fast occur diffusion occur? – Rate of diffusion (diffusion per time)

Steady State Diffusion and Non-steady State Diffusion

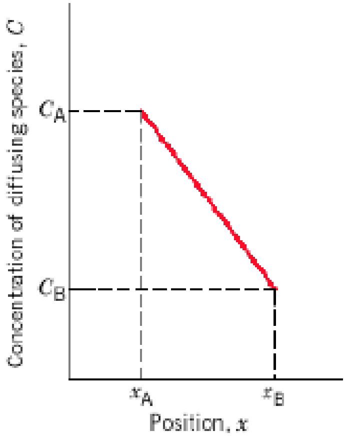
Fick’s First Law : Steady state diffusion through a constant concentration gradient:

Concentration gradient: dC/dx ($Kg.m^{-3}$): the slope at a particular point on concentration profile.

$$\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$



(a)



(b)

Diffusion Kinetics

Typically diffusion is explained on the basis of compositional gradients in an alloy which act as driving force for diffusion. Thermodynamically speaking, this amounts to gradient in the chemical potential which drives the migration of species from regions of higher chemical potential to lower chemical potential so that system reaches a chemical equilibrium. The atomic flux as a result of driving force is expressed in terms of chemical composition gradient, also called as Fick's law(s). These laws are briefly explained below. For detailed discussion on diffusion, readers are referred to standard text books on diffusion.[1,2]

Fick's First Law of Diffusion

It states that atomic flux, under steady-state conditions, is proportional to the concentration gradient. It can be stated as

$$\boxed{\text{Atomic flux } J \propto -\left(\frac{dc}{dx}\right) \qquad \textbf{OR}}$$

$$J = -D.\left(\frac{dc}{dx}\right) \qquad (3.1)$$

where

- J is the diffusion flux with units moles/cm^2-s, and basically means the amount of material passing through a unit area per unit time;
- D is the proportionality constant, called as diffusion coefficient or diffusivity in cm^2/s;
- x is the position in cm; and
- c is the concentration in cm^3 .

The negative sign on the R.H.S. indicates that diffusion takes place from regions of higher concentration to lower concentration i.e. down the concentration gradient. Diffusivity is a temperature dependent parameter and is expressed as $D = D_0 \exp(-Q/kT)$ where Q is the activation energy, k is Boltzmann's constant and D_0 is the pre-exponential factor in cm^2 /s.

Diffusivity: A Simple Model

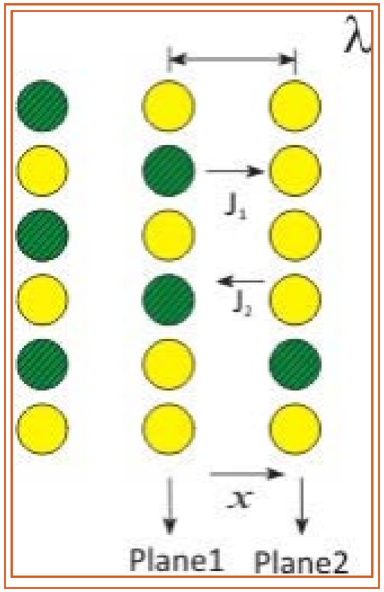


Figure 3. 1 Schematic of the planes of atoms with arrows showing the cross-movement of species

As shown in **Figure (3.1),** a schematic diagram shows atomic planes, illustrating 1-D diffusion of species across the planes .

Flux from position (1) to (2) is written as

$$J_1 = \frac{1}{2} n_1 \Gamma \qquad (3.3)$$

where n_1 is no. of atoms at position (1) and Γ is the jump frequency i.e number of atoms jumping per second (atoms/s)

Similarly, Flux from plane (2) to (1) is expressed as

$$J_2 = \frac{1}{2} n_2 \Gamma \qquad (3.4)$$

where n_2 is the number of atoms at (2) and Γ is the jump frequency in s^{-1}.

in both the above expressions, factor ½ is there because of equal probability of jump in +x and -x directions.

