

Thermal Properties of Materials

Heat Capacity, Content, Energy Storage – 6.1, .2, .4, .6

Theory of the equipartition of energy – “... at temperatures high enough that translational, vibrational and rotational degrees of freedom are fully excited, each type of energy contributes $\frac{1}{2}kT$ to the internal energy, U .”

Table 6.1

	degrees of <u>freedom</u>	<u>U</u>	<u>$C_v(\partial U/\partial T)_v$</u>	<u>$C_{v,m}$</u>
Translational	n (3)	$n \times \frac{1}{2} kT$	$n \times \frac{1}{2} k$	$n \times \frac{1}{2} R$
Rotational	n	$n \times \frac{1}{2} kT$	$n \times \frac{1}{2} k$	$n \times \frac{1}{2} R$
Vibrational	n	$n \times kT$	$n \times k$	$n \times R$

k = Boltzmann's constant = 1.38×10^{-23} J/K

T = Temperature in Kelvin

R = gas constant = 8.314 J/mol·K

The higher the heat capacity, the greater the heat storage capability. (p. 96)

Thermal Properties of Materials

Degrees of Freedom, Heat Capacity

An N-atom polyatomic molecule has $3N$ degrees of freedom. These are divided into translational, rotational and vibrational components.

	<u>Linear</u>	<u>Nonlinear</u>
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$

$$\text{H}_2\text{O } 3N = 9$$

	<u>dof</u>	<u>$C_{v,m}$</u>
Translational =	3	$3/2R$
Rotational =	3	$3/2R$
Vibrational =	3	<u>$3R$</u>
		$C_{v,m} = 6R$

$$C_{v,m} (\text{exp}) = 3.038R$$

Why?

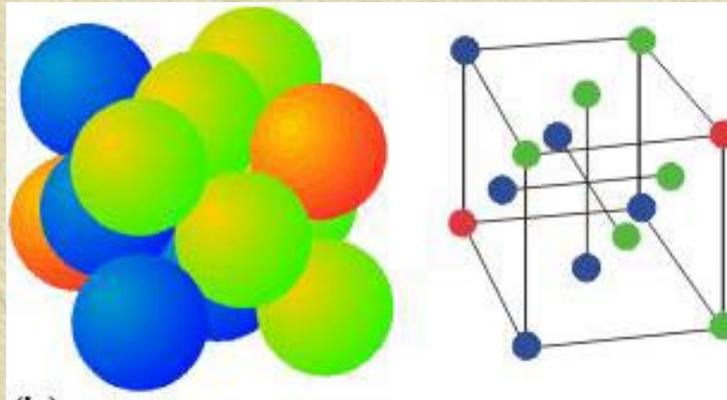
Translation and rotational energies are most easily excited ($3R$), while vibrations of gaseous water molecules at room temperature are only slightly active ($0.038R$).

Thermal Properties of Materials

Heat Capacities of Solids

1819, Dulong and Petit found for nonmetallic solids at room temperature, $C_{v,m} \sim 3R = 25 \text{ J/K}\cdot\text{mol}$. (Dulong-Petit Law)

Each atom in a solid has 3 degrees of freedom, and these are vibrational (simple monoatomic solids). $U = 3kT$; $C_{v,m} = 3R$



Not explained is why (experimentally) $C_{v,m} \rightarrow 0$ as $T \rightarrow 0\text{K}$?

Thermal Properties of Materials

Heat Capacities of Solids

Einstein model of the heat capacity of a solid – The thermal depopulation of vibrational energy levels is used to explain why $C_{v,m} \rightarrow 0$ as $T \rightarrow 0K$.
(but predicts values too low at low temperatures)

Debye model of the heat capacity of a solid – Considers the atoms in a solid to be vibrating with a distribution of frequencies, up to ν_D .

$\theta_D = h\nu_D / k$ - approximates strength of interatomic interactions
- materials with higher θ_D are harder to deform

	<u>θ_D (K)</u>
Diamond	2230
Gold	225
Neon	75
Mercury (solid)	72

Thermal Properties of Materials

Heat Capacities of Metals

For metals, there is the additional contribution of 'free' conducting electrons (above E_f).

If each atom had one free valence electron, the total internal energy would be: $U = 3 kT + 3/2 kT = 4.5 kT$ and $C_{v,m} = 4.5R$

(The first term is from vibrations alone, the second term is the translation of the free electron)

The experimentally observed molar heat capacity of a monoatomic metal is slightly over $3R$.

Only a small fraction of the valence electrons must be free to translate. (one of the first supporting facts for Fermi statistics)

In-Class Problem Set

Ch. 6, #11) A new product claims to protect seedlings from freezing by surrounding them with vertical cylinders of water. a) How does this device work? (explain in thermodynamic terms), b) Would this device be as effective filled with another liquid, like oil? Explain.

Ch. 6, #22) The sound velocity varies considerably with depth in the earth's crust, 8km/s in the upper mantle, and 12km/s in the lower mantle. a) How does θ_D vary with depth? b) What does the variation of the sound velocity indicate about the interactions within the crustal materials as a function of depth? c) Suggest an application of the variation of sound velocity with depth in the earth's crust.

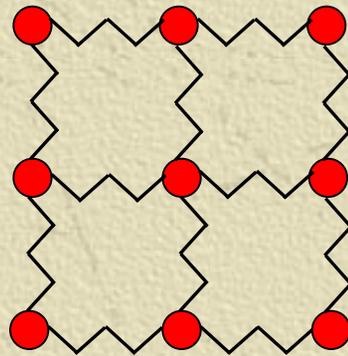
For next time: Read Ch. 7 (pp. 128-140)

Thermal Properties of Materials

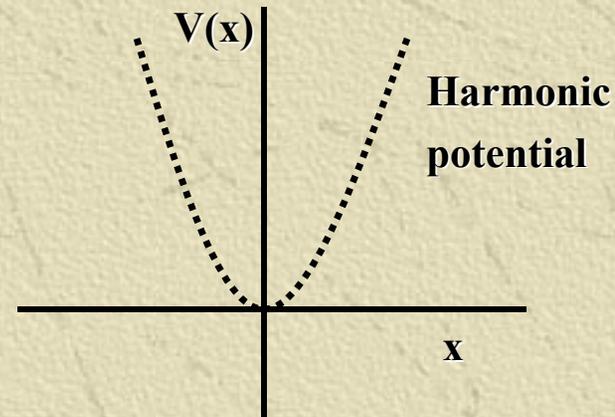
Thermal Expansion of Solids – 7.1, .3 (133-140)

