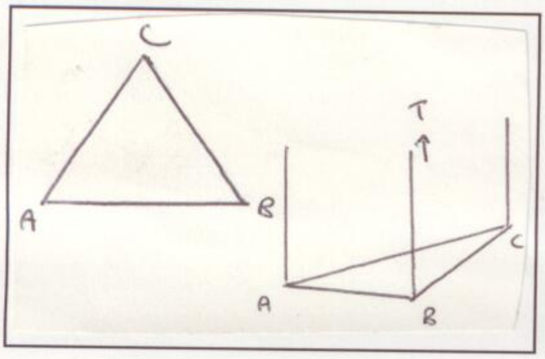
## TERNARY DIAGRAMS

These are like binary phase diagrams, but with three components instead of two.

**Represention:** There are several ways of represenation.
N.B. built incorporating three binary phase diagrams (which form the edges), so ternaries are similar, but more complicated.

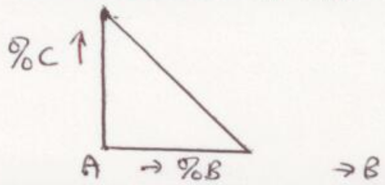



**Composition is represented on an equilateral triangular "space grid", this becomes the base, with the temperature shown by the vertical axis.**

Appropriate paper is used to express the concentations accurately.

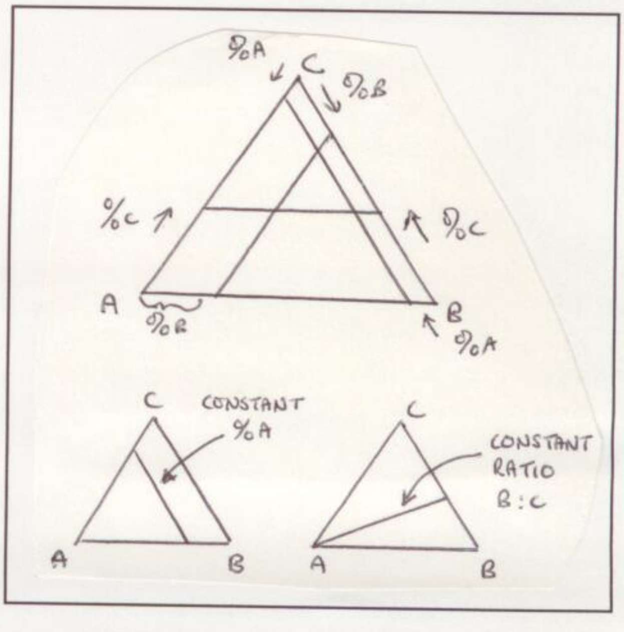
**N.B. All of the compositions should add up to 100%, therefore only need to define two compositions.**

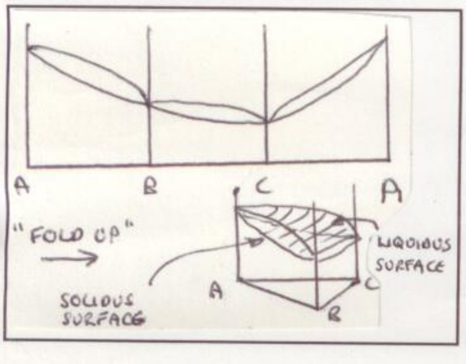
**For high concentrations of one component: e.g. A alloys - use a right angled triangle, and concentrate on the corner of interest. (e.g. Fe-C-Cr)**
**A = 100 - (A + B)**



