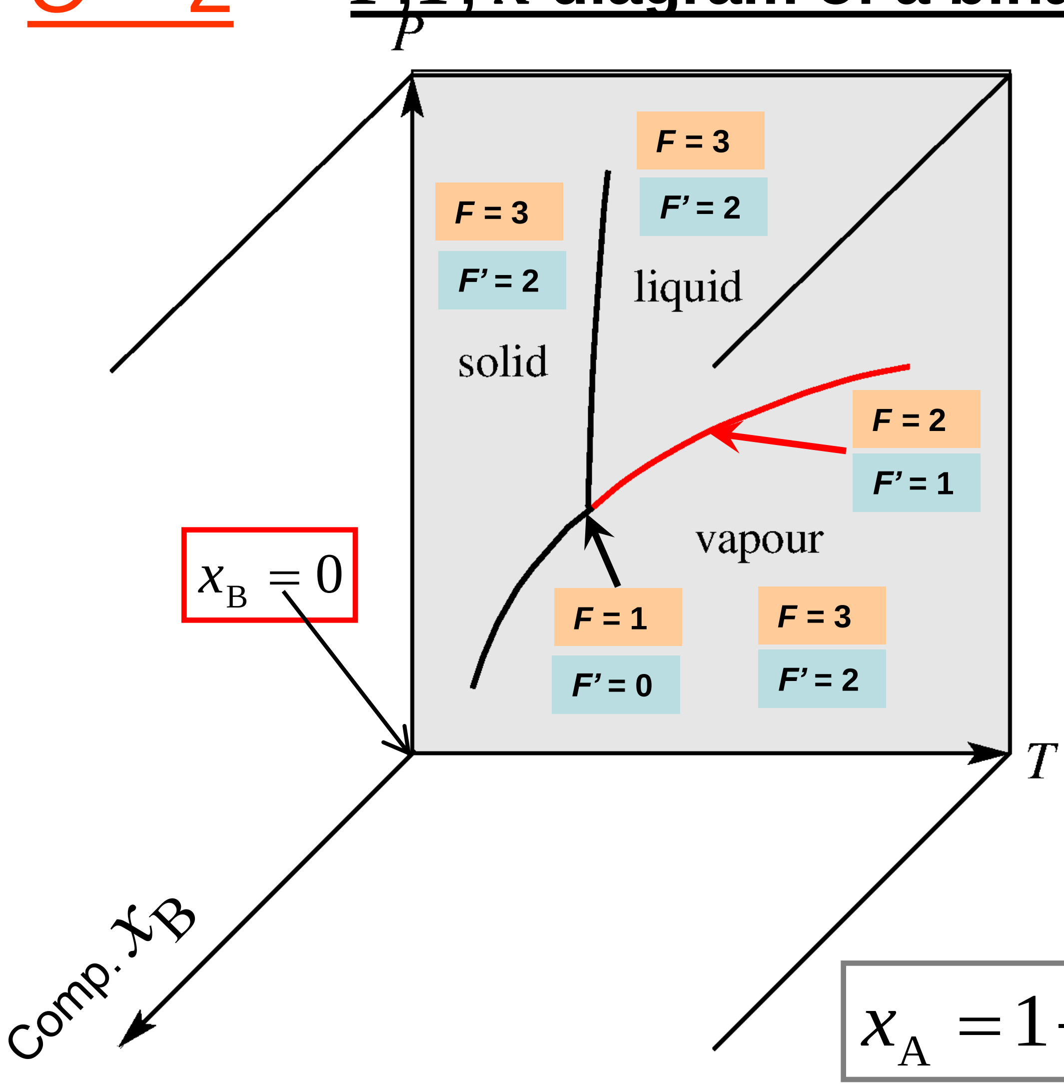
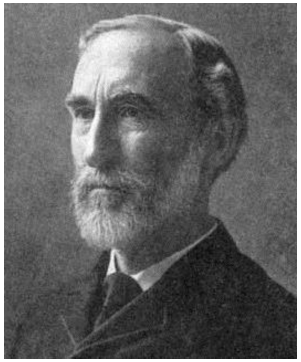
Summary of Lecture 4

