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8. Phase Diagrams of Two-Component Systems

8.1 Vapor Pressure Diagrams; the Lever Rule

If Raoult's law holds,then we predict completely the total vapor pressure of a binary solution at any temperature and the composition of the vapor:

partial vapor pressures:

$$p_A = p^*_A x_A \quad , \quad p_B = p^*_B x_B$$

total vapor pressure:

$$p = p_A + p_B$$

composition of the vapor:

$$y_A = p_A/(p_A+p_B) = p^*_A x_A /(p^*_A x_A + p^*_B x_B)$$

$$= p^*_A x_A /\{p^*_A x_A + p^*_B(1-x_A)\}$$

$$\boxed{y_A = p^*_A x_A/\{ p^*_B + (p^*_A - p^*_B)x_A)\}}$$

can also rearrange to find:

$$\boxed{x_A = p^*_B y_A/\{ p^*_A + (p^*_B - p^*_A)y_A)\}}$$

The total vapor pres$^{s}_{\wedge}$ure is therefore given by:

$$\boldsymbol{p} = p_A + p_B \quad = p^*_A x_A + p^*_B (1 - x_A)$$

$$= p^*_B + (p^*_A - p^*_B)\, \boldsymbol{x_A}$$

a straight line connecting p^*_A *and* p^*_B

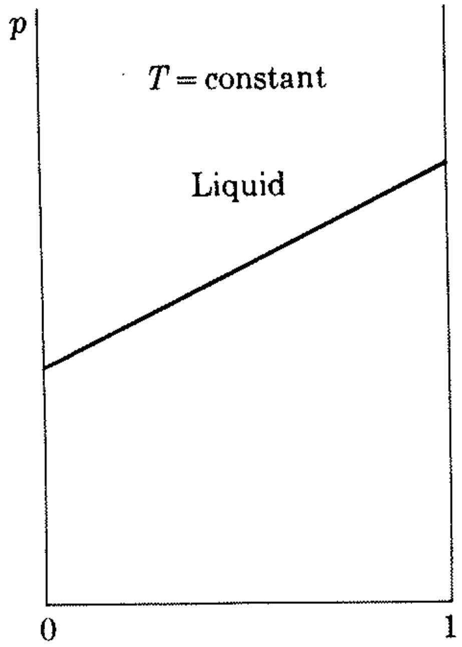
Alternatively, we can substitute x_A here by the expression in terms of y_A to get:

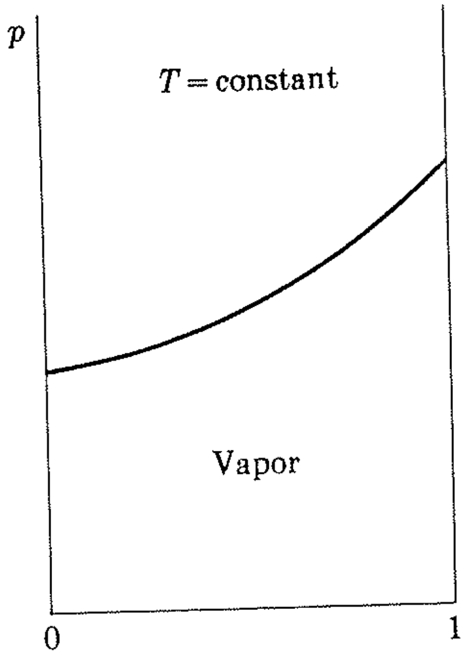
$$p = p^*_B + (p^*_A - p^*_B) p^*_B y_A / \{ p^*_A + (p^*_B - p^*_A) y_A)\}$$

which can be rearranged to give:

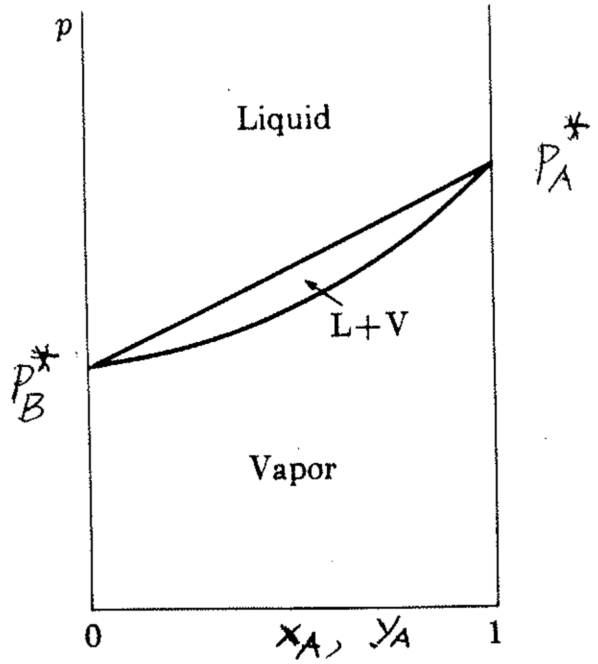
$$\boldsymbol{p} = p^*_A p^*_B / \{ p^*_A + (p^*_B - p^*_A) \boldsymbol{y_A})\}$$

a curve connecting p^*_A *and* p^*_B

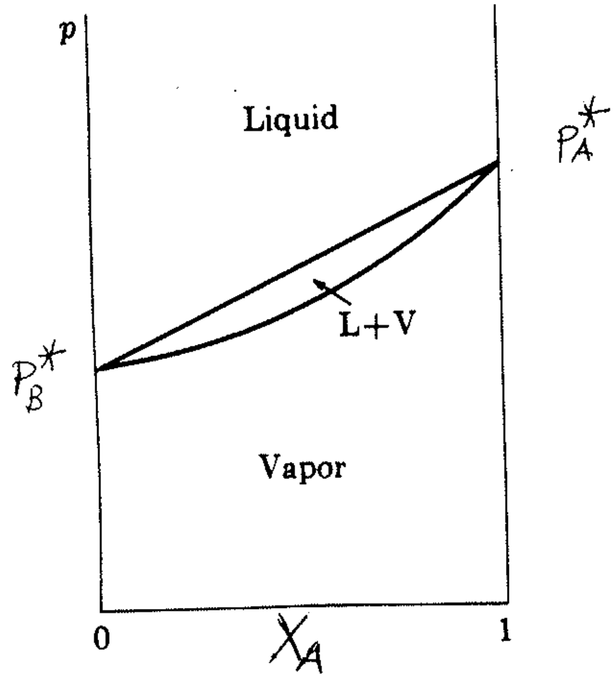


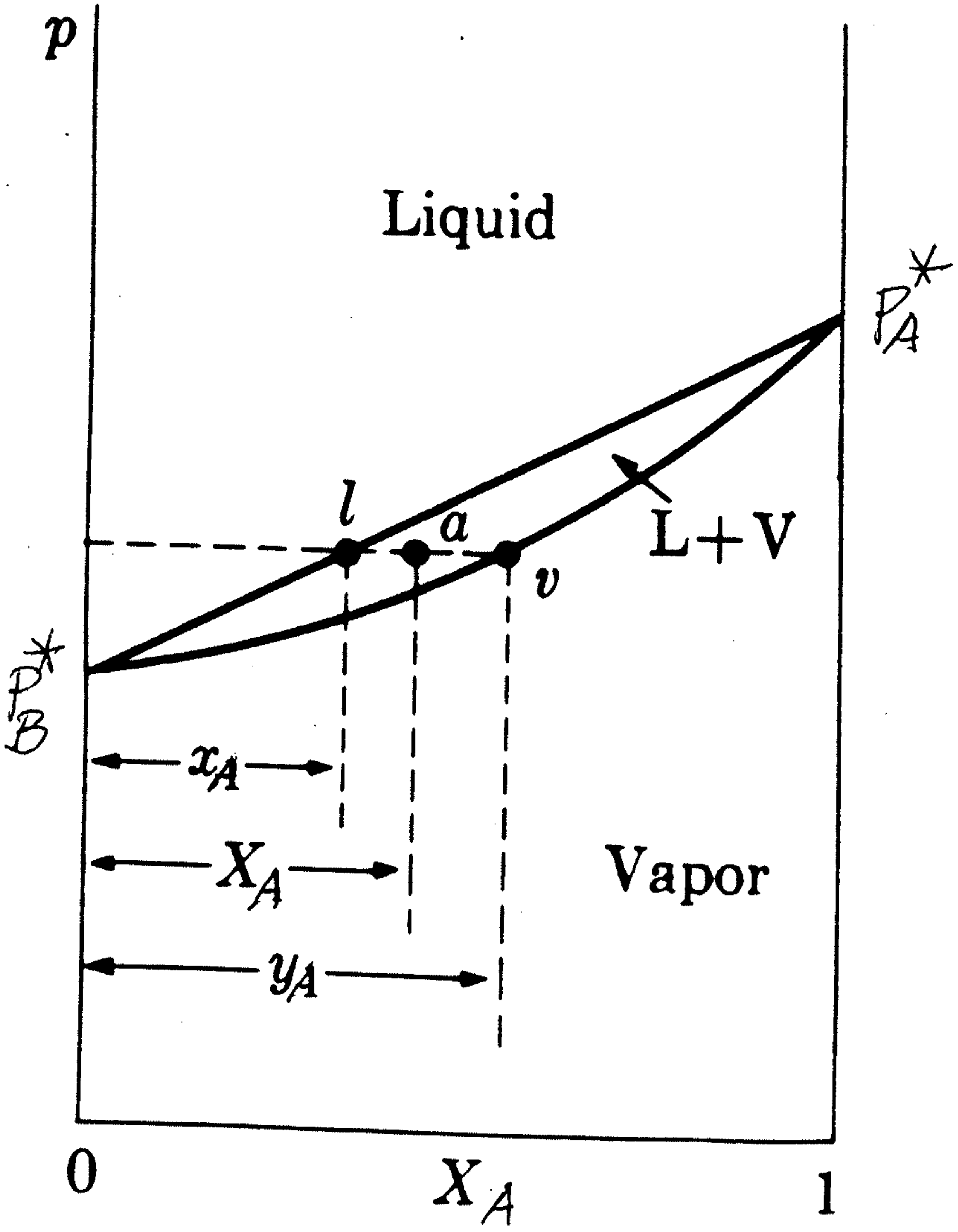


Put them in the same figure and use the x axis to read as x_A and also as y_A .



We can also plot against the overall mole fraction X_A of the whole system (vapor + liquid phase)




p
Liquid
p_A^*
l
a
v
L+V
p_B^*
x_A
X_A
y_A
Vapor
0
X_A
1

The lever rule:
line segment $(\underline{al})$ representing
$X_A - x_A = (n_A/n) - (n_{A(LIQ)} / n_{(LIQ)})$

line segment $(\underline{av})$ representing
$y_A - X_A = (n_{A(VAP)} / n_{(VAP)}) - (n_A/n)$

Multiply $(\underline{al})$ by n_{LIQ} and multiply $(\underline{av})$ by n_{VAP} then subtract, to get

$(\underline{al}) \bullet n_{LIQ} - (\underline{av}) \bullet n_{VAP}$
$=$
$(n_A/n)[n_{LIQ} + n_{VAP}] - (n_{A(LIQ)} + n_{A(VAP})$)
$= n_A - n_A = 0.$
Therefore,
$(\underline{al}) \bullet n_{LIQ} = (\underline{av}) \bullet n_{VAP}$ ***the lever rule***

Note that the lever rule depends only on a mass balance, so the rule is valid for calculating the relative amount of the two phases present in any two-phase region of a two-component system

Summary:

If we have a solution that obeys Raoult's law, all we need to know is

(a) X_A, the overall molefraction in the system (vapor+liquid) and the total vapor pressure p,

or else,

(b) the mole fraction in the liquid phase, x_A.