Now, the net flux, J, can be calculated as

$$J = J_1 - J_2 = \frac{1}{2}(n_1 - n_2)\Gamma \qquad (3.5)$$

Concentration is defined as

$$c_1 = \frac{n_1}{\lambda} \quad \text{and} \quad c_2 = \frac{n_2}{\lambda} \qquad (3.6)$$

if area is considered as unit area (=1) and λ is the distance between two atomic planes.

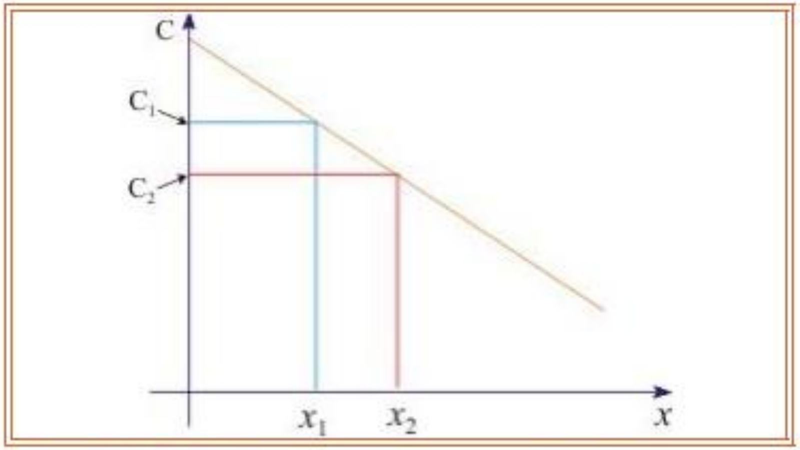


Figure 3. 2 Schematic diagram showing concentration gradient between two planes of atoms

Concentration gradient can be written as (note the minus sign)

$$-\frac{dc}{dx} = \frac{c_1}{\lambda} - \frac{c_2}{\lambda} = \frac{c_1 - c_2}{\lambda} = \frac{n_1 - n_2}{\lambda^2} \quad (3.7)$$

Hence, flux can now be expressed as

$$J = \frac{1}{2}\left(-\lambda^2 \frac{dc}{dx}\right) . \Gamma = -\left(\frac{1}{2}\lambda^2 \Gamma\right) . \frac{dc}{dx}$$

$$= - D \, . \, \frac{dc}{dx} \qquad (3.8)$$

where $D = ½ \lambda^2 t$ with unit cm^2/s in 1-D and can easily show to become $D = 1/6 \lambda^2 t$ in a 3-D cubic co-ordination scenario.

In general, diffusivity can be expressed as

$$D = \gamma \lambda^2 \Gamma \qquad (3.9)$$

where γ is governed by the possible number of jumps at an instant and λ is the jump distance and is governed by the atomic configuration and crystal structure.

Temperature Dependence of Diffusivity

Now, equation (3.9) can further be modified by replacing the jump frequency, Γ, which, by Boltzman statistics, is defined as

$$\Gamma = \nu . exp\left(-\frac{\Delta G^*}{kT}\right) \qquad (3.10)$$

where v is the vibration frequency in s^{-1}, ΔG^* is the activation energy of migration in J and k is Boltzmann Constant (J/K).

Further, ΔG^* can be written as

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (3.11)$$

where ΔH^* is the enthalpy of migration and ΔS^* is the associated entropy change. Now, substitution of equation (3.10) in equation (3.11) leads to

$$\mathrm{D} = \gamma.\lambda^2.\mathrm{v}.\exp\left(\frac{\Delta S^*}{\mathrm{k}}\right).\exp\left(-\frac{\Delta\,\mathrm{H}^*}{\mathrm{kT}}\right) \qquad \text{OR}$$

or

$$\mathrm{D} = \mathrm{D_o}\exp\left(-\frac{\Delta\,\mathrm{H}^*}{\mathrm{kT}}\right) \qquad (3.12)$$

where pre-exponential factor $\mathrm{D_o} = \gamma\,\lambda^2 \nu^* .\ \exp\left(\frac{\Delta\,S^*}{\mathrm{k}}\right)$.

Equation (3.12) explains the thermally activated nature of diffusivity showing an exponential temperature dependence resulting in significant increase in the diffusivity upon increasing the temperature.

