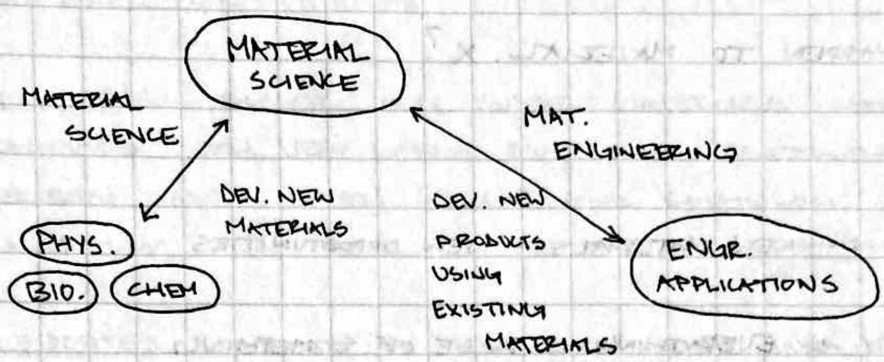
ENGR 321

MATERIAL SCIENCE AND ENGINEERING



* COMPOSITION AND PROCESSING

→ TURBINE BLADES, TOILETS, SiO_2, CARBON

- PROCESSING DETERMINES MATERIAL PROPERTIES

↓

* STRUCTURE:

- MACRO, MICRO, ATOMIC

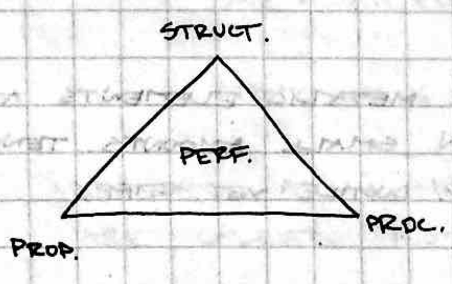
↓

* PROPERTIES

- SEVERAL CATAGORIES: MECHANICAL, THERMAL, ELECTRICAL, MAGNETIC, OPTICAL, DETERIORATIVE

↓

* PERFORMANCE



CHAPTER 2 READING NOTES

ATOMIC MASS UNIT = $\frac{1}{12}(^{12}C)$ ← CARBON 12

1 MOLE = 6.022×10^{23} ATOMS → $1\ ^{AMU}/_{ATOM} = 1\ ^{g}/_{MOL}$

BOTH BOHR'S MODEL AND WAVE-PARTICLE (MECHANICAL) MODEL ARE USED IN BOOK

* WAVE MECHANICS:

EVERY ATOM IS CHARACTERIZED BY 4 NUMBERS, CALLED QUANTUM NUMBERS

- PRINCIPLE QUANTUM NUMBER
- l, SPECIFIES THE SUBSHELL
- SPIN MOMENT, UP OR DOWN $(+\frac{1}{2}, -\frac{1}{2})$
- m_L, NUMBER OF ENERGY STATES PER SUBSHELL

PAULI EXCLUSION PRINCIPLE — EACH ELECTRON STATE CAN HOLD NO MORE THAN 2 ELECTRONS, WHICH MUST HAVE OPPOSITE SPINS

s = 2 ELECTRONS
p = 6 ELECTRONS
d = 10 ELECTRONS
f = 14 ELECTRONS

GROUND STATE = OCCUPYING LOWEST ENERGY LEVELS

3 TYPES OF BONDING FOUND:

- IONIC
- METALLIC
- COVALENT

- COVALENT: EACH ATOM CONTRIBUTES AN ELECTRON, SHARES. VERY STRONG OR VERY WEAK

CHAPTER 2 READING CONT.

- METALLIC BONDING: MINIMAL VALENCE ELECTRONS, FOUND IN METALS. VALENCE ELECTRONS FORM A "SEA" OF ELECTRONS

1/8/2012

* ATOMIC # → Z
ATOMIC MASS → A

AVAGODRO'S # → 6.023×10^{23} ATOMS = N_A

1 AMU/ATOM = 1 g/MOL

QUESTIONS:
- WHAT PROMOTES BONDING
- WHAT KIND OF BONDS
- WHAT PROPERTIES CAN BE INFERRED FROM BONDING

↳ ALL DICTATED BY VALENCE e's

THE STRUCTURE OF THE ATOM IS DICTATED BY QM

- e's HAVE WAVE / PARTICLE CHARACTERISTICS
- THEY ARE IN ORBITALS DEFINED BY PROBABILITY
- EACH ORBITAL IS AT A DISCRETE (QUANTIZED) ENERGY LEVEL

DESCRIBED BY 4 NUMBERS

① PRINCIPLE (n) → DISTANCE FROM NUCLEUS
② ANGULAR MOMENTUM → $0 \le l \le n-1$ → 0 1 2 3 / S P D F
③ MAGNETIC QN → m_L, NUMBER OF ORBITALS → $-l \le m_L \le l$
④ SPIN QN ↳ +½, -½

	n	l	S-STATE	m_L	e^-
1s	1	0		0	2
2p	2	1	P-STATE	-1, 0, 1	6
3d	3	2	D-STATE	-2, -1, 0, 1, 2	10
4f	4	3	f-STATE	-3, -2, -1, 0, 1, 2, 3	14

$0 \le l \le 2$

1/8/2012

IN ATOMS, ALL e^- WANT TO OCCUPY LOWEST ENERGY STATE

EX.

$H \rightarrow 1s^1$ $\quad$ $Be \rightarrow 1s^2 2s^2$

$He \rightarrow 1s^2$ $\quad$ $B \rightarrow 1s^2 2s^2 2p^1$

$Li \rightarrow 1s^2 2s^1$ $\quad$ $Si \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^2$

* NEED TO KNOW CATAGORIES ON PERIODIC TABLE *

↳ WILL BE TESTED ON

ALSO:

KNOW

WILL BE ON QUIZ NEXT WEEK

- COLUMNS HAVE SIMILAR VALENCE STRUCTURES
- ALKALI → Xs^1
- ALKALI EARTH → Xs^2
- TRANSITION METALS → Xd^{1-10}
- HALOGENS → Xp^5
- NOBEL GASSES → Xp^6
- ELECTRONEGATIVITY: MEASURE OF AN ATOMS AFFINITY TO ACCEPT AN EXTRA e^-

	n	ℓ	m_L	m_s
2s	2	0	0	1/2, -1/2
3p	3	1	-1, 0, 1	-1/2, 1/2
3d	3	2	-2, -1, 0, 1, 2	1/2, -1/2
4f	4	3	-3, -2, -1, 0, 1, 2, 3	1/2, -1/2

* ATOMIC BONDING:

DOMINATES

1. ELECTROSTATIC → 1-10 eV
2. GRAVITATIONAL → 10^{-6} eV
3. MAGNETIC → 10^{-32} eV

- TWO INTERACTIONS:

$F_{NET} = F_A + F_R$

ATTRACTIVE $\quad$ REPULSIVE

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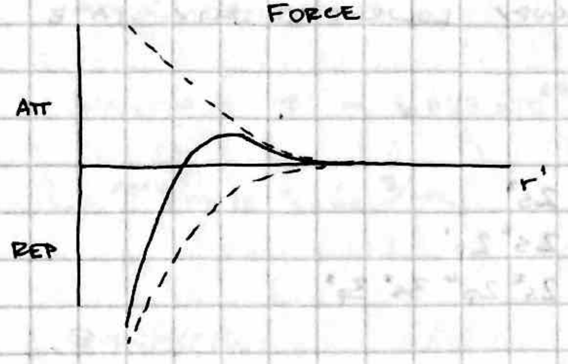
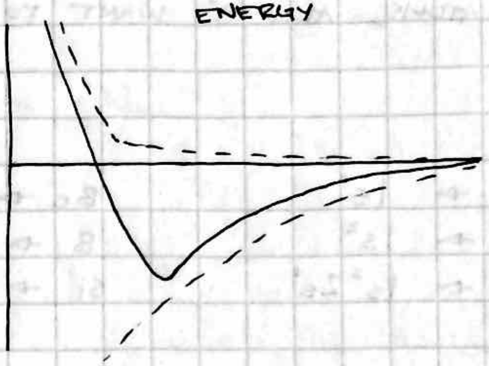




THE INTERATOMIC SPACING (BOND LENGTH)

- → AT ENERGY MINIMUM
- → HAS BOND ENERGY, E_0

* TYPES OF BONDING

- IONIC BONDING: ELECTROSTATIC, REQUIRES e^- TRANSFER

Na

$1s^2 2s^2 2p^6 3s^{①}$

↓

Na^+

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

↓

CATION

CL

$1s^2 2s^2 2p^6 3s^2 3p^5$

↓

Cl^-

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

↓

ANION

EX. OXIDES → MgO, TiO_2, Al_2O_3

SALTS → $NaCl$, $CaCl_2$

- HIGH BOND ENERGIES
- HIGH MELTING TEMPS

* IONIC BONDING IS <u>NON-DIRECTIONAL</u> *

↳ IMPORTANT

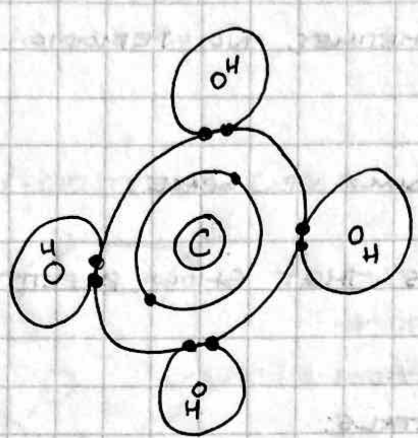
1/8/2013

* COVALENT BONDING : SHARING OF e^-'s

- HAPPENS BETWEEN ATOMS OF SIMILAR ELECTRONEGATIVITY

- METHANE : CH_4

$C: 1s^1 2s^2 2p^2$ → "WANTS 4 VALENCE e^-'s



* COVALENT BONDING IS VERY DIRECTIONAL *

EXAMPLES:

Si, C, GaAs, SiC

Bi → DIAMOND

USUALLY A VERY STRONG, HARD, SEMIBONDUCTING

* METALLIC BONDING

- ELECTRONS ARE DELOCALIZED FROM, FREE ELECTRON GAS
- BONDING OCCURS BETWEEN POSITIVELY CHARGED ION CORES AND THE "ELECTRON SEA"

NON-DIRECTIONAL

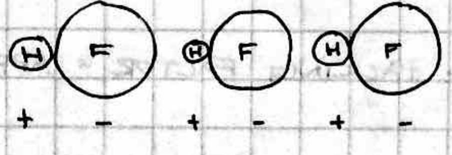
* SECONDARY BONDING : VANDER WALLS BONDING
- VERY WEAK
- ARISE FROM DIPOLAR INTERACTIONS
- SEPARATION OF CHARGE

* CHECK LECTURE SUMMARIES *

EX.

PERMANANT DIPOLE : HF

DIRECTIONAL



1/8/2013

* HW POSTED

* CHAPTER 3: CRYSTAL STRUCTURES

- CRYSTALLINE MATERIAL: PERIODIC ARRAY OF ORDER. 3D ARRAYS W/ LONG RANGE ORDER
  - METALS, CERAMICS, SOME POLYMERS

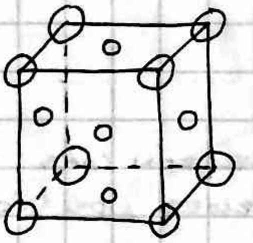
- NON-CRYSTALLINE: SHORT RANGE ORDER SOMETIMES, NO PERIODIC PACKING. NO LONG RANGE ORDER

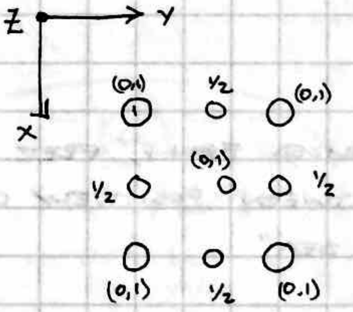
- LATTICE: A 3D ARRAY OF POINTS, DIVIDING UP SPACE.

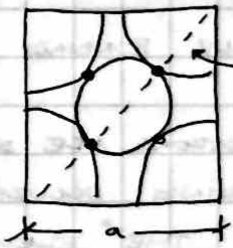
- UNIT CELL: SMALLEST GROUP OF ATOMS THAT SHOW REPETITION, "BUILDING" BLOCKS OF MATERIAL.

3 TYPES OF UNIT CELLS TO KNOW FOR METALS:

- FACE-CENTERED CUBIC (FCC) "OR" CUBIC CLOSE PACKED







$a^2 + a^2 = (4R)^2$

$$\boxed{a = \frac{4R}{\sqrt{2}} = 2R\sqrt{2}}$$

KNOW THIS EQUATION

- MUST ENVISION ATOMS AS "HARD-SPHERES"
- IN FCC, ATOMS TOUCH ALONG FACE DIAGONAL

- HOW MANY TOTAL ATOMS IN A UNIT CELL? → ONCE KNOWN, THEORETICAL DENSITY CAN BE CALCULATED

FOR FCC: $\frac{1}{8}(8) + 6(\frac{1}{2}) = 4$ ATOMS

- COORDINATION NUMBER: 12 FOR ~~ALL METALS~~ FCC, # OF ATOMS IN CONTACT WITH A GIVEN ATOM

- ATOMIC PACKING FACTOR = APF = $\frac{\text{VOL. OF ATOMS IN UC}}{\text{VOL. OF UC}}$

1/9/2013

FOR APF: $V_{UC} = a^3$, $V_{ATOMS} = 4(4/3\,\pi R^3)$, $a = \frac{4R}{\sqrt{2}}$

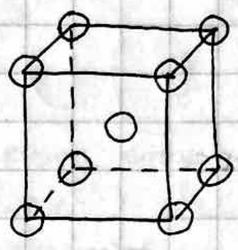
$$\frac{4(4/3\,\pi R^3)}{\left(\frac{4R}{\sqrt{2}}\right)^3} \rightarrow \text{FOR } \overset{\text{FCC;}}{\cancel{\text{APF}}} = \boxed{0.74}$$

HIGHEST PACKING FACTOR!

EX. OF FCC:

Ag, Ni, Cu, Pt, AL, γ-Fe

- BODY-CENTERED CUBIC



CN = 8 ← ALWAYS REMAINS THE SAME

\# OF ATOMS = 2

ATOMS TOUCH ALONG BODY DIAGONAL

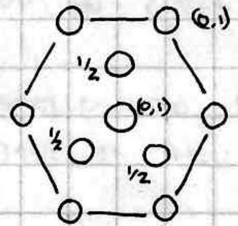
1 ATOM IN CENTER

APF = 0.68

EX. Cr, ALKALI METALS, α-Fe

$a = \frac{4R}{\sqrt{3}}$

- HEXAGONAL CLOSE PACKED – HCP



6 ATOMS / UC

CN = 12 } SAME AS FCC, ONLY ONE SMALL

APF = 0.74 } DIFFERENCE

* DENSITY:

$$\rho = \frac{nA}{V_c N_A}$$

n = # OF ATOMS

A = ATOMIC WEIGHT (g/mol)

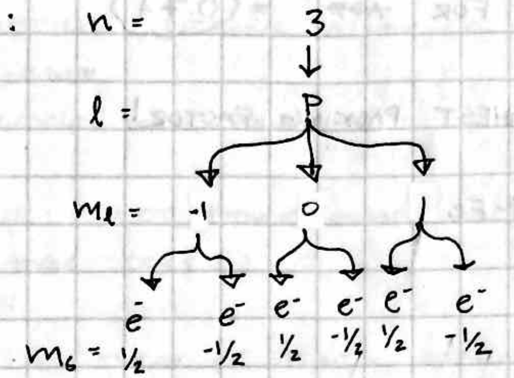
V_c = VOL CELL (m^3)

N_A = AVOGADRO'S # (atom/mol)

11/13/2013

n → SUBSHELL → # OF STATES PER SUBSHELL → 2 e^- PER SUBSHELL

EX. $3p^6$:



SUBSHELLS:
s = 1 → 2e^-
p = 3 → 6e^-
d = 5 → 10e^-
f = 7 → 14e^-

✻ BONDS:

COVALENT: TENDS TO FORM BETWEEN 2 NON-METALS

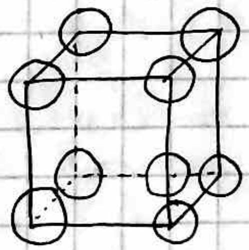
IONIC: GENERALLY BETWEEN 2 DISTANT ELEMENTS ON THE PERIODIC TABLE, MOSTLY BETWEEN A METAL AND NON-METAL

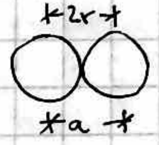
METALLIC: BETWEEN 2 METALS

1/14/2013 LECTURE NOTES:

✻ LAPTOPS ON WEDNESDAY

EX. SIMPLE CUBIC





a = 70.4 g/mol

R = 0.126 nm

$$\rho = \frac{nA}{V_c N_A}$$

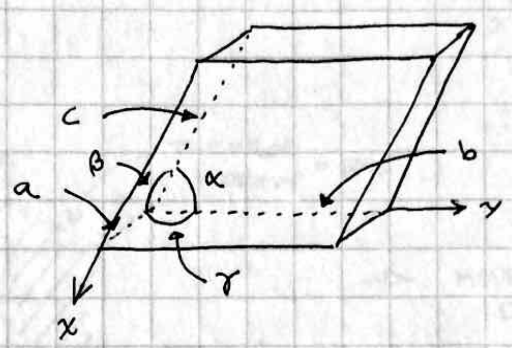
$$\frac{(1\ \text{atom/cell})(70.4\ \text{g/mol})}{[(2)(0.126\text{nm})]^3 \cdot (6.022\times10^{23}\ \text{atoms/mol})}$$

