MECHANICAL BEHAVIOUR

WHAT YOU APPLY!

Shear & shear stress

Static

The two forces are equal and opposite.

\[ F = \sum F_i \]

\[ \sigma = \frac{F}{A} \quad \text{(Stress, Tensile, Compression)} \]

\[ \tau = \frac{F_{\parallel}}{A} \quad \text{(Shear Stress)} \]

\[ \sigma = \text{Pascal} = \text{Newtons/m}^2 \]

\[ \tau = \text{Pascal} = \text{Newtons/m}^2 \]
WHAT YOU GET?

strain

$\varepsilon = \text{strain (no dimension } \Rightarrow \%)$

$\varepsilon = \frac{\Delta l}{l_0} > 0$ (hopefully)

Deformation!

$\sigma = \frac{F}{A}$

$\sigma \Rightarrow \varepsilon$

ELASTICITY $\Rightarrow \sigma \propto \varepsilon \Rightarrow \varepsilon \propto \sigma$ (some thing)

$\frac{\sigma}{\varepsilon} = E$ YOUNG MODULUS (PASCAL)

$E = \frac{\sigma}{\varepsilon}$

$\frac{d\sigma}{d\varepsilon} = Ed$ DIFFERENTIAL YOUNG MODULUS

loading

unloading

slope

$E$ good metals

$E$ small rubber?

$E$ big ceramics
E can depend on direction

\[ \Rightarrow \]

POISSON'S RATIO

\[ \Delta d < 0 !! \text{ (hopefully)} \]

\[ E_{axial} = \frac{\Delta l}{l_0} > 0 \]

\[ E_{transverse} = \frac{\Delta d}{d_0} < 0 \]

\[ \nu = \frac{E_t}{E_a} \text{ Poisson RATIO} \]

it's always > 0 ?

No!! some weird materials (metallic foams) can be \( \nu < 0 \)
**SHEAR STRAIN**

\[ \Delta \theta = \frac{\Delta W}{h} \]

\[ \tan \theta = \frac{\sin \theta}{\cos \theta} \]

\[ \theta \to 0 \quad \sin \theta \to \theta \]
\[ \cos \theta \to 1 \quad \tan \theta \to \frac{\theta}{\cos^2 \theta} \to \theta \]

\[ \Delta \theta = \frac{\Delta W}{h} \times \theta = \text{No Dim} \]

Apply \( z \) to get \( \frac{\Delta W}{h} \) in elasticity.

\[ \Rightarrow z \equiv G \quad \text{SHEAR MODULUS} \]

\[ E, G, \nu \text{ are called ELASTIC CONSTANTS} \]

\[ G = \frac{E}{2(1+\nu)} \quad \text{For isotropic materials} \]

\( \theta z = Gz \) if \( z \) different.

**EXAMPLE** put CUBIC
DEFORMATION / VISCOELASTICITY

Elastic for small $\sigma$, $\epsilon$ monomolecular materials, what about polymers?

2 REGIMES

$T < T_{\text{glass}}$ transition

$\sigma$ \rightarrow \text{STRETCHING, DEFORMATION, BUT NO SLIP}$

$\Rightarrow T > T_{\text{glass}}$

Temperature $\Rightarrow$ a lot of thermal movement $\Rightarrow$

$\Rightarrow$ \text{slip} $\Rightarrow$ \text{DEFORMATION, VISCOELASTICITY}$
DYNAMIC TESTS (STEPS)

2 common tests \( T > T_g \)

\[ \varepsilon = \text{constant} \quad \frac{\partial \varepsilon}{\partial t} = 0 \Rightarrow \sigma(t) \quad \text{STRESS RELAXATION} \]

\[ \begin{align*}
\varepsilon_{\text{relax}}(t) &= \frac{\sigma(t)}{\varepsilon_0} \\
\varepsilon_{\text{relax}}(t) &= \frac{\sigma_0}{\varepsilon(t)} \\
\sigma &= \text{constant} \\
\frac{\partial \sigma}{\partial t} &= 0 \Rightarrow \varepsilon(t) \quad \text{TIME DEPENDENT DEFORMATION}
\end{align*} \]

\[ \sigma \quad \Rightarrow \quad \sigma_0 \quad \text{DAMPING} \quad t = \frac{-t}{\lambda} \]

\[ \begin{align*}
\varepsilon(t) &= \text{damping} \\
\varepsilon(t) &= \text{relaxation} \\
\varepsilon(t) &= \text{time dependent viscosity} \\
\varepsilon(t) &= \text{exponential} \\
\varepsilon(t) &= \text{relaxation} \\
\varepsilon(t) &= \text{deformation}
\end{align*} \]
\[ \Delta W = FA \Delta L \]
\[ dW = FdL \]
\[ \varepsilon = \frac{\Delta L}{L_0} \]
\[ \Rightarrow \varepsilon = \frac{\Delta L}{L_0} \]
\[ L = L_0 + \varepsilon L_0 \]
\[ SL = L_0 \varepsilon \]
\[ \Rightarrow dL = L_0 d\varepsilon \]
\[ dW = \int F L_0 d\varepsilon \]
\[ \Rightarrow \frac{dW}{V} = \frac{dW}{A \cdot L_0} \]
\[ dw = \sigma de \]

**M7**

amount of work per unit volume you do with stress \( \sigma \), getting de deformation
**DYNAMIC CYCLING**

\[ e = \varepsilon_0 \sin\omega t \]

\[ \varepsilon = \varepsilon_0 \sin(\omega t + \phi) = \varepsilon_0 \left[ \sin(\omega t) \cos \phi + \cos(\omega t) \sin \phi \right] \]

\[ E_1 = \frac{\varepsilon_0}{\varepsilon} \quad \text{STORAGE MODULUS} \]

\[ \partial w = \sigma d\varepsilon \Rightarrow \omega \text{ a circle} \]

\[ \varepsilon(t) \Rightarrow \sigma = \varepsilon_0 \frac{E_1}{\varepsilon} \sin(\omega t) + \varepsilon_0 \frac{E_2}{\varepsilon} \cos(\omega t) \]

\[ \Rightarrow \quad \varepsilon(t) = \varepsilon_0 \frac{\sin(\omega t)}{\sigma} \quad \text{LOSS MODULUS} \]

\[ E^* = \frac{\varepsilon_0}{\varepsilon} e^{i\phi} = E_1 + iE_2 \]

Loss per cycle: \[ \Delta w = \int \partial w \]

\[ \sigma = \varepsilon_0 \frac{E_1}{\varepsilon} \sin(\omega t) + \varepsilon_0 \frac{E_2}{\varepsilon} \cos(\omega t) \]

\[ \Phi = \frac{\pi}{2}, \quad \phi = \frac{\pi}{2} \]

\[ \int \partial \varepsilon = \int_0^{2\pi} \varepsilon_0 \sin(\phi + \theta) \cos \phi \, d\phi = \]

\[ = \varepsilon_0 \cos \frac{\pi}{2} \left[ \cos \phi + \frac{\sin \phi}{2} \right]^{2\pi}_0 = 0 \]

\[ \cos \phi \, d\phi = \cos \phi \left[ \frac{\sin \phi}{2} \right]^{2\pi}_0 = 0 \]

\[ \sin \phi \, d\phi = \sin \phi \left[ \frac{\phi}{2} \right]^{2\pi}_0 = 0 \]

\[ = \varepsilon_0 \frac{E_1}{\varepsilon} \sin(\omega t) + \varepsilon_0 \frac{E_2}{\varepsilon} \cos(\omega t) \]

\[ \Delta w = \int \partial w = \frac{\varepsilon_0}{\varepsilon} \left( E_1 + iE_2 \right) \quad \text{LOSS small} \]

\[ \approx \frac{\varepsilon_0}{\varepsilon} E_2 \]

\[ E_1 \approx 1 \text{ GPa} \]

\[ E_2 \approx 0.01 \text{ GPa} \]

\[ \approx 10^6 \]
ELASTIC LIMIT

\[ \sigma - E \]

plastic = continuous increase of \( \sigma \)
\( \Rightarrow \) the material gets harder

STRAIN HARDENING

METALS ≠ POLYMERS ≠ CERAMICS (BRITTLE)

POLY: used to align molecules \( \Rightarrow \) stronger

TENSILE TESTING

\[ \sigma - E \]

yield strength \( \sigma_Y \)
yield stress \( E_Y \)

\( \sigma_U \) = ultimate strength

\( \varepsilon_f \) = fracture

\( \varepsilon_f \) = engineering strain at fracture

\( \varepsilon_f \) = DUCTILITY

[Samples I]

uniform strain (strain uniform)
IF NOT ELASTIC

Copper, Aluminum, Fe
always, plastic

IF DEFECTS ARE STUCK
(mobility of dislocations)

Carbon Steel

Toughness = energy to frac

\[ U = \int_0^{\epsilon_f} \sigma \, d\varepsilon = \frac{F}{m^3} \]
CERAMIC TEST

samples are hard to move = bending but not uniform stress

Compression = tension
Ionic bonding & pre-existing voids inside

POLYMERS

Fibers
Thermoplastic
Polyethylene
Necking
Stretching primary bonds

DUCTILE & BRITTLE FRACTURE

Metals: ductile = absorb energy, dislocations, defects move, deforming, necking = fracture

Ceramics: brittle = no absorbing energies, no dislocations, movement, defects get stuck = brittle
DUCTILE TO BRITTLE DBTT

TRANSITION TEMPERATURE

Some metals when cooled cannot absorb energy well (ferritic steel, steel with ferrite)

So their DBTT changes

Problem for equipment in cold weather slips, spares, planes

DBTT depends on chemical composition

For steel
\[ \text{C} \uparrow \text{DBTT} \downarrow \]

Amorphous: \( T>T_g \) viscous fluid (brittle)
\( T<T_g \) brittle

Polymers depend where DBTT is with respect to \( T_g \).
tensile testing of metals, and then describe the corresponding procedures for ceramics and polymers (testing of composites is described in Chapter 14).

Figure 9.2–7 shows two specimen geometries recommended by the American Society for Testing and Materials (ASTM) for tensile testing of metals. The choice of specimen geometry and size often depends on the product form in which the material is to be used or the amount of material available for samples. A flat specimen geometry is preferred when the end product is a thin plate or sheet. Round–cross section specimens are preferred for products such as extruded bars, forgings, and castings.

As shown in Figure 9.2–8a, one end of the specimen is gripped in a fixture that is attached to the stationary end of the testing machine; the other end is gripped in a fixture attached to the actuator (moving portion) of the testing machine. The actuator usually moves at a fixed rate of displacement and thus applies load to the specimen. The test usually continues until the specimen fractures.

During the test, the load on the specimen is measured by a transducer called a load cell; the strain is measured by an extensometer (a device for measuring the change in length of
FIGURE 9.2-23
Charpy impact test results for several types of materials: (a) the influence of carbon content on the DBTT of plain carbon steels, (b) the influence of manganese content on the DBTT of steels containing 0.05 percent carbon, and (c) a comparison of the data for FCC metal alloys, BCC steels, high-strength metal alloys, and ceramics. (Source: Metals Handbook, Desk Edition, 1984, p. 4.85, ASM International, Materials Park, OH. Reprinted by permission of the publisher.)
FRACTURE - BRITTLE

\[ \sigma - E \]

\[ \text{DUCTILE} \]

\[ \text{BRITTLE} \]

\[ \text{MAX LOAD} \Rightarrow \text{FRACTURE} \]

\[ \Rightarrow \text{CRACK GROWING CONTINUOUSLY} \]

Small defect allows growth with fatigue

GRIFFIT MODEL: ENERGY RELEASE RATE

CRACK RELEASE ELASTIC ENERGY

SURFACE ENERGY EXCEEDS GAPS IT!!

\[ \Delta W = \text{FRACTURE} \]

\[ \sigma = \partial W = \partial W_E + \partial W_S \]

\[ \partial W = \sigma \partial e \quad \text{Elasticity} \]

\[ \frac{\sigma}{E} = \epsilon \quad \epsilon = \frac{\sigma}{E} \Rightarrow \]

\[ \partial W = \frac{\sigma \partial \epsilon}{E} \]

\[ \frac{\sigma}{E} \]

\[ \text{Gullet} \]

\[ \sigma \]

\[ \sigma \]

\[ \Delta W = \sigma^2 \Delta V \]

\[ \Rightarrow - \frac{\sigma^2 \Delta a}{E} \]
\[ \Delta W_{\text{surface}} = x_s \Delta W_{\text{fracture}} \]

Energy to create 1 m² of surface

If you cut \( \Rightarrow \) create 2 holes

\[ \Rightarrow \quad 2 \Delta a_{\text{surface}} \quad \text{per circle} \Rightarrow \quad 4 \Delta a \]

\[ \Rightarrow \quad \Delta W_{\text{surface}} = x_s 4 \Delta a \quad \text{(per unit length)} \]

\[ \Rightarrow \quad \text{of fracture} \Rightarrow \text{self-sustaining phenomenon} \]

\[ \Rightarrow \quad 0 = \Delta W_E + \Delta W_{\text{surface}} = -\frac{\sigma^2}{E} a + 2 \Delta a + x_s 4 \Delta a \]

\[ = 2 \Delta a \left( -\frac{\sigma^2}{E} a + 2 x_s \right) \]

Critical \( \sigma_c \) for fracture with release of elastic energy (good mechanics)

For metal (plastic) ?? How? Orowan trick

\[ \sigma_c = \sqrt{\frac{2E}{a + \phi}} \frac{x_s}{x_s} \]

plastic deformation of surface

How to measure? A big hack.!

plastic deformation学科 by rock growth orientation CRAZES!
MODERN APPROACH

ISOTROPIC, ELASTIC, the stress can be written as

\[ \sigma_y = \frac{k}{\sqrt{2m}} f(\Theta) \]

\[ k \text{ is a stress intensity parameter} \]

\[ \text{for} \quad \frac{\text{sum, cos, sinh, complex}}{\text{inv.}} < 1 \]

\[ \Rightarrow \text{WORSE SCENARIO OVERESTIMATE} \sigma_y \]

\[ \sigma_y = \frac{k}{\sqrt{2m}} \]

\( K \) depends on the MODE (MICHELANGELO)

MODE I

MODE II

MODE III

and type of crock

MIS
\[ k = \sigma \sqrt{\frac{H}{a}} \]

**TUNNEL**

**PENNY**

\[ k = 2\sigma \sqrt{\frac{\alpha}{\pi}} \]

Wedge \ldots and so on:

\[ k = \frac{p}{B \sqrt{H a}} \]

\[ \sigma \] or \( \sigma (\sigma P) \) set \( k \),

\[ \sin \sigma \rightarrow k \] when:

\[ k = k_c e^{i\theta} \] (tables for modes and materials)

\[ \text{CRACK, fracture} \]

\[ \text{Weld for thick metals,} \]

\[ \text{for thin? thin is tough} \]

\[ \text{because more plasticity has to be built for unit value} \]

\[ \sigma - \text{thin} \]

\[ \sigma - \text{thin} \]

\[ \Sigma = 1 \text{m}^3 \]

\[ \text{(less plasticity)} \]
**EXPERIMENTALLY**

\[ \frac{k_{\text{mode}1}}{k_{\text{crit},\text{mode}1}} \text{ valid for} \]

**Thickness \( > \) critical thickness**

\[ B = 2.5 \left( \frac{K_{\text{ic}}}{\sigma_{ys}} \right)^2 \]

\[ \sigma \]

\[ \varepsilon \]

---

**FRACTURE RELATION WITH FRACTURE TOUGHNESS**

**METAL** HIGH \( K_{\text{ic}} \) known

**CERAMICS**

small area ! !

FOR METALS

\[ K_{\text{ic}} \propto \sqrt{E \sigma_{ys} \varepsilon_{ft}} \]

\[ \sigma \]

\[ \varepsilon \]

\( E = \frac{\sigma}{\varepsilon} \)

---

strain toughness exponent

(\( (\text{do second part of course)} \))

**M17**

measure of how much \( K_{\text{ic}} \) is strain driven, by entangling defects
\[
E \uparrow \quad \\nabla \downarrow \quad \varepsilon_f \downarrow
\]

\[
\nabla \varepsilon_f \uparrow \nabla \varepsilon \uparrow \varepsilon_f
\]

\[
\Rightarrow \quad E \uparrow \quad \varepsilon \uparrow \quad \varepsilon_f \downarrow \quad \Rightarrow \quad E \uparrow \quad \varepsilon \uparrow \quad \varepsilon_f \downarrow
\]

\[
\Rightarrow \quad \text{brittle fracture}
\]

Concern for high strength alloys and metal, AND NOT DUCTILE ONES!!

CERAMICS NO PLASTICITY \Rightarrow LEFM

Linear Elastic Fracture Mechanics.

\[
\sigma_{\text{max}} \sim \sqrt{\frac{a}{\rho}}
\]

MAX

\[
\nabla \sigma_{\text{max}}
\]

So: how to make it stiffer?

VOIDS? INCREASE p

work with solubility with bigger atomic expansion & quench

H18
Precipitates with lower thermal expansion may pre-load the matrix to low compressive stress, which can decrease 10 times stronger.

**Numbers**

- **Metals**: 20 - 150 MPa/√m; absorbs energy, plasticity
- **Ceramics**: 0.5 - 2 MPa/√m; no adhesion
- **Treated**: 9 - 15 MPa/√m; voids + precipitates
- **Polymers**: 0.5 - 10 MPa/√m; small area < Tg
  - > Tg: same viscoelasticity, no fracture but lose slope
Expressions for estimating $K$ can be found in handbooks. Some common load and crack geometries and their corresponding stress intensity parameter expressions are shown in Figure 9.4–2. For example, for a plate under uniform tensile stress containing a center crack, $K$ is given by:

$$K = \sigma \sqrt{\pi a}$$  \hspace{1cm} (9.4-2)

In Figure 9.4–2a through c, the dimensions of the body are assumed to be very large relative to the dimensions of the crack. When the crack size is not negligible compared with the planar dimensions of the component, the stress intensity parameter is obtained by applying a geometric correction factor to the corresponding expression for $K$ in a semi-infinite body. Although these geometric correction factors are beyond the scope of this text, we note that omitting their use, or, equivalently, assuming a geometric correction factor of 1, always leads to conservative design estimates.
FIGURE 9.4-4  Toughening mechanisms for ceramics. (a) Microcracking—when the advancing crack enters the microvoid, its length increases slightly but its crack tip radius increases significantly, decreasing the stress amplification and correspondingly reducing the driving force for crack extension. (b) Residual compression at the crack tip—selected regions of a microstructure are induced to expand in the vicinity of the crack tip so that a local state of compression counteracts the externally applied tensile stress.

microvoid, the tip radius increases by a much larger factor so that the ratio $a/o$ in Equation 9.4-6 decreases significantly. Thus, although the crack blunting mechanism is different in ceramics than in metals, the result is the same—a decrease in the driving force for crack extension.

How can these microvoids be inserted into the ceramic microstructure? One method is to obtain a microstructure that at elevated temperatures is composed of a roughly spherical phase surrounded by a second-phase matrix. If the coefficient of expansion for the spherical phase is greater than that of the matrix, then when the ceramic is cooled to room temperature, the spherical phase will contract more than the matrix. If the phase boundary is weak, this differential contraction results in the formation of a "gap" between the two phases that displays the desired characteristics.

The same mechanism is occasionally used to stop crack extension in large-scale metal structures. If the tip of an advancing crack can be located using a nondestructive testing method, then one can drill a hole in front of the crack so that when the crack enters the hole, its radius increases significantly. (This was used on the Liberty ships).

Let us return to the idea of a two-phase ceramic microstructure containing a spherical second phase. Suppose that the spherical phase has a lower expansion coefficient than the matrix. What happens when the ceramic is cooled from the fabrication temperature to room temperature? As shown in Figure 9.4-4b, the spherical phase contracts less than the matrix. The result is that the matrix material located between two nearby second-phase particles is placed in residual compression. A crack attempting to enter this volume of the matrix phase will experience an effective reduction in the stress component responsible for crack extension. The result is an increased toughness value for the ceramic. Although there are other methods for toughening ceramics, they are all based on the same principles: decrease the driving force for crack extension, increase the amount of energy required for crack extension, or both.

As an example of the effectiveness of these toughening mechanisms, pure zirconia (ZrO$_2$) has a $K_c$ value of $\approx 2$ MPa-V$\cdot$m, while transformation-toughened zirconia has a $K_c$ value of $\approx 9-13$ MPa-V$\cdot$m. It is important to note, however, that while the mechanisms described above can significantly increase the fracture toughness of ceramics, the data in Appendix D show that even the toughest ceramics generally have lower $K_c$ values than most metals.

---

There are other methods for creating a volume expansion in the spherical second phase, but the result is the same—the matrix between particles is placed in residual compression.
reasonable estimates of the fracture toughness can be obtained. An indentation on the surface of cubic zirconia is shown in Figure 9.4–5, with cracks emanating from the corners.

Typical fracture toughness values for some common metals, ceramics, and polymers are given in Appendix D.

9.5 FATIGUE FRACTURE

Fatigue is the most common mechanism of failure and is believed to be either fully or partially responsible for 90% of all structural failures. This failure mechanism is known to occur in metals, polymers, and ceramics. Of these three classes of structural materials, ceramics are least susceptible to fatigue fractures. The phenomenon of fatigue is best illustrated by a simple experiment. Take a metal paper clip and bend it in one direction until it forms a sharp kink. The clip undergoes plastic deformation in the region of the kink but does not fracture. If we now reverse the direction of bending and repeat this process a few times, the paper clip will fracture. Thus, under the action of cyclic loading, the paper clip breaks at a much lower load than would be required if it were pulled to fracture using a monotonically increasing load. While the initial loading causes the metal in the paper clip to strain-harden, repeated load application causes internal fatigue damage. In a simplified view of this process, the plastic deformation causes dislocations to move and to intersect one another. The intersections decrease the mobility of the dislocations, and continued deformation requires the nucleation of more dislocations. The increased dislocation density degrades the crystallographic perfection of the material, and eventually microcracks form and grow to a sufficiently large size that failure occurs.

9.5.1 Definitions Relating to Fatigue Fracture

Figure 9.5–1 shows a typical fatigue load cycle as characterized by a variation in stress as a function of time. The maximum and minimum levels of stress are denoted by $S_{\text{max}}$ and $S_{\text{min}}$, respectively. The range of stress, $\Delta S$, is equal to $S_{\text{max}} - S_{\text{min}}$, and the stress amplitude, $S_0$, is $\Delta S/2$. A fatigue cycle is defined by successive maxima (or minima) in load or

---

Footnote:

6 The symbol $S$ is used to represent engineering stress by most specialists in the area of fatigue. We have therefore elected to employ this convention in our discussion of fatigue.
ATOMIC STRUCTURE

ATOMS = DEMOCRITOS (GREECE!!)

UNITS THAT CANNOT BE SPLIT (WRONG BUT RIGHT)

NUCLEUS
  PROTONS / NEUTRONS

V ELECTRONS

10 TIMES MORE BIGGER THAN NUCLEUS

\[ Z = \# e = \# p = \# n \] atomic number

\[ \# n = \text{variable} > Z \]

electrons rotate fast as fast you need QM

ORBITALS LIKE PLANET AROUND SUN

4 UNSERIVED

SCHRODINGER EQUATION

A1
How to describe orbitals

Quantum numbers: \( n, l, m, s \)

- \( n \) - principal quantum number (positive integer)
- \( l \) - angular momentum quantum number (integer, \( 0 \leq l \leq n-1 \))
- \( m \) - magnetic quantum number (integer, \( -l \leq m \leq l \))
- \( s \) - spin quantum number (1/2, -1/2)

Pauli principle: \( 2e \) cannot occupy same 4 quantum numbers.

Rules:

- \( n = 1, 2, 3, \ldots \) integer
- \( l = 0, 1, \ldots n-1 \)
- \( m = -l, -l+1, \ldots 0, l-1, l \)
- \( s = \pm \frac{1}{2}, \frac{1}{2} \)

Special case: \( n = 1 \)
- \( l = 0 \) (\( s = 0 \), \( s = \text{spin-up} \))
- \( m = 0 \)
- \( s = +\frac{1}{2}, -\frac{1}{2} \) \( \Rightarrow \) 2 electrons
\[ 2s^1, 2s^2 \quad l = 0 \quad s = \pm \frac{1}{2} \quad m_s = 0 \quad m = 0 \quad \text{2 electrons} \]

\[ 2p^1 \quad l = 1 \quad m = -1, 0, 1 \quad P_x, P_y, P_z \quad S = \pm \frac{1}{2} \quad \text{each} \quad \Rightarrow 6 \text{ electrons} \]

\[ \text{S I M M E R T R I C} \]
\[ \text{RESPECT THE CENTER} \]

\[ m = 3 \quad l = 0 \quad 3s^1 \quad \Rightarrow 2 \quad 3s^1 \quad \Rightarrow 6 \text{ mo} \]

\[ 3d^{1...10} \quad l = 2 \quad m = -2, -1, 0, 1, 2 \quad \overbrace{5} \quad \text{S} \quad \text{d orbitals} \]

\[ S = \pm \frac{1}{2} \quad \Rightarrow 10 \text{ electrons} \]
Energy

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p

Increasing energy

Hund's Rule

In a set of orbitals with the same energy, if partially occupied, the electrons go to maximize total spin.

Example: 3d^5

Lower energy

\[ S = +\frac{1}{2} \]

\[ S = 2 \uparrow \]

Magnetic = both filled d & f

Hm, Fe, Co magnetic

Tl, Zn NO

Put AM table

Valence \# e in outer shell contributing to bond

BOON = SHARE ELECTRONS
THERMO & AIR

THERMODYNAMICS

Study of relationships between $p$, $T$, value, composition $\Rightarrow$ EQUILIBRIUM (phases, liquid, solid...)

KINETIC

Study of relationships out of EQUILIBRIUM

speed reaction occur

THERMO: increase $T$ - increase Energy

$E$

$T$

Phase

Solid

Liquid

Quartz

Melting

solid most favourable energy most favourable

low cost?

Rate $k(+) = Ce^{-\frac{Q}{RT}}$ (gas constant $T \uparrow k \downarrow p_e$

activation energy

EXAMPLE 2.3 1

plote A

plot B

$Q =$ energy you need to apply to see the bill

$\Rightarrow$ irreveibility
Bonds

Electronegativity = measure how _lone _pennous
is an atom!
for electrons

\[ \text{Na} \rightarrow \text{Na}^+ \]

\[ 1s^2, 2s^2, 2p^6, 3s^1 \]

\[ \text{Na}^+ \rightarrow \text{Na}^+^\rightarrow \text{Na}^+^+ \]

\[ 1s^2, 2s^2, 2p^6, 3s^1, 3p^5 \]

\[ \text{Ce} \rightarrow \text{Ce}^- \]

\[ -2.02 \text{ eV} \]

electron affinity

\[ \text{Na}^+ + \text{Ce}^- \]

\[ E = \text{eV} - 4.02 \text{ eV} \]

\[ 1.02 \text{ eV} > 0 \]

\[ \text{wholly they form} \]

\[ F = \frac{|Z_1 Z_2 |}{4 \pi \varepsilon_0 r^2} \]

attraction

\[ \nabla V \left( r \right) = \frac{F \nabla V \left( r \right)}{\varepsilon_0} \]

\[ V(r) = \text{attraction} \]

\[ \text{classical mechanics} \]

A6
the ionic force would fuse the two atoms together

but

\[ F = \frac{k}{r^2} \]

repulsion due to other electrons

much stronger than attraction

when \( r \) is small \( m \)

must why 12

\[ F = -\nabla V \Rightarrow V_{\text{repulsion}} = \frac{1}{r^2} \]

\( n = m - 1 \)

\( n = 12 \rightarrow 13 \)

\[ F_{\text{total}} = F_{\text{att}} + F_{\text{rep}} = -\nabla V_{\text{total}} = -\nabla (V_{\text{rep}} + V_{\text{att}} + V_{\text{form}}) \]

\[ V_{\text{for}} \to \text{form } Na^+ Cl^- \]

\[ V_{\text{att}} \to \text{form } Na, Cl \]

Read chap 2 up to 39

[\[ L_{12}O, 1s^2 2s^2 2p^9 \]

[\[ 1s^2 2s^2 \] an extra line \]
**COVALENT BOND**

- In 2 atoms, similar electronegativity:
  - No one gives away (C+) or gains one electron.
  - Then they share:
    - \( \text{Cl}_2, \ H_2, \ \text{CH}_4 \) all hydrocarbons.

**METALLIC BOND**

- Generous atoms give away electrons.
- Electrons form a sea/cloud of electrons called the FERMI SEA, it's homogeneous.
- Jello model:
- De-localized electrons, globally shared electrons.
**Ductility - Brittle behaviour**

- **Metals**
  - Metallic bonds
  - Easy

- **Ceramic**
  - Ionic bonds
  - Hard

**Electrical conductivity**

- Type of carrier (metals, solutions)
- Density of carriers (#/Volume)
- Mobility (e. heavy or light)

\[ \text{Speed} = \mu \cdot E \]

- Free electrons => Very mobile
- Ions and electrons => Not very mobile
ORIGIN OF YOUNG MODULUS

$V(x)$

$\varepsilon = \frac{\Delta x}{x}$

$F(x) = \frac{\partial V}{\partial x}$

$e = \frac{\partial E}{\partial x}$

$\Delta x$

$\sigma = E \varepsilon$

$F = E \frac{\Delta x}{\Delta x}$

$E = \frac{\sigma}{\varepsilon}$

$\varepsilon(\varepsilon) = \varepsilon \frac{\partial F}{\partial \varepsilon}$

$\text{curvature} = \frac{\partial^2 V}{\partial x^2}$

$E(x) = E_0 + \frac{F}{A}$

$E(x) = E_0 + \frac{F}{A}$

$\text{elastic}$

$\text{modulus}$

$\text{A10}$
THERMAL EXPANSION

parabola

\[ V(x) \sim V(x_0) + \frac{1}{2} \epsilon (x - x_0)^2 \]

\( \text{V}(t) \) not symmetric \( \Rightarrow \) expansion

\( x_e = x_0 (T = 0) + g x_0 (T - T_0) \)

\[ E_{\text{bond}} \uparrow \Rightarrow T_{\text{melting}} \uparrow \Rightarrow \frac{\partial n}{\partial T} \downarrow \]

more symmetric and \( \downarrow \)

All
**Coordination Number & Packing**

Ionic material (spherical, all dimensional consideration)

Cation (the one that gets the $\text{\textsuperscript{+}}$)

Anion (the one that gets the $\text{\textsuperscript{-}}$)

"usually" $r(\text{cation}) < r(\text{anion})$

Go right/left in Table

Use $R/s$ in Table

$r/R$ defines structure

$CN =$ coordination number

# of first neighbours

**Covalent**

$CN$ depends on the electron valence shells

**Layered**

Show PIC Beam 45
SECONDARY BONDS

\[ \text{vdW (temporary dipoles)} \Rightarrow \text{van der Waals} \]

\[ \text{electrons while rotating produce a temporary electric dipole (TEMPORARY DIPOLE)} \]

\[ \Rightarrow \text{dipole} = \frac{e}{r} \]

\[ \Rightarrow \text{Coulomb's distance vector} \]

\[ \Rightarrow \text{attraction between dipoles, else if the net charge is zero} \]

\[ \Rightarrow \text{van der Waals weak} \sim V_{\text{vdW}} \sim -\frac{1}{r^6} \]

PERMANENT DIPOLES

When they have a permanent asymmetric distribution:

\[ \text{H}_2\text{O} \Rightarrow \text{O} 1s^2 2s^2 2p^4 \]

\[ \text{Selection in } sp^3 \text{ hybridization} \]

\[ \text{Same for } \text{SeH}_2, \text{H}_2\text{S} \& \text{NH}_3 \]

\[ 2s^2 2p^3 \]

\[ sp^3 \text{ with Se} \]

Permanent Bonds \(\sim\) VdW
POLYMERS : MACROMOLECULES

Saturated

No free electrons to share

\[
\begin{align*}
\text{No C} = \text{C to break} \\
\text{No free electrons to share}
\end{align*}
\]

Soluble \( \Rightarrow \) bonding between molecules are secondary (volatil & gaseous remnant)

\( \Rightarrow \) Thermoplastic: They melt and can be reused many times (AGA)

Unsaturated

They have free orbitals to share

\[
\begin{align*}
\text{\( \text{H} - \text{C} = \text{C} - \text{C} = \text{C} - \text{C} \)} \\
\text{\( \text{H} \)}
\end{align*}
\]

\( \Rightarrow \) Less unsaturated

\( \Rightarrow \) Double bonds

\( \Rightarrow \) Upon heating up, these bonds break and join with other chains resulting cross-links

Thermoset polymers

Rubber comes from LATTICE (natural) with sulfurization

Good Year

A14
determined by the value of the quantum number \( l \) and is given by \( 2(2l + 1) \). Thus, the maximum numbers of electrons in an s, p, d, and f subshell are respectively 2, 6, 10, and 14.

