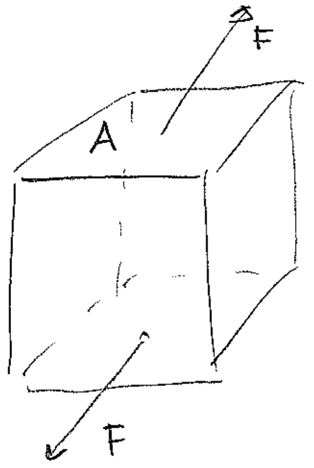
MECHANICAL BEHAVIOUR

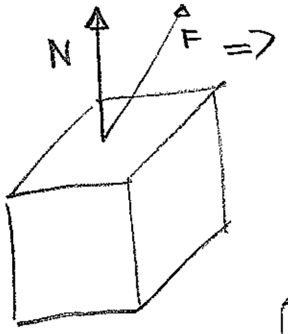
WHAT YOU APPLY!

Stress & shear stress

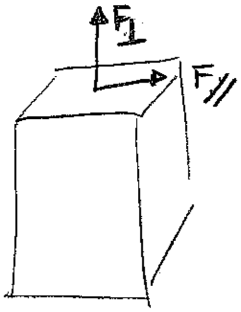
Static
the two
forces
are
opposite



⇒

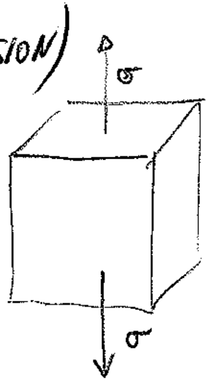


$\bar{F} = \bar{F}_{//} + \bar{F}_{\perp}$



⇒

STRESS (TENSILE, COMPRESSION)



sigma

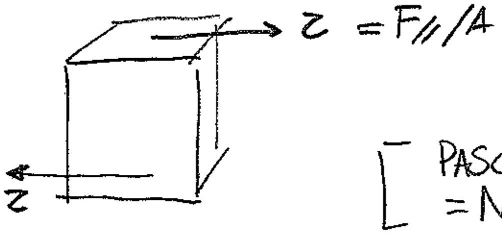
$$\sigma \equiv \frac{F_{\perp}}{A}$$ the parallel part

[pressure = PASCAL
= Newton/m^2]

SHEAR STRESS

tau

$$\tau \equiv \frac{F_{//}}{A}$$

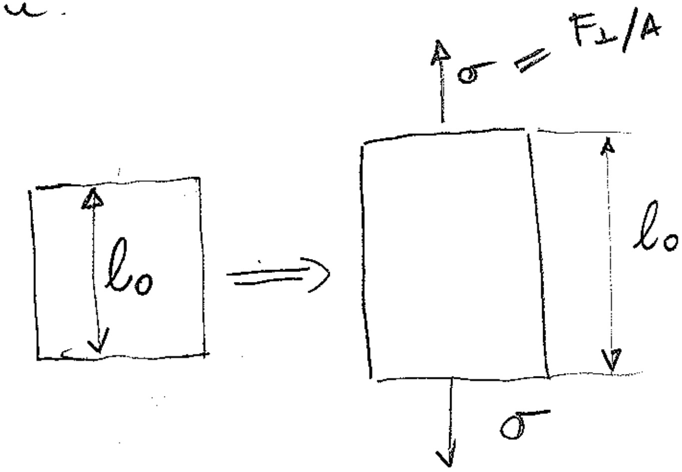


[PASCAL
$= N/m^2$]

WHAT YOU GET?

deformation!

STRAIN



$l_0 + \Delta l > l_0$ (HOPEFULLY)

$$\varepsilon \equiv \frac{\Delta l}{l_0} > 0$$

ε = strain (NO DIMENSION ⇒ %)

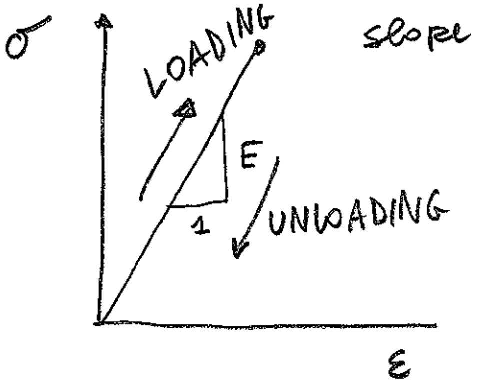
$$\sigma \Rightarrow \varepsilon$$

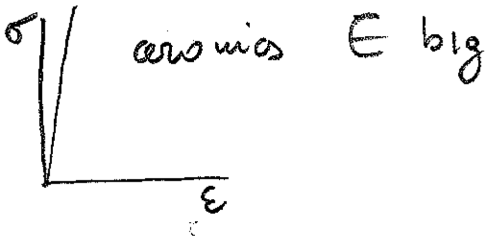
ELASTICITY ⇒ $\sigma \propto \varepsilon \Rightarrow \varepsilon \propto \sigma$ (same thing)

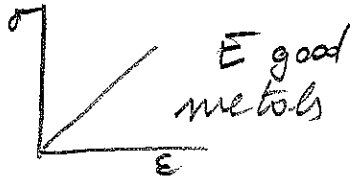
$\boxed{\frac{\sigma}{\varepsilon} = E}$ YOUNG MODULUS [PASCAL]

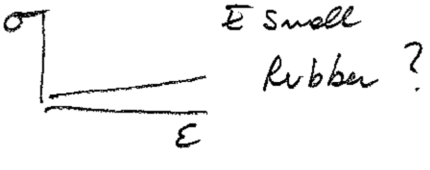
$\boxed{\varepsilon = \sigma / E}$

$\boxed{\frac{\partial \sigma}{\partial \varepsilon} = E_d}$ DIFFERENTIAL YOUNG MODULUS

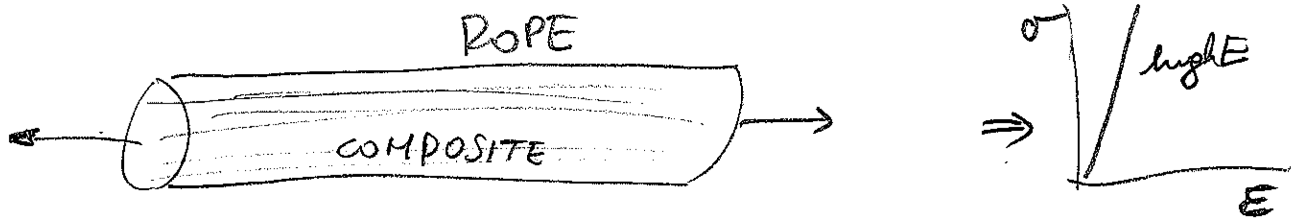


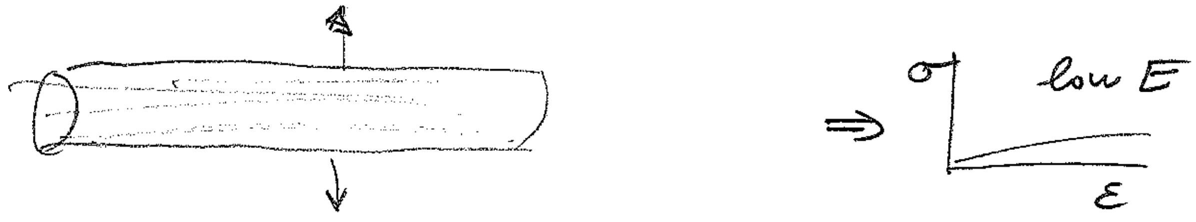




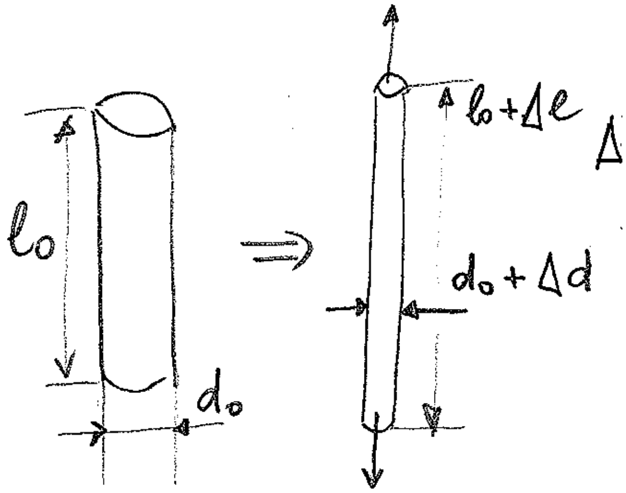


E can depend on direction





POISSON'S RATIO



$\Delta d < 0$!! (hopefully)

$$\varepsilon_{axial} \equiv \frac{\Delta l}{l_0} > 0$$

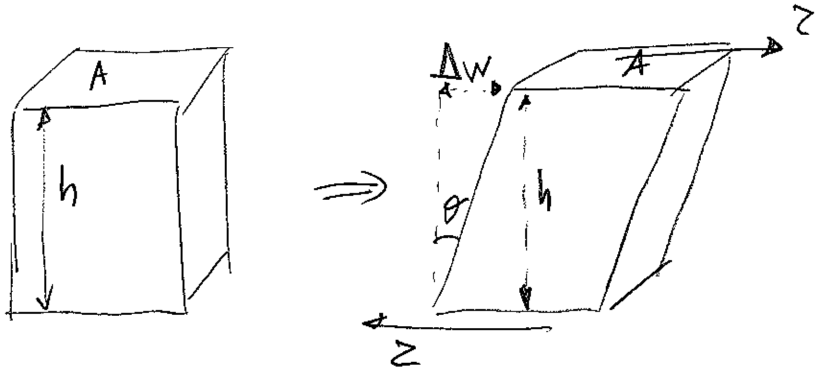
$$\varepsilon_{transverse} \equiv \frac{\Delta d}{d_0} < 0$$

$$\boxed{\nu \equiv \underset{\text{so} > 0}{-} \frac{\varepsilon_t}{\varepsilon_a} \quad \text{POISSON RATIO}}$$

it's always > 0 ?

No !! some weird materials (metallic foams) can have $\nu < 0$

SHEAR STRAIN



$$\gamma \equiv \frac{\Delta W}{h} = \tan\vartheta$$

$$\tan\vartheta = \frac{\sin\vartheta}{\cos\vartheta}$$

$\vartheta \to 0$ $\quad \sin\vartheta \to \vartheta$
$\cos\vartheta \to 1$
$\tan\vartheta \to \sin\vartheta \to \vartheta$

$$\gamma = \frac{\Delta W}{h} \approx \vartheta \quad = \underline{\underline{\text{NO DIM}}}$$

$\downarrow$

small τ

apply τ ~~get~~ γ

in elasticity $\tau \propto \gamma \propto \tau$!

$$\Rightarrow \boxed{\frac{\tau}{\gamma} \equiv \underset{[\text{Pascal}]}{G} \quad \text{SHEAR MODULUS}}$$

$$\boxed{\frac{\partial\tau}{\partial\gamma} = G_d \text{ diff shear Mod}}$$

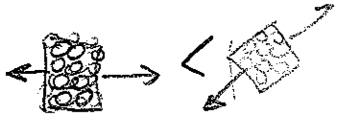
E, G, ν are called ELASTIC CONSTANTS

$$G = \frac{E}{2(1+\nu)}$$

For <u>isotropic materials</u>

(NO COMPOSITES LAYERED, FIBERS)

EXAMPLE put CUBIC

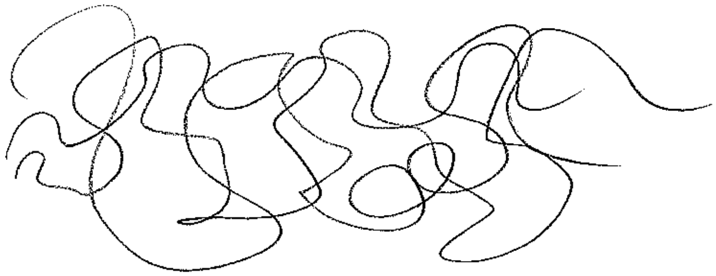


M4

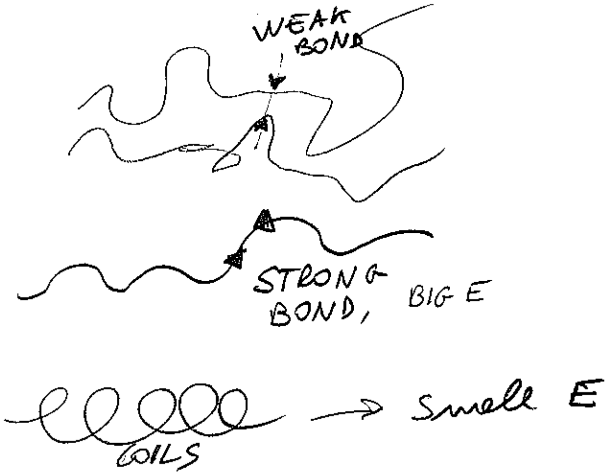
DEFORMATION / VISCOELASTICITY

elastic for small σ, ε normal materials.

what about polymers

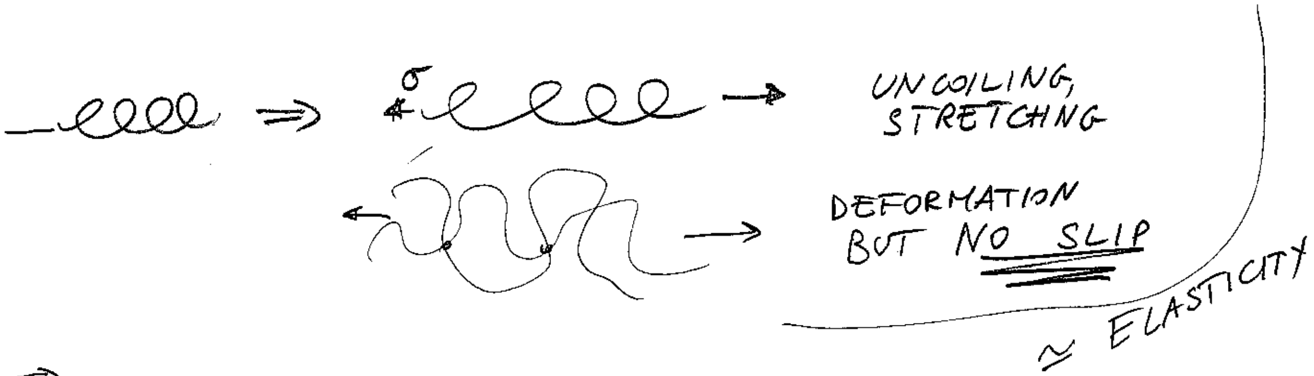


POLYMER



2 REGIMES

T < T glass transition



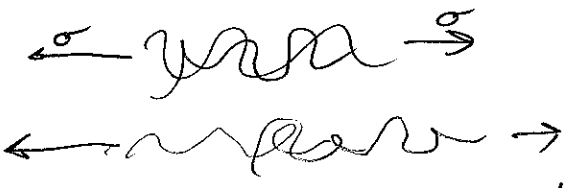
UNCOILING, STRETCHING

DEFORMATION BUT NO SLIP

≃ ELASTICITY

⇒ T > T glass

Temperature ⇒ a lot of thermal movement ⇒



slip ⇒ CONTINUOUS DEFORMATION

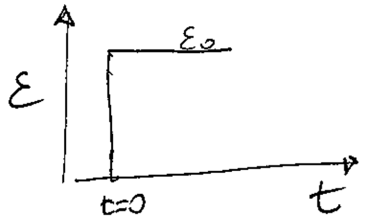
VISCOELASTICITY

DYNAMIC TESTS (STEPS)

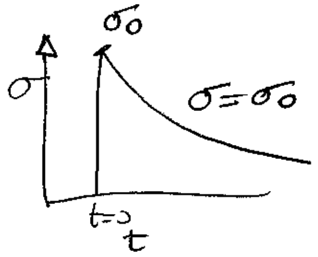
2 common tests $T > T_g$

ε = constant $\frac{\partial \varepsilon}{\partial t} = 0 \Longrightarrow \sigma(t)$ STRESS RELAXATION

$E_{relax}(t) = \frac{\sigma(t)}{\varepsilon_0}$



$\Longrightarrow$



$\sigma = \sigma_0 e^{-t/\tau_0}$

τ_0 → DAMPING → Relaxation time ∝ viscosity

$\tau_0 \propto$ viscosity $\propto \exp(-Q/RT)$

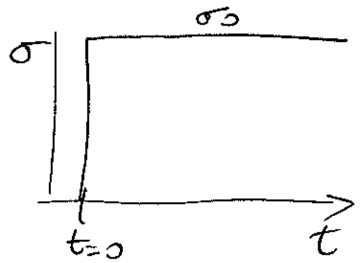
Q → materiale

RT → Arrenius

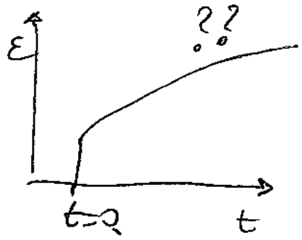
$\neq$

σ = constant $\frac{\partial \sigma}{\partial t} = 0 \Longrightarrow \varepsilon(t)$ TIME DEPENDENT DEFORMATION

$E_{relax}(t) = \frac{\sigma_0}{\varepsilon(t)}$



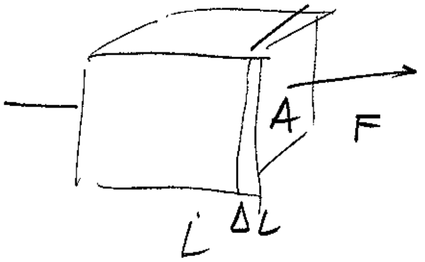
$\Longrightarrow$



M6

~~DYNAMIC TESTS~~ ~~(CYCLIC)~~
ENERGETICS

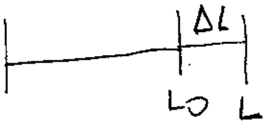
$$\Delta W = F \Delta L$$



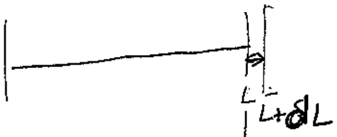
$$\Downarrow$$

$$dW = F\,dL$$

$$\varepsilon = \frac{\Delta L}{L_0}$$



$$\Rightarrow \varepsilon = \frac{\Delta L}{L_0}$$



$$= L = L_0 + \Delta L$$

$$\overset{!}{=} L_0 + \varepsilon L_0$$

$$\Rightarrow L = L_0 + \varepsilon L_0$$

$$\delta L = L_0\,\delta\varepsilon$$

$$\Rightarrow dL = L_0\,d\varepsilon$$

$$\Downarrow$$

Joules

$$dW = F L_0\,d\varepsilon$$

per unit volume
density Joules/m^3

$$\Rightarrow \frac{dW}{V} = \frac{dW}{A \cdot L_0}$$

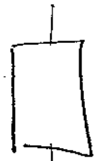
$$dw = \frac{dW}{A L_0} = \underset{\Downarrow\ \sigma}{\frac{F}{A}}\,\frac{\cancel{L_0}}{\cancel{L_0}}\,d\varepsilon \Rightarrow \sigma\,d\varepsilon$$

$$\boxed{dw = \sigma\,d\varepsilon}$$

amount of work per unit volume you do with stress σ, getting dε deformation

M7

DYNAMIC CICLING



$\varepsilon = \varepsilon_0 \sin \omega t$

$\sigma = \sigma_0 \sin(\omega t + \vartheta) \Rightarrow \sigma_0 [\sin(\omega t)\cos\vartheta + \cos\omega t \sin\vartheta)]$

$E_1 = \frac{\sigma_0}{\varepsilon_0}\cos\vartheta$ = STORAGE MODULUS

$dW = \sigma d\varepsilon \Rightarrow$ in a cycle

$\boxed{E_2 = \frac{\sigma_0}{\varepsilon_0}\sin\vartheta}$ LOSS MODULUS

$\Rightarrow \sigma = \varepsilon_0 E_1 \sin(\omega t) + \varepsilon_0 E_2 \cos(\omega t)$

$\Rightarrow \varepsilon = \varepsilon_0 e^{i\omega t}$

$\sigma = \sigma_0 e^{i(\omega t + \vartheta)}$

$E^* = \frac{\sigma_0}{\varepsilon_0} e^{i\vartheta} = E_1 + iE_2$

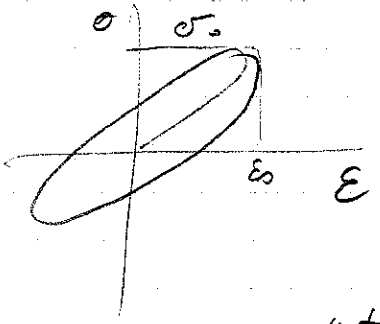
loss per cycle $\Delta W = \oint \sigma d\varepsilon$

$\pi \varepsilon_0^2 E_2$

$E_1 \sim 1$ GPA

$E_2 \sim 0.01$ GPA

losses ~ 1%



$\omega t = \varphi \qquad d\varepsilon = \frac{\partial\varepsilon}{\partial\varphi} d\varphi$

$$\int \sigma d\varepsilon = \int_0^{2\pi} \sigma_0 \sin(\varphi + \vartheta)\varepsilon_0 \cos\varphi \, d\varphi =$$

$$= \sigma_0 \varepsilon_0 \int_0^{2\pi} \cos\varphi [\sin\varphi \cos\vartheta + \cos\varphi \sin\vartheta] \, d\varphi$$

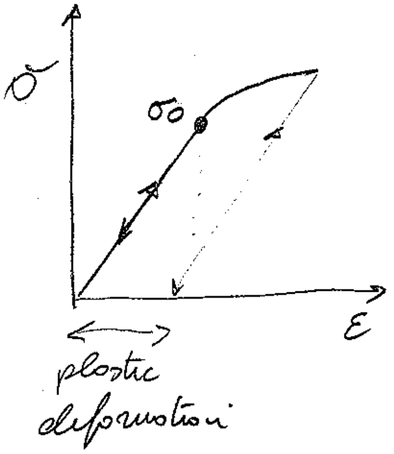
$$\cos\vartheta \int_0^{2\pi} \cos\varphi \sin\varphi \, d\varphi = \cos\vartheta \left[\frac{\sin^2\varphi}{2} \Big|_0^{2\pi} \right] = 0$$

$$\sin\vartheta \int_0^{2\pi} \cos^2\varphi \, d\varphi = \sin\vartheta \, \frac{\varphi + \sin\varphi\cos\varphi}{2} \Big|_0^{2\pi} = \pi \sin\vartheta$$

M8.

$$= \frac{\sigma_0}{\varepsilon_0} \varepsilon_0^2 \pi \sin\vartheta = \pi \varepsilon_0^2 E_2$$ loss small ~1%

ELASTIC LIMIT



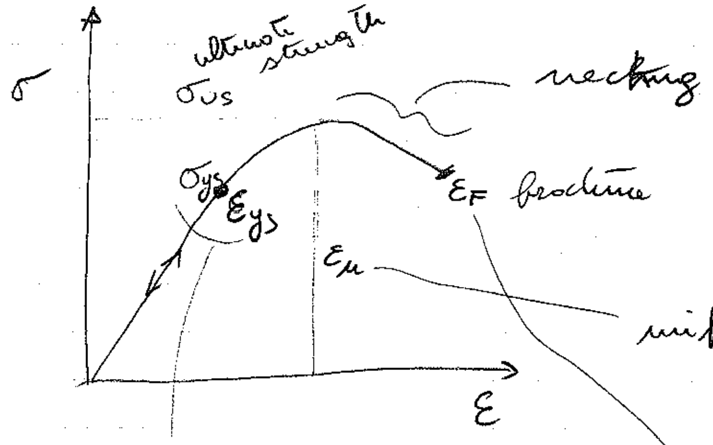
plastic = continuous increase of σ
⇒ the material gets harder

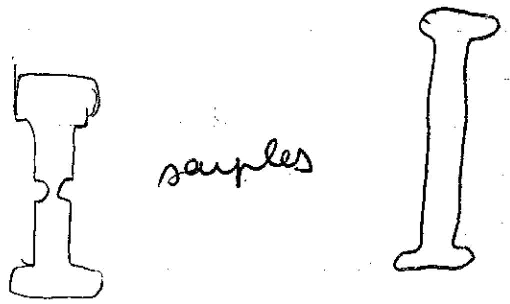
STRAIN HARDENING

METALS ≠ POLYMERS ≠ CERAMICS
(BRITTLE)

POLY: used to align molecules ⇒ stronger

TENSILE TESTING





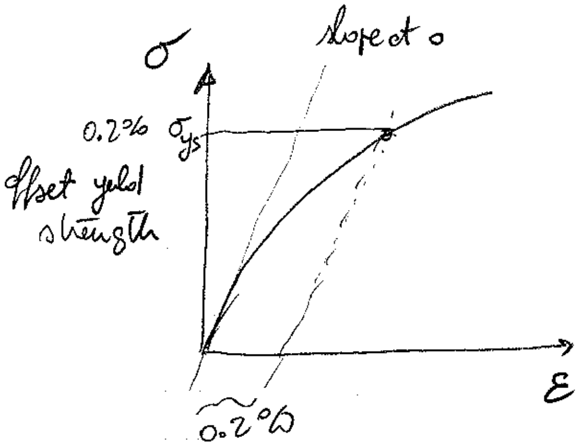
uniform strain (stress uniform)

yield strength σ_{ys}
yield strain ε_{ys}

ε_F engineering strain at fracture

= DUCTILITY

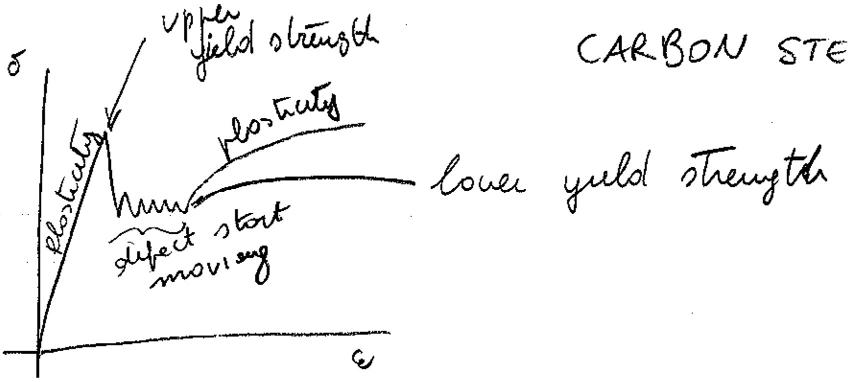
IF NOT ELASTIC



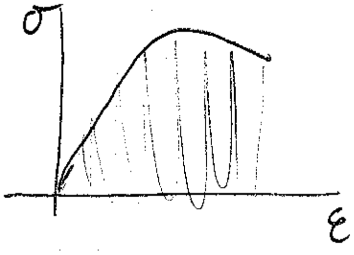
copper, Aluminum FCC
always plastic

IF DEFECTS ARE STUCK
(mobility of dislocations)

CARBON STEEL



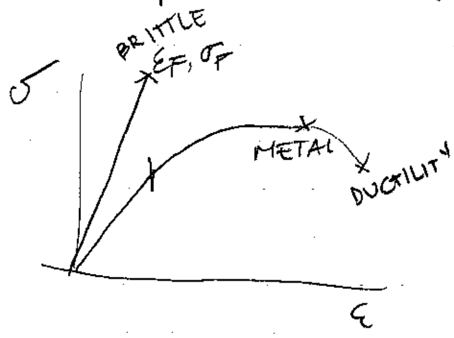
TOUGHNESS = energy to ~~b~~ fracture



$$U = \int_0^{\varepsilon_F} \sigma \, d\varepsilon = \left[\frac{J}{m^3}\right]$$

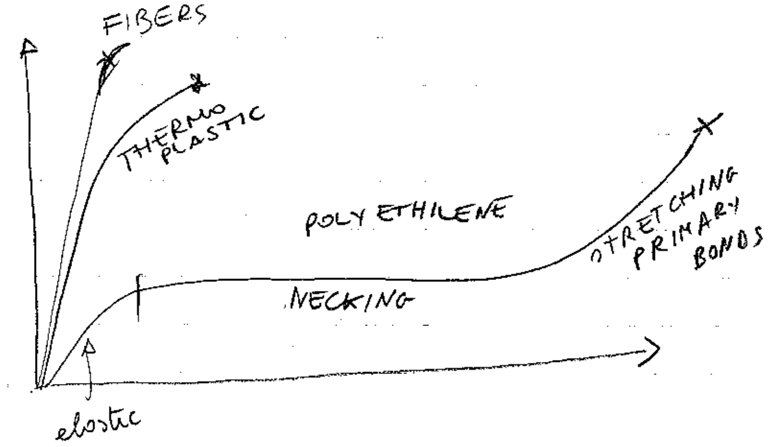
CERAMIC TEST

samples are hard to make ⇒ Bending but not uniform stress



compression ≠ tension
ionic BONDING & PREEXISTING VOIDS INSIDE

POLYMERS

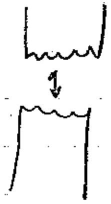


DUCTILE & BRITTLE FRACTURE

metals ; ductile ⇒ absorb energy, dislocation, defects move, deforming necking ⇒ fracture

ceramics, brittle ⇒ NO absorbing energies, no dislocations movement defects get stuck

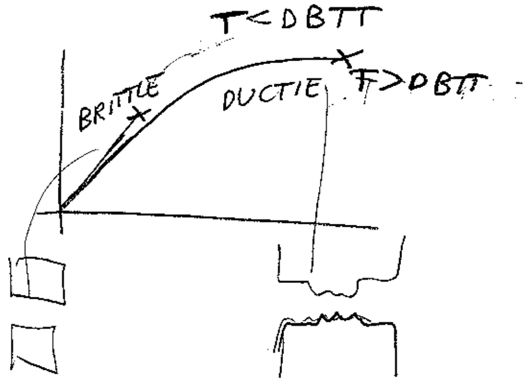
BRITTLE



DUCTILE TO BRITTLE TRANSITION TEMPERATURE DBTT

some metals when cooled cannot absorb plastic energy well
(ferritic BCC steel, [illegible] with ferrite)

so their σ/ε changes



problem for equipment
in cold weather
ships, space, planes

(FCC always DUCTILE
ceramics always BRTILE)

DBTT depends on chemical composition

FOR CARBON STEEL Mn↑ DBTT↓
C↓ DBTT↓

Amorphous: T>Tg viscous fluid (viscoelasticity)
T<Tg brittle

Polymers . depend where DBTT is with respect to Tg N_2

M12

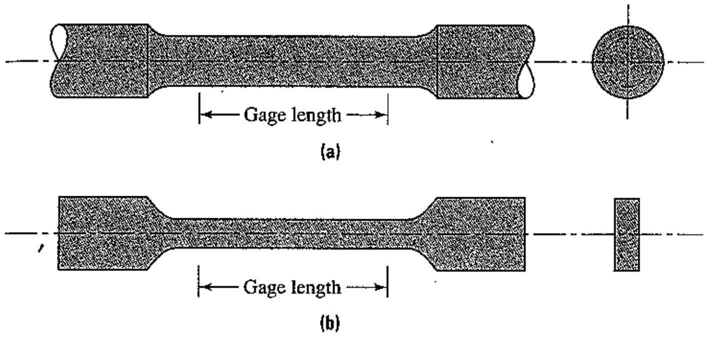


FIGURE 9.2–7 Specimen geometries used for tensile testing: **(a)** cylindrical and **(b)** flat specimens. *(Source: Copyright ASTM. Reprinted with permission.)*

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

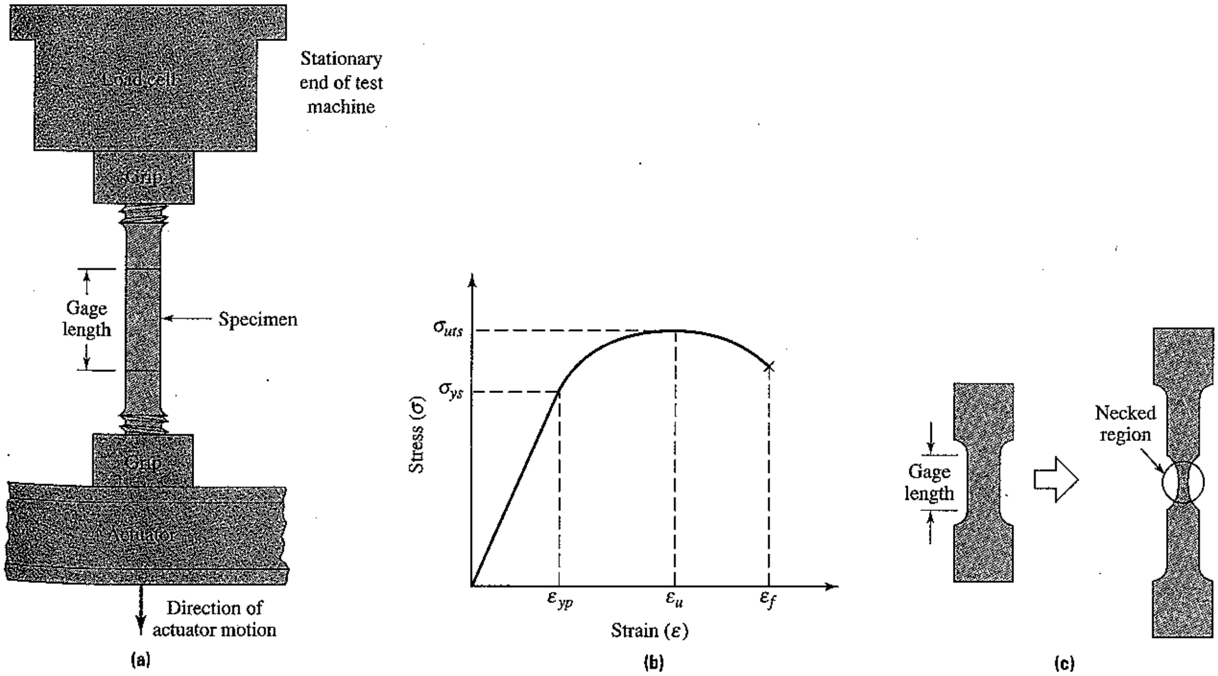
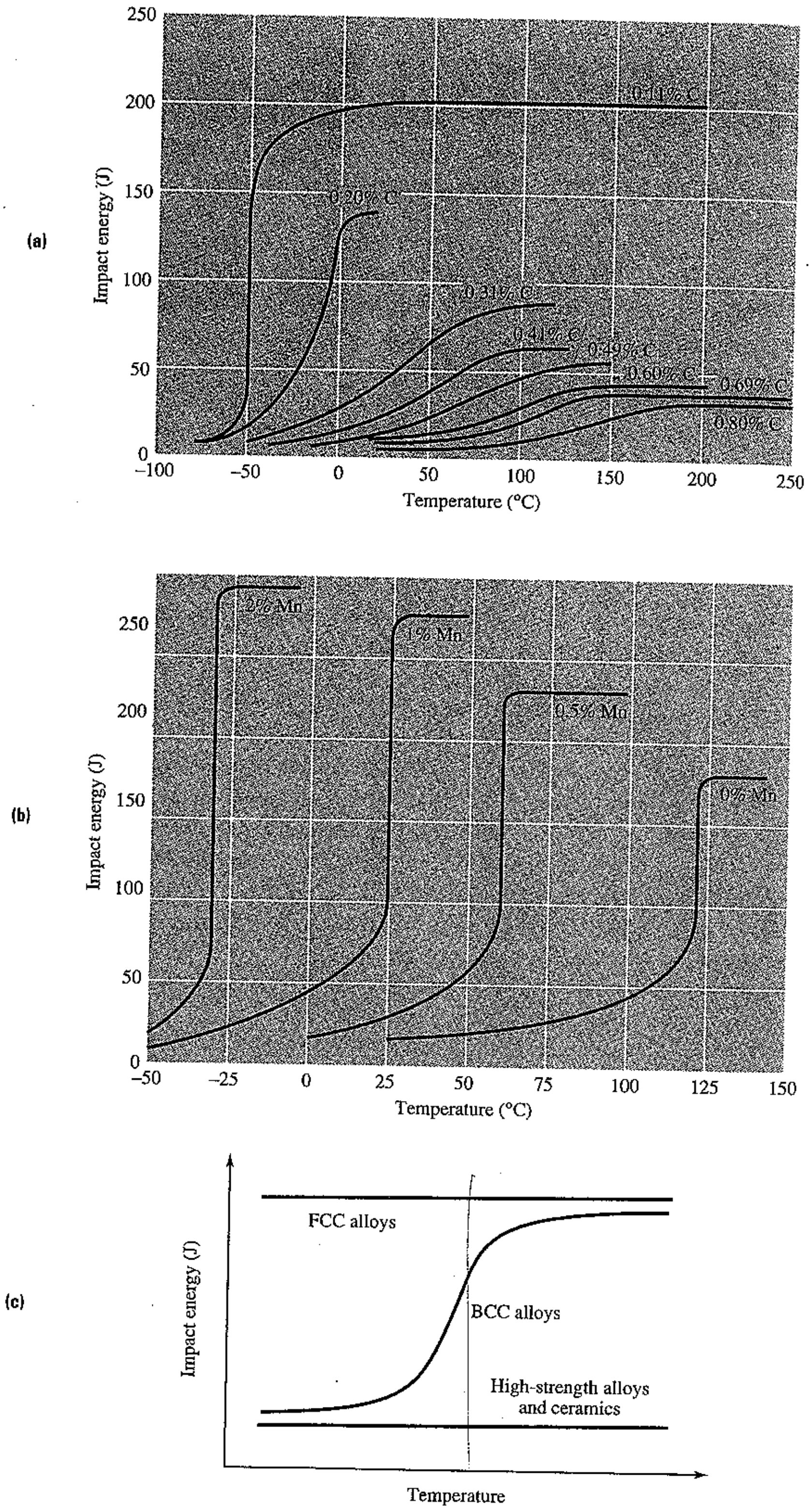


FIGURE 9.2–8 Tensile testing of materials: **(a)** a complete setup for tensile testing of metals, **(b)** stress versus strain behavior obtained from a tensile test, and **(c)** the formation of a "neck" within the gage length of the sample.

M 12b

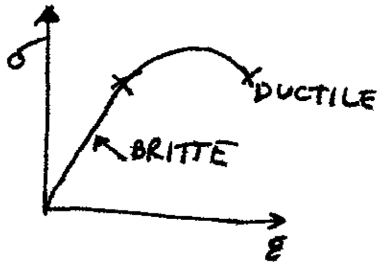
FIGURE 9.2–23

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.)*



M12c

FRACTURE - BRITTLE



MAX LOAD ⇒ FRACTURE

⇒ CRACK GROWING ~~[illegible]~~ CONTINUOSLY

small defect flow growth with fatigue

GRIFFIT MODEL : ENERGY RELEASE RATE

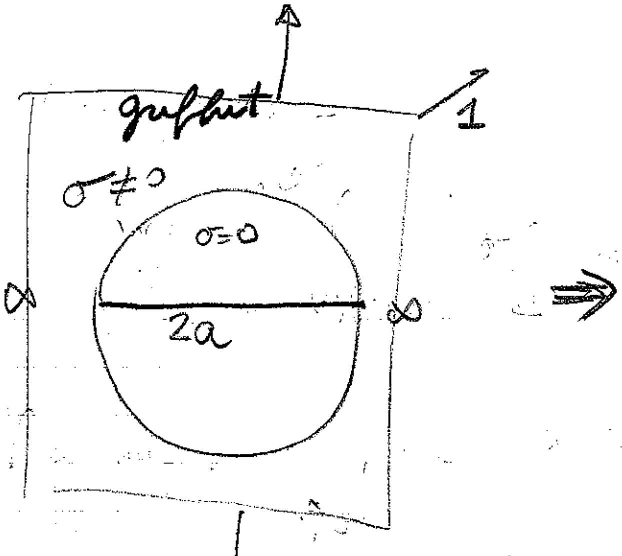
CRACK RELEASE ELASTIC ENERGY

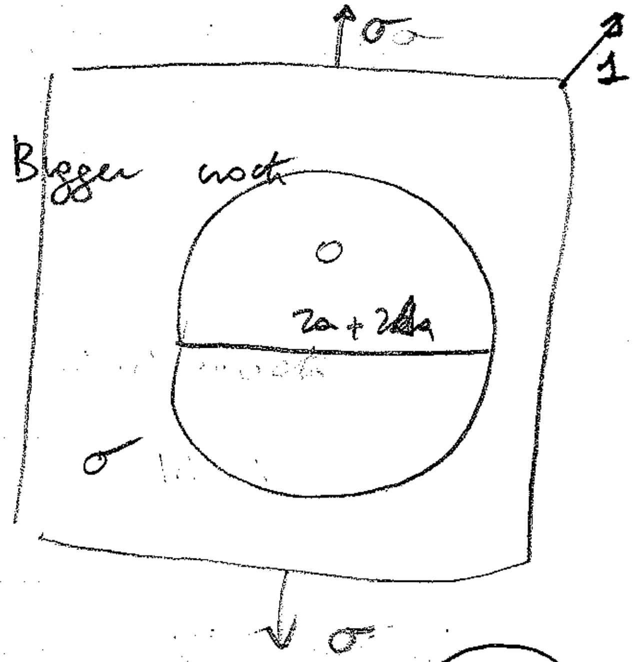
SURFACE ENERGY EXCESS EATS IT !!

Δa = FRACTURE $0 = dW = dW_E + dW_S$

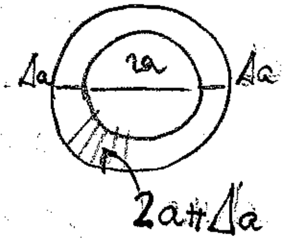
$dW = \sigma d\varepsilon$ Elasticity $\frac{\sigma}{\varepsilon} = E$, $\varepsilon = \frac{\sigma}{E} \Rightarrow$

$dW = \frac{\sigma d\sigma}{E}$





at constant extend stress ⇒ release of ELASTIC ENERGY



$dW_E = \frac{\sigma d\sigma}{E}$ griffit $\Delta W_E = \frac{\sigma^2}{E}\Delta V$ ⇒ $-\frac{\sigma^2}{E} 2aH\Delta a$

release

M13

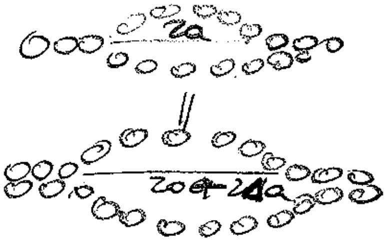
CREATION OF SURFACE

$$\Delta W_{SURFACE} = \gamma_S \, \Delta \text{surface}$$

Energy to create 1 m² of surface

atoms

break bonds



if you cut ⇒ create 2 halves

⇒ 2Δa surfaces per side ⇒ 4Δa

$$\Rightarrow \Delta W_{SURFACE} = \gamma_S \, 4\Delta a$$ (per unit length)

⇒ at fracture ⇒ self sustaining phenomenon

$$\Rightarrow 0 = \Delta W_E + \Delta W_{surface} = -\frac{\sigma^2}{E} a\pi 2\Delta a + \gamma_S 4\Delta a = 2\Delta a \underbrace{\left(-\frac{\sigma^2}{E} a\pi + 2\gamma_S\right)}_{=0}$$

Fracture

$$\Rightarrow \boxed{\sigma_G = \sqrt{\frac{2E\gamma_s}{a\pi}}}$$

fracture

crytical σ_G for fracture with release of elastic energy (good ceramics)

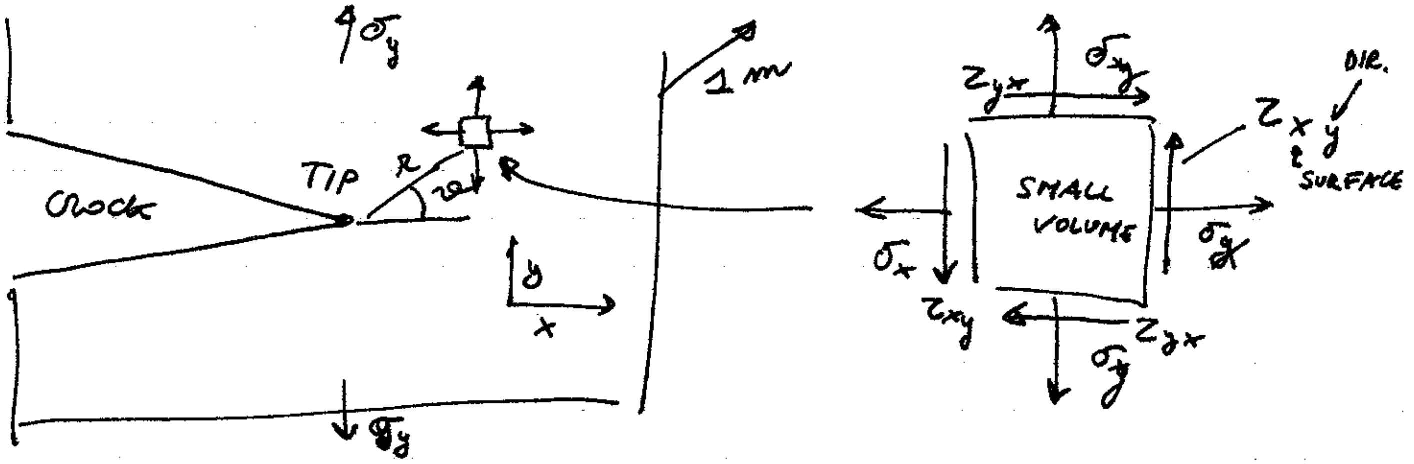
For metal (plastic)?? How? OROWAN TRICK

$$\sigma_g = \sqrt{\frac{2E}{a\pi}(\gamma_S + \gamma_p)}$$

HOW TO MEASURE? A BIG HACK!

plastic deformation of surface? what does it mean? plastic deformation due by crack growth ~ orientation CRAZES!

MODERN APPROACH



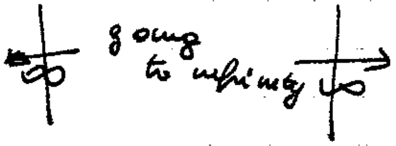
ISOTROPIC, ELASTIC, the stress can be written as

$$\sigma_y = \frac{K}{\sqrt{2\pi r}} f(\vartheta)$$

$\boxed{K \text{ is a stress intensity parameter}}$ K: Pa$\sqrt{m}$

$f(\vartheta)$: $\frac{\text{sin, cos inside}}{\text{complicate}} < 1$

for

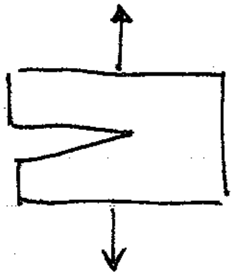


$\Rightarrow f(\vartheta) \to 1$

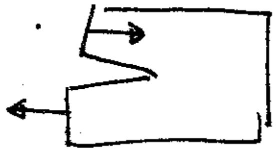
⇒ WORSE SCENARIO OVERESTIMATE σ

$$\sigma_y = \frac{K}{\sqrt{2\pi r}}$$

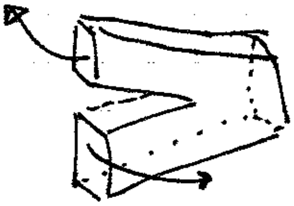
K depends on the MODE (MICHELANGELO)



MODE I



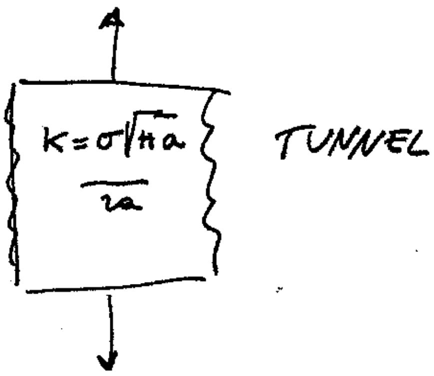
MODE II

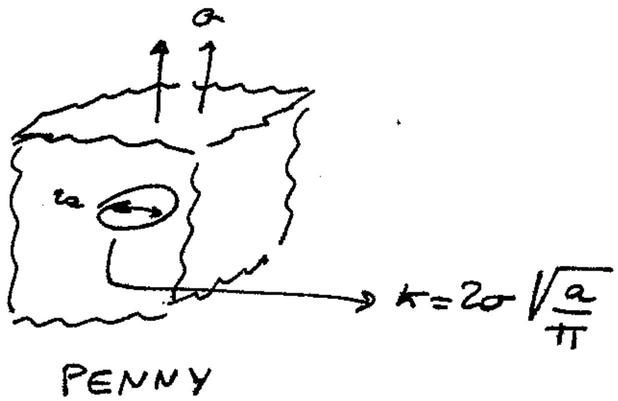


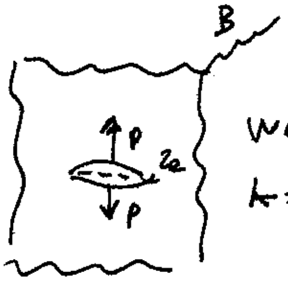
Mode III

and type of crack

MIS







Wedge : . . . and so on

$$k = \frac{P}{B\sqrt{\pi a}}$$

~~ot~~ put σ (∝P) get k,

increase $\sigma\uparrow \rightarrow k\uparrow$ when $\boxed{k = K_{CRIT}}$ (tables for modes and materials)

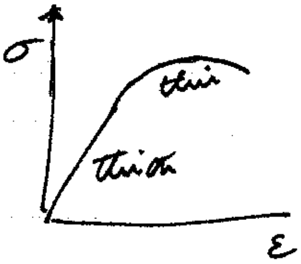
↓

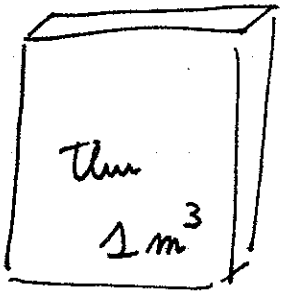
CRACK, fracture

Valid for thick materials,

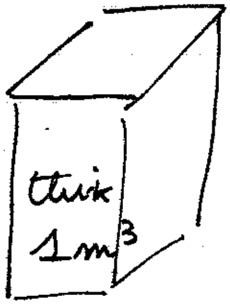
for thin? thin is tougher

because more plasticity has to be built for unit volume





same σ ⇒ more plasticity



↑ less plasticity

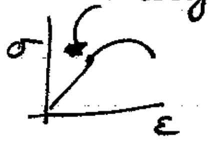
M16

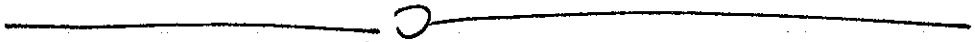
EXPERIMENTALLY

criterion $k_{MODE} \Rightarrow k_{CRIT, MODE}$, valid for

thickness > critical thickness $B = 2.5\left(\frac{K_{Ic}}{\sigma_{ys}}\right)^2$

yield strength



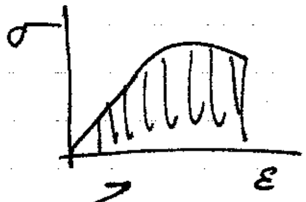


~~Rela~~

FRACTURE RELATION WITH FRACTURE TOUGHNESS

METAL HIGH K_{IC} because

Big area



CERAMICS
small
area !!

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

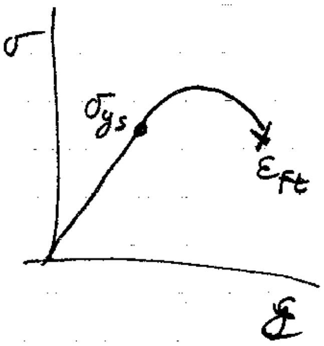
FOR METALS

$$K_{Ic} \propto n\sqrt{E\,\sigma_{ys}\,\varepsilon_{ft}}$$

true fracture strain

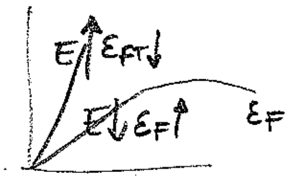
yield strength

strain hardening exponent
((DO second part of course)



M17 measure of how much I can
strain harden, by ~~one~~ entangling defects

$E \uparrow$ $n \downarrow$ $\varepsilon_f \downarrow$

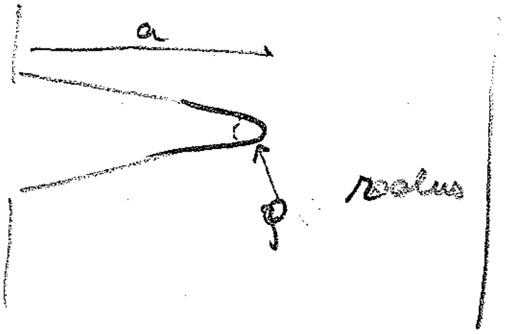


$\Rightarrow$ $E\uparrow$ $K_{Ic}\downarrow$

$\Rightarrow$ concerns for BRITTLE FRACTURE

high strength alloys
and metal
& NOT DUCTILE ONES!!

CERAMICS NO PLASTICITY $\Rightarrow$ LEFM
Linear
Elastic
Fracture
Mechanics.



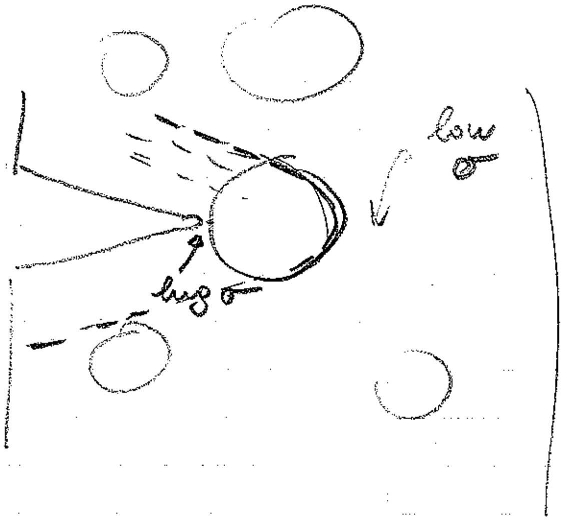
$\sigma_{max} \sim \sqrt{\frac{a}{\rho}}$

MAX

So: how to make it stronger?

VOIDS? INCREASE ρ

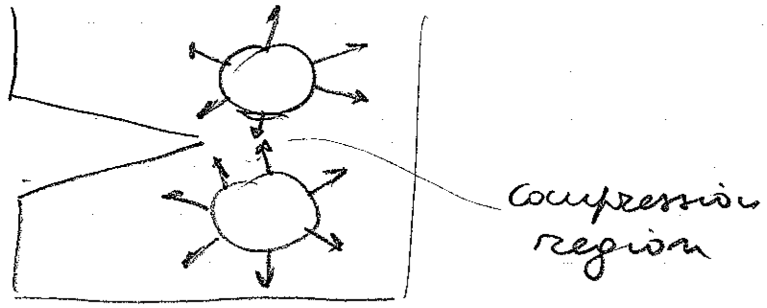
cook with something
with bigger thermal
expansion & quench



M18

OR

Precipitates with lower thermal expansion
so they preload the crystal @ low temperature



can become 10 times stronger

NUMBERS

METALS	20~150	$MPa\sqrt{m}$	absorb energy plasticity
CERAMICS	0.5~2	$MPa\sqrt{m}$	no adsorption
" TREATED	9~15	$MPa\sqrt{m}$	voids + precipitates
POLYMERS	0.5~10	$MPa\sqrt{m}$	small area $< T_g$

$> T_g$ some viscoelasticity
no fracture but lose slope!

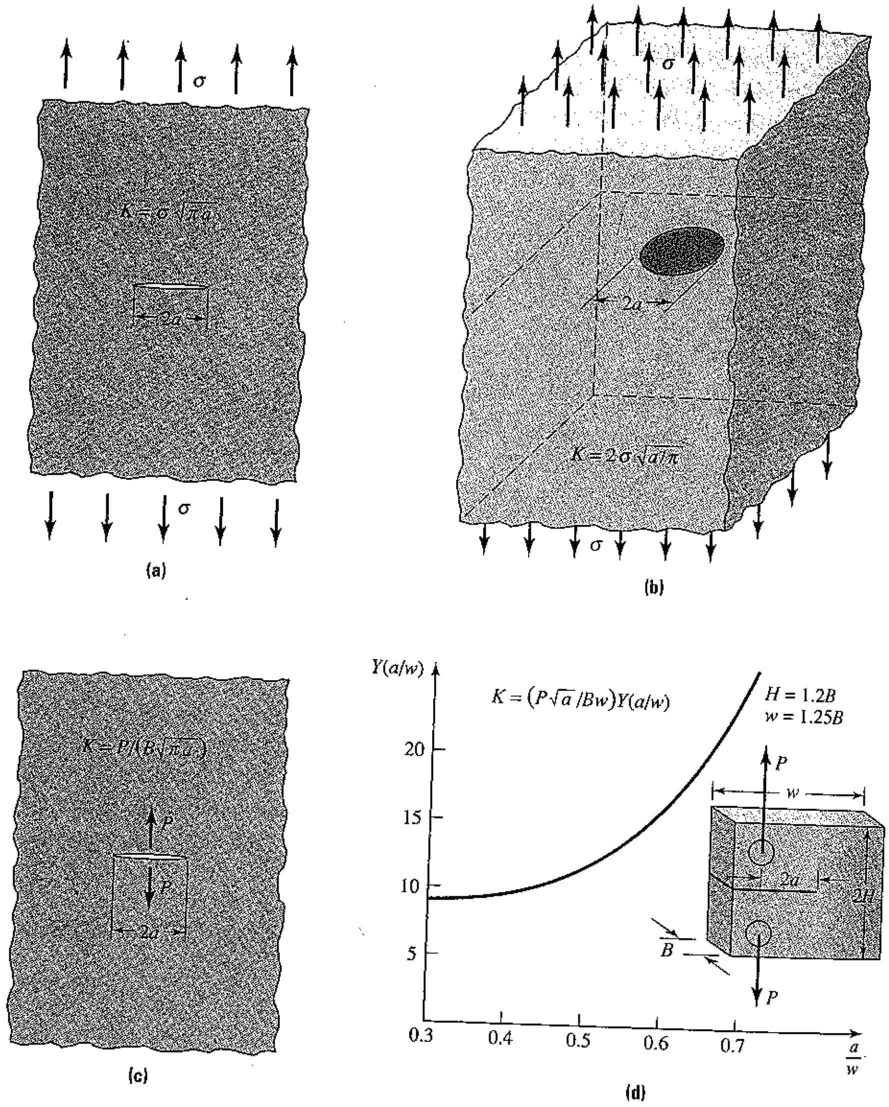


FIGURE 9.4–2

Some typical load/crack geometries and their corresponding stress intensity parameters: **(a)** a tunnel crack, **(b)** a penny crack, **(c)** a wedge-opened crack, and **(d)** an eccentrically loaded crack.

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:

$$K = \sigma\sqrt{\pi a} \tag{9.4–2}$$

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.

M19b

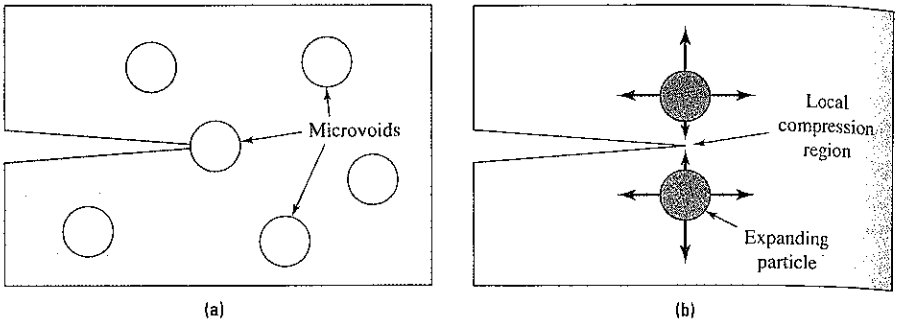


FIGURE 9.4–4 Toughening mechanisms for ceramics. **(a)** Microcracking—when the advancing crack enters the microvoid, its length increases slightly but its crack tip radius increases significantly, decreasing the stress amplification and correspondingly reducing the driving force for crack extension. **(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/ρ 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 matirx. The result is that the matrix material located between two nearby second-phase particles is placed in residual compression.[4] 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_{Ic} value of ~ 2 MPa-$\sqrt{\text{m}}$, while transformation-toughened zirconia has a K_{Ic} value of ~ 9–13 MPa-$\sqrt{\text{m}}$. It is important to note, however, that while the mechanism 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_{Ic} values than most metals.

---

[4] 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.

M12c

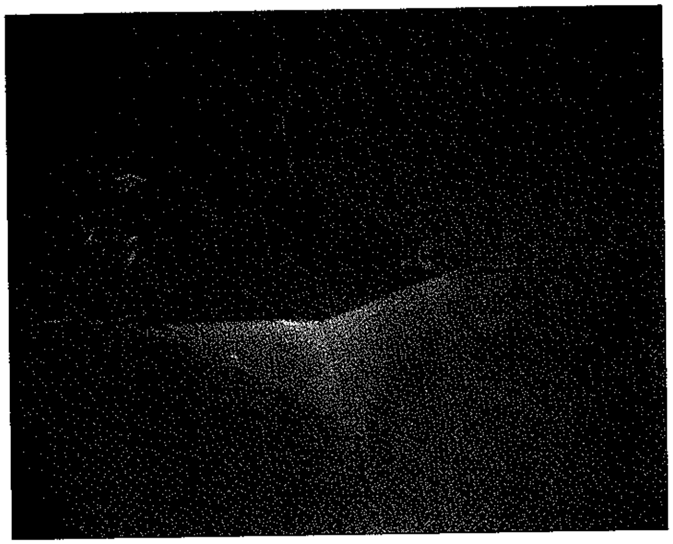


FIGURE 9.4–5

Vickers indentation in the surface of a single-crystal cubic zirconia (Y_2O_3-stabilized). Radial cracks are used to calculate the fracture toughness. *(Source: Courtesy of Joseph K. Cochran.)*

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_{max} and S_{min}, respectively.[6] The range of stress, ΔS, is equal to $S_{max} - S_{min}$, and the stress amplitude, S_a, is $\Delta S/2$. A fatigue cycle is defined by successive maxima (or minima) in load or

---

[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.

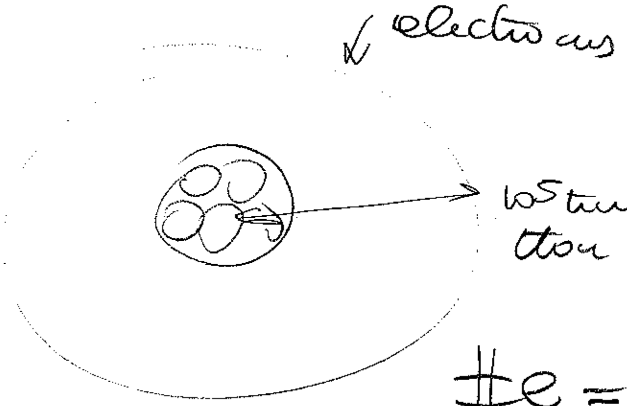
M19d

ATOMIC STRUCTURE

ATOMS = DEMOCRITOS (GREECE!!)

UNITS THAT CANNOT BE SPLIT (WRONG BUT RIGHT)

NUCLEUS
PROTONS
, NEUTRONS



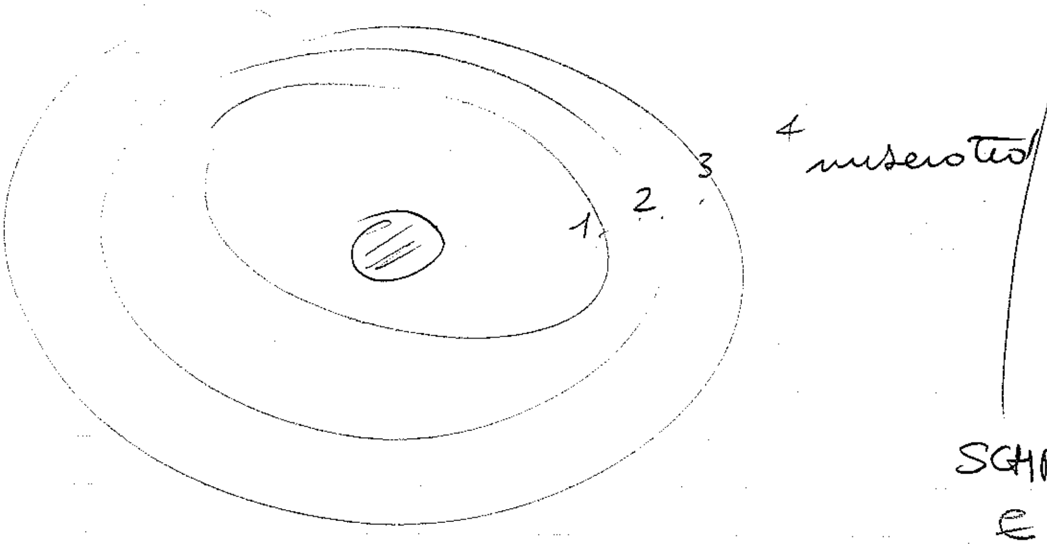
10^5 times more bigger than nucleus

$\#e = \#p = Z$ atomic number

$\#n =$ variable $\underline{\simeq} Z$

electrons rotate, fast so fast you need QM

⇒ orbitals like planet around the sun



SCHRÖDINGER
EQUATION

how to describe orbitals

quantum numbers n, l, m, s

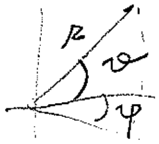
n ↑ energy

l ↑ shape

m ↑ orientation

s ↑ spin ↑ ↓

$\psi(r, \vartheta, \varphi)$



n boundary for r

l boundary for ϑ

m boundary for φ

2 ~~Boundary~~

PAULI ⇒ 2e can't have same 4 q. numbers.

$n = 1, 2, 3 \ldots \ldots$ integer

$l = 0, 1, \ldots n-1$

$m = -l, -l+1 \ldots 0, l-1, l$

$s = \cancel{\pm}\frac{1}{2}, \frac{1}{2}$

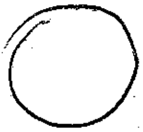
$n = 1$

1s

$l = 0$ (s $l=0$ s = spherical)

$m = 0$

$s = +\frac{1}{2}, -\frac{1}{2}$ ⇒ 2 electrons



$n=2$

$2s^1, 2s^2$ $\quad$ $l=0$ spherical

$m=0$

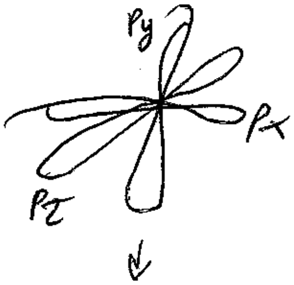
$s=\pm\frac{1}{2}$ $\quad$ 2 electrons

$l=1$ $\quad$ P $\rightarrow$

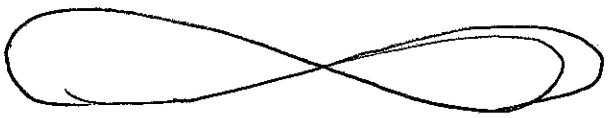
$m=-1, 0, 1$ $\leftarrow$ 3 types

P_x, P_y, P_z

$2p^{1\ldots6}$ $\quad$ $S=\pm\frac{1}{2}$ each



$\Rightarrow$ 6 electrons total



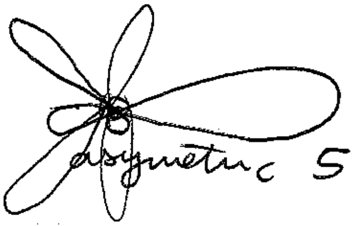
SIMMERTRIC RESPECT THE CENTER

$n=3$ $\quad$ $l=0$ $\quad$ $3s^{1..2} \rightarrow 2$

$l=1$ $\quad$ $3p^{1..6} \longrightarrow 6$ max

$l=2$

$3d^{1\ldots10}$ $\quad$ $m=\underbrace{-2,-1,0,1,2}_{5}$ $\quad$ d orbitals



asymetric 5

Ag $\quad$ $S=\pm\frac{1}{2}$, $\downarrow\uparrow$ each

$\Rightarrow$ 10 electrons

~~n =~~ 4

$l = 3$ $m = -3, -2, -1, 0, 1, 2, 3$

4s, 4d, 4p, 4f

2 6 10 14 electons

7 → 14 electons

Energy

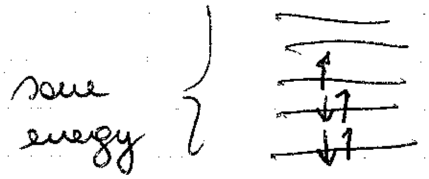
$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p \ldots$

increasing energy

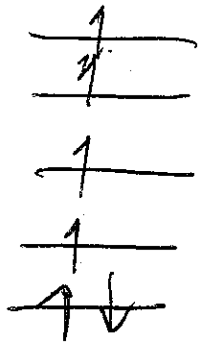
HUND RULE

~~in electrons~~ in set of orbitals, ~~two~~ with same energy, is partially occupied the electrons go to maximize total spin

Example $3d^5$



⇒ NO BUT



$\sum s = +\frac{1}{2}$

$\sum s = 2$!!

Magnetic ~ half filled d & f

Mn, Fe, Co magnetic

Ti, Zn NO Put AM table

Valence = # e in outer shell contributing to bond

BOND = SHARE ELECTRONS

A§4

THERMO & KIN

THERMODYNAMICS

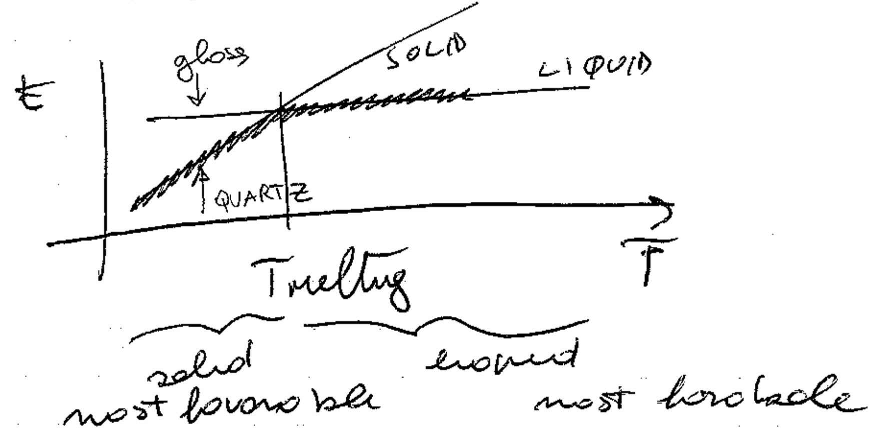
Study of relationships between p, T, Volume, composition @ EQUILIBRIUM
(phases, liquid, solid...)

KINETIC

study of relationships OUT of EQUILIBRIUM

~~[illegible]~~ speed reaction occur

THERMO : increase T - increase Energy



how fast?

kJ/mol activation energy

$$\text{Rate } k(T) = C\, e^{-\frac{Q}{RT}}$$

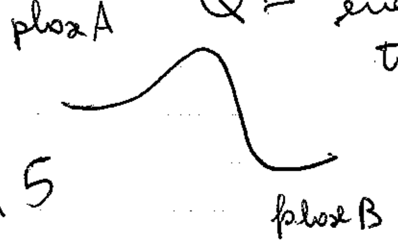
R ← gas constant

$T \uparrow k \uparrow exp$

EXAMPLE
Q 2.3-1

~~arr~~ ARRHENIOUS LAW
almost always true

Q = energy you need to apply to see the other side of the hill

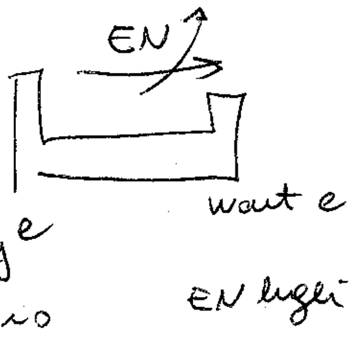


A5

IRREVERSIBILITY

BONDS

Electronegativity = measure how generous is an atom! for electrons



orbitals like to be as much as possible full or empty

Na $\qquad$ Cl

$1s^2, 2s^2, 2p^6, 3s^{①}$

$\Downarrow$ $\quad$ Na → Na^+ $\quad$ 5.14 eV IONIZATION POT

Na^+

$1s^2, 2s^2, 2p^6$

$\Downarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^{⑤}$

$\Downarrow$ Cl^-

$1s^2, 2s^2, 2p^6, 3s^2\ 3p^6$

Cl → Cl^-

−4.02 eV electron affinity AFFINITY

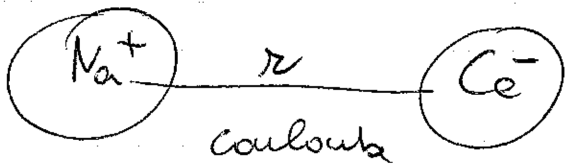
$Na + Cl \rightarrow Na^+ + Cl^-$

5.14 eV − 4.02 eV

$= 1.12\,\text{eV} > 0$

so unlikely they form

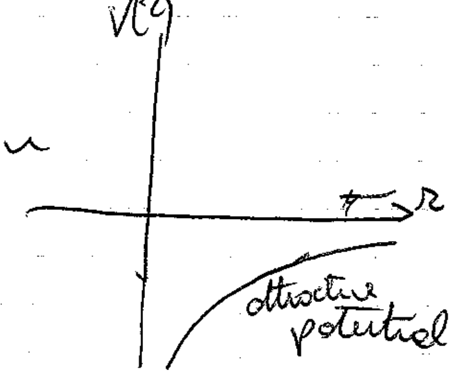
$Z_1 q = +e$ $\qquad$ $Z_2 q = -e$



$$F = \frac{|Z_1 Z_2| q^2}{4\pi\varepsilon_0 r^2}$$ attraction

$$= \frac{e^2}{4\pi\varepsilon_0 r^2}$$ attraction

conservative DYNAMICS CLASSICAL MECHANICS →



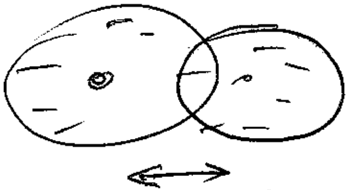
$$F(r) = +\nabla V(r) = \frac{\partial V}{\partial r}$$

Newton $\quad$ grad $\quad$ Joules

A6

the ionic force would fuse the two atoms together

but



repulsion due by other electrons

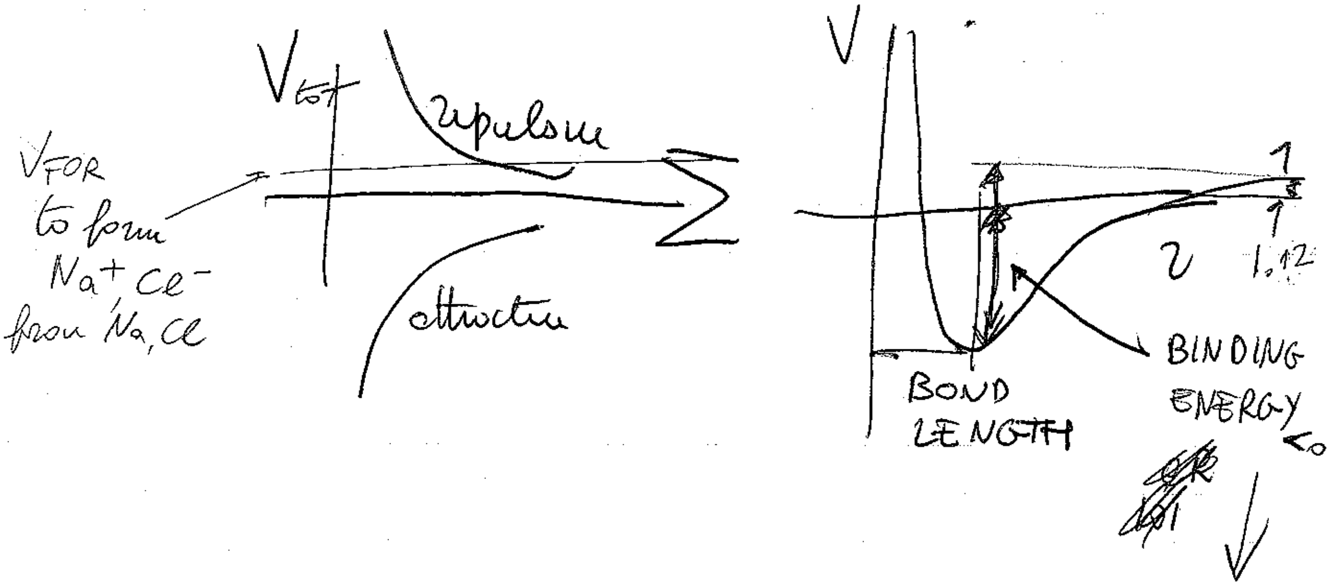
$F \sim \frac{k}{r^m}$ much stronger than attraction when r is small m

m ~~[illegible]~~ why 12

$F_{Rep} = \underset{\frac{\partial}{\partial r}}{\nabla} V \Rightarrow V_{repulsion} \sim \frac{c}{x^{\cancel{m}}}$ ~~[illegible]~~ $n = m - 1$

$\downarrow \sim 12 \quad \downarrow \sim 13$

$F_{total} = F_{att} + F_{rep} = \nabla V_{total} = \nabla(V_{REP} + V_{ATT} + V_{FORM})$

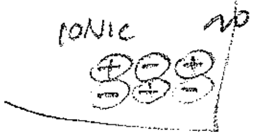


with respect of pure NaCl

Read chap 2 up to 34

Li_2O
$1s^2 2s^1$
$1s^2 2s^2 2p^4$
in extra line

A7



COVALENT BOND

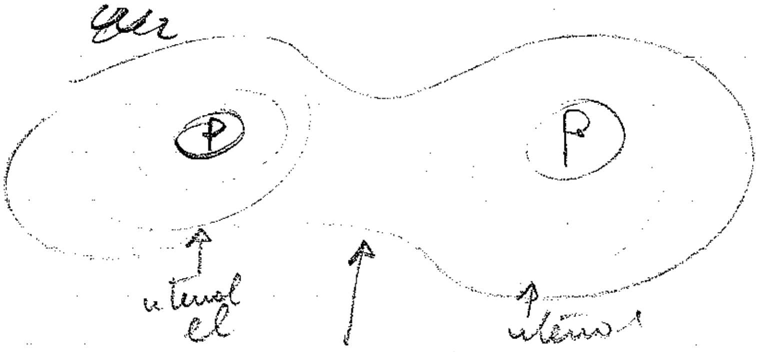
In 2 atoms similar electronegativity ⇒ but not ~~[illegible]~~ positive electro

⇒ no one gives away (+) or steals one electron (-)

then they share

Cl_2, H_2, C_xH_y are all hydrocarbons

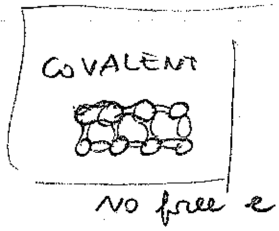
LOCALIZED

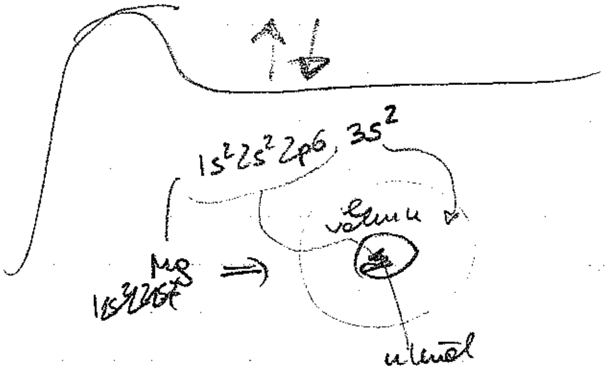


F_2 $1s^2 2s^2 2p^5$

AMMONIA NH_3 $1s^2 2s^2 2p^3$

covalent bonding orbital = guest 2 electrons





METALLIC BOND

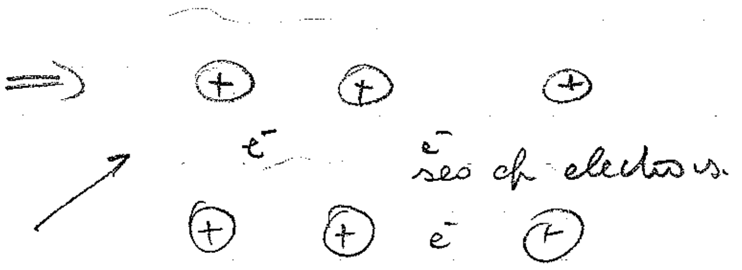
generous atoms give away electrons

⇒ electrons form a SEA / CLOUD OF ELECTRONS

called **FERMI SEA**, it's homogeneous.

JELLO MODEL

⇒



plenty of free electrons

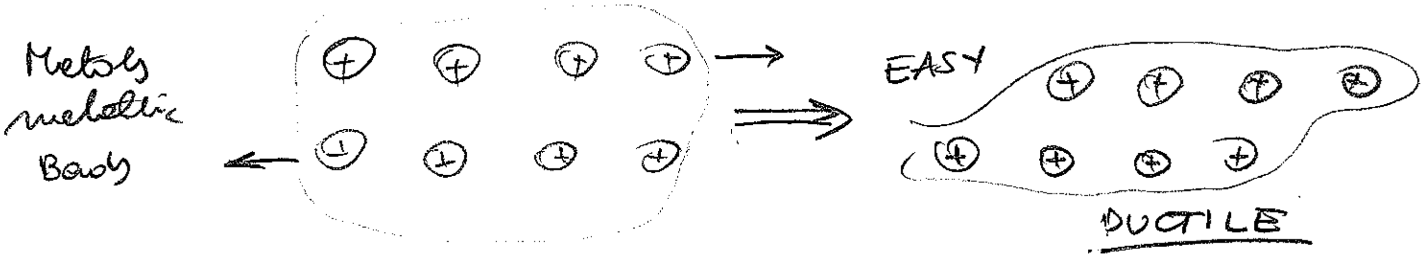
DELOCALIZED ELECTRONS.

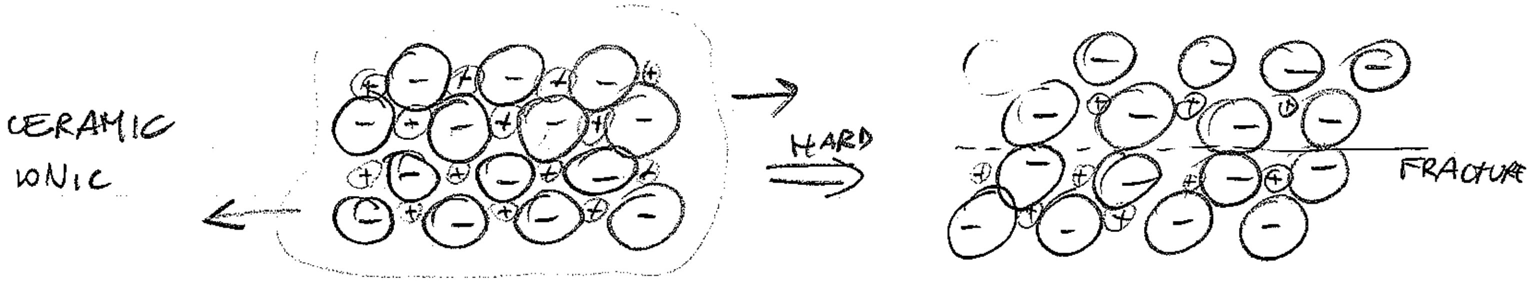
GLOBALLY SHARED ELECTRONS

A8

DUCTILITY – BRITTLE BEHAVIOUR

BOOK PIC





ELECTRICAL CONDUCTIVITY

- type of carrier (metals, solutions)
- density of carriers (#/Volume)
- mobility (heavy or light)

$v = \mu \bar{E}$

speed

electric field

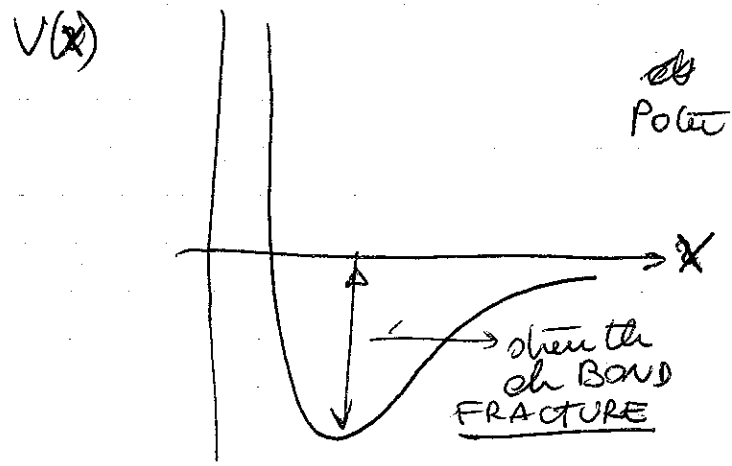
mobility

(ASK [redacted] LIONS)

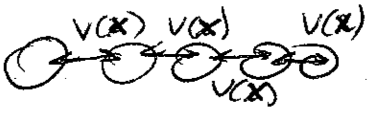
free electrons ⇒ very mobile

in bond electrons ⇒ not very mobile

ORIGIN OF YOUNG MODULUS

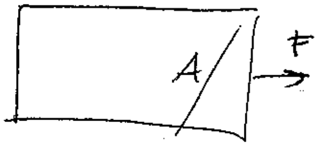


interatomic
Potential



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

$\varepsilon = \Delta x / l$



$\sigma = E \varepsilon$

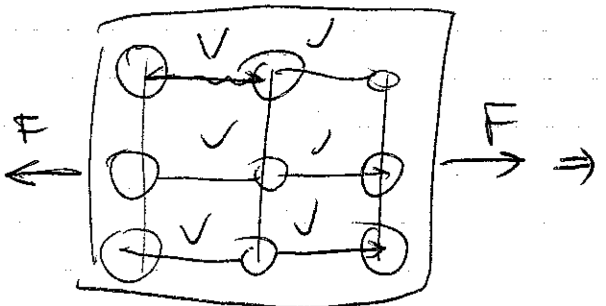
ELASTICITY

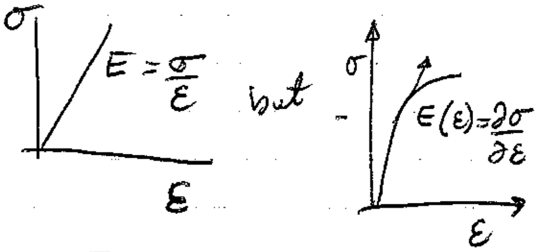
$\frac{E}{\rho}$

$F = E a \Delta x$

YOUNG

geometrical factor





$E(\varepsilon) = \frac{\partial \sigma}{\partial \varepsilon} \sim \frac{\partial F/A}{\partial \Delta x / x_0} \sim \frac{\partial F}{\partial x}$

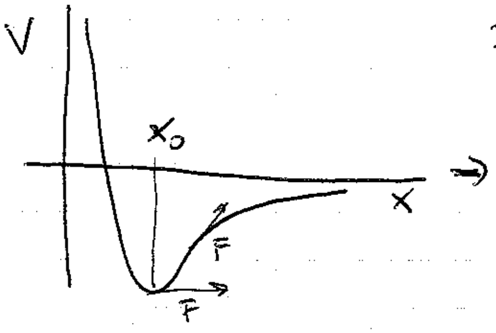
$= a \frac{\partial F}{\partial x}$

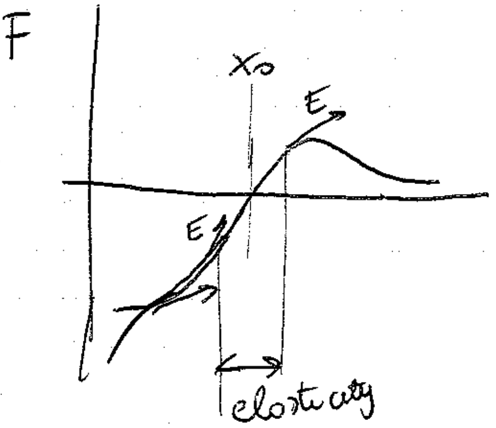
constant

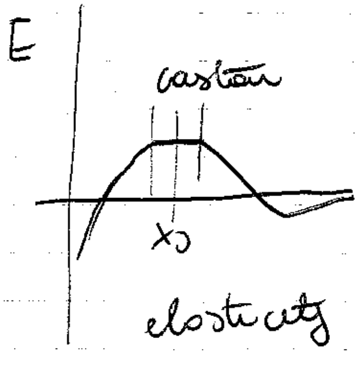
$E = a \frac{\partial F}{\partial x} = a \frac{\partial}{\partial x} \frac{\partial V}{\partial x}$

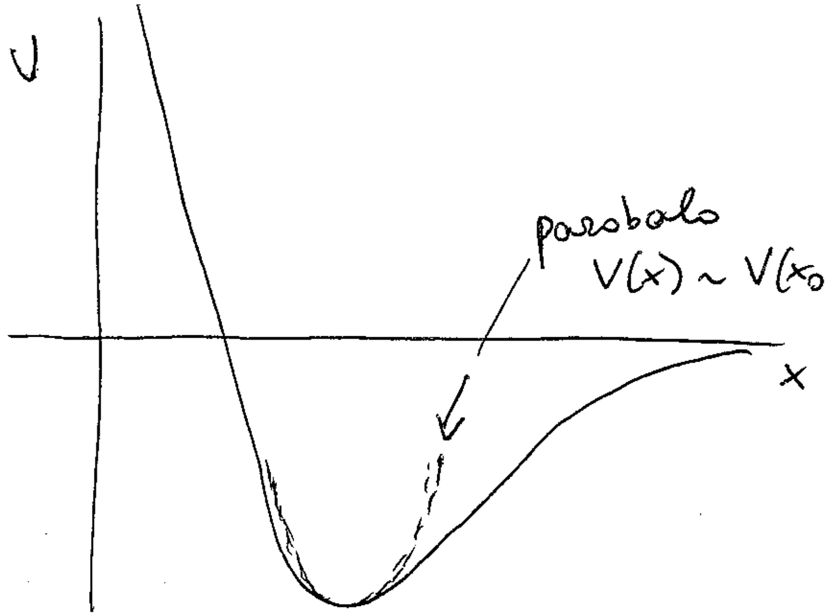
elastic modulus

$= a \frac{\partial^2 V}{\partial x^2}$ CURVATURE









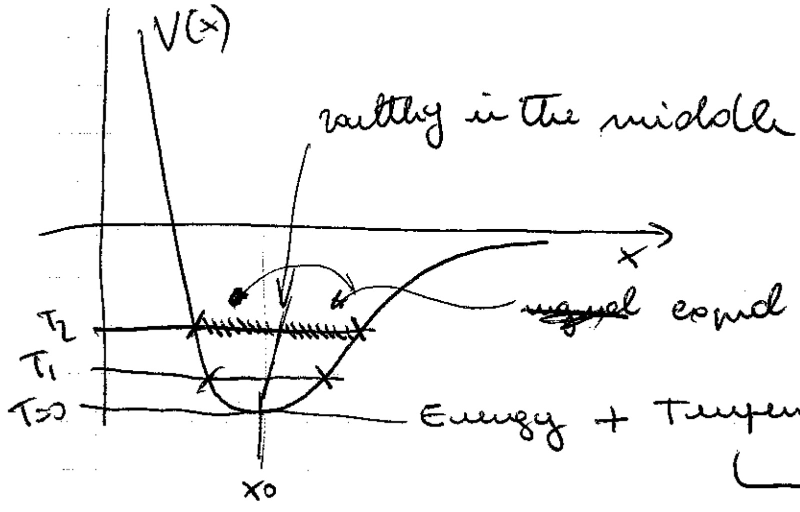
parabola

$V(x) \sim V(x_0) + \frac{1}{2}\epsilon(x - x_0)^2_{a}$

↑ imp

THERMAL EXPANSION

V(x) not symmetric
⇒ expansion



Energy + Temperature energy

↳ $\frac{1}{2}kT$ per degree of freedom (3 or 5)

↳ kT

$x_e = x_0(T=0) + \alpha x_0 (T - T_0)$

$\alpha \equiv \frac{1}{x_0}\frac{\partial x}{\partial T}$ $\sim 10^{-5} K^{-1}$

thermal expansion

$E_{BOND} \uparrow \Rightarrow T_{Melting} \uparrow \Longrightarrow \alpha_{th} \downarrow$

more symmetric and $\alpha \downarrow$

All

COORDINATION NUMBER & PACKING

ionic material (sferical, all dimensional consideration)

cation (the one that ~~the~~ gets the ⊕)

anion (the one that gets the (−))

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

$\leftarrow$ go ~~right~~ left in TABLE $\rightarrow$ go right in TABLE   then $r \leq R$

$\frac{r}{R}$ defines structure   CN= coordination number
\# of first neighbours

~~CN= 8 6 layered~~ 4   Show PIC BOOK 45

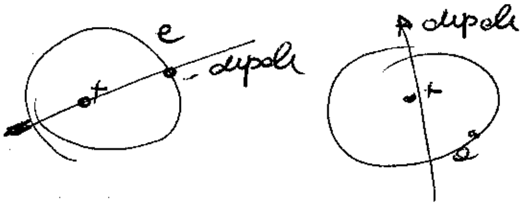
Covalent

CN depends on the electron valence shells

SECONDARY BONDS

vdW (temporary dipoles)   (weakest possible bonds ⇒ He crystals)
spherical

electrons while rotating produce a momentary electric dipole (TEMPORARY DIPOLE)



⇒ $\overline{\text{dipole}} = \bar{\ell}\, e$

$\bar{\ell}$ ↓ distance vector

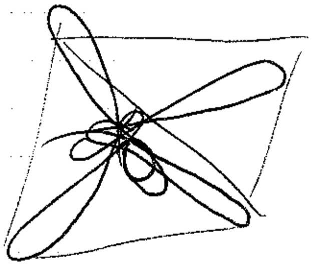
coulomb
⇒ attraction between dipoles, also if the net charge is zero!!