Phase diagrams of multicomponent systems

C = 2

P, *T*, *x* diagram of a binary sytem





Gibbs phase rule

$$\boxed{F = C - P + 2}$$

$$\boxed{F' = C - P + 2 - 1}$$

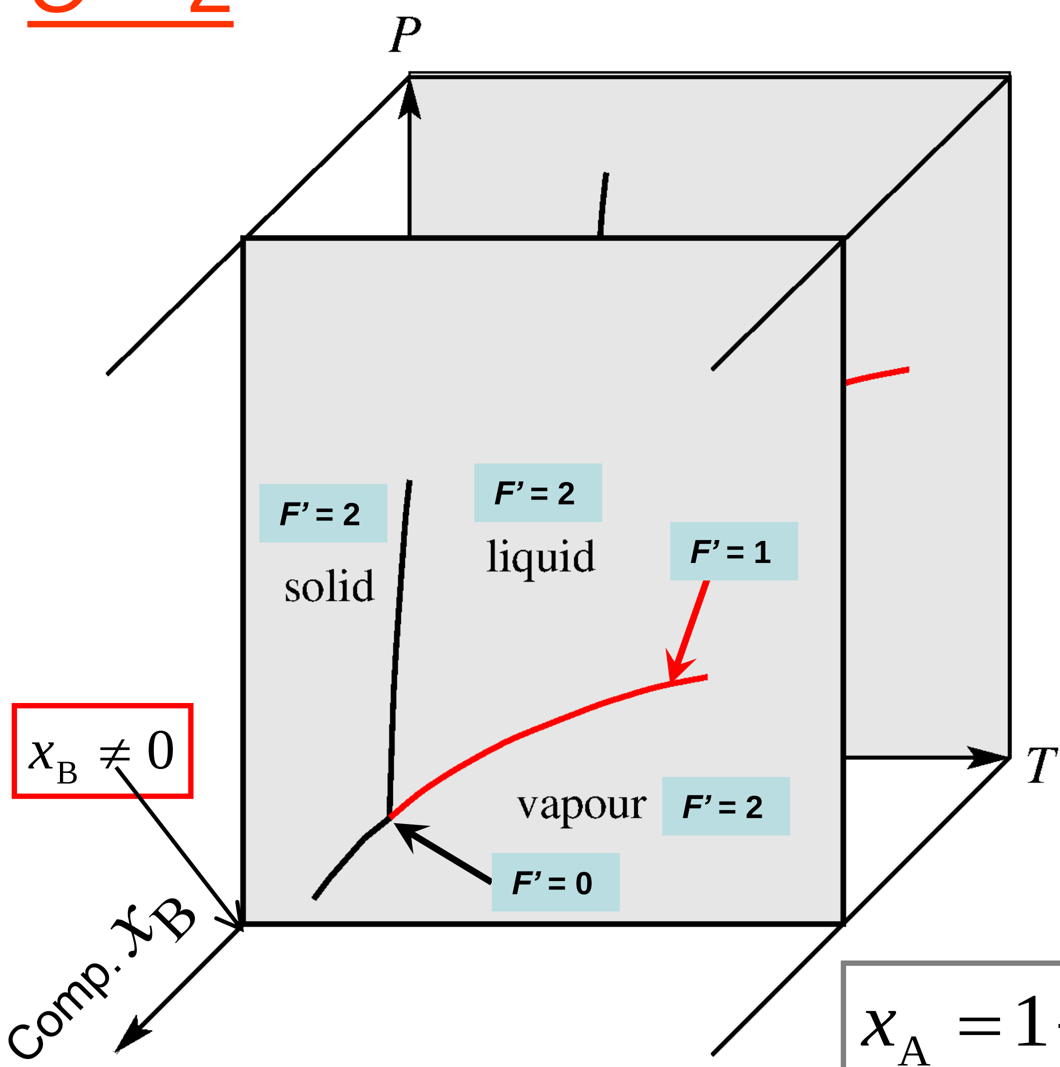
(if x is considered fixed)