1/14/2013

- POLYMORPHISM: WHEN A MATERIAL CAN HAVE MORE THAN ONE CRYSTAL STRUCTURE. EX: α-Fe → γFe

✳ CRYSTAL SYSTEMS:

- ORGANIZE STRUCTURES BY UNIT CELL GEOMETRY



• 7 CRYSTAL STRUCTURES:

- CUBIC
- HEXAGONAL
- RHOMBOHEDRAL
- ORTHORHOMBIC
- MONOCLINIC
- TRICLINIC

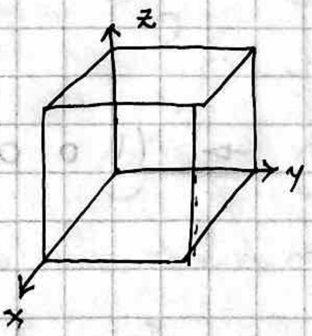
HIGHEST SYMETRY ↓ LOWEST SYMMETRY

✳ WEEK 2 HW POSTED TONIGHT:

- PP ON CUBES FOR DRAWING PRACTICE

✳ CRYSTALLOGRAPHIC DIRECTIONS / PLANES

- BASIS IS THE UNIT CELL W/ A RIGHT HANDED COORDINATE SYSTEM



- DIRECTIONS: 3-D VECTOR

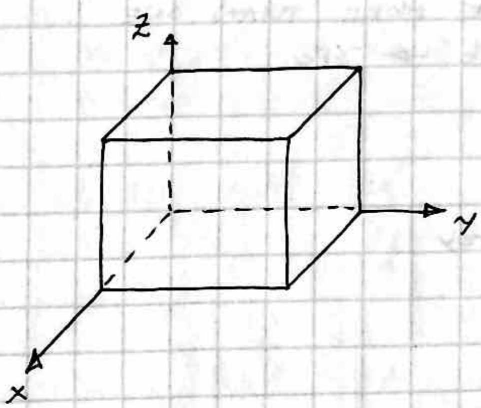
① VECTOR LENGTH IS MEASURED IN TERMS OF LATTICE PARAMETERS (a, b, c)

② REDUCE TO SMALLEST <u>INTEGER</u> VALUES

③ [U V W] → <u>NO</u> COMMA'S

④ IF NEGATIVE, USE BAR OVER #: $-2 \rightarrow \bar{2}$

1/14/2013



$[2\ 1\ 0] \rightarrow$ PROJECTION: $x = \frac{2}{2} = 1$

$y = \frac{1}{2} = \frac{1}{2}$

$z = \frac{0}{2} = 0$

DO <u>NOT</u> WRITE: ~~$[1\ \frac{1}{2}\ 0]$~~

EX. #2:

$[\bar{1}\ \bar{2}\ 1] \rightarrow x = -\frac{1}{2}$

$y = -1$

$z = \frac{1}{2}$

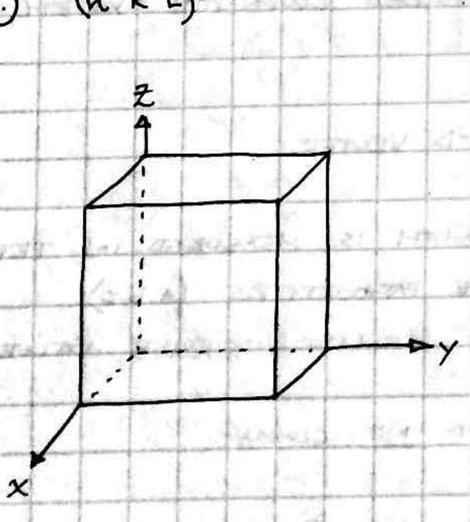
* PLANES
- SPECIFIED W/ MILLER INDICIES = h, K, L

① IF PLANE GOES THROUGH ORIGIN, MOVE ORIGIN

② DETERMINE WHERE PLANE INTERCEPTS EACH AXIS
- IF PLANE IS PARALLEL TO AXIS, USE ∞

③ TAKE RECIPROCAL

④ (h K L)

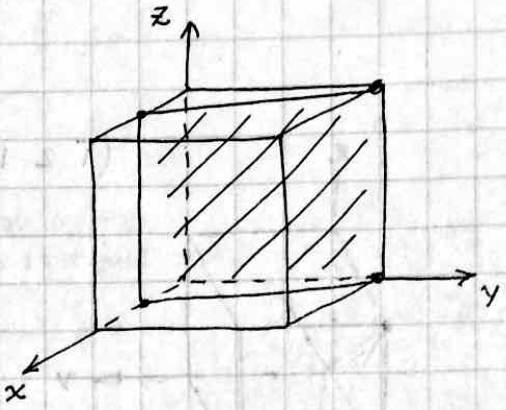


INTERCEPTS:	RECIP:
$x = 1$	1
$y = \infty$	0
$z = \infty$	0

$\rightarrow (1\ 0\ 0)$

1/14/2013:

FIND PLANE OF (2 1 0)

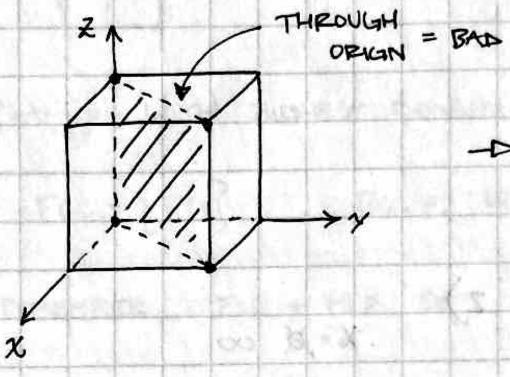


RECIP:

$x = 1/2$

$y = 1$

$z = \infty$

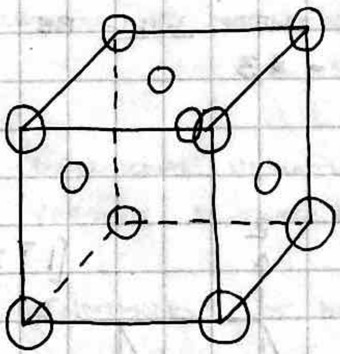


→ MOVE ORIGIN

1/15/2013

QUIZ TOMORROW (1/16)
- PLANES / DIRECTIONS
- ELECTRON STRUCTURE

* LECTURE NOTES:



FOR SOME CRYSTAL SYSTEMS (ie. CUBIC), SOME DIRECTIONS ARE EQUIVALENT

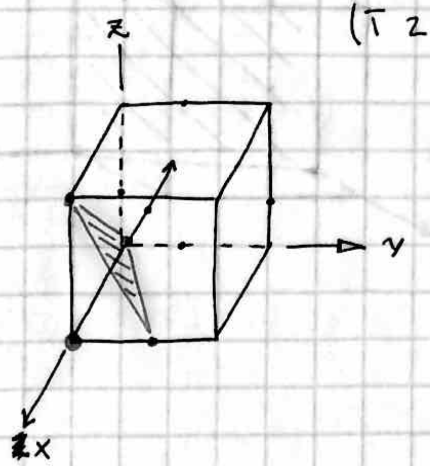
$$\left.\begin{array}{l}[001],\ [010],\ [100] \\ [00\bar{1}],\ [0\bar{1}0],\ [\bar{1}00]\end{array}\right\}$$ "FAMLY OF DIRECTIONS"

- ALSO HAVE FAMILIES OF PLANES

→ $\{h\ k\ \ell\}$

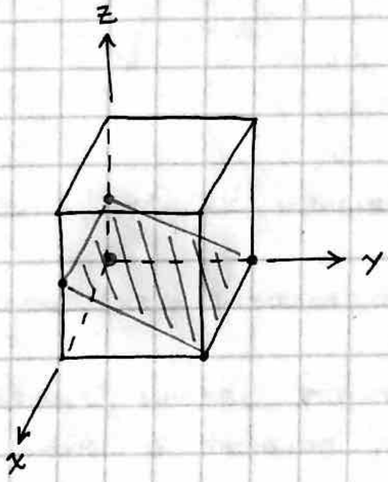
1|15|2013

$(\bar{1}\ 2\ 1) \rightarrow (\bar{1}/2\ \ 1/2\ \ 1/2)$



$(3\ \bar{1}\ 1)$

$(0\ 1\ 2)$



x = ~~0~~ ∞

y = ~~1/2~~ 1

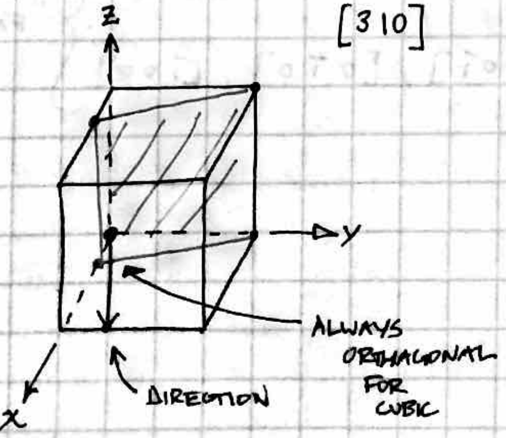
z = ~~X~~ 1/2

NOTE:

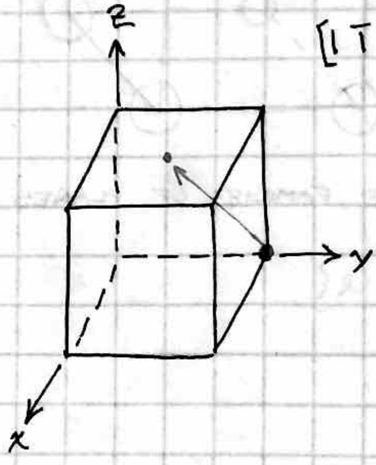
* IF ANY MILLER INDICICIES ARE ZERO, THERE WILL BE ONLY 4 SIDES. IF ~~ALL~~ ARE NON ZERO, - 3

- DIRECTIONS

[3 1 0]



$[1\ \bar{1}\ 2]$



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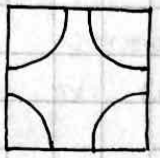
- PLANES CANNOT CROSS ORIGIN

* PLANAR DENSITY:

$$PD = \frac{\text{\# OF ATOMS}}{\text{AREA OF PLANE}} \quad OR \quad \frac{\text{AREA OF ATOMS}}{\text{AREA OF PLANE}}$$



$$\rightarrow \quad PD = \frac{\pi R^2}{a^2} \quad \rightarrow \quad PD = 0.59$$

- PLANES WITH HIGHEST DENSITY HAVE STRONGEST BONDING

$FCC = \{111\}$, $BCC = \{110\}$, HCP → BASAL PLAIN

- REMEMBER, FCC + HCP BOTH HAVE APF OF

HCP → AB AB AB AB PACKING
FCC → ABC ABC ABC ABC... PACKING

* CRYSTALLINE MATERIAL CATAGORIES

① SINGLE CRYSTAL : ONE UNIQUE CRYSTAL (UNIT CELL) GROWN TO A MACROSCOPIC SIZE

② POLYCRYSTALLINE : COLLECTIONS OF SMALL CRYSTALS (GRAIN) ON SCALE OF 1μm - 1mm

ANISOTROPY: DIRECTIONAL VARIATION OF PROPERTIES RESULTING FROM VARYING PLANAR + LINEAR DENSITIES

ISOTROPY: INDEPENDENT OF DIRECTION (LIQUIDS, GASSES, AMORPHOUS MATERIALS)

1/15/2013

* IMPERFECTIONS IN SOLIDS

- IRREGULARITY AT AN ATOMIC SCALE
- WE CLASSIFY DEFECTS BASED ON DIMENSIONALITY DEFECTS
- CRITICAL

0-D DEFECTS

① VACANCY: VACANT LATTISE SITE
- AT EQUILLIBRIUM, # OF VACANCIES GIVEN BY: $N_V = N \exp\left(\frac{-Q_V}{KT}\right)$

N_V = # OF VACANCIES
N = # OF LATTISE SITES
T = TEMPERATURE IN <u>KELVIN</u>
Q_V = ENERGY REQ. TO FORM VACANCY
K = BOLTZMANN'S CONSTANT

\# OF VACANCIES INCREASES EXPONENTIALLY W/ TEMP.

② SELF-INTERSTITIAL: EXTRA ATOM "SQUEEZED" INTO

- ENERGY IS MUSH GREATER THAN FOR A VACANCY

* IMPURITIES:

→ THE MOST PURE ARE 99.9999 % PURE
- INTENTIONAL IMPURITIES → ALLOYS, "DOPING"
- W/ AN IMPURITY, 2 THINGS CAN HAPPEN
  - SECOND PHASE FORMATION
  - SOLID SOLUTION FORMATION

- SOLID SOLUTION:
  - SOLVENT ATOMS = PRIMARY CONSTITUENT
  - SOLUTE ATOMS = MINOR

AS LONG AS CRYSTAL STRUCTURE DOESN'T CHANGE, LOOKS THE SAME

1/15/2013

- 2 MECHANISMS

① SUBSTITUTION: SOLUTE ATOM REPLACES ATOM ON LATTICE SIGHT

- DEGREE OF SOLID SOLUBILITY GOV. BY 4 THINGS

KNOW FOR EXAM {
- SIZE
- CRYSTAL STRUCTURE
- EN SHOULD BE SIMILAR FOR A COMPOUND
- VALENCE

- COMMON QUESTION

- DEGREE OF SOLUBILITY: RANGE FROM 0% → 100%

EX. $Cu \leftrightarrow Ni$

$r_{Cu} = 0.128$ nm BOTH FCC $EN_{Cu} = 1.9$

$r_{Ni} = 0.125$ nm $EN_{Ni} = 1.8$

② INTERSTITIAL SOLID SOLUTION

→ WHERE SOLUTE ATOMS SQUEEZE INTO FREE LATTICE SPACE

- EX. STEEL

1/16/2013

* EXAM TUESDAY, WEEK 3

- COVERS ALL MATERIAL THROUGH 1/16/2013 (1D DEFECTS)

* NOTES

INTERSTITIAL SOLID SOLUTION

- SOLUTE SHOULD BE SMALL TO "FIT-IN"
- EX. Fe-C → $\left.\begin{array}{l} R_C = 0.71\ \text{Å} \\ R_{Fe} = 1.24\ \text{Å} \end{array}\right\} \rightarrow$ MAX SOLUBILITY OF ~2%

ALLOY COMPOSITION:

- HOW DO WE DESCRIBE

1.) WEIGHT PERCENT = WT %

$$C_1(\text{wt}\%) = \frac{m_1}{m_1 + m_2} \times 100$$

1/16/2013

2.) ATOMIC PERCENT = MOLE PERCENT = at % OR MOL %

- BASIS IS # OF MOLES

$$n_1 = \frac{m_1 \rightarrow \text{WEIGHT (g)}}{A_1 \rightarrow \text{ATOMIC MASS (g/mol)}}$$

EX. Cu - Be → 98 wt % Cu + 2 wt % Be

$A_{Cu} = 63.55$ g/mol $\quad n_{Cu} = \frac{98\text{g}}{63.55 \text{ g/mol}} = 1.54$ mol ← ARBITRARY

$A_{Be} = 9.01$ g/mol $\quad n_{Be} = \frac{2\text{g}}{9.01 \text{ g/mol}} = 0.22$ mol

$$C'_{Cu} = \frac{1.54}{1.54 + 0.22} \times 100\% = 87.5 \text{ at } \%$$

$$C'_{Be} = 12.5 \text{ at } \%$$

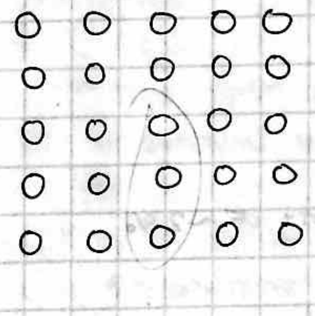
3.) MASS PER VOLUME (kg/m³)

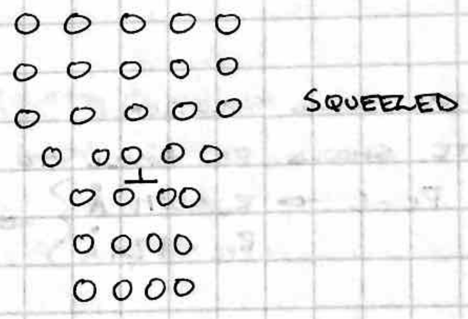
$$C''_1 = \frac{C_1}{\left(\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}\right)} \times 1000$$

* 1-D DEFECTS = LINEAR DEFECTS

- DISLOCATION → 2 TYPES

-PERFECT





- EXTRA HALF PLANE OF ATOMS
- DISLOCATION LINE OUT OF PAPER

1/16/2013

② SCREW DISLOCATION
- ARISE FROM SHEAR STRESS
- NAME COMES FROM HELICAL PATH ATOMS TAKE AROUND DISLOCATION LINE
- ↻

ALL REAL DISLOCATIONS ARE MIXED
ALL MATERIALS HAVE DISLOCATIONS

* 2-D DEFECTS = PLANAR DEFECTS
→ BOUNDARY
(.) - SURFACES

* MIDTERM REVIEW NOTES:

PLANAR DENSITY: 2 TYPES
- DIMENTIONED → (ATOMS/AREA) WHERE ATOMS = # OF COMPLETE CIRCLES
- NON-DIMENTIONED → (AREA/AREA)
- # OF ATOMS IN DENSITY CALCULATIONS IS ALWAYS THE SAME AND IS EQUAL TO THE # PRESENT IN THE PRINCIPLE PLANES

1/23/2012:

* 2-D DEFECTS - PLANAR DEFECTS
- BOUNDARIES
  - EXTERNAL
  - INTERNAL
  - TWIN BOUNDARY } SPECIAL
  - STACKING FAULTS } SPECIAL

EXTERNAL SURFACE:
- SURFACE ATOMS ARE NOT FULLY COORDINATED
- SURFACE ENERGY OF DANGLING BONDS $[J/m^2]$ UNITS γ

1/23/2013

LIQUID → FORMS SPHERICAL DROPLETS

INTERNAL DEFECTS:
- INTERFACE BETWEEN 2 SINGLE CRYSTAL ~~STRUCTURES~~ WITH DIFFERENT ORIENTATION

2-D DEFECTS CAN BE CREATED BY STACKING 1-D DEFECTS

GRAIN BOUNDARY ENERGY $\propto$ TO MISS ORIENTATION, IT ALSO LEADS TO GRAIN GROWTH. MINIMIZE SURFACE ENERGY BY REDUCING SURFACE AREA OF GRAIN BOUNDARIES. GRAIN SIZE ALSO CHANGES WITH TEMPERATURE

GRAIN BOUNDARIES ARE ALSO MORE CHEMICALLY REACTIVE, IMPURITIES OFTEN SEPARATE ALONG GRAIN BOUNDARIES

1/28/2013

* STACKING FAULT:
- OFTEN FOUND IN FCC METALS WHERE THERE IS A 'SCREW UP' IN STACKING SEQUENCE

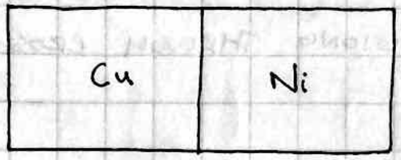
* 3D DEFECTS:
- HOW DO WE CHARACTERIZE DEFECTS

* MICROSCOPY
- LIGHT/ELECTRONS/PROBES TO IMAGE

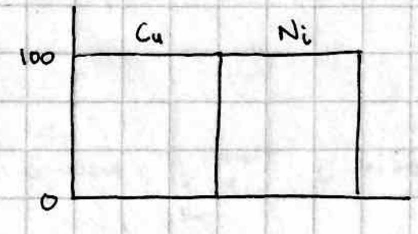
* CHAPTER 5:
- DIFFUSSION: MASS TRANSPORT BY ATOMIC MOTION
  - PHASE CHANGES
  - DEPENDENT ON STRUCTURE
  - CRYSTAL STRUCTURE
  - ORIENTATION AND CHEMISTRY

1/28/2013

"THOUGHT EXPERIMENT" – DIFFUSION COUPLE

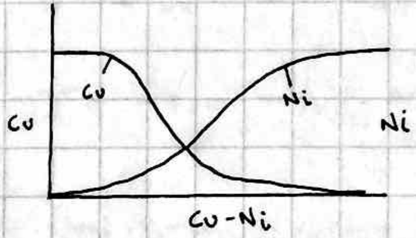


CONCENTRATION AT t=0



@ t=0

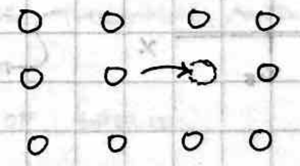
CONCENTRATION AT $\frac{2}{3}T_m$



* TWO THINGS THAT CONTROL DIFUSSION: <u>TIME</u> AND <u>TEMPERATURE</u>

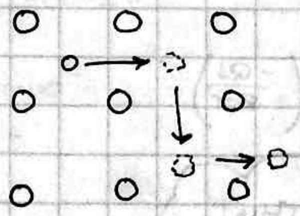
*THERE MUST BE A PLACE FOR THE DIFFUSING SPECIES TO GO:

① VACANCY DIFFUSION



- AT HIGH TEMPERATURES THERE ARE MORE VACANCIES SO DIFFUSION WILL INCREASE

② INTERSTITIAL DIFFUSION



- OCCURS WILL SMALL SPECIES: H, C, N, O.
- MORE TYPICAL IN <u>METALS</u>

<u>KNOW</u>
<u>FOR</u>
<u>EXAM</u>
<u>COMMON</u>
<u>QUESTION</u>

1/28/2013 :

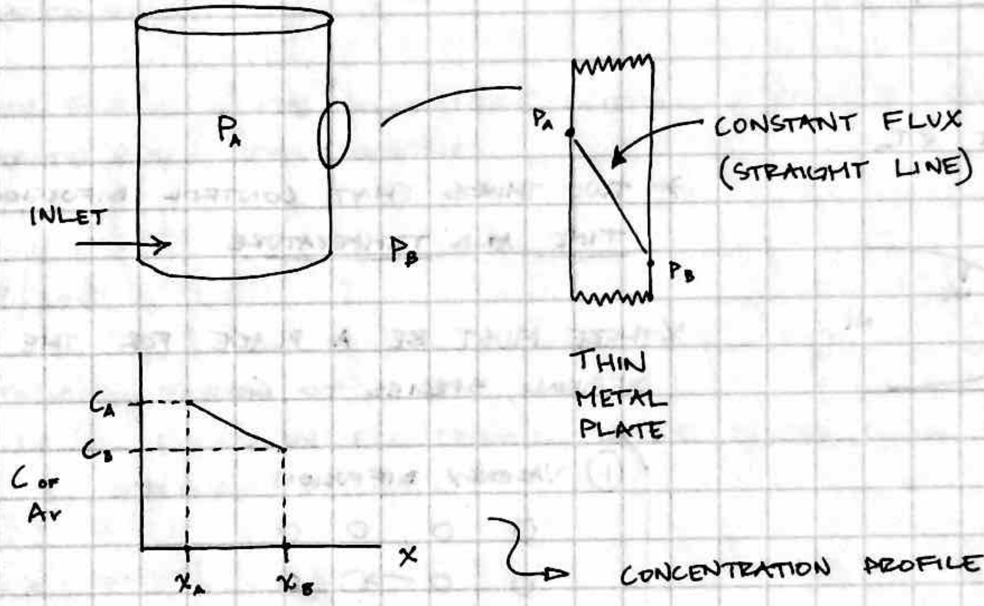
* STEADY STATE DIFFUSION :

- DIFFUSION FLUX = J = TOTAL MASS DIFFUSING THROUGH CROSS-SECTIONAL AREA PER UNIT TIME

$$J = \frac{M}{At} \left(\frac{Kg}{m^2 \cdot s}\right) \text{ OR } \left(\frac{\text{ATOMS}}{m^2 \cdot s}\right)$$

$$J = \frac{1}{A}\frac{dM}{dt}$$

EX. PRESSURE VESSEL WITH Ar



CONCENTRATION PROFILE:

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

THE GRADIENT CREATES THE FLUX THROUGH ACCORDING TO FICKS LAW:

$$J = -D\frac{dC}{dx}$$

└→ DRIVING FORCE

D = DIFFUSION COEFFICIENT

$$D = D_0 \exp\left(\frac{-Q_d}{RT}\right)$$

- D_0 = TEMP. IND. CONSTANT
- Q_d = ACTIVATION ENERGY FOR DIFFUSION
- R = GAS CONSTANT = 8.31 J/MOL·K
- T = ABS. TEMP.

"ACROSS A THIN METAL PLATE"

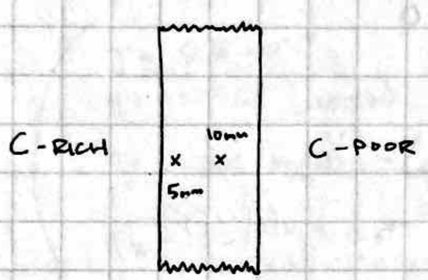
└→ STEADY STATE

1/29/2013

$$D = D_0 \exp\left(\frac{-Q_d}{RT}\right)$$

EX. 5.1

- STEADY STATE



KNOWNS:

$T = 700°C$

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

$C_c(5mm) = 1.2\ kg/m^3$

$C_c(10mm) = 0.8\ kg/m^3$

$$J = -D\frac{dC}{dx} \rightarrow \frac{dC}{dx} = \frac{\Delta C}{\Delta X} \rightarrow \frac{(0.8\ kg/m^3 - 1.2\ kg/m^3)}{10mm - 5mm} = -80\ kg/m^4$$

$$J = -(3 \times 10^{-11}\ m^2/s)(-80\ kg/m^4) = \boxed{2.4 \times 10^{-9}\ kg/m^2 \cdot s}$$

* NON-STEADY STATE DIFFUSION:

→ TIME DEPENDENT FLUX OF ATOMS ~~THROUGH~~ AND CONCENTRATION GRADIENT

→ ACCUMULATION OR DEPLETION OF SPECIES

- USE FICKS 2ND LAW:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \rightarrow \text{MULTIPLE SOLUTIONS}$$

BOUNDARY CONDITION: A SEMI-INFINATE SOLID WITH A CONSTANT SURFACE CONCENTRATION OF DIFFUSING SPECIES

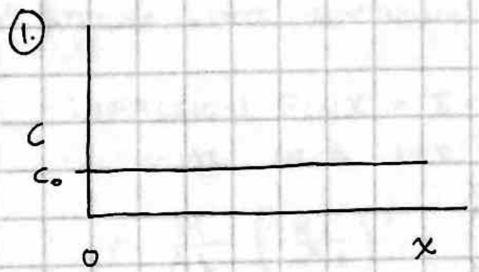
① At • $t = 0$, $C = C_0$ for $0 \leq x \leq \infty$

② FOR $t > 0$, $C = C_s$ AT $x = 0$

$C_x = C_0$ AT $x = \infty$

1/29/2013

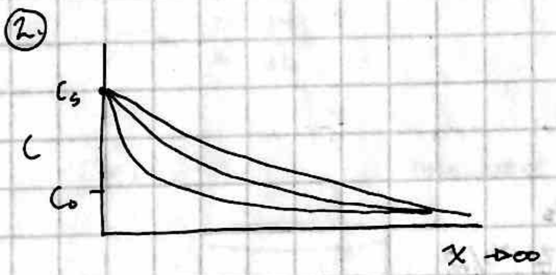
①



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

C_x = CONC. @ x
C_o = CONC @ ∞
C_s = CONC @ 0

②



$\ln(D) - 1/T$

$\rightarrow D = \exp(1/T)$

EX. 5.2

$C_o = 0.25$ WT %
$C_s = 1.2$ WT %
$C_x = 0.8$ WT %
$x = 0.5$ mm
$t = ?$
$D = 1.6 \times 10^{-11}\ m^2/s$

$$\frac{0.8 - 0.25}{1.2 - 0.25} = 0.579 = 1 - \mathrm{erf}\left(\frac{5\times10^{-4}\,m}{2\sqrt{(1.6\times10^{-11})t}}\right)$$

$$\mathrm{erf}\left(\frac{5\times10^{-4}\,m}{2\sqrt{1.6\times10^{-11}\,t}}\right) = 0.4210$$

$$\frac{Z - 0.35}{0.42 - 0.3794} - 0.421$$

- INTERPOLATE:

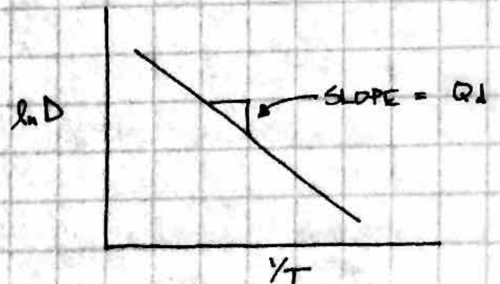
Z	erf(z)
0.35	0.3794
?	0.4210
0.4	0.4284

$$\frac{Z - 0.35}{0.4 - 0.35} \rightarrow Z = 0.392$$

$$0.392 = \frac{5\times10^{-4}\,m}{2\sqrt{Dt}} \rightarrow 7.1 \text{ hrs}$$

*FACTORS THAT INFLUENCE DIFFUSION:

① TIME
② TEMPERATURE → $D = D\exp\left(\frac{-Q_d}{RT}\right) \rightarrow \ln D = \ln D_o - \frac{Q_d}{R}\cdot\frac{1}{T}$



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③ SPECIES

- SMALL SPECIES MORE MOBILE
  - C IN α-Fe @ 900°C $D = 1.7 \times 10^{-10}$ m²/s
  - αFe IN α-Fe @ 900°C $D = 1.8 \times 10^{-15}$ m²/s

④ OTHER DIFFUSION PATHWAYS – "SHORT-CIRCUITS"

- GRAIN BOUNDARIES, SURFACE, DISL$^{\underline{NS}}$

$J = 5.4 \times 10^{-10}$

$T = 727°C$ (1000 K)

$\frac{dc}{dx} = -350$ kg/m⁴

$T_2 = 1027°$ 1300 K°

$Q_d = 125$

$J = -D\frac{dc}{dx} \rightarrow D = \frac{J_1}{\frac{dc}{dx}}$

$D = D_0 \exp\left(\frac{-Q_d}{RT}\right)$

$$D_1 = \frac{-5.4 \times 10^{-10}}{-350} = 1.54 \times 10^{-12}$$

$$D_0 = \frac{1.54 \times 10^{-12}}{\exp\left(\frac{-125}{8.314 \times 1000}\right)} = -1.56 \times 10^{-12}$$

FICK'S FIRST LAW:

$$\overset{\checkmark}{J} = -\underbrace{D}_{?}\overset{\checkmark}{\frac{dc}{dx}} \qquad T_1 = 1000\,K$$

FIND ~~D~~: $D = \frac{-J}{\frac{dc}{dx}} = \boxed{D_0}\exp\left(\frac{-Q_d}{RT}\right)$ ↳ NEED THIS GUY

$$\boxed{D_0 = 5.26 \times 10^{-6}\ m^2/s}$$

SOLVE FOR $D_{1300} = 5.26 \times 10^{-6}\ m^2/s\ \exp\left(\frac{-125000\ J/mol}{(8.314)(1300K)}\right)$

$$D_{1300} = 4.99 \times 10^{-11}\ m^2/s$$

$$J_{1300} = (-4.99 \times 10^{-11}\ m^2/s)(-350\ kg/m^4) = 1.75 \times 10^{-8}\ kg/m^2 \cdot s$$

* UNDERSTAND EVERY EXAMPLE PROBLEM IN CHAPTER 5 *

1/29/2013

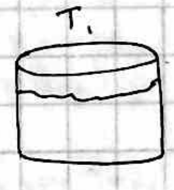
* PHASE DIAGRAMS

- HOW WE UNDERSTAND WHAT HAPPENS WHEN WE MIX TWO ELEMENTS
- PHASE DIAGRAM RELATES
  - WHAT PHASES ARE PRESENT
  - CHEMICAL COMPOSITION
  - RELATIVE AMOUNTS OF THE PHASES
  - ALL AS A FUNCTION OF TIME

- COMPONENT: PURE METALS OR COMPOUNDS THE ALLOY IS MADE OF

- PHASE: A HOMOGENEOUS PORTION OF A SYSTEM WHICH HAS UNIFORM CHEMICAL AND PHYSICAL CHARACTERISTICS

EX.| SYSTEM = 90% H_2O + 10% NaCl

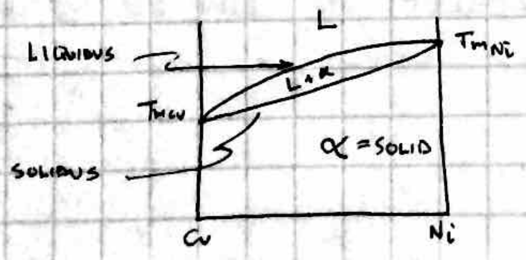


1 PHASE LIQUID	2 PHASES → L+S
90% H_2O + 10% NaCl	SOLID - 100% NaCl
100% L	LIQUID = 95% H_2O + 5% NaCl

- PHASE DIAGRAMS DESCRIBE EQUILLIBRIUM CONDITIONS
  - NUMBER AND RELATIVE AMOUNTS DON'T CHANGE WITH TIME
  - SYSTEM IS STABLE
  - IF EXPERIMENTAL CONDITIONS CHANGE RAPIDLY, A NON-EQUILLIBRIUM STATE MAY OCCUR. (METASTABLE)

(I.) BINARY PHASE DIAGRAMS

- ISOMORPHOUS : COMPLETE SOLID STABILITY EXISTS BETWEEN 2 COMPONENTS
  EX. Ni - Cu



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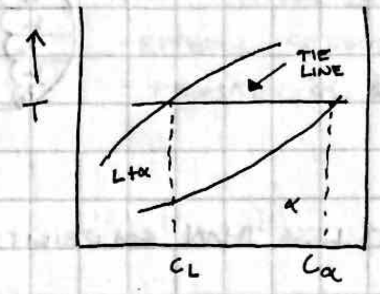
WE CAN FIND 3 IMPORTANT THINGS