Mobility and Diffusivity

In addition to diffusivity, another useful term to describe conduction in ionic compounds and ceramics is mobility which is defined as velocity (v) of an entity per unit driving force (F) and is expressed as

$$M = \frac{v}{F} \qquad (3.17)$$

The Force F can be defined as either of chemical potential gradient, electrical potential gradient, interfacial energy gradient, elastic energy gradient or any other similar parameter.

Absolute mobility

$$B_i\left(\frac{cm^2}{J.s}\right) = \frac{v_i\left(\frac{cm}{s}\right)}{\left(\frac{1}{N_A}\right)\left(\frac{\partial \mu_i}{\partial x}\right)} \qquad (3.18)$$

Where N_A is Avogadro's Number, μ_i is chemical potential in J/mol and x is the position in cm.

For atomic transport, Einstein first pointed out that the most general driving force is the virtual force that acts on a diffusing atom or species and is due to negative gradient of the chemical potential or partial molar free energy. It is expressed as

$$F_i(J/cm) = -\frac{1}{N_a}\left(\frac{d\mu_i}{dx}\right) \qquad (3.21)$$

Where μ_i is the chemical potential of i and N_A is the Avogadro's Number.

Absolute mobility, B_i is given by

$$B_i = \frac{v(\frac{cm}{s})}{F(\frac{J}{cm})} = -\frac{v_i}{\left[\frac{1}{N_A}.\left(\frac{d\mu_i}{dx}\right)\right]} cm^2/V.s \qquad (3.22)$$

To obtain the relation between mobility and diffusivity of species, *i*, we need to write the flux in a general form as a product of concentration, c_i, and velocity, v_i, *i.e.*

$$J_i = c_i.v_i = c_i B_i F_i \qquad (3.23)$$

Now, substituting for F_i from equation (3.21), we have

$$J_i = -\frac{1}{N_A}.\left(\frac{d\mu_i}{dx}\right)B_i c_i \qquad (3.24)$$

Now, for an ideal solution with unit activity of species i , chemical potential can be expressed as

$$\mu_i = \mu_i^{\circ} + RT\ln c_i \qquad (3.25)$$

where R is the gas constant. So, the change in the chemical potential can be written as

$$d\mu_i = RT.d\ln c_i = \frac{RT}{c_i}\ln c_i \qquad (3.26)$$

OR

$$\frac{d\mu_i}{dx} = \frac{RT}{c_i}\left(\frac{dc_i}{dx}\right) \qquad (3.27)$$

Substituting equation (3.27) into equation (3.24) leads to

$$J_i = -\frac{RT}{N_A}.B_i.\frac{dc_i}{dx} \qquad (3.28)$$

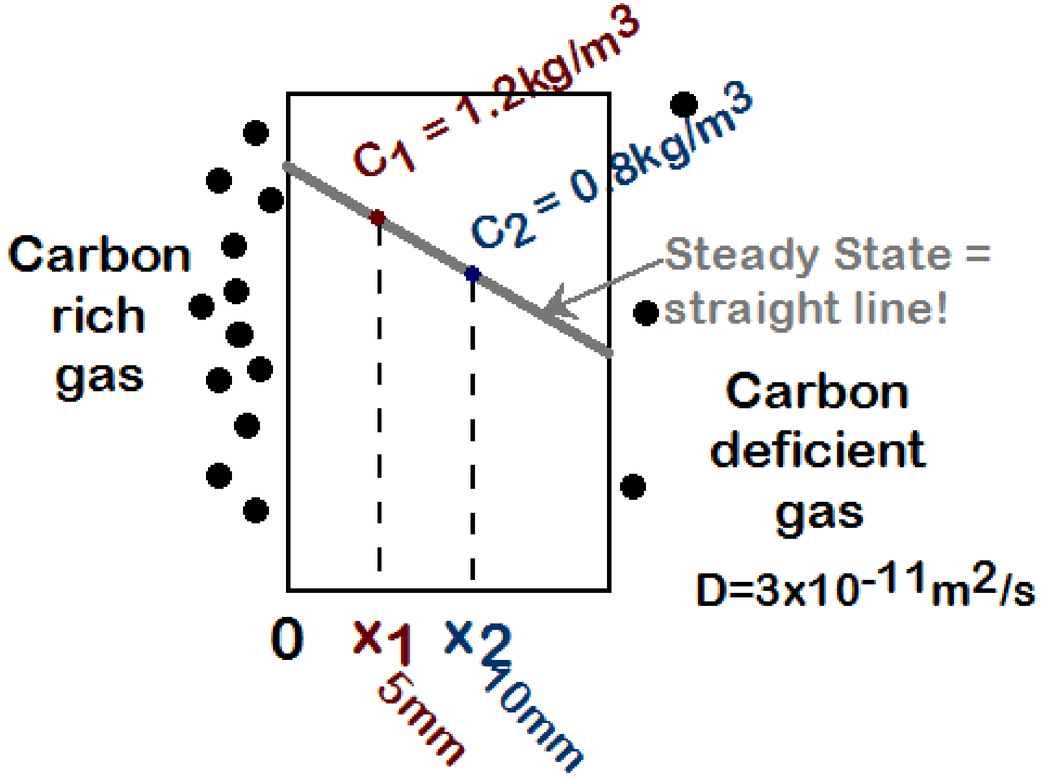
If we compare the above equation with Fick's first law, which is equation (3.1), diffusivity of species *i* can be written as