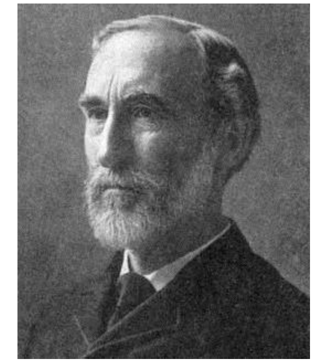
$$\boxed{x_A = 1 - x_B}$$

Vapour-liquid-composition diagram

P, T, x diagram of a binary sytem

$C = 2$





Gibbs phase rule

$$\boxed{F = C - P + 2}$$

$$\boxed{F' = C - P + 2 - 1}$$

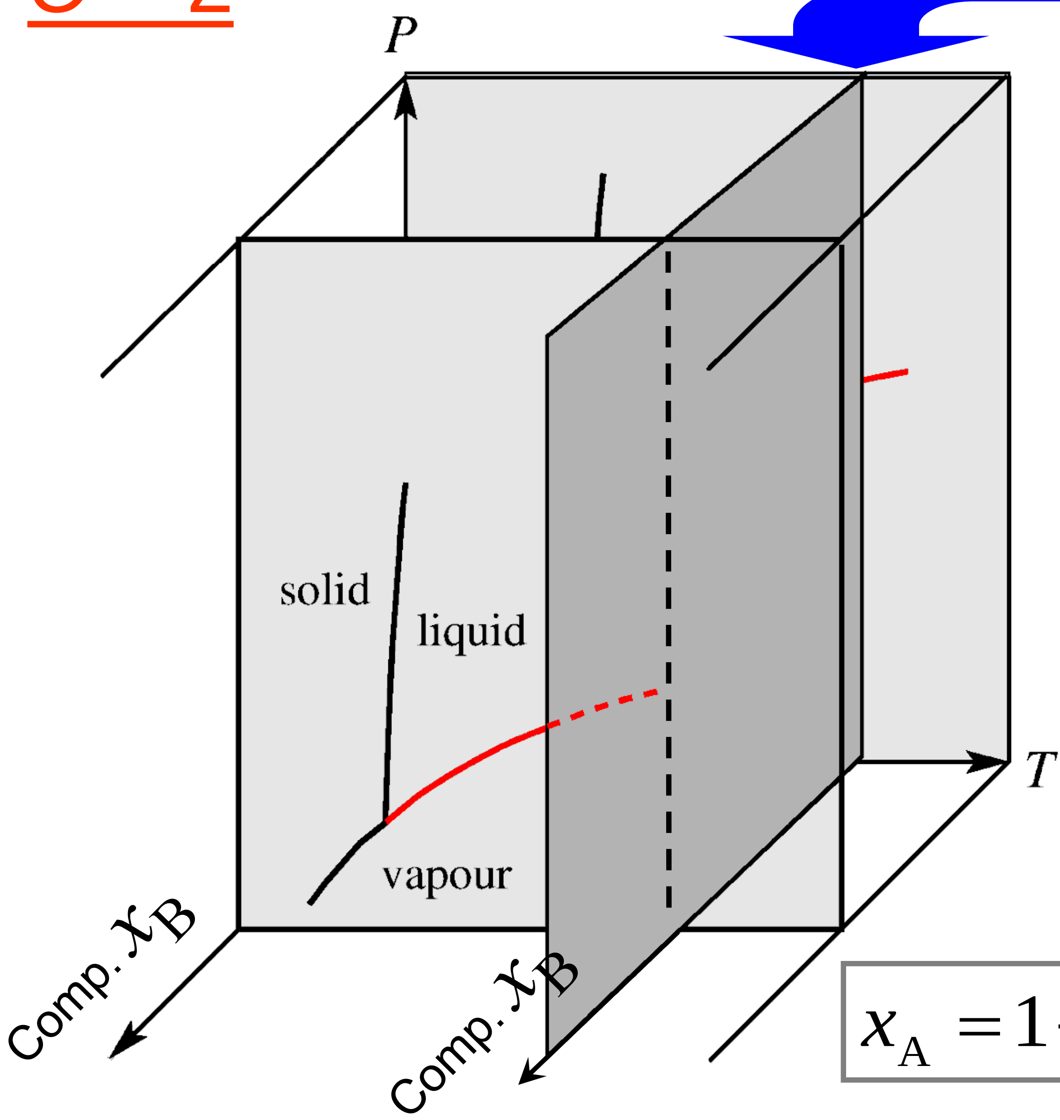
(x is fixed)

