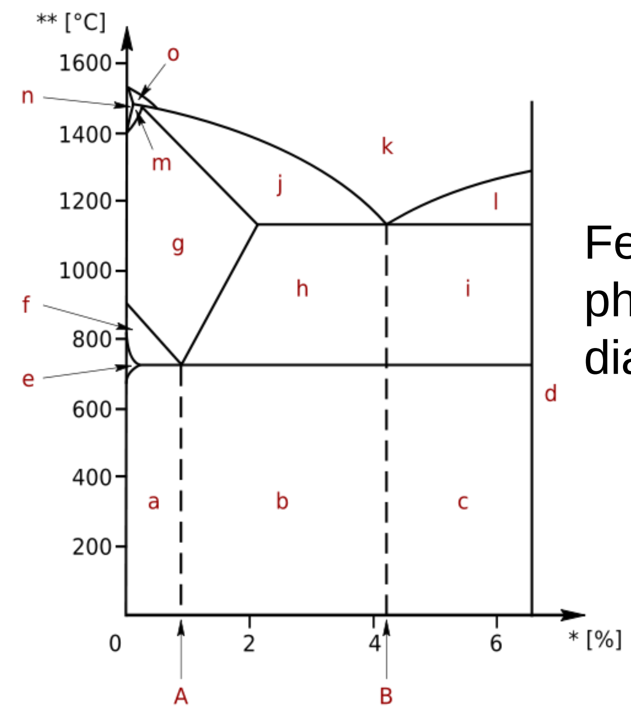
Phase Equilibria

Reading: West 7

PHASE DIAGRAMS

- Also called equilibrium or constitutional diagrams
- Plots of temperature vs. pressure, or T or P vs. composition, showing relative quantities of phases at equilibrium
- Pressure influences phase structure
  - Remains virtually constant in most applications
  - Most solid-state phase diagrams are at 1 atm
- Note: metastable phases do not appear on equilibrium phase diagrams



Fe–Fe_3C phase diagram

PHASES

A phase is a homogeneous portion of a system with uniform physical and chemical characteristics, in principle separable from the rest of the system.

A difference in <u>either</u> physical or chemical properties constitutes a phase

<u>gaseous state</u>

- seemingly only one phase occurs (gases always mix)

<u>liquid state</u>

- often only one phase occurs (homogeneous solutions)
  e.g., salt water, molten Na_2O-SiO_2
- two immiscible liquids (or liquid mixtures) count as two phases

<u>solid state</u>

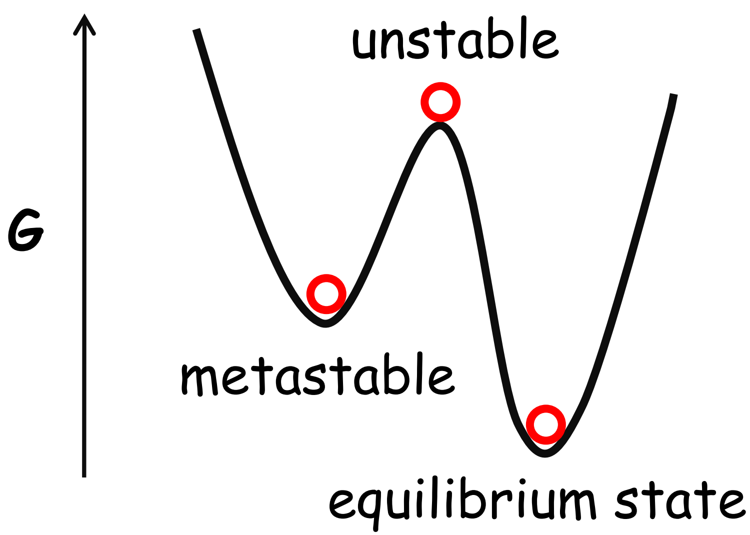
- crystalline phases: e.g., ZnO and SiO_2 = two phases
- polymorphs: e.g., wurtzite and sphalerite ZnS are different phases
- solid solutions = one phase (e.g., Al_2O_3-Cr_2O_3 solutions)

PHASE EQUILIBRIA

The equilibrium phase is always the one with the lowest free energy

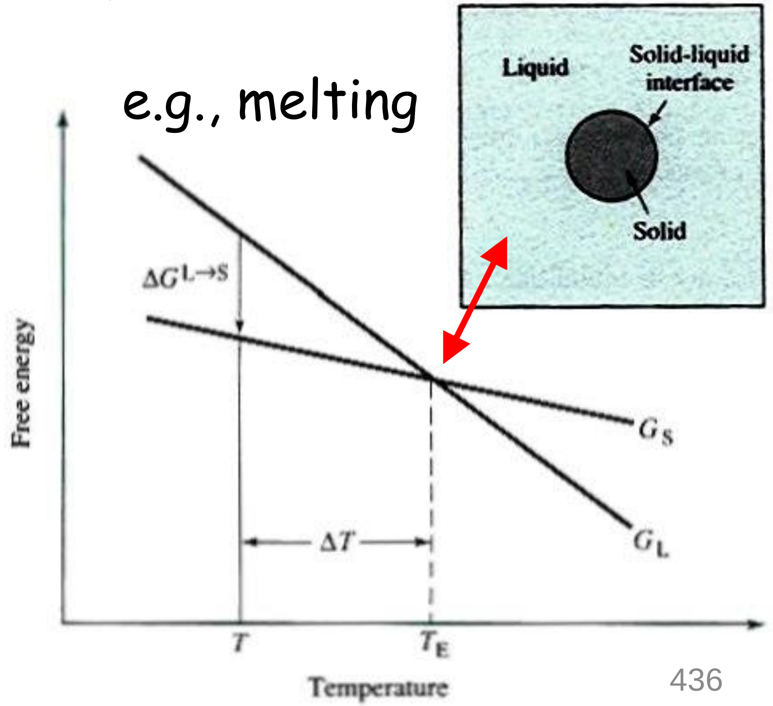
$$\Delta G = \Delta H - T\Delta S$$

Equilibrium → state with minimum free energy under some specified combination of *temperature, pressure, and composition*



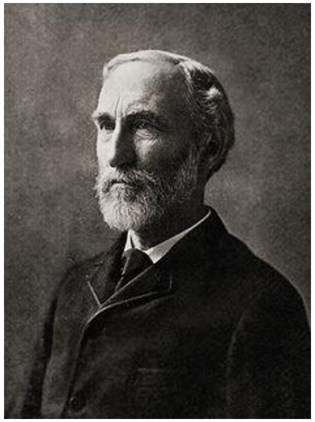
The driving force for a phase change is the minimization of free energy

e.g., melting



GIBBS PHASE RULE

"On the Equilibrium of Heterogeneous Substances" 1874-78



Gibbs

$$\mathbf{P + F = C + 2}$$

$$F = C - P + 2$$

P: number of **p**hases present at equilibrium
C: number of **c**omponents needed to describe the system
F: number of degrees of **f**reedom, e.g. T, P, composition

The *number of components* (C) is the minimum number of chemically independent constituents needed to describe the composition of the phases present in the system.

e.g.,
- salt water. *C* = 2 (NaCl and water)
- solid magnesium silicates. *C* = 2 (MgO and SiO_2)
- solid MgAl silicates. *C* = 3 (MgO, Al_2O_3, SiO_2)

The *degrees of freedom* (F) is the number of independent variables that must be specified to define the system completely.

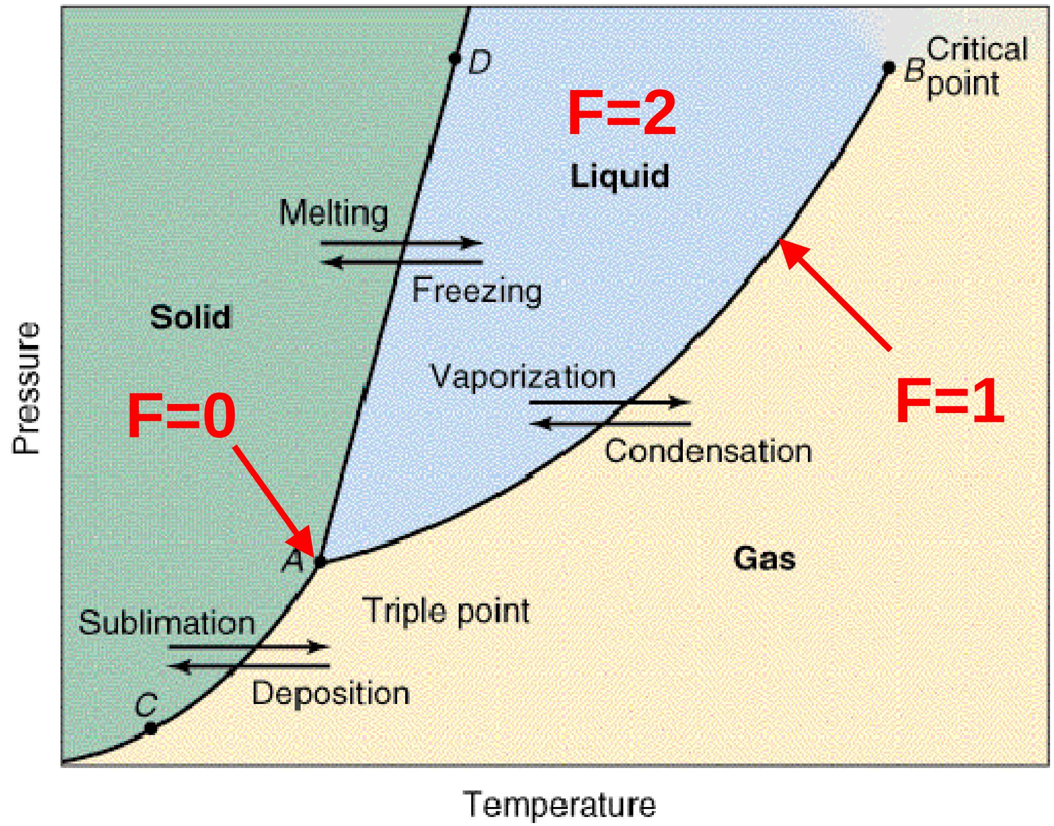
ONE COMPONENT PHASE DIAGRAMS

P + F = C + 2

with C = 1

P + F = 3

Composition is fixed, only T and P can vary



Three possibilities:

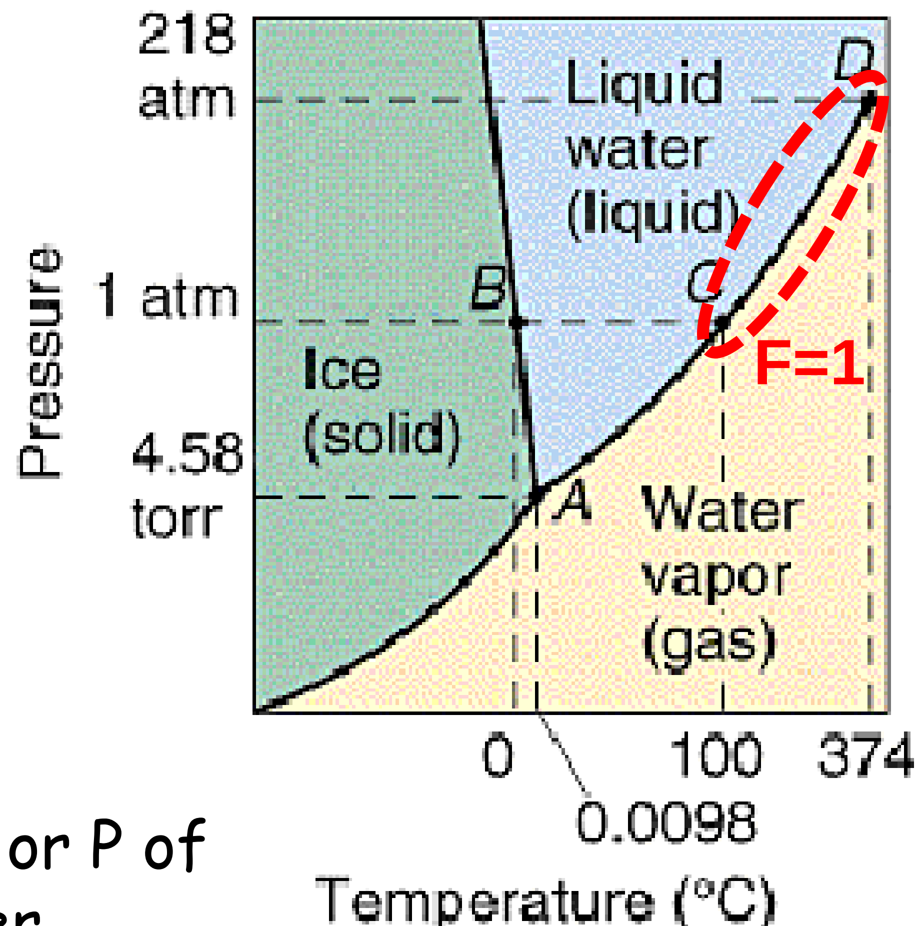
- P = 1 … F = 2 (bivariant phase <u>field</u>)
- P = 2 … F = 1 (univariant phase <u>curve</u>)
- P = 3 … F = 0 (invariant phase <u>point</u>)

EXAMPLE: BOILING WATER

$P + F = C + 2$

$C = 1$ (water)
$P = 2$ (vapor + liquid)

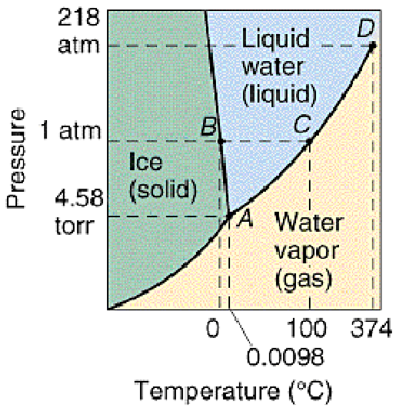
$F = 1$ (either T or P,
but not both)
→ coexistence curve

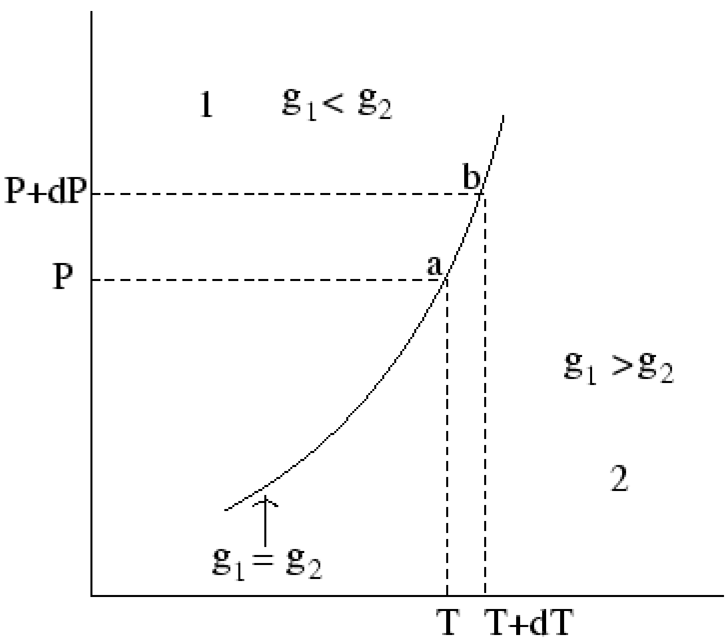


*once we specify either T or P of our boiling water, the other variable is specified automatically

CLAUSIUS-CLAPEYRON EQUATION

Expresses the pressure dependence of phase transitions as a function of temperature (gives slopes of coexistence curves).





From a to b, starting from Gibbs-Duhem equation:

$$d\mu_1 = -s_1 dT + v_1 dP$$

$$d\mu_2 = -s_2 dT + v_2 dP$$

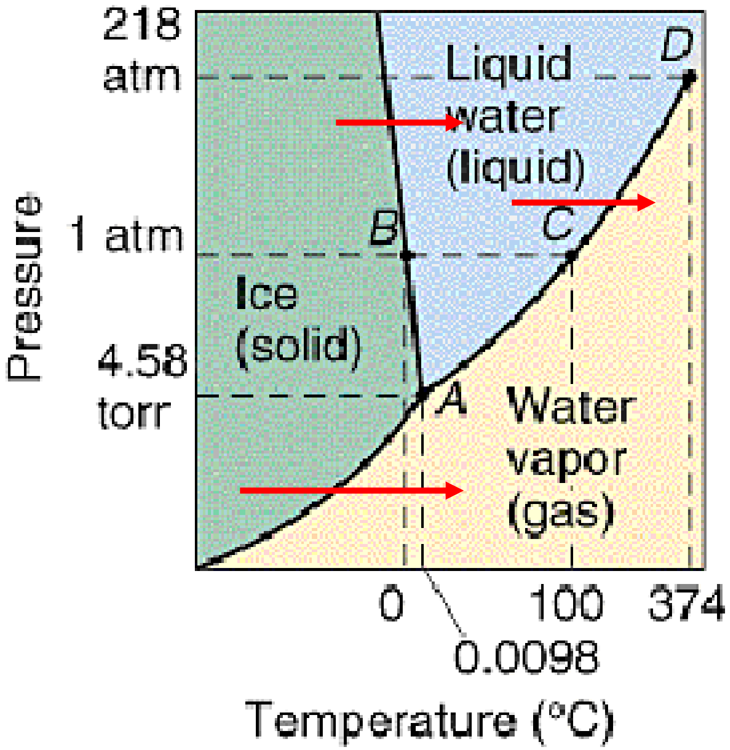
$$d\mu_1 = d\mu_2$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}$$

$$\Delta s = \frac{\Delta h}{T}$$

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

derived ~1834



Slope of the coexistence curves:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

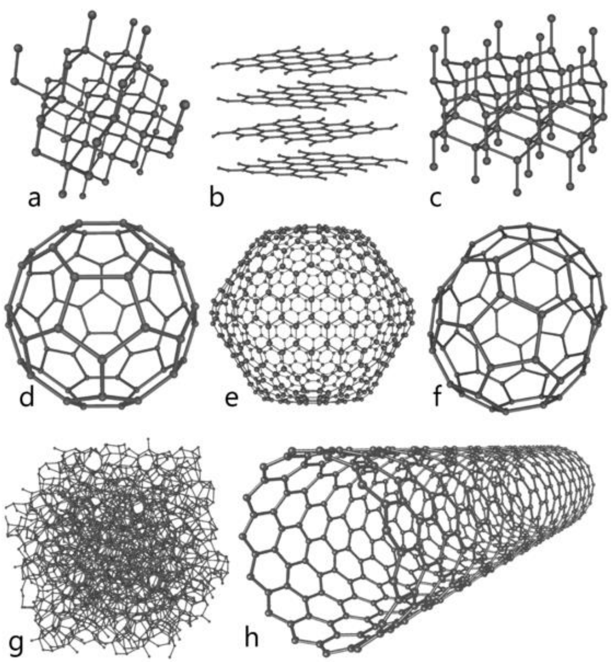
ΔH positive along arrows (melt, sublime, vaporize)

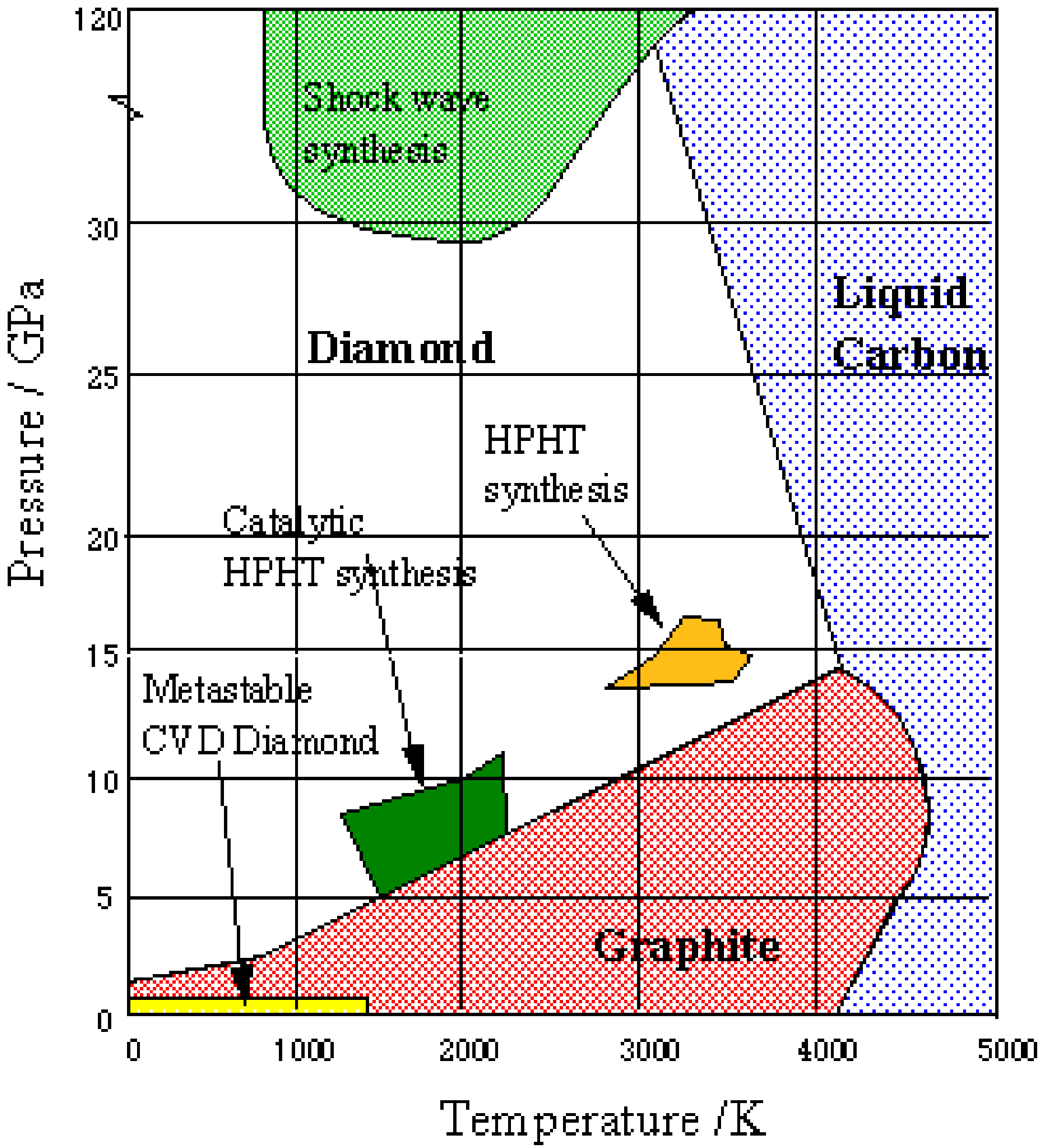
ΔV negative only for melting

*Ice less dense than water

ONE COMPONENT PHASE DIAGRAMS

Carbon



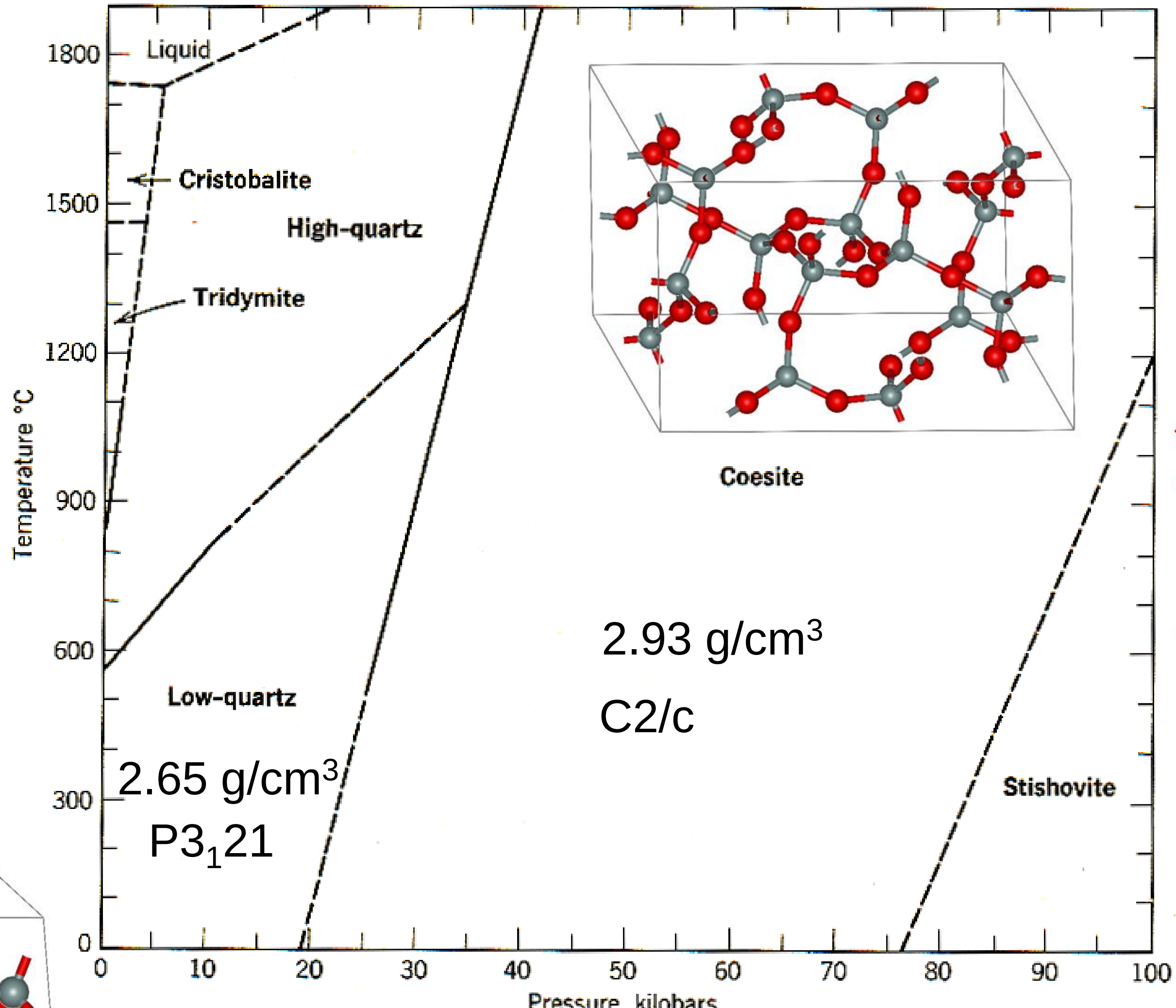


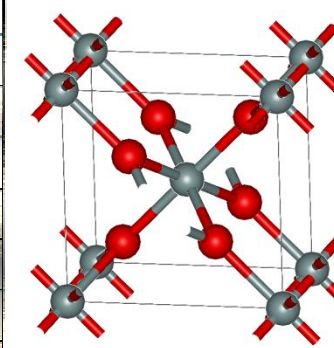
More than 100 tons of synthetic diamonds are produced annually worldwide by firms like Diamond Innovations (previously part of General Electric), Sumitomo Electric, and De Beers.

Gemesis, GE, Sumitomo Electric, and De Beers

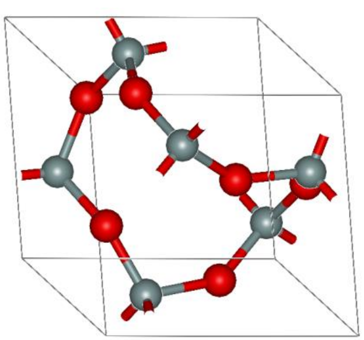
ONE COMPONENT PHASE DIAGRAMS

SiO_2





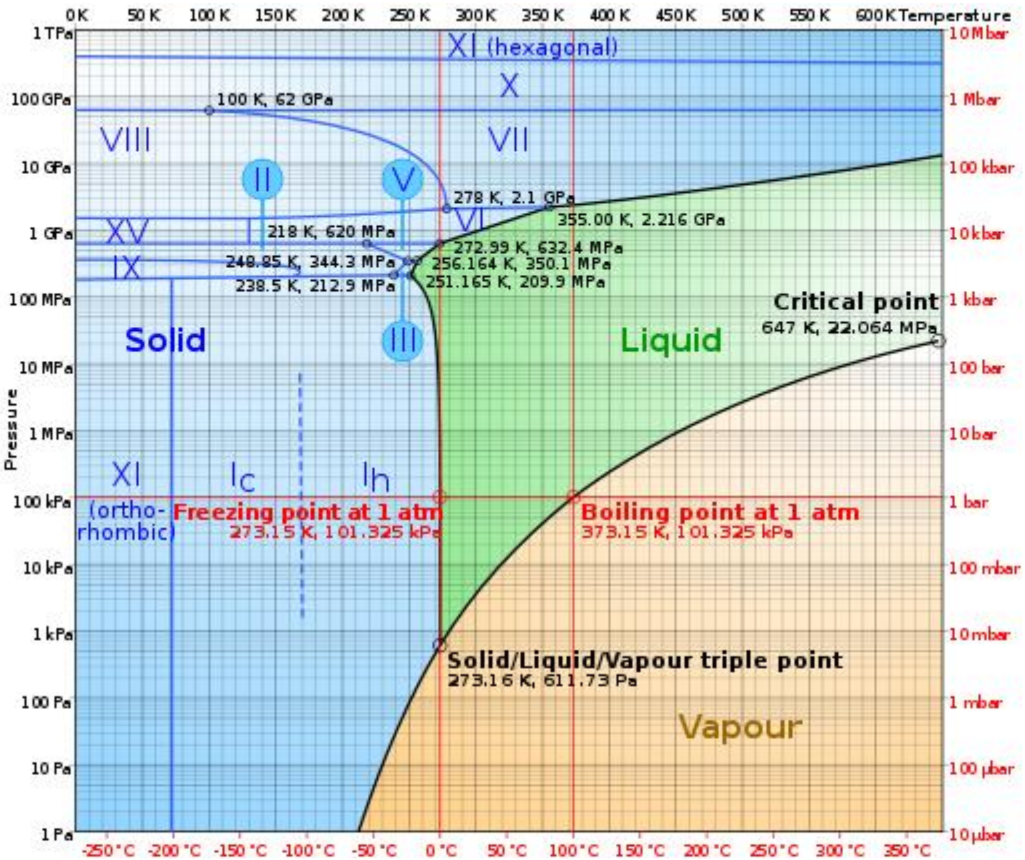
4.287 g/cm^3
$P4_2/mnm$

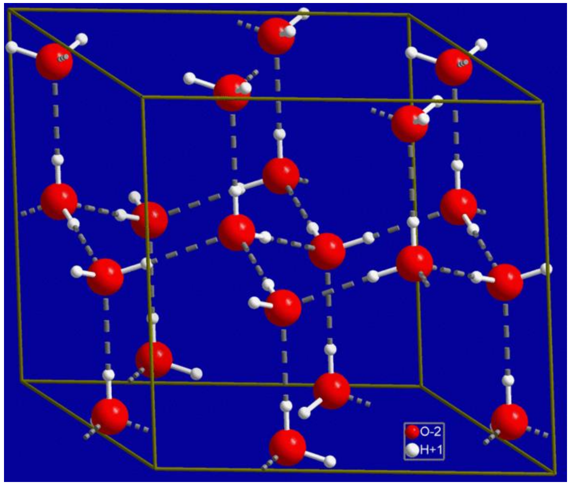


there are also many metastable phases (not shown)

OTHER EXAMPLES

Ice – 18 different crystalline phases!