“Almost all materials expand when heated, regardless of the phase of matter”

→ Related directly to the forces between atoms



To a 1st approximation, atoms in a solid can be considered connected to each other by ‘springs’



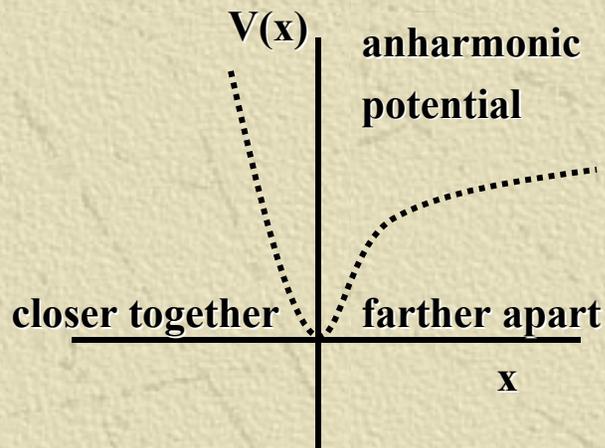
$$V(x) = cx^2; c = \text{spring stiffness,} \\ x = \text{displaced distance}$$

*The average value of x is independent of temperature

Thermal Properties of Materials

Thermal Expansion of Solids

An anharmonic potential more closely approximates the interatomic forces between atoms. → Atoms will separate when pushed far enough apart
→ Repulsion of inner electron clouds inhibits close contact



*The average value of x is dependent on temperature

$$V(x) = cx^2 - gx^3 - fx^4;$$

1st term – harmonic potential (stiffness)
2nd term – asymmetric mutual repulsion
3rd term – softening vibrations at large amplitudes

$$\langle x \rangle = 3gkT / 4c^2$$

The dimensions of a material will increase by a factor that is linear in temperature.

Thermal Properties of Materials

Thermal Expansion of Solids

$$\langle x \rangle = 3gkT / 4c^2$$

Equation for thermal expansion for
a specific direction of the solid:

$$da / a = (\alpha) dT$$

Values for the thermal expansion of
selected materials:

	<u>T(K)</u>	<u>alpha (K⁻¹)</u>
Al	50	3.8 x 10 ⁻⁶
Al	300	2.32 x 10 ⁻⁵
Diamond	50	4.0 x 10 ⁻⁹
Diamond	300	1.0 x 10 ⁻⁶
Cu	50	3.8 x 10 ⁻⁶
Cu	300	1.68 x 10 ⁻⁵
Ice	100	1.27 x 10 ⁻⁵
Ice	200	3.76 x 10 ⁻⁵

Why does alpha increase at higher
temperatures?

Why is the value for diamond so
small, and dramatically increase
at higher temperatures?

Thermal Properties of Materials

Negative Thermal Expansion of Solids

What would lead a solid to contract while it is being heated? (it must outweigh the normally tendency of bond lengthening)

Negative thermal expansion materials †

—— *J. Chem. Soc., Dalton Trans.*, 1999, 3317–3326 ——

John S. O. Evans

Solid-state transitions – the average of a short and long bond is always larger than one that is intermediate between the two. (e.g. Ti-O bonds in PbTiO_3)

Figure 2

Thermal Properties of Materials

Negative Thermal Expansion of Solids

What would lead a solid to contract while it is being heated? (it must outweigh the normally tendency of bond lengthening)

Figure 3

Transverse vibrational modes:
The M-O distance stays the same, but the M-M distance shortens.

These vibrational modes in a solid are low in energy, and preferentially excited.

Many solids exhibit NTE at very low temperature ($<1/20$ Debye Temp.), such as RbCl, H₂O(ice), Si, Ga, etc.

Thermal Properties of Materials

Negative Thermal Expansion of Solids

What would lead a solid to contract while it is being heated? (it must outweigh the normally tendency of bond lengthening)

Rigid unit modes (RUMs), or rocking modes, also reduces the volume of the material.

Figure 6

The M-O-M bending potentials are as much as 100 times weaker than the stiffness of the individual polyhedra.

Example solids: Quartz (SiO_2) and Perovskite structures (ABO_3)

Thermal Properties of Materials

Negative Thermal Expansion of Solids

What uses are possible for NTE materials?

High precision optical mirrors (a zero expansion substrate keeps optical properties from degrading as a function of temperature)

Fibre optic systems, where NTE can be used to compensate for changes in the dimensions of the glass fiber.

Adjusting the thermal expansion properties of printed circuit boards and heat sinks in the electronics industry to match those of silicon.

To have dental fillings match the thermal expansion coefficients of teeth.

Next Time: Thermal Conductivity of Materials (pp. 144-154)

Thermal Properties of Materials

Thermal Conductivity – Ch. 8, 144-154

$J_{(\text{energy})}$ = The rate of heat transfer per unit time (W) per unit area (m^2)

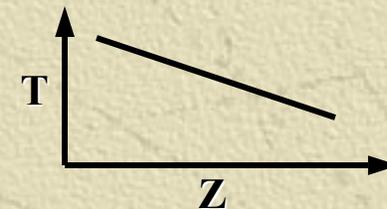
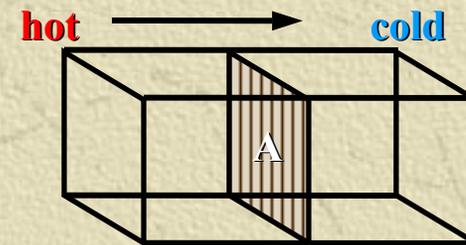
Thermal conductivity is a *transport property*
- effusion, diffusion, electrical conductivity...

$$\text{Flux, } J(i) = \frac{(\text{Amount } i \text{ flowing})}{(\text{unit time}) (\text{unit area})} = \frac{J}{\text{m}^2\text{s}} = \frac{W}{\text{m}^2}$$

$$J_z(\text{energy}) = -(\text{kappa}) (dT / dZ) \quad (= W / \text{m}^2)$$

since $dT/dZ < 0$; $J_z(\text{energy}) > 0$

→ The higher the kappa the better the heat conduction



Which would be the better thermal conductor, La or S ?