$D_i = \frac{RT}{N_A}.B_i = k\,T\,B_i$	(3.29)

The above equation is called **Nernst Einstein Equation**.

- Q: How much carbon transfers from the rich to the deficient side?

- Steel plate at 700° C



$D = 3\text{x}10^{-11}\text{m}^2/\text{s}$

$$\text{Flux;} \quad J = -D\frac{\Delta C}{\Delta x}$$

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9}\,\frac{\text{kg}}{\text{m}^2\text{s}}$$

$\boldsymbol{J} \rightarrow flow$

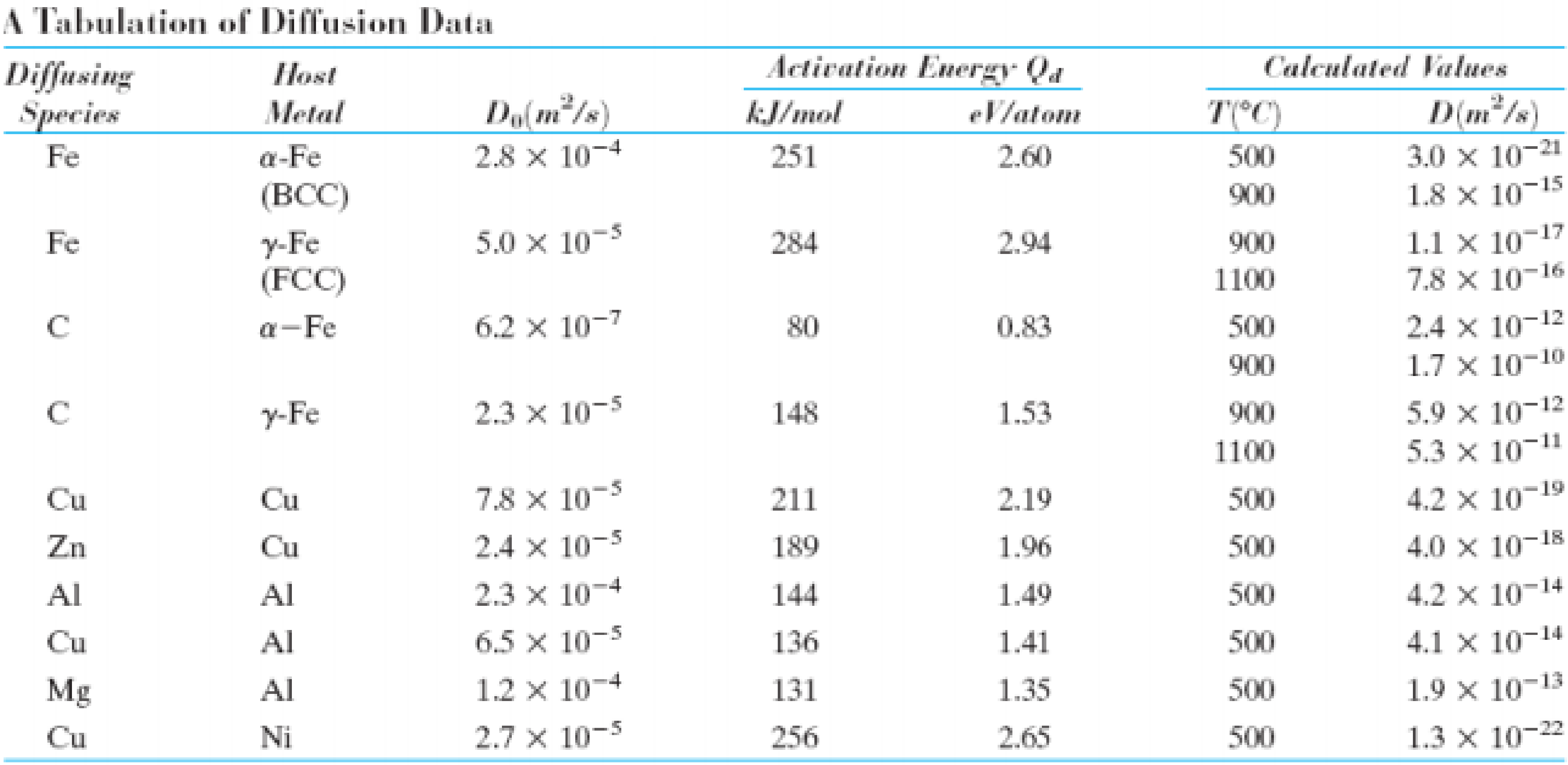
$\dfrac{\Delta \boldsymbol{C}}{\Delta \boldsymbol{x}} \rightarrow driving\ force$