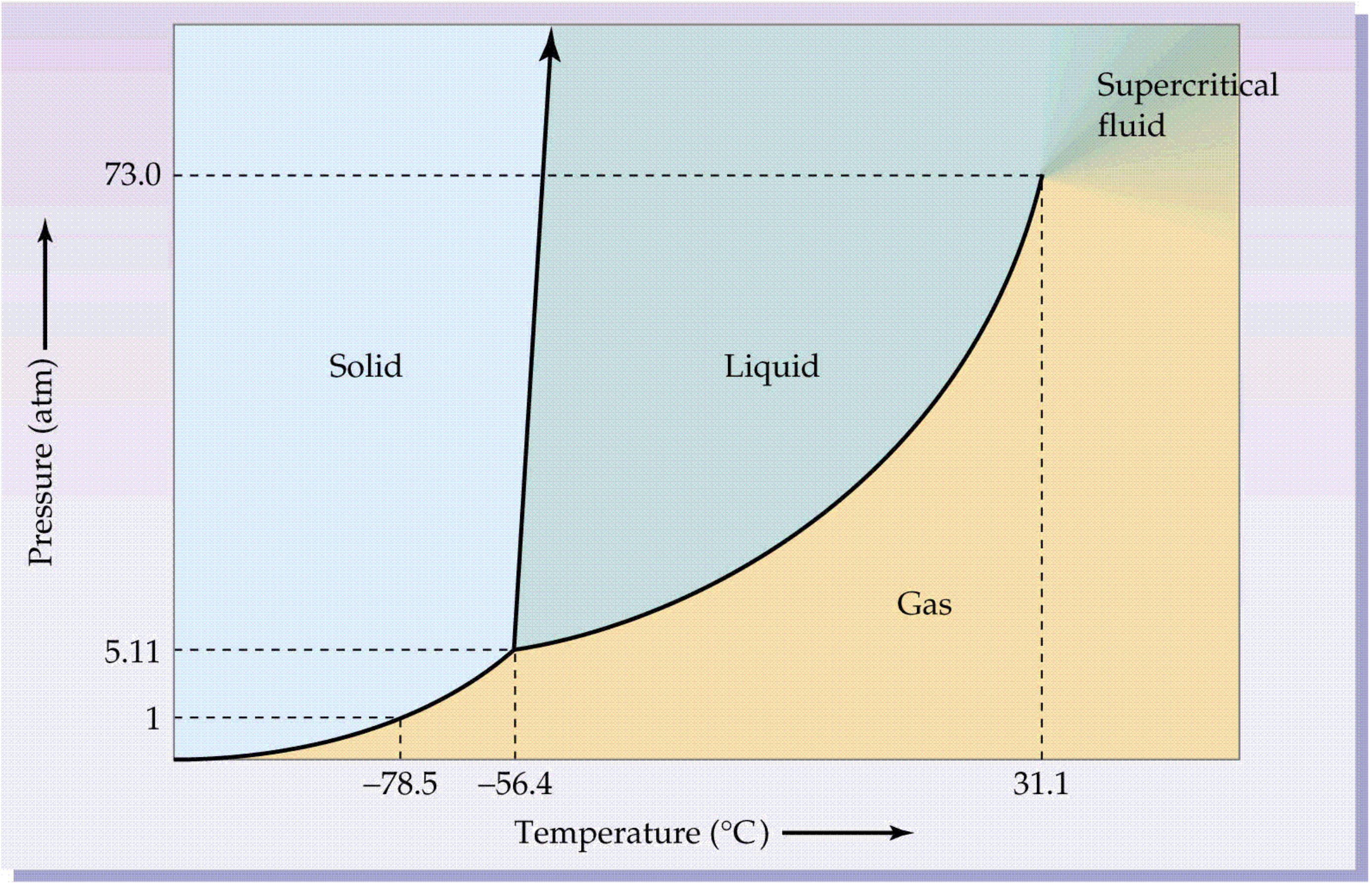




hex ice

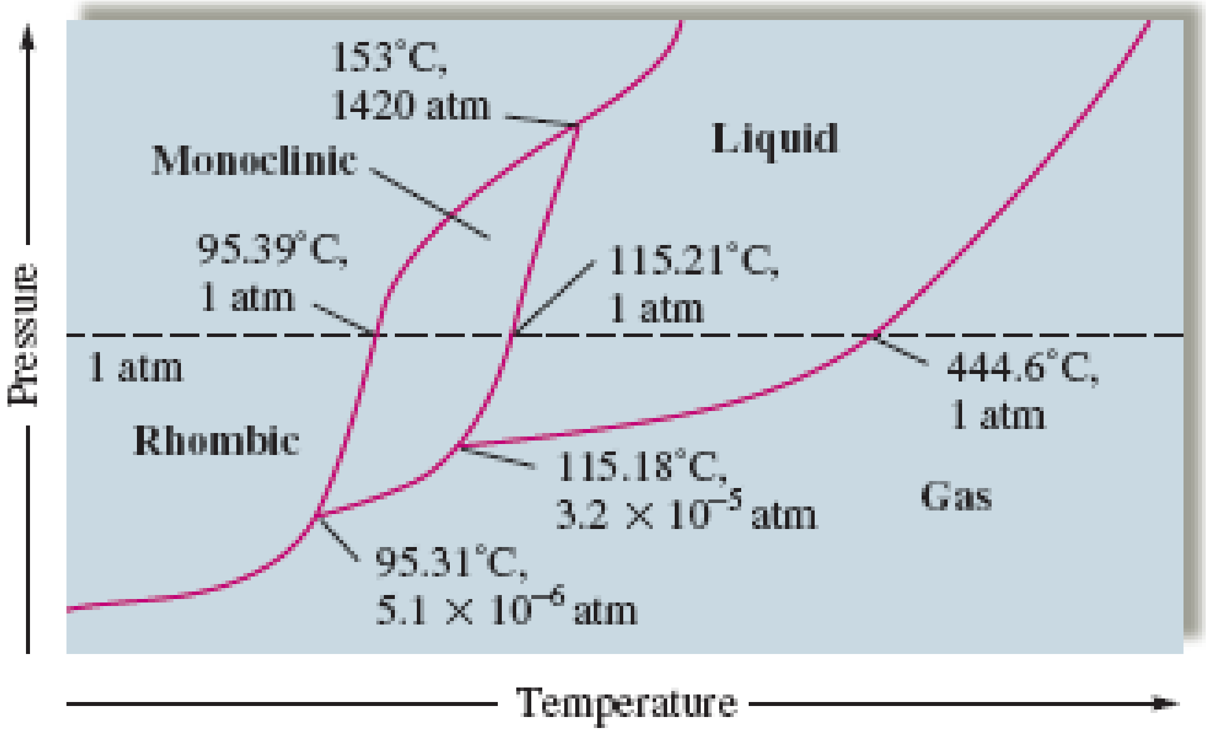
OTHER EXAMPLES

CO_2



OTHER EXAMPLES

Sulfur



TWO COMPONENT (BINARY) DIAGRAMS

$$P + F = C + 2$$

with $C = 2$

Composition is now variable: T, P, and composition can vary

When vapor pressures are negligible and nearly constant:

Condensed phase rule: $P + F = C + 1$

Pressure is no longer a variable: only T and composition matter

$$P + F = 3$$

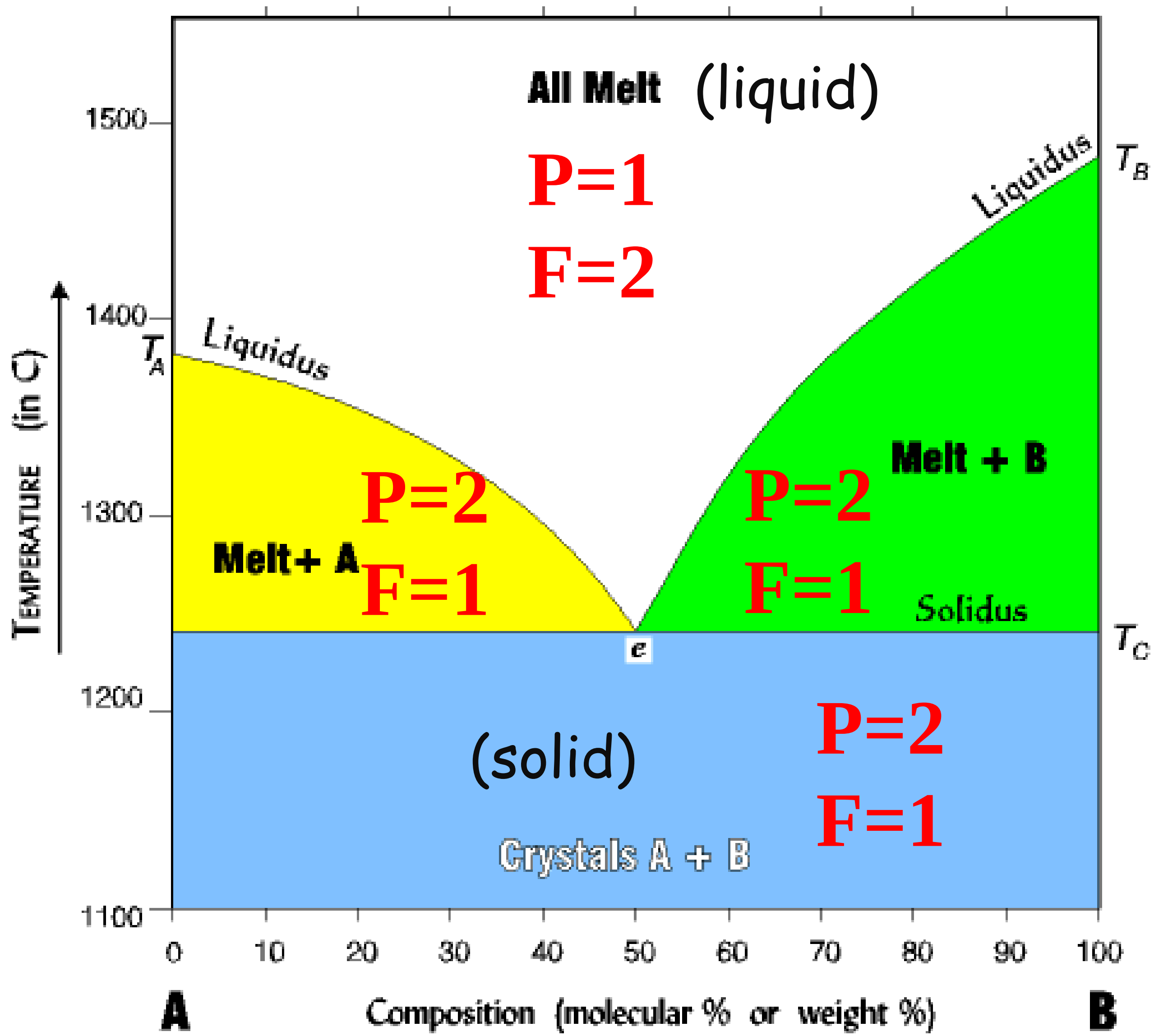
Three possibilities (as before):

- P = 1 … F = 2 (bivariant phase field)
- P = 2 … F = 1 (univariant phase curve)
- P = 3 … F = 0 (invariant phase point)

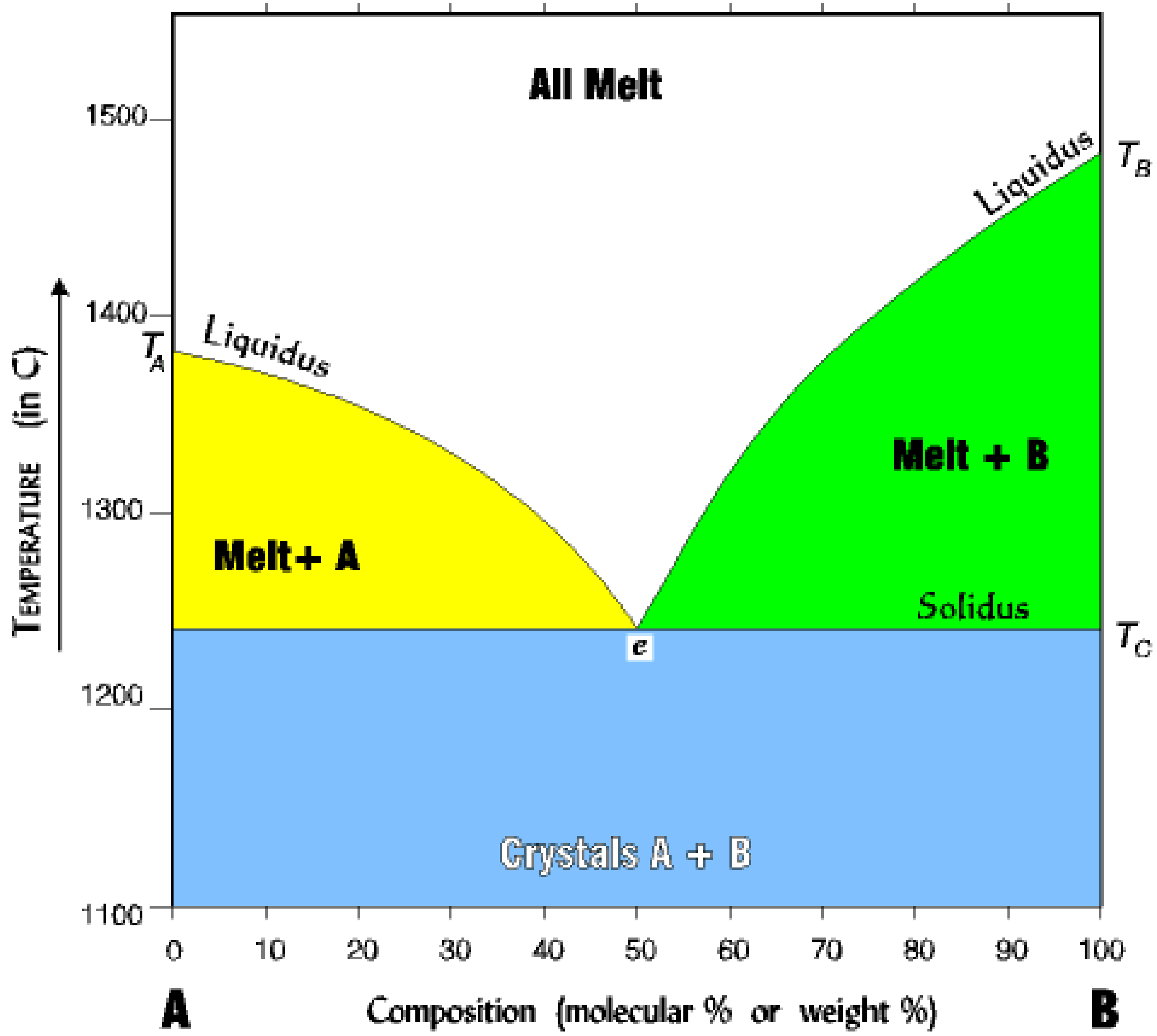
SIMPLE EUTECTIC SYSTEMS

simplest binary diagram for solids

P + F = 3

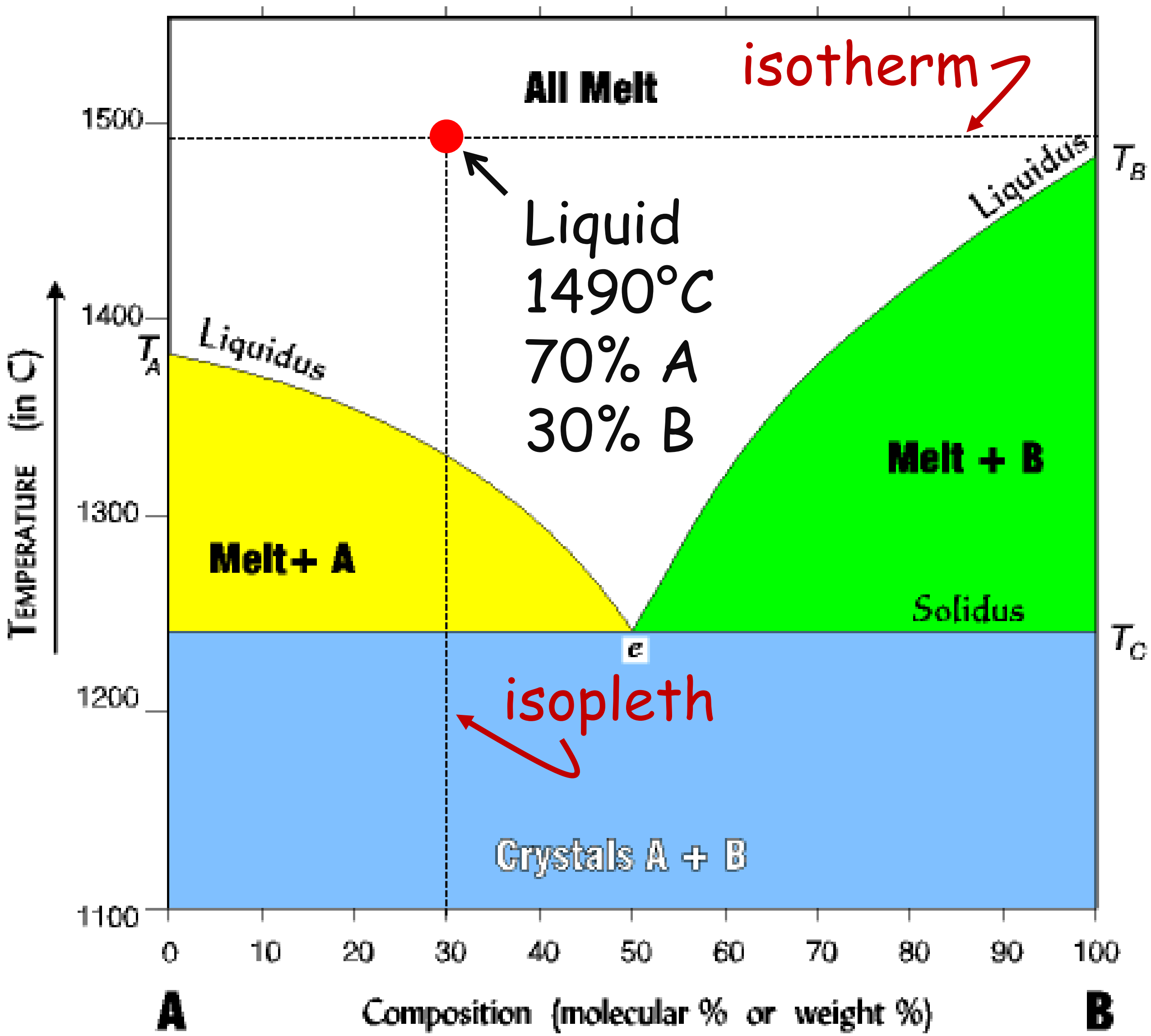


- no compounds/solid solutions in solid state
- only single phase liquid at high temperatures
- partial melting at intermediate temperatures

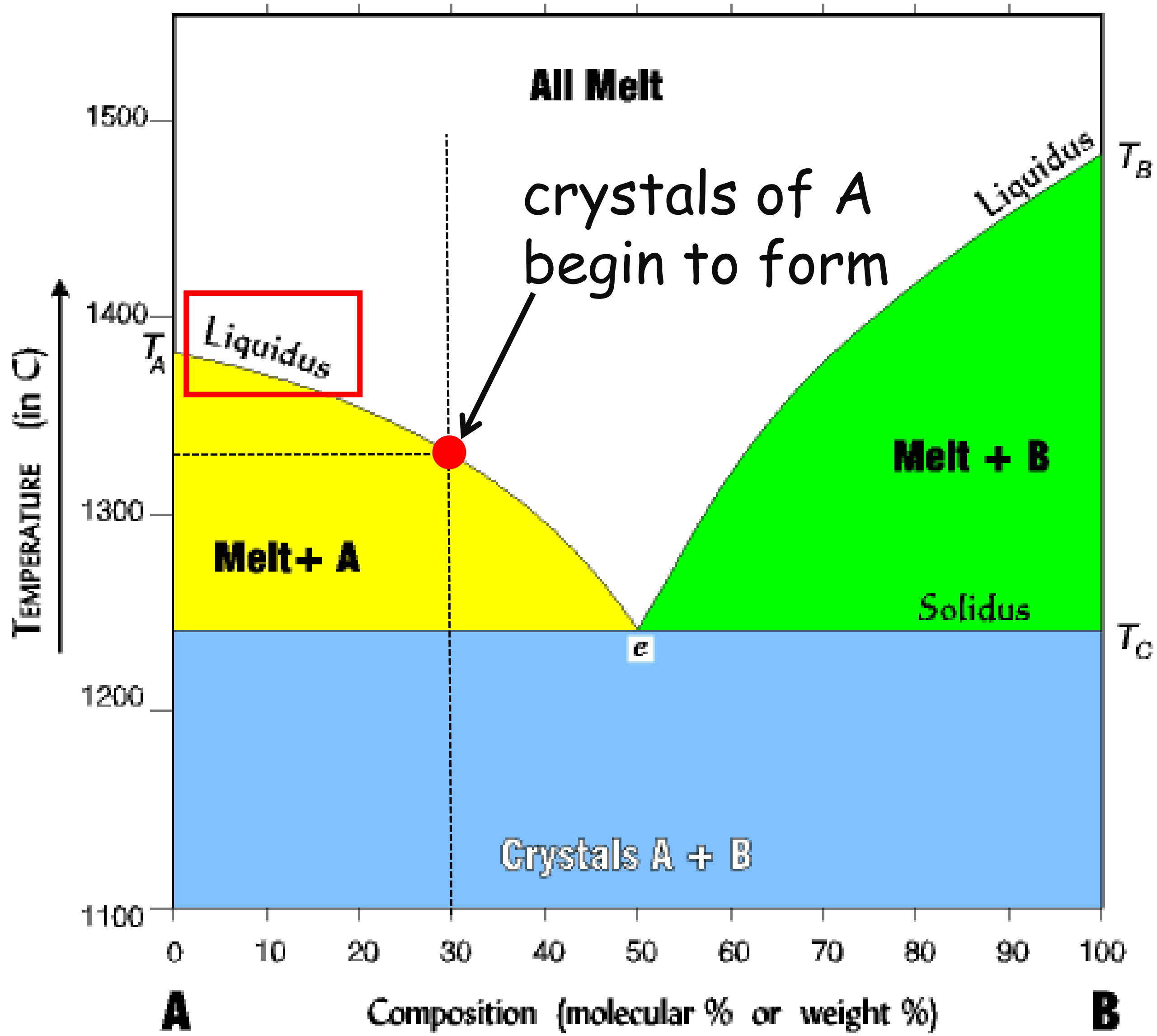


First, specify overall composition of the system
Second, pick a temperature.
→ The compositions of the phases (1 or 2) are then fixed

e.g., start with liquid at a certain composition



now, slowly cool liquid

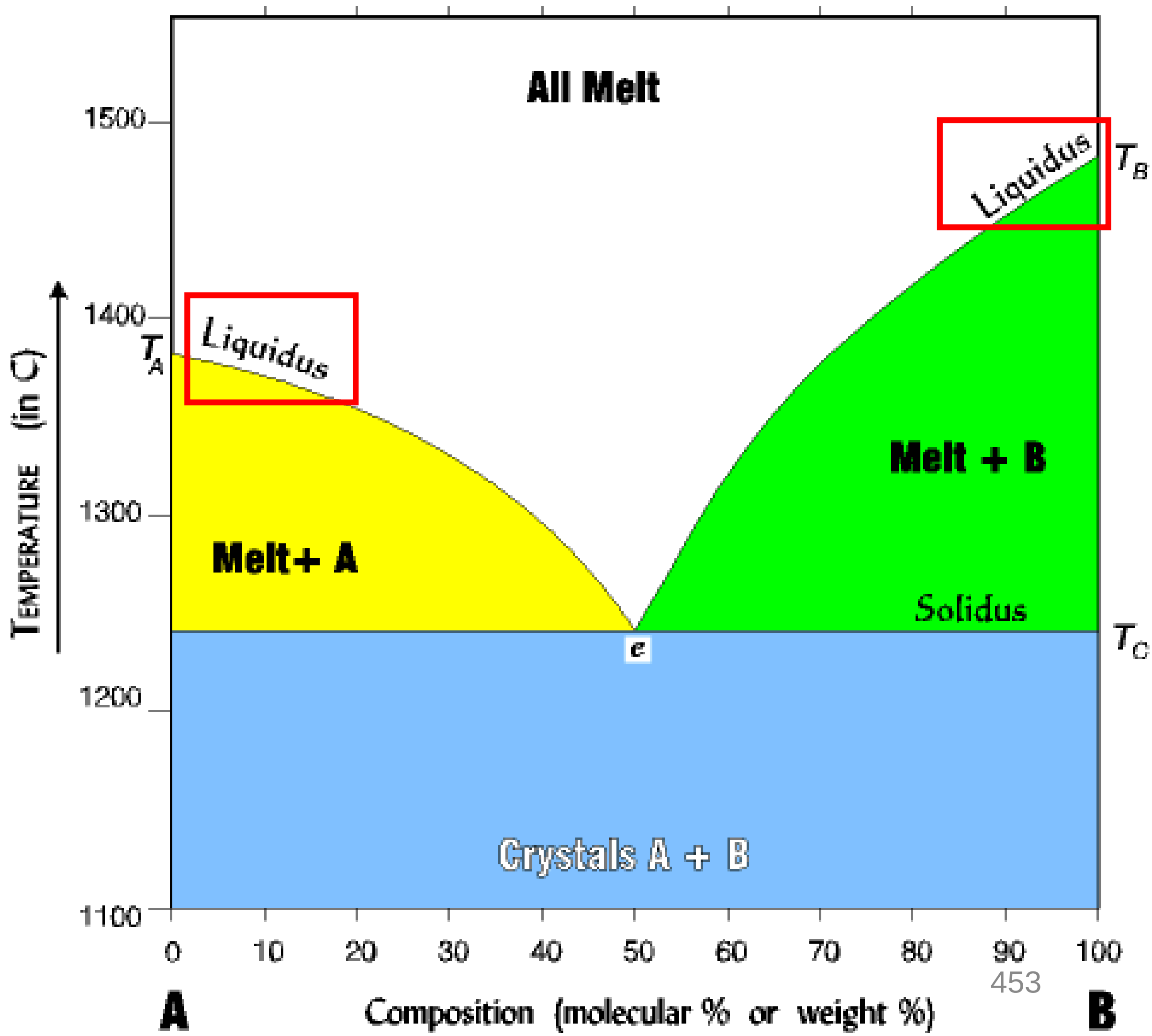


Liquidus curve: specifies the maximum temperature at which crystals can co-exist with the melt in thermodynamic equilibrium

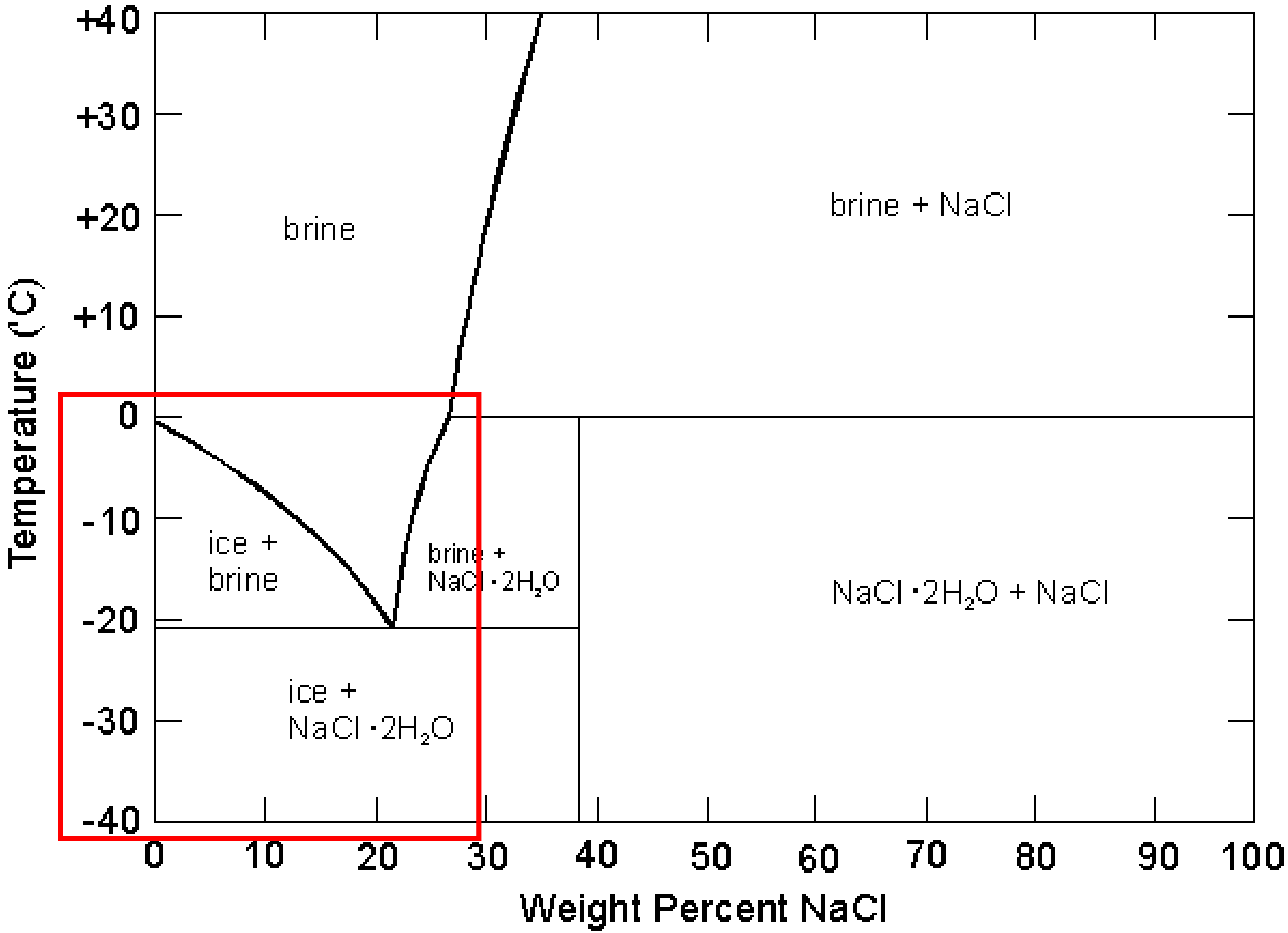
LIQUIDUS CURVE

Maximum T at which crystals can exist.
aka Saturation Solubility Curve

Melting point depression: the effect of a soluble impurity on the melting point of pure compounds.