The **electron configuration** represents the distribution of electrons within the permissible energy levels. In the **ground state**, an atom's electrons occupy the lowest-energy subshells consistent with the Pauli exclusion principle. The subshells can be arranged in order of increasing energy as follows:

\[ 1s, 2s, 2p, 3s, 3p, 4s, 4p, 5s, 5p, 6s, 6p, 7s, 7p, 6f, 7d, \ldots \]

In this notation, the number of electrons in each subshell is indicated using an integer superscript on the corresponding letter. For example, a half-filled subshell with quantum numbers \( n = 3 \) and \( l = 2 \) would be designated as \( 3d^5 \).

How can we use this notation to describe the ground-state electron configuration for an oxygen atom that contains eight electrons? In the ground state the subshells will “fill” in the order \( 1s, 2s, 2p \ldots \) and the maximum number of electrons in s and p subshells will be two and six, respectively. Thus, the ground-state electron configuration for oxygen is \( 1s^22s^22p^4 \), indicating two electrons in each of the (filled) \( 1s \) and \( 2s \) subshells and four electrons in the (partially filled) \( 2p \) subshell.

In addition to the quantization of energy, another key result of the wave model is that the exact position of an electron within an atom can never be known. Instead, probability density functions (PDFs) are used to describe the spatial location of electrons. As shown in Figure 2.2–2, the shape of the PDF depends on the value of the quantum number \( l \). Note that not all the distribution functions are radially symmetric. The consequence of a nonsymmetric PDF is that definite bond angles can be found in structures such as diamond, organic molecules, and polymeric chains. We will see that these specific bond angles influence the macroscopic engineering properties of the corresponding materials.

**Figure 2.2–2**
A highly schematic illustration of the probability density functions for electrons in certain subshells of an atom. Note that the s subshells are radially symmetric while the p subshells (and all other subshells) are highly directional.

\[ s \text{ orbitals are spherically symmetric} \]

\[ p \text{ orbitals have a dumbbell shape} \]
d. For CdTe, $\Delta EN = 2.1 - 1.9 = 0.2$. Using the table in Appendix B, this corresponds to a bond that is $\sim 1\%$ ionic. Therefore, the bonding in CdTe is either metallic or covalent. Since the average number of valence electrons in CdTe is $(2 + 6)/2 = 4$, we predict the bonding in CdTe is likely to be covalent.

### 2.4.4 Influence of Bond Type on Engineering Properties

At this point we can make a few preliminary observations concerning some of the mechanical and electrical properties of solids as a function of bond type.

Consider the difference in the response of a metal and an ionic solid (ceramics and oxide glasses are examples of solids with considerable ionic character) when each material is struck with a blow from a hammer. Atoms in the metal can slip and slide past one another without regard to electrical-charge constraints in response to the applied force and thus absorb the impact without breaking. This phenomenon is called ductile behavior of metals. On the other hand, as illustrated in Figure 2.4–5a, in an ionic solid, each ion is surrounded by oppositely charged ions. Thus, ionic slip may lead to like charges moving into adjacent positions, causing coulombic repulsion (see Figure 2.4–5b). This makes slipping much more difficult to achieve, and the material responds by breaking. This is one of the reasons why ceramics and oxide glasses fracture easily. Such behavior is known as brittle behavior.

---

**FIGURE 2.4–5** A comparison of the difference in the atomic scale response of a metal and an ionic solid to a hammer blow. **(a)** In an ionic solid before the hammer blow each ion is surrounded by oppositely charged ions. **(b)** When the ions attempt to slip past one another in response to the applied force, strong repulsive forces develop and lead to cracking. **(c)** In contrast, in a metal the electron cloud shields the positively charged atomic cores from each other so that the repulsive forces do not develop.
TABLE 2.5-1  Latent heat of fusion, melting temperatures, and coefficients of thermal expansion for some metallic elements.

<table>
<thead>
<tr>
<th>Material</th>
<th>Latent heat of fusion (J/g)</th>
<th>Melting temperature (K)</th>
<th>Coefficient of thermal expansion ($\times 10^{-6}$/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Row III metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>250</td>
<td>291</td>
<td>27</td>
</tr>
<tr>
<td>Re</td>
<td>28</td>
<td>925</td>
<td>37</td>
</tr>
<tr>
<td>Ta</td>
<td>37</td>
<td>620</td>
<td>54</td>
</tr>
<tr>
<td>Ti</td>
<td>160</td>
<td>566</td>
<td>90</td>
</tr>
<tr>
<td>Row IV metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>12</td>
<td>535</td>
<td>83</td>
</tr>
<tr>
<td>Ca</td>
<td>6.9</td>
<td>494</td>
<td>19</td>
</tr>
<tr>
<td>Zn</td>
<td>64</td>
<td>414</td>
<td>17</td>
</tr>
<tr>
<td>Mg</td>
<td>44</td>
<td>112</td>
<td>17</td>
</tr>
<tr>
<td>Al</td>
<td>26.8</td>
<td>1899</td>
<td>12</td>
</tr>
<tr>
<td>Si</td>
<td>277</td>
<td>1609</td>
<td>11</td>
</tr>
<tr>
<td>Fe</td>
<td>316</td>
<td>1768</td>
<td>12</td>
</tr>
<tr>
<td>Ni</td>
<td>230</td>
<td>1026</td>
<td>13</td>
</tr>
<tr>
<td>Cu</td>
<td>311</td>
<td>2300</td>
<td>12</td>
</tr>
<tr>
<td>Zr</td>
<td>2100</td>
<td>3189</td>
<td>6</td>
</tr>
</tbody>
</table>

*Although silicon is not usually considered a metal, it is included here for comparison.

sufficient accuracy to facilitate calculation of the absolute values of bond length, bond energy, modulus of elasticity, and coefficient of thermal expansion. The values of these properties for engineering materials are usually directly measured in the laboratory.

**DESIGN EXAMPLE 2.5-2**
The bond-energy curves for two engineering materials are shown in Figure 2.5-3. Your task is to select the better material for use in each application described below.

**FIGURE 2.5-3**
A comparison of the bond-energy curves for two hypothetical materials, A and B.
TABLE 2.6-1 The critical (r/R) ratio for each coordination number. (Note that the drawings are not to scale.)

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Critical (r/R) value</th>
<th>(r/R) Stability range</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0.2 ≤ (r/R) &lt; 0.125</td>
<td>Always positive</td>
</tr>
<tr>
<td>3</td>
<td>0.155</td>
<td>0.155 ≤ (r/R) &lt; 0.225</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.225</td>
<td>0.225 ≤ (r/R) &lt; 0.414</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.414</td>
<td>0.414 ≤ (r/R) &lt; 0.732</td>
<td>TETRAHEDRAL</td>
</tr>
<tr>
<td>8</td>
<td>0.752</td>
<td>0.752 ≤ (r/R) &lt; 1</td>
<td>BCC</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>(r/R) = 1</td>
<td>FCC</td>
</tr>
</tbody>
</table>

estimate the CN of the anion. Once the CN of the smaller ion is known, the CN of the larger ion can be determined based on the cation: anion ratio, or the stoichiometry of the compound.

EXAMPLE 2.6-1

Table 2.6-1 gives the ionic radius ratio range for CN = 6 as 0.414 ≤ (r/R) < 0.732. Derive these limiting values by investigating the critical geometry for CNs of 6 and 8.

Solution

The geometry for the critical (minimum) r/R ratio for CN = 6 is shown in Table 2.6-1. If a represents the length of the edge of the cube, then when all of the ions are just touching each other

\[ r + R = \frac{a}{2} \quad \text{and} \quad R + R = \frac{a}{\sqrt{2}} \]

Dividing the first equation by the second equation yields

\[ \frac{r + R}{2R} = \frac{1}{\sqrt{2}} \]
b. In the C$_2$H$_6$ molecule each H atom is bonded to one of the C atoms. Since each C atom must form four covalent bonds, there is a single covalent bond bridging the two C atoms (see Figure 2.6–3b).

c. In the compound C$_2$H$_2$Cl each H and Cl atom forms a single covalent bond with one of the C atoms. Each C atom must form four covalent bonds, so that there will be a double bond between the two C atoms (see Figure 2.6–3c).

d. In silicon, each atom must be bonded to four other Si atoms, and the resulting structure is similar to the diamond structure described previously (see Figure 2.6–2b).

Covalent bonds are directional and are characterized by specific bond angles. The bond angles can be determined by the geometry of the structure or vice versa. Shared electrons, or bond pairs, and lone electron pairs constitute mutually repulsive negative-charge centers that tend to separate as much as possible. As shown in Figure 2.6–4a, the bond angle in a tetrahedral structure such as diamond is 109.5°, which places nearest-neighbor C atoms (and their associated shared electron pairs) as far apart as possible in space while satisfying the valency requirements. In contrast, when carbon is bonded to only three other atoms (one of which involves a double bond), the resulting structure is planar with a bond angle of about 120°, as shown in Figure 2.6–4b. The existence of specific bond angles in covalent molecules is important in understanding the properties of polymers.

![Diagram of covalent bond angles](image)

**FIGURE 2.6–4** A schematic illustration of covalent bond angles in two compounds: (a) the bond angle in a tetrahedral structure such as diamond is 109.5°; (b) when the C is bonded to only three other atoms (one of which involves a double bond), the resulting structure is planar with a bond angle of ~120°.

**EXAMPLE 2.6–4**

Sketch the three-dimensional arrangement of covalent bonds in the H$_2$O molecule.

**Solution**

The geometry of the H$_2$O molecule can be envisioned by placing the O atom at the center of an imaginary cube and noting that its four pairs of electrons, two bonding and two nonbonding electron pairs, must be spatially separated as much as possible. This separation, shown in Figure 2.6–5, is obtained by placing the electron pairs along directions pointing to an alternating set of four corners of the imaginary cube. The H atoms are positioned at two of the cube corners associated with the
angles. The shared negative charge is possible in a double structure.

bonding electron pairs. The structure of H₂O deviates slightly from this model, since nonbonding electron pairs repel each other slightly more than bonding electron pairs. The result is that the H—O—H bond angle is 104.5°—slightly less than the predicted 109.5°.

The shared electrons in a metallic bond are delocalized. Thus, the CN of an atom in a metallic solid is determined primarily by geometrical considerations. Indeed, many pure metals (e.g., Al, Cu, and Ni), for which \( r/R = 1 \), have structures with a CN of 12; however, several common pure metals such as Fe, Cr, and W have CNs of only 8, even in their purest forms.

Coordination numbers are useful because they describe the short-range order, defined as the number and type of nearest neighbors, associated with a particular solid structure. All solids exhibit short-range order. As we expand the consideration to include second- and higher-order neighbors, we find that there are two distinct types of solids. Those that exhibit both short-range order (SRO) and long-range order are called crystalline materials while those with SRO only are termed amorphous, or noncrystalline, materials.

2.7 SECONDARY BONDS

Secondary bonds are fundamentally different from primary bonds in that they involve neither electron transfer nor electron sharing. Instead, attractive forces are produced when the center of positive charge is different from the location of the center of negative charge. The resulting electric dipole can be either temporary, induced, or permanent and can occur in atoms or molecules. As shown in Figure 2.7–1 for Ar, a temporary dipole is formed when the electrons, which are constantly in motion, are momentarily arranged so as to produce an asymmetric charge distribution. The temporary dipole can then induce another dipole in an adjacent Ar atom. The two dipoles then experience a coulombic force of attraction. This type of bonding is responsible for the condensation of noble gases at low temperatures and is known as van der Waals (or van der Waals–London) bonding. Van der Waals bonds can also occur between symmetric molecules such as CH₄ and CCl₄. The total attractive force between molecules due to the van der Waals bond generally increases as the number of atoms in the compound increases. Hence, large molecules can have a large net attractive force. This phenomenon explains why the melting temperatures of the hydrocarbons with chemical formulas CₙH₂ₙ₊₂ increase as \( n \) increases.
Figure 2.7–2 shows the charge distribution in H₂O, H₂S, and NH₃. These molecules are permanent dipoles, because their center of positive charge (indicated by the symbol $\delta^+$) is always different from their center of negative charge ($\delta^-$). Permanent dipole bonds are generally stronger than van der Waals bonds. One especially important type of permanent dipole bond is the hydrogen bond, which occurs whenever a hydrogen atom can be shared between two strongly electronegative atoms such as N, O, F, or Cl. The hydrogen bond is the strongest type of secondary bond, but it is still significantly weaker than a primary bond. Hydrogen bonds hold the wood fibers in a sheet of paper together.

**Figure 2.7–2** A schematic illustration of three permanent dipole molecules: (a) H₂O, (b) H₂S, and (c) NH₃. The x's represent the valence electrons from the H atoms and the •'s represent those from either O, S, or N. The $\delta^+$ and $\delta^-$ symbols represent the spatial centers of positive and negative charge for the molecule. Note that nonbonding electron pairs are local regions of negative charge and the isolated nucleus of an H atom is a local region of positive charge.
energy of the system. Thus, the formation of a PE polymer chain from a collection of identical monomers is a thermodynamically favored reaction. Note that in contrast to the monomer, the PE polymer chain is saturated, so there are no additional sites for primary bond formation. Thus, the only mechanism that remains for bond formation between PE chains is secondary bond formation. Linear polymers that form melts upon heating, such as PE, are called thermoplastic polymers.

The structure of rubber is fundamentally different from that of the thermoplastic polymers. Careful examination of the generic hydrocarbon rubber structure in Figure 2.9–2a shows that the polymer chains contain an unsaturated double bond. The existence of this double bond within the macromolecule permits the formation of additional primary bonds between chains (Figure 2.9–2b). The primary bonds between rubber chains formed by the opening of the unsaturated double bonds are known as crosslinks. When the crosslink density is low, only a small fraction of the double bonds have been opened, and the individual polymer chains retain their identity. There are only a “few” primary bonds between chains. As the crosslink density increases, the individual chains lose their identity and the structure begins to resemble a three-dimensional network of primary bonds. This 3-D primary bond structure is characteristic of many polymers that do not form a melt, or thermoset polymers.
Michelangelo Buonarroti

and architecture ... and the root of all sciences.

Design ... is the found and body of painting and sculpture.

Leonardo da Vinci

(Movement is the cause of all life)

Il moto e causa d'ogni vita
CRYSTAL STRUCTURE

ORDER

Sit on an atom & around

what do you see?

short range order (liquids, amorphous)

long range order (crystals)

disorder (gas)

WE CARE ABOUT CRYSTALS

CRYSTAL = solid material with periodic structure

periodicity is represented by a lattice (BRAVAIS)

LATTICE = infinite set of discrete points

invariant by translation / geometrical points, not necessary atoms

(BRAVAIS LATTICES)

sit on a lattice point and look around

then move to another lattice point, you will see the same thing

UNIT CELL = a part of volume (surface of 2D lattice)

that if replicated for every lattice point

covers all the space, once and only one

C1
Lattice points, many different unit cells

\[ \overrightarrow{a}, \overrightarrow{b}, \overrightarrow{c} \]

\[ a \]

\[ \text{lattice parameter} \]

\[ \text{in 2D} \]

3 possible lattices

\[ \text{square} \]
\[ \text{rectangular} \]
\[ \text{parallelogram} \]

LATTICE = geometrical set of points needed for translations

TRANSLATION OF WHAT? OF A BASIS

LATTICE + BASIS = CRYSTAL STRUCTURE

\[ \text{bas} \]

\[ \text{basis} \]

\[ \overrightarrow{\text{basis}} \]

\[ \text{but also} \]

FIGURE 3.2-2 Three examples of 2-D patterns all created using the same rectangular lattice but each having a different basis: (a) the basis is a single character, (b) the basis contains a repeated character, and (c) the basis contains two characters with different orientations.
COORDINATION NUMBER

The points in a Bravais lattice that are closest to a given point are called its *nearest neighbors*. Because of the periodic nature of a Bravais lattice, each point has the same number of nearest neighbors. This number is thus a property of the lattice, and is referred to as the *coordination number* of the lattice. A simple cubic lattice has coordination number 6; a body-centered cubic lattice, 8; and a face-centered cubic lattice, 12. The notion of a coordination number can be extended in the obvious way to some simple arrays of points that are not Bravais lattices, provided that each point in the array has the same number of nearest neighbors.

PRIMITIVE UNIT CELL

A volume of space that, when translated through all the vectors in a Bravais lattice, just fills all of space without either overlapping itself or leaving voids is called a *primitive cell* or *primitive unit cell* of the lattice. There is no unique way of choosing a primitive cell for a given Bravais lattice. Several possible choices of primitive cells for a two-dimensional Bravais lattice are illustrated in Figure 4.10.

![Figure 4.10](image)

Several possible choices of primitive cell for a single two-dimensional Bravais lattice.

A primitive cell must contain precisely one lattice point (unless it is so positioned that there are points on its surface). It follows that if \( n \) is the density of points in the lattice and \( v \) is the volume of the primitive cell, then \( nv = 1 \). Thus \( v = 1/n \). Since

---

Translated from the primitive cell may possess common surface points; the non-overlapping proviso is only intended to prohibit overlapping regions of nonzero volume.

The density \( n \) of Bravais lattice points need not, of course, be identical to the density of conduction electrons in a metal. When the possibility of confusion is present, we shall specify the two densities with different symbols.
14 different lattices in 7 families

I. Cubic lattices \( a = b = c; \alpha = \beta = \gamma = 90^\circ \)

1) CUBIC 3 SYMMETRY LATTICES

II. Tetragonal lattices \( a = b \neq c; \alpha = \beta = \gamma = 90^\circ \)

2) TETRAGONAL 2 SYMMETRY LATTICES

III. Hexagonal lattices \( a = b = c; \alpha = \beta = 90^\circ; \gamma = 120^\circ \)

3) HEXAGONAL 1 SYMMETRY LATTICES

IV. Orthorhombic lattices \( a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ \)

4) ORTHORHOMBIC LATTICES

V. Monoclinic lattices \( a \neq b = c; \alpha = \beta = \gamma \neq 90^\circ \)

VII. Triclinic lattices \( a \neq b \neq c; \alpha \neq \beta \neq \gamma \)

5) RHOMBOHEDRAL

6) MONOCLINIC 2 SYMMETRY LATTICES

7) TRICLINIC 1 SYMMETRY LATTICES

**Figure 3.2-3** The 14 Bravais lattices grouped into the 7 lattice types. The restrictions on the lattice parameters \( a, b, \) and \( c \) and the angles between the edges of the unit cell \( \alpha, \beta, \) and \( \gamma \) are listed for each unit cell.

**A UNIT CELL IS THE "SMALLEST" POSSIBLE VOLUME WHICH, IF TRANSLATED, COVER ALL THE SPACE.**
Some systems can be described with a basis or without a basis? Example: BCC

A few sites from a body-centered cubic Bravais lattice. Note that it can be regarded either as a simple cubic lattice formed from the points A with the points B at the cube centers, or as a simple cubic lattice formed from the points B with the points A at the cube centers. This observation establishes that it is indeed a Bravais lattice.

\[ \text{BCC} \]

\[ \alpha = \text{LATTICE PARAMETER} \]

Or without basis

\[ \Rightarrow \text{CUBIC} + \text{A BASIS OF } 2 \text{ POINTS LATTICE} \]

\[ \text{BCC OR CUBIC+BASIS} \]

\[ 0, \frac{a}{2} (x + y + z) \]

**ELEMENTS**

Table 4.2

**ELEMENTS WITH THE MONATOMIC BODY-CENTERED CUBIC CRYSTAL STRUCTURE**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>(a) (Å)</th>
<th>ELEMENT</th>
<th>(a) (Å)</th>
<th>ELEMENT</th>
<th>(a) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>5.02</td>
<td>Li</td>
<td>3.49 (78 K)</td>
<td>Ta</td>
<td>3.31</td>
</tr>
<tr>
<td>Cr</td>
<td>2.88</td>
<td>Mo</td>
<td>3.15</td>
<td>Ti</td>
<td>3.88</td>
</tr>
<tr>
<td>Cs</td>
<td>6.05 (78 K)</td>
<td>Na</td>
<td>4.23 (5 K)</td>
<td>V</td>
<td>3.02</td>
</tr>
<tr>
<td>Fe</td>
<td>2.87</td>
<td>Nb</td>
<td>3.30</td>
<td>W</td>
<td>3.16</td>
</tr>
<tr>
<td>K</td>
<td>5.23 (5 K)</td>
<td>Rb</td>
<td>5.59 (5 K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.6
Three primitive vectors, specified in Eq. (4.3), for the body-centered cubic Bravais lattice. The lattice is formed by taking all linear combinations of the primitive vectors with integral coefficients. The point $P$, for example, is $P = -a_1 - a_2 + 2a_3$.

$\mathbf{a}_1 = a\mathbf{x}$, $\mathbf{a}_2 = a\mathbf{y}$, $\mathbf{a}_3 = \frac{a}{2}(\mathbf{x} + \mathbf{y} + \mathbf{z})$. \hspace{1cm} (4.3)

Figure 4.7
A more symmetric set of primitive vectors, specified in Eq. (4.4), for the body-centered cubic Bravais lattice. The point $P$, for example, has the form $P = 2a_1 + a_2 + a_3$.

$\mathbf{a}_1 = \frac{a}{2}(\mathbf{y} + 2 - \mathbf{x})$, $\mathbf{a}_2 = \frac{a}{2}(2 + \mathbf{x} - \mathbf{y})$, $\mathbf{a}_3 = \frac{a}{2}(\mathbf{x} + \mathbf{y} - 2)$. \hspace{1cm} (4.4)
A set of primitive vectors, as given in Eq. (4.5), for the face-centered cubic Bravais lattice. The labeled points are $P = a_1 + a_2 + a_3$, $Q = 2a_1$, $R = a_2 + a_3$, and $S = -a_1 + a_2 + a_3$.

Table 4.1
ELEMENTS WITH THE MONATOMIC FACE-CENTERED CUBIC CRYSTAL STRUCTURE

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>5.26 (4.2 K)</td>
<td>Ir</td>
<td>3.84</td>
<td>Pt</td>
<td>3.92</td>
</tr>
<tr>
<td>Ag</td>
<td>4.09</td>
<td>Kr</td>
<td>5.72 (58 K)</td>
<td>δ-Pt</td>
<td>4.64</td>
</tr>
<tr>
<td>Al</td>
<td>4.65</td>
<td>La</td>
<td>5.30</td>
<td>Rh</td>
<td>3.80</td>
</tr>
<tr>
<td>Au</td>
<td>4.08</td>
<td>Ne</td>
<td>4.43 (4.2 K)</td>
<td>Sc</td>
<td>4.54</td>
</tr>
<tr>
<td>Ca</td>
<td>5.58</td>
<td>Ni</td>
<td>3.52</td>
<td>Sr</td>
<td>6.08</td>
</tr>
<tr>
<td>Ce</td>
<td>5.16</td>
<td>Pb</td>
<td>4.95</td>
<td>Th</td>
<td>5.08</td>
</tr>
<tr>
<td>β-Co</td>
<td>3.55</td>
<td>Pd</td>
<td>3.89</td>
<td>Xe (58 K)</td>
<td>6.20</td>
</tr>
<tr>
<td>Cu</td>
<td>3.61</td>
<td>Pr</td>
<td>5.16</td>
<td>Yb</td>
<td>5.49</td>
</tr>
</tbody>
</table>

**Fcc lattice, no basis**

**Or cubic lattice with basis of 4!**

\[0, \frac{a}{2} (x + y), \frac{a}{2} (y + z), \frac{a}{2} (z + x) \] (fcc).
**Some Important Examples of Crystal Structures and Lattices with Bases**

**Diamond Structure**

The diamond lattice\(^\text{16}\) (formed by the carbon atoms in a diamond crystal) consists of two interpenetrating face-centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal. It can be regarded as a face-centered cubic lattice with the two-point basis 0 and \((a/4)(\hat{x} + \hat{y} + \hat{z})\). The coordination number is 4 (Figure 4.18). The diamond lattice is not a Bravais lattice, because the environment of any point differs in orientation from the environments of its nearest neighbors. Elements crystallizing in the diamond structure are given in Table 4.3.

![Conventional cubic cell of the diamond lattice. For clarity, sites corresponding to one of the two interpenetrating face-centered cubic lattices are unshaded. (In the zincblende structure the shaded sites are occupied by one kind of ion, and the unshaded by another.) Nearest-neighbor bonds have been drawn in. The four nearest neighbors of each point form the vertices of a regular tetrahedron.](image)

**Table 4.3**

<table>
<thead>
<tr>
<th>Element</th>
<th>Cube Side (a) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (diamond)</td>
<td>3.57</td>
</tr>
<tr>
<td>Si</td>
<td>5.43</td>
</tr>
<tr>
<td>Ge</td>
<td>5.66</td>
</tr>
<tr>
<td>(\alpha)-Sn (grey)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

**Hexagonal Close-Packed Structure**

Though not a Bravais lattice, the hexagonal close-packed (hcp) structure ranks in importance with the body-centered cubic and face-centered cubic Bravais lattices; about 30 elements crystallize in the hexagonal close-packed form (Table 4.4).

\(^{16}\) We use the word "lattice," without qualifications, to refer either to a Bravais lattice or a lattice with a basis.
HEX is a Bravais lattice.

The simple hexagonal Bravais lattice. Two-dimensional triangular nets (shown in inset) are stacked directly above one another, a distance $c$ apart.

$$a_1 = a \hat{x}, \quad a_2 = \frac{a}{2} \hat{x} + \frac{\sqrt{3} a}{2} \hat{y}, \quad a_3 = c \hat{z}.$$ PRIMITIVE VECTORS.

HCP is NOT A BRAVAIS LATTICE

HCP = HEX + BASIS(2)

The hexagonal close-packed crystal structure. It can be viewed as two interpenetrating simple hexagonal Bravais lattices, displaced vertically by a distance $c/2$ along the common c-axis, and displaced horizontally so that the points of one lie directly above the centers of the triangles formed by the points of the other.
Table 4.4
ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
<th>$c$</th>
<th>$c/a$</th>
<th>ELEMENT</th>
<th>$a$ (Å)</th>
<th>$c$</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>2.29</td>
<td>3.58</td>
<td>1.56</td>
<td>Os</td>
<td>2.74</td>
<td>4.32</td>
<td>1.58</td>
</tr>
<tr>
<td>Cd</td>
<td>2.98</td>
<td>5.62</td>
<td>1.89</td>
<td>Pr</td>
<td>3.67</td>
<td>5.92</td>
<td>1.61</td>
</tr>
<tr>
<td>Ce</td>
<td>3.65</td>
<td>5.96</td>
<td>1.63</td>
<td>Re</td>
<td>2.76</td>
<td>4.46</td>
<td>1.62</td>
</tr>
<tr>
<td>α-Co</td>
<td>2.51</td>
<td>4.07</td>
<td>1.62</td>
<td>Ru</td>
<td>2.70</td>
<td>4.28</td>
<td>1.59</td>
</tr>
<tr>
<td>Dy</td>
<td>3.59</td>
<td>5.65</td>
<td>1.57</td>
<td>Sc</td>
<td>3.31</td>
<td>5.27</td>
<td>1.59</td>
</tr>
<tr>
<td>Er</td>
<td>3.56</td>
<td>5.59</td>
<td>1.57</td>
<td>Tb</td>
<td>3.60</td>
<td>5.69</td>
<td>1.58</td>
</tr>
<tr>
<td>Gd</td>
<td>3.64</td>
<td>5.78</td>
<td>1.59</td>
<td>Ti</td>
<td>2.95</td>
<td>4.69</td>
<td>1.59</td>
</tr>
<tr>
<td>He (2 K)</td>
<td>3.57</td>
<td>5.83</td>
<td>1.63</td>
<td>Ti</td>
<td>3.46</td>
<td>5.53</td>
<td>1.60</td>
</tr>
<tr>
<td>Hf</td>
<td>3.20</td>
<td>5.06</td>
<td>1.58</td>
<td>Tm</td>
<td>3.54</td>
<td>5.55</td>
<td>1.57</td>
</tr>
<tr>
<td>Ho</td>
<td>3.58</td>
<td>5.62</td>
<td>1.57</td>
<td>Y</td>
<td>3.65</td>
<td>5.73</td>
<td>1.57</td>
</tr>
<tr>
<td>La</td>
<td>3.75</td>
<td>6.07</td>
<td>1.62</td>
<td>Zn</td>
<td>2.66</td>
<td>4.95</td>
<td>1.86</td>
</tr>
<tr>
<td>Lu</td>
<td>3.50</td>
<td>5.55</td>
<td>1.59</td>
<td>Zr</td>
<td>3.23</td>
<td>5.15</td>
<td>1.59</td>
</tr>
<tr>
<td>Mg</td>
<td>3.21</td>
<td>5.21</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>3.66</td>
<td>5.90</td>
<td>1.61</td>
<td>&quot;Ideal&quot;</td>
<td></td>
<td></td>
<td>1.63</td>
</tr>
</tbody>
</table>

Ideal (with spheres)

$$c = \left(\frac{4}{\sqrt{3}}\right)a_0 = 1.633a_0 = 3.266r$$

Volume

$$V_{o_c}(\text{large HCP}) = \left(\frac{3\sqrt{3}}{2}\right)a_0^2c$$
MILLER INDICES

- CUBIC, TETRACOVAL, ORTHOROMBIC

for all the systems with angles $\alpha = \beta = \gamma = 90^\circ$

RIGHT-HAND CARTESIAN SYSTEM

TAKE "RECTANGULAR" UNIT CELL

$\alpha, \beta, \gamma$ in meters \[\text{[maybe } \AA \text{ or } \text{mm}]\]

$(h, k, l) = $ Bravais cell positions of $P$

with respect to $(a, b, c)$.

POINTS

(FRACTIONAL)

negative

put a $-\frac{1}{2}$ on the top

DIRECTIONS

put numbers in

and get

$(h, k, l)\quad$ maximum common denominator $\Rightarrow$ divide

minimum common multiplier

$\Rightarrow$ multiply

$(1\frac{\frac{3}{2}}{0}) \Rightarrow [2\ 3\ 0]$

$(2\ 2\ 0) \Rightarrow [1\ 1\ 0] \Rightarrow$ MILLER INDICES
2) identify intercepts in \((h, k, l)\) notation (fractional), in the \(x, y, z\) axis

3) take reciprocal
\[
\left(\frac{1}{h}, \frac{1}{k}, \frac{1}{l}\right) \Rightarrow \left(0, 2, 1\right)
\]

A) clear fractions but DO NOT REDUCE AT LOWER INTEGER

<table>
<thead>
<tr>
<th>Plane</th>
<th>Intercepts</th>
<th>Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>(\infty, \infty, 1)</td>
<td>(0, 0, 1)</td>
</tr>
<tr>
<td>(B)</td>
<td>(1, 1, 1)</td>
<td>(1, 1, 1)</td>
</tr>
<tr>
<td>(C)</td>
<td>(1, 1, \infty)</td>
<td>(1, 1, 0)</td>
</tr>
<tr>
<td>(D)</td>
<td>(\infty, \infty, -1)</td>
<td>(0, 0, 1)</td>
</tr>
<tr>
<td>(E)</td>
<td>(1, \infty, 1/2)</td>
<td>(1, 0, 2)</td>
</tr>
<tr>
<td>(F)</td>
<td>(1/3, 1/2, 1)</td>
<td>(2, 1, 1)</td>
</tr>
</tbody>
</table>
DENSITY, PACKING FACTORS OF CRYST.