⇒ van der Waals weak ~ $V_{vdW} \sim -\frac{1}{r^6}$

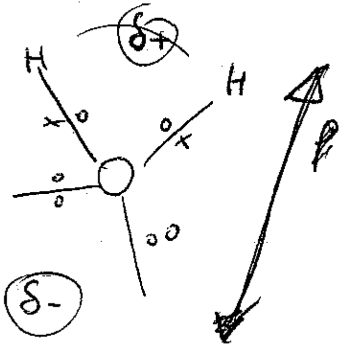
PERMANENT DIPOLES

when they have a permanent asymmetric distribution

$H_2O \Rightarrow$ ~~O~~ O $1s^2\ \underbrace{2s^2 2p^4}_{6\ \text{electrons}}$ in sp^3 hybridization



tetrahedron



p ~~dy~~ dipole

hydrogen bond
⇒ liquid water

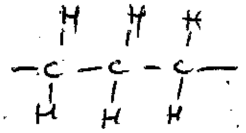
same for (S) ~~SH~~ H_2S & NH_3 $\underbrace{2s^2 2p^3}_{sp^3\ \text{with}\ 5}$

Permanent Bonds > VdW

AB

POLYMERS : MACROMOLECULES

— SATURATED



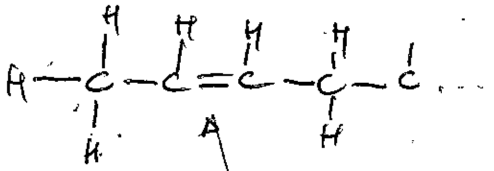
$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

NO C=C to break

NO ~~free~~ electrons to share ⇒ saturated ⇒ bonds between molecules are secondary (vdW & dipole permanent) ⇒ Termoplastic : they melt and can be reused many times ([illegible])

—UNSATURATED

they have free orbitals to ~~share~~ ⇒



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{A}{C}}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-C\ldots$$

⇒ have unsaturated double bonds

⇒

upon heating up, these bonds break and join with other chains making "cross links".

Thermoset polymers

Rubber comes from LATTICE (natural) with sulfurization
GOODYEAR

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, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d . . .

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 . . . 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 $1s^2 2s^2 2p^4$, 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.

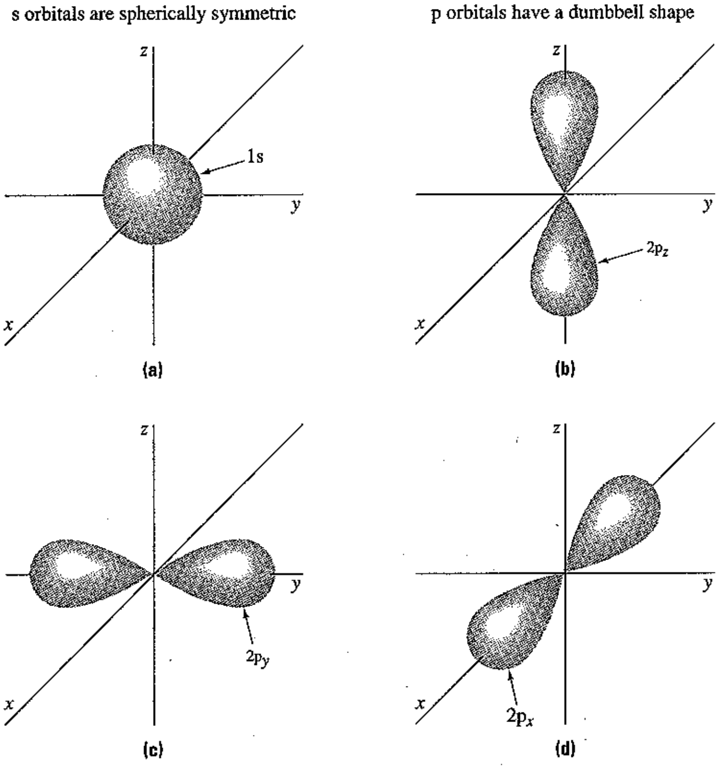


FIGURE 2.2–2

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.

d. For CdTe, ΔEN = 2.1 − 1.9 = 0.2. Using the table in Appendix B, this corresponds to a bond that is ~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.

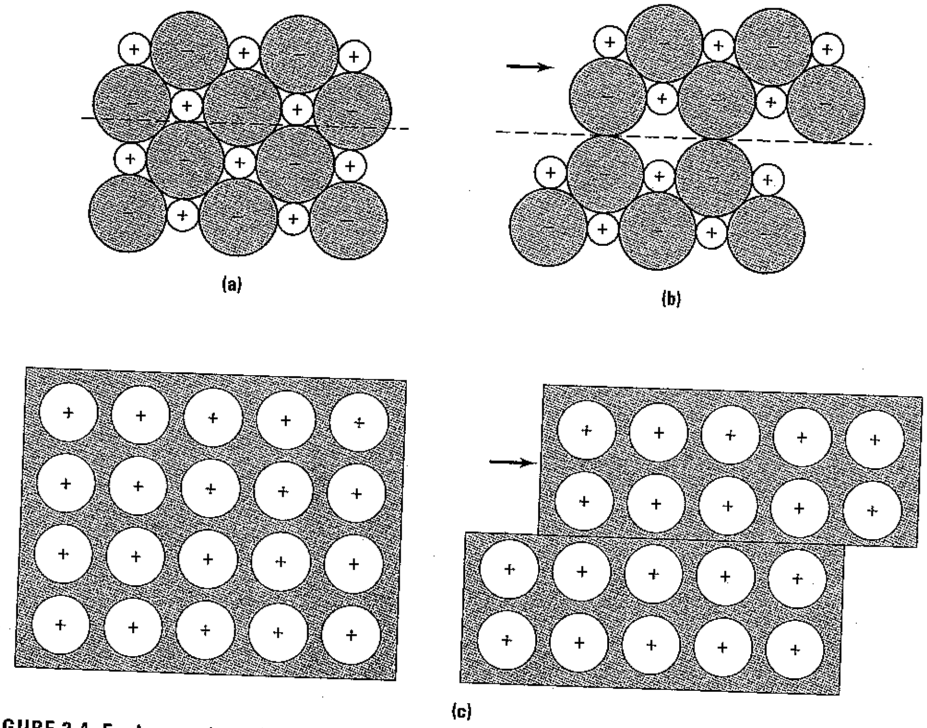


FIGURE 2.4–5 A comparison of the difference in the atomic scale response of a metal and an ionic solid to a hammer blow. **(a)** In an ionic solid before the hammer blow each ion is surrounded by oppositely charged ions. **(b)** When the ions attempt to slip past one another in response to the applied 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.

Material	Latent heat of fusion (J/g)*	Melting temperature (K)	Coefficient of thermal expansion ($\times 10^{-6}$ °C)*
Row III metals			
Na	113	371	70
Mg	368	922	25
Al	397	933	25
Si†	1800	1685	3
Row IV metals			
K	63	336	83
Se	67	494	37
Zn	113	693	35
Cu	205	1358	17
Mn	268	1517	22
Fe	272	1809	12
Co	276	1768	12
Ni	297	1726	13
Cr	331	2130	6
V	410	2175	8
Ti	418	1943	9

*Adapted from the *CRC Handbook of Tables for Applied Engineering Science*, copyright CRC Press, Boca Raton, FL, 1979.

† 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.

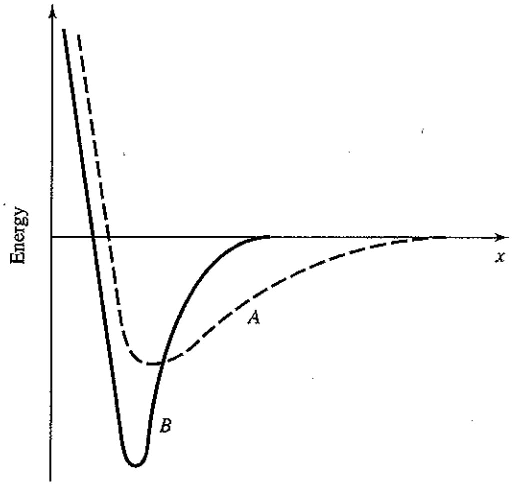
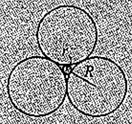
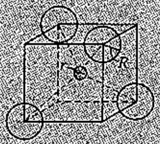
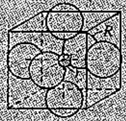
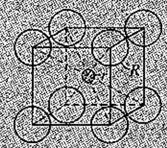
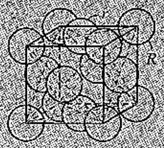


FIGURE 2.5–3

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.)

Coordination number	Critical (r/R) value	(r/R) Stability range	Geometry	
2	0	$0 < r/R < 0.155$	Always possible	DUNNO!
3	0.155	$0.155 \leq r/R < 0.225$		LAYERED
4	0.225	$0.225 \leq r/R < 0.414$		TETRAGONAL
6	0.414	$0.414 \leq r/R < 0.732$		[redacted] OCTAHEDRA
8	0.732	$0.732 \leq r/R < 1$		BCC
12	1	$r/R = 1$		FCC

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 $0.414 \leq (r/R) < 0.732$. 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

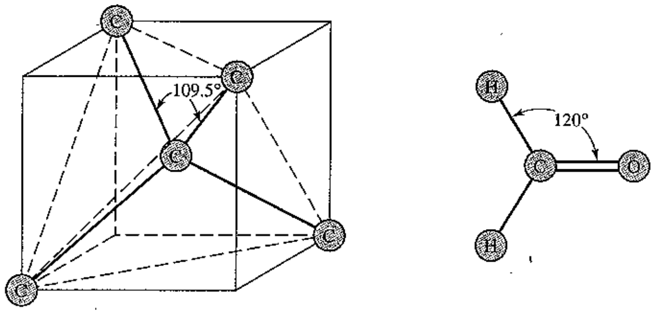
$$\frac{r + R}{2R} = \frac{1}{\sqrt{2}}$$

b. In the C_2H_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_2H_3Cl 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.



3-D structure, with all angles = 109.5°

(a)

2-D (planar) structure, with all angles = 120°

(b)

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_2O molecule.

Solution

The geometry of the H_2O 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

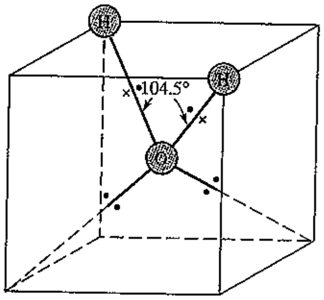


FIGURE 2.6–5 A schematic illustration of covalent bond angles in water. Note that the bond angle is 104.5°, which is slightly less than the tetrahedral angle of 109.5°.

bonding electron pairs. The structure of H_2O 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 CH_4 and CCl_4. 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 C_nH_{2n+2} increase as n increases.

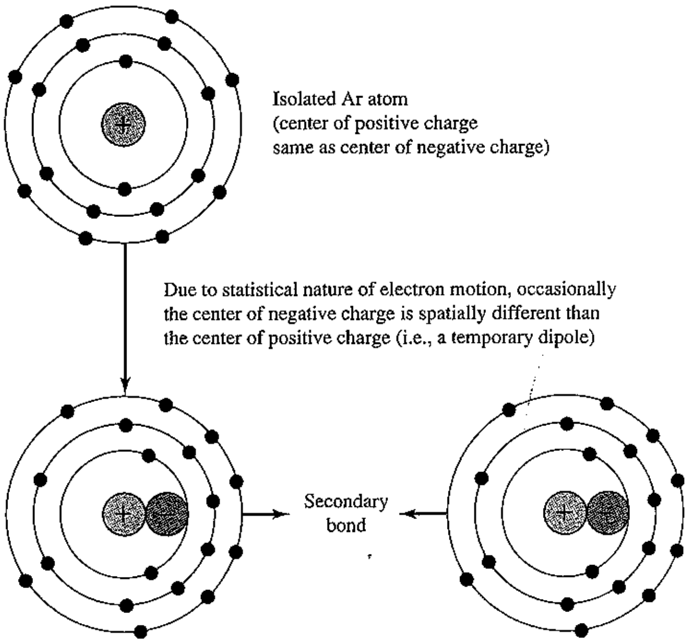


FIGURE 2.7–1 Formation of a temporary dipole in an Ar atom can induce a dipole in an adjacent Ar atom. This type of secondary bond is known as a van der Waals bond.

Figure 2.7–2 shows the charge distribution in H_2O, H_2S, and NH_3. These molecules are **permanent dipoles,** because their center of positive charge (indicated by the symbol δ^+) is always different from their center of negative charge (δ^-). 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.

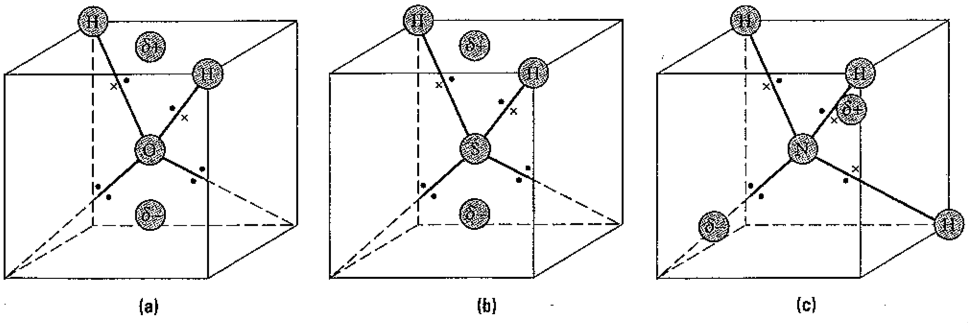


FIGURE 2.7–2 A schematic illustration of three permanent dipole molecules: **(a)** H_2O, **(b)** H_2S, and **(c)** NH_3. The x's represent the valence electrons from the H atoms and the •'s represent those from either O, S, or N. The δ^+ and δ^- symbols represent the spatial centers of positive and negative 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.

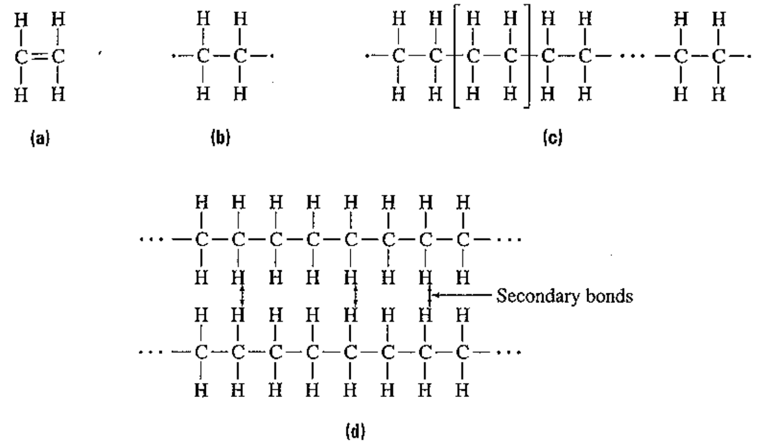


FIGURE 2.9–1 The structure of polyethylene, PE: **(a)** the basic building block for PE is the C_2H_4 monomer; **(b)** the double bond in the monomer is "opened" so that **(c)** many monomers can be linked together to form the PE polymer chain; **(d)** since the polymer chains are saturated, the only type of bond that can form between PE chains is the secondary bonds.

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.**

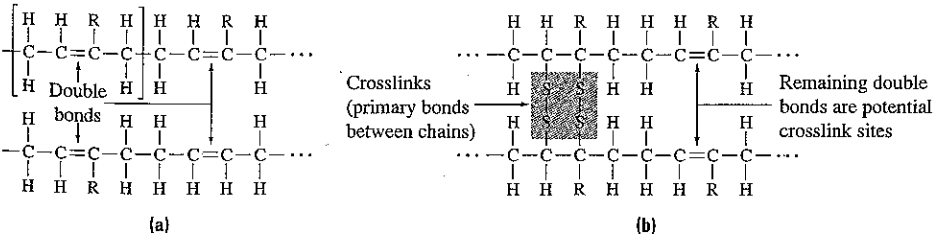
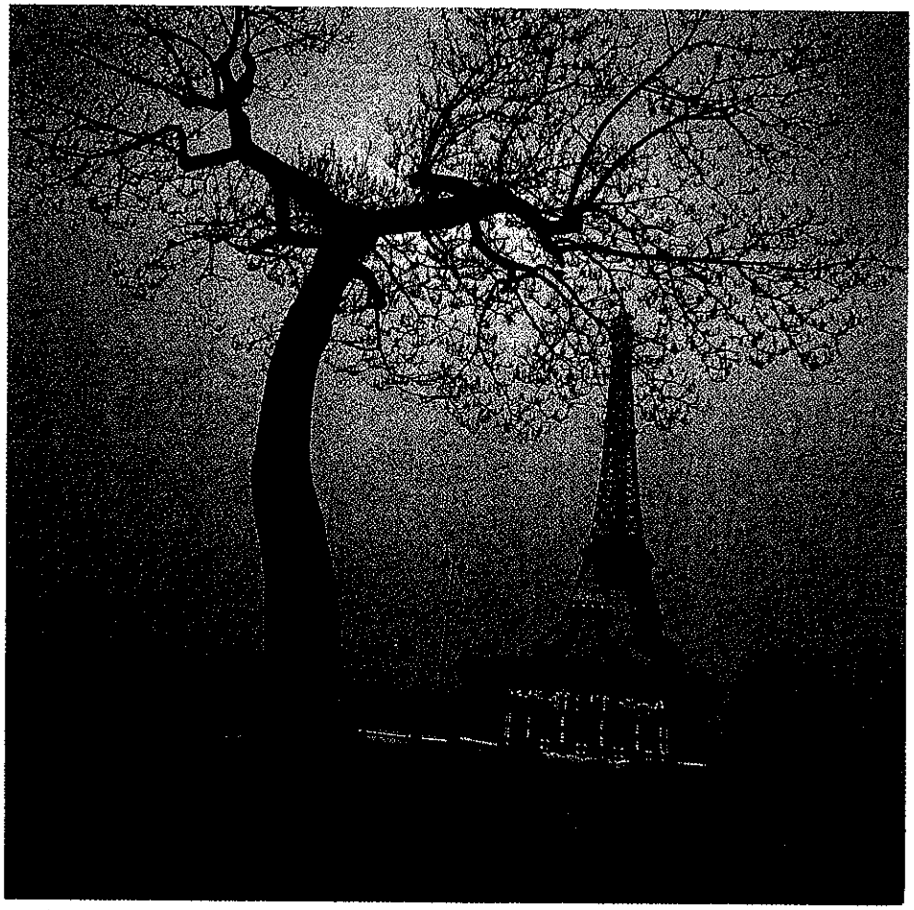


FIGURE 2.9–2 The structure of crosslinked rubber. The existence of double bonds along the length of the polymer chains shown in part **(a)** permits the formation of crosslinks between chains, as shown in part **(b)**. Note that in this case the crosslinks are composed of short chains of sulfur atoms.



Il moto é causa d'ogni vita

(Movement is the cause of all life)

Leonardo da Vinci

Design …. Is the fount and body of painting and sculpture
and architecture … and the root of all sciences.

Michelangelo Buonarroti

CRYSTAL STRUCTURE

ORDER

BOOK 61-78
STUDY

Sit on an atom & around around

what do you see ?

short range order (Liquids, amorphous)
long range order (crystals)
disorder (gas)

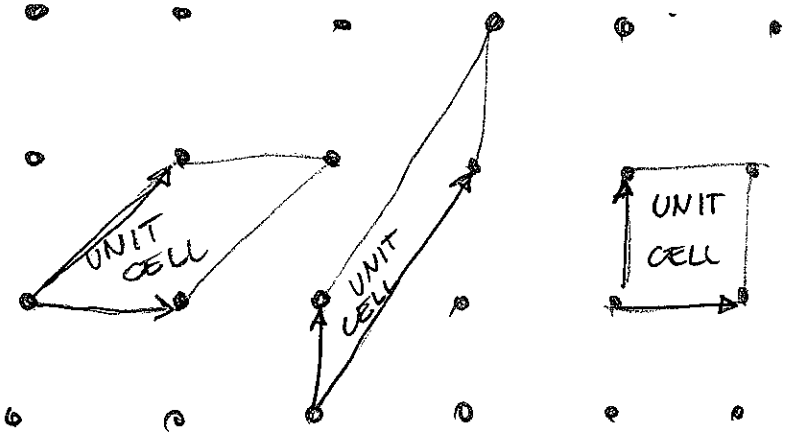
WE CARE ABOUT CRYSTALS

CRYSTAL = solid material with periodic structure!
periodicity is represented by a lattice (BRAVAIS)

LATTICE = infinite set of discrete points
invariant by traslation / 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

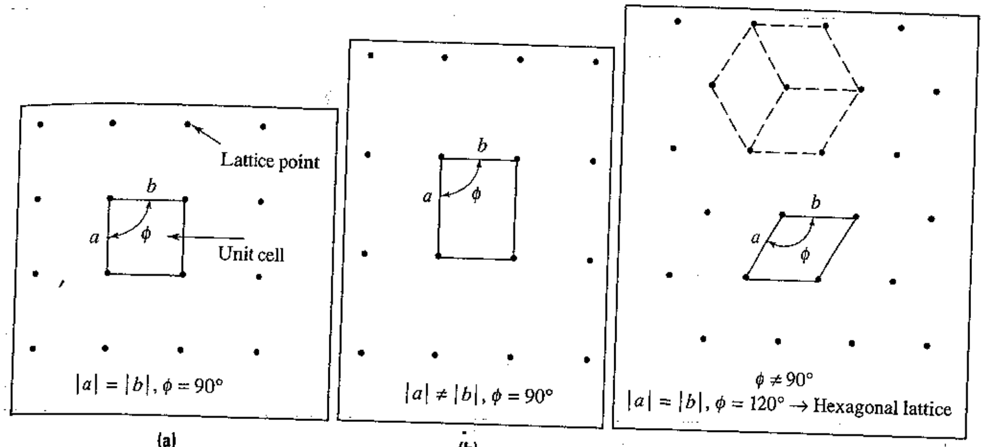
UNIT CELL = a part of volume (surface if 2D lattice) that if replicated for every lattice point covers all the space once and only one lattice points, many different unit cells



↗ = translational vectors, $\bar{a}, \bar{b}, \bar{c}$

|↗| = lattice parameter

IN 2D



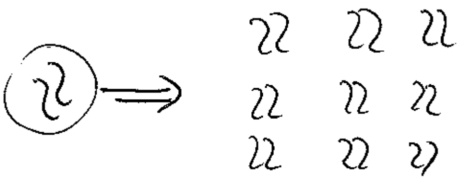
(a) (b) (c)

in 2D
3 possible lattices

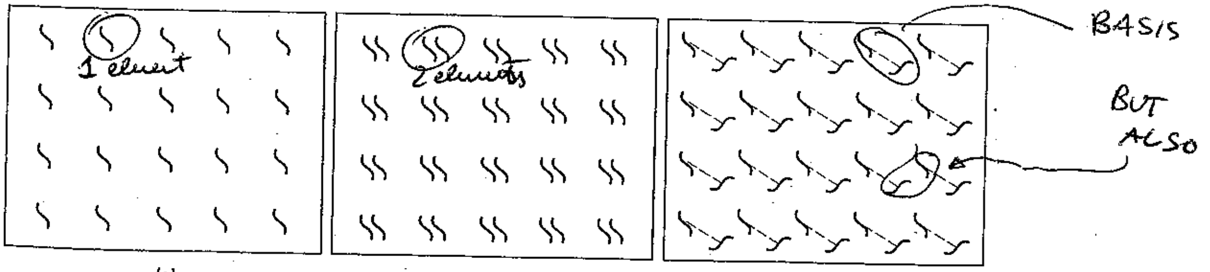
square rectangular parallelogram, if $\phi = 120 \Rightarrow$ HEX

LATTICE = geometrical set of points needed for translations

TRANSLATION OF WHAT? OF A BASIS



LATTICE + BASIS = CRYSTAL STRUCTURE



(a) (b) (c)

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.

D

ELEMENT	a (Å)
Pt	3.92
δ-Pu	4.64
Rh	3.80
Sc	4.54
Sr	6.08
Th	5.08
Xe (58 K)	6.20
Yb	5.49

ystal Structures, 2nd ed.,
aken at about room tem-
at exist in many forms the
letailed information, more
should be consulted.

RED

ELEMENT	a (Å)
Ta	3.31
Tl	3.88
V	3.02
W	3.16

to apply to a set of points, it
ining any one of these points
ice, this set of vectors does not
Yet another usage comes from
splacement, in which everything
rection of **R**. The term "Bravais
termined by the vectors, rather
clear from the context whether
are being referred to.[7]

---

nition of a Bravais lattice with the pre-
n (a): A Bravais lattice is a discrete set
traction (i.e., the sum and difference of

C2b

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.[8] 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.

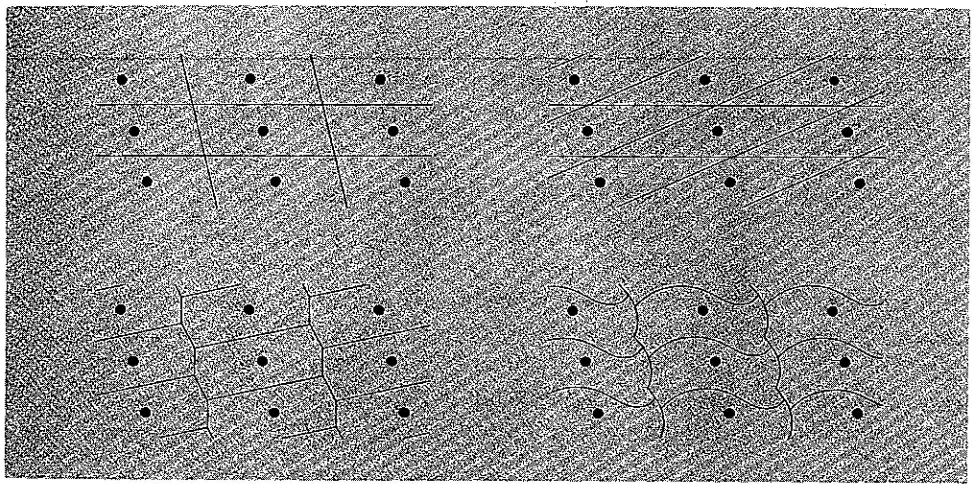


Figure 4.10
Several possible choices of primitive cell for a single two-dimensional Bravais lattice.

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[9] and v is the volume of the primitive cell, then $nv = 1$. Thus $v = 1/n$. Since

---

[8] Translations of the primitive cell may possess common surface points; the nonoverlapping proviso is only intended to prohibit overlapping regions of nonzero volume.

[9] 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.

IN 3D

14 different lattices BRAVAIS in 7 FAMILIES

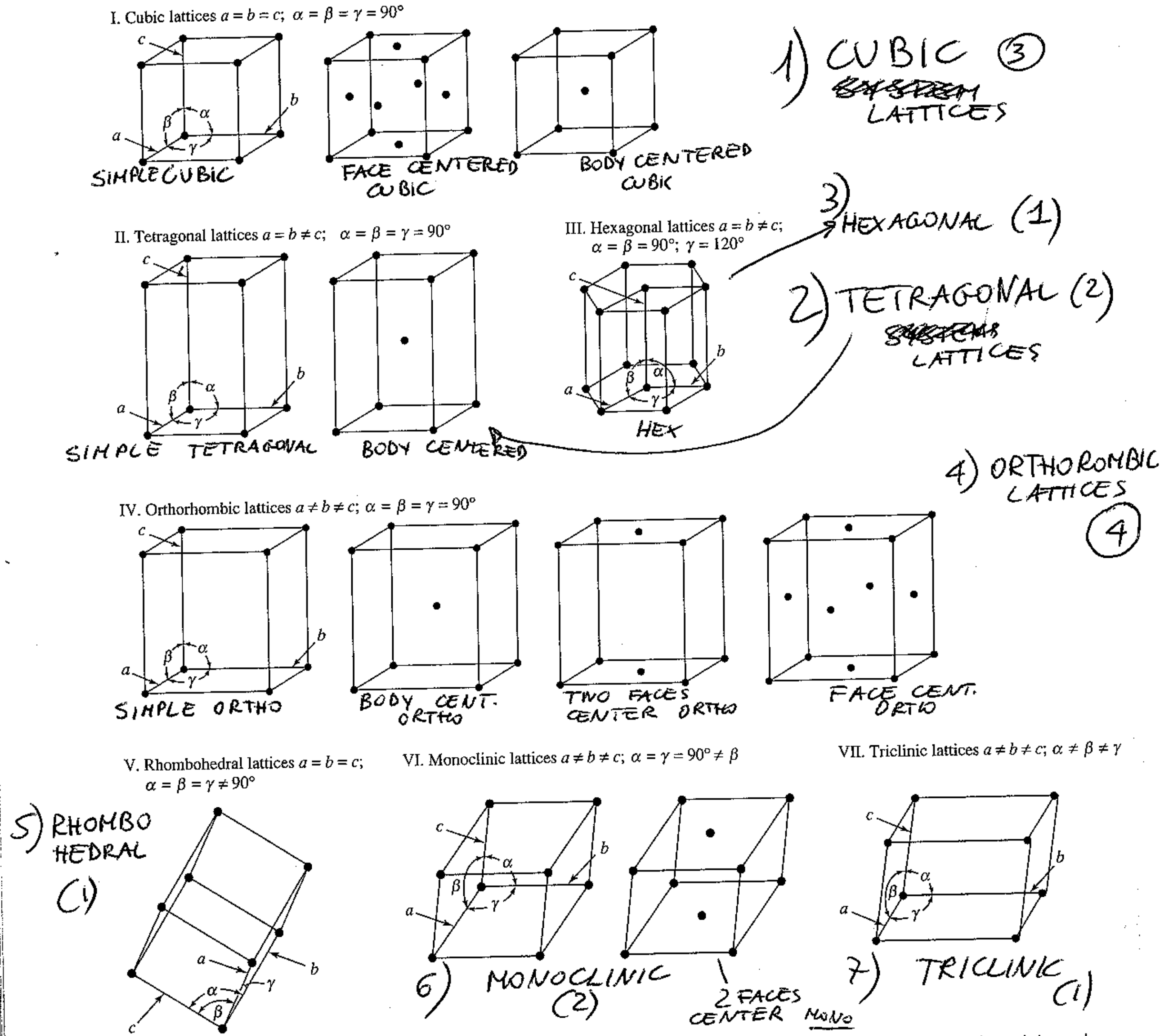


FIGURE 3.2–3 The 14 Bravais lattices grouped into the 7 lattice types. The restrictions on the lattice parameters a, b, and c and the angles between the edges of the unit cell α, β, and γ are listed for each unit cell.

There are 14 valid 3-D lattices

A UNIT CELL IS THE "SMALLEST" POSSIBLE VOLUME WHICH, IF TRANSLATED, COVER ALL THE SPACE.

C3

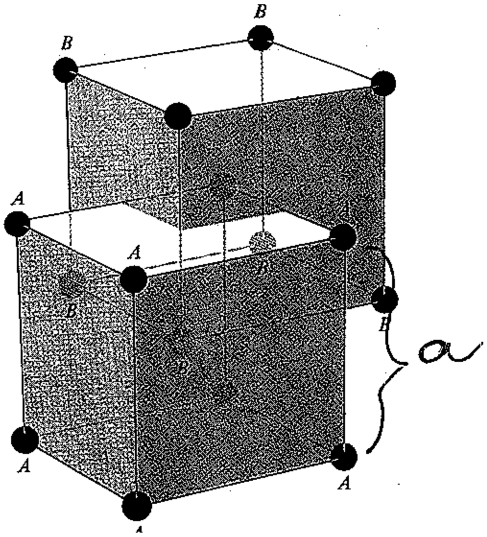
SOME SYSTEMS CAN BE DESCRIBED WITH A BASIS O WITHOUT BASIS ?

BCC

EXAMPLE BCC

Figure 4.5

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.



NO BASIS

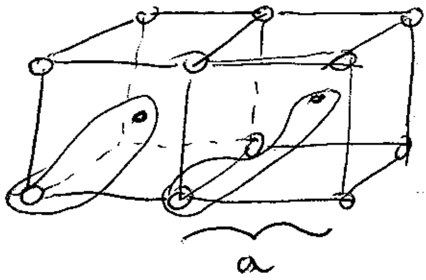
BCC = EVERY POINT IS A LATTICE POINT

a = LATTICE PARAMETER

OR WITHOUT BASIS

⇒ CUBIC LATTICE + A BASIS OF 2 POINTS

BCC OR CUBIC + BASIS



$$\mathbf{0},\quad \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \qquad \text{(bcc)}$$

ELEMENTS

Table 4.2
ELEMENTS WITH THE MONATOMIC BODY-CENTERED CUBIC CRYSTAL STRUCTURE

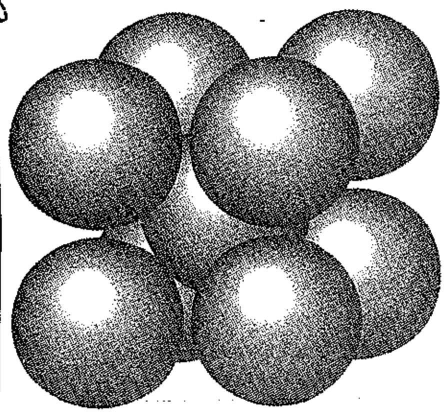
ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

↓ TUNGSTEN

C4

Bcc

ATOMS



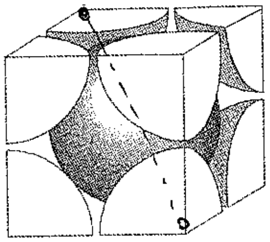
Again like

SHIFTED B

STACKING TYPE A

⇒ STACKING ABABAB

SECTION OF A UNIT CELL (CUBIC CHOICE) WITH BASIS



$a\sqrt{3}$ diagonal must FIT 2 spheres

$= 4r$

⇒

BCC WITHOUT BASIS

$a\sqrt{3} = 4r$

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

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}). \tag{4.3}$$

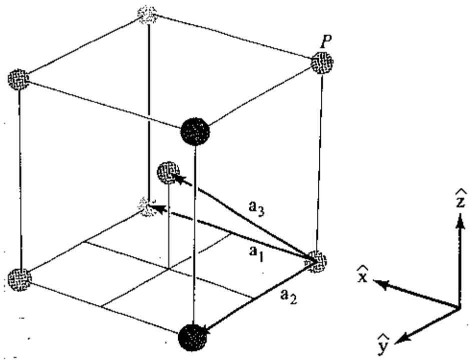


Figure 4.6
Three primitive vectors, specified in Eq. (4.3), for the body-centered cubic Bravais lattice. The lattice is formed by taking all linear combinations of the primitive vectors with integral coefficients. The point P, for example, is $P = -\mathbf{a}_1 - \mathbf{a}_2 + 2\mathbf{a}_3$.

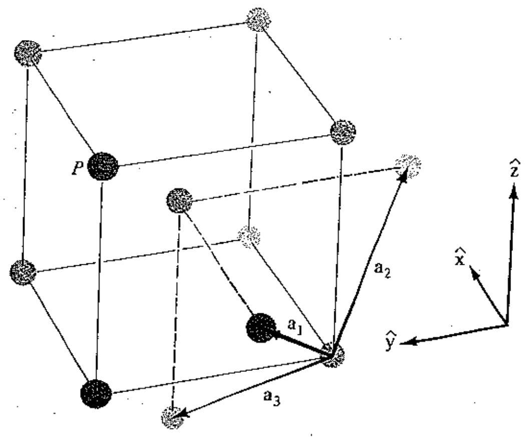


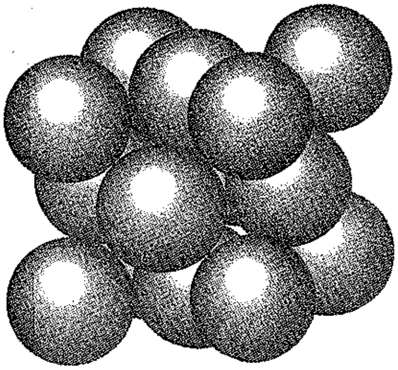
Figure 4.7
A more symmetric set of primitive vectors, specified in Eq. (4.4), for the body-centered cubic Bravais lattice. The point P, for example, has the form $P = 2\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$.

BCC WITHOUT A BASIS BUT MORE SYMMETRIC SET OF VECTOR

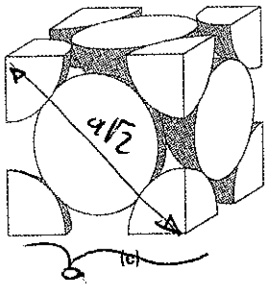
$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}). \tag{4.4}$$

C5

Fcc



(b)



(c)

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

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

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}). \quad \text{FCC} \tag{4.5}$$

Figure 4.9
A set of primitive vectors, as given in Eq. (4.5), for the face-centered cubic Bravais lattice. The labeled points are $P = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$, $Q = 2\mathbf{a}_2$, $R = \mathbf{a}_2 + \mathbf{a}_3$, and $S = -\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$.

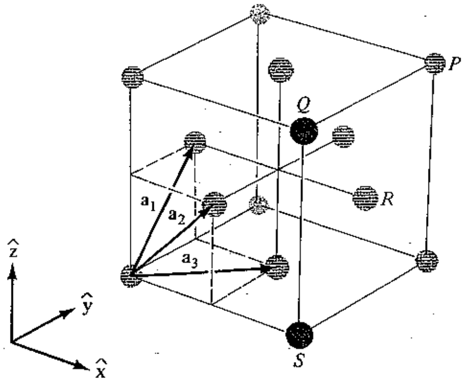


Table 4.1
ELEMENTS WITH THE MONATOMIC FACE-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ-Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β-Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

FCC LATTICE, NO BASIS

OR CUBIC LATTICE WITH BASIS OF 4!

C6

$$\mathbf{0}, \quad \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}), \quad \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}) \qquad \text{(fcc)}.$$

DIAMOND = FCC + BASIS (2)

SOME IMPORTANT EXAMPLES OF CRYSTAL STRUCTURES AND LATTICES WITH BASES

Diamond Structure

fcc, can base (1/8, 1/8, 1/8) and −( )

The diamond lattice[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 $(a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. 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.

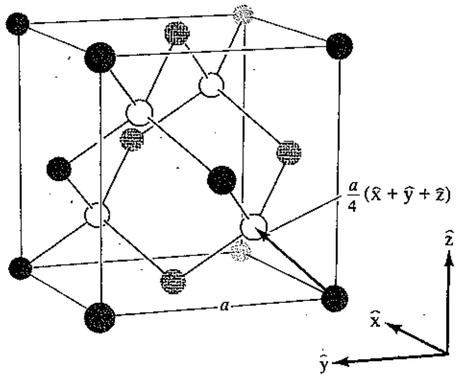


Figure 4.18
Conventional cubic cell of the diamond lattice. For clarity, sites corresponding to one of the two interpenetrating face-centered cubic lattices are unshaded. (In the zincblende structure the shaded sites are occupied by one kind of ion, and the unshaded by another.) Nearest-neighbor bonds have been drawn in. The four nearest neighbors of each point form the vertices of a regular tetrahedron.

Table 4.3
ELEMENTS WITH THE DIAMOND CRYSTAL STRUCTURE

ELEMENT	CUBE SIDE a (Å)
C (diamond)	3.57
Si	5.43
Ge	5.66
α-Sn (grey)	6.49

← total e density
$\simeq 1.05 \times 10^{24} \frac{ele}{cc}$

~~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.

C6b

HEX

IS A BRAVAIS LATTICE

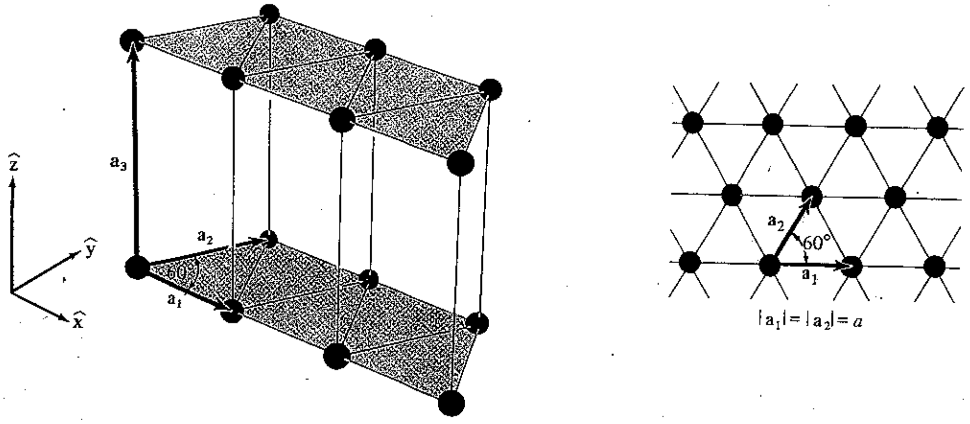


Figure 4.19
The simple hexagonal Bravais lattice. Two-dimensional triangular nets (shown in inset) are stacked directly above one another, a distance c apart.

⇓

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = \frac{a}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}a}{2}\hat{\mathbf{y}}, \quad \mathbf{a}_3 = c\hat{\mathbf{z}}.$$

PRIMITIVE VECTORS.

HCP IS NOT A BRAVAIS LATTICE

HEXAGONAL CLOSED PACKED

HCP = HEX + BASIS(2)

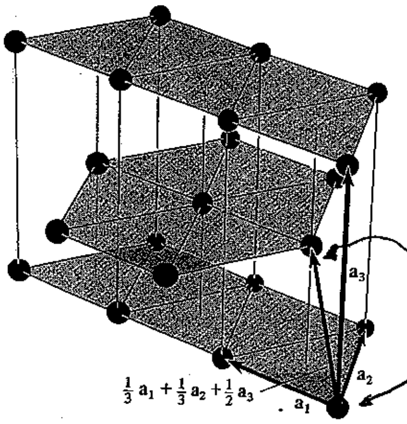
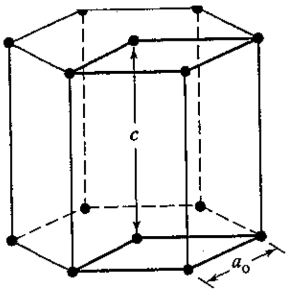


Figure 4.20
The hexagonal close-packed crystal structure. It can be viewed as two interpenetrating simple hexagonal Bravais lattices, displaced vertically by a distance $c/2$ along the common c-axis, and displaced horizontally so that the points of one lie directly above the centers of the triangles formed by the points of the other.

HCP = HEX + BASIS

C7

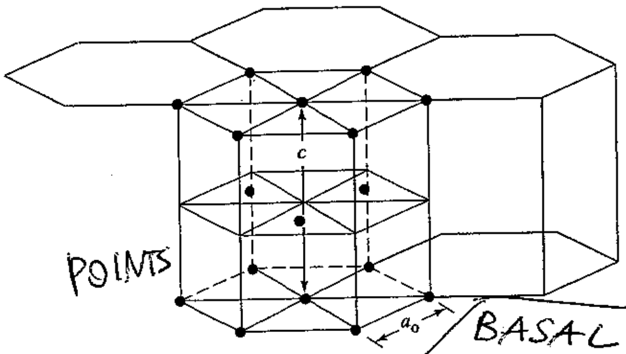
HCP



(a)

UNIT CELL

NEED
2 PARAMETERS

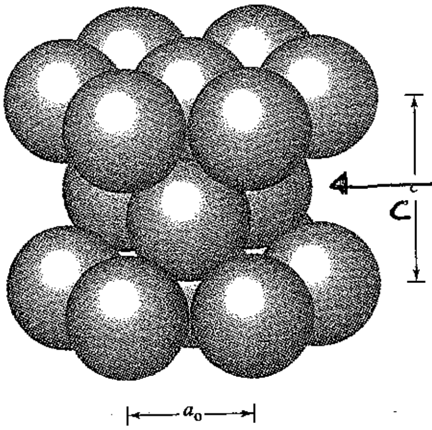


C-AXIS

POINTS

BASAL
PLANE

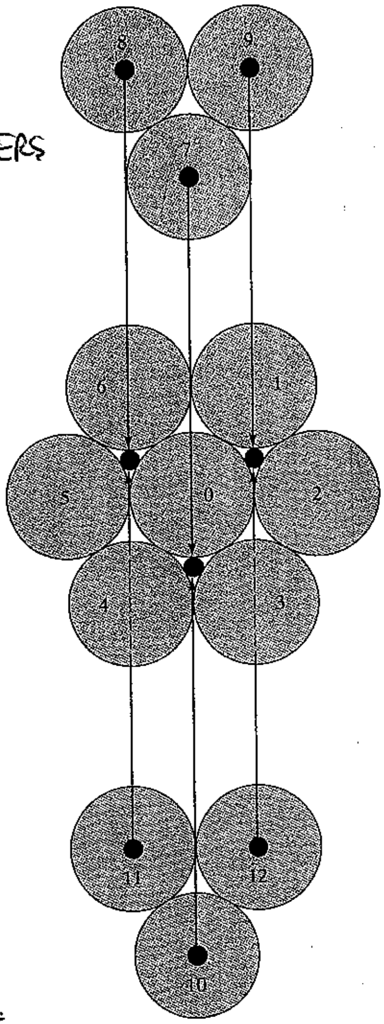
(b)



ATOMS

WITHOUT
THIS IS
NORMAL
HEXAGONAL

(c)



(d)

STACKING

Table 4.4
ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

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

IDEAL (WITH SPHERES)

$$c = \left(\frac{4}{\sqrt{6}}\right)a_0 = 1.633a_0 = 3.266r$$

VOLUME

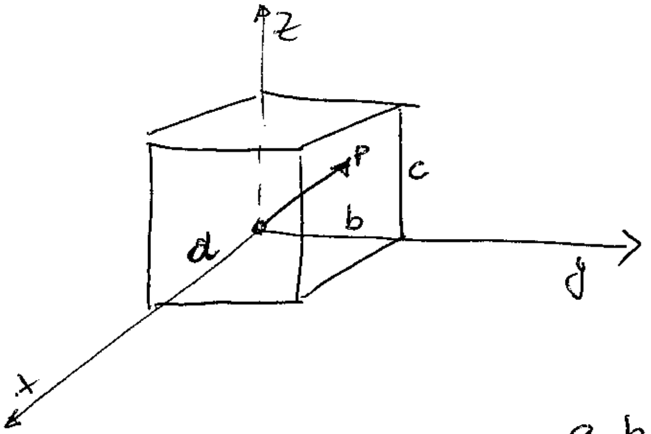
$$V_{uc}(\text{large HCP}) = \left(\frac{3\sqrt{3}}{2}\right)a_0^2c$$

C 8

MILLER INDICES

- CUBIC, TETRAGONAL, ORTHOROMBIC

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

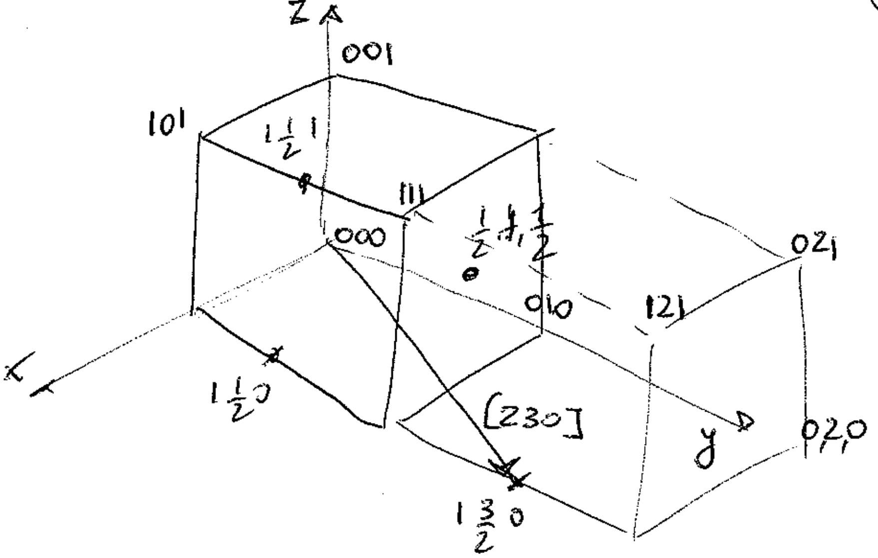


RIGHT HAND CARTESIAN SYSTEM

TAKE "RECTANGULOID" UNIT CELL

a, b, c in meters [maybe Å OR nm]

(h, k, l) = fractions of positions of P with respect to (a, b, c).



POINTS (FRACTIONAL

negative put a ‾ on the top

DIRECTIONS

put numbers in (h, k, l) and get MAXIMUM COMMON DENOMINATOR ⟹ DIVIDE

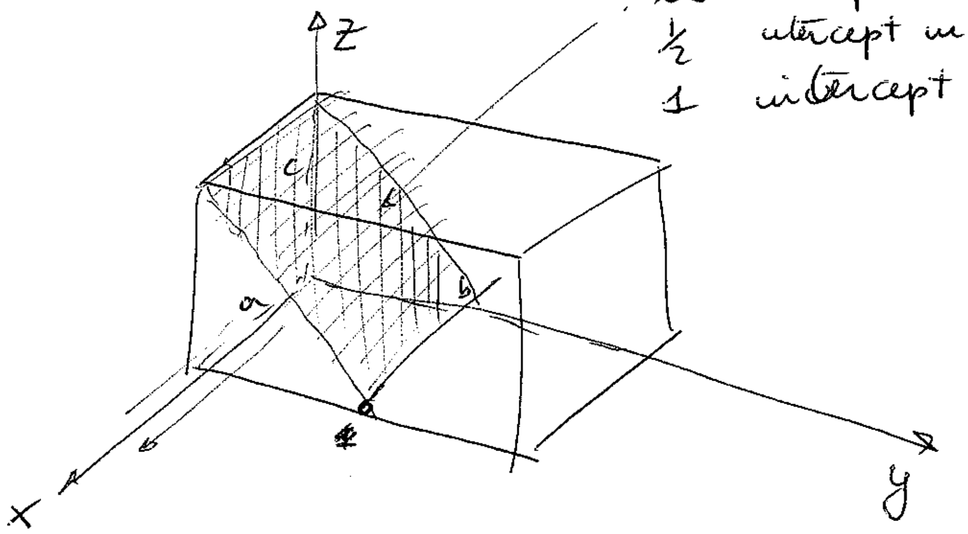
MINIMUM COMMON MULTIPLIER ⟹ MULTIPLY

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

$(2\ 2\ 0) \Rightarrow [1\ 1\ 0]$ ⟹ MILLER INDICES

PLANES

1) MAKE COORDINATES



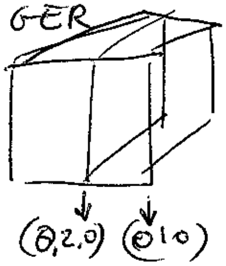
∞ intercept in $\hat{x}$
½ intercept in $\hat{y}$
1 intercept in $\hat{z}$

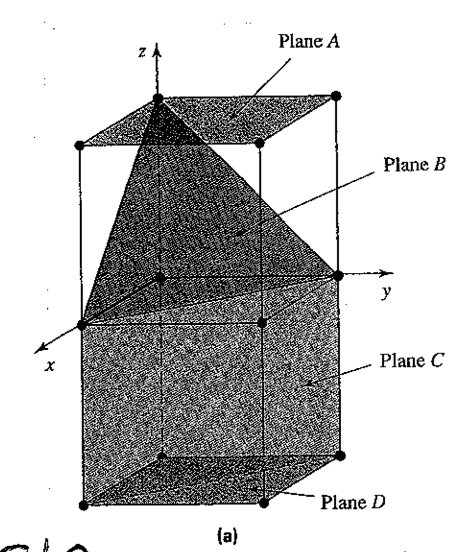
2) identify intercepts in (h k l) notation (fractional), in the $\hat{x}, \hat{y}, \hat{z}$ axis

3) take reciprocal

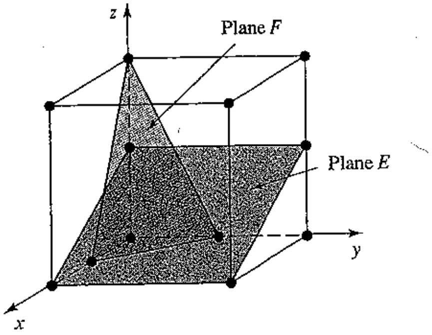
$\left(\frac{1}{h}, \frac{1}{k}, \frac{1}{l}\right) \to \left(\frac{1}{\infty}, \frac{1}{1/2}, \frac{1}{1}\right) \to (0, 2, 1)$ → put (−) on top if negative

4) clear fractions but DO NOT REDUCE AT LOWER INTEGER



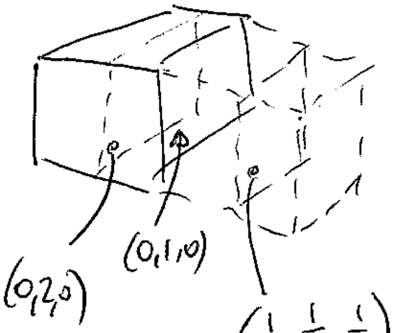


(a)



Plane	Intercepts	Indices
A	∞, ∞, 1	(0 0 1)
B	1, 1, 1	(1 1 1)
C	1, 1, ∞	(1 1 0)
D	∞, ∞, −1	$(0\,0\,\bar{1})$
E	1, ∞, 1/2	(1 0 2)
F	1/2, 1/2, 1	(2 2 1)

(b)



$\left(\frac{1}{\infty}, \frac{1}{\frac{3}{2}}, \frac{1}{\infty}\right) = \left(0, \frac{2}{3}, 0\right) \to = (0,2,0)$

C10

DENSITY, PACKING FACTORS OF CRYST.

MUST COUNT ONLY LATTICE POINTS (BRAVAIS) NOT ATOM NECESSARY (UNLESS BASIS = 1 element)

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

$$\Downarrow \quad \rho_L = \frac{\#\text{ of LATTICE POINTS ALONG DIRECTION } \cancel{\text{ONE}} \text{ IN UNIT CELL}}{\text{LENGTH OF LINE CONTAINED IN ONE UNIT CELL}} \quad \left[\frac{1}{m}\right]$$

EQUIVALENT NOTATION, BUT EASIER! (STEFANO'S)

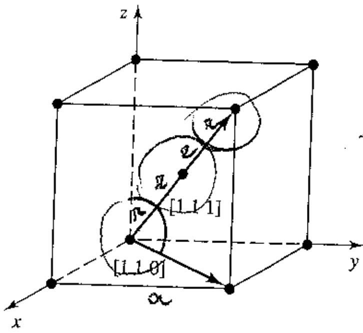
1) PICK 1 DIRECTION FROM ORIGIN (1 POINT 000)
2) ~~[illegible]~~ MEASURE DISTANCE WITH 1ST EQUIVALENT POINT ~~TO~~ ~~TO~~ OF ORIGIN = d

$$\Rightarrow \quad \rho_L(\text{DIRECTION}) = \frac{1}{d(\text{DIRECTION})}$$

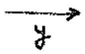
put DIST IN RADII OF SPHERES

EXAMPLE 3.5.1 (79)

BCC



(c)

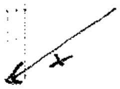


along [1 1 1]

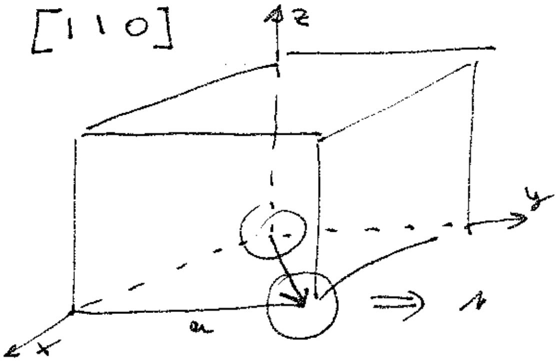
$\longrightarrow a\sqrt{3} = 4r$ (Relation $r \leftrightarrow$ lattice parameter for BCC)

start from (0,0,0)
go along [111] $\Rightarrow$ meet $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$
at position $\left(\frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2}\right)$ distance
$= 2r \Rightarrow \rho_L([111]) = \frac{1}{2r}$ //

C11



ALONG [1 1 0]



$a\sqrt{3} = 4r$

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

go along [110] $\Rightarrow$ 1 meet point (1,1,0) @ distance $a\sqrt{2}$

$$\Rightarrow \rho_L([110]) = \frac{1}{a\sqrt{2}} = \frac{\sqrt{3}}{r4\sqrt{2}} \simeq \frac{0.3}{r}$$

SYMMETRY

$$\rho_L[110] = \rho_L[101] = \rho_L[011] \simeq \frac{0.3}{r}$$

$$\rho_L[111] = \frac{0.5}{r}$$

$$\rho_L[100] = \rho_L[010] = \rho_L[001] \simeq \frac{0.43}{r}$$

~~HIGHEST CLOSE PACKING DIRECTION~~

CLOSE
PACKING
DIRECTION

ALONG [1 0 0]

go along [100]

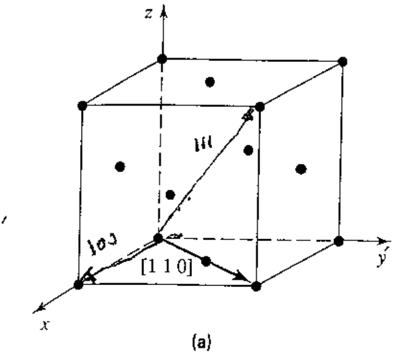
meet point (1,0,0) @ a

$$\rho_L([100]) = \frac{1}{a} = \frac{\sqrt{3}}{4r} \simeq \frac{0.43}{r}$$

CLOSE PACKING DIRECTION

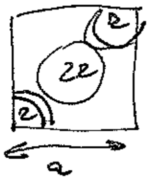
IS THE DIRECTION WHERE EQUIVALENT POINTS ARE CLOSEST!!! (HIGHEST ρ_L)

FCC



RATIO $a \leftrightarrow r$ for FCC

FACE



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

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

along $[111]$ find $(1,1,1)$ $\Rightarrow$ @ $a\sqrt{3} \Rightarrow$

$\rho_L[111] = \frac{1}{a\sqrt{3}} = \frac{\sqrt{2}}{4r\sqrt{3}} \simeq \frac{0.2}{r}$

along $[110]$ or $[101]$ OR $[011]$

find $(\frac{1}{2}, \frac{1}{2}, 0)$ @ $\frac{a\sqrt{2}}{2} = \frac{a}{\sqrt{2}} \Rightarrow$ $\rho_L[111] = \frac{\sqrt{2}}{a} = \frac{\sqrt{2}\sqrt{2}}{4r} = \frac{1}{2r}$ $\simeq \frac{0.5}{r}$

along $[100]$ or $[010]$ or $[001]$

find $(1,0,0)$ @ $a \Rightarrow \rho_L[100] = \frac{1}{a} = \frac{\sqrt{2}}{4r} \simeq \frac{0.35}{r}$

CLOSE-PACKING DIRECTION FOR FCC = $[110]$

~~CUBIC~~

C13

PLANAR DENSITY

PLANAR DENSITY IS THE DENSITY OF POINTS PER UNIT AREA

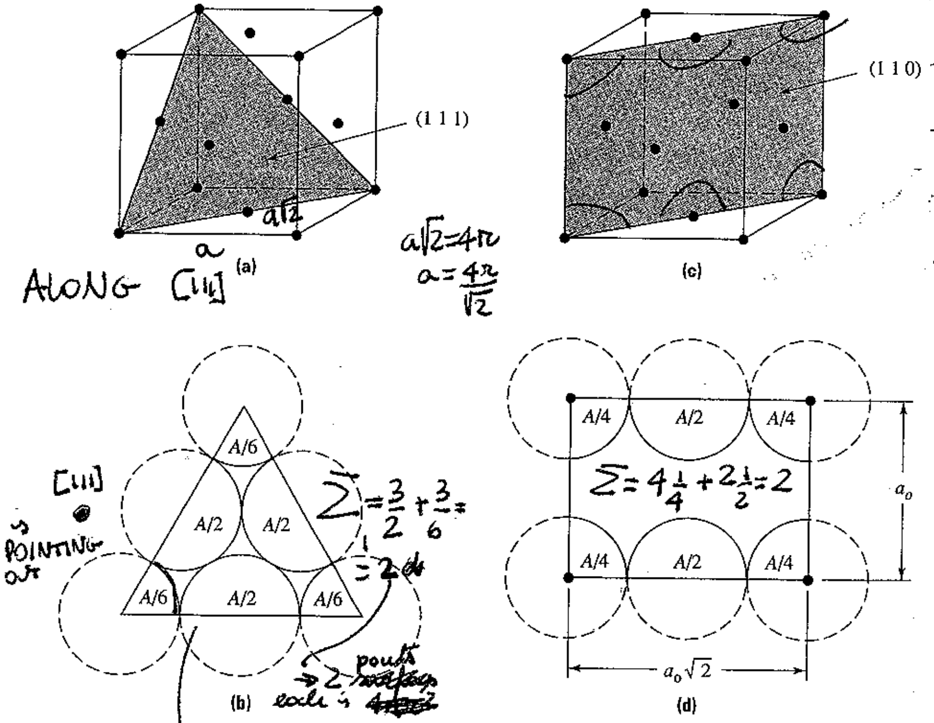
$$\rho_P(\text{PLANE}) = \frac{\#\text{ OF POINTS LATTICE}}{\text{AREA OF THE SURFACE CONSIDERED}}$$

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

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

FCC

EX 3.5-2



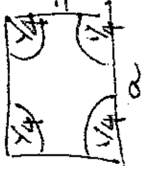
$a\sqrt{2} = 4r$

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

$\Sigma = \frac{3}{2} + \frac{3}{6} = 2$

$\Sigma = 4\frac{1}{4} + 2\frac{1}{2} = 2$

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.



$\rho_P[100] = \Rightarrow \Sigma 4 \cdot \frac{1}{4} = 1$

$\rho_P(100) = \frac{1}{a^2} = \frac{2}{16r^2} = \frac{1}{8r^2}$

$\rho_P[110] = \frac{2}{a\sqrt{2}\cdot a} = \frac{2}{a^2\sqrt{2}} = \frac{2}{\sqrt{2}\,\frac{16r^2}{2}}$

$$\Rightarrow \boxed{\rho_P(110) = \frac{1}{4\sqrt{2}\,r^2}}$$

NICE BOX

$\rho_P(100) = \rho(200) = \frac{1}{8r^2}$

NICE BOX

$$\boxed{\rho_P(111) = \frac{1}{r^2 2\sqrt{3}}}$$

~~$\rho_P[111] = \frac{2}{4\dots r^2} = \dots = \frac{1}{2\dots r^2} =$~~

C14

area $=$ △ $a\sqrt{2}$ $\updownarrow \frac{a\sqrt{3}}{\sqrt{2}} \Rightarrow$ ~~A~~

$a = 4r/\sqrt{2}$

$A = a\sqrt{2}\,\frac{a\sqrt{3}}{\sqrt{2}}\,\frac{1}{2} = \frac{a^2\sqrt{3}}{2} \Rightarrow \rho_P = \frac{2}{\frac{a^2\sqrt{3}}{2}}\ \Sigma = 2 = \frac{4}{a^2\sqrt{3}} = \frac{4}{\frac{16r^2}{2}\sqrt{3}} = \frac{1}{2\sqrt{3}\,r^2}$

HIGHEST DENSITY PLANE

⇒ FOR FCC ρ_P max is $\rho_P(111) = \frac{1}{2\sqrt{3}r^2}$ MAX OF EVERY THING

⇒ such $\rho_P = \frac{1}{2\sqrt{3}r^2}$ is called CLOSE-PACKED PLANE

in a system with HIGHEST DENSITY PLANE IS = to ~~CLOSEST~~ THEN → IT IS CALLED CLOSED PACKED

BCC $\underbrace{\rho_P^{BCC}(110)}_{\text{HIGHEST DENSITY PLANE}} = \frac{3}{8r^2\sqrt{2}} \simeq 92\%$ of $\rho_P^{FCC}(111)$

→ BCC IS NOT CLOSE-PACKED

FOR HOME $\rho_P^{BCC}(100)$, $\rho_P^{BCC}(111)$; $\rho_P^{BCC}(210)$? FAST ☹

$\rho_P^{FCC}(111)$ is THE HIGHEST DENSITY PLANE

CLOSE PACK. IF $\rho_P^{MAX} = \frac{1}{2\sqrt{3}r^2}$

TABLE 3.5–1 The close-packed directions and highest-density planes in the BCC, FCC, and HCP crystal structures.

Crystal structure	Close-packed directions	Highest-density planes	Are the highest-density planes close-packed?
BCC	⟨1 1 1⟩	{1 1 0}	No
FCC	⟨1 1 0⟩	{1 1 1}	Yes
HCP	a	Basal	Yes

BCC IS NOT C.P. —

FCC is C.P., along for planes {111}

→ HCP = HEX + BASIS is C.P. on the basal plane

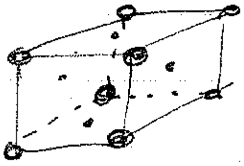
SEE LATER

VOLUMETRIC DENSITY:

$\rho_V = \frac{\text{\# of LATTICE POINT}}{\text{UNIT VOLUME}}$ → 1) put POINTS as sperical atoms
2) count them in UNIT CELL (TAKE an easy one)
3) $\rho_V = \#/\text{Volume}$

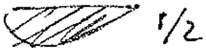
FCC

for simplicity we take CUBIC UNIT CELL



HAVE 8 corners spheres with 1/8 volume each

HAVE 6 face spheres with 1/2 volume



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

Volume $= a^3 \Rightarrow a = \frac{4r}{\sqrt{2}} \Rightarrow \rho_V = \frac{4\, 2^{3/2}}{4^3 r^3} =$

$$\boxed{\rho_V^{FCC} = \frac{1}{4\sqrt{2}\, r^3}}$$

HCP is same $\rho_V^{HCP} = \frac{1}{4\sqrt{2}\, r^3}$
if $c/a = 1.6$ theoretical one

EXERCISE
ρ_V^{BCC} ?

HCP & FCC are both CLOSED PACKED STRUCTURE

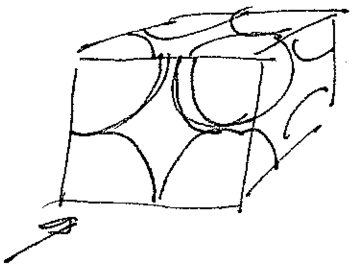
HEX CLOSED PACKED

ATOMIC PACKING FACTOR

measures the empty volume of the cell!!

APF ↑ empty volue ↓

$\overset{!}{=}$ occupied fraction of volume



SIMPLE CUBIC

$$APF \equiv \frac{\text{Volume atoms (if spherical)}}{\text{Volume cell}}$$

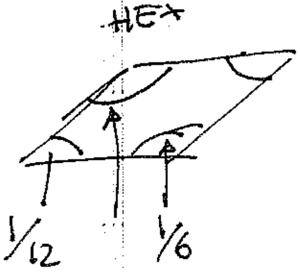
⇒

each sphere is $\boxed{\frac{4}{3}\pi r^3}$

	ATOMS/CUBIC CELL	a ↔ r relation	APF
SIMPLE CUBIC	$8*\frac{1}{8}=1$	$a=2r$	$\frac{1*\frac{4}{3}\pi r^3}{8r^3}=0.52$
BCC	$8*\frac{1}{8}+1=2$	$a=\frac{4r}{\sqrt{3}}$	0.68
FCC	$8*\frac{1}{8}+6*\frac{1}{2}=4$	$a=\frac{4r}{\sqrt{2}}$	0.74
HCP (ideal $c/a=1.6$)	$4*\frac{1}{6}+4*\frac{1}{12}+1=2$	$c=1.633a$ $=3.266r$ IDEAL	0.74

MOST DENSE!!

HCP = HEX + BASIS (2)
EXTRA ATOM IS IN CENTER



$c=\left(\frac{4}{\sqrt{6}}\right)a=1.633$

C17

CLOSE PACKED STRUCTURES

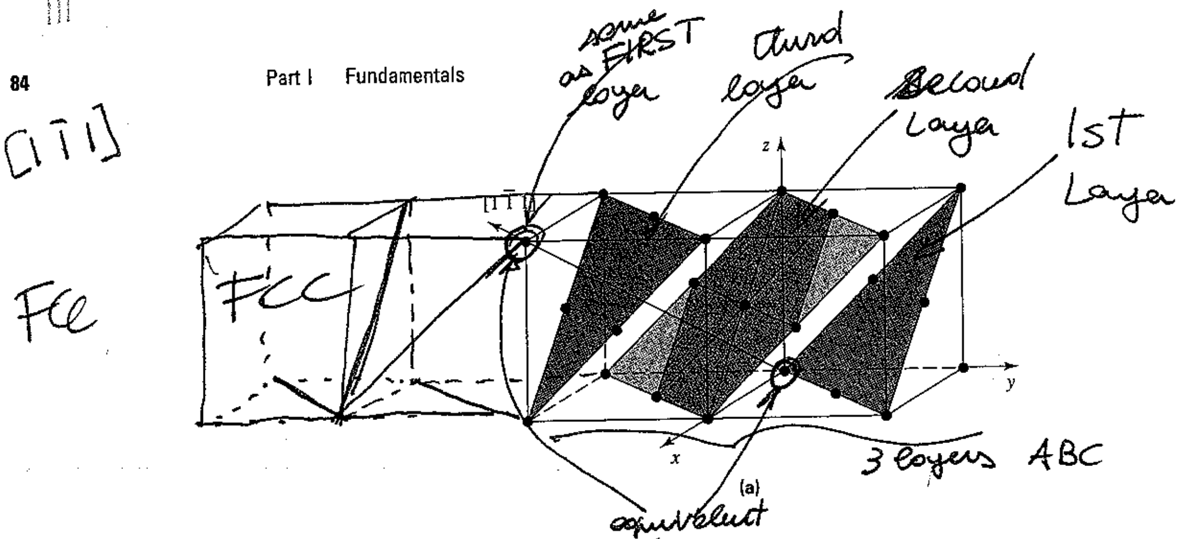
FCC & HCP are the most DENSE STRUCTURES

↓ LATTICE ↓ HEX + BASIS LATTICE — they are very SIMILAR

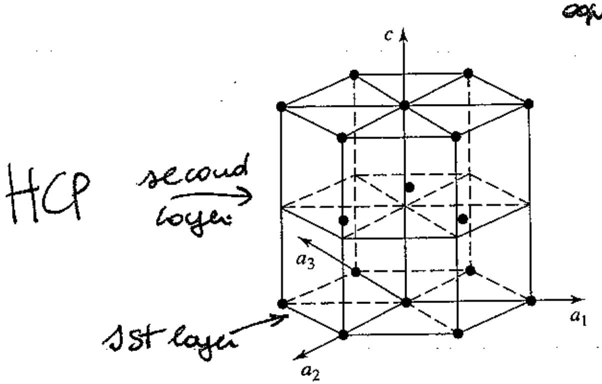
FCC in [111] direction is an HEX LATTICE + BASIS (3)

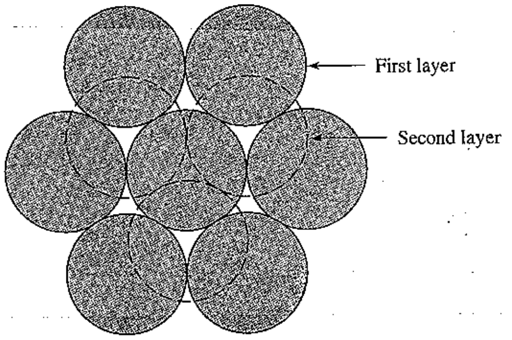
HCP in AXIS direction is an HEX LATTICE + BASIS (2)

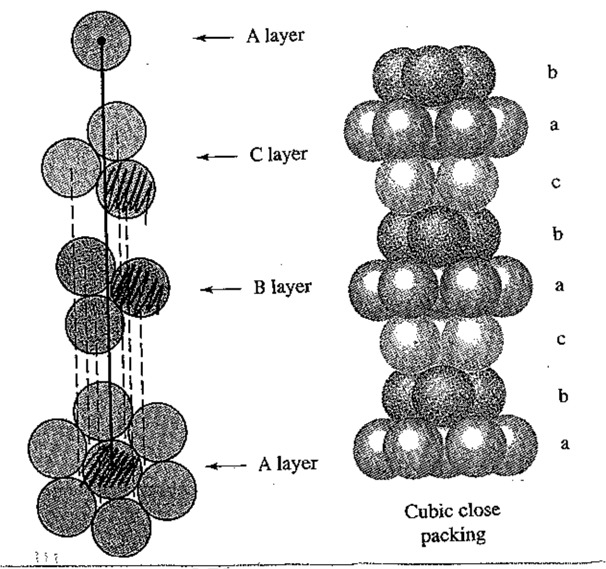
84 Part I Fundamentals



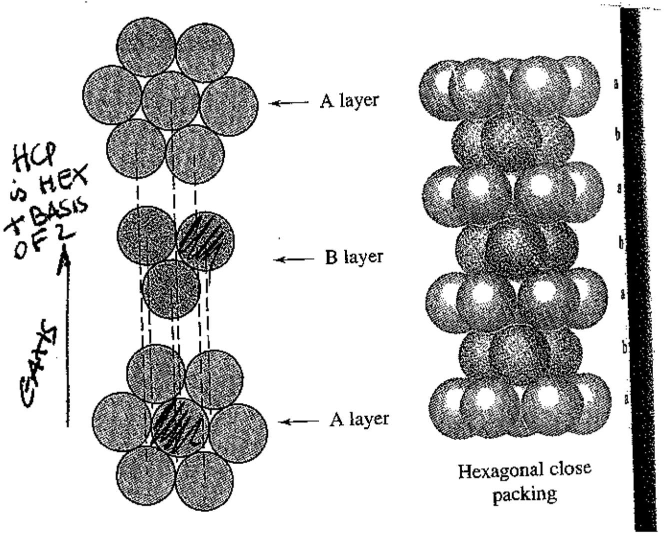
(a)







Cubic close packing

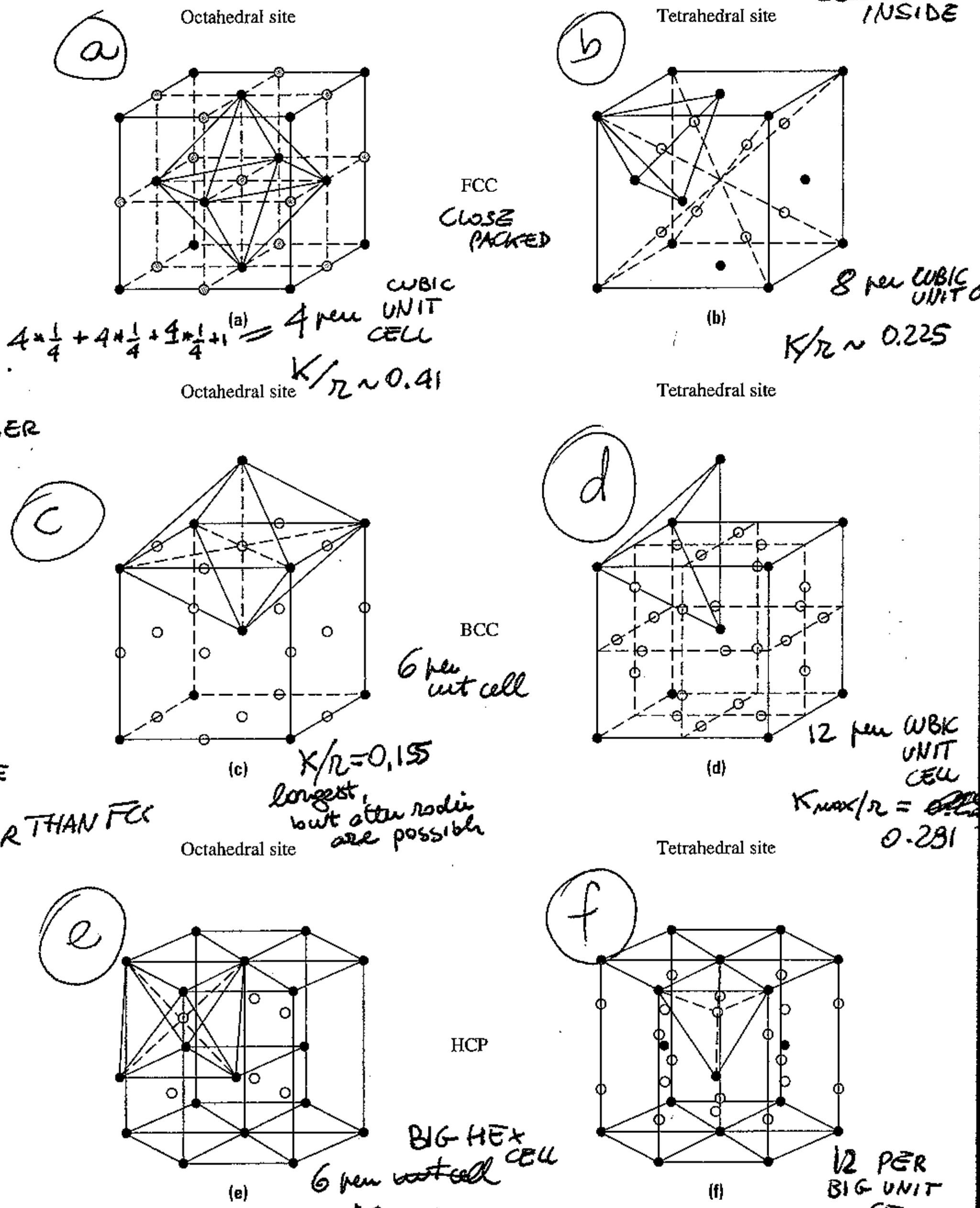


Hexagonal close packing

INTERSTITIAL POSITION → WHY? TO SQUEEZE SOMETHING ELSE INSIDE

FIGURE 3.6–1

The locations of the interstitial sites in the common crystal structures: **(a)** octahedral sites in FCC, **(b)** tetrahedral sites in FCC, **(c)** octahedral sites in BCC, **(d)** tetrahedral sites in BCC, **(e)** octahedral sites in HCP, and **(f)** tetrahedral sites in HCP.



CLOSE PACKED

$4*\frac{1}{4}+4*\frac{1}{4}+4*\frac{1}{4}+1 = 4$ per CUBIC UNIT CELL

$K/r \sim 0.41$

8 per CUBIC UNIT CELL

$K/r \sim 0.225$

x = max radius of an INTRUDER

6 per unit cell

$K/r = 0.155$ longest, but other radii are possible

12 per CUBIC UNIT CELL

K_{max}/r = 0.281

BCC is NOT C.P.
⇒ SOLUTION IS NOT EQUIDISTANT
⇒ BCC IS OPEN STRUCTURE
INTRUDERS CAN GET IN/OUT EASIER THAN FCC

6 per ~~unit cell~~ BIG HEX CELL

K/r = FCC

12 PER BIG UNIT CELL

$\frac{K}{r}$ = FCC

Because both close packed

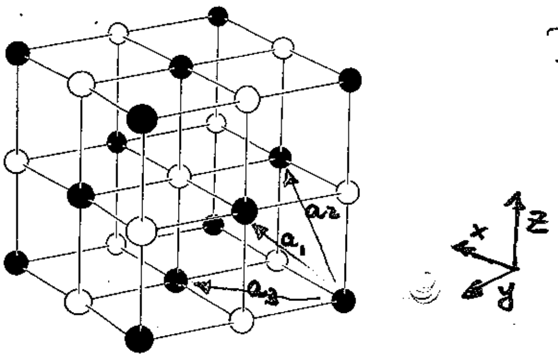
3.6.2 Interstices in the BCC Structure

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 ⟨1 0 0⟩ as measured from one central atom to

C19

CRYSTALS WITH 2 ATOMS/CELL

SODIUM CLORIDE STRUCT. Prototype NaCl Rocksalt
IONIC



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

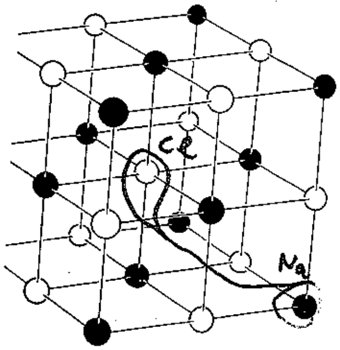
OR VICEVERSA

SODIUM CLORIDE STRUCTURE = FCC + BASIS(2)

⇓

FCC ⇒

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



(0,0,0) Na
$\frac{a}{2}(1,1,1)$ Cl

↓

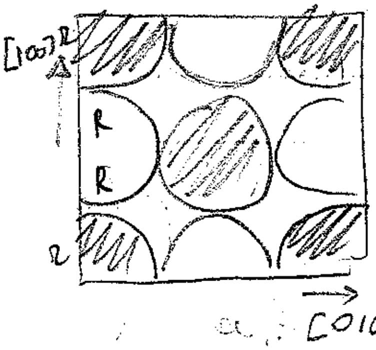
BUT EVERY COUPLE OF ● & ○ will work

SEE PHOTOCOPY FOR EXAMPLE

● OR YOU CAN CONSIDER AS 2 INTERPENETRATING FCC LATTICES

$a \Leftrightarrow r$

ALONG [100] DIR
FACE



$$\Rightarrow \boxed{2(r+R) = a}$$

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.[17] 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, $(a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$.

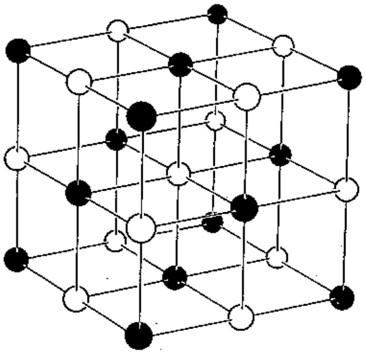


Figure 4.24
The sodium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating fcc lattices.

NACl
interpenetrating FCC

FCC + BASIS $\frac{a}{2}(\vec{x}+\vec{y}+\vec{z})$ Na

0 Cl

Table 4.5
SOME COMPOUNDS WITH THE SODIUM CHLORIDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
LiF	4.02	RbF	5.64	CaS	5.69
LiCl	5.13	RbCl	6.58	CaSe	5.91
LiBr	5.50	RbBr	6.85	CaTe	6.34
LiI	6.00	RbI	7.34	SrO	5.16
NaF	4.62	CsF	6.01	SrS	6.02
NaCl	5.64	AgF	4.92	SrSe	6.23
NaBr	5.97	AgCl	5.55	SrTe	6.47
NaI	6.47	AgBr	5.77	BaO	5.52
KF	5.35	MgO	4.21	BaS	6.39
KCl	6.29	MgS	5.20	BaSe	6.60
KBr	6.60	MgSe	5.45	BaTe	6.99
KI	7.07	CaO	4.81		

The Cesium Chloride Structure

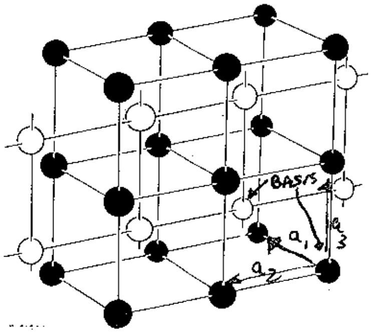
Similarly, cesium chloride (Figure 4.25) consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion

---

[17] For examples see Table 4.5.

C21

CESIUM CLORIDE STRUCTURE prototype CsCl



IONIC

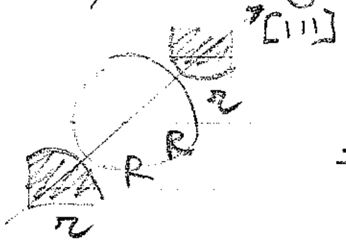
2 INTERPENETRATING CUBIC

CSCL = CUBIC + BASIS (2)

$a_1 = a\hat{x}$ $a_2 = a\hat{y}$ $a_3 = a\hat{z}$

→ $(0,0,0)$, $\frac{a}{2}(1,1,1)$

$a \Leftrightarrow r$ relation, along direction [111]



$$\Rightarrow \boxed{\boxed{a\sqrt{3} = 2(r+R)}}$$

CAN BE SEEN AS BCC WITH BLACK/WHITE ALTERNATING ATOMS

ımond lattices as lattices
 lattice points. A lattice
l structures in which the
:, but in which the crystal
y of the Bravais lattice
ɛample, sodium chloride
e ions placed at alternate
has six of the other kind
:ribed as a face-centered
. at **0** and a chlorine ion

:. One type of ion is repre-
:r type by white. The black
:trating fcc lattices.

ing FCC

$\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ Na

0 Cl

TRUCTURE

CRYSTAL	*a* (Å)
CaS	5.69
CaSe	5.91
CaTe	6.34
SrO	5.16
SrS	6.02
SrSe	6.23
SrTe	6.47
BaO	5.52
BaS	6.39
BaSe	6.60
BaTe	6.99

ıumbers of cesium and
lattice so that each ion

C23

---

has eight of the other kind as its nearest neighbors.[18] The translational symmetry of this structure is that of the simple cubic Bravais lattice, and it is described as a simple cubic lattice with a basis consisting of a cesium ion at the origin **0** and a chlorine ion at the cube center $(a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$.

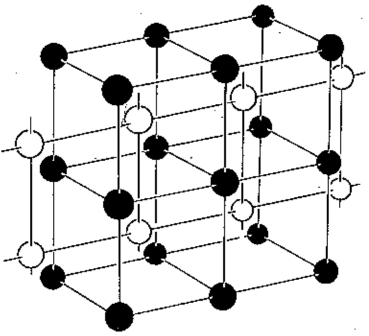


Figure 4.25
The cesium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating simple cubic lattices.

CsCl
2 interpenetrating
CUBIC
OR ~~BCC~~ — 0 Cs
CUBIC — $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ Cl

Table 4.6
SOME COMPOUNDS WITH THE CESIUM CHLORIDE STRUCTURE

CRYSTAL	*a* (Å)	CRYSTAL	*a* (Å)
CsCl	4.12	TlCl	3.83
CsBr	4.29	TlBr	3.97
CsI	4.57	TlI	4.20

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[19] 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
SOME COMPOUNDS WITH THE ZINCBLENDE STRUCTURE

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

---

[18] For examples see Table 4.6.
[19] For examples see Table 4.7.

DIAMOND & ZINCBLENDE

DIAMOND

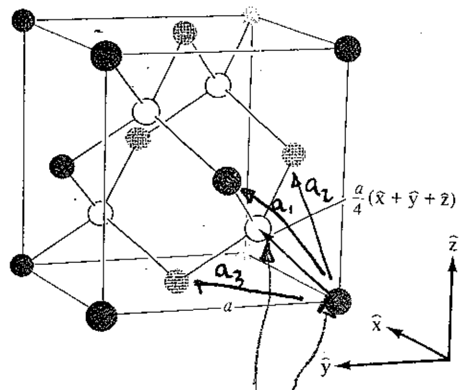


Table 4.3
ELEMENTS WITH THE DIAMOND CRYSTAL STRUCTURE

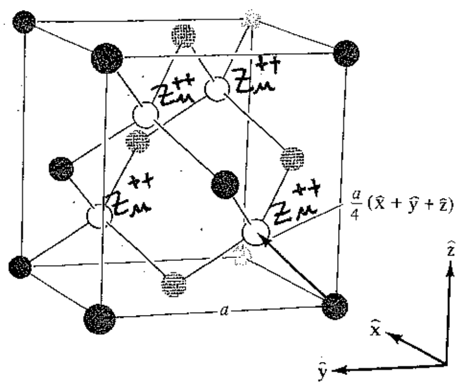
ELEMENT	CUBE SIDE a (Å)
C (diamond)	3.57 ← toth
Si	5.43
Ge	5.66
α-Sn (grey)	6.49

FCC $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ + BASIS (2)

BASIS

$(0,0,0), \frac{a}{4}(1,1,1)$

ZINCBLENE



$Zn^{++}S^{--}$

IONIC ⟷ ZnS

BASIS

$(0,0,0)$ SULFUR

$\frac{a}{4}(1,1,1)$ ZINC

which GaAs (SEMICONDUCTOR)

CdTe (QUANTUM DOTS)

~~[illegible]~~ ZrO_2

CaF_2

$MX_2 \Rightarrow M = FCC$

X are 8 interstitial sites cubic

ASSIGNMENT ~~FLUORITE~~ (92)

CRYSTOBALITE (92-93)

METHANE SOLID (94)

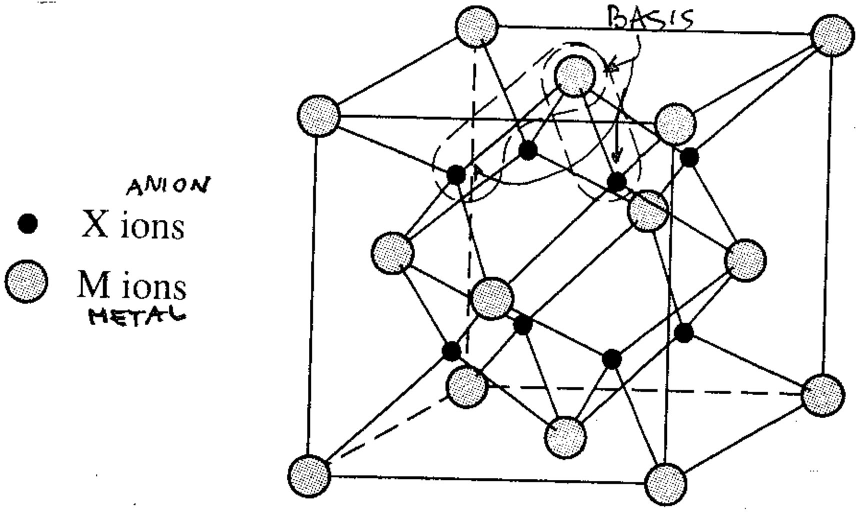
POLYETHYLENE (95-95)

LIQUID CRYSTALS

(long molecules that can orient on some external field (ELECTRIC)

C24

FLUORITE - ANTIFLUORITE



FLUORITE

= FCC + INTERSTITIAL

= FCC + BASIS (3)

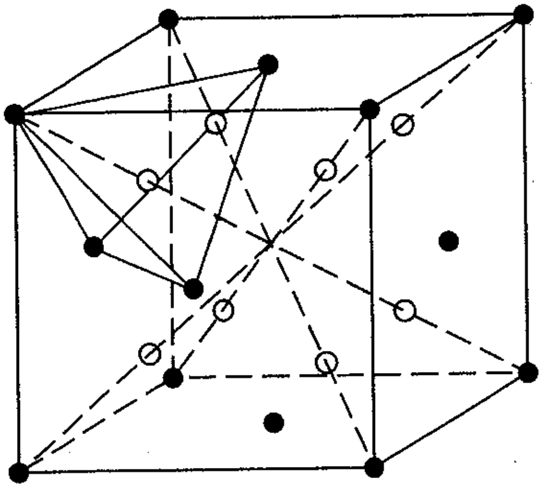
twice as many interstitials

CaF_2, ~~[illegible]~~ ZrO_2, MX_2
4
↑ Metal
↑ ION

Tetrahedral site

INTERSTITIAL

8 PER CUBE



METAL

~~[illegible]~~ ION

ANTIFLUORITE M_2X

Same as FLUORITE

BUT METAL INVERTED

Li_2O,

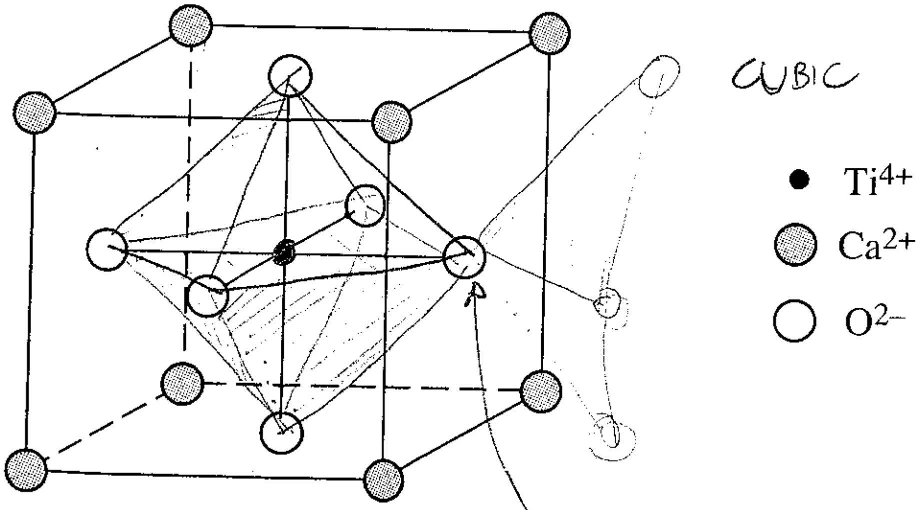
C25

PEROVSKITE STRUCTURE

USUALLY ABO_3

A, B metals

O oxigen



CUBIC

Oxygen takes all electrons O^{2-}
one metal gives 4
the other gives 2

↓ a total of 6 electrons must come from the metals

$CaTiO_3$
CALCIUM TITANATE

SHARE CORNERS

CUBIC CALCIUM (A) STRUCTURE
OXIGEN IN THE FACES (6) ⟹ OCTAHEDRA
METAL TITANIUM (B) IN THE CENTRE

$LiCoO_3$ in BATTERIES

BARIUM TITANATE

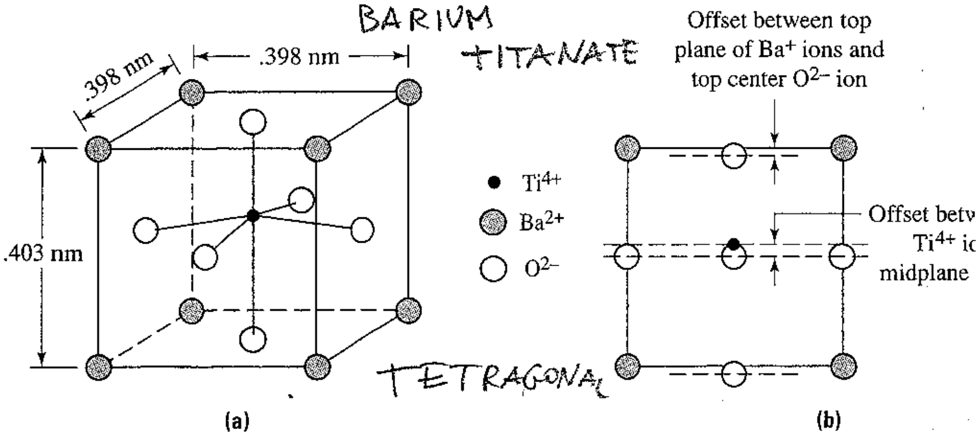
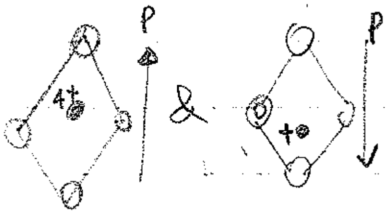
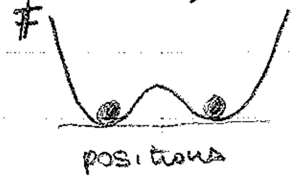


FIGURE 3.7–8 The tetragonal unit cell of $BaTiO_3$ shown **(a)** in 3-D, and **(b)** in 2-D.