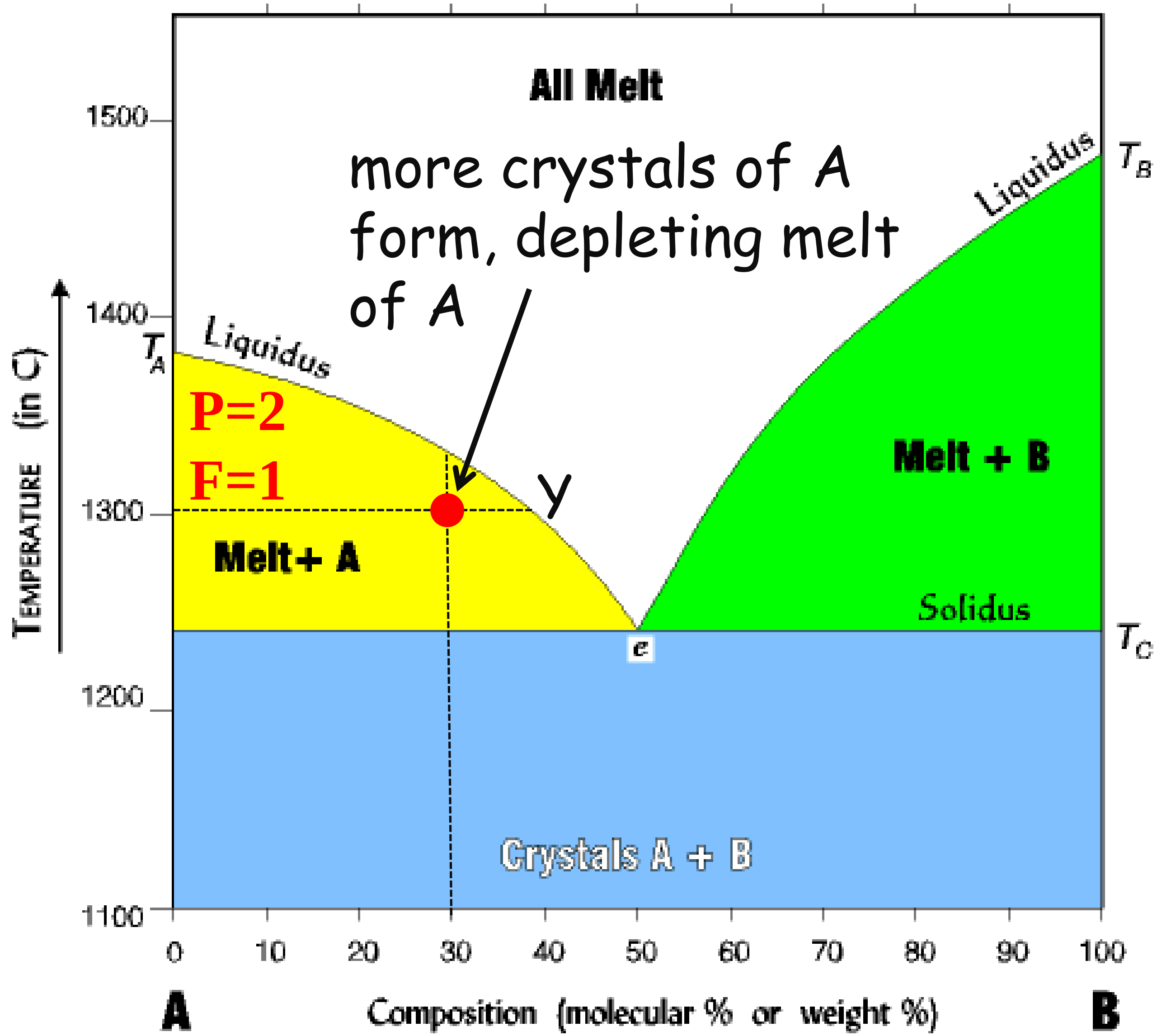


For example, consider salty ice:

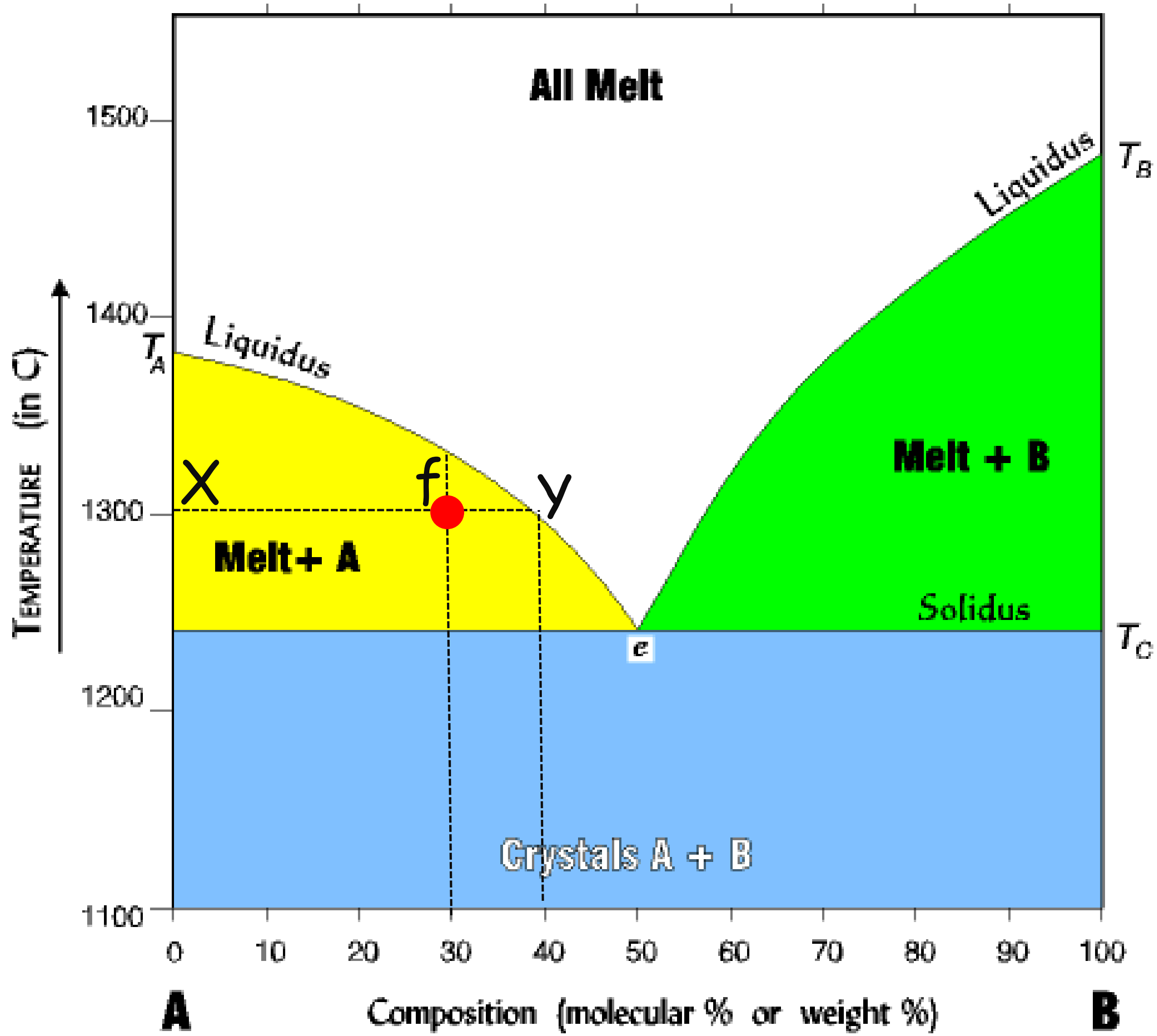


add salt, freezing point falls…

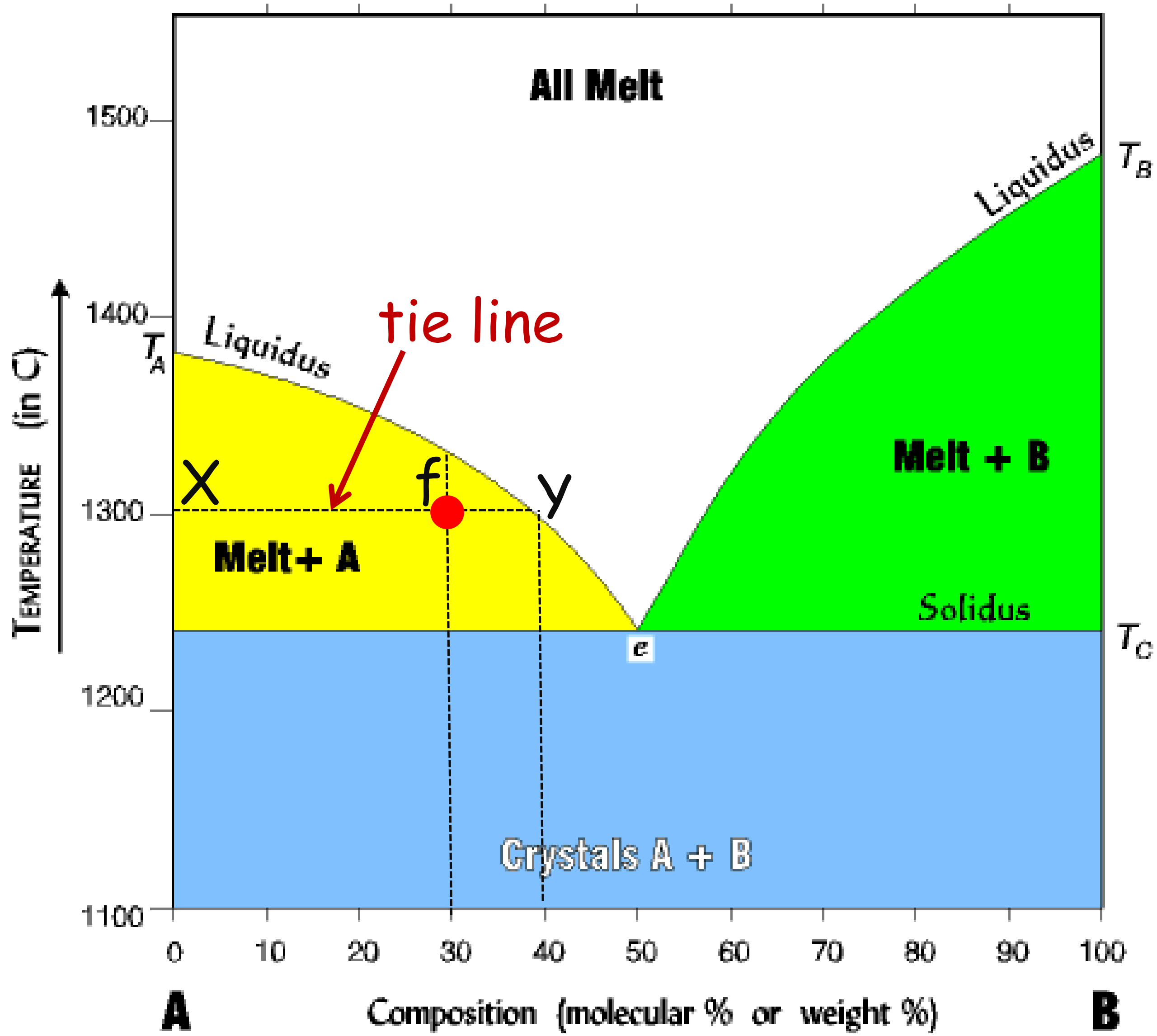
keep cooling



the system is now a mixture of crystals of pure A and the melt of composition y

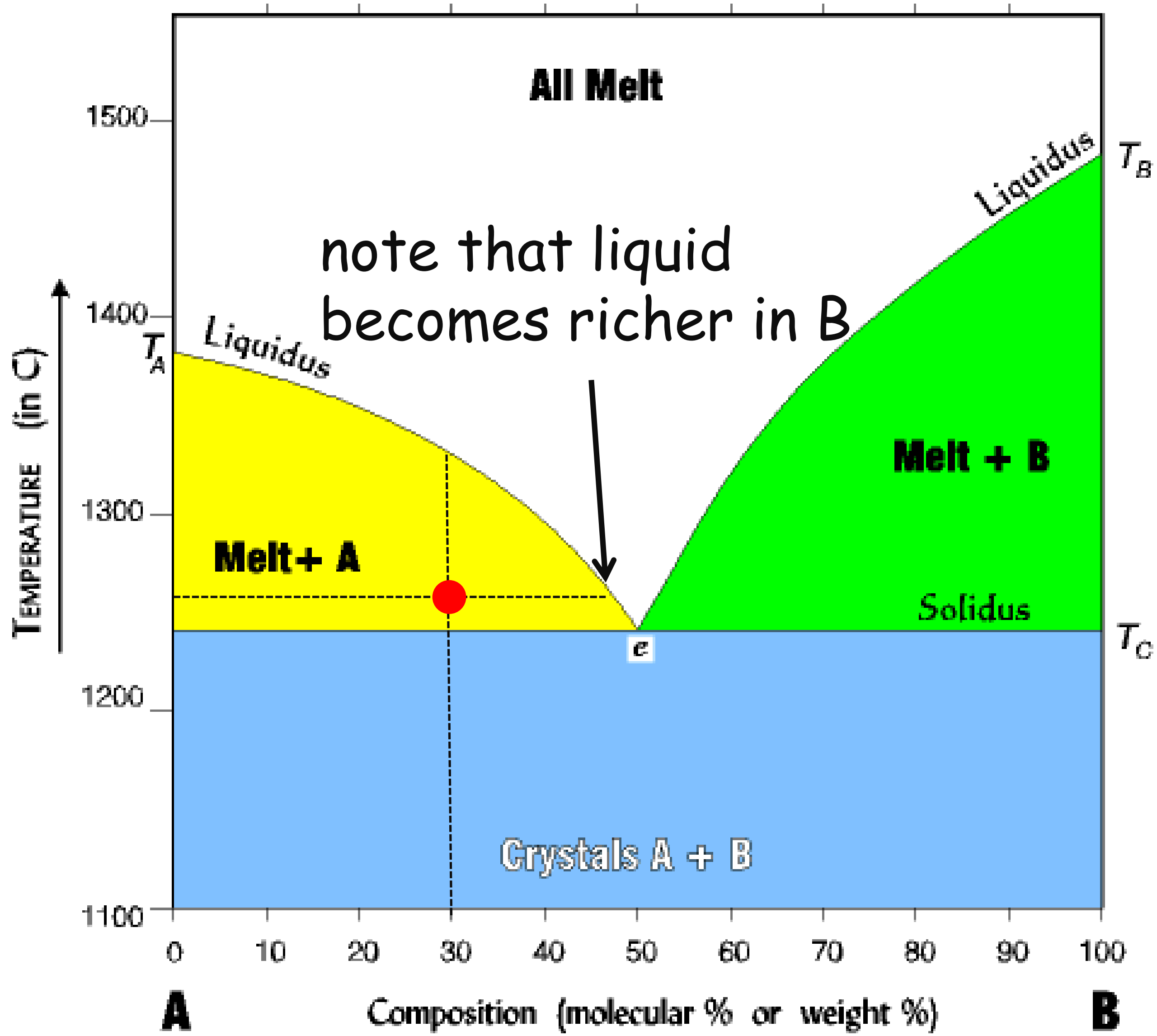


Along the isotherm XfY, the relative amounts of the phases A and melt vary but the composition of the individual phases does not vary.
Along XfY, the two phases are **pure A** and **melt of ~60% A & 40% B.**



The relative amounts of the two phases ("**phase composition**") can be determined by using the **lever rule** along the **tie line** XfY:
Amount of A = fY/XY and amount of liquid = Xf/XY.

cool more



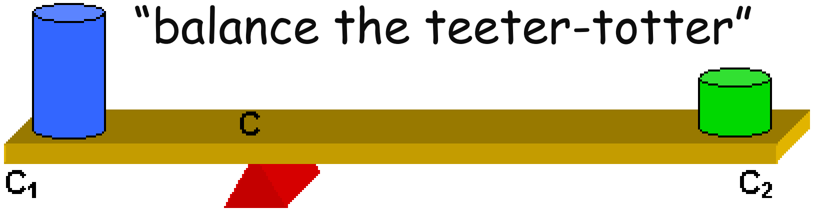
We can use the phase diagram to determine the phase composition, the *relative amounts* of A and melt at a certain T and bulk comp.

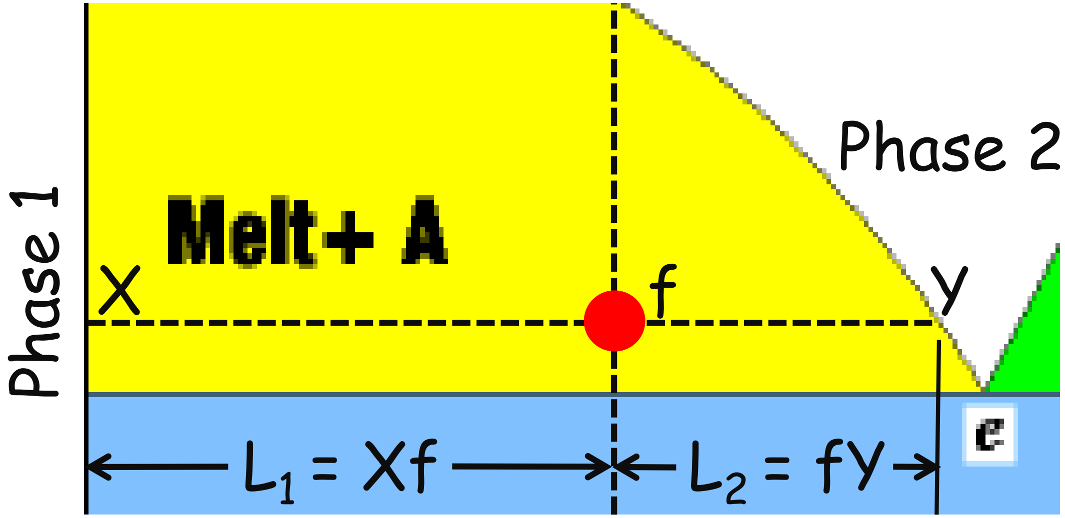
PHASE COMPOSITION AND LEVER RULE

Lever rule: the fractional amounts of two phases are inversely proportional to their distances along the **tie line** (isotherm) from the bulk composition axis

$$f_1 L_1 = f_2 L_2$$

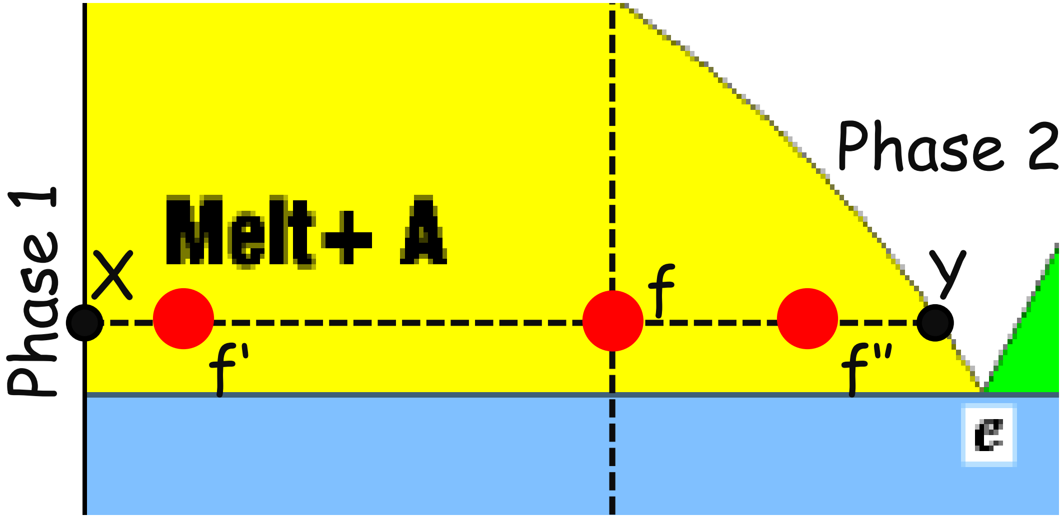
"balance the teeter-totter"





$$\frac{f_1}{f_2} = \frac{f_1}{1 - f_1} = \frac{L_2}{L_1}$$

$$f_1 = \frac{L_2}{L_1 + L_2} = \frac{\mathrm{fY}}{\mathrm{XY}}$$

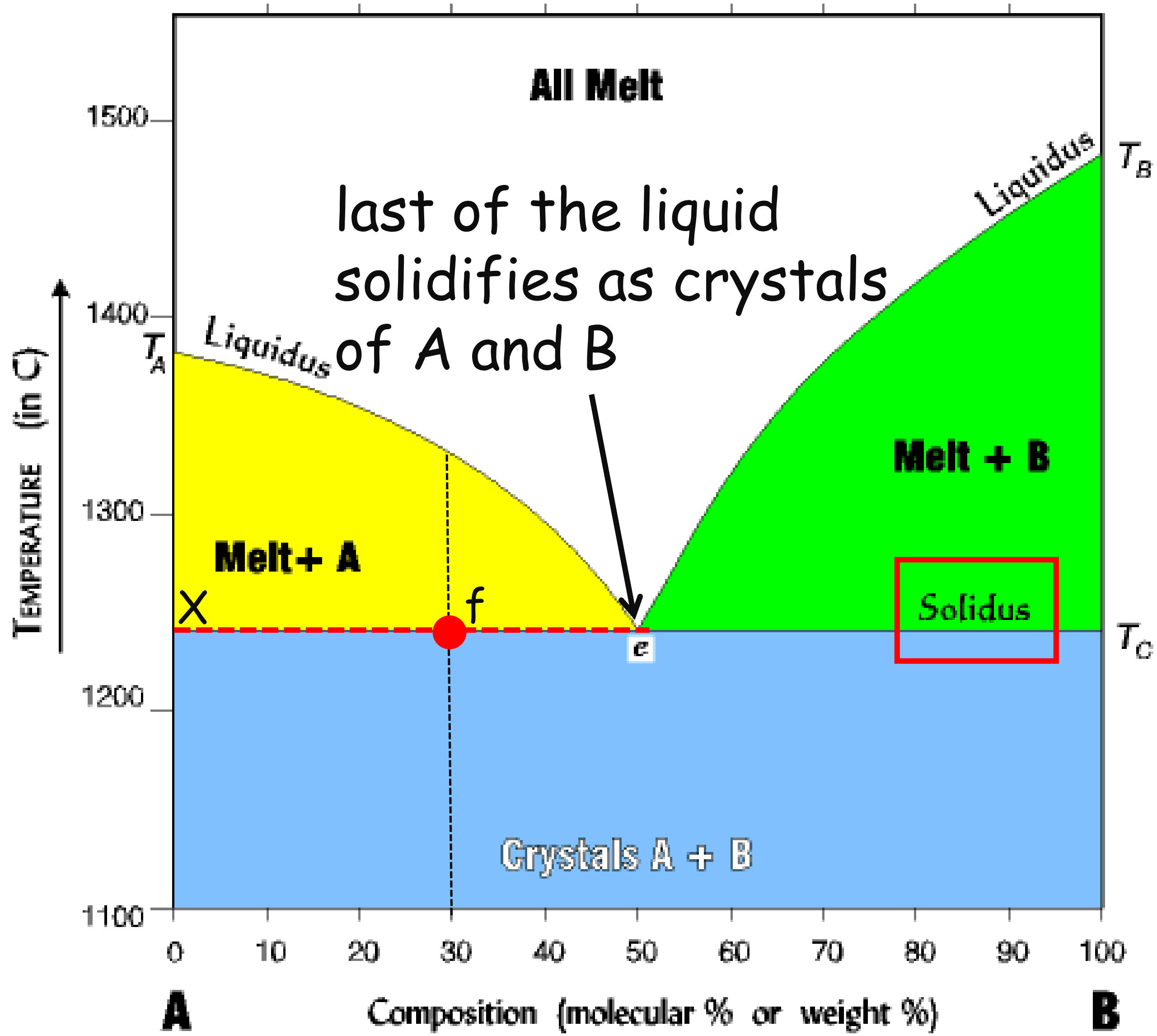


Overall Composition	Fraction of liquid
f'	Xf' /XY = 10%
f	Xf/XY = 60%
f''	Xf'' /XY = 85%

cool some more

just above solidus:

fraction A: fe/Xe
melt fraction: Xf/Xe



passing through the solidus is called the **eutectic reaction:**

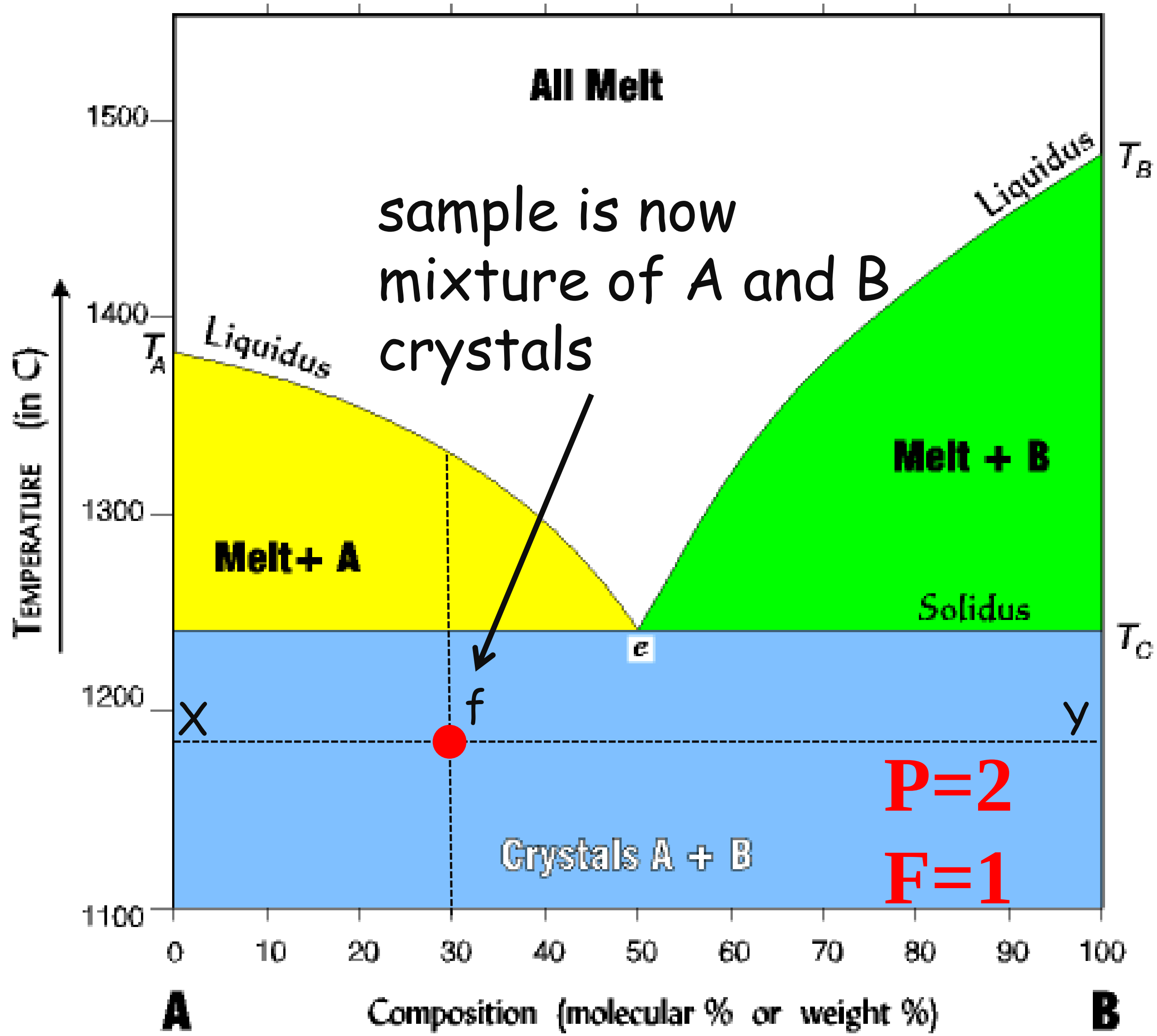
Liq. e + A → A + B

Solidus curve: gives the lowest temperature at which liquids can exist in equilibrium over a given compositional range cool some more

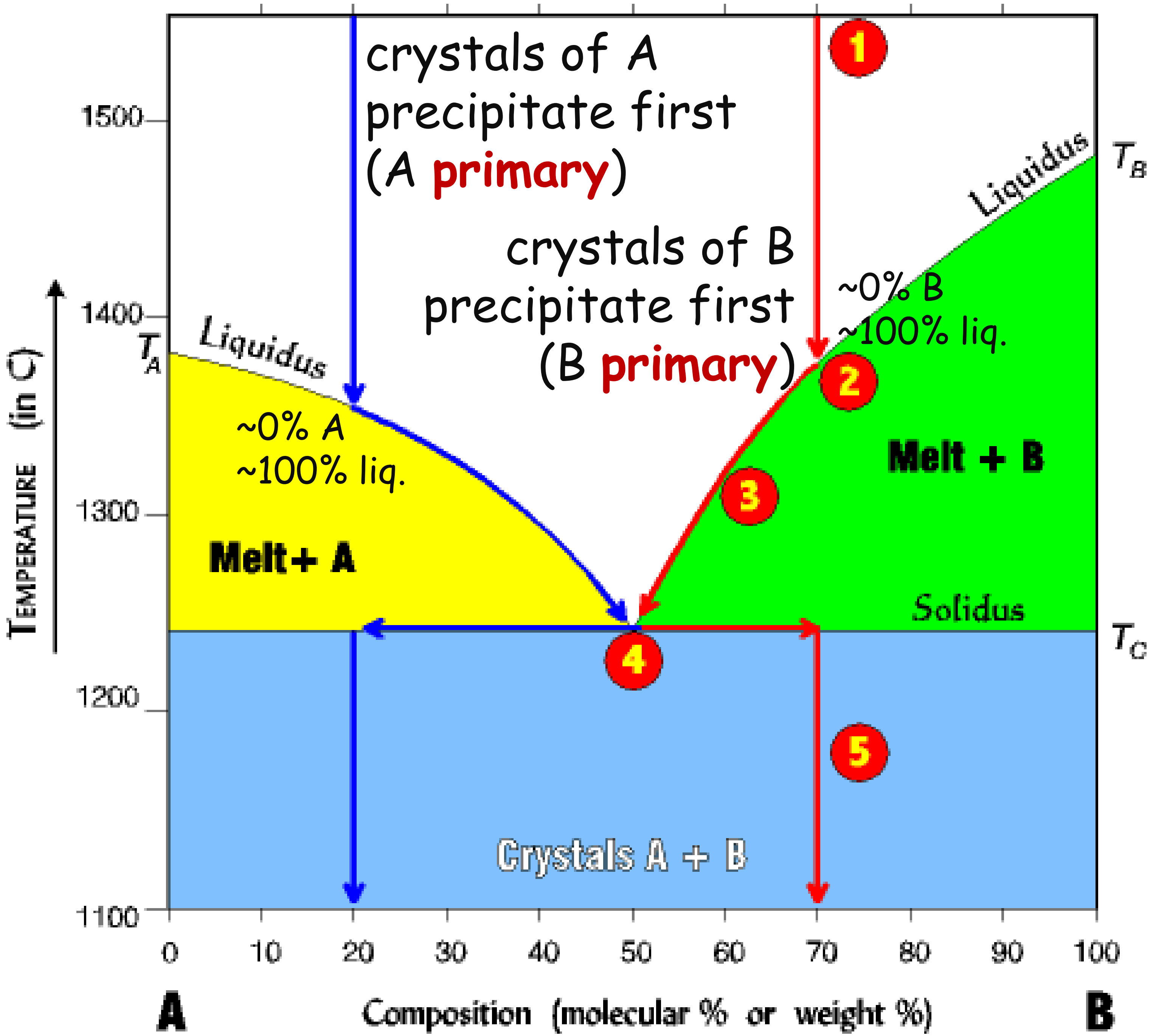
below solidus:

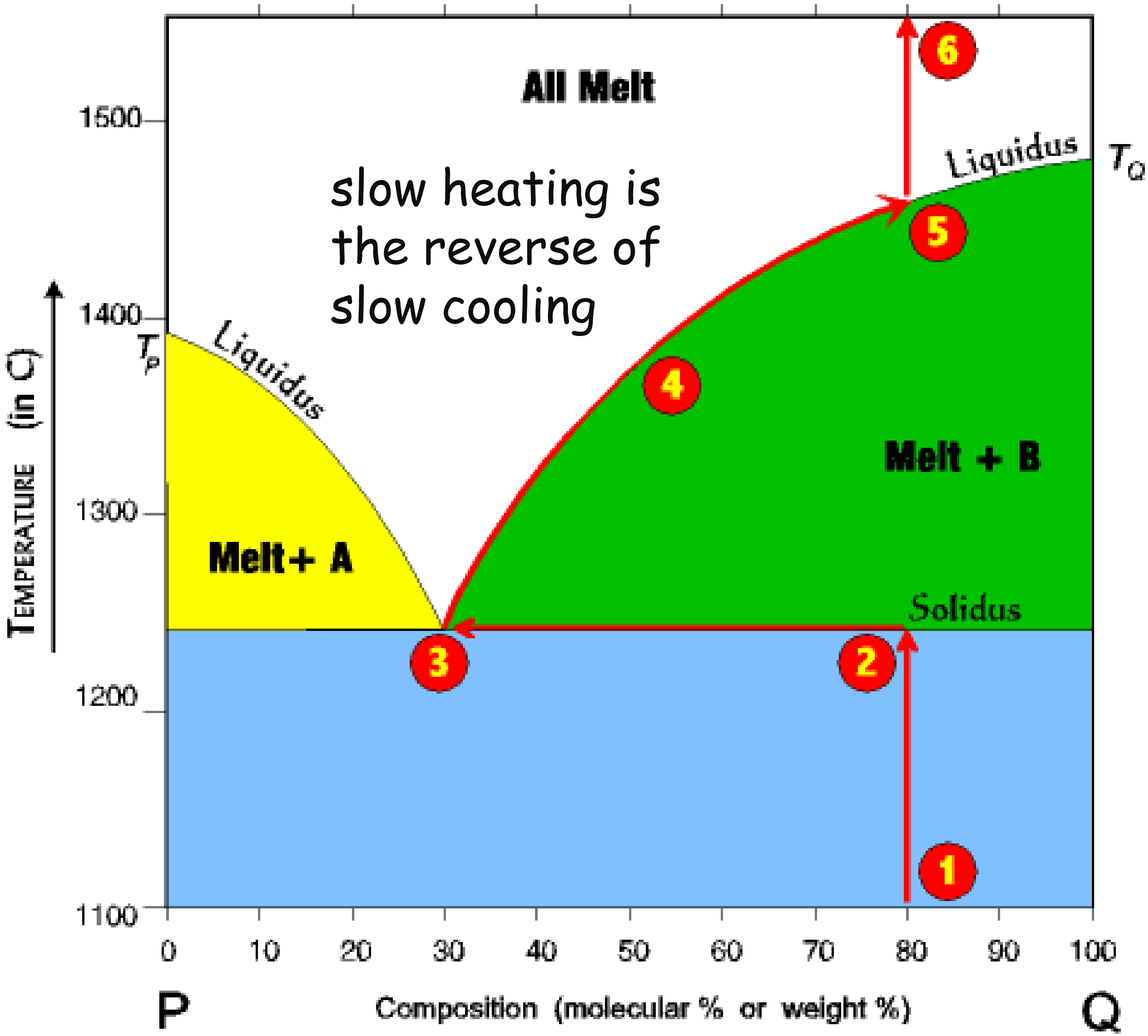
fraction A constant at fY/XY

fraction B constant at Xf/XY



not much interesting happens below the solidus line. The solid just further cools with no change in composition.