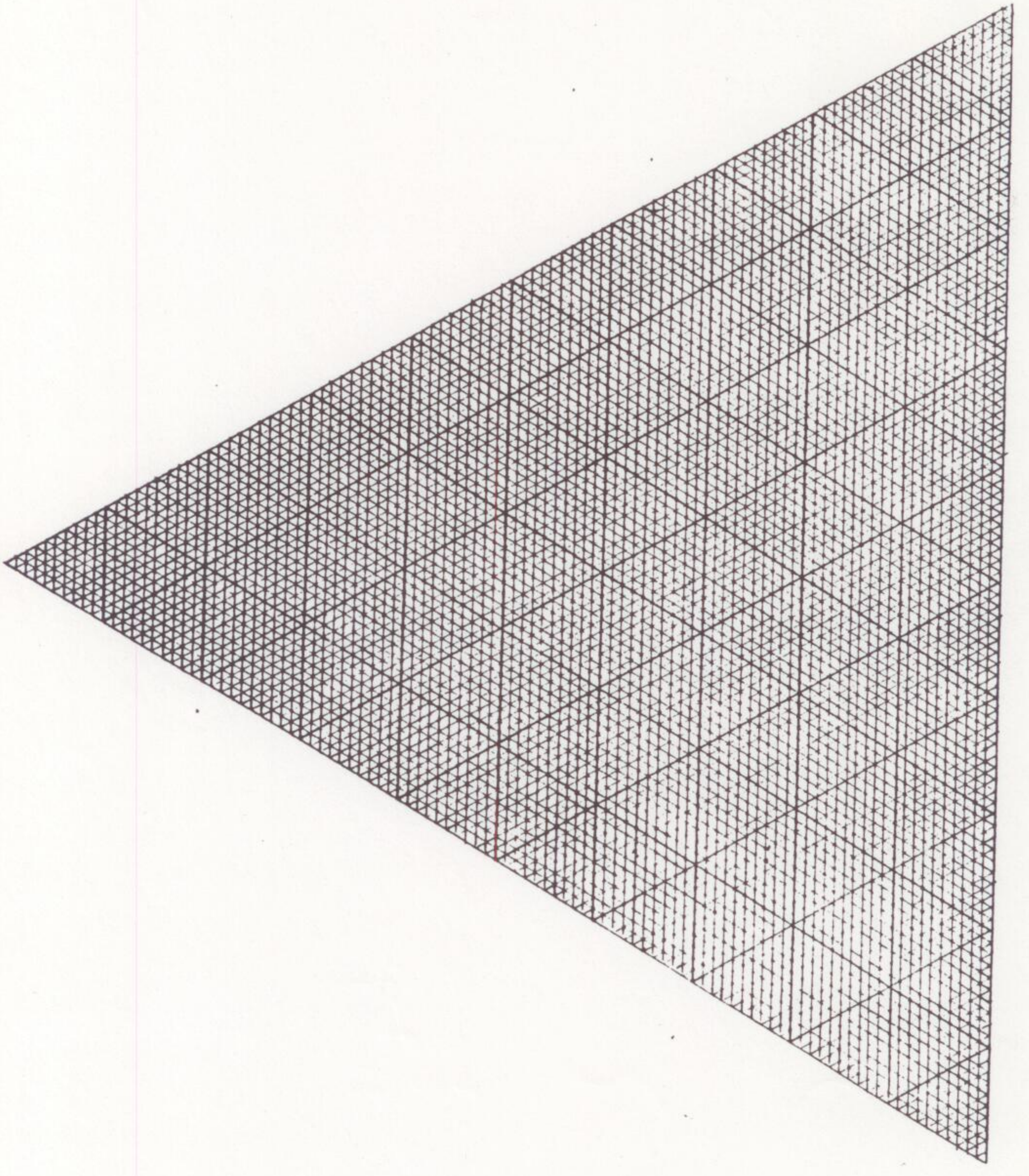

**N.B. All phases n the binary diagram HAVE to appear, if only to a limited extent, on the ternary.**

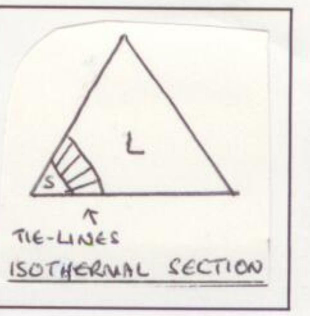
**Space diagram:** This is a **3-D representation** of the entire ternary phase diagram, and usually shows only lines (i.e. NOT the surfaces) between the different phase fields. **Binary phase diagrams form the edges.**



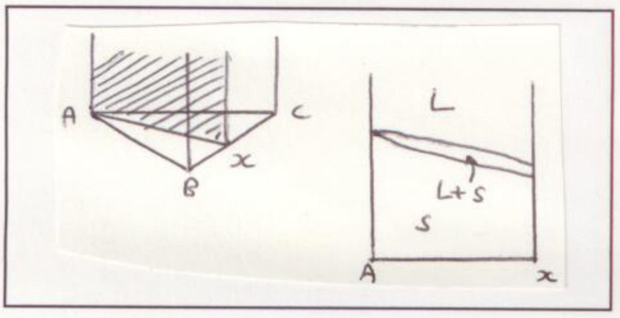

**Isothermal section:** i.e. **horizontal slice through the space diagram.** **The slices are at the same temperature.** Typically, there are **tie triangles of 3 phases in equilibrium** with each other. Lines are produced where the surface boundaries are cut. **Tie lines [kossols] denote 2 phase compositions which are in equilibrium.**






The isothermal section shows which phases are in equilibrium at a particular temperature, and is a very useful representation.

**Slice/"Compositional Slice"/Section/"pseudo binary"/"quasi-binary"/isopleths/vertical section:** This is a **less useful representation**, because the **compositions of the phases do not necessarily lie in the same vertical plane as the temperature changes, even if the overall composition does**. It is also more complicated and difficult to draw.

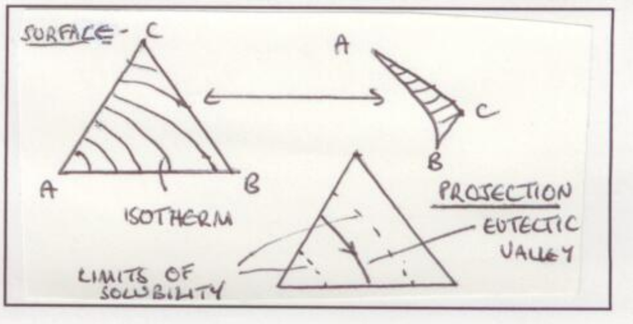



**N.B. A pseudo-binary or quasi-binary is USUALLY taken to have a compound at the stipulated edge.**

The A and x edges are obtained from binary diagrams.

**Surface:** This is a **3-D surface which shows a particular REACTION**, e.g. onset of solidification, i.e. liquidus. (Could use a computer representation?) Difficult to represent in 2-D, thus often have a projection of the surface (e.g. liquidus/solidus) on to the base.

**Projection/Projected view on the Base:** This is a plot the loci of the various reactions. N.B. this is a **PROJECTION on to the plane**.




**RULES OF TERNARY DIAGRAMS:** These should help with the logistics of construction of ternaries.

**"Noddy Rule":** Whatever phase is in the binary **MUST exist in the ternary (EVEN if only to a limited extent).**

**Phase Rule:** $$P + F = C + 2$$

Where: P = number of phases
F = Degrees of freedom
C = number of components

**ALTERNATIVELY**, if **PRESSURE IS ASSUMED TO BE CONSTANT** (i.e. most metallurgical phase diagrams):

$$P + F = C + 1$$

In a ternary system, C = 3. Note that the 3 **components MIGHT not necessarily be elements**. It is possible to have compounds at the corners:

e.g. **"triaxial ceramics"**: comprise the three compounds:

**SILICA** $SiO_2$
**LEUCITE** $K_2O.Al_2O_3.4SiO_2$
**MULLITE** $3Al_2O_3.2SiO_2$

For comparison with binary systems, use the **"Reduced Binary Phase Rule"**. I.e. substitute C=2. Thus P+F=3, then work out the alternatives:

| **P** | 1 | 2 | 3 |
|---|---|---|---|
| **F** | 2 | 1 | 0 |

1 phase has 2 degrees of freedom e.g. **single phase region**
2 " " 1 " " " e.g. **liquidus**
3 " " 0 " " " e.g. **eutectic point**

**Ternary "Reduced Ternary Phase Rule":**

**C=3 therefore P+F=4**

1 phase → 3 degrees freedom i.e. T+2 for composition, e.g. liquid
2 phase → 2 degrees freedom i.e. surface, e.g. liquidus
3 phase → 1 degree freedom e.g. eutectic valley
4 phase → 0 degree freedom e.g. ternary eutectic point

**Rules for horizontal sections (Isothermal sections):**

1. On **crossing a boundary line** (NOT at a point), the **number of phases must change by 1**, the rest are common.

2. **3-phase fields are bounded by straight lines joining the compositions of the three phases which are in equilibrium.**

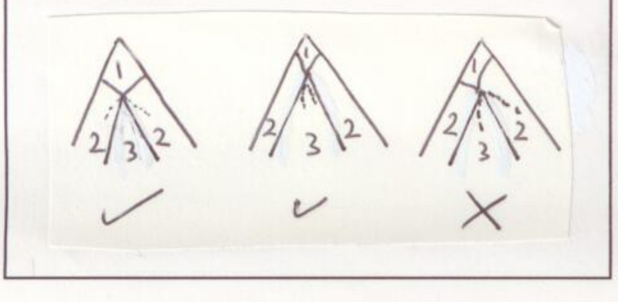
3. Different **3-phase fields do NOT meet, except possibly at a point.**

4. **3-phase fields and 2 phase fields are separated from each other by straight lines.** (See 1 and 2 above.)