Thermal Properties of Materials

Re-expression of J_z and κ in terms of materials' parameters

Lattice vibrations, also known as *phonons*, transport heat in solids.

→ Phonons are a quantum of crystal wave energy, traveling at the speed of sound in the medium and manifested by thermal energy. The more heat, the greater the number of phonons (more excited lattice waves).

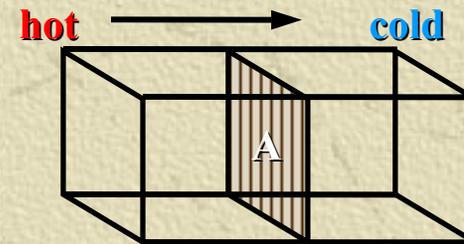
$$J_z \text{ (energy)} = -1/3 \nu(\lambda)C (dT/dZ) \quad (8.14)$$

$$\kappa = -1/3 \nu(\lambda)C \quad (8.15)$$

C = heat capacity per unit volume

λ = mean free path of phonons

ν = average speed of phonons



In materials, what would tend to give the highest values for κ ?

C (3R limit or better)

ν (proportional to force constant, or θ_D)

λ (crystalline materials)

Thermal Properties of Materials

What causes thermal resistance?

Phonon-phonon collisions (and anharmonicity)

What is the dependence of thermal resistance with temperature?

$$\kappa = -1/3 \nu(\lambda)C \quad (8.15)$$

At high temperatures ($T > \theta_D$)

$C \sim$ constant

ν is independent of temperature

λ decreases with T

Kappa decreases with increasing temperature

At lower temperatures ($T < \theta_D$)

C increases with T

ν is independent of temperature

$\lambda \sim$ constant (maximum reached)

Kappa increases with increasing temperatures

Thermal Properties of Materials

Thermal Conductivity of Metals

In metals, there are two mechanisms to carry heat:

- 1) Phonons,
- 2) Electrons

$$\kappa = \kappa_{\text{phonon}} + \kappa_{\text{electron}}$$

$$\kappa_{\text{elec}} = \frac{1}{3} v_{\text{elec}} (\lambda)_{\text{elec}} C_{\text{elec}} \quad (8.21)$$

The thermal conductivity of a metal is 10-100x that for a nonmetal.
Most of the heat is carried by conducting electrons, not phonons.

What are applications for thermally conductive or nonconductive materials?

In-Class Problem Set

Make a plot of how the thermal conductivity vs. temperature will change for a pure semiconductor. How will this plot compare to that for a metal (show on the same figure)?

Discuss your assumptions of the changes in *heat capacity*, *mean free path*, *average speed* and *type and number* of the heat carriers as a function of temperature.

Ch. 8, #8) Two countertop materials look very similar; one is natural marble and the other is synthetic polymer. They can be easily distinguished by their feel: one is cold to the touch and the other is not. Explain which is which and the basis in the difference of their thermal conductivities.

Next time: Research article on thermoelectric materials

Thermal Properties of Materials

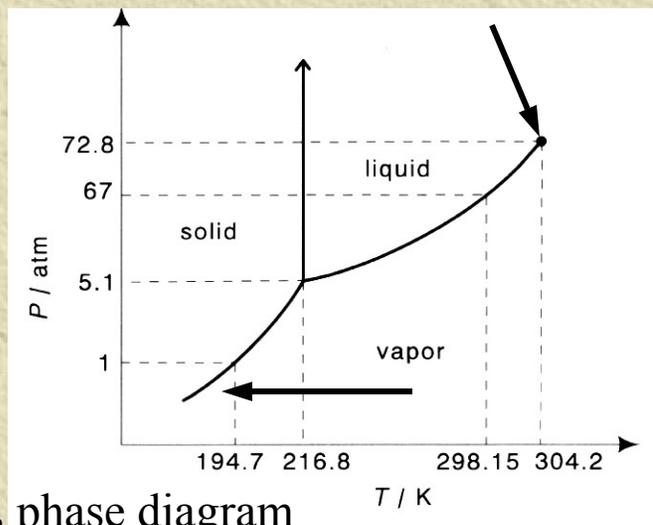
Thermal Stability of Materials (9.1, 9.3-9.5, 9.8-9.10)

Phase Diagrams – P-T plots provides useful information about the properties, structures and stability of materials; show the ranges of temperature, pressure and composition over which phases are thermodynamically stable.

Clapeyron Equation $dP / dT = \Delta_{\text{trs}} H / T \Delta_{\text{trs}} V$

Solid to vapor transitions: $\Delta_{\text{trs}} H > 0$;
 $\Delta_{\text{trs}} V > 0$; so slope of solid/vapor
equilibrium line (dP / dT) is > 0 .

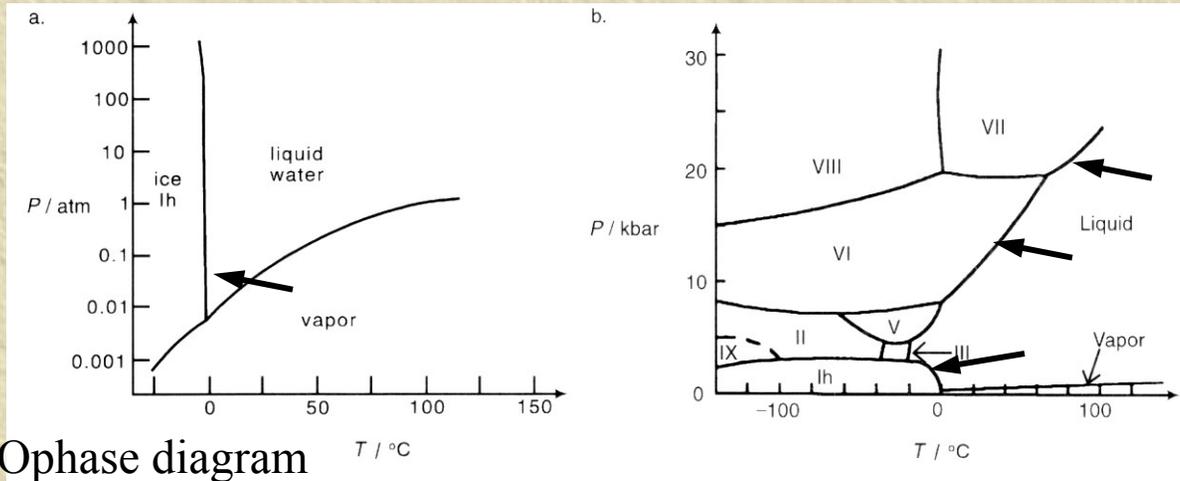
Solid to liquid transitions: $\Delta_{\text{trs}} H > 0$;
 $\Delta_{\text{trs}} V$ usually > 0 ; so slope of solid-
liquid line (dP / dT) is usually > 0 .