MUST COUNT ONLY LATTICE POINTS (BRAVAIS) NOT ATOM NECESSARY (UNLESS BASIS = 1 e. g. Cu)

1) PICK 1 DIRECTION / PUT IN MILLER NOTATION
2) COUNT # OF EQUIVALENT LATTICE POINTS &
3) DIVIDE BY THEIR DISTANCE

↓ \( p_L \) # of LATTICE POINTS ALONG ONE DIRECTION IN UNIT CELL

\[
\begin{align*}
\text{LENGTH OF LINE CONTAINED IN ONE UNIT CELL} & = \frac{1}{M} \\
\end{align*}
\]

EQUIVALENT NOTATION, BUT EASIER! (STEFANO S)

1) PICK 1 DIRECTION FROM ORIGIN (1 POINT 000)
2) MEASURE DISTANCE WITH 1ST EQUIVALENT POINT TO # OF ORIGIN = \( d \)

\[ p_L \text{(DIRECTION)} = \frac{1}{d \text{(DIRECTION)}} \]

EXAMPLE 3.5.1 (79)

BCC

\[
\alpha \sqrt{3} = 4r \quad \text{(Relation)} \quad \text{for BCC}
\]

along [111]

\( \alpha \sqrt{3} = 4r \) (Relation between lattice parameter)

Start from (000)

go along [111] ⇒ meet \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\)
at position \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) distance = 2r ⇒ \( p_L(111) = \frac{1}{2r} \)
Along [110] \[ a\sqrt{3} = 4R \Rightarrow a = 4R/\sqrt{3} \]

Go along [110]

Meet point (1,1,0) at distance \( a/\sqrt{2} \)

\[ s_{l}(110) = \frac{1}{a\sqrt{2}} = \frac{\sqrt{3}}{24\sqrt{2}} \approx 0.3 \]

SYMMETRY

\[ s_{l}[110] = s_{l}[101] = s_{l}[011] \approx 0.3 \]

\[ s_{l}[111] = 0.5 \]

\[ s_{l}[100] = \frac{2}{a} = s_{l}[010] = s_{l}[001] = 0.43 \]

Along [100]

Go along [100]

Meet point (1,0,0) at \( a \)

\[ s_{l}(100) = \frac{1}{a} = \frac{\sqrt{3}}{4R} \approx 0.43 \]

CLOSE PACKING DIRECTION

Is the direction where equivalent points are closest!! (highest \( s_{l} \))

C12
Close-packing direction for FCC = [110]

C13
PLANAR DENSITY

PLANAR DENSITY IS THE DENSITY OF POINTS PER UNIT AREA

$$\rho_p(\text{plane}) = \frac{\# \text{ of points lattice}}{\text{area of the surface considered}}$$

(PICK SURFACE INSIDE UNIT CELL FOR SIMPLICITY BUT NOT NECESSARY!)

AS FOR LINEAR DENSITY, SUBSTITUTE POINTS WITH SPHERES OF RADIUS $$\varepsilon$$ SO YOU CAN COMPARE DIFFERENT STRUCTURES (AND YOU ARE READY TO RUN IF THE BASIS IS MONOATOMIC!)

FCC

Ex 35-2

$$T = \frac{4}{3} \Rightarrow \frac{4}{3} \cdot \frac{1}{2} = \frac{2}{3} \cdot \frac{1}{2}$$

$$\rho_p \left[ \langle 100 \rangle \right] = \frac{2}{a \sqrt{2} \cdot a}$$

$$\rho_p \left[ \langle 110 \rangle \right] = \frac{2}{a \sqrt{12} \cdot \sqrt{6} \cdot a}$$

$$\rho_p \left[ \langle 110 \rangle \right] = \frac{4}{12 \pi 2}$$

$$\rho_p \left[ \langle 100 \rangle \right] = \rho_p \left[ \langle 001 \rangle \right] = \frac{2}{8 \pi 2}$$

$$\rho_p \left[ \langle 111 \rangle \right] = \frac{1}{\pi 2 \sqrt{3}}$$

Figure 3.5-2 (a) The portion of the (1 1 1) plane contained within a single FCC unit cell is sketched in 3-D; (b) the same plane sketched in 2-D; (c) the portion of the (1 1 0) plane contained within a single FCC unit cell is sketched in 3-D; (d) the same plane sketched in 2-D.
For FCC, \( \rho_p \text{ max is} \)

\[
\rho_p (111) = \frac{1}{2\sqrt{3}a^2} \text{  MAX OF EVERY THING}
\]

\[
\text{HIGHEST DENSITY PLANE}
\]

\[
\text{CLOSE-PACKED PLANE}
\]

\[
\text{in a system with}
\]

\[
\text{CLOSEST IT IS CALLED}
\]

\[
\text{CLOSED PACKED}
\]

\[
\text{HIGHEST DENSITY PLANE}
\]

\[
\text{BCC IS NOT CLOSE-PACKED}
\]

\[
\text{FOR THEE} \quad \rho_p^{BCC} (100), \rho_p^{BCC} (111), \rho_p^{BCC} (210) \quad \text{? FAST}
\]

\[
\rho_p^{C}(111)
\]

\[
\text{FCC IS THE HIGHEST DENSITY PLANE}
\]

\[
\text{HIGHEST DENSITY PLANE}
\]

\[
\text{CLOSE-PACKED IF} \quad \rho_p^{MAX} = \frac{1}{2\sqrt{3}a^2}
\]

\[
\text{HCP IS HIGHER + BASIS IS C.P. ON THE BASIS PLANE}
\]

\[
\text{SEE LATER}
\]

\[
\text{TABLE 3.5-1  The close-packed directions and highest-density planes in the BCC, FCC, and HCP crystal structures.}
\]

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Close-packed directions</th>
<th>Highest-density planes</th>
<th>Are the highest-density planes close-packed?</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td>111</td>
<td>111</td>
<td>Yes</td>
</tr>
<tr>
<td>FCC</td>
<td>111</td>
<td>111</td>
<td>Yes</td>
</tr>
<tr>
<td>HCP</td>
<td>111</td>
<td>111</td>
<td>Yes</td>
</tr>
</tbody>
</table>

CIS
VOLUME TRIC DENSITY:

$\rho V = \frac{\text{# of lattice point}}{\text{unit volume}}$

1) put points as spherical atomic
2) count them in unit cell (TAKE one easy one)
3) $\rho V = \frac{\# \text{Value}}{1}$

FCC

for simplicity
we take
CUBIC
UNIT CELL

HAVE 8 spheres with $\frac{1}{8}$ value each

HAVE 6 face spheres with $\frac{1}{2}$ value

$\Rightarrow \# \text{atoms} = 8 \ast \frac{1}{8} + 6 \ast \frac{1}{2} = 4$

Value = $a^3 \Rightarrow a = \frac{4 \rho V}{a^3} \Rightarrow \rho V = \frac{4 \sqrt[3]{\frac{2}{3}}}{\frac{4 \sqrt[3]{2}}{3}}$

FCC is same $\rho V = \frac{1}{4 \sqrt{2} \pi}$

If $\gamma_a = 1.6 \text{ theoretical only}$

HCP & FCC are both close packed structure

HEX
CLOSED
PACKED

C16
ATOMIC PACKING FACTOR

The packing factor measures the empty volume of the cell!!

$\text{APF} = \frac{\text{empty volume}}{\text{occupied fraction of volume}}$

$\Rightarrow$

Each sphere in a sphere is $\frac{4}{3}\pi r^3$

$\Rightarrow$

$\text{APF} = \frac{\text{Volume atoms (in sphere)}}{\text{Volume cell}}$

$\Rightarrow$

$8\times \frac{1}{8} = 1$

$\Rightarrow a = 2r$

$\Rightarrow \frac{1}{3} \times \frac{4}{3} \pi r^3 = 0.52$

$BCC$

$8\times \frac{1}{8} + 1 = 2$

$\Rightarrow a = \frac{4r}{\sqrt{3}}$

$\Rightarrow 0.68$

$FCC$

$8\times \frac{1}{8} + 6\times \frac{1}{2} = 4$

$\Rightarrow a = \frac{4r}{\sqrt{2}}$

$\Rightarrow 0.74$ (most dense)

$HCP$ (ideal $c/a = 1.6$)

$4\times \frac{1}{6} + 4\times \frac{1}{12} + 1 = 2$

$\Rightarrow a = \frac{1.633}{3.266} = 0.50$

$HCP = \text{HEX} + \text{BASE} + (2)$

EXTRA ATOMIC ORBIT

Ideal $c = \frac{1}{16} a = 1.633$

$C17$
CLOSE PACKED STRUCTURES

FCC & HCP are the most dense structures

\[ \downarrow \quad \downarrow \]

LATTICE  LATTICE

HEX + BASIS

FCC in [111] direction is an HEX LATTICE + BASIS (2)

HCP in [110] direction is an HEX LATTICE + BASIS (2)

Part 1 Fundamentals

[111]

FCC

HCP

First layer

Second layer

Cubic close packing

A layer

B layer

C layer

Hexagonal close packing

A layer

B layer

A layer

First layer

Second layer

1st layer

2nd layer

3rd layer

Equivalent to FIRST layer

Second layer

Cubiac close packing

C18
3.6.2 Interstices in the BCC Structure

Like the FCC structure, the BCC structure also contains both octahedral and tetrahedral sites. As shown in Figure 3.6–1c, the octahedral sites are located in the center of each face and the center of each edge, giving a total of six sites per unit cell. The diameter of the octahedral site cannot be determined by examination of the face diagonal. The BCC structure is not a close-packed structure, and the atoms that surround the interstitial site are not all equidistant neighbors. When the largest possible atom occupies the octahedral position, the atoms touch only along \( \langle 100 \rangle \) as measured from one central atom to...
CRYSTALS WITH 2 ATOMS / IONIC

SODIUM CHLORIDE STRUCTURE. Prototype NO CE (SODIUM CLORIDE) ionic

BLACK ATOMS FORM FCC LATTICE
WHITE ATOMS ARE SECOND ATOM IN BASIS

OR VICE VERSA

SODIUM CHLORIDE STRUCTURE =

FCC + BASIS(2)

\[ a_1 = \frac{a}{2} (\hat{x} + \hat{y}) \]
\[ a_2 = \frac{a}{2} (\hat{z} + \hat{x}) \]
\[ a_3 = \frac{a}{2} (\hat{z} + \hat{y}) \]

SEE PHOTOCOPY FOR EXAMPLE

OR YOU CAN CONSIDER AS
2 INTERPENETRATING FCC LATTICES

1 1 1

ALONG [100] DIR
FACE

\[ 2(2R + R) = a \]
The Sodium Chloride Structure

We are forced to describe the hexagonal close-packed and diamond lattices as lattices with bases by the intrinsic geometrical arrangement of the lattice points. A lattice with a basis is also necessary, however, in describing crystal structures in which the atoms or ions are located only at the points of a Bravais lattice, but in which the crystal structure nevertheless lacks the full translational symmetry of the Bravais lattice because more than one kind of atom or ion is present. For example, sodium chloride (Figure 4.24) consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice, in such a way that each ion has six of the other kind of ions as its nearest neighbors. This structure can be described as a face-centered cubic Bravais lattice with a basis consisting of a sodium ion at \(0\) and a chlorine ion at the center of the conventional cubic cell, \((a/2)(\hat{x} + \hat{y} + \hat{z})\).

![Figure 4.24](image)

The sodium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating fcc lattices.

$N_aCe$

$[\text{interpenetrating fcc}]

\[\frac{a}{2}(\hat{x} \hat{y} \hat{z})\] Na

$0 \text{ c}e$

Table 4.5

<table>
<thead>
<tr>
<th>CRYSTAL</th>
<th>$a$ (Å)</th>
<th>CRYSTAL</th>
<th>$a$ (Å)</th>
<th>CRYSTAL</th>
<th>$a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>4.02</td>
<td>RbF</td>
<td>5.64</td>
<td>CsS</td>
<td>5.69</td>
</tr>
<tr>
<td>LiCl</td>
<td>5.13</td>
<td>RbCl</td>
<td>6.58</td>
<td>CsSe</td>
<td>5.91</td>
</tr>
<tr>
<td>LiBr</td>
<td>5.50</td>
<td>RbBr</td>
<td>6.85</td>
<td>CsTe</td>
<td>6.34</td>
</tr>
<tr>
<td>LiF</td>
<td>6.00</td>
<td>RbI</td>
<td>7.34</td>
<td>SrO</td>
<td>5.16</td>
</tr>
<tr>
<td>NaF</td>
<td>4.62</td>
<td>CaF</td>
<td>6.01</td>
<td>SrS</td>
<td>6.02</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.64</td>
<td>AgF</td>
<td>4.92</td>
<td>SrSe</td>
<td>6.23</td>
</tr>
<tr>
<td>NaBr</td>
<td>5.97</td>
<td>AgCl</td>
<td>5.55</td>
<td>SrTe</td>
<td>6.47</td>
</tr>
<tr>
<td>NaI</td>
<td>6.47</td>
<td>AgBr</td>
<td>5.77</td>
<td>BaO</td>
<td>5.52</td>
</tr>
<tr>
<td>KF</td>
<td>5.35</td>
<td>MgO</td>
<td>4.21</td>
<td>BaS</td>
<td>6.39</td>
</tr>
<tr>
<td>KCl</td>
<td>6.29</td>
<td>MgS</td>
<td>5.20</td>
<td>BaSe</td>
<td>6.60</td>
</tr>
<tr>
<td>KBr</td>
<td>6.60</td>
<td>MgSe</td>
<td>5.45</td>
<td>BaTe</td>
<td>6.99</td>
</tr>
<tr>
<td>KI</td>
<td>7.07</td>
<td>CaO</td>
<td>4.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Cesium Chloride Structure

Similarly, cesium chloride (Figure 4.25) consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion...
Cesium Chloride Structure Matrix CsCl

Ionic

2 Interpenetrating Cubic

\[ CsCl = \text{Cubic} + \text{Basis} (2) \]

- \( a_1 = a \hat{x} \)
- \( a_2 = a \hat{y} \)
- \( a_3 = a \hat{z} \)

- \( \frac{a}{2} (0,0,0) \)
- \( \frac{a}{2} (1,1,1) \)

Plane relation, along direction \([111]\):

\[ a\sqrt{3} = 2 (a + R) \]

Can be seen as BCC with black/white alternating atoms
monad lattices as lattices lattice points. A lattice l structures in which the ion placed at alternate has six of the other kind of ions treated as a face-centered at 0 and a chlorine ion.

Table 4.6

<table>
<thead>
<tr>
<th>CRYSTAL</th>
<th>a (Å)</th>
<th>CRYSTAL</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsCl</td>
<td>4.12</td>
<td>TiCl</td>
<td>3.83</td>
</tr>
<tr>
<td>CsBr</td>
<td>4.29</td>
<td>TiBr</td>
<td>3.97</td>
</tr>
<tr>
<td>CsI</td>
<td>4.57</td>
<td>TiI</td>
<td>4.20</td>
</tr>
</tbody>
</table>

The Zincblende Structure

Zincblende has equal numbers of zinc and sulfur ions distributed on a diamond lattice so that each has four of the opposite kind as nearest neighbors (Figure 4.18). This structure is an example of a lattice with a basis, which must be so described both because of the geometrical position of the ions and because two types of ions occur.

Table 4.7

<table>
<thead>
<tr>
<th>CRYSTAL</th>
<th>a (Å)</th>
<th>CRYSTAL</th>
<th>a (Å)</th>
<th>CRYSTAL</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuF</td>
<td>4.26</td>
<td>ZnS</td>
<td>5.41</td>
<td>AlSb</td>
<td>6.13</td>
</tr>
<tr>
<td>CuCl</td>
<td>5.41</td>
<td>ZnSe</td>
<td>5.67</td>
<td>GaP</td>
<td>5.45</td>
</tr>
<tr>
<td>CuBr</td>
<td>5.69</td>
<td>ZnTe</td>
<td>6.09</td>
<td>GaAs</td>
<td>5.65</td>
</tr>
<tr>
<td>CuI</td>
<td>6.04</td>
<td>CdS</td>
<td>5.82</td>
<td>GaSb</td>
<td>6.12</td>
</tr>
<tr>
<td>AgI</td>
<td>6.47</td>
<td>CdTe</td>
<td>6.48</td>
<td>InP</td>
<td>5.87</td>
</tr>
<tr>
<td>BeS</td>
<td>4.85</td>
<td>HgS</td>
<td>5.85</td>
<td>InAs</td>
<td>6.04</td>
</tr>
<tr>
<td>BeSe</td>
<td>5.07</td>
<td>HgSe</td>
<td>6.08</td>
<td>InSb</td>
<td>6.48</td>
</tr>
<tr>
<td>BeTe</td>
<td>5.54</td>
<td>HgTe</td>
<td>6.43</td>
<td>SiC</td>
<td>4.35</td>
</tr>
<tr>
<td>MnS (red)</td>
<td>5.60</td>
<td>AlP</td>
<td>5.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSe</td>
<td>5.82</td>
<td>AlAs</td>
<td>5.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

18 For examples see Table 4.6.
19 For examples see Table 4.7.
DIAMOND & ZINC BLEND

Table 4.3
ELEMENTS WITH THE DIAMOND CRYSTAL STRUCTURE

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CUBE SIDE a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (diamond)</td>
<td>3.57</td>
</tr>
<tr>
<td>Si</td>
<td>5.43</td>
</tr>
<tr>
<td>Ge</td>
<td>5.66</td>
</tr>
<tr>
<td>α-Sn (grey)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

FCC \( (\overline{a}, \overline{a}, \overline{a}) \) + BASIS \( \overline{a} \)

\[ L(0,0,0), \frac{a}{4} (1,1,1) \]

IONIC \( \leftrightarrow \) \( \text{ZnS} \)

BASIS \[ \frac{a}{4} (111) \]

SULFUR

ZINC

which \( \text{GeAs} \) \( \text{(semiconductor)} \)

CoTe \( \text{(quantum dots)} \)

ELECTROLYSIS \( \text{(92-93)} \)

CRYSTOBALITE \( \text{(92-93)} \)

METHANE SODIUM \( \text{(99)} \)

POLYETHYLENE \( \text{(95-95)} \)

C2A

LIQUID CRYSTALS (long molecules tilted can orient on some external field (electrical))
Fluorite - Antifluorite

Fluorite = FCC + Interstitial
= FCC + Basis (g)

Tetrahedral site
Interstitial
8 per cube

Twice as many interstitials
CaF₂, MgZrO₂, Mₓ²⁺ + L⁺ ion
Metal

Antifluorite
Some as Fluorite but Metal Inverted
L₂O₁

C₂S
PEROVSKITE STRUCTURE

CUBIC
• Ti⁴⁺
• Ca²⁺
• O²⁻

Ca₅TiO₃
CALCIUM TITANATE

CUBIC CALCIUM (A) STRUCTURE
OXGEN IN THE FACES (6) = OCTAHEDRA
METAL TITANIUM (B) IN THE CENTRE

OFFSET BETWEEN TOP PLANE OF Ba⁺ IONS AND TOP CENTER O²⁻ ION

BARIUM TITANATE

Offset between Ti⁺⁺ ions and midplane

FIGURE 3.7-8 The tetragonal unit cell of BaTiO₃ shown (a) in 3-D, and (b) in 2-D.

C₂G
FIGURE 3.9-1
A schematic illustration of a polycrystalline sample. The polycrystal is composed of many grains separated by thin regions of disorder known as grain boundaries. Note that the unit-cell alignment within grain A (shown in the high-magnification insert) is different from that in grain B.

Many ceramic materials are also in the form of polycrystalline solids. With inorganic solids, such as silica, it can be relatively easy to cool the material sufficiently quickly that crystal formation does not occur. Hence, these materials may be either crystalline or noncrystalline (amorphous), depending on thermal history. The structure of noncrystalline and partially crystalline materials will be discussed in Chapter 6.

Polymers are unique in that because of the nature of long-chain molecules, they recombine to form structures that are entirely crystalline. Hence, polymers are either semicrystalline or amorphous. Although there are no commercial single-crystal polymers, Spectra® is one of the strongest materials known, has a structure similar to that of a single crystal. Spectra consists of long polyethylene chains that are processed in such a way that molecular are highly aligned. Crystallinity is very high, and defects, principally ends, are randomly dispersed through the continuous crystal.

Few materials are used in a single-crystal form; however, those few are commercially significant. Single-crystal materials have no grain boundaries, so they offer unique optical, and electrical properties. Single-crystal quartz (SiO₂) and perovskites are used as transducers in a variety of applications, such as in high-quality receivers. Single-crystal germanium and silicon are used extensively in the microelectronics industry. Single-crystal nickel alloys are used in turbine blades in high-performance jet aircraft. Sapphire (Al₂O₃) and diamond (C) single crystals are precious stones.

3.10 ALLOTROPY AND POLYMORPHISM

Many materials can exhibit crystal structures that change from one unit cell to another. These changes are known as allotropes. Polyphosphates are a good example of such behavior. Polyphosphates are a series of compounds in which the number of phosphorus atoms increases. As the number of phosphorus atoms increases, the number of oxygen atoms also increases, leading to a change in the unit cell structure. This change is referred to as allotropy.
X-RAY DIFF (LIGHT)

$\lambda \text{ in phase} + \lambda \text{ out of phase} \rightarrow \lambda$ constructive interference

$\lambda \text{ in phase} \rightarrow \lambda$ destructive interference

Phase or out of phase: depends on the distance traveled.

ON A CRYSTAL, PLANES REFLECT LIKE MIRRORS

$\theta = \text{incidence angle}$
$\lambda$ is known
$
\frac{1}{\lambda^2} = 2d \sin \theta = \text{extra distance}
$
$\sin \theta = \frac{n \lambda}{2d}$

2$\sin \theta = n \lambda$

BRAGG LAW
But which plane am I totting?

DUNNO!

\[ \rightarrow \text{matrix powder} \rightarrow \text{gas in crystals and X-ray powder} \]

\[ \text{Intensity} \]

\[ \text{FCC} \]

\[ \text{For atom a} \quad d(\text{III}) \]

\[ \text{FCC (III)} \]

\[ a_{\sqrt{3}} \]

\[ d(\text{III}) = \frac{a_{\sqrt{3}}}{3} \]

for FCC \[ d(h k l) = \frac{a_{\frac{1}{2}}}{(h^2 + k^2 + l^2)^{\frac{1}{2}}} \] \( \text{family of } d \)

\[ \text{line for every plane} \]

IF SOMETHING IS MISSING?
WHAT ABOUT MISSING LINES

EXAMPLE
TAKE CUBIC (100) YOU HAVE LINE for d(100)

> second ray has ext. path
= m\lambda

3 ray has extra m\lambda
but 2 ray has m\lambda/2

⇒ DESTRUCTIVE DIFFRACTION

SAME for FCC (100)

⇒ RULES
BCC: (h+k+l) even ⇒ LINE (h,k,l)  
FCC: h,k,l all even or one odd (h,k,l)

ALL X-RAY TECHNOLOGY IS AN
EVOLUTION OF THESE IDEAS

⇒ EXTREMELY POWERFUL

C30
DEFECT: POINT DEFECT (SMALL)

IN MONOTOMIC SYSTEMS

VACANCIES: SOMETHING MISSING

INTERSTITIALS: SOMETHING EXTRA

LOWER ENERGY
PERFECT CRYSTAL, NO DEFECT, BUT NOBODY IS PERFECT 😊
AT T=0

WHAT ABOUT @ T>0 ??

SYSTEM DOES NOT MINIMIZE ENERGY BUT

GIBBS FREE ENERGY

\[ \Delta G = \Delta E - PV + TS \]

Gibbs \( G = E + PV - ST \)

Free energy

\[ \Delta G = \Delta E + d(PV) - d(CTS) \]

\[ dG = \nabla \Delta E + dPV + \nabla TdS + \nabla PdV - TdS - SdT \]

\[ d\Delta G = \nabla PV + SdT \]

at \( P = \text{const}, \ T = \text{const} \)

\( \Rightarrow \) MOST STABLE IS \( \min G \) !!!

\( \frac{\text{NOT} E}{E} \)!!

PROPER THERMODYNAMIC POTENTIAL TO DESCRIBE SYSTEMS OF CONST Press, & Temp
DEFECTS increase energy (show Hess's rule)

BUT PRESENCE OF DEFECTS INCREASES ENTROPY (MEASURE OF CONFUSION)

\[ S = k_B \log \mathcal{Z}(E) \]

boltzmann definition

\[ \mathcal{Z}(E) = \# \text{ of states with energy } E \]

\[ \omega(E) = V dP - s dT \Rightarrow s = E + PV - TS \]

per unit volume \( V = 1 \)

pick 1 vacancy, how many possibilities? \( N \)!! atoms per unit volume

\[ \Rightarrow V \approx N a^3 \approx 10^{23} \]

\[ \Rightarrow S \approx k_B \log(10^{23}) \approx 100 k_B \]

\[ \Rightarrow E = E + PV - 100 k T \]!!!

thermal temperature can be large !!

\( \Rightarrow \) DEFECTS GROW NATURALLY !!

@ \( T > 0 \) most stable configuration has defects!

FIGHT PERFECTION, HAVE DEFECTS

D2
How many defects? How to make one you need an activation energy.

\[ \text{Vacancy formation} \]

If defects are independent \( \Rightarrow \) probability that one site has defect is Boltzmann.

\[ \text{prob} \sim \exp \left( - \frac{\Phi_f v}{k_B T} \right) \]

\( \Phi_f v \) and \( \Phi_f \) come from books or quantum mechanics calculations.

If you will be a grad student in my group 😊

Entropy: How many ways I can pick \( N_V \) atoms on a pool of \( N_T \)?

\[ \mathcal{S} = \frac{N_T!}{N_V! (N_T - N_V)!} \]

\[ \mathcal{S} = \log \mathcal{S} = \frac{N_T!}{N_V! (N_T - N_V)!} \]

\[ S = k \log \mathcal{S} = k \left[ \log N_T! - \log N_V! - \log (N_T - N_V)! \right] \]

D3
\[
\frac{S}{K} = \log N_T! - \log N_V! - \log (N_T - N_V)!
\]

Using Sterling formula: \( \log n! \approx n \log n - n \log(\ln n) \)

\[
\begin{align*}
\frac{S}{K} &= N_T \log N_T - N_T - N_V \log N_V + N_V - (N_T - N_V) \log (N_T - N_V) + N_T - N_V \\
&= N_T \log N_T - N_V \log N_V - (N_T - N_V) \log (N_T - N_V)
\end{align*}
\]

Divide by \( N_T \)

\[
\frac{S}{K} = \frac{N_T \log N_T - N_V \log N_V - (N_T - N_V) \log (N_T - N_V)}{N_T}
\]

Reduce and set \( \log \) terms:

\[
\frac{S}{K} = \frac{N_T \log N_T - N_V \log N_V - (1 - \frac{N_V}{N_T}) \log (N_T - N_V)}{N_T}
\]

\[
\begin{align*}
\frac{S}{K} &= \frac{N_T \log N_T - N_V \log N_V - (1 - \frac{N_V}{N_T}) \log (N_T - N_V)}{N_T} \\
&= \frac{N_T \log N_T - N_V \log N_V - (1 - \frac{N_V}{N_T}) \log (N_T - N_V)}{N_T}
\end{align*}
\]

Add and subtract \( \frac{N_V \log N_T}{N_T} \): 

\[
\begin{align*}
\frac{S}{K} &= \frac{N_T \log N_T + \frac{N_V \log N_T}{N_T} - N_V \log N_V - \log (N_T - N_V)}{N_T} + \frac{N_V \log (N_T - N_V)}{N_T} \\
&= \frac{N_T \log N_T + \frac{N_V \log N_T}{N_T} - N_V \log N_V - \log (N_T - N_V)}{N_T}
\end{align*}
\]

\[
\begin{align*}
\frac{S}{K} &= \left[ -\log \frac{N_T - N_V}{N_T} - \frac{N_V \log N_V}{N_T} + \frac{N_V \log (N_T - N_V)}{N_T} \right] \\
&= \left[ -\log \frac{N_T - N_V}{N_T} - \frac{N_V \log N_V}{N_T} + \frac{N_V \log (N_T - N_V)}{N_T} \right]
\end{align*}
\]

\[\text{D4}\]
\[ x \equiv \frac{N_v}{N_T} = \text{concentration of vacu庆祝} \]

\[ \frac{S}{k_B T} = \frac{N_T}{N_T} \left[ \frac{-x \log(1-x) - x \log x + x \log(1-x)}{1} \right] \]

\[ = N_T \left[ -x \log x + (1-x) \log(1-x) \right] \]

\( \text{divide per Volume} \implies \text{get per unit volume} \)

\[ S = - k_B T \rho \left[ -x \log x + (1-x) \log(1-x) \right] \]

\( \quad \rho = \frac{N_T}{V} \)

\[ TS = -k_B T \rho \left[ -x \log x + (1-x) \log(1-x) \right] \]

\( \text{BIGG} \)
DEFEAT IN IONIC CRYSTALS.

Ionic? Troubles

If a vacancy makes non-neutral you must need this vacancy (close) to get neutrality.

NaCl

Schottky defect
(1 V_{Cr} and 1 V_{Na}^{+})

(a)

MgCl_{2}

Schottky defect
(1 V_{Mg}^{++} and 2 V_{Cr}^{+})

(b)

Schottky Defects

For NaCl \Rightarrow Miss. 1Na^{+}, V_{Na}^{-} and 1Ce^{+}, V_{Ce}^{-}

For MgCl_{2} \Rightarrow Miss. 1Mg^{++}, 1Ce^{+}, 1Ce^{-} \Rightarrow V_{Mg}^{-}, V_{Ce}^{+}, V_{Ce}^{-}

D6
Other point defects in ionics:

Frenkel defects!

Interstitial of an ion.

But to respect neutrality you need a vacancy of the same ion somewhere (Why not an interstitial of the other species? Because cations (+) are small anions (−) are big).

\[
\begin{array}{c}
\text{Cations} \\
\text{Anions}
\end{array}
\]

⇒ Only cations available for interstitial.

Being honest: This is not really true mathematically.