5. **2- and 1-phase fields are usually separated from each other by curved lines.**

6. **Concerning the extrapolation of 3-phase Δ and 2-phase lines:**

**3- and 1-phase fields** **can** **meet at a point**, and:



**Plotting the continuation of the lines from the 2-phase lines:**
**BOTH go into the 3-phase field**
**OR**
**or both do not go into the 3-phase field!**

**Rules of tie-lines:** Tie lines are straight lines joining phases in equilibrium at a specific temperature. N.B. has to be **same**

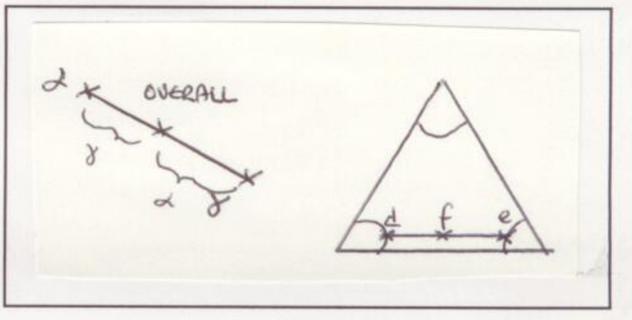
**temperature in EQUILIBRIUM phase diagram.**

1. **Tie-lines HAVE to be horizontal** (i.e. isothermal!).

2. **Tie lines Must NOT cross other tie-lines**

3. **Tie lines MUST coincide with binaries** i.e. the binaries are the limiting tie-lines, and/or tie-lines at a 3-phase triangle.

4. **CANNOT guess tie-lines**; they have to be determined experimentally.



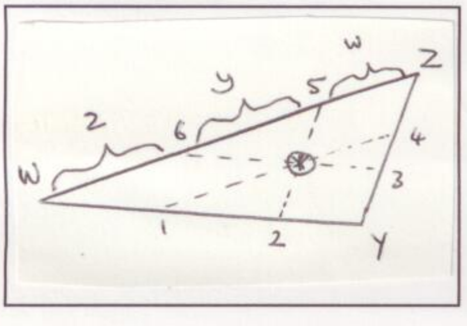

**Use experimental compositions and the lever rule to deduce tie-lines**

**Use lever rule:**

$$\% \ d = \frac{ef}{de} \times 100$$

$$\% \ e = \frac{fd}{de} \times 100$$

$$\frac{amount\ d}{amount\ e} = \frac{ef}{df}$$




**Three-Phase region:**
Alloy composition = *

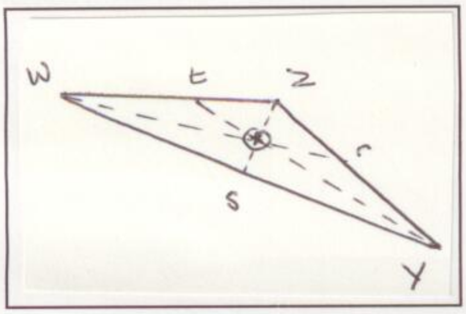
Can read off **compositions** and **relative concentrations** if know where X,Y,Z are (i.e. these are the actual compositions of the phases themselves).

Draw parallel lines to each side, passing through *. Can then deduce the relative concentrations (i.e. proportions) from each side: N.B. The concentrations given below are the relative lengths of the lines specified.

| | CONC$^N$. W | CONC$^N$.Y | CONC$^N$. Z |
|---|---|---|---|
| **WY side** | Y-2 | W-1 | 1-2 |
| **YZ side** | 3-4 | Z-4 | Y-3 |
| **WZ side** | Z-5 | 5-6 | W-6 |

**Possible to work out absolute percentages:**
Draw lines from tie triangle corners through *:

$$\% \ W = \frac{xr}{wr} \times 100$$




$$\% Y = \frac{xt}{ty} \times 100$$

$$\% Z = \frac{xs}{sz} \times 100$$

## MAJOR TYPES OF TERNARY SYSTEM

**1) Systems containing 2 phases:**
(solid + liquid)

**i) Isomorphous phase diagram.**

**2) Systems containing 3 phases:**
i) **Liquid (L) + 2 primary solid solutions** ($\alpha$ + $\beta$) with a **3-phase eutectic reaction L → $\alpha$ + $\beta$.**

ii) **Liquid (L) + 2 primary solid solutions** ($\alpha$ + $\beta$) with a **3-phase peritectic reaction L + $\alpha$ → $\beta$.**

iii) **Transition between eutectic and peritectic reactions.**

iv) **Two liquids ($L_1$ + $L_2$) and one primary solid solution** ($\alpha$) with a **3-phase monotectic reaction $L_1$ → $L_2$ + $\alpha$.**

v) Systems containing a **solid state miscibility gap which closes within the system.**
...