crystals of A
precipitate first
(A primary)
crystals of B
precipitate first
(B primary)
~0% B
~100% liq.
~0% A
~100% liq.
Liquidus
Liquidus
Solidus
Melt + A
Melt + B
Crystals A + B
T_A
T_B
T_C
1
2
3
4
5
Temperature (in C)
1500
1400
1300
1200
1100
0
10
20
30
40
50
60
70
80
90
100
A
B
Composition (molecular % or weight %)



All Melt
slow heating is
the reverse of
slow cooling
Liquidus
T_Q
Liquidus
T_P
Melt + B
Melt+ A
Solidus
1
2
3
4
5
6
1500
1400
1300
1200
1100
TEMPERATURE (in C)
0
10
20
30
40
50
60
70
80
90
100
P
Composition (molecular % or weight %)
Q

EUTECTIC COMPOSITION ("easily melted")

system with the eutectic composition will melt/freeze **congruently** (i.e., completely, with no change in composition) and at the lowest T

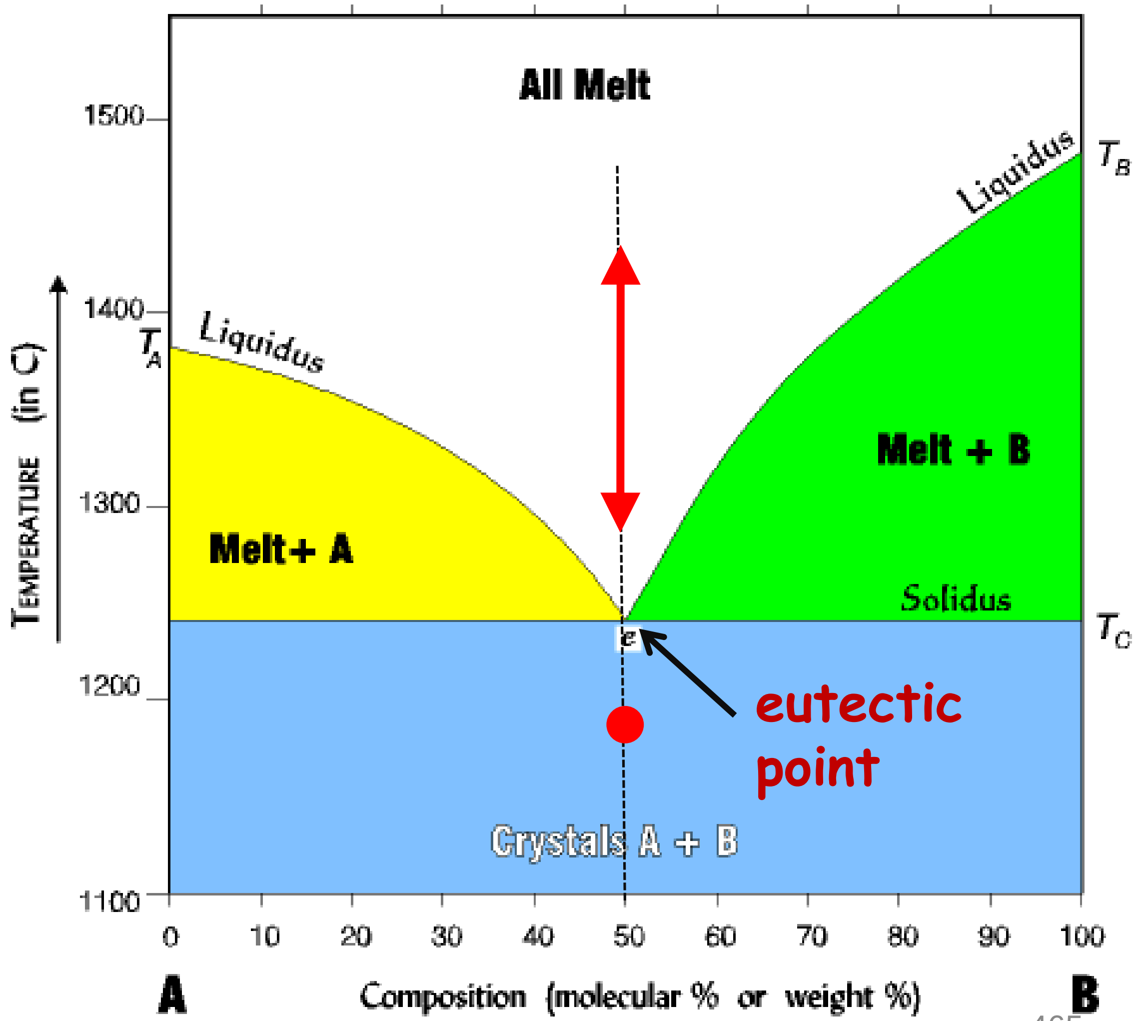
composition with the lowest melting point

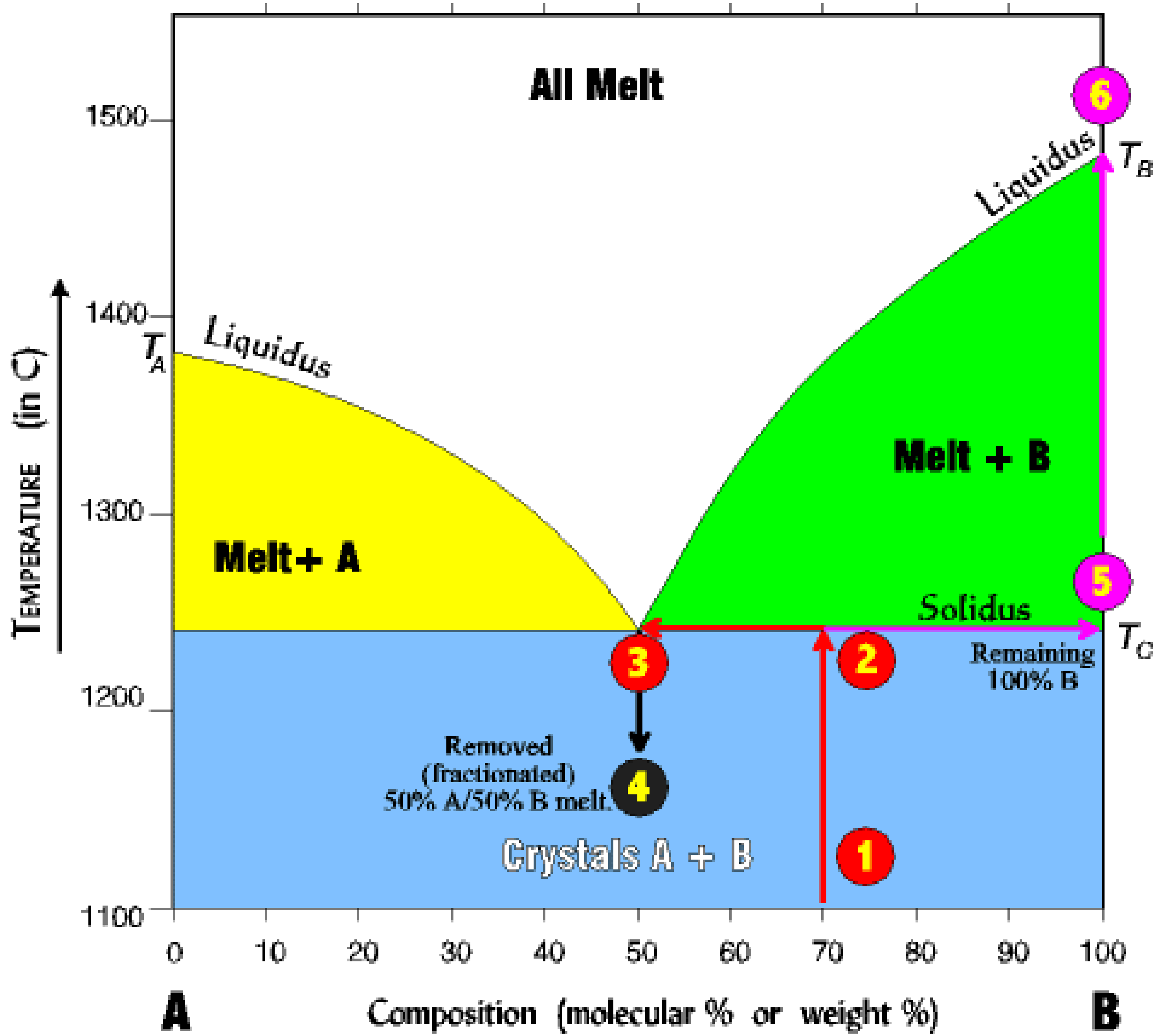
eutectic point is invariant

$$P + F = 3$$

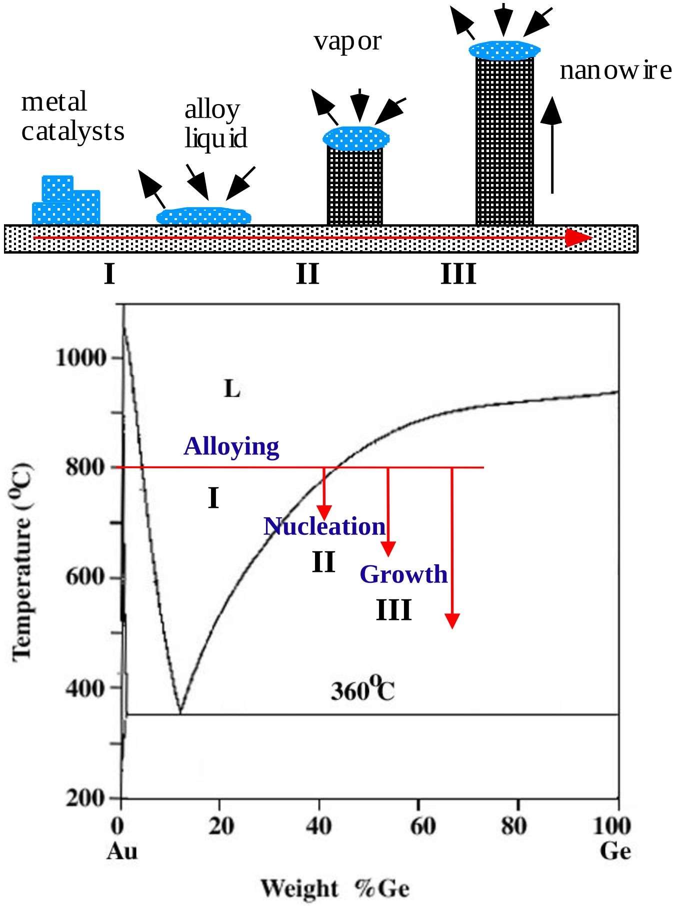
$$F = 0$$

- 3 phases present (A, B, liquid e)

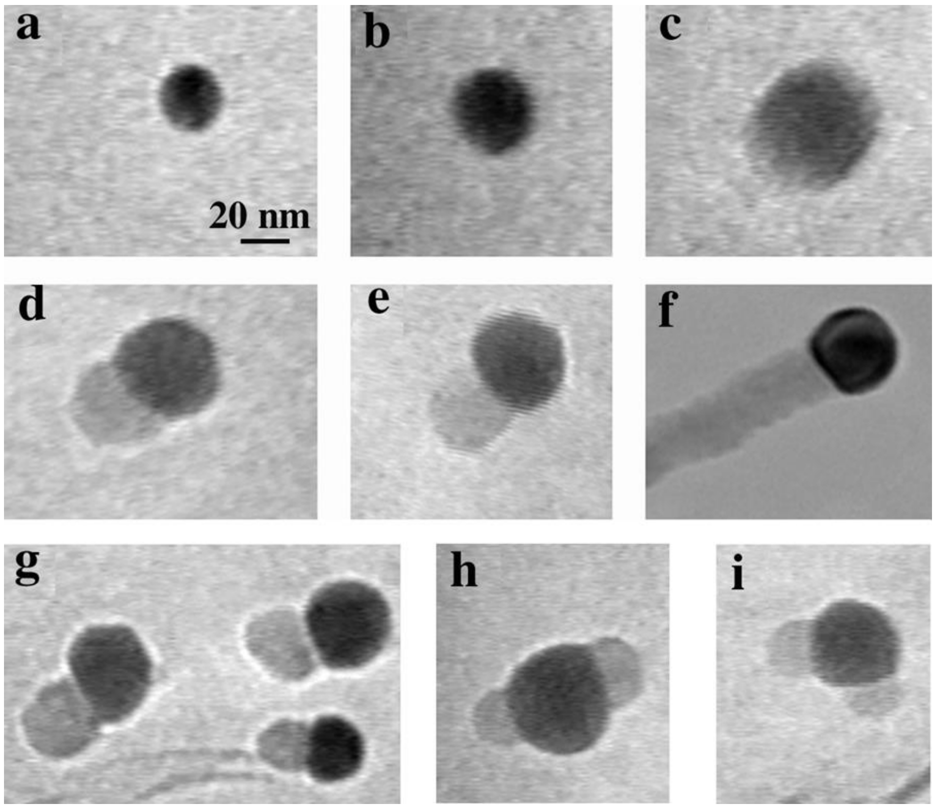



All Melt
1500
1400
1300
1200
1100
Temperature (in C)
T_A
Liquidus
Liquidus
T_B
Melt+ A
Melt + B
Solidus
T_C
Remaining
100% B
Removed
(fractionated)
50% A/50% B melt.
Crystals A + B
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90
100
A
Composition (molecular % or weight %)
B

Vapor-Liquid-Solid Nanowire Growth



800 deg. In-situ TEM

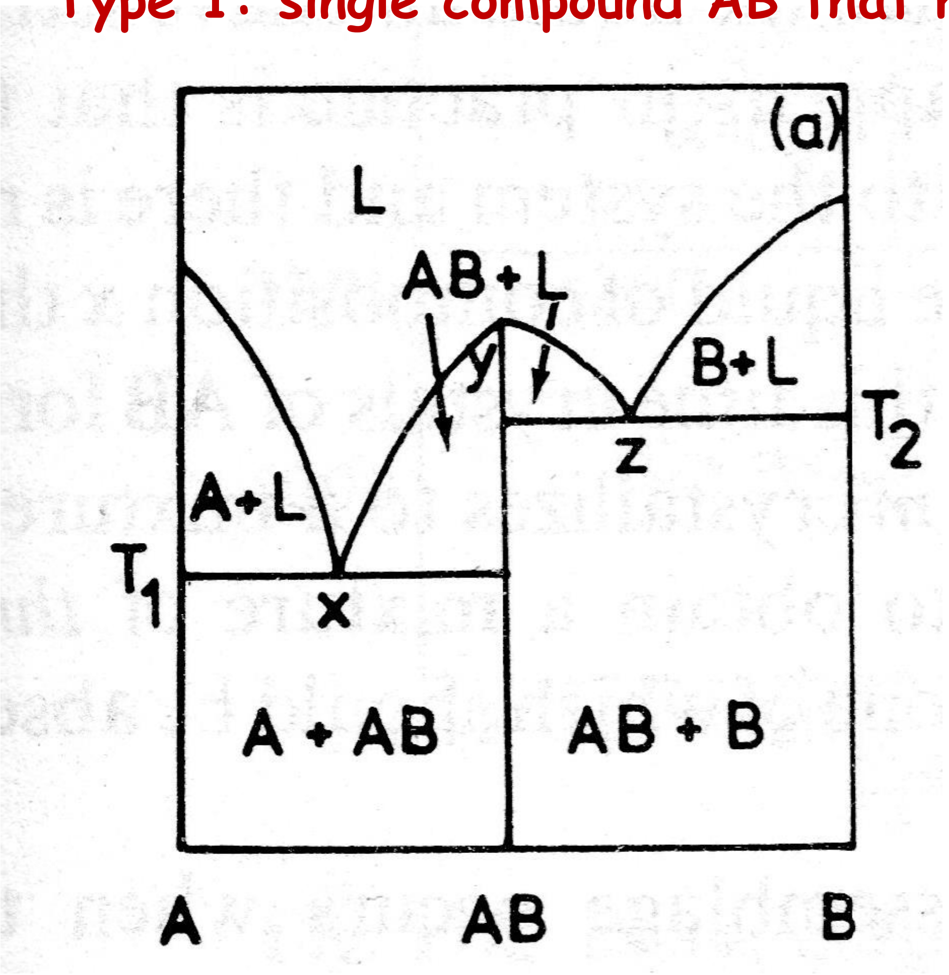


Unidirectional growth is the consequence of an anisotropy in solid-liquid interfacial energy.

Y. Wu et al. *J. Am. Chem. Soc*. **2001**, *123*, 3165

BINARY SYSTEMS WITH COMPOUNDS

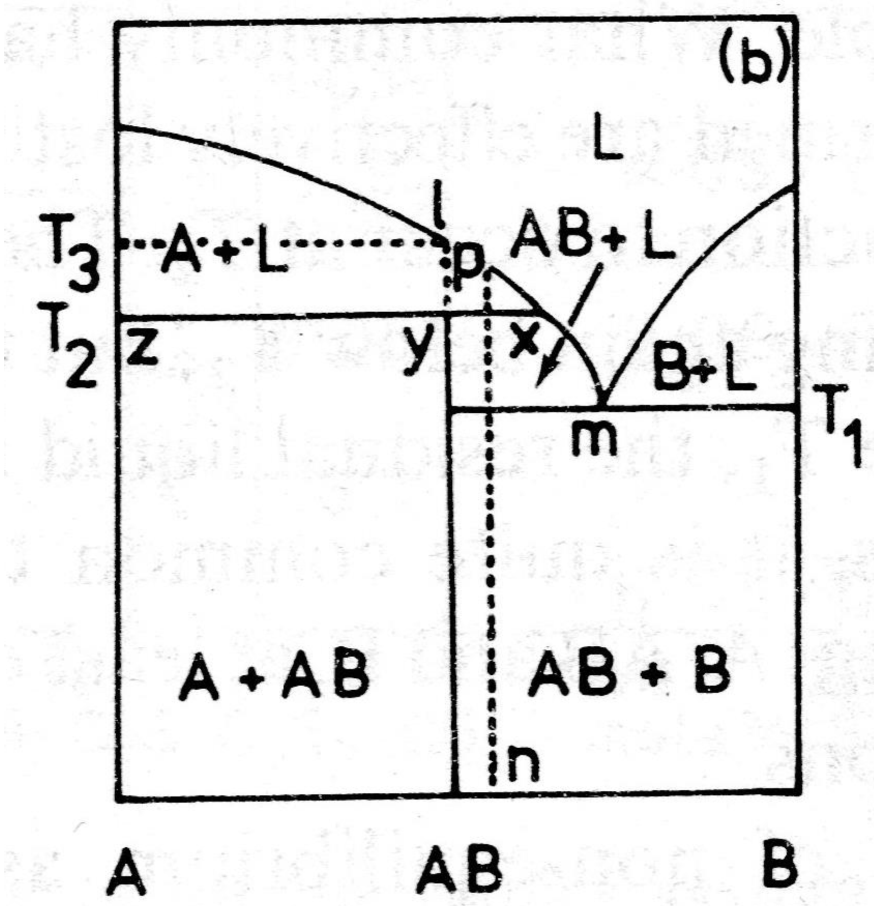
Type 1: single compound AB that melts congruently



- AB melts congruently (no change in composition)
- looks like two simple eutectic systems stitched together

BINARY SYSTEMS WITH COMPOUNDS

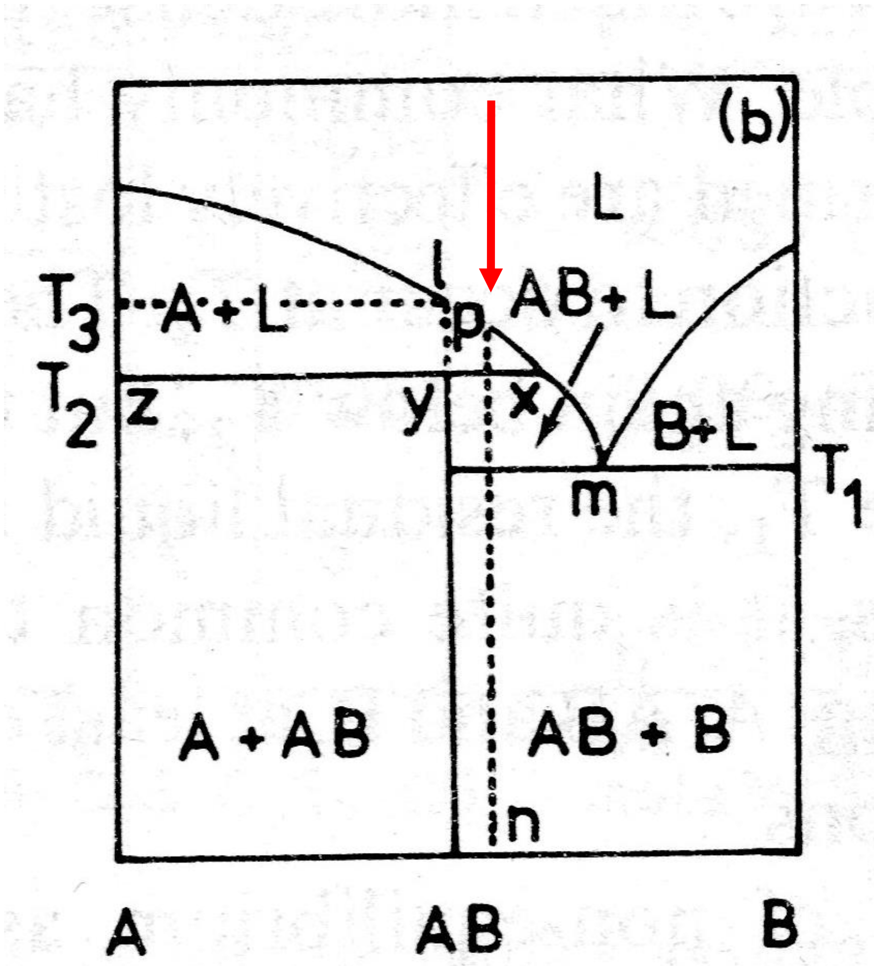
Type 2: single compound AB that melts incongruently



- **AB melts incongruently at T_2 (liquid composition is x, liquid fraction is zy/zx)**
- **x is a peritectic point (3 phases: A, AB, liquid x)**
- **AB melts completely at T_3**
- **liquid compositions between x and m precipitate AB first**

Peritectic point: an invariant point (liquid & two solids) in which the composition of the liquid phase is not between that of the two solids (not a minimum in the intersection between two liquidus lines)

let's cool liquid of composition n:



1) crystal of A form at ~T_3

2) more A forms until liquid reaches composition x

3) At T_2, peritectic reaction occurs:

Liq. x + A → Liq. x + AB

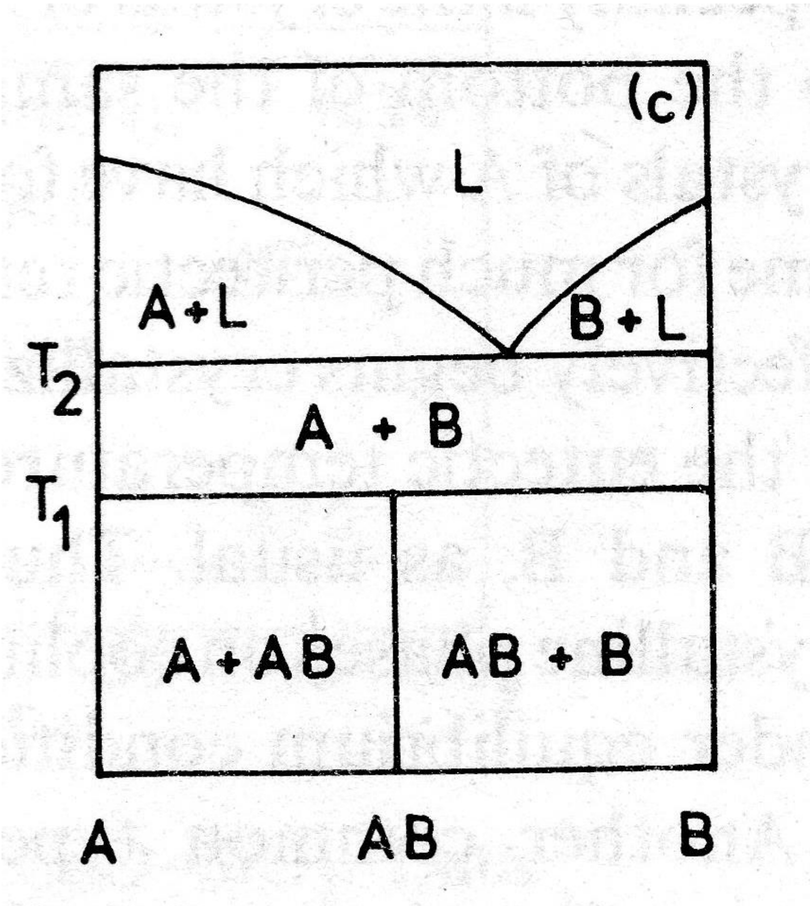
(crystalline phase changes from A to AB, often *very slowly*)

4) Cooling to T_1, more AB forms, liquid composition moves to m, eutectic reaction occurs

5) below T_1, we have AB and B

BINARY SYSTEMS WITH COMPOUNDS

Type 3: single compound AB with upper limit of stability



- **AB decomposes before melting**
  (it disproportionates to A and B)
- **AB has upper limit of stability**
- **simple eutectic system above T_1**

THE CaO – SiO_2 BINARY DIAGRAM

11 compounds!

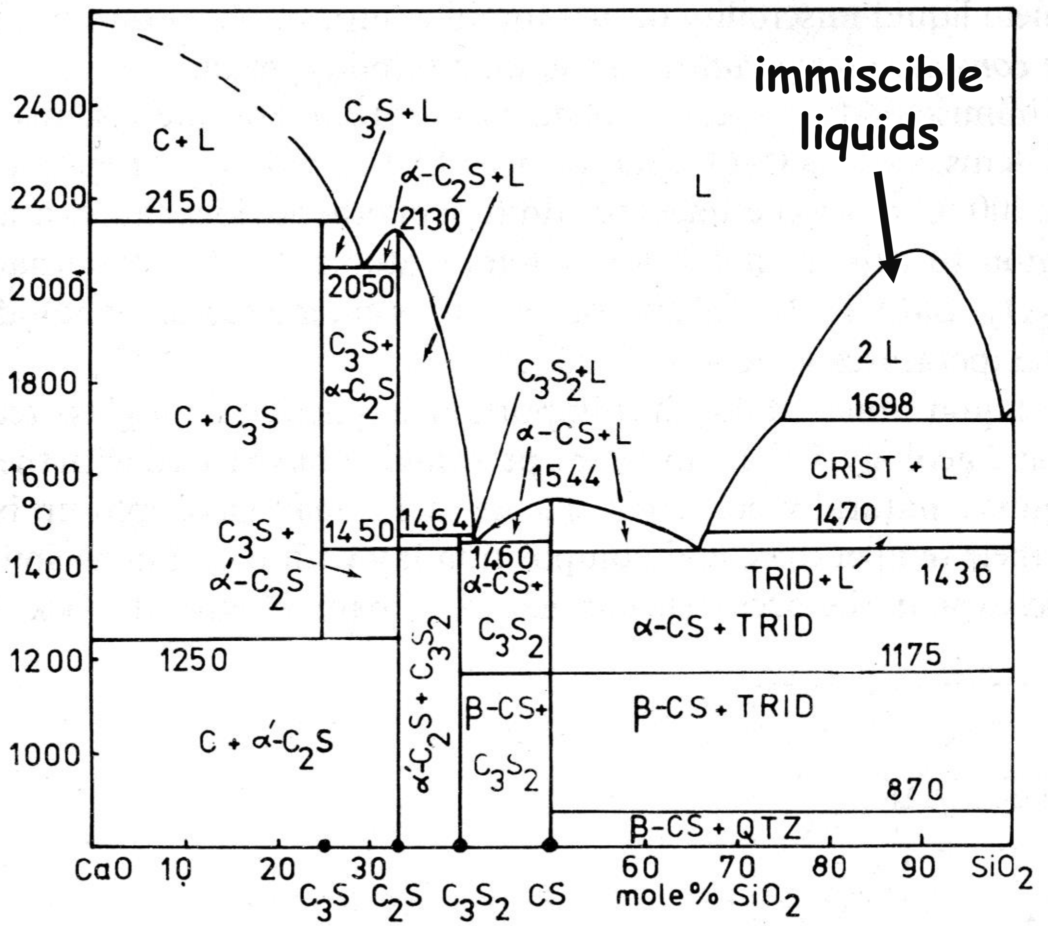
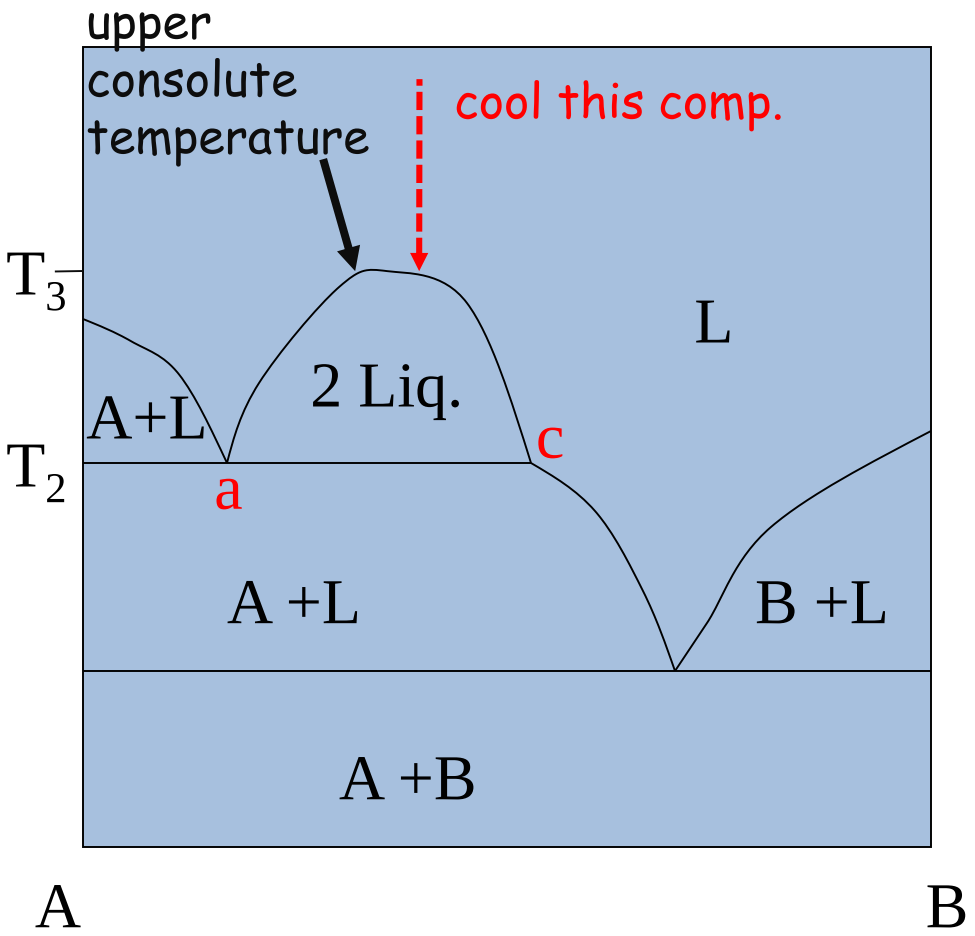