CO₂ phase diagram

However, if $\Delta_{\text{trs}} V < 0$ (H₂O, Ga, Sb, Bi, etc); then slope (dP / dT) is < 0 .

Thermal Properties of Materials



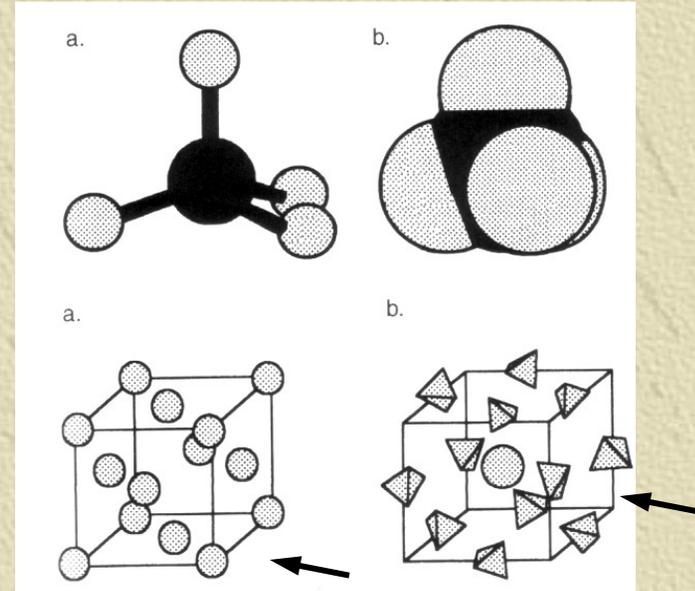
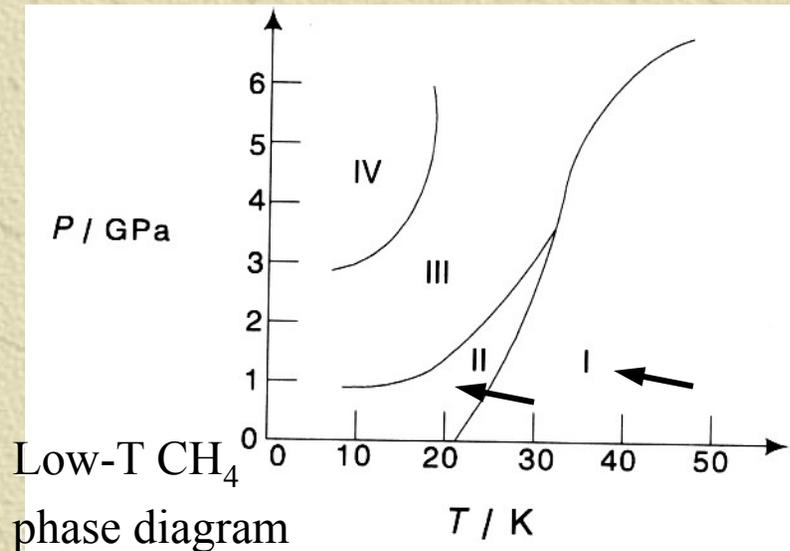
H₂O phase diagram

At low P, negative P-T solid-liquid line is negative; the solid is less dense than the liquid; decrease in freezing point with P

The hexagonal form of ice (Ih) has an open structure; structure is not close packed because of hydrogen bonding optimization.

Ice(s) has many *polymorphs* at high pressures owing to many ways to form hydrogen bonds to neighbors; more compressed.

Thermal Properties of Materials



Four solid phases, *polymorphism* arising from shape of molecule; nearly spherical shape with protuberances at tetrahedral locations.

Very little energy to rotate molecules – CH₄ molecules in solid I are nearly freely rotating, but located on particular lattice sites; orientationally disordered.

Other examples: H₂, N₂, O₂, F₂, CCl₄, C₆₀, etc.

Thermal Properties of Materials

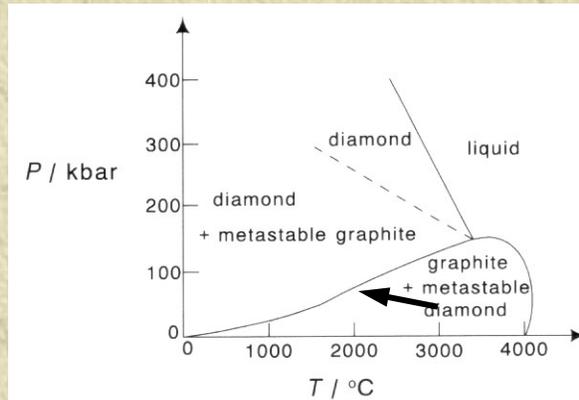
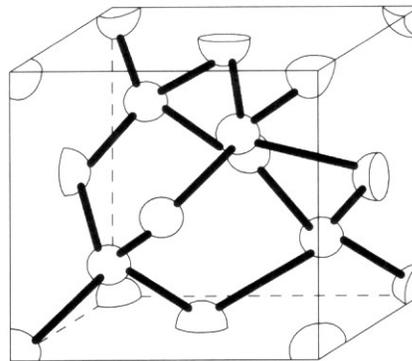


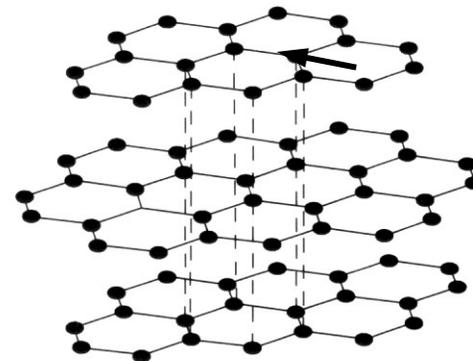
Figure 9.13. The pressure–temperature phase diagram of carbon. Solid lines indicate the regions of stable phases; metastability is indicated with dashed lines.