① PHASES PRESENT

② CHEMICAL COMPOSITION OF PHASE

- 1 PHASE REGION: EQUAL TO SYSTEM COMPOSITION
- 2 PHASE REGION: DETERMINED BY DRAWING A TIE-LINE

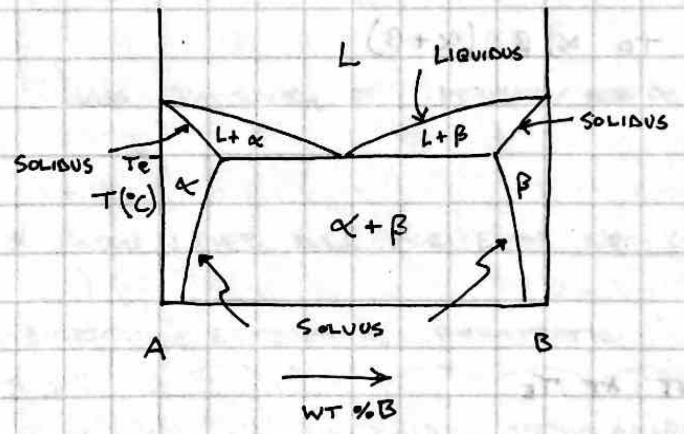


2/4/2013

QUIZ THIS WEEK → PHASE DIAGRAMS

EXAM → NEXT WEEK

* BINARY EUTECTIC PHASE DIAGRAMS



AT THE EUTECTIC POINT:

$$L(C_E) \underset{\substack{\uparrow \\ \text{COOLING}}}{\longrightarrow} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

"ALWAYS USE THE TIE LINE AND THE LEVER RULE"

3 THINGS TO LEARN FROM A PHASE DIAGRAM:

- WHAT PHASES ARE PRESENT

$$W_\alpha = \frac{\qquad}{WT\%_\beta - WT\%_\alpha}$$

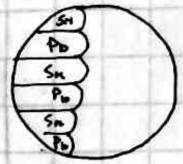
$$W_\beta = \frac{\qquad}{\cdots}$$

* PHASE DIAGRAM EXAMPLE ON BB *

2/4/2013

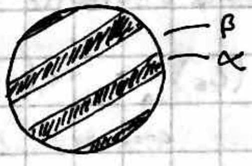
* READING THE PHASE DIAGRAM

1.) LESS THAN SOLID SOLUBILITY AT R.T.
- LIQUID STATE
- α (OR β) BEGINS TO SOLIDIFY AT LIQUIDUS
  - → L COMPOSITION FOLLOWS LIQUIDUS
  - → S COMPOSITION FOLLOWS SOLIDUS
- END W/ SOLID POLYCRYSTALLINE α OR β



2.) GREATER THAN SOLUBILITY AT R.T. BUT LESS THAN SOLUBILITY AT T.E.
- LIQUID STATE
- α (OR β) BEGINS TO SOLIDIFY AT LIQUIDUS
- AT THE SOLVUS, $\alpha \rightarrow \alpha+\beta$ OR $\beta \rightarrow \alpha+\beta$
  - → SECOND PHASE APPEARS
  - → SECOND PHASE WILL GROW AS T DECREASES

3.) AT EUTECTIC COMPOSITION (C_E)
- LIQUID STATE
- AT T_E ALL LIQUID SOLIDIFIES TO α, β ($\alpha+\beta$)
- UNIQUE MICROSTRUCTURE



4.) BETWEEN C_E AND SOLUBILITY LIMIT AT T_E
- LIQUID STATE
- α (OR β) FORMS AT LIQUIDUS
- JUST CROSSING T_E
  - → THE α (OR β) THAT HAS ALREADY FORMED DOES NOT CHANGE
  - → L TURNS INTO EUTECTIC MICROSTRUCTURE

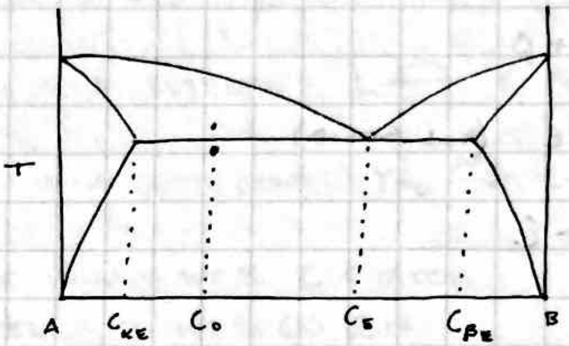
2/5/2013

✳ HELP SESSION: MONDAY, FEB. 11TH 6-7:30 pm, KEARNEY 112

→ 2 MICROCONSTITUANTS IN THE MICROSTRUCTURE

↳ A PART OF THE MICROSTRUCTURE WITH AN IDENTIFYABLE AND CHARACTERISTIC STRUCTURE.

- EUTECTIC STRUCTURE
- PRIMARY α (OR PRIMARY β)



MASS FRACTIONAL EUTECTIC MICROCONSTITUANT $= \dfrac{C_0 - C_{\alpha E}}{C_E - C_{\alpha E}}$

MASS FRACTIONAL OF PRIMARY [redacted] α $= \dfrac{C_E - C_0}{C_E - C_{\alpha E}}$

✳ KNOW LEVER RULE FOR EXAM, NOT GIVEN ✳

- EUTECTIC, EUTECTOID, PERATECTIC

✳ KNOW THE DEFINITION OF A PHASE ✳

2/5/2013

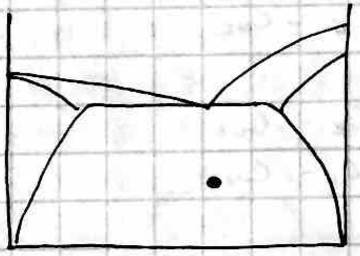
PHASE DIAGRAMS CAN BE MORE COMPLICATED

- INTERMEDIATE SOLID SOLUTIONS
  - → Cu - Zn
- LINE COMPOUNDS = INTERMEDIATE PHASES
  - → PHASES THAT ONLY EXIST IN A PARTICULAR CHEMICAL COMPOSITION
    - Mg_2Pb IN THE Mg - Pb SYSTEM

OTHER INVARIENT POINTS:

- EUTECTIC = $L \longrightarrow \alpha + \beta$
- EUTECTOID = $\delta \longrightarrow \gamma + \epsilon$ (ALL SOLID)
- PERITECTIC = $\delta + L \rightarrow \varepsilon$

✱ QUIZ QUESTION



$C_\alpha = 55$ WT% B

$C_\beta = 90$ %WT B

$$W_\alpha = 0.5 = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

$$\boxed{C_\alpha = 20 \text{ WT\% B}}$$

✱ PHASE DIAGRAM OF STEEL

- THERE IS A EUTECTOID (VERY IMPORTANT)
- IRON CARBON SYSTEM (STEEL)
- INCREDIBLY IMPORTANT
  - → REFER TO AS $Fe - Fe_3C$ SYSTEM

Fe_3C = LINE COMPOUND CALLED CEMENTITE

= FORMED AT 6.7 WT % C

2/5/2013

PURE Fe = 3 PHASES

α FERRITE $\longrightarrow$ γ AUASENITE $\longrightarrow$ δ - Fe
BCC FCC

INTRODUCE C:

α - Fe CAN TAKE 0.022 WT % C
γ - Fe CAN TAKE 2.14 WT % C

- IN BOTH CASES, Fe_3C FORMS PAST SOLUBILITY LIMIT

- THERE IS A EUTECTIC: $L \xrightarrow{\text{COOL}} \gamma\text{-Fe} + Fe_3C$

- THERE IS A EUTECTOID: $\gamma_{Fe} \xrightarrow{\text{COOL}} \alpha\text{-Fe} + Fe_3C$

  - PURE IRON = WT % $C < 0.008$
  - STEEL = WT % $C < 2.14$
  - CAST IRON = WT% $2.14 \leq$ WT% ≤ 6.17

* STEEL MICROSTRUCTURES

EUTECTOID STEEL: = 0.76 WT % C

- ON COOLING FROM γ-Fe, THE RESULTING MICROSTRUCTURE IS VERY SIMILAR TO THE EUTECTIC STRUCTURE, BUT LESS WELL DEVELOPED

EUTECTOID MICROSTRUCTURE = PEARLITE

HYPOLELTOID ALLOY

- STEEL W/ LESS THAN 0.76 % WT C

ON COOLING:

$$\gamma \longrightarrow \alpha + \gamma \longrightarrow \alpha' + [\alpha + Fe_3C]$$

2/6/2013

* HYPERTECTOID STEEL

WT % C IS GREATER THAN 0.76 WT %

$$\gamma \xrightarrow{\text{COOL}} \gamma + Fe_3C \xrightarrow[727°C]{\text{COOL}} Fe_3C' + \underbrace{(\alpha + Fe_3C)}_{\text{PEARLITE}}$$

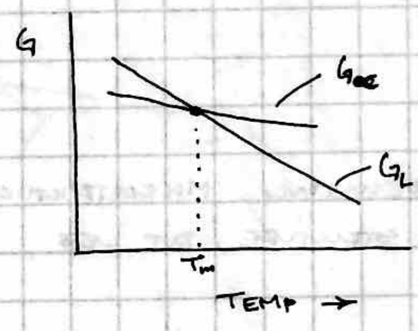
- USE LEVER RULE TO DESCRIBE THE MASS FRACTIONS OF PHASES AND MICROCONSTITUANTS

* CHAPTER 10, 2/11/2013

NUCLEATION THEORY - WHY AND HOW DO PHASE TRANSFORMATIONS OCCUR?

→ $L \rightarrow \alpha$ OR $\alpha \rightarrow \alpha + \beta$

GIBBS FREE ENERGY : G = TOTAL SYSTEM ENERGY



→ WE PAY ATTENTION TO ΔG FOR PHASE TRANSFORMATIONS.

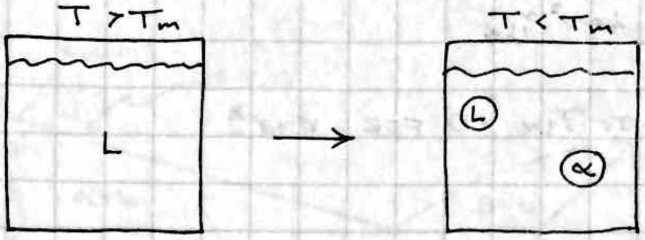
→ THE $L \rightarrow \alpha$ PHASE TRANSITION OCCURS BECAUSE AT $T < T_m$ $G_\alpha < G_L$ OR ΔG IS <u>NEGATIVE</u>

→ WHERE DOES NUCLEATION OCCUR?

① HOMOGENEOUS → UNIFORMLY THROUGOUT
② HEDEROGENEOUS → AT INHOMOGENEOUS (DEFECTS, SURFACES)

2/11/2013

CONSIDER A "PURE MATERIAL"



FORMATION OF NUCLEUS DECREASES TOTAL FREE ENERGY

2 FACTORS

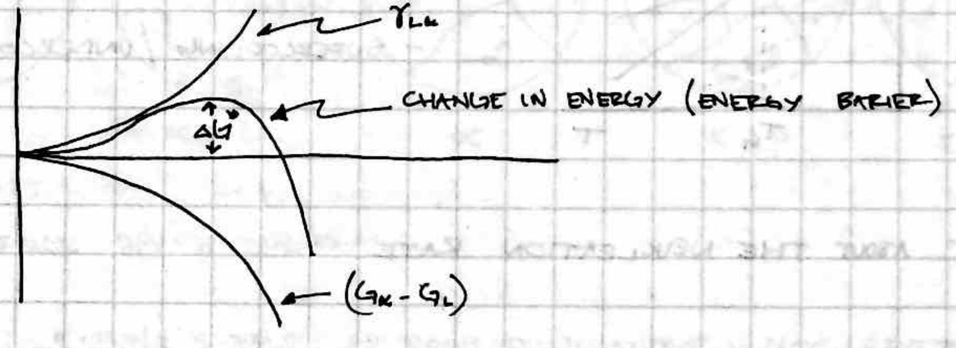
① ΔG DUE TO CONVERSION OF $L \rightarrow \alpha$

$$-\Delta G_{L\alpha} = (G_\alpha - G_L)\left(\tfrac{4}{3}\pi r^3\right)$$

② WE HAVE CREATED A SURFACE – THIS RAISES THE SYSTEM ENERGY
→ THIS DEPENDS ON THE "SURFACE ENERGY" ⇒ $\gamma = J/m^2$

$$\Delta G_\gamma = 4\pi r^2 \cdot \gamma_{L\alpha}$$

$$\Delta G_{HOMOGENEOUS} = \tfrac{4}{3}\pi r^3 (G_\alpha - G_L) + 4\pi r^2 \gamma_{L\alpha}$$



→ THERE IS A CRITICAL NEUCLEI SIZE (r^*) AND A CRITICAL ENERGY THAT MUST BE OVER COME (ΔG^*)

→ DIRECTLY AT Tm THERE IS NO DRIVING FORCE FOR NEUCLEATION
→ PHASE TRANSITIONS OCCUR BELOW THE TRANSITION TEMP

→ NEUCLEATION OCCURS VIA RANDOM THERMAL VIBRATIONS IN THE MELT (HOMOGENEOUS)

2/11/2013

→ WE CAN FIND r^* AND ΔG^* WITH SIMPLE MATH

$$\Delta G = \frac{4}{3}\pi r^3 (\Delta G_v) + 4\pi r^2 \gamma_{L\alpha}$$

$$\frac{dG}{dr} = 4\pi r^2 (\Delta G_v) + 8\pi r \gamma_{L\alpha} = 0 \text{ FOR } r = r^*$$

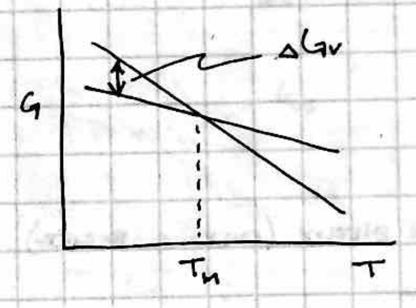
$$\boxed{r^* = \frac{-2\gamma_{L\alpha}}{\Delta G_v}}$$

→ THE ENERGY BARRIER TO NEUCLEATION = ΔG^*

$$\Delta G_{HOMO}(r^*) = \frac{4}{3}\pi \left(\frac{-2\gamma_{L\alpha}}{\Delta G_v}\right)^3 \Delta G_v + 4\pi \left(\frac{-2\gamma_{L\alpha}}{\Delta G_v}\right)^2 \gamma_{L\alpha}$$

$$\Delta G^* = \frac{16}{3}\frac{\pi \gamma_{L\alpha}^3}{\Delta G_v^2}$$ → - $\gamma_{L\alpha}$ IS INDEPENDENT OF T

- BUT ΔG_v IS STRONGLY DEPENDENT ON T



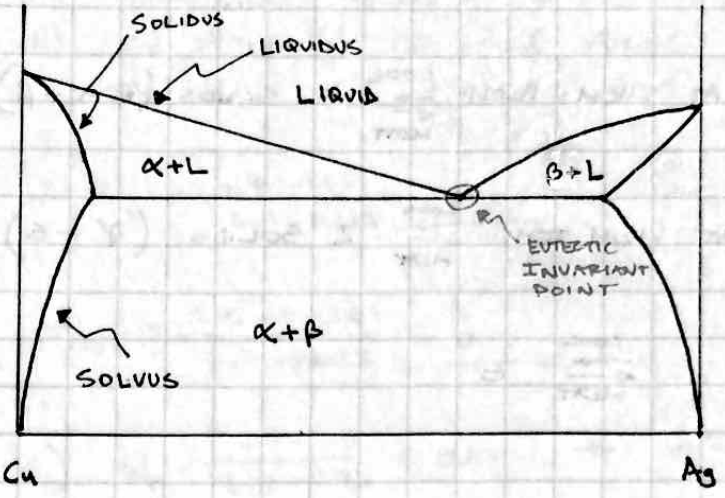
→ ΔG_v GETS MORE NEGATIVE AS T↓

- $\Delta G_v^* \propto \frac{1}{(T_m - T)^2}$ → $T_m - T = \Delta T$

- SUPERCOOLING / UNDERCOOLING

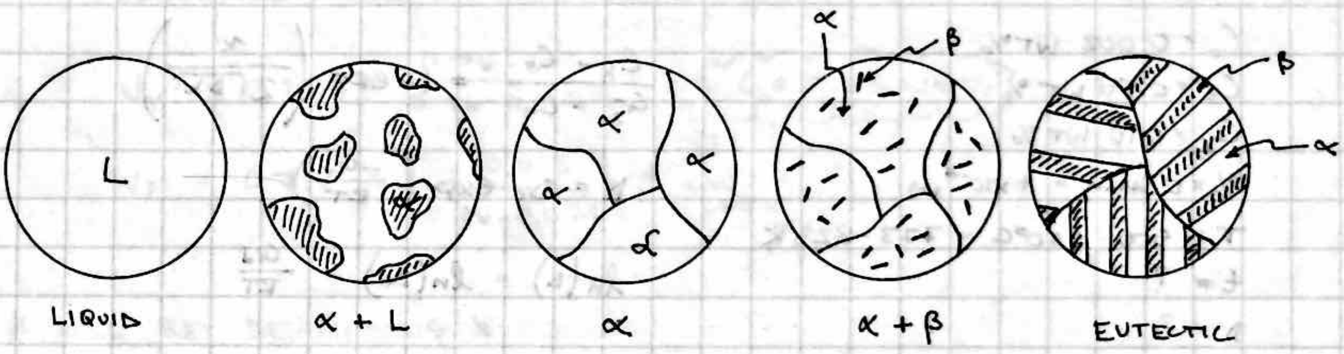
→ WHAT ABOUT THE NEUCLEATION RATE

2/11/2013 READING NOTES (MIDTERM STUDY)