Fig. 11.8 Phase diagram for the binary system CaO–SiO_2. Data from B. Philips and A. Muan, J. Am. Ceram. Soc., **42** 414 (1959) $C = CaO$, $C_3S = Ca_3SiO_5$, $C_2S = Ca_2SiO_4$, $C_3S_2 = Ca_3Si_2O_7$, $CS = CaSiO_3$, CRIST = cristobalite, TRID = tridymite, QTZ = quartz, L = liquid

- Ca_2SiO_4 and $CaSiO_3$ melt congruently
- Ca_3SiO_5 and $Ca_3Si_2O_7$ melt incongruently
- Ca_3SiO_5 has a **lower limit of stability** (decomposes to CaO and Ca_2SiO_4 below 1250°C)
- **liquid immiscibility dome** at the silica-rich end of the diagram

BINARY SYSTEMS WITH IMMISCIBLE LIQUIDS



immiscibility dome

Below T_3, the liquid phase separates into two liquids of different comp.

invariant monotectic points at points a and c

P + F = 3

- 3 phases present (liquid a, liquid c, A)

At T_2, monotectic reaction occurs:

Liq. a + Liq. c → Liq. c + A

THERMODYNAMICS OF LIQUID IMMISCIBILITY

<u>Enthalpy</u> of mixing determines whether two liquids A and B mix

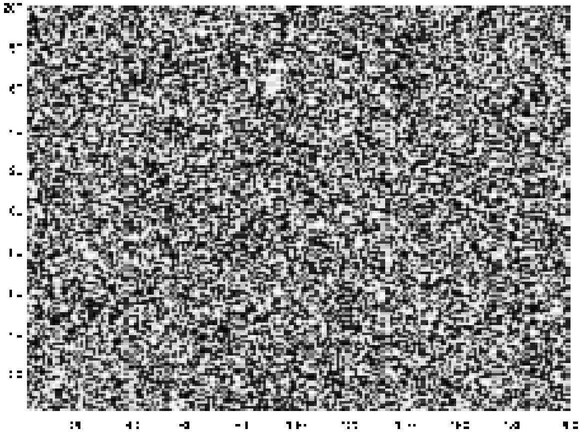
$$\Delta G_{mix} = \Delta H - T\Delta S$$

- $\Delta S > 0$ for mixing
- if $\Delta H < 0$ (stronger A-B attraction), the liquids are miscible at all temps
- if $\Delta H > 0$ (stronger A-A, B-B attraction):
  - possibly miscible if $\Delta H < T\Delta S$ (high T)
  - immiscible when $\Delta H > T\Delta S$ (low T)

when a liquid enters the immiscibility dome, the unmixing process (phase separation) occurs by one of two major mechanisms:

1) nucleation and growth
(large compositional fluctuations required for $\Delta G<0$)

2) spinodal decomposition
(even infinitesimal compositional fluctuations give $\Delta G<0$)



SOLID SOLUTIONS

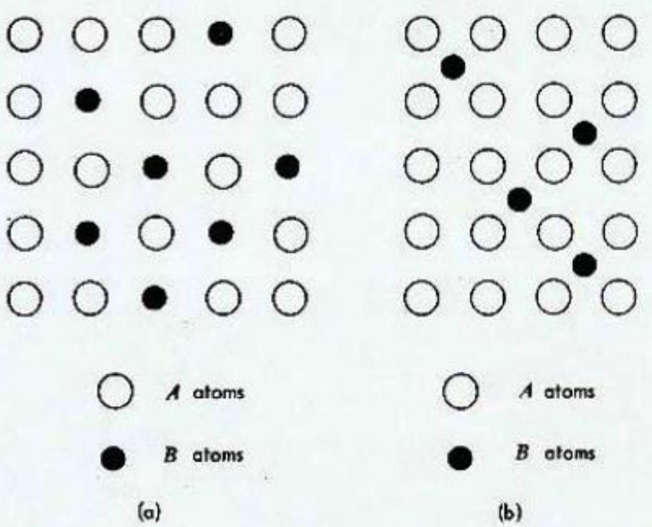
a solid-state solution; a crystalline material with variable composition

Two types:

- substitutional (solute atom/ion replaces solvent atom/ion)
- interstitial (solute atom/ion occupies interstitial site)

Formation of substitutional solid solutions favored by:

- similar atomic/ionic radii (15%)
- same crystal structure
- similar electronegativities
- same valency



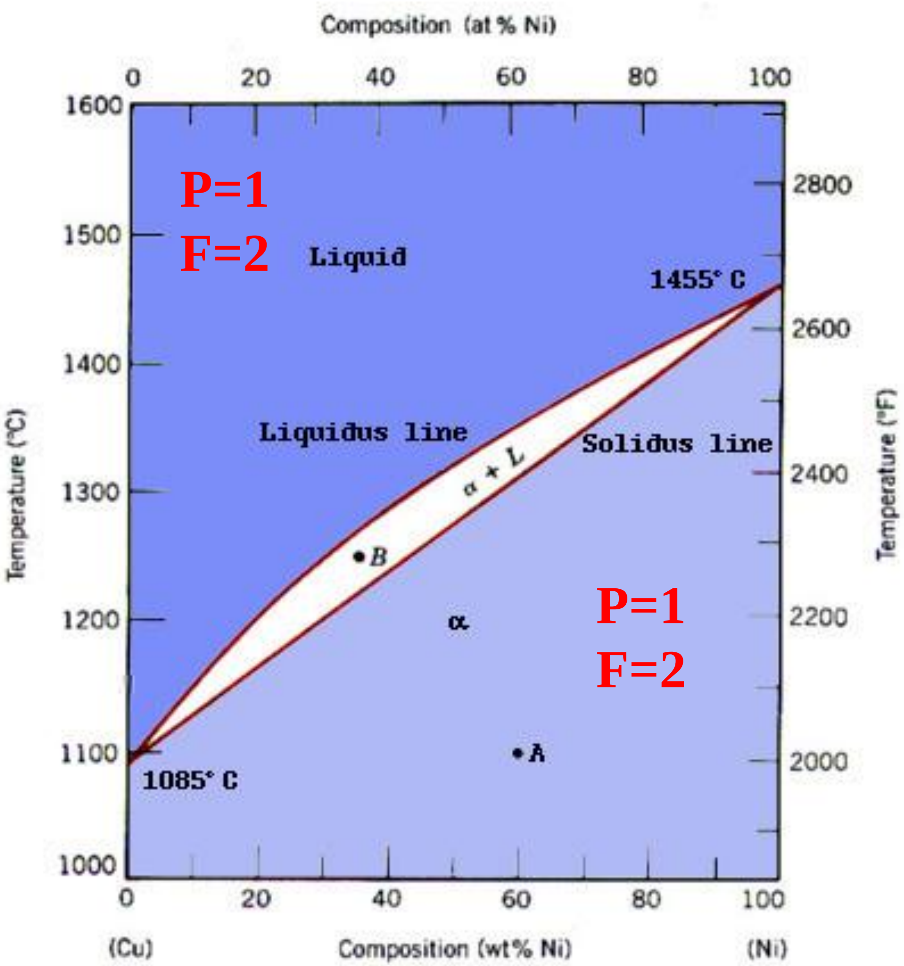
Substitutional (a) and interstitial (b) solid solutions

Examples:

- Al_2O_3 – Cr_2O_3 (substitutional, complete)
- Si-Ge (substitutional, complete)
- Fe-C (interstitial, partial)

BINARY SYSTEMS WITH SOLID SOLUTIONS

simplest solid solution system has complete miscibility in both solid and liquid states

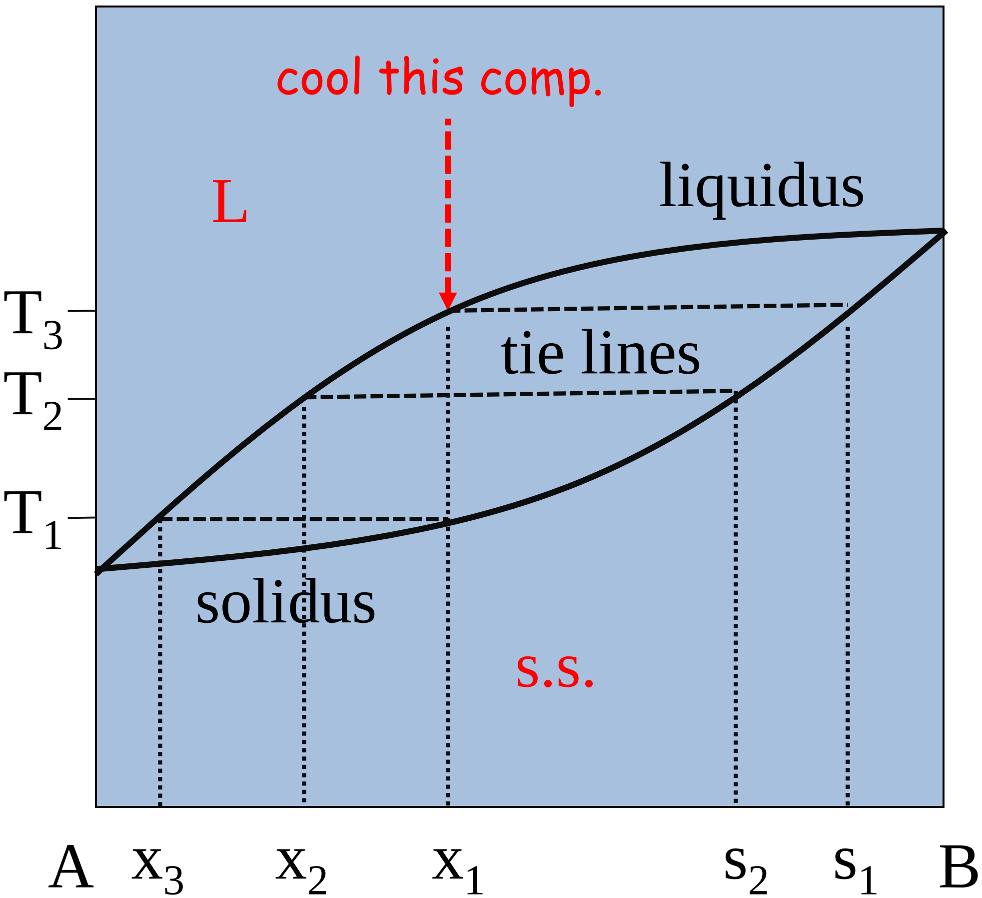


- copper melts at 1085 C
- nickel melts at 1455 C
- above liquidus: single phase liquid
- between liq. and sol.: two phases
- below solidus: single phase solid a

α-phase is a substitutional solid consisting of both Cu and Ni and on an FCC lattice

CRYSTALLIZATION

the composition of the solid solution has to change continuously during crystallization in order to maintain equilibrium

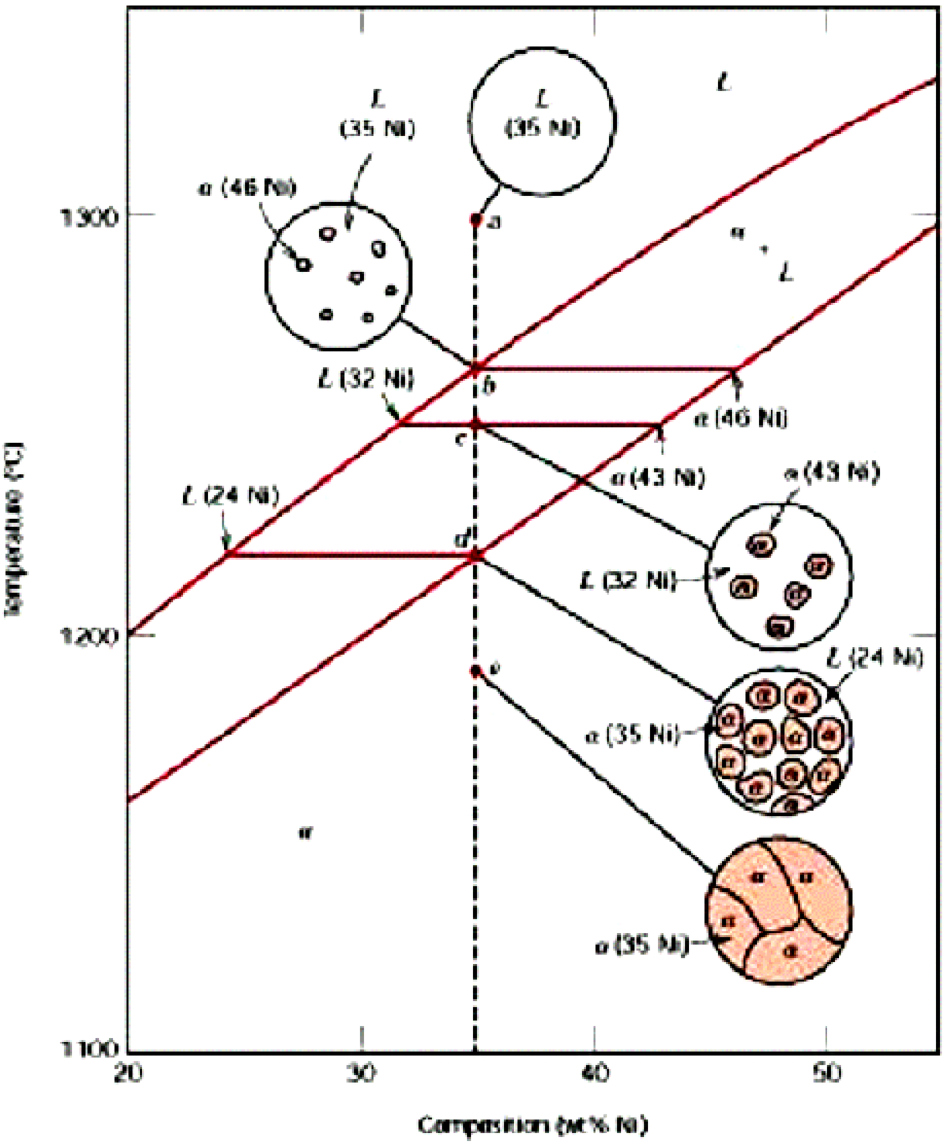


- at T_3, s.s. of composition s_1 forms (lever rule shows ~100% liquid of composition x_1)
- at T_2, s.s. is composition s_2, richer in A, and liquid is composition x_2, depleted of B (lever rule shows 33% s.s. and 67% liquid)
- at T_1, s.s. is composition x_1 and the final liquid is composition x_3 (lever rule shows ~100% s.s.)

The amount of s.s. and it's A content continuously increases during cooling.

Equilibrium solidification requires very slow cooling

microstructure during cooling

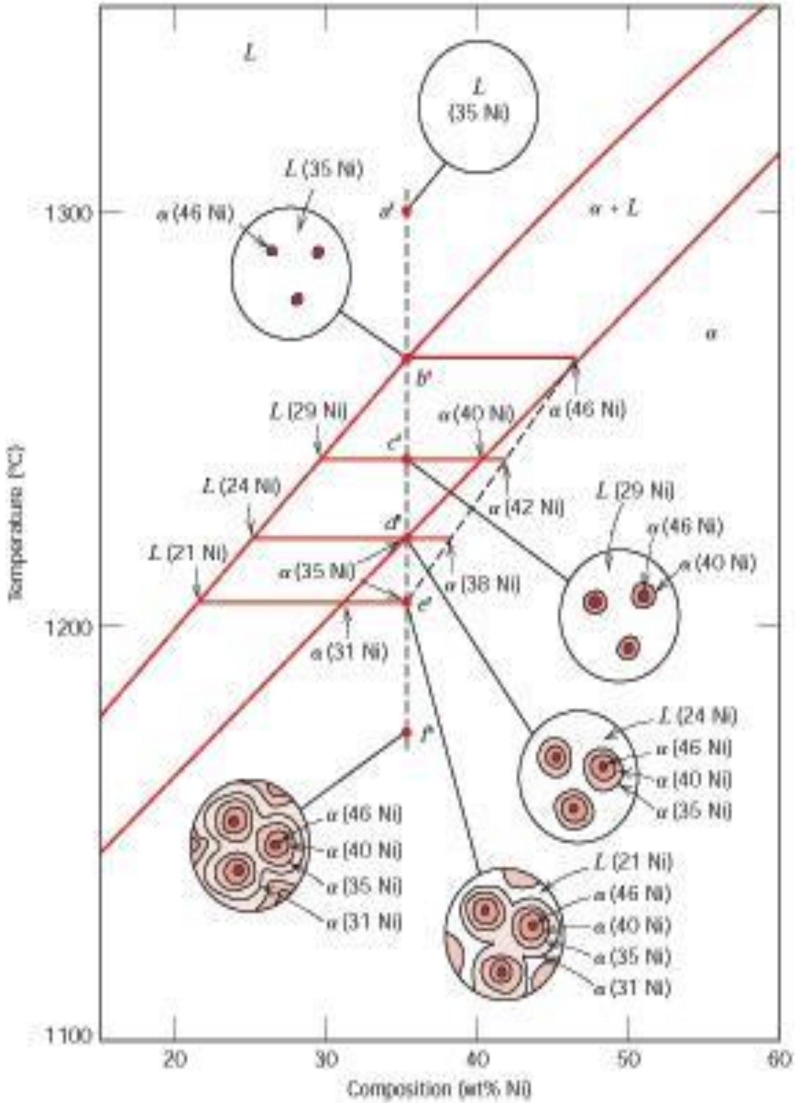


- No microstructural changes until the liquidus line is reached at b
- From b to d: α-phase increases as dictated by lever rule and composition changes as dictated by tie lines and their intersection with solidus/liquidus

maintaining equilibrium during cooling results in a *homogeneous* alpha phase

Somewhat faster cooling results in fractional crystallization

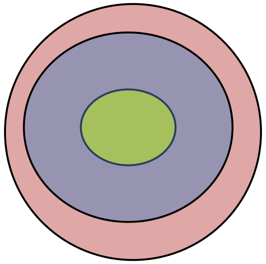
microstructure during cooling



- diffusion in solids is very slow, requires time
- non-equilibrium (fast) cooling causes:

1) cored structures (inhomogeneous s.s.)
2) metastable phases
3) undercooled liquid

Consequences of non-equilibrium solidification: segregation, cored structure.
upon reheating: grain boundaries will melt first causing loss of structural integrity



coring…
"onions"

coring in metals can be eliminated by heating just below the solidus for sufficient time

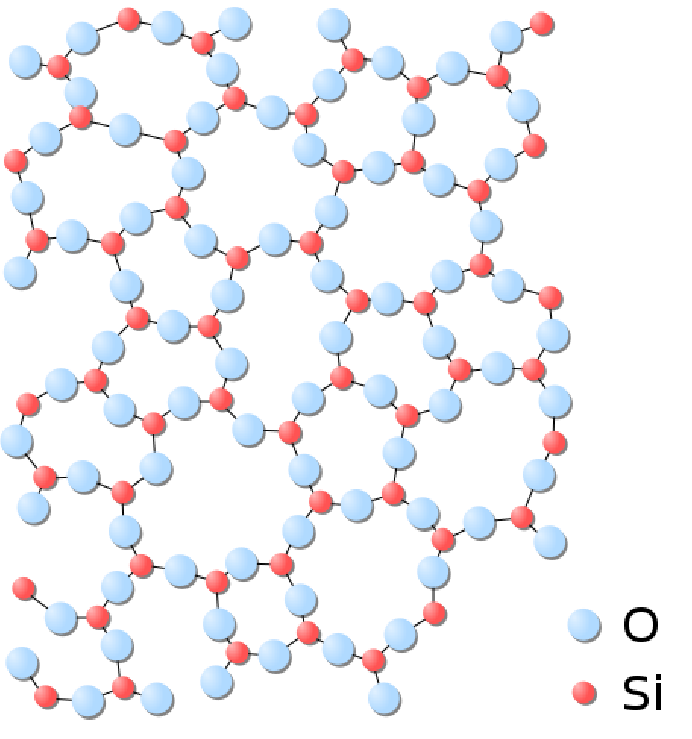
CRYSTALLIZATION

Very slow cooling rate: crystallization to the same composition

Slightly faster: fractional crystallization

Very fast (quenched): no time for crystallization, glass forms

A glass is a non-crystalline (amorphous) solid, such as glassy silica



METALLIC GLASSES

amorphous metallic alloys

small samples often produced by rapid cooling (millions of degrees a second) of molten metal, e.g., by melt spinning

bulk metallic glasses (**BMG**), 1990s, often formed from alloys with much lower critical cooling rates. These alloys contain many elements (Fe, Ti, Cu, Mg, Pd, etc.), thus "frustrating" the elements in their ability to form an ordered lattice.

properties:

- better wear/corrosion resistance (no grain boundaries)
- lower thermal conductivity (low phonon mean free path)
- higher strength (no line defects, no grain boundaries)
- easy processing (they soften and flow with heating)

e.g., $Ti_{40}Cu_{36}Pd_{14}Zr_{10}$, believed to be noncarcinogenic, is about 3 times stronger than titanium → potential artificial bone

BINARY SOLID SOLUTIONS WITH THERMAL MAX/MIN

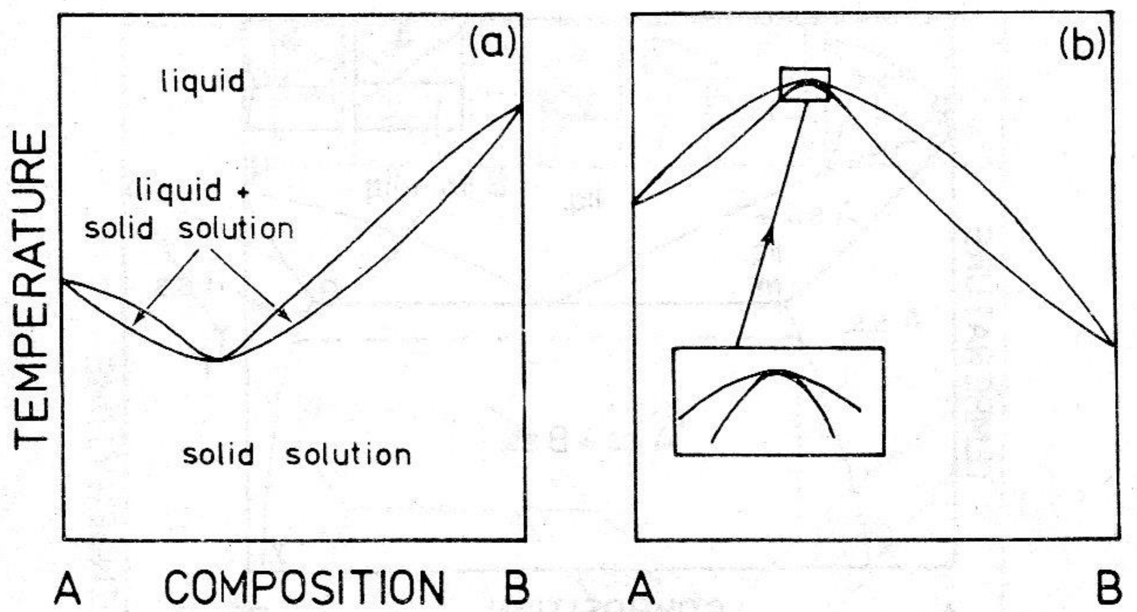


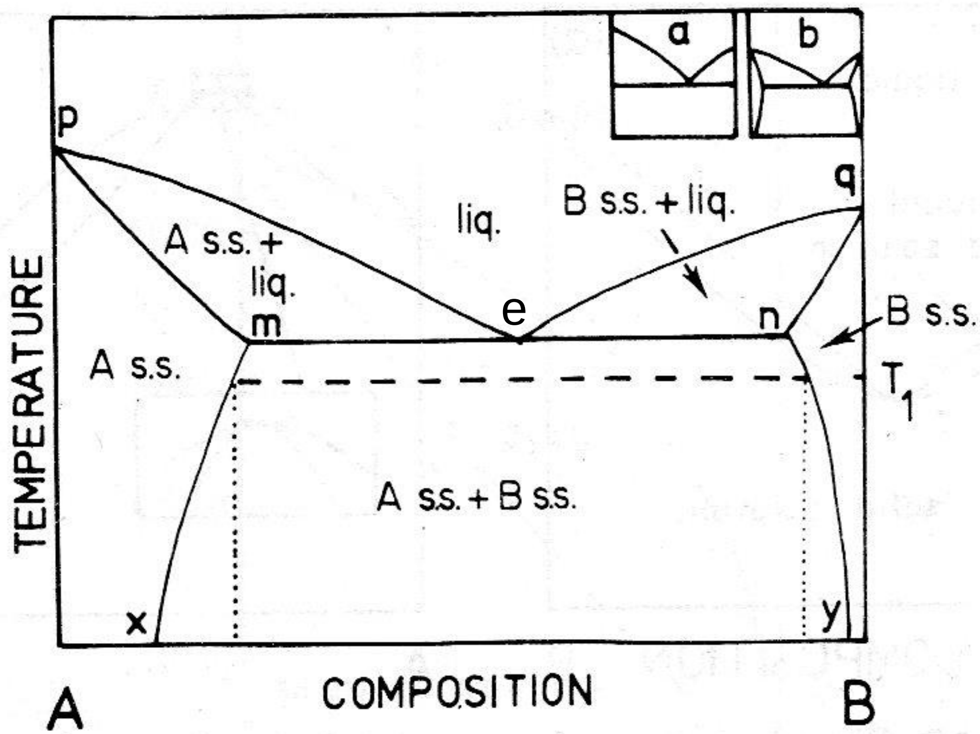
Fig. 11.13 Binary solid solutions with (a) thermal minima and (b) thermal maxima in the liquidus and solidus curves

Indifferent point (P = 2, F = 1), NOT invariant point

There are NEVER three phases.

BINARY EUTECTIC WITH PARTIAL SOLID SOLUTION

very commonly crystalline phases have only partial solubility in each other (immiscible solid solutions)

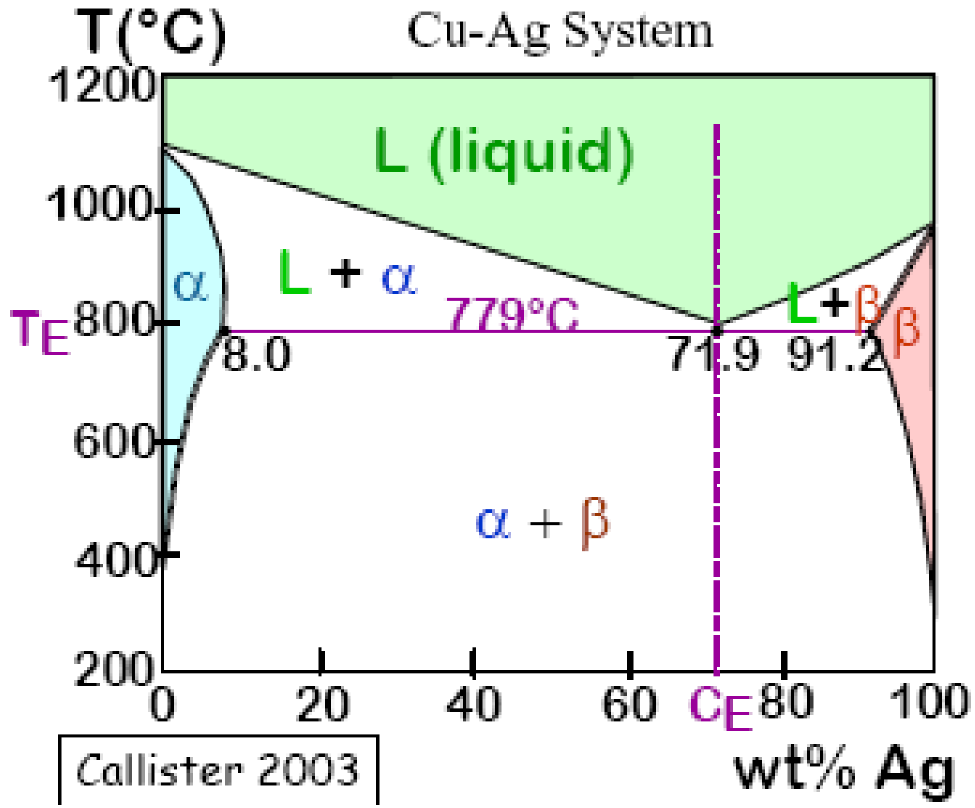


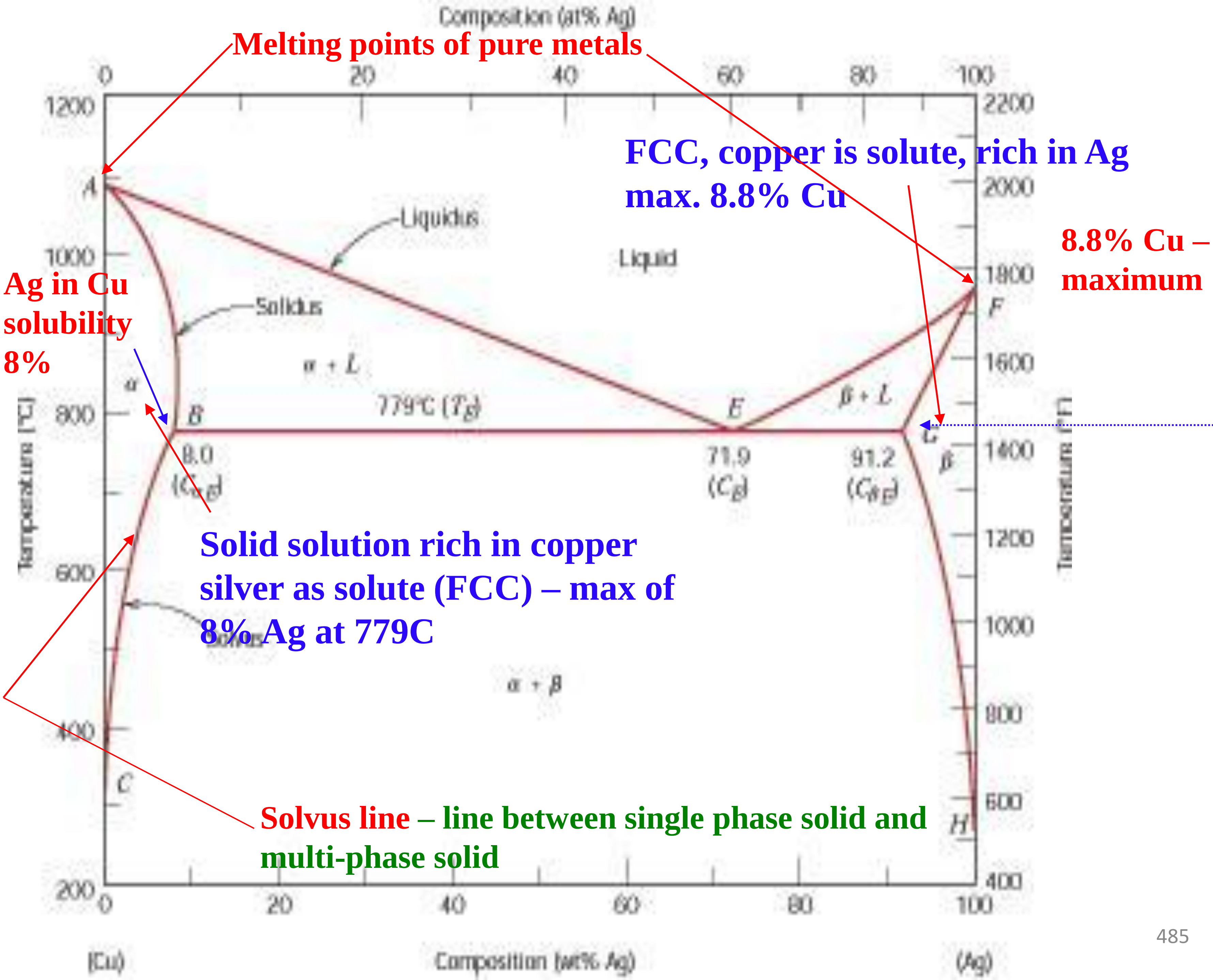
- **3 two phase regions**
- **3 one phase regions**
- **one invariant point**
- **compositional range of the two s.s. depends on temperature**
- **usually, the maximum solubility of B in A (and vice versa) occurs at solidus temp**