In fact energy \(Q_{\text{anion}}\) \(\gg\) \(Q_{\text{cation}}\) is prob:

\[
\exp\left(-\frac{Q_{\text{anion}}}{kT}\right) \gg \exp\left(-\frac{Q_{\text{cation}}}{kT}\right)
\]

\[\text{Energetic good} \rightarrow \text{V}^{+}\text{Ce}^- \& \text{I}^-\text{Ce}^+. \text{are more rare.}
\]

\[\text{V}_{\text{Ag}}^- \& \text{I}_{\text{Ag}}^+ \text{Frequent.}\]

**Figure 4.2-3** Frenkel defects in AgCl. The defect consists of vacancy/interstitial pairs. Frenkel defects involving cations (a) are more common than those involving anions (b), since cations are usually smaller.
CONCENTRATIONS OF DEFECTS

FRENKEL

\[ C_V = \frac{N_N}{N_T} = \exp \left( - \frac{\Phi_{Frenk}}{2RT} \right) = \frac{N_{C_i}}{N_T} \]

because 2 defects are built

SCHOTTKY

\[ C_{V, \text{cath}} = \frac{N_N}{N_T} = \exp \left( - \frac{\Phi_{Schottk}}{2RT} \right) = \frac{N_{C_{\text{an}, i}}}{N_T} = C_{\text{an}, i} \]

Can be proved for Schottky in \( H_{\text{m}, X_p} \) compounds

\[ H_{\text{m}, X_p} \rightarrow P C_{V, \text{cath}} = m_p \left[ \frac{\Phi_{\text{Schottk}}}{(m^2 + p^2)RT} \right] = m \cdot C_{V, \text{an}} \]

IMPURITIES IN CRYSTALS

Matrix or atom = SOLVENT

+ SOLUTE

Substitution (solute)

Substitutional

MUST BE SIMILAR SIZES

Interstitial (solute)

INTERSTITIAL

MUST BE COMPATIBLE SIZES
SUBSTITUTIONAL

EXAMPLE: steel (iron + C)

C → Fe dissolution 0.022% @ 725°C

Big C makes iron stronger
(Prevents movement of dislocations)

OTHER IMPURITIES

H, O, N → small, BAD

But if AlN → big particles
System very strong

RULES: HUME ROTHERY

1) Δ size < 15%
2) Similar electro negativity (giving to big e)
3) Similar valence (how many electrons for bonds)
4) Same crystal structure (Cr BCC & HCP can mix well)

No 4) → STRAIN
No (2, 3) → different bond characteristics
No 4) → Because atoms prefer similar environments

STEEL: Fe & BCC @ Room, BCC has fractures temperature

Add Ni, (2 → SOLID SOLUTION)
8% 18% @ Room

FCC

Better change electrical properties:
Better corrosion resistance
ASSIGNMENT

- DO IMPURITIES IN POLYMERIC CRYSTALS

- 4.3-2 EXAMPLE
  4.3-1

IMPURITIES IN IONIC CRYSTALS ⇒ need to maintain electroneutrality.

- EXAMPLE 4.3-3

- STUDY 111 - 122 WELL
FIGURE 5.2-1 Illustration of (a) a normal stress, given the symbol $\sigma$ and defined as $F/A$ when $F$ is parallel to the plane normal $N$, and (b) a shear stress, given the symbol $\tau$ and defined as $F/A$ when $F$ is perpendicular to $N$.

FIGURE 5.2-3 Model for computation of the theoretical critical resolved shear strength. Under the application of a shear stress $\tau$, the top plane of atoms is assumed to slide over the bottom plane as a unit to produce permanent offset. Parts (a) and (b) represent a macroscopic view, while parts (c) and (d) represent an atomic scale view of the process. As discussed in the text, this model requires that an entire plane of bonds be broken simultaneously.
TENSILE STRESS PRODUCES SLIP TOO!!

\[ \theta = \text{angle \ force \ \wedge \ slip \ direction} \]

\[ \phi = \text{angle \ force \ \wedge \ normal \ slip \ plane} \]

\[ A_s = \frac{A}{\cos \phi} \Rightarrow \text{area of the slip plane} \]

\[ F_s = F \cos \alpha \Rightarrow \text{force parallel to the slip plane and in the direction of the slip direction} \]

\[ \tau = \frac{F_s}{A_s} = \frac{F \cos \alpha}{A/\cos \phi} = \sigma \cos \phi \cos \phi \]

\[ \frac{1}{E/10} \text{ (SCHMID'S LAW)} \]

\[ \sigma_{cr} = \frac{2 \sigma_{cr}}{\cos \theta \cos \phi} \]

\[ \text{BAD THEORY} \]

\[ \text{THEORETICAL BAD!! need defects} \]

\[ \text{\# critical shear} \Rightarrow \text{to get slip \Rightarrow\text{stress \ deformation}} \]
SLIP IS MUCH EASIER THAN THEORETICAL

⇒ HAVE DEFECTS

---

**DISLOCATION**

1) EXTRA PLANE

2) NORMALLY GROWING CRYSTAL

3) OTHER DEFECTS RELEASING ENERGY

4) INTERACTIONS BETWEEN DISLOCATION

⇒ MOVEMENT IS EASIER DEFORMATION

ONE RAN AT EACH TIME

**DISLOCATION GUIDE MOVE** (IF FORCE APPLIED)

UNTIL IT'S OUT OF THE CRYSTAL

---

**FIGURE 5.2-4** (a) A 3-D representation of an edge dislocation. The dislocation is not the extra half plane of atoms that had been inserted but rather the line that runs along the bottom of the extra half plane. Parts (b) and (c) illustrate the motion of an edge dislocation in response to the application of a shear stress $\tau$. The details of this motion are described in the text.
HOW TO MEASURE DISLOCATIONS?
MAKE A CIRCLE AROUND ATOMS AND SEE WHAT IS LEFT?

BURGER CIRCLE (CLOCKWISE)

=) BURGER VECTOR!

FIGURE 5.2-6 Illustration of Burgers circuit and Burgers vector for an edge dislocation. (a) A 3D view of an edge dislocation. (b) A Burgers circuit closes upon itself when it surrounds a dislocation-free region of a crystal. (c) When the Burgers circuit surrounds a dislocation, the start and stop points are not coincident and the vector pointing from the stop point to the start point is defined to be the Burgers vector for the dislocation.

CLOCKWISE RESPECT TO THE SCREW DRIVER RULE APPLIED TO THE UNIT TANGENT VECTOR \( \mathbf{t} \), TANGENT TO THE DISLOCATION. (LOCALLY =)

\( \text{DEFECT } b \Rightarrow (\text{PERFECT}) b = 0 \)
HILLER INDICES OF
SLIP PLANE (IN CUBIC SYSTEMS ARE $\{100\}$
because
PLANE (111) $\perp$ direction $[1\bar{1}2]$. 

SCREW DISLOCATION

\[ \text{Burger's vector} \quad b \]

**Figure 5.2-8:** Illustrations of four types of dislocations: (a) an edge dislocation, (b) a screw dislocation, (c) a mixed dislocation, and (d) a dislocation loop. (Source: (b) William D. Callister, Jr., Materials Science and Engineering, 2nd ed., Copyright © 1991 by John Wiley & Sons. Used with permission of John Wiley & Sons, Inc. (c) James F. Shackelford, Introduction to Materials Science for Engineering, 3rd ed. Copyright © Macmillan Publishing Company, Inc. Used with permission of Macmillan College Publishing Company.)
**Loops**

**Dislocation**

**Loop**

![Dislocation Diagram]

Remove atoms here (e.g., clustering of vacancies)

(a)

(b)

Climbing!!

![Climbing Dislocation Diagram]

**Figure 5.2-10** Climb of edge dislocation. The dislocation moves up one atomic spacing when it absorbs a vacancy.
SLIP PLANES

WHERE DOES IT MOVE?

dislocation = elastic energy in a region

cylinder containing
"distorsional" energy
radius = |\( \mathbf{b} \) |

value per unit length
\( \propto |\mathbf{b}|^2 \)

\[ F_{\text{dislocation}} \propto |\mathbf{b}|^2 \Rightarrow \text{MINIMUM ENERGY} \]
\( \Rightarrow \text{MINIMUM BURGERS VECTORS} \)

BURGERS VECTOR:

vector contained in the slip plane, vector connecting two sites. Look for shortest possible in (h k l) plane.

FCC LATTICE ATOMS

FIGURE 5.2-12 Burgers vectors and slip systems in the FCC structure: (a) an FCC unit cell showing the location of the (1 1 1) slip plane and the six valid Burgers vectors in the (1 1 1) plane. Note that the Burgers vectors occur in pairs, such that only three of the Burgers vectors are independent. (b) The tetrahedron formed by four members of the (1 1 1) family of planes in the FCC structure, including the three independent Burgers vectors in each plane.
\[ 1 \leq h + l + f \leq \text{hollwy on planes:} \]
\[ \{ (h) (h+1) \} \text{ (h+1) (h+1) (h+1) (h+1) (h+1) (h+1) (h+1) } \]

Length each hollwy is \( \sqrt{2} \) long.

There are 12 possible Burgers \( \text{Vectors} \)!

In FCC 12 possible Burgers \( \text{Vectors} \)

\( h = \{ 111 \} \) hollwy, \( \Rightarrow \) slip plane is one of the \( \{ 111 \} \) planes \( \Rightarrow \) \( \{ 111 \} \)

Slip direction is one of the \( \text{directions} \) of Burgers. \( \Rightarrow \frac{\{ 110 \}}{2} \text{ hollwy oh direction!} \)

\( \Rightarrow \) 12 slip systems FCC (directions + planes)

BCC is not closed packed \( \Rightarrow \) solution is complicated

\[ \text{Figure 5.2-13} \quad \text{Slip planes and directions in the BCC structure: (a) a member of the \{1 1 0\}\{1 1 1\} system, (b) a member of the \{1 1 2\}\{1 1 1\} system, and (c) a member of the \{1 1 3\}\{1 1 1\} system.} \]

\( \Rightarrow \) a total of 48 slip system

\[ \text{IN SPECIFICATIONS, MURPHY'S LAW SUPPERSDES OHN'S.} \]
SLIP ALONG BASAL PLANES.

![Basal planes diagram](image)

**FIGURE 5.2-14** The slip planes and directions in the HCP structure are the basal planes and the a directions.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Slip planes</th>
<th>Slip directions</th>
<th>Number of slip systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>{1 1 1}</td>
<td>{1 1 0}</td>
<td>12</td>
</tr>
<tr>
<td>BCC</td>
<td>{1 1 0}</td>
<td>{1 1 1}</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>{2 1 1}</td>
<td>{1 1 1}</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>{3 2 1}</td>
<td>{1 1 1}</td>
<td>24</td>
</tr>
<tr>
<td>HCP</td>
<td>Basal</td>
<td>a</td>
<td>3</td>
</tr>
</tbody>
</table>

**TABLE 5.2-2** Primary slip systems in the BCC, FCC, and HCP systems.

**SUMMARY:**

**HINTS**

For the exam you must be able to calculate \( \mathbf{b} \) & \( \mathbf{e} \) for the systems listed here.

\[ \text{DI8} \]
Dislocations in Ions

Always remember that Burger vector must connect equivalent points: \( \text{NiO} \)

KCL

Dislocation must be neutral

\( \text{NiO} \)

\( |V_3| < |V_2| \)

G

\( \text{v} \)

Yes/No

Not of repulsion

Small repulsion!

Assignment

Ex: 6.2-4

Burgers for CsCl

\( \mathbf{b} = (a/2)(101) \)

\( \text{good!} \)
Planar Defects

Adatom & Pit Have High Energy $\Rightarrow$ Try to Get Adsorbed by Terraces

Remember that at T>0, need for defects since entropy!!

Terraces Growth!!!

Assignment Study $\Rightarrow S.3.1$
$S.3.2$
$S.3.3$ (No S.3.4)
$S.3.5$
$S.4$ /\_\_\_

D20
**DIFFUSION**

Living things move \(\Rightarrow\) Atoms are very small things, therefore they move with temperature

Temperature \(> 0\)

Random walks jump around (Drunk man) example

\(T \uparrow \Rightarrow \text{More jumps} \)

Gases = constant jumps (Pressure)

Liquids = frequent jumps

Solids = occasional jumps

**Solid Diffusion**

Modeling like atoms between two planes

- Pick 2 layers \(\mathbb{A}\) and think \(\mathbb{A}\) is solute in an environment of \(\mathbb{B}\)

\(\Rightarrow\) Define \(C_A = \text{concentration}\)

\[
\begin{align*}
\mathbb{A} & \xrightarrow{J_{12}} \mathbb{R} & \xleftarrow{\frac{J_{21}}{2}} \mathbb{B} \\
& \text{IF } C_2 > C_1 & \Rightarrow \frac{J_{21}}{2} > J_{12} \\
& \text{IF } C_2 < C_1 & \Rightarrow \frac{J_{21}}{2} < J_{12}
\end{align*}
\]

DF1 \(\mathbb{J}_{\text{total}} \propto -(C_2 - C_1) \approx \Delta C\) Assumption
2) WHAT ABOUT $\Delta x$?
FURTHER THEY ARE AND LESS LIKELY THEY JUMP! WHY?

$\Delta x$ SMALL $\Rightarrow$ $J_{21} > J_{12}$

$\Delta x$ BIG $\Rightarrow$ $J_{21} \approx J_{12}$

$\Rightarrow$ $\int_{\text{total}} \propto \frac{1}{\Delta x}$

ASSUMPTION

3) ATOMS TRY TO JUMP AT A FREQUENCY, THIS FREQUENCY DEPENDS ON TEMPERATURE

$\Rightarrow$

FICK'S LAW

$\overline{J} = D \left( -\frac{\Delta C}{\Delta x} \right)$

$\overline{J} = \frac{\text{# particles crossing}}{\text{UNIT AREA} \times \text{SECOND!}}$

$J = \frac{\text{# particles crossing}}{\text{UNIT AREA} \times \text{SECOND}}$

$\frac{\text{# particles crossing}}{\text{UNIT AREA} \times \text{SECOND}}$

$D = \left[ \frac{m^2}{s} \right]$

$C = \left[ \frac{1}{m^3} \right]$

$\frac{\text{# particles crossing}}{\text{UNIT AREA} \times \text{SECOND}}$

$C = \text{FRACTION OF PARTICLES}$

$\Rightarrow$ $C = \left[ \frac{1}{m^3} \right]$
TEMPERATURE DEPENDENCE

\[ D(T) = D_0 \exp \left( -\frac{\Delta f}{RT} \right) \]

\[ D(T) = D_0 \exp \left( -\frac{\Delta f}{kT} \right) \]

\[ \log D \propto \frac{\Delta f}{kT} \]

\[ \log D \approx \text{slope} \]

\[ \frac{\Delta f}{k} \]

\[ \text{(if) NEED TO KNOW} \]

\[ \text{where do they come from} \]

Book is misleading

IF SOLID HOMOGENEOUS

\[ \Delta C = 0 \Rightarrow \frac{\partial C}{\partial x} = 0 \]

\[ \Rightarrow J_{\text{tot}} = 0 \quad \text{CORRECT} \]

BUT \[ J_{\text{tot}} = J_{21} - J_{12} = 0 \]

\[ J_{21} \rightarrow \]

Remember \( J > 0 \) if same DIRECTION of \( D \)

IF \( T > 0 \)

\[ \& \text{ YOU ALWAYS HAVE STUFF MOVING ! !} \]

BUT IF \( \frac{\partial C}{\partial x} = 0 \) (HOMOGENEOUS)

THEN \( \text{SAME AMOUNT GOES RIGHT \\ & \\ LEFT} \)

\[ \Rightarrow \text{OVERALL} = 0 \quad \text{ULTRA-HEGA-IMPORTANT} \]
MECHANISM OF DIFFUSION

IN COVALENT AND METALLIC CRYSTALS

EXAMPLE: CARBON IN STEEL — IMPURITY DIFFUSION!

IN SOLIDS WITH EXTRAS

INTERSTITIAL

NO VACANCY HELP

SPACE ALWAYS AVAILABLE

IN SOLID SOLUTIONS WITH DEFECTS

THE DARK ATOM NEEDS HELP OF A VACANCY

= PROPORTIONAL TO CONCENTRATION OF VACANCIES

USUALLY ACTIVATION ENERGIES

\[ Q_v > Q_i \]

NEED ENERGY TO FORM VACANCY TOO!!

WHAT ABOUT WITHOUT IMPURITIES

IN PURE SYSTEMS ATOMS DIFFUSE TOO!

IT'S SELF DIFFUSION

FIGURE 4.4-5 Diffusion of radioactive isotopes in a matrix of the same atomic species. Increasing time is indicated in (a), (b), and (c). With time the radioactive species diffuse into the surrounding material. By measuring the concentration profiles at different times, the tracer diffusion constant can be determined.

DF4 SINCE ATOMS ARE IDENTICAL YOU CANNOT RECOGNIZE \( \Rightarrow \) NEED FOR COLOR!! \( \Rightarrow \) TAKE ISOTOPE
FIGURE 4.4-6 Self-diffusion coefficients for selected metals. The data were extrapolated to "infinite" temperature to demonstrate $D_0$. Data obtained from several sources.

TABLE 4.4-1 Diffusion coefficients for selected systems.

<table>
<thead>
<tr>
<th>Material</th>
<th>$D_0$ (m/s)</th>
<th>$Q$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-diffusion coefficients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>$4.0 \times 10^{-3}$</td>
<td>270</td>
</tr>
<tr>
<td>Cu</td>
<td>$2.0 \times 10^{-3}$</td>
<td>197</td>
</tr>
<tr>
<td>Zr</td>
<td>$4.0 \times 10^{-3}$</td>
<td>184</td>
</tr>
<tr>
<td>Au</td>
<td>$9.0 \times 10^{-3}$</td>
<td>205</td>
</tr>
<tr>
<td>Fe</td>
<td>$1.8 \times 10^{-3}$</td>
<td>225</td>
</tr>
<tr>
<td>Sn</td>
<td>$1.8 \times 10^{-3}$</td>
<td>280</td>
</tr>
<tr>
<td>Fe in melt</td>
<td>$1.2 \times 10^{-3}$</td>
<td>28</td>
</tr>
<tr>
<td>Impurity diffusion coefficients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu in Ag</td>
<td>$2.0 \times 10^{-3}$</td>
<td>193</td>
</tr>
<tr>
<td>Cu in Al</td>
<td>$1.5 \times 10^{-3}$</td>
<td>225</td>
</tr>
<tr>
<td>Zn in Ag</td>
<td>$3.4 \times 10^{-3}$</td>
<td>174</td>
</tr>
<tr>
<td>Zn in Cu</td>
<td>$3.4 \times 10^{-3}$</td>
<td>191</td>
</tr>
<tr>
<td>Ni in Cu</td>
<td>$2.7 \times 10^{-3}$</td>
<td>280</td>
</tr>
<tr>
<td>Ni in Fe</td>
<td>$7.7 \times 10^{-3}$</td>
<td>280</td>
</tr>
<tr>
<td>Cu in BCC Fe</td>
<td>$2.0 \times 10^{-3}$</td>
<td>84</td>
</tr>
<tr>
<td>Cu in FCC Fe</td>
<td>$2.0 \times 10^{-3}$</td>
<td>147</td>
</tr>
<tr>
<td>Ni in Fe</td>
<td>$3.0 \times 10^{-3}$</td>
<td>75</td>
</tr>
<tr>
<td>Al in AlG</td>
<td>$2.8 \times 10^{-3}$</td>
<td>477</td>
</tr>
<tr>
<td>Cr in AlG</td>
<td>$1.2 \times 10^{-3}$</td>
<td>608</td>
</tr>
<tr>
<td>Mg in MgO</td>
<td>$2.4 \times 10^{-3}$</td>
<td>398</td>
</tr>
<tr>
<td>Ce in MgO</td>
<td>$4.3 \times 10^{-3}$</td>
<td>388</td>
</tr>
<tr>
<td>Ni in NiO</td>
<td>$1.7 \times 10^{-3}$</td>
<td>262</td>
</tr>
<tr>
<td>Cr in CrO</td>
<td>$2.5 \times 10^{-3}$</td>
<td>181</td>
</tr>
<tr>
<td>Cu in copper (PET)</td>
<td>$6.0 \times 10^{-3}$</td>
<td>20</td>
</tr>
<tr>
<td>CO in PE</td>
<td>$2.0 \times 10^{-3}$</td>
<td>28</td>
</tr>
<tr>
<td>CO in PVC</td>
<td>$4.2 \times 10^{-4}$</td>
<td>42</td>
</tr>
<tr>
<td>O in PET</td>
<td>$5.3 \times 10^{-3}$</td>
<td>4</td>
</tr>
<tr>
<td>O in PS</td>
<td>$6.2 \times 10^{-3}$</td>
<td>4</td>
</tr>
<tr>
<td>O in PVC</td>
<td>$6.2 \times 10^{-3}$</td>
<td>55</td>
</tr>
</tbody>
</table>

DFS
EXAMPLE 4.4-4

Explain each of these observations:

a. The activation energy for the diffusion of H in FCC iron is less than that for self-diffusion in FCC iron.
b. The activation energy for the diffusion of H in BCC iron is less than that for the diffusion of H in FCC iron.

a) H SMALL! FE BIG

b) BCC OPEN, FCC IS CLOSED PACKED

MECHANISM IN IONICS

YOU HAVE BOTH IONS JUMPING AROUND!

\[ \text{MgO} \rightarrow \text{D}_{\text{Mg}} + \text{D}_{\text{O}} \]

IONS \(\Rightarrow\) COULOMB BONDED, NO FREE CHARGE

\(\Rightarrow\) ELECTRICAL CONDUCTIVITY IS ALL GIVEN

\(\Rightarrow\) SMALL CONDUCTIVITY, BUT I CAN GET DIFFUSION MEASURING CONDUCTIVITY!

MECHANISM IN POLYMERS

POLYMERS \(\Rightarrow\) LIKE SPAGHETTI (MOVING WORMS!

COMPLETELY DIFFERENT MECHANISM

\[ D = D_0 e^{-Q/R T} \]

\(\Rightarrow\) ALL MUST MOVE

\[ D_0 \propto \frac{1}{N^2} \]
**Figure 4.4–8**

Diffusion coefficients of various organic molecules in natural rubber as a function of temperature. Note that at any given temperature, the smaller species diffuse more rapidly than the larger species.

**But very fast for impurities!**

**Need to tailor proper length where the first goes through and the second does not!**

**What about time evolution?**

\[ \mathbf{J} = -\mathbf{D} \frac{\partial \mathbf{c}}{\partial \mathbf{x}} \]

But \( \mathbf{J} \) = stuff per unit second \( \equiv \) changes \( \mathbf{c} \Rightarrow \frac{\partial \mathbf{c}}{\partial \mathbf{t}} \) ?

**Take the box!**

DF 7
\[ J_{\text{out}}(x + dx) = J(x + dx) = J(x) + \frac{\partial J}{\partial x} \, dx \quad \text{TAYLOR} \]

\[ J_{\text{in}}(x) = J(x) \]

\[ J = \text{FLUX} \Rightarrow \text{# PARTICLES FLOWING PER UNIT AREA PER UNIT SECOND} \]

\[ J_{\text{in}} \, dA \Rightarrow \text{# PART GETTING IN \ PER UNIT SECOND} \]

\[ J_{\text{out}} \, dA \Rightarrow \text{# PART GETTING OUT \ PER UNIT SECOND} \]

\[ (J_{\text{out}} - J_{\text{in}}) \, dA = \text{# PART INCREASING INSIDE \ PER UNIT SECOND} \]

\[ (J(x) - J(x) - \frac{\partial J}{\partial x} \, dx) \, dA = \frac{d(C \, dA \, dx)}{dt} \]

VOLUME DOES NOT CHANGE IN TIME

\[ \Rightarrow \frac{d(C \, dA \, dx)}{dt} = dA \, dx \, \frac{dc}{dt} \]

\[ \Rightarrow \frac{\partial J}{\partial x} = \frac{dc}{dt} \]

\[ \text{CONSERVATION OF PARTICLES} \]
\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

**DIFFERENTIAL EQUATION**

**NEED BOUNDARY CONDITIONS**

**EXAMPLE**

\[ C_t = C_{surf} \]
\[ C_0 = C_{bulk \ FE \ before \ t=0} \]
\[ C_s > C_0 \Rightarrow \text{Carbide enters} \]

\[ C(x,t) = C_0 + [C_s - C_0] \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \]

\[ x_{eff} = 2\sqrt{Dt} \]

**CARBURIZATION OF STEEL**

**TO MAKE IT WEAR RESISTENT!**

\[ \operatorname{erfh}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} \, dy \]

\[ \text{DF9} \]
DEPLETING SOURCE

\[
C(x,t) = \left( \frac{8}{\pi \sqrt{4Dt}} \right) \exp \left( -\frac{x^2}{4Dt} \right) e^{-t}
\]

\( x_{\text{eff}} \) is where SHAPE IS \( \approx 1/3 \) OF ORIGINAL

\[ x_{\text{eff}} \approx 2\sqrt{Dt} \]

EFFECTIVE PENETRATION DISTANCE

ploe \( x_{\text{eff}} \) where \( C(x_{\text{eff}},t) = \frac{C_0 + C}{2} \)

\[ \Rightarrow \text{FOR PLATE} \Rightarrow \frac{1}{2} \approx \text{erf} \left( \frac{x_{\text{eff}}}{2\sqrt{Dt}} \right) \text{erf}(0.5) \]

\[ \Rightarrow x_{\text{eff}} \approx \sqrt{Dt} ! \]

\[ x_{\text{eff}} \approx 2\sqrt{Dt} \quad \text{for cylinders} \]

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} \, dx
\]

\[
\text{erf}(z) = -\text{erf}(-z)
\]

\[ \lim_{z \to 0} \text{erf}(z) = 0 \]

\[ \lim_{z \to \infty} \text{erf}(z) = 1 \]

\[ \text{erf}(z) \approx \frac{2}{\sqrt{\pi}} z \quad \text{for} \quad z \approx 0 \]

\[ \text{erf}(z) \approx \frac{1}{2} \]

DF10
THERMODYNAMICS

DETAILS

FOUNDATIONS ARE BASED ON EMPIRICAL OBSERVATIONS

LAWs

1ST LAW

\[ dE = SW + SQ \]

\[ E \rightarrow \text{total energy} \quad \Rightarrow \quad dE \rightarrow \text{variation of energy due by some process} \]

\[ W \rightarrow \text{mechanical work} \quad \Rightarrow \quad SW \rightarrow \text{mechanical work mode on the system} \]

\[ Q \rightarrow \text{heat} \quad \Rightarrow \quad SQ \rightarrow \text{heat given to the system} \]

Why \( dE \& SW \)? What is the difference between \( d(c.) \& SC(.) \)? FUNDAMENTAL!

\( E \) is a function of state of the system \((x)\)

\[ \Rightarrow \quad \text{going from } x_0 \text{ to } x_1 \text{ (states)} \]

is function only on FINAL \& INITIAL position, not path !!!

\[ \Delta E = \int_{x_0}^{x_1} dE \]

\[ \Rightarrow \quad \Delta E(\text{closed loop}) = \int_{x_0}^{x_0} dE = 0 \]

CHANGE OF A STATE FUNCTION ON A REVERSIBLE PROCESS IS ZERO
In Mathematical Terms

\[ dE = \text{differential} \]

**Example**  \( f(x, y) = \text{state function} \)

Differential:  \( df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \)

\[ \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \text{, are they identical?} \]

If  \( \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \Rightarrow f \) is **called close form**

**If and only if**

\[ \int df = 0 \text{ integral on a loop} = 0 \]

\[ \int_{(x, y_1)}^{(x, y_0)} df = \text{does not depend on path} \]

\[ \Rightarrow \text{dE is differential of E} \]

\& \( E \) is a function of state (for the 1st law)

T2
What about $S$?

$S$ represents a tiny amount of something but it is not a differential $!!!$

$S \neq d$

**Example**

$SW = \frac{\text{tiny amount of work}}{\text{from close states}}$

$F \rightarrow$

$W = F d l$

$\hat{e} \rightarrow \hat{e} + d \hat{e}$

$SW$ is not differential of $W$!!

$W = F \hat{e}$

$dW = \partial F \hat{e} = dF \hat{e} + F d \hat{e}$

$\downarrow$

$SW = F d \hat{e}$

$\therefore$ NOT HU$S$

$S$ (SOMETHING) symbol is applied when the variation depends on the path.

$\therefore S \rho_1 \neq S \rho_2$ depends on the path, the way you go from 1 to 2.

So

$df = \frac{df}{dx} dx + \frac{df}{dy} dy \Rightarrow$ if $\frac{df}{dx} \neq \frac{df}{dy} \Rightarrow$

**PATH DEPENDENCE $\Rightarrow$**

**NEED $S$ & NOT $d$**

**USUALLY CALLED**

$d = \text{PERFECT DIFFERENTIAL, DIFFERENTIAL FOR STATE FUNCTIONS}$

$S = \text{DELTA, VARIATION OF, FOR NO-STATE FUNCTIONS}$
we know \[ SW = -pdV \]

if \( V \) is a state function, \( dV \) is \( dV \)

of course, \( V \) is a state by itself.

\[ \Rightarrow \quad dE = -pdV + SQ \]

comes from \(-pV\)

\[ H = E + (-pV) = E + pV \]

ENTHALPY

\[ \Rightarrow \quad dH = Vdp + SQ \]

ENTHALPY, at constant pressure, contain HEAT VARIATION!

\[ \frac{dH}{dp} = SQ \]

\[ SQ = \frac{dH}{dp} = \frac{dE}{dV} \]

\[ C = \frac{SQ}{ST} \]

specific heat: HOW MUCH HEAT TO GIVE TO RAISE TEMPERATURE OF 1 DEGREE

\[ C_p = \frac{SQ}{ST} = \frac{dH}{dT} \bigg|_p \]

\[ C_v = \frac{SQ}{ST} = \frac{dE}{dT} \bigg|_V \]

USE \( H \) to describe system \( T \) \( = \) CONSTANT

NOTE
II) SQ is not a function of state but

**There is a state function, S, entropy, for which**

For all reversible processes \( dS = \frac{Q_{rev}}{T} \)

And all irreversible processes \( dS > \frac{Q}{T} \)

Equilibria are not always reversible

Rev of eq: small variation taken & given back brings to the same point

\[ \Rightarrow \text{If in a close loop} \]

I get some extra entropy \( \Rightarrow \text{This measures degradation} \)

(More heat exchange \( \Rightarrow \) more entropy)

\[ \Rightarrow \]

\[ dE = -p\,dV + T\,ds \]

\[ dH = V\,dp + T\,ds \]

\[ dA = -p\,dV + S\,dT \]

\[ dG = -V\,dp - S\,dT \]

\[ H = E + PV \] Energy

\[ A = E - ST \] (Helmholtz)

\[ G = E + PV - ST \] (Gibbs)

Good @ V, T constant

Like normal life

(Total entropy of universe \( \downarrow \))
III )

Stability? What to minimize?

Second law Irrev. Rev. \( TdS \geq SQ \) if irr
\( SQ \leq TdS \) if rev

A variation \( S \) (not a differential)

\[
dE = \Delta S + SQ \leq SW + TdS
\]

\[
\Rightarrow dE - SW - TdS \leq 0 \quad \text{suppose} \quad SW = -pdV
\]

\[
dE + pdV - TdS < 0 \quad \text{for all irreversible processes}
\]

Process = something moving \( SQ \leq TdS \), irr \( SQ < TdS \)

If equilibrium, no process \( \Rightarrow SQ \geq TSS \)

\[
\Rightarrow \Delta S \text{ equilibrium (variation back/forth does not change)} \quad \text{Virtual}
\]

If you vary \( S \rightarrow SS \), you need to violate the irreversible process

(because you need to come back)

\[
\frac{dE}{dS} = 0 \Rightarrow \frac{\partial}{\partial S} \text{ equilibrium}
\]

\[
\frac{dE}{dT} = 0 \Rightarrow \frac{\partial}{\partial T} \text{ irreversible non eq}
\]

\( SS \leq SQ/T \)

Virtual variation applies to state functions too

\[
\Rightarrow SE - TSS + PSV \geq 0 \Rightarrow
\]

\( SZ = SE - TSS + PSV \geq 0 \quad \text{equilibrium} \)
at $T=0$, constant volume $\Rightarrow$

equilibrium $\Rightarrow$ 

the point $E_i = 0$ where every variation of $E_i \geq 0$

$\min(E)$

what about $H$? ENTHALPY

\[ dH = dE + Vdp + Tds \]

\[ dH|_s = Vdp \Rightarrow dH|_{s,p} = 0 \]

\[ \boxed{\begin{align*}
S_Z|_{s,p} &= (SE - TSS + PSV)|_{sp} = (SE + PSV)_{sp} \\
&\geq 0 \text{ always}
\end{align*}} \]

at constant $P$ $\Rightarrow$ $VSP = 0$ $\Rightarrow$

\[ \frac{dS}{dE+PV} = \frac{S}{E+PV} \]

\[ \Rightarrow S_Z \geq 0 \Rightarrow S_{H,sp} \geq 0 \]

For $G$?

\[ dG = Vdp - SdT \Rightarrow S_Z \geq 0 \Rightarrow S_{G,PT} \geq 0 \]

if you like

at $T,P$ constant $\Rightarrow$ need to $\frac{\min(G)}{\not E}$
$\text{MELTING } \Rightarrow \text{ where the heat of melting goes?}$

\[ T = 0 \] \text{ Solid} \quad \text{Const pressure!}

\[ Q \Rightarrow \text{Solid} \quad T \text{ const} \]
\[ Q \Rightarrow \text{Liquid} \quad T \text{ const} \]
\[ Q \Rightarrow \text{Liquid} \quad T \uparrow \]

$\Delta Q$ to melt?