FOR A EUTECTIC REACTION (C_E, T_E)

- $L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$



* IRON-CARBIDE PHASE DIAGRAM

- FERRITE: α-IRON, STABLE AT ROOM TEMPERATURE - BCC CRYSTAL STRUCTURE
- AUSTINITE: γ-IRON, FCC (NON-MAGNETIC)

ALL STEEL IS ≤ 6.70 WT% CARBON

- CEMENITE: NOT AN EQUILLIBRIUM COMPOUND, VERY HARD AND BRITTLE

EUTECTIC REACTION FOR IRON-CARBIDE:

$$\boxed{L \rightleftharpoons \gamma + Fe_3C}$$

* PURE β IS <u>STILL</u> β

- KNOW ALL POINTS ON A EUTECTIC PHASE DIAGRAM

* INVARIENT POINTS

KNOW THESE

- EUTECTIC: LIQUID AT HIGH TEMP $\underset{\text{HEAT}}{\overset{\text{COOL}}{\rightleftarrows}}$ 2 SOLIDS ($\alpha+\beta$)
- EUTECTOID: SOLID AT HIGH TEMP $\underset{\text{HEAT}}{\overset{\text{COOL}}{\rightleftarrows}}$ 2 SOLIDS ($\gamma+\epsilon$)
- PARITECTIC: SOLID + L $\underset{\text{HEAT}}{\overset{\text{COOL}}{\rightleftarrows}}$ ϵ

* HARDENING A SURFACE → NON-STEADY STATE

- QUIZ 2 REDO:

$C_0 = 0.002$ WT%
$C_s = 0.50$ WT%
$C_x = 0.10$ WT%
$x = 0.4\text{mm} = 4\times10^{-4}\,\text{m}$
$T = 500-550°C = 773-823\,K$
$t = ?$
$D = ?$

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$D = D_0 \exp\left(\frac{-Q_d}{RT}\right)$$

$$\ln(D) = \ln(D_0) - \frac{Q_d}{RT}$$

$Q_d = 74{,}800$ J/MOL
$D_0 = 2.5\times10^{-7}\,\text{m}^2/\text{s}$

* MAKE SURE WE CAN DO ALL SAMPLE PROBLEMS IN CHAPTER 5 (NOT 5.6)

STEEL:

- HYPO: < 0.76
- HYPER: > 0.76

WHAT IS THE PROEUTECTOID PHASE? - COMMON QUESTION

* REVIEW SESSION *

1Kg OF γ-Fe 1.15 WT% C, COOLED TO JUST BELOW 727

A.) PROEUTECTOID PHASE = Fe_3C

B.) HOW MANY Kg's OF Fe_3C FORM?

HOW MANY Kg's OF α-Fe FORM?

$$WT\%_\alpha = \frac{6.7-1.15}{6.7-0.022} = \underline{0.83}$$

$$WT_{Fe_3C} = \frac{1.15-0.022}{6.7-0.022} = \underline{0.17\ Kg}$$

C.) $W_p = \frac{6.7-1.15}{6.7-0.76} = 0.93 \rightarrow 0.93\ Kg$

$$W_{Fe_3C} = \frac{1.15-0.76}{6.7-0.76} = 0.07 \rightarrow 0.07\ Kg$$

→ PROEUTECTOID FERRITE → PEARLITE

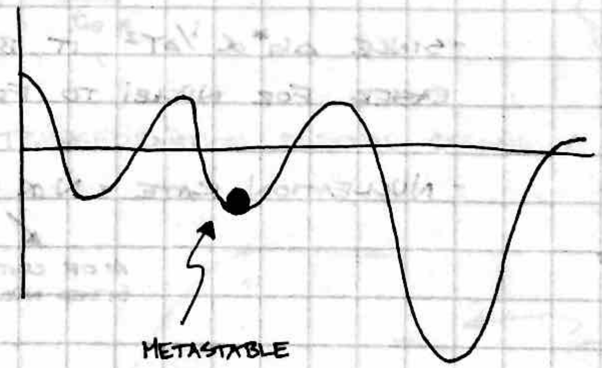
$W_{\alpha}' = 0.286 = \frac{0.76-x}{0.76-0.022} \rightarrow C_0 = 0.55\ WT\%$

$W_p = 0.714 = \frac{x-0.022}{0.76-0.022}$ ← CAN CHECK WITH THIS

* WILL BE DEFINITIONS *

* BRIEFLY OVERVIEW BOUNDARIES *

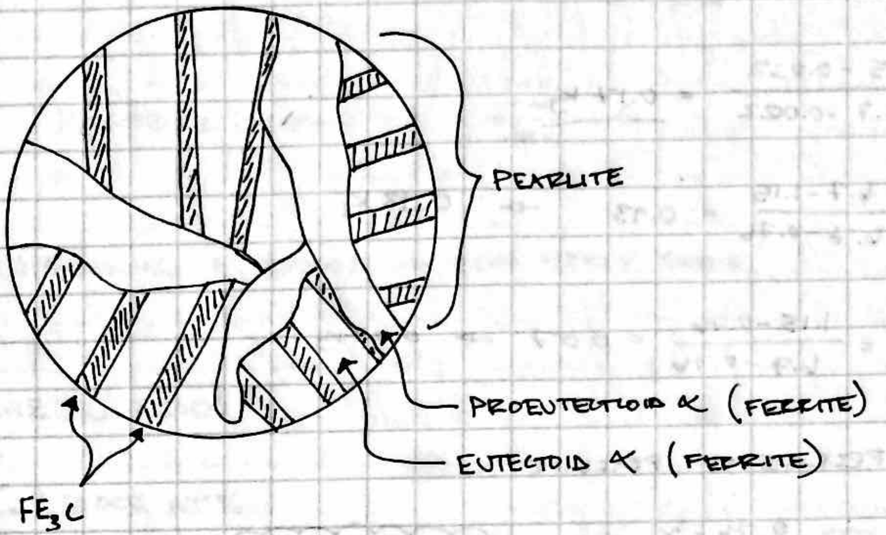
* QUANTITATIVE QUESTIONS ON DIFFUSION AND PHASE DIAGRAMS



2/11/2013

* MICROSTRUCTURE IN IRON-CARBON ALLOYS

- PEARLITE: EUTECTOID STRUCTURE OF α AND $\underbrace{Fe_3C}_{\text{CEMENTITE}}$
  PROPERTIES INBETWEEN FERRITE (SOFT) AND CEMENTITE (HARD)

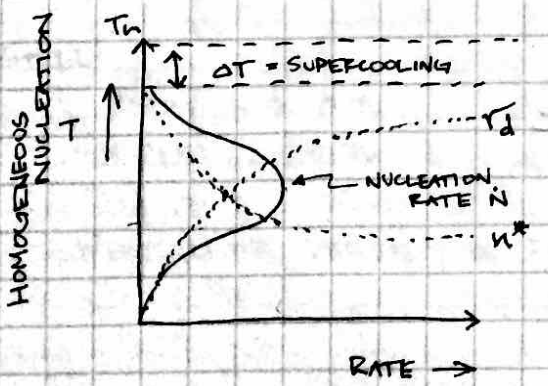


- HYPOEUTECTOID ALLOYS (LESS THAN EUTECTOID) – TO THE LEFT OF EUTECTOID POINT

- HYPEREUTECTOID (BETWEEN 0.76 AND 2.14 WT% CARBON)

2/13/2013

WHAT ABOUT THE NUCLEATION RATE?



- SINCE $\Delta G^* \propto 1/\Delta T^2$ IT BECOMES EASIER FOR NUCLEI TO FORM

- NUCLEATION RATE = $\dot{N} \propto n^* \cdot \nu_d$

  # OF CRIT. SIZED NUC.

  FREQ. OF ATOMIC ATTACHMENT

2/13/2013

→ WE'VE ONLY TALKED ABOUT NUCLEATION → THE SECOND STEP IS <u>GROWTH</u>

→ WITH NUCLEI FORMED, ATOMS MUST DIFFUSE TO CAUSE GROWTH
  → DIFFUSION INCREASES WITH T

CONCEP. QUESTION

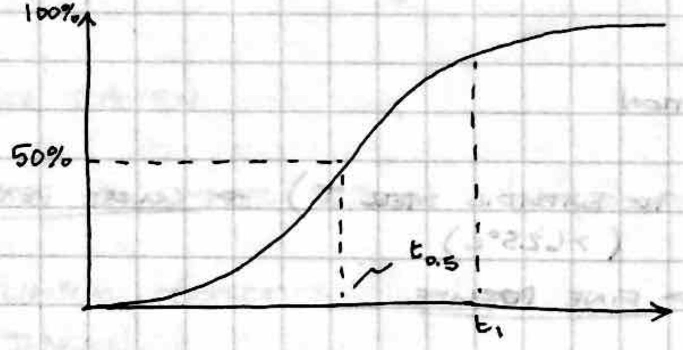
* WHY DOES THE GRAPH LOOK THE WAY IT LOOKS, DRAW GRAPH *

- ALL PHASE TRANSFORMATIONS ARE GOVERNED BY THESE RULES

→ WHEN APPLYING THESE CONCEPTS TO OTHER TYPES OF TRANSITIONS THERE CAN BE OTHER FACTORS TO CONSIDER.

CONCEP. QUESTION

* WHAT IS THE DIFFERENCES BETWEEN HEDROGENEOUS AND HOMOGENEOUS *



ARAMI EQUATION: $= 1 - \exp(-Kt^n)$

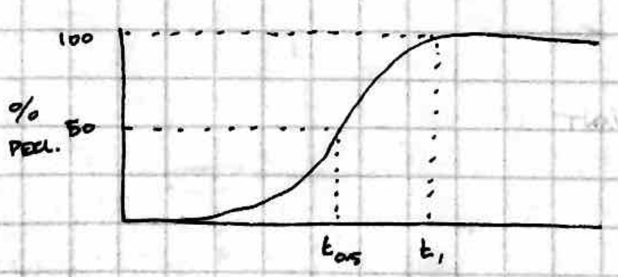
t = TIME
K, n, = CONSTANTS

PHASE TRANSFORMATION RATE

$$r = \frac{1}{t_{0.5}}$$

* KNOW HOW TO DO PROBLEM 10.18

* PHASE TRANSFORMATION DEPENDS STRONGLY ON KINETICS (TIME/TEMP)

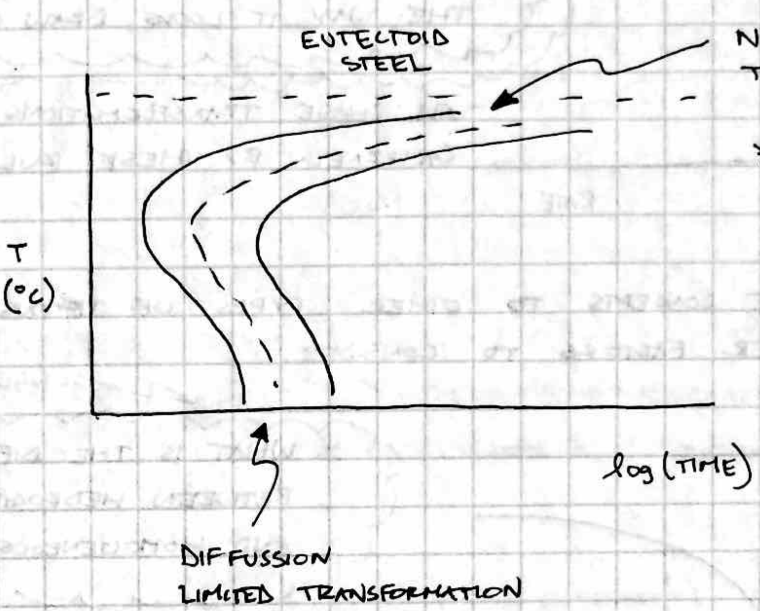


LOOK AT FIGURE IN BOOK

✱ 2/18/2013

- 10.18 POSTED
- START CH. 6 READING (MECHANICAL PROPERTIES)

COARSE PEARLITE
FINE PEARLITE
SPHEROIDITE



✱ WHAT IS CONTROLING THE PHASE TRANS. AT TOP OR BOTTOM? ✱

- AT HIGHER TEMPS (CLOSER TO EUTECTOID STEEL T) → COURSE PEARLITE ($>625°C$)
- LOWER WILL RESULT IN → FINE PEARLITE
- FOR VERY LONG TIMES NEAR THE EUTECTOID TEMP, THE MICROSTRUCTURE CHANGES FROM EUTECTOID M.S. TO SPHERICAL Fe_3C IN A α MATRIX
  → SPHEROIDITE ←
  ✱ THE DRIVING FORCE FOR SPHEROIDITE IS A REDUCTION IN INTERFACIL AREA ✱
- AT EVEN LOWER TEMPS (250°C - 550°C) PEARLITE CANNOT FORM.
  - LIMITED DIFFUSION
  - A NANOSTRUCTURED MICROCONSTITUANT

2/18/2013

IF COOLED RAPIDLY, A NON-EQUILLIBRIUM "MARTINITE"

WHEN γ IS RAPIDLY COOLED (QUENCHED), NEITHER PEARLITE OR BAINITE FORM
- → MARTENSITE FORM
- → IT IS A BODY CENTERED TETRAGONAL UNIT CELL
- → IT IS A METASTABLE MICROCONSTITUANT
- → IF ANNEALED, MARTENSITE WILL TRANSFORM + $\alpha + Fe_3C$

EX. 10.2

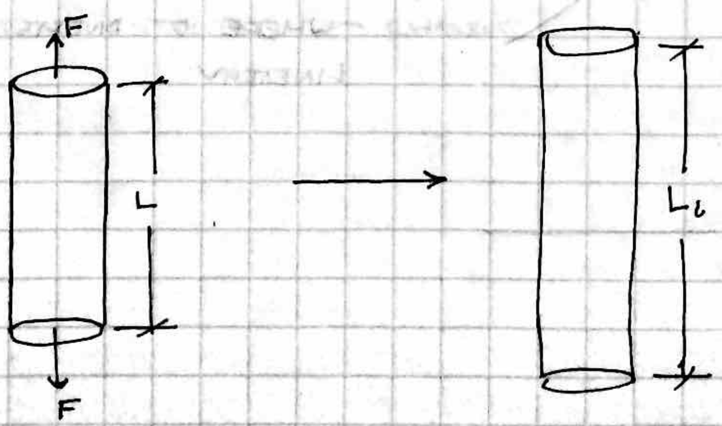
* TEMPERED MARTENSITE

- → BY ITSELF MARTENSITE IS USELESS
- → HOWEVER IF YOU TREAT (HEAT) (ANNEAL)
  - 250° - 600°C FOR 10MIN - 2HRS.
  - TEMPERING → TEMPERED MARTENSITE $(\alpha + Fe_3C)$
- → EXCELLENT MECHANICAL PROPERTIES

* QUIZ TOMORROW

-10.18 → SIMPLER VERSION (NUCLEATION / GROWTH)

MECHANICAL PROPERTIES:
- TENSION
- COMPRESSION
- SHEAR (TORSION)
- BIAXIAL TENSION
- HYDROSTATIC COMPRESSION



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

$$\epsilon = \frac{l_i - l_0}{l_0} = \frac{\Delta l}{l}$$

2/19/2013

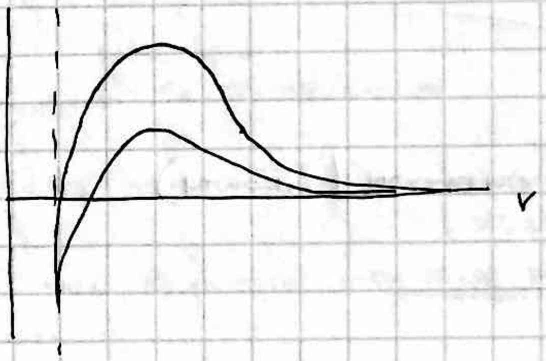
E: Mg = 45 GPa
Cu = 110 GPa
Steel - 100-250 GPa
Al_2O_3 = 392 GPa
LDPE = 0.2 GPa

→ HOOKE'S LAW FOR S.S

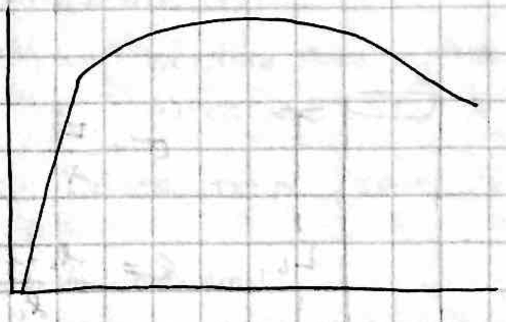
$$\tau = G\gamma$$

* IN CLASS ASSIGNMENT POSTED ONLINE

AT THE ATOMIC LEVEL, ELASTIC STRAIN IS SIMPLY SMALL CHANGES IN INTERATOMIC SPACING



THE MODULUS IS PROPORTIONAL TO THE SLOPE OF F VS. r AT r_0



PROPORTIONAL LIMIT
-WHERE σ DIVERTS FROM LINEARITY

* CHAPTER 10 READING NOTES

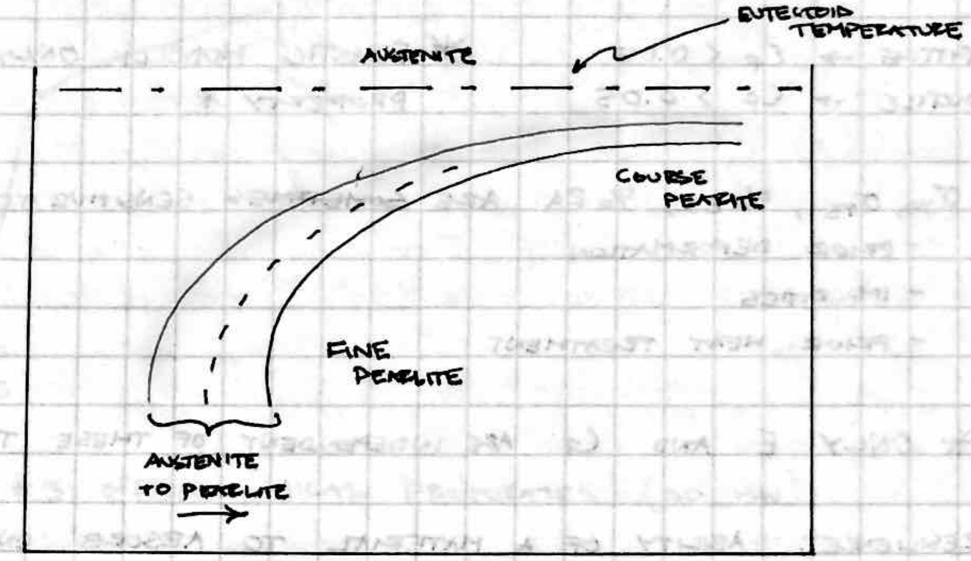
- PHASE TRANSFORMATIONS BROKEN INTO TWO DISTINCT GROUPS:
  - NUCLEATION
  - GROWTH

<u>NUCLEATION</u>: THE APPEARANCE OF VERY SMALL PARTICLES (OR NUCLEI) OF THE NEW PHASE. TWO TYPES: HEDEROGENEOUS, HOMOGENEOUS.