The vapor pressures of the pure liquids at the given temperature (p^*_A and p^*_B) are known from the Clapeyron eqn.

From x_A , p^*_A and p^*_B we can calculate

- partial pressure of A in the vapor, p^*_A
- partial pressure of B in the vapor, p^*_B
- total vapor pressure over the liquid solution, p
- mole fraction of A in the vapor phase, y_A

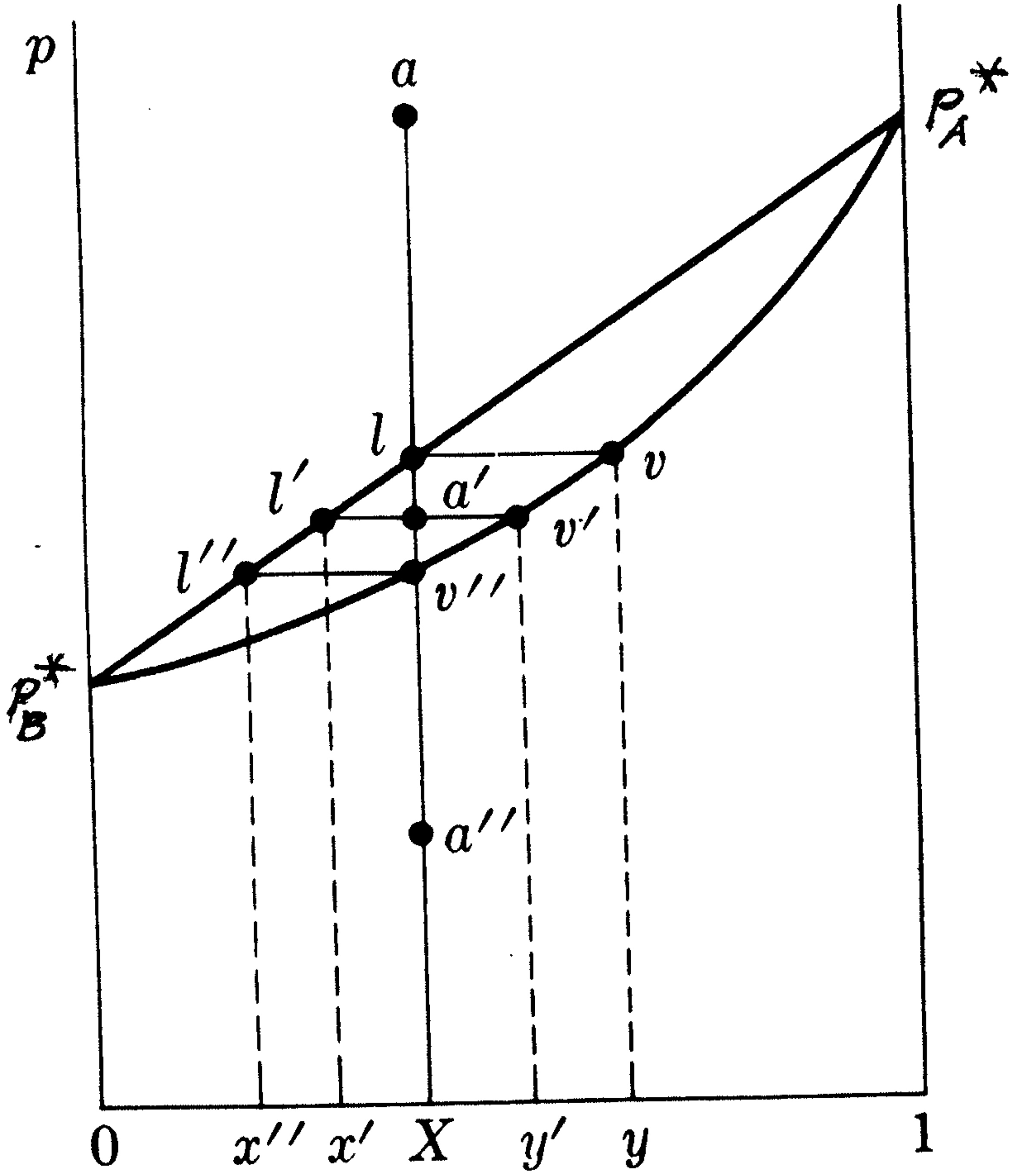
On the other hand, from only p, we can calculate:

- x_A and y_A

and from these and X_A we can calculate, using the lever rule,

- the ratio (n_{LIQ}/n_{VAP})

Changes in state as the pressure is reduced isothermally:

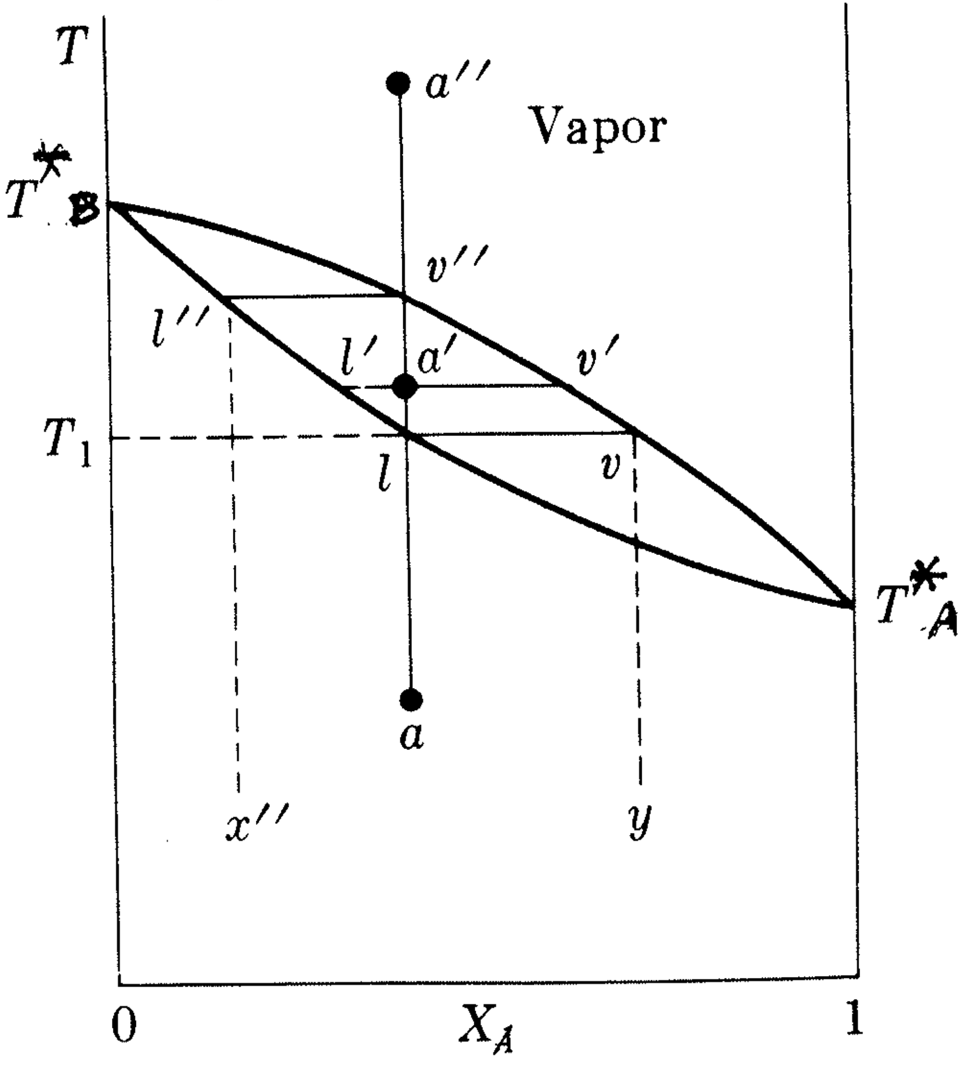


- $\boldsymbol{a}$ entirely liquid
- $\boldsymbol{l}$ first trace of vapor appears, having a composition y. *First vapor to appear is considerably richer in A than the liquid (component A is the more volatile)*
- $\boldsymbol{ll'}$ composition of the liquid moves along the line $\boldsymbol{ll'}$ while the composition of the vapor moves along $\boldsymbol{vv'}$
- $\boldsymbol{a'}$ liquid has composition x' while vapor has composition y'.The ratio of the number of moles of liquid to vapor is $(\boldsymbol{a'v'})/(\boldsymbol{a'l'})$, from the lever rule.
- $\boldsymbol{v''}$ only a trace of liquid of composition x'' remains, the vapor has the composition X. The liquid which remains is richer in the less volatile B.
- $\boldsymbol{a''}$ the pressure is reduced further (expansion of the vapor) at $\boldsymbol{a''}$ the vapor has the same composition as the original liquid.

8.2 Temperature Composition Diagrams; Fractional Distillation, Azeotropes

p^*_A and p^*_A are functions of temperature. (Clapeyron equation)

Plot of boiling points versus composition at constant pressure:



Component A had the higher vapor pressure, therefore has the lower boiling point.