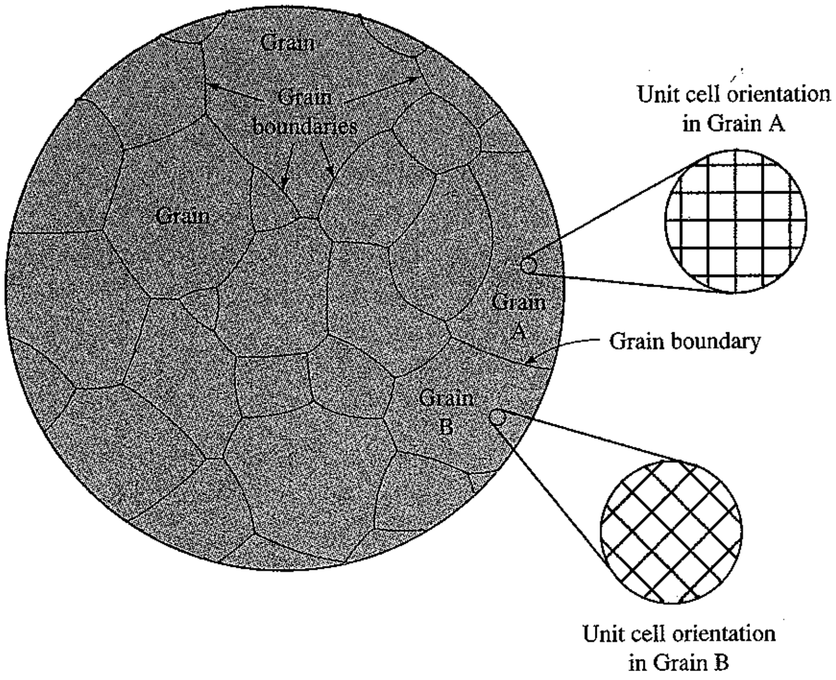
dipole ⟹
SWITCHABLE
→ direction



POLYCRISTALLINE

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 s inorganic solids, such as silica, it can be relatively easy to cool the material sufficie quickly that crystal formation does not occur. Hence, these materials may be ei crystalline or noncrystalline (amorphous), depending on thermal history. The structu 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 ra form structures that are entirely crystalline. Hence, polymers are either semicrysta or amorphous. Although there are no commercial single-crystal polymers, Spectra® f one of the strongest materials known, has a structure similar to that of a single cry Spectra consists of long polyethylene chains that are processed in such a way tha molecules are highly aligned. Crystallinity is very high, and defects, principally c ends, are randomly dispersed through the continuous crystal.

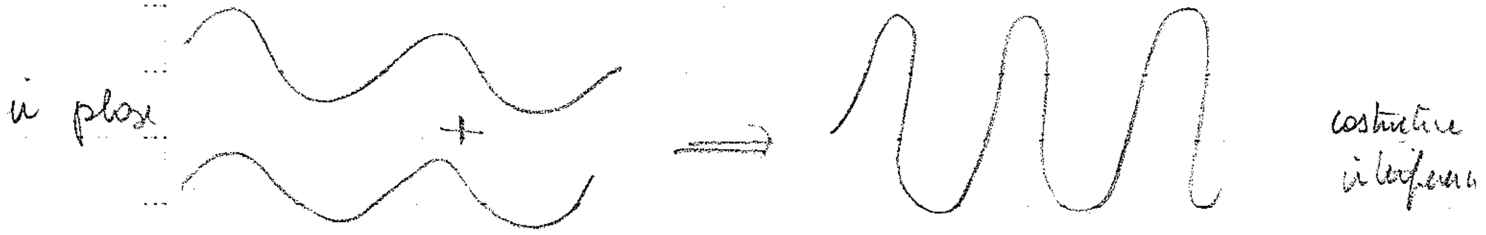
Few materials are used in a single-crystal form; however, those few are commerc significant. Single-crystal materials have no grain boundaries, so they offer unique chanical, optical, and electrical properties. Single-crystal quartz (SiO_2) and perovs are used as transducers in a variety of applications, such as in high quality receivers pickups (phonograph cartridges). Single-crystal germanium and silicon are used e sively in the microelectronics industry. Single-crystal nickel alloys are used in tu blades in high-performance jet aircraft. Sapphire (Al_2O_3) and diamond (C) single cry are precious stones.

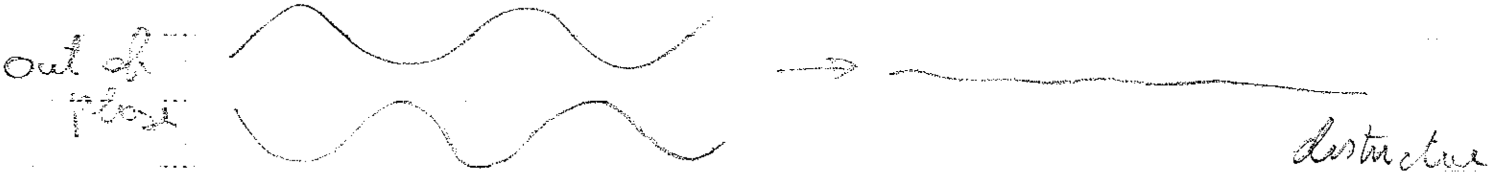
C27

3.10 ALLOTROPY AND POLYMORPHISM

Many materials can exhibit crystal structures that change from one unit cell to an

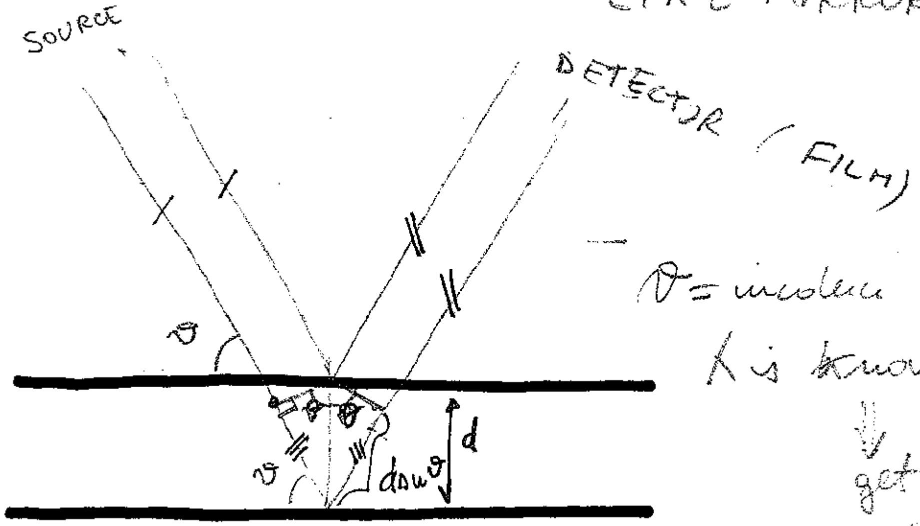
X-RAY DIFF (LIGHT)





phase or antiphase: depends on the distance travelled

ON A CRISTAL, PLANES REFLECT LIKE MIRRORS



θ = incident angle

λ is known

⇓

get d

// + /// = ~~2ldsin~~ $2d\sin\theta$ = extra distance

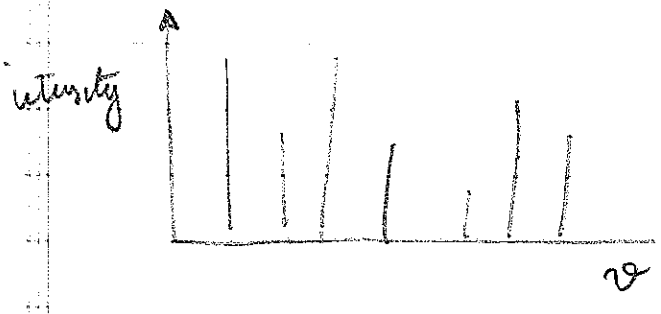
if this distance = $n\lambda$ ⇒ positive interference

$$\boxed{2d\sin\theta = n\lambda}$$ BRAGG LAW

C28

But which plane am I testing?
DUNNO!

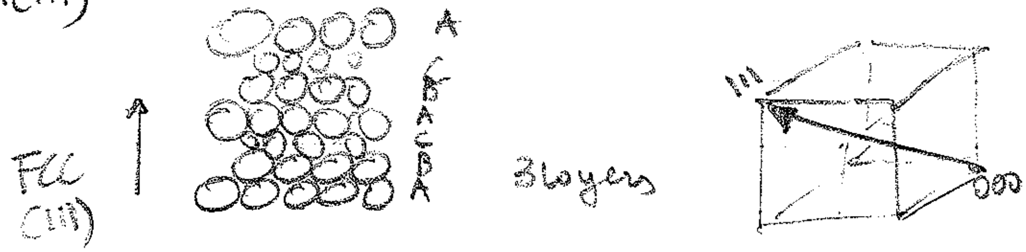
⇒ make powder ⇒ grind crystal and X-RAY
POWDER



one for every plane

FCC

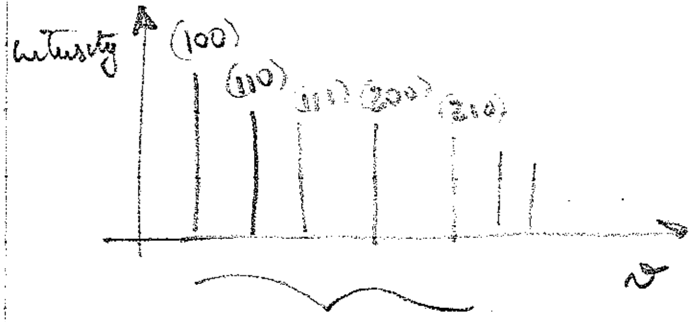
For instance d(111)



a√3

$$d(111) = \frac{a\sqrt{3}}{3} \Leftarrow$$

for FCC $d(hkl) = \dfrac{a_0}{(h^2+k^2+l^2)^{1/2}}$ ⇒ family of ds ⇒ family of θ with position interference



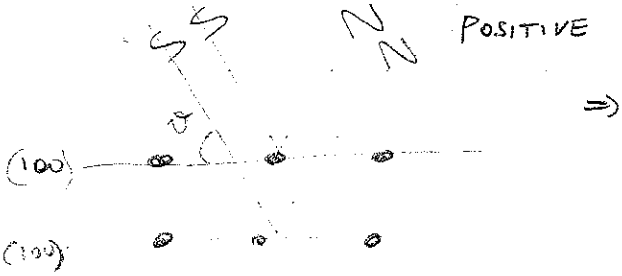
line for every plane.

IF SOMETHING IS MISSING?

WHAT ABOUT MISSING LINES

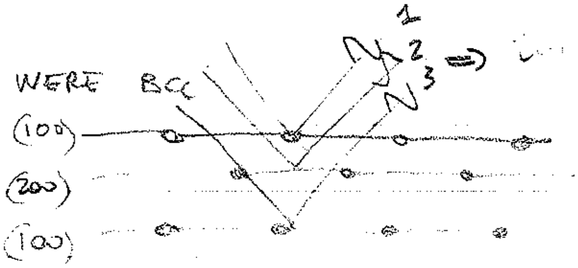
EXAMPLE

TAKE CUBIC ⓓ $\vartheta, \lambda \propto$ YOU HAVE LINE for $d(100)$



$\Rightarrow$ second ray has extra path $= n\lambda$

IF IT WERE BCC



3 ray has extra $n\lambda$
but 2 ray has $n\lambda/2$
$\Rightarrow$ DESTRUCTIVE DIFFRACTION

same for FCC (100)

$\Rightarrow$ RULES BCC: $(h+k+l)$ even $\Rightarrow$ LINE (h,k,l)
FCC: h,k,l all even OR all odd (h,k,l)

ALL X-RAY TECHNOLOGY IS AN EVOLUTION OF THESE IDEAS

$\Rightarrow$ EXTREMELY POWERFUL ☆ WEB

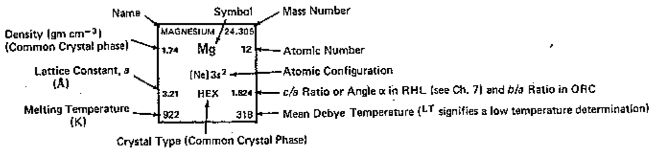
C30

R value = $\frac{a^3}{2 \quad 4}$
↑ BCC ↑ FCC

STEFANO
CURTAROLO
MIT

~~MILTON COLE~~
~~PHYSICS DEPT.~~
~~104 Davey Lab~~

LEGEND



FCC – Face-Centered Cubic
BCC – Body-Centered Cubic
SC – Simple Cubic
CUB – Cubic
TET – Tetragonal
ORC – Orthorhombic
HEX – Hexagonal
DIA – Diamond
RHL – Rhombohedral
MCL – Monoclinic

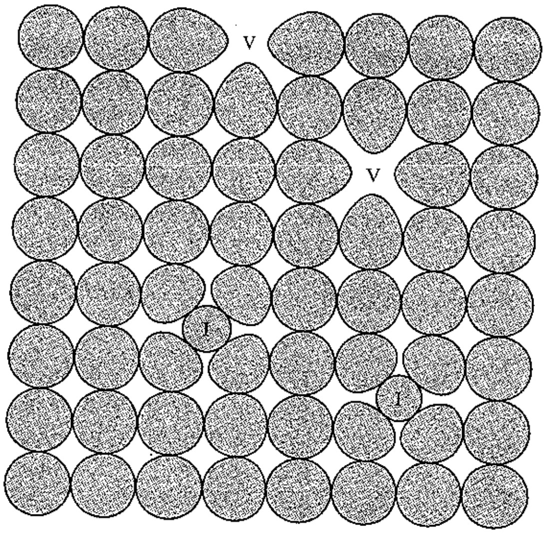
	1A	2A	3B	4B	5B	6B	7B	← 8		→	1B	2B	3A	4A	5A	6A	7A	NOBLE ELEMENTS
1	HYDROGEN 1.0079 0.089 H 1 $1s^1$ 3.75 HEX 1.731 14.0 110																	HELIUM 4.0026 0.179 He 2 $1s^2$ 3.57 HEX 1.633 ~1.0 (26 Atm) 26^{LT}
2	LITHIUM 6.941 0.53 Li 3 $1s^2 2s^1$ 3.49 BCC 453 400	BERYLLIUM 9.0122 1.85 Be 4 $1s^2 2s^2$ 2.29 HEX 1.567 1550 1000											BORON 10.81 2.34 B 5 $1s^2 2s^2 2p^1$ 8.73 TET 0.576 2600 1250	CARBON 12.01 2.26 C 6 $1s^2 2s^2 2p^2$ 3.57 DIA (4300) 1860	NITROGEN 14.007 1.03 N 7 $1s^2 2s^2 2p^3$ 4.039 HEX 1.651 63.3 (β) 79^{LT}	OXYGEN 15.999 1.43 O 8 $1s^2 2s^2 2p^4$ 6.83 CUB 54.7 (γ) 46^{LT}	FLUORINE 18.998 1.97 (α) F 9 $1s^2 2s^2 2p^5$ MCL 53.5	NEON 20.18 1.56 Ne 10 $1s^2 2s^2 2p^6$ 4.43 FCC 24.5 63
3	SODIUM 22.9898 0.97 Na 11 [Ne] $3s^1$ 4.23 BCC 371.0 150	MAGNESIUM 24.305 1.74 Mg 12 [Ne] $3s^2$ 3.21 HEX 1.624 922 318											ALUMINUM 26.982 2.70 Al 13 [Ne] $3s^2 3p^1$ 4.05 FCC 933 394	SILICON 28.086 2.33 Si 14 [Ne] $3s^2 3p^2$ 5.43 DIA 1683 625	PHOSPHORUS 30.974 1.82 (white) P 15 [Ne] $3s^2 3p^3$ 7.17 CUB 317.3	SULFUR 32.064 2.07 S 16 [Ne] $3s^2 3p^4$ 10.47 ORC 2.339 1.229 386	CHLORINE 35.453 2.09 Cl 17 [Ne] $3s^2 3p^5$ 6.24 ORC 1.324 0.718 172.2	ARGON 39.948 1.78 Ar 18 [Ne] $3s^2 3p^6$ 5.26 FCC 83.9 85
4	POSTASSIUM 39.09 0.86 K 19 [Ar] $4s^1$ 5.23 BCC 337 100	CALCIUM 40.08 1.54 Ca 20 [Ar] $4s^2$ 5.58 FCC 1111 230	SCANDIUM 44.956 2.99 Sc 21 [Ar] $3d^1 4s^2$ 3.31 HEX 1.594 1812 359^{LT}	TITANIUM 47.90 4.51 Ti 22 [Ar] $3d^2 4s^2$ 2.95 HEX 1.588 1933 380	VANADIUM 50.942 6.1 V 23 [Ar] $3d^3 4s^2$ 3.02 BCC 2163 390	CHROMIUM 52.00 7.19 Cr 24 [Ar] $3d^5 4s^1$ 2.88 BCC 2130 460	MANGANESE 54.938 7.43 Mn 25 [Ar] $3d^5 4s^2$ 8.89 CUB 1518 400	IRON 55.85 7.86 Fe 26 [Ar] $3d^6 4s^2$ 2.87 BCC 1808 420	COBALT 58.93 8.9 Co 27 [Ar] $3d^7 4s^2$ 2.51 HEX 1.622 1768 385	NICKEL 58.71 8.9 Ni 28 [Ar] $3d^8 4s^2$ 3.52 FCC 1726 375	COPPER 63.55 8.96 Cu 29 [Ar] $3d^{10} 4s^1$ 3.61 FCC 1356 315	ZINC 65.38 7.14 Zn 30 [Ar] $3d^{10} 4s^2$ 2.66 HEX 1.856 693 234	GALLIUM 69.72 5.91 Ga 31 [Ar] $3d^{10} 4s^2 3p^1$ 4.51 ORC 1.695 1.001 303 240	GERMANIUM 72.59 5.32 Ge 32 [Ar] $3d^{10} 4s^2 4p^2$ 5.66 DIA 1211 360	ARSENIC 74.922 5.72 As 33 [Ar] $3d^{10} 4s^2 4p^3$ 4.13 RHL 54°10' 1090 285	SELENIUM 78.96 4.79 Se 34 [Ar] $3d^{10} 4s^2 4p^4$ 4.36 HEX 1.136 490 150^{LT}	BROMINE 79.91 4.10 Br 35 [Ar] $3d^{10} 4s^2 4p^5$ 6.67 ORC 1.307 0.672 266	KRYPTON 83.80 3.07 Kr 36 [Ar] $3d^{10} 4s^2 4p^6$ 5.72 FCC 116.5 73^{LT}
5	RUBIDIUM 85.47 1.53 Rb 37 [Kr] $5s^1$ 5.59 BCC 312 56^{LT}	STRONTIUM 87.62 2.60 Sr 38 [Kr] $5s^2$ 6.08 FCC 1043 147^{LT}	YTTRIUM 88.91 4.48 Y 39 [Kr] $4d^1 5s^2$ 3.65 HEX 1.571 1796 258^{LT}	ZIRCONIUM 91.22 6.49 Zr 40 [Kr] $4d^2 5s^2$ 3.23 HEX 1.593 2125 250	NIOBIUM 92.91 8.4 Nb 41 [Kr] $4d^4 5s^1$ 3.30 BCC 2741 275	MOLYBDENUM 95.94 10.2 Mo 42 [Kr] $4d^5 5s^1$ 3.15 BCC 2890 380	TECHNETIUM 98.91 11.5 Tc 43 [Kr] $4d^5 5s^2$ 2.74 HEX 1.604 2445	RUTHENIUM 101.07 12.2 Ru 44 [Kr] $4d^7 5s^1$ 2.70 HEX 1.584 2583 382^{LT}	RHODIUM 102.90 12.4 Rh 45 [Kr] $4d^8 5s^1$ 3.80 FCC 2239 350^{LT}	PALLADIUM 106.40 12.0 Pd 46 [Kr] $4d^{10} 5s^0$ 3.89 FCC 1825 275	SILVER 107.87 10.5 Ag 47 [Kr] $4d^{10} 5s^1$ 4.09 FCC 1234 215	CADMIUM 112.40 8.65 Cd 48 [Kr] $4d^{10} 5s^2$ 2.98 HEX 1.886 594 120	INDIUM 114.82 7.31 In 49 [Kr] $4d^{10} 5s^2 5p^1$ 4.59 TET 1.076 429.8 129	TIN 118.69 7.30 Sn 50 [Kr] $4d^{10} 5s^2 5p^2$ 5.82 TET 0.546 505 170	ANTIMONY 121.75 6.62 Sb 51 [Kr] $4d^{10} 5s^2 5p^3$ 4.51 RHL 57°6' 904 200	TELLURIUM 127.60 6.24 Te 52 [Kr] $4d^{10} 5s^2 5p^4$ 4.45 HEX 1.330 723 139^{LT}	IODINE 126.90 4.94 I 53 [Kr] $4d^{10} 5s^2 5p^5$ 7.27 ORC 1.347 0.659 387	XENON 131.30 3.77 Xe 54 [Kr] $4d^{10} 5s^2 5p^6$ 6.20 FCC 161.3 65^{LT}
6	CESIUM 132.91 1.90 Cs 55 [Xe] $6s^1$ 6.05 BCC 302 40^{LT}	BARIUM 137.34 3.5 Ba 56 [Xe] $6s^2$ 5.02 BCC 998 110^{LT}	LANTHANUM 138.91 6.17 La 57 [Xe] $5d^1 6s^2$ 3.75 HEX 1.619 1193 132	HAFNIUM 178.49 13.1 Hf 72 [Xe] $4f^{14} 5d^2 6s^2$ 3.20 HEX 1.582 2495	TANTALUM 180.95 16.6 Ta 73 [Xe] $4f^{14} 5d^3 6s^2$ 3.31 BCC 225	TUNGSTEN (WOLFRAM) 183.85 19.3 W 74 [Xe] $4f^{14} 5d^4 6s^2$ 3.16 BCC 3683 310	RHENIUM 186.2 21.0 Re 75 [Xe] $4f^{14} 5d^5 6s^2$ 2.76 HEX 1.615 3453 416^{LT}	OSMIUM 190.20 22.6 Os 76 [Xe] $4f^{14} 5d^6 6s^2$ 2.74 HEX 1.579 3318 400^{LT}	IRIDIUM 192.22 22.5 Ir 77 [Xe] $4f^{14} 5d^7 6s^2$ 3.84 FCC 2683 430	PLATINUM 195.09 21.4 Pt 78 [Xe] $4f^{14} 5d^{10} 6s^0$ 3.92 FCC 2045 230	GOLD 196.97 19.3 Au 79 [Xe] $4f^{14} 5d^{10} 6s^1$ 4.08 FCC 1337 170	MERCURY 200.59 13.6 Hg 80 [Xe] $4f^{14} 5d^{10} 6s^2$ 2.99 RHL 70°45' 234.3 100	THALLIUM 204.37 11.85 Tl 81 [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$ 3.46 HEX 1.599 577 96	LEAD 207.19 11.4 Pb 82 [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$ 4.95 FCC 601 88	BISMUTH 208.98 9.8 Bi 83 [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$ 4.75 RHL 57°14' 544.5 120	POLONIUM 210 9.4 Po 84 [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$ 3.35 SC 527	ASTATINE 210 At 85 [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$ (575)	RADON 222 (4.4) Rn 86 [Xe] $4f^{14} 5d^{10} 6s^2 6p^6$ (FCC) (202)
7	FRANCIUM 223 Fr 87 [Rn] $7s^1$ (BCC) (300)	RADIUM 226 (5.0) Ra 88 [Rn] $7s^2$ 973	ACTINIUM 227 10.1 Ac 89 [Rn] $6d^1 7s^2$ 5.31 FCC 1323															

RARE EARTHS

LANTHANIDES 6	CERIUM 140.12 6.77 Ce 58 [Xe] $4f^2 5d^0 6s^2$ 5.16 FCC 1071 139^{LT}	PRASEODYMIUM 140.91 6.77 Pr 59 [Xe] $4f^3 5d^0 6s^2$ 3.67 HEX 1.614 1204 152^{LT}	NEODYMIUM 144.24 7.00 Nd 60 [Xe] $4f^4 5d^0 6s^2$ 3.66 HEX 1.614 1283 157^{LT}	PROMETHIUM 145 Pm 61 [Xe] $4f^5 5d^0 6s^2$ (1350)	SAMARIUM 150.35 7.54 Sm 62 [Xe] $4f^6 5d^0 6s^2$ 9.00 RHL 23°13' 1345 166	EUROPIUM 151.96 7.90 Eu 63 [Xe] $4f^7 5d^0 6s^2$ 4.61 BCC 1095 107^{LT}	GADOLINIUM 157.25 8.23 Gd 64 [Xe] $4f^7 5d^1 6s^2$ 3.64 HEX 1.588 1585 176^{LT}	TERBIUM 158.92 8.54 Tb 65 [Xe] $4f^9 5d^0 6s^2$ 3.60 HEX 1.581 1633 188^{LT}	DYSPROSIUM 162.50 8.78 Dy 66 [Xe] $4f^{10} 5d^0 6s^2$ 3.59 HEX 1.573 1680 186^{LT}	HOLMIUM 164.93 8.05 Ho 67 [Xe] $4f^{11} 5d^0 6s^2$ 3.58 HEX 1.570 1743 191^{LT}	ERBIUM 167.26 9.37 Er 68 [Xe] $4f^{12} 5d^0 6s^2$ 3.56 HEX 1.570 1795 195^{LT}	THULIUM 168.93 9.31 Tm 69 [Xe] $4f^{13} 5d^0 6s^2$ 3.54 HEX 1.570 1818 200^{LT}	YTTERBIUM 173.04 6.97 Yb 70 [Xe] $4f^{14} 5d^0 6s^2$ 5.49 FCC 1097 118^{LT}	LUTETIUM 174.97 9.84 Lu 71 [Xe] $4f^{14} 5d^1 6s^2$ 3.51 HEX 1.585 1929 207^{LT}
ACTINIDES 7	THORIUM 232.04 11.7 Th 90 [Rn] $6d^2 7s^2$ 5.08 FCC 2020 100	PROTACTINIUM 231 15.4 Pa 91 [Rn] $5f^2 6d^1 7s^2$ 3.92 TET 0.825 1470	URANIUM 238.03 19.07 U 92 [Rn] $5f^3 6d^1 7s^2$ 2.85 ORC 2.056 1.736 1406 210^{LT}	NEPTUNIUM 237.05 20.3 Np 93 [Rn] $5f^5 6d^0 7s^2$ 4.72 ORC 1.411 1.035 913 188^{LT}	PLUTONIUM 244 19.8 Pu 94 [Rn] $5f^6 6d^0 7s^2$ MCL 914 150^{LT}	AMERICIUM 243 11.8 Am 95 [Rn] $5f^7 6d^0 7s^2$ 1267	CURIUM 247 Cm 96 [Rn] $5f^7 6d^1 7s^2$ 1600	BERKELIUM 247 Bk 97 [Rn] $5f^7 6d^2 7s^2$	CALIFORNIUM 251 Cf 98 [Rn] $5f^9 6d^1 7s^2$	EINSTEINIUM 254 Es 99	FERMIUM 257 Fm 100	MENDELEVIUM 256 Md 101	NOBELIUM 254 No 102	LAWRENCIUM 257 Lw 103

DEFECT : POINT DEFECT (SMALL)

IN MONOATOMIC SYSTEMS



VACANCIES : SOMETHING MISSING

INTERSTITIALS : SOMETHING EXTRA

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

Read 111-122 ☹

what about @ $T>0$?

SYSTEM DOES NOT MINIMIZE ENERGY BUT GIBBS FREE ENERGY

Thermo $dE = -pdV + TdS$ (~~@~~ E good for costant V, S)

$G = E + PV - ST$ Gibbs Free energy

~~dG=~~

$dG = dE + d(PV) - d(TS)$

$$dG = -\underline{pdV} + \underline{TdS} + \underline{pdV} + Vdp - \underline{TdS} - SdT$$

$$dG = Vdp - SdT$$

(PROPER THERMODYNAMIC POTENTIAL TO DESCRIVE SISTEMS at CONST Pres, & Temp

at $P=$ cost, $T=$ const

⇒ MOST STABLE IS $\underline{\min G}$!!!

NOT $\underline{E}$!!

DEFECTS increase Energy (strain stress $\sigma d\epsilon$)

BUT PRESENCE OF DEFECTS INCREASE ENTROPY (MEASURE OF CONFUSION

$$S \equiv k_B \log \Omega(E)$$ BOLTZMANN DEFINITION

given E = Energy, $\Omega(E)$ = # of states with energy $= E \Rightarrow$

$dG = VdP - SdT \Leftrightarrow G = E + PV - TS$

per unit Volume $V = 1$

pick 1 vacancy, how many possibilities? N !! atoms per unit volume.

$\Rightarrow \sim N_A$ Avogadro 10^{23}

$\Rightarrow$ ~~[illegible]~~ $S \simeq 100 k_B$

$\Rightarrow G = E + PV - 100\, \underset{\sim}{kT}$!!!

thermal temperature

can be large !!

$\Rightarrow$ DEFECTS GROW NATURALLY !!

@ $T > 0$ most stable configuration has defects!

FIGHT PERFECTION, HAVE DEFECTS

HOW MANY DEFECTS? → ~~AR~~ TO MAKE ONE YOU NEED AN ACTIVATION ENERGY

$Q_{\text{VACANCY FORMATION}}$

IF DEFECTS ARE INDIPENDENT ⇒ PROBABILITY THAT ONE SITE HAS DEFECT IS BOLTZMANN

$$\text{prob} \sim \exp\left(-\frac{Q_{fv}}{K_B T}\right)$$

↑ OR R if Q is kJ/mol

⇒ IF N_T AVAILABLE SITES

$$\Rightarrow \quad N_V = N_T \exp\left(-\frac{Q_{FV}}{kT}\right)$$

in EQUILIBRIUM

Q_{FV} & Q_{FI} come from BOOKS OR QUANTUM MECHANICS CALCULATIONS IF YOU WILL BE A GRAD STUDENT IN MY GROUP ☺

ENTROPY: IN HOW MANY WAYS I CAN PICK N_V ATOMS ON A POOL OF N_T?

$$\cancel{\Omega = \binom{N_V}{N_T} = \frac{N_V!}{N_T!\,(N_T-N_V)!}} \qquad \Omega = \binom{N_T}{N_V} = \frac{N_T!}{N_V!\,(N_T-N_V)!}$$

$$\Rightarrow \quad S = k \log \Omega = k\left[\log N_T! - \log N_V! - \log (N_T-N_V)!\right]$$

D3

$$\frac{S}{K} = \log N_T! - \log N_V! - \log (N_T - N_V)!$$

USING STERLING FORMULA $\log n! \sim n(\log n - 1)$

$$= N_T \log N_T - \cancel{N_T} - N_V \log N_V + \cancel{N_V} - (N_T - N_V)\log(N_T - N_V) \cancel{+ N_T} \cancel{- N_V}$$

$$= N_T \log N_T - N_V \log N_V - (N_T - N_V)\log(N_T - N_V)$$

divide by N_T ⇒ $N_T\left[\log N_T - \frac{N_V}{N_T}\log N_V - \left(1 - \frac{N_V}{N_T}\right)\log(N_T - N_V)\right]$

~~$= N_T\left[\log\frac{N_T}{N_T - N_V} - \frac{N_V}{N_T}\log\frac{N_V}{N_T - N_V}\right.$~~

~~Rearrange and get Logs together~~

~~$= N_T\left[-\log\frac{N_T - N_V}{N_T}\right.$~~

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

add and subtract $\pm \frac{N_V}{N_T}\log N_T$

$$= N_T\left[\underset{\textcircled{1}}{\log N_T} \overset{\textcircled{3}}{\mp} \frac{N_V}{N_T}\underset{(4)}{\log N_T} - \frac{N_V}{N_T}\underset{(5)}{\log N_V} - \underset{(2)}{\log(N_T - N_V)} + \frac{N_V}{N_T}\underset{(6)}{\log(N_T - N_V)}\right]$$

$$= N_T\left[\underset{(1)+(2)}{-\log\frac{N_T - N_V}{N_T}} \underset{(3)+(5)}{- \frac{N_V}{N_T}\log\frac{N_V}{N_T}} \underset{(4)+(6)}{+ \frac{N_V}{N_T}\log\frac{N_T - N_V}{N_T}}\right]$$

D4

$\Rightarrow \quad x \equiv \frac{N_V}{N_T}$ = concentration of vacancies

$$\Rightarrow \quad \frac{S}{K} = N_T\left[-\log(1-x) - x\log x + x\log(1-x)\right]$$

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

⇒ divide per Volume ⇒ so get per unit volume

$$\rho = N_T/V$$

$$S = -k_B\underbrace{\rho\,[\underbrace{x\log x + (1-x)\log(1-x)}_{<0}]}_{>0 \quad \text{BIG} \Rightarrow} \qquad 0\le x\le 1$$

$$\underbrace{TS = -k_B T\rho\left[x\log x + (1-x)\log(1-x)\right]}_{\text{BIGGGG}}$$

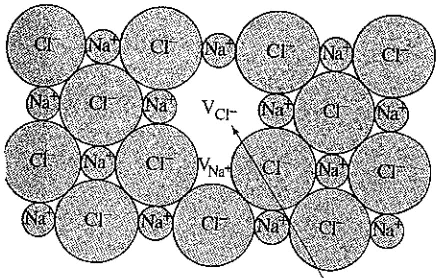
DS

DEFECT IN IONIC CRYSTALS.

Ionic? TROUBLES

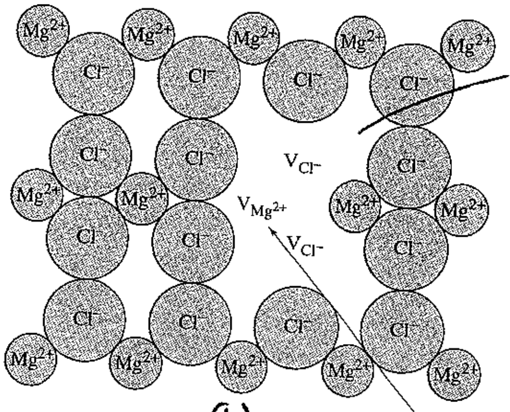
if vacancy notes non neutral
you ~~have to~~ need two vacancies
(CLOSE) TO get neutrality.

NaCl



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

(a)



Schottky defect
(1 $V_{Mg^{2+}}$ and 2 V_{Cl^-})

(b)

SCHOTTKY ~~DEFECTS~~

FOR NaCl ⇒ MISS 1Na $V^{-}_{Na^{+}}$
& 1Cl $V^{+}_{Cl^{-}}$

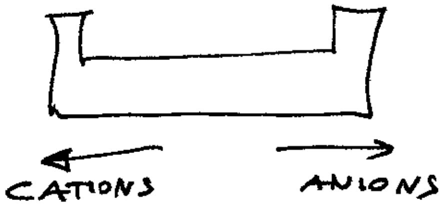
$Na^{+}\ Cl^{-} \Rightarrow V^{-}_{Na^{+}}\ V^{+}_{Cl^{-}}$

For $MgCl_2$ ⇒ Miss. 1 Mg^{++}
1 Cl^{-}
1 Cl^{-}
⇒ $V^{=}_{Mg^{++}}$
$V^{+}_{Cl^{-}}$
$V^{+}_{Cl^{-}}$

OTHER POINT DEFECTS IN IONICS

FRENKEL DEFECTS!

INTERSITITIAL OF AN ION
BUT TO RESPECT NEUTRALITY YOU NEED
A VACANCY OF THE SAME ION SOMEWERE
(WHY NOT AN INTERSITIAL OF THE OTHER SPECIE? BECAUSE
CATIONS (+) ARE SMALL ANIONS (−) ARE BIG)



⇒ ONLY CATIONS AVAILABLE FOR INTERSTITIAL

BEING HONEST: THIS IS NOT REALLY TRUE

MATHEMATICALLY IN ACT ENERGY $Q^{\text{ANION}}_{FI} \gg Q^{\text{CATION}}_{FI}$

prob: $\Rightarrow \exp\left(-\frac{Q^{AN}}{KT}\right) \lll \exp\left(-\frac{Q^{CAT}}{KT}\right)$

almost ~ 0 good

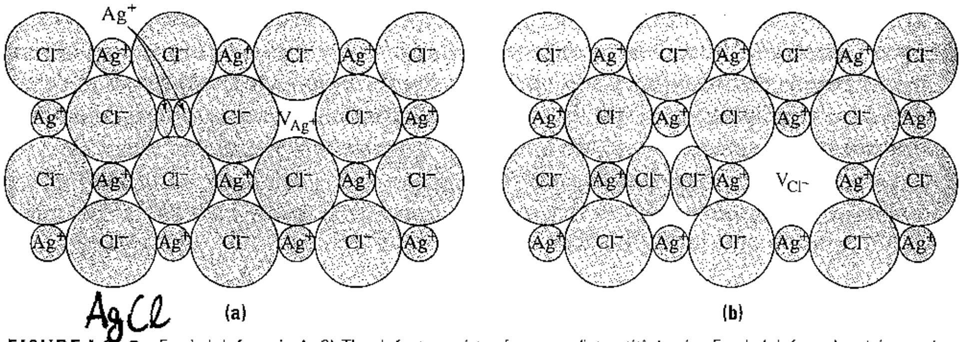


FIGURE 4.2–3 Frenkel defects in AgCl. The defect consists of vacancy/interstitial pairs. Frenkel defects involving cations (a) are more common than those involving anions (b), since cations are usually smaller.

→ $V^{+}_{Cl^-}$ & $I^{-}_{Cl^-}$ are more RARE

$V^{-}_{Ag^+}$ & $I^{+}_{Ag^+}$ Frequent

CONCENTRATIONS OF DEFECTS

FRENKEL

$$\overset{\downarrow \text{concentration}}{C_V} = \frac{N_V}{N_T} = \exp\left(-\frac{\varphi_{FVI}}{\underset{\uparrow}{2RT}}\right) = \frac{N_i}{N_T} = C_i$$

because 2 defects are built

SCHOTTKY

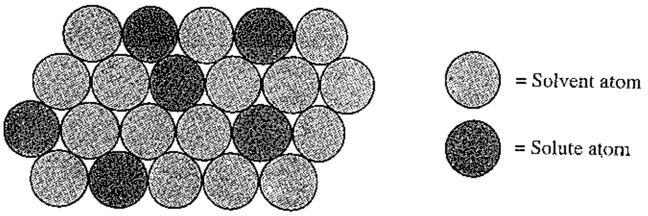
$$C_{V,cation} = \frac{N_{V,cat}}{N_T} = \exp\left(-\frac{\varphi_{FVP}}{2RT}\right) = \frac{N_{V,ANION}}{N_T} = C_{ANION}$$

CAN BE PROOVED FOR SCHOTTKY IN M_mX_p compounds

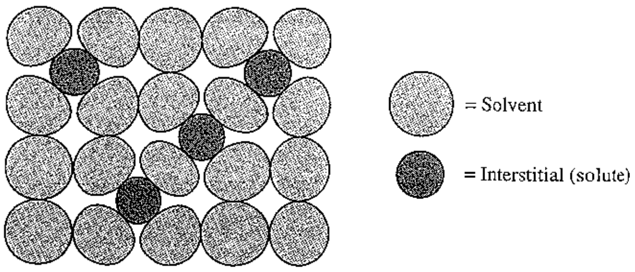
$$M_mX_p \longleftrightarrow pC_{V,cat} = \exp\left[-\frac{\varphi_{FVc}}{(m^2+p^2)RT}\right] = mC_{V,AN}$$

IMPURITIES IN CRYSTALS

Matrix of atom = SOLVENT + SOLUTE $\left\langle \begin{array}{l} \text{SUBSTITUTION (SOLUTE)} \\ \text{INTERSTITIAL (SOLUTE)} \end{array} \right.$



SUBSTITUTIONAL
MUST BE
SIMILAR SIZES



INTERSTITIAL
MUST BE ~~[illegible]~~
COMPATIBLE
SIZES

SUBSTITUTIONAL

EXAMPLE : steel (IRON + C)

C > Fe dimesion 0.022% @ 725°C
1000 K

— 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 electronegativity (giving, taking e^-)
3) similar valence (how many electrons for bonds)
4) same crystal structure (relax condition)
FCC & HCP can mix well)

NO 1) ⇒ STRAIN
NO (2,3) ⇒ different BOND CHARACTERISTICS
NO 4) ⇒ Because atoms prefere similar environments

STEEL : Fe is BCC @ T_{ROOM}, BCC HAS BRITTLE TRANSITION FRACTURES TEMPERATURE

add Ni, Cr ⇒ SOLID SOLUTION (FCC) @ T_{ROOM}.
8% 18%

} ~~BCI~~ CHANGE ELECTRICAL PROPERTIES: BETTER CORROSION RESISTENCE

D9

ASSIGMENT

— DO IMPURITIES IN POLYMERIC CRYSTALS 119

— 4.3-2 EXAMPLE
4.3-1

IMPURITIES IN IONIC CRYSTALS ⇒ need to maintain electroneutrality.

— EXAMPLE 4.3-3

— STUDY 111 — 122 WELL

LINEAR DEFECTS

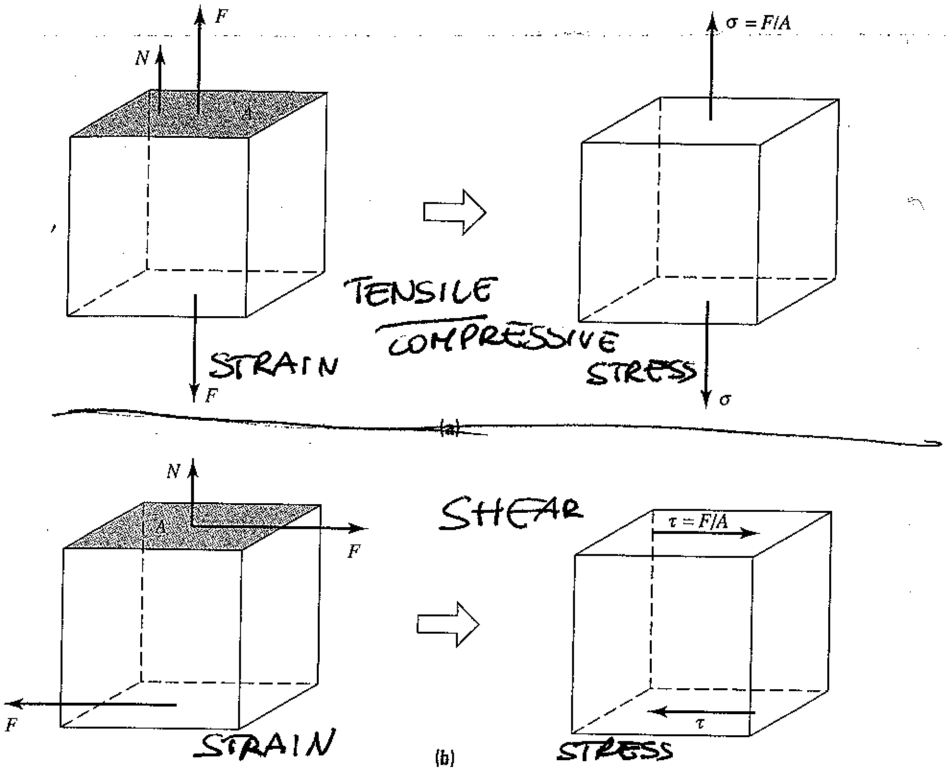


FIGURE 5.2–1 Illustration of **(a)** a normal stress, given the symbol σ and defined as F/A when F is parallel to the plane normal N; and **(b)** a shear stress, given the symbol τ and defined as F/A when F is perpendicular to N.

NOT FORGET DEFINITION

⇒ PULL TOO MUCH YOU GET DEFORMATION

⇓

SLIP PLANE
SLIP DIRECTION

⇓

SLIP SYSTEM.
(NOT ONLY BY SHEAR)

D10

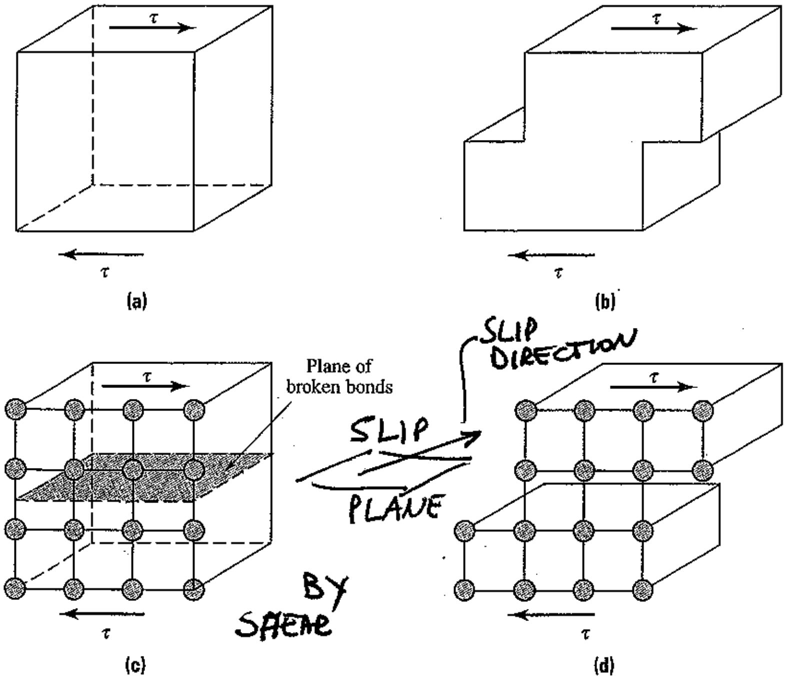
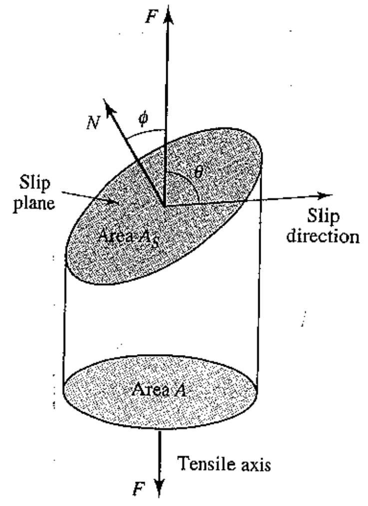
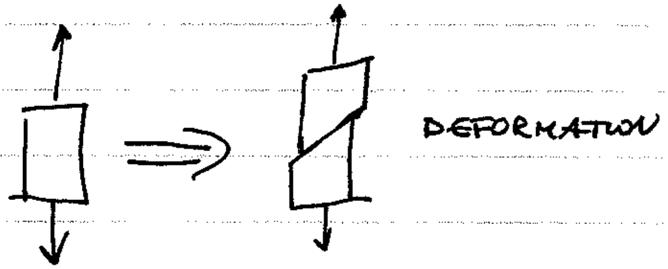


FIGURE 5.2–3 Model for computation of the theoretical critical resolved shear strength. Under the application of a shear stress τ, the top plane of atoms is assumed to slide over the bottom plane as a unit to produce permanent offset. Parts **(a)** and **(b)** represent a macroscopic view, while parts **(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.

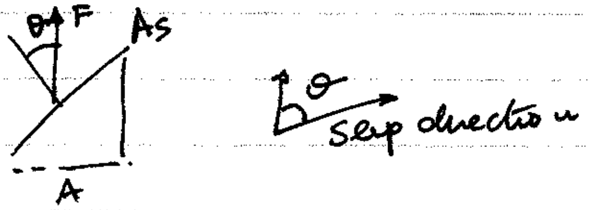
TENSILE STRESS PRODUCES SLIP TOO !!





ϑ = angle FORCE ∧ SLIP DIRECTION.

ϕ = angle FORCE ∧ NORMAL SLIP PLANE



$A_S = \dfrac{A}{\cos\phi}$ ⇒ area of the slip plane.

$F_S = F\cos\vartheta$ ⇒ Force parallel to the slip plane ~~and~~ in the direction of the slip direction.

$$\tau = \frac{F_S}{A_S} = \frac{F\cos\vartheta}{A/\cos\phi} = \sigma\cos\vartheta\cos\phi$$

Critical resolved shear stress (MPa)		
Metal	Experimental	Theoretical (E/10)
Cu	0.49	10.3×10^3
Ag	0.37	9.2×10^3
Al	0.78	7.0×10^3
Fe	27.44	21.0×10^3
Ti	13.72	11.0×10^3

if critical shear ⇒ to get slip ⇒ stress critical tensile to get deformation

$$\boxed{\sigma_{CR} = \frac{\tau_{CR}}{\cos\vartheta\cos\phi}}$$

BAD THEORY

SCHMID'S LAW

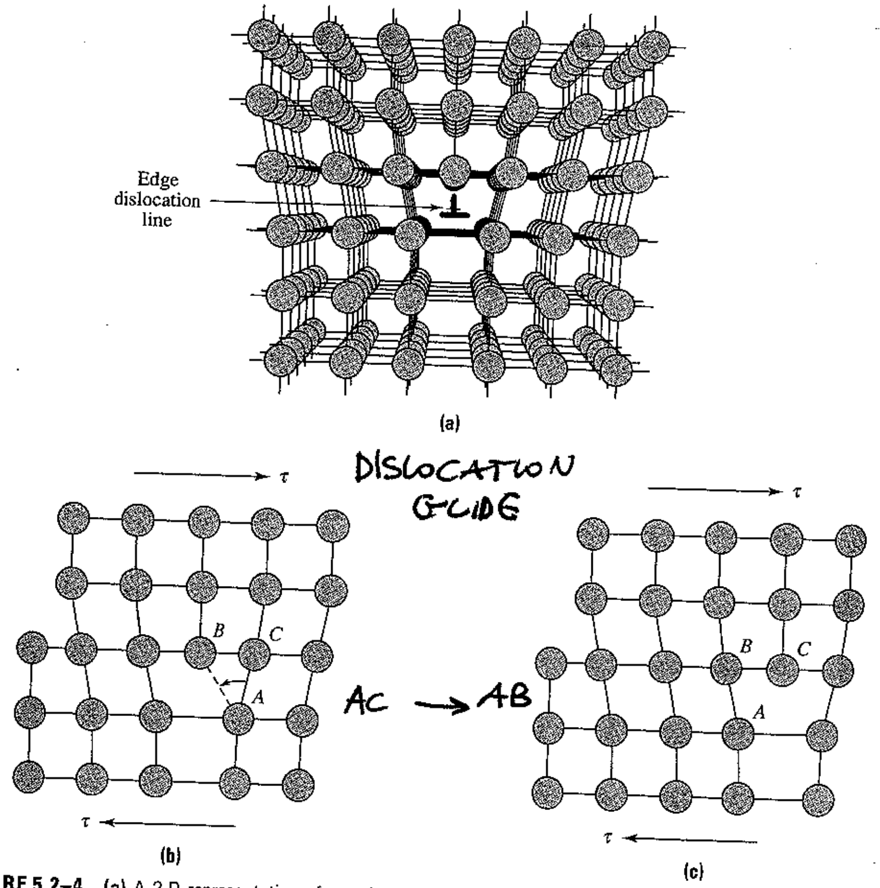
$\approx E/10$

THEORETICAL BAD!! need defects

D II

SLIP IS MUCH EASIER THAN THEORETICAL

→ HAVE DEFECTS.



(a)

DISLOCATION GLIDE

AC → AB

(b)

(c)

FIGURE 5.2–4 (a) A 3-D representation of an edge dislocation. The dislocation is not the extra half plane of atoms that has 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 τ. The details of this motion are described in the text.

DISLOCATION

~~[illegible]~~ ⊥

EXTRA PLANE

THEY FORM

1) NATURALLY GROWINGH CRYSTAL

2) OTHER DEFECTS RELEASING ENERGY

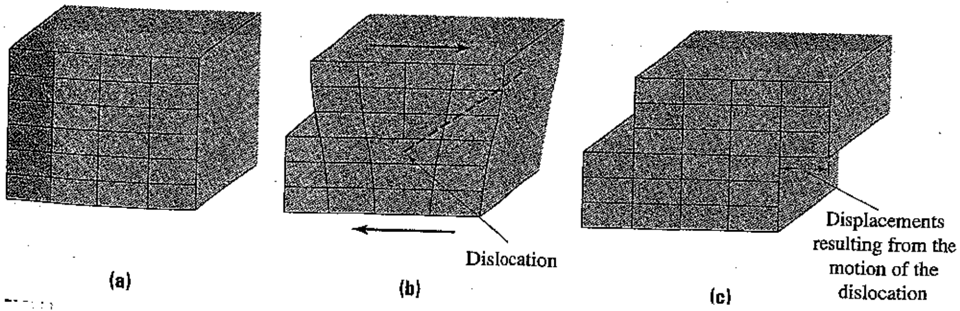
3) INTERACTIONS BETWEEN DISLOCATION

⇓

SINCE ⊥ MOVEMENT IS EASIER

DEFORMATION ONE PLANE AT EACH TIME

DISLOCATION GLIDE → MOVES (IF FORCE APPLIED) UNTIL IT'S OUT OF THE CRYSTAL



(a)

(b)

(c)

D12

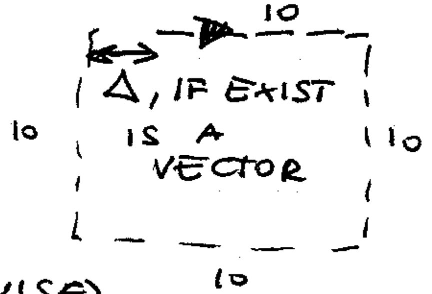
HOW TO MEASURE DISLOCATIONS?

MAKE A CIRCL~~E~~ AROUND ATOMS AND SEE WHAT IS LEFT:

⇓

~~BURGREE~~

BURGER CIRCLE (CLOCK WISE) ⇒ BURGER VECTOR!



EDGE

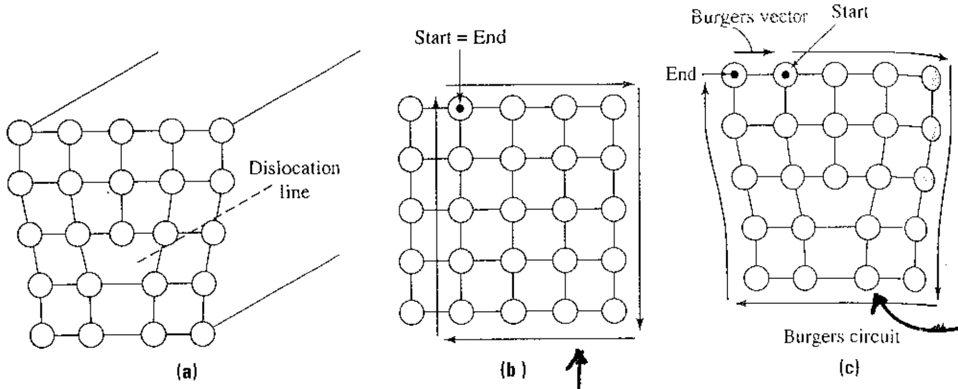


FIGURE 5.2–6 Illustration of Burgers circuit and Burgers vector for an edge dislocation. (a) A 3-D view of an edge dislocation. (b) A Burgers circuit closes upon itself when it surrounds a dislocation-free region of a crystal. (c) When the Burgers circuit surrounds a dislocation, the start and stop points 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.

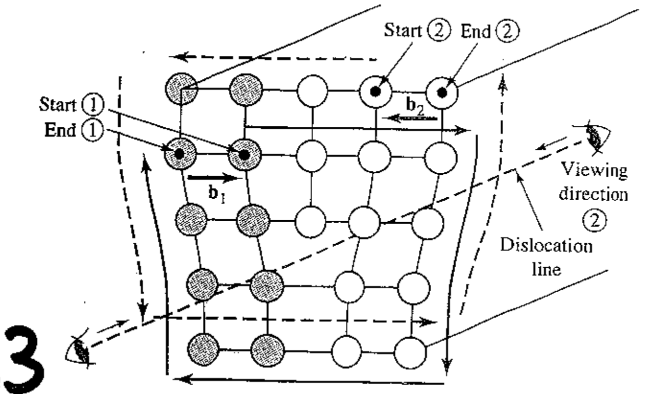
BURGER IS INVARIANT

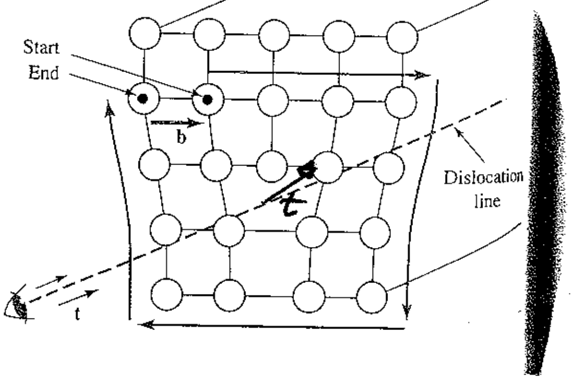
DEFECT

b = →

(PERFECT ⇒ B = 0)

CLOCKWISE RESPECT TO THE SCREWDRIVER RULE APPLIED TO THE UNIT TANGENT VECTOR t, TANGENT TO THE DISLOCATION, LOCALLY ⇒





D13

$\bar{b}$ & $\bar{t}$ are in the slip plane (EDGE $b \perp t$)

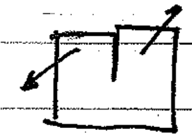
⇒ MILLER INDICES OF SLIP PLANE IN CUBIC SYSTEMS ARE $\propto \bar{b} \times \bar{t}$

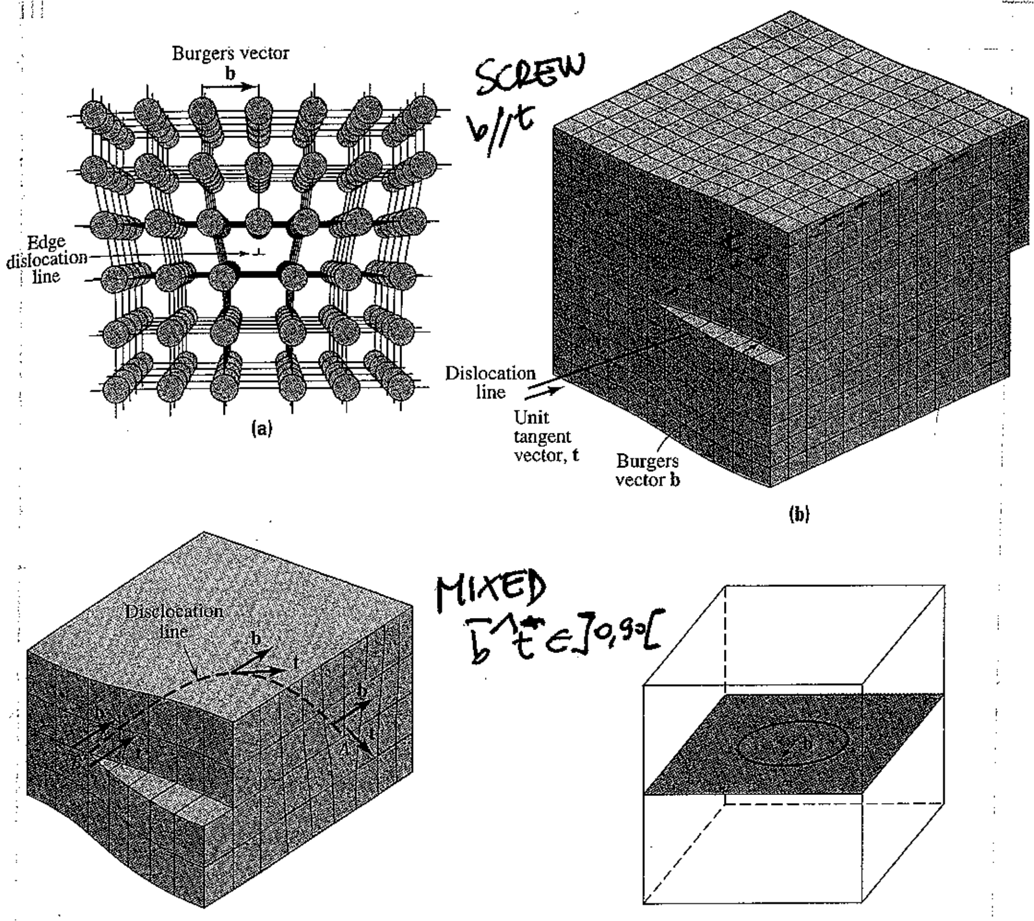
because

PLANE (h k l) ⊥ direction [h k l] in CUBIC SYSTEMS

$\bar{b} \times \bar{t}$ b t

SCREW DISLOCATION





SCREW $b // t$

MIXED $\hat{b\,t} \in]0, 90[$

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.)*

~~BURGER IS~~ INVARIANT

SCREW

$b // t$

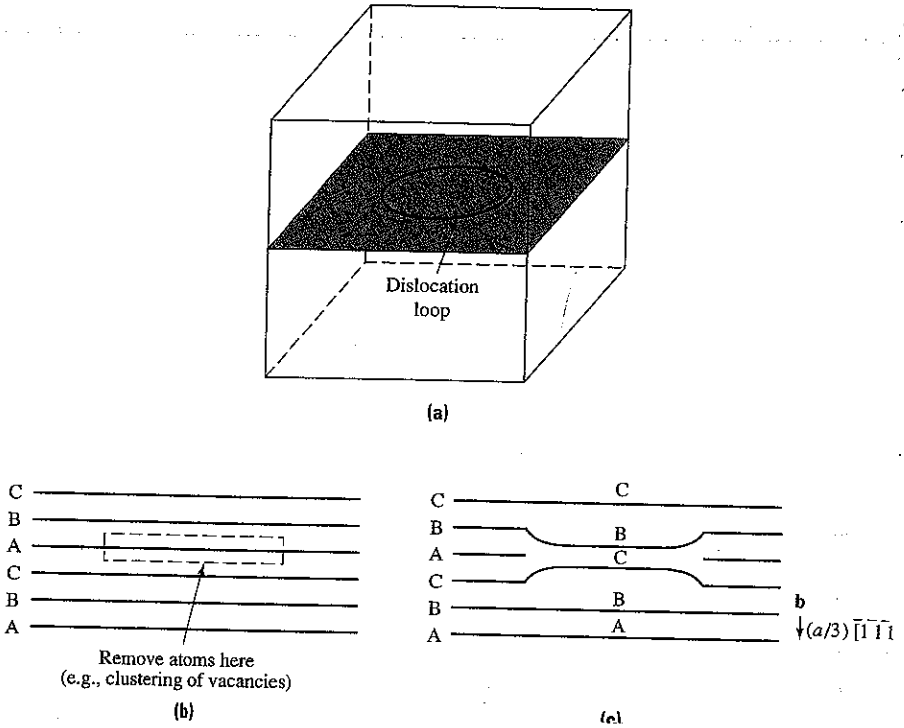
MIXED, LOOP

DIS

D14

- BURGER VECTOR IS INVARIANT !!
- DISLOCATION ENDS IN ANOTHER DISL., ON ITSELF, OR AT THE SURFACE

LOOPS DISLOCATION LOOP



CLIMBING!!

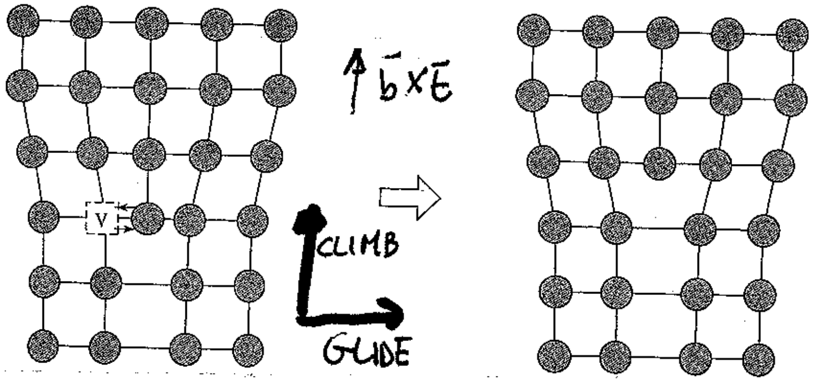


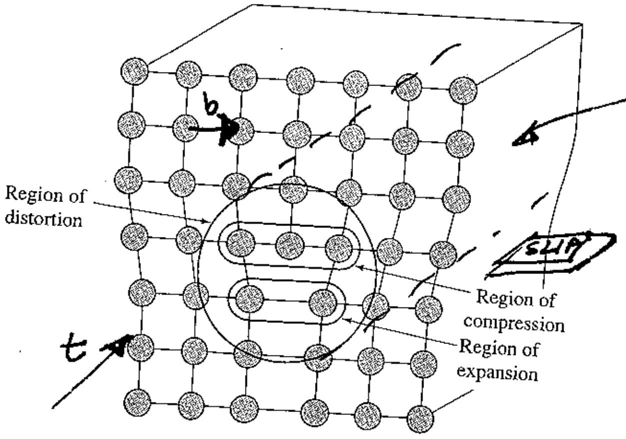
FIGURE 5.2–10 Climb of edge dislocation. The dislocation moves up one atomic spacing when it absorbs a vacancy.

DIS

SLIP PLANES (where is? ~~[illegible]~~)

WHERE DOES IT MOVE?

dislocation = elastic energy in a region



CYLINDER CONTAINING "DISTORSIONAL" ENERGY

RADIUS $\propto |\bar{b}|$

$\Rightarrow$ ~~stuck~~

Volume per UNIT LENGTH $\propto |\bar{b}|^2$

$E_{dislocation} \propto |\bar{b}|^2 \Rightarrow$ MINIMUM ENERGY

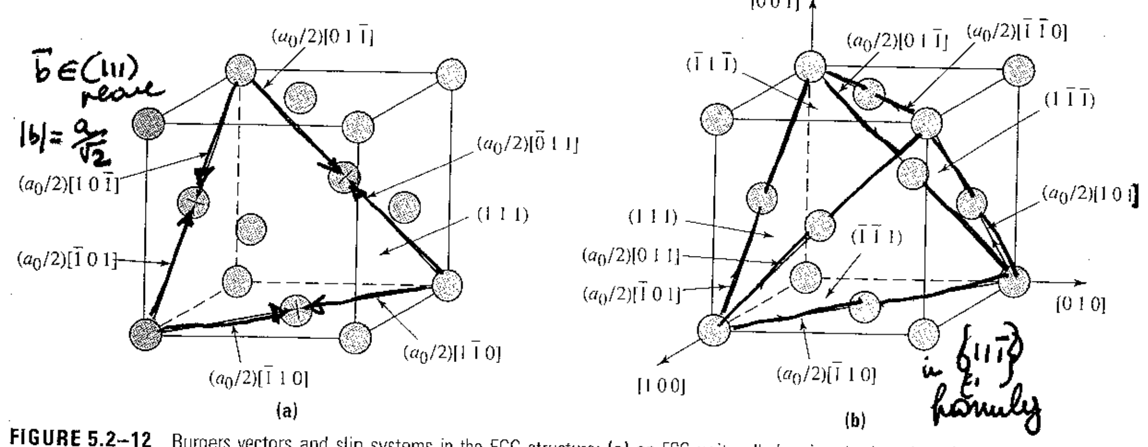
$\Rightarrow$ MINIMUM BURGERS VECTORS

BURGER VECTOR : ~~the vector containing~~

vector contained in the slip plane, vector connecting two ~~atoms~~ LATTICE ATOMS $\Rightarrow$ look for shortest possible in (the) planes

FCC

POSSIBLE BURGERS VECTORS [illegible] CONTAINED IN (111) PLANE



D16

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.

FOR FCC $\{111\}$ FAMILY

⇒ $|\bar{b}|$ in $\{1\ 1\ 1\}$ family of planes:

↳ (111) $(11\bar{1})$ $(1\bar{1}1)$ $(\bar{1}11)$ $(1\bar{1}\bar{1})$ $(\bar{1}1\bar{1})$ $(\bar{1}\bar{1}1)$ $(\bar{1}\bar{1}\bar{1})$

FAMILY

$|b|$ in such family is $a/\sqrt{2}$ long.

there are 12 possible BURGERS ~~PLANES~~ VECTORS!

IN FCC 12 POSSIBLE BURGERS VECTORS in {111} family, ⇒ SLIP PLANE IS ONE OF THE ~~8~~ PLANES in {111}

SLIP DIRECTION IS ONE OF THE DIRECTION OF BURGERS. ⇒ $\frac{a}{2}\langle 110\rangle$ family of direction!

⇒ $\boxed{\text{12 slip systems FCC (directions + PLANES)}}$

< > move 0 where you want and put ±1 ⇒ 1 or $\bar{1}$ everywhere!!

BCC is NOT CLOSED PACKED ⇒ SOLUTION IS ~~[illegible]~~ COMPLICATE

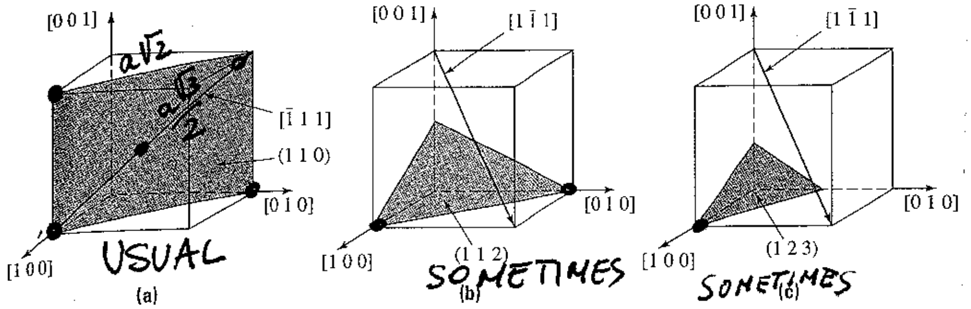


FIGURE 5.2–13 Slip planes and directions in the BCC structure: **(a)** a member of the {1 1 0}⟨1 1 1⟩ system, **(b)** a member of the {1 1 2}⟨1 1 1⟩ system, and **(c)** a member of the {1 2 3}⟨1 1 1⟩ system.

from {110} family get 12, then 36 from others

⇒ a total of. 48 slip system

D17

IN SPECIFICATIONS, MURPHY'S LAW SUPERSEDES OHM'S.

HCP. (a mess!)

SLIP ALONG BASAL PLANES. + OTHER SLIP DEPENDING ON LOADING

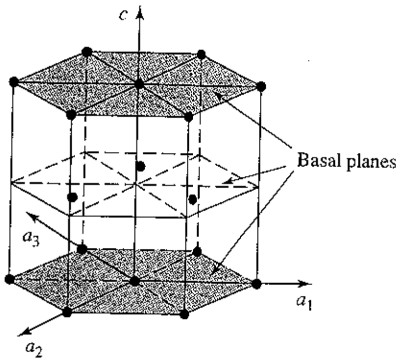


FIGURE 5.2–14 The slip planes and directions in the HCP structure are the basal planes and the *a* directions.

ANYWAY: THE MOST COMMON IS THE BASAL (3 SYSTEMS SLIP)

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

Crystal structure	Slip planes	Slip directions	Number of slip systems
FCC	{1 1 1}	⟨1 1 0⟩	12
BCC	{1 1 0}	⟨1 1 1⟩	12
	{2 1 1}	⟨1 1 1⟩	12
	{3 2 1}	⟨1 1 1⟩	24
HCP	Basal	*a*	3

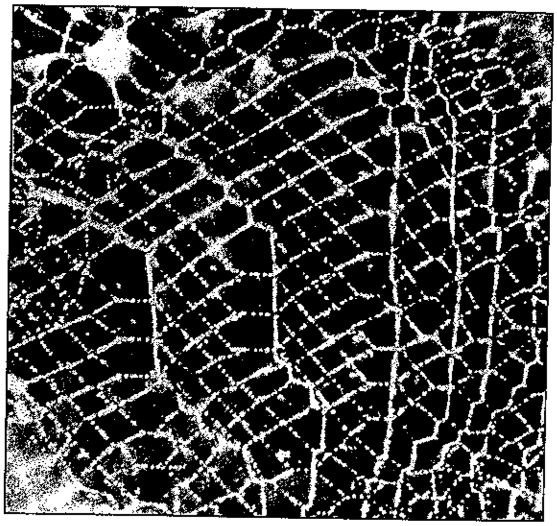
SUMMARY: HINTS

FOR THE EXAM YOU MUST BE ABLE TO CALCULATE $|\bar{b}|$ & $\bar{E}$ for THE SYSTEMS LISTED HERE ☺

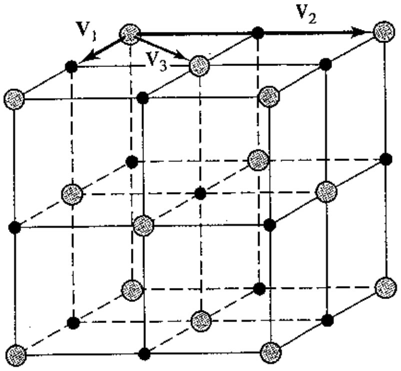
D18

DISLOCATIONS IN IONS

Always remember that BURGER VECTOR MUST CONNECT EQUIVALENT POINTS : NiO



KCL



NaCl OR CsCl ?

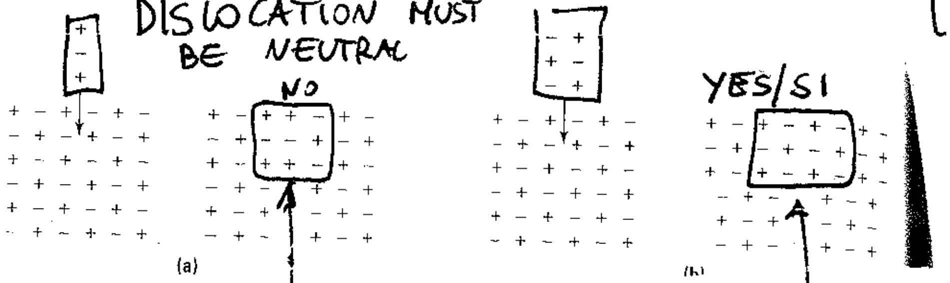
NiO

V_1 NOT Good why?

$|V_3| < |V_2|$

↑ $\bar{b}$

DISLOCATION MUST BE NEUTRAL

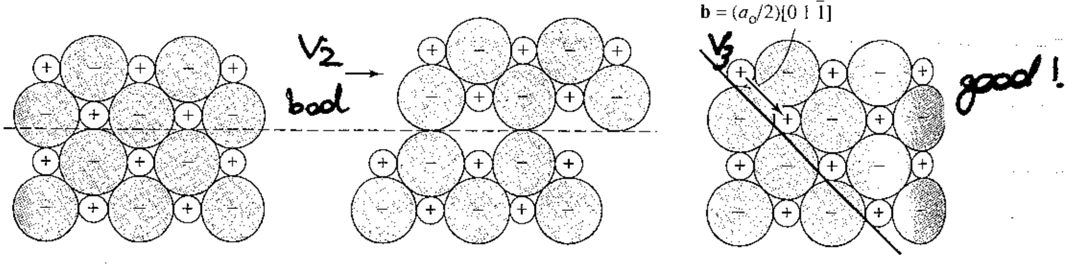


Lot of Repulsion

small repulsion!

ASSIGMENT

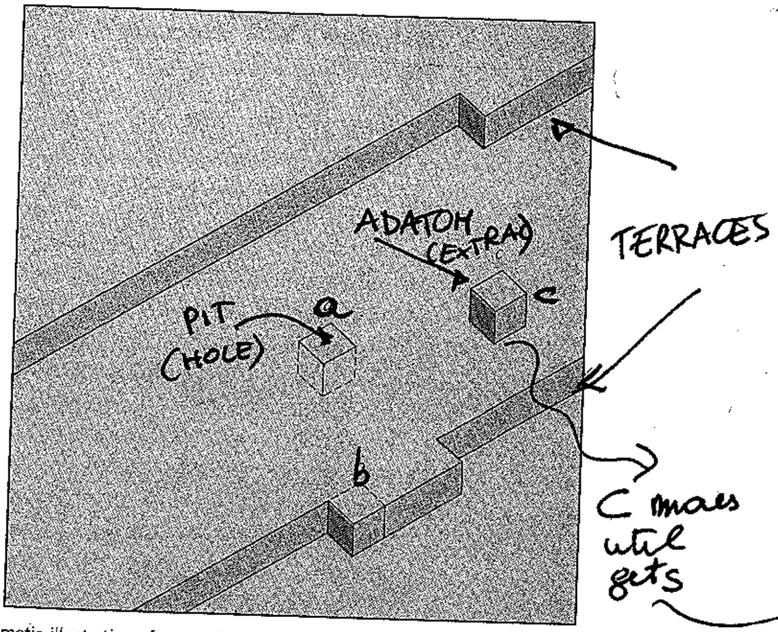
Ex: 5.2-4 Burgers for CsCl



(a) (b) (c)

D19

PLANAR DEFECTS



C moves until gets → absorbed by a terrace (b) USUALLY

FIGURE 5.3–1 Schematic illustration of atoms (assumed to be cubes) adsorbed at a free surface. The lowest-energy location for adsorption is at *a*, since the atom is attached with a reduction in the surface area and, hence, a reduction in the surface energy. At position *b* the surface energy remains unchanged, while at *c* the energy increases, since the surface area increases. The site at *b* is a "repeatable step," since the process may be repeated continually with no change in energy.

MINIMIZE SURFACE ENERGY (PROP α NUMBER OF OPEN BONDS)

ADATOM & PIT HAVE HIGH ENERGY ⟹ TRY TO GET ADSORBED BY TERRACES

REMEMBER THAT @ T>0
NEED FOR DEFECTS SINCE ENTROPY !!!!

TERRACES GROWTH !!

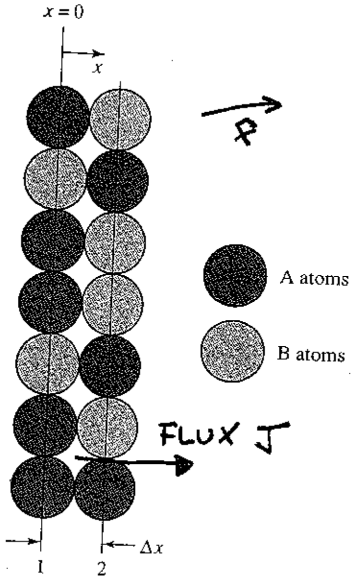
ASSIGNMENT STUDY
5.1 ALL
5.2 ALL + → 5.3.1
5.3.2
5.33 (NO 5.3.4)
5.36
5.4 //

D20

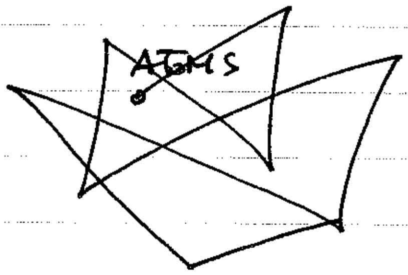
ASSIGNMENT !
STUDY ALL 4.4

DIFFUSION

Living things MOVE ⇒ ATOMS ARE VERY SMALL THINGS, THEREFORE THEY MOVE WITH TEMPERATURE



Temperature > 0



RANDOM WALKS
JUMP AROUND
(DRUNK MAN) EXAMPLE

T↑ ⇒ MORE JUMPS
GAS > CONSTANT JUMPS (PRESSURE)
LIQUIDS > FREQUENT JUMPS
SOLIDS = OCCASIONAL JUMPS

SOLID DIFFUSION
MODELING LIKE ATOM'S BETWEEN TWO PLANES

- PICK 2 LAYERS AND THINK A IS SOLUTE IN AN ENVIROMENT OF B
- ⇒ DEFINE C_A = CONCENTRATION

1) $A\ \underset{1 \qquad\qquad 2}{\xrightarrow{J_{12}}}$ & $\underset{1 \qquad\qquad 2}{\xleftarrow{J_{21}}}$ ⇒ TOTAL FLUX $J_{12} - J_{21}$ $\longrightarrow$?

IF $C_2 > C_1$ ⇒ $J_{21} > J_{12}$ ←
IF $C_2 < C_1$ ⇒ $J_{21} < J_{12}$ →

DF1 $J_{total} \propto -(C_2 - C_1) = -\Delta C$ ASSUMPTION

2) WHAT ABOUT Δx ?

FURTHER THEY ARE AND LESS LIKELY THEY JUMP ! WHY ?

Δx SMALL

$J_{21} \gg J_{12}$

$J_{TOT} \longleftarrow$

~~Δx~~ BIG

$J_{21} \gtrsim J_{12}$

$J_{TOT} = \leftarrow$

$\Rightarrow \quad J_{TOTAL} \propto \frac{1}{\Delta x}$ ASSUMPTION

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

$\Rightarrow$

FICK'S LAW $\quad \bar{J} = D\left(-\frac{\Delta c}{\Delta x}\right)$

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

$$\boxed{\bar{J} \equiv -D\frac{\partial c}{\partial x}}$$

$\bar{J} = [m^{-2} s^{-1}]$
$c = [\cancel{1}/m^3]$
$x = [m]$

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

$c = [\text{FRACTION OF PARTICLES}]$

$\Rightarrow$ TOTAL NUMBER $\Rightarrow \propto \frac{1}{(\text{VOLUME PART})^3}$

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

IDENTICAL TO HEAT FLUX $\Rightarrow$ FLUX OF HEAT

~~SQ~~ $J_Q = K\frac{T_{HOT} - T_{COLD}}{\Delta x}$

$= -k\frac{\partial T}{\partial x}$!!

SAME

DF2

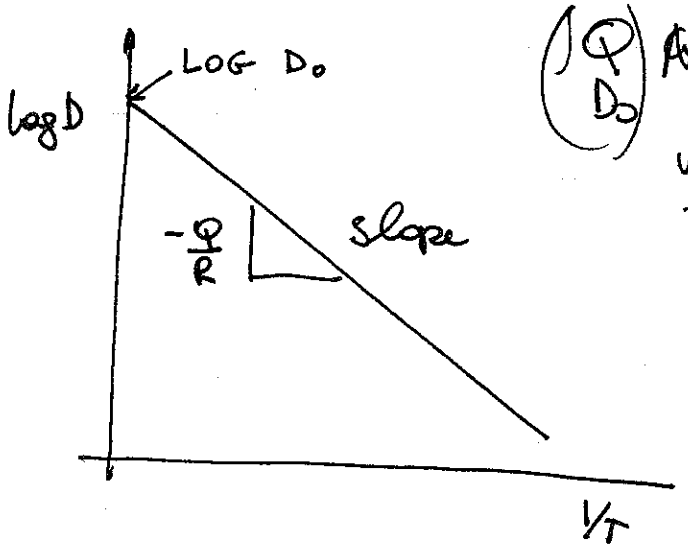
TEMPERATURE DEPENDENCE ?

IN D !! $D(T) = D_0 \exp\left(-\frac{Q}{RT}\right)$ → KJ/MOL

ARRHENIUS

$= D_0 \exp\left(-\frac{Q}{kT}\right)$ → JOULES

⇒ log D plot



$\left(\begin{matrix} Q \\ D_0 \end{matrix}\right)$ NEED TO KNOW where do they COME FROM

BOOK IS MISLEADING

IF SOLID HOMOGENEOUS $\Delta C = 0 \Rightarrow \frac{\partial c}{\partial x} = 0$

$\Rightarrow J_{TOT} = 0$ CORRECT

BUT $J_{TOT} = J_{12} - J_{21} = 0$

$J_{12} \longrightarrow = J_{21} \longleftarrow$

DF3

Remember $J > 0$ if in same DIRECTION OF $\hat{x}$

IF $T > 0$

& YOU ALWAYS HAVE STUFF MOVING !!

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

THEN SAME AMOUNT GOES RIGHT & LEFT

⇒ OVERALL $= 0$ ULTRA-MEGA-IMPORTANT

MECHANISM OF DIFFUSION

IMPURITIES

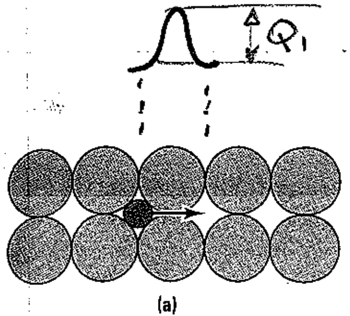
IN COVALENT AND METALLIC CRYSTALS

EXAMPLE EXTRA CARBON IN STEELE, IMPURITY DIFFUSION!

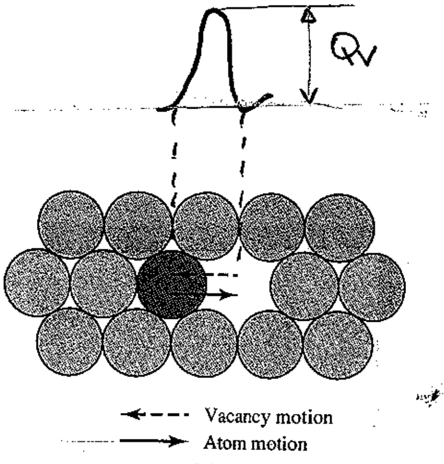
IN SOLIDS WITH EXTRA INTERSTITIAL

⇓

SPACE ALWAYS AVAILABLE



INTERSTITIAL
NO VACANCY HELP



SUBSTITUTIONAL
NEED HELP OF A VACANCY

IN SOLID SOLUTIONS WITH DEFECTS

THE DARK ATOM NEEDS HELP OF A VACANCY

⇒ PROP DEPENDS ON CONCENTR. OF VACANCIES

⇒ D(C)!!

USUALLY ACTIV. ENERGIES

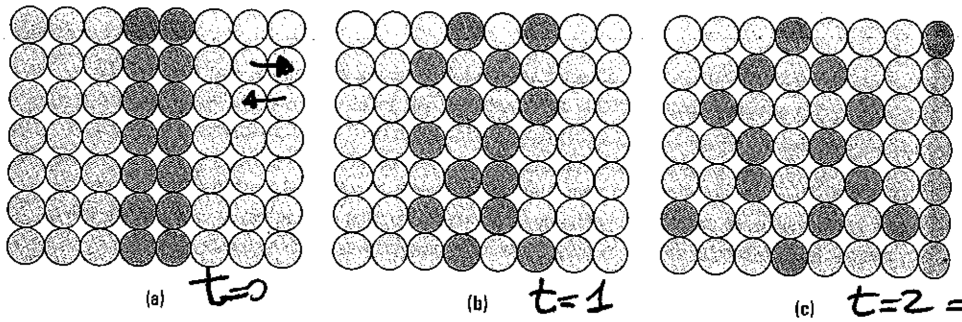
$$Q_V > Q_I$$

↳ NEED ENERGY TO FORM VACANCY TOO!!

WHAT ABOUT WITHOUT IMPURITIES

IN PURE SYSTEMS ATOMS DIFFUSE TOO!

IT'S SELF DIFFUSION



⇒ MIX

TRACER

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 ⇒ NEED FOR COLOR!! ⇒ TAKE ISOTOPE

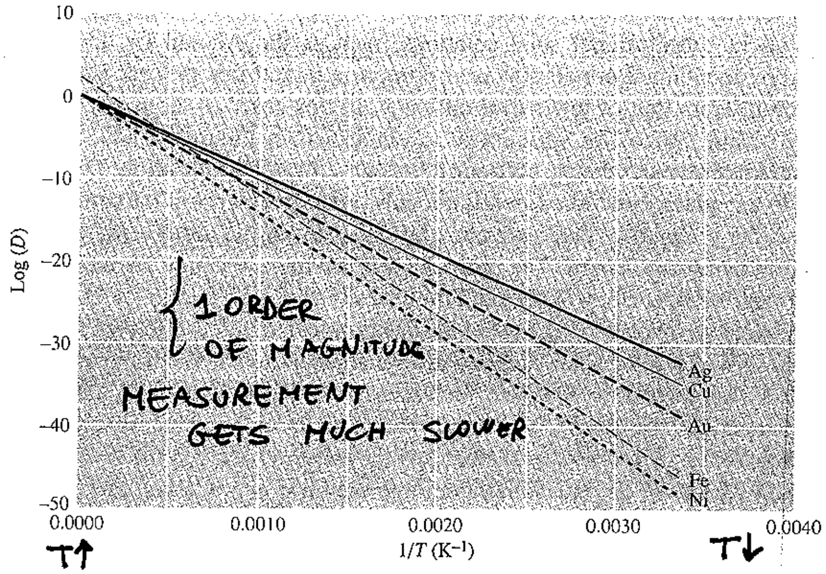


FIGURE 4.4–6 Self-diffusion coefficients for selected metals. The data were extrapolated to "infinite" temperature to demonstrate D_0. Data obtained from several sources.

TABLE 4.4–1 Diffusion coefficients for selected systems.