- HOMOGENEOUS: NUCLEI FORM UNIFORMLY THROUGHOUT
- HEDEROGENEOUS: NUCLEATION @ GRAIN BOUNDARIES, STRUCTURAL INHOMOGENETIES

* ISOTHERMAL TRANSFORMATION DIAGRAMS:

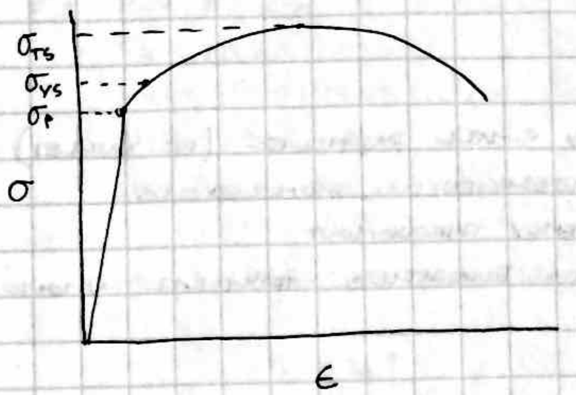
- ABOVE THE EUTECTOID TEMP LINE (727°C) ONLY AUSTINITE WILL EXIST



* BANITE:

- PEARLITIC AND BANITIC TRANSFORMATIONS VERY COMPETITIVE. ONE EITHER ONE HAS FORMED, IT MUST BE RE-HEATED ABOVE EUTECTIC TO CHANGE.

2|20|2013



TENSILE STRENGTH:
- MAX ON $\sigma - \epsilon$ CURVE
- ABOVE σ_{TS}, NECKING OCCURS
- ABOVE σ_{TS}, ALL DEFORMATION IN CONC. IN NECKED REGION

④ DUCTILITY = DEGREE OF PLASTIC DEFORMATION AT FRACTURE
- % ELONGATION $(EL) = \left(\frac{\ell_f - \ell_0}{\ell_0}\right) \times 100$
- % REDUCTION IN AREA $= RA\% = \left(\frac{A_0 - A_f}{A_0}\right) \times 100\%$

→ GENERAL RULE ←

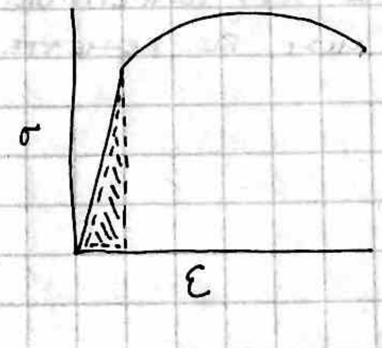
- BRITTLE → $\varepsilon_f < 0.05$
- DUCTILE → $\varepsilon_f > 0.05$

* ELASTIC MODULLI ONLY INHERENT PROPERTY *

⑤ σ_{YS}, σ_{TS}, % EL, % RA ARE ~~SOMETIMES~~ SENSITIVE TO:
- PRIOR DEFORMATION
- IMPURITIES
- PRIOR HEAT TREATMENT

* ONLY E AND G ARE INDEPENDENT OF THESE THINGS

⑥ RESILIENCE: ABILITY OF A MATERIAL TO ABSORB ENERGY IN THE ELASTIC REGION



$$U_r = \frac{1}{2}\sigma_{ys}\varepsilon_y = \frac{\sigma_{ys}}{2E}$$

2/20/2013 :

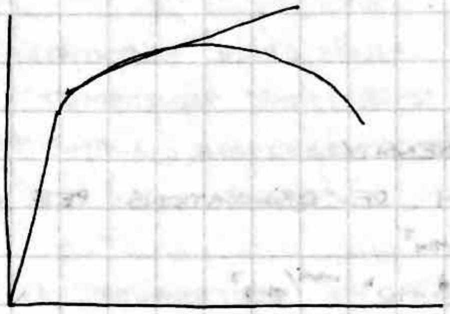
⑦ <u>TOUGHNESS</u> : ABILITY OF A MATERIAL TO ABSORB ENERGY UP TO FRACTURE.

- @ LOW STRAIN RATES = AREA UNDER ENTIRE $\sigma - \epsilon$ CURVE

- ALTHOUGH IT SEEMS THE MATERIAL IS GETTING WEAKER PAST σ_{TS} IT IS NOT
  - → ACTUALLY GETTING STRONGER
  - → THE AREA IS DECREASING
  - → INTRODUCE TRUE STRESS + TRUE STRAIN

$\sigma_T = \frac{F}{A_i}$ INSTANTANEOUS AREA

$\epsilon_T = \ln\left(\frac{l_i}{l_0}\right)$ INSTANTANEOUS LENGTH



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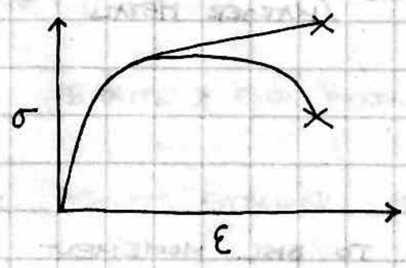
- QUIZ: #5 ON MECHANICAL PROPERTIES (DO HW)

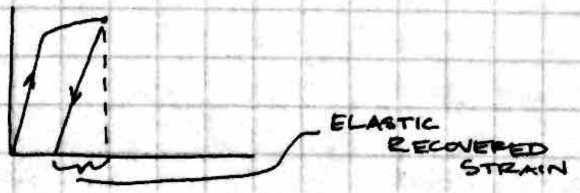
TRUE STRESS, TRUE STRAIN



$\sigma_T = \frac{F}{A_i}$, $\sigma_T = \sigma(1+\epsilon)$

$\epsilon_E = \ln\left(\frac{l_i}{l_0}\right)$, $\epsilon_t = \ln(1+\epsilon)$

THERE IS ELASTIC RECOVERY AFTER PLASTIC DEFORMATION



* WHEN RELOADED, MATERIAL ACTUALLY BECOMES STRONGER *

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→ MECHANISM BEHIND PLASTIC DEFORMATION

- ✱ NET MOVEMENT OF ATOMS IN RESPONSE TO STRESS
- ✱ HAPPENS BY DISLOCATION MOVEMENT
  - → CALLED DISLOCATION "SLIP" OR "GLIDE"

- DISLOCATIONS HAPPEN SEQUENTIALLY, NOT ALL AT ONCE

→ SIMPLY, ONE PLANE OF ATOMS IS SLIPPING OR SLIDING OVER ANOTHER

- USUALLY HAPPENS IN PARTICULAR PLANES AND DIRECTIONS
- ARISES FROM SHEAR STRESS

→ ALL MATERIALS HAVE DISLOCATIONS

- CHARACTERISED BY DISLOCATION DENSITY
- DISL. DENSITY IS TOTAL LENGTH OF DISLOCATIONS PER VOLUME
  - DEFORMED METAL ~ 10^{10} mm/mm^3
  - HEAT TREATED METAL ~ $10^{4}-10^{6}$ mm/mm^3
  - Si SINGLE CRYSTAL ~ 0.1 ~ 10 mm/mm^3

→ IT IS DISLOCATIONS WE WANT TO CONTROL

- THE ABILITY OF A METAL TO PLASTICALLY DEFORM DEPENDS ON HOW EASY DISLOCATIONS CAN MOVE
  - → LIMIT MOVEMENT = STRONGER/HARDER METAL

4 WAYS:

① REDUCE GRAIN SIZE
- GRAIN BOUNDARIES ARE BARRIERS TO DISL. MOMEMENT DUE TO CRYSTALLAGRAPHIC DISORDER
  - → DISL. CANNOT EASILY PASS THROUGH

CONCEPT. QUESTIONS.

WHY??

2/25/2013

② SOLID SOLUTION STRENGTHENING

- IMPURITY ATOMS DISTORT LATTICE AND CAUSE STRESS / STRAIN

- DISL. ALSO HAVE STRESS / STRAIN ASSOCIATED WITH THEM.
- THESE STRESS / STRAIN FIELDS INTERACT WHICH IMPEDES DISL. MOTION

③ STRAIN HARDENING = WORK HARDENING = COLD WORKING
  - THE MORE A MATERIAL IS PLASTICALLY DEFORMED, THE MORE DISL. ARE FORMED
  - THESE DISL. THEN INTERACT AND IMPEDE EACH OTHERS MOTION

④ PRECIPITATION HARDENING:
  - TEMPERED MARTENSITE
  - SMALL, DISPERSED, SECOND PHASES ACT AS BARRIERS TO DISL. MOVEMENT.

MECHANICAL PROPERTIES OF Fe-C ALLOYS

→ ANYTHING THAT HINDERS DISL. MOMEMENT

IN GENERAL → INCREASE WT %C (UP TO ~1.5 WT %)

$\uparrow \sigma_{TS}$, σ_{YS}, $\downarrow$ % RA

- FOR σ_{TS}:

BANITE > FINE PEARLITE > COARSE PEARLITE > SPHEROIDITE

✱ ALL ABOUT STOPPING DISLOCATIONS FROM MOVING ✱

HELP SESSION, MONDAY 3/4, KEARNEY 112
6 - 7:30

* CERAMIC MATERIALS

→ CERAMICS ARE LARGELY DOMINATED BY IONIC BONDING

→ FAR MORE COMPLEX STRUCTURES THAN METALS

→ MOST IMPORTANT CONSIDERATIONS:

- CATION / ANION CHARGE
- CATION / ANION SIZE → r_c / r_A

- **CHARGE** → A STABLE COMPOUND MUST BE NEUTRAL, CHARGES MUST BALANCE

$Na^{+} CL^{-}$ $Ti^{4+} O_2^{2-}$

$Mg^{2+} O^{2-}$ $AL_2^{3+} O_3^{2-}$

CHARGE DICTATES STOICIOMETRY

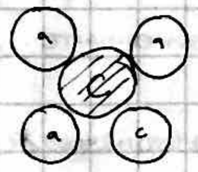
- **SIZE**:

CATIONS ARE GENERALLY SMALL

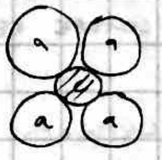
$Al^{3+} \sim 0.053$ nm
$Mg^{2+} \sim 0.072$ nm

ANIONS ARE GENERALLY LARGE (GAINED e'S)

$O^{2-} \sim 0.14$ nm
$Cl^{-} \sim 0.18$ nm



STABLE



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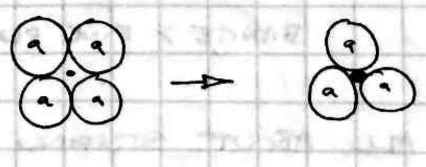


UNSTABLE

2/26/2013

$A_{(m)}X_{(p)}$ → DEPENDS ON IONIC CHARGE

r_c/r_a → DETERMINES CN

- DESCRIBE A FEW STRUCTURES

Cs^+Cl^- CRYSTAL STRUCTURE → <u>NOT</u> BCC

* TUESDAY PROBLEM:

A.) ~~PLASTIC~~ → $\sigma = \frac{F}{A} = \frac{38{,}000}{12.7\times10^{-3}\cdot 6.4\times10^{-3}} = 468\times10^{6}\,Pa = 468\,MPa$

B.) ~~0.004~~ → ELASTIC + PLASTIC

B.) TOTAL STRAIN = 0.02

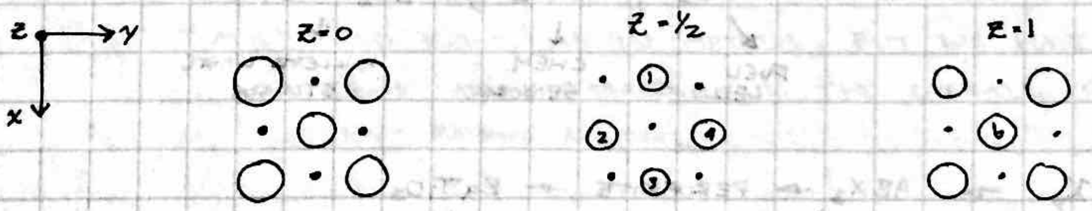
ELASTIC STRAIN → USE HOOKES LAW

$\sigma = E\varepsilon \rightarrow \varepsilon_p = \frac{468\times10^{6}\,Pa}{207\times10^{6}\,Pa} = 0.0023$

PLASTIC STRAIN = 0.2 - 0.0023

→ POSTED, TYPICAL EXAM PROBLEM

* ROCK SALT : HALLITE

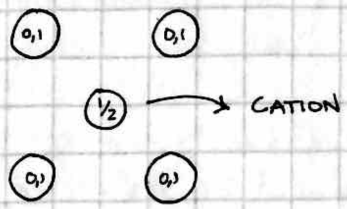


→ MgO, FeO, CaO

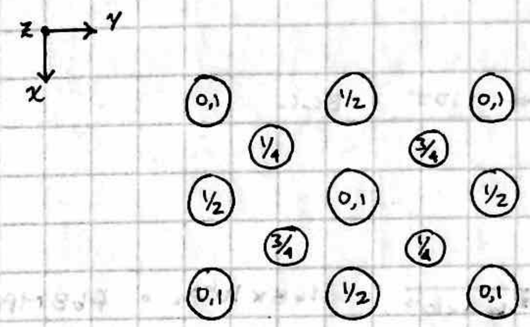
1 FORMULA UNIT = (NaCL)

2/26/2013

CESIUM CHLORIDE



ZINC BLENDE



<u>EXAMPLE:</u> WE HAVE A NEW COMPOUND, Mi^{2+} Lt^{2-}

- WHAT STRUCTURES MIGHT IT FORM

$r_{Mi} \sim 0.04\,nm$ $r_{Lt} \sim 0.12\,nm$

$$\frac{r_c}{r_a} = 0.33$$

FROM TABLE THIS PREDICTS CN = 4

→ PROBABLY ZINC BLENDE

OTHER IMPORTANT STRUCTES:

AX_2 → FLUORITE → ZrO_2, SnO_2, $Er_2Zr_2O_7$

ZrO_2 ↓ FUEL CELLS

SnO_2 ↓ CHEM. SENSORS

$Er_2Zr_2O_7$ ↓ NUCLEAR WASTE STORAGE

$A_mB_nX_p$ → ABX_3 → PEROFKITE → $BaTiO_3$

$BaTiO_3$ ↓ CAPACITORS

$PbZrO_3$, $FeSiO_3$

$PbZrO_3$ ↓ PIEZOELECTRIC

$FeSiO_3$ ↓ EARTHS CRUST

ROCK SALTS
CESIUM CHLORIDE } → LECTURE SUMMARIES. NEED TO KNOW FOR EXAM (MC QUESTION)

DENSITY:

$$\boxed{\rho = \frac{n'\left(\Sigma A_c + \Sigma A_A\right)}{V_c n_A}}$$

n' = # OF FORMULA UNITS / CELL
ΣA_c = ATOMIC WEIGHTS OF CATIONS
ΣA_A = " " " ANIONS
V_c = VOLUME OF CELLS

* CERAMICS

- BONDING IS LARGELLY IONIC
  - → HIGH T_m, MECHANICALLY HARD
- CRYSTAL STRUCTURES GOVERNED BY IONIC CHARGE AND SIZE

PHASE EQUILLIBRIA

- VERY SIMILAR TO METALS, BUT EQUILLIBRIUM TAKES LONGER TO ACHIEVE
  DUE TO LOWER THERMAL CONDUCTIVITY
- SAME RULES APPLY
  - TIE LINE
  - LEVER RULE
- MANY CERAMICS ARE OXIDES
  - → WE NEED TO BE AWARE OF O_2 ATMOSPHERE WHEN PROCESSING.
  - → IN AIR, $P_{O_2} \sim 0.21$