Melt happens at const $T$

$\Delta E = -p \Delta V + T \Delta S = \Delta Q$

$\Delta H = \Delta U + \Delta \text{WS}$

at $P = \text{const}$ \quad $\Delta H_p = \Delta Q$

$\Rightarrow \Delta Q_{\text{MELTING}} = \Delta H_p$ molar molar.

$\Rightarrow T_m \Delta S_m = \Delta H_m \Rightarrow \Delta S_m = \frac{\Delta H_m}{T_m}$

$\Rightarrow H$

$\Delta H_m$

$\Delta H_{\text{wp}}$

$H$

$T$
WHERE S COMES FROM?

F, L, P, V, T, W, are all easy to measure!

where S comes from? What is it? It's functional slope?

2nd law tells that \( S \) is function of state

\[
\frac{\partial S}{\partial Q} \leq 0
\]

INTENSIVE PROPERTIES:

\( T, P, F \) ... properties and quantities that do not depend on the size of the system

EXTENSIVE PROPERTIES

\( E, Q, S, V \) ... depend on the size!

EXAMPLE: 1kg of WATER @ 100°C contains 1*E100 J J O U L E S

3kg of WATER @ 100°C contains 3*E100 J J O U L E S!

\( \Rightarrow \) Energy is extensive, Volume too (obvious)

Heat too \( \Rightarrow \) (therefore \( S \))

IN THERMODYNAMICS INTENSIVE & EXTENSIVE ARE ASSOCIATED

\[
\begin{align*}
\downarrow & \quad \downarrow & \quad \downarrow & \quad \downarrow \\
\text{Int} & \quad \text{Ex} & \quad \text{Int} & \quad \text{Ex}
\end{align*}
\]

\[
-PdV \quad TdS \quad \& \quad \text{soon}.
\]
Boltzmann idea

1) At constant energy, the system can be in $S(E)$ number of states (definition)

2) all states are equiprobable (assumption)
   (Why a state should be more probable?)

3) \[ \frac{1}{\text{state}} \Rightarrow P_E(x) = \frac{1}{S(E)} \text{ for every state,} \]
   \[ \Rightarrow \sum_{\text{states}} P_E(x) = 1 \]

Boltzmann says

entropy measures the most probable distribution

\[ S(E) = f(\frac{1}{S(E)}) = f[-\beta(E)] \]

but $S$ is extensive \implies take system of energy $E$ & cut in two $\Rightarrow E_1, E_2$

\[ S(E) = f(-\beta(E)) \]

but if \[ \begin{align*} &\text{1) has } S(E_1) \text{ states} \quad &\text{& \quad 2) has } S(E_2) \text{ states}, \end{align*} \]
then \[ \begin{align*} &\text{1 + 2 for a total of } S(E_1) \times S(E_2) \text{ possible configurations} \end{align*} \]

\[ \begin{array}{c}
\text{E} \\
\hline
\text{1} \quad \text{2} \\
\text{E_1} \quad \text{E_2}
\end{array} \]

\[ \begin{align*}
S(E) &= f(-\beta(E)) \\
S(E) &= f(-\beta(E_1)) \quad f(-\beta(E_2))
\end{align*} \]
\[ S(E) \propto \log R(E) \Rightarrow \]

\[ S(E) = k_B \log R(E) \]

\[ k_B \text{ set (units: } \text{ ergs/deg)} \]

\[ \text{to get joules after multiplying for } T \]

DEFECTS (FRENETTE)

\[ N_1 = N_A \exp \left( -\frac{\Phi I}{kT} \right) \]

\[ \Rightarrow N_A \text{ sites} \]
\[ N_1 \text{ possible defects} \Rightarrow \]

\[ \text{choose } N_1 \text{ on a set of } N_A \text{ places} \]

\[ \# \text{ on a set of } N_A \text{ identical places} \]

\[ \binom{N_A}{N_1} = \frac{N_A!}{N_1!(N_A-N_1)!} \]

\[ \text{identical places must contain } N_1 \text{ identical defects} \]

\[ \& \] (N_A-N_1) identical good places
and remember Sterling \( \log m! \approx m \log m - m \)

\[ x = \frac{N_x}{N_x^*} \]

\[ S = - kN_0 \left[ x \log x + (1-x) \log (1-x) \right] \]

No defect: how many choices? \( I \Rightarrow 2 = 1 \Rightarrow S = 0 \)

All defects: how many choices? \( I \Rightarrow 2 = 1 \Rightarrow S = 0 \)

\[ y = - \left[ x \log x + (1-x) \log (1-x) \right] \]

To form FRENkel (Frenkel double vacancy)

\[ N_x = N_x^* e^{-\Delta Q / 2kT} \]

\[ \frac{\Delta Q}{2kT} = - \log x \]

\[ Q = -2kT \log x \] **MUST PROVE!**

Is this true??

T12

ELECTRICAL PROPERTIES

OBSERVATION

OHM'S LAW

\[ V = IR \]

Chapter 10  Electrical Properties

\[ R = \frac{V}{I} \]

\[ V = V_{ref} \]

\[ I = \text{Ampere} = \frac{C}{\text{sec}} \]

R \propto \frac{L}{A}

R \propto \frac{L}{A}

\[ R = \rho \frac{L}{A} \]

\[ \rho \frac{m}{m^2} \]

\[ \sigma = \frac{1}{\rho} \]

\[ \sigma = \text{conductivity} \]

\[ \rho = \text{resistivity} \]

\[ V = RI \]

\[ V = \sigma J \]

\[ V = E \cdot L \]

\[ E = \text{volts} \]

\[ J = \text{electric field} \]

\[ J = \sigma E \]

\[ I = \frac{J}{A} \]

\[ \text{density} \]

\[ V = \text{volt} \]

\[ L = \text{length} \]

\[ A = \text{area} \]

\[ m = \text{mass} \]

\[ m^2 = \text{area} \]

\[ L = \text{length} \]

\[ m = \text{mass} \]

\[ m^2 = \text{area} \]

\[ V = \text{volt} \]

\[ m = \text{mass} \]

\[ m^2 = \text{area} \]

\[ L = \text{length} \]

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\[ m^2 = \text{area} \]

\[ L = \text{length} \]

\[ m = \text{mass} \]

\[ m^2 = \text{area} \]

\[ L = \text{length} \]
E = \frac{V}{R}

\begin{align*}
3 \text{ Lions} & \rightarrow x = \frac{1}{2} \times 30 \text{ mph} \\
\text{Ratios} & \rightarrow \text{Ratio Speed} \quad \text{Ratio Mobility} \quad \text{Ratio Electric Field}
\end{align*}

\begin{align*}
1) \text{ Mobility} & \quad \text{Charge per unit volume} \\
2) \text{ Conductivity depends on} & \quad \text{Charge of Carrier} \\
3) \text{ Ratio} & \quad \text{Density of Carriers} \\
\text{Of Electrolytes} & \quad \text{Factor}
\end{align*}

Top Silver: \sigma = 6.3 \times 10^{-8} \text{ (Ohm's)}

\begin{align*}
\text{Good Conductors} & \quad \text{Big} \\
\text{Insulators} & \quad \text{Small} \\
\text{Of Magnitude} & \quad \text{23 orders of magnitude}
\end{align*}

\begin{align*}
\text{Ohm's Law} & \rightarrow J = \sigma E
\end{align*}
FIGURE 10.2–2
Particle model of an electron, $e^-$, moving through a crystal lattice. (a) Under an applied electric field, the mobile electrons are accelerated toward the positive potential and occasionally suffer collisions with the surrounding ion cores. (b) A plot of electron velocity versus time for an electron assumed to continuously undergo the acceleration-collision cycle ($F$ is the mean time between collisions and $\bar{v}$ is the average velocity).

**COLLISIONS:**
- START FROM $v=0$
- ACCELERATION TO $v_{\text{max}}$
- COLLISION & RESTART

**COLLISION every $\tau$ relaxation time!**

\[ F = ma \]
\[ \vec{a} \cdot \vec{m} = E \vec{e} \Rightarrow N_{\text{max}} = a \tau \]

\[ a \cdot E \]

$N_{\text{avg}} = \text{DRIFT VELOCITY}!! \sim \text{cm/s, mm/s, SMALL}$

$N_{\text{DRIFT}} = \mu E$

$E_3$

MOBILITY $\Rightarrow$ BUILD $\sigma$
CONDUCTOR

\[ V_{\text{drift}} \Delta t \]

How much "charge" exits surface in time \( \Delta t \)?

All the charge stored \( \text{closer than } N_{\text{drift}} \Delta t \) from surface!!

\[ \Delta Q = \left( N_{\text{drift}} \Delta t \right) A \cdot V_{\text{density}} \cdot \text{density} \]

\[ \text{PARTICLES.} \]

\[ \Rightarrow \frac{\Delta Q}{\Delta t} = A N_{\text{drift}} \cdot m \cdot q \]

\[ \Rightarrow I = \frac{\Delta Q}{\Delta t} \quad J = \frac{1}{A} \frac{\Delta Q}{\Delta t} \]

\[ J = N_{\text{drift}} m q = \frac{m q \mu E}{\mu e} \]

\[ \sigma = m q / \mu \]

If more then 1 species \( \sigma = \sum_i m_i q_i \mu_i \)

Example: \( \text{LiO}_2 \)

\[ q_{Li} = e \quad m_{Li} \]

\[ q_{O} = -2e \quad m_{O} \]

But \( m_{O} < 0 \) \& \( m_{Li} > 0 \)

(because \( q_{O} < 0 \)) \( \Rightarrow \) CONVENTION \( q_{O} \) \( \text{POSITIVE} \)

\[ \sigma = M_{Li} q_{Li} \mu_{Li} + M_{O} q_{O} \mu_{O} + Me \mu_{e} \]

\( E_4 \)
**FIGURE 10.2–3** A schematic illustration of the effects of temperature and point defects on electron motion. (a) As temperature increases, the amplitude of the thermally induced atomic vibrations increases. This causes a decrease in the mean time between collisions and, therefore, a corresponding decrease in the electron mobility. (b) The mean time between collisions and, therefore, the electron mobility decrease with increasing defect concentration.

**HOWEVER** \( \Theta = m_q \mu \)

\( \frac{\partial m}{\partial t} < 0 \)

\( \Theta m < 0 \)

or \( \frac{\partial m}{\partial n_D} < 0 \)

**BUT TEMPERATURE OR IMPURITIES CAN BOOST \( m \)!! \( \Theta m < \text{HUGE,} \)

\( \frac{\partial m}{\partial n_D} > 0 \) \( \mu \text{ LIKE SEMICONDUCTORS} \)

\( \frac{\partial m}{\partial t} = 0 \text{ METALS} \)

\( E_5 \)
CRYSTALLINE STRUCTURE ⇒ MANY LEVELS

From Quantum Mechanics: Take my course if you want to know.

1 atom (isolated) ⇒ LEVELS 1s 2s 2p 3s 3p 3d ... discrete

- ISOLATED
- OUTER ELECTRONS = VALENCE (LOCALIZED)

Atoms close! ⇒ LEVELS ARE FUNCTION OF SEPARATION (a)

CRYSTAL ⇒
- DISCRETE BANDS & ISOLATED
- SPREAD INTO ENERGY BANDS

- OUTER ELECTRONS NOT SPATIALLY LOCALIZED ANYMORE

![Diagram]

**FIGURE 10.2-4** Energy bands in solids. (a) The energy band structure as a function of interatomic separation distance. (b) For large separation distances, the electrons associated with any atom are independent of those of all other atoms. (c) For separation distance $x_3$, the isolated energy levels in a single atom split into a band of discrete levels separated by small energy differences. (d) For separation distance $x_4$, the 2s and 2p energy bands overlap to form an extended energy band.
ELECTRONS FILL FROM LOWEST ENERGY!

HIGHEST ENERGY BAND AT LEAST PARTIALLY OCCUPIED VALENCE BAND

PROPERTY: COMPLETELY FILLED & COMPLETELY EMPTY BANDS ARE NOT CAPABLE OF TRANSPORTING ELECTRIC CHARGE THROUGH THE SOLID

COMES FROM LIOUVILLE THEOREM (ASK!!!)

ONLY PARTIALLY OCCUPIED LEVELS GIVE CONDUCTIVITY!

\[ q = e \]
\[ m_e > 0 \]
\[ m_h < 0 \]

\[ \frac{m}{m_e} \]
generically \[ m_h < m_e \]
TEMPERATURE EFFECT
FERMI DIRAC DISTRIBUTION

\( T=0 \)

\[ \text{EF} = \text{FERMI ENERGY} \]

\[ f(E) = \frac{1}{e^{\frac{E-\text{EF}}{kT}} + 1} \]

\( T>0 \)

SOME ELECTRONS ARE Excited & Pop up from CORE BECAUSE TEMPERATURE

\[ n = \frac{N}{V} \text{ density of electrons} \]

\[ K_F = \frac{3^{3/2}N^2}{8\pi^2} \]

\[ E_F = \frac{k^2}{2m^*} K_F^2 \]

FERMI - DIRAC DISTRIBUTION

\( T=0 \)

\[ f(E<E_F) = 1 \]

\[ f(E>E_F) = 0 \]

\( T>0 \)

\[ f(E<E_F) \xrightarrow{\text{no cond}} 1 \]

\[ f(E>E_F) \xrightarrow{\text{no cond}} 0 \]

\[ f(E \approx E_F) \sim \frac{N}{V} \text{ not 0, 3, cond} \]

\( K_B T_{\text{room}} \approx 25 \text{ meV} \)

\( K_B \approx 8.6 \times 10^{-5} \text{ eV/k} \)

FIGURE 10.2-8
(a) The change in the probability of occupation, as described by the Fermi-Dirac distribution function \( f(E) \), as a function of temperature; and (b) the probability that energy level \( E^* \) is occupied, given by \( f(E^*) \), as a function of temperature.

E8
FIGURE 9.2-9
The relationship between the occupied energy levels and $f(E)$ as a function of temperature for solids with a partially filled energy band: (a) at $T = 0 \text{ K}$, (b) at $T_1 > 0 \text{ K}$, and (c) at $T_2 > T_1$.

$T \uparrow$ OCCUPATION IS SPREADING ALONG BANDS

STUDY CHAP 10
**ELECTRICAL PROPERTIES**

**OBSERVATION**

**OHM'S LAW**

\[ V = IR \]

\[ R = \frac{V}{I} \]

\[ I = \frac{V}{R} \]

Convection

Current from \( \bigtriangledown \) to \( \bigcirc \)

Only convention depends on carrier

\[ \rho = \text{Resistivity} \]

\[ \sigma = \text{Conductivity} \]

\[ \rho = \frac{1}{\sigma} \]

\[ \rho = \frac{L}{A} \]

\[ \sigma = \frac{E}{L} \text{ (or Siemens?!!) CHECK IT OUT} \]

\[ V = RI \]

\[ J = \frac{E}{L} \]

**Symblos**

\[ \text{Volts} \]

\[ \text{Amps} \]

\[ \text{Ohms} \]

\[ \text{Ampere} = \frac{C}{Sec} \]
TABLE 10.2-1 Electrical conductivities for a variety of materials at room temperature.

<table>
<thead>
<tr>
<th>Class of material</th>
<th>( \sigma [(\Omega \cdot \text{cm})^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td></td>
</tr>
<tr>
<td>Nylon</td>
<td>( 10^{-1} )</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Polyvinylacetate</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>( 10^{-13} )</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Phenolformaldehyde</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Polyesters</td>
<td>( 10^{-10} )</td>
</tr>
<tr>
<td>Silicon</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Acetal</td>
<td>( 10^{-11} )</td>
</tr>
<tr>
<td>Metals and alloys</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>( 2.8 \times 10^{-5} )</td>
</tr>
<tr>
<td>Cu</td>
<td>( 6.2 \times 10^{-5} )</td>
</tr>
<tr>
<td>Ag</td>
<td>( 1.6 \times 10^{-5} )</td>
</tr>
<tr>
<td>Cu (soft)</td>
<td>( 8.9 \times 10^{-6} )</td>
</tr>
<tr>
<td>Cu (hard)</td>
<td>( 1.7 \times 10^{-5} )</td>
</tr>
<tr>
<td>Zn</td>
<td>( 6.3 \times 10^{-6} )</td>
</tr>
<tr>
<td>Zr</td>
<td>( 5.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>Zn (ZnO)</td>
<td>( 10^{-4} )</td>
</tr>
<tr>
<td>Stainless steel (18-8)</td>
<td>( 10^{-2} )</td>
</tr>
<tr>
<td>Gray cast iron</td>
<td>( 10^{-3} )</td>
</tr>
</tbody>
</table>

**GOOD CONDUCTORS**

\( \sigma \text{ BIG} \) show 23 orders of magnitude.

- **TOP SILVER** \( \sigma_{Ag} = 6.3 \times 10^5 \text{ (}\Omega \cdot \text{cm})^{-1} \)
- **TO POLYMERS** \( \sigma \approx 10^{-18} \)

**INSULATORS**

- Si & Ge are **insulators** \( \sigma \approx 10^{-4} \text{ to } 10^{-2} \)

**CONDUCTIVITY DEPENDS ON FACTOR**

1. **DENSITY OF CARRIERS PER UNIT VOLUME** \( N \left( \text{m}^{-3} \right) \)
2. **CHARGE OF CARRIER**
3. **MOBILITY** \( \mu \left( \frac{\text{m}^2}{\text{V} \cdot \text{s}} \right) \)

\( \frac{\text{RATIO \, SPEED}}{\text{ELECTRIC \, FIELD}} \)

- **1 LION** \( N = \text{1 km} \times 10 \text{ mph} \)
- **3 LIONS** \( N = 30 \text{ mph} \) \( \Rightarrow \text{MOBILITY OF THE TEACHER} \)
**MOBILITY** ➞ **BUILD σ**

**FIGURE 10.2-2**
Particle model of an electron, $e^-$, moving through a crystal lattice. (a) Under an applied electric field, the mobile electrons are accelerated toward the positive potential and occasionally suffer collisions with the surrounding ion cores. (b) A plot of electron velocity versus time for an electron assumed to continuously undergo the acceleration-collision cycle. $F$ is the mean time between collisions and $\bar{v}$ is the average velocity.

**COLLISIONS**:
- START FROM $V=0$
- ACCELERATION TO $V_{\text{max}}$
- COLLISION & RESTART

Collision every $T$ revolution time!

\[ v = at \Rightarrow a = \frac{F}{m} \Rightarrow \bar{v} = \frac{1}{T} \]

\[ N_{\text{avg}} = N_{\text{max}} \]

\[ N_{\text{avg}} = \text{DRIFT VELOCITY}!! \quad \text{cm/s, mm/s small} \]

\[ N_{\text{DRIFT}} = \mu E \]

\[ \text{MOBILITY} \]
CONDUCTOR

\[ \Delta Q = (N_{\text{drift}} \Delta t) A \frac{\text{VOLUME}}{\text{DENSITY}} \times \frac{\text{PARTICLES}}{\text{CHARGE \ EACH \ PARTICLE}} \]

\[ \Rightarrow \frac{\Delta Q}{\Delta t} = A N_{\text{drift}} m q \]

\[ \Rightarrow J = \frac{\Delta Q}{\Delta t} \quad J = \frac{1}{A} \frac{\Delta Q}{\Delta t} \]

\[ J = N_{\text{drift}} m q = \frac{m q / m e}{\sigma} \]

\[ \Rightarrow \sigma = n q m \]

IF MORE THEN A SPECIES \[ \sigma = \sum_i m_i q_i m_i \]

EXAMPLE \[ \text{Li}_2 \]

\[ q_{\text{Li}} = e \quad m_{\text{Li}} \]

\[ \text{Li}^+ + \text{Li}^+ + e^- \]

\[ q_0 = -2e \quad m_0 \]

\[ \text{BUT} \quad m_0 < 0 \quad \& \quad m_{\text{Li}} > 0 \]

\[ \text{(BECAUSE } 0^- < 0 \text{)} \Rightarrow \text{CONVENTION } q \text{ POSITIVE } \]

\[ \sigma = m_{\text{Li}} q_{\text{Li}} m_{\text{Li}} + m_0 q_0 / m_0 + m_e e / m_e \]

\[ E4 \]
**Figure 10.2-3** A schematic illustration of the effects of temperature and point defects on electron motion. (a) As temperature increases, the amplitude of the thermally induced atomic vibrations increases. This causes a decrease in the mean time between collisions and, therefore, a corresponding decrease in the electron mobility. (b) The mean time between collisions and, therefore, the electron mobility decrease with increasing defect concentration.

\[ \text{TEMPERATURE} \]
\[ T \uparrow \mu \downarrow \text{(electrons get slower, more collision)} \]
\[ \frac{\partial \mu}{\partial T} < 0 \]

\[ \text{IMPURITIES} \]
\[ N_{\text{defects}} \uparrow \mu \downarrow \]
\[ \text{MORE COLLISIONS, MORE TIGHT SPACES} \]
\[ \frac{\partial \mu}{\partial N_D} < 0 \]

**However**
\[ \sigma = n q \mu \downarrow \frac{\partial \mu}{\partial T} < 0 \]
\[ \text{or} \frac{\partial \mu}{\partial N_D} < 0 \]

**But** TEMPERATURE or IMPURITIES
\[ \text{can boost } \mu!! \]
\[ \Theta_m \text{ huge, } \frac{\partial \mu}{\partial T} \text{ like semiconductor} \]
\[ \frac{\partial n}{\partial T} > 0 \]
\[ \frac{\partial \mu}{\partial n} \]

\[ \frac{\partial n}{\partial T} = 0 \text{ metastable} \]
CRYSTALLINE STRUCTURE ⇒ MANY LEVELS
FROM QUANTUM MECHANICS: TAKE MY COURSE IF YOU WANT TO KNOW

1 ATOM (ISOLATED) ⇒ LEVELS 1s, 2s, 2p, 3s, 3p, 3d, ... DISCRETE

• ISOLATED

• OUTER ELECTRONS = VALENCE (LOCAL)!

ATOMS CLOSE! ⇒ LEVELS ARE FUNCTION OF SEPARATION ε
CRYSTAL ⇒

• DISCRETE BECOME NON-ISOLATED
SPREAD INTO ENERGY BANDS

• OUTER ELECTRONS NOT SPATIALLY LOCALIZED ANYMORE

WIDER

NARROWER

ENERGY

\[ x_4 \quad x_2 \quad x_1 \]
Interatomic spacing
(a)

\[ x_2 \quad x_1 \]
Interatomic spacing
(b)

ENERGY

\[ x_3 \]
Interatomic spacing
(c)

\[ x_4 \]
Interatomic spacing
(d)

\{ BAND GAP \}

\{ REGION OF BAND OVERLAP \}

\{ EACH ATOM BRINGS ALL ITS LEVELS \}

\{ ISOLATED ENERGY LEVELS IN A SINGLE ATOM SPILL INTO A BAND OF DISCRETE LEVELS SEPARATED BY SMALL ENERGY DIFFERENCES \}

\{ FOR SEPARATION DISTANCE \[ x_4 \], THE 2S AND 2P ENERGY BANDS OVERLAP TO FORM AN EXTENDED ENERGY BAND. \}

\[ E_0 \]

\[ \{ \text{LEVELS} \}

\[ \text{const} \]

FIGURE 10.2-4: Energy bands in solids. (a) The energy band structure as a function of interatomic separation distance. (b) For large separation distances, the electrons associated with any atom are independent of those of all other atoms. (c) For separation distance \[ x_2 \], the isolated energy levels in a single atom split into a band of discrete levels separated by small energy differences. (d) For separation distance \[ x_4 \], the 2s and 2p energy bands overlap to form an extended energy band.
ELECTRONS FILL FROM
LOWEST ENERGY!

HIGHEST ENERGY BAND
AT LEAST PARTIALLY OCCUPIED

CORE BANDS

VALENCE BAND

PROPERTY:  COMPLETELY FILLED & COMPLETELY EMPTY BANDS ARE NOT
CAPABLE OF TRANSPORTING ELECTRIC CHARGE
THROUGH THE SOLID

COMES FROM LIOUVILLE THEOREM
(ASK!)

ONLY PARTIALLY OCCUPIED LEVELS GIVE CONDUCTIVITY!

$\Rightarrow$ GIVE CURRENT,
THE OTHER
DO NOT
GIVE
ANYTHING.

1 ELECTRON

$\Rightarrow$ EMPTY $\Rightarrow$ NO CURR

$\Rightarrow$ FULL $\Rightarrow$ NO CURR

$\Delta e$
$q = e$

$\text{me} > 0$

$\text{me}$

$\text{m}_h < 0$

$\text{m}_h$

generically

$\text{m}_h < \text{me}$
Example

$N_{\text{Drift}}$ ? Big or small?

recall $V_{\text{Drift}}$ for all wires

\[
\begin{align*}
R &= 0.0283 \Omega \\
L &= 1\,\text{m} \\
\mu_e &= 1.22 \times 10^{-3} \frac{\text{m}^2}{\text{Vs}}
\end{align*}
\]

with $SA = 1$

\[
V = RI \Rightarrow \frac{V}{L} = E
\]

\[
E = \frac{RI}{L} \Rightarrow \quad N_{\text{Drift}} = \frac{\mu_e E}{L} = \frac{\mu_e \frac{RI}{L}}{L} = \frac{1.22 \times 10^{-3} \times 2.83 \times 10^{-2}}{1} \approx 0.1 \text{ mm/s} \quad \text{small}
\]

$V_{\text{Drift}} \sim \text{mm/s}$

Vibration $\sim \frac{1}{2} m_e V_{\text{th}}^2 = \frac{3}{2} kT$

\[
V_{\text{th}} \approx 1000 \text{km/sec}
\]

but what moves at $c$ ? (Speed of Light)

ASK!
**Figure 10.2-8**

(a) The change in the probability of occupation, as described by the Fermi-Dirac distribution function \( f(E) \), as a function of temperature; and (b) the probability that energy level \( E_n \) in part a is occupied, given by \( N(E_n) \), as a function of temperature.

\[ f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \]

\( T = 0 \)
\[ f(E < E_F) = 1 \]
\[ f(E > E_F) = 0 \]

\( T > 0 \)
\[ f(E < E_F) \xrightarrow{\text{no cond.}} 1 \]
\[ f(E > E_F) \xrightarrow{\text{no cond.}} 0 \]
\[ f \left( E \approx E_F \right) \xrightarrow{\text{not op cond. or s cond.}} \]

\( k_B T_{\text{room}} \approx 25 \text{ meV} \)
\( k_B \approx 8.6 \times 10^{-5} \text{ eV/K} \)
FIGURE 10.2-9
The relationship between the occupied energy levels and \( n(E) \) as a function of temperature for solids with a partially filled energy band: (a) at 0 K, (b) at \( T_1 > 0 \) K, and (c) at \( T_2 > T_1 \).

\[ T = 0 \text{ K} \]

\[ T_1 > 0 \text{ K} \]

\[ T_2 > T_1 \]

\[ n(E) \]

\[ f(E) \]

\[ 0 \]

\[ 0.5 \]

\[ 1.0 \]

OCCUPATION IS SPREADING ALONG BANDS

STUDY CHAP 10
Pick 1 electron, its probability that this electron is in the conduction band, is \( p(E > E_c) \)

\[
P(E > E_c) = \int_{E_c}^{\infty} f(E) \, dE = P(T) \quad \text{(depends on temperature)}
\]

Number of electrons in conduction band is not the product of available electrons \( \times \) prob\(E > E_c)\)

But you must multiply \((\#\text{ availability of level})\)

\[
N_e = 2 \int_{E_c}^{\infty} f(E) g(E) \, dE = N_0 \exp \left( \frac{-E_c}{2kT} \right)
\]

\(f(E)\) is density of states, \(g(E)\) is population (depends on \(T\))

**Measure availability!**

**Example**

\(g(E)\) is very close \(g(E)\) big

\(g(E)\) is very close \(g(E)\) small

\(g(E)\) is \# of levels between \(E, E + dE\)
Remember 

$E_F$ is the 

HOR energy 

electrons can HAVE

@ $T=0$, in a level exist @ $E_F$

CONDUCTORS

$E_F$ happens in a region with bands =>

there are partially POPULATED BANDS @T!!

SEMICONDUCTOR

$E_F$ happens inside a GAP $< 2.5eV$

are partially occupied BANDS likely at T=DECENT

INSULATOR

GAP IS SO BIG 

you need $T > T_{mf}$ $> 2.5eV$
**Figure 10.2-12** Electron band structures for metallic Na and Mg: (a) electron energy levels for an isolated Na atom, (b) splitting of the energy levels as a function of distance between two Na atoms, (c) the energy band diagram for Na showing a half-filled 3s band, (d) electron energy levels for an isolated Mg atom, (e) splitting of the energy levels as a function of distance between two Mg atoms, and (f) the energy band diagram for metallic Mg showing a partially filled 3s/3p extended band.

Mg

\[ \text{3s}^2 \]

\[ \text{3p}^0 \]

\[ \text{EF} \]

\[ \text{FULL} \]

\[ \text{EF} \]

\[ \text{FULL} \]

\[ \text{CONDUCTOR} \]
CONDUCTORS: SUMMARY

\[ \sigma = N_e q_e m_e \]

available electrons for conduction

\[ N_e = N_{\text{cond}} = \text{const} \text{ with } T \]

\[ q_e = \text{charge } e \]

\[ m = \text{mobility } \quad T \uparrow \text{mob} \quad \frac{\partial m}{\partial T} < 0 \]

\( \sigma < 0 \) because \( \sigma \) is PHYSICS \( \neq \) ENGINEERING

\[ \rho = \rho_0 (1 + \alpha_\rho T) \]

more precisely

\[ \rho = \rho_0 \left[ 1 + \frac{T - T_0}{T_0} \right] \]

FOR TABLE

\[ \rho = \rho_0 \left[ 1 + \alpha_\rho (T - T_0) \right] \]

**TABLE 10.2-2** Electrical resistivities \( \rho_0 \) and temperature coefficients of resistivity \( \alpha_\rho \) for selected conductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>( \rho_0 ) (Ω·m)</th>
<th>( \alpha_\rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0003</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>200</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>300</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>400</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>500</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>600</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>700</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>800</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>900</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1000</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1100</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1200</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1300</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1400</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1500</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1600</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1700</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1800</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>1900</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
<tr>
<td>Au</td>
<td>2000</td>
<td>2.25 \times 10^{-8}</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

### Table 10.2.3

<table>
<thead>
<tr>
<th>Material</th>
<th>Band Gap (eV)</th>
<th>Activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.4</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>1.1</td>
<td>100</td>
</tr>
<tr>
<td>Ge</td>
<td>0.7</td>
<td>50</td>
</tr>
</tbody>
</table>

**Some facts about semiconductors:**

- Longest timescale: 10⁻¹² s
- Huge boost:
  \[ \frac{\Delta N_s}{N_e} = \frac{N_i - N_e}{N_e} \]
- Some facts:
  \[ N_s = N_e - \frac{E_g}{kT} \]

**Some notes:**

- H₂O: O₂, N₂
- 2H₂O → O₂ + N₂
- Some notes on quantum dots.