$$\boxed{x_A = 1 - x_B}$$

Vapour-liquid-composition (P,x) diagram

$C = 2$

Fixed T



Gibbs phase rule

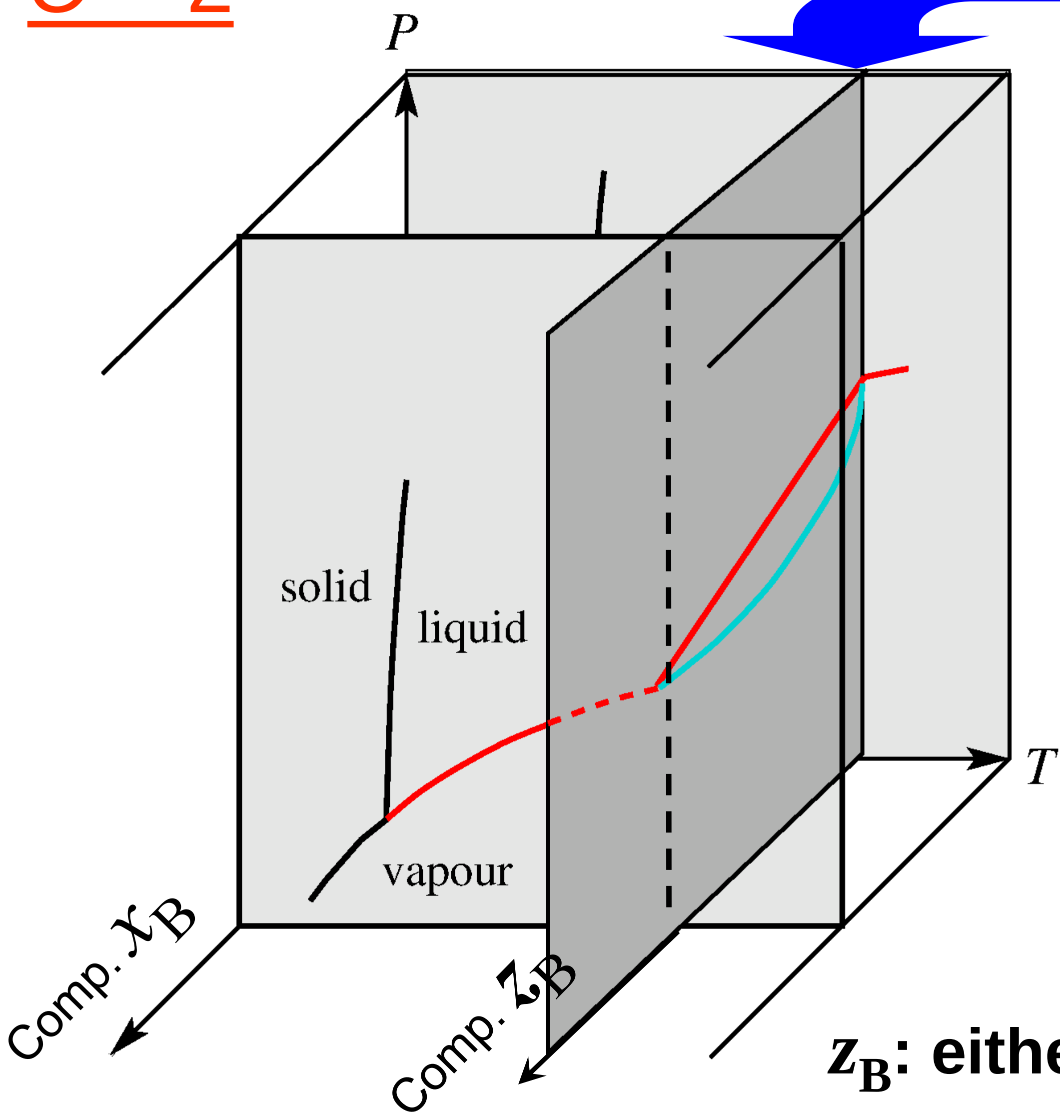
$$\boxed{F = C - P + 2}$$

$$\boxed{x_A = 1 - x_B}$$

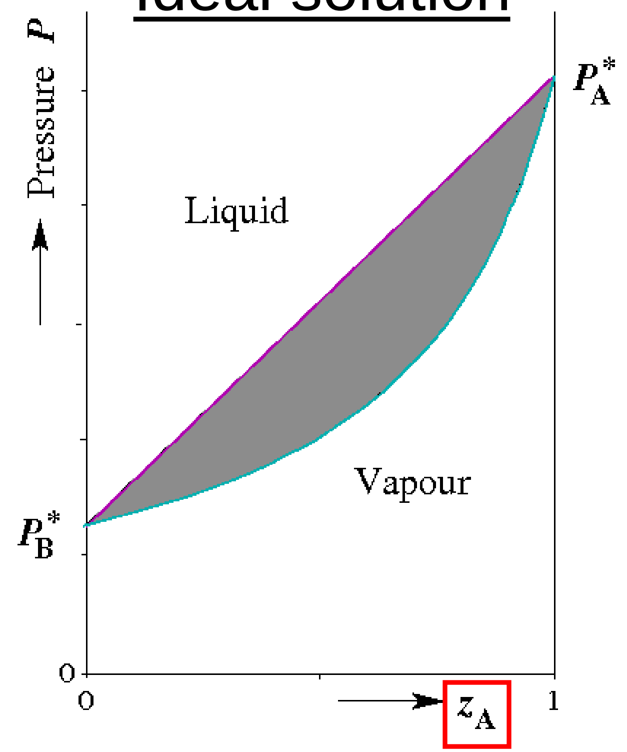
Vapour-liquid-composition (P,x) diagram