Carbon phase diagram

a.



b.



Graphite is favored at low pressures, diamond at high pressures. Their interconversion is slow at room T and P – activation energy is high.

Great rearrangement is required; drastically different structures and properties.

Thermal Properties of Materials

Gibbs' Phase Rule – defines relationship between # of free variables specifying state of system, chemical components and phases.

$$F = c - p + n$$

F = # degrees of freedom

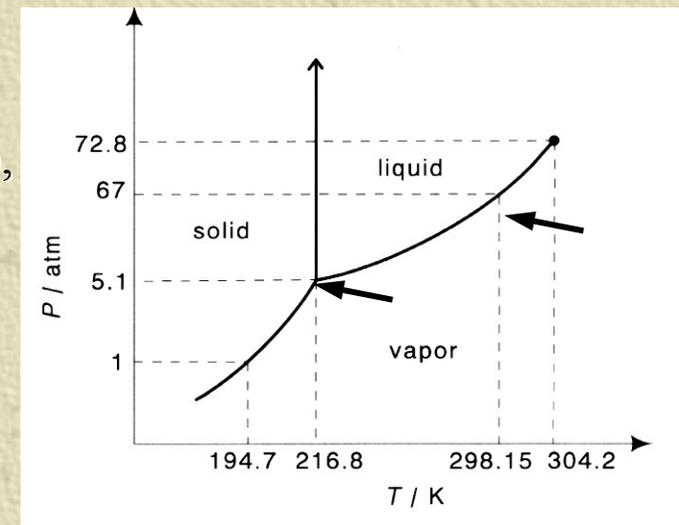
c = # chemical components; # independent chemical species (i.e. CaO-SiO₂, c = 2; MgO, c = 1)

p = # of phases (i.e. solids, liquids, gases)

n = # free variable specifying state of system; n = 2 (T and P) or 1 (T or P)

For example: H₂O (boiling); c = 1, p = 2 (gas, liquid),
F = 1 (T or P). Either only T or P can vary independently (a line).

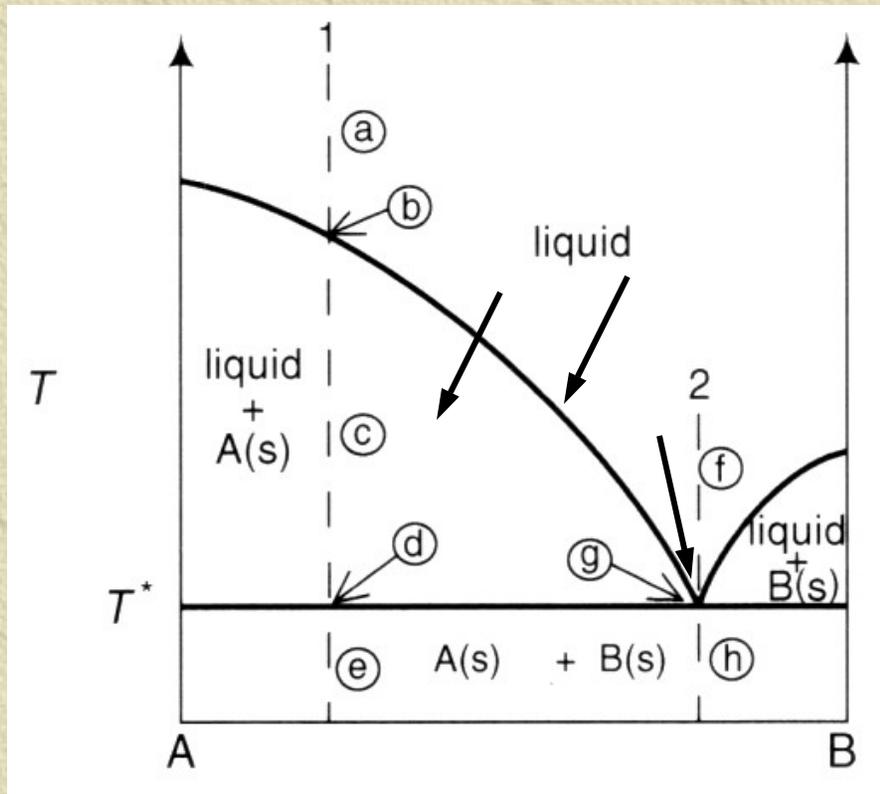
H₂O (triple point); c = 1, p = 3 (gas, liquid, solid),
F = 0. Invariant point, neither T or P can vary.



Thermal Properties of Materials

Two Component System – Binary Phase Diagrams

Condensed Phase Rule – Can assume the vapor pressure is negligible ($n = 1$; only T varies). $F = c - p + 1$; $c = 2$; $P + F = 3$



No intermediate compounds (AB) or solid solutions.

Solidus – two solids coexist; lowest T that liquids exist.

Liquidus – solid/liquid coexists; liquid changes composition

Eutectic – three phases (A, B, liquid) coexist; invariant.

Thermal Properties of Materials

Liquid-Solid Binary Phase Diagrams – Two component system

Lever Principle – Mole ratio of phases (on passing through liquidus) is proportional to tie lines connecting to the liquidus and solid vertical lines.