EXAMPLE OF PARTIAL SOLID SOLUTION EUTECTIC

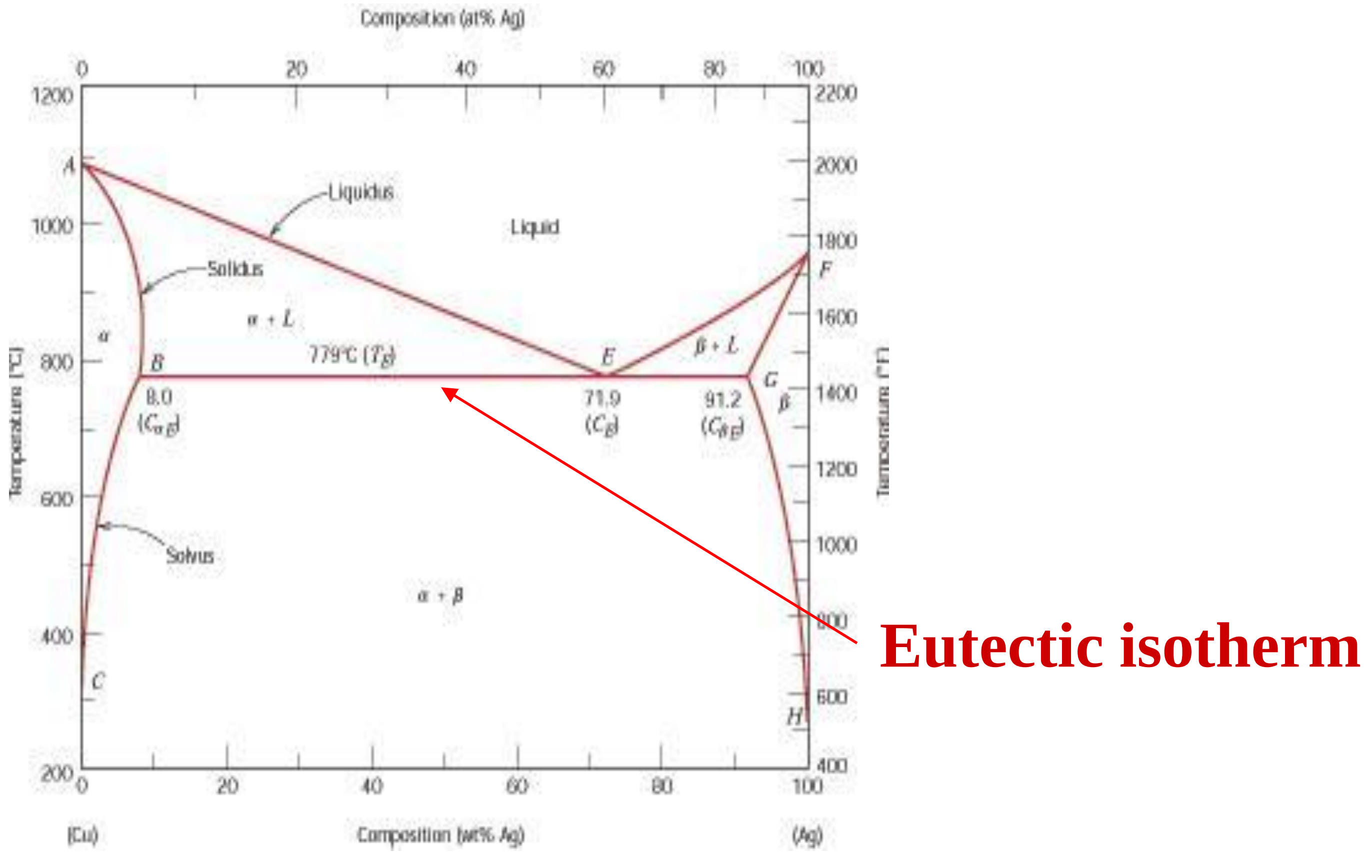
α: Cu containing fraction of Ag

β: Ag containing fraction of Cu




Composition (at% Ag)
Melting points of pure metals
0
20
40
60
80
100
1200
2200
A
FCC, copper is solute, rich in Ag
max. 8.8% Cu
2000
Liquidus
8.8% Cu –
maximum
1000
Liquid
1800
Ag in Cu
solubility
8%
Solidus
F
α + L
1600
α
β + L
800
B
779°C (TE)
E
G
8.0
(CαE)
71.9
(CE)
91.2
(CβE)
1400
β
Temperature (°C)
Temperature (°F)
1200
Solid solution rich in copper
silver as solute (FCC) – max of
8% Ag at 779C
600
1000
Solvus
α + β
800
400
C
600
Solvus line – line between single phase solid and
multi-phase solid
H
200
400
0
20
40
60
80
100
(Cu)
Composition (wt% Ag)
(Ag)

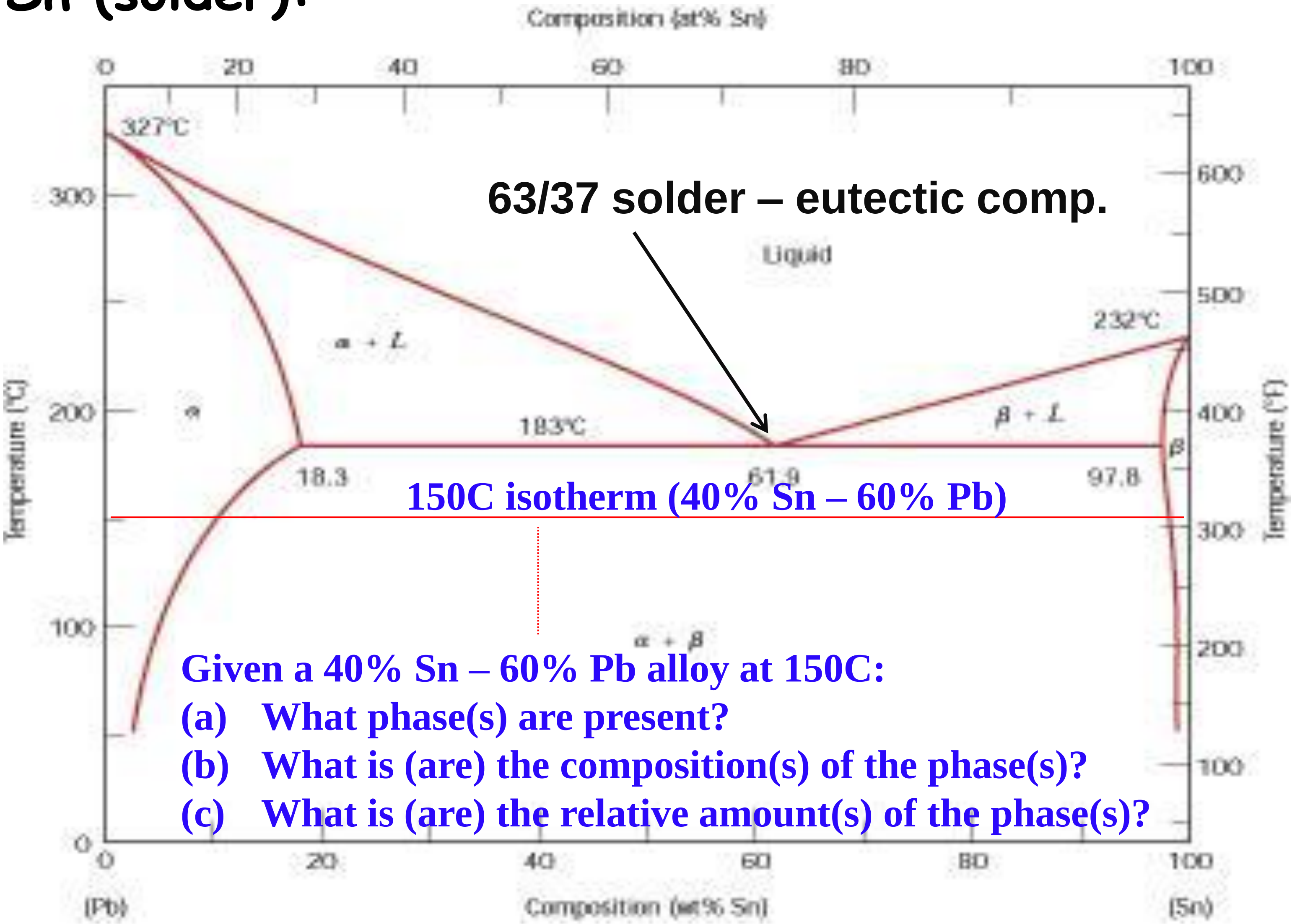
Eutectic isotherm



Eutectic reaction:

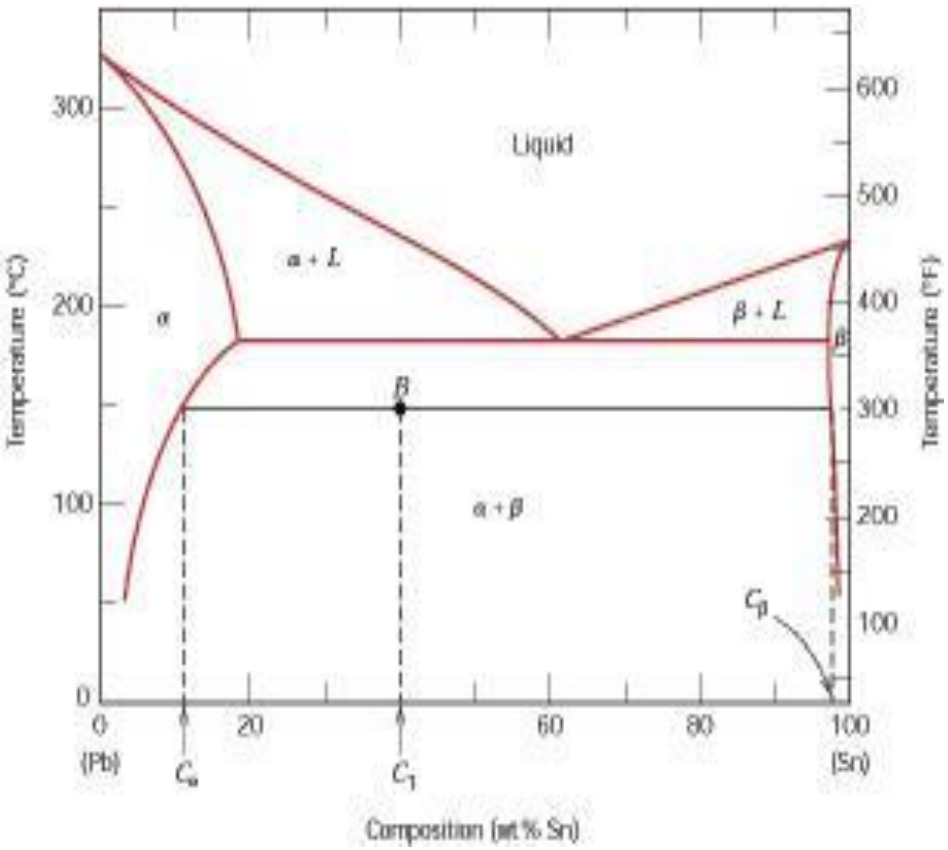
$$\text{Liq. E } (71.9\%\ Ag) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha\ (8.0\%\ Ag) + \beta\ (91.2\%\ Ag)$$

Pb-Sn (solder):



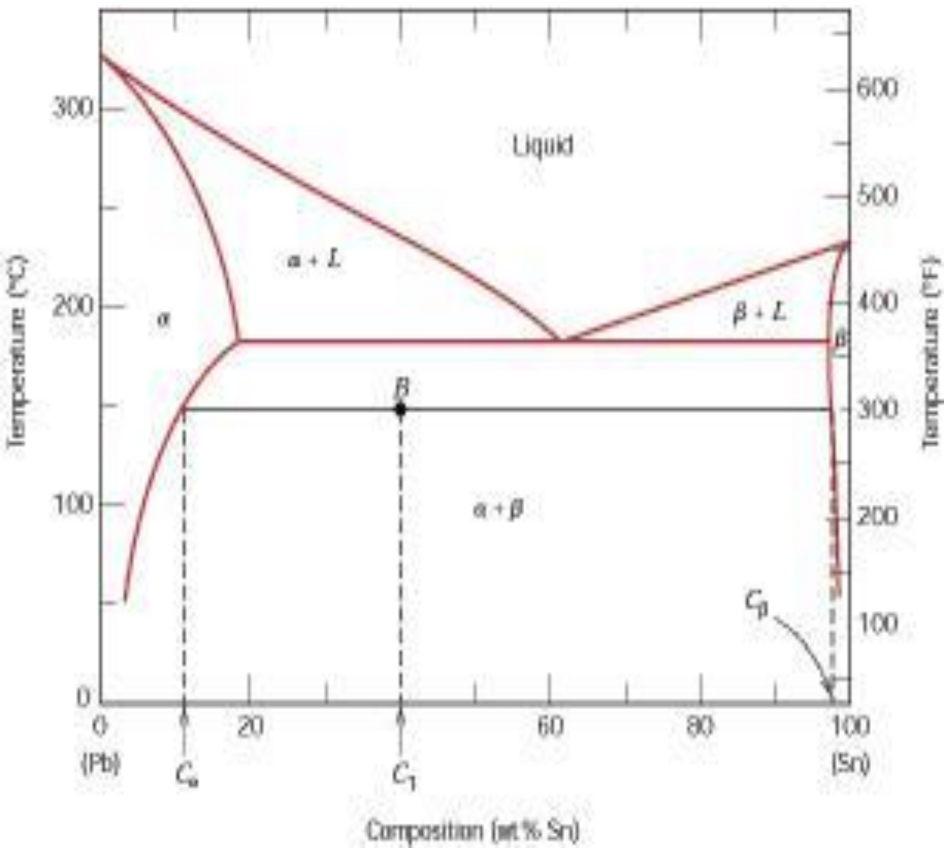
use tie line and Lever Rule!

composition of the two phases: use tie line



- 40% Sn – 60% Pb alloy at 150^{0}C
- Phases present
    - Temperature – composition point in α + β region (α and β will coexist)
    - C_α (10% Sn – 90% Pb)
    - C_β (98% Sn – 2% Pb)

phase composition: use Lever Rule

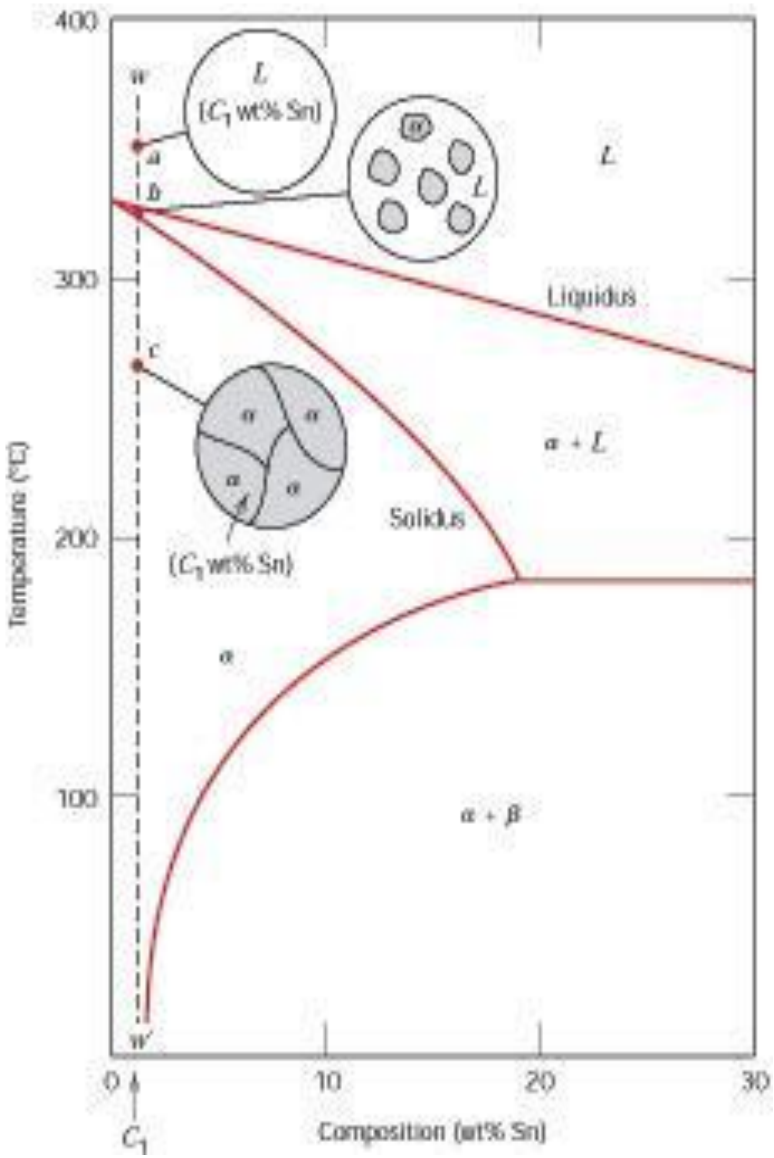


Relative amounts of each phase (weight)

$$W_\alpha = \frac{C_\beta - C_1}{C_\beta - C_\alpha} = \frac{98-40}{98-10} = 0.66$$

$$W_\beta = \frac{C_1 - C_\alpha}{C_\beta - C_\alpha} = \frac{40-10}{98-10} = 0.34$$

MICROSTRUCTURAL CHANGES IN BINARY EUTECTICS



Pure element to maximum solubility at room temperature

Cooling composition C_1:

Alloy is liquid until it passes through liquidus at b: α-phase begins to form

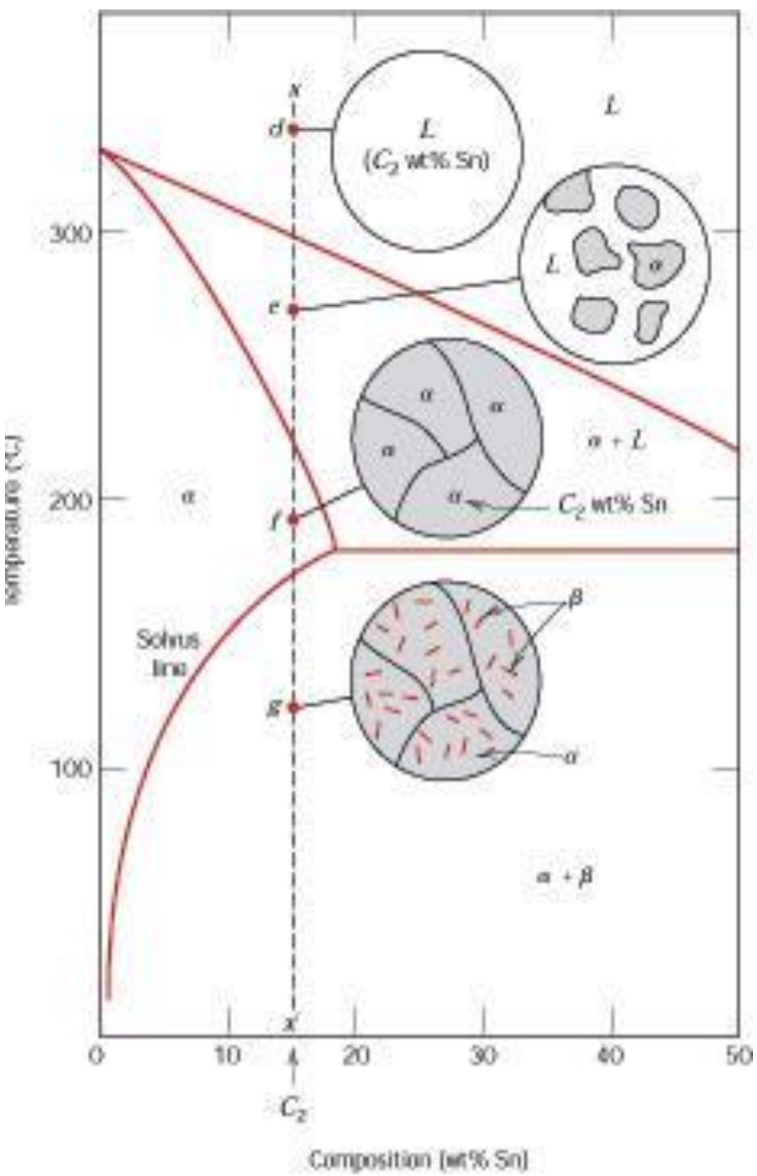
More α is formed while passing through α+L region – compositional differences dictated by tie lines and boundaries

All liquid crystallizes to α-phase with C_1

Results in polycrystalline solid with uniform composition

Note crystal maintains α-structure all the way to room temperatures (at equilibrium).

MICROSTRUCTURAL CHANGES IN BINARY EUTECTICS



Composition range between room temperature max solubility and max. solid solubility at eutectic temperature

Cooling composition C_2:

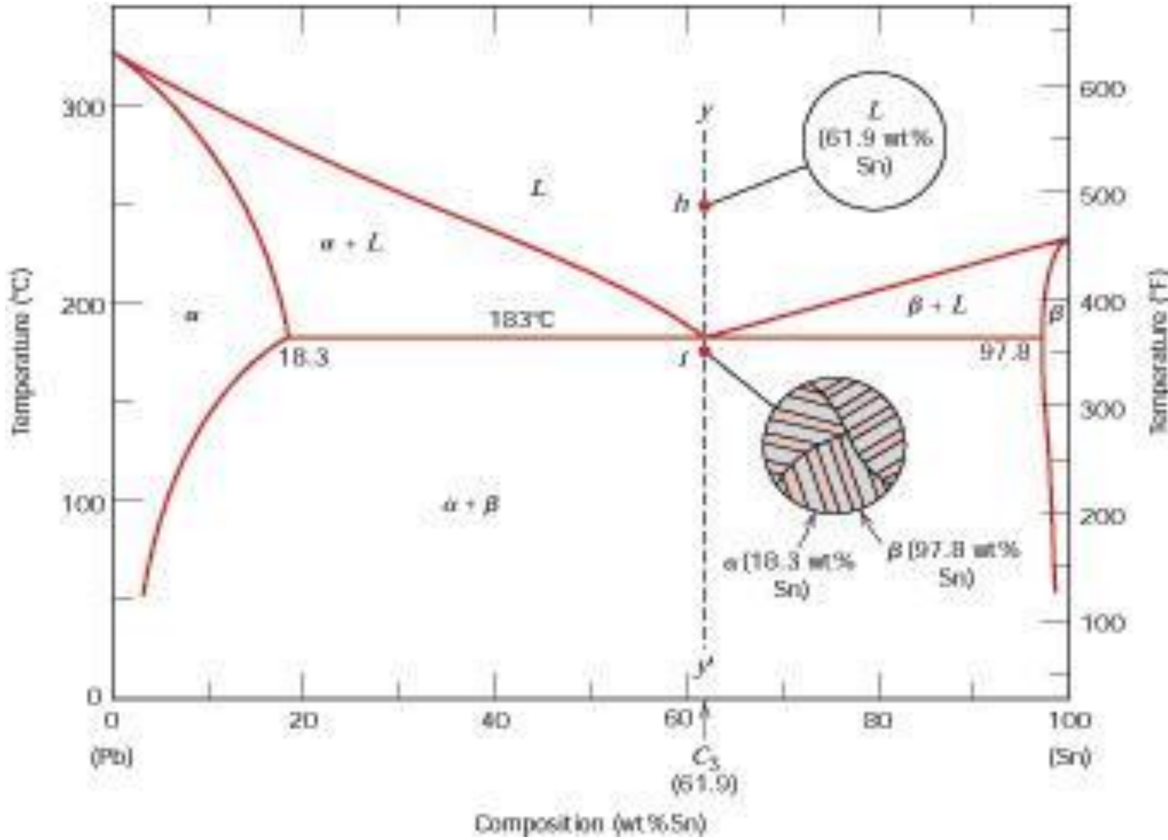
Changes are similar to previous case as we move to solvus line

Just above solvus line, at point f, microstructure consists of grains with composition C_2

Upon crossing the solvus line, the α-solid solubility is exceeded → formation of β-phase particles

With continued cooling, β particles will continue to grow in size because the mass fraction of β increases slightly with decreasing temperature

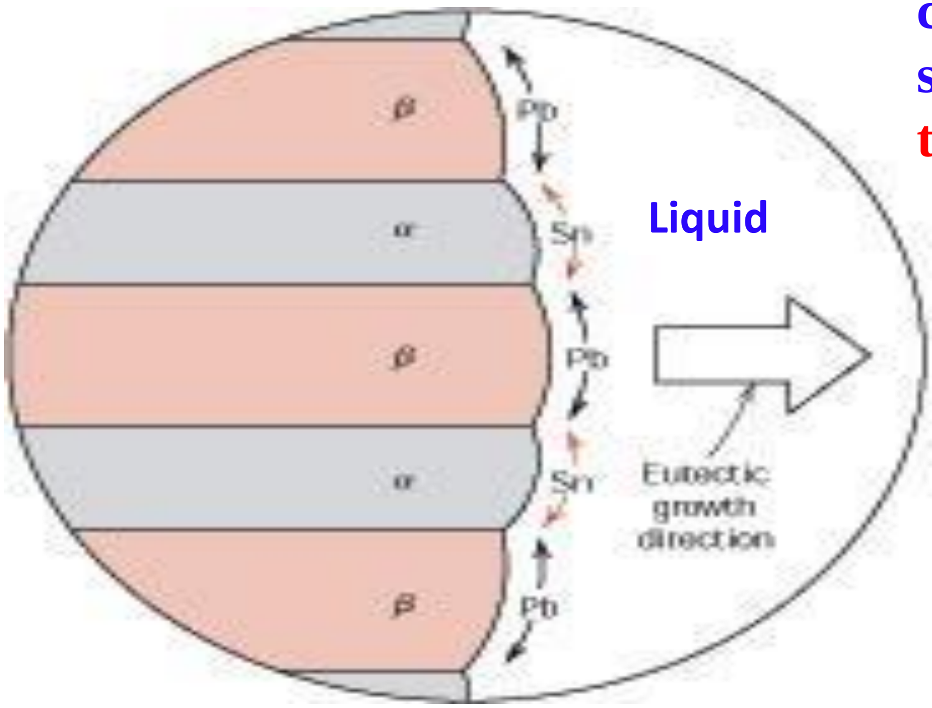
EUTECTIC MICROSTRUCTURES



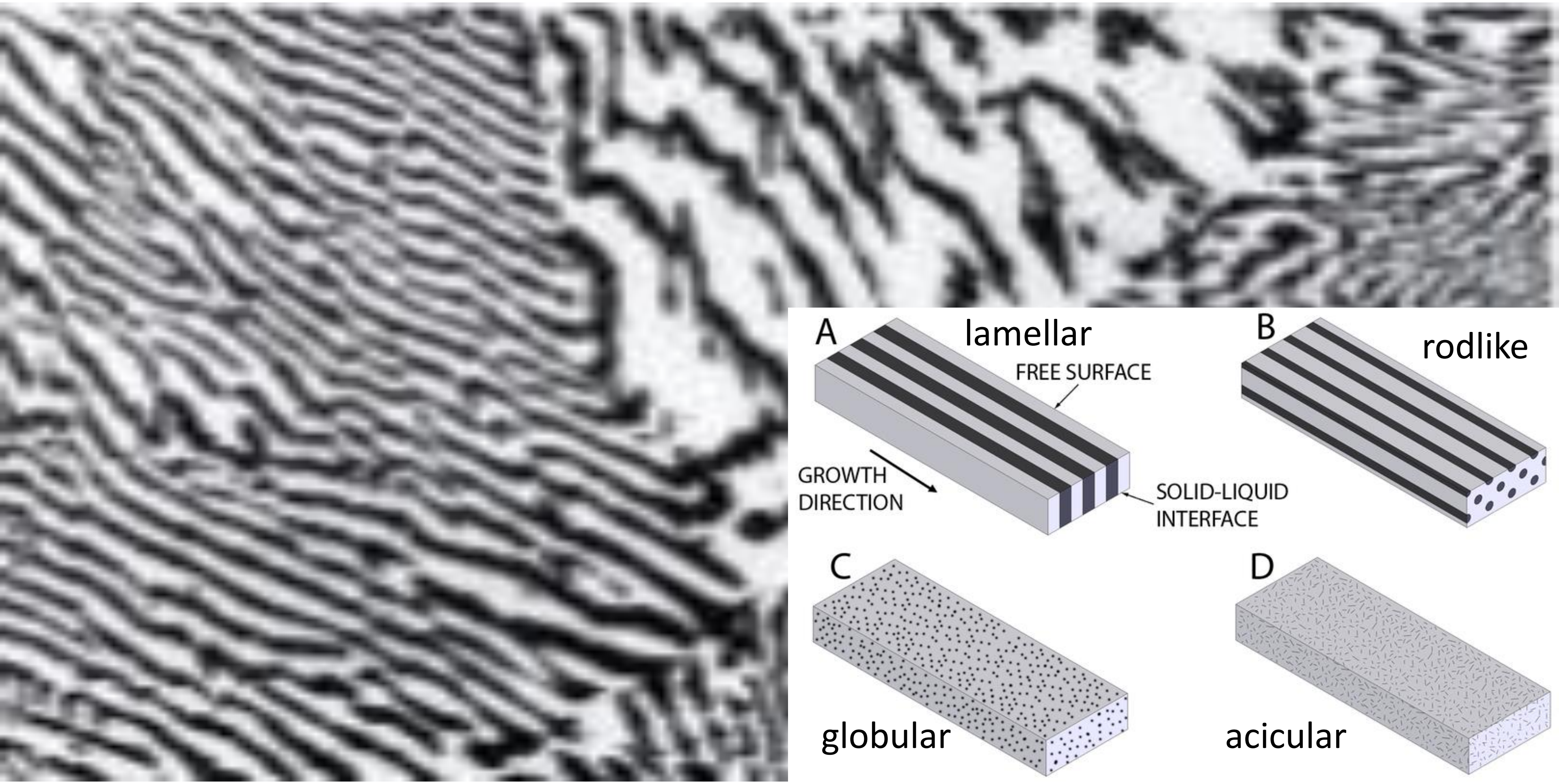
Solidification of eutectic composition:

L (61.9% Sn) ⇆ α (18.3% Sn) + β (97.8% Sn) – redistribution of tin and lead at eutectic temperature

Redistribution is accomplished by diffusion – microstructure is lamellae or columnar structure. This lamellae/columnar configuration: atomic diffusion of lead and tin need only occur over relatively short distances

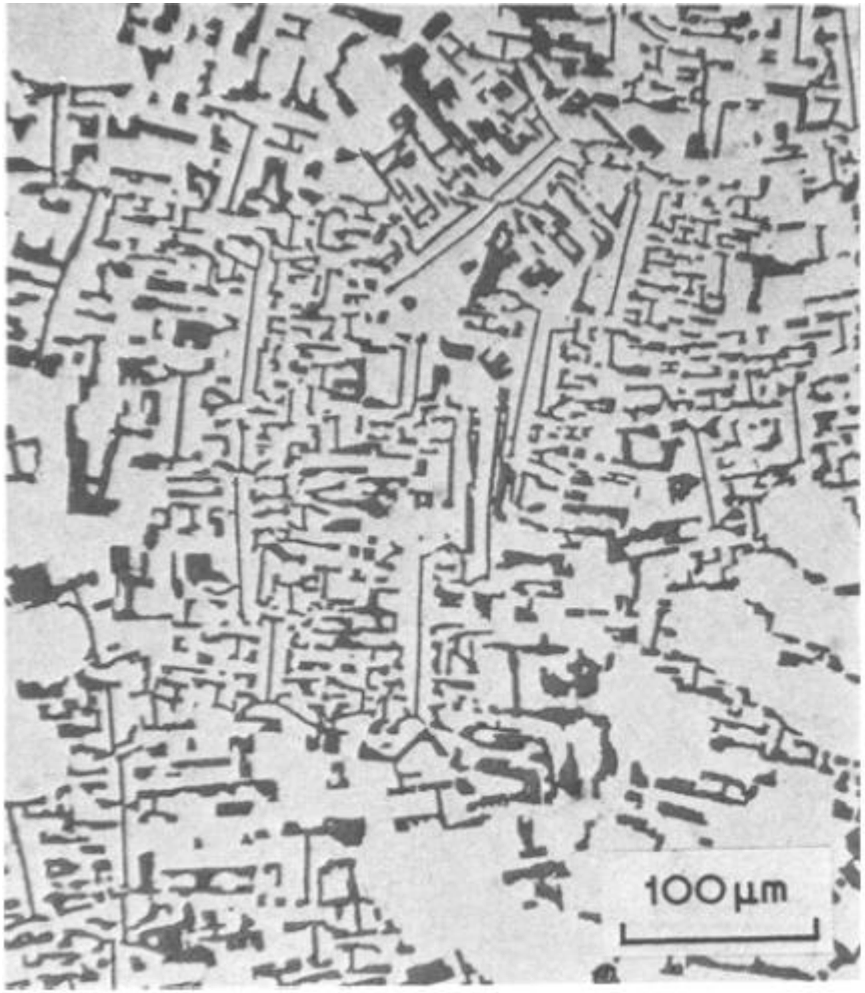


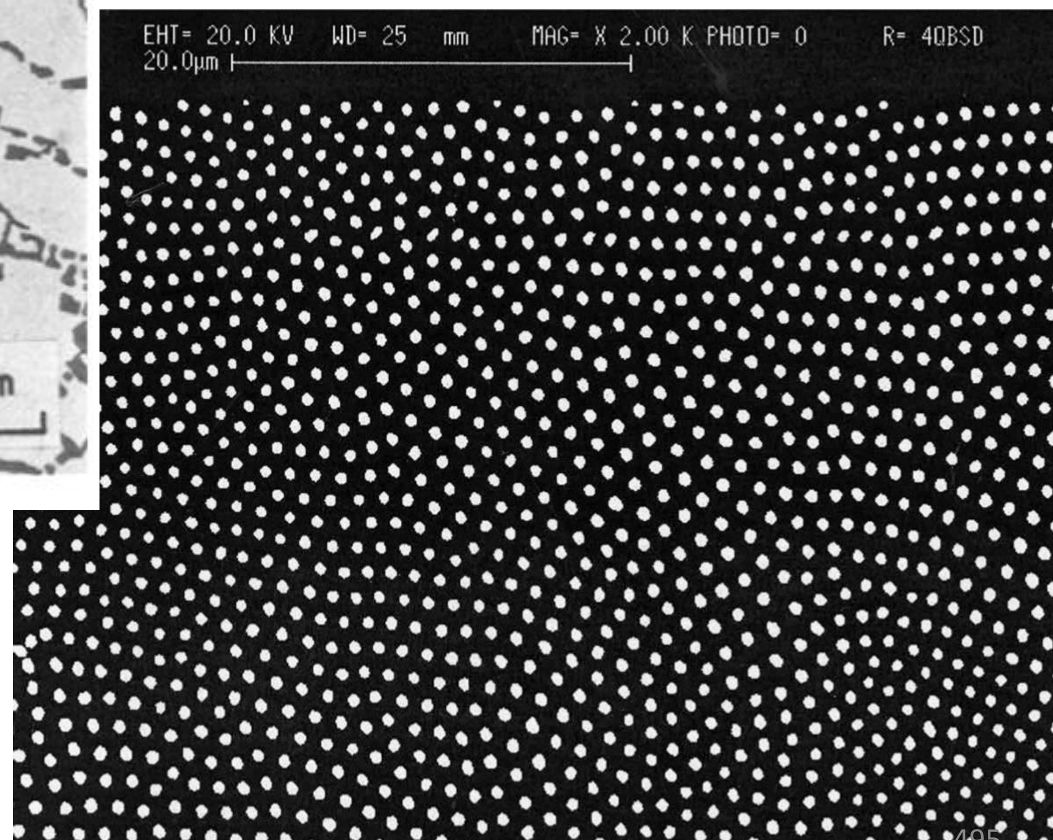
During the eutectic transformation from liquid to solid (α + β), a redistribution of and tin is necessary because and α and β have different compositions, neither of which is the same as the liquid. Redistribution is through diffusion.