Material	D_0 (m²/s)	Q (kJ/mol)
Self-diffusion coefficients		
Ni	1.30×10^{-4}	279
Cu	2.00×10^{-5}	197
Ag	4.00×10^{-5}	184
Au	9.10×10^{-6}	174
Fe	1.18×10^{-2}	281
Si	1.80×10^{-1}	460
PE in melt	1.20×10^{-11}	28
Impurity diffusion coefficients		
Cu in Ag	1.20×10^{-4}	193
Cu in Al	1.50×10^{-5}	126
Zn in Ag	5.40×10^{-5}	174
Zn in Cu	3.40×10^{-5}	191
Ni in Cu	2.70×10^{-4}	236
Ni in Fe	7.70×10^{-5}	280
C in BCC Fe	2.00×10^{-6}	84
C in FCC Fe	2.00×10^{-5}	142
N in Fe	3.00×10^{-7}	76
Al in Al_2O_3	2.8×10^{-3}	477
O in Al_2O_3	1.9×10^{-1}	636
Mg in MgO	2.49×10^{-5}	330
O in MgO	4.3×10^{-9}	344
Ni in MgO	1.8×10^{-9}	202
O in SiO_2	2.7×10^{-8}	111
CO_2 in polyester (PET)	6.0×10^{-5}	51
CO_2 in PE	2.0×10^{-4}	38
CO_2 in PVC	4.2×10^{-2}	64
O_2 in PET	5.2×10^{-5}	47
O_2 in PE	6.2×10^{-4}	41
O_2 in PVC	4.1×10^{-3}	54

DF S

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 !

$MgO \Rightarrow D_{Mg}$ & D_O

IONS ⇒ COULOMB BONDED, NO FREE CHARGE

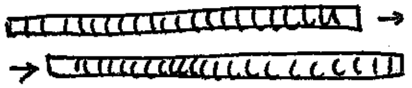
⇒ ELECTRICAL CONDUCTIVITY IS ALL GIVEN BY IONIC DIFFUSION

⇒ SMALL CONDUCTIVITY, BUT I CAN GET DIFFUSION MEASURING CONDUCTIVITY !

MECHANISM IN POLYMERS

POLYMERS ⇒ LIKE SPAGHETTI (MOVING WORMS) ENTANGLED

COMPLETELY DIFFERENT MECHANISM

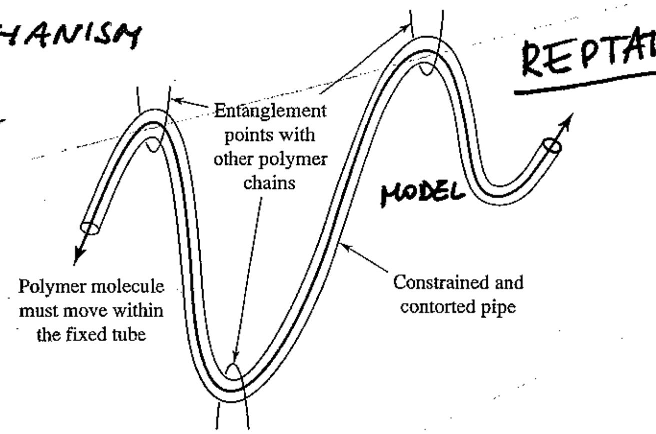


ALL MUST MOVE

$$\Rightarrow D = D_0 e^{-Q/RT}$$

$$\hookrightarrow D_0 \propto \frac{1}{N^2}$$

REPTATION



DF6

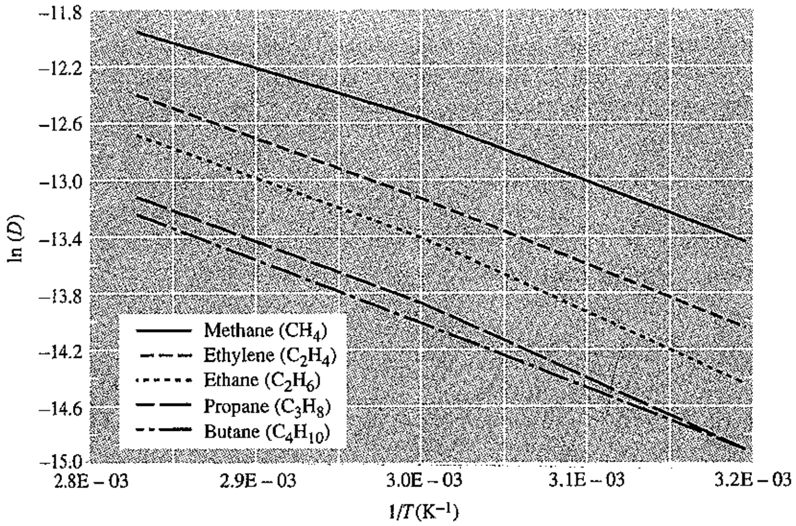


FIGURE 4.4–8 Diffusion coefficients of various organic molecules in natural rubber as a function of temperature. Note that at any given temperature, the smaller species diffuse more rapidly than the larger species.

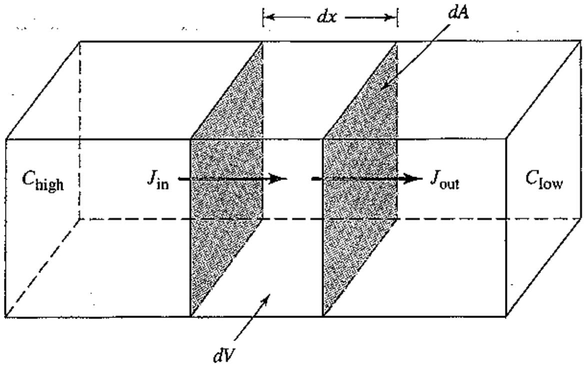
BUT VERY FAST FOR IMPURITIES !

NEED T SEPARATE TWO ORGANIC SPECIES ?

NEED TO TAYLOR PROPER LENGTH WHERE THE FIRST GOES THROUGH & THE SECOND DOES NOT!

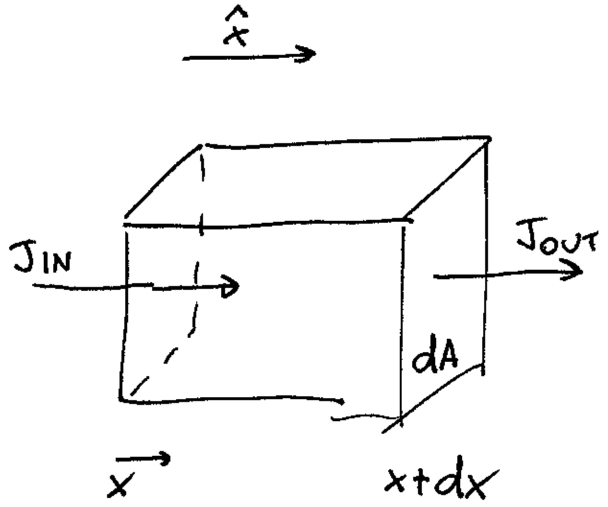
WHAT ABOUT TIME EVOLUTION ?

$J = -D\frac{\partial c}{\partial x}$, but J = STUFF per unit second $\overset{J}{\Rightarrow}$ changes $C \Rightarrow \frac{\partial c}{\partial t}$??



TAKE THE BOX!

DF 7



IF $J_{OUT} \neq J_{IN}$
SOMETHING
CHANGES INSIDE!!

PARTICLES DO. NOT
GET DESPROYED ⇒ CONC
CHANGES

$$J_{OUT}(x+dx) \equiv J(x+dx) = J(x) + \frac{\partial J}{\partial x}dx \quad \text{TAYLOR}$$

$$J_{IN}(x) = J(x)$$

J = FLUX ⇒ # PARTICLES FLOWING PER UNIT AREA
PER UNIT SECOND

⇒ $J_{IN}\,dA$ ⇒ # PART getting IN / UNIT SECOND

$J_{OUT}\,dA$ ⇒ # PART getting OUT / UNIT SECOND

⇒ ~~$(J_{OUT} - J_{IN})\,dA$ = # PART DISAPPEARING INSIDE / UNIT SECONDS~~

$(J_{IN} - J_{OUT})\,dA$ = # PART INCREASING INSIDE PER UNIT SECOND!!

$$\Rightarrow \left(J(x) - J(x) - \frac{\partial J}{\partial x}dx\right)dA = \frac{d}{dt}(c\,dA\,dx) \qquad = \cancel{\frac{\partial c}{\partial t}\Delta t} = \frac{dN}{dt}\Delta t$$

$$\frac{d}{dt}(\underbrace{c}_{\text{CONC}} \cdot \underbrace{dA\,dx}_{\text{VOLUME}})\,\Delta t$$

⇒ VOLUME DOES NOT
CHANGE IN TIME

$$\Rightarrow \frac{d(c\,dA\,dx)}{dt} = dA\,dx\,\frac{dc}{dt}$$

$$\Rightarrow \boxed{-\frac{\partial J}{\partial x} = \frac{dc}{dt} \;!!}$$

~~SECOND FICK'S LAW~~

← CONSERVATION
OF PARTICLES

BUT

$$J = -D\frac{\partial c}{\partial x}$$

$$\Rightarrow \quad -\frac{\partial J}{\partial x} = D\frac{\partial^2 c}{\partial x^2} = \frac{dc}{dt}$$

$$\boxed{\frac{\partial c}{dt} = D\frac{\partial^2 c}{\partial x^2}}$$

FOURIER LAW!!

HEAT

$$\boxed{\frac{\partial T}{\partial t} = D_{TH}\frac{\partial^2 T}{\partial x^2}}$$

Thermal diffusivity

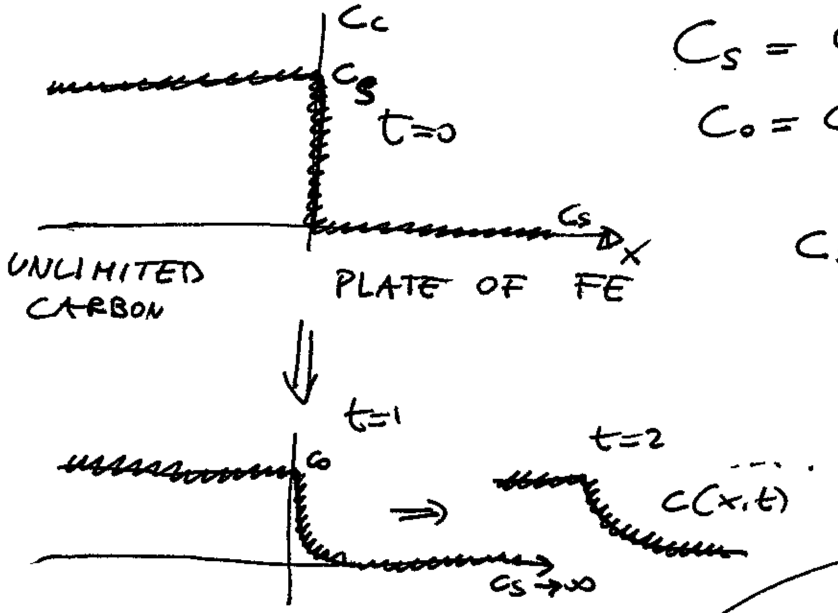
CONST D(T) NOT D(C)!!

DIFFERENTIAL EQUATION

NEED BOUNDARY CONDITIONS

EXAMPLE C & FE

INFINITELY FEEDING SURFACE



$C_s = C_{surface}$

$C_o = C_{BULK\ FE}$ BEFORE $t=0$

$C_s > C_o \Rightarrow$ Carbon enters

$$C(x,t) = C_o + [C_S - C_o]\left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

erf function!

$x/2\sqrt{Dt} = 1\,\overset{2}{\cdot}$

$x_{eff} \simeq 2\sqrt{Dt}$ is space/time relation

1/10 to get [illegible]

CONCENTRATION!

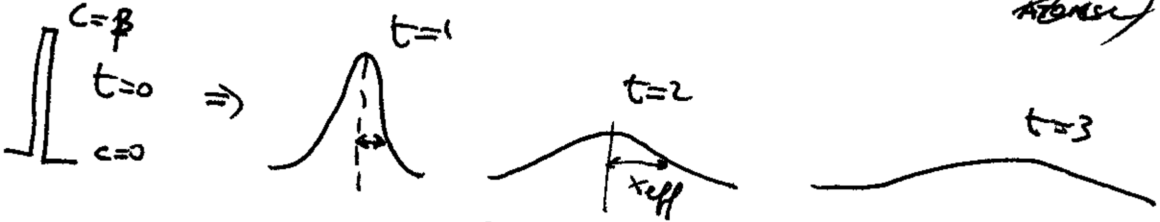
CARBURIZATION OF STEELE

TO MAKE IT WEAR RESISTENT!

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}dy$$

DF9

DEPLETING SOURCE (~~[illegible]~~)



$$C(x,t) = \left(\frac{\beta}{2\sqrt{\pi D t}}\right) \exp\left(-\frac{x^2}{4Dt}\right)$$

xeff is where ~~slope~~ SHAPE IS $\overset{e^{-1}}{\approx 1/3}$ OF ORIGINAL

$$x_{eff} \simeq 2\sqrt{Dt}$$

EFFECTIVE PENETRATION DISTANCE

place xeff ~~[illegible]~~ where $C(x_{eff},t) = \frac{C_0 + C_s}{2}$

$\Rightarrow$ FOR PLATE $\Rightarrow$ $\frac{1}{2} = \mathrm{erf}\left(\frac{x_{eff}}{2\sqrt{Dt}}\right)$ $\quad \mathrm{erf}(0.5) \sim 0.5$

$\Rightarrow x_{eff} \simeq \sqrt{Dt}$!

$x_{eff} \simeq 2\sqrt{Dt}$ for cylinders

ERF(Z)

$$\mathrm{erf}(z) \equiv \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} dx$$

$\mathrm{erf}(-z) = -\mathrm{erf}(z)$

$\lim_{z \to \infty} \mathrm{erf}(z) \to 1$

$\mathrm{erf}(z) \sim \frac{2}{\sqrt{\pi}} z$ for $z \approx 0$

$\mathrm{erf}\left(\frac{1}{2}\right) \sim \frac{1}{2}$

DF10

THERMODYNAMICS DETAILS

FOUNDATIONS ARE BASED ON EMPIRICAL OBSERVATIONS

⇒ LAWS

I) 1ST LAW

CONSERVATION OF ENERGY

<u>1st IN ANY PROCESS ENERGY IS CONSERVED</u>

$$dE = \delta W + \delta Q$$

E ⇒ total energy ⇒ dE variation of energy due by some process

W ⇒ MECHANICAL WORK ⇒ δW mechanical work made on the system

Q → HEAT ⇒ δQ heat given to the system.

Why dE & δW? What is the difference between $d(\cdot)$ & $\delta(\cdot)$? FUNDAMENTAL!

E is a <u>function of state</u> of the system $(\bar{x})$

⇒ going from x_0 to x_1 (states) is function only on FINAL & INITIAL position, not path!!!

$$\Delta E = \int_{x_0}^{x_1} dE$$

DOES NOT DEPEND ON PATH

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

CHANGE OF A STATE FUNCTION ON A REVERSIBLE PROCESS IS <u>ZERO</u>

IN MATHEMATICAL TERMS

d = <u>DIFFERENTIAL</u>

EXAMPLE
(x,y) STATE

$f(x,y)$ = STATE FUNCTION

DIFFERENTIAL $df = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy$

∂^2? $\frac{\partial^2 f}{\partial x \partial y}$ & $\frac{\partial^2 f}{\partial y \partial x}$, are they identical?

IF $\underline{\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}} \Rightarrow f$ is CALLED CLOSE FORM.

$\Updownarrow$ IF & ONLY IF

$\oint = 0$

$\oint_{loop} dF = 0$ integral on a loop = 0

$\Updownarrow$

$\int_{(x_0,y_0)}^{(x_1,y_1)} df$ = does **NOT** depend on path

$\Rightarrow$ dE is differential of E
& E is a function of <u>state</u> (for the 1st Law)

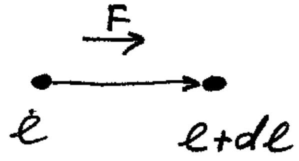
T2

What about δ?

δ represents a tiny ~~amount~~ variation of something but it is not a differential !!!!

$$\underset{\text{NO DIFF}}{\delta} \neq \underset{\text{DIFF}}{d}$$

EXAMPLE δW = tiny amount of work to go from close states



$$\delta W = F\,dl$$

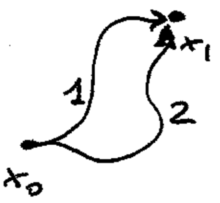
δW is not differential of W !!

$$W = Fl$$

$$dW = d(FL) = \underset{\overset{\|}{\delta W}}{F dl} + \underset{\underset{\text{NOTHING}}{\Downarrow}}{l dF}$$

$$\delta W = F dl$$

δ(SOMETHING) symbol is aplyed when the variation depends on the path



$\delta Q_1 \neq \delta Q_2$ depends on the path, the way you go from 1 to 2

so $$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy \Rightarrow \text{if } \frac{\partial^2 f}{\partial x \partial y} \neq \frac{\partial^2 f}{\partial y \partial x} \Rightarrow$$

PATH DEPENDENCE ⇒ need δ & not d

USUALLY CALLED

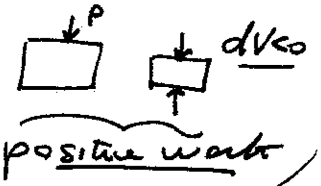
d = PERFECT DIFFERENTIAL, DIFFERENTIAL ... FOR STATE FUNCTIONS

δ = DELTA, VARIATION OF, ... FOR NO-STATE FUNCTIONS!

T3

we know $$\delta W = -p\,dV$$

(— because if V decreases with positive pressure, we make work



)

V is a state function!! ⇒ dV

of course, V is a state variable by itself.

$$\Rightarrow \quad dE = \underbrace{-p\,dV}_{\text{comes from } -PV} + \delta Q$$

$$H \equiv E - (-PV) = E + PV$$

ENTHALPY

(Legendre transformation = subtract conjugate variables

$$\Rightarrow \quad dH = V\,dP + \delta Q$$

ENTHALPY, at constant pressure, contains HEAT VARIATION!!

$$dH\Big|_P = \delta Q \quad \Rightarrow$$

EPERIMENT:
IN OPEN AIR (CONSTANT 1 APM)
RAISE TEMPERATURE OF ONE SOLID ⇒ MAKE ΔH NOT ΔE!!

$$\delta Q = dH\Big|_P = dE\Big|_V$$

$$C \equiv \frac{\delta Q}{\delta T}$$

specific heat: HOW MUCH HEAT TO GIVE TO RAISE TEMPER OF 1 DEGRRE

$$C_P = \frac{\partial Q}{\delta t}\Big|_P = \frac{dH}{dT}\Big|_P$$

$$C_V = \frac{\delta Q}{\delta T}\Big|_V = \frac{dE}{dT}\Big|_V$$

T4

USE H to describe systems @ P=COST
NOT E

II)

δQ is NOT A FUNCTION OF STATE BUT

THERE IS A STATE FUNCTION, S, ENTROPY, FOR WHICH
FOR ALL REVERSIBLE PROCESSES $dS = \frac{\delta Q_{rev}}{T}$
AND ALL IRREVERSIBLE PROCESSES
$dS > \frac{\delta Q}{T}$

EQUILIBRA ARE NOT ALWAIS REVERSIBLE

REV OF EQ ! SMALL VARIATION TAKEN & GIVEN
BACK BRINGS TO THE SAME POINT

$\Rightarrow$ IF in a <u>close loop</u>

I get some extra ENTROPY $\Rightarrow$ THIS MEASURES DEGRADATION

(MORE HEAT EXCHANGE $\Rightarrow$ MORE ENTROPY)

$\Rightarrow$ $dE = -pdV + TdS$ ENERGY

$dH = Vdp + TdS$ $H \equiv E + PV$ ENTHALPY

$dA = -pdV \cancel{+} SdT$ $A \equiv E - ST$ (HELMOLTZ)

good @ V, T constant

$dG = \cancel{-} Vdp - SdT$ $G \equiv E + PV \cancel{+} ST$ (GIBBS)

good @ P, T costant

Like normal <u>Life</u>

(TOTAL ENTROPY OF UNIVERSE $\uparrow$)

TS

III) STABILITY? WHAT TO MINIMIZE?

SECOND LAW IRREV. REV $Tds \geq \delta Q$

IF IRR

$$\delta Q \underset{\uparrow}{\overset{\downarrow}{\leq}} Tds$$

IF REV

A VARIATION δ (NOT A DIFFERENTIAL)

$$dE = \delta W + \delta Q \leq \delta W + TdS$$

$$\Rightarrow dE - \delta W - Tds \leq 0$$

suppose $\delta W = -pdV$ for mech work

$$dE + pdV - Tds < 0$$

FOR ALL IRREVERSIBLE <u>PROCESSES</u>

PROCESS = SOMETHING MOVING $\delta Q \leq T ds$, IRR $\delta Q < Tds$

IF EQUILIBRIUM, NO PROCESS $\Rightarrow$ $\delta Q \geq T\overset{\uparrow}{\delta} S$ Virtual Variation

$\Rightarrow$ at equilibrium (variation back/forth does not change state)

if you vary $S \to \delta S$, you need to violate THE irreversible process (because you need to come back)

$$\Rightarrow \underset{\substack{\downarrow \\ \text{VIRTUAL VARIATION}}}{\delta S} \leq \delta Q/T$$

APPLIES TO STATE FUNCTIONS TOO

$$\Rightarrow \quad \delta E - T\underset{\substack{\downarrow \\ \text{vv}}}{\delta S} + P\underset{\substack{\downarrow \\ \text{vv}}}{\delta V} \geq 0 \Rightarrow$$

~~δQ~~

$$\delta Z = \delta E - T\delta S + P\delta V \geq 0$$

EQUILIBRIUM

T6

$\Rightarrow$ at $T=0$, constant Volume $\Rightarrow$

equilibrium is $\delta E \geq 0 \Rightarrow$

the point where every variation of E is ≥ 0 → MIN(E)

---

what about H? ENTHALPY (IF NO EXTRA HEAT MOVES $\delta Q=0$ $Tds=0$)

$$dH = \cancel{dE}\ Vdp + Tds$$

$$dH|_S = VdP \Rightarrow dH|_{S,P} = 0$$

d

$(\cancel{\delta Z})$ $$\delta Z|_{S,P} = \underbrace{(\delta E - T\delta S + P\delta V)}_{\geq 0 \text{ always}}\Big|_{SP} = (\delta E + P\delta V)_{SP} =$$

at constant P $\longrightarrow$ $V\delta P = 0 \Rightarrow$

$$= (\delta E + P\delta V + \underbrace{V\delta P}_{=0})_{SP} = \delta(E+PV)_{SP} = \delta H_{SP}$$

$$\Rightarrow \delta Z \geq 0 \Longrightarrow \delta H_{SP} \geq 0$$

FOR G?

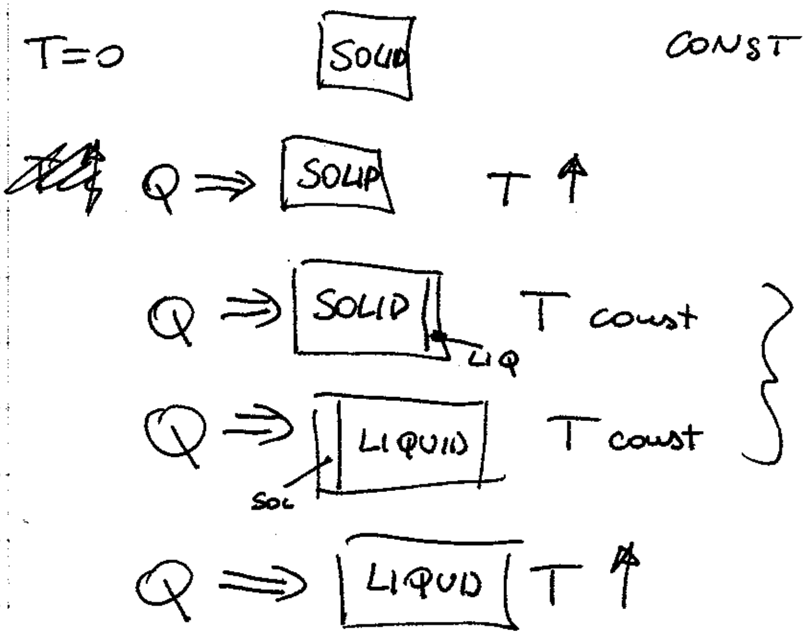
$$dG = VdP - SdT \Rightarrow \delta Z \geq 0 \Rightarrow \delta G_{P,T} \geq 0$$

if you like at T,P const ⇒ need to MIN(G) NOT E !!!

T7

IIII) MELTING ⇒ where the HEAT OF MELTING GOES?

CONST PRESSURE!



ΔQ to MELT?

Melt happens at cost T

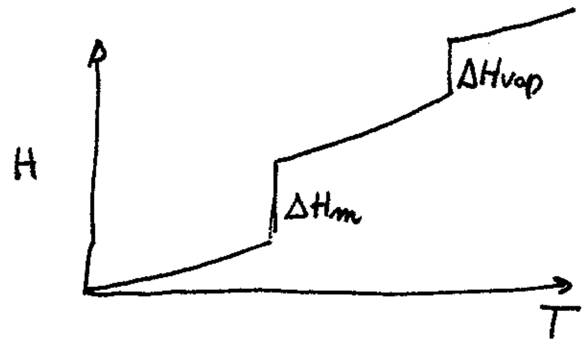
$$dE = -p\,dV + \overset{=\delta Q}{\boxed{T\,dS}}$$

$$dH = V\,dP + \delta Q \quad \text{at } P = \text{cost} \quad dH_P = \delta Q$$

$$\Rightarrow \Delta Q_{\text{MELTING}} = \Delta H_P \text{ measurable}$$

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

⇒



WHERE S COMES FROM?

F, L, P, V, T, W, are all easy to measure!
where S comes from? What is It's functional slope?

2nd law tells that S is function of state & $\frac{\delta Q}{T} \le dS$!!

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 ~~steam~~ WATER @ 100° CONTAINS
E^{100} JOULES ⇒
3kg of WATER @ 100° CONTAINS
$3*E^{100}$ JOULES!

⇒ Energy is Extensive, Volume too (obvious)
Heat too (⇒ therefore S)

IN THERMODYNAMICS INTENSIVE & EXTENSIVE ARE ASSOCIATED

$$\underset{\text{Int}}{\underset{\downarrow}{-P}}\,\underset{\text{Ext}}{\underset{\downarrow}{\underbrace{dV}}} \qquad \underset{\text{INT}}{\underset{\downarrow}{T}}\,\underset{\text{EXT}}{\underset{\downarrow}{\underbrace{dS}}}$$

& so on.

Φ is extensive $\Rightarrow$ S is extensive

BOLTZMANN IDEA

1) at constant Energy the system can be in $\underset{\text{\# of states}}{\Omega(E)}$ number of states (DEFINITION)

2) all <u>states</u> are equiprobable (ASSUMPTION)
(why a state should be more probable ?)

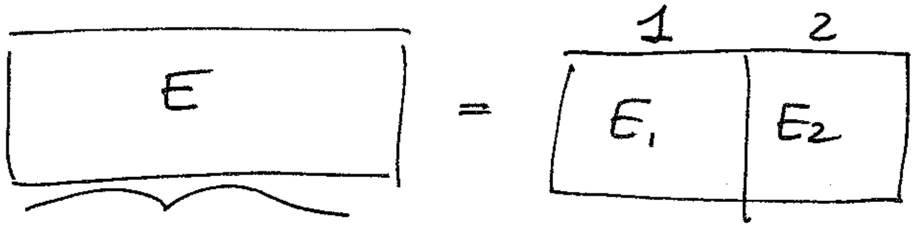
3) ①+② $\Rightarrow$ $P_E(\underset{\substack{\uparrow\\ \text{state}}}{\vec{x}}) = \dfrac{1}{\Omega(E)}$ | for every state,
then are $\Omega(E)$

$$\boxed{\Rightarrow \sum_{\Omega(E)} P_E(\vec{x}) = 1}$$

0) BOLTZMAN SAYS
ENTROPY MEASURES THE ~~MAX~~ PROBABILITY DISTRIBUTION

$$S(E) = f_{uni}(P_E(\vec{x})) = f[\Omega(E)]$$

BUT S is EXTENSIVE $\Rightarrow$ TAKE SYSTEM OF ENERGY E & CUT IN TWO $\Rightarrow E_1, E_2$



$E_1+E_2=E$

$\underbrace{\qquad}_{S(E)=f(\Omega(E))}$ $\quad S_1(E_1) = f(\Omega(E_1)) \quad S_2 = f(\Omega(E_2))$

but if ① has $\Omega(E_1)$ states & ② has $\Omega(E_2)$ states,
then ①+② has a total of $\Omega(E_1) * \Omega(E_2)$ possible configurations
(for every one of one, pick Ω of the other)

T10

$\Rightarrow \quad \Omega(\epsilon_1+\epsilon_2) = \Omega(\epsilon_1) * \Omega(\epsilon_2)$ obvious.

$\Rightarrow \quad f(\Omega_1(\epsilon_1) * \Omega(\epsilon_2)) = f(\Omega(\epsilon_1)) + f(\Omega(\epsilon_2))$

which function has this property?

$f(a*b) = f(a) + f(b)$? log

$\Rightarrow \quad S(E) \propto \log \Omega(\epsilon) \Rightarrow$

$$\boxed{S(\epsilon) \equiv \underset{\uparrow}{k_B} \log \Omega(\epsilon)}$$

to get Joules after multiplying for T

$\Rightarrow$ DEFECTS (FRENKEL)

$$N_I = N_A \exp\left(-\frac{Q_I}{RT}\right)$$

$\Rightarrow$ N_A sites

N_I ~~possible~~ defects $\Rightarrow$

choose N_I on a set of N_V places

$\Omega =$ # choose N_I identical defects on a set of N_A identical places

$$\binom{N_A}{N_I} = \frac{N_A!}{N_I!\,(N_A-N_I)!}$$

identical places ~~has~~ contains N_I identical defects & (N_A-N_I) identical good places

T11

and remember Sterling $\log n! \sim n \log n - n$

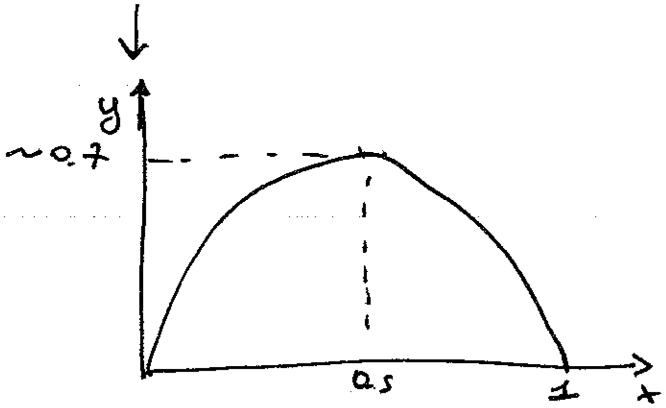
and $x \equiv \frac{N_I}{N_A}$

$$\Rightarrow \quad S = -kN_A\left[x \log x + (1-x)\log(1-x)\right]$$

No defect : how many choices? $1 \Rightarrow \Omega = 1 \Rightarrow S = 0$

ALL defects : how many choices! $1 \Rightarrow \Omega = 1 \Rightarrow S = 0$

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



To form FRENKEL (form double vacancy)

I TOLD THIS !! $\quad N_I = N_A e^{-Q/2kT}$

$$\Rightarrow \quad \frac{Q}{2kT} = -\log x$$

IS THIS TRUE?? $\quad Q = -2kT \log x \qquad$ MUST PROVE !

T12

T, P, const $\Rightarrow$ min G!

$G = E - TS + PV$

$\Delta G = \Delta E - T\Delta S + P\Delta V$

dT, dP = 0

defects do not change volume !!

$\Rightarrow$

$\frac{Q}{2}$ because every Q gets 2 defects $\Rightarrow \frac{Q}{2}$ per defects

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

$N_A x \Rightarrow \Delta G = N_A * \left[x\frac{Q}{2} - T\Delta S(x) \right]$

$\downarrow$

$S(x) - \cancel{S(0)} = S(x)$

$\Rightarrow N_A * \left[x\frac{Q}{2} + kT\left[x\log x + (1-x)\log(1-x) \right] \right]$

suppose few $\Rightarrow x \approx 0 \Rightarrow (1-x)\log(1-x) \approx 0$

$\Rightarrow$ min $\Delta G \Rightarrow$ min ΔG over all possible configuration $\{x\}$

$$\Rightarrow \quad \frac{\partial \Delta G}{\partial x} = 0$$

$$\Rightarrow 0 = \frac{\partial}{\partial x}\left[x\frac{Q}{2} + kT\, x\log x + kT(1-x)\log(1-x) \right]$$

$\Rightarrow$

$$\frac{Q}{2} + kT\log x + \cancel{kT\frac{x}{x}} - kT\log(1-x) + \cancel{\frac{(1-x)}{(1-x)}(-1)kT}$$

$$0 = \frac{Q}{2} + kT\log x \underbrace{- kT\log(\underbrace{1-x}_{\approx 1})}_{\approx 0} = 0$$

$$\Rightarrow -\frac{Q}{2kT} \log x \Rightarrow \Rightarrow \boxed{N_D = N_A e^{-Q/2kT}}$$

EQ CONCENTRATION

T13

ELECTRICAL PROPERTIES

OBSERVATION   OHM'S LAW $V=RT$

$$\boxed{V=IR}$$

$R = \Omega$
$V =$ Volt
$I =$ Ampere $= \frac{C}{Sec}$

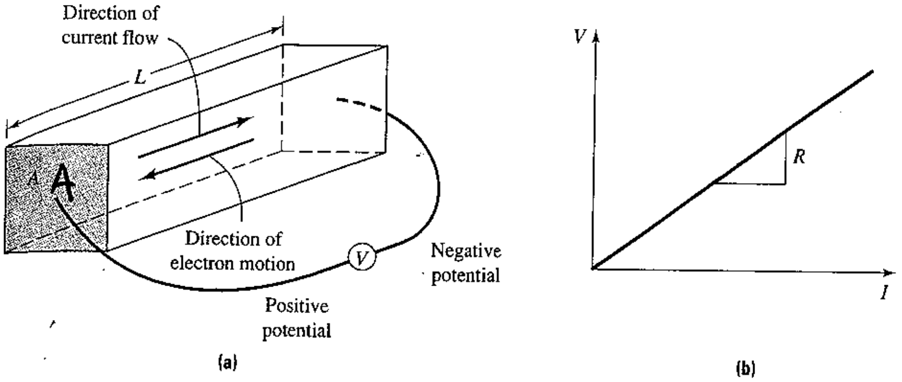
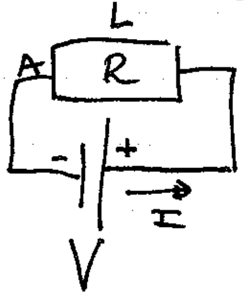


FIGURE 10.2–1 A simple electrical conduction experiment. **(a)** A bar of material of length L and cross-sectional area A is subjected to a voltage V. **(b)** The response of the system, current flow I, is a linear function of the magnitude of the driving force, voltage V. The constant of proportionality, or slope, is the resistance R.

SIMBOLS



CONVENTION

CURRENT FROM
$\oplus \longrightarrow \ominus$
(ONLY CONVENTION
DEPENDS ON CARRIER)

$R(L,A)$ experimental

$L \rightarrow 2L \Rightarrow R \rightarrow 2R$
$R \propto L$

$A \rightarrow 2A \Rightarrow R \rightarrow \frac{R}{2}$
$R \propto \frac{1}{A}$

$R \propto \frac{L}{A}$ ρ = RESISTIVITY

$$\Rightarrow \boxed{R \equiv \rho \frac{L}{A}} \Rightarrow \rho\,[\Omega m]$$

$R\,[\Omega]$
$L\,[m]$ $A\,[m^2]$

$\Omega = \rho \frac{m}{m^2}$

$$\boxed{\rho \equiv \frac{1}{\sigma}}$$

$\sigma \equiv$ CONDUCTIVITY
$\hookrightarrow [\Omega m]^{-1}$ (OR SIEMENS ?? CHECK IT OUT)

$\rho = \sigma^{-1}$

$$V=RI \Rightarrow V = \rho \frac{L}{A} I = \rho L J \Rightarrow \frac{V}{L} = \rho J \Rightarrow E = \rho J$$

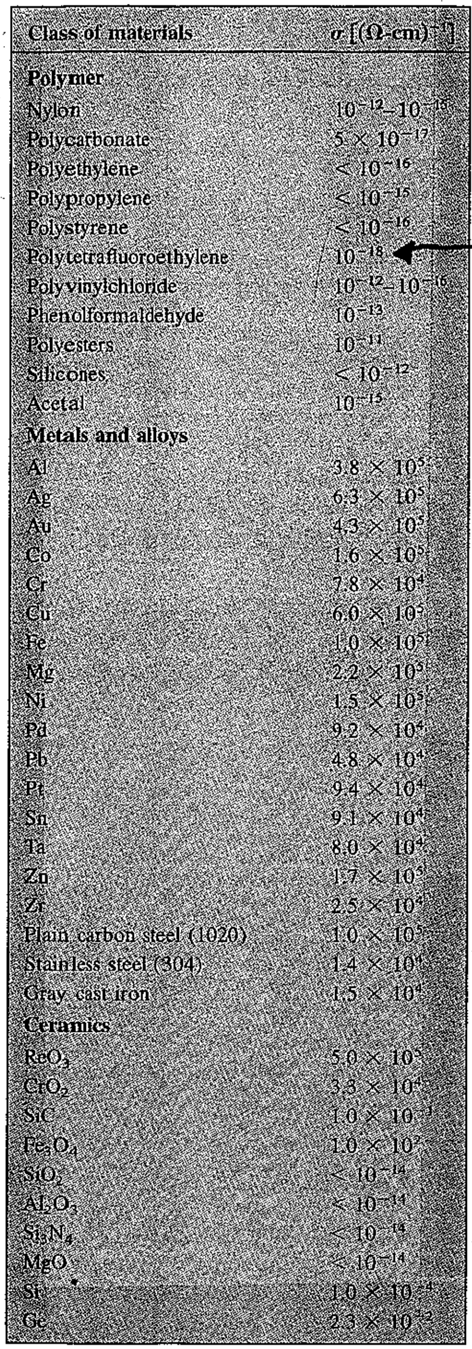
$\frac{I}{A} = J$ DENSITY

$V = E \cdot L$
Volt electric FIELD

$\hookrightarrow \boxed{J = \sigma E}$

E1

TABLE 10.2–1 Electrical conductivities for a variety of materials at room temperature.



Class of materials	$\sigma\,[(\Omega\text{-cm})^{-1}]$
Polymer	
Nylon	10^{-12}–10^{-15}
Polycarbonate	5×10^{-17}
Polyethylene	$< 10^{-16}$
Polypropylene	$< 10^{-15}$
Polystyrene	$< 10^{-16}$
Polytetrafluoroethylene	10^{-18}
Polyvinylchloride	10^{-12}–10^{-16}
Phenolformaldehyde	10^{-13}
Polyesters	10^{-11}
Silicones	$< 10^{-12}$
Acetal	10^{-15}
Metals and alloys	
Al	3.8×10^{5}
Ag	6.3×10^{5}
Au	4.3×10^{5}
Co	1.6×10^{5}
Cr	7.8×10^{4}
Cu	6.0×10^{5}
Fe	1.0×10^{5}
Mg	2.2×10^{5}
Ni	1.5×10^{5}
Pd	9.2×10^{4}
Pb	4.8×10^{4}
Pt	9.4×10^{4}
Sn	9.1×10^{4}
Ta	8.0×10^{4}
Zn	1.7×10^{5}
Zr	2.5×10^{4}
Plain carbon steel (1020)	1.0×10^{5}
Stainless steel (304)	1.4×10^{4}
Gray cast iron	1.5×10^{4}
Ceramics	
ReO_3	5.0×10^{5}
CrO_2	3.3×10^{4}
SiC	1.0×10^{-10}
Fe_3O_4	1.0×10^{2}
SiO_2	$< 10^{-14}$
Al_2O_3	$< 10^{-14}$
Si_3N_4	$< 10^{-14}$
MgO	$< 10^{-14}$
Si	1.0×10^{-4}
Ge	2.3×10^{-2}

OHM'S $V=RI \iff J=\sigma E$

RESULT MOVEMENT ← FORCE

GOOD CONDUCTORS

σ BIG spans 23 ORDERS OF MAGNITUDE

TOP SILVER $\sigma_{Ag} = 6.3\ 10^{5}\ (\Omega\cdot cm)^{-1}$

TO POLYMERS $\sigma \simeq 10^{-18}$!!

INSULATORS

Si & Ge are INSULATORS $\sigma \sim 10^{-4}, 10^{-2}$

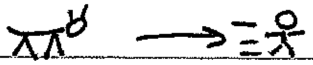
CONDUCTIVITY DEPENDS ON FACTOR

1) DENSITY OF CARRIERS PER UNIT VOLUME N $\left(m^{-3} / cm^{-3}\right)$
2) CHARGE OF CARRIER COLLOMB C
3) MOBILITY μ $\left(\frac{m^2}{V\cdot s}\right)$

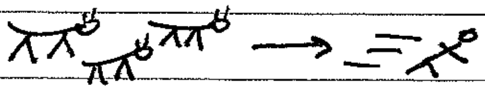
$\downarrow$ RATIO $\frac{\text{SPEED}}{\text{ELECTRIC-FIELD}}$

~~YOUR SPE~~

1 LION $\rightarrow v =$ ~~10mi~~ 10 mph



3 LIONS

 $v =$ 30 mph

RATIO $\frac{\text{SPEED}}{\#\text{ OF LIONS}}$ $\Rightarrow$ MOBILITY OF THE TEACHER

E2

MOBILITY ⇒ BUILD σ

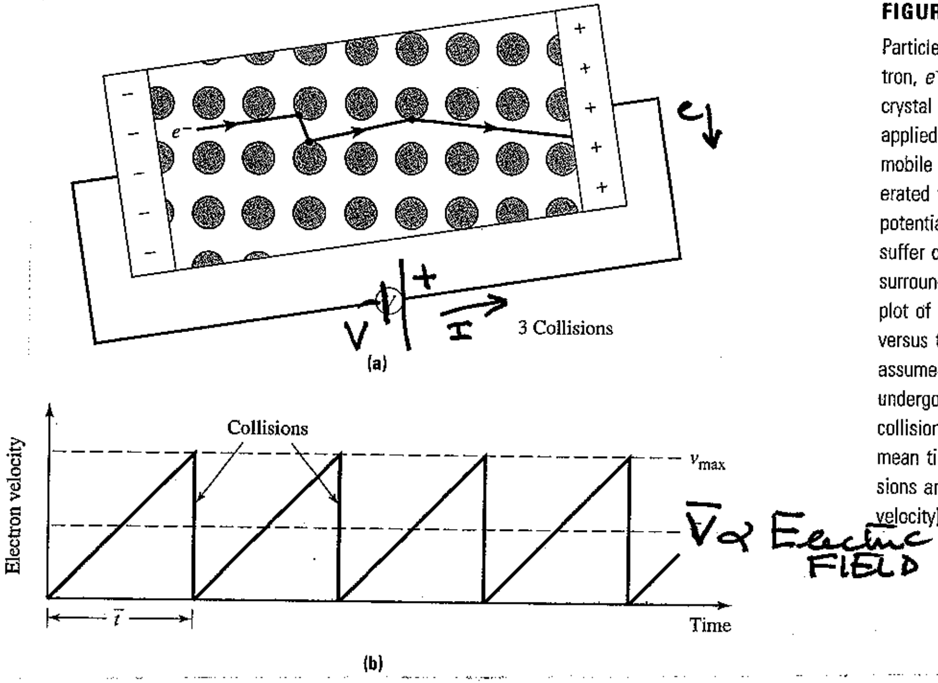


FIGURE 10.2–2
Particle model of an electron, e^-, moving through a crystal lattice. **(a)** Under an applied electric field, the mobile electrons are accelerated toward the positive potential and occasionally suffer collisions with the surrounding ion cores. **(b)** A plot of electron velocity versus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

COLLISIONS :- START FROM V=0
- ACCELERATION TO V_{max}
- COLLISION & RESTART

~~Vaverage ∝ E~~

COLLISION every τ relaxation time !

$$(F = ma)$$

$$v = at \Rightarrow \underbrace{am}_{acc} = \underbrace{Ee}_{Force} \Rightarrow v_{max} = a\tau$$

$$a \propto E$$

$$v_{avg} \propto v_{max} \propto E_{\text{FILED}}$$

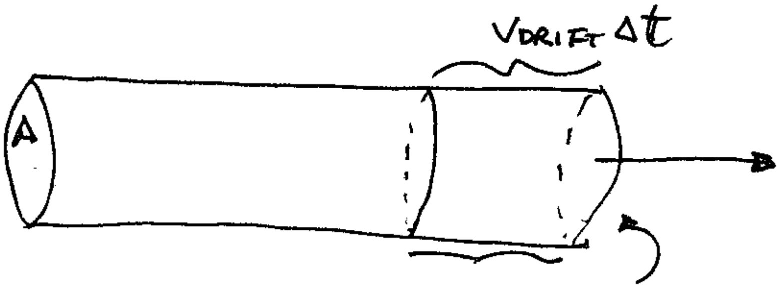
v_{AVG} = DRIFT VELOCITY !! ~ cm/s mm/s SMALL

$$\boxed{v_{DRIFT} \equiv \mu E}$$

μ → MOBILITY

E3

CONDUCTOR



HOW MUCH "CHARGE" EXITS SURFACE IN TIME Δt?
All the ~~one~~ CHARGE ~~STORED in~~ CLOSER THAN $v_{DRIFT}\,\Delta t$ from SURFACE !!

$$\Delta Q = \underbrace{\overbrace{(v_{DRIF}\Delta t)\,A}^{\text{VOLUME}} \cdot * \overset{\text{DENSITY}}{n}}_{\text{PARTICLES}} * \underset{\text{CHARGE EACH PARTICLE}}{q}$$

$$\Rightarrow \frac{\Delta Q}{\Delta t} = A\, v_{DRIFT} * n * q \qquad J = \sigma E$$

$$\Rightarrow I = \frac{\Delta Q}{\Delta t} \qquad J = \frac{1}{A}\frac{\Delta Q}{\Delta t}$$

$$J = \underset{\mu E}{\underset{\downarrow}{v_{DRIFT}}}\, n\, q = \underset{\sigma}{(n q \mu)}\, E \Rightarrow \boxed{\sigma = n q \mu}$$

IF MORE THEN 1 specie $\sigma = \sum_i n_i q_i \mu_i$

EXAMPLE Li_2O $\quad q_{Li} = e \quad n_{Li}$

$Li^+ + Li^+ + O^{--}$ $\quad q_O = -2e \quad n_O$

BUT $\mu_O < 0$ & $\mu_{Li} > 0$

(BECAUSE $O^{--} < 0$) ⇒ CONVENTION
q POSITIVE !
μ POSITIVE !

$$\sigma = n_{Li} q_{Li} \mu_{Li} + n_O q_O \mu_O + n_e e \mu_e$$

E4

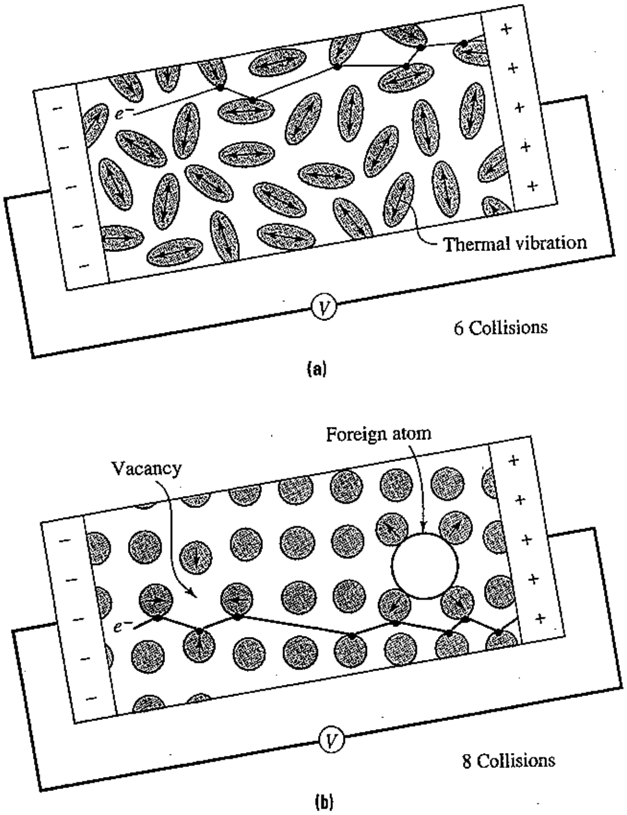


FIGURE 10.2–3 A schematic illustration of the effects of temperature and point defects on electron motion. **(a)** As temperature increases, the amplitude of the thermally induced atomic vibrations increases. This causes a decrease in the mean time between collisions and, therefore, a corresponding decrease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

TEMPERATURE

$T\uparrow \ \mu\downarrow$ (electrons get slower, more collision)

$\frac{\partial \mu}{\partial T} < 0$

IMPURITIES

$N_{DEFECTS}\uparrow \ \mu\downarrow$

(MORE COLLISIONS, MORE TIGHT SPACES)

$\frac{\partial \mu}{\partial N_D} < 0$

HOWEVER $\sigma = nq\mu$

$\downarrow$ $\partial\mu/\partial T < 0$

OR $\frac{\partial \mu}{\partial N_D} < 0$

BUT TEMPERATURE OR IMPURITIES CAN BOOST n!!

$\frac{\partial n}{\partial T}$ ← HUGE, LIKE SEMICONDUCTORS

$\frac{\partial n}{\partial N_D} > 0$

$\frac{\partial n}{\partial T} \approx 0$ METALS

ES

CRYSTALLINE STRUCTURE ⇒ MANY LEVELS

FROM QMECHANICS : 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 ⇒ a

• DISCRETE ~~BECAUSE~~ & ISOLATED SPREAD INTO ENERGY BANDS

• OUTER ELECTRONS NOT SPATIALLY LOCALIZED ANYMORE

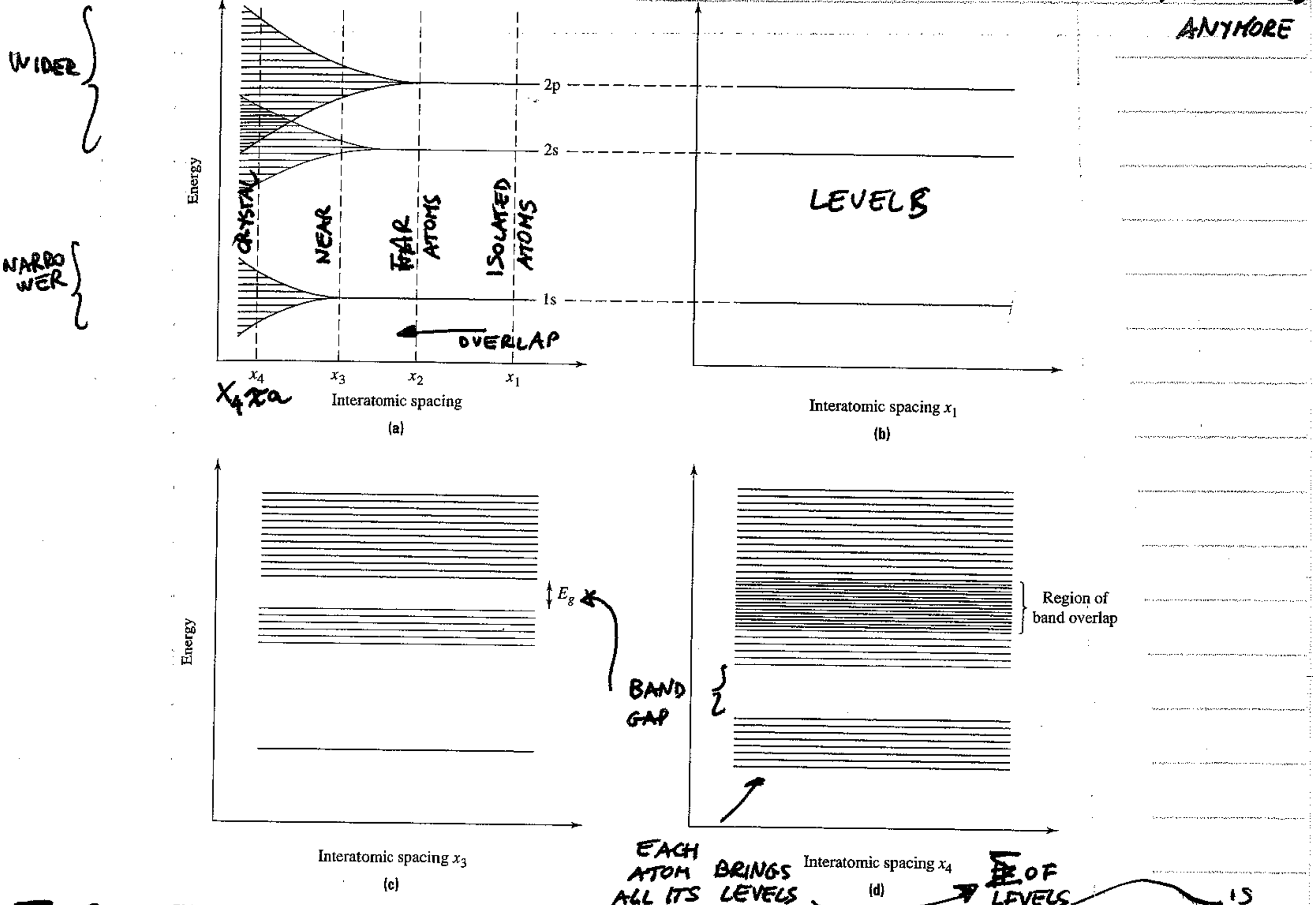


FIGURE 10.2–4 Energy bands in solids. **(a)** The energy band structure as a function of interatomic separation distance. **(b)** For large separation distances, the electrons associated with any atom are independent of those of all other atoms. **(c)** For separation distance x_3, the isolated energy 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

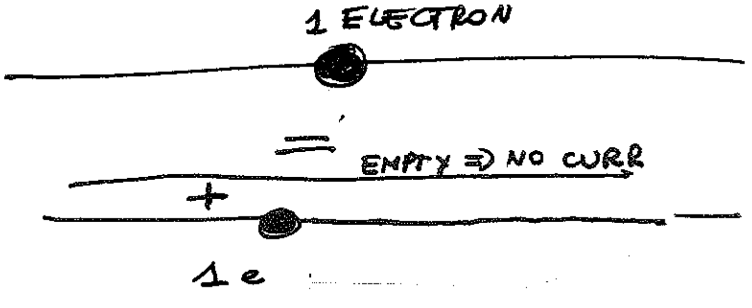
<u>VALENCE BAND</u>

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

COMES FROM LIOUVILLE THEOREM
ASK!!

ONLY PARTIALLY OCCUPIED LEVELS GIVE CONDUCTIVITY!!

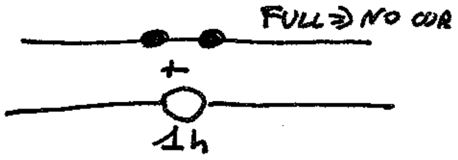
⇒ GIVE CURRENT, THE OTHER DO NOT GIVE ANYTHING



1e

$q=-e$

OR



1h

$q=e$

$m_e > 0$

μ_e

$m_h < 0$

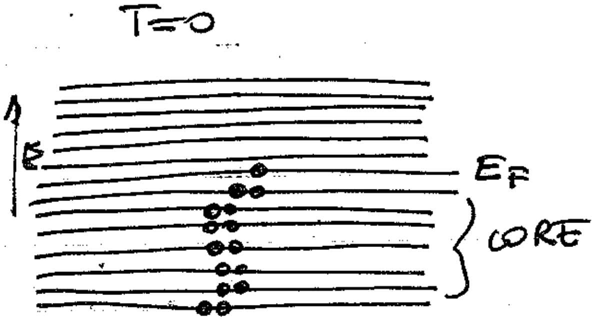
μ_h

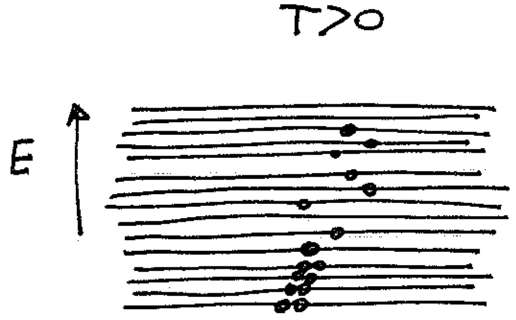
generically

$\mu_h < \mu_e$

E7

TEMPERATURE EFFECT
FERMI DIRAC DISTRIBUTION





E_F = FERMI ENERGI

SOME ELECTRONS ARE EXCITED & POP UP FROM CORE BECAUSE TEMPERATURE

$n = \frac{N}{V}$ density of electrons

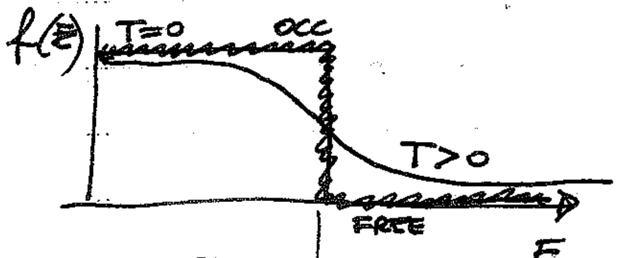
$K_F = \sqrt[3]{3\pi^2 n}$ FERMI MOMENTUM

$E_F = \frac{\hbar^2}{2m_e} K_F^2$

PROBABILITY DISTRIBUTION OF OCCUPATION

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

FERMI – DIRAC DISTRIBUTION



T=0 $f(E<E_F) = 1$

$f(E>E_F) = 0$

⇒ T>0 $f(E \ll E_F) \rightarrow 1$ NO COND

$f(E \gg E_F) \rightarrow 0$ NO COND

$f(E \approx E_F)$ in (kT) ~ NOT 0 OR 1 } COND

$K_B T_{ROOM} \approx 25$ meV

$K_B \sim 8.6\ 10^{-5}$ 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^* in part a is occupied, given by $f(E^*)$, as a function of temperature.

E8

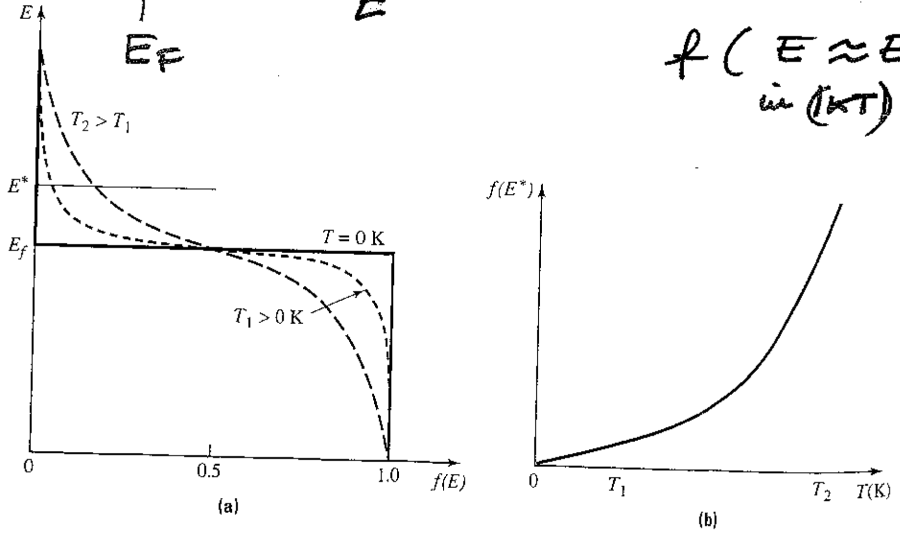
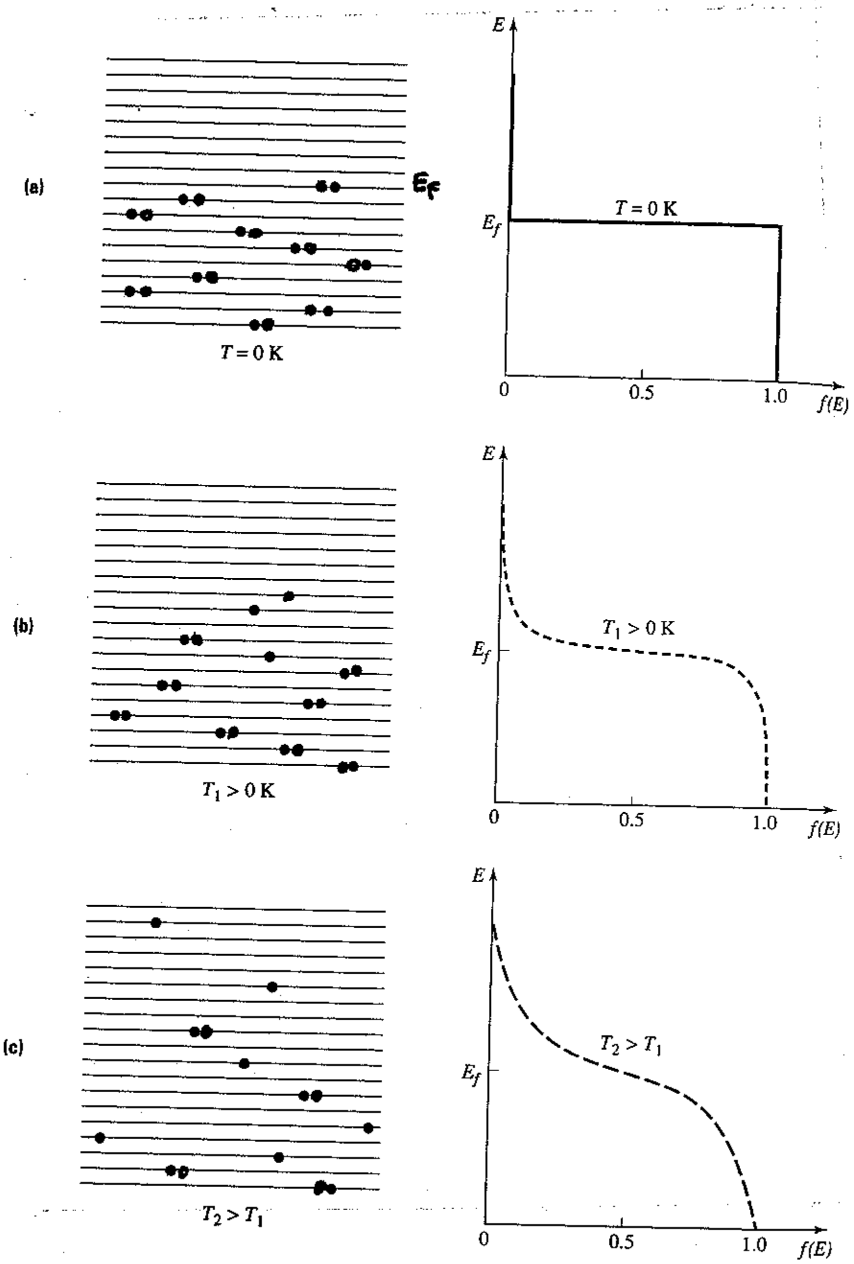


FIGURE 10.2-9 The relationship between the occupied energy levels and $f(E)$ as a function of temperature for solids with a partially filled energy band: **(a)** at 0 K, **(b)** at $T_1 > 0$ K, and **(c)** at $T_2 > T_1$.



T ↑ OCCUPATION IS SPREADING ALONG BANDS

STUDY CHAP 10

E9

ELECTRICAL PROPERTIES

OBSERVATION   OHM'S LAW   V=RT

$$\boxed{V=IR}$$

R = Ω
V = Volt
$I = \text{Ampere} = \frac{C}{Sec}$

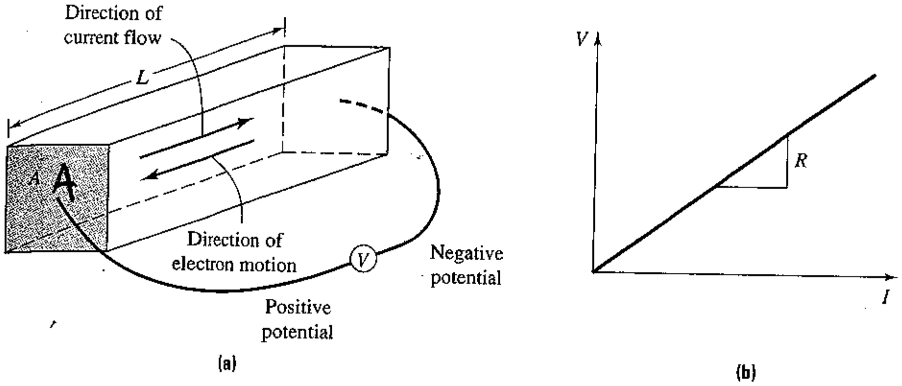
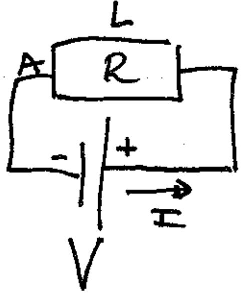


FIGURE 10.2–1 A simple electrical conduction experiment. **(a)** A bar of material of length L and cross-sectional area A is subjected to a voltage V. **(b)** The response of the system, current flow I, is a linear function of the magnitude of the driving force, voltage V. The constant of proportionality, or slope, is the resistance R.

SIMBOLS



CONVENTION

CURRENT FROM
⊕ → ⊖
(ONLY CONVENTION DEPENDS ON CARRIER)

R(L, A) experimental

$L \rightarrow 2L \Rightarrow R \rightarrow 2R$
$R \propto L$
$A \rightarrow 2A \Rightarrow R \rightarrow \frac{R}{2}$
$R \propto \frac{1}{A}$

$R \propto \frac{L}{A}$ ρ=RESISTIVITY

$\Rightarrow \boxed{R \equiv \rho \frac{L}{A}} \Rightarrow \rho\,[\Omega m]$

$R\,[\Omega]$
$L\,[m]$ $A\,[m^2]$

$\Omega = \rho \frac{m}{m^2}$

$$\boxed{\rho \equiv \frac{1}{\sigma}}$$

σ ≡ CONDUCTIVITY
↳ $[\Omega m]^{-1}$ (OR SIEMENS?? CHECK IT OUT)

$V=RI \Rightarrow V = \rho \frac{L}{A} I = \rho L J \Rightarrow \frac{V}{L} = \rho J \Rightarrow E = \rho J$

$\frac{I}{A} = J$ DENSITY

$\rho = \sigma^{-1}$

↳ $\boxed{J = \sigma E}$

$V = E \cdot L$
Volt ↑ electric FIELD

E1

TABLE 10.2–1 Electrical conductivities for a variety of materials at room temperature.

Class of materials	$\sigma\,[(\Omega\text{-cm})^{-1}]$
Polymer	
Nylon	10^{-12}–10^{-15}
Polycarbonate	5×10^{-17}
Polyethylene	$< 10^{-16}$
Polypropylene	$< 10^{-15}$
Polystyrene	$< 10^{-16}$
Polytetrafluoroethylene	10^{-18}
Polyvinylchloride	10^{-12}–10^{-16}
Phenolformaldehyde	10^{-13}
Polyesters	10^{-11}
Silicones	$< 10^{-12}$
Acetal	10^{-15}
Metals and alloys	
Al	3.8×10^{5}
Ag	6.3×10^{5}
Au	4.3×10^{5}
Co	1.6×10^{5}
Cr	7.8×10^{4}
Cu	6.0×10^{5}
Fe	1.0×10^{5}
Mg	2.2×10^{5}
Ni	1.5×10^{5}
Pd	9.2×10^{4}
Pb	4.8×10^{4}
Pt	9.4×10^{4}
Sn	9.1×10^{4}
Ta	8.0×10^{4}
Zn	1.7×10^{5}
Zr	2.5×10^{4}
Plain carbon steel (1020)	1.0×10^{5}
Stainless steel (304)	1.4×10^{4}
Gray cast iron	1.5×10^{4}
Ceramics	
ReO_3	5.0×10^{5}
CrO_2	3.3×10^{4}
SiC	1.0×10^{-1}
Fe_3O_4	1.0×10^{2}
SiO_2	$< 10^{-14}$
Al_2O_3	$< 10^{-14}$
Si_3N_4	$< 10^{-14}$
MgO	$< 10^{-14}$
Si	1.0×10^{-4}
Ge	2.3×10^{-2}

OHM'S $V = RI \Longleftrightarrow J = \sigma E$

RESULT MOVEMENT ← FORCE

GOOD CONDUCTORS

σ BIG spans 23 ORDERS OF MAGNITUDE

TOP SILVER $\sigma_{Ag} = 6.3\ 10^{5}\ (\Omega\cdot cm)^{-1}$

TO POLYMERS $\sigma \simeq 10^{-18}$!!

INSULATORS

Si & Ge are INSULATORS $\sigma \sim 10^{-4}, 10^{-2}$

CONDUCTIVITY DEPENDS ON FACTOR

1) DENSITY OF CARRIERS PER UNIT VOLUME N $\left(\frac{m^{-3}}{cm^{-3}}\right)$

2) CHARGE OF CARRIER COULOMB C

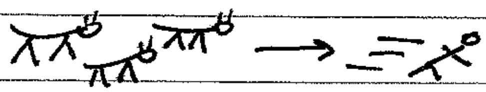
3) MOBILITY μ $\left(\frac{m^2}{V\cdot s}\right)$

↓ RATIO $\frac{\text{SPEED}}{\text{ELECTRIC-FIELD}}$

~~YOUR SPE~~

1 LION → $v =$ ~~10mi~~ 10 mph

3 LIONS



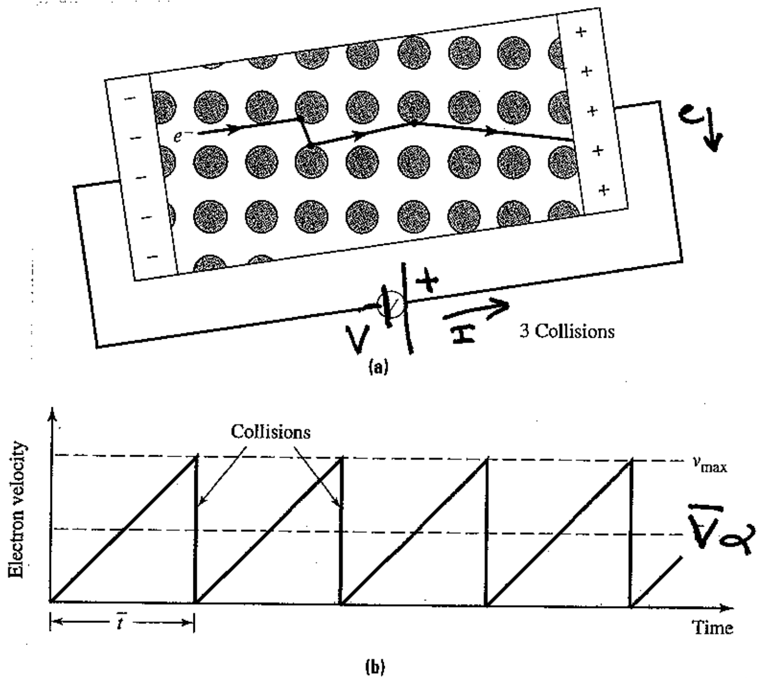
$v = 30$ mph

RATIO $\frac{\text{SPEED}}{\#\text{ OF LIONS}}$

⇒ MOBILITY OF THE TEACHER

E2

MOBILITY ⇒ BUILD σ



$\bar{V} \propto$ Electric FIELD

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 ($\bar{t}$ is the mean time between collisions and $\bar{v}$ is the average velocity).

COLLISIONS :- START FROM $V=0$
- ACCELERATION TO V_{max}
- COLLISION & RESTART

~~$V_{average} \propto E$~~

COLLISION every τ relaxation time !

$$(F = ma)$$

$$v = at \Rightarrow \underbrace{am}_{acc} = \underbrace{Ee}_{Force} \Rightarrow v_{max} = a\tau$$

$$a \propto E$$

$$v_{avg} \propto v_{max}$$

$$v_{max} \propto E_{FILED}$$

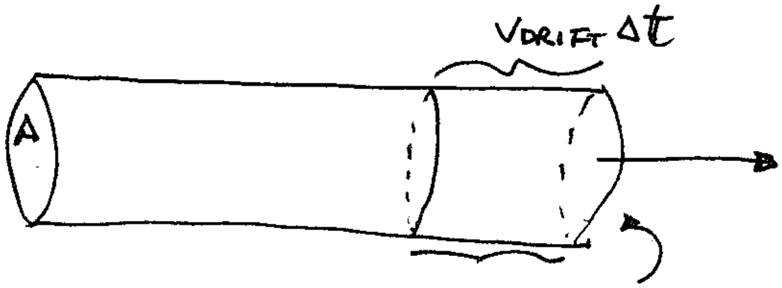
v_{AVG} = DRIFT VELOCITY !! ~ cm/s mm/s SMALL

$$\boxed{v_{DRIFT} \equiv \mu E}$$

μ → MOBILITY

E3

CONDUCTOR



HOW MUCH "CHARGE" EXITS SURFACE IN TIME Δt?

All the ~~ove~~ CHARGE ~~STORED IN~~ CLOSER THAN $v_{DRIFT}\,\Delta t$ from SURFACE !!

$$\Delta Q = \underbrace{\overbrace{(v_{DRIF}\Delta t)\,A}^{\text{VOLUME}} \cdot * \overset{\text{DENSITY}}{n}}_{\text{PARTICLES}} * \underset{\text{CHARGE EACH PARTICLE}}{q}$$

$$\Rightarrow \frac{\Delta Q}{\Delta t} = A\, v_{DRIFT} * n * q \qquad J = \sigma E$$

$$\Rightarrow I = \frac{\Delta Q}{\Delta t} \qquad J = \frac{1}{A}\frac{\Delta Q}{\Delta t}$$

$$J = \underset{\substack{\downarrow \\ \mu E}}{v_{DRIFT}}\, n\, q = \underbrace{(n q \mu)}_{\sigma} E \quad \Rightarrow \quad \boxed{\sigma = n q \mu}$$

IF MORE THEN 1 specie $\sigma = \sum_i n_i q_i \mu_i$

EXAMPLE Li_2O $\quad q_{Li} = e \quad n_{Li}$

$Li^+ + Li^+ + O^{--}$ $\quad q_O = -2e \quad n_O$

BUT $\mu_O < 0$ & $\mu_{Li} > 0$

(BECAUSE $O^{--} < 0$) $\Rightarrow$ CONVENTION

q POSITIVE !

μ POSITIVE !

$$\sigma = n_{Li} q_{Li} \mu_{Li} + n_O q_O \mu_O + n_e e \mu_e$$

E4

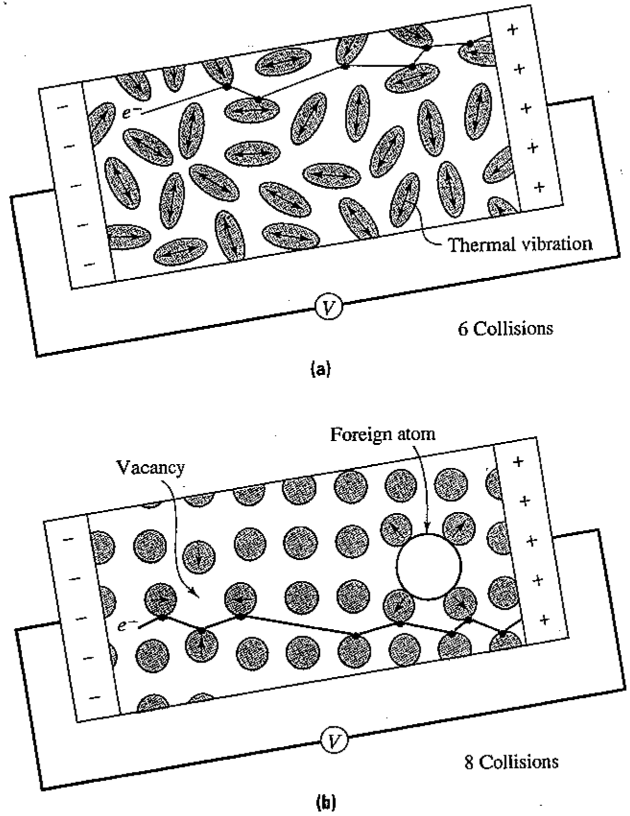


FIGURE 10.2–3 A schematic illustration of the effects of temperature and point defects on electron motion. **(a)** As temperature increases, the amplitude of the thermally induced atomic vibrations increases. This causes a decrease in the mean time between collisions and, therefore, a corresponding decrease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

TEMPERATURE

$T \uparrow \ \mu \downarrow$ (electrons get slower, more collision)

$\frac{\partial \mu}{\partial T} < 0$

IMPURITIES

$N_{DEFECTS} \uparrow \ \mu \downarrow$

(MORE COLLISIONS, MORE TIGHT SPACES)

$\frac{\partial \mu}{\partial N_D} < 0$

HOWEVER $\sigma = n q \mu$

$\downarrow$ $\partial \mu / \partial T < 0$

OR $\frac{\partial \mu}{\partial N_D} < 0$

BUT TEMPERATURE OR IMPURITIES CAN BOOST n!!

$\frac{\partial n}{\partial T}$ ← HUGE, LIKE SEMICONDUCTORS

$\frac{\partial n}{\partial N_D} > 0$ ↗

$\frac{\partial n}{\partial T} \approx 0$ METALS

ES

CRYSTALLINE STRUCTURE ⇒ MANY LEVELS

FROM QMECHANICS : 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 ⇒ a

- DISCRETE & ISOLATED SPREAD INTO ENERGY BANDS
- OUTER ELECTRONS NOT SPATIALLY LOCALIZED ANYMORE

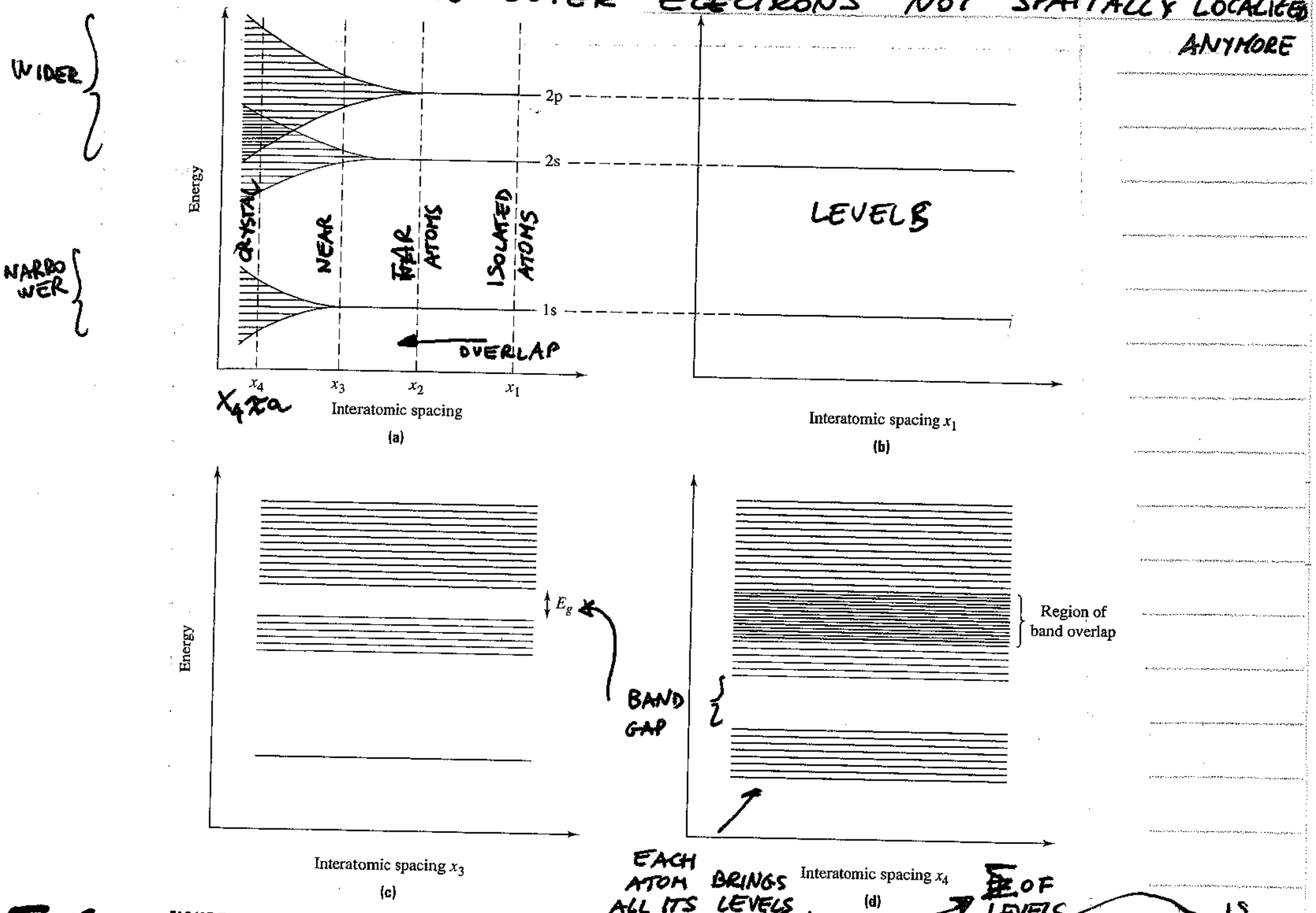


FIGURE 10.2–4 Energy bands in solids. **(a)** The energy band structure as a function of interatomic separation distance. **(b)** For large separation distances, the electrons associated with any atom are independent of those of all other atoms. **(c)** For separation distance x_3, the isolated energy 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.

E6

ELECTRONS FILL FROM LOWEST ENERGY!

HIGHEST ENERGY BAND AT LEAST PARTIALLY OCCUPIED

VALENCE BAND

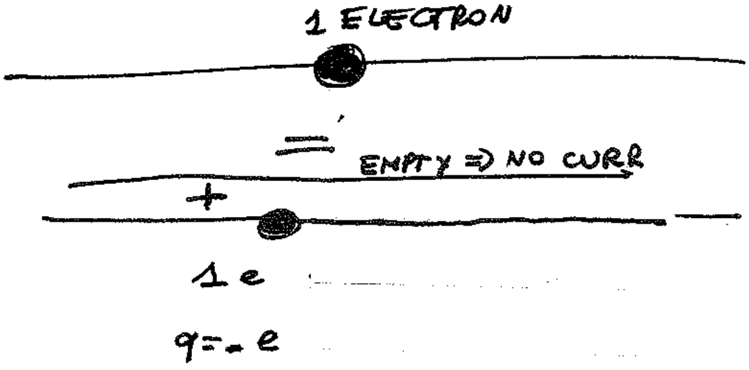
PROPERTY : COMPLETELY FILLED & COMPLETELY EMPTY BANDS ARE ~~DO~~ NOT CAPABLE OF TRANSPORTING ELECTRIC CHARGE THROUGH THE SOLD

COMES FROM LIOUVILLE THEOREM

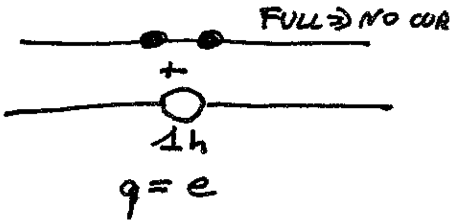
ASK !!

ONLY PARTIALLY OCCUPIED LEVELS GIVE CONDUCTIVITY !!

⇒ GIVE CURRENT, THE OTHER DO NOT GIVE ANY THING



OR



$m_e > 0$

μ_e

$m_h < 0$

μ_h

genericaly

$\mu_h < \mu_e$

E7

EXAMPLE

v_{DRIFT} ? BIG OR SMALL ?

~~[illegible]~~ V_{DRIFT} for Al wire

$R = 0.0283\ \Omega$

$L = 1\ m$

$\mu_e = 1.22 \cdot 10^{-3} \frac{m^2}{Vs}$

$\Bigg\}$ with $3A = I$

with 3~~A~~ ?

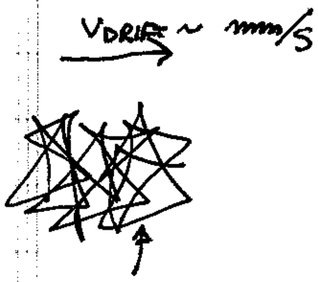
$$V = RI \Rightarrow \frac{V}{L} = E$$

$$\Rightarrow E = \frac{RI}{L} \Rightarrow v_{DRIFT} = \mu_e E = \mu_e \frac{RI}{L}$$

$$= \frac{1.22 \cdot 10^{-3}\ 2.83\ 10^{-2}\ 3}{1} =$$

$$\sim 0.1 \frac{mm}{s}$$ **SMALL**

mm & cm/sec NOT speed of Light



VIBRATION $\sim \frac{1}{2} m_e V_{th}^2 \simeq \frac{3}{2} kT$ $\quad v_{th} \simeq 1000\ km/sec$

Temp ROOM

FAST !!

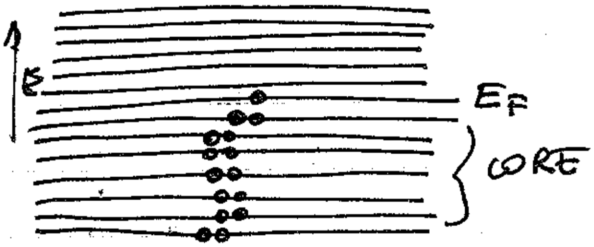
but what moves at c? (SPEED OF LIGHT) ASK!

E7b

TEMPERATURE EFFECT

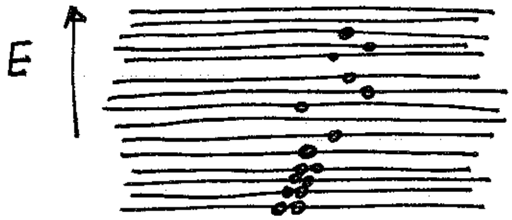
FERMI DIRAC DISTRIBUTION

T=0



E_F = ~~[illegible]~~ ~~[illegible]~~ FERMI ENERGI

T>0



SOME ELECTRONS ARE ~~[illegible]~~ EXCITED & POP UP FROM CORE BECAUSE TEMPERATURE

$n = \frac{N}{V}$ density of electrons

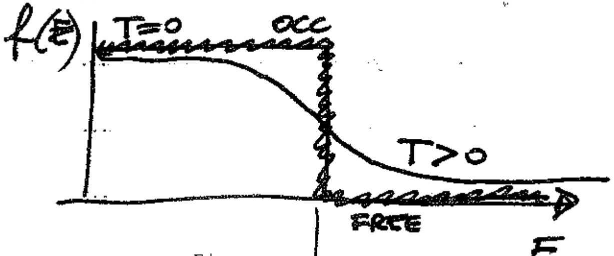
$K_F = \sqrt[3]{3\pi^2 n}$ FERMI MOMENTUM

$E_F = \frac{\hbar^2}{2m_e} K_F^2$

PROBABILITY DISTRIBUTION OF OCCUPATION

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

FERMI — DIRAC DISTRIBUTION



$T=0 \quad f(E<E_F) = 1$

$f(E>E_F) = 0$

⇒ $T>0 \quad f(E \ll E_F)$ ~~[illegible]~~ $\rightarrow 1$ NO COND

$f(E \gg E_F)$ ~~[illegible]~~ $\rightarrow 0$ NO COND

$f(E \approx E_F) \sim$ NOT 0 OR 1 } COND

in (kT)

~~[illegible]~~

$K_B T_{ROOM} \approx 25$ meV

$K_B \sim 8.6\ 10^{-5}$ eV/K

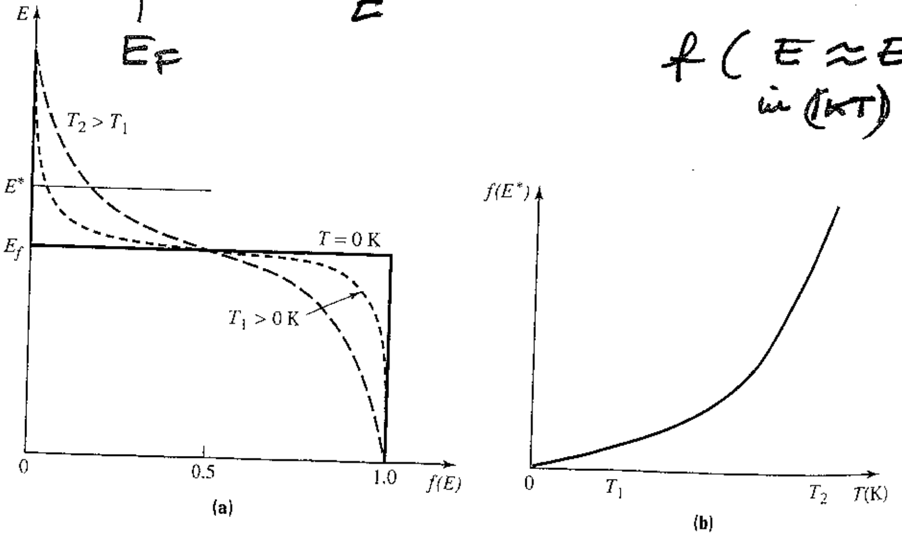
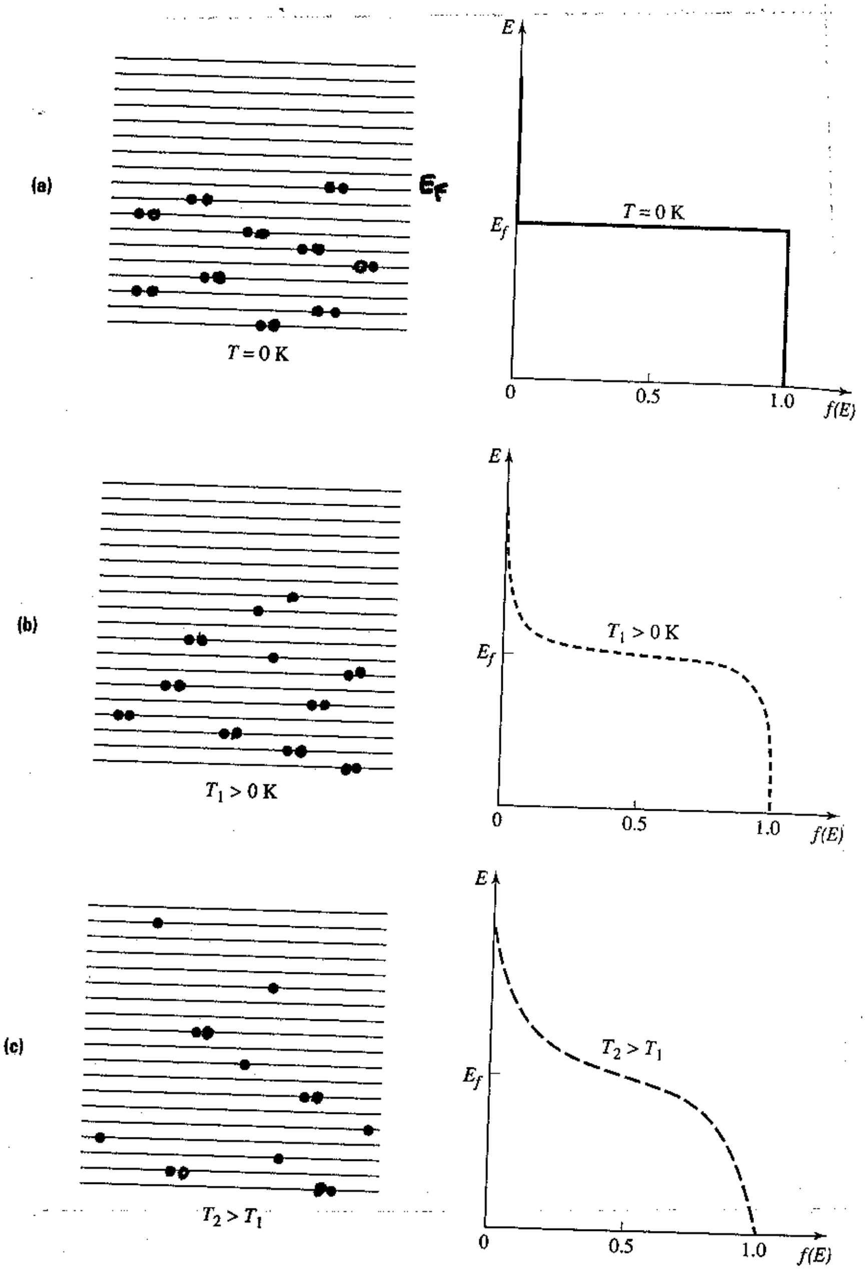


FIGURE 10.2–8

(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^* in part a is occupied, given by $f(E^*)$, as a function of temperature.