**3) Systems containing 4 phases:**

i) **Ternary eutectic.**

ii) **Ternary peritectic.**

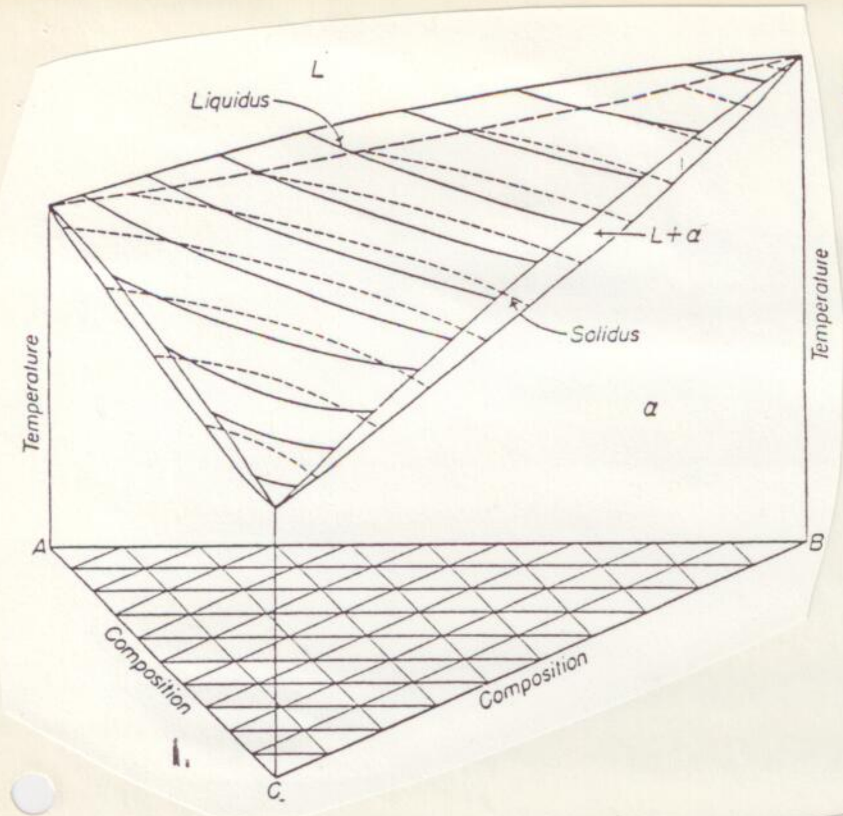
## SIMPLE TYPES OF TERNARY PHASE DIAGRAM

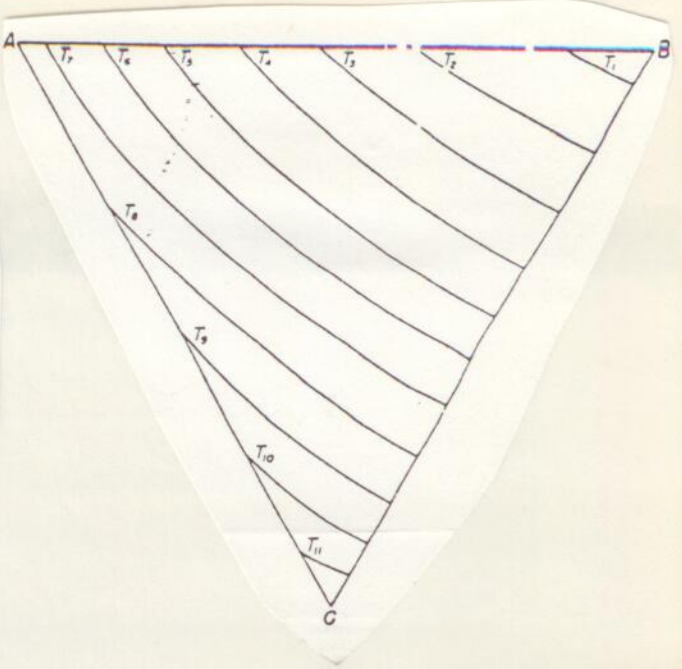
**2 PHASE SYSTEM: Isomorphous Ternary:** This is **complete solution in the liquid AND solid states**. The **liquidus and solidus surfaces curve away from each other**, except at the corners (where they coincide because these are the melting points of the pure elements/compounds).

The second diagram is a vertical view, NOT a section. The tie-lines are horizontal, but are in a number of different vertical planes. $S_1$ denotes the composition nearest to the highest melting point component.

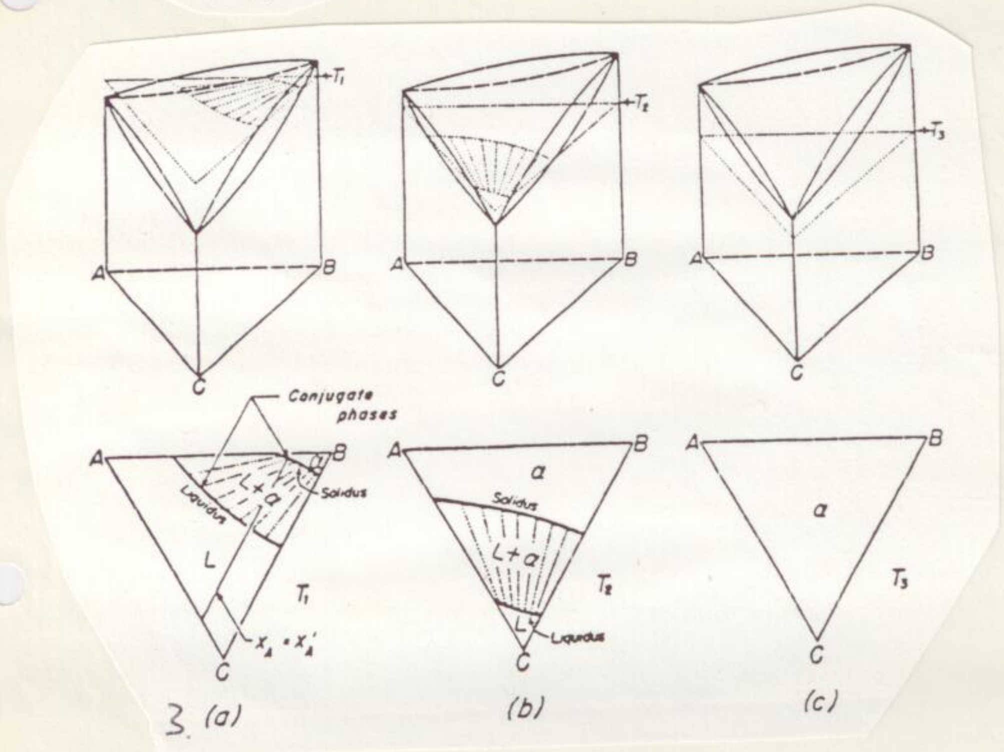
**In the projection on the base, a vertical section would not contain all of the tie-line because the curved surfaces slope different ways.**