DEFECTS IN CERAMICS

- ALL KINDS EXIST, AS IN METALS, BUT WE HAVE AN ISSUE...
  - → IONS ARE CHARGED, AND THE OVERALL CHARGE MUST REMAIN NEUTRAL
- DISLOCATION SLIP IS VERY DIFFICULT, BECAUSE IT BRINGS SAME CHARGED IONS TOGETHER
  - → VERY ENERGETICALLY UNFAVORABLE = BRITTLE (IT WOULD RATHER BREAK)

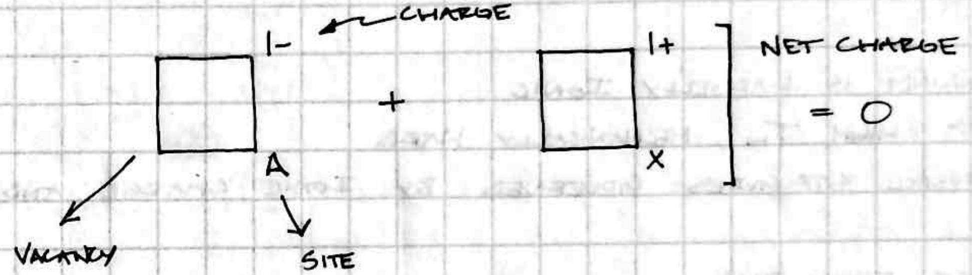
2/27/2013

- HOW DOES CHARGE IMPACT 0-D DEFECTS
  - → TO CREATE A VACANCY IN AN IONIC CRYSTAL, YOU CANNOT SIMPLY REMOVE A POSITIVE OR NEGATIVE ION
  - → DEFECTS MUST BE PAIRED

FOR $A^{1+}X^{1-}$ STRUCTURES

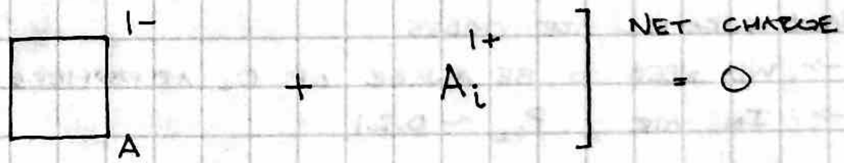
①. SCHOTTKY DEFECT

→ CATION VACANCY + ANION VACANCY



② FRENKEL DEFECT

→ CATION VACANCY + CATION INTERSTITIAL



* FRENKEL → INTERSTITIAL *

THE GENERATION OF THESE IS TEMP. DEPENDENT

FRENKEL → $N_f = N \exp\left(\frac{-Q_{fr}}{2kT}\right)$

SCHOTTKY → $N_s = N \exp\left(\frac{-Q_s}{2kT}\right)$

* MIDTERM #3 REVIEW:

- GIBBS FREE ENERGY (LIQUID → SOLID)
  - 2 TERMS:
    - DIFFERENCE BETWEEN SOLID / LIQUID PHASES → ΔG_v THE VOLUME FREE ENERGY. MAGNITUDE IS $\frac{1}{3}\Delta G_v \rightarrow \frac{4}{3}\pi r^3 \Delta G_v$
    - SECOND RESULTS FROM FORMATION OF THE SOLID-LIQUID PHASE BOUNDARY. MAGNITUDE $\gamma A \rightarrow \gamma 4\pi r^2$

SOLIDIFICATION (IF $T < T_{EQ,SOLID}$) LOWERS THE TOTAL FREE ENERGY, BUT DOING SO ALSO RAISES THE ENERGY BY THE FORMATION OF A PHASE BOUNDARY. THE BALANCE OF THE TWO (OR PROPORTION) DETERMINES IF GROWTH WILL CONTINUE.

- CRITICAL RADIUS: RADIUS REQUIRED TO NUCLEATE
- ACTIVATION ENERGY: ENERGY TO NUCLEATE (MINIMUM FREE)

* CERAMICS

- GENERALLY MORE COMPLEX CRYSTAL STRUCTURES (COMPRISED OF 2 + ELEMENTS)
- BONDING MOSTLY IONIC
  - → METALLIC IONS = CATIONS (+ CHARGE)
  - → NON-METALLIC IONS = ANIONS (- CHARGE)

2 FACTORS AFFECT CRYSTAL STRUCTURE

- AMOUNT OF CHARGE (MAGNITUDE)
- RELATIVE SIZES OF ANION / CATION.

* MUST BE ELECTRICALLY NEUTRAL *

3/4/2013

* POINT DEFECTS

→ GENERATION IS DEPT. (EXPONENTIALLY) ON TEMPERATURE

AX_2 STRUCTURES:

→ FOR EXAMPLE: ZrO_2

* OXYGEN ALWAYS 2^- *

* FRENKEL DEFECT:

$$\square_{Zr}^{4-} + Zr^{4+}$$

* SCHOTTKY DEFECT:

$$\square_{Zr}^{4-} + 2\,\square_{O}^{2+}$$

- A SIMILAR NOTATION IS USED FOR IMPURE OR 'DOPED' CERAMICS

→ FOR DOPING W/ SAME CHARGE

$$\underbrace{Na^{1+}Cl^{1-} \text{ DOPED WITH } K^{1+}Cl^{1-}}$$

K_{Na}^{0} → FOR A SOLID SOLUTION $(K_x Na_{1-x})Cl$

→ FOR DOPANTS (OR IMPURITIES) WITH A DIFFERENT CHARGE

- NEUTRALITY DEMANDS A COMPENSATING DEFECT IS FORMED

$Na^{1+}Cl^{1-}$ DOPED WITH $Ca^{2+}Cl^{1-}_2$

Ca_{Na}^{1+} → NEEDS TO BE COMPENSATED WITH A 1- DEFECT

3/4/2013

① INTERSTITIAL Cl → Cl_i^{1-}

* ② VACANT Na SITE → $\square_{Na}^{1-}$ * ← EASIEST TO FORM

– INTERSTIAL → $CaCl_2 \xrightarrow{NaCl} Ca_{Na}^{1+} + Cl_{Cl}^{\circ} + Cl_i^{1-}$

↑ INTERSTIAL SITE

– VACANT SITE → $\square_{Na}^{1-} \longrightarrow CaCl_2 \xrightarrow{2NaCl} \underbrace{Ca_{Na}^{1+} + Cl_{Cl}^{\circ} + Cl_{Cl}^{\bullet} + \square_{Na}^{1-}}_{(Ca_x \square_x Na_{1-2x})Cl}$

↑ "VACANCY"

$Zr^{4+}O_2^{2-}$ DOPED WITH $Ca^{2+}O^{2-}$

$\underbrace{CaO \xrightarrow{ZrO_2} Ca_{Zr}^{2-} + O_O^{\circ} + \square_O^{2+}}$ ← MORE LIKELY

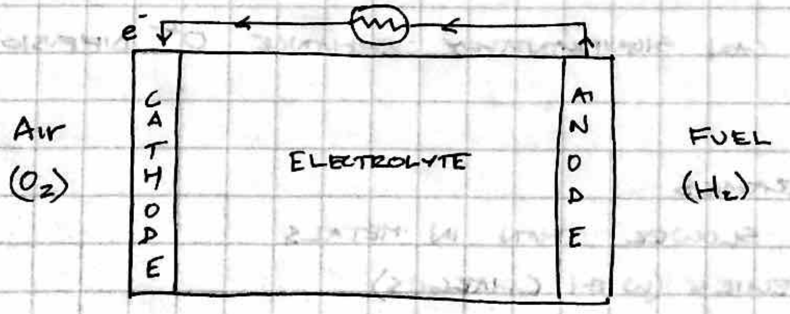
$2CaO \xrightarrow{ZrO_2} Ca_{Zr}^{2-} + O_O^{\circ} + O_O^{\circ} + Ca_i^{2+}$

→ SOLID OXIDE FUEL CELL - SOFC

→ ELECTROCHEMICAL ENERGY CONVERSION DEVICES WITH 4 MAIN COMPONENTS

→ NORMALLY 50-60% EFFICIENT (UP TO 85%)

→ OPERATE BETWEEN 500-1000°C



3/4/2013

① AIR / CATHODE :

$$\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}_{\text{SURFACE}}$$

②. THROUGH ELECTROLYTE

$$\text{CATHODE} \xrightarrow[\text{DIFFUSION}]{O^{2-}} \text{ANODE}$$

③. ANODE / FUEL

$$O^{2-} + H_{2\,(\text{GAS})} \longrightarrow \boxed{H_2O} + 2e^-$$

④. THROUGH INTERCONNECT

$$\text{ANODE} \xrightarrow[\text{CURRENT}]{2e^-} \text{CATHODE}$$

→ ELECTROLYTE IS THE CRITICAL COMPONENT
  → ELECTRICAL INSULATOR
  → OXYGEN CONDUCTOR
  → HIGH TEMP STABLE

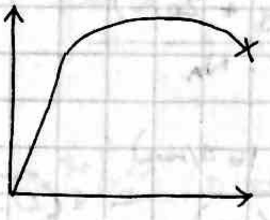
✱ USE ZIRCONIUM - ZrO_2

→ HIGH TEMP. STABLE CERAMIC
→ INSULATOR
→ CONTROL O VACANCIES BY DOPING WITH CaO

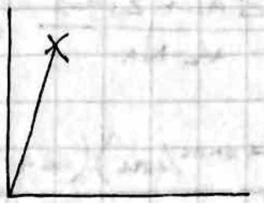
- MEANS WE CAN SIGNIFICANTALLY ENHANCE O^{2-} DIFFUSION

✱ DIFFUSION IN CERAMICS
  → TYPICALLY SLOWER THAN IN METALS
  → MORE SPECIES (WITH CHARGES)
  → USUALLY OCCURS BY

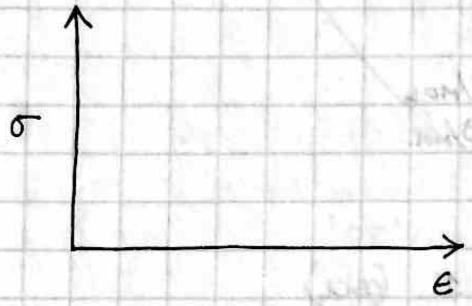
$\epsilon_F <$ 0.05 → BRITTLE



DUCTILE



BRITTLE



* IF THE LOAD IS <u>STILL</u> APPLIED, DRAW LINE STRAIGHT DOWN. IF RELEASED, DRAW PARALLEL TO MODULUS LINE

* NECKING BEGINS AFTER ULTIMATE

* NEED TO KNOW CN #'S OF STRUCTURES

RS → CN = 6
ZB → CN = 4
CS → CN = 8

MgO → ROCK SALT → $\rho = 3.58\ g/cm^3$

A.) WHAT IS THE LATTICE PARAM. (UNIT CELL EDGE LENGTH)?

$$\rho = \frac{m}{V} = \frac{n'(\Sigma A_c + \Sigma A_c)}{V_c N_A} = \frac{n'(\Sigma A_{mg} + \Sigma A)}{a^3 \cdot N_A}$$

$$a = \frac{(4\ \text{FORMULA UNITS/CELL})(24.31\ g/mol + 16\ g/mol)}{(3.58\ g/cm^3)(6.02 \times 10^{23}\ \#/mol)} = \boxed{0.421\ nm}$$

#4.) AX $\rho = 2.65\ g/cm^3$, CUBIC

$a = 0.43\ nm$, $A_A = 86.6\ g/mol$

$A_X = 40.3\ g/mol$

$$\rho = \frac{n'(\Sigma A_A + \Sigma A_c)}{V_c \cdot N_A}$$

$n' = 1$ (CsCl)

$n' = 4$ (ROCK SALT)

$n' = 4$ (ZINC BLENDE)

→ EITHER GOING TO BE REALLY CLOSE TO 1, OR REALLY CLOSE TO 4

#5.) $Li_2^{1+}O^{2-}$ IS DOPED INTO $Ca^{2+}O^{2-}$

$Li_{CA}^{1-} \longrightarrow Li_i^{1+}$

NEED A POSITIVE AND NEGATIVE DEFECT

$\square_O^{2+}$

REVIEW SESSION :

$CaCl_2$ DOPED INTO $Ca^{2+}O^{2-}$

$$2Cl_{O}^{1+} \xrightarrow[\text{VACANCY}]{} 1\,\square_{Ca}^{2-}$$

$Al_2^{3+}O_3^{2-}$ DOPED INTO $Mg^{2+}O^{2-}$

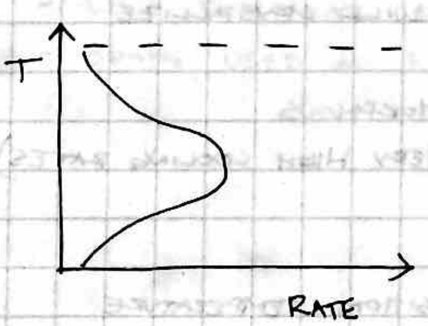
$$\begin{tikzcd} Al_{Mg}^{1+} \arrow[r] \arrow[dr] & O_i^{2-} \\ & \square_{Mg}^{2-} \end{tikzcd}$$

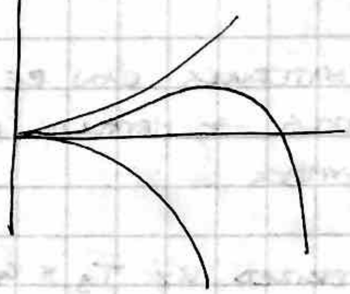
'OR'

$$Al_2O_3 \xrightarrow{2MgO} 2Al_{Mg}^{1+} + 2O_O^{0} + O_i^{2-}$$

$$Al_2O_3 \xrightarrow{3MgO} 2Al_{Mg}^{1+} + 3O_O^{0} + \square_{Mg}^{2-}$$

* DISLOCATIONS ARE DIFFICULT TO MOVE IN A CERAMIC BECAUSE OF THE <u>CHARGE.</u>





10.18

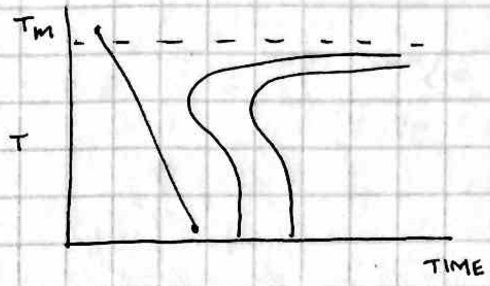
ISOTHERMAL T-DIAGRAM
STRENGTHANING DIAGRAMS
MECHANICAL PROPERTIES

3/6/2013

PHASE TRANSFORMATIONS

→ SAME PRINCIPLES OF NUC./GROWTH APPLY

→ SLOW DIFFUSION + LOW THERMAL



PROPERTIES OF GLASS:

1. GLASS FORMING SYSTEMS NEED A COMPLEX BUILDING BLOCK → INHIBITS FORMATION OF LONG RANGE ORDER

   → $(SiO_4)^{4-}$ TETRAHEDRON

2. GLASSES BEHAVE LIKE FLUIDS
   - → VISCOSITY IS TEMP. DEPENDENT
   - → ISOTROPIC
   - → HIGH SOLUBILITY
   - → TRANSPARENT (MOSTLY)

3. AT HIGH TEMPERATURES, GLASSES WILL CRYSTALLIZE

4. OTHER MATERIALS CAN BE MADE AMORPHOUS
   - → METALS → METALLIC GLASSES (VERY HIGH COOLING RATES)
   - → POLYMERS

5. CHARACTERIZED BY T_g = GLASS TRANSITION TEMPERATURE

   → STRUCTURAL RELAXATION

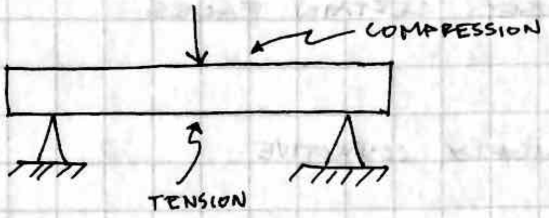
   RIGID BRITTLE $< T_g <$ SOFT DEFORMABILITY

6.