C = 2

Fixed *T*



Ideal solution

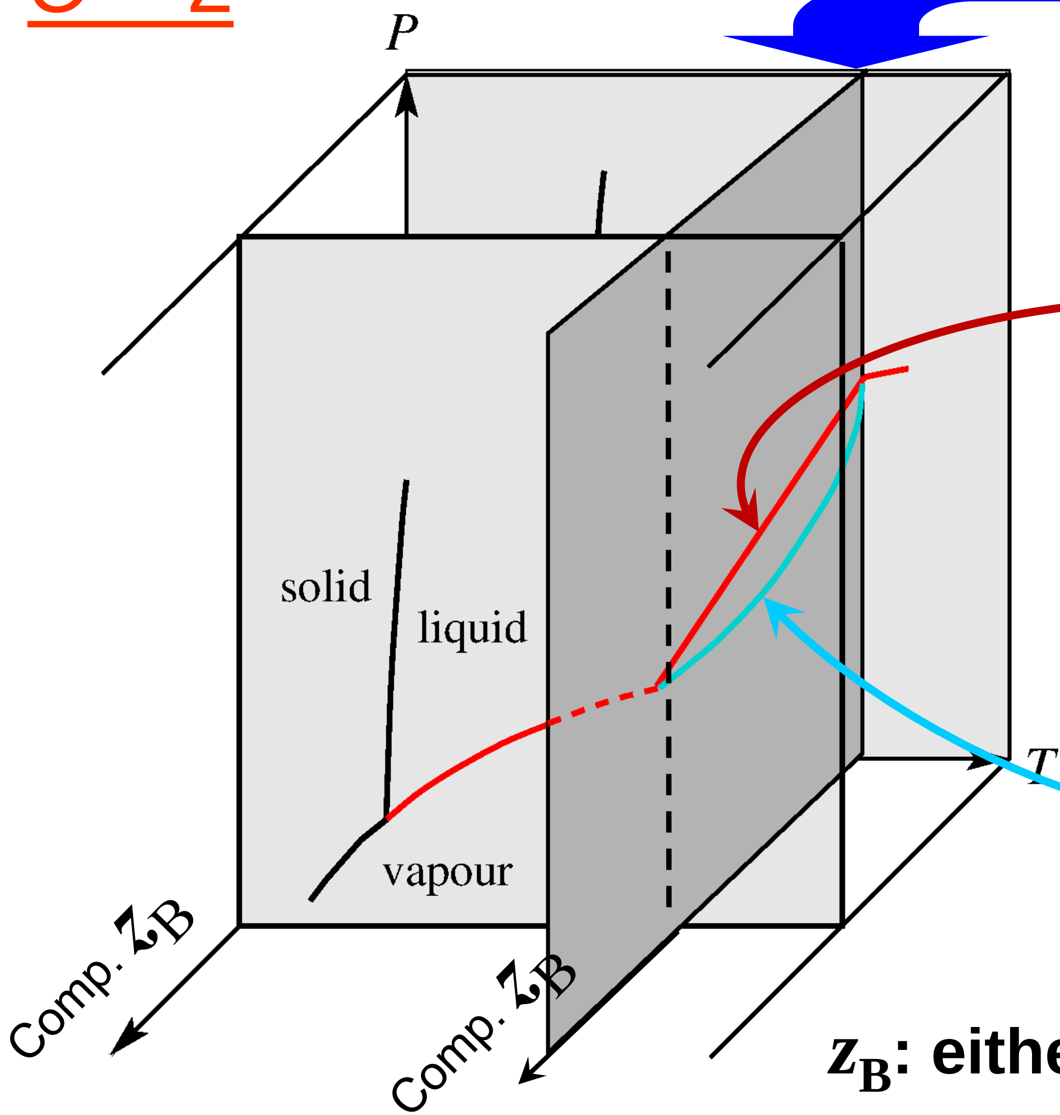


z_B: either x_B or y_B

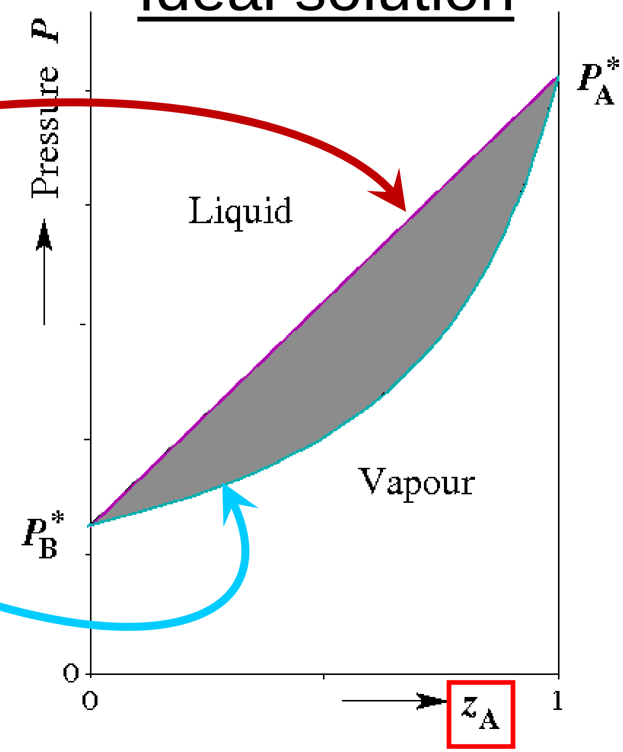
Vapour-liquid-composition (P,x) diagram

C = 2

Fixed T



Ideal solution

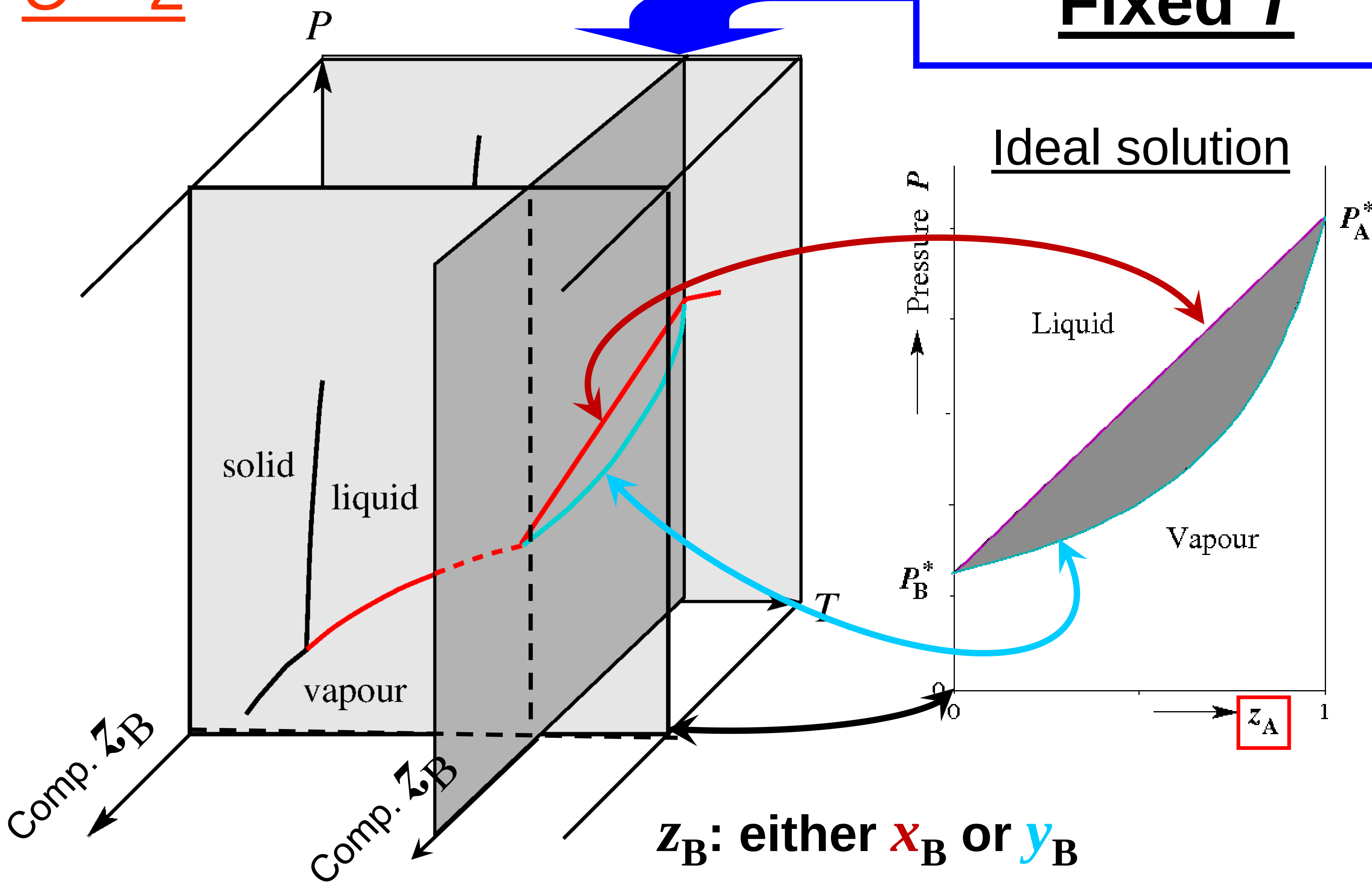