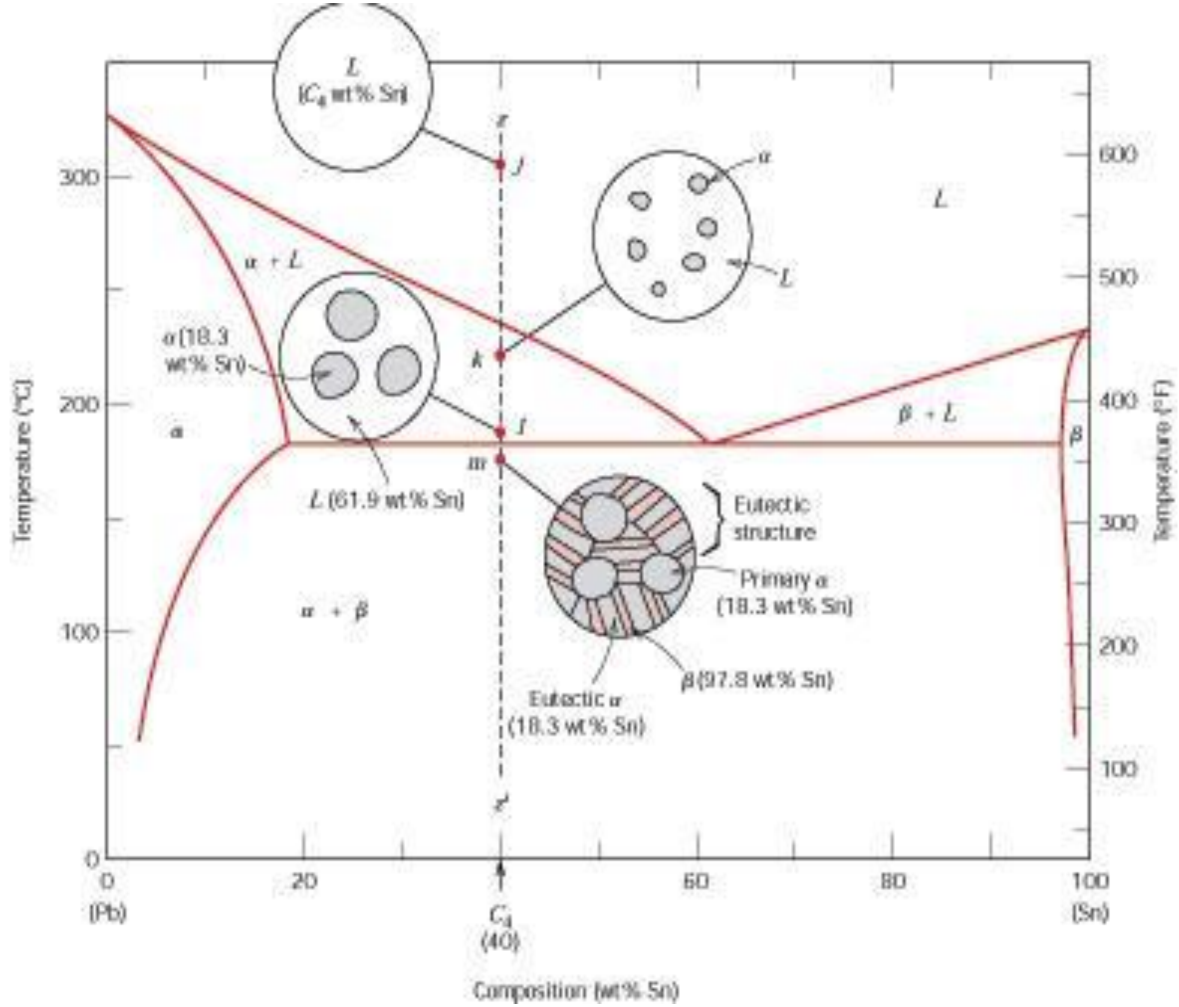


Each eutectic alloy has its own characteristic microstructure

spheroidal, nodular, or globular; acicular (needles) or rod; and lamellar (platelets, Chinese script or dendritic, or filigreed)

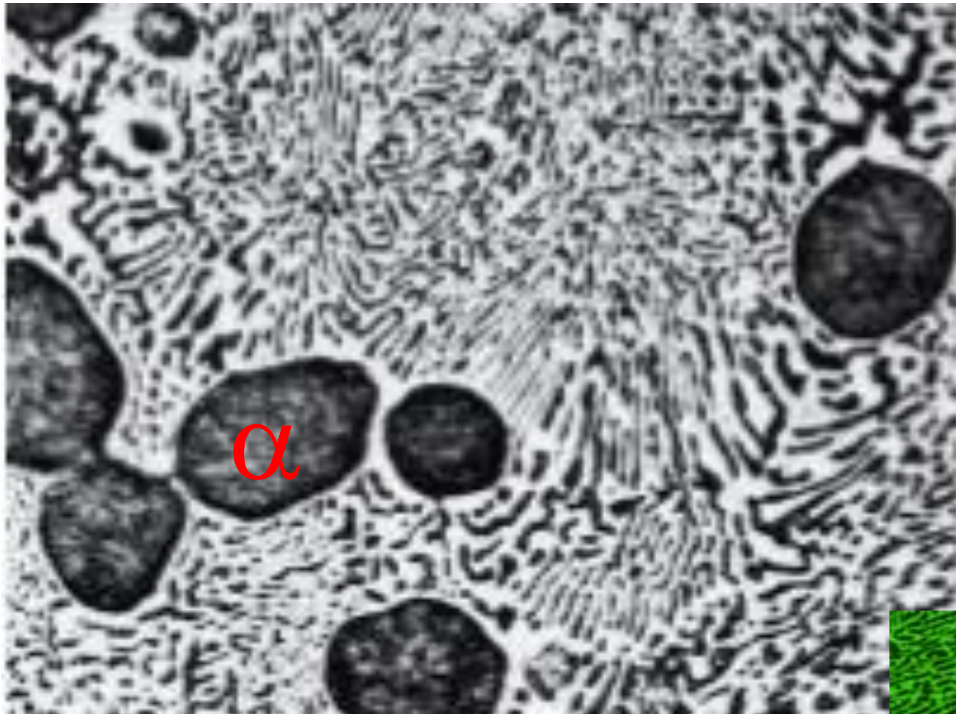

100 µm


EHT= 20.0 KV WD= 25 mm MAG= X 2.00 K PHOTO= 0 R= 4QBSD
20.0µm

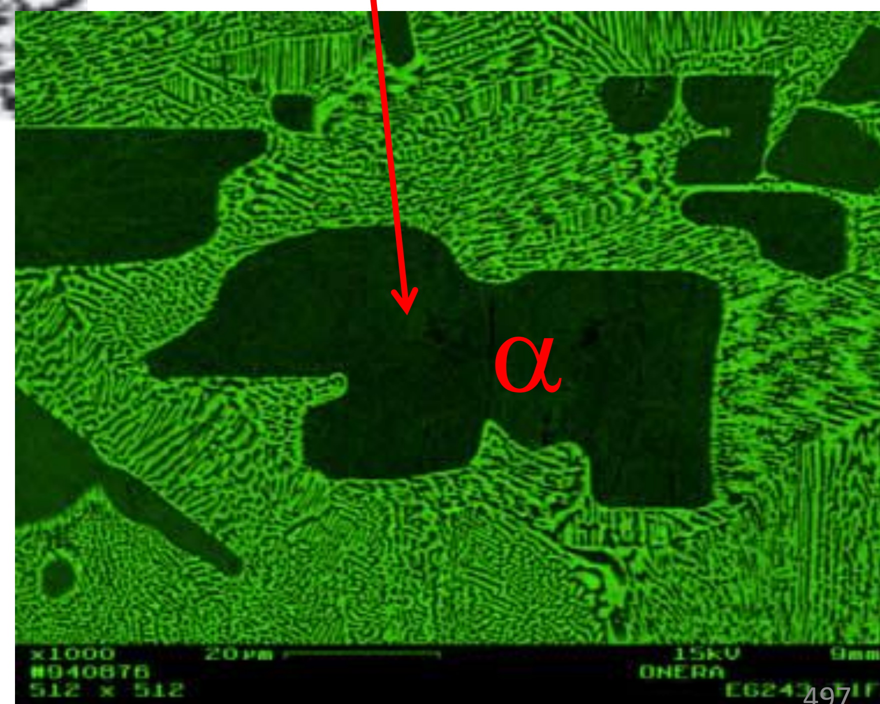


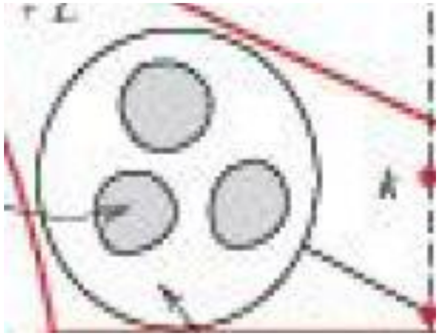
Compositions other than eutectic that, when cooled, cross the eutectic point

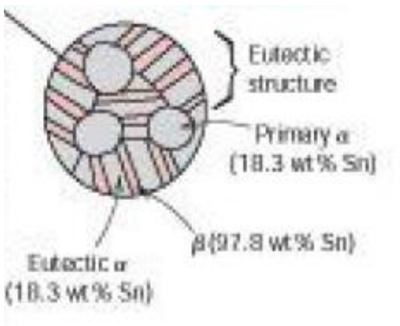
As eutectic temperature line is crossed, liquid phase, which is of the eutectic composition, will transform to eutectic structure (often lamellae)

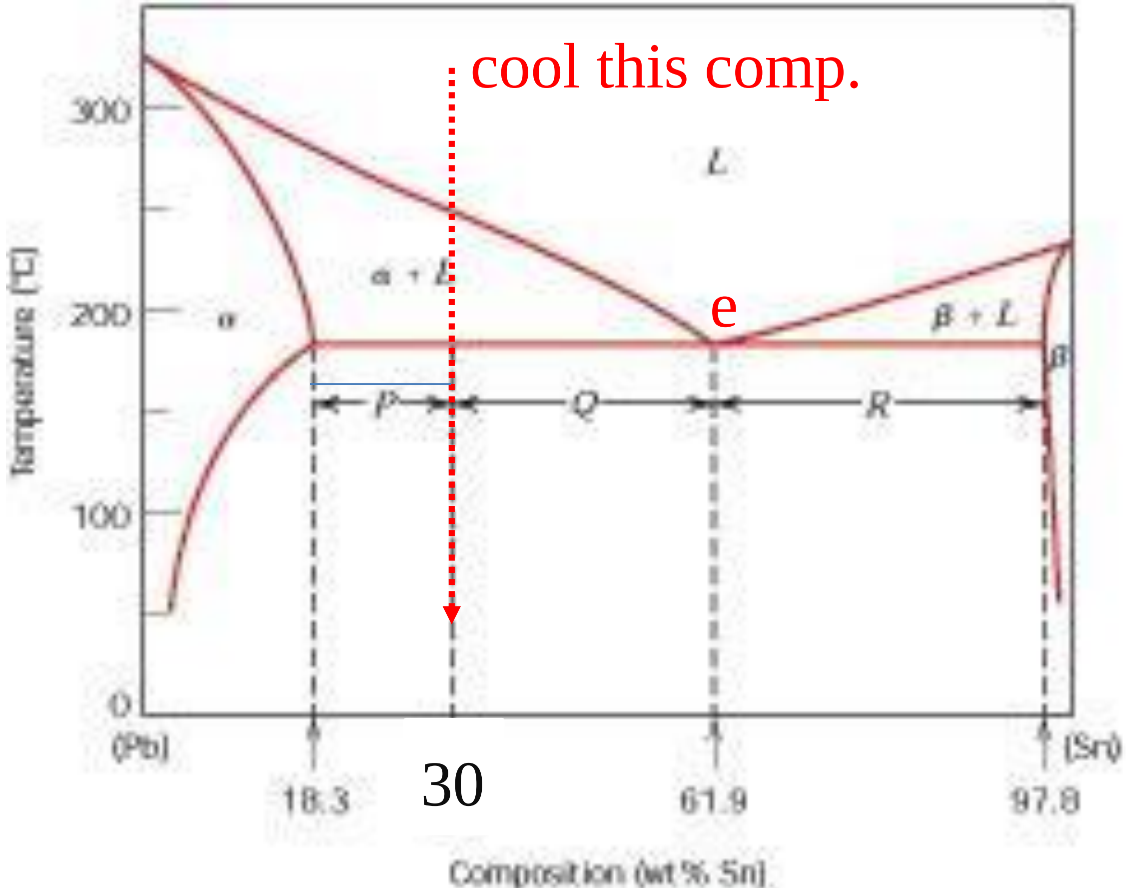


Anteater inclusion









Relative amounts of microconstituents just below solidus:

Primary microconstitutent, $f_{\alpha'}$ = Q/(p + Q) = (61.9 – 30)/(61.9 – 18.3) = 73% is primary alpha

Eutectic microconstituent, f_e = same as liquid phase from which it was transformed, f_e

f_e = p/(p + Q) = (30 – 18.3)/(61.9 – 18.3) = 27% is liquid

The eutectic liquid fractionates into alpha and beta solid solutions:

f_α = R/(p + Q + R) = (97.8 – 61.9)/(97.8 – 18.3) = 45% alpha

Total α = 73% + 27% × 0.45 = 85% ; 73% is primary α, 12% is eutectic α, 15% is β

ADVANCED MATERIALS

DOI: 10.1002/adma.200700726

Well-Aligned Nanocylinder Formation in Phase-Separated Metal-Silicide–Silicon and Metal-Germanide–Germanium Systems

By *Nobuhiro Yasui*, *Ryoko Horie*, *Yoshihiro Ohashi*, *Koichi Tanji*, and *Tohru Den**

Table 1. List of the examined materials and their eutectic temperatures

Materials [silicide]	Eutectic Temperature [°C]	Materials [germanide]	Eutectic Temperature [°C]
Al-Si [11,18]	577	Al-Ge [12, 18]	420
Cu_3Si-Si [18]	802	Cu_3Ge-Ge [18]	644
Pd_2Si-Si [19]	825	Ag-Ge [18]	651
$NiSi_2$-Si [20]	960	$Mn_{11}Ge_8$-Ge [28]	720
PtSi-Si [18]	979	PdGe-Ge [18]	725
RhSi-Si [21]	1060	NiGe-Ge [18]	762
$Mn_{11}Si_{19}$-Si [18]	1142	$PtGe_2$-Ge [18]	802
$FeSi_2$-Si [18]	1207	$Co_{0.875}Ge_2$-Ge [18]	810
$IrSi_3$-Si [22]	1221	Rh_3Ge_4-Ge [18]	850
$CoSi_2$-Si [18]	1259	$Cr_{11}Ge_{19}$-Ge [18]	895
$NbSi_2$-Si [18]	1302		
$CrSi_2$-Si [18]	1305		
$TiSi_2$-Si [18]	1330		
$ZrSi_2$-Si [23]	1353		
$HfSi_2$-Si [18]	1360		
Ru_2Si_3-Si [24]	1370		
VSi_2-Si [25]	1382		
$TaSi_2$-Si [18]	1385		
$ReSi_{1.75}$-Si [26]	1380		
$MoSi_2$-Si [18]	1400		
WSi_2-Si [27]	1400		

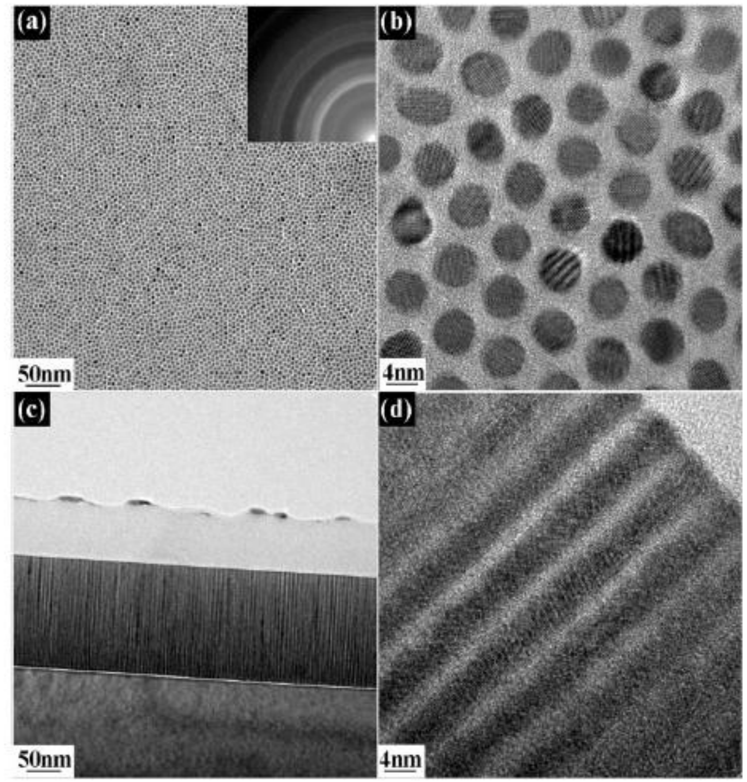


Figure 4. HRTEM images of the Pd_2Si-Si system sputtered by using deposition condition 1. a) A low-magnification image and b) high-magnification lattice image in plane view. c) A low-magnification image and d) high-magnification image in cross-sectional view.

longer time available to phase separate yields larger phase domains

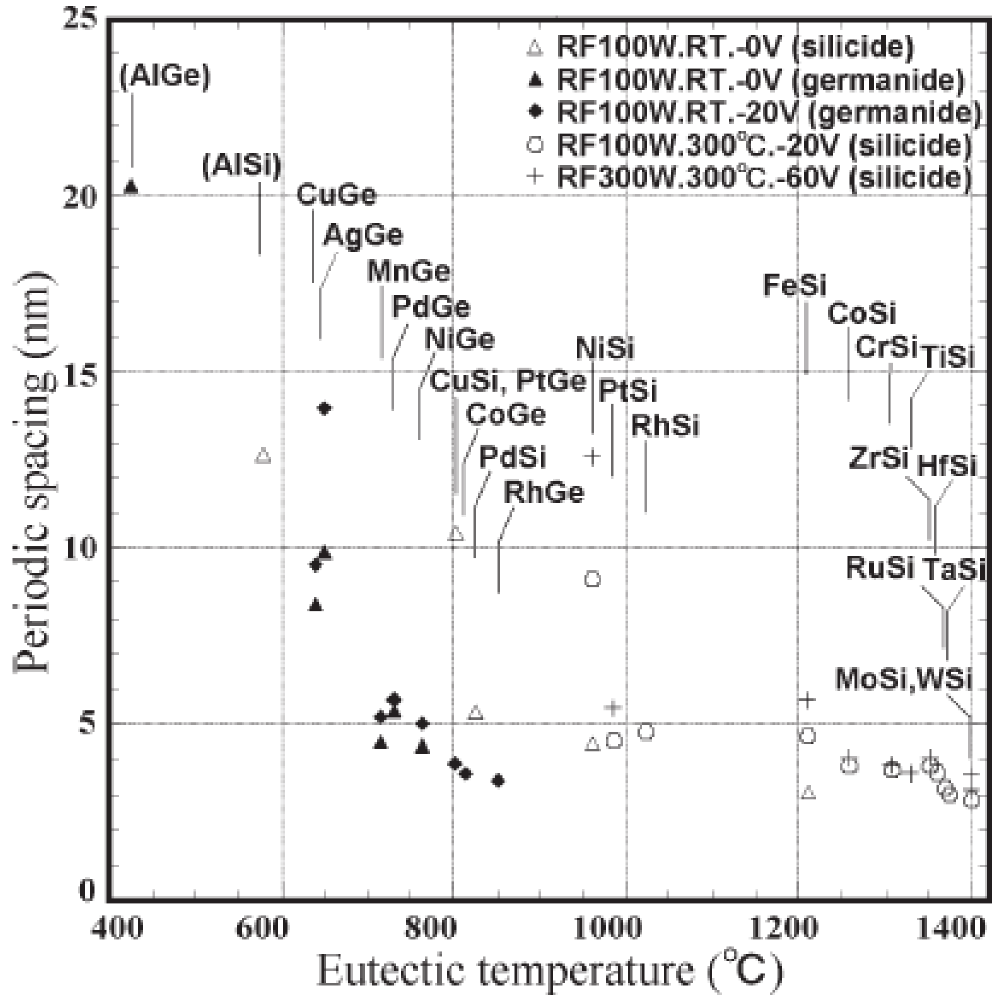


Figure 3. Plot of periodic spacing versus eutectic temperature for various phase-separated silicide and germanide systems. △ represents silicide systems deposited under condition 1; ▲ represents germanide systems deposited under condition 1; ◆ represents germanide systems deposited under condition 2; ○ represents silicide systems deposited under condition 3; + represents silicide systems deposited under condition 4.

BINARIES WITH SOLID-SOLID PHASE TRANSITIONS

in systems without solid solutions, solid-solid phase transitions are indicated by isotherms

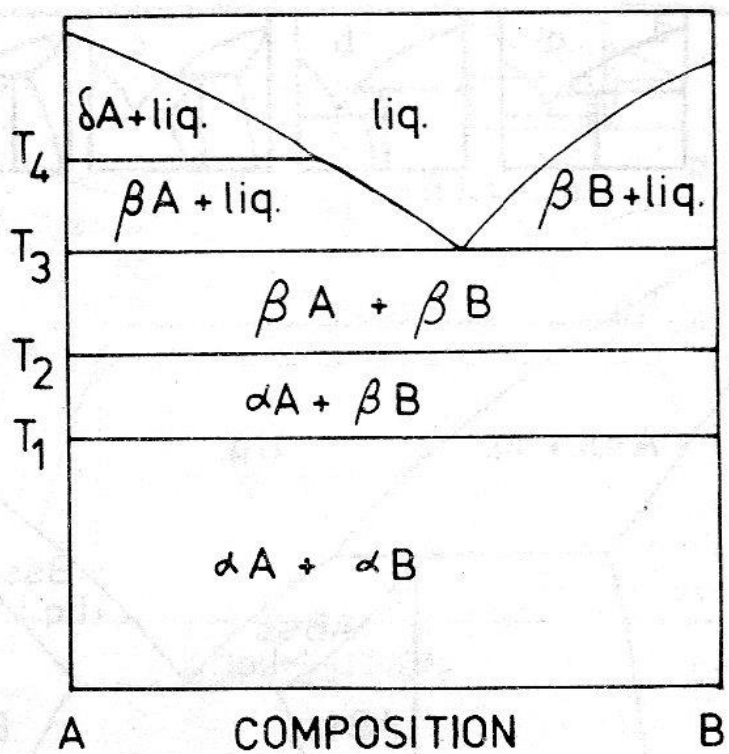


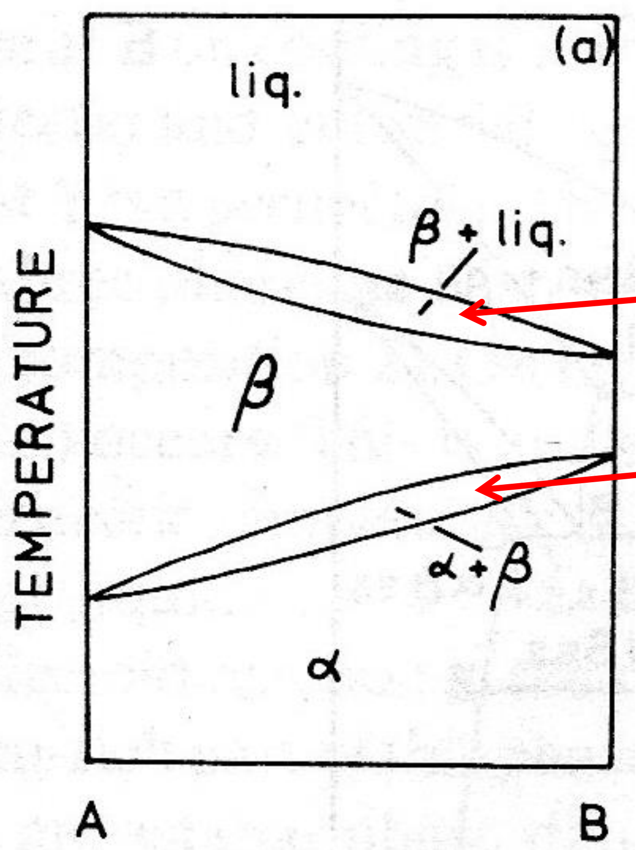
Fig. 11.17 Simple binary system with polymorphic transitions

T_1: $\alpha B \leftrightarrows \beta B$

T_2: $\alpha A \leftrightarrows \beta A$

BINARIES WITH SOLID-SOLID PHASE TRANSITIONS

in systems with complete solid solubility, the solid-solid phase transition temperature usually varies with composition



two-phase region contains one solid and one liquid phase

two-phase region contains two solid phases

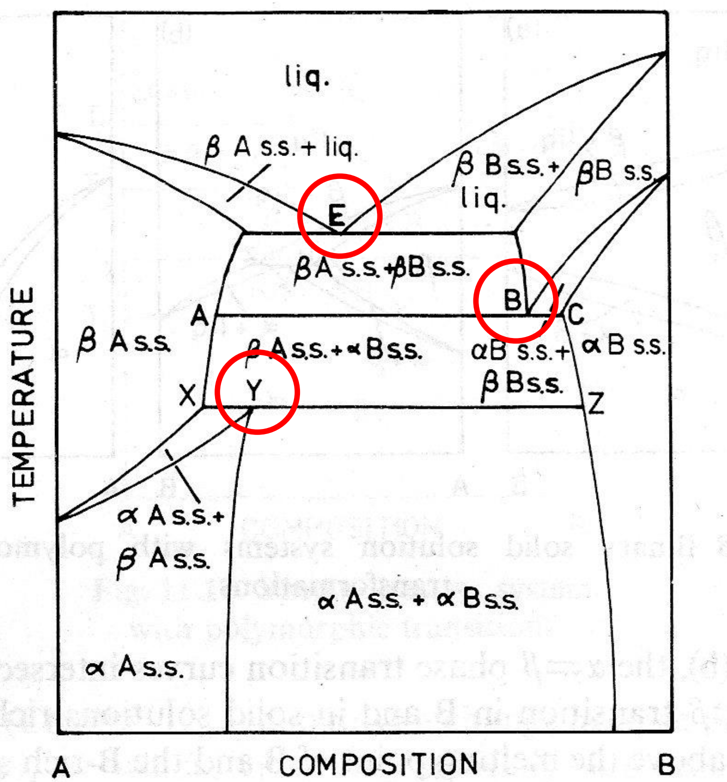
ALL SOLID INVARIANT POINTS

Eutectic point E: Liq. E → βA + βB

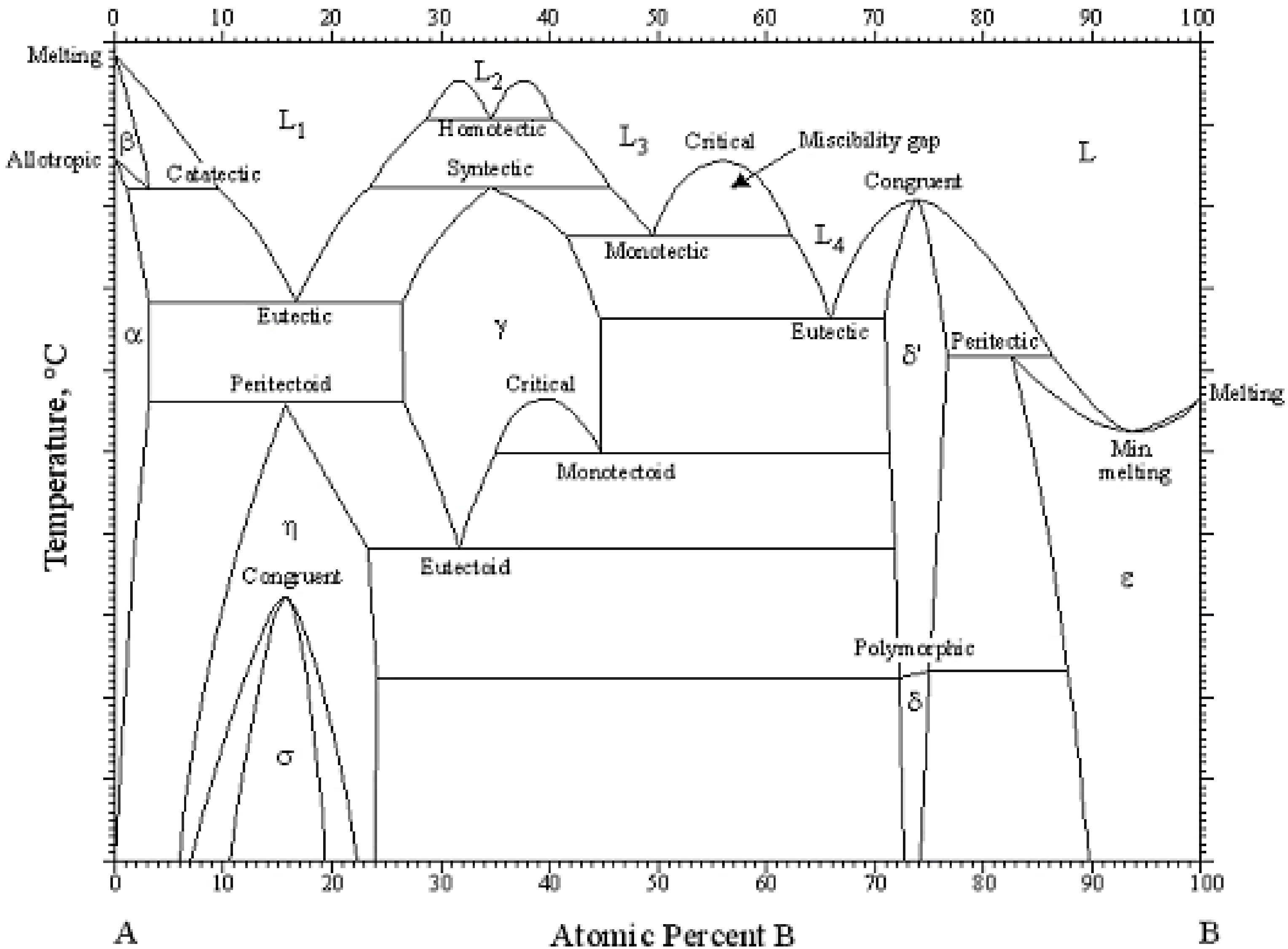
Eutectoid point B: βB → βA + αB

Peritectoid point Y: βA + αB → αA

} disproportionation reactions



BINARIES: THE BIG PICTURE



Invariant Reactions

Eutectic: $L \rightarrow \alpha\ (s) + \beta\ (s)$; e.g., Pb-Sn

Peritectic: $\alpha\ (s) + L \rightarrow \beta\ (s)$; e.g., Pb-In

Monotectic: $L_1 \rightarrow \alpha\ (s) + L_2$; e.g., Cu-Pb

Syntectic: $L_1 + L_2 \rightarrow \alpha\ (s)$; e.g., Na-Zn

Metatectic: $\beta\ (s) + \alpha\ (s) \rightarrow L_1$ e.g., U-Mn

Note: "oid" analogues of each these reactions may exist

Determination of Phase Diagrams

- Cooling Curves
- Differential Scanning Calorimetry
- Thermomechanical Analysis
- Differential Thermal Analysis
- Metallography/Petrography
- Energy Dispersive X-ray Spectroscopy
- Electron Microprobe Analyzer
- X-ray Diffraction
- Transmission Electron Microscopy