Liquid region is at the bottom of the diagram (under constant pressure the liquid is stable at low temperatures)

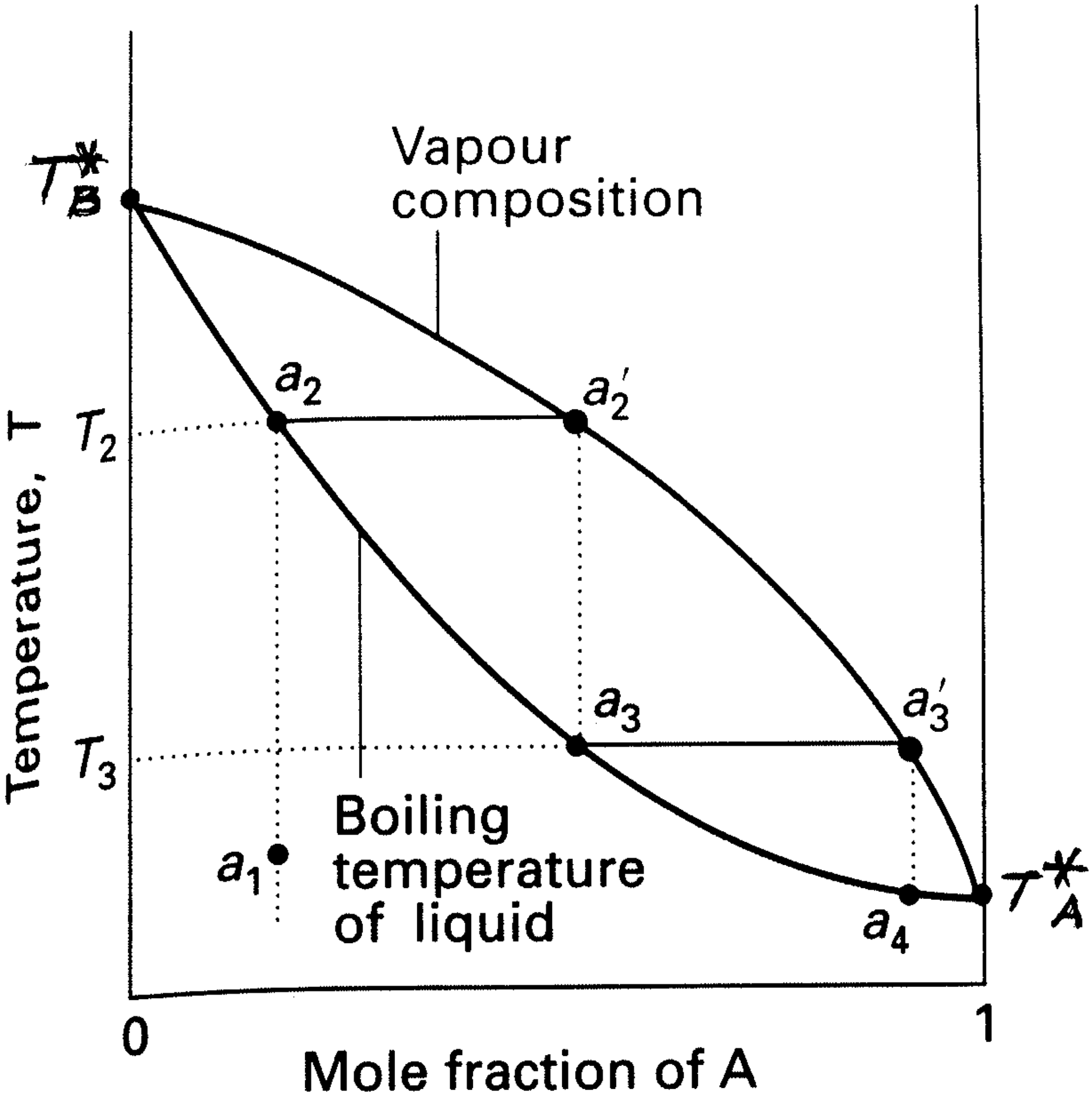
Lower curve describes the liquid composition, the upper curve describes the vapor composition

- ***a*** entirely liquid
- ***l*** first trace of vapor appears, having a composition *y*. *First vapor to appear is considerably richer in A than the liquid (component A is the lower boiling component)*
- ***ll′*** composition of the liquid moves along the line ***ll′*** while the composition of the vapor moves along ***vv′***
- ***a′*** The ratio of the number of moles of liquid to vapor is $(a'v')/(a'l')$, from the lever rule.
- ***v″*** only a trace of liquid of composition x″ remains. The liquid which remains is richer in the higher boiling B.
- ***a″*** the system exists entirely as vapor.

Fractional Distillation

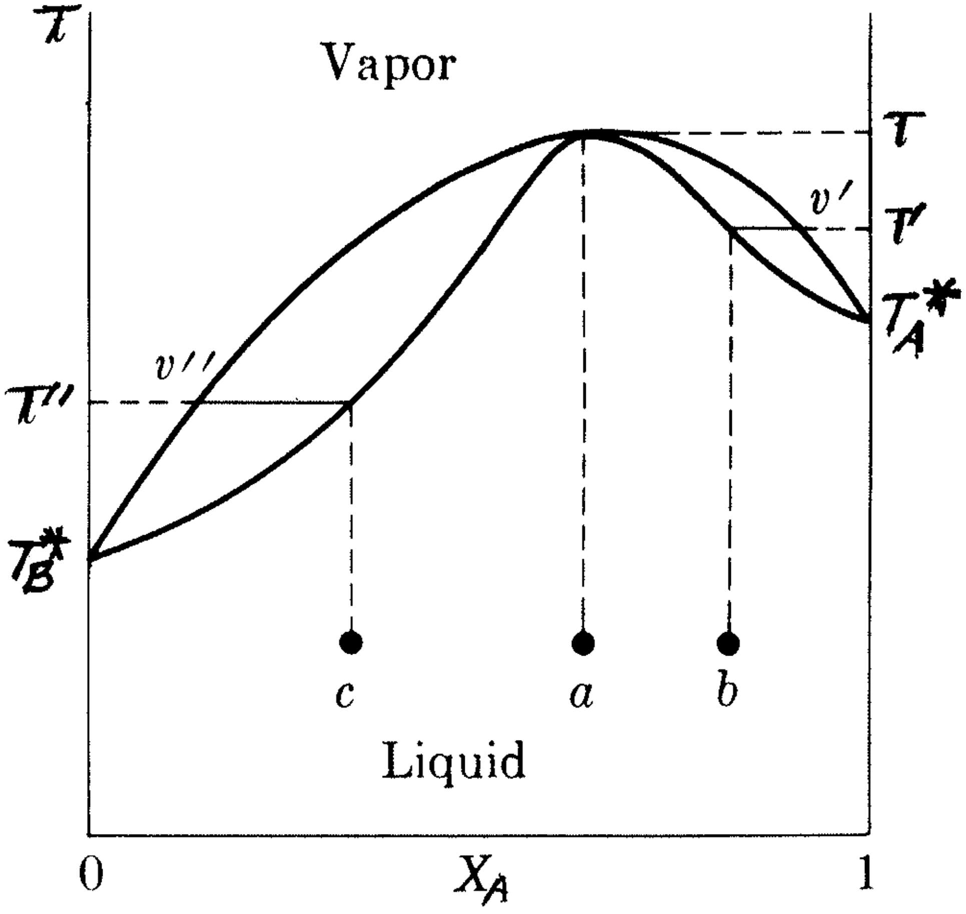
a_1 a liquid of this composition is heated. It boils when the temperature reaches T_2. Then the liquid has composition **a_2** (still), while the first trace of vapor has the composition **a_2'** (the vapor is richer in the component with the lower boiling point).

If the vapor is condensed completely it will be liquid at the same composition **a_3**. If the liquid is heated, it boils when the temperature reaches T_3, yielding a vapor of composition **a_3'**. That vapor, if drawn off and condensed (**a_4**) will have a boiling temperature very close to that of the pure A.


Vapour composition
T_B^*
a_2
a_2'
T_2
Temperature, T
a_3
a_3'
T_3
Boiling temperature of liquid
a_1
a_4
T_A^*
0
1
Mole fraction of A

Azeotropes

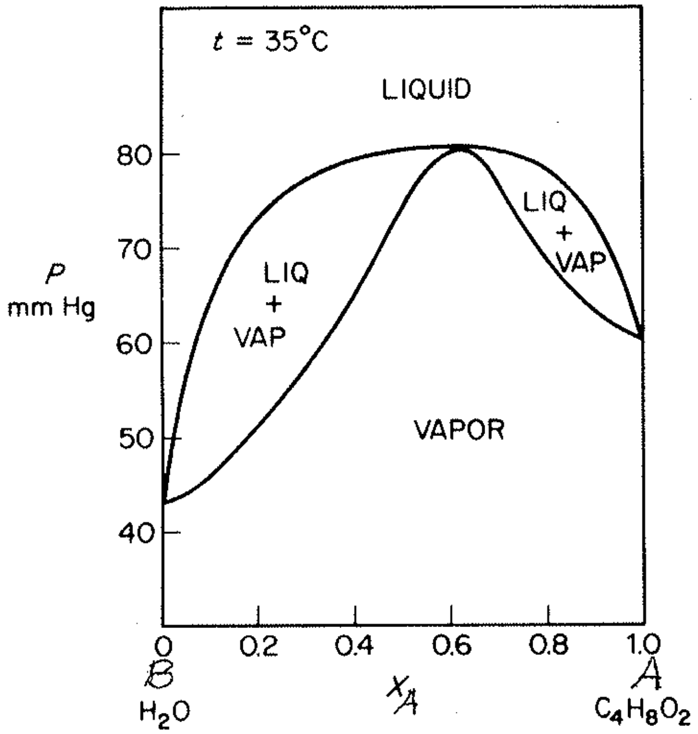
If the deviations from Raoult's law are large there may be a maximum or minimum in the vapor pressure curve. It can be shown that if the vapor pressure curve has a maximum or minimum, then at that point the *liquid and vapor curves must be tangent to one another and the liquid and the vapor must have the same composition*.



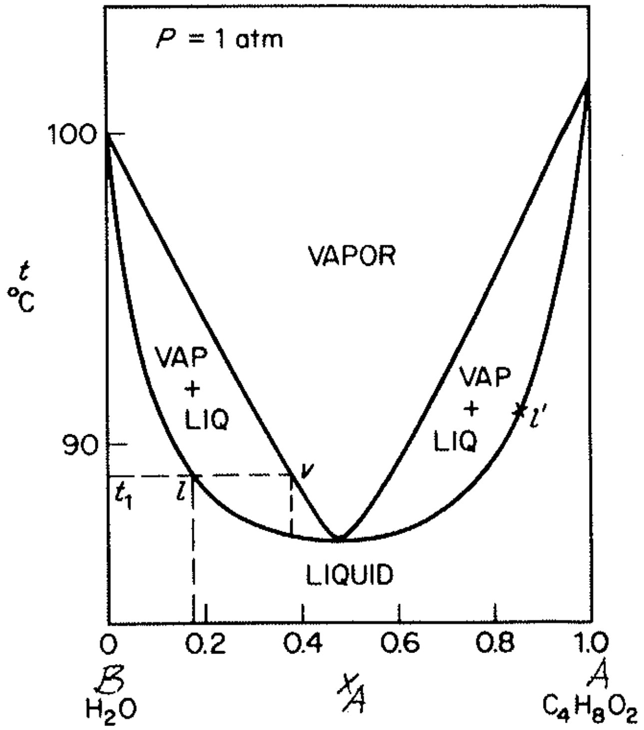
- ***a*** a liquid mixture having the azeotropic composition: If heated the vapor will first form at temperature T; that vapor has the same composition as the liquid, consequently no separation can be effected
- ***b*** This liquid mixture if heated, the first vapor appears forms at T′ and has a composition ***v′*** *the vapor is richer in the higher boiling component.* Fractionation would separate the mixture into pure component A in the distillate and leave the azeotropic mixture in the pot.
- ***c*** This liquid mixture if heated, would boil first at T″ and has a composition ***v″***. Fractionation would separate the mixture into pure component B in the distillate and leave the azeotropic mixture in the pot.