**More notes:**

- although out of classroom is an outline by our definition, it is included here for completeness.
- Source: Adapted from Handbook of Chemistry and Physics, 91st ed. Copyright CRC Press, Boca Raton, FL.
IONICS: No free electrons (or holes)

But ions move? Atoms $Na^+ e^- $ move

jumping left $\&$ right $\Rightarrow$ by Diffusion

$\Rightarrow \mu \sim \text{Diff.}$

$\mu_{\text{ion}} = \frac{q}{kT}$

$\Gamma_{\text{diff.}}$

$\sim e^{-R/KT}$

EINSTEIN RELATIONS

$\Rightarrow \delta_r = \frac{N_e \mu_e e + N_h \mu_h e}{N_{\text{ions}}}$

IF SMALL

$\Delta G \Rightarrow \text{CONSIDERABLE CURRENT!}$

$\leq 2.5 eV$

TRANSFERENCE NUMBER $= \% \text{ of conductivity}$

of a sample

$\% \text{ of the species vs the total of the IONIC}$

$\kappa e^- = k^+ e^-$

$\downarrow$

$\sigma_{k^+} / \sigma_{k^+ e^-} = 96\% \quad \Theta$ $435^{\circ}C$

$\sigma_{e^-} / \sigma_{k^+ e^-} = 4\%$

$\delta_{k^+} / \sigma_{k^+ e^-} = 88\% \quad \Theta \ 600^{\circ}C$

$\delta_{e^-} / \sigma_{k^+ e^-} = 12\%$
DEFECTS & IMPURITIES

reduce $\sigma$ in conductors, metals & ionic!

$\partial \mu / \partial N_d < 0$!!

BUT FOR

FOR METAL

$T = 0$

$p = p_0 + qT$

removing one due by defect

in $p_0 \sim 0$

SUPERCONDUCTOR

$\rho$

$\rho_0$...

SUPERCONDUCTOR

$\rho$ vs $T$

MAX

Cu

Ni

Cu IMPURITIES

N$_1$ IMPURITIES

$1.6 \times 10^{-6}$

$6.8 \times 10^{-6}$ (Cu)

$E16$
SEMICONDUCTORS: INTRINSIC

PURE ELEMENT HAS CHARGES (e & h) CREATED ONLY BY TEMPERATURE CALLED INTRINSIC SEMICONDUCTOR

\[ \sigma = \text{Me}_q \text{e}_e + \text{M}_h \text{q}_n \text{h}_n = e(\text{Me}_e \text{Me} + \text{M}_h \text{M}_n) \]

\[ \frac{e}{k^2} > 0 \quad \frac{e}{k} > 0 \]

EC = CONDUCTION ENERGY = MIN OF CONDUCTION BANDS

Ev = VALANCE ENERGY = MAX OF VALANCE BANDS

\[ E_g = \text{energy gap} \]

1) \( q \) is NOT function of \( T \), it's just \( e \)!!

2) \( \frac{\Delta q}{\Delta T} < 0 \) but small v. rouge!

\[ q > q_0 (1 + (\gamma T)) \Rightarrow \mu \sim \mu_0 - \beta T \]

\[ \Rightarrow \] CONDUCTION LINEARLY

3) \( \frac{\Delta M}{\Delta T} \) \& \( \frac{\Delta M}{\Delta T} \) ARE HUGE!! EXPONENTIAL THING

FOR INTRINSIC, THERE IS NO EXTRA CHARGE

\[ E_{17} \]

\[ \Rightarrow M_n = M_e \] IF YOU PRODUCE 1 E YOU PRODUCE 1 h
\[ M_e = m_n = N_0 \exp \left( -\frac{E_g}{2kT} \right) \]

From integrals.

\[ \sigma = \frac{N_0 e^2 (m_e + m_h)}{\left( \frac{m_e}{2kT} \right)} \]

\[ \approx \sigma_0 \text{ constant} = N_0 e (m_e + m_h) \]

\[ \approx \sigma_0 \exp \left( -\frac{E_g}{2kT} \right) \]

\[ \Rightarrow \text{plot } \log \sigma = \log \sigma_0 - \left( \frac{E_g}{2k} \right) \frac{1}{T} \]

\[ \Rightarrow \text{avalanche effect.} \]
SEMICONDUCTORS: EXTRINSIC

N-type

What happens if we add impurities?

Remove some Si & add P

⇒ extra electron

Each impurity creates

One extra level

Donor level with Ed

Conduction band

Extra electrons from Group V dopants

Ed is very close to Ec

⇒ Ec - Ed ≈ 40 meV

at room temp

KT_{room} ≈ 25 meV

\[ \exp \left(-\frac{E_c - E_d}{kT} \right) \approx 0.2 \]

at room temperature

All donor up electrons

have jumped out their

donor levels & are FREE

⇒ plenty of conductivity

⇒ \[ N_h = N_0 \exp \left(-\frac{E_{gap}}{2kT} \right) \neq N_c \]

in-work range

Mc = Concentration of donors

⇒ Low TEMP: \[ n_c = N_d \exp \left(-\frac{E_v - E_d}{kT} \right) \]
\[
\sigma = N_0 e^m e \exp \left( -\frac{E_c - E_d}{kT} \right)
\]

**EXTRINSIC : P-TYPE (Add holes):**

Extra holes from Group III dopants

---

**ACCEPTOR LEVELS:**

Localized Levels with Holes INSIDE!

\[ \text{1 electron from VALENCE CORE TO THE ACCEPTOR LEVEL} \]

\[ \Rightarrow \sigma_h \]

\[ \Rightarrow \text{a \# \# \# ONLY INTRINSIC} \]

\[ \Rightarrow \text{extr } \sim \text{ intrinsic} \]

\[ \Rightarrow N_h \gg N_e \Rightarrow \sigma = \sigma_h = N_0 q n_h \exp \left( -\frac{E_a - E_V}{kT} \right) \]

E20
**CONDUCTIVITY**

**P-type**

\[ \text{Slope} = -\frac{E_a}{2k} \text{ (intrinsic behavior)} \]

**Saturation region**

\[ \text{Slope} = -\frac{E_a}{k} \text{ (extrinsic behavior)} \]

---

**SUMMARY**

**INTRINSIC** \(\Rightarrow\) **ONLY THERMAL GENERATION** \(\Rightarrow\) **CARRIERS = SMALL**

**EXTRINSIC** \(\Rightarrow\) **INTRINSIC + CARRIERS OF IMPURITIES (DOPANTS)** \(\Rightarrow\) **SMALL** __extra__ \(e\) \(\Delta\) \(h\) \(\text{ (N\& P-type)}\)

---

**TABLE 10.3-1** Impurity energy levels \(E_a\) or \(E_o\) in Si and Ge.

<table>
<thead>
<tr>
<th>Host</th>
<th>Doping</th>
<th>Energy Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>C</td>
<td>0.12 eV</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.14 eV</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>0.07 eV</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.06 eV</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.04 eV</td>
</tr>
<tr>
<td>Ge</td>
<td>T</td>
<td>0.12 eV</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.08 eV</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>0.09 eV</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>0.01 eV</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>0.001 eV</td>
</tr>
</tbody>
</table>

---

**FREE SEMI CONDUCTOR TYPE**

**INTRINSIC** \(\text{N}_h = \text{N}_m = \text{M}_e\)

**EXTRINSIC N-TYPE** \(\text{M}_e > \text{N}_p > \text{M}_h\)

**EXTRINSIC P-TYPE** \(\text{N}_h > \text{N}_p > \text{M}_e\)

---

\(\sigma = \sigma_0 \text{ exp} \left(\frac{-E_a - E_V}{kT}\right)\)

---

**NOT** \(E_a\) **but** \(E_a - E_V\)** in book**

\(\sigma = \sigma_0 \text{ exp} \left(\frac{-E_a - E_V}{kT}\right)\)

**Ea** \(\Rightarrow\) **Ea - E_V**.

---

**E21**
DEFECTS

DEFECTS: SOURCES OF TROUBLES
- about charge mobility but
- introduce extra localized electron levels that
  mess up mechanism
- act like a carrier - charge recombination sites!
  (electron falls & meet its hole & vici versa!)

- FAST SEMICONDUCTORS
  ⇒ minimize defects,
  need for big crystals (small crystals, no poly!)

SIMPLE DEVICES

- measure temp: intrinsic
  \[ \log \sigma = \frac{E_g}{2kT} \]

- light detector: light \( \lambda \Rightarrow E = \frac{\hbar c}{\lambda} \)
  \( \frac{\hbar}{\lambda} \) : PLANCK
  \( \hbar \geq E > E_{\text{gap}} \Rightarrow \) generation of extra charge
  ⇒ boost of conductivity

But, more important is
JUNCTIONS ⇒ PN, ⇒ TRANSISTORS!
N-TYPE @ ROOM TEMPERATURES

- Free electrons
- Frozen holes

P-TYPE @ ROOM TEMPERATURES

- Free holes
- Frozen electrons

Free electrons in N region feel free holes in P.
\[ q_{\text{free}} + q_{\text{frozen}} \]

\[ \text{q-free + h-frozen} \]

\[ \text{JUNCTION} \]

\[ \text{Recombination Region} \]

\[ q_{\text{tot}} = q_{\text{free}} + q_{\text{frozen}} \]

\[ \Rightarrow \text{NON BALANCE OF CHARGE BY JUNCTION} \]
\[ \Delta V \approx 0.7 \text{ eV for Si} \]

**Reverse Bias**

- \[ V_{out} \]
- \[ V = \Delta V + (V_{out}) = \Delta V - V_{out} \]
- \[ I = I_0 (e^{\frac{\Delta V}{kT}} - 1) \]

**Forward Bias**

- \[ V = \Delta V - V_{out} \]
- \[ V = \Delta V - V_{out} \]

**External Act.**

- \[ \Delta V \Rightarrow \text{Free Electron} \]
- \[ \Delta V \Rightarrow \text{Free Hole} \]
- \[ \Delta V \Rightarrow \text{No Current} \]
- \[ \Delta V \Rightarrow \text{No Barrier} \]

**Recombination Region**

- \[ \text{Small Barrier} \]
- \[ \text{Open Circuit (Rev)} \]
- \[ \text{Close Circuit (Fwd)} \]
Extra electrons

(a)

Extra holes

(b)

EXTERNAL LOAD

(c)

V_{be}, I_{be} vary.

BASE IS THINNER THAN RECOMBINATION REGION

⇒ V_{be}, electrons flow

E to B, but

B is thin ⇒ not enough space for recombination

⇒ travel to C

⇒ V_{be} controls

CONDUCTION BETWEEN E & C

⇒ amplification

E26
FIGURE 10.3-9
Three methods for fabricating a p-n junction diode: (a) diffusion of an n-type dopant into a p-type substrate, (b) diffusion of a p-type dopant into an n-type substrate, or (c) sequential diffusion of n-type and p-type dopants into an intrinsic substrate.

FIGURE 10.3-10
The method for introducing a controlled amount of a dopant into a silicon substrate: (a) the oxidized wafer, (b) the SiO₂ surface oxide layer is removed from the region to be doped, (c) dopant atoms are introduced onto the surface, and (d) the dopant is thermally diffused into the underlying silicon.

FIGURE 10.3-11
A metal-oxide-semiconductor (MOS) capacitor.
**POLYMERS**

- They are not crystalline! < rubber > some stuff, but depends on temperature

- above \( T_g \) = rubber
- under \( T_g \) = glass

\[ \text{Volume is function of Temperature} \]

\[ \varepsilon_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

\[ \varepsilon_v \sim \frac{B_v}{T^2} \]

\[ \text{Thermal expansion} \]

\[ q_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

\[ q_v \sim 3B_v \]

**Figure 6.2-1** Specific volume as a function of temperature for a series of materials. (a) The liquid-to-crystalline solid transformation. A discontinuous change in volume occurs at the melting temperature \( T_m \). (b) The liquid-to-glass transformation (the liquid-to-crystalline curve is shown for reference). The temperature range in which the slope of the liquid-glass curve changes is the glass transition temperature \( T_g \). (c) Specific volume versus temperature for a semicrystalline material. The discontinuous change in volume occurs at \( T_m \) and a change in slope occurs at \( T_g \).
Molecular motion \( \Rightarrow \) depends on time frame of experiment.

\[ \xrightarrow{\text{slow}} \quad \text{pull slowly} \quad \xrightarrow{\text{to}} \quad \text{break} \quad \xrightarrow{\text{fast}} \quad \text{pull fast} \]

\[ \Rightarrow T_g \text{ depends on time frame of events!} \]

Example of polymers = poly\((\text{mer})\)

\[ \text{polymer} \times n \text{ mer.} \]

**Figure 6.2-2** Repeat units in two different structures: (a) the \((\text{SiO}_2)_x\) tetrahedron in \(\text{SiO}_2\), and (b) the \(\text{C}_2\text{H}_4\) mer in polyethylene. In this figure we show the polymer molecule in a simplified linear (stretched-out) orientation. In fact, as discussed later in the chapter, polymer molecules rarely look like this. When drawn in the linear fashion, however, the backbone carbon atoms are in the plane of the paper but the side groups (H, etc.) stick out of, or go into, the plane of the paper.
VISCOITY

SHEAR STRESS

\[ F \rightarrow Z = \frac{F}{A} \rightarrow \]

SHEAR STRAIN

\[ \gamma \rightarrow x \rightarrow \frac{dy}{dx} \rightarrow \]

even better \( \frac{dy}{dx} = \gamma \)

SOLID RESPONSE

\[ Z \Rightarrow Z = G \gamma \rightarrow \frac{dy}{dx} = \gamma \rightarrow \]

\[ \text{SHEAR MODULUS} \]

A liquid responds to shear stress?

NO STRAIN but STRAIN RATE

\[ \Rightarrow \text{constant deformation} \]

\[ \begin{array}{c}
t = 0 \\
t = 1 \\
t = 2 \\
t = 3 \
\end{array} \]

\[ \begin{array}{c}
X, X_1 \\
X_2 \\
X_3 \\
\end{array} \]

\[ \Rightarrow \frac{dx}{dt} \propto Z \rightarrow \text{bigger } Z \& \text{ faster } \frac{dx}{dt} \]

\[ \Rightarrow Z = \mu \frac{dx}{dt} \]

NEWTON VISCOITY LAW

\[ \mu \text{ is measure of work done for deformation} \]
\[ \eta (\cdot) \]

\[ F = \frac{1}{\eta} \frac{m}{s} \Rightarrow \frac{g \cdot m}{s} \text{ Pa} \cdot \text{s} \]

\[ \Rightarrow \frac{g \cdot m}{s} \cdot \frac{s}{s^2} \cdot \frac{m}{m} = \frac{g \cdot m}{s^2} \]

\[ \eta \downarrow \text{ water, solvent, liquid metals (Hg)} \]

\[ \eta \uparrow \text{ solid liquid, solid} \]

\[ \text{Caramel} \sim 10^5 \text{ Pa} \cdot \text{s} \]

\[ \text{Windows, glasses} \sim 10^2 \text{ Pa} \cdot \text{s} \]

\[ \text{Fluidity} \]

\[ \phi = \frac{1}{\eta} \]

\[ \eta \sim T \]

\[ \phi \sim \frac{1}{T} \]

\[ \text{Arrhenius} \]

\[ \phi = \phi_0 \exp \left( \frac{-\Theta}{kT} \right) \]

\[ \eta = \eta_0 \exp \left( \frac{-\Theta}{kT} \right) \]

**Figure 6.3-2** The effect of temperature on the viscosity of a soda-lime-silicate glass. (Source: W. D. Kingery et al., Introduction to Ceramics, 2nd ed. Copyright © 1976 by John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.)
STRUCTURES!

- Classification

polyethylene

UNIT ⇒ \( \left( \begin{array}{c}
C \\
H
\end{array} \right) \) = MER

If \( n \) small ⇒ polyethylene

WAX OR PARAFFIN OR OIL

HUNDREDS.

If \( n \) large ⇒ polyethylene

Degree of polymerization

\( m \sim 10^4 \sim 10^7 \) MILLIONS

VINYl POLYMER

\[ R = \text{vinyl polymer} \]

\[ R = CH_3 \Rightarrow \text{polypropylene} \]

HYDROCARBONS RUBBERS

C C C double bond

POLYOLEFIN (If C & H only) = FAMILY

If not only C in backbone ⇒

POLYESTER

ESTER \(-O-C-\)

FAMILY

PET

FIBERS

TRANSPARENT, PROJECTOR

NYCAR, DACRON, FORTREL, TERYLENE
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyls and related polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CH_2})</td>
<td>Clear film, flexible bottles</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CHCl})</td>
<td>Floors, pipes, hoses</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CH})</td>
<td>Containers (clear or foam), toys</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CH})</td>
<td>Shoe, pipe, film, containers</td>
</tr>
<tr>
<td>Polymethylmethacrylate (Plexiglas)</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-C})</td>
<td>Lenses, transparent enclosures, windows</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>(CF_2=CF_2 \rightarrow {CF_2-C})</td>
<td>Nonstick coatings, gaskets, seals</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CN})</td>
<td>Fibers—synthetic wool</td>
</tr>
<tr>
<td>Rubbers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CH})</td>
<td>Tires and molded parts</td>
</tr>
<tr>
<td>Polyisoprene (natural rubber)</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CH})</td>
<td>Tires and gaskets</td>
</tr>
<tr>
<td>Polychloroprene</td>
<td>(CH_2=CH_2 \rightarrow {CH_2-CH})</td>
<td>Belts, bearings, and foams</td>
</tr>
<tr>
<td>Polydimethylsiloxane (silicone rubber)</td>
<td>(CH_3 \rightarrow {CH_3})</td>
<td>Gaskets, insulation, and adhesives</td>
</tr>
<tr>
<td>Polymer</td>
<td>Structure</td>
<td>Applications</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>--------------</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td></td>
<td>Films (magnetic tape), fibers, and clothing</td>
</tr>
<tr>
<td>Thermoset variation</td>
<td></td>
<td>Bond and auto body parts, fiberglass, hoses, and chairs</td>
</tr>
<tr>
<td>Polyamides</td>
<td></td>
<td>Carrafe, parachute, rope, gear, insulation, and bearings</td>
</tr>
<tr>
<td>Nylons 66</td>
<td></td>
<td>Fiber, bulletproof vests</td>
</tr>
<tr>
<td>Kevlar or poly-piphenylene-terephthalamide (PPTA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other common polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td></td>
<td>Lenses, helmets, lamp casings, machine parts</td>
</tr>
<tr>
<td>Thermoset-durene</td>
<td></td>
<td>Casings, fuses and telephone, electrical components, distribution, etc.</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td></td>
<td>Foam, floor and lining, wall tiles, baskets, etc.</td>
</tr>
<tr>
<td>Adhesive, used in composites</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Page 7**
Relation with adjacent groups

\[
\begin{align*}
\text{ISOTACTIC} & \quad \text{Stereoblock} \\
\text{SYNDIOTACTIC} & \quad \text{Stereoblock} \\
\text{ATACTIC} & \quad \text{Random} \quad \text{Stereocenter}
\end{align*}
\]

**FIGURE 6.4-5** A planar illustration of the (a) isotactic, (b) syndiotactic, and (c) atactic configurations of polystyrene. Note: The C\(_6\)H\(_5\) rings are actually much larger than indicated in these sketches.

**TACTICITY (STereochemistry)** is **very** dependent on polymer formation (can be modified randomly at HIGH TEMP) because they affect secondary bonds:

\( \text{Isotactic} \quad \text{Syndiotactic} \quad \text{Atactic} \)

\[\text{C} \quad \text{H} \]
**THERMO PLASTIC & THERMOSET**

1) Secondary bond (VDWALCS, Dipole) $\Rightarrow$ weak, can be destroyed by temperature $\Rightarrow$ $T \uparrow \Rightarrow$ polymer melts

2) Primary and double bonds inside chain $\Rightarrow$ $T \uparrow$ + extra atoms

\[ \text{THERMOPLASTIC (TP)} \]

- Break double bonds inside chain $\Rightarrow$ lose EXTRA BOND CROSS LINK

\[ \text{THERMOSET (TS)} \]

- UNSATURATED: HAVE C=C
PHENOLFORMALDEHYDE (Bakelite) → Polymer Surface

FIGURE 6.4-2
The structure of the TS polymer phenolformaldehyde (Bakelite®) showing:
(a) the basic building block for the structure (the numbers 1–3 correspond to the three sites for primary bond formation with neighboring mes), (b) a simplified representation of the basic building block, and (c) a 2-D representation of the 3-D primary bond network in this TS polymer.

CELLULOSE

FIGURE 6.4-3 (a) The structure of cellulose, and (b) schematic of the structure of lignin.

PROTEINS

---

DIFFERENT

R & R' mobes different aminocids!
Molecular Weight

\[ (\text{MER})_n \rightarrow M = mn \]

*degree of polymerization \( n \)

If a mixture of different polymers \( M \)

\( \Rightarrow \) different molecular weights \( \left[ \frac{\overline{M}}{n} = \frac{\sum M_i M_i}{\sum N_i} \Rightarrow \overline{M_W} = \frac{\sum w_i M_i}{\sum w_i} \right] \)

\[ N_i = \# \text{ of polymers with weight } M_i \Rightarrow w_i = N_i M_i \]

Different definition:

\[ w_i = \text{total weight of polymers with weight } M_i \Rightarrow w_i = N_i M_i \]

\[ PD = \frac{\overline{M_W}}{\overline{M_n}} \]

Polydispersity \( \sim 2 \) to 20

Polymer Configuration

Very rarely they are linear ...

Commonly kinked:

![Polyethylene Structure](image)

**Figure 6.4-4** The 3-D structure (conformation) of a polyethylene chain. (a) The C—C bond angle in PE. (b) The bond angle does not define the location of the neighboring C atoms but only restricts their location to a specific cone of rotation. (c) If all of the C atoms in the chain backbone lie in the same plane, the planar zigzag conformation results. (d) The more common (lower-energy) conformation of PE is the random coil structure.
CRYSTALLIZATION OF POLYMER

THERMOPLASTIC partially crystalline

\[ \Rightarrow \text{go } T^\uparrow \text{ and cool slowly.} \]

CRYSTALLIZATION DEPENDS ON

1) SIZE OF SIDE GROUPS \((R)\) \(<\) DEFECTS.
2) EXTENT OF BRANLING
3) TACTICITY
4) COMPLEXITY OF MER
5) TYPE OF SECONDARY BONDS (DIPOLAR OR VDW)

1) SIZE - small polymers crystallize better
   simple polymers crystallize better

POLY PROPYLENE \(\left( \text{C}_2\text{H}_3\text{C}_2\text{H}_3 \right)^n\)
   crystallize less than
POLY ETHYLENE \(\left( \text{C}_2\text{H}_2\text{C}_2\text{H}_2 \right)^n\)

2) BRANCHING

\[ \text{PVC} \]

More branches 
less crystalline

small concentration of branches
\[ \Rightarrow \]
more open spaces, polymer less compact

FIGURE 6.4-7 A schematic illustration of chain branching in polyvinylchloride.
3) TACTICITY affects crystallization.

Atactic (random) with big side groups cannot easily be packed. It's easier to pack isotactic (-----) and syndiotactic (-----).

⇒ this influences property.

Example: Polypropylene isotactic (~50% crystalline) = hard & rigid
Polypropylene atactic (~0% crystalline) = useless, gummy substance.

4) COMPLEXITY OF MER

Big repeated unit (mer) ⇒ need more extreme chain segment to create L.R.O.

⇒ they crystallize slowly.

Then short mer

5) TYPE OF SECONDARY BONDS

Existence of small space polar side groups helps formation of crystals

⇒ Ex: Polyvinyl chloride (-----) crystallizes better than Polypropylene (-----) P13

⇒ PVC stronger than PP
**Semi-Crystalline Polymer**

Polymers = long spaghetti need to roll up

- **Spherulite**
  - Disorder = No Crystal
  - Order = Crystal
  - *Interlamellar Non-crystalline Polymer*

- **Semi-Crystalline**
  - Degree of Cristallinity
    - % of the polymer that is crystalline

  (Metal, Ceramic = ~99%)
  - Poly = 90 to 95%
  - Non-crystal 0%

---

(a) Diagram of crystalline and non-crystalline regions.

(b) Image of spherulites.
Tgloss vs. Tmelting

Simple rule: longer MERS, HEAVIER side groups

\[ T_g \text{ ~increases~} \frac{T_m}{2} \]

because you need a higher T to get the "motion" going on.

In addition

- Symmetric MERS (C<sub>2</sub>H<sub>4</sub> or PE for instance)

\[ T_g \sim \frac{T_m}{2} \]

- Asymmetric MERS (-C<sub>2</sub>H<sub>3</sub>C= or PVC)

\[ T_g \sim \frac{T_m}{2} \]

It's an entropy EFFECT (Symmetric MERS has one more DEGENERATION \( \rightarrow S=0 \) for symmetric.)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T&lt;sub&lt;dim&gt;&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&lt;glass&gt;&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density polyethylene</td>
<td>175</td>
<td>-120</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>20</td>
<td>87</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>110</td>
<td>16</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>240</td>
<td>110</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>320</td>
<td>107</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>527</td>
<td>220</td>
</tr>
<tr>
<td>Poly(methylmethacrylate)</td>
<td>320</td>
<td>100</td>
</tr>
<tr>
<td>Acetal</td>
<td>181</td>
<td>85</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>265</td>
<td>80</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>230</td>
<td>89</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>270</td>
<td>145</td>
</tr>
<tr>
<td>Polysulfone tetraphthalate</td>
<td>255</td>
<td>90</td>
</tr>
<tr>
<td>Silicons</td>
<td>-</td>
<td>123</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>120</td>
<td>-80</td>
</tr>
<tr>
<td>Polychloroprene</td>
<td>48</td>
<td>-80</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>38</td>
<td>-73</td>
</tr>
</tbody>
</table>

TABLE 6.5-3 Observed melting and glass transition temperatures for selected polymers.
GLASSES
STRUCTURE & PROPERTY

Take a piece of a window ⇒ X-ray, wait it becomes crystalline.

Chapter 6  Noncrystalline and Semicrystalline Materials

FIGURE 6.5-1
A comparison of the X-ray scans for (a) amorphous silica and (b) a crystalline polymorph of silica (crystal-silicate). (Source: Adapted from B. E. Warren and J. Boscoi, Journal of American Ceramic Society, 2149, 1938.)

FIGURE 6.5-2 The 2-D representations of (a) silica glass and (b) a crystal of silica.

P16
Gloss: variety of materials (amorphous) = random

$\Rightarrow$ metal, ionic & covalent

Requirement: Material must be cooled from liquid phase, rapidly enough to "freeze" the liquid phase, and kinetic to of crystalline phase must be slow so the system does not become ordered fast.

Table 6.5-1 Glass-forming systems

<table>
<thead>
<tr>
<th>Elements</th>
<th>S, Se, P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>$\text{B}_2\text{O}_3, \text{SiO}_2, \text{GeO}_2, \text{P}_2\text{O}_5, \text{As}_2\text{O}_3, \text{Sb}_2\text{O}_3, \text{In}_2\text{O}_3, \text{SnO}_2, \text{PbO},$ and $\text{SeO}_2$</td>
</tr>
<tr>
<td>Halides</td>
<td>$\text{BeF}_2, \text{AlF}_3, \text{ZnCl}_2, \text{AgCl, Br, I}, \text{PbCl}_2, \text{Br}_2, \text{I}_2,$ and multicomponent mixtures</td>
</tr>
<tr>
<td>Sulfides</td>
<td>$\text{As}_2\text{S}_3, \text{Sb}_2\text{S}_3, \text{CS}_2,$ and various compounds of B, Ga, In, Te, Ge, Sn, N, P, and S</td>
</tr>
<tr>
<td>Selenides</td>
<td>Various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, and P</td>
</tr>
<tr>
<td>Tellurides</td>
<td>Various compounds of Tl, Sn, Pb, As, Sb, Bi, and Ge</td>
</tr>
<tr>
<td>Nitrates</td>
<td>KNO$_3, \text{Ca(NO}_3)_2,$ and many other binary mixtures containing alkali and alkaline earth nitrates</td>
</tr>
<tr>
<td>Sulfates</td>
<td>KHSO$_4$ and other binary and ternary mixtures</td>
</tr>
<tr>
<td>Carbonates</td>
<td>K$_2$CO$_3, \text{MgCO}_3$</td>
</tr>
<tr>
<td>Polymers</td>
<td>Polysyrrene, polymethylmethacrylate, polycarbonate, polyethylene terephthalate, and nylon</td>
</tr>
<tr>
<td>Metallic alloys</td>
<td>Au$_3$Si, Pd$_3$Si, (Fe-Si-B) alloys</td>
</tr>
</tbody>
</table>


Ionic glasses

An ionic compound can live in a disordered state, can form glasses

Example: Oxide glasses ($\text{SiO}_2$) for which a set of rules was developed if oxygen + metal is present
**Zachariasen Rules**

**For Ionic Oxide Glasses**

1) Oxide glass networks are composed of oxygen polyhedra → metal + oxygen

2) Coordination of oxygen is 2! \( CN(0) = 2 \rightarrow O^{2-} \)

3) Coordination of metal is 3 or 4
   \( CN(M) = 4 \rightarrow \text{Tetrahedra} \quad \text{(SiO}_4\text{)}^4 \)
   \( \text{of Silica (SiO}_2\text{)} \)
   \( CN(3) = 3 \rightarrow \text{Triangles Li} \)
   \( \text{like (BO}_3\text{)}^3^- \) of \( \text{B}_2\text{O}_3 \) & \( \text{Boron O}^{1+} \text{ ion} \)

4) Oxygen polyhedra share corners, not edge or face (to minimize metal repulsion!)

5) Each polyhedra shares at least 3 corners

---

**Figure 6.5-3** The structure of amorphous \( \text{B}_2\text{O}_3 \): (a) the basic building block, a triangular polyhedron \( \text{B(O}_3\text{)}^3^- \); (b) two polyhedra sharing an edge; (c) two polyhedra sharing a corner, with the B—O—B angle slightly different from 180°; and (d) two polyhedra sharing a corner, with the B—O—B angle equal to 180°.
COVALENT GLASSES

lost time: ionic glasses & ZACHARIASEN'S Rule for ionic glasses!

what about covalent glasses?
MUST BE POLYMERS, must love \( T_g > T_{room} \) 
& must be able to COOL DOWN FAST & must love viscous melt.

GLASS = NO DEFECTS

SEMICONDUCTORS: usually build from crystals (reduce defects to increase \( \mu \)), but when \( \mu \) is not a problem, then we can use amorphous semiconductors.

EXAMPLES: solar cells, greed

\( \text{Surface} \rightarrow \text{very expensive Si crystalline, best amorphous Si works fine & no grain boundaries which are the places where corrosion starts!} \)

TABLE 8.5-3 Observed melting and glass transition temperatures for selected polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_m (^\circ \text{C}) )</th>
<th>( T_g (^\circ \text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density polyethylene</td>
<td>137</td>
<td>54</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>170</td>
<td>101</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Polyethylene carbonate</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>Acrilan</td>
<td>185</td>
<td>95</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>265</td>
<td>50</td>
</tr>
<tr>
<td>Cellophane acetate</td>
<td>140</td>
<td>141</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>265</td>
<td>100</td>
</tr>
<tr>
<td>Silica</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Polymethylpentene</td>
<td>120</td>
<td>96</td>
</tr>
<tr>
<td>Polychloroprene</td>
<td>85</td>
<td>20</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>80</td>
<td>50</td>
</tr>
</tbody>
</table>

P19
METALLIC GLASSES

Metals are very fluid once melted
=> hard to remove heat fast
Removing 10^5 K/s, we can make more 20% glass of a metal matrix => 80% metal & 20% polymer
=> only small parts & strips & ribbons & wires

Dope with
IF I NEED A NON METAL OR BAD METAL
Au-Si (80 & 20), Fe-Si-B (78, 9, 13) => tin free
Melt is more viscous and easy to form glasses.