(-) → flow down the conc. gradient

$\boldsymbol{J}\ - flux\ \left[\dfrac{atoms}{cm^2 s}\right]$

$\boldsymbol{D}\ - diffusion\ coefficient\ or\ diffusivity\ \left[\dfrac{cm^2}{s}\right]$

$\dfrac{\Delta \boldsymbol{C}}{\Delta \boldsymbol{x}} - concentration\ gradient\ \left[\dfrac{atoms}{cm^3}\dfrac{1}{cm}\right]$



A Tabulation of Diffusion Data

Diffusing Species	*Host Metal*	$D_0 (m^2/s)$	*Activation Energy Q_d*		*Calculated Values*	
			kJ/mol	*eV/atom*	*T(°C)*	$D (m^2/s)$
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α−Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

DIFFUSION AND TEMPERATURE

- Diffusivity increases with T.

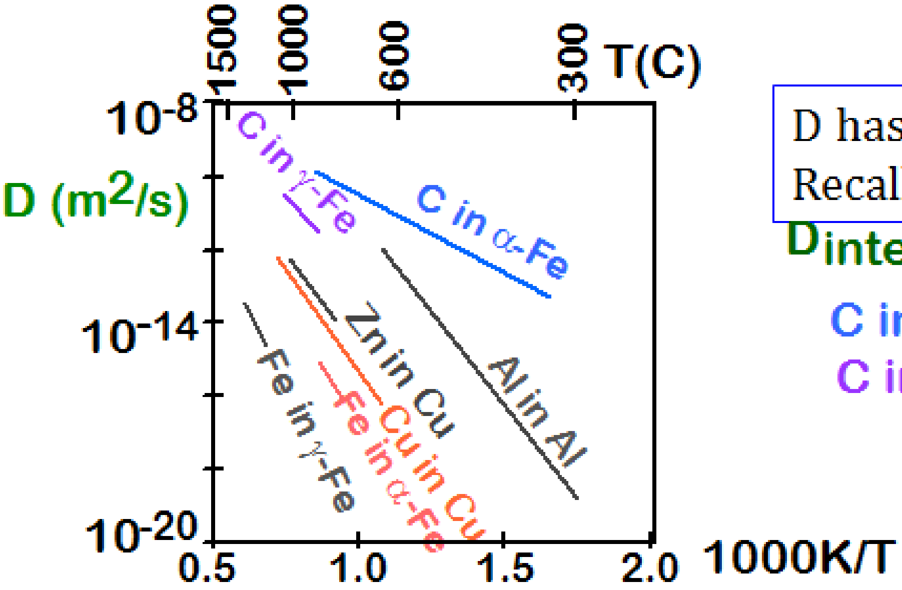
pre-exponential [m^2/s]

activation energy
[J/mol],[eV/mol]

diffusivity $$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

gas constant [8.31J/mol-K]

- Experimental Data:



(Date taken from E.A. Brandes and G.B. Brook (Ed.) *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

D has exp. dependence on T
Recall: Vacancy does also!