THREE-COMPONENT CONDENSED SYSTEMS

$$P + F = C + 1$$ **with C = 3**

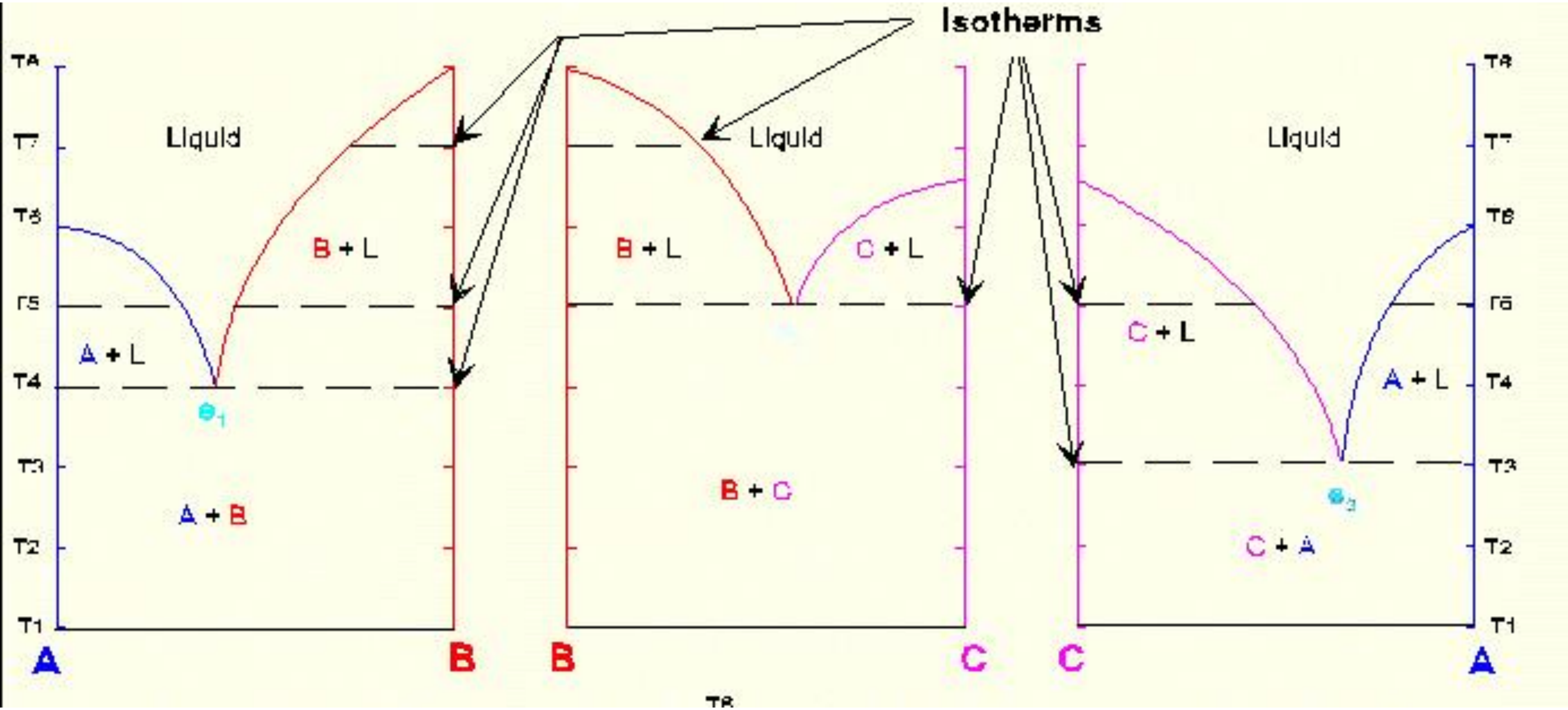
$$P + F = 4$$

If pressure is constant, three independent variables:
T & the concentrations of <u>two</u> components

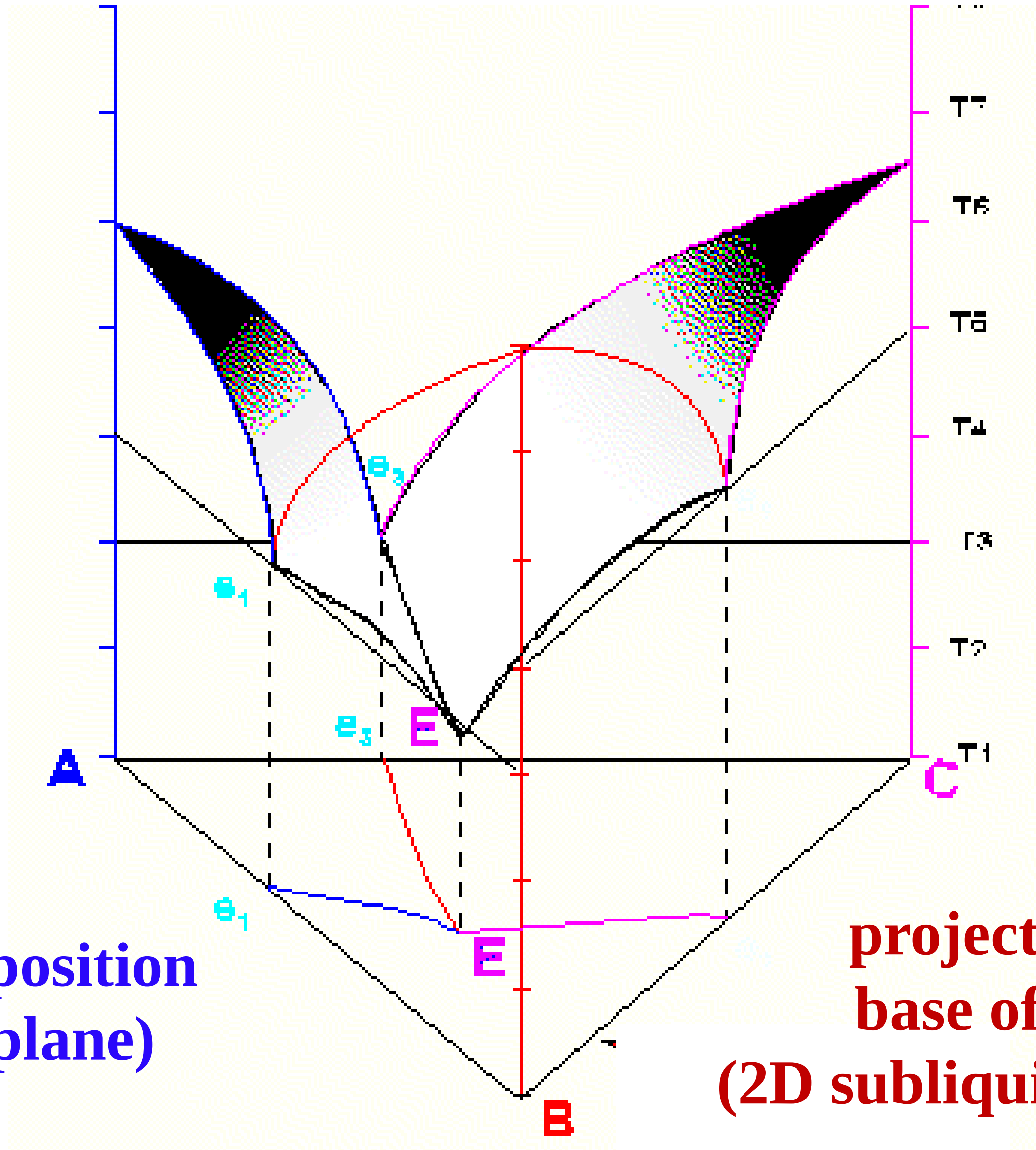
The presence of four phases: F = 0, invariant point
(usually three crystalline phases and liquid)

EUTECTIC SYSTEM WITHOUT COMPOUNDS

Take 3 simple binary eutectic systems …



… combine to form a triangular prism phase space



Temperature

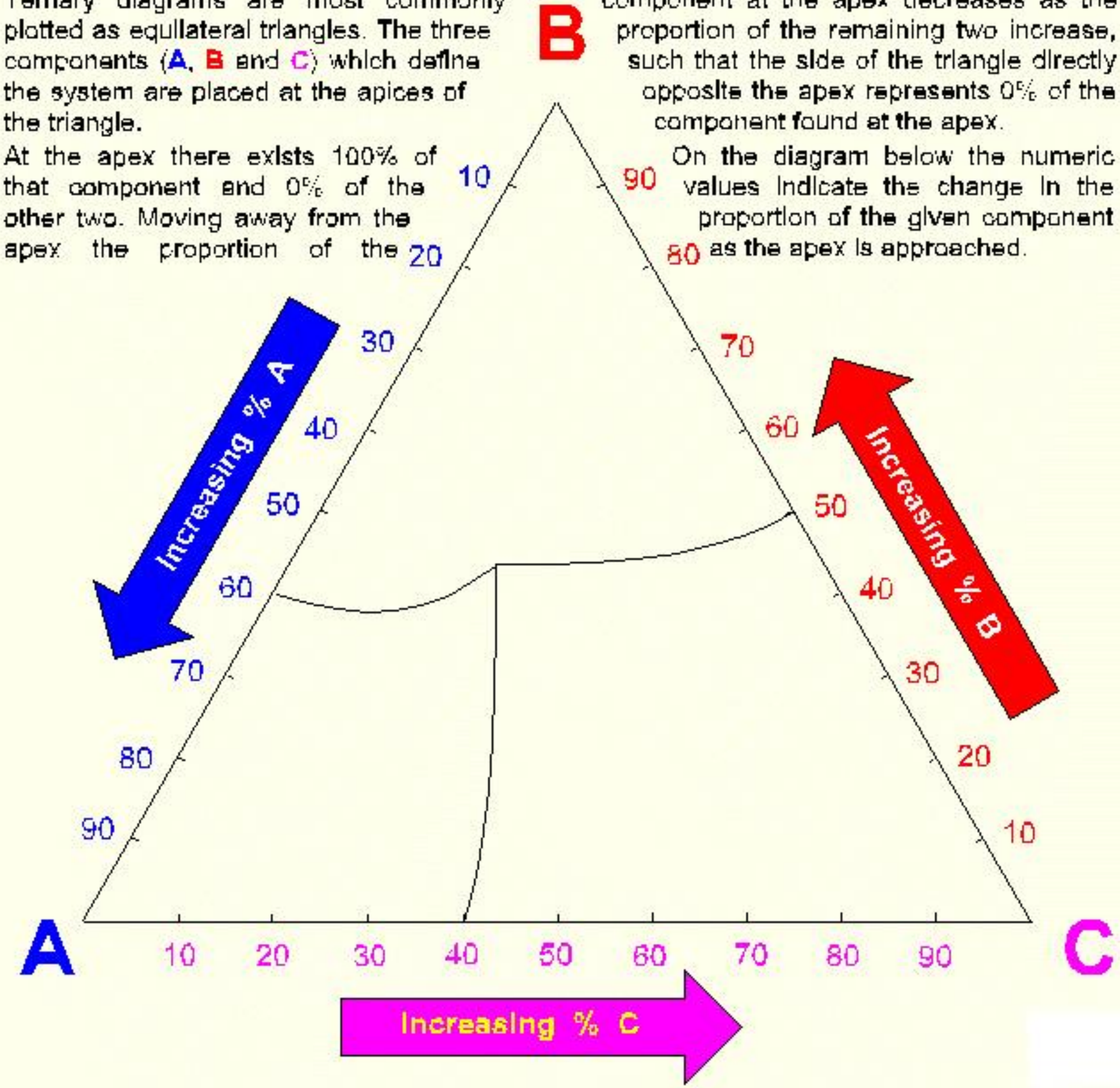
Composition
(in plane)

projection onto
base of triangle
(2D subliquidus diagram)

Ternary diagrams are most commonly plotted as equilateral triangles. The three components (A, B and C) which define the system are placed at the apices of the triangle.

At the apex there exists 100% of that component and 0% of the other two. Moving away from the apex the proportion of the component at the apex decreases as the proportion of the remaining two increase, such that the side of the triangle directly opposite the apex represents 0% of the component found at the apex.

On the diagram below the numeric values indicate the change in the proportion of the given component as the apex is approached.

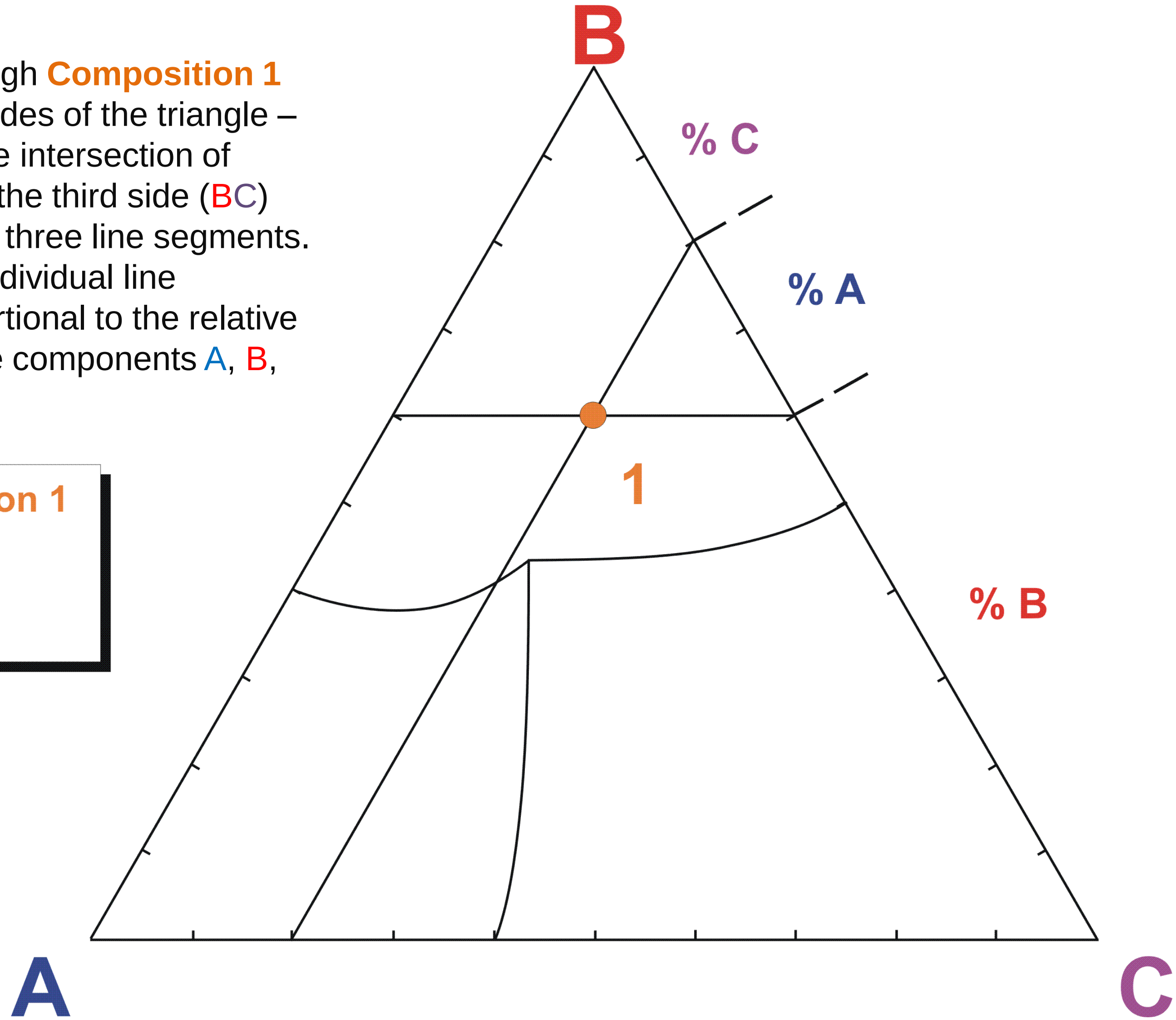


FINDING COMPOSITION ON A TERNARY DIAGRAM

Two Line Method

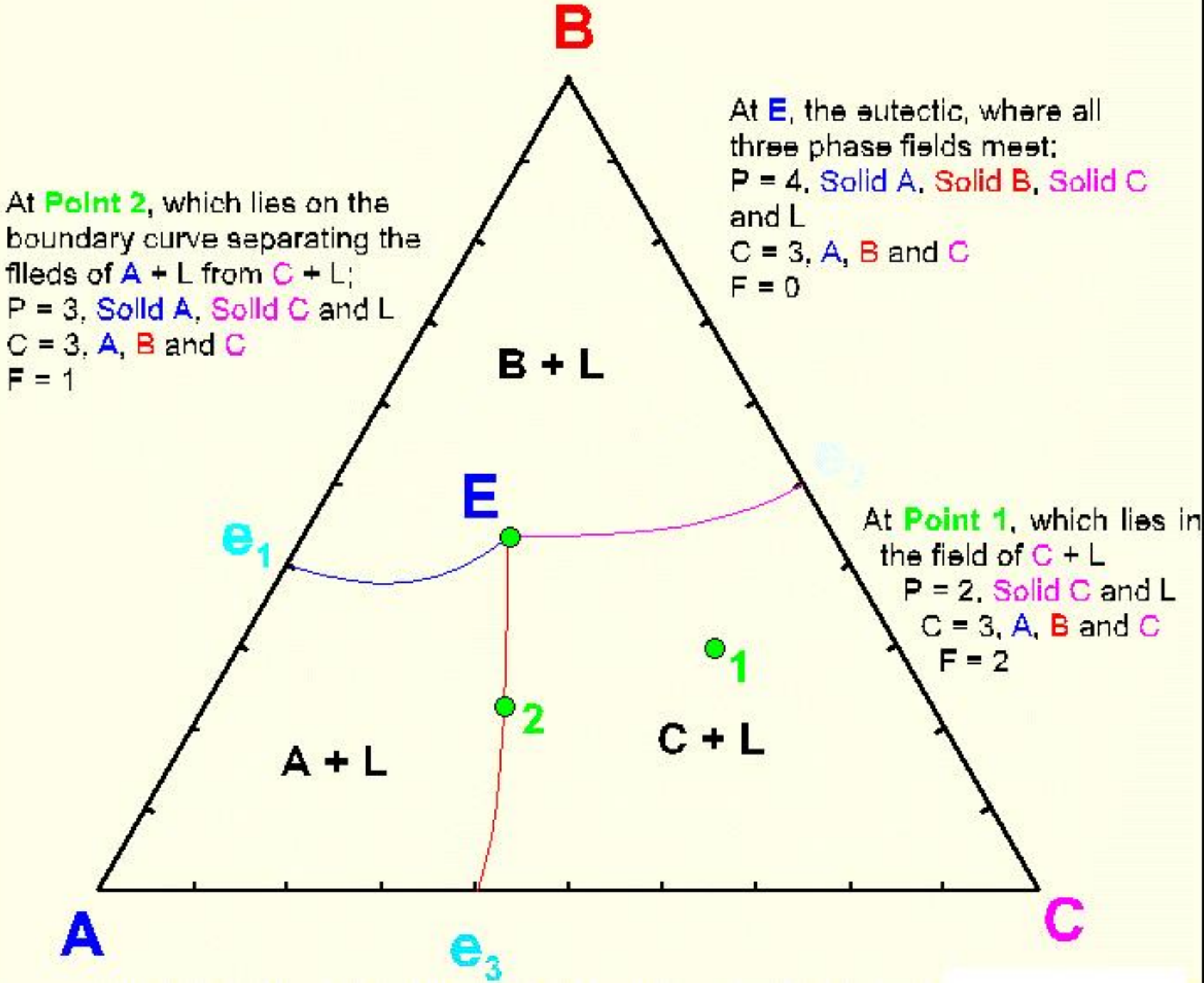
Draw two lines through **Composition 1** parallel to any two sides of the triangle – here AB and AC. The intersection of these two lines with the third side (BC) divides this side into three line segments. The lengths of the individual line segments are proportional to the relative amounts of the three components A, B, and C.

Composition 1
20% A
60% B
20% C



Phase Rule $P + F = C + 1$

subliquidus equilibria



CRYSTALLIZATION PATHWAY

For a general composition:

1) start at primary phase field
2) proceed along univariant boundary curve
3) finish at eutectic point

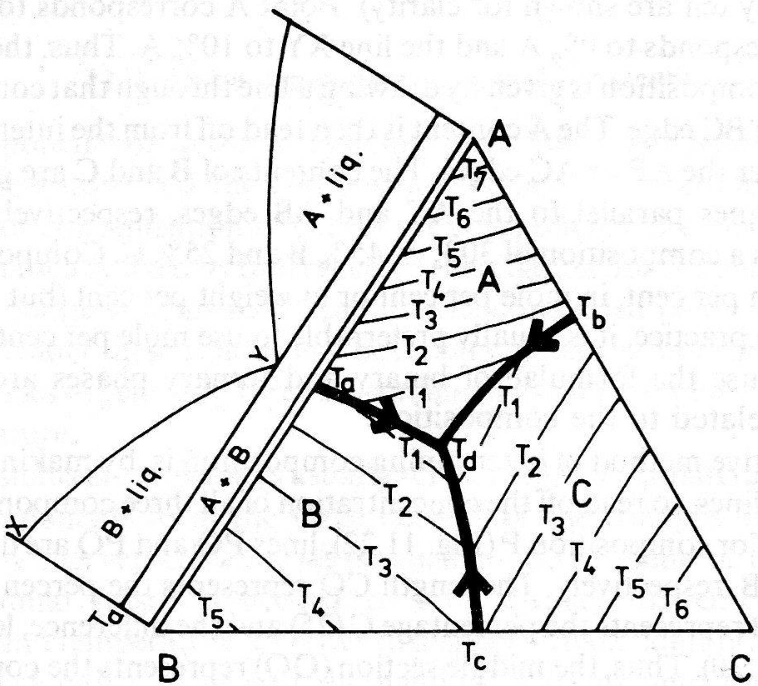


Fig. 11.23 Simple ternary eutectic system showing univariant curves and liquidus isotherms

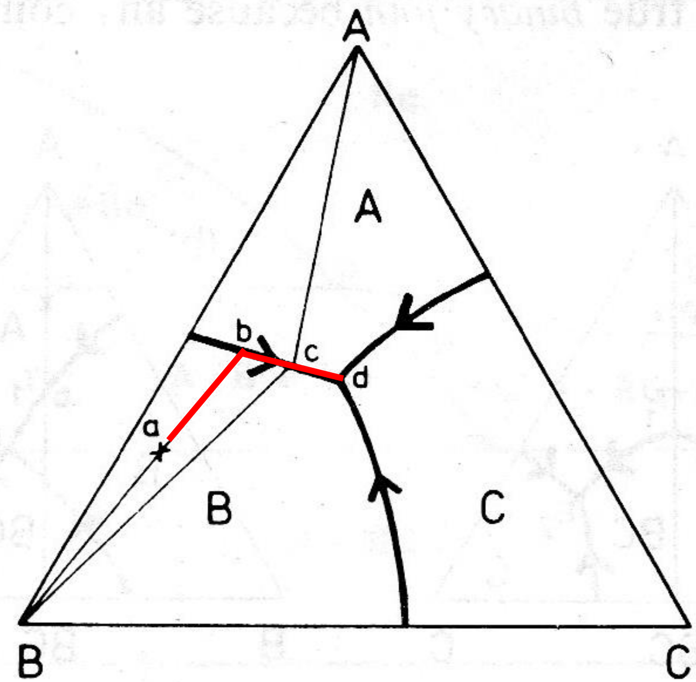
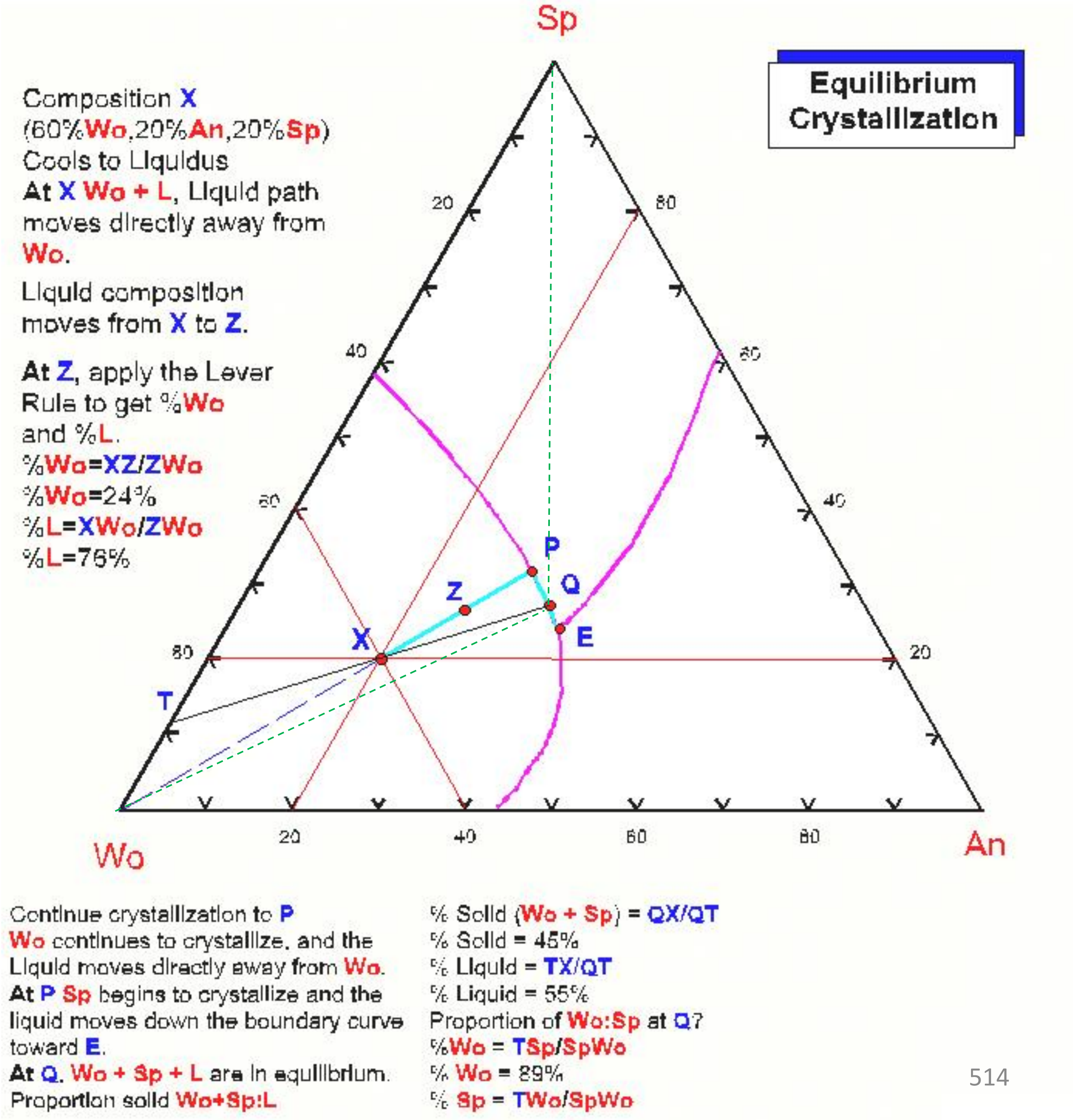


Fig. 11.24 Crystallization pathway in a simple ternary eutectic system

CRYSTALLIZATION PATHWAY - EXAMPLE

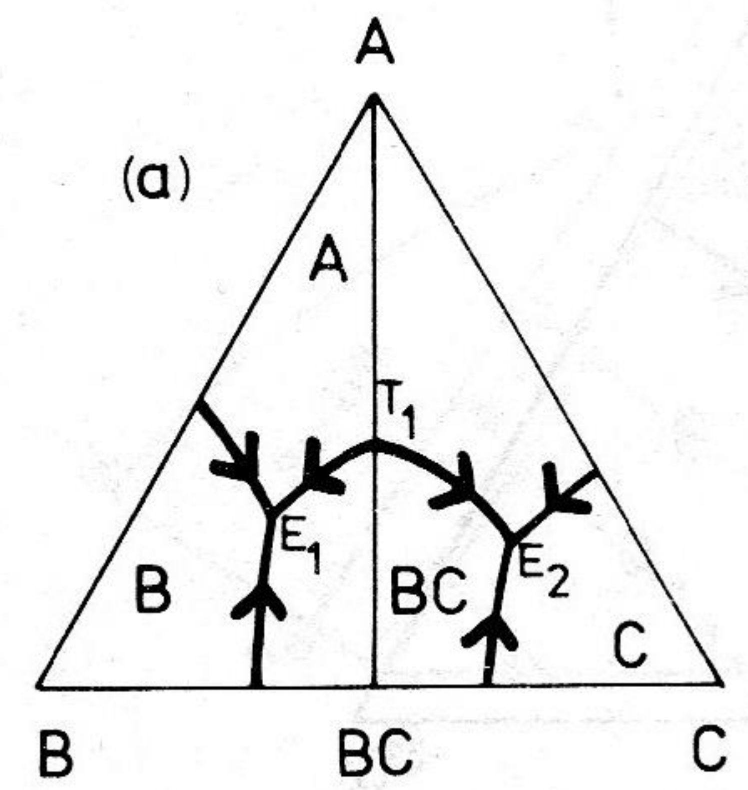
Anorthite – Wollastonite – Sphene System

Anorthite – $CaAl_2Si_2O_8$
Wollastonite – $CaSiO_3$
Sphene – $CaSiTiO_5$



EUTECTIC SYSTEM WITH ONE COMPOUND

simplest case is one binary compound on a *binary join*



- binary join A-BC
  (only A and BC along this line)
- two eutectic triangles
  (A-B-BC and A-BC-C)

ternary diagrams with multiple compounds, solid solutions, etc.
become very complicated very quickly