The opposite behavior is also observed, that is, a minimum boiling azeotrope:

plot of
vapor pressures

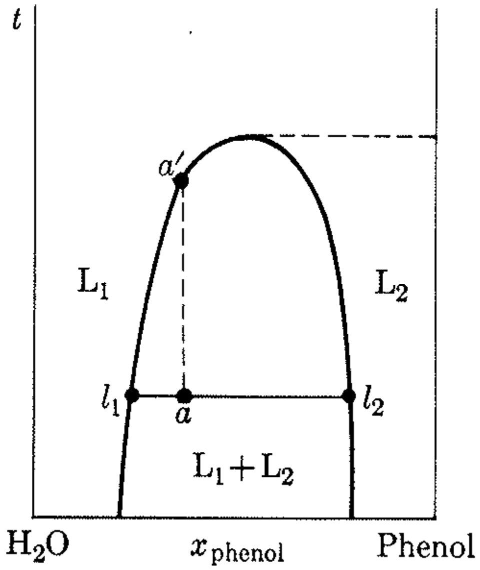


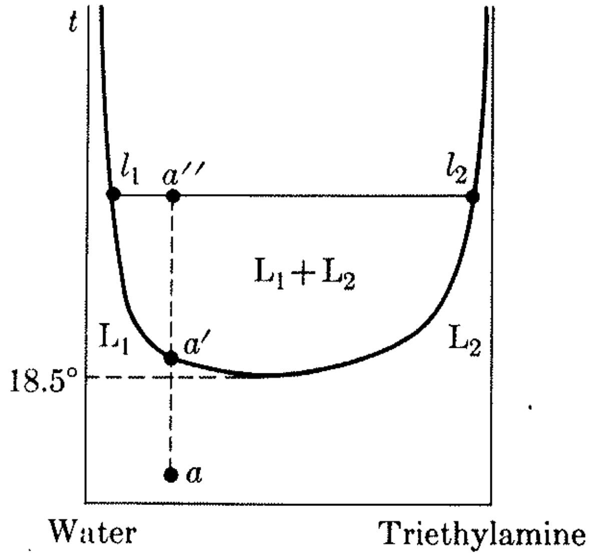
plot of
boiling points

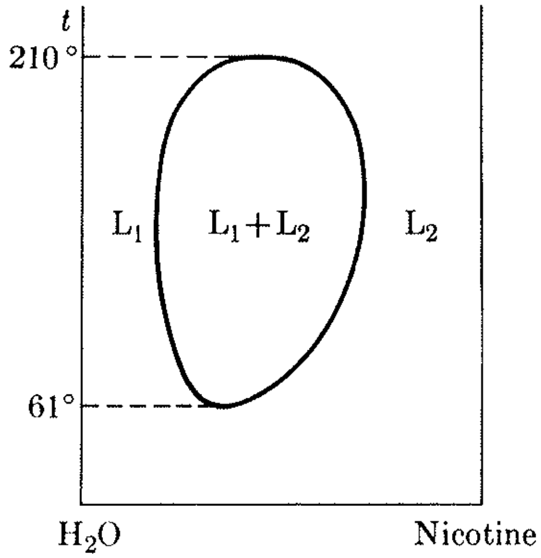


8.3 Liquid-Liquid Equilibria, Partially Miscible Liquids, Critical Solution Temperature

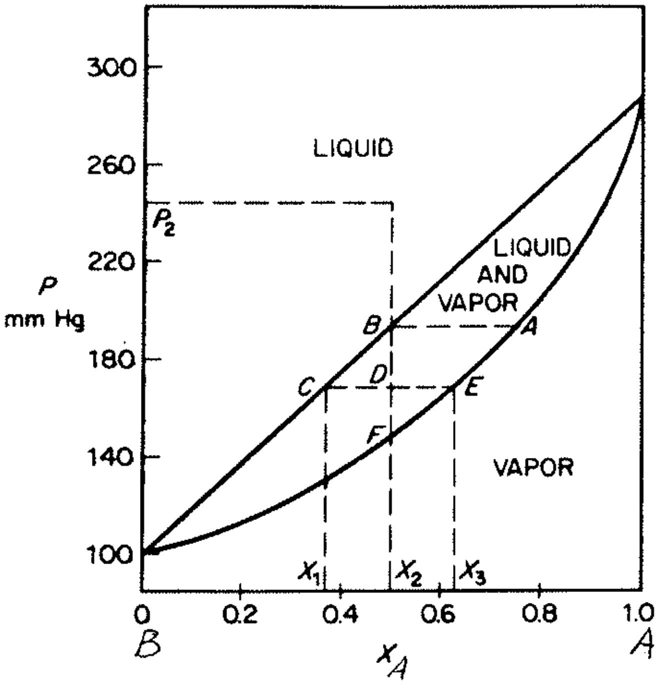
Substances that form ideal solutions are completely miscible in each other. Liquids that are only partially miscible form solutions that are far from ideal.

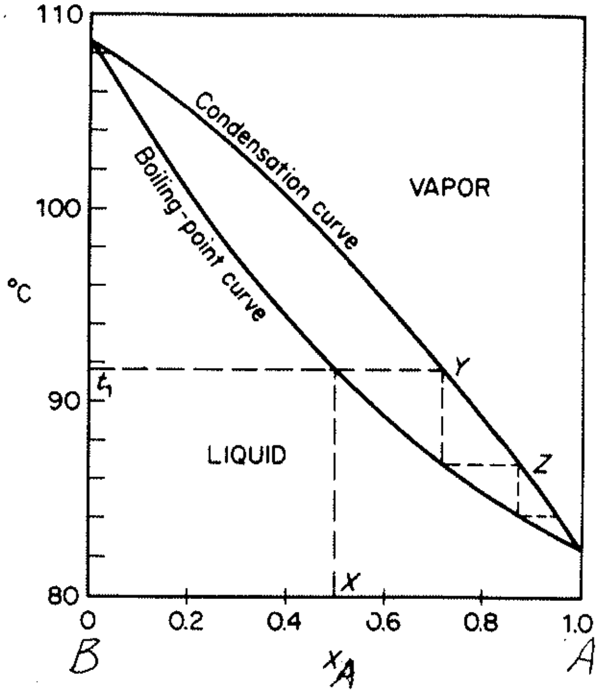




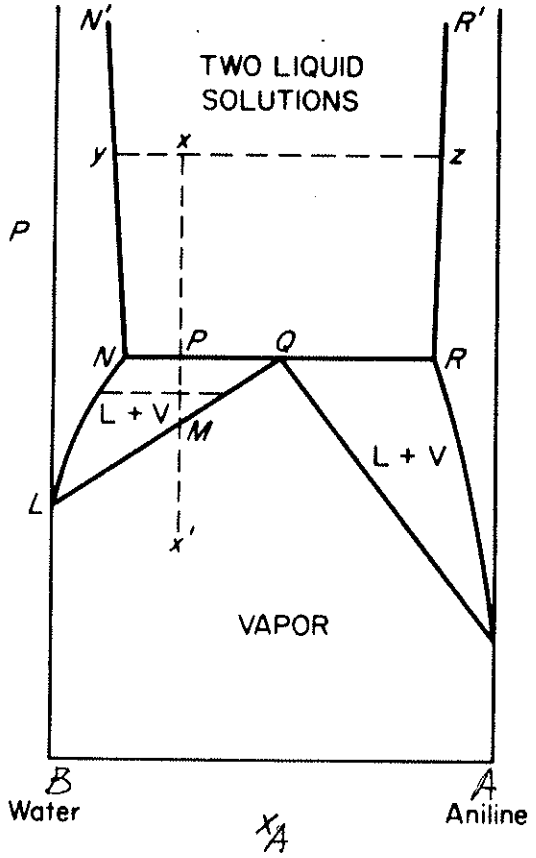


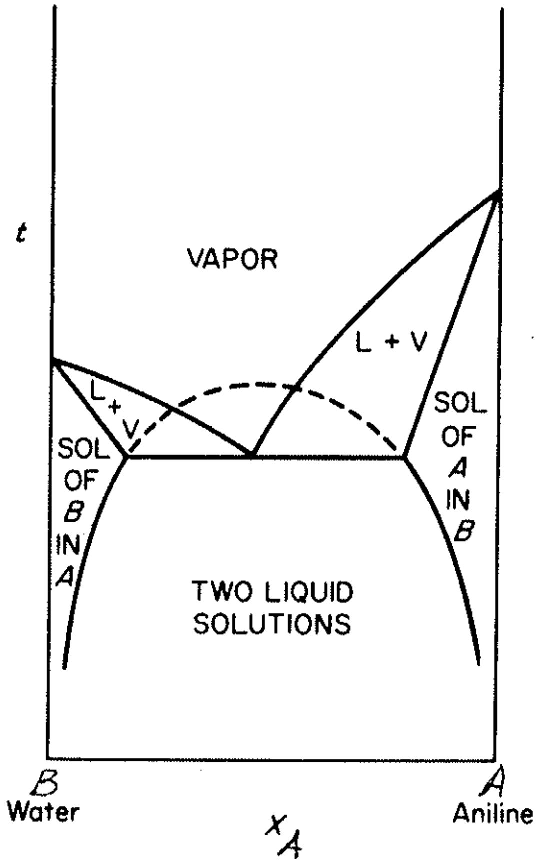
Completely miscible and ideal:



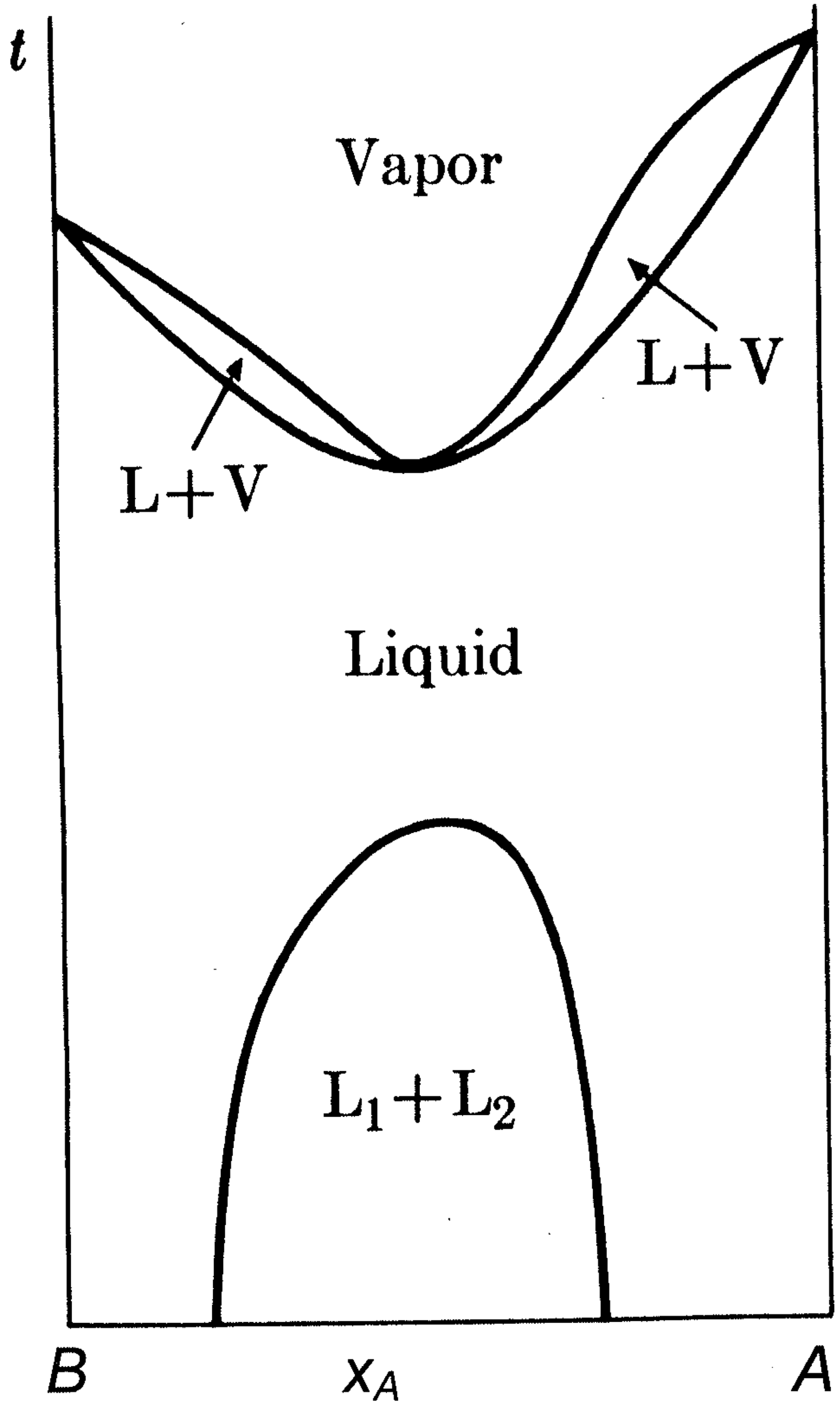


Partially miscible liquids:

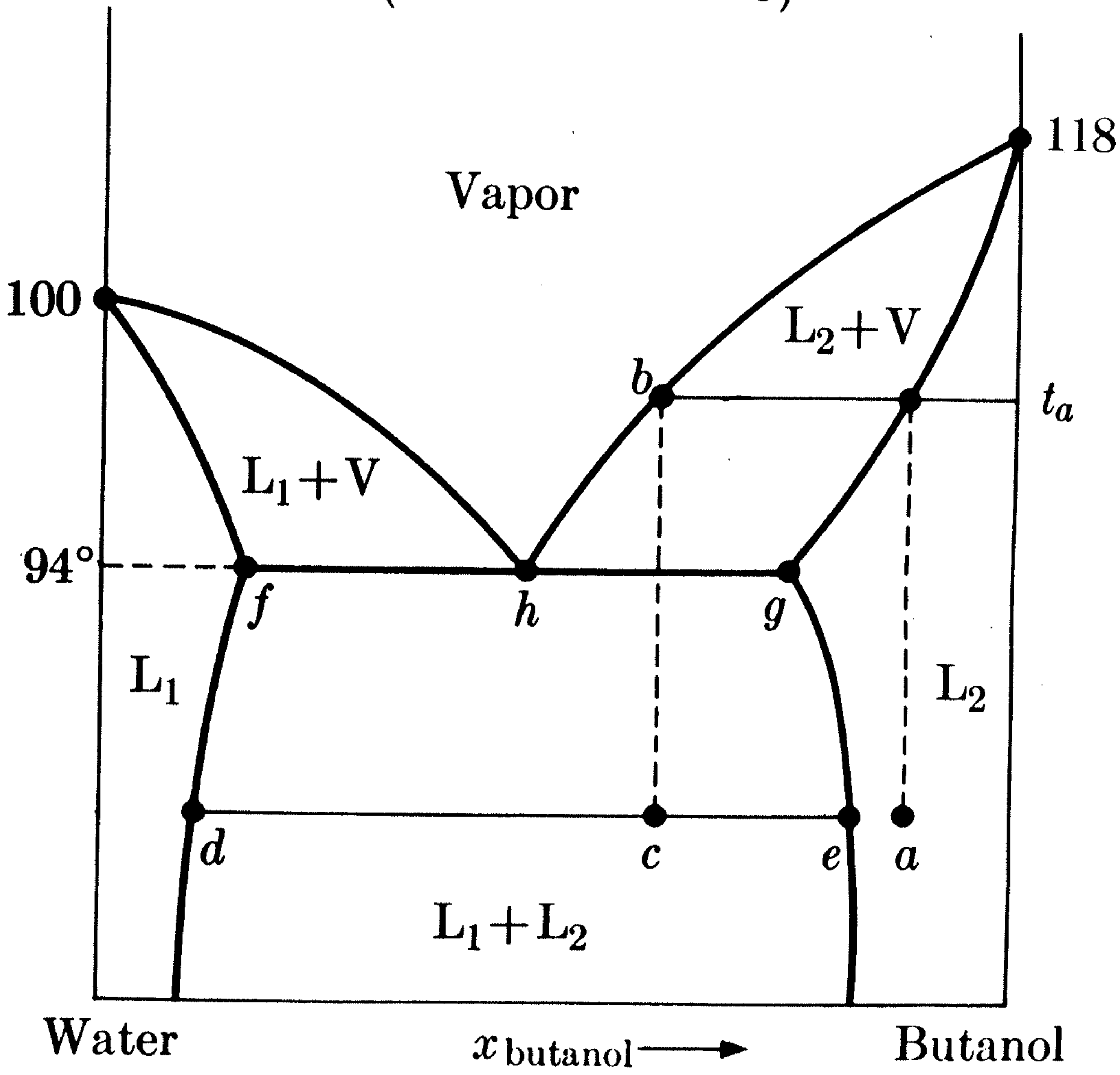




Other possible *T* versus *X* behavior:

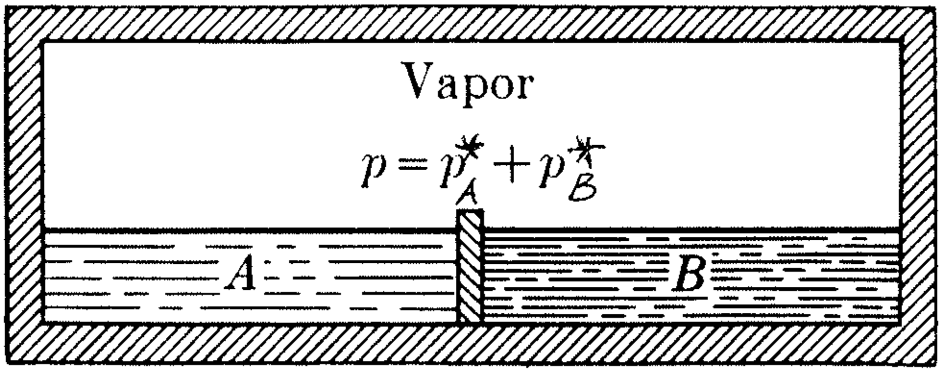


At h three phases are present. At a fixed pressure, the system has zero degrees of freedom. ($F' = C - P + 1 = 0$)



Immiscible liquids

Since the liquids are immiscible, having them be physically separated by a barrier does not change anything:



Total vapor pressure of the pure liquids:

$$p = p^*_A + p^*_B .$$

The mole fractions in the vapor are:

$$y_A = p^*_A / p \qquad y_B = p^*_B / p$$

Then,

$$\frac{(n_A)_{\mathrm{VAP}}}{(n_B)_{\mathrm{VAP}}} = \frac{y_A}{y_B} = \frac{p^*_A / p}{p^*_B / p} = \frac{p^*_A}{p^*_B}$$

The masses of A and B are

$$w_A = (n_A)_{\mathrm{VAP}} M_A \quad w_B = (n_B)_{\mathrm{VAP}} M_B$$

so that

$$\frac{w_A}{w_B} = \frac{M_A\, p^*_A}{M_B\, p^*_B}$$

This is applied to steam distillation of liquids. For example, A is aniline, B is water. At 98.4°C, the vapor pressures of the pure substances are 42 and 718 mm Hg which add up to 760, so that any mixture of aniline and water boils at 98.4°C. Since the vapor pressure is greater than that of either pure component, the boiling point of the immiscible mixture is lower than either pure boiling temperature.

The weight of aniline which distills for each 100 g of water which comes over is

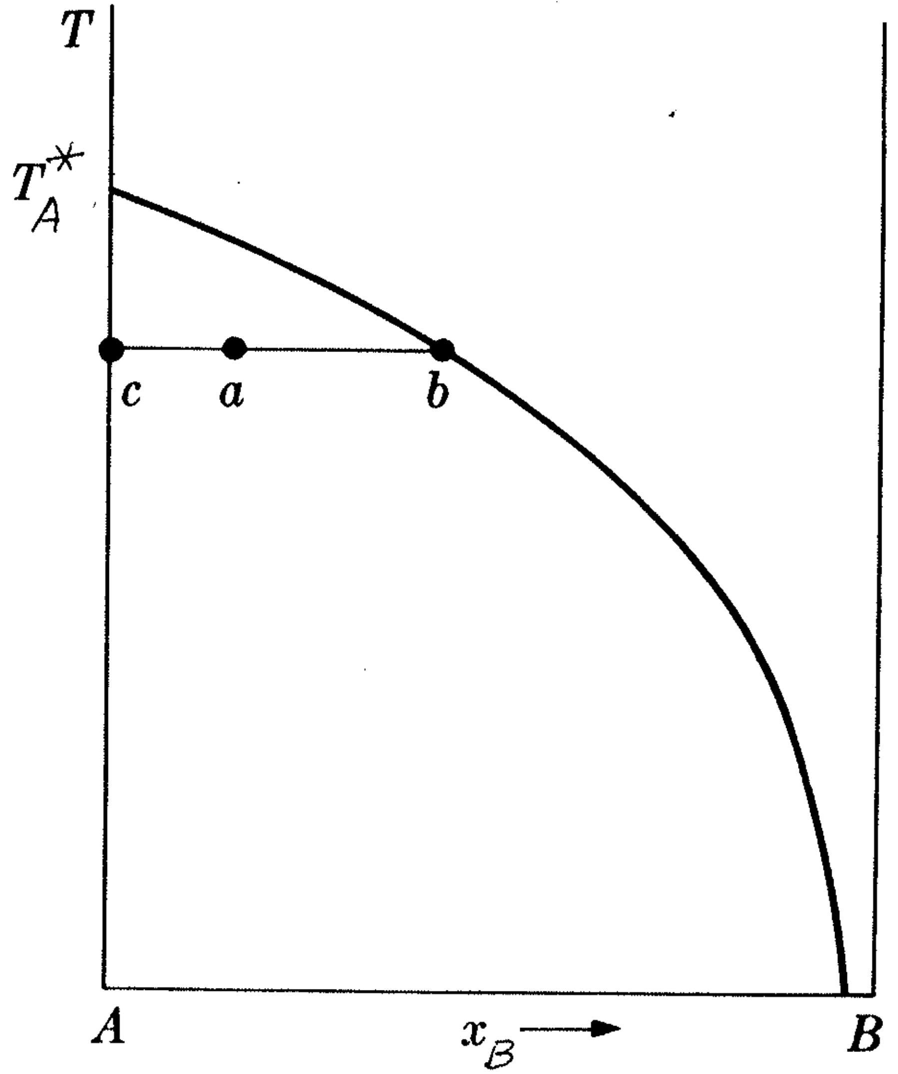
$$\frac{w_A}{100} = \frac{94 \times 42}{18 \times 718}$$