E8

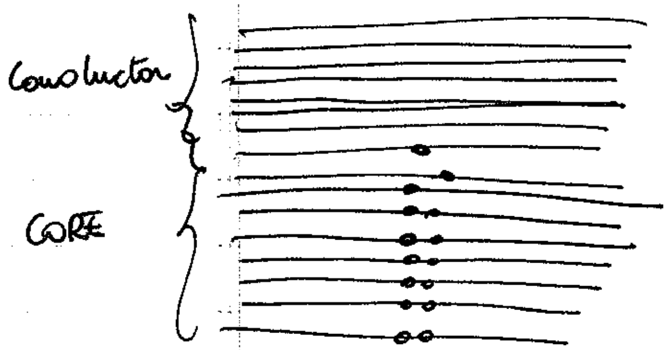
FIGURE 10.2–9 The relationship between the occupied energy levels and $f(E)$ as a function of temperature for solids with a partially filled energy band: **(a)** at 0 K, **(b)** at $T_1 > 0$ K, and **(c)** at $T_2 > T_1$.

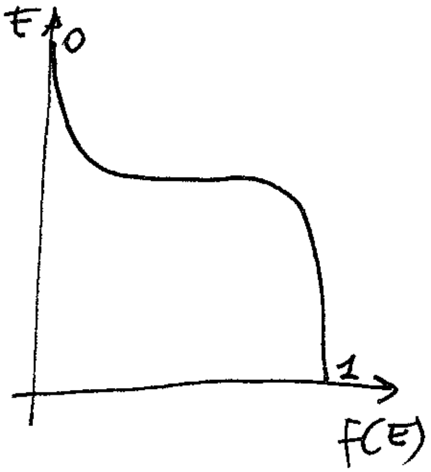


T ↑ OCCUPATION IS SPREADING ALONG BANDS

STUDY CHAP 10

E9





PICK 1 electron,

probability that this electron is in the conduction band, is Prop $E>E_c$

$$P[E>E_c] = \int_{E_c}^{\infty} f(E)\,dt = P(\underset{\uparrow}{T})$$

depends on Temperature

Number of electrons in <u>CONDUCTION BAND</u> is not the product of AVAILABLE ELECTRONS * PROB($E>E_c$)
BUT you MUST MULTIPLY (* AVAILABILITY OF LEVEL)

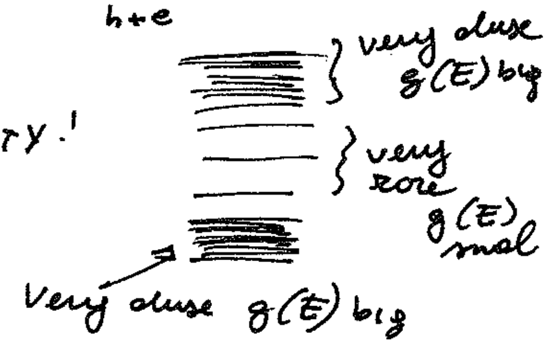
$$N_e = \underset{\uparrow}{2}\int_{E_c}^{\infty} \underset{\uparrow}{f(E)}\,\underset{\uparrow}{g(E)}\,dE = N_0 \exp\left(\frac{-E_G}{2kT}\right)$$

h+e

SPIN

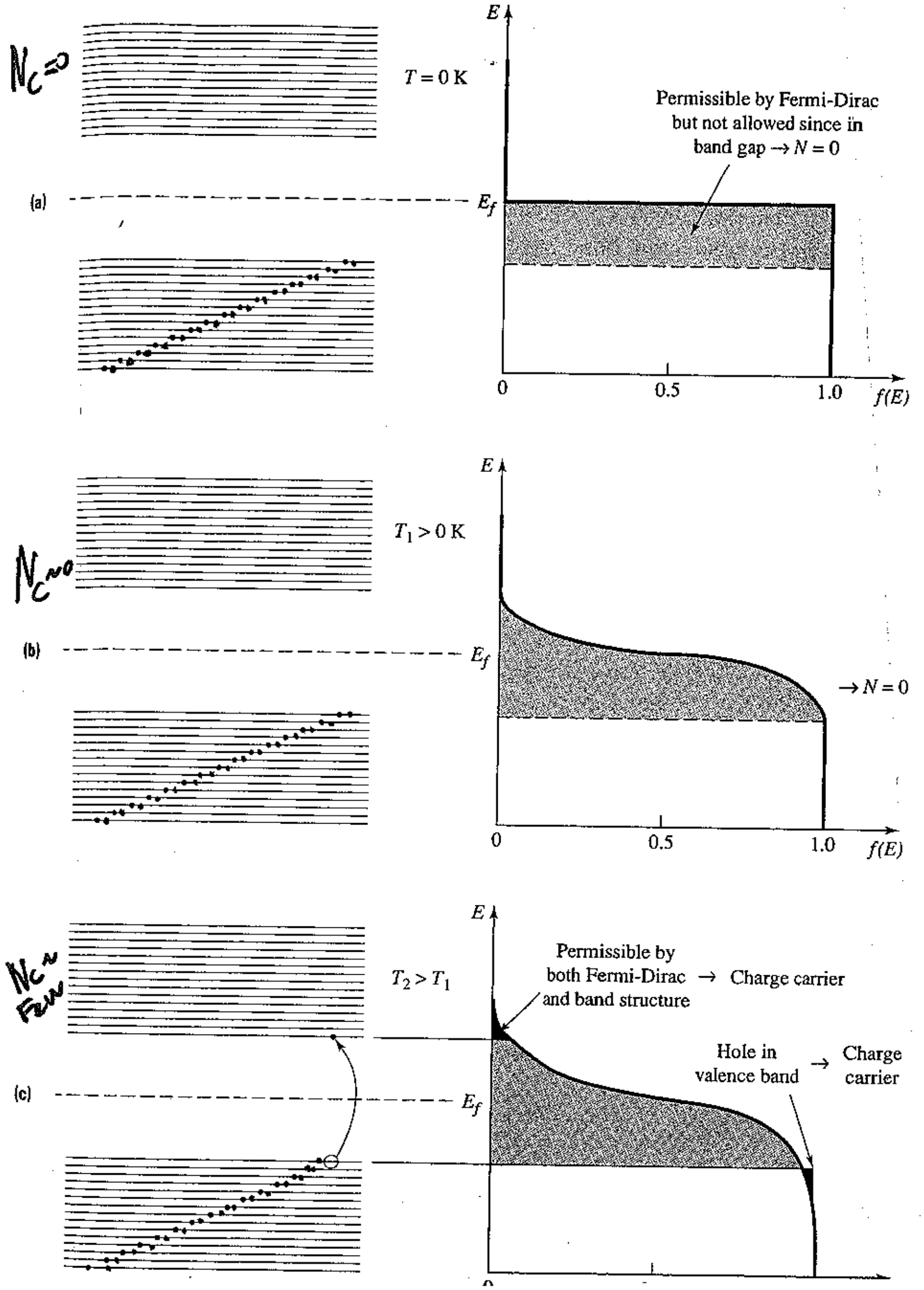
density of states
MEASURE AVAILABILITY!
EXAMPLE

prob that
level, which exist with
density $g(E)$, is populated
(depends on T)



$\Rightarrow$ $g(E)dE$ = # of levels between $[E, E+dE[$

E10



Remember E_F is the Max Energy electrons can HAVE @ $T=0$, if a level exist @ $E=E_F$

↓

CONDUCTORS

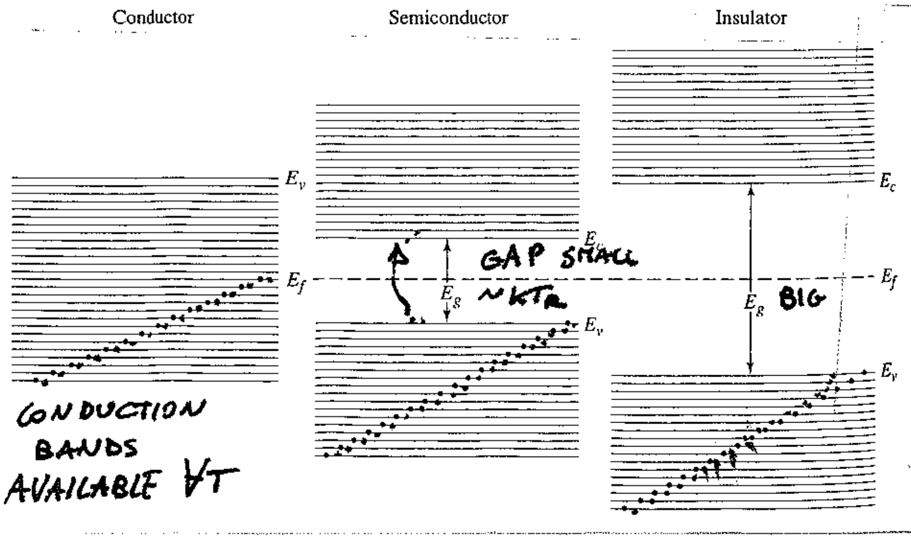
E_F happens in a region with bands ⇒ there are partially POPULATED BANDS ∀T!!

SEMICONDUCTOR

E_F happens inside a GAP < 2.5 eV, there are partially occupied BANDS only at T ~ DECENT

INSULATOR

GAP IS SO Big you need $T > T_{melt}$ > 2.5 eV



CONDUCTION BANDS AVAILABLE ∀T

E11

CONDUCTORS Na & Mg !

EAMPLE

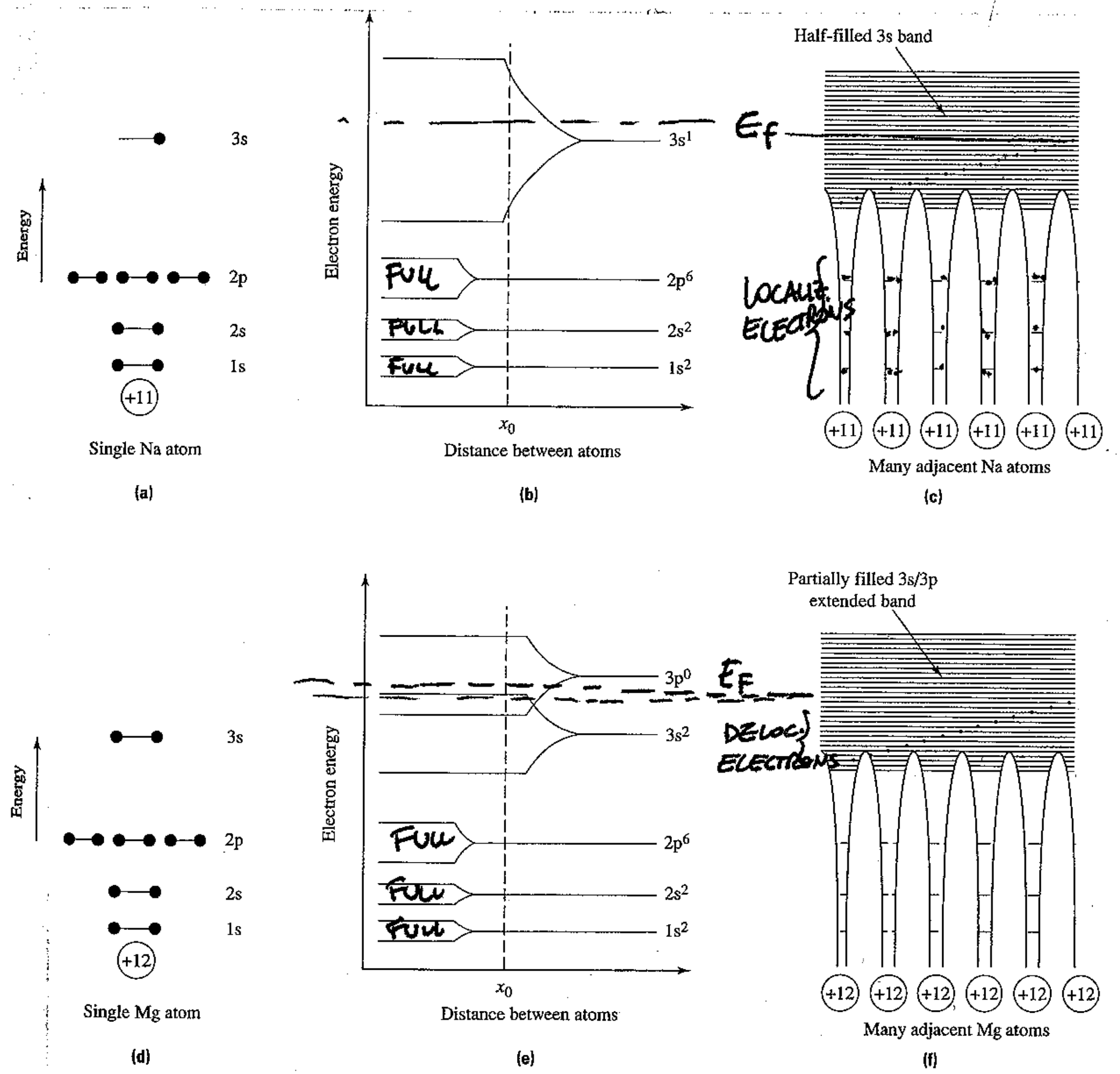
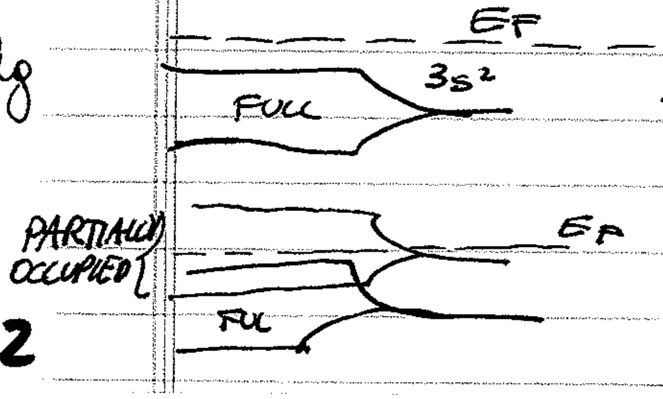


FIGURE 10.2–12 Electron band structures for metallic Na and Mg: **(a)** electron energy levels for an isolated Na atom, **(b)** splitting of the energy levels as a function of distance between two Na atoms, **(c)** the energy band diagram for Na showing a half-filled 3s band, **(d)** electron energy 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



⇒ should BE NO CONDUCTOR

BUT

⇒ CONDUCTOR !!

E12

CONDUCTORS: SUMMARY ⇒

⇒ $\sigma = N_e q_e \mu_e$

available electrons for conductions

$N_e \simeq N_{COND}$ = CONST with T

q_e = charge : e

μ_e = mobility $T \uparrow \mu_e \downarrow$ $\frac{\partial \mu}{\partial T} < 0$

$\sigma \Rightarrow \frac{1}{\rho}$ BECAUSE σ IS PHYSICS ⇒ ρ is ENGINEERING

Resistivity

⇒ $\rho = \rho_0 (1 + \alpha_e T)$

↳ coefficient

more precisely

~~coefficient of temperature of~~

↑ Temperature coefficient of resistivity

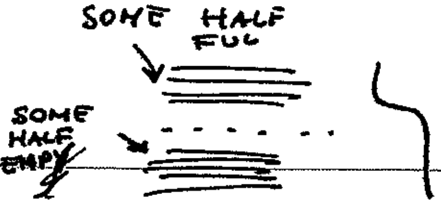
FOR TABLE $\rho = \rho_0 \left[1 + \alpha_e (T - T_{Ref}) \right]$

TABLE 10.2–2 Electrical resistivities ρ_0 and temperature coefficients of resistivity α_e for selected conductors.

Conductor	Reference temperature (°C)	ρ_0 (Ω-cm)	α_e (°C^{-1})
Al	20	2.65×10^{-6}	0.0043
Ag	20	1.59×10^{-6}	0.0041
Au	20	2.35×10^{-6}	0.0040
Co	20	6.24×10^{-6}	0.0060
Cr	0	1.29×10^{-5}	0.0030
Cu	20	1.67×10^{-6}	0.0068
Fe	20	9.71×10^{-6}	0.0065
Mg	20	4.45×10^{-6}	0.0065
Ni	20	6.84×10^{-6}	0.0069
Pd	20	1.08×10^{-5}	0.0038
Pb	20	2.06×10^{-5}	0.0034
Pt	20	1.06×10^{-5}	0.0039
Sn	0	1.10×10^{-5}	0.0047
Ta	25	1.25×10^{-5}	0.0038
Zn	20	5.92×10^{-6}	0.0042
Zr	20	4.00×10^{-5}	0.0044

Source: Adapted from *Handbook of Materials Science*, Vol. I. Copyright CRC Press, Boca Raton, FL.

SEMICONDUCTORS!



$$\sigma = N_h e \mu_h + N_e e \mu_e$$

$\frac{\partial \mu_h}{\partial T} < 0$ $\frac{\partial \mu_e}{\partial T} < 0$ but $N_h, N_e \uparrow$ BOOST

$\frac{\partial N_h}{\partial T} = \frac{\partial N_e}{\partial T}$ HUGE EXPONENTIAL

$$N_h = N_e = N_0 e^{-E_g/2kT}$$

FUNDAMENTAL

TABLE 10.2–3 Band gaps and charge-carrier mobilities for a variety of semiconductors.

Material	Band gap (eV)	μ_e (cm²/V-s)	μ_h (cm²/V-s)
C* DIAMOND	5.4	1800	1400
Si	1.107	1900	500
Ge	0.67	3800	1820
III-V compounds with the zinc blende crystal structure			
BN	~4	—	—
AlP	2.5	—	—
AlAs → FOR LED	2.16	1,200	420
AlSb	1.60	200–400	550
GaP → for LED	2.24	300	100
GaAs → HIGH speed EL.	1.35	8,800	400
GaSb	0.67	4,000	1400
InP → for LED	1.27	4,600	150
InAs	0.36	33,000	460
InSb	0.165	78,000	740
II-VI compounds with the zinc blende crystal structure			
ZnS	3.54	180	5
ZnSe	2.58	540	28
ZnTe	2.26	340	100
CdTe → QUANTUM DOTS	1.44	1200	50
Other crystalline semiconductors			
β-SiC	2.3	4000	—
α-SiC	2.9	4000	~2000
ZnO	3.2	180	—
CdS	2.42	400	—
CdSe → QUANTUM DOTS	1.74	650	—
$CuAlS_2$	2.5	—	—
$CuFeSe_2$	0.16	—	—
$AgInSe_2$	1.18	—	—
$ZnSiAs_2$	1.7	—	50
PbS	0.37	600	600
CdO	2.5	100	—
$BaTiO_3$	2.8	—	—
Polymers			
Polyacetylene	1.4	—	—
Poly(*p*-phenylene sulfide)	4.0	—	—
Polypyrrole	3.0	—	—

*Although carbon (diamond) is an insulator by our definition, it is included here for comparison.

Source: Adapted from *Handbook of Chemistry and Physics*, 61st ed. Copyright CRC Press, Boca Raton, FL.

IONICS : No free electrons (or few)

BUT IONS MOVE? ATOMS Na^+ Cl^- move
jumping left & right ⇒ by DIFFUSION

$$\Rightarrow \mu \sim \text{Diff.} \qquad \mu_{ION} = \frac{\overset{\text{charge}}{q}}{\underset{\text{temp}}{kT}} \, \underset{\text{diffi}}{D_{ION}}(\underset{\sim e^{-Q/kT}}{T, \text{Defect}})$$

μ_{ION} ↓ EINSTEIN RELATIONS

$$\Rightarrow \sigma = \underbrace{\overset{\exp T}{N_e}\,\overset{\text{small } T}{\mu_e}\, e + \overset{\exp T}{N_h}\,\overset{\text{small } T}{\mu_h}\, e}_{\substack{\text{IF SMALL} \\ \text{GAP} \Rightarrow \text{CONSIDERABLE CURRENT!} \\ <2.5\text{eV}}} + \sum_{IONS} \underset{\text{NOT } T}{N_{ion}}\, q_{ion}\, \underset{\sim \frac{1}{T}}{\mu_{ion}}$$

TRANSFERENCE NUMBER of a specie = % of conductivity of the specie VS the total of the IONIC

$KCl = K^+ + Cl^-$
↓

$\sigma_{K^+}/\sigma_{KCl} = 96\%$ @ 435°C
$\sigma_{Cl^-}/\sigma_{KCl} = 4\%$

$\sigma_{K^+}/\sigma_{KCl} = 88\%$ @ 600°C
$\sigma_{Cl^-}/\sigma_{KCl} = 12\%$

} change with Temperature

DEFECTS & IMPURITIES

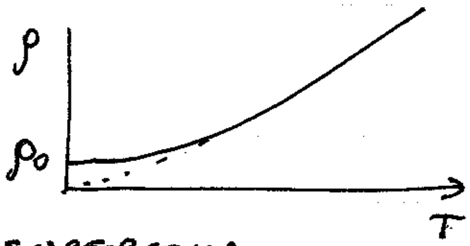
reduce σ in conductors, metals & ionics!

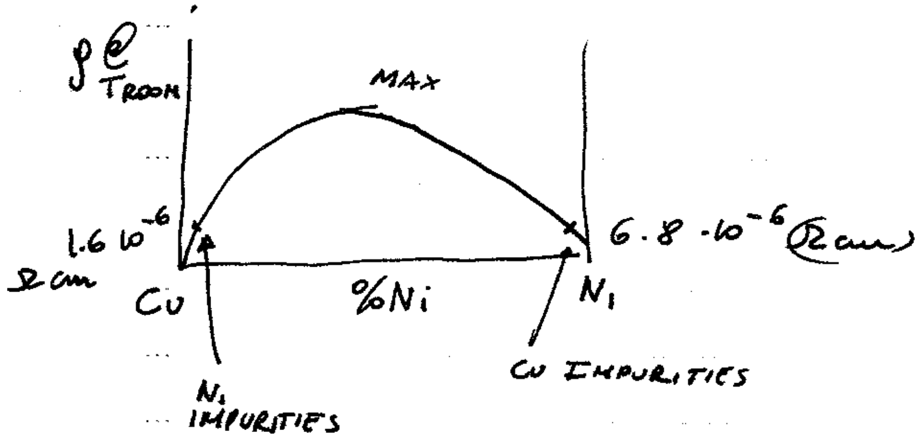
$\frac{\partial \mu}{\partial N_D} < 0$!!   BUT FOR SEMICONDUCTORS $\Longrightarrow$ COMPLETELY DIFFEREN!

@ $T=0$ FOR METAL

$$\underset{\substack{\uparrow \\ \text{Remaining one} \\ \text{DUE BY DEFECT}}}{\rho = \rho_0} + \alpha T$$

if $\rho_0 \sim 0$ SUPERCONDUCTOR





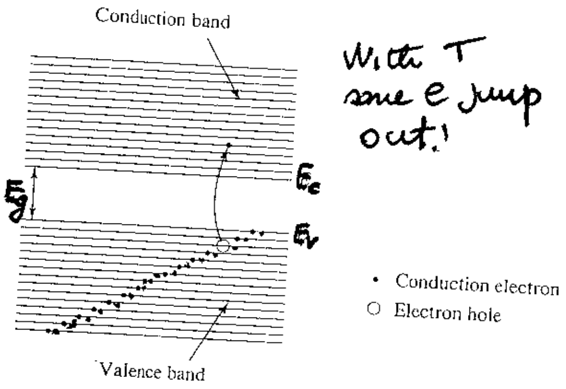
SEMICONDUCTORS : INTRINSIC

PURE ELEMENT HAS CHARGES (e & h) ~~EACH~~ CREATED ONLY BY TEMPERATURE

CALLED INTRINSIC SEMICONDUCTOR

ch NO IONIC DIFFUSION CONTRIBUTION

$$\sigma = n_e' \underset{\substack{\downarrow\\ e}}{q_e} \underset{\substack{\downarrow\\ \Rightarrow >0}}{\mu_e} + n_h \underset{\substack{\downarrow\\ e}}{q_h} \underset{\substack{\downarrow\\ \Rightarrow >0}}{\mu_h} = e(n_e\mu_e + n_h\mu_h)$$



With T some e jump out!

E_c = conduction energy
= min of conduction BANDS

E_V = valence energy
= max of valence bands

E_g = energy gap

1) q is NOT function of T, it's just $\underline{\underline{e}}$!!
2) $\frac{\partial \mu}{\partial T} < 0$ but small in range!
since $\rho = \rho_0(1 + \alpha\Delta T) \Rightarrow \mu \sim \mu_0 - \gamma T$
$\Rightarrow$ ~~$\frac{\partial\mu}{\partial T}$ linearly in~~ decrease linearly.
3) ~~$\frac{\partial M}{\partial T}$~~ $\frac{\partial n_e}{\partial T}$ & $\frac{\partial n_h}{\partial T}$ are HUGE!!
exponentially HUGE

FOR INTRINSIC, THERE IS NO EXTRA CHARGE

E17 $\Rightarrow n_h = n_e$ IF YOU PRODUCE 1 e YOU PRODUCE 1 h

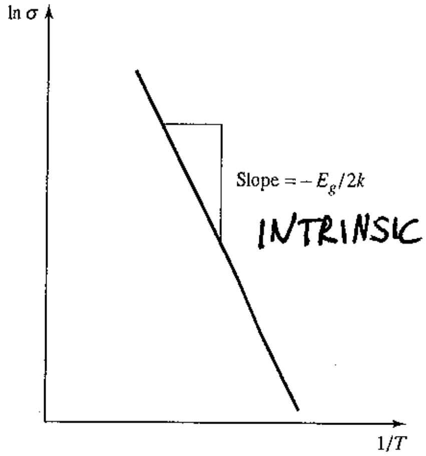
$$\Rightarrow \quad n_e = n_h = N_0 \exp\left(-\frac{E_g}{2kT}\right)$$ from $\int f(E)\,g(E)\,dE$ integrals!

$$\Rightarrow \quad \sigma = \underbrace{N_0\, e(\mu_e+\mu_h)}_{\text{small T variation}}\ \underbrace{\exp(-E_g/2kT)}_{\text{Big T variation}}$$

$$\approx \sigma_0 \text{ constant} = N_0\, e(\mu_e+\mu_h)$$

$$\Rightarrow \quad \sigma = \sigma_0 \exp\left(-E_g/(2kT)\right)$$

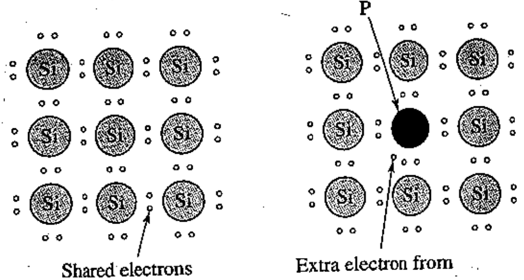
$$\Rightarrow \text{plot} \quad \log\sigma = \log\sigma_0 - \left(\frac{E_g}{2k}\right)\left(\frac{1}{T}\right)$$



⇒ AVALANCHE effect.

SEMICONDUCTORS : EXTRINSIC ! N-type

what happens if we add impurities ?

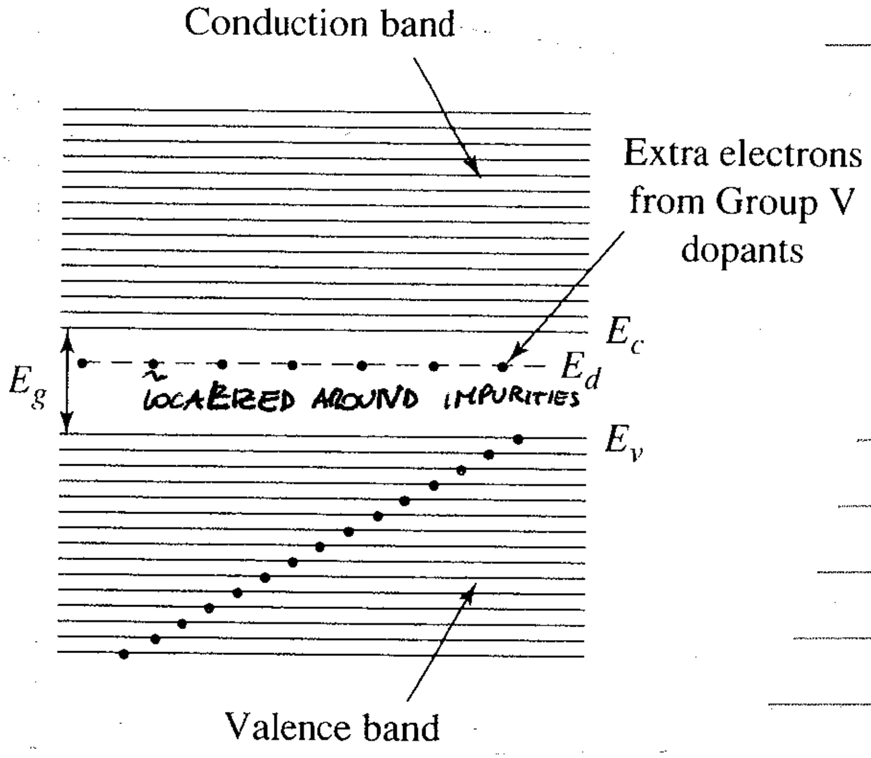


Shared electrons in a covalent bond
(a)

Extra electron from Group V dopant atom
(b)

Remove Some Si & add P
⇒ extra electron

EACH IMPURITY CREATES
ONE EXTRA LEVEL
DONOR LEVEL WITH E_d



E_d is very close to E_c

$\Rightarrow E_c - E_d \simeq 40\,meV$

at ROOM TEMP

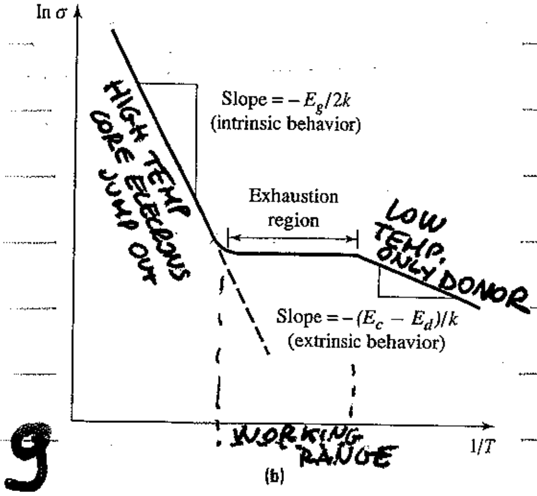
$KT_{ROOM} \simeq 25\,meV$

$$\Rightarrow \exp\left(-\frac{\overbrace{E_c-E_d}^{\sim 40}}{\underbrace{KT}_{\sim 25}}\right) \sim 0.2$$

1

[illegible]

BIG!!!



(b)

at ROOM Temperature all donor ~~lev~~ electrons have jumped out their donor levels & are FREE

⇒ plenty of conductivity

$\Rightarrow n_h \simeq N_0 \exp(-E_{gap}/2kT) \neq n_e$ } in WORK RANGE

$n_e \simeq$ Concentrations of donors $\rightarrow N_d$

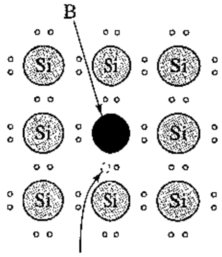
all jumped out

@ LOW TEMP $n_e = N_d \exp(-(E_c-E_d)/KT)$

N: type $\sigma = \underset{\Rightarrow}{N_0} e \mu_e \exp(-(E_c - E_d)/kT)$

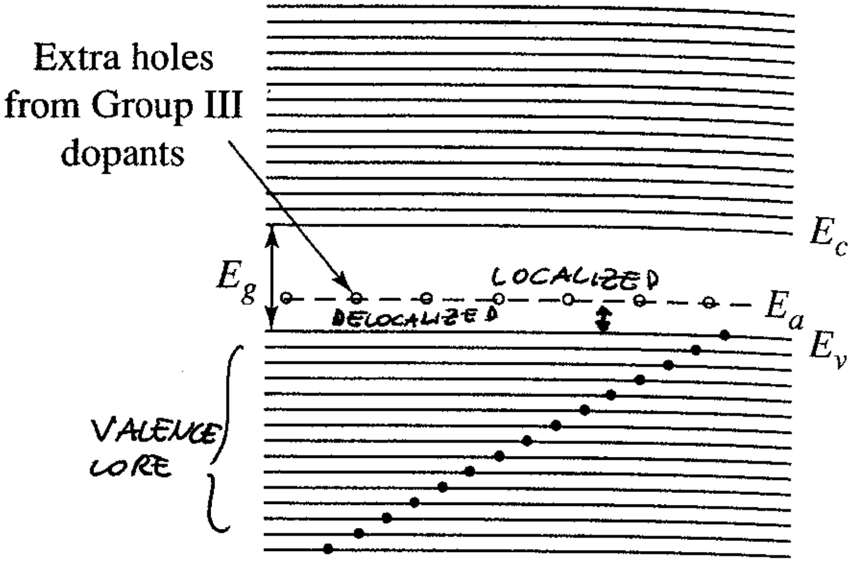
EXTRINSIC : P- TYPE (add holes)

we add holes:



Hole (missing electron) from Group III dopant atom

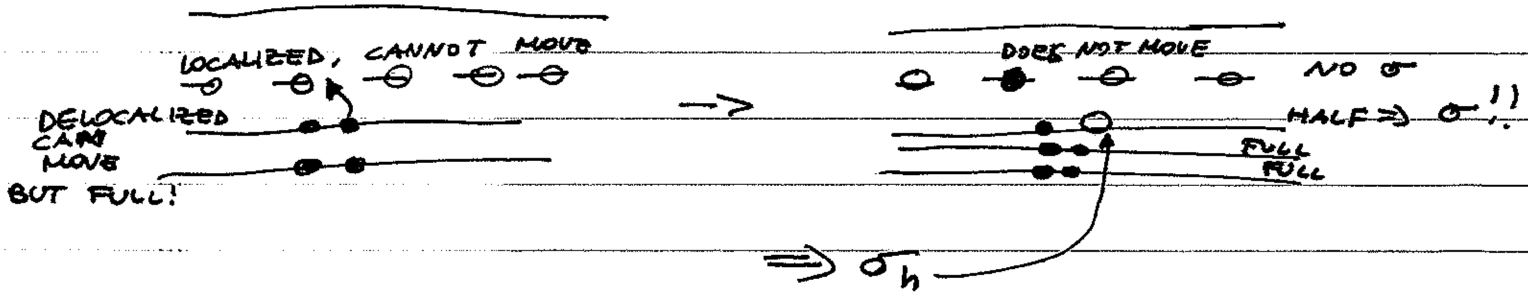
(a)



(b)

ACCEPTOR LEVELS
LOCALIZED LEVELS
WITH HOLES INSIDE!

the 1 electron
from VALENCE CORE TO THE ACCEPTOR LEVEL



⇒ n_e ~ ONLY INTRINSIC

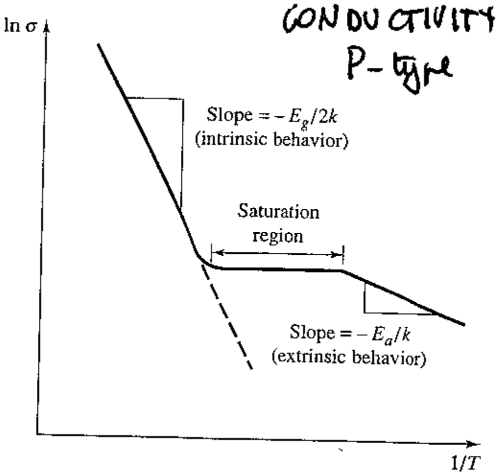
n_h ~ goes with $\exp\left(-\frac{E_a-E_v}{kT}\right)$

1 because only 1 positive "hole" is generated.

⇒ $\overset{EXTR}{n_h} \gg \overset{INTR}{n_e}$ ⇒ $\sigma = \sigma_h = N_0 q \mu_h \exp\left(-\frac{E_a-E_v}{kT}\right)$

≈ CONCENTRATION OF IMPURITIES

NOT E_a but $E_a - E_v$ in book



(c)

$$\sigma_h = N_0 q \mu_h \exp\left(-\frac{E_a - E_v}{kT}\right)$$

SUMMARY

INTRINSIC ⇒ ONLY Temperature generated carriers = SMALL

EXRINSIC ⇒ $\underbrace{\text{INTRINSIC}}_{\text{small}}$ + CARRIERS OF IMPURITIES (DOPANTS) extra e or h (N & P-types)

TABLE 10.3–1 Impurity energy levels (E_a or E_d) in Si and Ge.

Host	Dopant	Energy level
Silicon	Sb	$E_c - E_d = 0.039$ eV
	P	$E_c - E_d = 0.044$ eV
	As	$E_c - E_d = 0.049$ eV
	Bi	$E_c - E_d = 0.069$ eV
	B	$E_a = 0.045$ eV
	Al	$E_a = 0.057$ eV
	Ga	$E_a = 0.065$ eV
	In	$E_a = 0.160$ eV
	Tl	$E_a = 0.260$ eV
Germanium	P	$E_c - E_d = 0.012$ eV
	As	$E_c - E_d = 0.013$ eV
	B	$E_a = 0.010$ eV
	Al	$E_a = 0.010$ eV

$E_a \rightarrow E_a - E_v$.

FREE

SEMICONDUCTOR	TYPE	σ_0	Act Energy
INTRINSIC	$n_h = n_e$	$N_0 e(\mu_e + \mu_h)$	$\exp(-E_g/2kT)$
EXTRINSIC N-TYPE	$n_e \simeq N_D >> n_h$	$N_0 e \mu_e$	$\exp(-(E_c - E_D)/kT)$
EXTRINSIC P-TYPE	$n_h \simeq N_A >> n_e$	$N_0 e \mu_h$	$\exp(-(E_a - E_v)/kT)$

E21

DEFECTS

DEFECTS : SOURCES OF TROUBLES

- dont change mobility but
- introduce extra localized ~~electro~~ levels that mess up mechanism
- act like a carrier-charge recombination sites! (electron falls & meet its hole & viceversa!)

- FAST SEMICONDUCTORS
  ⇒ minimize defects,
  need for big crystals (single crystals, no poly!)

SIMPLE DEVICES

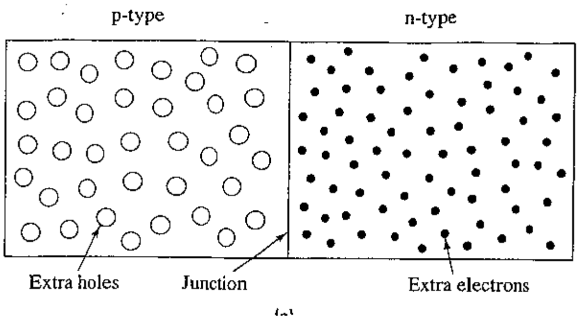
- measure temp : intrinsic $\log \sigma \sim \frac{E_g}{2k} \frac{1}{T}$

- ligth detector : ligth $\lambda \Rightarrow E = \frac{\hbar c}{\lambda}$ DE-BROGLIE

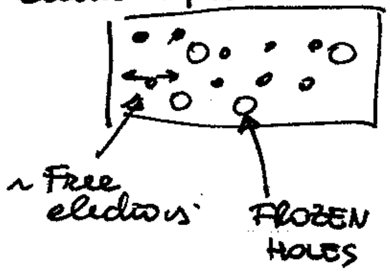
  $\hbar$: PLANK CONSTANT

  ⇒ if $E > E_{gap} \Rightarrow$ generation of extra charges
  ⇒ boost of conductivity

But, more important is
JUNCTIONS ⇒ PN ⇒ TRANSISTORS!



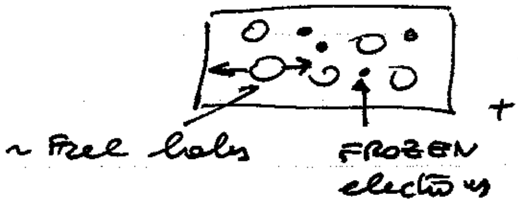
N-TYPE @ ROOM ...
electrons promoted in conduction bands

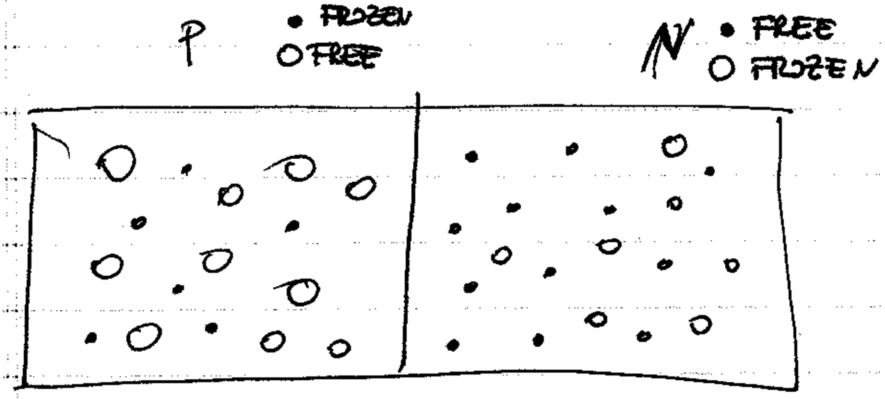


⇒ holes stuck in DONOR!

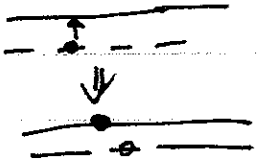
P-TYPE @ ROOM TEMPERATURE

holes promoted to be free + electrons stuck



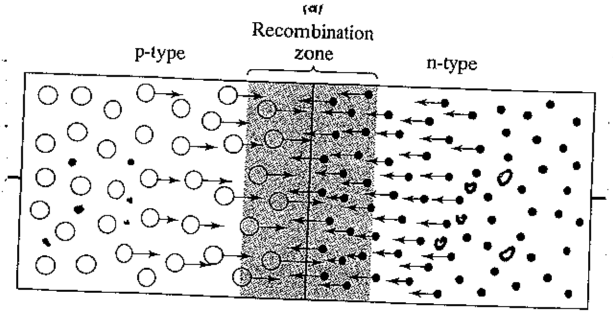


N-TYPE



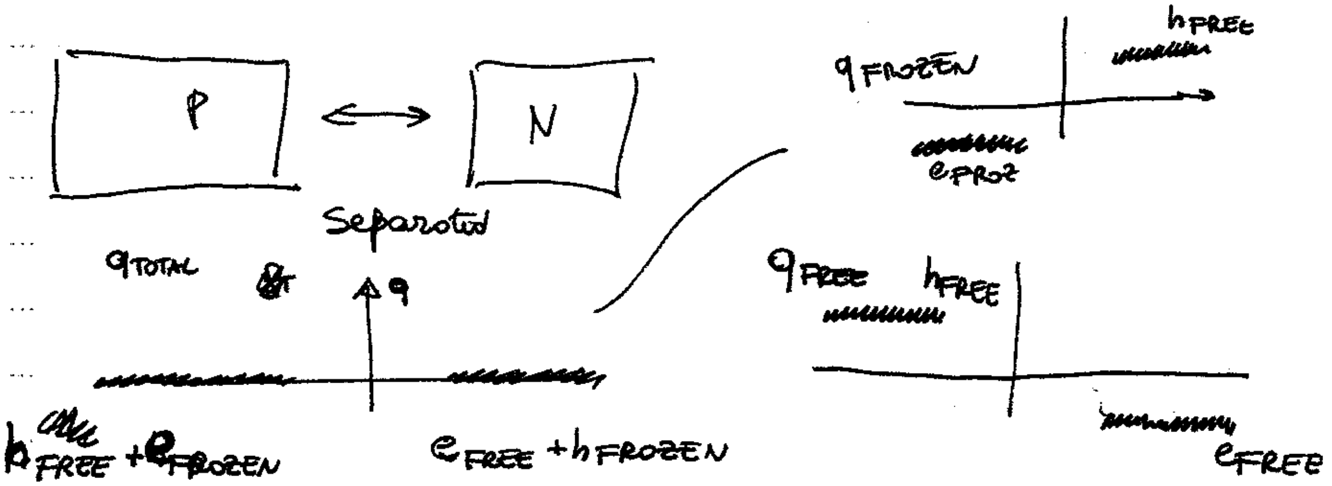
= FREE ELECTRON + FROZEN HOLE

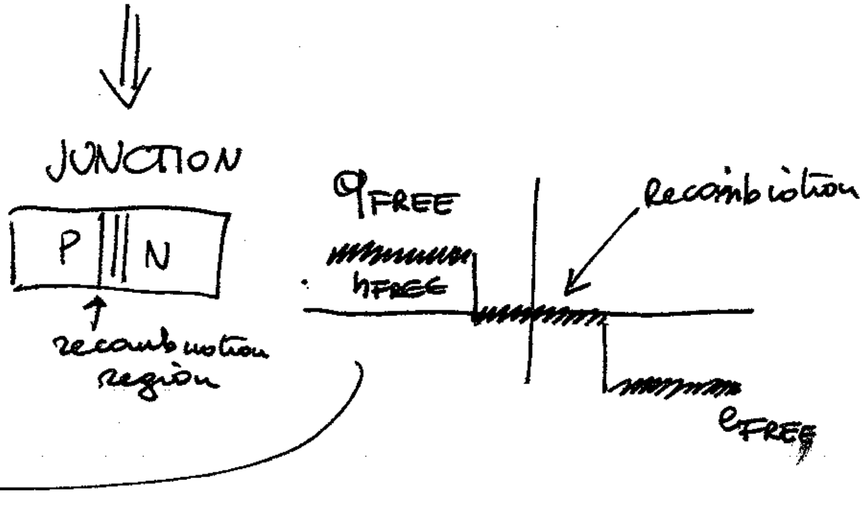
Free electrons in N region feel free Holes in P.



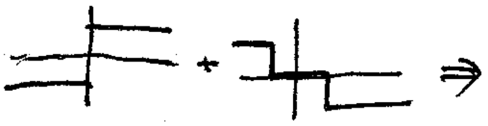
E23

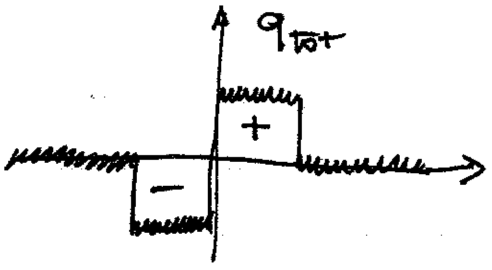
~~FREE~~ TOTAL CHARGE



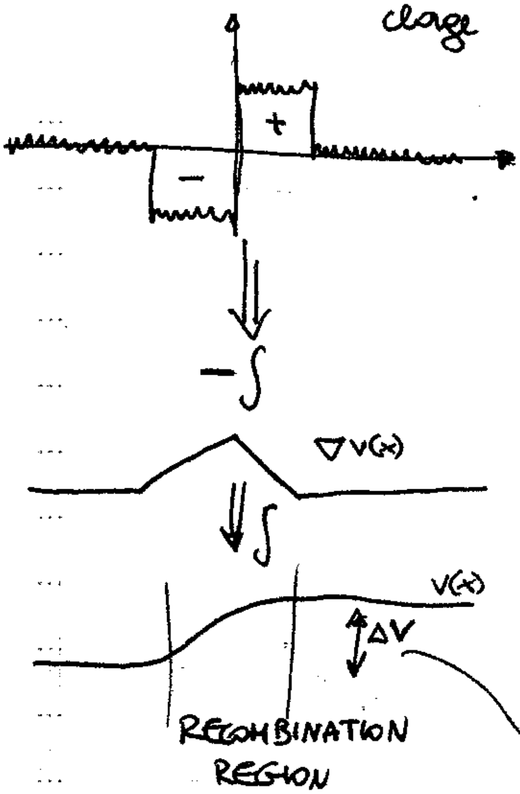


$q_{TOT} = q_{FREE} + q_{FROZEN}$





⇒ NON BALANCE OF <u>CHARGE</u> BY JUNCTION



⇒ FROM MAXWELL

$$\nabla^2 V(x) = -q(x)/\varepsilon_0 \Rightarrow \text{forget the } \varepsilon_0 !$$

$$V(x) = -\iint q(x)\,dx\,dx$$

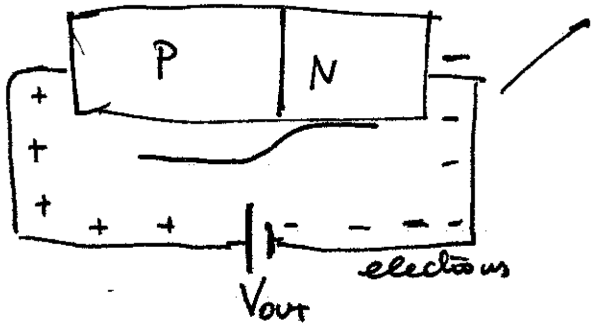
JUNCTION CAUSES A JUMP ON THE INTERNAL POTENTIAL

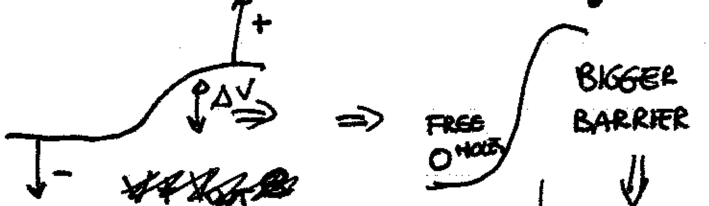
⟹

AFFECT ELECTRIC CURRENT!!

ΔV ~ 0.7 eV for Si !

REVERSE BIAS

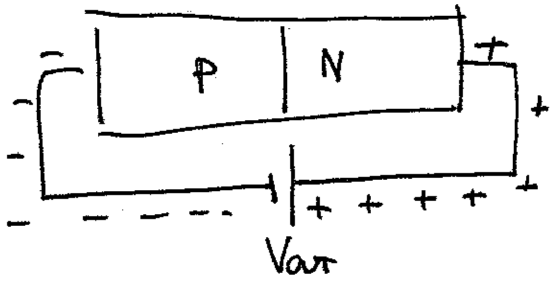


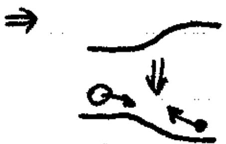


$$\Delta V + (\underbrace{V_{OUT}\,q}_{\uparrow\ \text{electron} < 0}) = V - V_{OUT}\,e$$

NO CURRENT
⇓
BIGGER RECOMBINATION REGION

FORWARD BIAS





$$V = \Delta V + (V_{OUT}\,q) = \Delta V - V_{OUT}\,e$$

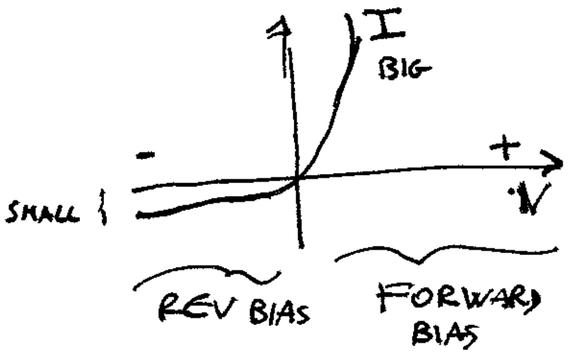
$$V = \Delta V - V_{OUT}$$

$$I = I_0\left(e^{eV/kT} - 1\right)$$

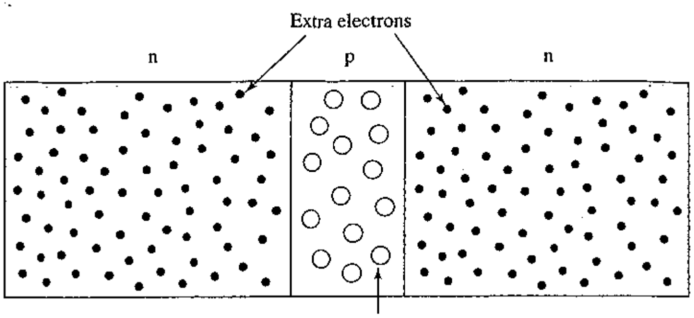
⇓

~ OPEN CIRCUIT (REV)
~ CLOSE CIRCUIT (FWD).

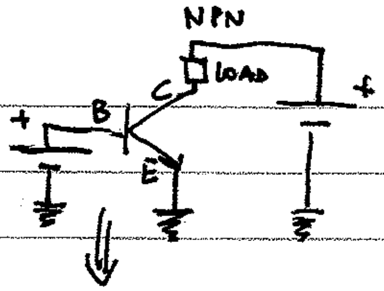
SMALL BARRIER
NO BARRIER
⇓
PLENTY OF CURRENT
⇓
SMALL RECOMB REGION



E25

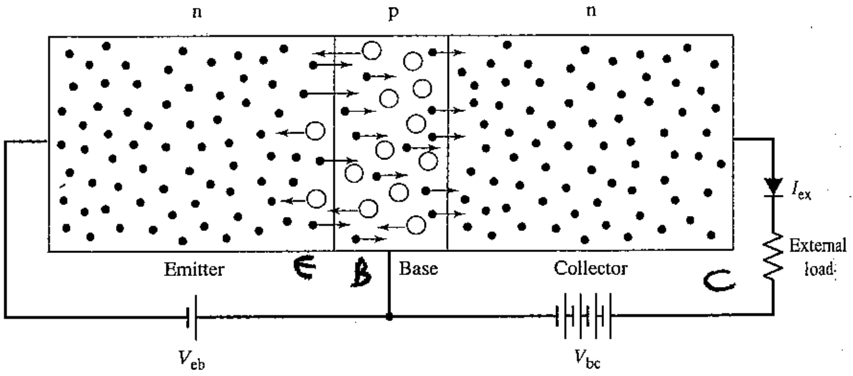


(a)

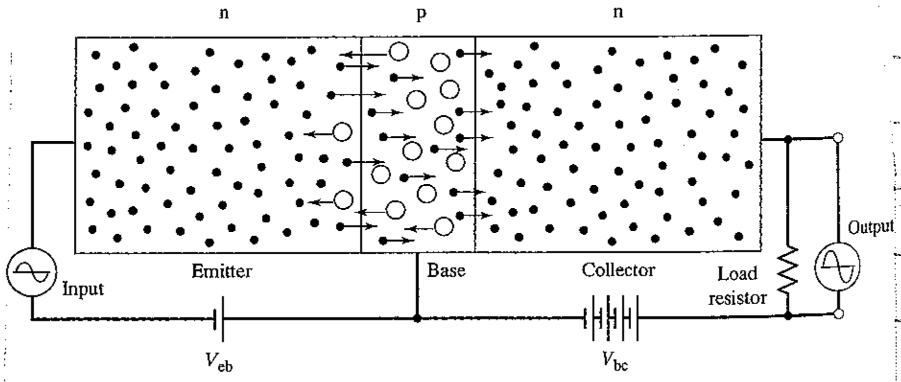


⇓

V_{Bc}, I_{Be} like diode.



(b)



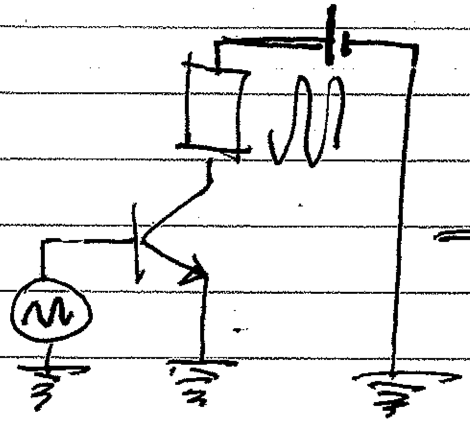
(c)

BASE is THINNER THAN RECOMBINATION REGION

⇒ V_{BE}, accelerates electrons from E TO B, but B is thin ⇒ not enough space for recombination

⇒ travel to C

⇒ V_{BE} controls CONDUCTIVITY BETWEEN E & C



⇒ amplification

INTEGRATED CIRCUITS

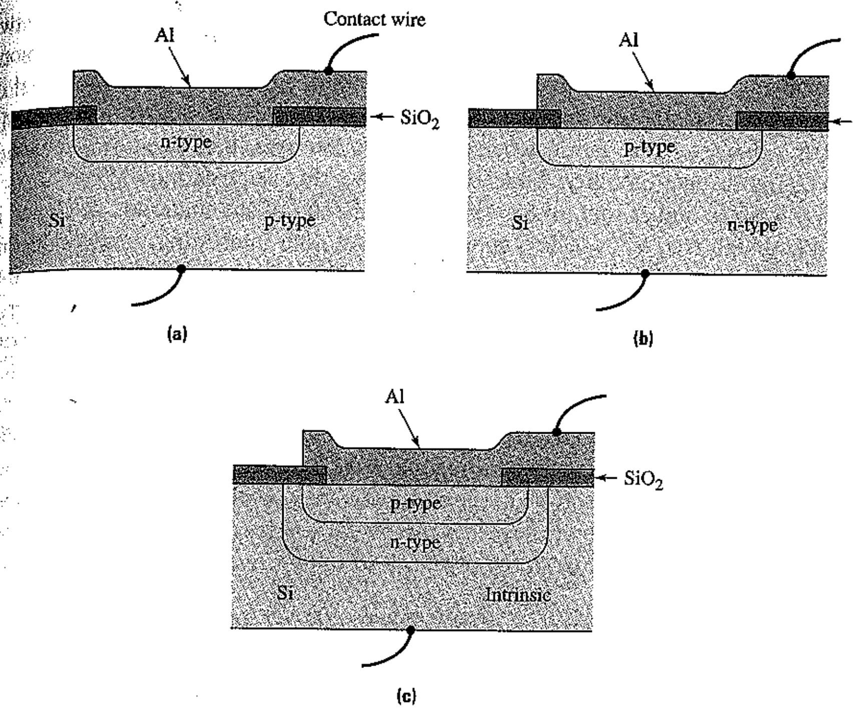


FIGURE 10.3–9

Three methods for fabricating a pn 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.

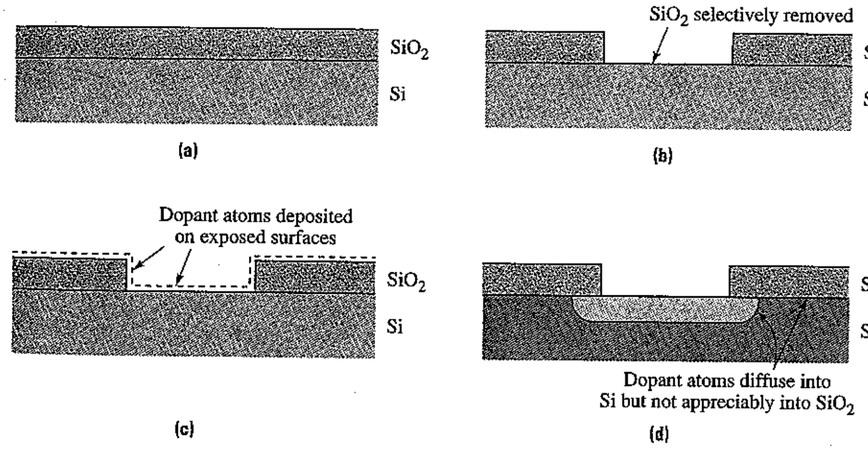


FIGURE 10.3–10

The method for introducing a controlled amount of a dopant into a silicon substrate: **(a)** the oxidized wafer, **(b)** the SiO$_2$ 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.

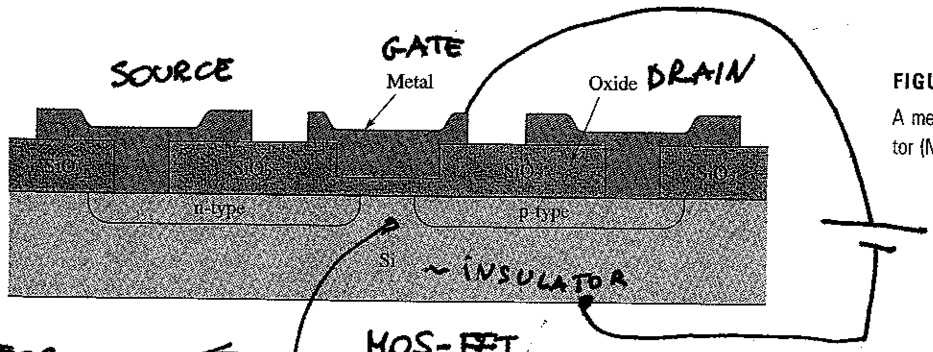


FIGURE 10.3–11

A metal-oxide-semiconductor (MOS) capacitor.

Voltage ⟸ MOS-FET
regulated Resistor

Electric Field controls availability of Free charges diffusing in

POLYMERS ;

AMORPHOUS ⟹ NO LONG RANGE ORDERING

- they are not crytalline! < glass / rubber } same stuff but depends on Temperature

- above T_g ⟹ rubber (MOLECULAR REARRANGEMENT) → are times comparable with experiment

  under T_g ⟹ glass no molecular rearrangement (FROZEN)

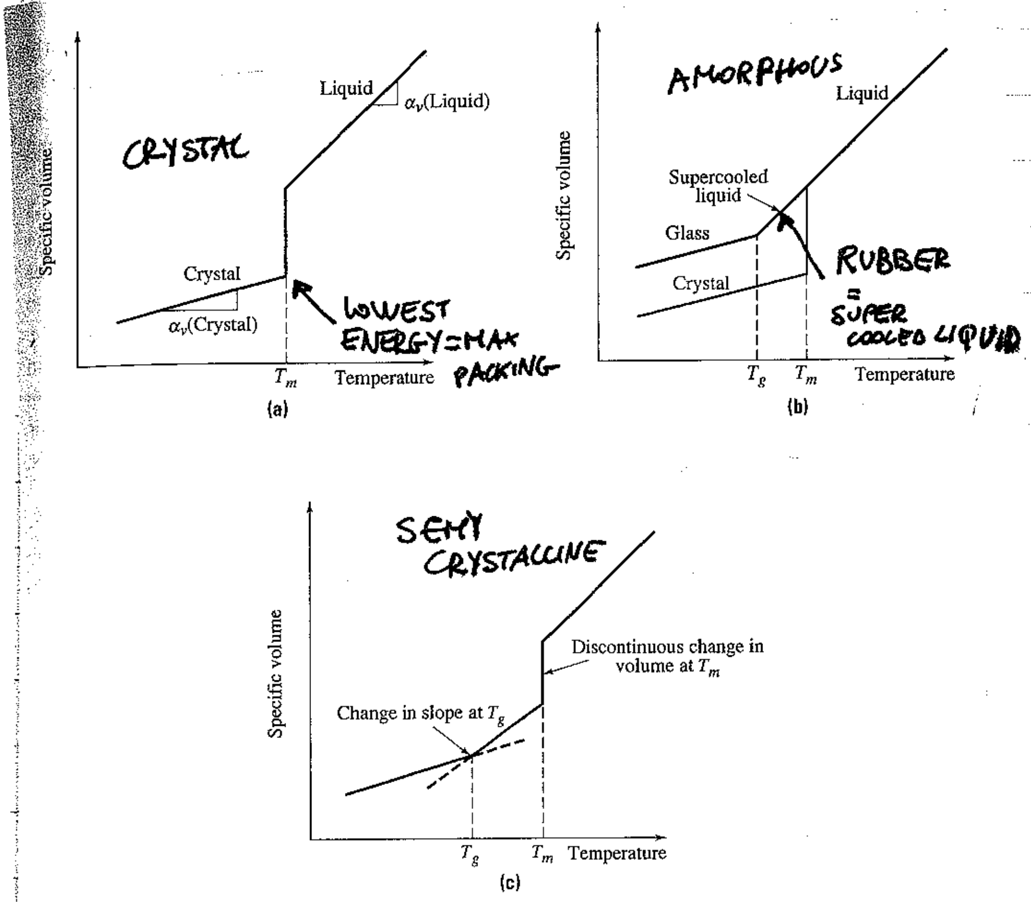
  T_g glass transition temperature

Volume is function of Temperature

$$\Rightarrow \quad \alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$ volumetric thermal expansion

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P$$

$$\alpha_V \sim 3\alpha_L$$



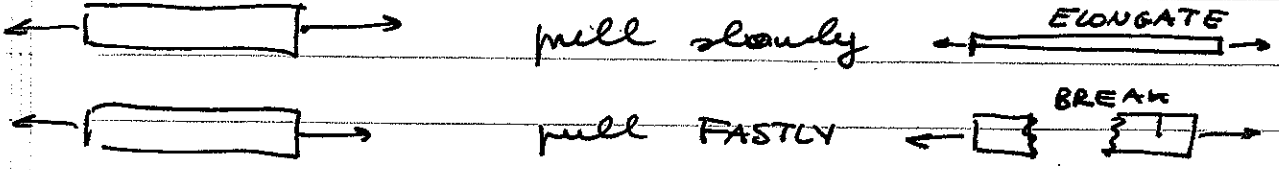
$\alpha_V^{liq} > \alpha_V^{sol}$

MOST OF MATERIALS

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-crystal 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.

P1

MOLECULAR MOTION ⇒ depends on time frame of experiment
REARRANGEMENT



⇒ T_g depends on Time frame of events!

EXAMPLE OF POLYMERS = POLY + (MER)
↑
many times * mer.

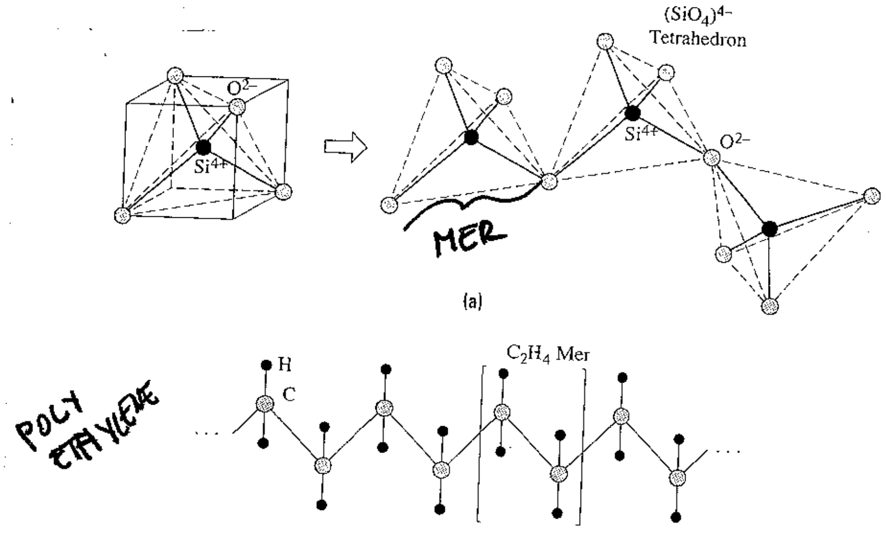
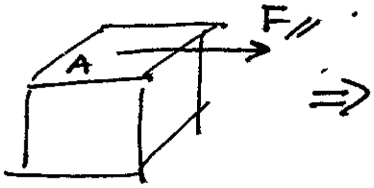


FIGURE 6.2-2 Repeat units in two different structures: **(a)** the $(SiO_4)^{4-}$ tetrahedron in SiO_2, and **(b)** the C_2H_4 mer in polyethylene. In this figure we show the polymer molecule in a simplified linear (stretched-out) orientation. In fact, as discussed later in the chapter, polymer molecules 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.

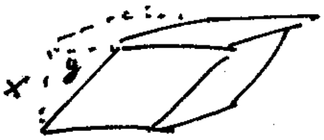
VISCOSITY

SHEAR STRESS



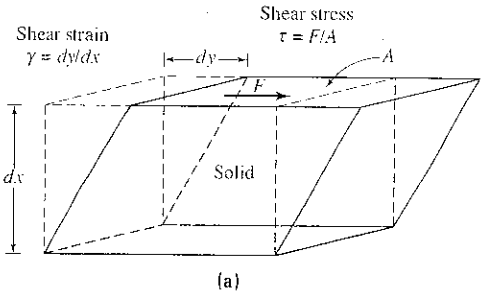
$$\Rightarrow \tau \equiv \frac{F_{\parallel}}{A} \Rightarrow$$

SHEAR STRAIN



~~$\frac{y}{y}$~~ $\frac{y}{x}$ is shear strain;

even better $\frac{dy}{dx} \equiv \gamma$ SHEAR STRAIN



(a)

SOLID RESPONSE

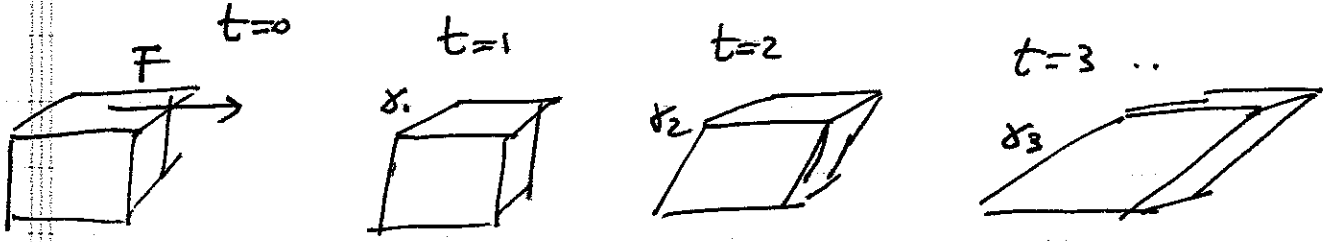
$\tau \Rightarrow \gamma \propto \tau$ $\quad \tau = G\gamma$

$\downarrow$ SHEAR MODULUS

A liquid responds to shear STRESS?

NO STRAIN but STRAIN RATE

⇒ constant deformation

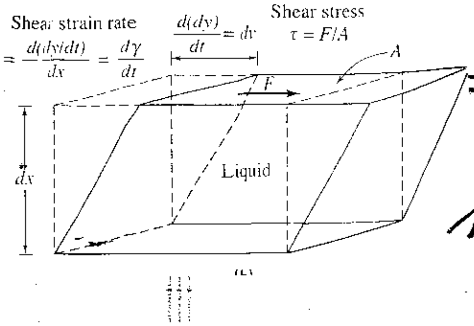


$\gamma \uparrow$ $\quad \gamma(t) \uparrow$ is function of time

P3 $\Rightarrow \frac{\partial \gamma}{\partial t} \propto \tau$ bigger τ & Faster $\frac{\partial \gamma}{\partial t}$

SHEAR STRAIN

$\Rightarrow$ ~~τ~~ $\frac{\partial \gamma}{\partial t} \propto \tau$



$\Rightarrow$

$$\boxed{\tau = \eta \frac{\partial \gamma}{\partial t}}$$

NEWTON VISCOSITY LAW

η is measure of work done for deformation

~~μ~~ $\eta\ (\overset{?}{\cdot})$

$$\tau\ \left(\frac{F}{A}\right) = \eta\ \frac{1}{s}\ \frac{m}{m} \Rightarrow \boxed{\frac{g\,m}{s}}\ \text{POISE}\ \frac{g}{cm \cdot s}$$

$F = g \cdot \frac{m}{s}^{2}$

$$\Rightarrow\ g\,\frac{\cancel{m^2}}{s\,\cancel{s^2 m^2}}\ \cancel{s}\,\frac{\cancel{m}}{\cancel{m}} = \frac{g\,m}{s}$$

$\eta\downarrow$ water, solvent, ~~liquid metals~~, } still liquid

H_2O, liquid metals (Hg) ~ 0.01 P

~~Metal liquid metal~~

$\eta\uparrow$ ~~of liquid metals~~ viscous materials

CARAMEL $\sim 10^5$ P

WINDOWS glasses 10^{25} } FLUIDITY $\boxed{\phi \equiv \frac{1}{\eta}}$

viscosity (& fluidity) are TEMPERATURE DRIVEN PROCESSES

@ $T\uparrow$ ~~μ~~ $\eta\downarrow, \phi\uparrow$

ARRHENIUS

$$\phi \equiv \frac{1}{\eta} = \phi_0 \exp\left(\frac{-Q}{KT}\right)$$

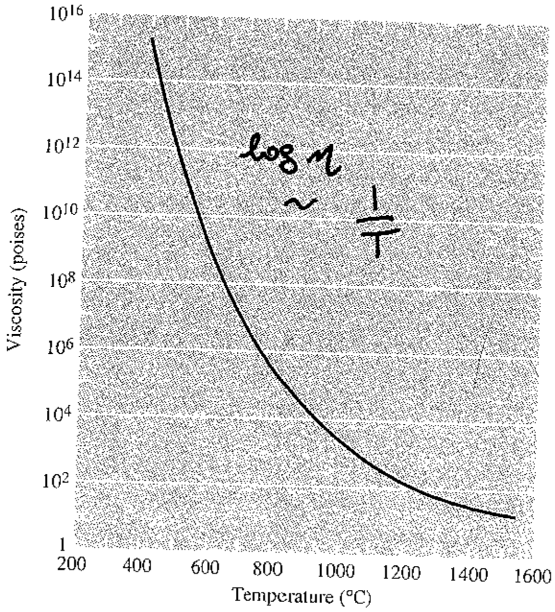
→ activation energy

$\Rightarrow$ when the system is viscous

~~at~~ good FIT @ $T > T_g$

$$\eta = \eta_0 \exp\left(\frac{Q}{KT}\right)$$

T in kelvin, NOT celsius

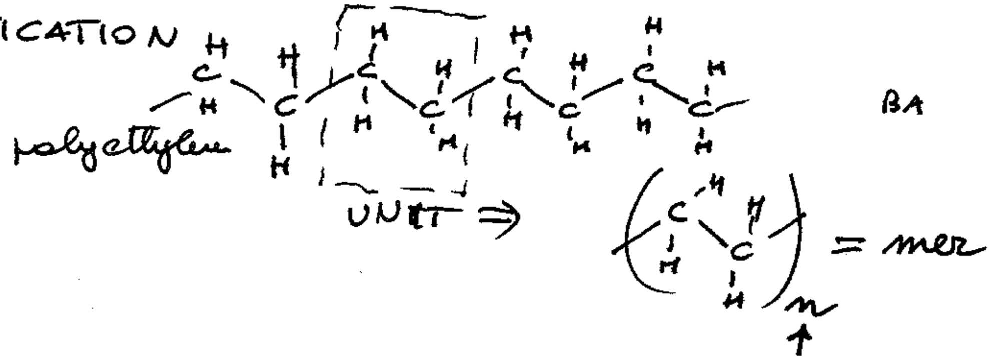


P4

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



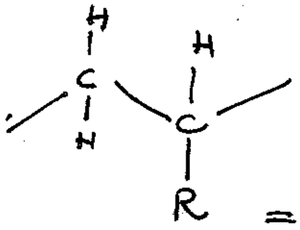
BA

Degree of polimerization
n ~ 50k, 500k
MILLIONS

if n small ⇒ polyethylene
WAX OR PARAFFIN OR OIL

↓
HUNDREDS.

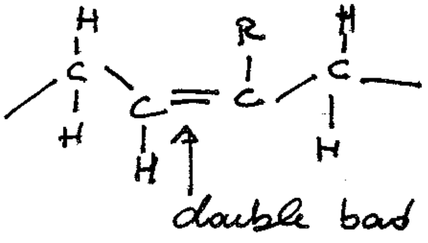
VINYL POLYMER



= VINYL POLIMER

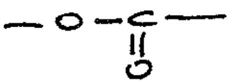
$R= CH_3$ ⇒ POLYPROPYLENE

HYDROCARBONS RUBBERS (double bond

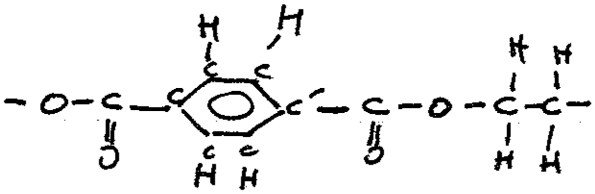


R=H POLYBUTADIENE

- POLYOLEFIN (if C & H only) = FAMILY
  if not only C in BACKBONE ⇒
- POLYESTER FAMILY

ESTER

$-O-\underset{\overset{\|}{O}}{C}-$

PET POLYESTER ⟸



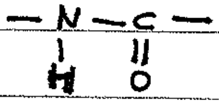
Films & FIBERS
TRANPARENT, PROJECTOR

MYLAR, DACRON, FORTREL,
TERYLENE

P5

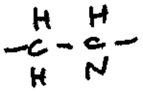
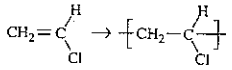
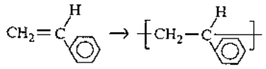
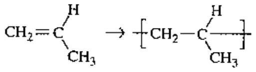
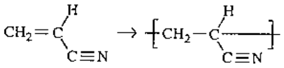
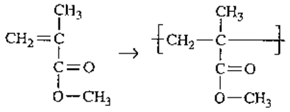
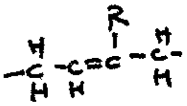
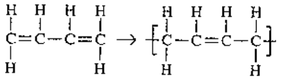
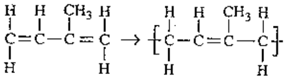
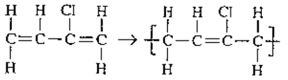
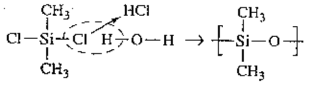
AMIDE GROUP

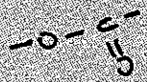
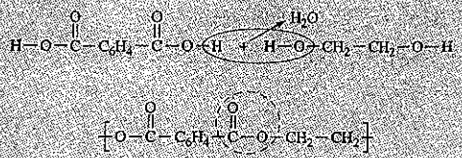
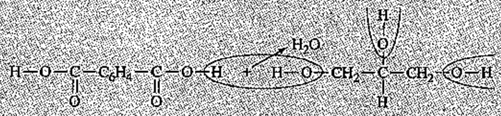
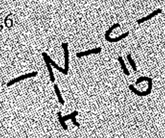
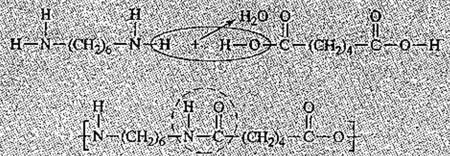
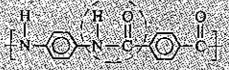
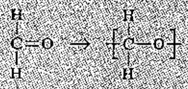
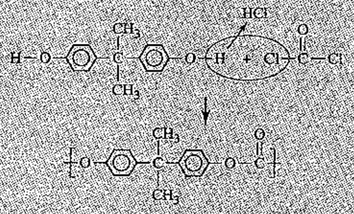
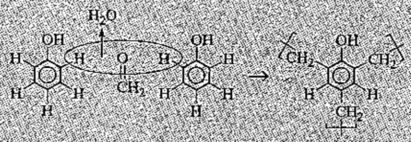
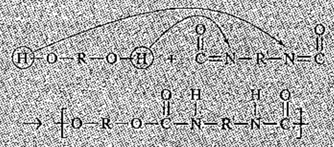
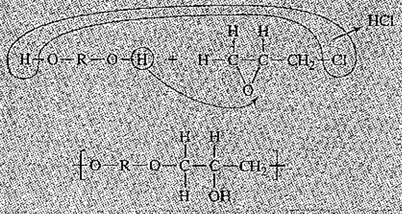
- POLYAMIDES or NYLON



$-\underset{H}{N}-\underset{O}{\overset{}{C}}-$

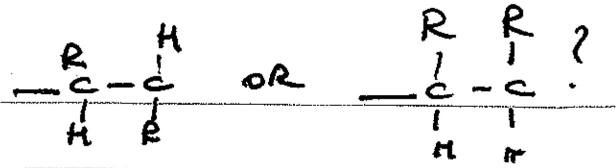
CARPET, SILK, WOOL,

Polymer	Structure	Applications
Vinyls and related polymers		
Polyethylene	$CH_2{=}CH_2 \rightarrow -[CH_2-CH_2]-$	Clear film, flexible bottles
Polyvinylchloride 	 $CH_2{=}C(H)(Cl) \rightarrow -[CH_2-C(H)(Cl)]-$	Floors, pipes, hoses
Polystyrene	 $CH_2{=}C(H)(C_6H_5) \rightarrow -[CH_2-C(H)(C_6H_5)]-$	Containers (clear or foam), toys
Polypropylene	 $CH_2{=}C(H)(CH_3) \rightarrow -[CH_2-C(H)(CH_3)]-$	Sheet, pipe, film, containers
Polyacrylonitrile	 $CH_2{=}C(H)(C{\equiv}N) \rightarrow -[CH_2-C(H)(C{\equiv}N)]-$	Fibers—synthetic wool
Polytetrafluoroethylene (Teflon)	$CF_2{=}CF_2 \rightarrow -[CF_2-CF_2]-$	Nonstick coatings, gaskets, seals
Polymethylmethacrylate (Plexiglas)	 $CH_2{=}C(CH_3)(C{=}O)(O-CH_3) \rightarrow -[CH_2-C(CH_3)(C{=}O)(O-CH_3)]-$	Lenses, transparent enclosures, windows
Rubbers		
Polybutadiene 	 $CH_2{=}CH-CH{=}CH_2 \rightarrow -[CH_2-CH{=}CH-CH_2]-$	Tires and molded parts
Polyisoprene (natural rubber)	 $CH_2{=}CH-C(CH_3){=}CH_2 \rightarrow -[CH_2-CH{=}C(CH_3)-CH_2]-$	Tires and gaskets
Polychloroprene	 $CH_2{=}CH-C(Cl){=}CH_2 \rightarrow -[CH_2-CH{=}C(Cl)-CH_2]-$	Belts, bearings, and foams
Polydimethylsiloxane (silicone rubber)	 $Cl-Si(CH_3)_2-Cl + H-O-H \xrightarrow{HCl} -[Si(CH_3)_2-O]-$	Gaskets, insulation, and adhesives

Polymer	Structure	Applications
Polyesters		
Polyethyleneterephthalate 		Films (magnetic tape), fibers, and clothing
(Thermoset variation)		Boat and auto body parts (fiberglass), helmets, and chairs
Polyamides		
Nylon 6,6 		Carpets, parachutes, rope, gears, insulation, and bearings
Kevlar, or poly p-phenyleneterephthalamide (PPTA)		Fibers, bulletproof vests
Other common polymers		
Polyacetal		Gears and machine parts
Polycarbonate		Lenses, helmets, lamp casings, machine parts
Phenolformaldehyde		Casings, (motor and telephone), electrical components, distributor caps
Polyurethane [R, R' → complex molecules]		Foam, sheet and tubing, in-line skate wheels
Epoxy		Adhesives, used in composites

P7

Relation with adjacent groups



$-\overset{R}{\underset{H}{C}}-\overset{H}{\underset{R}{C}}$ OR $-\overset{R}{\underset{H}{C}}-\overset{R}{\underset{H}{C}}$?

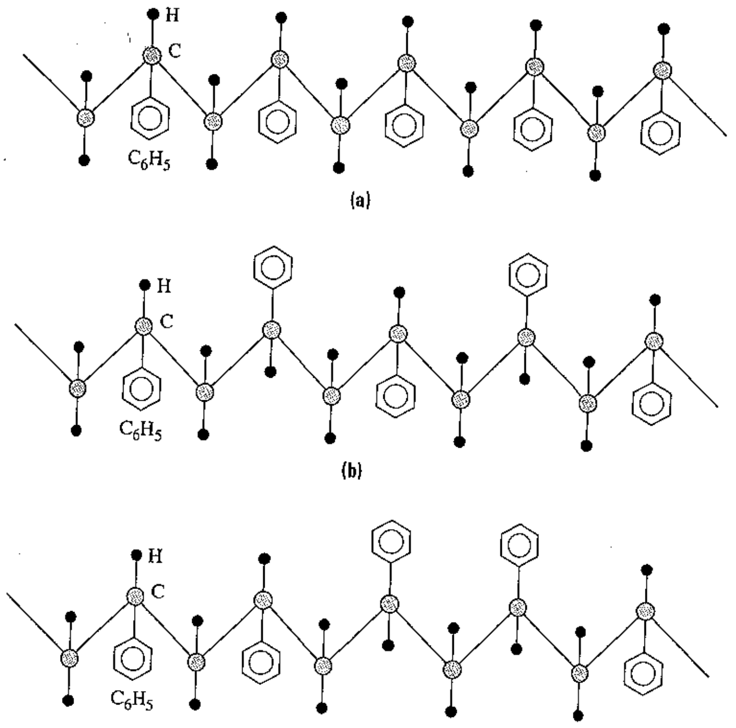


FIGURE 6.4–5 A planar illustration of the **(a)** isotactic, **(b)** syndiotactic, and **(c)** atactic configurations of polystyrene. Note: The C_6H_5 rings are actually much larger than indicated in these sketches.

....

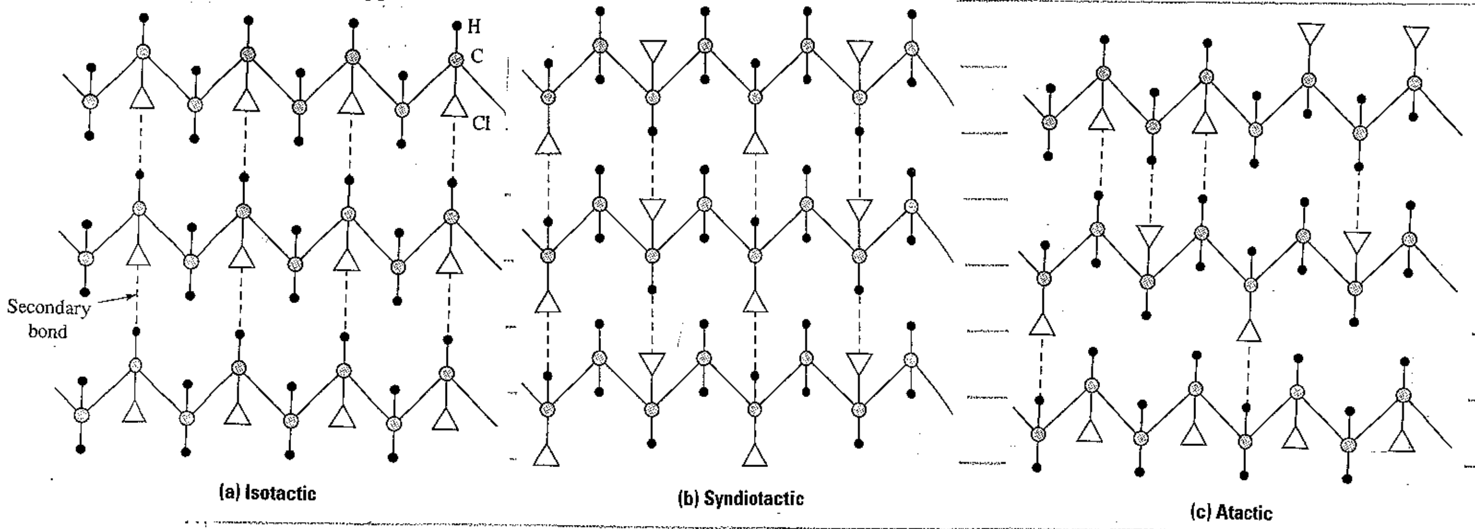
ISOTACTIC

SYNDIOTACTIC

ATACTIC
Random.

it's decided during production

TACTICITY (STEREOCHEMISTRY) ~~[illegible]~~ depends on polymer formation (can be modified randomly at HIGT TEMP) because they affect secondary bonds:



(a) Isotactic

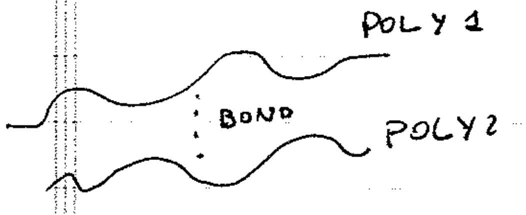
(b) Syndiotactic

(c) Atactic

P11

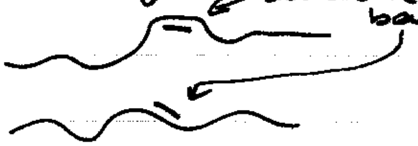
⟹ CRYSTALS ?
Some do!

THERMO PLASTIC & THERMOSET

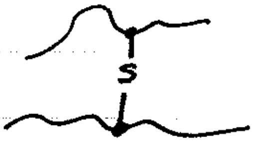


BOND: 1) secondary ; (VDWAALS , DIPOLE) ⇒ weak, can be destroied by Temperature ⇒ T ↑ ⇒ polymer melts
THERMOPLASTIC (TP)

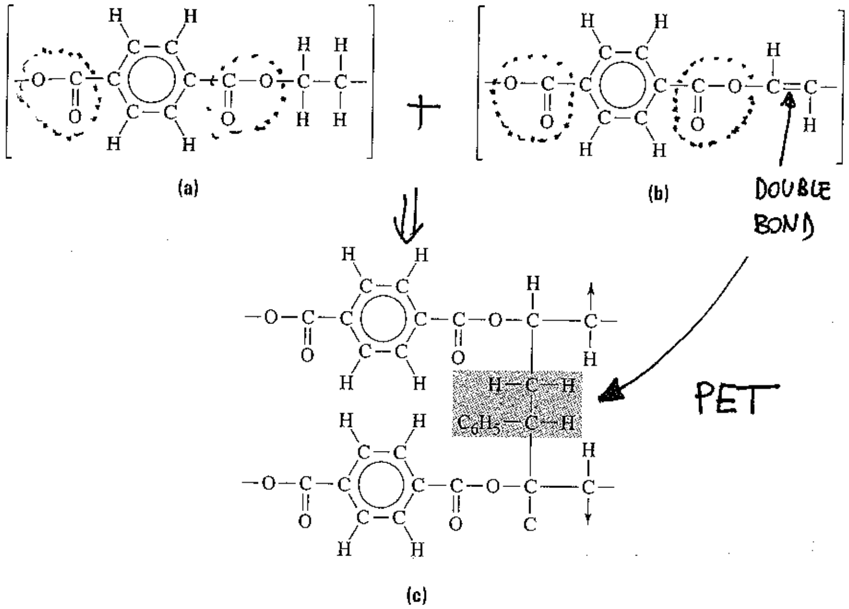
2) primary ← double bonds inside chain



T ↑ + extra atoms
⇒ BREAK double Bonds inside chain ⇒
create EXTRA BOND
CROSS LINK
THERMOSET (TS)



UNSATURATED: HAVE C=C

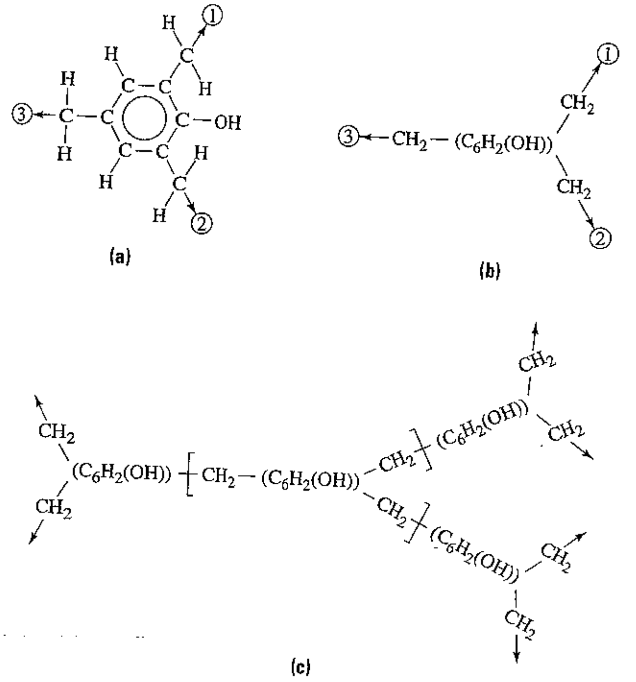


(a) (b) (c)

PET

PHENOLFORMALDEIDE (BAKELITE)

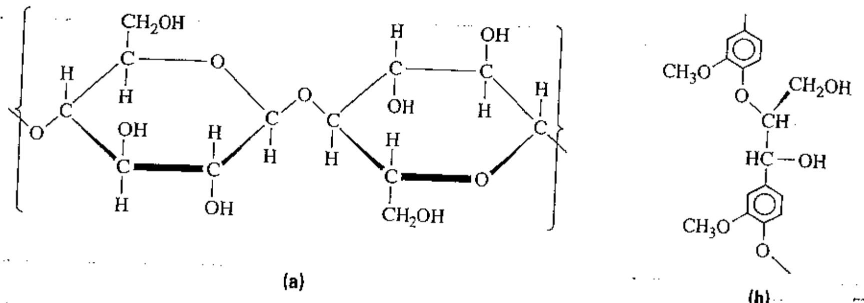
PHENOLFORMALDEIDE (BAKELITE) ⇒ ~~NO~~ POLYMER SURFACE



(a) (b) (c)

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 bold formation with neighboring mers), **(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.