T1 = all liquid; 75% A, 25%B

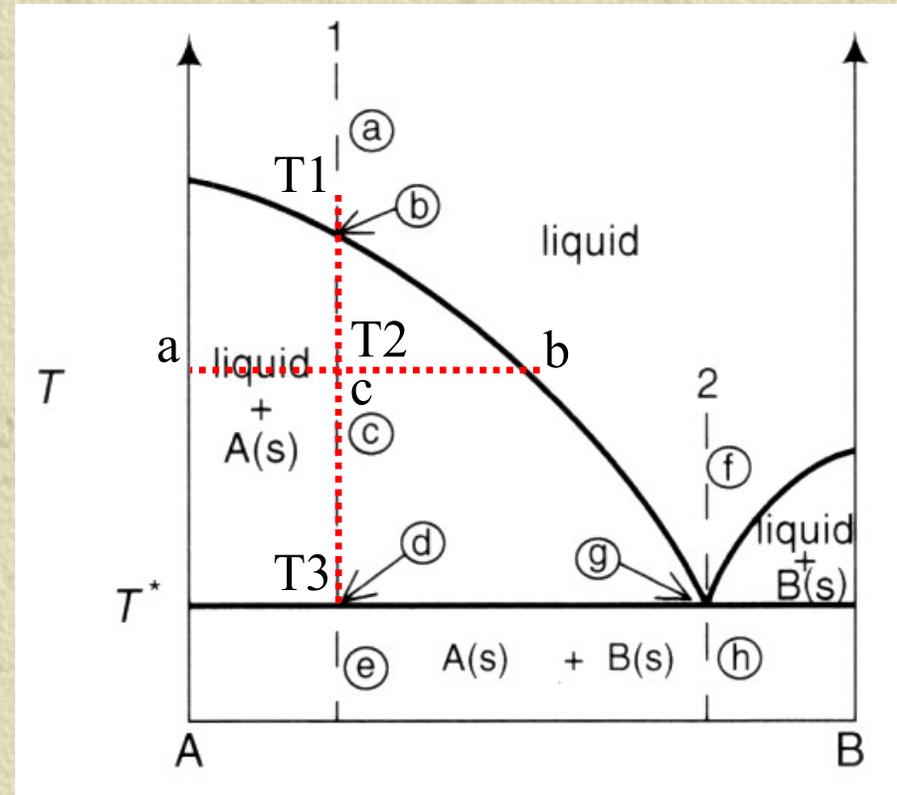
T2 = liquid + A(s)

Liquid composition = point b
(50% A, 50% B)

% liquid = $ac / ab = 25/50 = 50\%$

% solid = $cb / ab = 25/50 = 50\%$

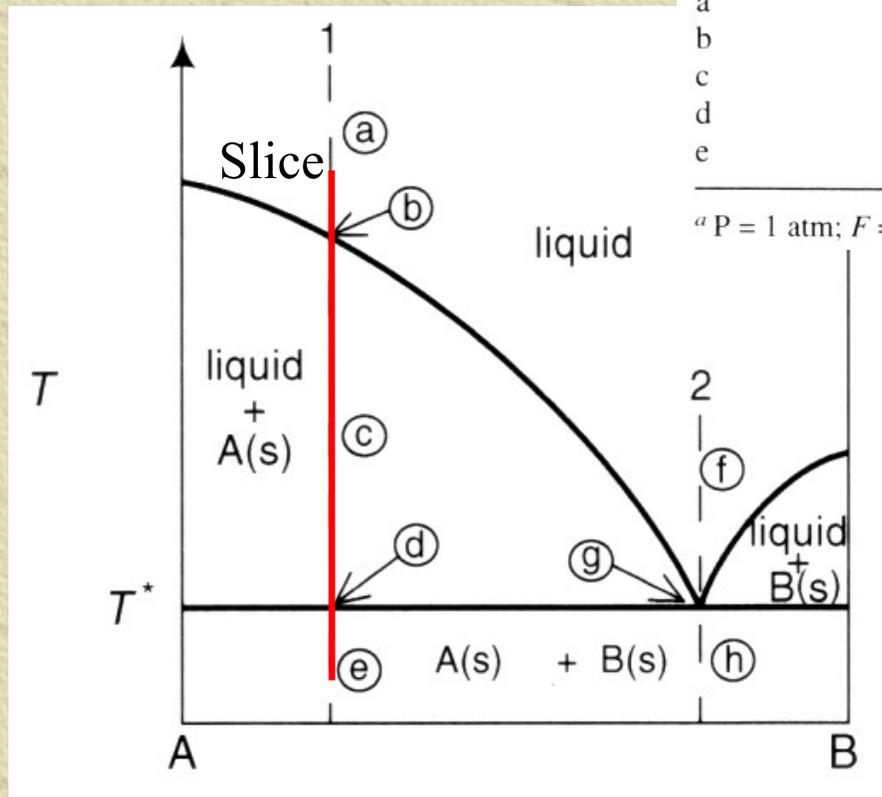
T3 = all solid; 75%A, 25%B



Thermal Properties of Materials

Liquid-Solid Binary Phase Diagrams – Two component system

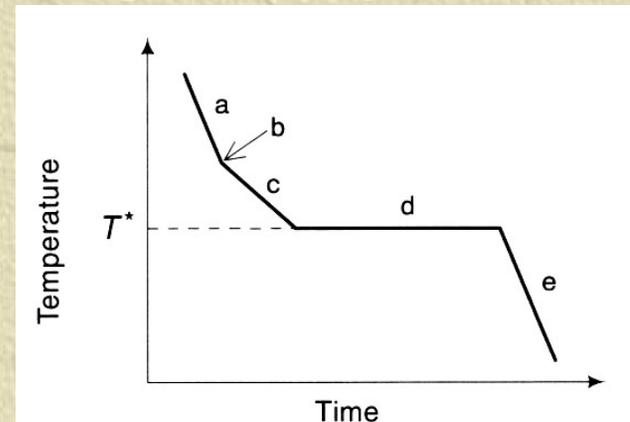
Phase diagrams can be investigated using cooling curves (temperature-time profiles).