8.4 Solid-Liquid Equilibria, Eutectics, Incongruent Melting

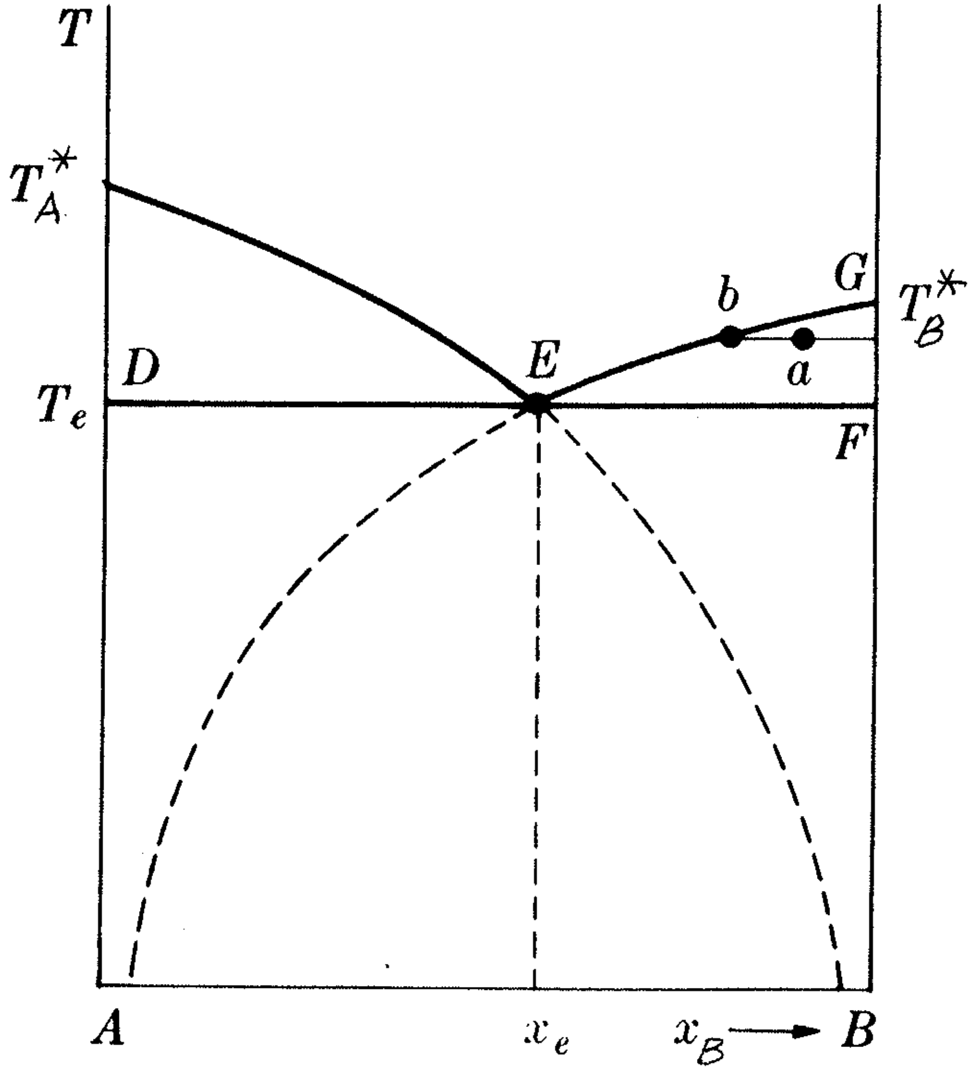
In the discussion of freezing p[oint depression we found, assuming that pure solid A is in equilibrium with an ideal liquid solution,

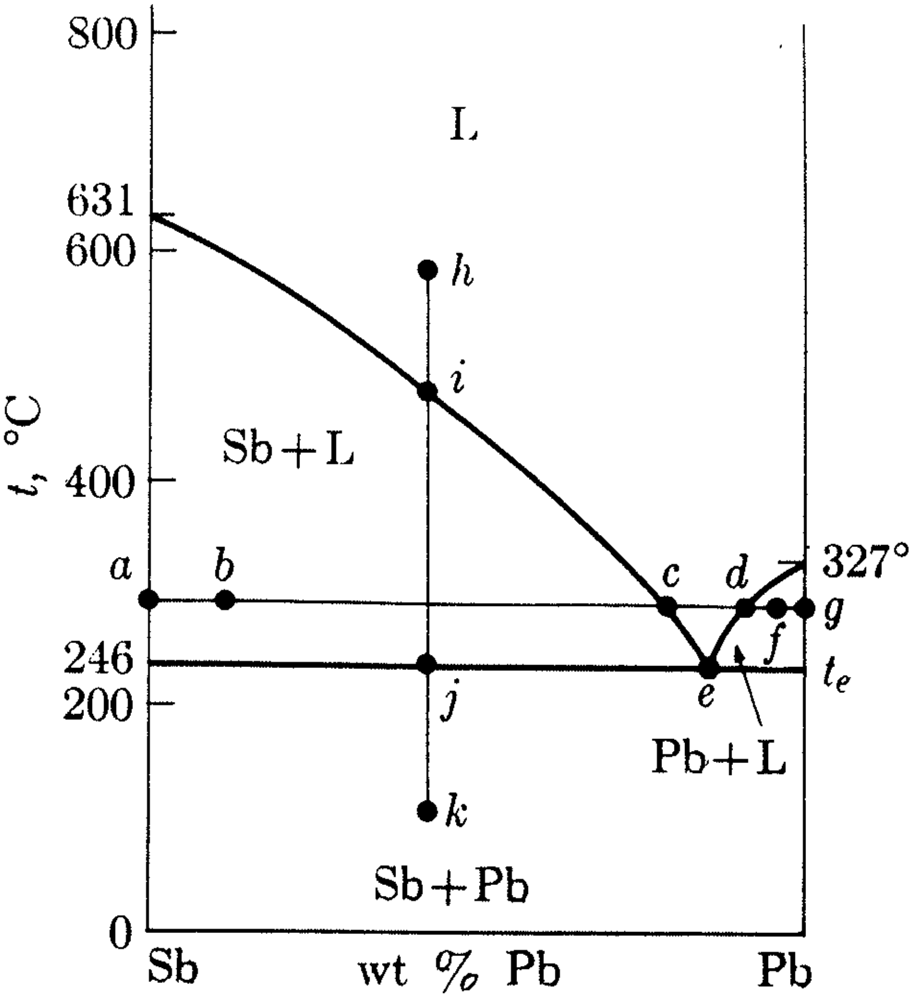
$$\ln x_A = \Delta_{fus} \boldsymbol{H}/R \left[-\frac{1}{T} + \frac{1}{T^*} \right]$$

A plot of this function is :



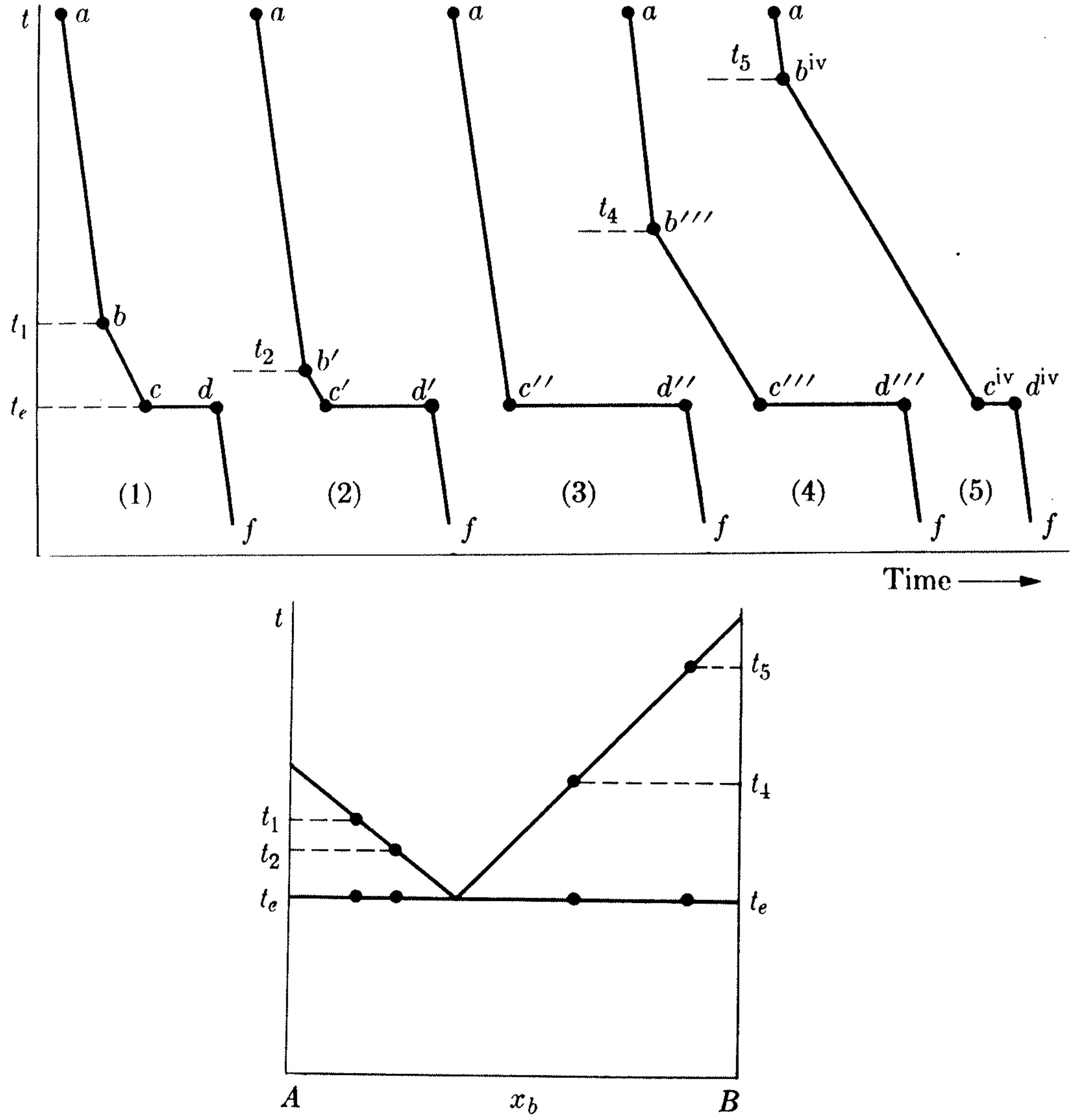
If the solution is ideal, the same holds for the freezing point of a solution in which B is the major component. Pure solid B is in equilibrium with the ideal liquid solution. The curves intersect at a temperature called the ***eutectic temperature***, at which the composition of the system is the ***eutectic composition***.