3/6/2013

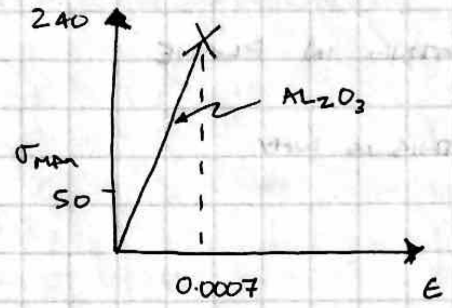
MECHANICAL PROPERTIES: (OF CERAMICS)

→ CERAMICS + GLASSES ARE TESTED IN FLEXURE MODE



→ MEASURE σ_{FS} → FLEXURAL STRENGTH

→ DEPENDS ON SAMPLE GEOMETRY

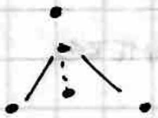


* NO PLANES IN GLASS, IT BREAKS BECAUSE IT HAS FLAWS *

CARBON STRUCTURES:

→ DIAMOND:

- BASIC STRUCTURAL UNIT IS C-TETRAHEDRON



- CN OF CARBON = 4
- VERY STRONG BONDING = HARDEST MATERIAL KNOWN
- LOW ELECTRICAL CONDUCTIVITY
- OFTEN USED AS A COATING

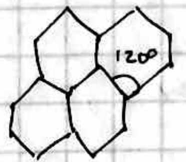
3/11/2013

✱ FINAL: THURSDAY OF FINALS WEEK ✱

- DIAMOND CUBIC STRUCTURE: SIMILAR FORMATION AS ZINC BLENDE

- LIKES TO "FACET" → EXPOSED CERTAIN FACES

✱ GRAPHITE: 3 COORDINATED, HIGHLY CONDUCTIVE



→ STRONG INPLANE BONDING, WEAK OUT OF PLANE BONDING

→ ELECTRICALLY CONDUCTING IN PLANE

$\rightarrow 1s^2 2s^2 \underbrace{2p^2}$

↳ THIS IS WHY

✱ OTHERS:
- FULLERENES (USELESS)
- NANOTUBES
- GRAPHENE

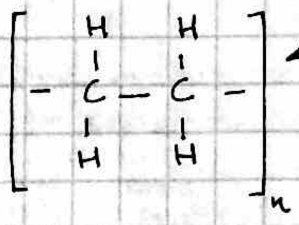
✱ POLYMERS

KNOW DEFINITIONS FOR FINAL

- NATURAL, WOOD, RUBBER, LEATHER
- SYNTHETIC — NYLON, PVC, TEFLON, RUBBER

I. POLYMER CHEMISTRY

→ PRIMARILY BASED ON C-C BONDING WITH VARIOUS SIDE GROUPS.

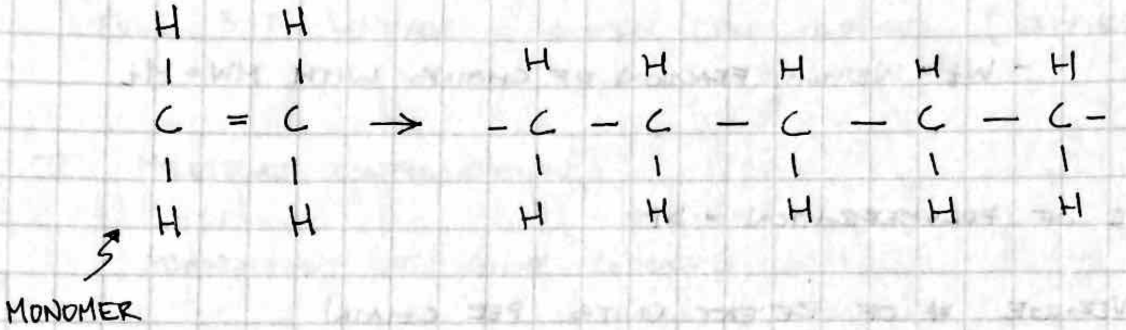


$$\left[-\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \right]_n$$

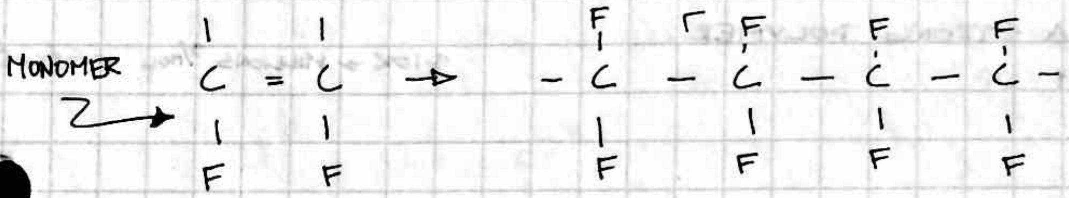
'MER'

3/11/2013

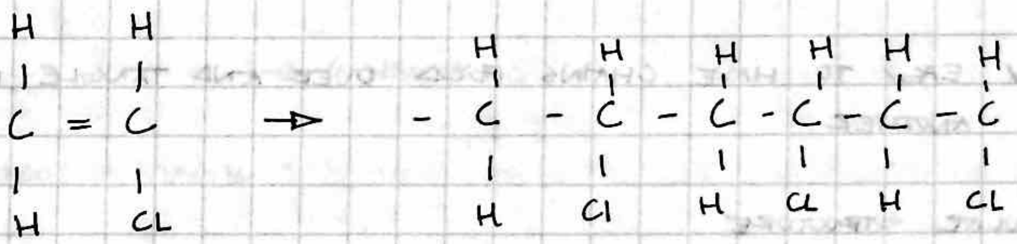
→ POLYETHYLENE



→ POLYTETRAFLUOROETHYLENE - PTFE



→ POLYVINYLCHLORIDE = PVC



II. MOLECULAR WEIGHT

- LENGTH OF POLYMER CHAIN WILL VARY, DEPENDING ON PROCESSING

- NUMBER AVERAGED MOLECULAR WEIGHT

$\overline{M}_N = \sum x_i M_i$ → x_i = NUMBER FRACTION OF TOTAL # OF CHAINS WITH MOLECULAR WEIGHT M_i

M_i = MW OF A GROUP

3/11/2013

- WEIGHT AVERAGE:

$$\overline{M}W = \sum w_i M_i$$

  - W_i = WEIGHT FRACTION OF CHAINS WITH $MW = M_i$

- DEGREE OF POLYMERIZATION = DP
  - AVERAGE # OF REPEAT UNITS PER CHAIN

$$DP = \frac{\overline{M}_n}{m}$$ ← MW OF 1 MER

FOR A GIVEN POLYMERS

~100 g/mol = LIQ/GAS

~1000 g/mol = WAXY/SOFT SOLID

~10K → MILLIONS g/mol = SOLID

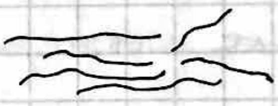
* HOW TO GET A STRONG POLYMER:
- TANGLE THEM UP

III MOLECULAR SHAPE:

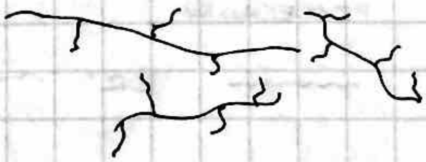
- C-C BOND ANGLE IS 109°, BUT IT IS FREE TO ROTATE IN 3-D
- VERY EASY TO HAVE CHAINS FOLD OVER AND TANGLE W/ ONE ANOTHER

IV MOLECULAR STRUCTURE

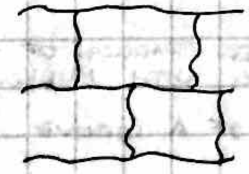
- LINEAR POLYMERS: FLEXIBLE HDPE



- BRANCHED POLYMER: LDPE



- CROSSLINKED POLYMERS:



→ VERY STIFF

→ VULCANIZED RUBBER

3/11/2013

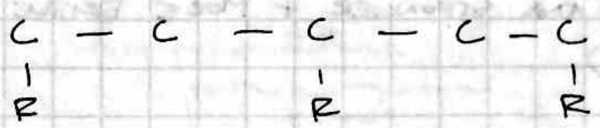
→ CROSSLINKED POLYMERS CONT.

CALLED "NETWORK" POLYMERS

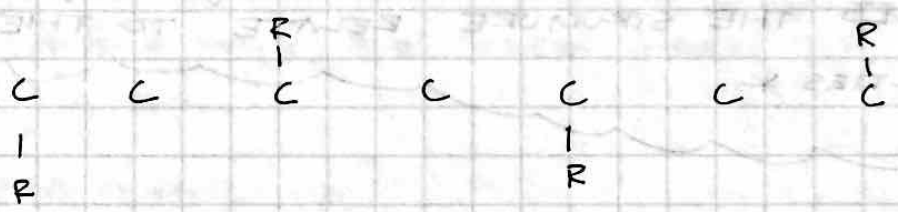
FULL 3-D LINKAGE - HIGHLY CROSS-LINKED (EPOXIES)

V MOLECULAR CONFIGURATION

ARANGEMENT OF SIDE GROUPS



→ ISOTACTIC ←



→ SYNDIOTACTIC ←

RANDOM = ATACTIC

3/12/2013

* OVERALL CLASSES OF POLYMERS

- THERMOPLASTIC: SOFTENS ON HEATING, MELTS ABOVE T_m.
  ON COOLING THE REVERSE OCCURS
  USUALLY SOFT AND DUCTILE
  TYPICALLY LINEAR OR BRANCHED POLYMERS

- THERMOSET: BECAME PERMANENTLY HARD ON SYTHNTHESIS
  FORMATION IS IRREVERSIBLE
  NETWORKED.
  HARDER AND STRONGER + MORE BRITTLE (EPOXY, VULCANIZED RUBBER)

- COPOLYMERS: 2 POLYMERS BLENDED TOGETHER IN VARIOUS WAYS

AAAA - BBBB - AAAA - BBBB

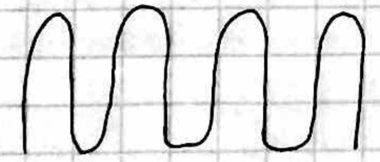
* HOW DOES THE STRUCTURE RELATE TO THE PROPERTIES *

POLYMERS LIKE TO FOLD OVER ON THEMSELVES

* CRYSTALLINE POLYMERS:

- IT IS POSSIBLE FOR POLYMERS TO HAVE LONGE RANGE ORDER

- HAPPENS BY "CHAIN FOLDING"



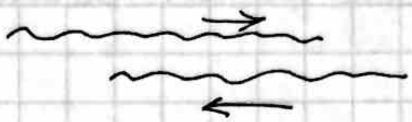
GROW INTO "SPHERULITES"

3/12/2013

* DEGREE OF CRYSTALLINITY, DEPENDS ON PROCESSING
- SLOW COOLING
- SIMPLY OR HIGHLY ORDERED PAIRS CRYSTALLIZE EASIER

* PROPERTIES OF POLYMERS

① - STRENGTH IN C-C BACKBONE IS VERY HIGH
- BONDING BETWEEN CHAINS IS SECONDARY ⇒ WEAK
- WHY MANY POLYMERS ARE FLEXIBLE



② PHASE EQUILLIBRIA EXISTS IN POLYMERS
- LOW PROCESSING TEMPS LIMIT DIFFUSION
- AMORPHOUS PHASES ARE VERY COMMON

③ DIFFUSION → IS FAST BETWEEN CHAINS

T_g EXISTS IN POLYMERS TOO,

GLASSY, RIGID, SOLID < T_g < RUBBERY, FLEXIBLE, SOFT

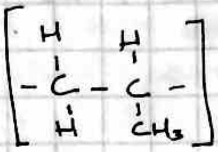
TYPICALLY THE DIFFERENCE BETWEEN T_g, T_m IS 200 ≈ 300°C

EX.	T_g	T_m
HDPE	-90°C	137°C
PTFE	-97°C	327°C
PVC	87°C	212°C

3|12|2013

→ CONTROL T_g WITH:

① BULKY OR POLAR SIDE GROUPS

POLYPROPYLENE 

$$\left[\begin{matrix} & H & & H & \\ - & C & - & C & - \\ & H & & CH_3 & \end{matrix}\right]$$

② MOLECULAR WEIGHT

③ CROSSLINKING INCREASES

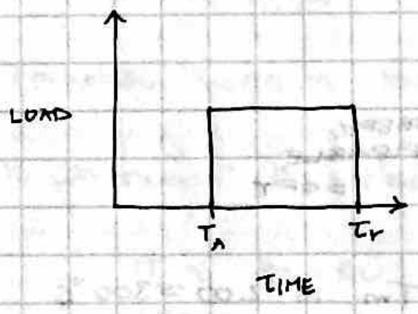
* NETWORKED POLYMERS DO NOT EXPERIENCE T_g *

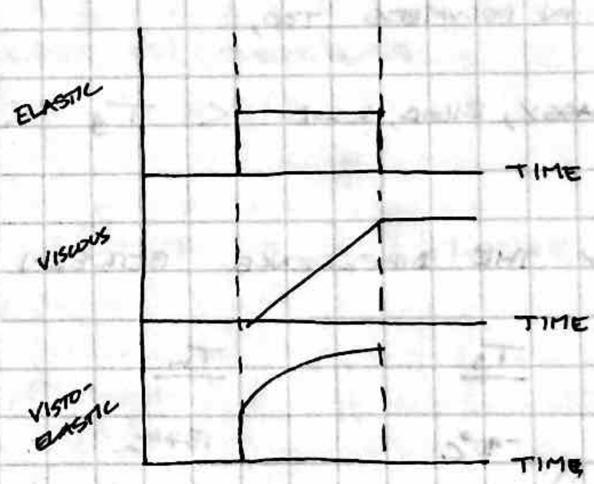
*TUESDAY PROBLEM WILL BE ON EXAM

* VISCOELASTIC DEFORMATION

-VERY TYPICAL OF POLYMERS

-APPLY THE LOAD TO THE GRAPH





ELASTIC → STRAIN IS INSTANTANEOUS AND FULLY RECOVERED

VISCOUS → STRAINS (FLOW) AT A CONSTANT RATE, STRAIN IS NOT REVERSIBLE

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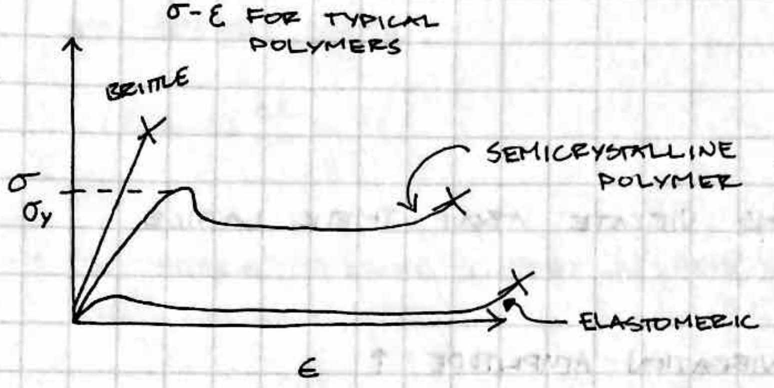
* VISCO-ELASTIC → IMPORTANT *



→ NECK FORMS AT σ_y
- CHAINS BECOME ORIENTED W/ APPLIED STRESS
- NECK REGION GETS LONGER AND LONGER

* STRENGTHENING MECHANISMS:

- BULKY/ POLAR SIDE GROUPS } SIMILAR
- INCREASE SECONDARY BINDING } SIMILAR
- INCREASE MOLECULAR WEIGHT
- SOMEHOW INCREASE CRYSTALLINITY

* THERMAL PROPERTIES:

- RESPONSE OF A MATERIAL TO HEAT
  - HEAT CAPACITY (SPECIFIC HEAT)
  - THERMAL EXPANSION
  - THERMAL CONDUCTION

HEAT CAPACITY:

$$\Delta T = \frac{\Delta Q}{C}$$

← QUANT. OF HEAT (J/MOL)

← HEAT CAPACITY ($J/MOL \cdot K$)

TEMP RISE

- MEASURE OF A MATERIALS ABILITY TO ABSORB HEAT

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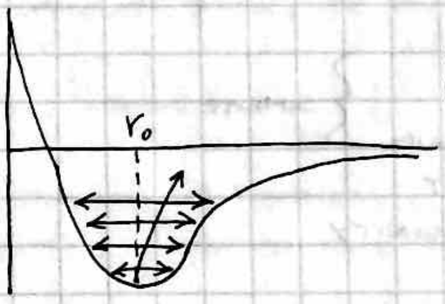
WHERE DOES THE HEAT GO?

→ FREE ELECTRONS (METALS)
→ CRYSTAL LATTICE → PHONONS

THERMAL EXPANSION:

→ ABOVE 0 K, ATOMS VIBRATE ABOUT THEIR LATTICE POSITION

→ AS T ↑, THE VIBRATION AMPLITUDE ↑



✳ CONCEPT. QUESTION:

- THE ENERGY WELL IS NOT SYMMETRIC, SO AS T INCREASES THE ASSYMETRY RESULTS IN AN INCREASE IN EQ. BOND DISTANCE
  = THERMAL EXPANSION

$$\boxed{\frac{\Delta l}{l_0} = \alpha_e \Delta T = \varepsilon}$$

✳ TYPICAL VALUES

$5 - 25 \ \mathrm{PPM}/C^0$ → $5 - 25 \times 10^{-6}/C$ → METALS
$0.5 - 15 \ \mathrm{PPM}/C$ → CERAMICS
$50 - 400 \ \mathrm{PPM}/^0C$ → POLYMERS

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* THERMAL CONDUCTIVITY :

AT STEADY STATE :

$$q = -K \frac{dT}{dx}$$

→ IN METALS, THERMAL ENERGY IS CARRIED BY BOTH ELECTRONS AND PHONONS

→ IN CERAMICS, ONLY PHONONS CAN CONTRIBUTE

- LOW K
- $SiO_2 = 6.5$ W/m·K
- $NaCl = 6.5$ W/m·K

→ IN POLYMERS :

- VERY WEAK LATTICE VIBRATIONS OR PHONONS EXIST, SO VERY LOW K
  - → HDPE = 0.5 W/m·K

* DISORDER = BAD FOR Q
ORDER = GOOD *