$D_{interstitial} \gg D_{substitutional}$

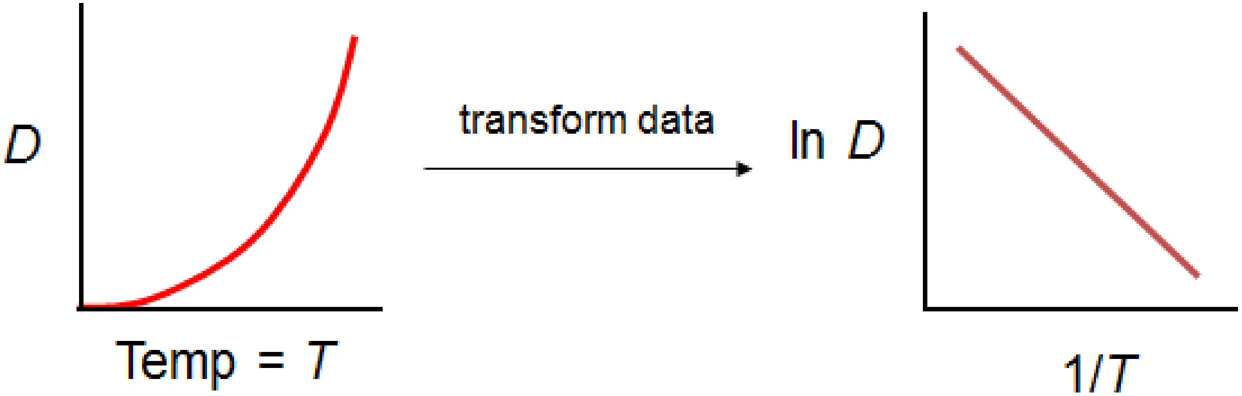
C in α-Fe	Cu in Cu
C in γ-Fe	Al in Al
	Fe in α-Fe
	Fe in γ-Fe
	Zn in Cu

Example: At 300ºC the diffusion coefficient and activation energy for Cu in Si are

D(300ºC) = 7.8 x 10-11 m2/s
Qd = 41.5 kJ/ mol

What is the diffusion coefficient at 350ºC?

$$D = D_o \exp\left(-\frac{Qd}{RT}\right)$$



$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\therefore \quad \ln D_2 - \ln D_1 = \ln \frac{D_2}{D_1} = -\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$D_2 = D_1 \exp\left[-\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

T1 = 273 + 300 = 573 K

T2 = 273 + 350 = 623 K

$$D_2 = (7.8 \text{ x } 10^{-11} \text{ m}^2/\text{s}) \exp\left[\frac{-41{,}500 \text{ J/mol}}{8.314 \text{ J/mol - K}}\left(\frac{1}{623 \text{ K}} - \frac{1}{573 \text{ K}}\right)\right]$$

D2 = 15.7 x 10-11 m2/s

Fick’s Second Law ; Non-steady State Diffusion

In most practical cases, J (flux) and dC/dx (concentration gradient) change with time (t).

Net accumulation or depletion of species diffusing

How do we express a time dependent concentration?

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x} \right) = D\,\frac{\partial^2 C}{\partial x^2}$$

Concentration at a point *x*
Changing with time

Flux, J, changes at any point *x* !

How do we solve this partial differential equation ?