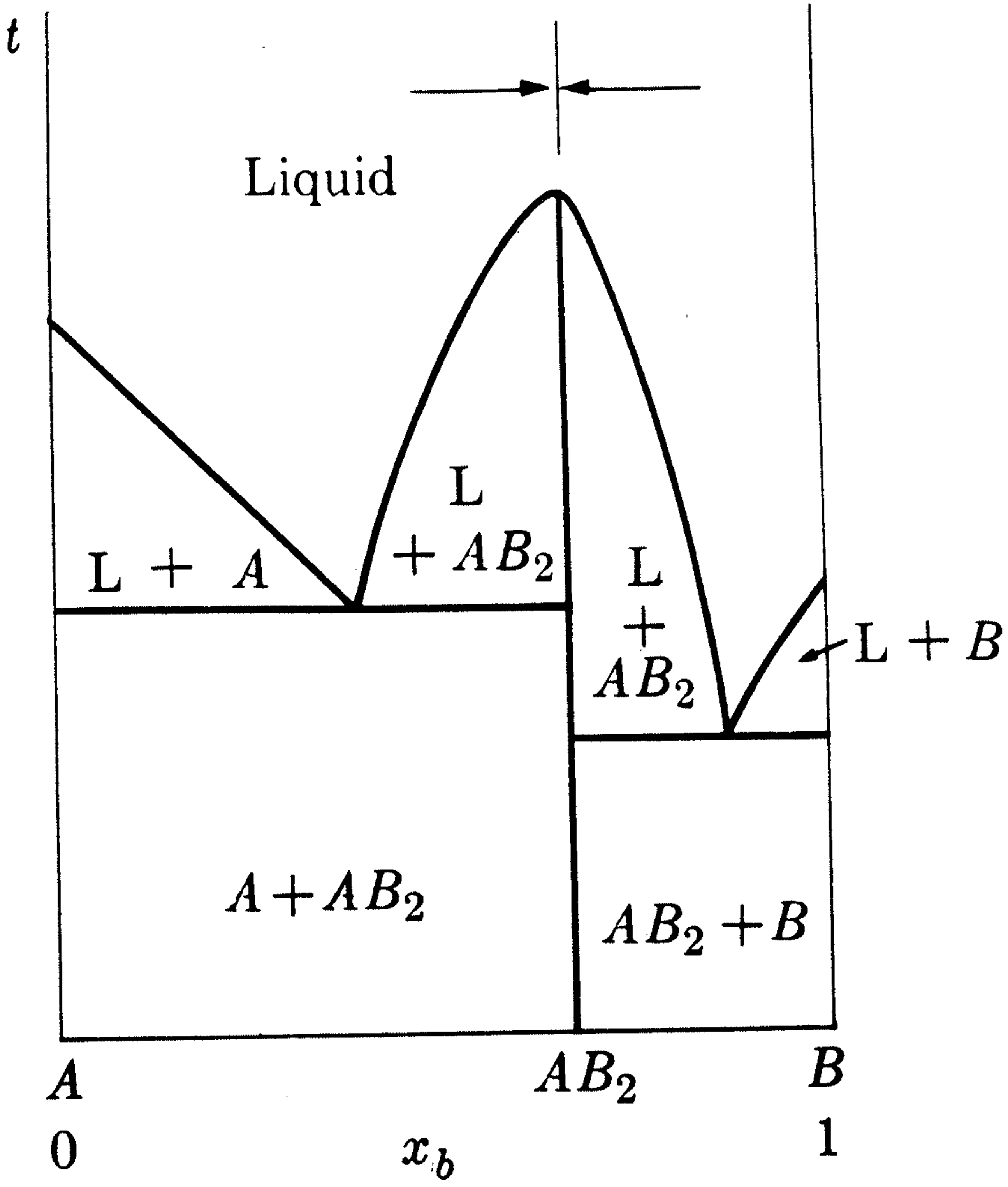


Thermal analysis

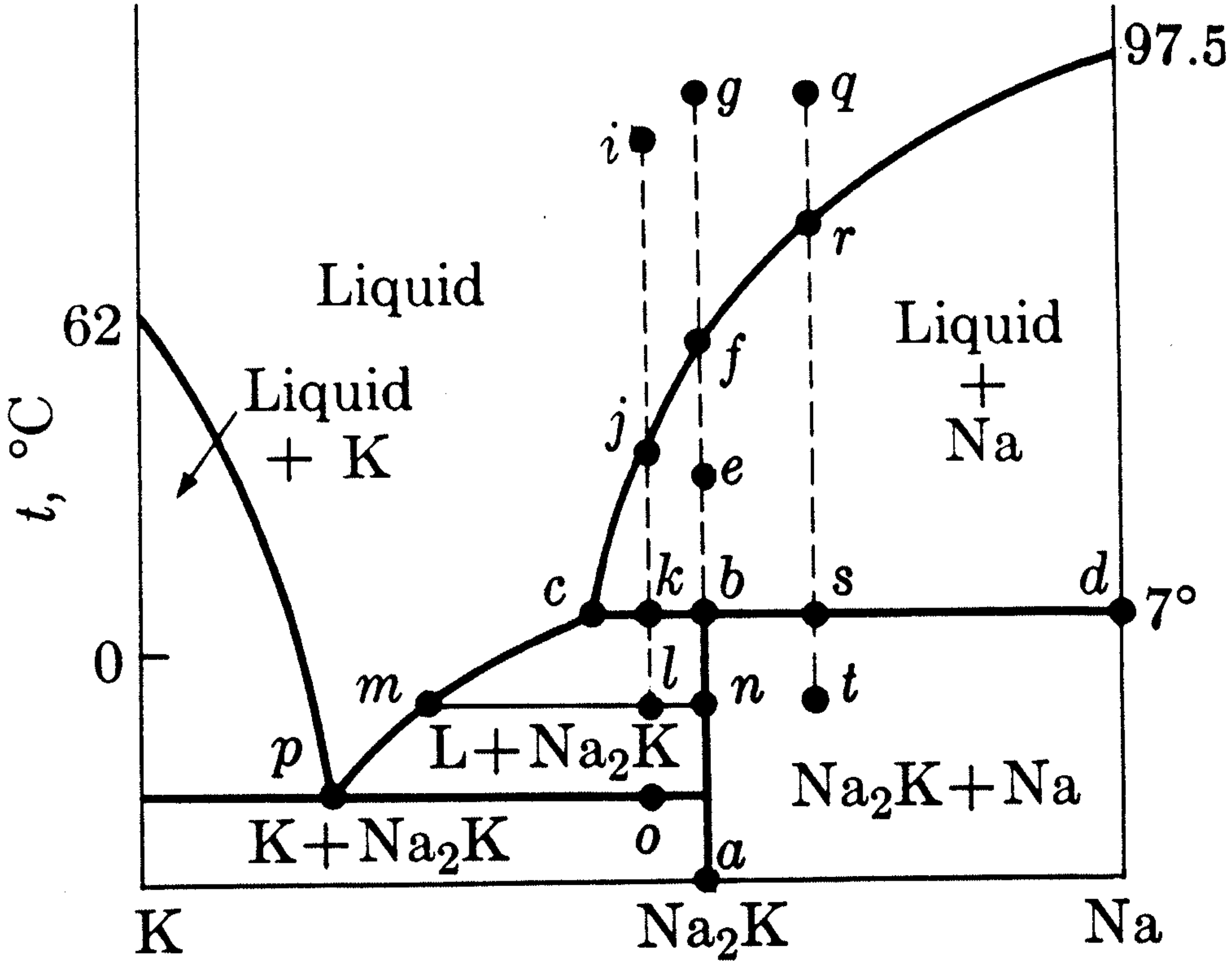
The shape of freezing point curves can be determined experimentally. A mixture of known composition is heated to a high enough temperature so that it is homogeneous. Then it is allowed to cool at a regulated rate. The ***cooling curve*** is a plot of temperature vs. time. The horizontal plateau is the ***eutectic halt***.


t
a
b
c
d
f
t1
te
(1)
a
b′
c′
d′
f
t2
(2)
a
c′′
d′′
f
(3)
a
t4
b′′′
c′′′
d′′′
f
(4)
a
t5
biv
civ
div
f
(5)
Time
t
t1
t2
te
t5
t4
te
A
xb
B

Compound Formation



Compounds having incongruent melting points



When the solubility curve of one component (A) does not drop rapidly enough to intersect the other curve between the composition of the compound and pure A but instead intersects the other curve at the ***peritectic point***. (*c*).The compound is said to melt ***incongruently*** since the melt differs from the compound in composition.

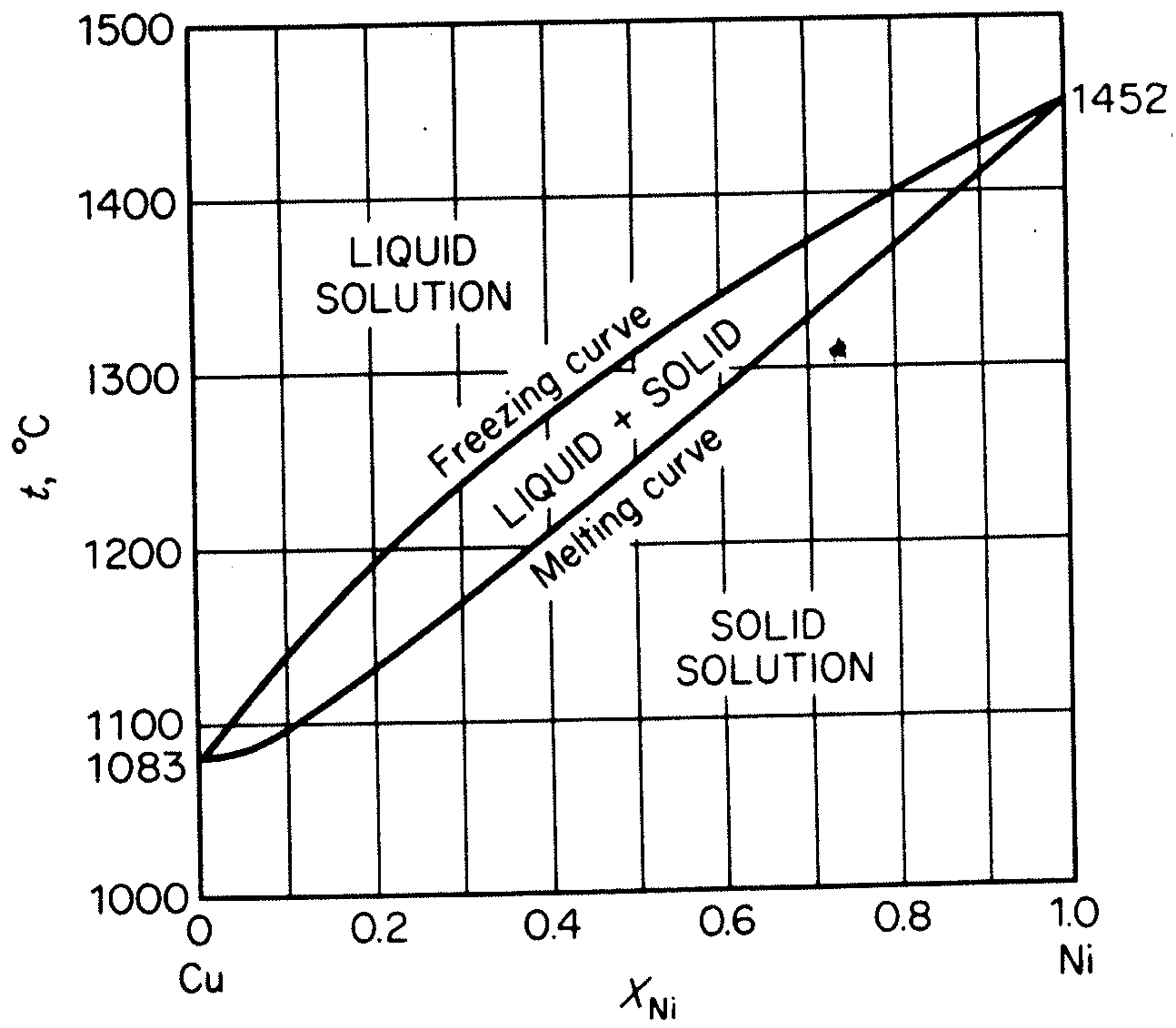
- Start with the pure solid compound Na_2K. On increasing temperature
- the state point moves along line ***ab***
- ***b*** liquid having composition ***c*** forms
  $Na_2K(s) \rightarrow Na(s) + c(liquid)$
  3 phases in equilibrium
- the state point moves along ***bef***
- ***f*** the last trace of solid Na melts
- above ***f*** the system consists of one phase