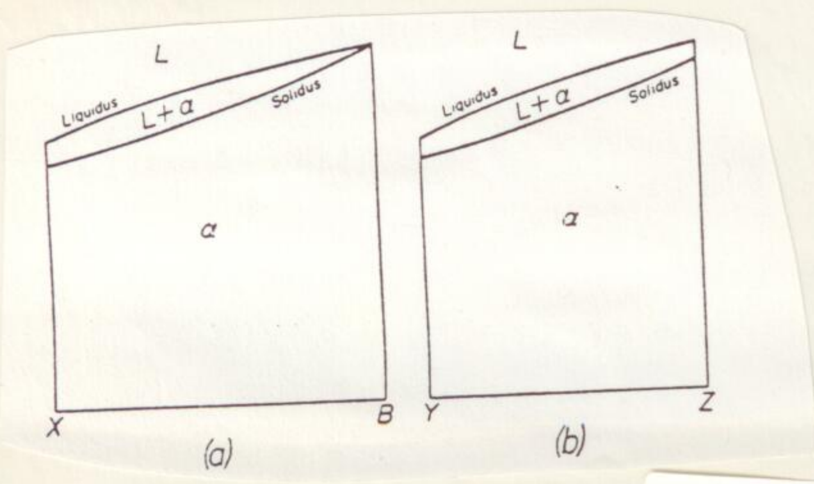
**Conditions for isomorphous system:** Same structure, valency, similar



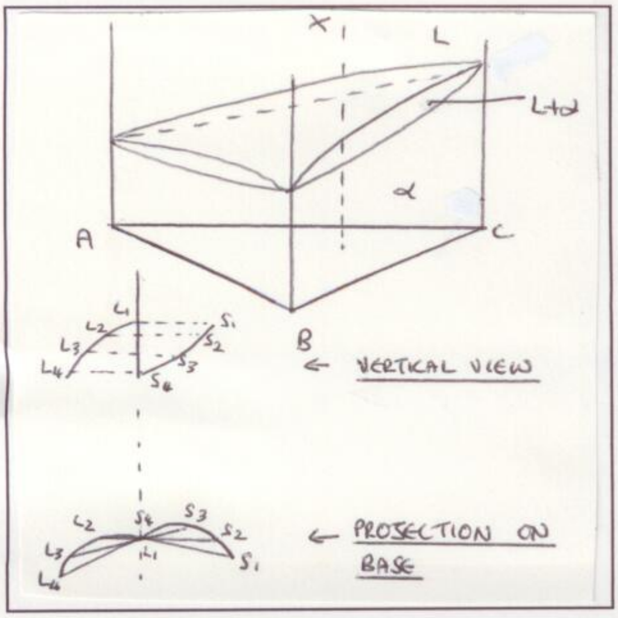




2. Liquidus projection




4. Example of isopleths. (a) Constant $X_B/X_C$ ratio. (b) Constant $X_B$




electronegativities (i.e. no intermetallic compounds formed), atom sizes within 15% of each other, ideal thermodynamic behaviour.
E.g. Ag-Au-Pd system.

**<u>3 PHASE SYSTEMS:</u>**

**<u>i) L + 2 primary solid solutions (α + β) giving 3-phase eutectic reaction L → α + β</u>**

E.g. AC isimorphous i.e. complete miscibility in L and S.
AB, BC: eutectic systems showing partial solubility.

- **<u>3 single phase regions:</u>** L, α, β.
Each has three degrees of freedom.

- **<u>Two-phase regions:</u>** are between the single phase regions: α + β, L + α, L + β.
Each 2-phase region has two degrees of freedom.

Assume that the temperature of binary AB eutectic reaction > eutectic reaction BC, and so there is a "valley" running from M to N, i.e. the **liquidus has 2 adjacent surfaces because there are two different reactions:**

**L → α**
**L → β.**

The intersection of these is the **eutectic valley which has the reaction:**

**L → α + β.**

BUT it must be remembered that the **compositions change as move down the valley**.

In this example, the valley flows straight(ish) downwards, but it is possible to have a **maximum** or a **minimum** (which are **shown by arrows**):

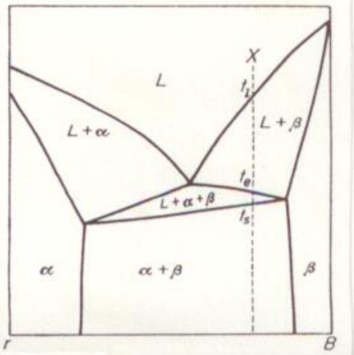
D → G is the composition locus of the α-phase from the eutectic reaction. E → F is the composition locus of the β-phase from the eutectic reaction.

<u>N.B.</u> **MN, DG, and EF do NOT lie in the same plane:**
ABOVE the surface of DEFG have 2 surfaces: DMNG and MEFN, with DEFG being the third, and lowest one. Thus **three surfaces enclose the 3-phase region: L + α + β.**

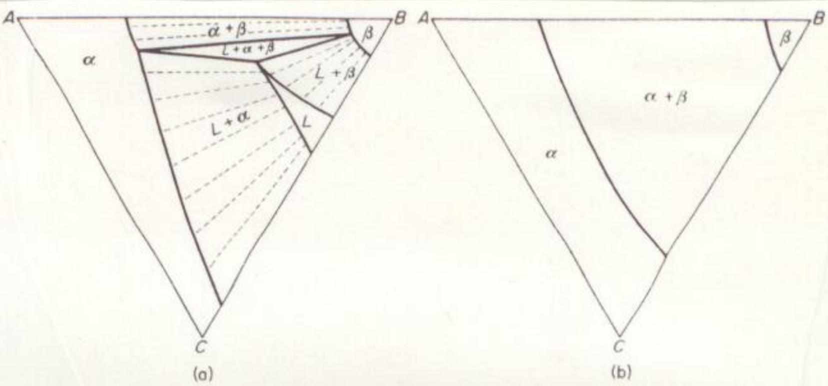
**<u>2-phase regions</u>** lie on the outside of the 3-phase region:

DMNG → L + α
MEFN → L + β
DEFG → α + β.