GLASSY METALS ARE SENSITIVE TO HEAT!! HEAT destroys the glass & becomes metal crystalline!!

Again, glass metals have no grain boundaries =>
1) Strong against corrosion
2) Isotropic properties (used for magnetic applications)

METALLIC FOAMS

Increased temperature, melt, and decrease fast while bubbling with inert gas => METALLIC FOAMS, LIKE SPONGES

Used for biomaterials => strong & adsorbent & lightweight (bones)
good tissue good
Rubbers & Elastomers

It's when $T_g < \text{Troom}$, but not only.

Remember

Thermoplastic $\Rightarrow$ no secondary bonds, $\Rightarrow$ when $T > T_g$ viscosity decreases and material flows

Thermoset $\Rightarrow$ plenty of bonds $\Rightarrow T > T_g$ get more linked and material gets strong

Thermoset Elastomers

$\Rightarrow$ have few available bonds to make few cross links

Thermoset

Heavy, brittle, stiff

Much cross linking (1/10)

Few extra

Thermoset Elastomers

Soft, rubbery, rubber band style

Little cross linking (1/1000)

Controlling concentration of "extra"

We can control final product

Medium (1/1000)

Tires for cars!

Thermoset Elastomers do not really melt.

They get stiffer and then burn!
Figure 6.6-1: The structure of polybutadiene: (a) as a thermoplastic polymer, and (b) as a crosslinked rubber.

Silicone rubber (CAULKING COMPOUNDS)

Polydimethylsiloxane

$\text{Si} + \text{Oxygen}$
Thermoplastic Elastomers

When thermoplastic is heated, becomes viscous: loses shape

⇒ How can we fit the shape and make it elastic?

⇒ Need to fight viscosity keeping elasticity

Block Copolymers!

\[(HRA)_A - -(HRA)_B -(HRA)_B - (HRA)_A \ldots\]

- A \(N_A\) times
- B \(N_B\) times

KEEP FLEXIBLE & NOT CROSS LINKED! SO IT MAKES CROSS LINKS

⇒ GETS HARD & RIGID

⇒ ELASTIC

When high temperature melts because the long soft segments (no secondary bonds) but at lower temperature is elastomeric
can stretch properly with site on blocks!

Figure 6.1-3 Copolymers and thermoplastic rubbers: (a) a schematic illustration of a block copolymer, and (b) the structure of the triblock copolymer thermoplastic rubber: polystyrene-polybutadiene-polybutadiene.
CRYSTALLIZATION OF RUBBERS

melted

monomer

\[ \text{parallel} \]

\[ \text{crystallization} \]

\[ \text{stretch} \]

\[ \text{ favors plasticity} \]

\[ \text{remove heat} \]

\[ \text{free elasticity} \]

\[ \text{get cold} \]

\[ \text{keep shape} \]

\[ \text{go back to the original shape} \]

\[ \text{set heat} \]

\[ \text{at} \]

EXAMPLE

THERMO SHRINKING MATERIALS

usefull in electronics

PILES that shrink with heat gun

FIGURE 6.5-4 Changes in polymer structure as a result of an applied load: (a) unaligned chains in an unloaded polymer, and (b) chains aligned under an applied load.

P24
Young's Modulus $\&$ Temp

\[ \sigma = E \varepsilon \]

\[ E(t) \]

- **Newton's Laws**
- Viscosity

**Figure 6.6-5** The relationship between modulus and temperature. (a) An amorphous uncrosslinked polymer. (b) The influence of increasing percent crystallinity. (c) The influence of increasing crosslink density.

With semicrystalline and cross-linked density the glossy transition "disappears", softens!!
Rubber Elasticity

Elastomers = stretch 10 times and come back to original shape!!

How? stretching original fiber directions

---

Figure 6.6-6: A comparison of (a) the random coil conformation of an unstretched rubber, and (b) the stretched, or planar zigzag, conformation in which the separation distance between the chain ends is maximum.

---

Stretch A to get B

Resarrangement of bond directions!

No elongation of bonds

Therefore no elastic energy, only few % from bond stretching but in elastic entropy change

---

Stress from bond stretching only few %
Now all logs of $c^{\frac{S}{T}}c$ are along the same diagonal!!!

$$L_{\text{ext}} = m \log_2 \left( \frac{\theta}{\sigma} \right) \quad \text{for extended}$$

$$L_{\text{coil}} \approx 2\sqrt{m} \frac{1 + \cos \theta}{1 - \cos \theta}$$

Max strain $= \frac{L_{\text{ext}} - L_{\text{coil}}}{L_{\text{coil}}} = \frac{L_{\text{ext}}}{L_{\text{coil}}} - 1 \geq 1.15 \sqrt{m} = \text{HUGE}$

$m \geq 10^2 \text{ to } 10^5$

Max strain $\approx 10$ to $300$ times

HUGE

all elastic energy goes in uncoiling.

ENTROPIC EFFECT

$$S = k \log_2 \mathcal{F}(E)$$

fold configurations with energy

$S \approx 0$

many confi.

$S = \text{HIGH}$

on stretching $S \downarrow$

$\Rightarrow \text{TAS} \rightarrow \Delta \Psi$ produced

P27

Elastomers SHRINK UPON HEATING
PHASE EQUILIBRIA & DIAGRAMS

→ Many identical "things" join together creating phases!

PHASE = A CHEMICALLY & STRUCTURALLY HOMOGENEOUS REGION OF THE MATERIAL

→ If I choose T, P, or composition, it can happen that the phase of a system changes!

⇒ I need to plot a "phase diagram" to describe such behavior

→ We show phase diagrams @ EQUILIBRIUM, therefore we do not represent superheated solids & supercooled liquids!

→ Components of a phase

THE CHEMICALLY DISTINCT & ESSENTIALLY INDIVISIBLE SUBSTANCES

EXAMPLE: take pure Al

Pure Al ⇒ Form FCC structure

⇒ 1 COMPONENT (Al) @ 1 PHASE (FCC)

• Take FCC, add water (liquid)

⇒ 1 component (H2O) & 2 PHASES (solid ice) + (liquid water)

• Take copper (is FCC), take Ni, is FCC

Cu + Ni mixed together FORM a random solution of Cu & Ni ⇒ SOLID SOLUTION

⇒ 2 components (Cu) + (Ni) @ 1 PHASE (solid solution random FCC)

• Window's glass

SiO2 + Na2O + CaO ⇒ 3 components (SiO2) + (Na2O) + (CaO)

& 1 PHASE (amorphous)!
ONE COMPONENT SYSTEM

WHAT can I change? P, T, Comp (No) \Rightarrow P&T only

How many degrees of freedom? 2 ⇒

P \quad PHASE
\downarrow \quad DIAGRAM
T \quad const \ P = \text{ISOBARS}
\quad \text{(V = const, ISOCONCENTRATES)}
\quad \text{const} \ T = \text{ISOTHERMS}

ONE COMPONENT
PHASE DIAGRAM

LINES =
PHASE'S
BOUNDAIES

REGION =
PHASES

\text{TT, PT, Tc, Pc} \quad \text{TRIPLE POINT}
\quad \text{SOLID, LIQUID & VAPOR CONEFFECT}

\text{Tc, Pc} \quad \text{CRITICAL POINT}
\quad \text{LIQUID & VAPOR BECOME A SINGLE CAR}

\text{PE2}
**GIBBS PHASE RULE**

*At Equilibrium:*
- \( F = \# \text{ number of degrees of freedom} \)
- \( C = \# \text{ of components} \)
- \( P = \# \text{ of coexisting phases} \)
- \( Z = \# \text{ of state variables} \)

\[ F = C - P + 2 \]

**(If P is Fixed)\( \Rightarrow F = C - P + 1 \)**

**Example:** Pick \( H_2O \) with water liquid and ice
- \( C = 1 \)
- \( P = 2 \)

\[ F = 1 - 2 + 2 = 1 \Rightarrow \text{ there are 2 phases} \]

I can change only one variable, \( T \) or \( P \),

\[ \begin{array}{c}
\text{IF I change } P \\
T \text{ will follow } T(p) \text{.}
\end{array} \]

\[ \begin{array}{c}
\text{IF I change } T \\
P \text{ will follow } P(T) \text{.}
\end{array} \]

\( \Rightarrow \) coexistence of 2 phases, with 1 component
leads to a curve 1-dimensional \( T(P) \) or \( P(T) \)

**Locus**

\[ \begin{array}{c}
\text{need only 1 coordinate to describe!}
\end{array} \]
2nd Example: Pick $\text{H}_2\text{O}$ at when ice, liquid, vapour coexist $\Rightarrow C = 1 \quad P = 3$

$F = 1 - 3 + 2 = 0$

$\Rightarrow$ triple point is a 0-dimensional locus

OD = NO FREEDOM = INVARIANT $\Rightarrow$ A POINT

3rd Example: Pick $\text{H}_2\text{O}$ vapour $\Rightarrow C = 1 \quad P = 2$

$F = 1 - 1 + 2 = 2$

$\Rightarrow$ Vapour is a 2-dimensional locus,
a part of a plane with 2 coordinates to be described $\Rightarrow$ A REGION

\[ \text{DIMENSION OF THE LOCUS} \]
MORE COMPLEX ONE-MEMBER-COMPONENT SYSTEMS

Temperature (°C)

Pressure (kbar)

Iron

Pressure (GPa)

Temperature (°C)