Region	Phase(s)	p	F
a	Liquid	1	2
b	Liquid + A(s)	2	1 (break)
c	Liquid + A(s)	2	1
d	Liquid + A(s) + B(s)	3	0 (halt)
e	A(s) + B(s)	2	1

^a $P = 1 \text{ atm}; F = 3 - p.$

break point (b) is a change in slope, or change in F

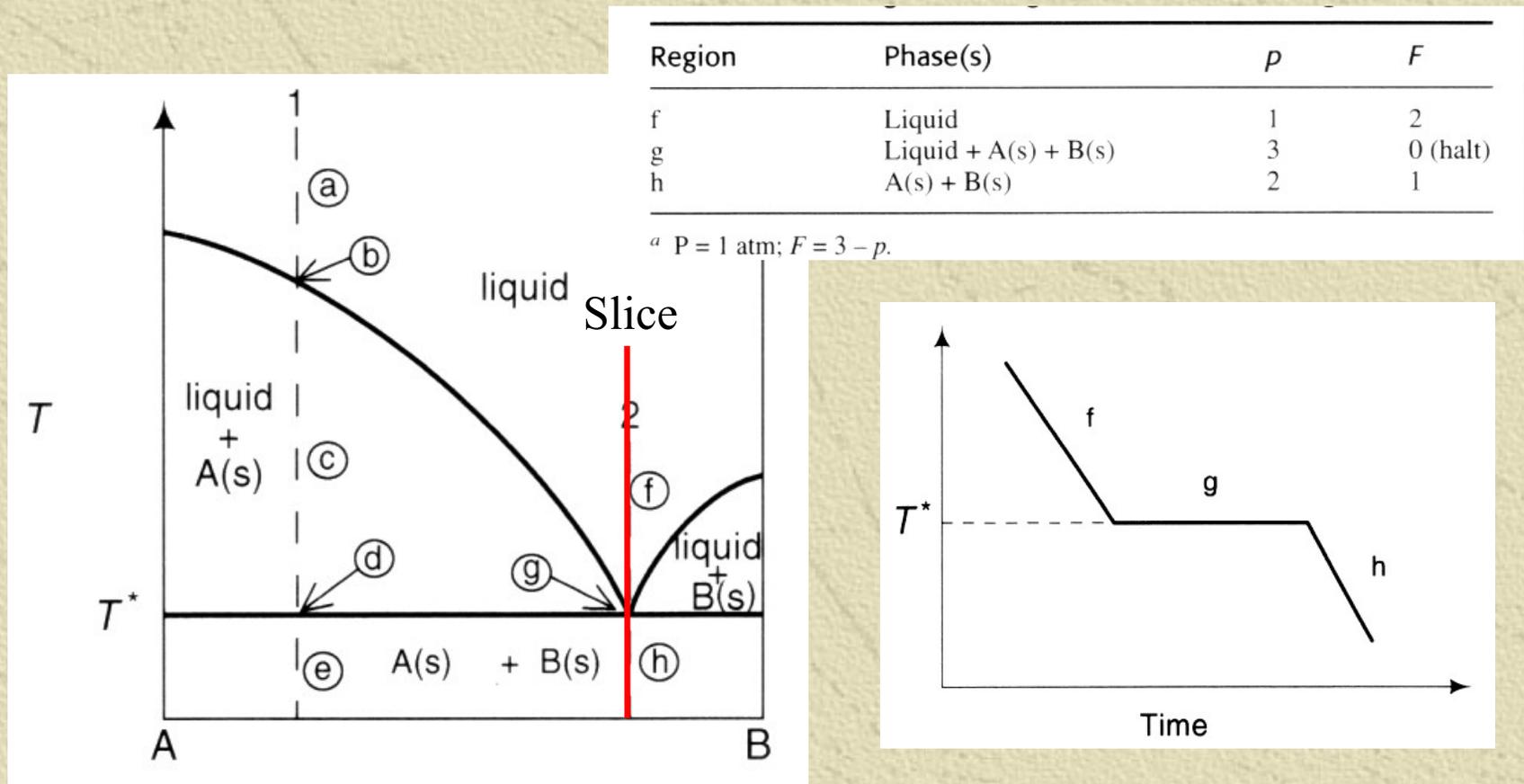


At halt point(d), $F = 0$ and $p = 2$.

Thermal Properties of Materials

Liquid-Solid Binary Phase Diagrams – Two component system

Evaluation of a cooling curve through the eutectic point.



Eutectic composition melts at a single T without change in composition.
(example: Sn/Pb solder, Na/K flux, etc.)

Worked Problem

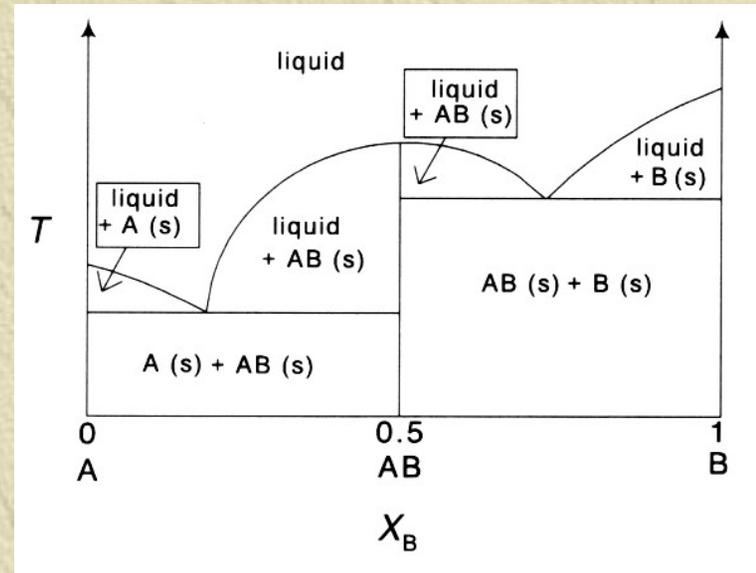
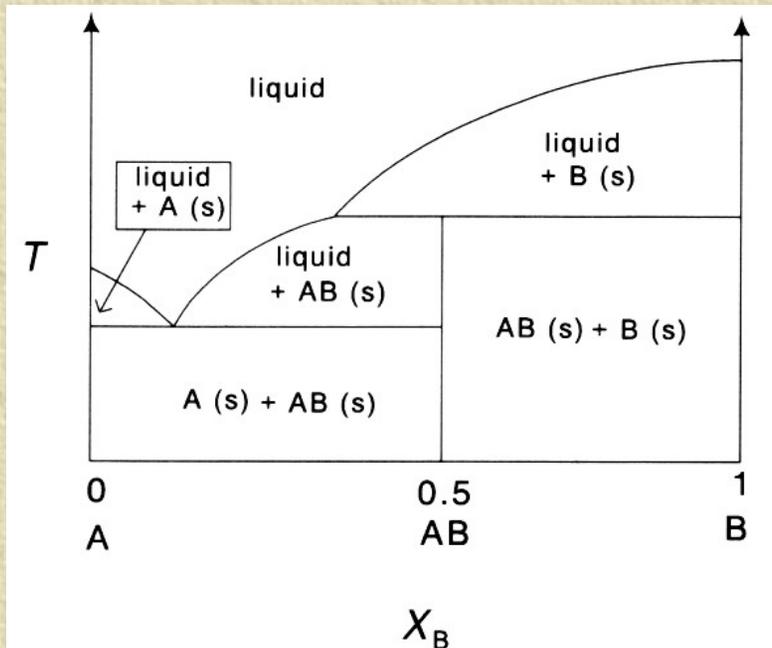
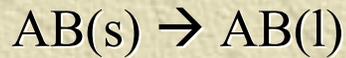
Ch 9, #8) Sketch the Sb-Cd phase diagram (T vs. X_{cd}) based on the following information obtained from a set of cooling curves.