Note that DEFG is part of the solidus surface, which shrinks to a horizontal in the binary phase diagrams. This is because in the

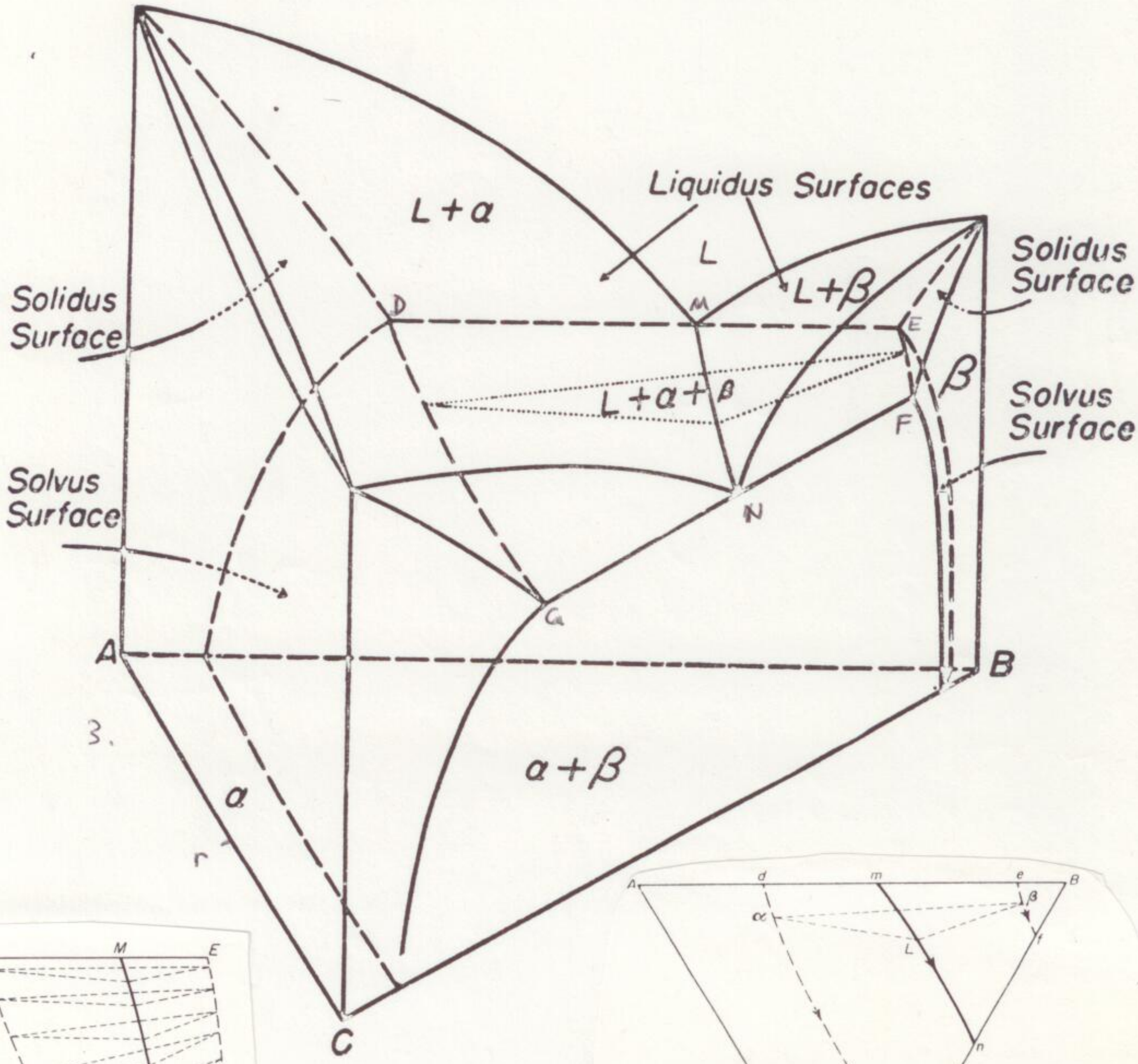


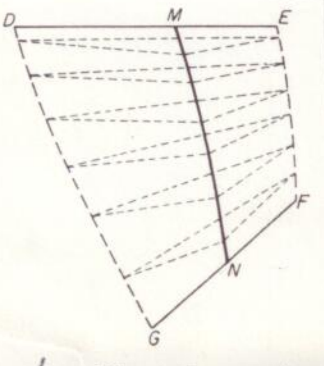

1. Vertical section from corner *B* to the mid-point *r* of side *AC*



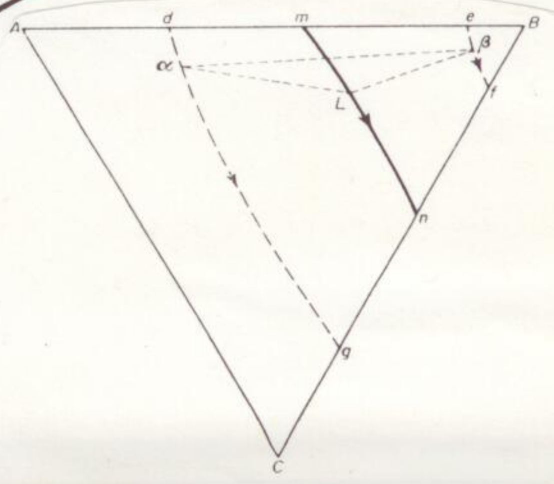

2. Representative isothermal sections through the space model

(*a*) at a temperature between that of the eutectics in systems *AB* and *BC*
(*b*) at a temperature below that of eutectic *BC*




4. Three-phase region (liquid, α and β)




5. Projected view on the base of the space model of the system including a typical tie-triangle

binary phase diagram the eutectic is an invarient reaction (i.e can only occur at one temperature and composition)., and in the ternary the eutectic reaction is NOT an invariant one. Thus it can occur over a **range of temperatures**, thus instead of ONE set composition, there are a **range of compositions for any eutectic reaction in the ternary**.

Thus, at any given temperature in the ternary there will be different compositions of L, $\alpha$ and $\beta$ in equilibrium with each other. This is shown by a **series of tie-triangles** for the different temperatures. **Each corner of the triangle represents the composition of ONE of the phases**, i.e. MN → L
DG → $\alpha$
EF → $\beta$

**E.g. Cooling path of alloy of composition, X:** (lying over L + $\beta$ surface):
The alloy is liquid above the liquidus. At the liquidus, the **liquid composition moves DOWN the the liquidus surface as the temperature decreases, and the $\beta$ composition also DOWNdown the solidus surface.**

N.B. **with solid solutions, one CANNOT deduce the directions that the compositions move down the surface. When pure components are solidifying, i.e NO solid solution, then the liquidus composisition moves in a STRAIGHT LINE AWAY FROM THAT COMPNOENT**. Thus, solid $\beta$ is formed...