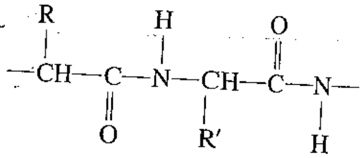
CELLULOSE



(a) (b)

FIGURE 6.4–3 **(a)** The structure of cellulose, and **(b)** schematic of the structure of lignin.

PROTEINS



$$-\underset{}{\overset{R}{\overset{|}{CH}}}-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\underset{\underset{R'}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$$

—DIFFERENT R&R' makes different aminoacids!

MOLECULAR WEIGHT

$$\left.\begin{array}{l}1 \text{ mer} = m \\ \# \text{ degree of polimerization } n\end{array}\right\} (\text{MER})_n \Rightarrow M = mn$$

if a bunch of different polymers $\bar{M}$
⇒ different molecular weights ⇒

$N_i = \#$ of polymers with weight M_i ⇒ $\boxed{\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}}$

different definition:
w_i = total weight of polymers
with weight M_i ⇒ $w_i = N_i M_i$ ⇒ $\boxed{\bar{M}_W = \frac{\sum w_i M_i}{\sum w_i}}$

$\boxed{PD = \bar{M}_W / \bar{M}_n}$ PD = 1.0 ⇒ all same polymers.
Polydispersion

~ 2 to 20

POLYMERS CONFIGURATION

very rarely they are linear —X—
usually KINKED :

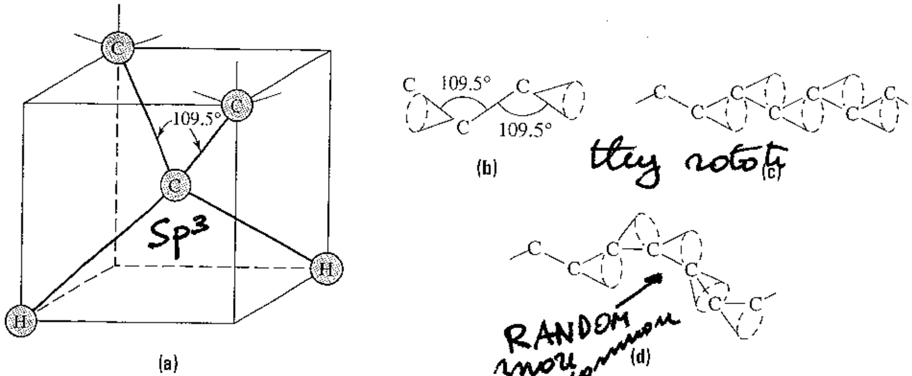
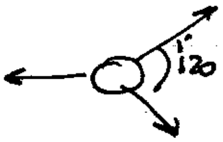


FIGURE 6.4–4 The 3-D structure (conformation) of a polyethylene chain. **(a)** The C—C—C bond angle in PE. **(b)** The bond angle does not define the location of the neighboring C atoms but only restricts their location to a specific cone of rotation. **(c)** If all of the C atoms in the chain backbone lie in the same plane, the planar zigzag conformation results. **(d)** The more common (lower-energy) conformation of PE is the random coil structure.

C sp² is



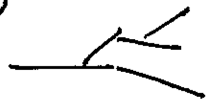
CRYSTALLIZATION OF Pol.

THERMOPLASTIC partially crystallize

-> go T↑ and cool slowly.

CRYSTALLIZATION DEPENDS ON

1) SIZE OF SIDE GROUPS (R)
2) EXTENT OF BRANCHING



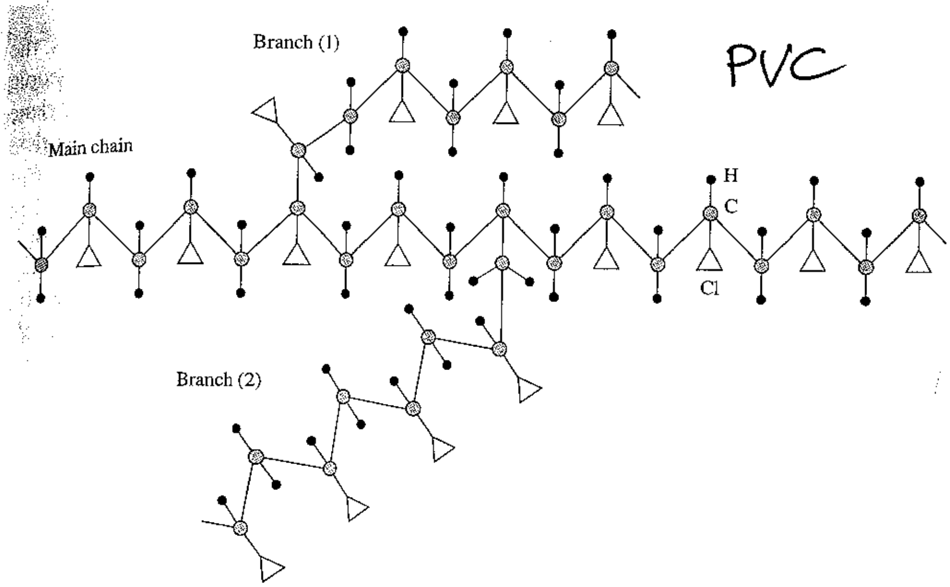
DEFECTS.

3) TACTICITY
4) COMPLEXITY OF MER
5) TYPE OF SECONDARY BONDS (DIPOLE OR VdW)

1) SIZE — small polymers crystallize better
simple polymers crystallize better

POLY PROPYLENE $-(C_2H_3(C_2H_3))_n-$
crystallize less than
POLY ETHYLENE $-(C_2H_2\ C_2H_2)-$

2) BRANCHING



PVC

FIGURE 6.4–7 A schematic illustration of chain branching in polyvinylchloride.

More branches less crystal!!
small concentration of branches
⇓
branches ⇒ more open spaces, polymer less compact!!

HIGH density PE ⇒ STRUCTURAL

LOW density PE ⇒ storage Box Bags

3) TACTICITY affects crystallization

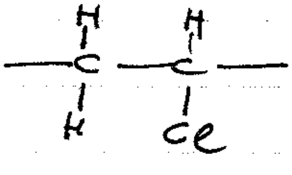
Atactic (Random) with big side groups cannot ~~easly~~
easily be packed.
It's easier to pack ~~isota~~ ISOTACTIC (-ııııı)
and SYNDIOTACTIC (-╵╷╵╷╵╷-)

⇒ this influences property.
Ex: POLYPROPYLENE ISOTACTIC (~50% crystalline) = HARD & RIGID
POLYPROPYLENE ATACTIC (~0% crystalline) = USELESS gummy substance

4) COMPLEXITY OF MER
big repeated unit (mer) ⇒ need more extensive chain segment to create L.R.O.
⇓
⇒ they crystallize slowly.
Then short mer

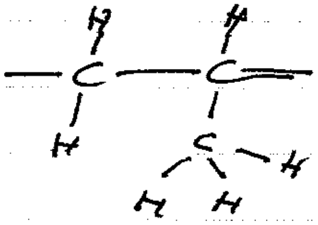
5) TYPE OF SECONDARY BONDS
existence of small space polar side groups
helps formation of crystals

⇒ Ex



POLY VINIL CLORIDE

crystallize better than

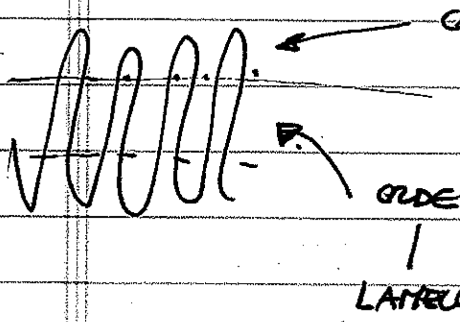


POLYPROPYLENE

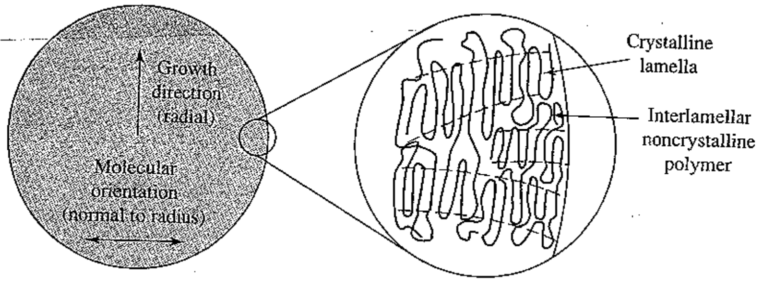
⇒ PVC stronger than PP

SEMICRYSTALLINE POLYMER

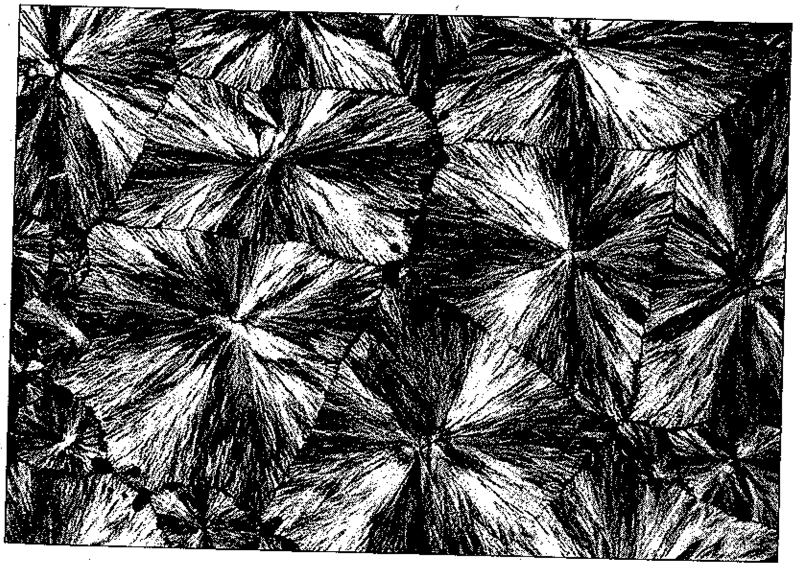
polymers = long spagetti need to roll up



~~SPER~~ SPHERULITE
= AGLOMERATE OF
LAMELLAE
+ INTERLAMELLAR NONCRYSTALLINE POLYMER



(a)



(b)

SEMY CRISTAL

⇓

X_i DEGREE OF CRISTALLINITY
= % of the polymer that is crystaline

(METAL, CERAMICS $X_i \sim 99\%$)
POLY ~ 40 to 95%
non crystal ~ 0%

T_{gloss} V.S. $T_{melting}$

Simple rule: longer MERS, HEAVIER side groups $\Rightarrow$ ~~lower~~ increase T_g (RUBBER simple and light)

because you need higher T to get the "motion" going on.

in ADDITION Symmetric MER (C_2H_4 PE ~~for~~ instance)

$$T_g \sim \frac{T_m}{2}$$

Asymmetric MER ($-C_2H_3Cl$ PVC)

$$T_g \sim T_m \frac{2}{3}$$

IT'S an entropy EFFECT (symmetric MER HAS ONE MORE DEGENERATION → $S = k \log \Omega$ is ↓ for symmetric !!)

TABLE 6.5–3 Observed melting and glass transition temperatures for selected polymers.

Polymer	T_m (°C)	T_g (°C)
High-density polyethylene	137	−120
Polyvinylchloride	—	87
Polypropylene	170	−16
Polystyrene	240	110
Polyacrylonitrile	320	107
Polytetrafluoroethylene	327	—
Polychlorotrifluoroethylene	220	—
Polymethylmethacrylate	—	100
Acetal	181	−85
Nylon 6,6	265	50
Cellulose acetate	230	—
Polycarbonate	230	145
Poly(ethylene terephthalate)	255	90
Silicone	—	−123
Polybutadiene	120	−90
Polychloroprene	80	−50
Polyisoprene	30	−73

GLASSES
STRUCTURE & PROPERTY

take a piece of a window ⇒ X-RAY, wait it becomes

crystalline

RANDOM

$(SiO_4)^{4-}$

tetrahedra OR SiO_2

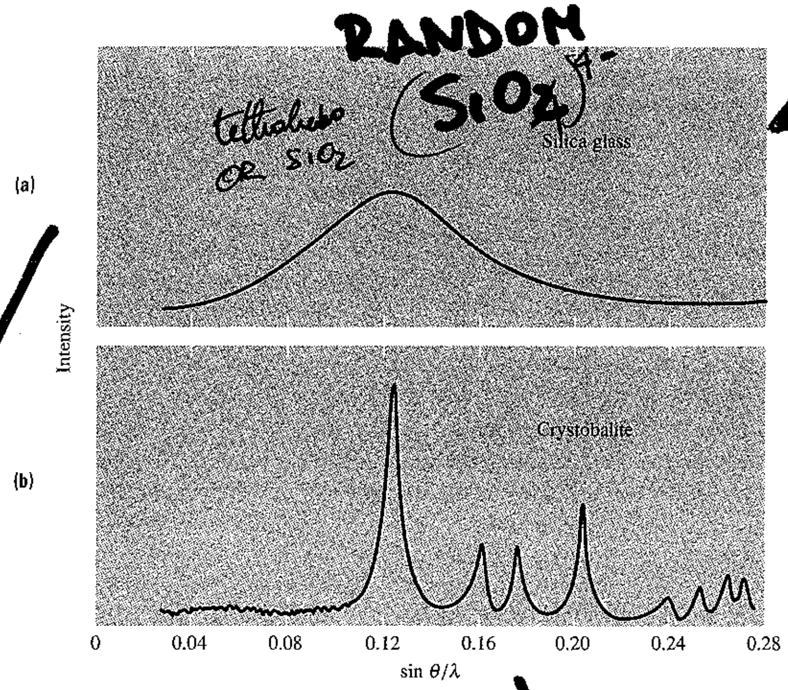


FIGURE 6.5–1 A comparison of the X-ray scans for **(a)** amorphous silica and **(b)** a crystalline polymorph of silica (crystobalite). *(Source: Adapted from B. E. Warren and J. Biscal,* Journal of American Ceramic Society, *2149, 1938.)*

Silica glass = covalent bonding

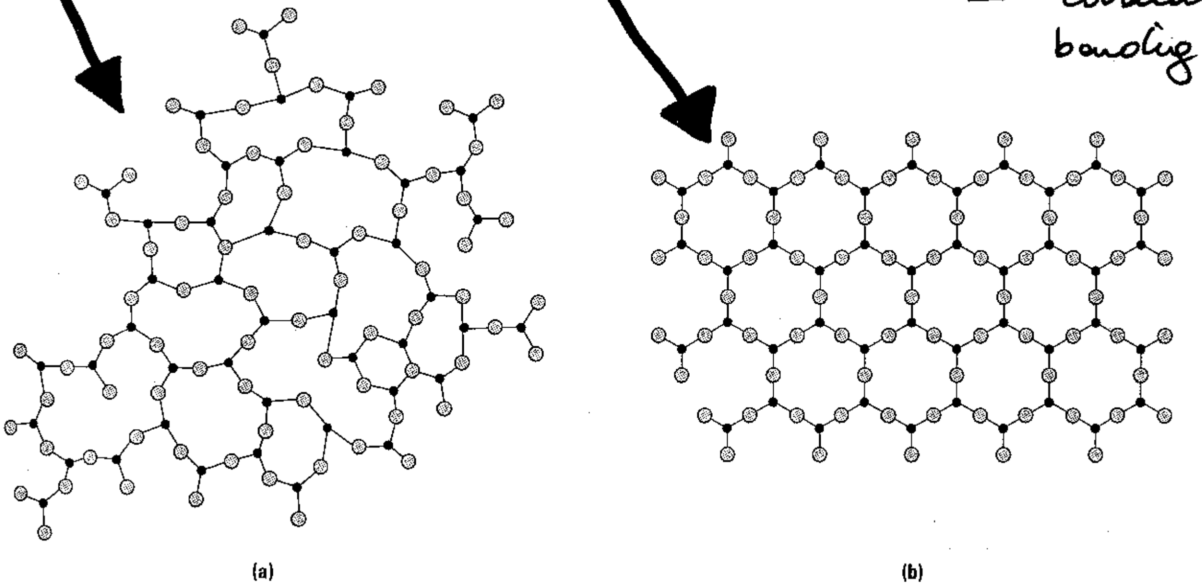


FIGURE 6.5–2 The 2-D representations of **(a)** silica glass and **(b)** a crystal of silica.

P16

Glass: variety of materials (AMORPHOUS) ≡ RANDOM

∀ ⇒ 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 ~~BE~~ BECOME ORDERED FAST,

(MELT MUST BE VISCOUS)

TABLE 6.5–1 Glass-forming systems.

Elements:	S, Se, P
Oxides:	B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, Sb_2O_3, In_2O_3, SnO_2, PbO_3, and SeO_2
Halides:	BeF_2, AlF_3, $ZnCl_2$, Ag(Cl, Br, I), Pb(Cl_2, Br_2, I_2), and multicomponent mixture
Sulfides:	As_2S_3, Sb_2S_3, CS_2, and various compounds of B, Ga, In, Te, Ge, Sn, N, P, and B
Selenides:	Various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, and P
Tellurides:	Various compounds of Tl, Sn, Pb, As, Sb, Bi, and Ge
Nitrides:	KNO_3-$Ca(NO_3)_2$ and many other binary mixtures containing alkali and alkaline earth nitrates
Sulfates:	$KHSO_4$ and other binary and ternary mixtures
Carbonates:	K_2CO_3-$MgCO_3$ ← STATUES
Polymers:	Polystyrene, polymethylmethacrylate, polycarbonate, polyethylene terephthalate, and nylon
Metallic alloys:	Au_4Si, Pd_4Si, (Fe-Si-B) alloys

← OXIDES

Source: Robert H. Doremus, *Glass Science*, 1st ed., Copyright © 1973 by John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.

IONIC GLASSES

If IONIC COMPOUND CAN LIVE IN A DISORDERED STATE, ⇒ CAN FORM GLASSES

EXAMPLE: OXIDE GLASSES (SiO_2) for which a set of RULES WAS DEVELOPED IF OXYGEN + METAL IS PRESENT

ZACHARIASEN RULES FOR IONIC OXIDE GLASSES

NEED NETWORKS : METAL + OXIGEN.

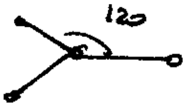
1) OXIDE GLASS NETWORKS ARE COMPOSED OF OXYGEN POLYHEDRA → METAL + OXIGEN

2) COORDINATION OF OXYGEN IS 2! $CN(O)=2 \Rightarrow O^{--}$

3) COORDINATION OF METAL IS 3 OR 4

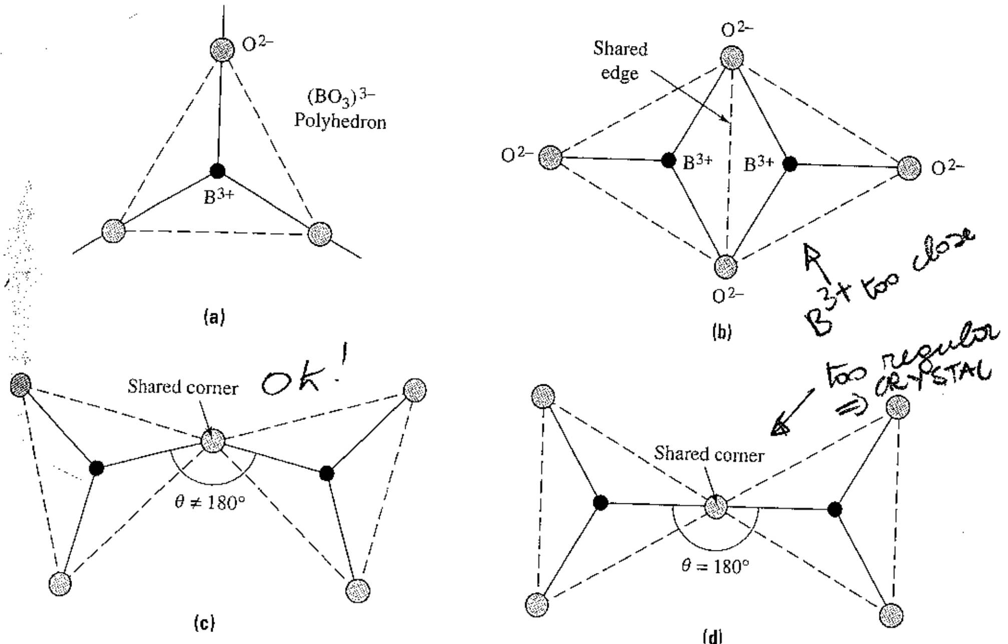
$CN(M) = 4 \Rightarrow$ TETHAHEDRA $(SiO_4)^4$ of SILICA (SiO_2)

$CN(3) = 3 \Rightarrow$ TRIANGLES Li LIKE $(BO_3)^{3-}$ of B_2O_3 Boron oxide



4) OXYGEN POLYHEDRA SHARE CORNERS, NOT EDGE OR FACE (TO MINIMIZE METAL+ REPULSION!!)

5) EACH POLYHEDRA SHARES at least 3 CORNERS



RANDOM NETWORK ⇒ FORMERS

FIGURE 6.5–3 The structure of amorphous B_2O_3: **(a)** the basic building block, a triangular polyhedron $(BO_3)^{3-}$; **(b)** two polyhedra shown 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

last time: ionic glasses & ZACHARIASEN'S Rule for ~~oxide~~ Oxide glasses!

what about covalent glasses:?

MUST BE POLYMERS, ~~with~~ & have $T_g > T_{Room}$ & must be able to COOL DOWN FAST & must have viscous melt,

GLASS = NO DEFECTS

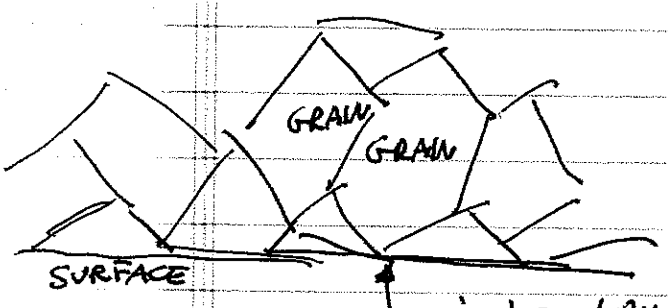
$\xrightarrow{\text{ISOTROPY}}$

TABLE 6.5–3 Observed melting and glass transition temperatures for selected polymers.

Polymer	T_m(°C)	T_g(°C)
High-density polyethylene	137	−120
Polyvinylchloride	—	87
Polypropylene	170	−16
Polystyrene	240	110
Polyacrylonitrile	320	107
Polytetrafluoroethylene	327	—
Polychlorotrifluoroethylene	220	—
Polymethylmethacrylate	—	100
Acetal	181	−85
Nylon 6,6	265	50
Cellulose acetate	230	—
Polycarbonate	230	145
Poly(ethylene terephthalate)	255	90
Silicone	—	−123
Polybutadiene	120	−90
Polychloroprene	80	−50
Polyisoprene	30	−73

SEMICONDUCTORS: usually build from crystals (reduce defects to increase μ), but when μ is not a problem then we can use amorphous semiconductors

EXAMPLES: Solar cells, need surface ⇒ very expensive Si crystalline, but amorphous Si works fine & no grain boundaries which are the places where corrosion starts!!



grain boundary @ surface ⇒ start corrosion

METALLIC GLASSES

metals are very fluid once melted

⇒ hard to remove heat fast

Removing 10^5 K/s (huge) we can make max 20% glass of a metal material ⇒ 80% crystalline metal & 20% glassy metal!!

⇒ ONLY SMALL PARTS & STRIPS & RIBBONS & WIRES

IF I ~~MEET~~ DOPE WITH A NON METAL OR BAD METAL

Au-Si (80 & 20), Fe Si B (78, 9, 13) ⇒ then the melt is more viscous and easy to form glasses.

GLASSY METALS are sensitive to heat!! HEAT destroy the glass & becomes metal crystalline!!

Again glass metals have no grain boundary ⇒

1) strong against corrosion
2) isotropic properties (used for magnetic applications)

METALLIC FOAMS

increase temperature, melt, and decrease fast while <u>bubbling</u> with inert gas ⇒ METALLIC FOAMS, LIKE SPOUNGES

USED FOR BIOMATERIALS (BONES) ⇒ STRONG & ADSORBENT & LIGHT

↑ good ↑ tissue ↑ good

RUBBERS & ELASTOMERS

it's when $T_g < T_{room}$, but NOT ONLY

REMEMBER

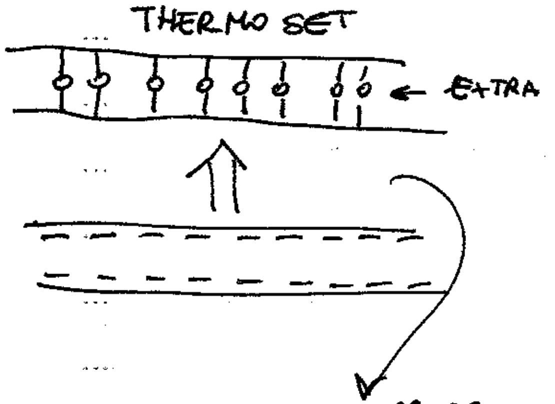
THERMOPLASTIC ⇒ no secondary bonds, ⇒ when $T > T_g$ viscosity deformation

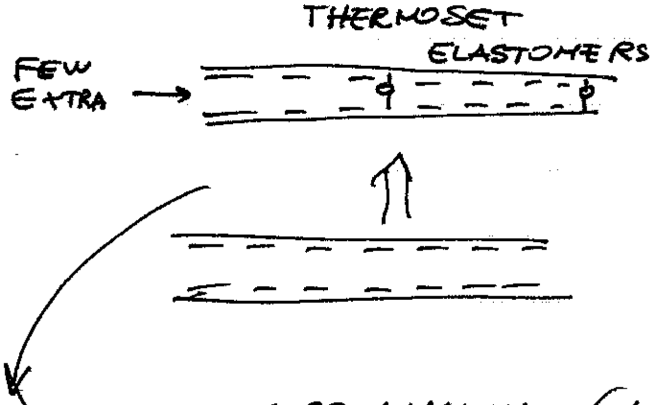
THERMOSET ⇒ PLENTY OF ~~secondary~~ double bonds ⇒ $T > T_g$ get cross linked!! and material gets strong

THERMOSET ELASTOMER

⇒ have few available bonds to mate

few cross links





MUCH CROSS LINKING (1/10)

⇓

HEAVY BRITTLE STIFF

LITTLE CROSS LINKING (1/1000) (1/100000)

⇓

SOFT, RUBBER, RUBBER BAND STYLE!!

CONTROLLING CONCENTRATION OF "EXTRA" WE CAN CONTROL FINAL PRODUCT

⇓

MEDIUM (1/100)
~ TIRES FOR CARS!

THERMOSET ELASTOMERS DO NOT REALLY MELT, THEY GET STIFFER & THEN BURN!

P21

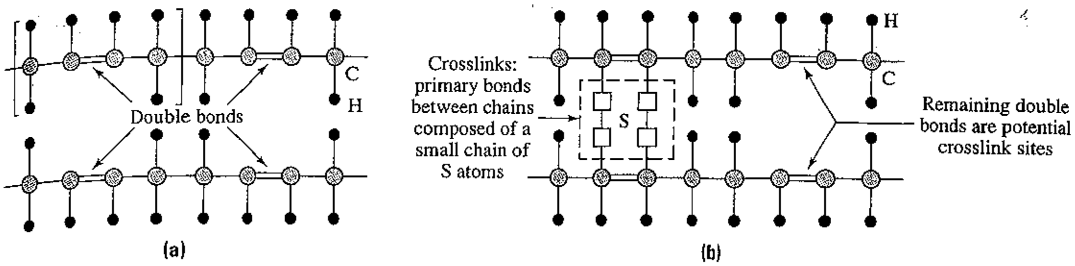
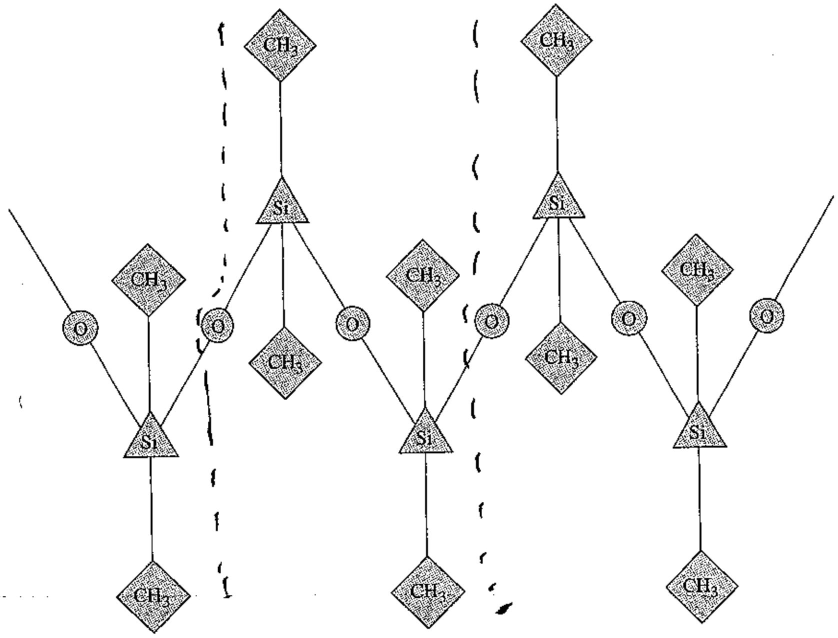


FIGURE 6.6–1 The structure of polybutadiene: **(a)** as a thermoplastic polymer, and **(b)** as a crosslinked rubber.



↑ SILICONE RUBBER (CAULKING COMPOUNDS)

POLY DYMETHYL SILOXANE

Si + Oxygen

THERMOPLASTIC ELASTOMERS

when Thermoplastic is heated, becomes viscous : loses slope

=> HOW CAN WE FIX THE SHAPE AND MAKE IT ELASTIC?

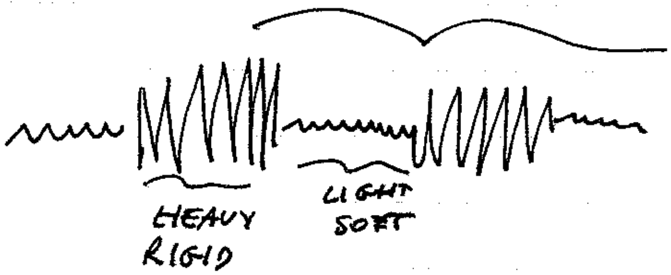
=> NEED TO FIGHT VISCOSITY KEEPING ELASTICITY

BLOCK COPOLYMERS !!

$$\underbrace{(\text{MER A}) \cdots (\text{MER A})}_{A \quad N_A \text{ times}} - \underbrace{(\text{MER B}) \cdots (\text{MER B})}_{B \quad N_b \text{ times}} - (\text{MER A}) \cdots$$

↓ KEEP FLEXIBLE & NOT CROSS LINKED! =>

↓ DOUBLE BONDS (UNSATURATED) SO IT MAKES CROSS LINKS & GETS HARD & RIGID



=> ELASTIC & when high temperature melts because the light & soft mers (no secondary bonds) but at lower temperature is elastic

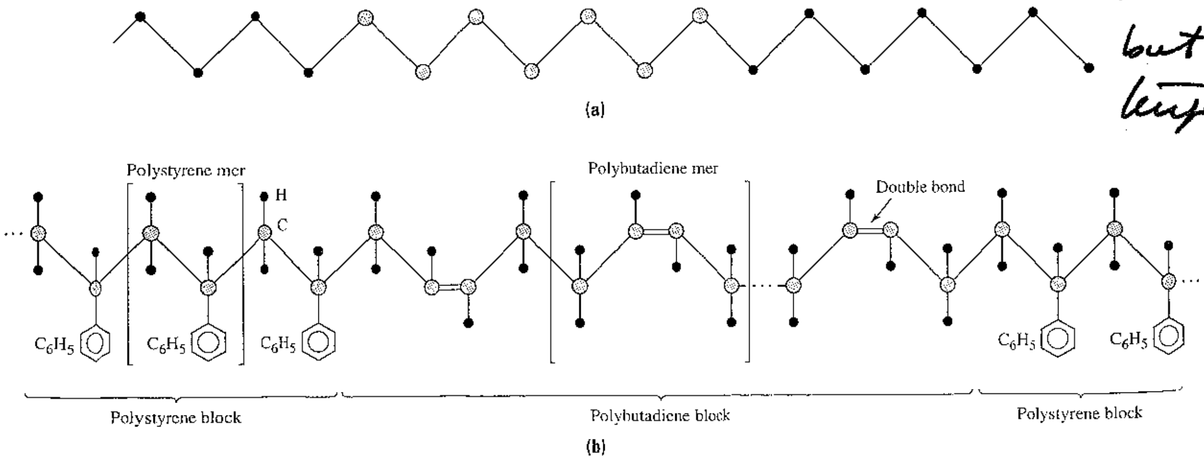
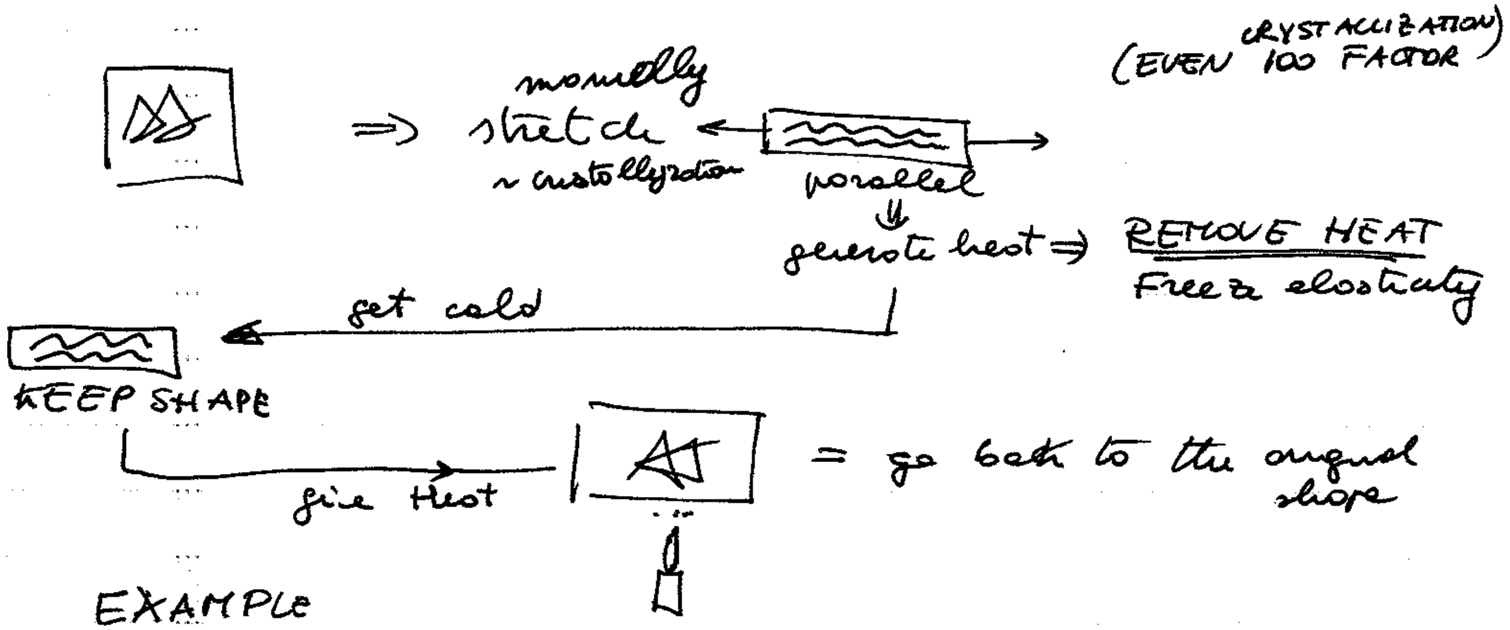


FIGURE 6.6–3 Copolymers and thermoplastic rubbers: **(a)** a schematic illustration of a block copolymer, and **(b)** the structure of the triblock copolymer thermoplastic rubber polystyrene-polybutadiene-polystyrene.

can decide property with size of BLOCKS!

P23

CRYSTALLIZATION OF RUBBERS



EXAMPLE

THERMOSHRINKING MATERIALS !! usefull in electronics

PIPES that shrink with heat gun !!

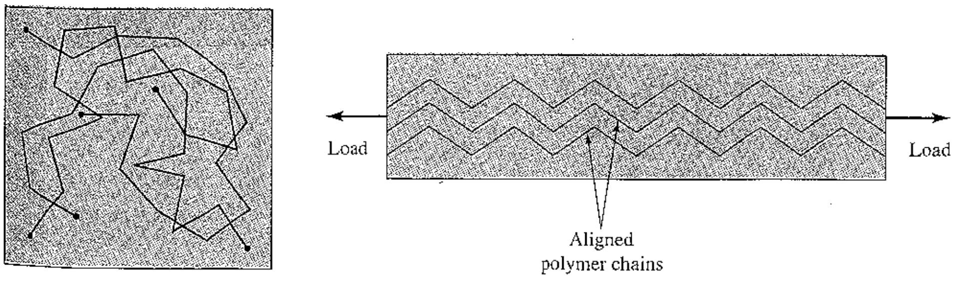
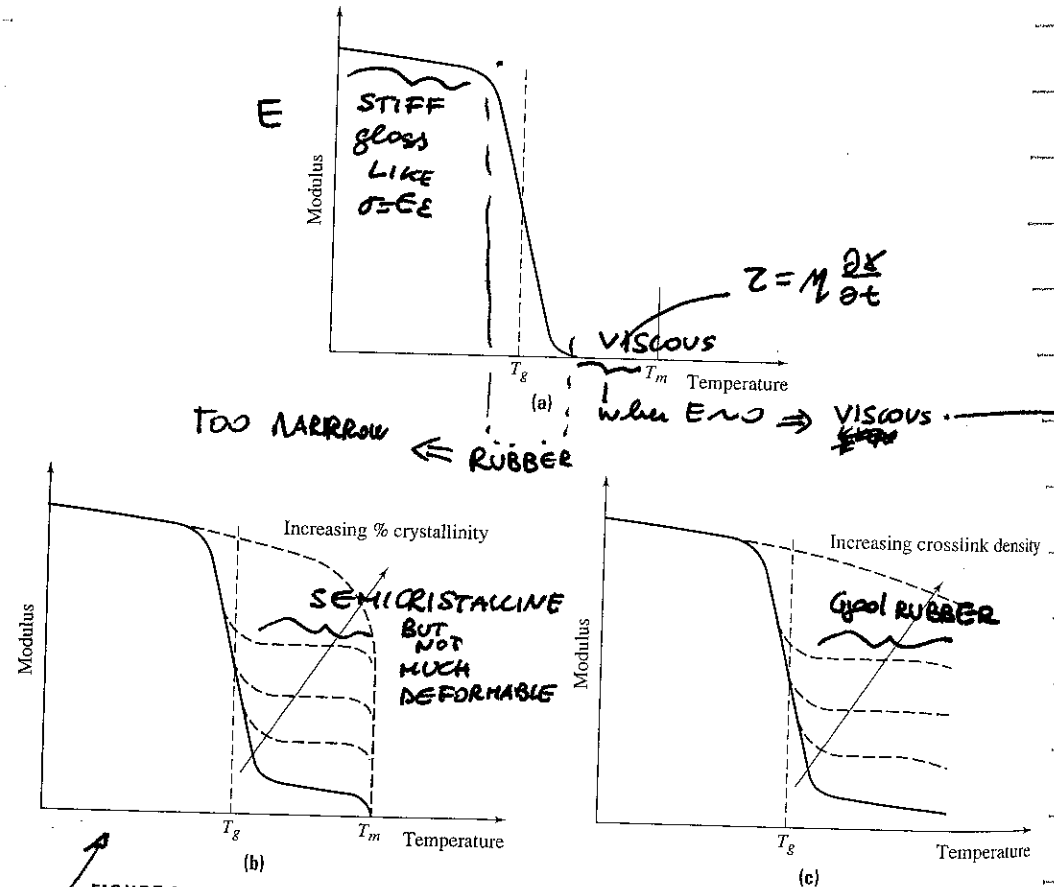


FIGURE 6.6–4 Changes in polymer structure as a result of an applied load: **(a)** unaligned chains in an unloaded polymer, and **(b)** chains aligned under an applied load.

YOUNG'S MODULUS & TEMP

$\sigma = E\varepsilon$

$E(t)$



VISCOSITY
NEWTON LAW'S

good RUBBER
MODERATE CROSS-LINK,
BUT NO 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.

EPOXIES & PHENOLICS

with semicrystalline and cross-link density the glossy transition "disappears", softens!!

RUBBER ELASTICITY

ELASTOMERS = stretch 10 times and come back to original shape !!

HOW? stretching original fiber directions

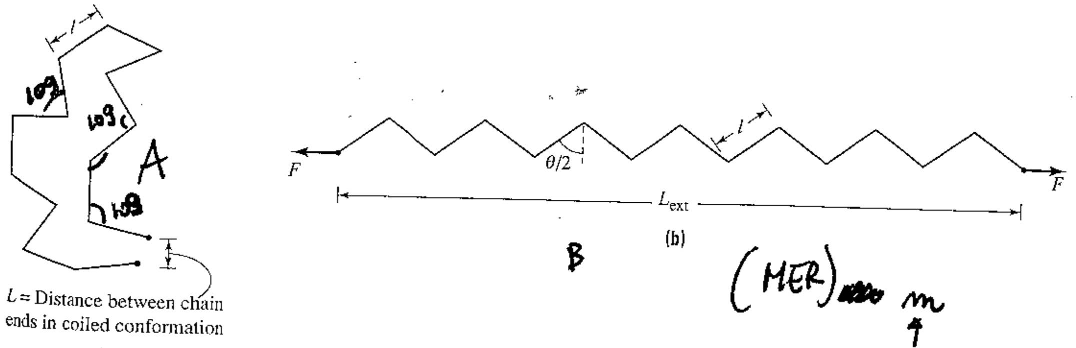


FIGURE 6.6–6 A comparison of **(a)** the random coil conformation of an unstretched rubber, and **(b)** the stretched, or planar zigzag, conformation in which the separation distance between the chain ends is maximum.

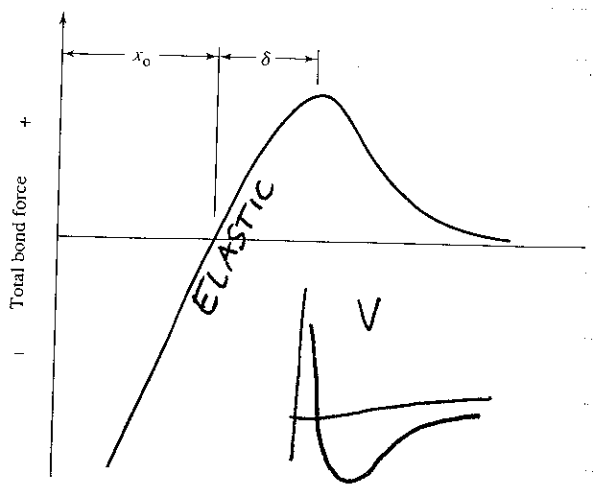
Stretch A to get B S_A & S_B (which is Bigger)

Rearrangement of bond directions!

PRODUCE OR ADSORB ~~HEAT~~ ?

NO elongation of Bonds O~~O ⇒ O~~~~O NO

therefore ~~no~~ ELASTIC ENERGY, does not go in bond stretching but in ENTROPY CHANGE



← FROM BOND STRETCHING ONLY FEW %

now all log°s of $C\overset{C}{\underset{\vartheta}{\wedge}}C$ are along the same direction!!!

$$\Rightarrow \quad L_{ext} = m\,\ell \cos\left(\frac{\vartheta}{2}\right) \quad \text{for extended}$$

$$L_{COILED} \simeq \ell\sqrt{m}\,\frac{1+\cos\vartheta}{1-\cos\vartheta} \qquad L_{COILED} \lll L_{EXT}$$

$$m \gg 1 \Rightarrow \sqrt{m} \gg 1$$

$$\text{Max strain} = \frac{L_{EXT} - L_{COIL}}{L_{COIL}} = \frac{L_{EXT}}{L_{COIL}} - 1 \simeq \underline{\underline{1.15\sqrt{m} = HUGE}}$$

$$m \simeq 10^2 - 10^5$$

~~m~~

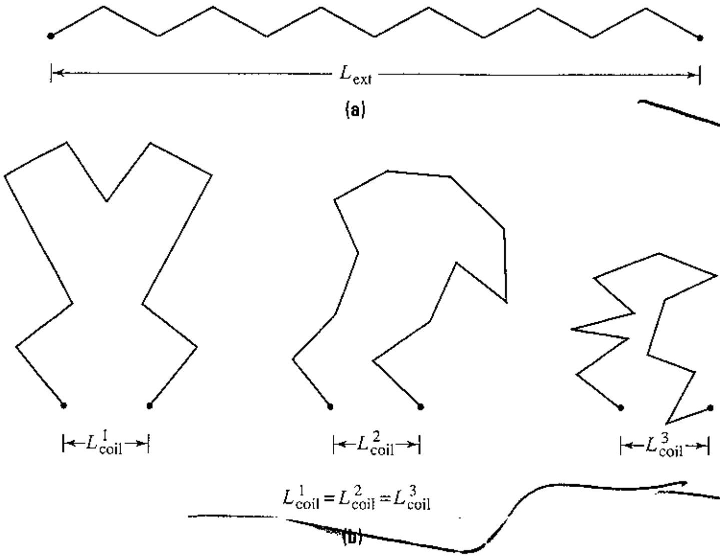
Max strain ~ 10 to 300 times

HUGE

all elastic energy goes in uncoiling.
ENTROPIC EFFECT

$$S = k \log \underset{\sim}{\Omega(E)}$$

# of configurations with Energy E



→ 1 confi
S ~ 0

→ many conf
S = HIGH

FIGURE 6.6–8 A comparison of the number of equivalent conformations for **(a)** the planar zigzag conformation and **(b)** a partially coiled chain.

on stretching S↓
$\Rightarrow T\Delta S \rightarrow \Delta Q$ produced

P27

ELASTOMERS SHRINK UPON HEATING

PHASE EQUILIBRIA & DIAGRAMS

(NOT interesting for polymers)

→ many identical "things" JOIN together creating PHASES!
└ atoms, molecule.

PHASE = A CHEMICALLY & STRUCTURALLY HOMOGENEOUS REGION OF THE MATERIAL

→ if I change 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 SUBSTANCE"

EXAMPLE • take PURE Al

pure Al ⇒ forms FCC structure

⇒ 1 COMPONENT (Al) @ 1 PHASE (SOLID FCC)

- TAKE ICE, add water (liquid)

  ⇒ 1 component (H_2O) & 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)

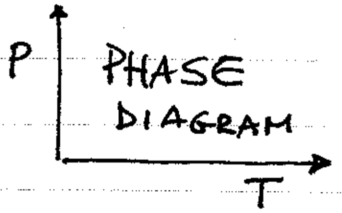
- Window's glass

  $SiO_2 + NaO_2 + CaO \longrightarrow$ 3 components (SiO_2)+(NaO_2)+(CaO_2) & 1 PHASE (amorphous)!

ONE COMPONENT SYSTEM

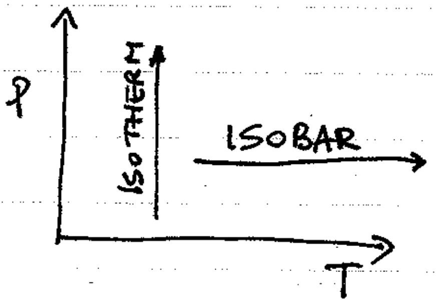
WHAT can I change ? P, T, Comp (No) ⇒ P&T only

how many degrees of freedom ? 2 ⇒



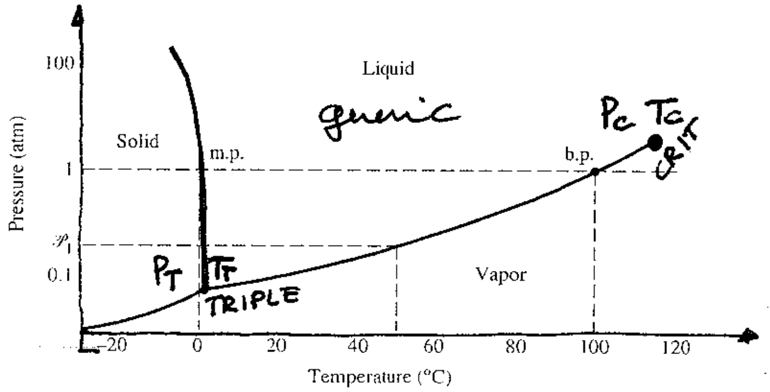
const P = ISOBARS (V const ISOCORES)

const T = ISOTHERMS



ONE COMPONENT PHASE DIAGRAM

LINES = PHASE'S BOUDARIES

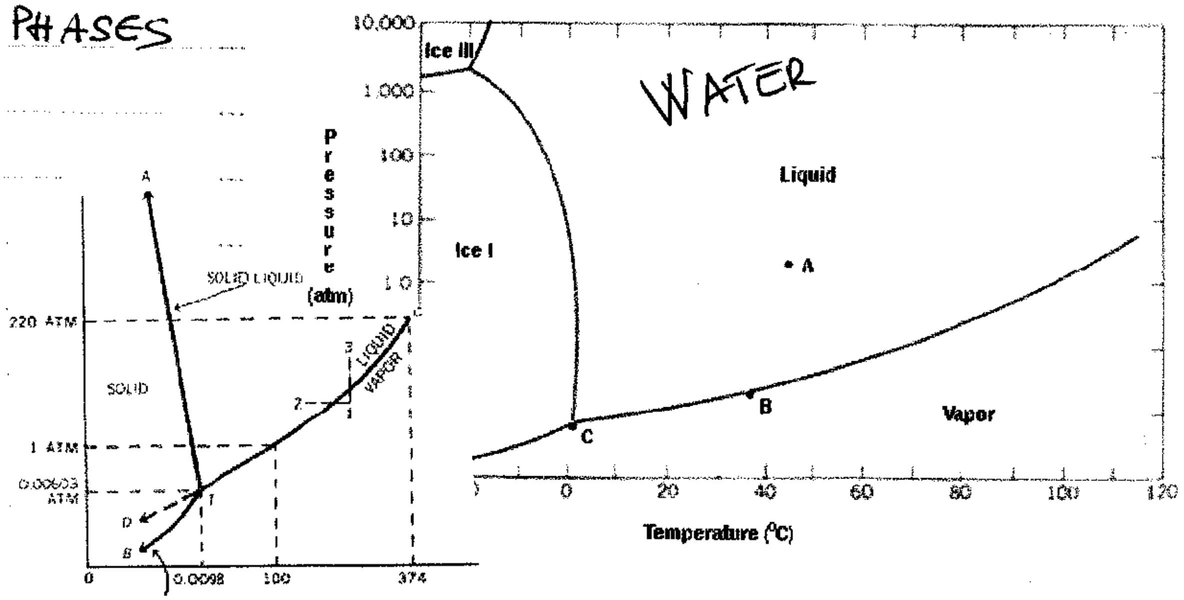


T_T, P_T

TRIPLE POINT

SOLID & LIQUID & VAPOUR COEXIST

REGIONS = PHASES



T_c, P_c

CRITICAL POINT

LIQUID & VAPOUR BECOME A SIMILAR FLUID

PE2

GIBBS PHASE RULE

at Equilibrium

connects the F = # number of degrees of freedom (things that we can change)
with C = # of components
with P = # of coexisting phases:
with 2 = # of state variables (things that we wish to ~~[illegible]~~ change)
P,T

$$F = C - P + 2$$

(if P is Fixed ⇒ $F = C - P + 1$)

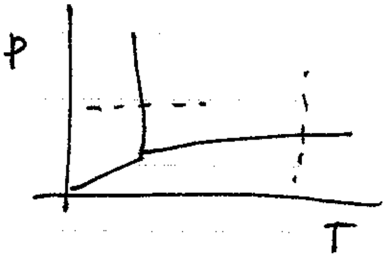
Example: Pick H_2O with water liquid and ice

⇒ $C = 1$ $P = 2$

$F = 1 - 2 + 2 = 1$ ⇒ to have 2 phases I can change only one variable T OR P,

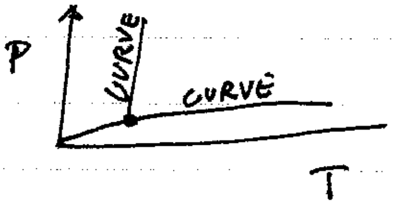
↓

IF I change P, T will follow T(P).
IF I change T, P will follow P(T)



⇒ coexistence of 2 phases, with 1 component leads to a curve 1DIMENSIONAL T(P) OR P(T)!!

LOCUS
↑
need only 1 coordinate to describe!



PE3

2nd Example Pick H_2O ~~at~~ when ICE, LIQUID, VAPOUR coexist ⇒ $C = 1$ $P = 3$

$F = 1 - 3 + 2 = 0$

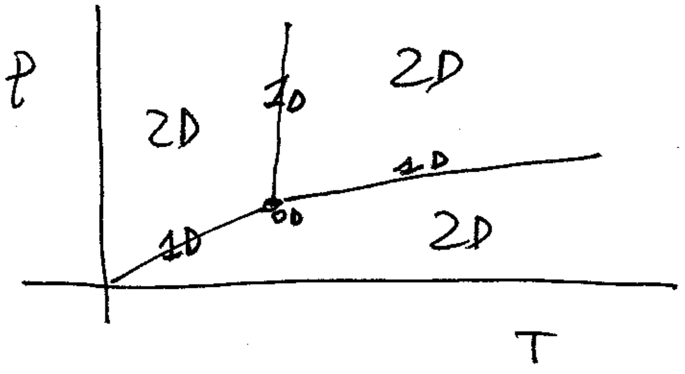
⇒ triple point is a 0Dimensional ~~do~~ ~~lo~~ LOCUS

0D = NO FREEDOM = <u>INVARIANT</u> ⇒ A POINT

3rd Example Pick H_2O vapour ⇒ $C = 1$ $P = 1$

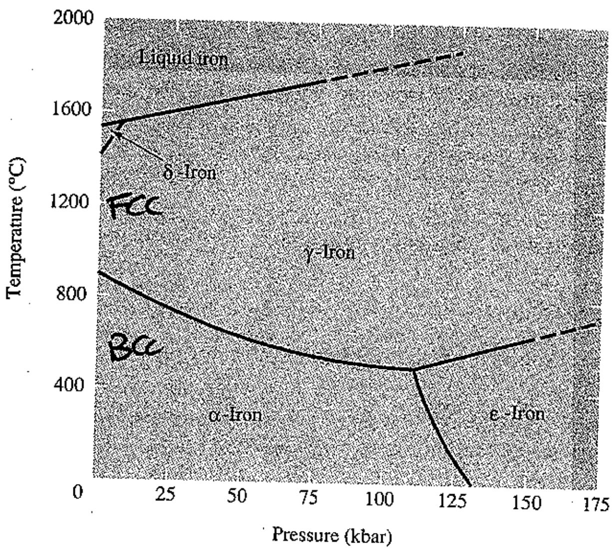
$F = 1 - 1 + 2 = 2$

⇒ Vapour is a 2Dimensional LOCUS, a part of a plane with 2 coordinates to be described ⇒ A REGION

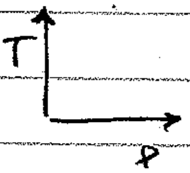


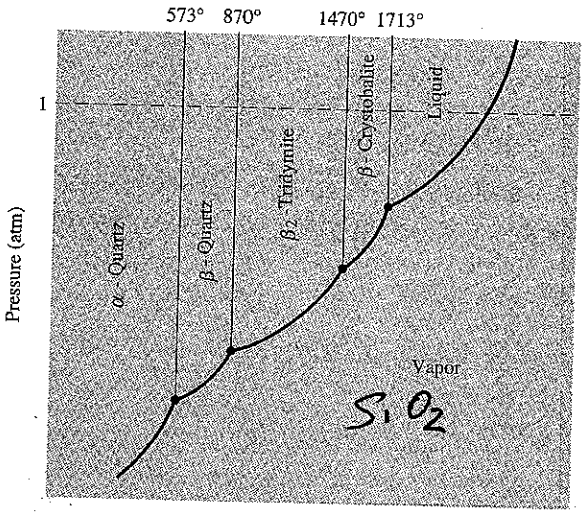
DIMENSION OF THE LOCI

MORE COMPEX ~~SINGLE~~ ONE-COMPONENT SYSTEMS

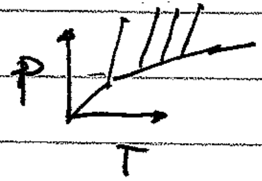


IRON





SiO_2



PE5

TWO-COMPONENT SYSTEMS

as [illegible] can change another variable C!!
concentration of A or B in a MIX of A & B!!

C_A? weight or ATOMIC ?
in weight #atoms

EXAMPLE

$$C_H^a(H_2O) = \frac{2}{2+1} = 2/3$$

$$C_H^w(H_2O) = \frac{2}{2+16} = \frac{1}{9}$$

Concentrations

WEIGHT ⇒ ATOMIC

$$C_A^{at} = \frac{C_A^w / W_A^{at}}{C_A^w/W_A^{at} + C_B^w/W_B^{at}} \quad [\text{in } 100\%]$$

$$C_A^{at} + C_B^{at} = 1$$

W_A^{at} & W_B^{at} atomic weight of A & B

C_A^{at} & C_B^{at} atomic concentrations

C_A^w & C_B^w weight concentrations

ATOMIC ⇒ WEIGHT

$$C_A^w = \frac{C_A^{at} * W_A^{at}}{C_A^{at} * W_A^{at} + C_B^{at} * W_B^{at}} \quad [\text{in } 100\%]$$

$$C_A^w + C_B^w = 1.$$

MOLAR mix n_A MOLES of A & n_B moles of B

$$N_A = n_A/(n_A + n_B) \quad \& \quad N_B = n_B/(n_A + n_B)$$

$$N_A + N_B = 1$$

- SOLUBILITY

put sugar in water = solute & solvent

if $C_{sugar} \leq C_{sugar}^{MAX}$ ⇒ sugar does not precipitate

$\boxed{C_{SUGAR}^{MAX}(T) = \text{SOLUBILITY LINE}}$ → max solute without precipitation

$T\uparrow \; C^{MAX}\uparrow$

$T\downarrow \; C^{MAX}\downarrow$

PE6

SIMPLEST CASE

2-COMPONENTS SYSTEM A&B
ISOMORHOUS 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 MAX 15%
2) ELECTRONEGATIVITIES ARE COMPARABLE
3) VALENCES ARE SIMILAR.
4) CRYSTAL STRUCTURE OF PURE A & B IS IDENTICAL

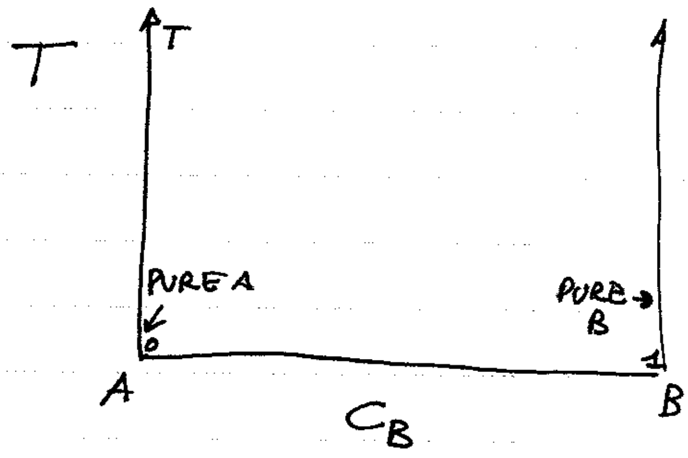
ISOMORPHOUS ⇐ { 1)–4)

Ex Cu+Ni form A SOLID-SOLUTION = RANDOM MIX OF A&B WITH A STRUCTURE

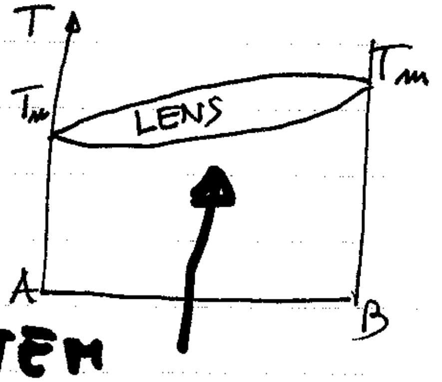
Cu ≃ Ni : they are ISOMORPHOUS

CONSTANT Pressure (1 ATM)

DRAW COMPOSITION DIAGRAM



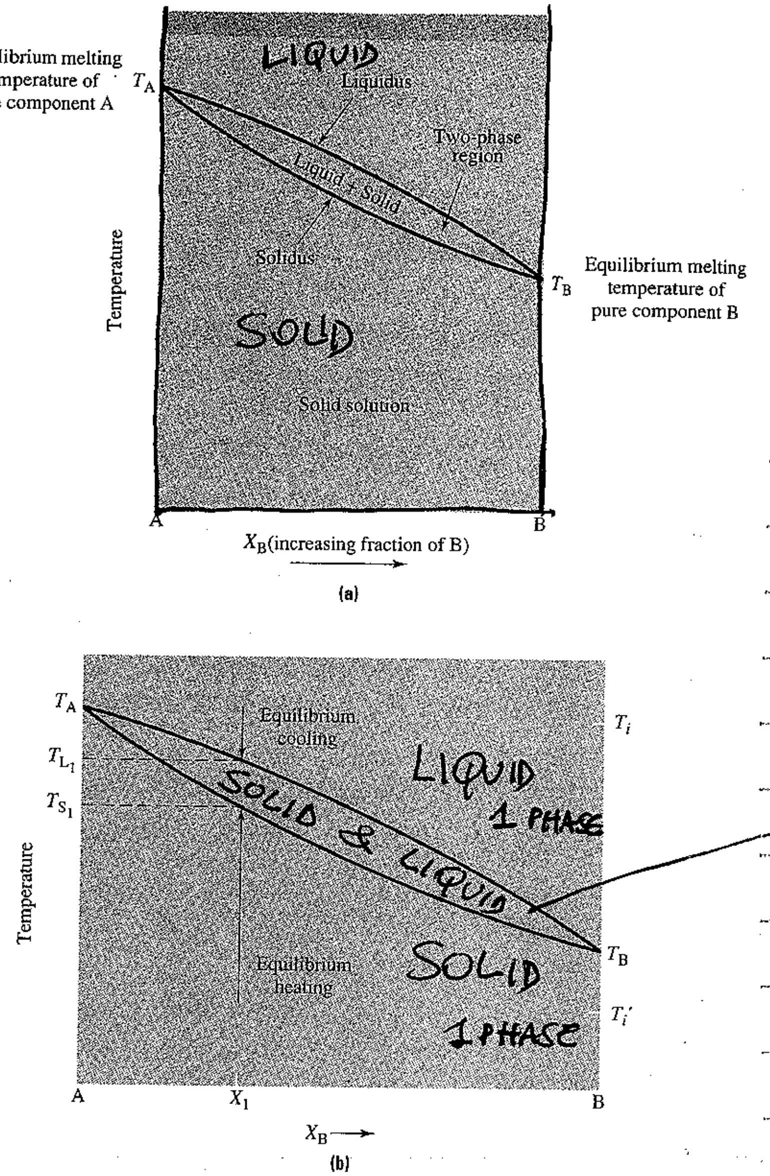
SUPPOSE $T_m(A) < T_m(B)$



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_1.



IDEAL
SYSTEM
=
SOLID SOLUTION
+
LENS

P = cost ⇒ $F = C - P + 1$ **WHY?** ORIGIN IS GIBBS RULE ~~COEXISTENCE~~

LOOK FOR TWO PHASE ~~REGIONS~~ CC

PURE A (OR B)

L $C = 1$ $F = 1 - 2 + 1 = 0$

⇒ POINT @ 2 PHASES COEXISTING HAS NO FREEDOM

⇒ POINT ⇒ $T_m(A)$

MIX A+B → $C = 2$

$F = 2 - 2 + 1 = 1$ ⇒

THERE IS AN INTERVAL (ΔT)

~~FOR WHICH 2 PHASES COEXIST!~~

PE8

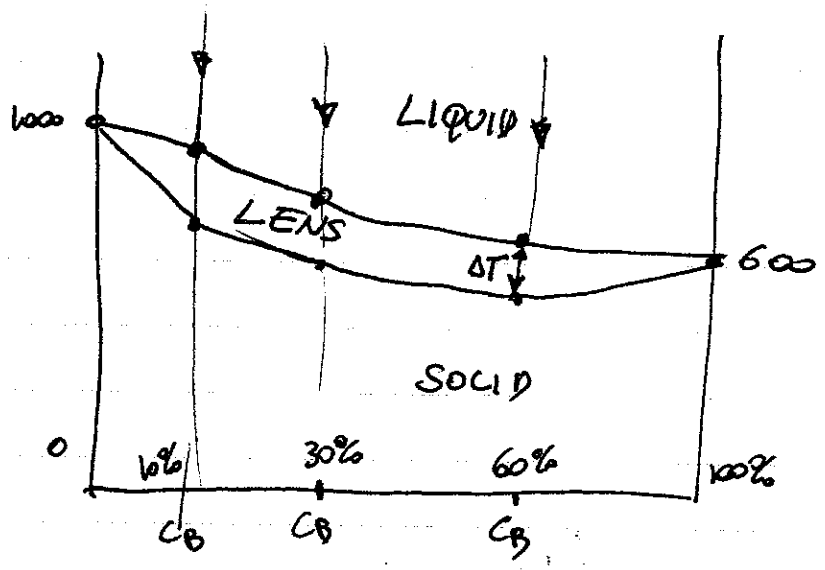
MEASUREMENT SCHEME   PURE A $T_m(A) = 1000$ K

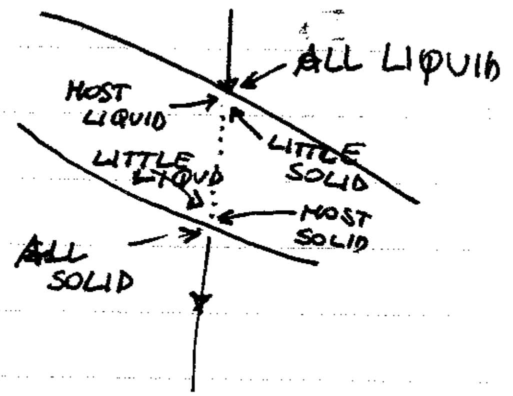
MIX A & B $C_B = 10\%$ $\Rightarrow$ 2 PHASE INTERVAL [900, 700] K

$C_B = 30\%$ $\Rightarrow$ 2 PHASE INTERVAL [800, 600] K

$C_B = 60\%$ 2 PHASE INTERVAL [700, 500] K

Pure B $C_B = 100$ $\Rightarrow$ $T_m =$ 600°K   2 PHASE POINT





PE9

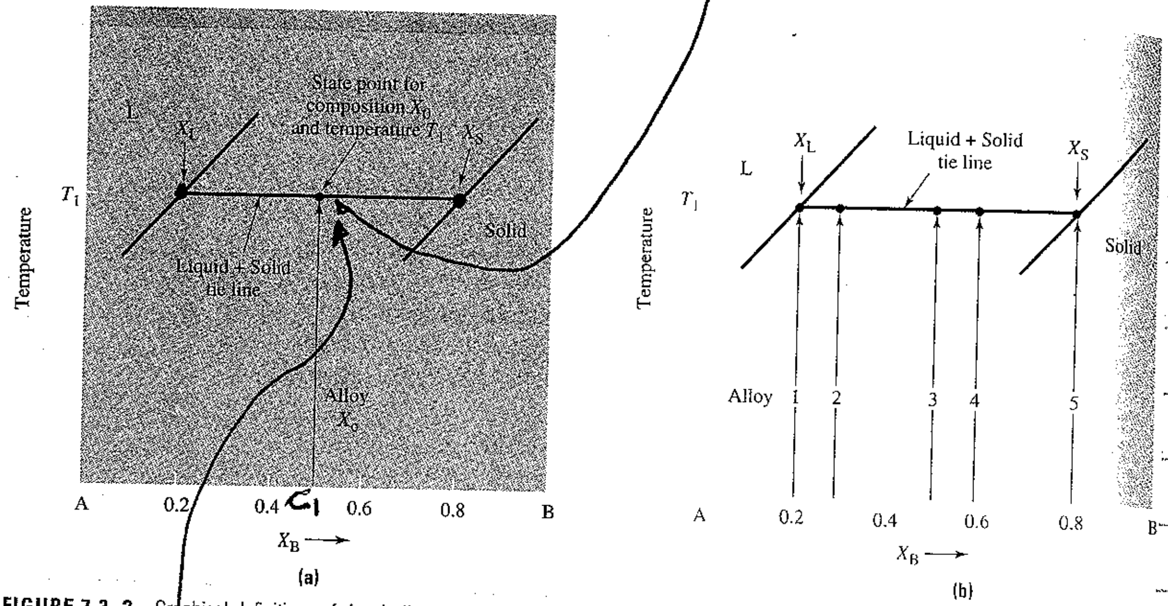
HOW MUCH LIQUID & SOLID AND WHICH COMPOSITION THEY HAVE?

Remember that you are at equilibrium (go up down in Temperature VERY SLOWLY)

INSIDE A 2-PHASES REGION which concentrations?

Pick concentration & Temperature of your MIX

(C, T) = STATE POINT



(a)

(b)

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_0, and **(b)** the same tie line shared by all five alloy compositions at temperature T_1.

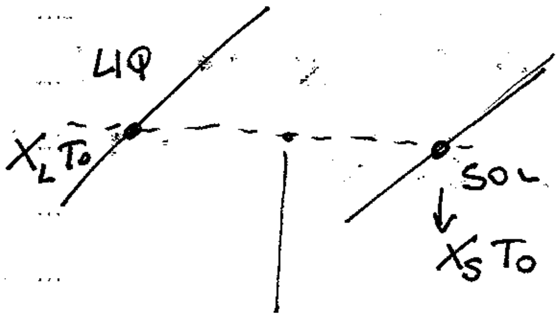
at (T_1, C_1) then is DRAW HORIZONTAL LINE

TIE LINE

C or X (Book uses X so I use X but you should try to use c)

PE 10

LEVER RULE



X = conc of B

$X_0 T_0 \Rightarrow$ Have M_0 mass

$\Rightarrow$ M_L is liquid @ conc X_L

M_S is solid @ conc X_S

$\Rightarrow$ CONSERVATION OF MASS

CONSERVATION OF B

$$\overset{\text{total mass of B}}{M_0X_0} = \overset{\text{tot MASS B in LIQUID}}{M_LX_L} + \overset{\text{tot B in MASS SOLID}}{M_SX_S}$$

$$\Rightarrow X_0 = \left(\frac{M_S}{M_0}\right)X_S + \left(\frac{M_L}{M_0}\right)X_L$$

$$\Downarrow$$

$$X_0 = f_SX_S + f_LX_L$$

CONSERVATION OF TOTAL MASS

$$M_0 = M_L + M_S \Rightarrow 1 = f_L + f_S$$

$$\left\{\begin{array}{l} f_L + f_S = 1 \\ f_SX_S + f_LX_L = X_0 \end{array}\right. \Rightarrow \begin{array}{l} f_SX_S + (1-f_S)X_L = X_0 \\ f_S(X_S - X_L) = X_0 - X_L \end{array}$$

Solutions
But difficult to remember
TRY RULE

$$\left\{\begin{array}{l} f_S = \dfrac{X_0 - X_L}{X_S - X_L} = \dfrac{X_L - X_0}{X_L - X_S} \\[2ex] f_L = \dfrac{X_0 - X_S}{X_L - X_S} = \dfrac{X_S - X_0}{X_S - X_L} \end{array}\right.$$

PE II

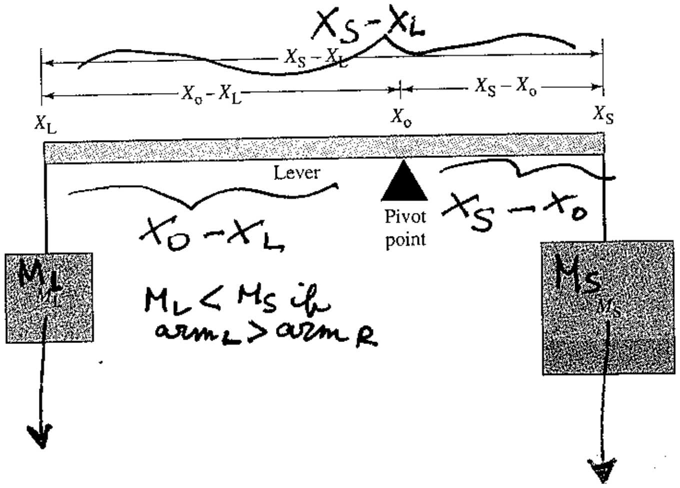


FIGURE 7.3–3
A schematic illustration of the lever rule. The tie line represents a "lever" with its pivot point located at the alloy composition X_0, its left end fixed at "position" X_L, and its right end located at X_S with blocks of mass M_L and M_S resting on either end.

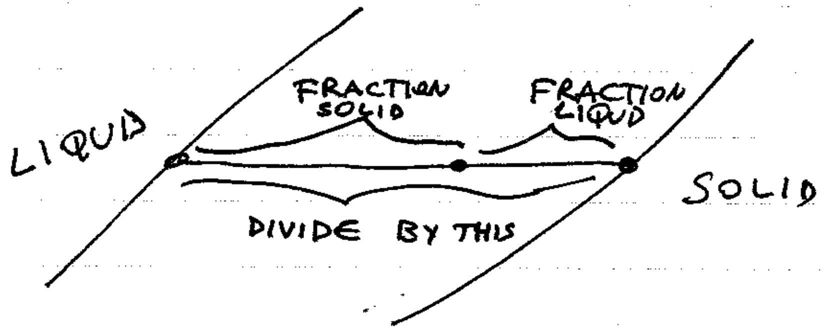
M_S at the ~~left~~ RIGHT depends on the LEFT part of the pivot

$$f_S = \frac{X_0 - X_L}{X_S - X_L}$$

M_L at the LEFT depends on the LEFT part of the pivot

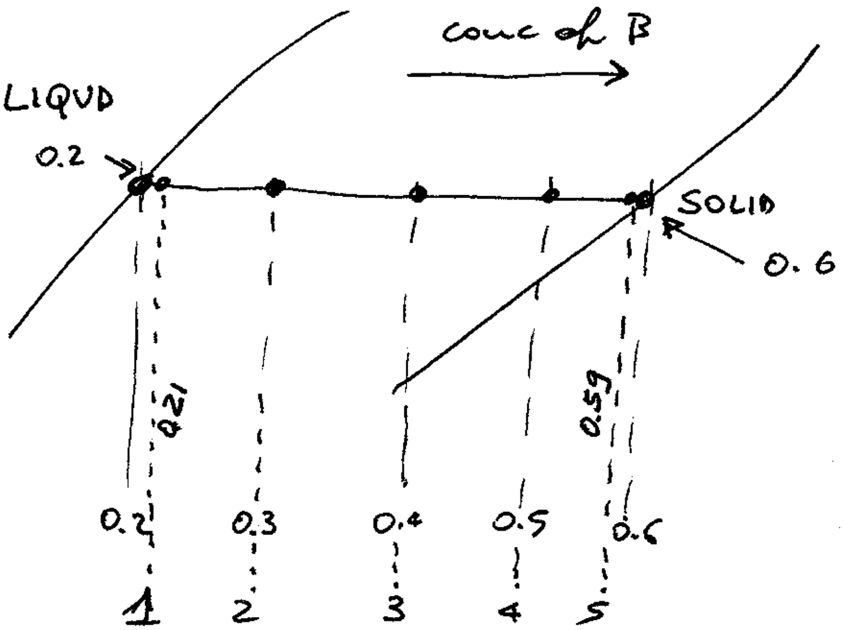
$$f_L = \frac{X_S - X_0}{X_S - X_L}$$

⇒

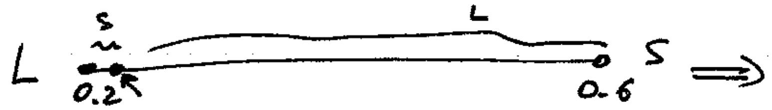


PE12

EXAMPLE



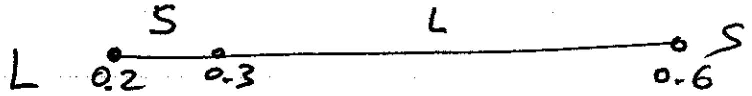
Alloy 1
$X_B = 0.21$



$\Longrightarrow$ NORM = 0.6 − 0.2 = 0.4

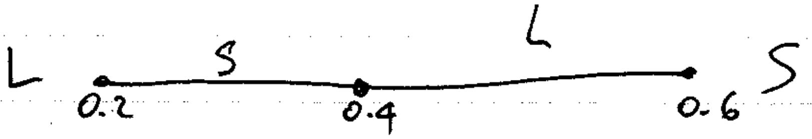
$f_S = \frac{0.21-0.2}{0.4} = 0.025$ $f_L = 0.975$ almost ALL LIQUID

Alloy 2
$X_B = 0.3$



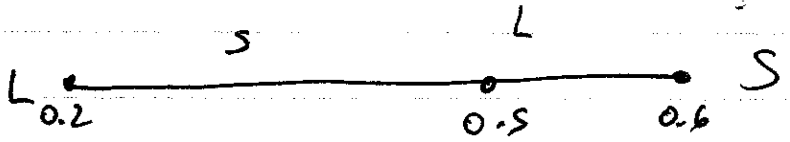
$f_S = \frac{0.3-0.2}{0.4} = 25\%$ $f_L = 75\%$ Most liquid

Alloy 3
$X_B = 0.4$



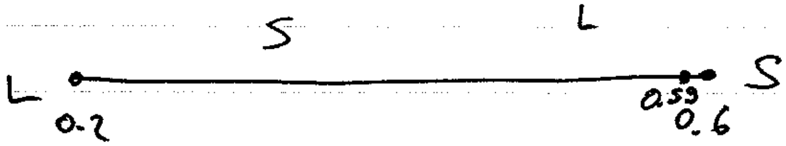
$f_L = \frac{0.4-0.2}{0.4} = 50\%$
$f_S = 50\%$

Alloy 4
$X_B = 0.5$



$f_L = \frac{0.5-0.2}{0.4} = 60\%$
$f_S = 40\%$

Alloy 5
$X_B = 0.59$



$f_L = \frac{0.59-0.2}{0.4} = 97.5\%$
$f_S = 2.5\%$
almost ALL LIQUID

PE 13

SOLIDIFIKATION & MICROSTRUCTURE of an ISOMORPHOUS IDEAL ALLOY

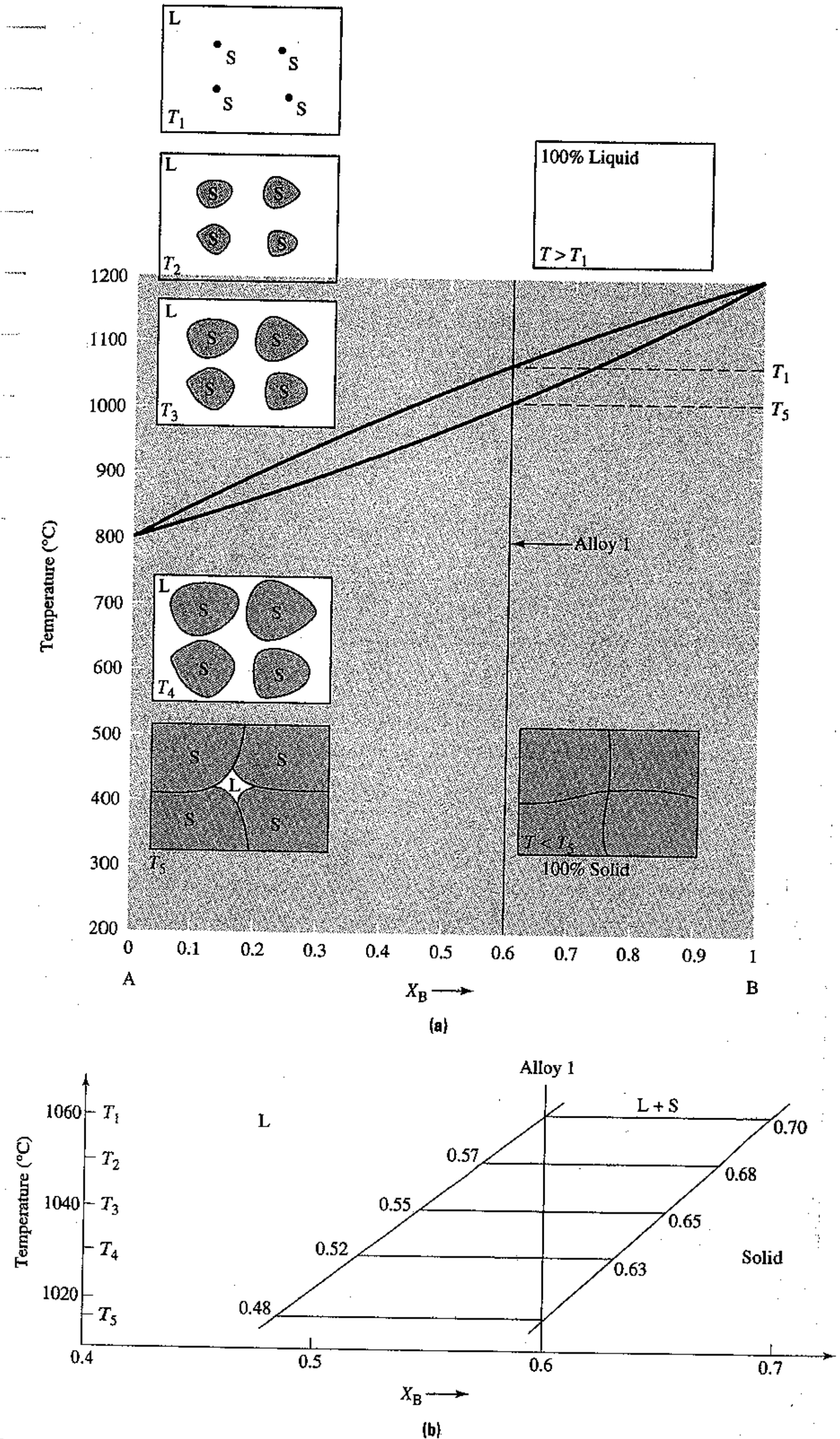
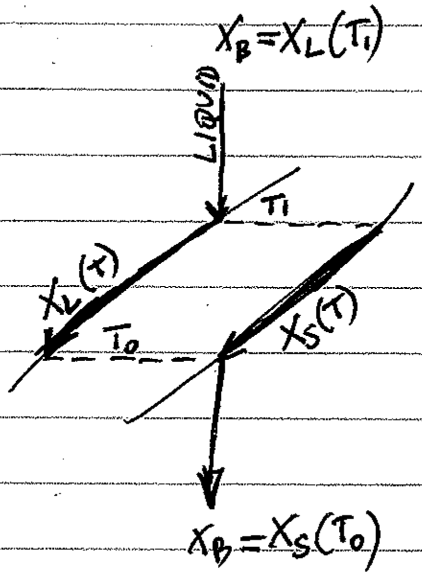
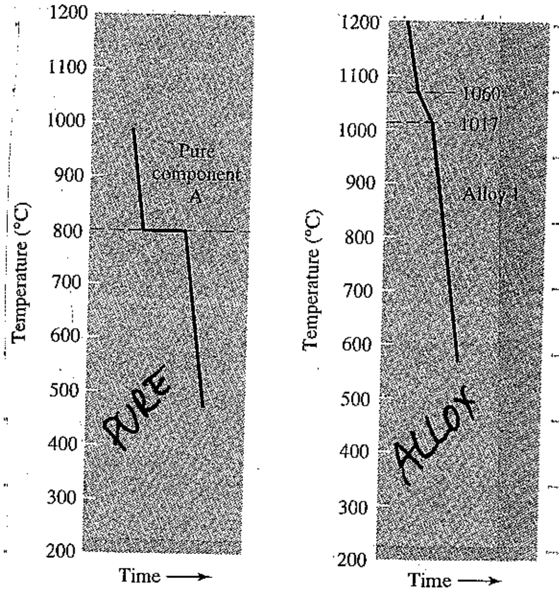


FIGURE 7.3–4 Equilibrium solidification of alloy 1 (composition 0.6 B): **(a)** the cooling path and sketches showing the development of the microstructure, and **(b)** an expanded section of part **(a)** showing the compositions of the liquidus and solidus boundaries in the range of 1010°C to 1060°C.

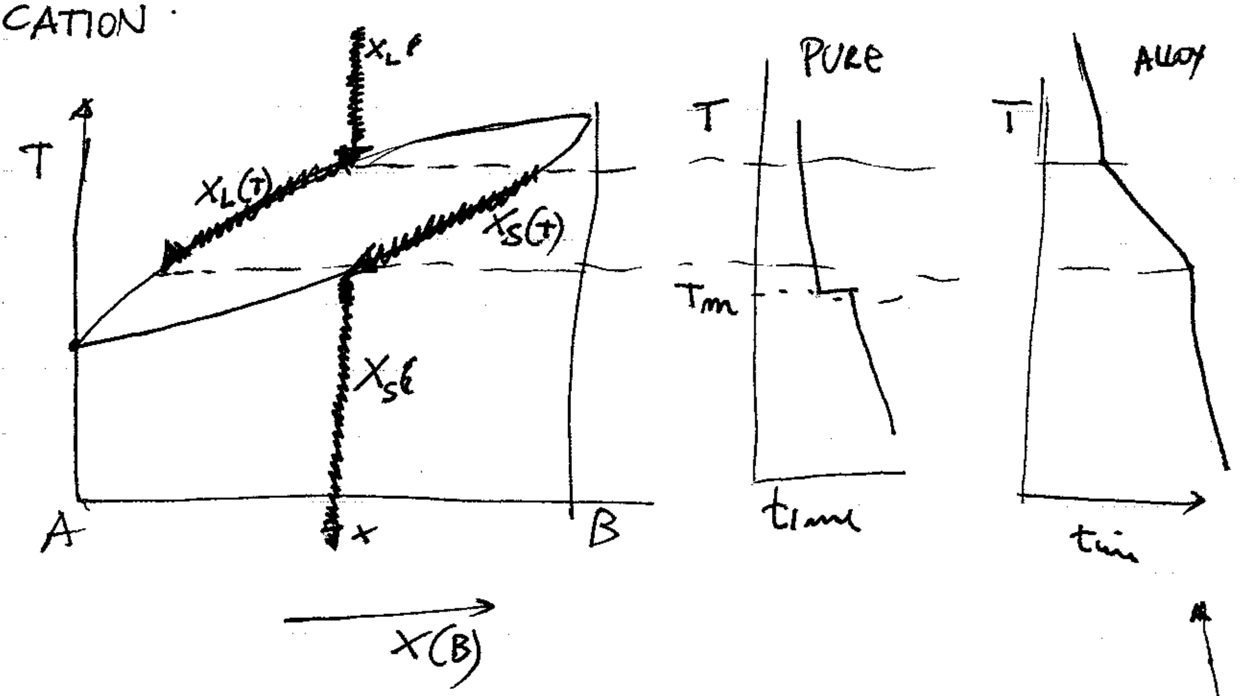


TIME TEMPERATURE PROFILE



PE14

SOLIDIFICATION



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 NaCl) = FCC with basis one anion O^{--}
and one cation
Ni OR Mg]

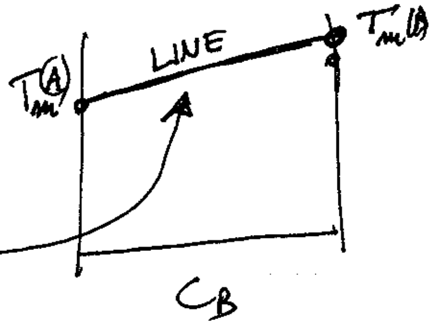
WHY I HAVE LENS ? Because of ENTROPY!

A-A Bond E_{AA}

B-B Bond E_{BB}

A-B Bond $E_{AB} = \frac{1}{2}(E_{AA}+E_{BB})$ IDEAL ⇒

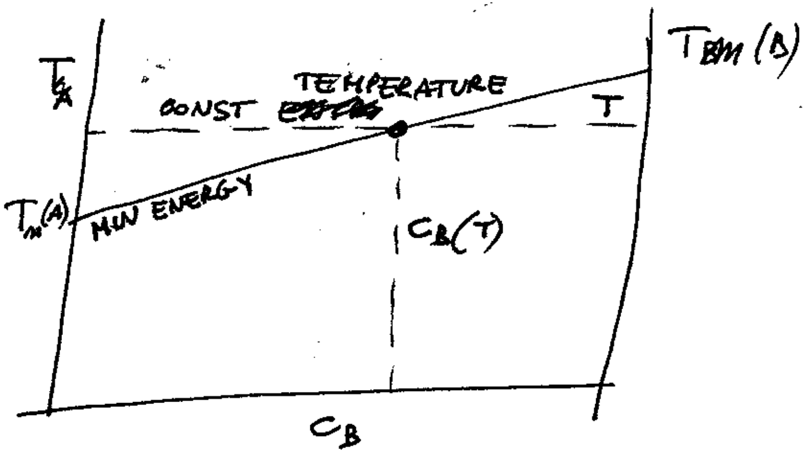
⇒ MIN ENERGY



@ const P, & T

But remember THAT we have to minimize $G = E + PV - TS$

have entropy effect



@ T $C_B(T)$ the ideal straight line ⇒

$C_B(T) \xrightarrow[\not\Leftarrow]{} X_B$ & $x_A = 1 - x_B$,

but have Temperature ⇒ defects form ⇒ some B are A & viceversa

⇒ $X_B \to x_B + \Delta x \quad x_A \to x_A - \Delta x$

⇒ Δx depends on energy required to form (with Arrhenius)

⇒ $S(\Delta x) = -k[\cancel{\log}(x_B + \Delta x)\log(x_B + \Delta x) + (x_A - \Delta x)\log(x_A - \Delta x)]$

same way I have

$x_B \to x_B - \Delta x' \quad x_A \to x_A + \Delta x'$

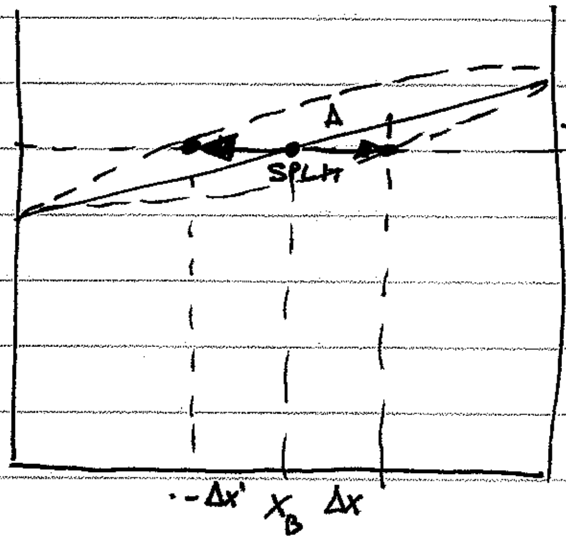
⇒ $S(\Delta x')$

$\Delta x'$ depends on energy to form defect with the ARRENIOUS

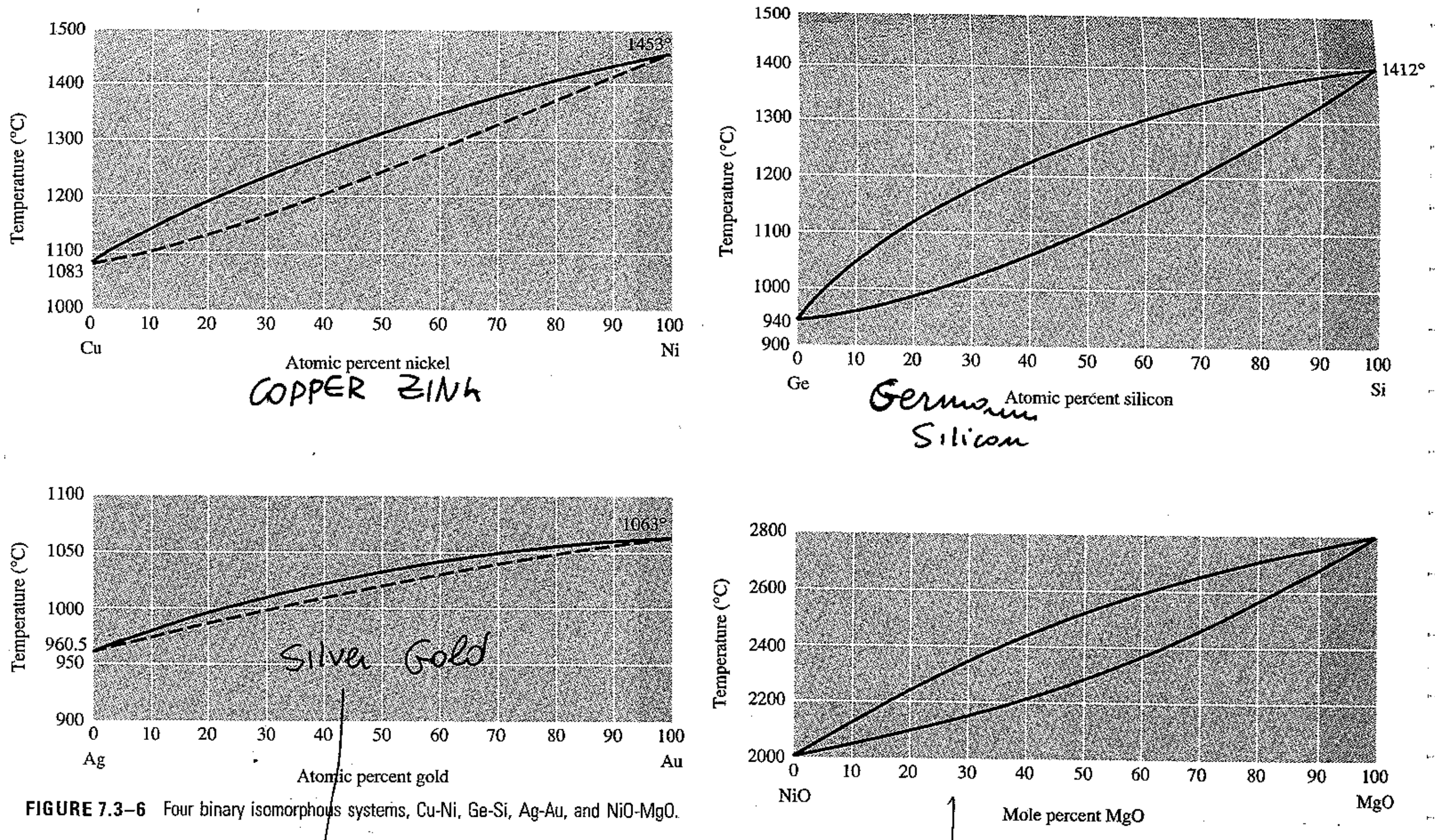
PE16 min $(E + PV - T(S(\Delta x) - S(\Delta x'))]$

⇓

C



Temperature rules → ENTROPY ⇒
Formation of
defects OR
OFF-STOCHIOMETRY
PHASES.