Start with melt ***i***. On cooling,

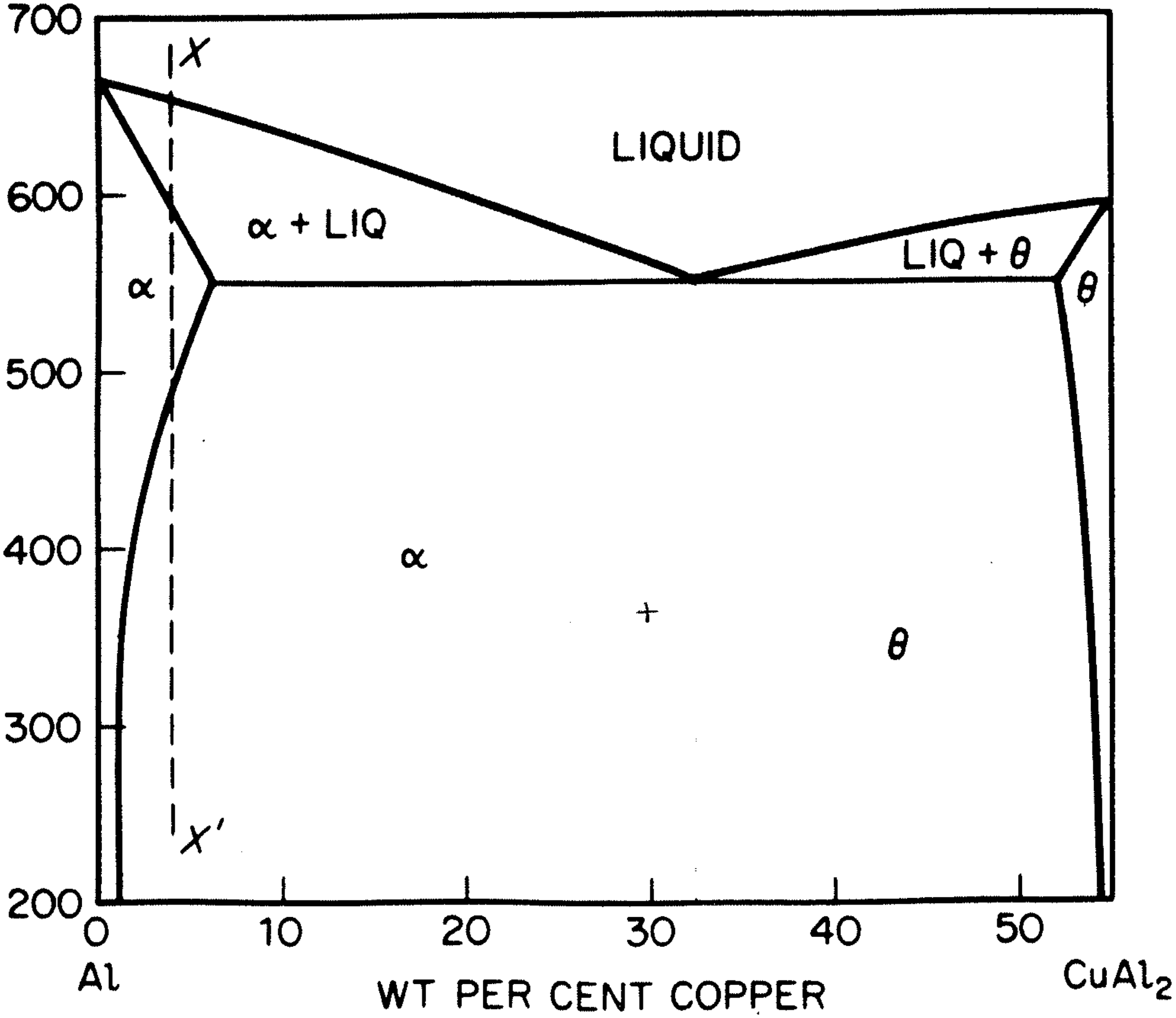
- ***j*** crystals of Na(s) form, liquid composition moves along ***jc*** as more Na(s) crystallizes
- ***k*** Na_2K(s) forms:
  c(liquid) + Na(s) → Na_2K(s)
  The amount of Na in composition ***i*** is insufficient to convert the liquid ***c*** completely into compound.
- After the Na(s) is consumed, the temperature drops, Na_2K crystallizing and the liquid composition moving along ***cm***
- ***l*** the tie line shows that Na_2K coexists with liquid ***m***.
- ***o*** pure K(s) begins to crystallize, the liquid has the eutectuic composition ***p***
- When the liquid disappears, a mixture of K(s) and Na_2K(s) appear.

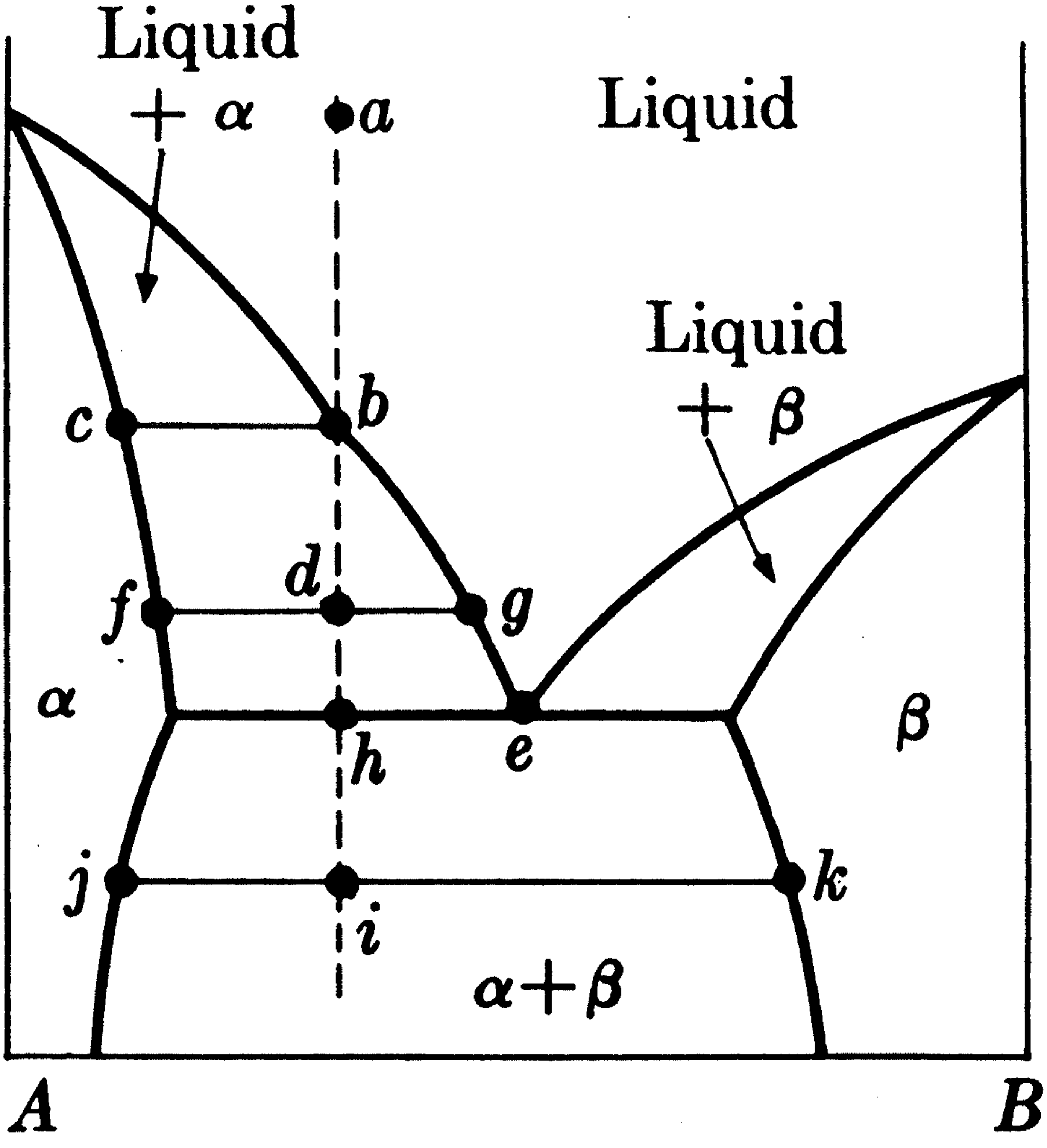
Solid solutions

Addition of a foreign substance always <u>lowers the melting point of a pure solid</u>. An *increase in melting point* can occur if the solid in equilibrium with the melt is not pure but is a solid solution.



Partially miscible solids




Liquid
+ α
a
Liquid
Liquid
+ β
b
c
d
f
g
α
e
h
β
j
i
k
α+β
A
B

α solid solutions of B in A
β solid solutions of A in B
$\alpha+\beta$ two phases (both are saturated solid solutions) coexist in equilibrium

Cooling a system at state point ***a***,

- state point moves along ***ab***
- ***b*** solid solution α having composition ***c*** appears
- temperature drops, state point moves along ***bd***
- ***d*** two phases of composition ***f*** and ***g*** are in equilibrium
- ***h*** liquid has eutectic composition ***e***, solid β appears, 3 phases in equilibrium
- ***i*** two phases of composition ***j*** and ***k*** coexist, both are saturated solid solutions)

No eutectic point, but a transition point

At any point on the line **abc** three phases coexist: α, β, and a melt of composition **c**. The temperature of **abc** is the transition temperature.