Eventually when the temperature has decreased, such that the liquid composition is at the VALLEY, and at the same time, the solid composition has reached somewhere on EF, **now in a 3-phase region.** The equilibrium between the 3 phases is shown with tie triangles.

Initially, X lies on the L$\beta$ side of the tie triangle.

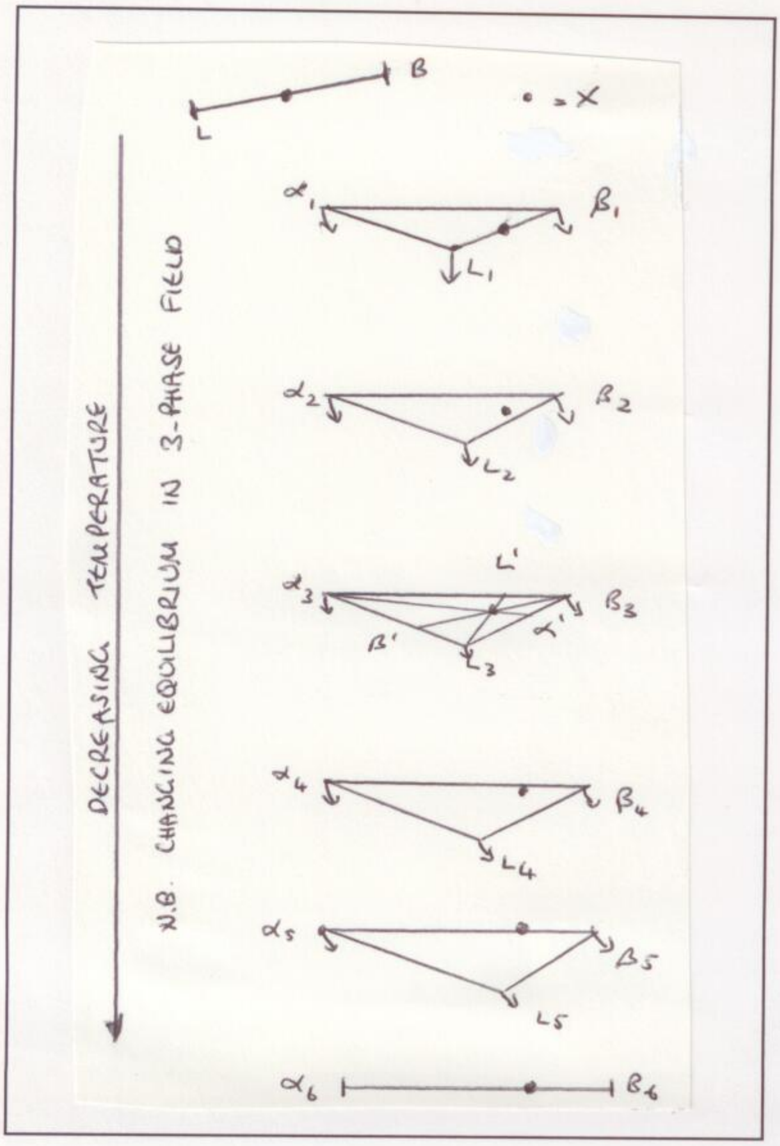
**N.B. Eutectic reaction, thus the NOSE LEADS.**

$$\%L = \frac{XL'}{L_3L'} X\,100$$

$$\%\beta = \frac{X\beta'}{\beta_3\beta'} X\,100$$

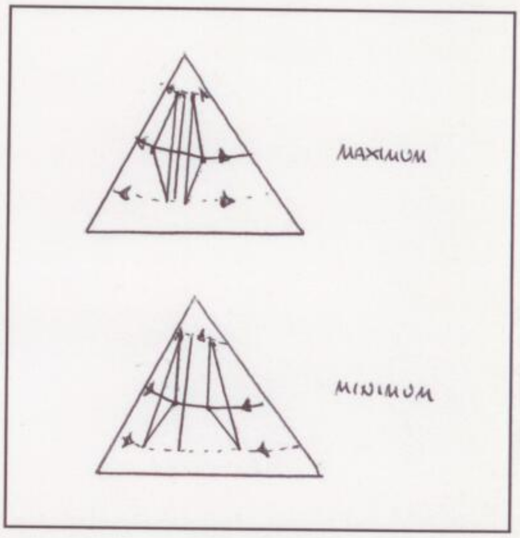
$$\%\alpha = \frac{X\alpha'}{\alpha_3\alpha'} X\,100$$

At the temperature decreases, the triangles are such that apparently X moves into the triangle. I.e. more correctly, **the triangles flow past X**. Eventually, X reaches the $\alpha$ + $\beta$ side. Now the composition




has left the 3-phase field, and is in the solid 2-phase region.