COPPER ZINh

Germanium
Silicon

Silver Gold

FIGURE 7.3–6 Four binary isomorphous systems, Cu-Ni, Ge-Si, Ag-Au, and NiO-MgO.

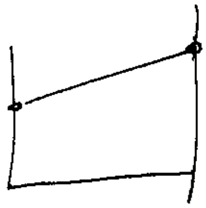
thought to have
SOLID SOLUTION AT
LOW TEMPERARURE (NO)

NICKEL-OXIDE +
MAGNESIUM
OXIDE

PE 17

DEVIATION FROM IDEALITY

- IDEAL $E_{AB} = \frac{1}{2}(E_{AA}+E_{BB})$ MIN(E) ⇒



Random

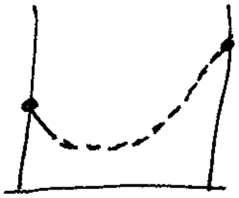
- CLUSTERING TENDENCY $E_{AB} > \frac{1}{2}(E_{AA}+E_{BB}) \Rightarrow E_{AB}$ is not "welcome" higher than ideal

it means that A prefer A to B & B prefers B to A! they do not want to mix too much in the solid phase

minimize # A-B Bonds

⇒ to minimize total energy temperature trys to destroy as soon as possible the solid phase

⇒ min(E)



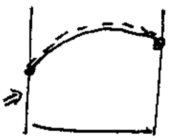
- ORDERING TENDENCY $E_{AB} < \frac{1}{2}(E_{AA}+E_{AB}) \Rightarrow E_{AB}$ is "welcome" lower than ideal

it means that A prefers B to A & B prefers A to B!

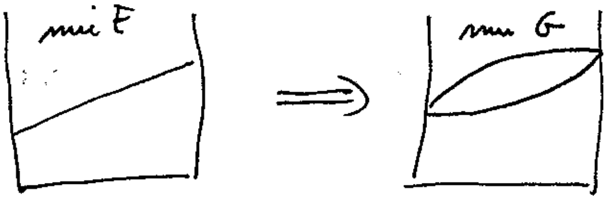
they WANT to ordered mix and they resist to temperature (disorder) as much as possible!

maximize # of A-B bonds

PE18 ⇒ Temperature needs to work hard to destroy ordering! ⇒ min(E) ⇒

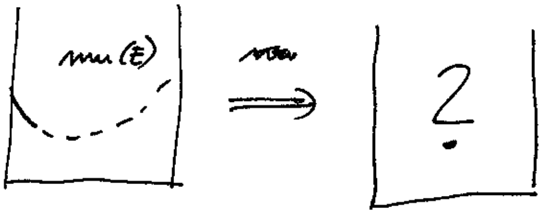


NOW IDEAL

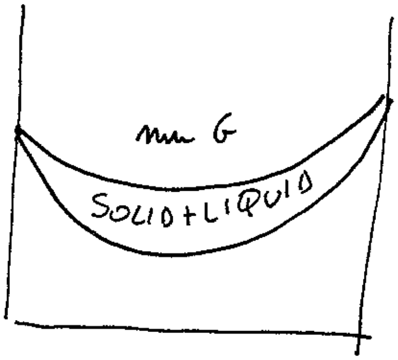


(Entropy)

CLUSTERING TENDENCE $E_{AB} > \frac{E_{AA}+E_{BB}}{2}$

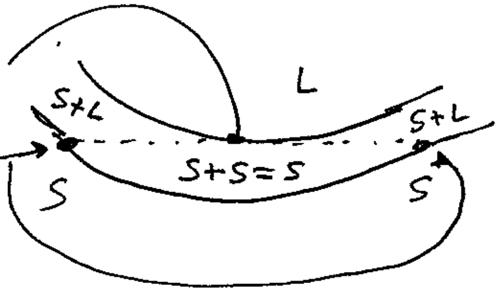


CAN BE A "BANANA"

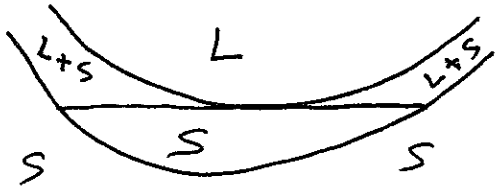


? No

becouse here I woud split it → therefore the lower part woud be just SOLID



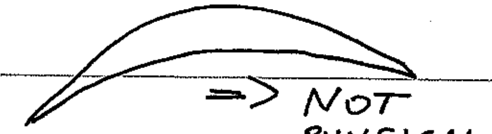
"BANANA" LENS DOES NOT EXIST!! ⟸



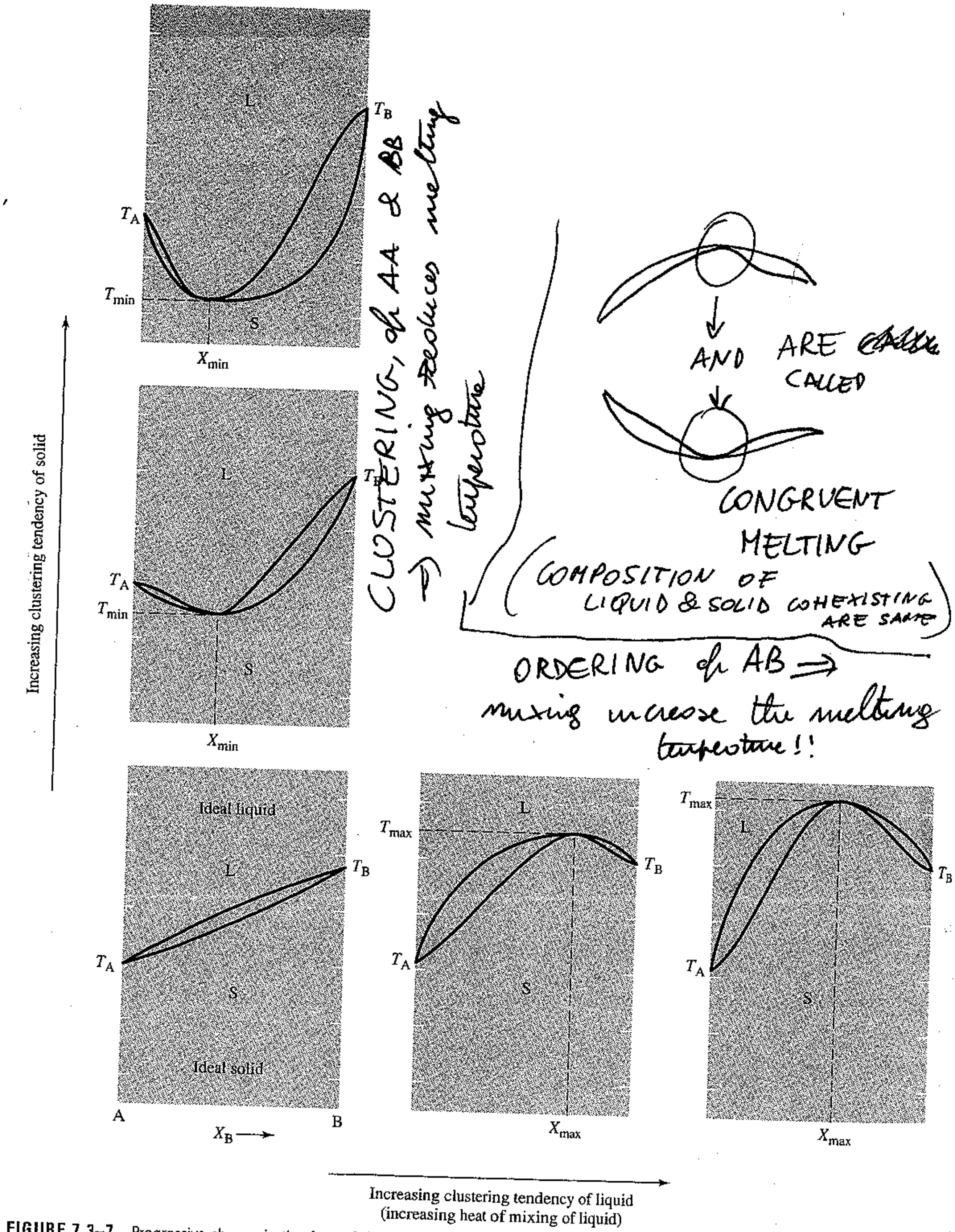
PE19

- CONGRUENT MELTING

SAME FOR ORDERING



the LIQUIDUS & SOLIDUS
⇒ must "touch" at the min AND max



CLUSTERING of AA & BB
⇒ mixing reduces melting temperature

AND ARE ~~calle~~ CALLED
CONGRUENT MELTING
(COMPOSITION OF LIQUID & SOLID COEXISTING ARE SAME)

ORDERING of AB ⇒
mixing increase the melting temperature!!

FIGURE 7.3–7 Progressive change in the form of the isomorphous phase diagram as the solid and liquid phases deviate from ideal behavior.

PE20

AT CONGRUENT MELTING POINT THE ALLOY SOLIDIFIES/MELTS AT A GIVEN TEMPERATURE ($T_m(c)$) AND CONCENTRATION (C) AND NOT IN A TEMPERATURE INTERVAL

X_{L_1} and X_{L_2} for alloys X_1 and X_2, respectively.

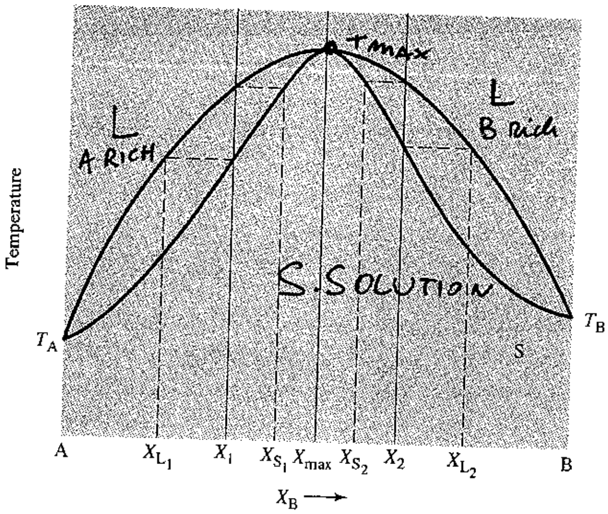


FIGURE 7.3–8 A binary phase diagram showing a congruently melting alloy of composition X_{max}. Two additional alloy compositions are shown.

IF YOU WANT TO MAKE AN ALLOY WHICH RESISTS AT HIGHER TEMPERATURE THAN THE CONSTITUENTS, THAN YOU NEED SOMETHING LIKE THIS

PLANES
ENGINES

IF YOU WANT TO MAKE AN ALLOY WHICH MELTS AT LOWER TEMPERATURE THAN THE CONSTITUENTS, THAN YOU NEED SOMETHING LIKE THIS

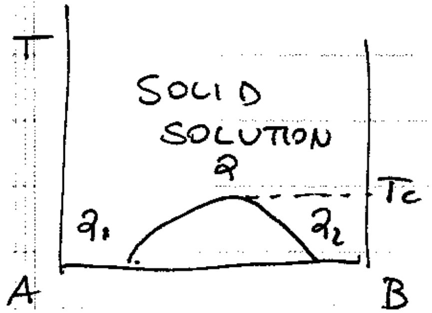
WELDING
SOLDERING
CAST

PE21

EUTECTIC PHASE DIAGRAM

if CLUSTERING (A likes A better than B) then at low Temperature the two elements do not mix well ~~ad~~ and solid solution disappear

⇒



α = solid solution above T_c (critical)

α_1 = solid solution A-Rich

α_2 = solid solution B-Rich

A =

B =

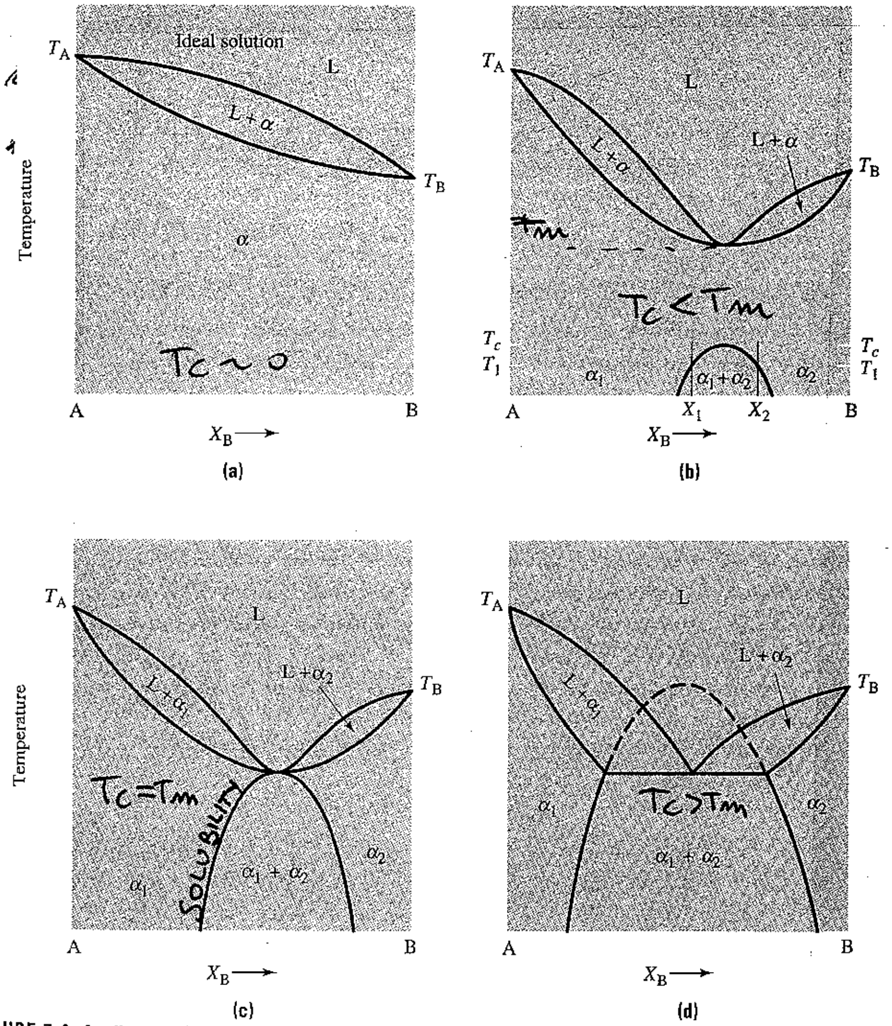
depending on the

Above T_c
COMPLETE
SOLUBITITY

UNDER T_c
PARTIAL
SOLUBILITY

A with B with Sol B in A
&
B with A with Sol A in B

PE 22



(a) (b) (c) (d)

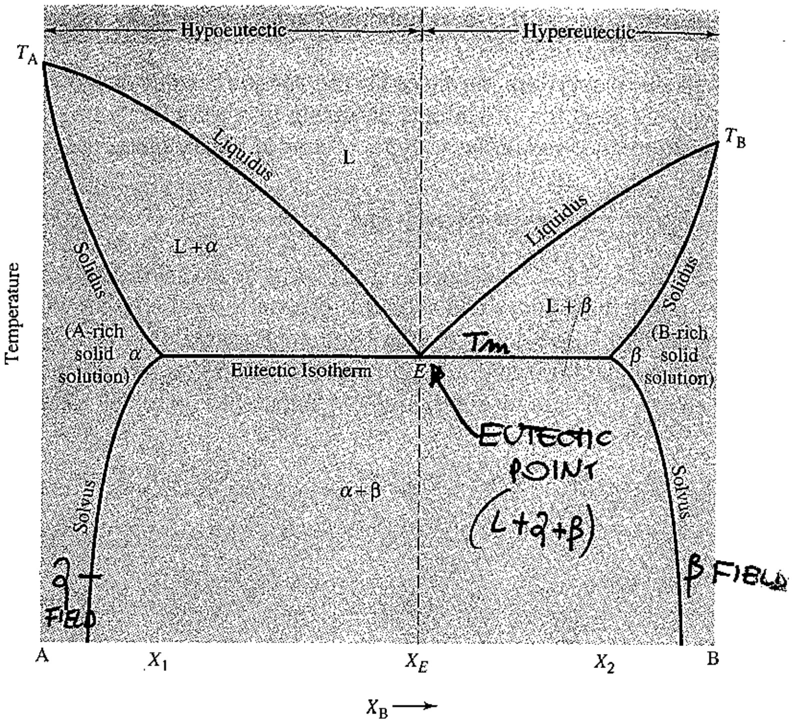
FIGURE 7.4–1 The development of a eutectic reaction by increasing the clustering tendency in the solid phase: **(a)** the diagram for an ideal system, and **(b–d)** increasing clustering tendency in the solid phase.

↓

Like water + alcohol ~~sugar~~ at low temperature

High temp
MIXING

low temp
Separation
water with little alcohol solute
+
alcohol with little water solute



IE 7.4–2 A binary eutectic phase diagram and the associated terms used to describe regions of a eutectic system.

~~[illegible]~~

SOLVUS = max solubility of a ~~[illegible]~~ specie in the other.

EUTECTIC POINT

Coexistence of 3 phases

⇒ $F = C - P + 2$

↓ ↑ is 1 Becaus P is FIXED

$\underbrace{2 - 3 + 1}$

$F = 0$

INVARIANT ← Eutectic point

SOLVUS

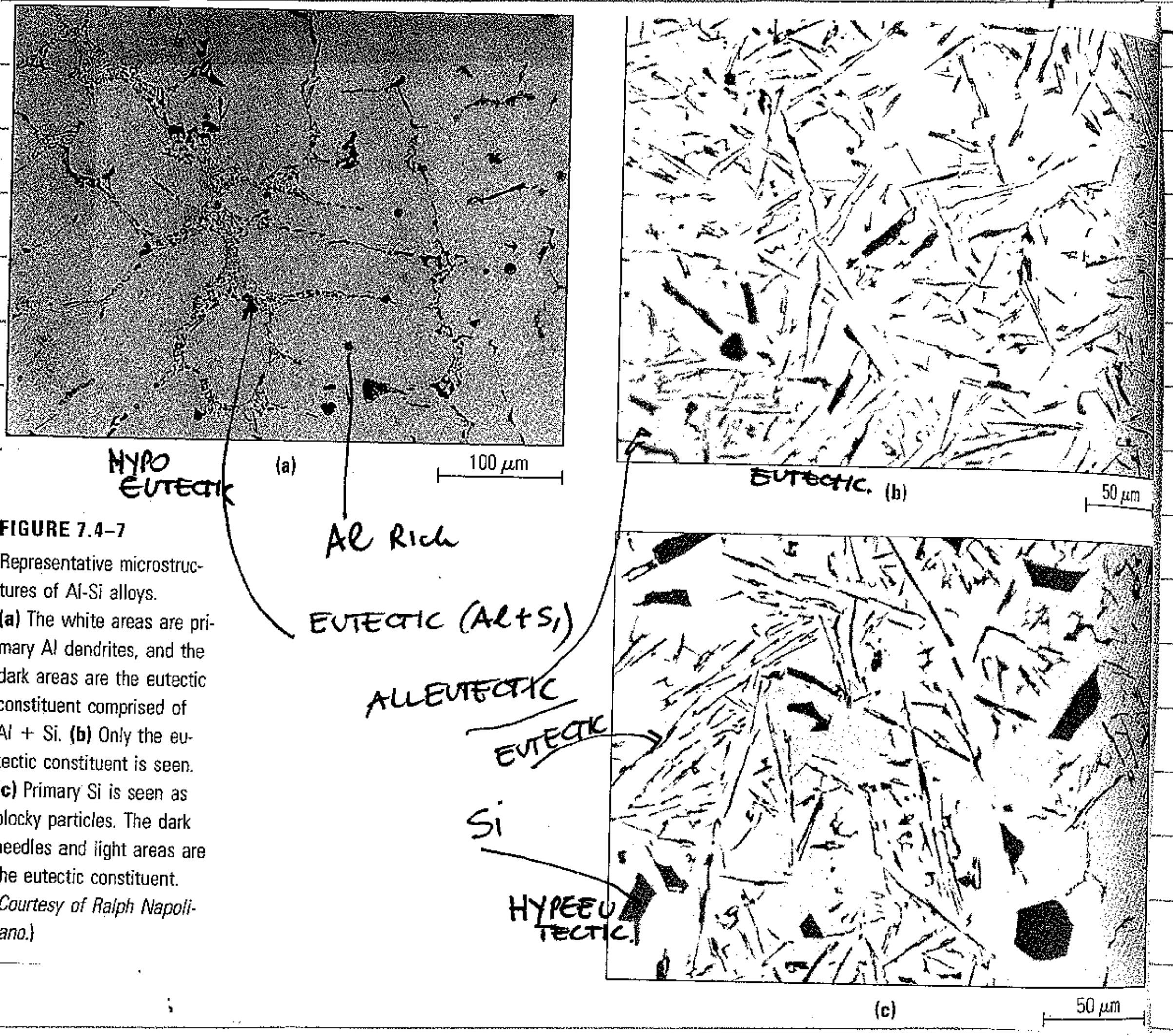


FIGURE 7.4–7 Representative microstructures of Al-Si alloys. **(a)** The white areas are primary Al dendrites, and the dark areas are the eutectic constituent comprised of Al + Si. **(b)** Only the eutectic constituent is seen. **(c)** Primary Si is seen as blocky particles. The dark needles and light areas are the eutectic constituent. (*Courtesy of Ralph Napolitano.*)

PE23

MELTING OF AN EUTECTIC ALLOY

go down at X_E concentration through the T~~m~~ point

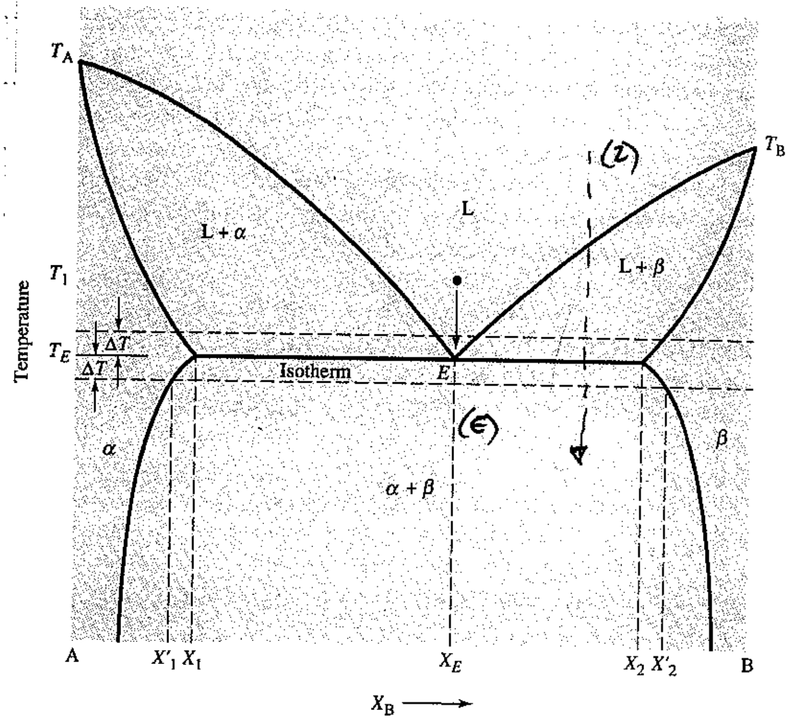
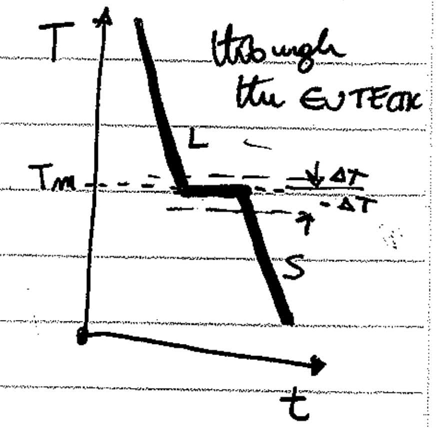
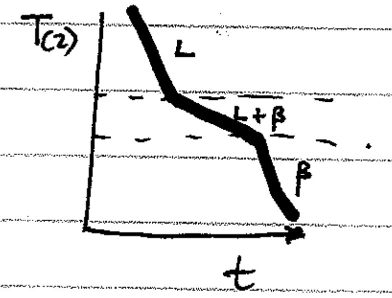


FIGURE 7.4–3 A binary eutectic equilibrium phase diagram showing the changes in composition of the phases present as the temperature is changed by an amount ΔT above and below the eutectic isotherm.





potte (ε) $L \rightleftarrows \alpha+\beta$

at EUTECTIC POINT
Wery nice if ΔT ↑ all Liquid!
if ΔT ↓ all solid!

EUTECTIC $X=X_E$

$L^{X_E} \rightleftarrows \alpha^{X_1} + \beta^{X_2}$

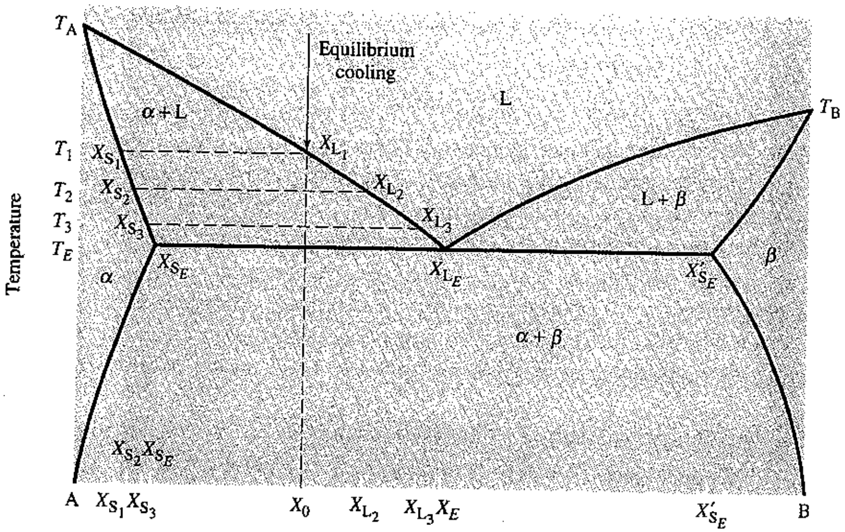


FIGURE 7.4–4 Equilibrium solidification of an off-eutectic alloy of composition X_0.

PE
24

~~OFF EUTECTIC $(X=X_0)$~~

~~@ T_1~~

~~$L_E^{X_0} \rightleftarrows L^{X_0} + \alpha^{X_{S_1}}$~~

~~@ T_2 $\alpha^{X_{S_2}} + L^{X_{L_2}}$~~

~~@ T_m $\alpha^{X_{S_E}}$ +~~ NEXT PAGE

SOLIDIFICATION OF AN EUTECTIC ALLOY BUT OFF-EUTECTIC COMPOSITION

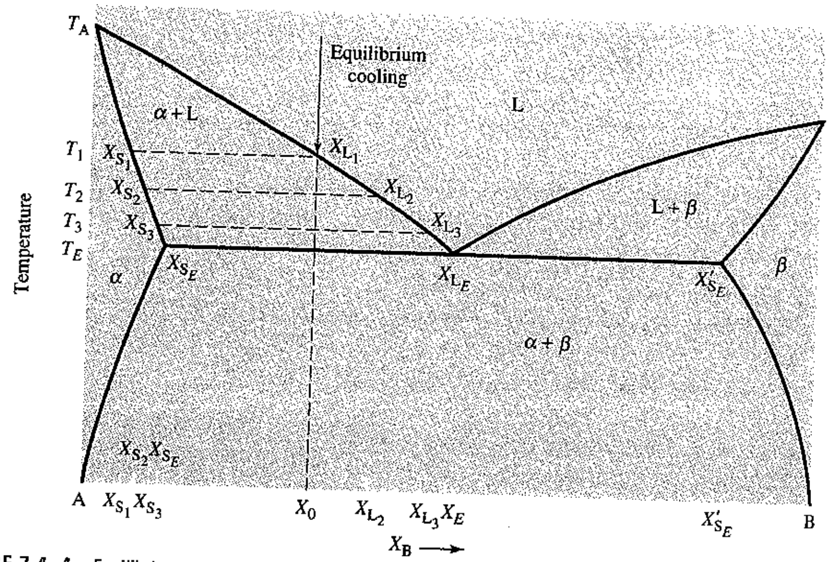


FIGURE 7.4–4 Equilibrium solidification of an off-eutectic alloy of composition X_0.

@ T_1 $\quad L(X_{L_1}) \longleftrightarrow \underset{\Downarrow\; f_{S_1}}{\alpha(X_{S_1})} + \underset{\Downarrow\; f_{L_1}}{L(X_{L_1})}$

$$f_{S_1} = \frac{X_{L_1} - X_0}{X_{L_1} - X_{S_1}} \quad \text{and} \quad f_{L_1} = \frac{X_0 - X_{S_1}}{X_{L_1} - X_{S_1}}$$

@ T_2 $\quad \underset{\Rightarrow f_{S_2}}{\alpha(X_{S_2})} + \underset{\Downarrow f_{L_2}}{L(X_{L_2})}$

$$f_{S_2} = \frac{X_{L_2} - X_0}{X_{L_2} - X_{S_2}} \quad \text{and} \quad f_{L_2} = \frac{X_0 - X_{S_2}}{X_{L_2} - X_{S_2}}$$

in $T_M \gtrsim T_E$

@ $T_M = T_E^{(+)}$ $\quad \alpha(X_{SE}) + ~~\beta~~ L(X_{LE})$

$$f_{SE} = \frac{X_{LE} - X_0}{X_{LE} - X_{SE}} \quad \text{and} \quad f_{LE} = \frac{X_0 - X_{SE}}{X_{LE} - X_{SE}}$$

$T_M = T_E^{(-)}$ $\quad \alpha(X_{SE}) + \beta(X'_{S_E})$ } 3 PHASES

α X_{SE} — L — x_0 — $S(\alpha)$ — X_{LE} L ⇒ fractions
NORM

BUT A LOT of α & β FORM SIMULTANEOUSLY

in $T \lesssim T_E$ (IF IT HAS TIME TO REARRANGE)

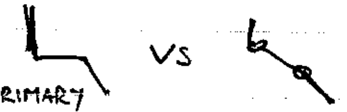
α X_{SE} — $S(\beta)$ — X_0 — $S(\alpha)$ — X'_{SE} β
NORM

in the same way fractions!

$$f_{S\alpha} = \frac{X'_{SE} - X_0}{X'_{SE} - X_{SE}} \Longleftarrow \qquad f_{S\beta} = \frac{X_0 - X_{SE}}{X'_{SE} - X_{SE}} \quad !!$$

PE
25

AT EUTECTIC POINT, a lot of α and β form SIMULTANEOUSLY, and their MORPHOLOGY IS DIFFERENT FROM THE PRIMARY α and β! (IT'S BECAUSE OF THE SPEED (T(t)) ~~THE MORPHO~~ [illegible] IT'S CALLED EUTECTIC (α+β)

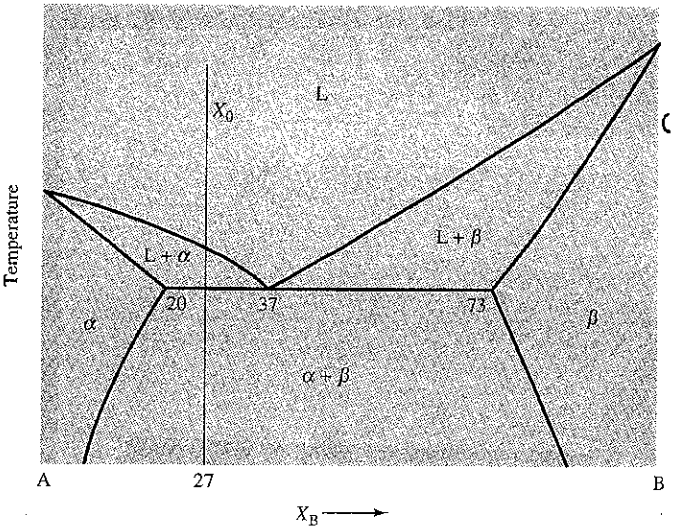

VS

⟹ therefore below EUTECTIC POINT the ALLOY IS A MIXTURE of $\overset{\downarrow \text{PRIMARY}}{\alpha}$ + EUTECTIC (α+β) ← EUT.

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 α and β of compositions X_{SE} and X'_{SE}, and that the relative amounts of α and β formed from this liquid will be constant. In fact, this is what makes the eutectic reaction invariant.

UNLESS you go superslow, you always get EUTECTIC (α+β)

EXAMPLE



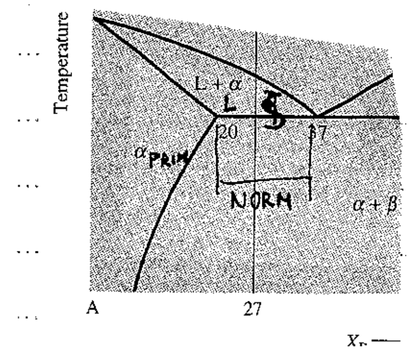
(

mposition 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 α and β that will form from the liquid just below the eutectic isotherm.
- *d.* The total amount of α phase in the alloy at a temperature just below the eutectic temperature.

a)

a. The fraction of primary solid that forms under equilibrium cooling at the eutectic temperature.



$$f_\alpha^P = \frac{X_L - X_0}{X_L - X_\alpha} = \frac{\overbrace{37 - 27}^{S}}{\underbrace{37 - 20}_{NORM}} = 0.588$$

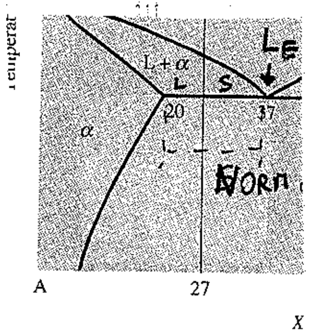
THIS IS α-PRIMARY

α primary has $X_{SE} = 20\%$

b) *b.* The fraction of liquid with the eutectic composition that will transform to two solid phases below the eutectic isotherm.

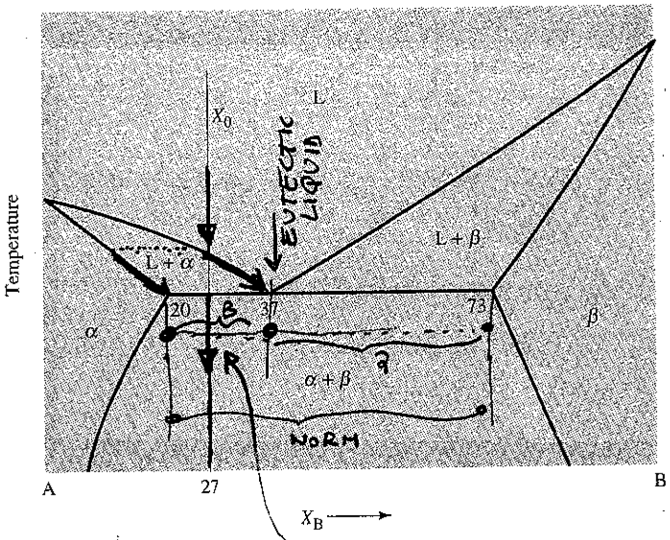
is the one at Liquid just before solidification.

L_{Eut} has $X_{LE} = 37\%$



$$f_L^{\text{eut}} = \frac{X_0 - X_\alpha}{X_L - X_\alpha} = \underbrace{\frac{27 - 20}{37 - 20}}_{\text{NORM}} = 0.412 = 1 - f_\alpha^{\text{Prim.}}$$

c) *c.* The amount of α and β that will form from the liquid just below the eutectic isotherm.



Liquid at T_E has concentration $X_{EE} = 37\%$ (EUT. LIQUID just below the EUTECTIC POINT it becomes SOLID EUT SOLID $\alpha+\beta$ with f_α, f_β

$$f_\alpha = \frac{X_\beta - X_L^{\text{eut}}}{X_\beta - X_\alpha} = \frac{73 - 37}{73 - 20} = 0.679$$

$$f_\beta = \frac{X_L^{\text{eut}} - X_\alpha}{X_\beta - X_\alpha} = \frac{37 - 20}{73 - 20} = 0.321$$

⇒ also here I HAVE $\underset{(a)}{\alpha^P} + \underbrace{\text{EUT}(\alpha+\beta)}_{(b).}$

$f_\alpha^P = 0.588$

$f_L^E = f_S^E = 0.412$

⇓

of which

$f_\alpha = 0.679$

$f_\beta = 0.321$

$$\underset{0.588}{f_\alpha^P} + \underset{f_L^E * f_\alpha = 0.412 * 0.679 = 0.280}{f_\alpha^{\text{EUT}}} + f_\beta^{\text{EUT}} = f_\alpha^{\text{TOT}} + f_\beta^{\text{TOT}}$$

$f_L^E * f_\beta = 0.412 * 0.321 = 0.132$

PE27

d) *d.* The total amount of α phase in the alloy at a temperature just below the eutectic temperature.

$$f_\alpha^{TOT} = f_\alpha^{P} + f_\alpha^{EUT}$$

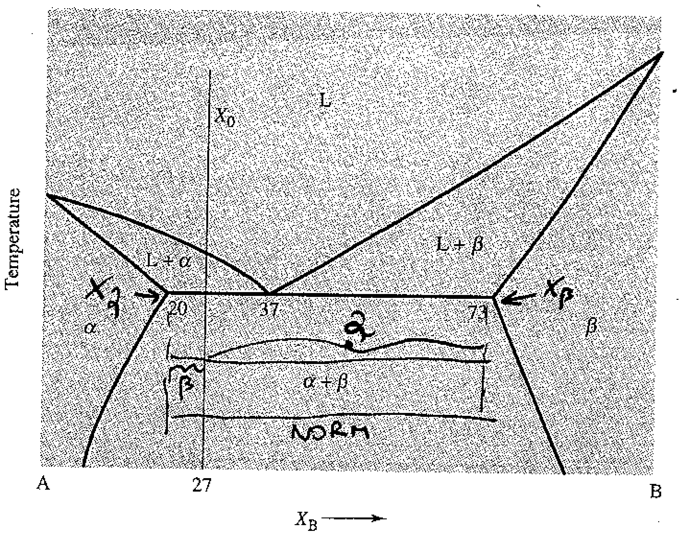
OR $1 - f_\beta^{EUT}$

OR

$$f_\alpha^{\text{total}} = f_\alpha^{P} + f_\alpha^{\text{eut}} = 0.588 + 0.280 = 0.868$$

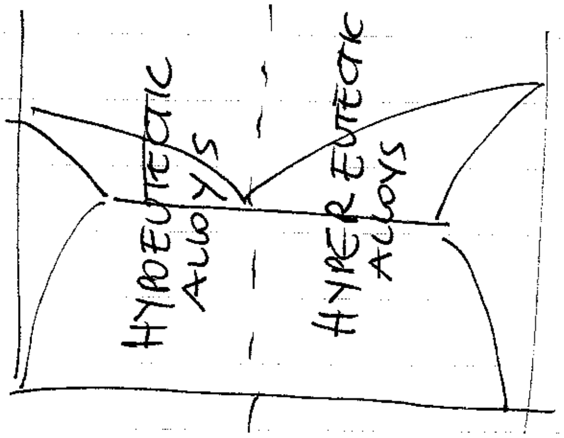
Alternatively, since the microstructure is composed of just two phases, $\alpha + \beta$, the total fraction of α must be given by:

$$f_\alpha^{\text{total}} = 1 - f_\beta^{\text{eut}} = 1 - 0.132 = 0.868$$



$$f_\alpha = \frac{X_\beta - X_0}{X_\beta - X_\alpha}$$

$$f_\alpha^{\text{total}} = \frac{X_\beta - X_0}{X_\beta - X_\alpha} = \frac{73 - 27}{73 - 20} = 0.868$$



PE28

ALUMINUM- SILICON (CHIPS)

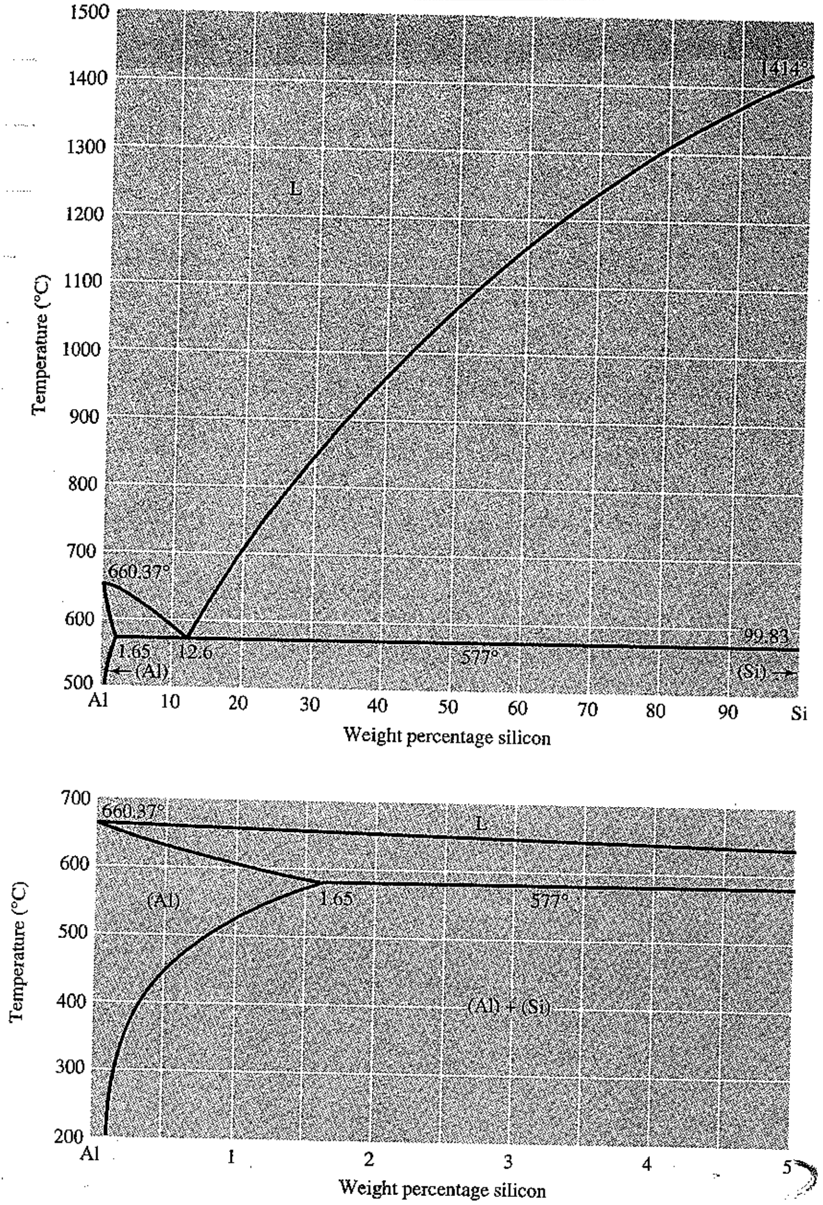


FIGURE 7.4–6
The Al-Si eutectic phase diagram. (*Source: F. Shunk, Constitution of Binary Alloys, McGraw-Hill. Reproduced with permission of McGraw-Hill.*)

CARS
(PISTONS)

(HARD, Si ⇒ Wear Resistance)

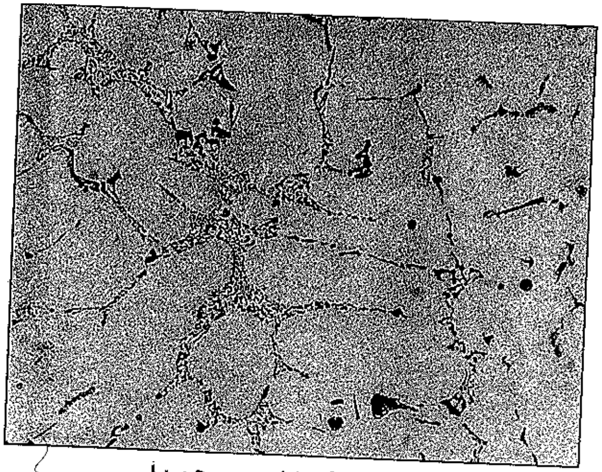
look at Page PE23

~~STRO~~

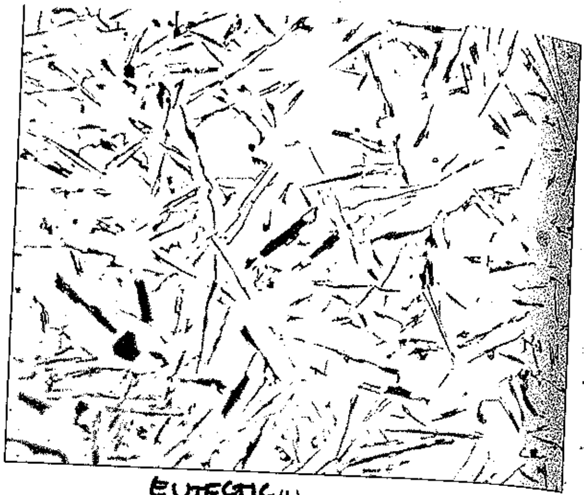
CLUSTERING) = TENDENCE

Al = LIGHT

PE 29



HYPOEUTECTIC
$X_{Si} < X_E = 12.6$

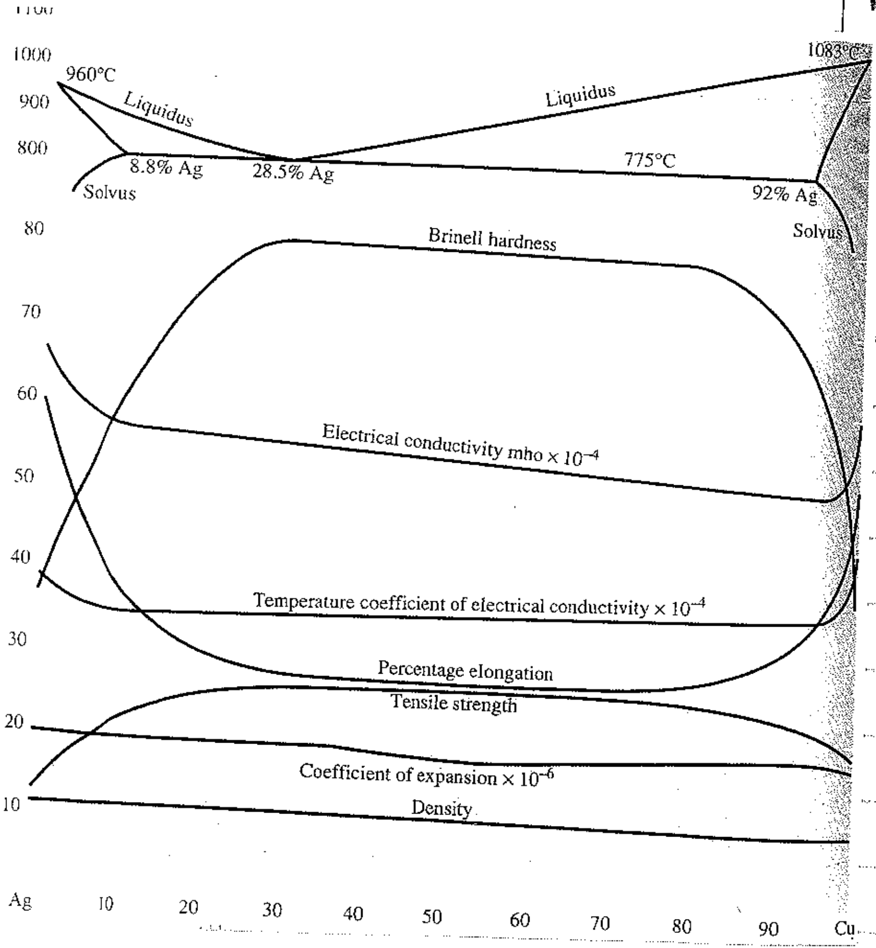


EUTECTIC

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.*)

HYPER EUTECTIC

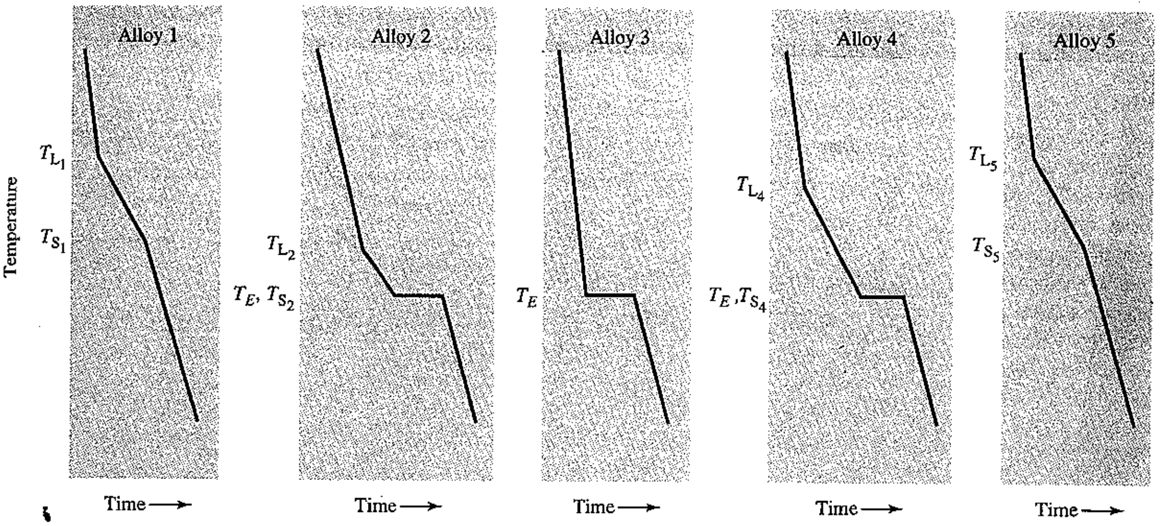


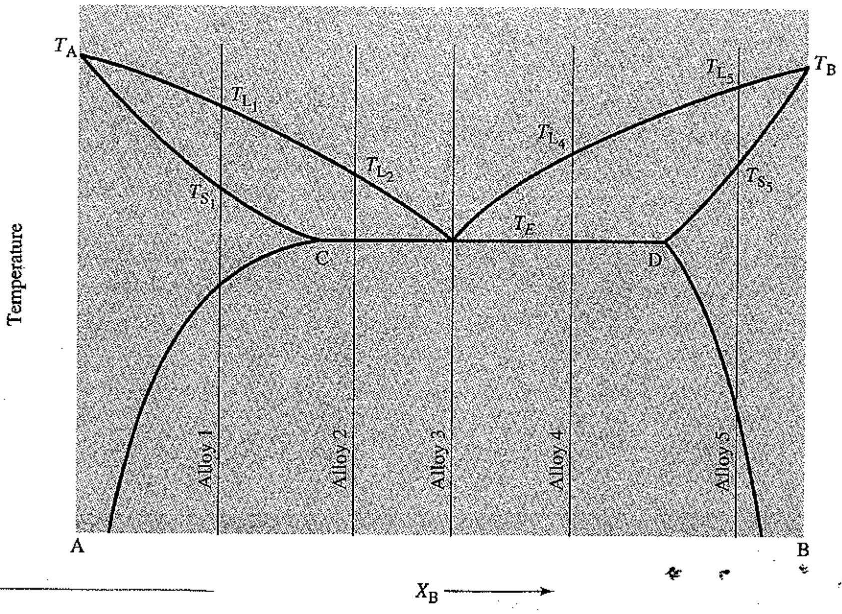
← PROPERTIES
VS
CONCENTRATION

PE 30

HOW TO MEASURE

melt & watch T(t) behaviour.





Temperature PROFILES (c)

Properties PROFILE (c)

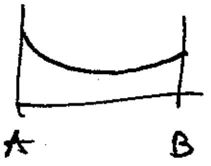
PE31

TWO EUTECTICS

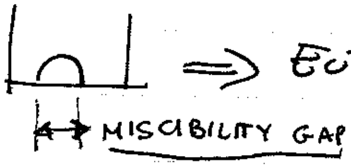
A likes A more than B ⇒ $E_{AB} > \frac{1}{2}(E_{AA}+E_{AB})$ ⇒ CLUSTERING TEND

⇒ WEAKER SOLID SOLUTION

⇒ STRONGER LIQUID



\+ low Temp

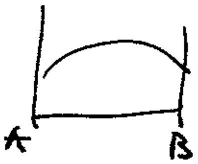


⇒ Eutectic

A likes B more than A ⇒ $E_{AB} < \frac{1}{2}(E_{AA}+E_{AB})$ ⇒ ORDERING TEND

⇒ STRONGER SOLID SOLUTION

⇒ WEAKER LIQUID



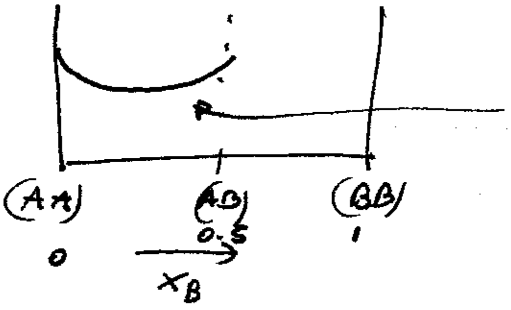
* * *

TAKE 2 ATOMS (AA), (AB), (BB)

If (AA) likes (AA) more than (AB) (depends upon structure!)

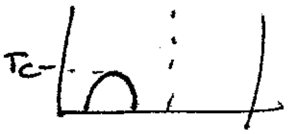
⇒ $E_{AA-AB} > \frac{1}{2}(E_{AA-AA}+E_{AA-BB})$

⇒



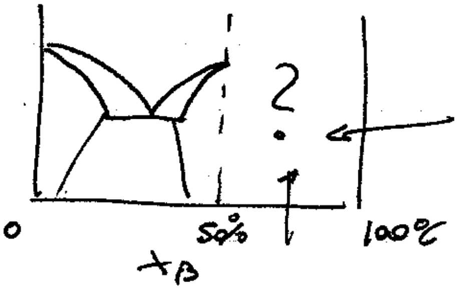
STOPS AT 50% or elsewhere

If low temperature IMMISCIBILITY of AA & AB (NO SOLID SOLUTION) ⇒



⇒

the system can form an eutectic between 0 & 50%



may be another eutectic between AB & BB

Rule: between two strong chemical compounds you can form an eutectic (CAN=MAY ≠ MUST=HAS TO).

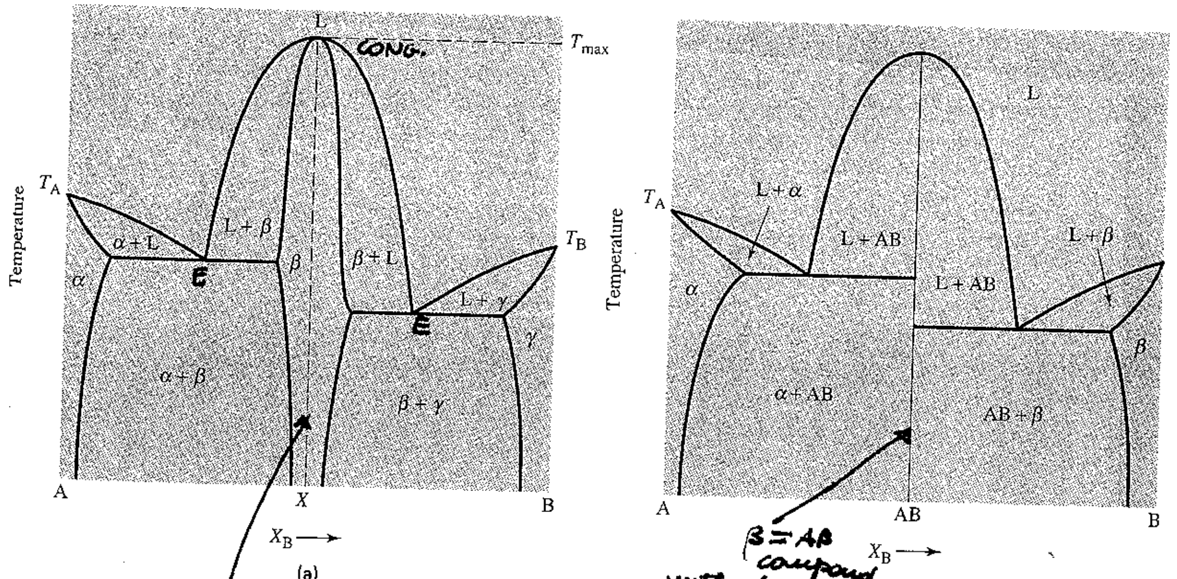


FIGURE 7.4–11 **(a)** A binary equilibrium phase diagram containing two eutectic reactions illustrating solid solution ranges, an intermediate phase β, and a congruent melting reaction. **(b)** When the solubility of the intermediate phase becomes limited, the line compound AB results.

β = AB compound without solubility

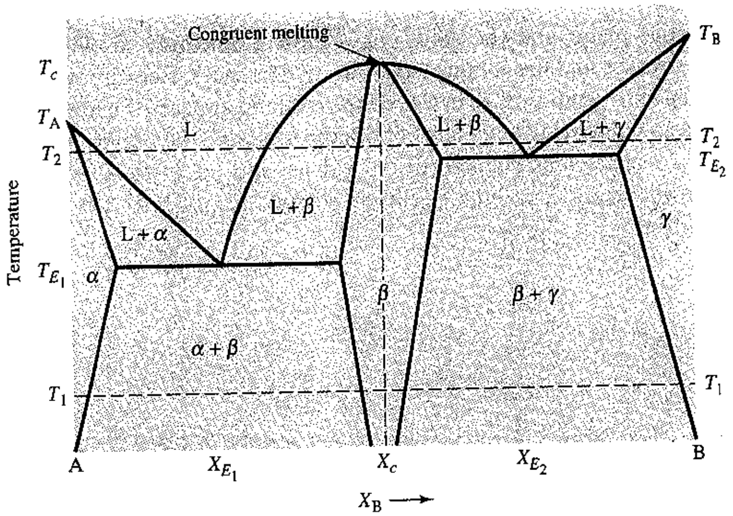
intermediate phase β

α+β) β)β+γ

solubilities of β in α & γ

PE 33

EXAMPLES



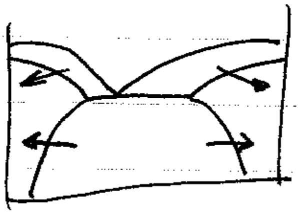
(changing T)

Reactions @ the invariant points (∞)

1. Eutectic reaction at T_{E_1} and X_{E_1}: $L \leftrightarrows \alpha + \beta$
2. Eutectic reaction at T_{E_2} and X_{E_2}: $L \leftrightarrows \beta + \gamma$
3. Congruent melting at T_c and X_c: $L \leftrightarrows \beta$

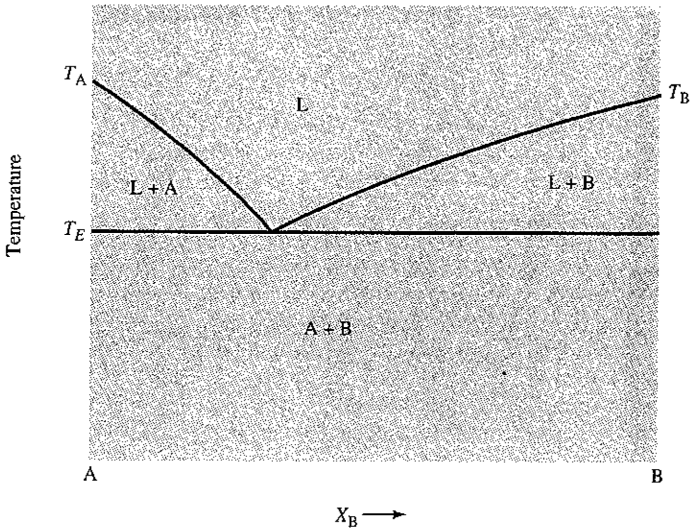
or

only



IF NO SOLUBILITIES

A Hates mixing with B
but only in the liquid
phase they do, because the higher entropy of
the Liquid



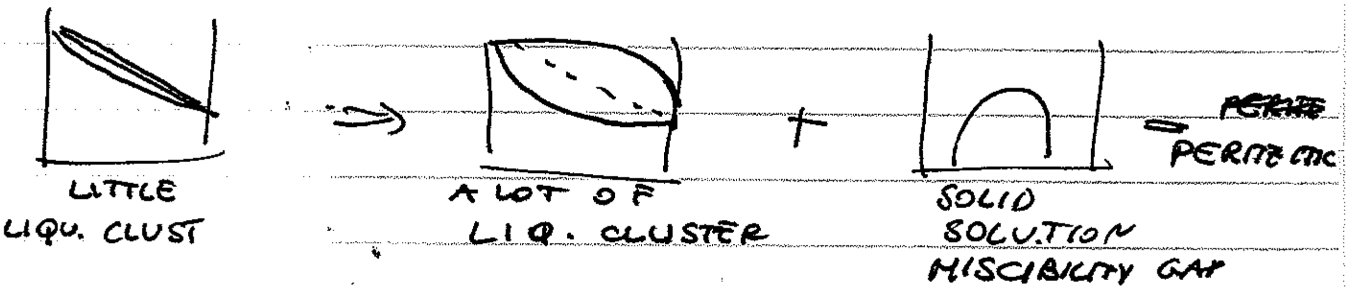
PE34

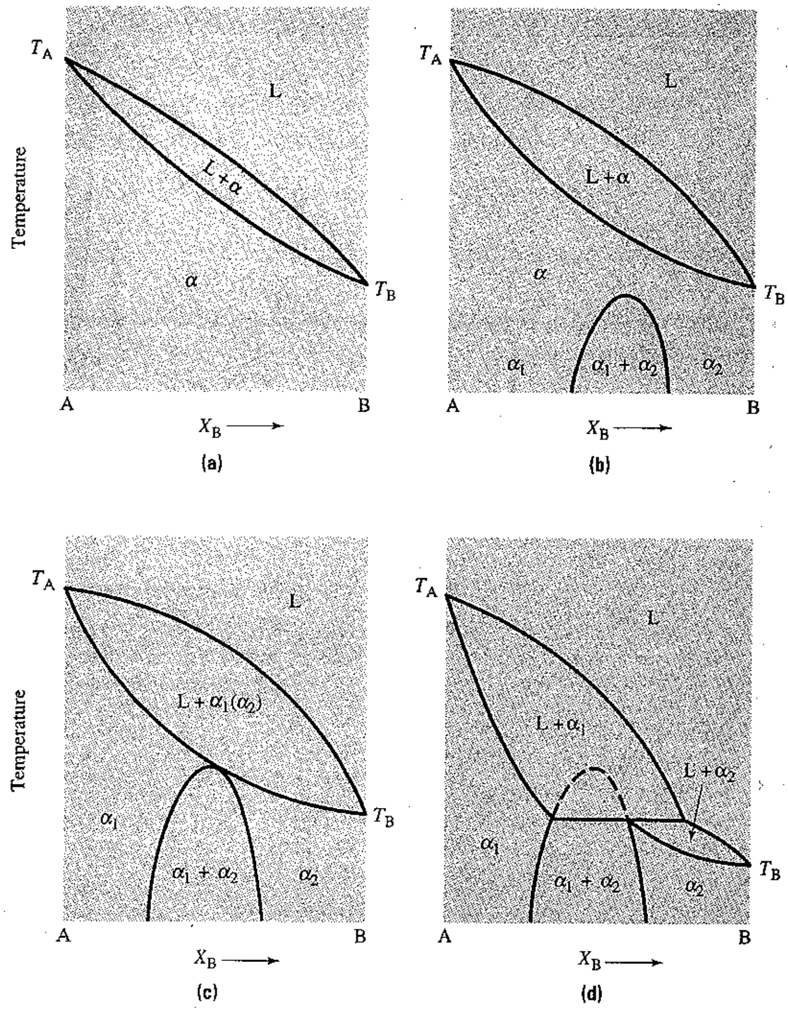
PERITECTIC SYSTEMS

1) if ~~[illegible]~~ A likes A more than B (SOLID CLUSTERING) at low temperature (MISCIBILITY GAP)

2) melting point very different

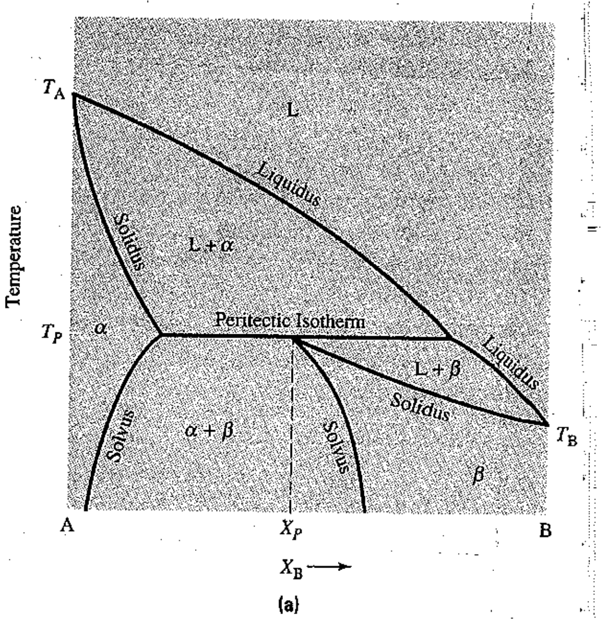
3) if A likes A more than B also at high temperature (CLUSTERING OF LIQUIDS) ⇒ LENS BECOME WIDER





(a) (b) (c) (d)

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,*



(a)

PE 35

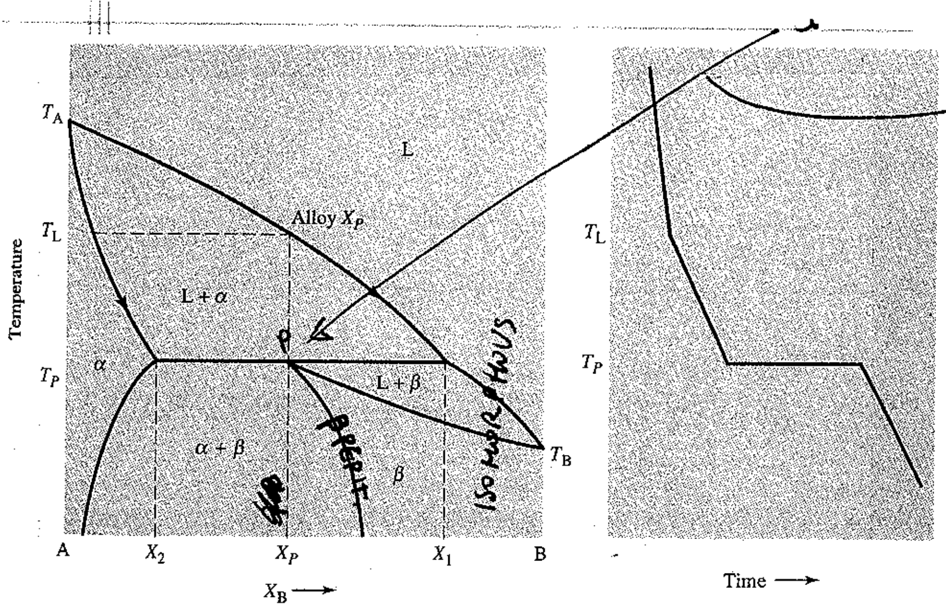
at Peritectic point

INVARIANT TRANSORMATION

$L+\alpha \rightleftarrows \beta$

but ±ΔT ⇒ produce α!!

TEMPERATURE BEHAVIOUR OF PER.



(b) (c)

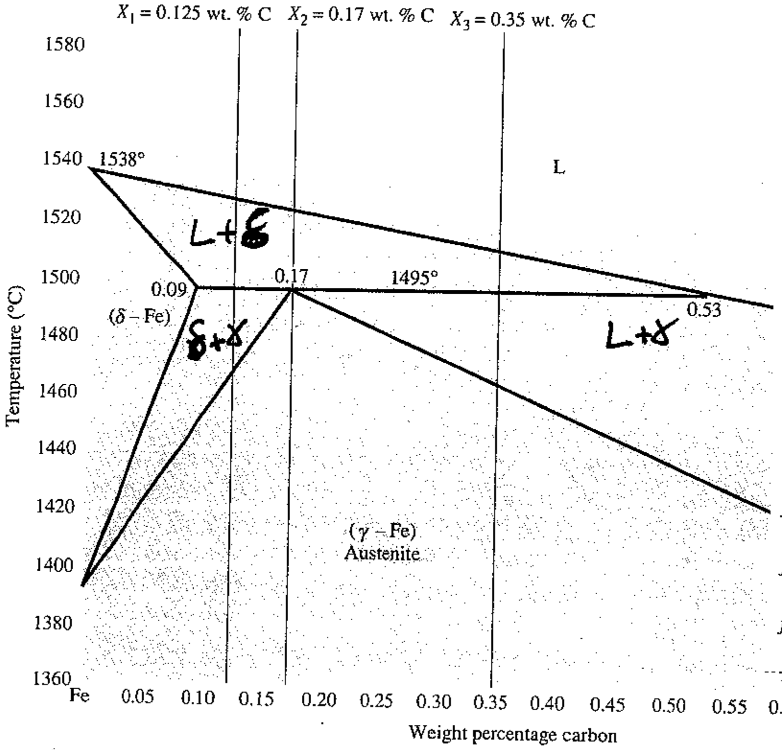
FIGURE 7.5–2 (a) A binary peritectic phase diagram and the associated terms used to describe regions of a peritectic system, (b) a simple peritectic system showing the equilibrium cooling of an alloy whose composition is the peritectic composition X_P, and (c) the corresponding cooling curve for alloy X_P.

at Perit

$L + \alpha \rightleftarrows \beta$

β gets frozen
and changes
concentration
with T.

X in weight ⇒ f in weight



	Above peritectic	Below peritectic
Alloy 1	T=Tp+ε	T=Tp−ε
f_L	$\frac{0.125-0.09}{0.53-0.09} = 0.080$	0
f_δ	$\frac{0.53-0.125}{0.53-0.09} = 0.920$ δPRIM	$\frac{0.17-0.125}{0.17-0.09} = 0.563$
f_γ	0	$\frac{0.125-0.09}{0.17-0.09} = 0.437$ γPER
Alloy 2		
f_L	$\frac{0.17-0.09}{0.53-0.09} = 0.182$	0
f_δ	$\frac{0.53-0.17}{0.53-0.09} = 0.818$ δPRIM	0 γPER
f_γ	0	1.0 (single phase)
Alloy 3		
f_L	$\frac{0.35-0.09}{0.53-0.09} = 0.591$	$\frac{0.35-0.17}{0.53-0.17} = 0.500$
f_δ	$\frac{0.53-0.35}{0.53-0.09} = 0.409$ δPRIM	0 γPER
f_γ	0	$\frac{0.53-0.35}{0.53-0.17} = 0.500$

$x_L = 12$
$x_S = 9$
$x_\gamma = 17$

$L + \delta \rightleftarrows \gamma$

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.

PE 36

MONO TECTIC PHASE DIAGRAM

like eutectic but for liquids!
liquid A hates liquid B ⟹ don't mix
⟹ miscibility gap for liquids (region L_1+L_2)
and results Liquid 1 & liquid 2 outside.

OIL + WATER

Mix only at high temp

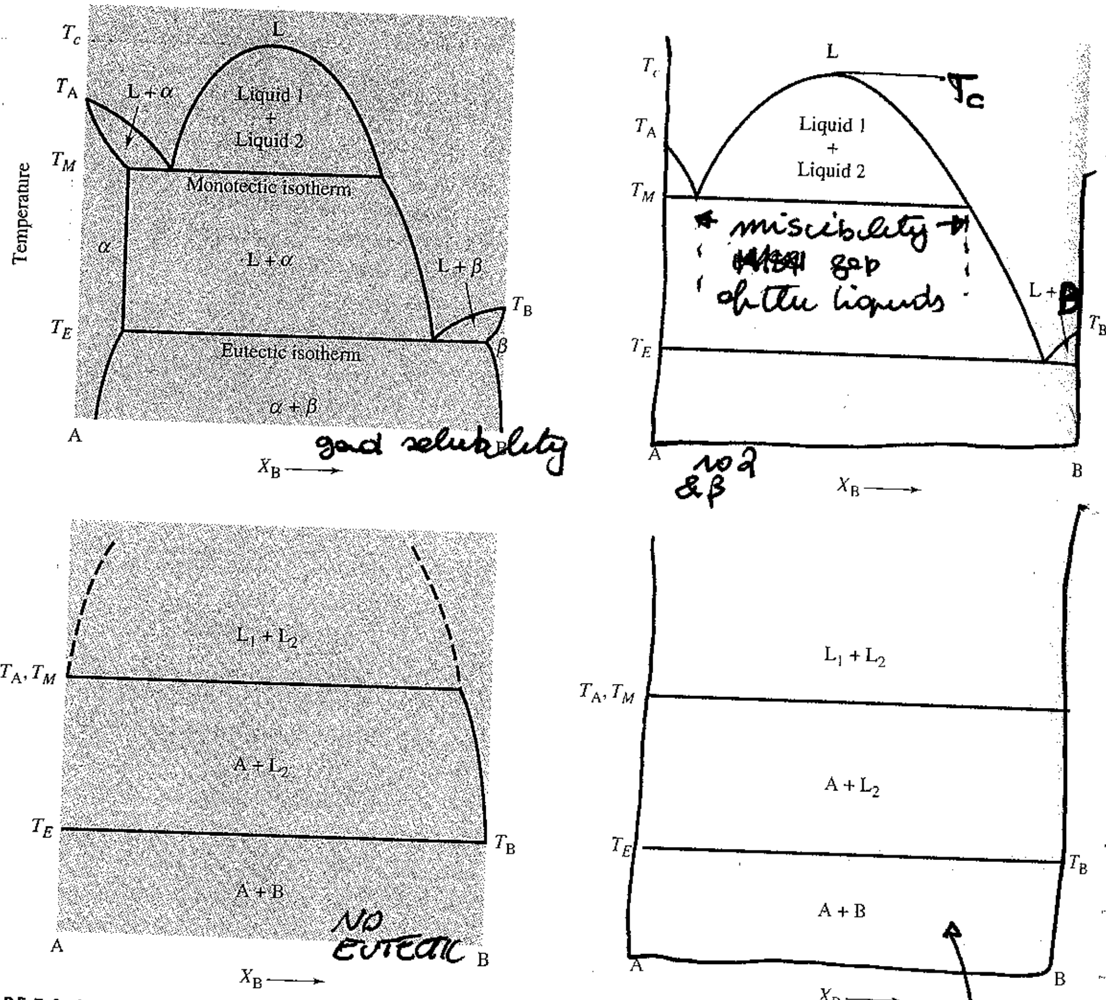
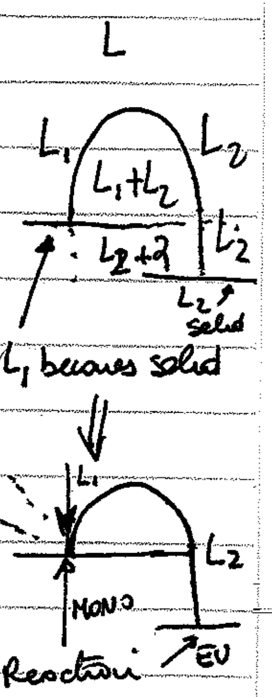


FIGURE 7.6–1 The limiting case of the monotectic reaction occurs when there is effectively no mutual solubility in either the liquid or solid phase.



$$L_1 \rightleftarrows L_2+\alpha$$

another invariant point!

3 phases

$$\begin{aligned}F&=C-P+\underset{\downarrow}{2}\\&=2-3+1\\&=0\end{aligned}$$

0D point INVARIANT

⟹ α is not α PRIMITIVE but MONOTECTOID

SUMM:
EU $L \rightleftarrows \alpha+\beta$
PER $L+\alpha \rightleftarrows \beta$
MONO $L_1 \rightleftarrows L_2+\alpha$
C.Melt $L \rightleftarrows \alpha$

NO SOLUBILITY FOR SOLIDS & LIQUIDS!

CuW
only way to MIXING is sintering

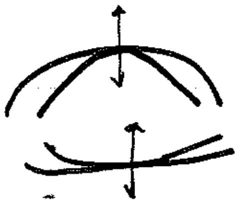
PE 37

COMPLEX DIAGRAMS : diversity IS FUN!

1) for students everything is complex
2) for professors complex systems = many 2 phase regions & invariant points

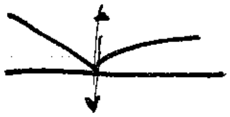
Remember

- CONGRUENT MELTING



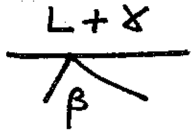
$L \rightleftarrows \alpha$

- EUTECTIC POINT



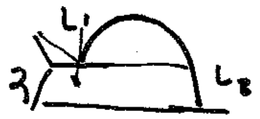
$L \rightleftarrows \alpha + \beta$ (eutectic)

- PERITECTIC POINT

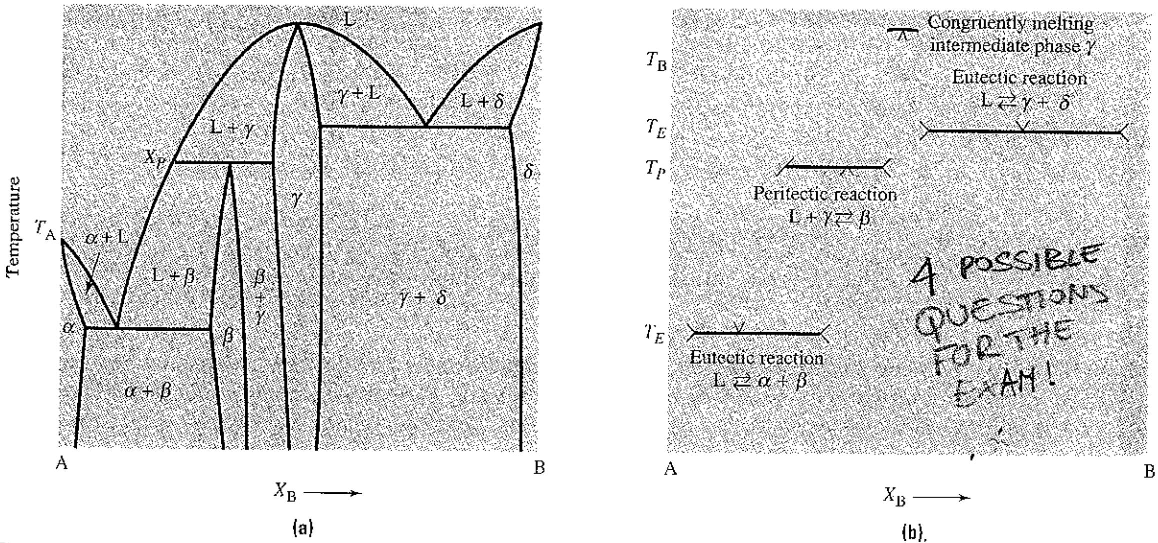


$L + \gamma \rightleftarrows \beta$ (peritectic)

- MONO~~E~~TECTIC POINT



$L_1 \rightleftarrows L_2 + \alpha$ α non eutectoid



(a)

(b)

4 POSSIBLE QUESTIONS FOR THE EXAM!

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 symbolic representations. When the β phase is heated to the peritectic temperature, an incongruent melting reaction occurs at T_P, the peritectic temperature.

PE38

IDEA: BREAK PHASE DIAGRAMS IN "AS MANY PART AS POSSIBLE" $\Rightarrow$ IT BECOMES EASIER

EXTRA TROUBLE:

- INCONGRUENT MELTING: if Liquid solidifies to a phase with different concentration?

$L + ? \rightleftharpoons \beta$

HOW IS THIS POSSIBLE?

$L + ? \rightleftharpoons \beta$

x_L ↙ ↑ some thing else ↘ $x_\beta \neq x_L$

$L + \alpha \rightleftharpoons \beta$ = like in peritectic

IF NO SOLUBILITIES ON intermediate phases

PHASES (BROAD CONCENTRATION) $\xrightarrow{\text{NO SOLUBILITIES}}$ COMPOUNDS

$\alpha, \beta, \gamma \ldots \Rightarrow A, B, A_2B \ldots$

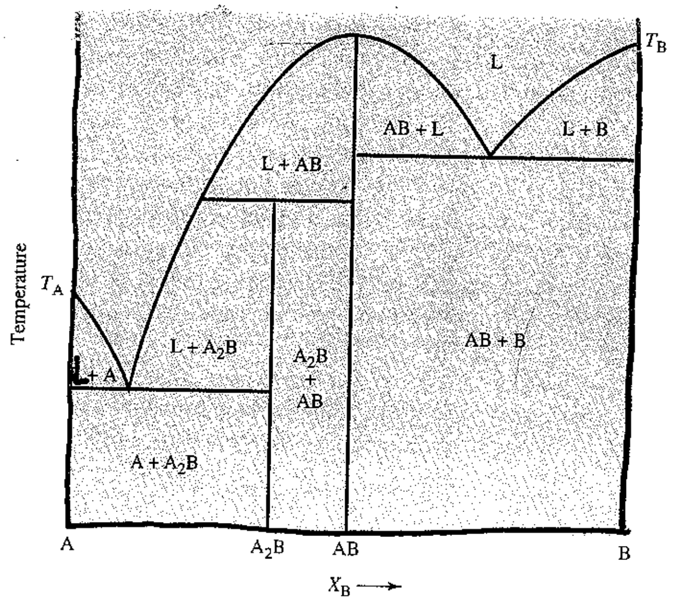


FIGURE 7.7–2 A diagram similar to Figure 7.7–1, but the β and γ are seen as line compounds. The α and δ phases are terminal solid solutions with essentially no solubility. Thus, they are simply labeled A and B, corresponding to the pure components.

NICKEL- ALUMINUM

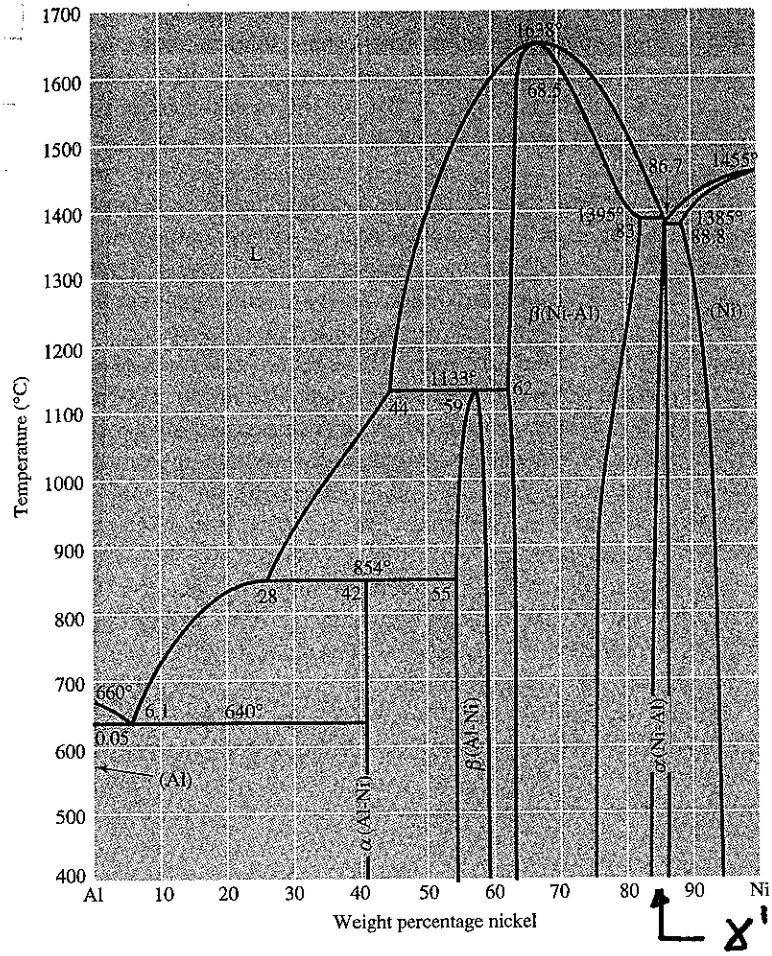


FIGURE 7.7–3
The Al-Ni binary phase diagram.

↑ └ γ' = FUNDAMENTAL IN STRENGTHENING OF NI-SUPERALLOYS

It is worth noting that α(Ni-Al) is often called γ' and is the basis of strengthening in Ni-base superalloys.

(PRECIPITATES OF γ'
FORM AGLOMERATES THAT
STOP DISLOCATION MOVEMENTS
BREAK PLASTICITY } NO DEFORMATION PERMANENT
KEEP ELASTICITY }
⇓
SUPERALLOY !!

PE
40

PHASE EQUILIBRA WITH SOL-SOL REACTION

LIQUID REACTION

$L \rightleftarrows \alpha+\beta$ EUTECTIC

$L+\alpha \rightleftarrows \beta$ PERITECTIC

$L_1 \rightleftarrows L_2+\alpha$ NONOTECTIC

SUBSTITUTE

L with a phase solid γ

$\gamma \rightleftarrows \alpha+\beta$ EUTECTOID

$\gamma+\alpha \rightleftarrows \beta$ PERITECTOID

$\gamma_1 \rightleftarrows \gamma_2+\beta$ MONOTECTOID

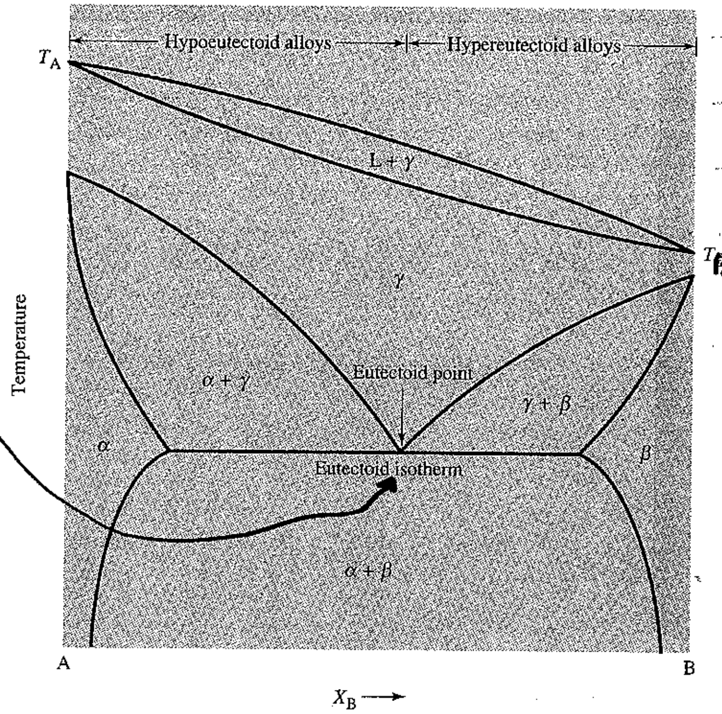
FIGURE 7.8–1

A general eutectoid equilibrium phase diagram with associated definitions.

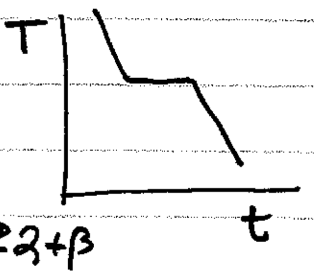
EUTECTOID SYSTEM

SOLID PH. decomposes in 2 SOLID PHASES

$\gamma \rightleftarrows \alpha+\beta$



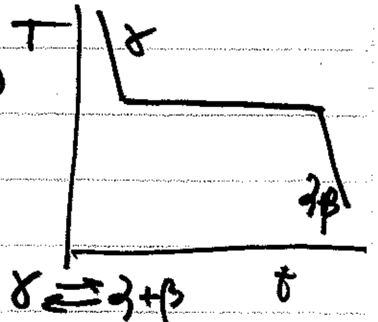
EUTECTIC



$L \rightleftarrows \alpha+\beta$

Reactions are fast because diffusion in L is fast ⇒ α, β low time to FORM & separate

EUTECTOID



$\gamma \rightleftarrows \alpha+\beta$

[diff is Faster along grain boundaries ⇒ EUT. α, β growth FROM G.B]

Reaction are slow diffusion in solid is slow ⇒ α, β slowly growing!

[redacted]
PE41

IRON · CARBON HAS EUTECTOID

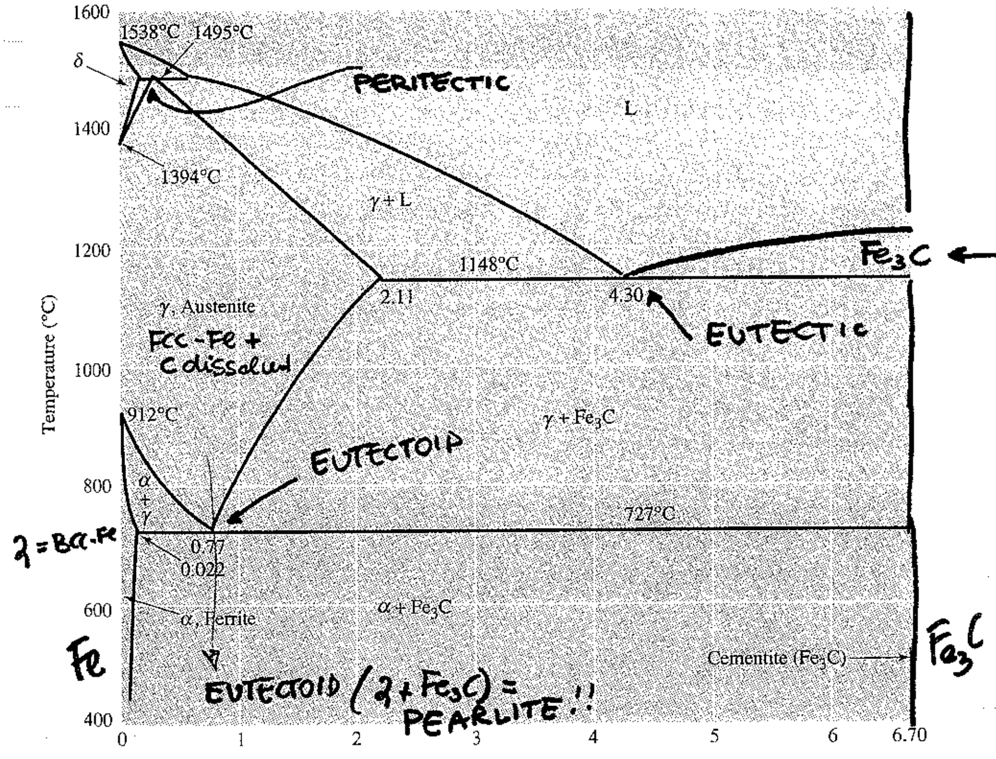


FIGURE 7.8–2 The Fe-Fe$_3$C system with the important phase fields defined.