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

Use proper boundary conditions:

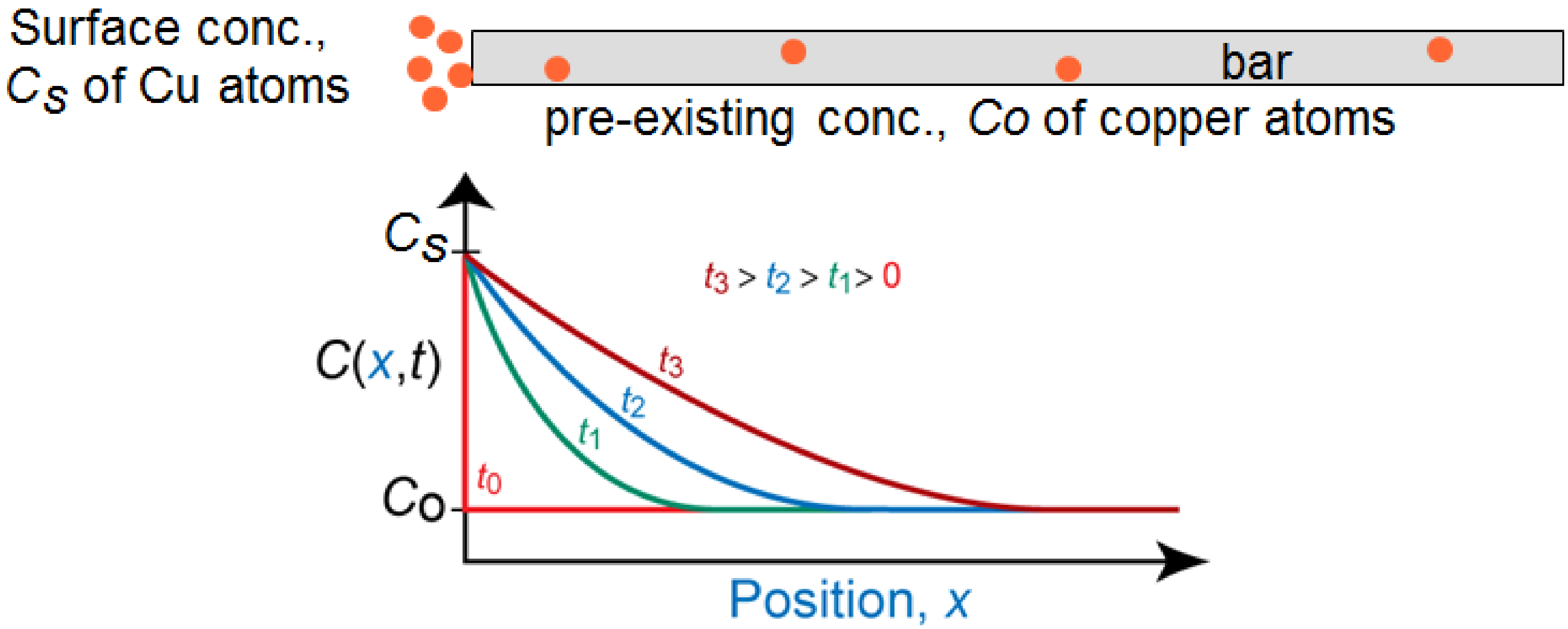
$t=0$, $C = C_0$, at $0 \le x \le \infty$

$t>0$, $C = C_s$, at $x = 0$

$C = C_0$, at $x = \infty$

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.



B.C. at $t = 0$, $C = Co$ for $0 \le x \le \infty$

at $t > 0$, $C = CS$ for $x = 0$ (const. surf. conc.)

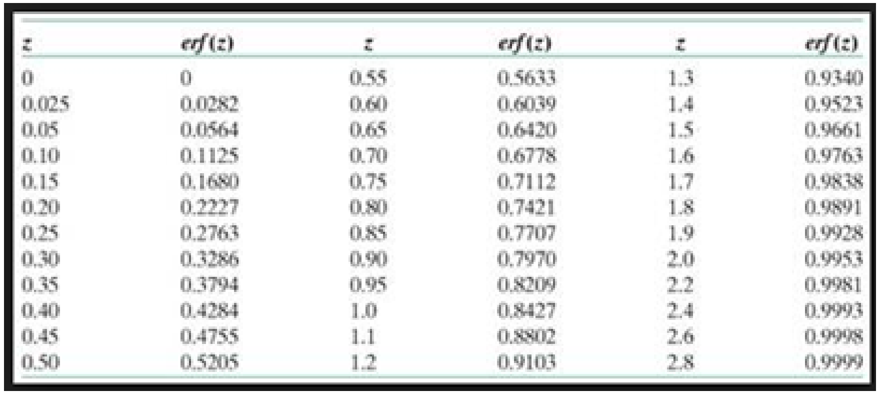
$C = Co$ for $x = \infty$

$$\boxed{\frac{C(x,t)-C_o}{C_s-C_o}=1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