z_B: either x_B or y_B

Vapour-liquid-composition (P,x) diagram

C = 2

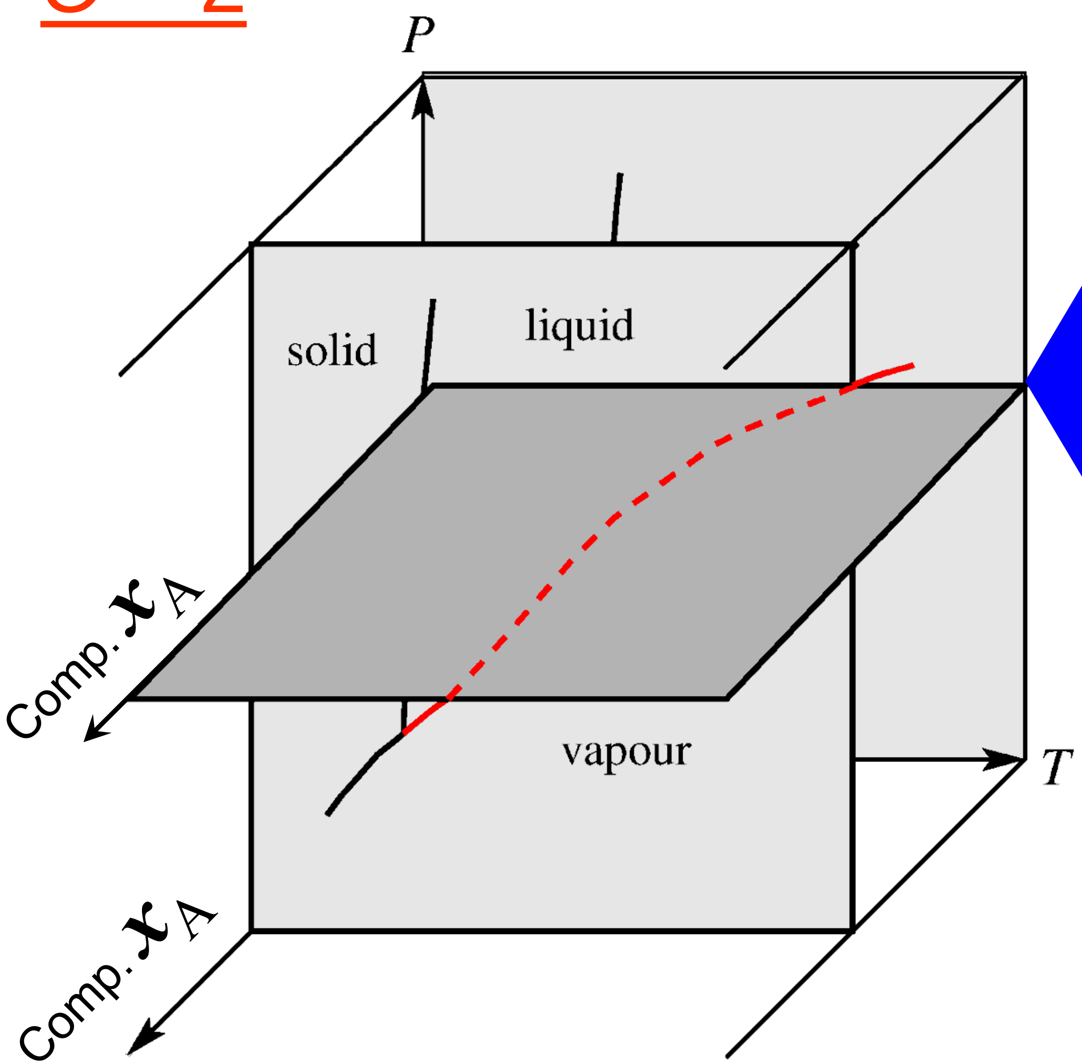
Fixed T



z_B: either x_B or y_B

Vapour-liquid-composition (T,x) diagram

C = 2



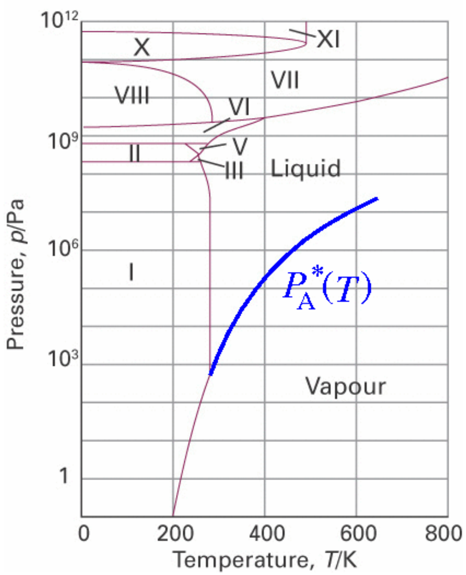
Fixed *P*