← CEMENTITE

See: NO SOLUBILITY OF Fe in Fe$_3$C

BOOK: TAKE γ (austenite) with 0.77% w of C & cool down

EUTECTOID @ 727°C

$$\underset{\text{Austenite}}{\underset{\swarrow}{\gamma}} \rightleftharpoons \underset{\text{Ferrite}}{\underset{\downarrow}{\alpha^{\text{PRIM}}}} + \underbrace{(\alpha+Fe_3C)}_{\text{Pearlite}}^{\text{EUTECTOID}}$$

SEE: solubility OF C in γ (FCC-Fe) is bigger than in α (BCC-Fe)

WHY?

↳ as long as you have γ (with > 0.022 % w of C ⇒ you get pearlite)

PE42

IN PRACTICAL WORDS:

WE HAVE PEARLITE ALL OVER THE PLACE

EUTECTOID (α + Fe_3C) = PEARLITE

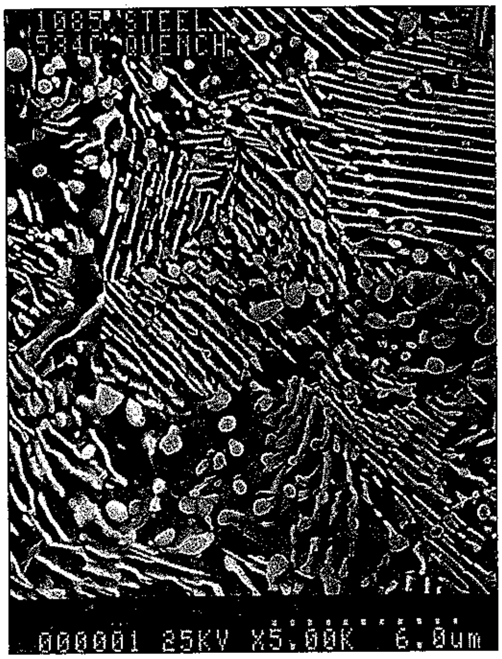


FIGURE 7.8–3 Structure of the eutectoid composition 0.77 wt. % C steel. The eutectoid constituent, called pearlite, has a lamellar (layered) morphology consisting of alternating plates of α Fe (light areas) and Fe_3C (dark areas).

COPPER-ALUMINUM.

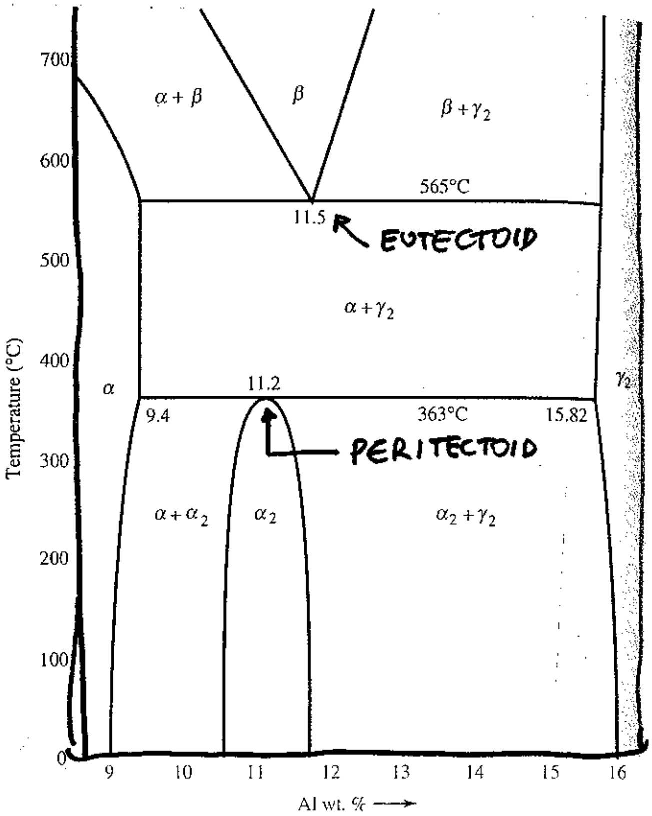


FIGURE 7 The copper-rich side of the Cu-Al system shows a peritectoid reaction in the approximate temperature range of 300–400°C. Symbolically the reaction is written $\alpha + \gamma_2 \rightleftarrows \alpha_2$. *(Source: Adapted from Albert Prince,* Alloy Phase Equilibria, *1966. Permission granted from Elsevier Science.)*

ZINC
ALUM.

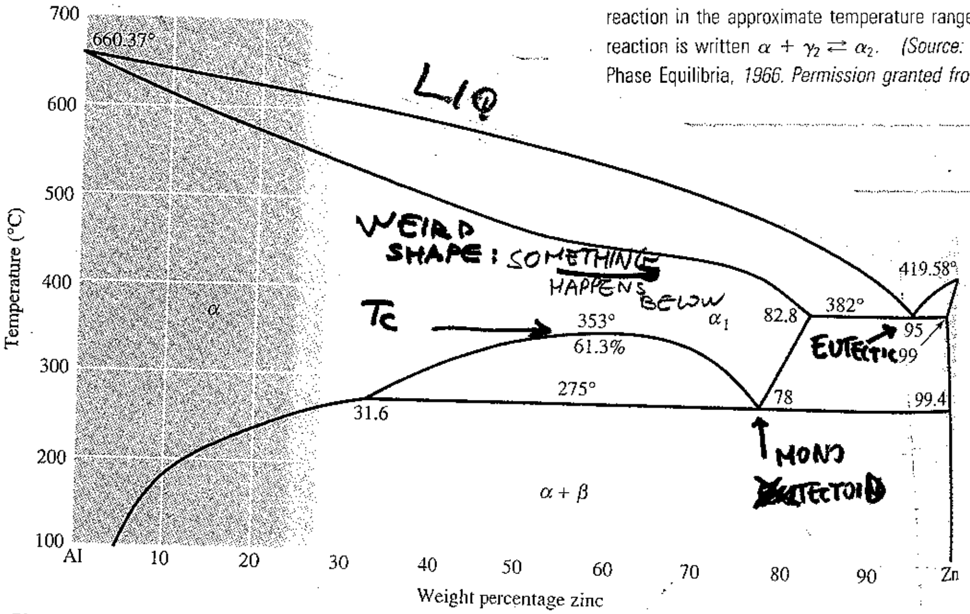


FIGURE 7.8–5 The Al-Zn systems contain a monotectoid reaction at 275°C. Symbolically the reaction is $\alpha_1 \rightleftarrows \alpha + \beta$.

PE 43

KINETICS

KINETIC OF PHASE TRANSFORMATIONS

Equilibrium ⇒ PHASE DIAGRAMS
NON equilibrium ⇒ KINETIC OF PHASE TRANSFORMATIONS

Kinetic = things change (evolve) ⇒ KINETIC = evolution = rate ~~of~~ ~~speed~~ at which the phenomenon occurs.

Example: liquid → solid ⇒ transformation has time to occur
⇒ liquid copper to solid copper ⇒ NO ENERGY STRAIN
⇒ volume adapts inside liquid

but solid ⇒ solid ⇒ transformation has troubles
⇒ plenty of ENERY STRAIN → volume of α must squeeze (expand) β to make you for α

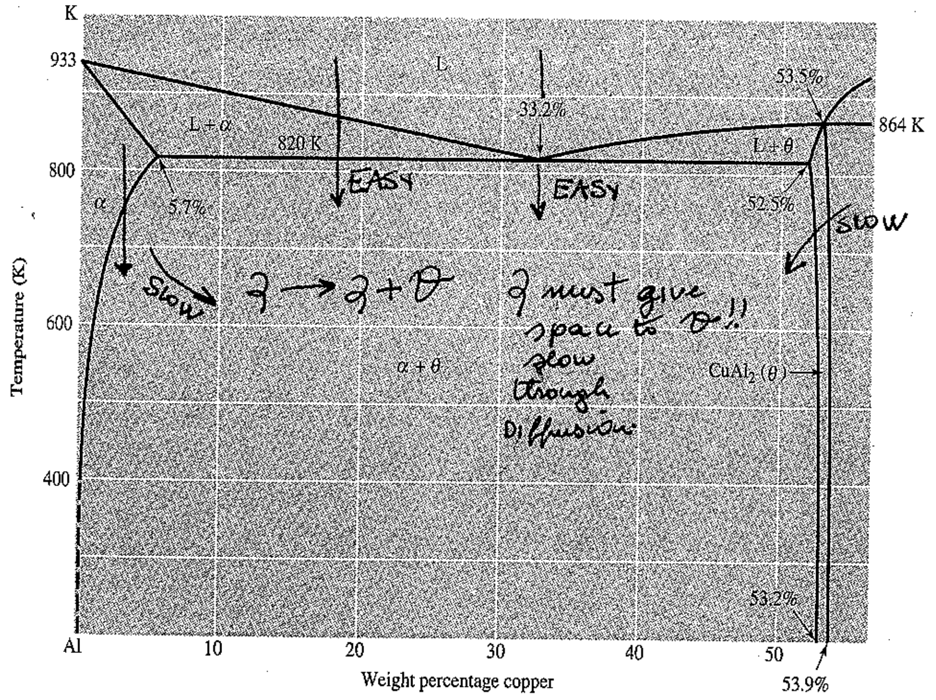


FIGURE 8.2–1
The aluminum-rich end of the Al-Cu binary phase diagram.

SLOW
SLOW KINETIC
⟷
EASY
FAST KINETIC

K1

IF I Remove Heat too fast (T↓ FAST)
then I create some microstructures that I might not want

for practical alloys, many heat treatments are necessary! (to get rid of microstructures)
form

It's all a matter of temperature ⇒ NOT E but G!!

DRIVING FORCE OF A TRANSFORM.

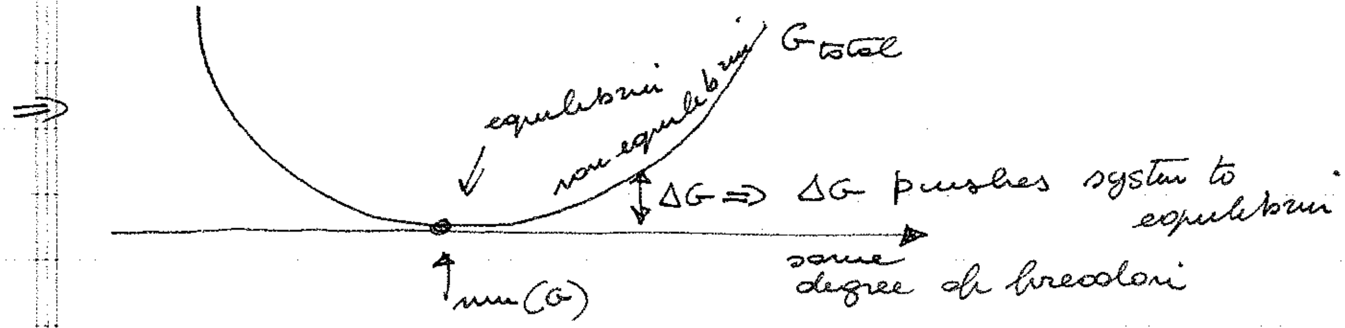
→ for const V & S problems ⇒ min(E)

$E \rightarrow dE = -p\,dV + T\,dS$ (or $\sigma d\varepsilon$ instead of $-p\,dV$)

enthalpy $H = E + PV \Rightarrow dH = V\,dP + T\,dS$ for costant pressure & entropy problems ⇒ min(H)

gibbs free energy $G = \underbrace{E + PV}_{H} - TS$ $dG = V\,dP - S\,dT$

$\hookrightarrow$ min(G) → stable equilibrium



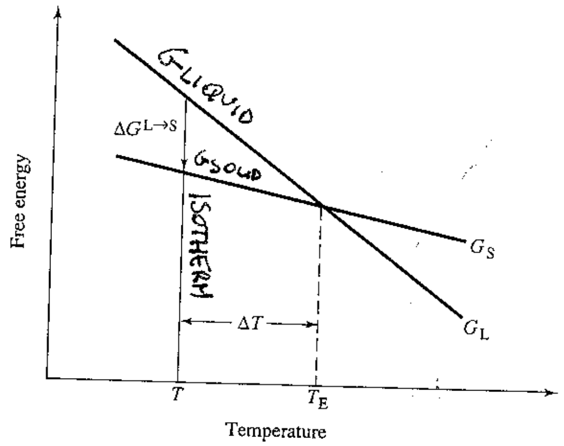
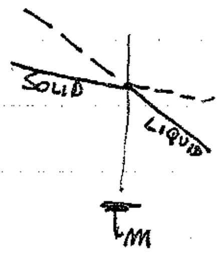


FIGURE 8.2–2
An approximation of the variation in free energy for the liquid and solid phases close to the equilibrium melting temperature.

⇒ equilibrium min(G) →



K2

LIQUID & SOLIDS have different S & E ⇒ different slopes!!

trousformation LIQ → SOLID $\Delta G^{L\to S}$ is driving force

at cost T

$G = H - TS$

$$\left(\Delta G^{L\to S} = \Delta H^{L\to S} - T\Delta S^{L\to S}\right) = ~~G~~$$

FINAL − INITIAL

$\Delta G^{L\to S} = G^{S} - G^{Liq}$ $\quad \Delta S^{L\to S} = S^{S} - S^{L}$

$\Delta H^{L\to S} = H^{S} - H^{L}$

Remember $dH = Vdp + Tds$ so if you keep always $p = 1$ = cost

$\Rightarrow dH = TdS = \delta Q$ = internal hot

$$\Rightarrow \boxed{\Delta H^{L\to S}_{P_{co}} = \delta Q^{L\to S}} =$$ Release or adsorption of heat during L→S reaction !!

LATENT HEAT

EXOTERMIC
ENDOTERMIC

$$\Delta G^{L\to S} = \Delta H^{L\to S} - T\Delta S^{L\to S}$$

@ melting T_M $\quad \Delta G^{L\to S} = 0 \Rightarrow$ & system switches status

$$\Delta H^{L\to S} - T_M\,\Delta S^{L\to S} = 0$$

$$\Delta S^{L\to S} = \frac{\Delta H^{L\to S}}{T_M} = \frac{\delta Q^{L\to S}}{T_M}$$

$$\Rightarrow \Delta G^{L\to S} = \Delta H^{L\to S} - T\,\frac{\Delta H^{L\to S}}{T_M}$$

$\Delta T \equiv T_M - T$

↓

$$\Delta G^{L\to S} = \Delta H^{L\to S}\left(1 - \frac{T}{T_M}\right) = \Delta H^{L-S}\,\frac{\Delta T}{T_M}$$

$$\boxed{\begin{array}{c}\Delta G^{L\to S} = \dfrac{\Delta H^{L-S}}{T_M}\,\Delta T \\ \Delta T = T_M - T\end{array}}$$

$\Delta H^{L\to S} = \delta Q$

K3

which is Favorite ?

depends on sign of $\Delta H^{L\to S}$

$$\Delta H^{L\to S} = H^S - H^L = \delta Q^{L\to S}$$

$$\Delta G^{L\to S} = \frac{\Delta H^{L\to S}}{T_M}\Delta T$$

higher (lower) is the temperature (& bigger is ΔT) ⇒ the stronger is ΔG ⇒ stronger is driving force

Temperature is EVERYTHING

1) T gives defects (necessary)
2) T gives entropy (diversity of configurations)
3) ΔT gives transformation driving force.

EXAMPLE = PURE SUBSTANCE

Pure substance

liquid has more energy in L than in S $\Rightarrow H^S < H^L$

$\Rightarrow \delta Q^{L\to S} < 0$ HEAT↓ INTERNAL ⇒

⇒ HEAT IS EXPELLED

EXOTHERMIC

$\Delta H^{L\to S} < 0$

at high temp $T > T_M$

$\Delta T = T_M - T < 0$

$\Rightarrow \Delta G^{L\to S} = \frac{\overset{<0}{\Delta H^{L\to S}}}{T_M}\overset{<0}{\Delta T} > 0$

$\Rightarrow L\to S$ IS DISFAVORED

$\Rightarrow S\to L$ TRANSFORMATION

at low temperature $T < T_m$

$\Delta T > 0$

$\Delta G^{L\to S} = \frac{\overset{<0}{\Delta H^{L\to S}}}{T_M}\overset{>0}{\Delta T} < 0$

G↓ gets better minimum with L→S

L→S is FAVORED !!

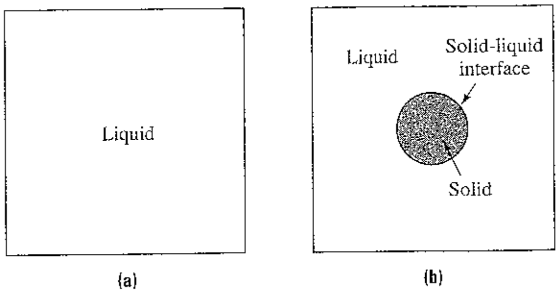
NUCLEATION

HOMOGENEOUS
if particles
appears randomly

HETEROGENEOU
if particles
appear in specific
places

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.

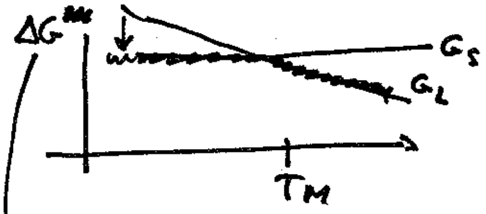


K4

HOMOGENEOUS NUCLEATION

- HAVE LIQUID
- COOL IT UNDER T_M ⇒ wants to SOLIDIFY

$$\boxed{\begin{array}{l} \Delta G^{L\to S} = \Delta H^{L-S}\dfrac{\Delta T}{T_m} \\ \Delta T = T_M - T \\ \Delta G^{L\to S} = G^S - G^L \end{array}}$$



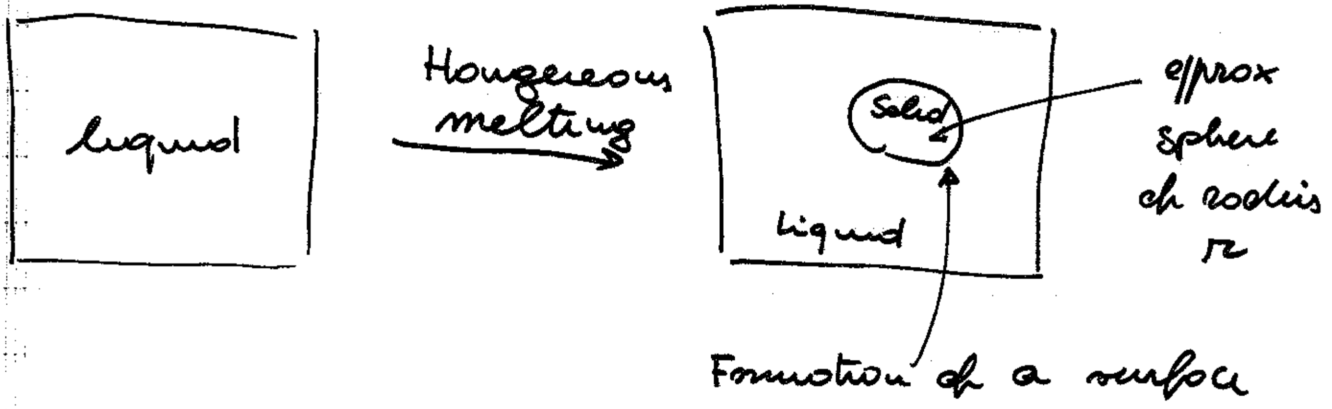
EXOTERMIC ~ release heat
$\Rightarrow \Delta H^{L\to S} < 0$
(wants to solidify)

(like E, S, ...)

this ΔG is extensive (2V → 2ΔG)
⇒ let's introduce ΔG_v = Free energy per unit volume.

$$\Rightarrow \Delta G = V \underbrace{\Delta G_v}_{(J/m^3)} \quad \text{simple.} \quad < 0$$

(sistem wants to solidify)



CREATION OF SURFACE ⇒ REQUIRES ENERGY
(like making a chew-gum bubble)

Energy $\propto$ surface
$= \gamma_s \cdot$ surface

(J/m^2)
γ_s = surface energy

K5

⇒ to create (nucleate) sphere of radius r

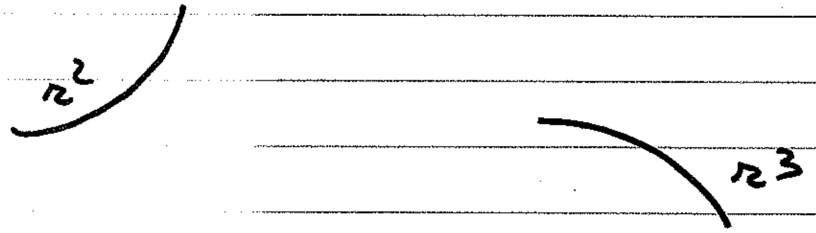
surface = $4 \pi r^2$

Volume = $\frac{4}{3} \pi r^3$ $\qquad \underbrace{\frac{4}{3} \pi r^3 \Delta H^{L \to S} \frac{\Delta T}{T_m}}$

$$\Rightarrow \quad \Delta G = \underbrace{4 \pi r^2 \gamma_s}_{\text{POSITIVE} > 0} + \underbrace{\frac{4}{3} \pi r^3 \Delta G_v^{L \to S}}_{\text{NEGATIVE} < 0}$$

the system ~~does~~ HATES SURFACE

the system LOVES TO SOLIDIFY



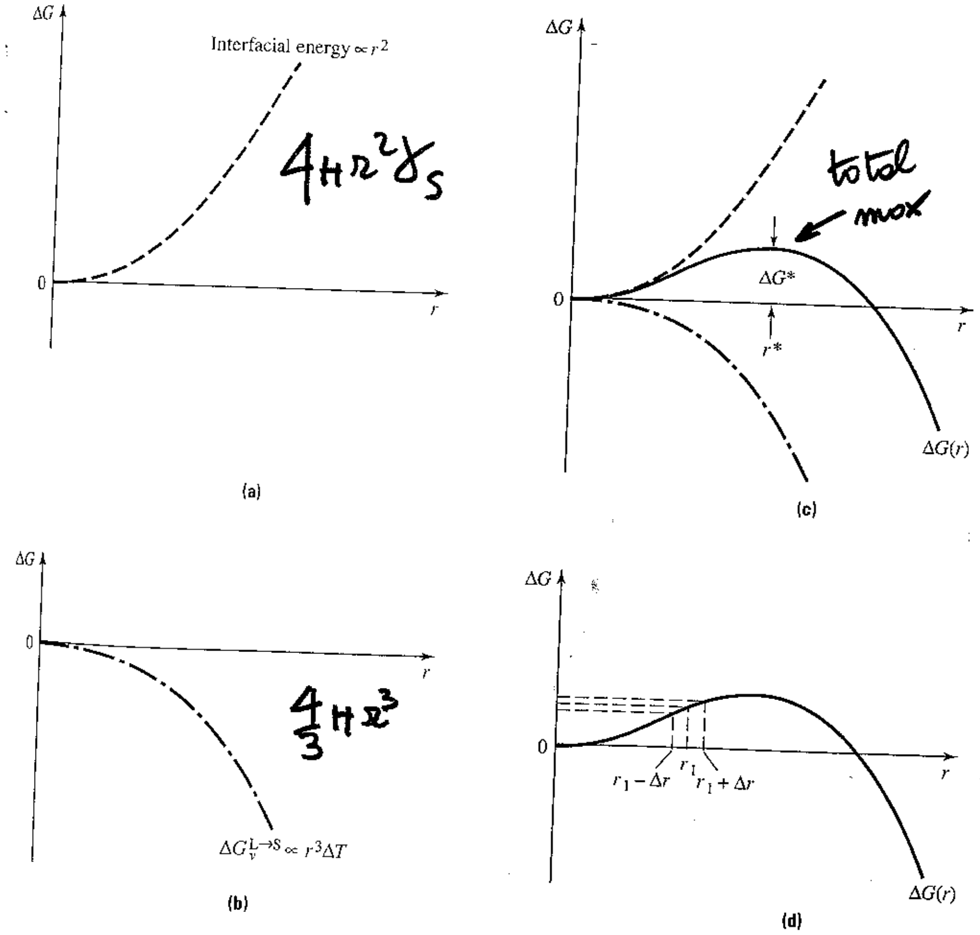
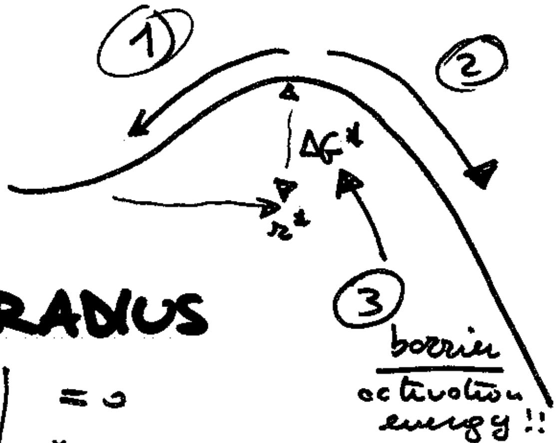


FIGURE 8.2–4

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 $\Delta G_v^{L \to S}$, **(c)** the sum of the previous two curves, and **(d)** an annotated version of ΔG plotted versus r (see footnote 1 on page 294).

Remember that $\min(G) =$ thermodynamical equilibrium

$\Rightarrow$ 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 ΔG^* to start nucleation

sort of activation energy

CRITICAL RADIUS

$$r^* \Rightarrow \left.\frac{\partial \Delta G}{\partial r}\right|_{r^*} = 0$$

$$0 = \frac{\partial \Delta G}{\partial r} = \frac{\partial}{\partial r}\left[4\pi r^2 \gamma_S + \frac{4}{3}\pi r^3 \Delta G_v^{L\to S}\right]$$

$$= 8\pi r \gamma_S + 4\pi r^2 \Delta G_v^{L\to S} = 0 \Rightarrow \cancel{\Delta G_v^{L\to S} = \frac{8\pi r \gamma_S}{4\pi r^2}}$$

$$\Downarrow$$

$$2\gamma_S + r\Delta G_v^{L\to S} = 0$$

$$r^* = -\frac{2\gamma_S}{\Delta G_v^{L\to S}}$$

$$= -\frac{2\gamma_S}{\Delta H_v^{L\to S}}\frac{T_M}{\Delta T}$$

$$r^* \propto \frac{1}{\Delta T}$$

$\Delta T \uparrow$ $r^* \downarrow$ $\Rightarrow$ easy to nucleate

K7

so $$\boxed{r^* = \frac{-2\gamma_s}{\Delta H_v^{L\to s}} \frac{T_m}{\Delta T}}$$

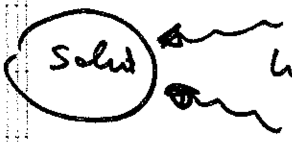
$\Delta G^* = \Delta G(r^*) \Rightarrow$ plug r^* inside $\Delta G(r)$ and obtain

$$\boxed{\Delta G^* = \frac{16\pi \gamma_s^3 T_M^2}{3(\Delta H_v^{L\to s})^2} * \frac{1}{\Delta T^2}}$$

$\Delta T\uparrow$ $\Delta G^*\downarrow$ barrier.

UNDERCOOLING INCREASES ($\Delta T\uparrow$), THE ENERGY BARRIER DECEASES.

another problem : ~~[illegible]~~ MOBILITY OF LIQUID DUE By difference of concentration



Particles in the liquid must touch the surface to become solid (particles move throu DIFFUSION)
$\Rightarrow$ at low temperature
Diffusion $\propto \exp(-Q/T)$ #
$T\downarrow$ $D\downarrow$ $\Rightarrow$ small ~~flux~~ of particles! to feed the solid.

at very low T ~~cooling~~ solidification decreases.

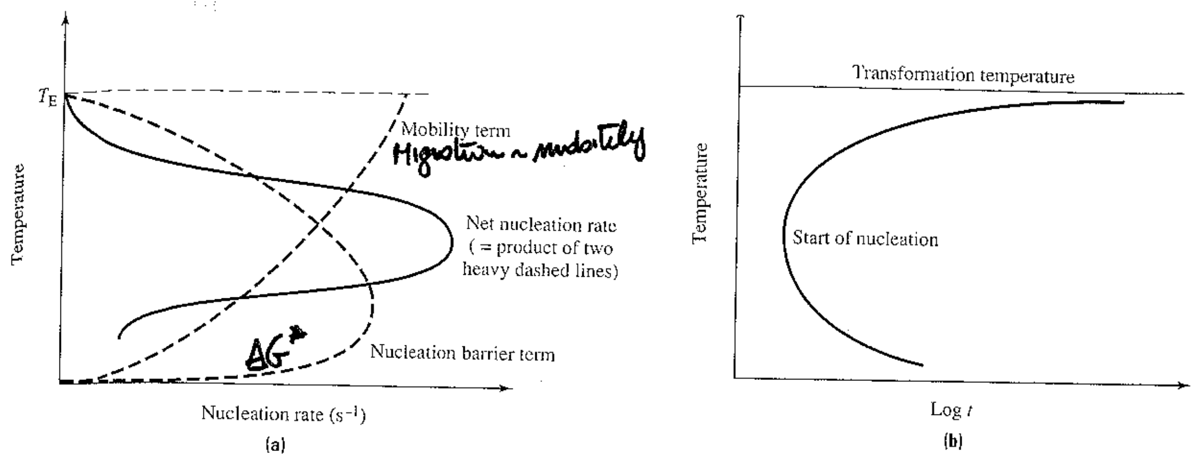


FIGURE 8.2-5 **(a)** The influence of temperature on the mobility term and the nucleation barrier term. The opposing processes result in a maximum in the nucleation rate at an intermediate temperature. **(b)** Since the time for nucleation is inversely related to the nucleation rate, the time curve exhibits a minimum at an intermediate temperature. Because of its shape, this curve is often referred to as a C curve.

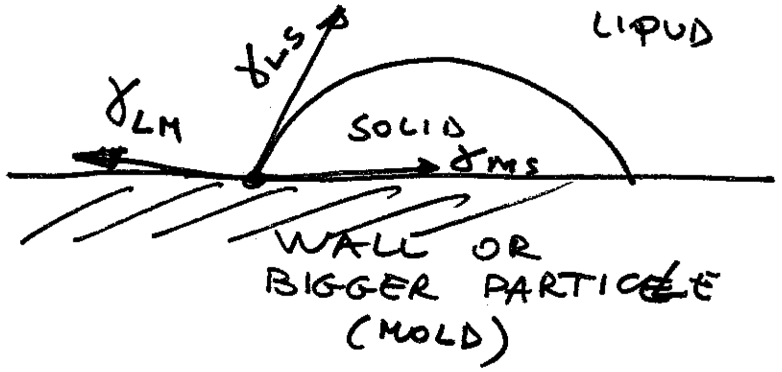
HOMOGENEOUS
~ NEVER.
always start
in some place
HOMOGENEOUS = need SPACE

K8

HETEROGENEOUS NUCLEATION

- IF WE ADD SOME SUBSTANCE (ANOTHER BIG PARTICLE) TO HELP NUCLEATION $\gamma \downarrow$
- WALLS, CORNERS $\gamma \downarrow$

} How? WETTING PROBLEM



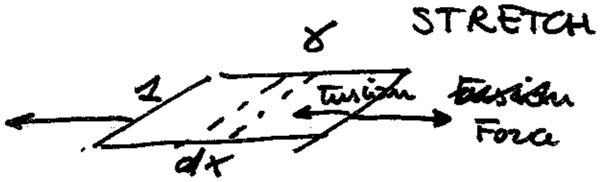
↓

3 surface energies:

Liquid ⇔ solid
liquid ⇔ mold (wall)
mold → solid

surface energies = surface tension

P



$$\underbrace{-\text{tension}\; dx}_{\text{WORK MADE}} = \underbrace{\gamma\, \overset{1dx}{\overset{\parallel}{dA}}}_{\text{energy gained}} = \gamma dx$$

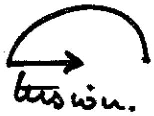
surface tension $\Longleftarrow$

= (surface energy) with direction of ~~tangent~~ tangent to direction when surface grows

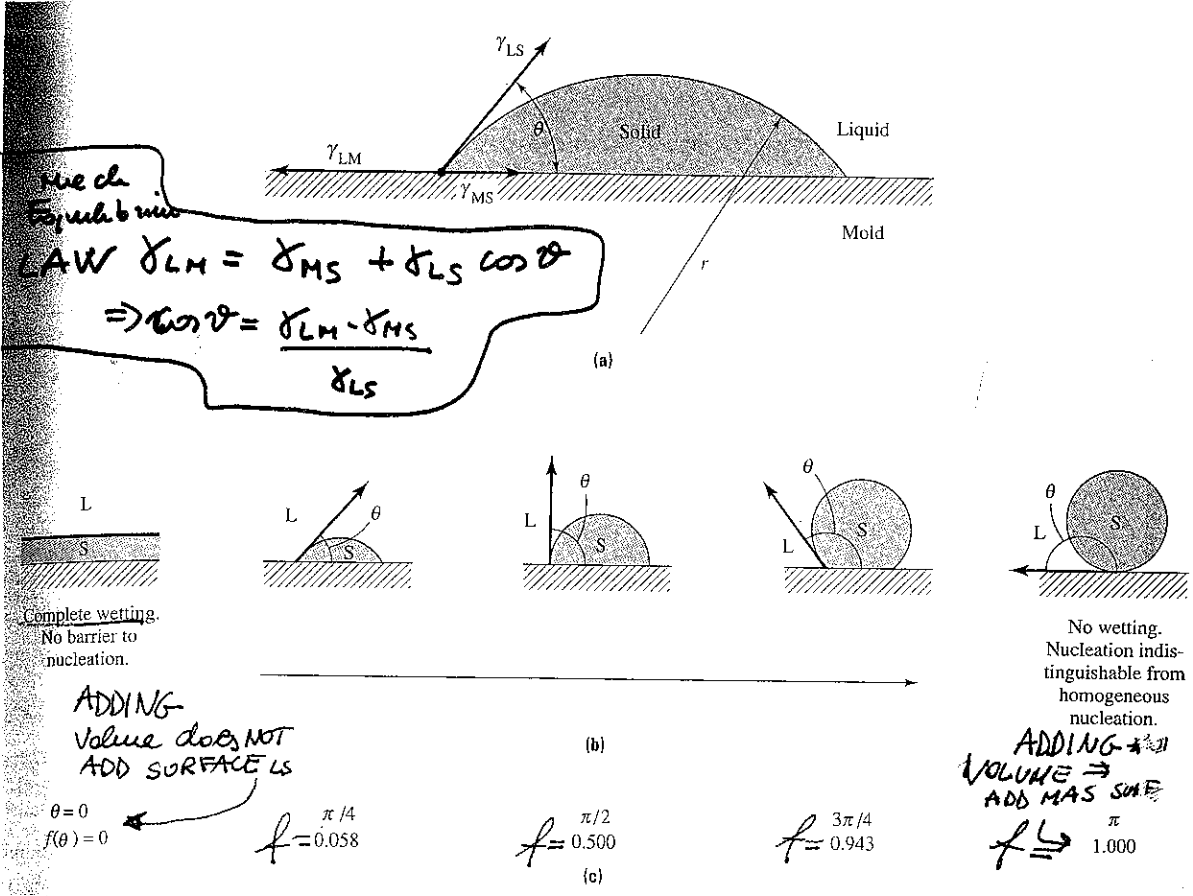
SOLID-LIQUID surface grows (

LIQ.—MOLD surface grows

SOLID-MOLD Surface growth



⇒ and γ_{LS}, γ_{LM}, γ_{SM} ⇒ determine slope bubble.



mech Equilibrium

YOUNG'S LAW $\gamma_{LM} = \gamma_{MS} + \gamma_{LS}\cos\vartheta$
1805

$$\Rightarrow \cos\vartheta = \frac{\gamma_{LM} - \gamma_{MS}}{\gamma_{LS}}$$

ADDING Volume does NOT ADD SURFACE LS

ADDING VOLUME ⇒ ADD MAS SURF

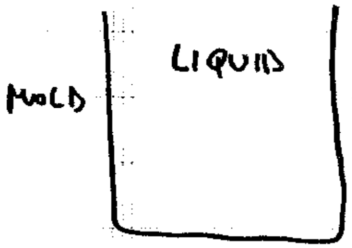
FIGURE 8.2–6 The wetting characteristics of a number of solid-liquid systems: **(a)** The angle θ, as defined in the illustration, is an indication of the wettability of the system; **(b)** as θ increase from $\theta = 0$ to $\theta = \pi$, the wettability decreases; **(c)** the function $f(\theta)$ varies from 0 to 1 as θ varies from 0 to π.

$$\Rightarrow \Delta G^*_{HET} = \Delta G^*_{HOM} * f(\vartheta)$$

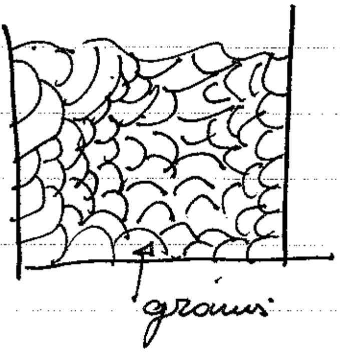
↳ ch 0 (complete wetting)

NO BARRIER TO SOLIDIFICATION

K10



SOLIDIFICATION → FROM THE WALLS

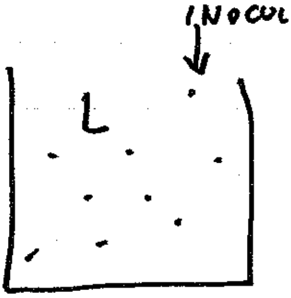


IF WE PREVENT WETTING ON SURFACE OF THE MOLD

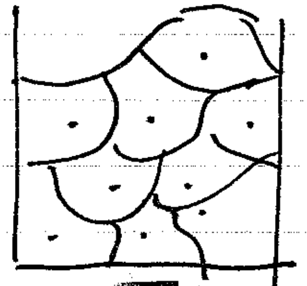
(TiB2 particles in Al) INOCULANT

⇓

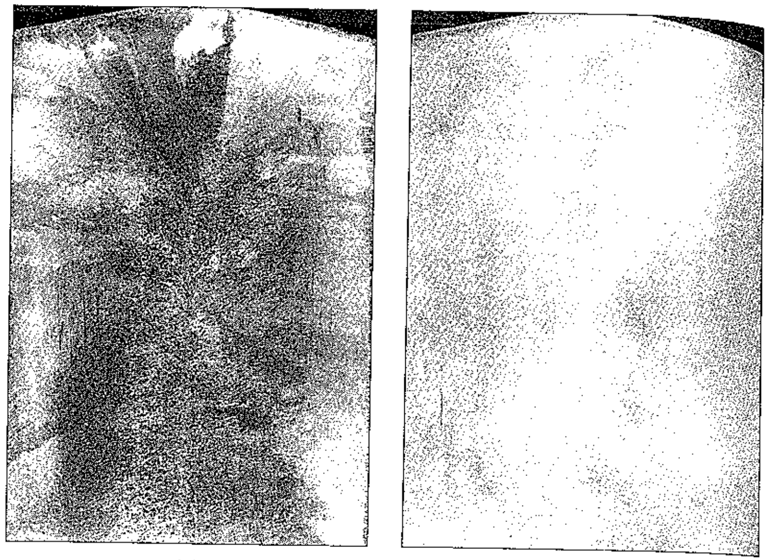
NO WETTING ON SURFACE ⇒ NUCLEATION HETEROGENEOUS ~~A~~ IN RANDOM POSITIONS (LIKE HOMOGENEOUS)



SOLIDIFICATION →



bigger grains ⇒ better CAST



(a) (b)

FIGURE 8.2–7 Photomicrographs of a transverse section from a 20-in × 54-in cast aluminum alloy: **(a)** with no ingot grain refiner, and **(b)** with an ingot grain refiner. Illustration is half the cross section.

KII

SOLID - SOLID INTERFACES (WHEN IN 2 o + PHASE SOLID REGIONS)

Liquid ⇔ Solid interfaces & γ's generate different nucleation. $\boxed{\alpha(\alpha+\beta)\beta}$

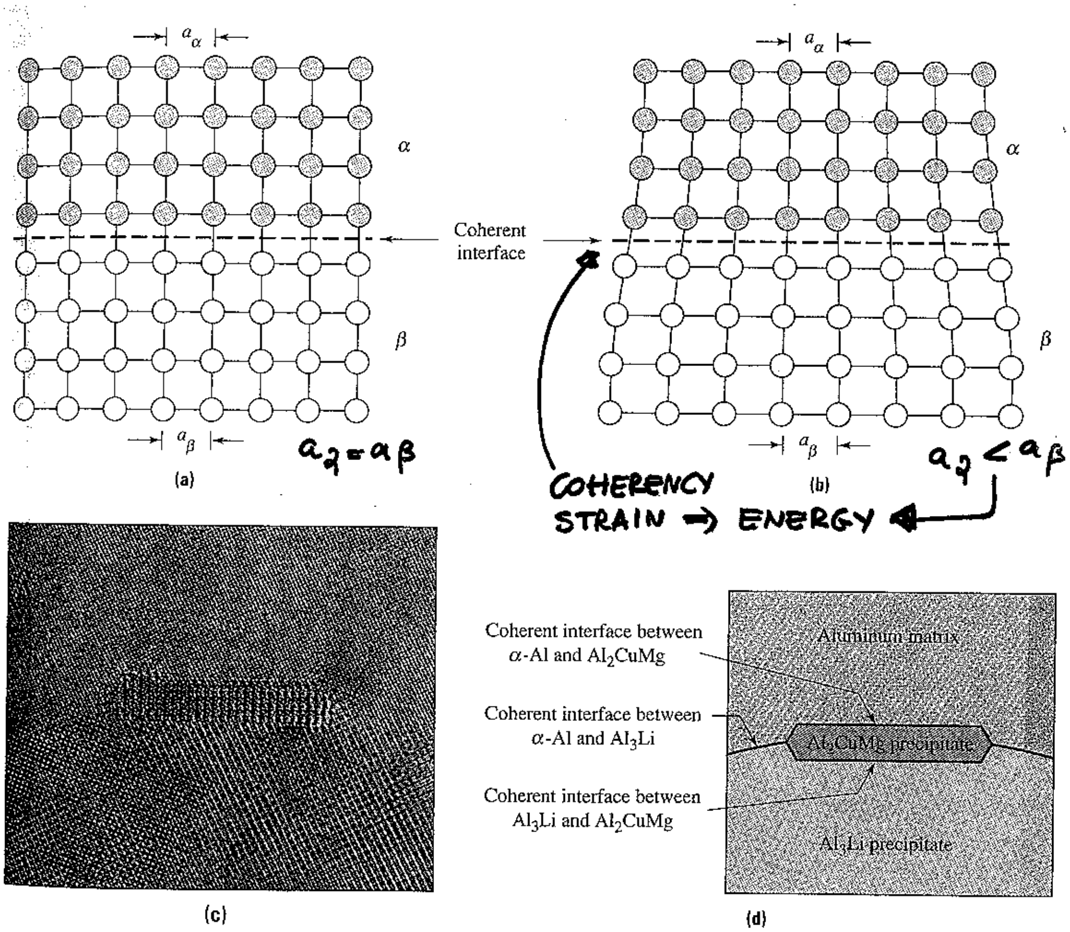
Solid ⇔ Solid interfaces, what happens if I have a big particle inside a sea (matrix) of atoms
($A_x B_y$) A (parent)

MATIRIX ⇔ PRECIPITATE interfaces

COHERENT (α, β same lattice type)

COHERENT INTERFACES: one to one atom corresponding

ONLY if
$a_\alpha = a_\beta$
or
$a_\alpha \simeq a_\beta$
they adjust!
A LITTLE



$a_\alpha = a_\beta$

$a_\alpha < a_\beta$

COHERENCY STRAIN ⇒ ENERGY

FIGURE 8.2–8 Schematic illustration of coherent interface between two phase α and β. **(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.

K12

SEMICOHERENT (α, β same ~~class~~ ~~FCC~~, lattice type)

$a_\alpha < a_\beta$, pump $a_\beta \uparrow$ ⇒ every once in a while one atom slips out the COHERENCY STRAIN

⇒ INTRODUCE PERIODIC DISLOCATION (depend on DIRECTION)

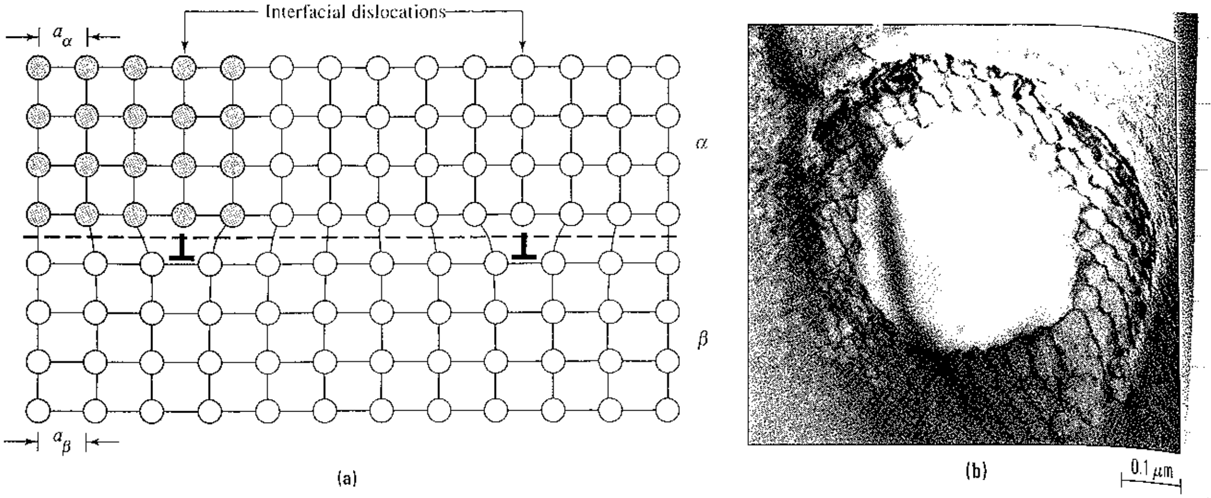


FIGURE 8.2–9 **(a)** Schematic of a semicoherent interface between two phases. The insertion of the periodically spaced dislocations eliminates coherency strains but increases the interfacial energy. **(b)** Regular array of dislocations at the matrix/precipitate interface of a semicoherent precipitate in Astroloy, a high-temperature Ni-base superalloy. *(Source: Photomicrograph courtesy of Mario Luis Maciá).*

INCOHERENT (α, β different lattice types and $a_\alpha \leq a_\beta$)

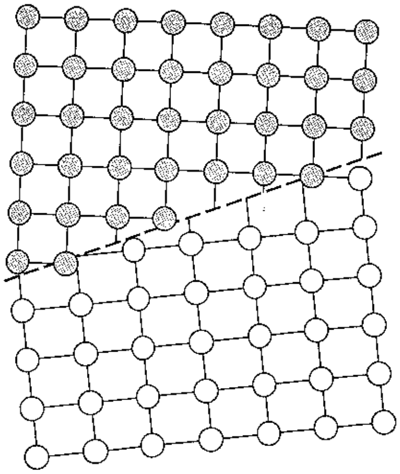


FIGURE 8.2–10 An incoherent interface occurs when the crystal structures and lattice parameters of two phases are different.

largest interfacial energy $\gamma_{\alpha\beta}$

Fe_3C in Fe

COMPLICATE ↔ α BCC

FERRITE

PEARLITE

K13

REMEMBER $$\Delta G^* = \frac{16\pi (\gamma_{SL})^3 T_M^2}{3(\Delta H_V^{L\to S})^2} \cdot \frac{1}{(\Delta T)^2}$$ for solidification

TABLE 8.2.–1 Relationship among interfacial energy, the nature of the nucleation process, and the precipitate.

Type of interface	$\gamma_{\alpha\beta}$ Interfacial energy	Nucleation process	Location of precipitates	Number of precipitates per unit volume
Coherent	Increasing ↓	Homogeneous EASY	Throughout the matrix	$\sim 10^{18}/\text{cm}^3$ many
Semicoherent		Heterogeneous MEDIUM need defect to $\gamma\downarrow$	Mostly at dislocations	Orders of magnitude less than homogeneous nucleation Few
Noncoherent		Heterogeneous HARD TO FORM	At grain boundaries	Orders of magnitude less than homogeneous nucleation Fewest

$\gamma_{\alpha\beta}$

$\sim 200\ \text{mJ/m}^2$

$\sim 500\ \text{mJ/m}^2$

$\sim 1000\ \text{mJ/m}^2$

for solid → solid nucleation $\Delta G^{\alpha\to\beta}$, $\gamma_{\alpha\beta}$, $\Delta H_V^{\alpha\to\beta}$

$$\Longleftarrow \quad \Delta G^*_{\alpha\to\beta} \propto (\gamma_{\alpha\beta})^3 \Rightarrow$$ NONCOHERENT REALLY DOES NOT WANT TO ~~[illegible]~~ APPEAR

$\gamma \to \alpha + \beta$

COHERENT → Precipitates precipitate everywhere (EASY)

SEMICOHERENT → precipitates precipitate around dislocations (which relieve $\gamma\downarrow$) (MEDIUM)

~~HETERG~~ NON-COHERENT → precipitates precipitate ONLY IN regions of grain boundaries where plenty of γ relieve (HARD)

HETEROGENEOUS FORMING PARTICLES GROWTH FAST BEAUSE DEFECTS ARE DIFFUSION CHANNELS

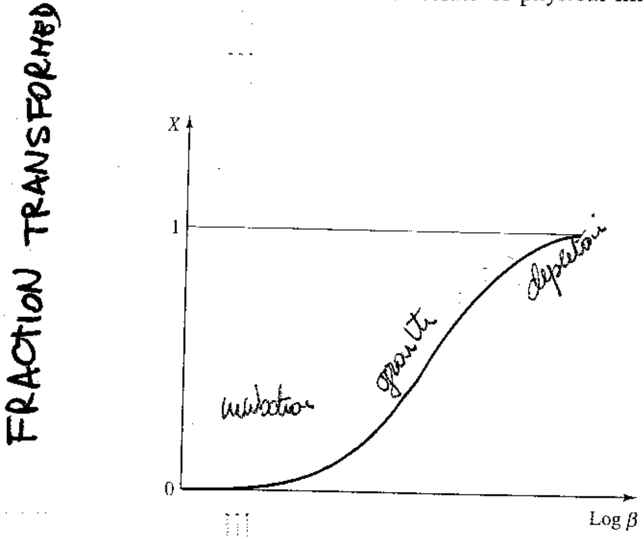
K14

GROWTH OF A PHASE

Nucleation ⇒ growth of phase:
how it works in time

INCUBATION
⇓
GROWTH
⇓
SATURATION

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.



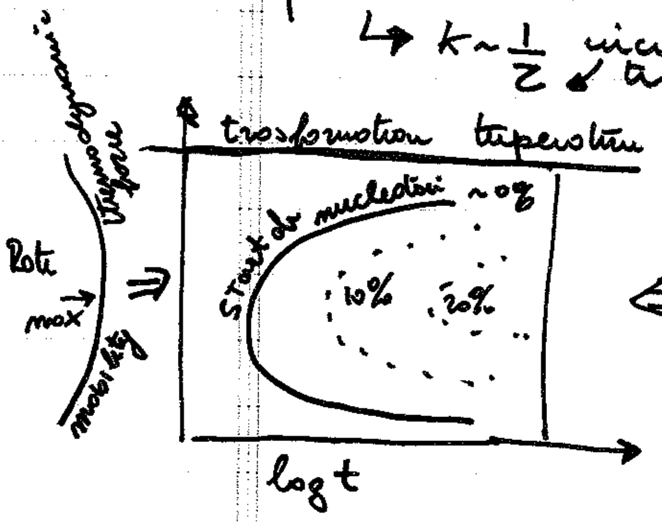
AVRAHI EQUATION

$$x = 1 - \exp\left[-\underbrace{(kt)}_{\beta \equiv kt}{}^{n}\right]$$

INCUBATION = time ~~required~~ ~~reach~~ th before some particle appears with $r > r^*$

$\beta = kT$
↳ $k \sim \frac{1}{\tau}$ incubation time

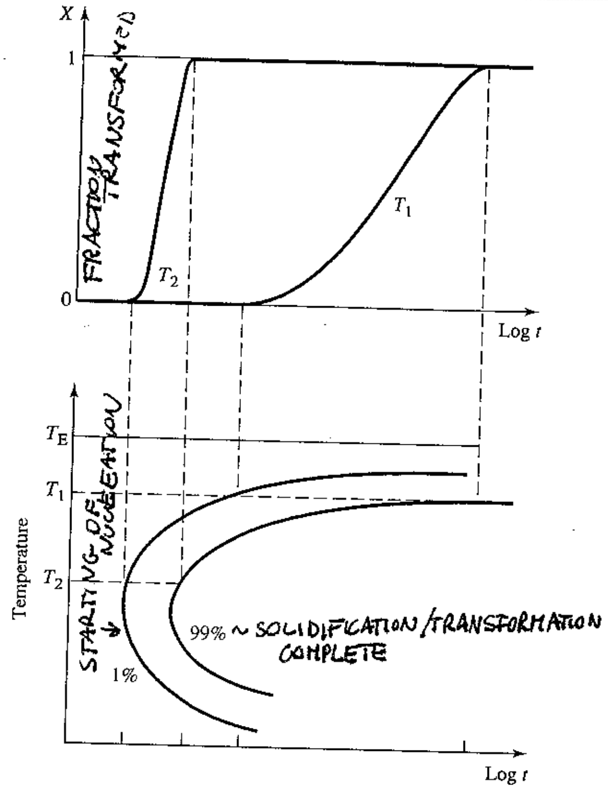
$(\ )^{n} \leftrightarrow 0.5$ to 5 depend on system & structure

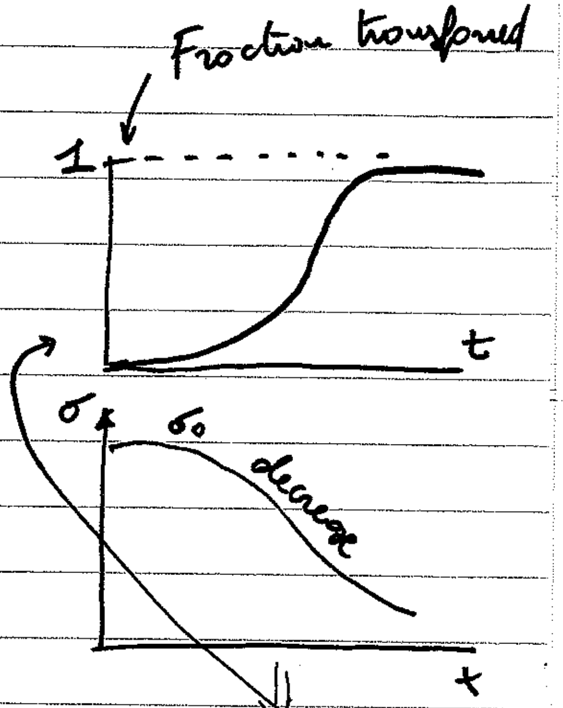


⇐ % transformed

K15

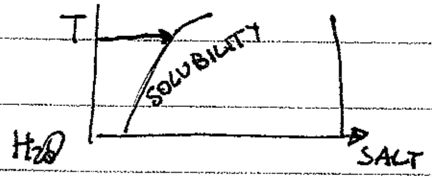
⇒ ISOTHERMAL GROWTH (T= cost)



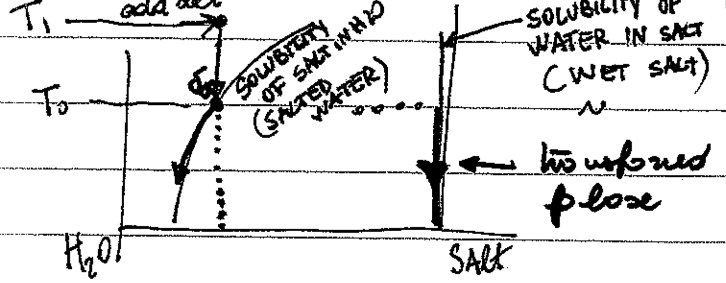


CAN GET NUCLEATION & TRANSFORMATION CURVES WITH MULTIMETER

EXAMPLE : WATER + SALT



1) • HEAT WATER
2) • PUT SALT (A LOT)
3) • GO DOWN IN TEMP
4) • SALT WILL PRECIPTATE



5) @ T_1 salted water looses salt & SALT NUCLEATES

6) SALT PARTICLES DO NOT CONDUCE

7) SALTED WATER CONDUCES

$\sigma = \mu n q$

mobility ~ const

const charge

$n(T)$ = conc of salt in water

⇒ = 1 − fraction of transformed phase ⇒

K16

Homo Nucl

⇒ intergranular precipitates

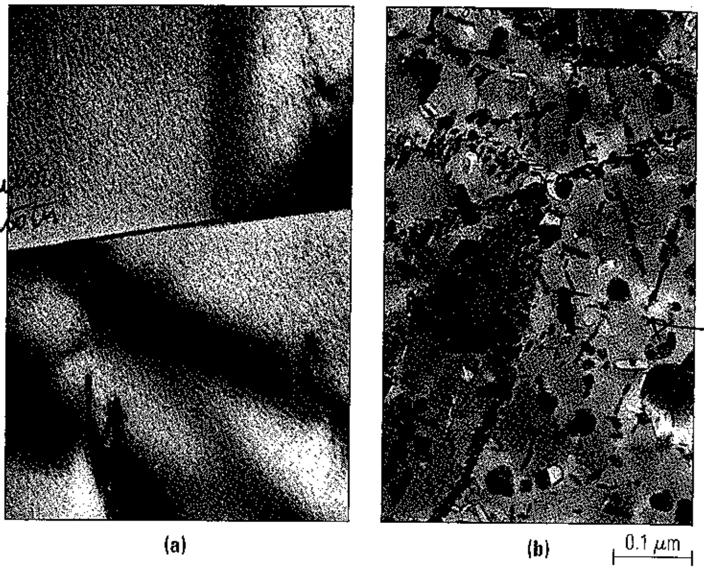
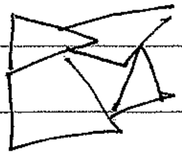


FIGURE 8.2–13 The distribution of precipitates in an aluminum alloy: **(a)** precipitates that homogeneously nucleated, and **(b)** those that heterogeneously nucleated. In part a, the precipitates are the fine, pepperlike features that are scattered throughout.

GRAINS



Heterogeneous nucleation
⇒ precipitates start from defect:
INTRA GRANULAR
(Between grains)

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 depends strongly on the size and spatial distribution of the phases, heat treatment is a powerful tool for modifying the properties of engineering materials.

⇒ Heat treatment twist properties!!

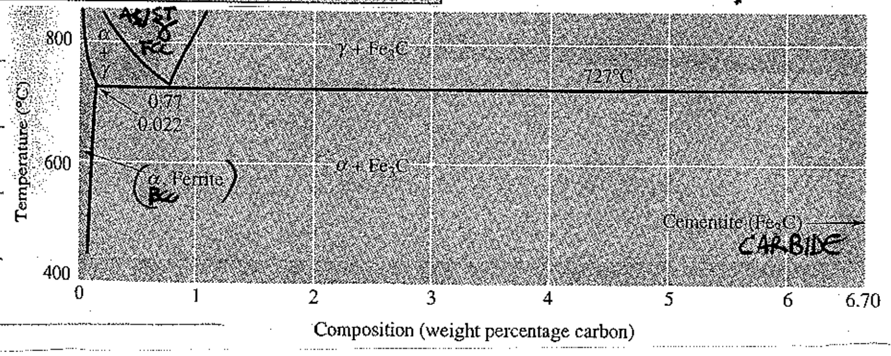
PHASES IN STEEL

Microstructure name	Description
δ-ferrite	An interstitial solid solution of carbon in δ iron (BCC).
Austenite	An interstitial solid solution of carbon in γ iron (FCC).
α-ferrite	An interstitial solid solution of carbon in α iron (BCC).
Pearlite	Eutectoid of α-ferrite and cementite with a lamellar microstructure of alternate α-Fe and cementite plates.
Bainite	Eutectoid of α-ferrite and cementite. The α-ferrite either has a feathery appearance or occurs as plates. Carbide particles lie between the α-ferrite regions.
Spheroidite	Spherical particles of cementite in a matrix of α-ferrite.
Martensite	An interstitial solid solution of carbon in a body-centered tetragonal (BTC) Fe crystal structure.
Hypoeutectoid steels	Alloys with compositions to the left of the eutectoid reaction.
Hypereutectoid steels	Alloys with compositions to the right of the eutectoid reaction.
Proeutectoid ferrite	Ferrite that forms prior to the eutectoid ferrite.
Proeutectoid cementite	Cementite that forms prior to the eutectoid cementite.

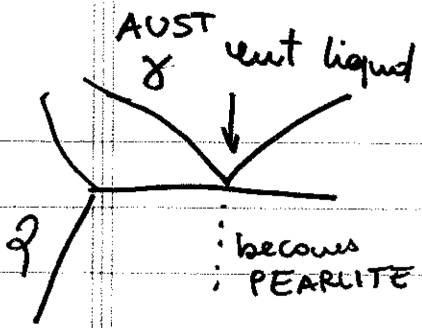
EUTECTOID

$\gamma \rightarrow \alpha + Fe_3C$

(NO SOLUBILITY OF Fe in Fe_3C ⇒ compound)

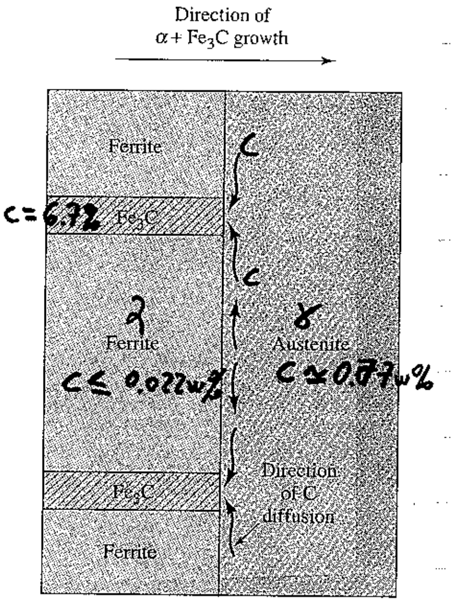


K17

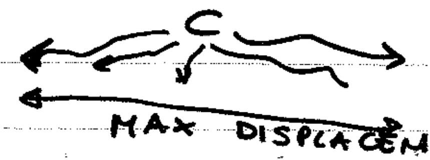


becomes PEARLITE = lamellar alternation of α-ferrite & cementite

INTERFACE
γ-austenite & pearlite MOVES during phase transformation



MIGRATION OF C inside γ-austenite toward Fe_3C ⇒
C cannot move more than a distance

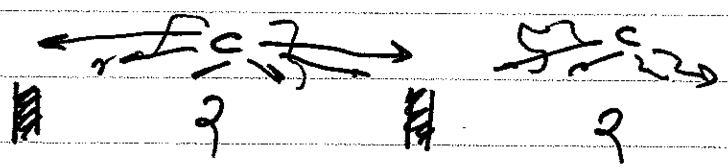


= ~~size~~ thickness of α- inside PEARLITE

MIGRATION = DIFFUSION (T)

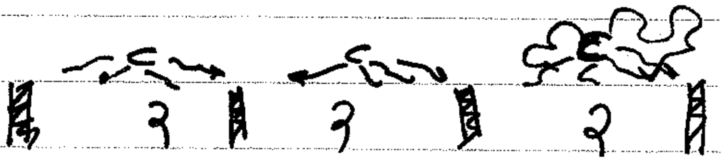
at T high T↑

Pearlite IS COARSED ⇐



at T low T↓

PEARLITE IS THIN!



different EXTERNAL Temperature ⇒ DIFFERENT PEARLITE density!!!

K 18

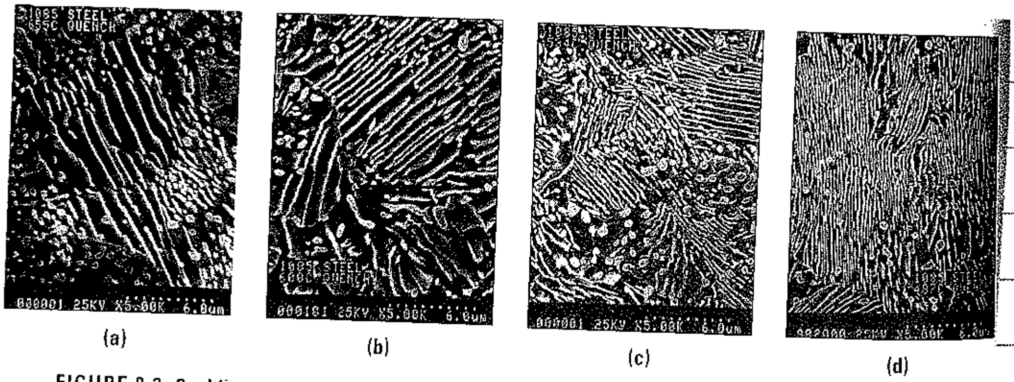
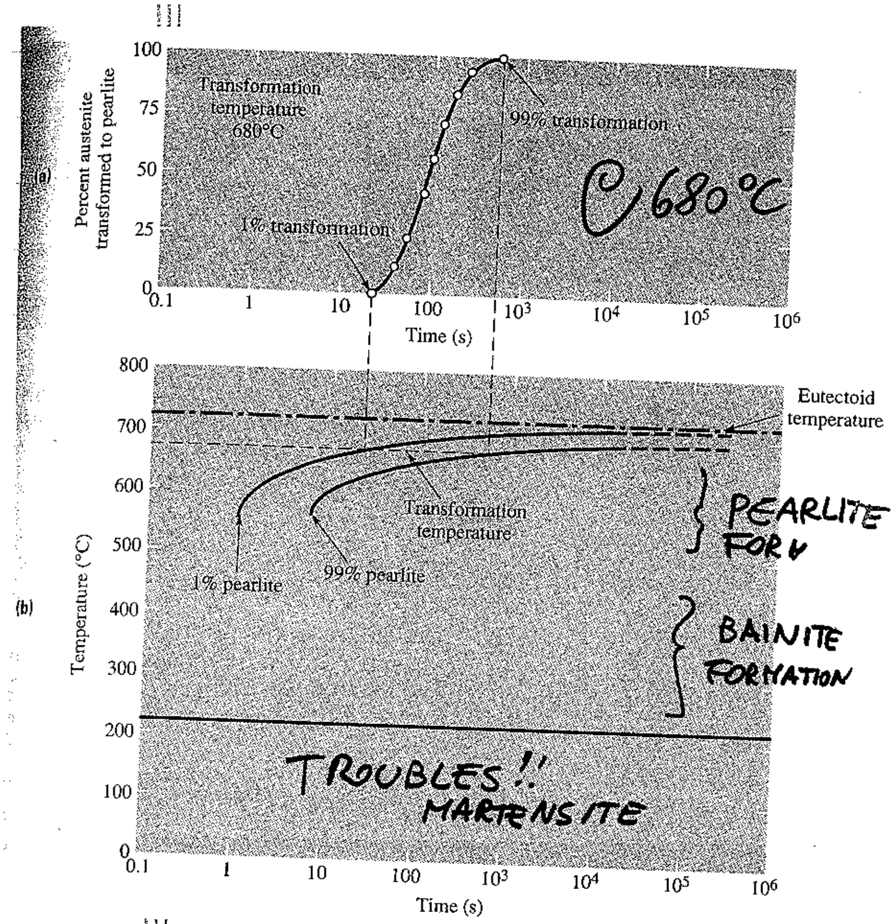


FIGURE 8.3–2 Microstructure of pearlite formed at different isothermal hold temperatures: **(a)** 655°C, **(b)** 600°C, **(c)** 534°C, and **(d)** 487°C. Notice that the morphologies of the two-phase structure are similar but their spacings decrease with decreasing isothermal hold temperature.

lower T (and bigger ΔT)
and smaller
are the size of
the carbides (Fe_3C)
⇒
smaller, finer
is PEARLITE



PEARLITE
FORMS FROM
γ-AUSTENITE
@ EUTECTOID
COMPOSITION
ONLY IF
UNDERCOOLING
IS MODERATE
≳ 550 °C

IF UNDERCOOLING IS
BELOW ~~[illegible]~~ 550°C, EUTECTOID γ-AUSTENITE
BECOMES BAINITE ($\alpha + Fe_3C$)

α-Ferrite LATHS OR PLATES

with CEMENTITE BETWEEN α-Ferrite
PLANES!!!

K19

⟹ THE ISOTHERMAL TRANSFORMATION DIAGRAM LOOKS LIKE

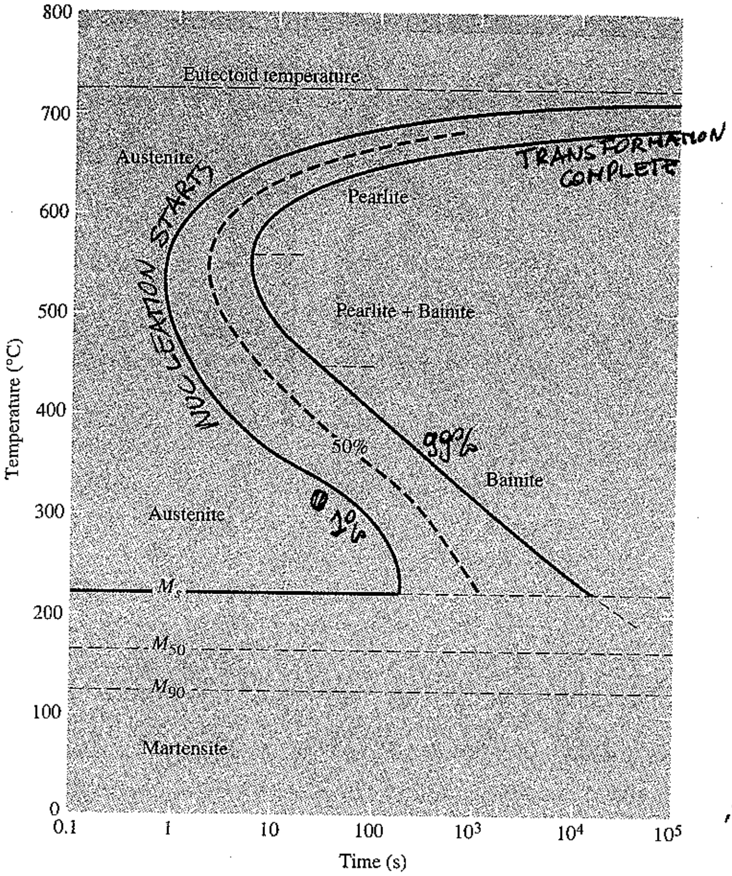
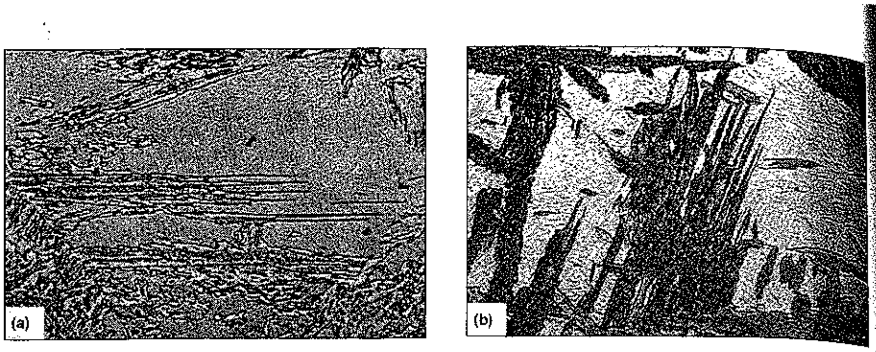


FIGURE 8.3–6 Schematic of an isothermal transformation (IT) diagram for a eutectoid steel.

TEMPERING
HEAT UP STEEL
AND COOL IT DOWN
DRAMATICALLY
WITH COLD WATER
OR OIL !!

ASK TO STUDENTS

& BAINITE (PLANES , LATHS) + PLENTY OF DISLOCATION



(a) (b)

FIGURE 8.3–5 The microstructure of bainite in an alloy steel isothermally transformed at: **(a)** 495°C, and **(b)** 410°C. *(Source: R. F. Hehman, "Ferrous and Nonferrous Bainite Structures,"* Metals Handbook, *8th ed., pp. 194–96. ASM International, Materials Park, Ohio. Reprinted* WITHOUT *permission of the publisher.)*

PAG 309

K20

- Pearlite & Bainite Form iF UNDERCOOLING has T. between 220°C to 727°C (EUTECTOID TEMP.)

  C inside γ-AUSTENITE DIFFUSES through the γ structure FEC to reach iT'S FRIENDLY CARBIDE (Fe_3C)

- IF UNDERCOOLING has T below ~200°C
  ⇒ C has NO TIME TO DIFFUSE (COOLING & solidification are fast, T↓ migration ~ 0)
  ⇒ There is a change of phase without diffusion

$$\underbrace{\text{DIFFUSIONLESS TRANSFORMATION}}_{\text{ATOMS FREEZE in THEIR POSITIONS BUT LATTICE DEFORMS!!}} \qquad \gamma\text{-AUSTENITE (Fcc)} \Downarrow \text{MARTENSITE (Bcc)}$$

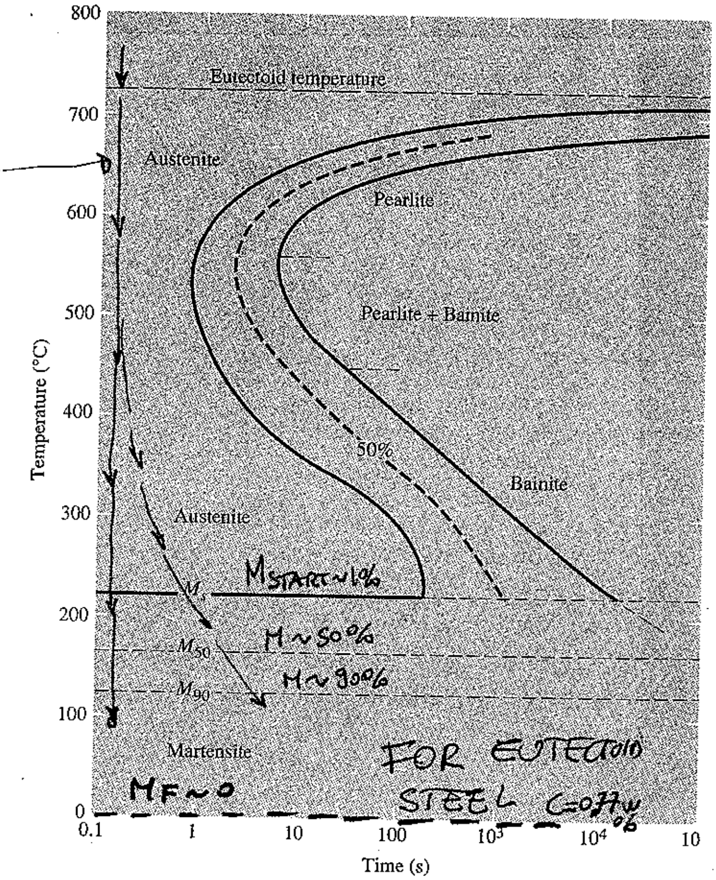
This is what you make if you put hot-red IRON in COLD WATER ⇒ MARTENSITE

K21

MARTENSITIC TRANSFORMATION

- FROM γ-AUSTENITE TO MARTENSITE (FCC → BCC)
- DIFFUSIONLESS (C does not move)
  DISPLACIVE (change shape of LATTICE, deform without diffusing atoms)
- happens if UNDERCOOLING IS BIG
  $T \leq 220°C \Rightarrow \Delta T > 500°C$ (HUGE)

VIOLENT
COOLING
TO 100°C
MADE BY
THE
"IRON AGE"
METALLURGIST
"
WARRIOR



ARROW OF THE "IRON AGE" WARRIOR

FOR EUTECTOID STEEL

$M_S \sim 220°C$

$M_{50} \sim 170°C$

$M_{90} \sim 120°C$

$M_F = M_{100} \simeq 0°C$

DURING "IRON AGE" ONLY HUMAN IN THE NORTH HAD ICE TO COOL STEEL

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

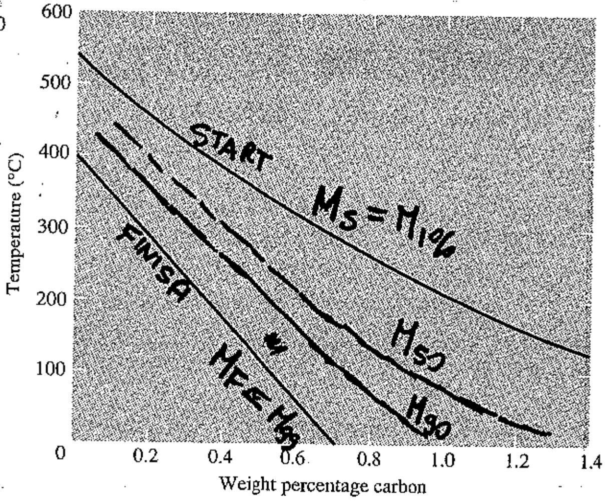


FIGURE 8.3–7 The effect of carbon on the M_s and M_f temperatures for a plain carbon steel.

K22

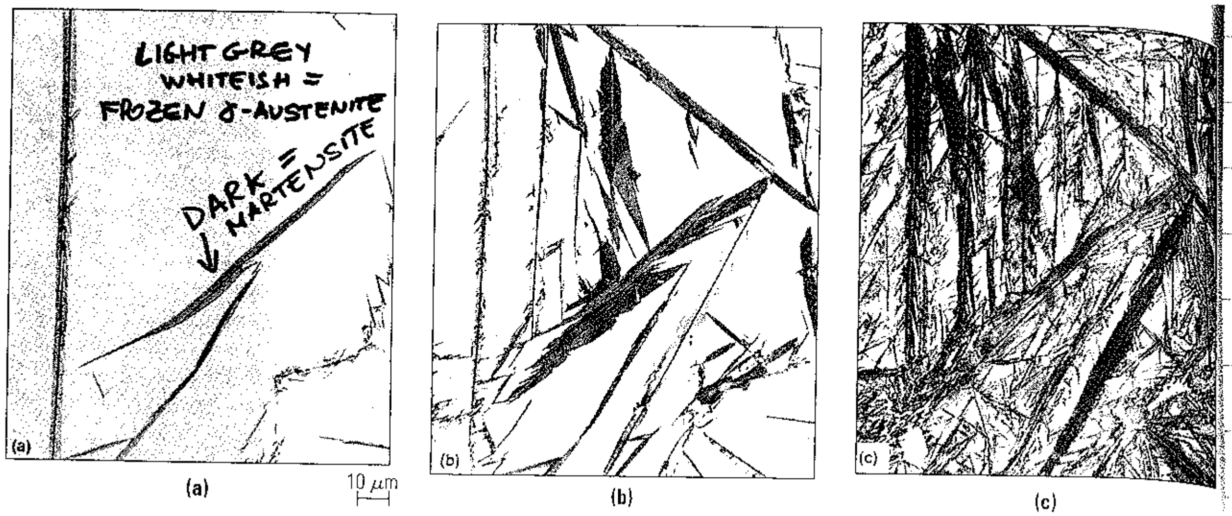
MARTENSITE IS DIFFUSIONLESS

⇒ SAME CONCENTRATION OF STARTING γ-AUSTENTE (HOT IRON)

$C = 1.8$ w%

$M_S \sim 25^\circ C$

$M_F \sim -200^\circ C$



(a) (b) (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. *(Source: G. Kraus and A. R. Marder,* The Morphology of Martensite in Iron Alloys. Metallurgical Transactions, *Vol. 2, 1971, pp. 2343–57. Reprinted by permission of the publisher.)*

NEEDLE LIKE ⇒ DIRECTION OF M are same from γ

HOW TO GO FROM γ-AUST TO MARTENSITE?

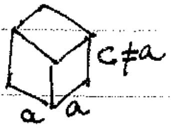
K23

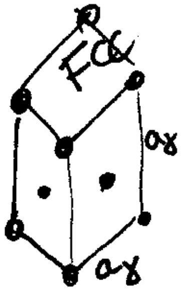
γ-AUSTENITE ⟹ MARTENSITE

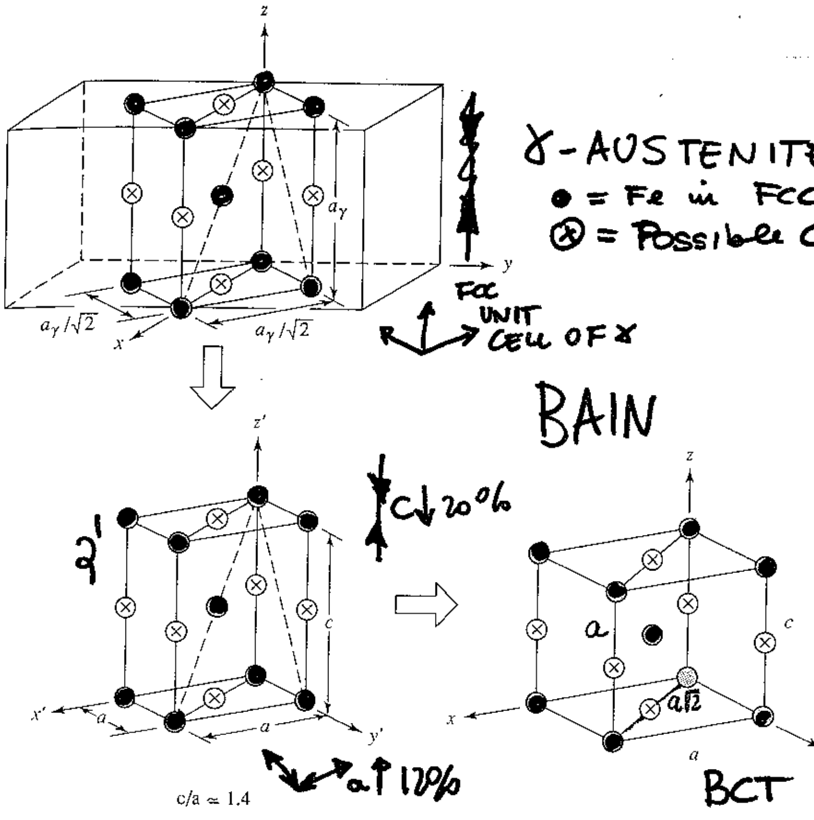
Only LATTICE $\overset{\text{FCC}}{\text{DISTORSIONS!}}$ Body Centered

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.

BCT = Body Center Tetragonal







γ-AUSTENITE
● = Fe in FCC
⊗ = Possible C OR nothing to FILL UP CONCENTRATION

FIGURE 8.3–9 The relationship between the FCC γ 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 α′ phase from the γ unit cell, the c axis must contract about 20% and the a axis must expand about 12%.

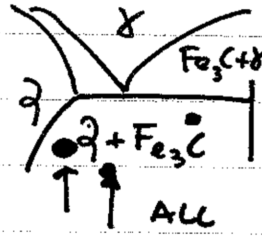
[illegible] $a_\gamma \Rightarrow c\downarrow$
⟹ CONTRACT 20%
$a_\gamma = a\uparrow$ 12%

γ → M
Volume increase!!

⇓

BCT

BUT @ low Temp



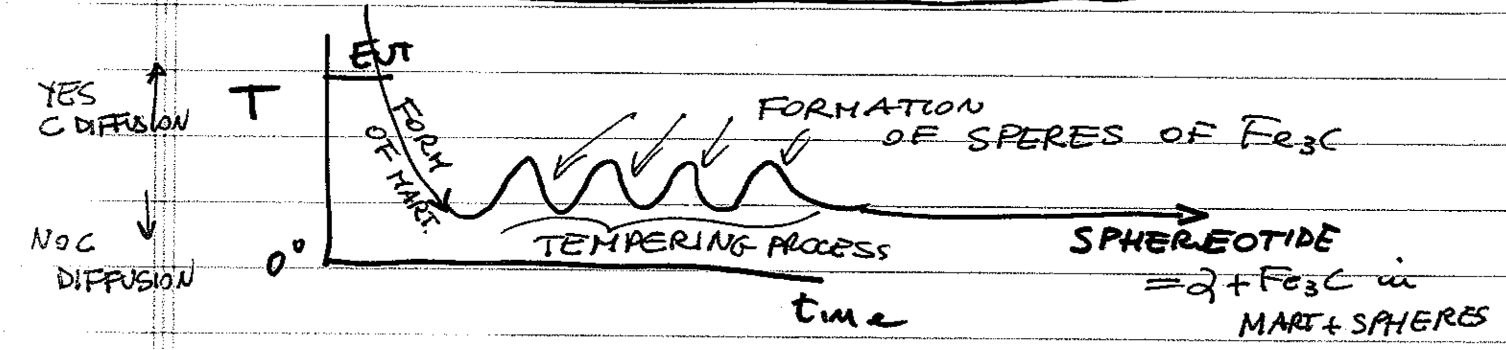
ALL THESE MARTENSITES ARE UNSTABLE TOWARD DECOMPOSITION OF α + Fe₃C

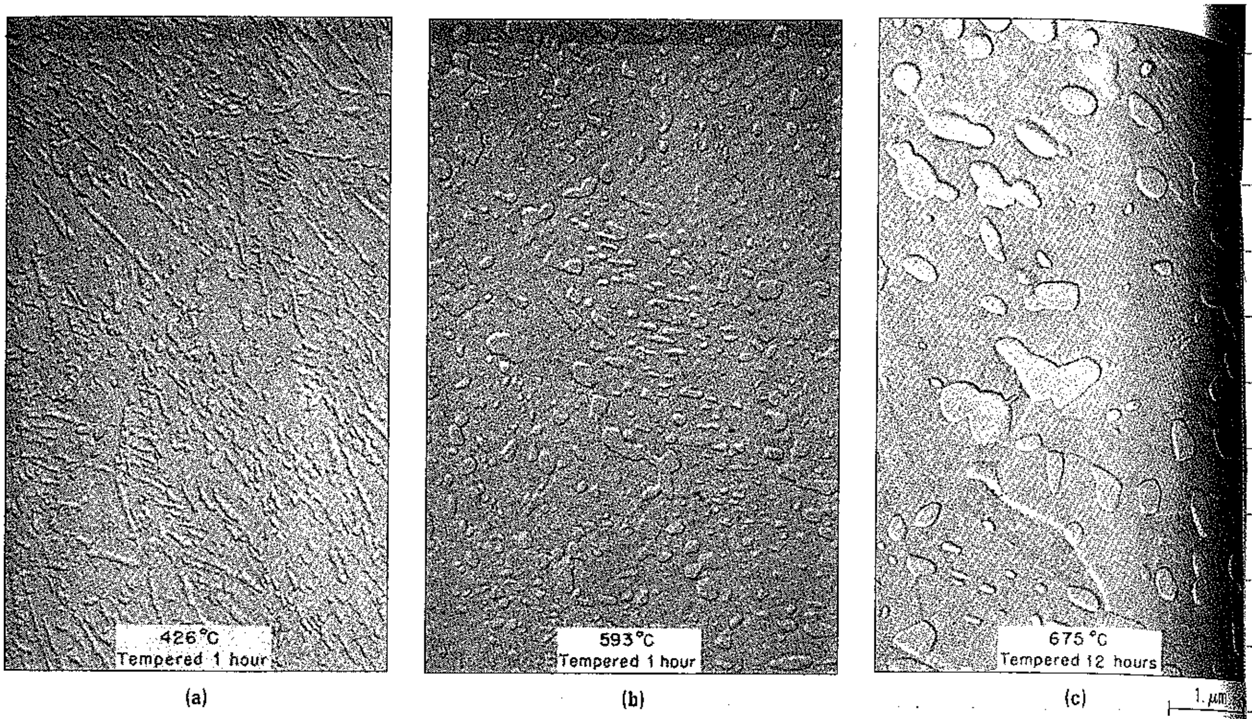
K24

TEMPERING

IF I KEEP MARTENSITE COLD WILL REMAIN MART.
BUT IF I HEAT IT UP A LITTLE IT WILL
ALLOW C TO DIFFUSE & PRECIPITATE ON
~SPHERES OF Fe_3C (CEMENTITES) (AND BCT becomes
BCC)
SUCH SPHERES ARE CALLED

SPHEROIDITE = MARTENSITE + SPHERES OF CEMENTITE





(a) (b) (c)

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), 1958, a publication of the Minerals, Metals & Materials Society, Warrendale, PA. Reprinted by permission of the publisher.)*

K25

EXAMPLE

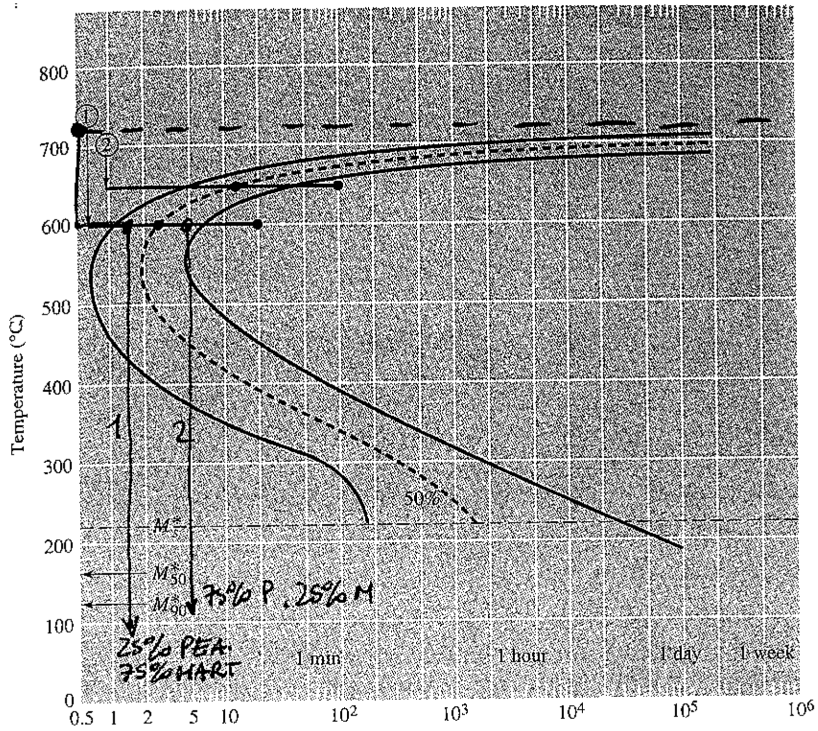


FIGURE 8.3–11 Examples of time-temperature paths on the isothermal transformation diagram of a eutectoid steel.

1) @ t=0 T= 727°C

- COOL FAST (QUENCH) to 600°C
- WAIT 1.5 secs
- COOL FAST TO 100°C ⟹ ≃ 25% PEARLITE ≃ 75% MARTENSITE BCT.

K26

2) • COOL FAST to 600°C, WAIT 5 secs, COOL FAST TO 100°C ⟹ 75% PEARL 25% MART

3) • COOL FAST TO 650°C, WAIT 2 MINS, COOL TO 100°C ⟹ 100% PEARL

4) COOL SUPER SLOWLY (to ALLOW TH. EQ) to 500, WAIT 2 YEARS, COOL TO 100°C ⟹ ALL α + Fe_3C NO M, NO B, NO P

5) DO LIKE 1) but THEN HAT UP TO 200°C, WAIT 10 SECS & QUENCH, REPAT MANY TIMES ⟹ 25% P, MUCH Fe_3C, SOME α, SOME BCC M,