X_{Cd}	Break/(°C)	Halt /(°C)
0	—	630
0.188	550	410
0.356	461	410
0.412	—	410
0.480	419	410
0.600	—	439
0.683	400	295
0.925	—	295
1	—	321

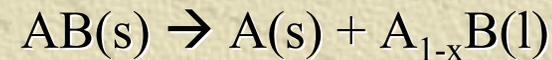
Thermal Properties of Materials

Liquid-Solid Binary Phase Diagrams – Solid Formation

Congruently melting compound:

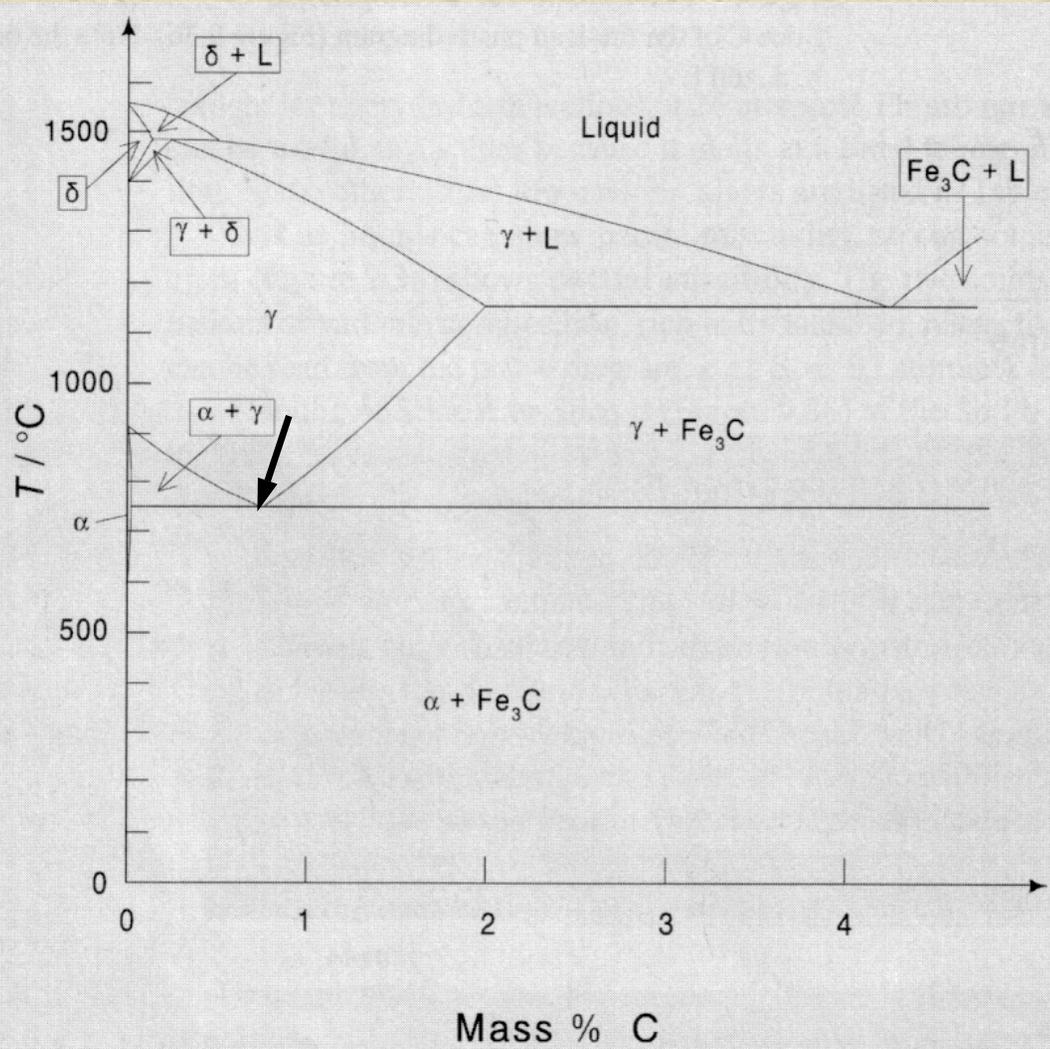


Incongruently melting compound:



Thermal Properties of Materials

The Iron Phase Diagram



Fe exists in three polymorphs (bcc < 910C; fcc 910-1400C; bcc >1400C)

Only bcc (gamma) dissolves appreciable C - *Austenite*

Eutectoid decomposition occurs >723C at grain boundaries to give lamellar textures – *Pearlite*

- if cooled rapidly, *Martensite* forms.

In-Class Problem Set

Ch 9, #6) The following are cooling data obtained for solutions of Mg and Ni. Two solids form in this system, Mg_2Ni and MgNi_2 . Plot and label the phase diagram.

X_{Ni}	0.00	0.044	0.139	0.202	0.383	0.669	0.752	1.00
$T_{\text{break}}/^\circ\text{C}$	—	608	—	—	1050	—	—	—
$T_{\text{arrest}}/^\circ\text{C}$	651	510	510	510 and 770	770	1180	1080	1450

Ch. 9, #28) Label the regions in the Mg/Pb phase diagram. Include labels for the solidus, liquidus, eutectic(s), and congruent or incongruent melting solid.