**N.B.** the tie triangles drawn above are hypothetical. The **shapes**



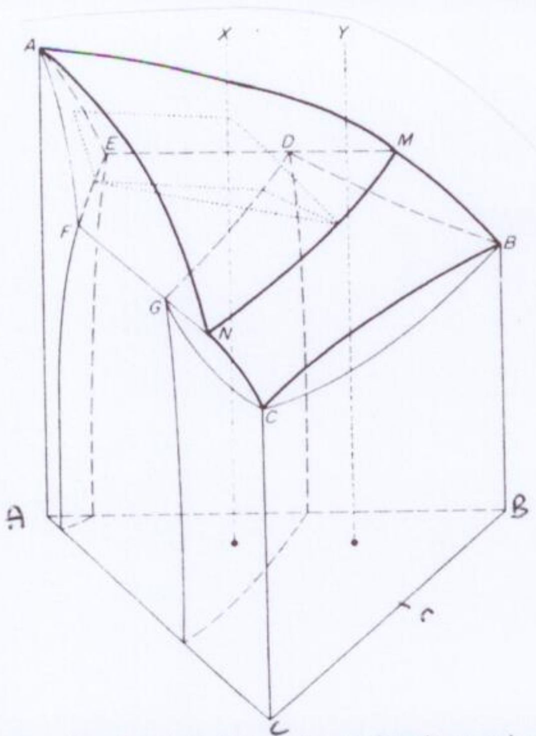

**often change in the series: narrow → wider → narrow** as cross the ternary.

**N.B.** the **tie triangles MUST become straight lines at the binary edges**.

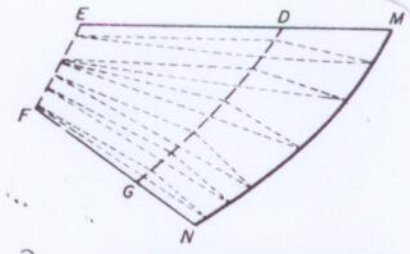
Note that the **projected view show the limits of the solid solution as well as the eutectic valley**. The directions of "flow" of the eutectic valley are always shown, and a maximum or minimum can be denoted. The **projected view shows the condition after solidification**, i.e. shows **primary** phases, and not necessarily the **final** ones. There are usually differences in the positions of the solvi for these phases, but the differences are usually so slight as to be negligible, unless there is a subsequent (solid state) phase change.

**Vertical Sections: N.B.** One probably **CANNOT trace the solidifcation properly using only a vertical section because the liquidus and solidus surfaces are CURVED, and the vertical section is highly unlikely to be situated on the right part of the curve**. I.e. the vertical section CANNOT contain and show what phase are in equilibrium, nor their compositions, but it **CAN give an indication ONLY of the temperatures at which the reactions occur**.

**N.B.** The **lines bounding 3-phase regions here are NOT necessarily straight lines, because they are NOT tie triangles**, i.e. they are not at the same temperature.




1. Space model of system showing a peritectic reaction $L + \alpha \longrightarrow \beta$

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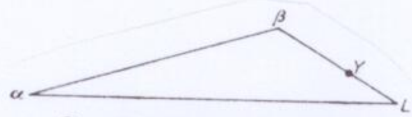
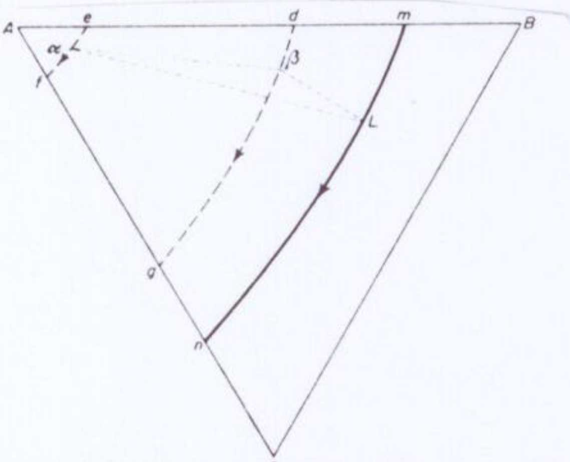
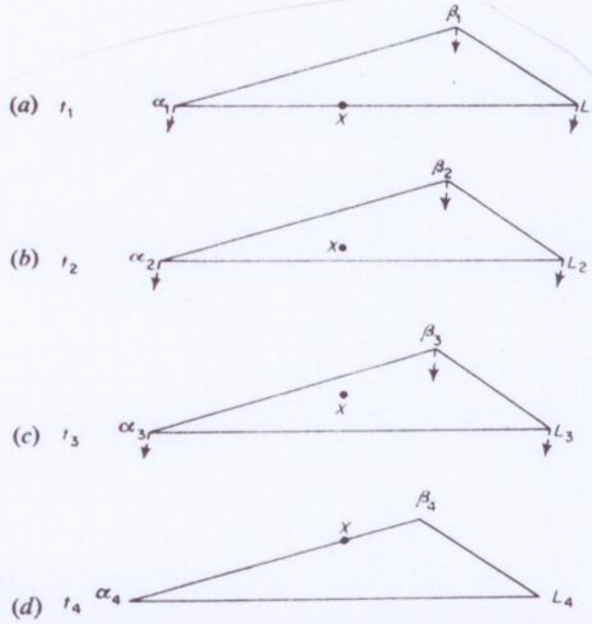


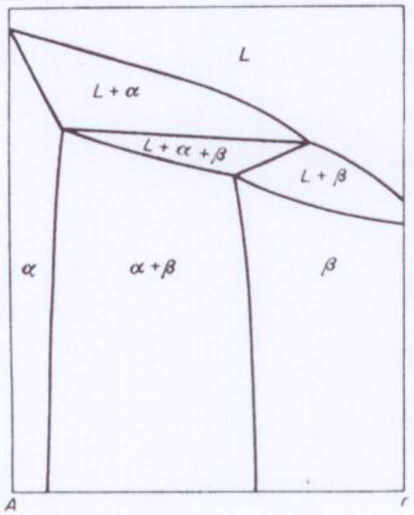

3. Tie-triangle illustrating the completion of the peritectic reaction in an alloy Y, that consists only of β-phase when solidification is finally completed




4. Projected view on the base of the space model of the system

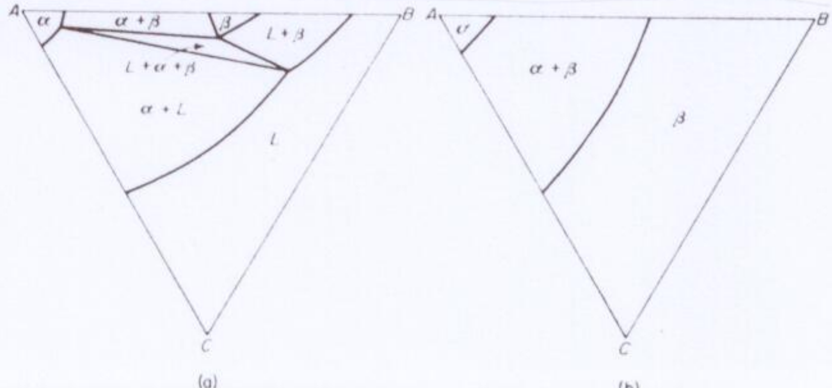



5. Tie-triangles at various temperatures illustrating the progress of the peritectic reaction in an alloy, X, that is $\alpha + \beta$ when solid




Vertical section of system

6.




7. Representative isothermal sections through the space model
(*a*) at a temperature between that of the peritectic reactions in systems *AB* and *AC*
(*b*) at a temperature below that of the peritectic reaction in system *AC*