SiO2
**TWO-COMPONENT SYSTEMS**

```
CONCENTRATIONS
WEIGHT = ATOMIC

\[ C_{A}^{\text{at}} = \frac{C_{A}^{W}}{W_{A}} = \frac{C_{A}^{W}}{C_{A}^{W} + C_{B}^{W}} \]

\[ C_{A}^{\text{at}} + C_{B}^{\text{at}} = 1 \]

ATOMIC \( \Rightarrow \) WEIGHT

\[ C_{A}^{W} = \frac{C_{A}^{\text{at}} \times W_{A}}{C_{A}^{\text{at}} + C_{B}^{\text{at}} \times W_{B}} \]

\[ C_{A}^{W} + C_{B}^{W} = 1 \]

EXAMPLE

\[ C_{H}^{\text{at}} (\text{H}_{2}O) = \frac{2}{2+1} = \frac{2}{3} \]

\[ C_{H}^{W} (\text{H}_{2}O) = \frac{2}{2+16} = \frac{1}{9} \]

\[ W_{A}^{\text{at}} \& W_{B}^{\text{at}} \text{ atomic weight of } A \& B \]

\[ C_{A}^{\text{at}} \& C_{B}^{\text{at}} \text{ atomic concentrations} \]

\[ C_{A}^{W} \& C_{B}^{W} \text{ weight concentrations} \]

MOLAR mix \( n_{A} \) moles of A \& \( n_{B} \) moles of B

\[ N_{A} = \frac{n_{A}}{n_{A} + n_{B}} \quad \& \quad N_{B} = \frac{n_{B}}{n_{A} + n_{B}} \]

\[ N_{A} + N_{B} = 1 \]

**SOLUBILITY**

Put sugar in water = solute \& solvent

If \[ C_{\text{sugar}} < C_{\text{MAX sugar}} = \text{sugar does not precipitate} \]

\[ C_{\text{sugar}} (T) = \text{SOLUBILITY LINE} \rightarrow \text{max solute without precipitation} \]

PE6
2-COMPONENTS SYSTEM A&B

ISOMORPHOUS DIAGRAM FOR IDEAL

DEFINITIONS
ISOMORPHOUS = if you mix A & B, at low temperature they form a solid-solution

WHEN SOLID-SOLUTIONS? when A & B similar?

HUME-ROTHERY RULES:
1) SIZE A & B OFF OF NA+ 15%
2) ELECTRONEGATIVITIES ARE OXIDE
3) VALENCE ARE SIMILAR
4) CRYSTAL STRUCTURE OF PURE A & B IS IDENTICAL

EX: Cu+Ni form a solid-solution = random mix of A & B with a structure

Cu = Ni; they are isomorphous

DRAW CONSTANT PRESSURE (1 ATM)

COMPOSITION DIAGRAM

T

PURE A

A

PURE B

B

Tm(A) < Tm(B)

SUPPOSE

IDEAL LENS SYSTEM

PE7
FIGURE 7.3-1
The idealized binary [A-B] isomorphous system: (a) the composition-temperature phase diagram with associated definitions, and (b) a similar diagram showing the liquidus and solidus temperatures for a specific alloy of composition $X_0$.

---

IDEAL SYSTEM

\[ \text{Solid Solution} \]

LENS

---

\[ P = \text{const} \quad \Rightarrow \quad F = C - P + 1 \]

Origin is Gibbs Rule Consistency

Look for Two Phase Regions

Pure A (or B)

\[ L = C = 1 \quad F = 1 - 2 + 1 = 0 \]

\[ \Rightarrow \text{Point } \theta \text{ Coexisting Has No Freedom} \]

Mix $A + B \rightarrow C = 2$

\[ F = 2 - 2 + 1 = 1 \quad \Rightarrow \]

THERE IS AN INTERVAL (1)

FOR WHICH 2 PHASES COEXIST!

PE8
MEASUREMENT SCHEME

**PURE A** \( T_m(A) = 1000 \) K

Mix A & B \( C_B = 10\% \Rightarrow 2 \) PHASE INTERVAL \([900, 700]\) K

\[ C_B = 30\% \Rightarrow 2 \) PHASE INTERVAL \([800, 600]\) K

\[ C_B = 60\% \Rightarrow 2 \) PHASE INTERVAL \([700, 500]\) K

**PURE B** \( C_B = 100\% \Rightarrow T_m = 600 \) K

PEG
How much liquid & solid and now which composition they have?

Remember that you are at equilibrium (go up down in temperature). Inside a 2-phases region which concentration?

Pick concentration & temperature of your mix

\[(C, T) = \text{STATE POINT}\]

**Figure 7.3-2** Graphical definitions of the tie line and the lever rule in a two-phase field. (a) the tie line through the state point defined by temperature \(T_1\) and alloy composition \(X_b\), and (b) the same tie line shared by all five alloy compositions at temperature \(T_1\).

Draw horizontal line at \((T_1, C_1)\) then is \(\text{TIE LINE}\)

C or + (both works if so I use + but you should try to use c)
**LEVER RULE**

\[ X = \text{conc of } B \]

**CONSERVATION OF MASS**

\[ M_0 X_0 = M_L X_L + M_S X_S \]

\[ X_0 = \left( \frac{M_S}{M_0} \right) X_S + \left( \frac{M_L}{M_0} \right) X_L \]

\[ X_0 = f_S X_S + f_L X_L \]

**CONSERVATION OF TOTAL MASS**

\[ M_0 = M_L + M_S \Rightarrow 1 = f_L + f_S \]

\[ f_L + f_S = 1 \]

\[ f_S X_S + f_L X_L = X_0 \]

\[ f_S = \frac{X_0 - X_L}{X_S - X_L} = \frac{X_L - X_S}{X_L - X_S} \]

\[ f_S = \frac{X_0 - X_S}{X_L - X_S} = \frac{X_S - X_0}{X_S - X_L} \]

**Solutions**

**But difficult**

**If not**

**TRY RULE**
A schematic illustration of the lever rule. The tie line represents a "lever" with its pivot point located at the alloy composition \(X_0\), its left end fixed at "position" \(X_L\), and its right end located at \(X_S\) with blocks of mass \(M_L\) and \(M_S\) resting on either end.

\[ M_S \text{ at the right depends on the LEFT part of the pivot} \]
\[ f_S = \frac{X_0 - X_L}{X_S - X_L} \]

\[ M_L \text{ at the LEFT depends on the LEFT part of the pivot} \]
\[ f_L = \frac{X_S - X_0}{X_S - X_L} \]

\[ \Rightarrow \text{ LIQUID} \]

FRACTION SOLID  
FRACTION LIQUID

DIVIDE BY THIS

SOLID
**Example**

![Graph showing liquid and solid phases for different alloys]

**Alloy 1**

$X_B = 0.21$

$\text{fs} = \frac{0.21 - 0.2}{0.4} = 0.025$

$\text{fL} = 0.975$ (almost all liquid)

**Alloy 2**

$X_B = 0.3$

$\text{fs} = \frac{0.3 - 0.2}{0.4} = 0.25\%$

$\text{fL} = 75\%$ (most liquid)

**Alloy 3**

$X_B = 0.4$

**Alloy 4**

$X_B = 0.5$

**Alloy 5**

$X_B = 0.59$

\[PE 13\]
SOLIDIFICATION of an ISOMORPHOUS IDEAL ALLOY

FIGURE 7.3–4 Equilibrium solidification of alloy 1 (composition 0.6 B): (a) the cooling path and sketches showing the development of the microstructure, and (b) an expanded section of part (a) showing the compositions of the liquidus and solidus boundaries in the range of 1010°C to 1060°C.
SOLIDIFICATION

DIAGRAM:

Determination: Mix, T↑, T↓ & Watch Liquid, Solid
OR: T↓ and watch for heat flow out

ISOMORPHOUS SYSTEMS: Form solid solution @ low temp

Cu-Ni: FCC
NiO-MgO (both NiOCC) = FCC with basic oxide amide

WHY I HAVE LENS? Because of ENTROPY!

A-A Bond \( E_{AA} \)
B-B Bond \( E_{BB} \)
A-B Bond \( E_{AB} = \frac{1}{2} (E_{AA} + E_{BB}) \) IDEAL →

⇒ MIN ENERGY

PE15
But remember that we have to minimize $G = E + PV - TS$ for entropy effect.

\[ T_{BM}(B) \]

\[ T_B(A) \]

\[ C_B(T) \]

\[ C_B(T) \] in ideal straight line $\Rightarrow x_B \& x_A = 1 - x_B$

\[ T \]

but here temperature $\Rightarrow$ defects form $\Rightarrow$ some B are A & vice versa

$\Rightarrow x_B \rightarrow x_B + \Delta x \quad x_A \rightarrow x_A - \Delta x$

$\Rightarrow \Delta x$ defects on energy required to form (with Arrhenius)

$\Rightarrow S(\Delta t) = k \left[ \log (x_B + \Delta x) \log (x_B + \Delta x) + (x_A - \Delta x) \log (x_A - \Delta x) \right]$

\[ \mu_{\text{mi}} (E + PV - T(S(\Delta t) - S(\Delta t)')) \]

$\Delta t$ depends on energy to form defect with Arrhenius
FIGURE 7.3–6 Four binary isomorphous systems, Cu-Ni, Ge-Si, Ag-Au, and NiO-MgO.
DEVIATION FROM IDEALITY

- IDEAL
  \[ E_{AB} = \frac{1}{2} (E_{AA} + E_{BB}) \]

- CLUSTERING TENDENCY
  \[ E_{AB} > \frac{1}{2} (E_{AA} + E_{BB}) \Rightarrow E_{AB} \text{ is not "welcome" higher than ideal} \]
  
  It means that A prefers A to B
  & B prefers B to A.
  They do not want to mix too much.

  \[ \Rightarrow \text{to minimize total energy} \]
  
  Temperature tries to destroy as soon as possible the solid phase.

  \[ \Rightarrow \min(E) \]

- ORDERING TENDENCY
  \[ E_{AB} < \frac{1}{2} (E_{AA} + E_{BB}) \Rightarrow E_{AB} \text{ is "welcome" lower than ideal} \]
  
  It means that A prefers B to A
  & B prefers A to B.
  They want to order

  \[ \Rightarrow \text{Temperature needs to work hard to destroy ordering!} \]
Now ideal

\[ E_{AB} > \frac{E_{AA} + E_{BB}}{2} \]

Can be a "banana" solid + liquid

because here I would split therefore the lower part would be just solid

"banana" lens does not exist!!
CONGRUENT MELTING

SAME FOR ORDERING

⇒ NOT PHYSICAL

⇒ THE LIQUIDUS & SOLIDUS

MUST "TOUCH" AT THE MIN AND MAX

CONGRUENT MELTING

(COMPOSITION OF LIQUID & SOLID CONEXISTING ARE SAME)

ORDERING OF AB ⇒ mixing increase the melting temperature!

FIGURE 7.3-7 Progressive change in the form of the isomorphic phase diagram as the solid and liquid phases deviate from ideal behavior.
At the congruent melting point, the alloy solidifies/wets the crucible at a given temperature \( T_{\text{m}}(c) \) and concentration \( c \) and not in a temperature interval.

**Figure 7.3-8**
A binary phase diagram showing a congruently melting alloy of composition \( \chi_{\text{m}} \). Two additional alloy compositions are shown.

If you want to make an alloy which resists at higher temperature than the constituents, than you need something like this

![Planes](image)

If you want to make an alloy which melts at lower temperature than the constituents, than you need something like this

![Welding Soldering Cast](image)

PE21
EUTECTIC PHASE DIAGRAM

If CLUSTERING (A like A better than B) slow at low temperature the two elements do not mix well and solid solution disappears.

\[ \begin{align*}
Q_1 &= \text{solid solution A-rich} \\
Q_2 &= \text{solid solution B-rich}
\end{align*} \]

Depending on the

Above Tc COMPLETE SOLUBILITY

UNDER Tc PARTIAL SOLUBILITY

A with B with sol & B with A with sol

FIGURE 7.4-1 The development of a eutectic reaction by increasing the clustering tendency in the solid phase:
(a) the diagram for an ideal system, and (b-d) increasing clustering tendency in the solid phase.
**SOLVUS**

Solvus = max solubility of a specie in the other.

**EUTECTIC POINT**

Coexistence of 3 phases

\[ F = C - P + 2 \]

\( F = 0 \)

**INVARINT** \(
= \text{Eutectic point}
\)

**FIGURE 7.4-7**

Representative microstructures of Al-Si alloys.

(a) The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. (b) Only the eutectic constituent is seen. (c) Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent.

(Courtesy of Ralph Napolitano)
Melting of an eutectic alloy

go down at $X_E$ concentration through the T epollut

FIGURE 7.4–3 A binary eutectic equilibrium phase diagram showing the changes in composition of the phases present as the temperature is changed by an amount $\Delta T$ above and below the eutectic isotherm.

with (E) $L \xrightarrow{\beta} \alpha + \beta$

at eutectic point $\beta$ at $\Delta T$ all liquid! $\alpha + \beta$ all solid!

Eutectic $X = X_E$

$X_E \xrightarrow{\beta} X_1 + X_2$

OFF EUTECTIC ($X = X_E$)

$X_0 \xrightarrow{\beta} L_{X_0} \xrightarrow{\beta} X_5$

$T_2

$X_5 \xrightarrow{\beta} \alpha + \beta$

$T_m \xrightarrow{\beta} 2X_5 + \text{NEXT PAGE}$

FIGURE 7.4–4 Equilibrium solidification of an off-eutectic alloy of composition $X_0$. 
SOLIDIFICATION OF AN EUTECTIC ALLOY BUT OFF-EUTECTIC COMPOSITION

FIGURE 7.4-4 Equilibrium solidification of an off-eutectic alloy of composition $X_E$

@ $T_1$

$L(X_{L_1}) \rightarrow \delta(X_{S_1}) + L(X_{L_1})$

\[ f_{S_1} = \frac{X_{L_1} - X_0}{X_{L_1} - X_{S_1}} \quad \text{and} \quad f_{L_1} = \frac{X_0 - X_{S_1}}{X_{L_1} - X_{S_1}} \]

@ $T_2$

$\delta(X_{S_2}) + L(X_{L_2}) \rightarrow f_{S_2} \downarrow f_{L_2}$

\[ f_{S_2} = \frac{X_{L_2} - X_0}{X_{L_2} - X_{S_2}} \quad \text{and} \quad f_{L_2} = \frac{X_0 - X_{S_2}}{X_{L_2} - X_{S_2}} \]

@ $T_0 = T_E$ (+) \[ \delta(X_{S_E}) + L(X_{L_E}) \]

\[ f_{S_E} = \frac{X_{L_E} - X_0}{X_{L_E} - X_{S_E}} \quad \text{and} \quad f_{L_E} = \frac{X_0 - X_{S_E}}{X_{L_E} - X_{S_E}} \]

@ $T_0 = T_E$ (-)

$\delta(X_{S_E}) + \beta(X_{S_E}) \rightarrow 3 \text{ PHASES}$

\[ \delta(X_{S_E}) \rightarrow \frac{L(X_{S_E})}{\delta(X_{S_E}) + \beta(X_{S_E})} \]

\[ f_{S_E} = \frac{X_{S_E} - X_0}{X_{S_E} - X_{S_E}} \quad \text{and} \quad f_{L_E} = \frac{X_0 - X_{S_E}}{X_{S_E} - X_{S_E}} \]

but a lot of $\delta$ and $\beta$ form simultaneously in the same way fractions:

\[ f_{S_1} = \frac{X_{S_E} - X_0}{X_{S_E} - X_{S_E}} \quad f_{S_2} = \frac{X_0 - X_{S_E}}{X_{S_E} - X_{S_E}} \]

\[ f_{S_2} = \frac{X_0 - X_{S_E}}{X_{S_E} - X_{S_E}} \]

in the time it has to rearrange

\[ \beta \leftrightarrow \delta(X_{S_E}) \quad \text{NORM} \]

25
AT EUTECTIC POINT, a lot of $\alpha$ and $\beta$ form SIMULTANEOUSLY, and their MORPHOLOGY IS DIFFERENT FROM THE PRIMARY $\alpha$ and $\beta$! (IT'S BECAUSE OF THE SPEED (TC))

$\implies$ therefore below EUTECTIC POINT $\downarrow$ PRIMARY $\uparrow$ EUTECTIC ($\alpha + \beta$) $\iff$

...The alloy is a mixture of $\alpha +$ EUTECTIC ($\alpha + \beta$)

Note that for any alloy with composition in the range $X_{SE} < X_0 < X_{SE}'$, at the eutectic temperature liquid of composition $X_{LE}$ will transform to $\alpha$ and $\beta$ of compositions $X_{SE}$ and $X_{SE}'$, and that the relative amounts of $\alpha$ and $\beta$ formed from this liquid will be constant. In fact, this is what makes the eutectic reaction invariant.

UNLESS... you go super slow, you always get EUTECTIC ($\alpha + \beta$)

---

**EXAMPLE**

Composition 0.27 B. Calculate the following quantities:

a. The fraction of primary solid that forms under equilibrium cooling at the eutectic temperature.

b. The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

c. The amount of $\alpha$ and $\beta$ that will form from the liquid just below the eutectic isotherm.

d. The total amount of $\alpha$ phase in the alloy at a temperature just below the eutectic temperature.

---

**a)**

The fraction of primary solid that forms under equilibrium cooling at the eutectic temperature.

$$f_p = \frac{X_L - X_0}{X_L - X_\alpha} = \frac{37 - 27}{37 - 20} = 0.588$$

**This is 2-PRI**

 Primary $\implies X_{SE} = 20%$
b. The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

\[ f_L^\text{tr} = \frac{X_\text{L} - X_a}{X_a - X_n} = \frac{27 - 20}{37 - 20} = 0.412 \]

\[ L_{\text{Eut}} \text{ loss} \]

\[ X_{nE} = 37\% \]

\[ = 1 - f_\text{Pb} \text{ hesson.} \]

c. The amount of \( \alpha \) and \( \beta \) that will form from the liquid just below the eutectic isotherm.

Liquid at \( T = 600^\circ \text{C} \) concentration:

\[ X_{nE} = 37\% \] (Eut. Liquid just below the Eutectic Point it becomes Solid Eut Solid \( \alpha + \beta \) with \( f_\alpha f_\beta \))

\[ f_\alpha = \frac{X_\beta - X_a'}{X_a' - X_a} = \frac{73 - 37}{73 - 20} = 0.679 \]

\[ f_\beta = \frac{X_a' - X_\beta}{X_\beta - X_a} = \frac{37 - 20}{73 - 20} = 0.321 \]

\[ \Rightarrow \text{ I have } \]

\[ \alpha^p + \text{ Eut } (\alpha + \beta) \]

\[ f_\alpha^p = 0.588 \]

\[ f_\text{Eut} \]

\[ f_\beta \]

\[ f_\text{L} = f_\text{S} = 0.412 \]

\[ \Rightarrow \text{ which } \]

\[ f_\alpha = 0.679 \]

\[ f_\beta = 0.321 \]

\[ 0.412 \times 0.321 = 0.132 \]

\[ 0.588 \times f_\alpha = 0.412 \times 0.679 = 0.280 \]

\[ \Rightarrow f_\text{L} f_\beta = 0.412 \times 0.321 \]

\[ f_\alpha = 0.588 \]

PE27
d) The total amount of $\alpha$ phase in the alloy at a temperature just below the eutectic temperature.

\[ f_{\alpha}^{\text{total}} = f_\alpha^0 + f_\alpha^{\text{eut}} \]

\[ 1 - f_\beta = \frac{X_\beta - X_0}{X_\beta - X_\beta^\alpha} \]

Alternatively, since the microstructure is composed of just two phases, $\alpha + \beta$, the total fraction of $\alpha$ must be given by:

\[ f_{\alpha}^{\text{total}} = 1 - f_\beta^{\text{total}} = 1 - 0.132 = 0.868 \]
Figure 7.4-8

Cars (Pistons)
HARD, Si ⇒ Wear
Look at page PE 23

Clusters (Tendency) = RESIST

Al = LIGHT

PE 29
**Figure 7.4-7**
Representative microstructures of Al-Si alloys.
(a) The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. (b) Only the eutectic constituent is seen. (c) Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent.
(Courtesy of Ralph Napolitano)
HOW TO MEASURE

melt & watch T(x) behaviour

Temperature profiles (c)

Properties profile (c)

PE31
TWO EUTECTICS

A likes A more than B \( \Rightarrow \) \( E_{AB} > \frac{1}{2} (E_{AA} + E_{AB}) \) \( \Rightarrow \) CLUSTERING TEM
\[ \Rightarrow \text{WEAKER SOFT SOLUTION} \]
\[ \Rightarrow \text{STRONGER LIQUID} \]
\[ \text{Low Temp} \quad \text{MISCEIBILITY GAP} \]

A likes B more than A \( \Rightarrow \) \( E_{AB} < \frac{1}{2} (E_{AA} + E_{AB}) \) \( \Rightarrow \) ORDERING TEM
\[ \Rightarrow \text{STRONGER SOLID SOLUTION} \]
\[ \Rightarrow \text{WEAKER LIQUID} \]

TAKE 2 ATOMS \( (AA) \), \( (AB) \), \( (BB) \)

If \( (AA) \) likes \( (AA) \) more than \( (AB) \) (depends from structure)
\[ \Rightarrow \] \( E_{AA-AA} > \frac{1}{2} (E_{AA-AA} + E_{AA-AB}) \)
\[ \Rightarrow \]

IF low temperature IMMISCIBILITY of \( AA \& AB \)
\( (NO \ SOLID \ SOLUTION) \) \( \Rightarrow \)
The system can form an eutectic between 0 & 50%.

**Rule:** Between two chemical compounds, you can form an eutectic (can = may ≠ must = has to).

**Figure 7.4-11** (a) A binary equilibrium phase diagram containing two eutectic reactions illustrating solid solution ranges, an intermediate phase \( \beta \), and a congruent melting reaction. (b) When the solubility of the intermediate phase becomes limited, the line compound \( AB \) results.
If no solubilities

A does mixing with B
But only in the liquid, please they do because the higher entropy of the liquid.
PERITECTIC SYSTEMS

1) If A clusters A + more than B (CLUSTERING) at low temperature (MISCIBILITY GAP)
2) Melting point very different
3) If A clusters A more than B else at high impurity (CLUSTERING OF LIQUIDS) LENS BECOME WIDER

![Diagram of peritectic system]

**Figure 7.5-1** Development of a peritectic system by increasing the clustering tendencies of the solid and liquid phases. The clustering tendency for the solid is greater than that of the liquid. (Source: Adapted from Albert Prince)
**Figure 7.5-2**  (a) A binary peritectic phase diagram and the associated terms used to describe regions of a peritectic system. (b) A simple peritectic system showing the equilibrium cooling of an alloy whose composition is the peritectic composition $X_p$, and (c) the corresponding cooling curve for alloy $X_p$.

**Figure 7.5-3**  A simple peritectic diagram showing three specific alloy compositions. Refer to Example 7.5-1 for a discussion of this phase diagram.
**MONOTECTIC PHASE DIAGRAM**

- The eutectic but for liquids.
- Liquid A solv. liquid B = Eutectic point
-miscibility gap for Formols (region L, L) and results: Liquid 1 & Liquid 2 outside.

\[ \text{Oil + Water} \]

Mix only at high temp.

\[ \text{L} \]

- L becomes solid
  - L

\[ \text{Nono} \]

\[ \text{Invariant Point} \]

3 phases

\[ F = C - P + \frac{3}{2} \]

- Only real 2
- Mix not +

PE 37
Remember:

- **CONGRUENT MELTING**
  
- **EUTECTIC POINT**
  \[ L \leftrightarrow \gamma \]
  \[ L \leftrightarrow \gamma + \beta \text{ (eutectic)} \]

- **PERITECTIC POINT**
  \[ L + \gamma \xrightarrow{\beta} \]

- **NONEUTECTIC POINT**
  \[ L_1 \leftrightarrow L_2 + \gamma \text{ (more eutectic)} \]

**FIGURE 7.7-1** (a) Complex phase diagram containing a peritectic and two eutectic reactions, and (b) the invariant reactions in (a) emphasized along with their isometric representations. When the \( \beta \) phase is heated to the peritectic temperature, an incongruent melting reaction occurs at \( T_p \), the peritectic temperature.
Idea: Break phase diagrams in as many parts as possible. It becomes easier.

Extra trouble:

- **Incongruent Melting**: If liquid solidifies to a phase with different concentration?

  \[ L + ? \rightarrow \beta \]

  How is this possible?

  \[ X_L \quad \text{something else} \quad X_B \neq X_A \]

  \[ L + A \rightarrow \beta \quad \Rightarrow \quad \text{euh...} \]

  \[ \text{in peritectic} \]

If no solubilities on intermediate phases, no solubilities. Phases (broad concentration) \( \rightarrow \) compounds \( \gamma, \beta, \ldots \rightarrow A, B, A_2B, \ldots \)

**Figure 7.7-2**: A diagram similar to Figure 7.7-1, but the \( \beta \) and \( \gamma \) are seen as line compounds. The \( \alpha \) and \( \delta \) phases are terminal solid solutions with essentially no solubility. Thus, they are simply labeled A and B, corresponding to the pure components.
It is worth noting that α(Ni-Al) is often called γ' and is the basis of strengthening in Ni-base superalloys.

\( \gamma' \) is fundamental in strengthening of Ni-superalloys.

Precipitates of \( \gamma' \) form and agglomerates that stop dislocation movements, break plasticity, no DR formation, keep elasticity permanent.

Superalloy!!
PHASE EQUILIBRIA WITH SOL-SOL REACTION

LIQUID REACTION

L → γ + β EUTECTIC
L + γ → β PERITECTIC
L + γ → L₂ + γ NONSTECTIC

SUBSTITUTE

EUTECTIC

γ + β → L with a slow solid

PERITECTIC

γ + L → β, γ + L₂ → γ + β

NONSTECTIC

γ + L₂ → γ + β

FIGURE 7.8-1

A general eutectoid equilibrium phase diagram with associated phase definitions.

EUTECTOID SYSTEM

SOLID PH. decomposes in 2 SOLID PHASES

γ → γ + β

EUTECTIC

T

L → γ + β

Reactions are fast because diffusion in L is fast → γ, β low time to form & separate

EUTECTOID

T

γ → γ + β

Reaction are slow

diffusion in solid is slow → γ, β slowly growing
IRON-CARBON HAS EUTECTOID

See: No solubility of Fe in Fe₃C

Figure 7.8-2 The Fe-Fe₃C system with the important phase fields defined.

Book: Take 3 (austenite) with 0.77% w of C & cool down

Eutectoid @ 727°C

\[ \gamma \xrightarrow{\text{PRIH}} \delta + (\gamma + \text{Fe}_3\text{C}) \xrightarrow{\text{EUTECTOID}} \]

\[ \text{Austenite} \xrightarrow{\text{Ferrite}} \text{Pearlite} \]

\[ \rightarrow \text{as long as you have } \gamma \]

(with \( > 0.022 \% \) w of C \( \Rightarrow \) you get pearlite)

In practical words:

We have pearlite all over the place.

PE42
EUTECTOID (α + Fe₃C) = PEARLITE

FIGURE 7.8-3  Structure of the eutectoid composition 0.77 wt. % C steel. The eutectoid constituent, called pearlite, has a lamellar (layered) morphology consisting of alternating plates of α-Fe (light areas) and Fe₃C (dark areas).

COPPER-ALUMINUM

FIGURE 7  The copper-rich side of the Cu-Al system shows a peritectoid reaction in the approximate temperature range of 300-400°C. Symbolically the reaction is written α + γ₂ → α₁. (Source: Adapted from Albert Prince, Alloy Phase Equilibria. 1966. Permission granted from Elsevier Science.)

ZINC

Alum

FIGURE 7.8-5  The Al-Zn systems contain a monotectoid reaction at 275°C. Symbolically the reaction is α₁ → α + β.
KINETICS

KINETIC OF PHASE TRANSFORMATIONS

Equilibrium $\Rightarrow$ PHASE DIAGRAMS
Non equilibrium $\Rightarrow$ KINETIC OF PHASE TRANSFORMATIONS

Kinetic = things change (evolve) $\Rightarrow$ kinetic = evolution = rate at which the phenomenon occurs.

Example: liquid $\Rightarrow$ solid $\Rightarrow$ transformation has time to occur
   - liquid copper to solid copper $\Rightarrow$ no ENERGY STRAIN = volume adopts unde
   - liquid

but solid $\Rightarrow$ solid $\Rightarrow$ transformation has trouble
   $\Rightarrow$ plenty of EVERY STRAIN $\Rightarrow$ value of $\beta$ must (expand) $\beta$ to make you fast.

FIGURE 3.2-1
The aluminium-rich end of the Al-Cu binary phase diagram.

Slow
Slow KINETIC
EASY
PAST KINETIC

K1

IF I remove that too fast (TK FAST)
then I create some microstructures that I might
for practical alloys, many heat treatments are necessary! (to get rid of microstructure)

It's all a matter of temperature! not E but G!!

**Driving Force of a Transform**

\( E \rightarrow \Delta G = -\Delta H + T \Delta S \)

\( H = E + pV \rightarrow \Delta H = Vdp + T \Delta S \)

\( G = E + pV - TS \rightarrow \Delta G = Vdp - SdT \)

\( \therefore \min (G) \rightarrow \) stable equilibrium

**Figure 8.2-2**

An approximation of the variation in free energy for the liquid and solid phases close to the equilibrium melting temperature.

**K2**

Liquid & solids have different S & E ⇒ different slopes!!
transformation: $L \rightarrow S$  

$\Delta G^L \rightarrow S$ is driving force

at constant $T$

$G = H - TS$

$\left( \Delta G^L \rightarrow S = \Delta H^L \rightarrow S - T \Delta S^L \rightarrow S \right) = 0$

**FINAL - INITIAL**

$\Delta G^L \rightarrow S = G^S - G^L$

$\Delta S^L \rightarrow S = S^L - S^S$

$\Delta H^L \rightarrow S = H^S - H^L$

Remember:

$dH = Vdp + Tds$

so if you keep always $p = 1$

$\Rightarrow \ dH = Tds = SdP = \text{internal heat}$

$\Rightarrow \Delta H^L \rightarrow S = S \Delta P = \text{Release or Absorption}$

$\Rightarrow \text{heat during} \ L \rightarrow S$

$\Rightarrow \text{Reaction!!}$

**EXOTHERMIC**

**LATENT HEAT**

**ENDOTHERMIC**

$\Delta G^L \rightarrow S = \Delta H^L \rightarrow S - T \Delta S^L \rightarrow S$

@ melting $T_m$

$\Delta G^L \rightarrow S = 0 \Rightarrow \text{system}$

**SWITCHED STATUS**

$\Delta H^L \rightarrow S - T \Delta S^L \rightarrow S = 0$

$\Delta S^L \rightarrow S = \Delta H^L \rightarrow S \over T_m = S \Delta P \over T_m$

$\Rightarrow \Delta G^L \rightarrow S = \Delta H^L \rightarrow S - T \left( \frac{\Delta H^L \rightarrow S}{T_m} \right)$

$\Rightarrow \Delta T = T_m - T$

$\Delta G^L \rightarrow S = \Delta H^L \rightarrow S \left( 1 - \frac{T}{T_m} \right) = \frac{\Delta H^L \rightarrow S \Delta T}{T_m}$

$\Delta G^L \rightarrow S = \frac{\Delta H^L \rightarrow S \Delta T}{T_m}$

$\Delta T = T_m - T$

$\Delta H \rightarrow S = S \Delta P$

K3
Which is favorite?

\[ \Delta H^{L \rightarrow S} = H^S - H^L = SQ^{L \rightarrow S} \]

\[ \Delta G = \Delta H - T \Delta S \]

Liquids (lower) is the Temptation
(\& bigger is \( \Delta T \)) \( \Rightarrow \) the
stronger is \( \Delta G \) \( \Rightarrow \) stronger
is driving force

Temperature is EVERYTHING

1) \( T \) gives defects (necessity)
2) \( T \) gives entropy (diversity)
3) \( \Delta T \) gives transformation driving force

Nucleation

\[ \Delta H^{L \rightarrow S} < 0 \]
\( \Rightarrow \) at high temp \( T > T_m \)
\( \Delta T = T_m - T < 0 \)
\( \Rightarrow \) \( \Delta G = \frac{\Delta H^{L \rightarrow S}}{T_m} \Delta T < 0 \)
\( \Rightarrow \) \( L \rightarrow S \) is DISFAVORED

\( \Rightarrow \) \( S \rightarrow L \) TRANSFORMATION

\( \Rightarrow \) at low temperature \( T < T_m \)
\( \Delta T > 0 \)
\( \Delta G^{L \rightarrow S} = \Delta H^{L \rightarrow S} \Delta T \frac{L}{T_m} \)
\( \Rightarrow \) \( L \) gets better \( T_m \)
\( \Rightarrow \) \( L \rightarrow S \) is FAVORED!!

FIGURE 8.2-3
Schematic showing (a) a region containing only liquid, and (b) a region containing liquid with a solid and a solid-liquid (S/L) interface.
**Homogeneous Nucleation**

- **Have liquid**
- Cool it under $T_m$ → *solidify*  

$$\Delta G \rightarrow s = \Delta H \frac{\Delta T}{T_m}$$

$$\Delta T = T_m - T$$

$$\Delta G \rightarrow s = G_s - G_l$$

*Exothermic → release heat → $\Delta H \rightarrow s < 0$ (wants to solidify)*

Let $E, S, ...$

This $\Delta G$ is extensive $\left(2V \rightarrow 2\Delta G\right)$

Let's introduce $\Delta G_v = \text{Free energy per unit volume}$

$$\Rightarrow \Delta G = V \frac{\Delta G_v}{(J/m^3)}$$

**Formation of a surface**

Creation of surface requires energy

(like making a chewing gum bubble)

$$\text{Energy} = \frac{\Delta S}{\Delta S_{\text{surf}}} \text{ Surface energy}$$
$\Delta G = 4\pi r^2 \sigma_s + \frac{4}{3} \pi r^3 \Delta G_v^{\text{L-S}}$

The system 

HATES SURFACE LOVES TO SOLIDIFY

**Figure 8.2-4**

The dependence of the various energy terms associated with nucleation as a function of the radius of the growing phase: (a) the relationship between cluster radius and surface energy of growing spherical solid phase in a liquid, (b) the relationship between the cluster radius and $\Delta G_r^{\text{L-S}}$, (c) the sum of the previous two curves, and (d) an annotated version of $\Delta G$ plotted versus $r$ (see footnote 1 on page 294).
Remember that

\[ \min (\alpha) = \text{thermodynamical equilibrium} \]

\[ \Rightarrow \text{G WANTS TO DECREASE} \]

1) all particles \( r < r^* \) will disappear, become liquid & DIE . . .

2) all particles \( r > r^* \) will grow, eating liquid and becoming bigger and bigger solids!!

3) we need to feed the system with more than \( \Delta G^{*} \) to start nucleation

\[ \Delta T / \partial T \Rightarrow \text{easy to nucleate} \]

**Critical Radius**

\[ r^* = \frac{\partial \Delta G}{\partial r} \bigg|_{r^*} = 0 \]

\[ 0 = \frac{\partial \Delta G}{\partial r} = \frac{2}{3} \left[ 4 \pi r^2 x_S^2 + \frac{1}{3} 4 \pi r^3 \Delta G^{L \rightarrow S} \right] \]

\[ = 8 \pi r^2 x_S + 4 \pi r^2 \Delta G^{L \rightarrow S} = 0 \]

\[ 2 x_S + r \Delta G^{L \rightarrow S} = 0 \]

\[ r^* = - \frac{2 x_S}{\Delta G^{L \rightarrow S}} \]

\[ = - \frac{2 x_S T_m}{\Delta H^{L \rightarrow S} \Delta T} \]
So

\[ z^* = -\frac{2 \Delta s}{\Delta H_{lv}^\ddagger} \frac{T_m}{\Delta T} \]

\[ \Delta G^* = \Delta G (z^*) \Rightarrow \text{plug } z^* \text{ into } \Delta G (z) \text{ and obtain} \]

\[ \Delta G^* = \frac{16 \pi \Delta s^3 T_m^2}{3(\Delta H_{lv}^\ddagger)^2} + \frac{1}{\Delta T^2} \]

\[ \Delta T \uparrow \Delta G^* \downarrow \text{ barrier} \]

UNDERCOOLING INCREASES (\( \Delta T \uparrow \)), THE ENERGY BARRIER DECREASES.

**Another problem:** UNDERESTIMATING MOBILITY OF LIQUID DUE TO DIFFUSION OF PARTICLES IN THE LIQUID. The liquid must touch the surface to become solid (particles must be close). At low temperature, diffusion \( \propto \exp (-Q/RT) \) becomes small.

\( T \downarrow D \downarrow \) small feed of particles to seed solid.

**Figure 8.2-5 (a)** The influence of temperature on the mobility term and the nucleation barrier term. The opposing processes result in a maximum in the nucleation rate at an intermediate temperature. (b) Since the time for nucleation is inversely related to the nucleation rate, the time curve exhibits a minimum at an intermediate temperature. Because of its shape, this curve is often referred to as a C curve.
**HETEROGENEOUS NUCLEATION**

- IF WE ADD SOME SUBSTANCE (ANOTHER BIG PARTICLE) TO HELP NUCLEATION.
- WALLS, CORNERS

\[ \Delta G \]

\[ \Delta G \text{? HOW? WETTING PROBLEM} \]

\[ \gamma_{SL} \]

\[ \gamma_{SL} \text{? WETTING PROBLEM} \]

\[ \gamma_{SL} \text{? WETTING PROBLEM} \]

\[ \gamma_{SL} \text{? WETTING PROBLEM} \]

- \( 3 \) SURFACE ENERGIES:
  - Liquid-Solid
  - Liquid-Mold
  - Mold-Solid

\[ \text{Surface energy} = \text{surface tension} \]

\[ \gamma \]

\[ \Delta \gamma \text{STRETCH FILM} \]

\[ \frac{\Delta \gamma}{dx} \text{Tension Force} \]

\[ \gamma \text{Tension, } dx = \gamma \text{d}A \text{d}x \text{ WORK MADE} \]

\[ \text{surface tension} \leq \text{(surface energy)} \]

\[ \text{with direction of tension tangent to direction when surface grows} \]

**SOLID-LIQUID SURFACE GROWTH**

\[ \gamma \text{vapor} \]

\[ \gamma \text{vapor} \]

\[ \text{LIQUID-MOLD SURFACE GROWTH} \]

\[ \gamma \text{vapor} \]

\[ \gamma \text{vapor} \]

\[ \text{SOLID-MOLD SURFACE GROWTH} \]
YOUNG'S LAW $\gamma_{LM} = \gamma_{MS} + \gamma_{LS} \cos \theta$

$\Rightarrow \cos \theta = \frac{\gamma_{LM} - \gamma_{MS}}{\gamma_{LS}}$

Complete wetting:
No barrier to nucleation.

$\theta = 0$
$\theta = \pi/2$
$\theta = \pi/4$

Adding value does not add surface is

$\theta = 0$
$\theta = \pi/2$
$\theta = 3\pi/4$

Adding $\gamma_{	ext{surf}}$

No wetting:
Nucleation indistinguishable from homogeneous nucleation.

Adding $\gamma_{	ext{surf}}$

Volume $\Rightarrow$
ADD HAS SURF

$3\theta/4$
$0.500$
$0.943$
$1.000$

Figure 8.2-6 The wetting characteristics of a number of solid-liquid systems: (a) The angle $\theta$, as defined in the illustration, is an indication of the wetting of the system; (b) as $\theta$ increases from $\theta = 0$ to $\theta = \pi$, the wetting decreases; (c) the function $f(\theta)$ varies from 0 to 1 as $\theta$ varies from 0 to $\pi$.

$\Rightarrow \Delta G_{\text{het}} = \Delta G_{\text{hom}} \cdot f(\theta)$

$\Rightarrow \Delta G^*$

$\eta \rightarrow 0$ (Complete wetting)

No barrier to solidification
IF WE PREVENT WETTING ON SURFACE OF THE MOLD (TiB₂ particles w/ Al)

\[ \text{NO WETTING} \Rightarrow \text{NUCLEATION HETEROGENEOUS} \]

INOCULANT

INOCULANT

\[ \text{NUCLEATION IN RANDOM POSITIONS} \]

\[ \text{LISS HOMOGENEOUS} \]

\[ \text{Larger grains} \Rightarrow \text{better cast} \]

---

**FIGURE 8.2-7** Photomicrographs of a transverse section from a 20-in × 54-in cast aluminum alloy: (a) with an ingot grain refiner, and (b) with an ingot grain refiner. Illustration is half the cross section.
Solid–solid interfaces are different nucleation.

Solid–solid interfaces: what happens if I have a big particle inside a sea (matrix) of other (AₓBᵧ)

MATRIX ← PRECIPITATE ← interface

COHERENT (γ, β same lattice type)

COHERENT INTERFACES: one-to-one atom correspondence.

ONLY

If \( a_\alpha = a_\beta \)

or\( a_\alpha \neq a_\beta \)

then adjust! A LITTLE

\[ a_\alpha = a_\beta, \quad a_\alpha \neq a_\beta \]

**Figure 8.2-8** Schematic illustration of coherent interface between two phases \( \alpha \) and \( \beta \). (a) The crystal structures and lattice parameters are identical. (b) The crystal structures are identical but the lattice parameters are different. The difference in lattice parameters leads to coherency strains. (c) High-resolution image showing the coherent interface that exists between the aluminum matrix and two precipitates that form during artificial aging of an Al-Cu-Mg-Li alloy. The white dots are columns of atoms that form the phase. (d) A schematic of the photomicrograph in part c identifying the phases and the coherent interfaces.
SEMI COHERENT (\( \gamma, \beta \) same lattice, \( a_\gamma < a_\beta \), \( p_{\gamma \beta} \rightarrow \) every once in a while one atom slips out the coherency straw

\[ \Rightarrow \text{INTRODUCE periodic dislocation (depends on direction)} \]

![Interfacial dislocations](image)

**FIGURE 8.2–9**  (a) Schematic of a semi coherent interface between two phases. The insertion of the periodically spaced dislocations eliminates coherence strains but increases the interfacial energy. (b) Regular array of dislocations at the matrix/precipitate interface of a semi coherent precipitate in Astrolay, a high-temperature Ni-base superalloy.  (Source: Photomicrograph courtesy of Mario Luis Maciel).

INCOHERENT (\( \gamma, \beta \) different lattices, \( \gamma_{\alpha r} \) and \( a_\gamma \neq a_\beta \))

![Incoherent Interface](image)

**FIGURE 8.2–10**  An incoherent interface occurs when the crystal structures and lattice parameters of two phases are different.
Remember \[ \Delta G^t = \frac{16\pi (\Delta g)^3 V}{3 (\Delta H_{298})^2} \cdot \frac{1}{(\Delta T)^2} \] for solidification.

<table>
<thead>
<tr>
<th>Type of interface</th>
<th>( \frac{\Delta g}{\beta} )</th>
<th>Interfacial energy</th>
<th>Nucleation process</th>
<th>Location of precipitates</th>
<th>Number of precipitates per unit volume</th>
<th>( \Delta g \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coherent</td>
<td>Increasing</td>
<td>Homogeneous</td>
<td>Easy</td>
<td>Throughout the matrix</td>
<td>(-10^{13} \text{cm}^{-1} \cdot \text{molv}^{-1})</td>
<td>~200 mJ/m²</td>
</tr>
<tr>
<td>Semi-coherent</td>
<td></td>
<td>Homogeneous</td>
<td>Mosty at dislocations</td>
<td>Mostly at dislocations</td>
<td>Orders of magnitude less than homogeneous nucleation</td>
<td>~500 mJ/m²</td>
</tr>
<tr>
<td>Non-coherent</td>
<td></td>
<td>Homogeneous</td>
<td>At grain boundaries</td>
<td>Hard to form</td>
<td>Orders of magnitude less than homogeneous nucleation</td>
<td>~1000 mJ/m²</td>
</tr>
</tbody>
</table>

\( \Delta G_{3\gamma' \rightarrow \beta} \) is called the activation energy for solidification. A lower value of \( \Delta G_{3\gamma' \rightarrow \beta} \) means easier solidification. The \( \Delta g \beta \) for solidification is given by:

\[ \Delta G_{3\gamma' \rightarrow \beta} \propto (\Delta g \beta)^3 \propto \text{NON-COHERENT REALLY DOES NOT WANT TO SEMICHERENT APPEAR} \]

\( \Delta \sigma^* \)

**Coherent** → Precipitates precipitate everywhere (EASY)

**Semi-coherent** → Precipitates precipitate around obstacles (MEDIUM)

**Non-coherent** → Precipitates precipitate only in region of grain boundaries (HARD)

K14

Heterogeneous forming particles growth fast because defects are diffusion channels.
GROWTH OF A PHASE

Nucleation $\Rightarrow$ growth of phase: how it works in time

1. There is a time period, often called the incubation time, required to nucleate the phase; the incubation time is a function of undercooling. No measurable phase transformation occurs during the incubation time.

2. Once nucleated, the phase begins to grow and there is a rapid increase in the amount of new phase present.

3. Eventually, the growth rate of the new phase decreases because of either depletion of solute or physical impingement of the growing phase.

AVRAHI EQUATION

$$x = 1 - \exp\left[ -\frac{(kt)^{m}}{\beta} \right]$$

$\beta \approx kt$

INCUBATION = time required to before some particle appears with $\beta > \beta^*$

$\beta = kT \rightarrow k \approx \frac{1}{2} \text{ incubation}$

$m \rightarrow 0.5 \leftrightarrow 5$

$%$ depend on system & structure

$\%$ transformed
1) Salts and water condenses.
2) Molten salt changes to salt.
3) Water is oxidized and salt condensed.
4) Salt is salted water.
5) Water will go down in temp.
6) Heat water.
7) Put salt on ice.

Example:

Water + Salt

Starting or Nucleation

Fraction Transformed

Transformation Complete

Freedom bound

\[ T_1 \to T_2 \to T_3 \to T_4 \]

\[ T_1 \to T_2 \to T_3 \to T_4 \]
FIGURE 8.2-13 The distribution of precipitates in an aluminum alloy: (a) precipitates that homogeneously nucleated, and (b) those that heterogeneously nucleated. In part a, the precipitates are the fine, perrite-like features that are scattered throughout.

This example illustrates two key points: (1) altering the heat treatment has a significant effect on the size and spatial distribution of the precipitates through its influence on the nucleation and growth rate, and (2) since macroscopic material properties depend strongly on the size and spatial distribution of the phases, heat treatment is a powerful tool for modifying the properties of engineering materials.

PHASES IN STEEL

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perlite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BCT) Fe crystal structure.</td>
</tr>
<tr>
<td>Martensite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BCT) Fe crystal structure.</td>
</tr>
<tr>
<td>Bainite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BCT) Fe crystal structure.</td>
</tr>
<tr>
<td>Spheroid</td>
<td>Spheroidal particles of cementite in a matrix of a ferrite.</td>
</tr>
<tr>
<td>Upper bainite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BCT) Fe crystal structure.</td>
</tr>
<tr>
<td>Upper bainite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BCT) Fe crystal structure.</td>
</tr>
<tr>
<td>Upper bainite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BCT) Fe crystal structure.</td>
</tr>
<tr>
<td>Lower bainite</td>
<td>Ferrite, pearlite, or the dendritic ferrite.</td>
</tr>
<tr>
<td>Cementite</td>
<td>Cementite that forms prior to the austenite transformation.</td>
</tr>
</tbody>
</table>

EUTECTOID

\[ \gamma \rightarrow \alpha + Fe_3C \]

_NO SOLUBILITY of Fe in Fe_3C \_
AUST = liquid

because: PEARLITE = alternation of $\gamma$-ferrite & austenite

INTERFACE

$\gamma$-austenite & pearlite moves during phase transformation

Direction of $\alpha + \text{Fe}_3\text{C}$ growth

Migration of C via $\gamma$-austenite toward $\text{Fe}_3\text{C}$

C cannot move more than a distance

Max displacement (t) = speed of $\gamma$-austenite

Migration = diffusion (D)

\( C \rightarrow \text{higher} \)

Pearlite is coarser

\( C \rightarrow \text{lower} \)

Pearlite is thinner

different external temperature $\Rightarrow$ different pearlite density!!!
IF UNDERCOOLING IS
BELOW 250°C, EUTECTOID AUSTENITE (Γ + F) FORMS.

FIRST, LAWS OR PLANES
WITH CARBENITE BETWEEN γ-FOURIER
PLANE!!
THE Isothermal Transformation Diagram Looks Like

![Isothermal Transformation Diagram](image)

**FIGURE 8.3-6** Schematic of an isothermal transformation (T) diagram for a eutectoid steel.

& Bainite (Planes, Laths) + Plenty of Dislocation

**FIGURE 8.3-5** The microstructure of bainite in an alloy steel isothermally transformed at: (a) 405°C, and (b) 412°C.
- Pearlite & Bainite Form if undercooling lies T between 220°C to 727°C (Eutectoid Temp.)

C inside γ-AUSTENITE DIFFUSES through the γ structure FEC to reach its FRIENDLY CARBIDE (Fe₃C)

- If undercooling lies T below ~220°C

⇒ C has no time to diffuse (cooling & solidification are fast, Ti migration ~0)

⇒ There is a change of phase without diffusion

DIFFUSIONLESS TRANSFORMATION γ-AUSTENITE (Fe₃) \[ \rightarrow \] MARTENSITE (B₂)

ATOMS FREEZE IN THEIR POSITIONS BUT LATTICE DEFORMS!!

This is what you make if you put hot-red iron in cold water \[ \Rightarrow \] MARTENSITE
MARTENSITIC TRANSFORMATION

- From δ-AUSTENITE to MARTENSITE (FCC → BCC)
- DIFFUSIONLESS (C does not move)
  DISPLACIVE (change slope of LATTICE, deform without diffusing atoms)
- helps if UNDERCOOLING is BIG
  \[ T \leq 220°C \Rightarrow \Delta T > 500°C \] (HUGE)

---

**Figure 8.3-6** Schematic of an isothermal transformation (IT) diagram for a eutectoid steel.

IF WE CHANGE C% we can get MARTENSITE ALL OVER THE PLACE

**Figure 8.3-7** The effect of carbon on the \( M_s \) and \( M_f \) temperatures for a plain carbon steel.

<table>
<thead>
<tr>
<th>ARROW OR THE &quot;IRON AGE&quot; WARRIOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOR EUTECTOID STEEL</td>
</tr>
<tr>
<td>( M_s \sim 220°C )</td>
</tr>
<tr>
<td>( M_{50} \sim 170°C )</td>
</tr>
<tr>
<td>( M_{90} \sim 120°C )</td>
</tr>
<tr>
<td>( M_f = M_{100} \sim 0°C )</td>
</tr>
</tbody>
</table>

DURING "IRON AGE" ONLY HUMAN IN THE NORTH HAD ICE TO COOL STEEL
MARTENSITE IS DIFFUSIONLESS

⇒ SAME CONCENTRATION OF STARTING \( \gamma \)-AUSTENITE (NOT IRON)

\[ C = 1.8 \text{ wt.\%} \]
\[ H_s \approx 25^\circ \text{C} \]
\[ M_f \approx -200^\circ \text{C} \]

**FIGURE 8.3-8** Progress of athermal martensitic transformation in an Fe-1.8 wt. % C alloy after cooling to (a) 24°C, (b) -60°C, and (c) -100°C.

NEEDLE LIKE ➞ DIRECTION OF \( \gamma \) OR SAME LTEM \( \delta \)

HOW TO GO FROM \( \gamma \)-AUST TO MARTENSITE?
1. An FCC to BCT transformation.
2. Distortion of the BCT lattice parameters to match those of the martensite. This is called the Bain distortion after the person who first proposed it.
3. Rotation to produce the appropriate habit planes and directions between the martensite and the parent austenite.

**FIGURE 8.3-9** The relationship between the FCC $\gamma$ phase and the BCT martensite phase. The possible sites for carbon atoms are located at the x's, and the iron atoms are located at the open circles. To obtain the $\alpha'$ phase from the $\gamma$ unit cell, the $c$ axis must contract about 20% and the $a$ axis must expand about 12%.

**BUT @ Low Temp**

All these martensites are unstable toward decomposition of $\gamma + Fe_3C$. 

K24
If I keep martensite cold, it will remain martensite. But if I heat it up a little, it will allow C to diffuse and precipitate on spheres of $\text{Fe}_3\text{C}$ (cementite) (and BCT become BCC).

Such spheres are called spheroidite.

Spheroidite = martensite + spheres of cementite.

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**FIGURE 8.3-10** Microstructure of a tempered martensite (spheroidite) in a steel with 0.7 wt. % C. (Source: Transactions of the Metallurgical Society (212), 1968, a publication of the Minerals, Metals & Materials Society, Warrandale, PA. Reprinted by permission of the publisher.)
1) \( t = 0 \)  \( T = 727^\circ C \)
   - COOL FAST (QUENCH) TO 600\(^\circ\)C
   - WAIT 1.5 sec
   - COOL FAST TO 100\(^\circ\)C \( \Rightarrow \) \( \approx 25\% \) PEARLITE
      \( \approx 75\% \) HARRTENSR
      BCT.

2) COOL FAST TO 600\(^\circ\)C, WAIT 5 sec, COOL FAST TO 100\(^\circ\)C
   \( \Rightarrow 75\% \) PEARL
   \( 25\% \) HARRT.

3) COOL FAST TO 650\(^\circ\)C, WAIT 2 MINS, COOL TO 100\(^\circ\)C
   \( \Rightarrow 100\% \) PEARL

4) COOL SUPER SLOWLY TO 500, WAIT 2 YEARS, COOL TO 100\(^\circ\)C
   \( \Rightarrow \) ALL B + Fe\(_3\)C

5) DO LIKE 1) BUT THEN HAT UP TO 200\(^\circ\)C, WAIT 300 SEC & QUENCH, REPAT MANY TIMES
   \( \Rightarrow 25\% \) P, MUCH Fe\(_3\)C, SOME B, SOME BCC M.