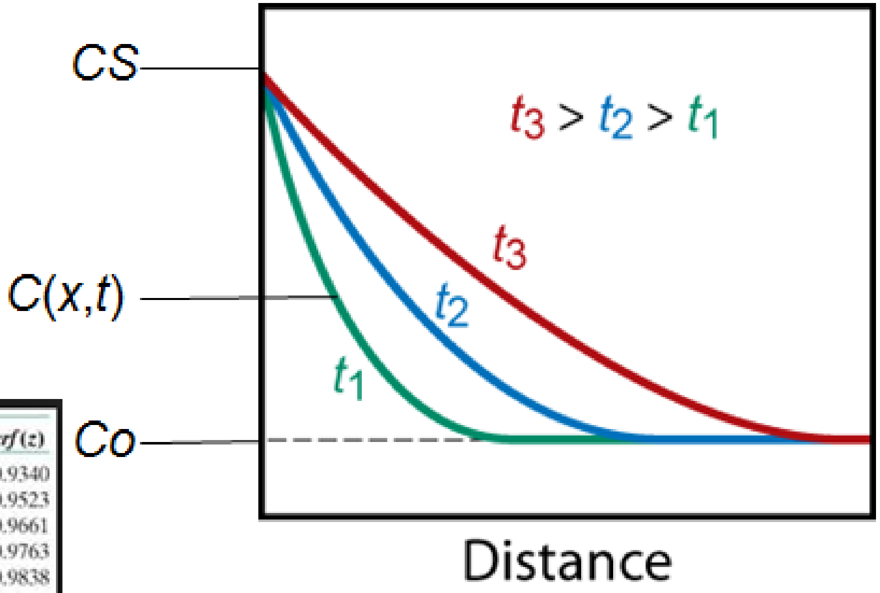
$C(x,t)$ = Conc. at point x at
time t

erf (z) = error function

$$= \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy$$



z	$erf(z)$	z	$erf(z)$	z	$erf(z)$
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999



Sample Problem for Non-steady State Diffusion

An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.

Solution:

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

t = 49.5 h $\quad$ x = 4 x 10-3 m

Cx = 0.35 wt% $\quad$ Cs = 1.0 wt%

Co = 0.20 wt%

$$\frac{C(x,t)-C_o}{C_s-C_o}=\frac{0.35-0.20}{1.0-0.20}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)=1-\mathrm{erf}(z)$$

$\therefore$ erf(z) = 0.8125

Solution (cont.)

We must now determine from Table the value of *z* for which the error function is 0.8125. An interpolation is necessary as follows

z	erf(z)
0.90	0.7970
z	0.8125
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for *D*

$$z = \frac{x}{2\sqrt{Dt}} \qquad D = \frac{x^2}{4z^2t}$$

$$\therefore D = \left(\frac{x^2}{4z^2t}\right) = \frac{(4 \text{ x } 10^{-3} \text{ m})^2}{(4)(0.93)^2(49.5 \text{ h})} \frac{1 \text{ h}}{3600 \text{ s}} = 2.6 \text{ x } 10^{-11} \text{ m}^2/\text{s}$$

Solution (cont.):

To solve for the temperature at which D has above value, we use a rearranged form of Equation;

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

from Table, for diffusion of C in FCC Fe

D_o = 2.3 x 10-5 m2/s Q_d = 148,000 J/mol

$$T = \frac{148{,}000 \text{ J/mol}}{(8.314 \text{ J/mol - K})(\ln 2.3\text{x}10^{-5} \text{ m}^2/\text{s} - \ln 2.6\text{x}10^{-11} \text{ m}^2/\text{s})}$$

$$\boxed{T = 1300\ K = 1027\ ℃}$$