Temperature-composition diagrams

$$x_{\mathrm{A}}(T) = \frac{P - P_{\mathrm{B}}^{*}(T)}{P_{\mathrm{A}}^{*}(T) - P_{\mathrm{B}}^{*}(T)}$$

$$y_{\mathrm{A}}(T) = \frac{P_{\mathrm{A}}^{*}(T)\left[P - P_{\mathrm{B}}^{*}(T)\right]}{P\left[P_{\mathrm{A}}^{*}(T) - P_{\mathrm{B}}^{*}(T)\right]}$$

Ideal solution

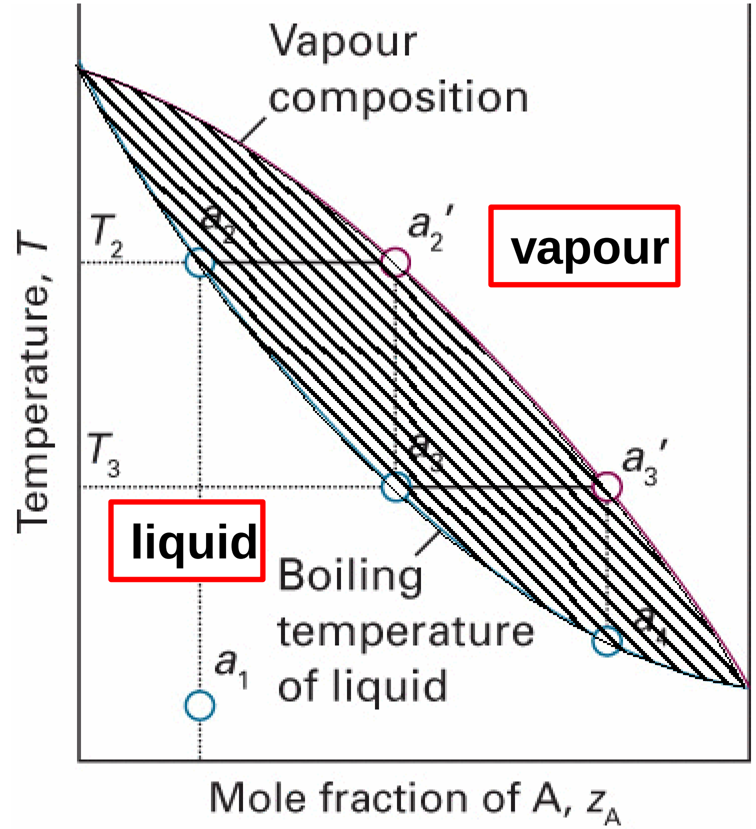


$$\frac{\mathrm{d}P_{\mathrm{A}}^{*}}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{A}}^{*}(T)}{T\Delta_{\mathrm{vap}}V_{\mathrm{A}}^{*}(T)}$$

(Clapeyron)

(*P*,*T*)-diagram

Component A



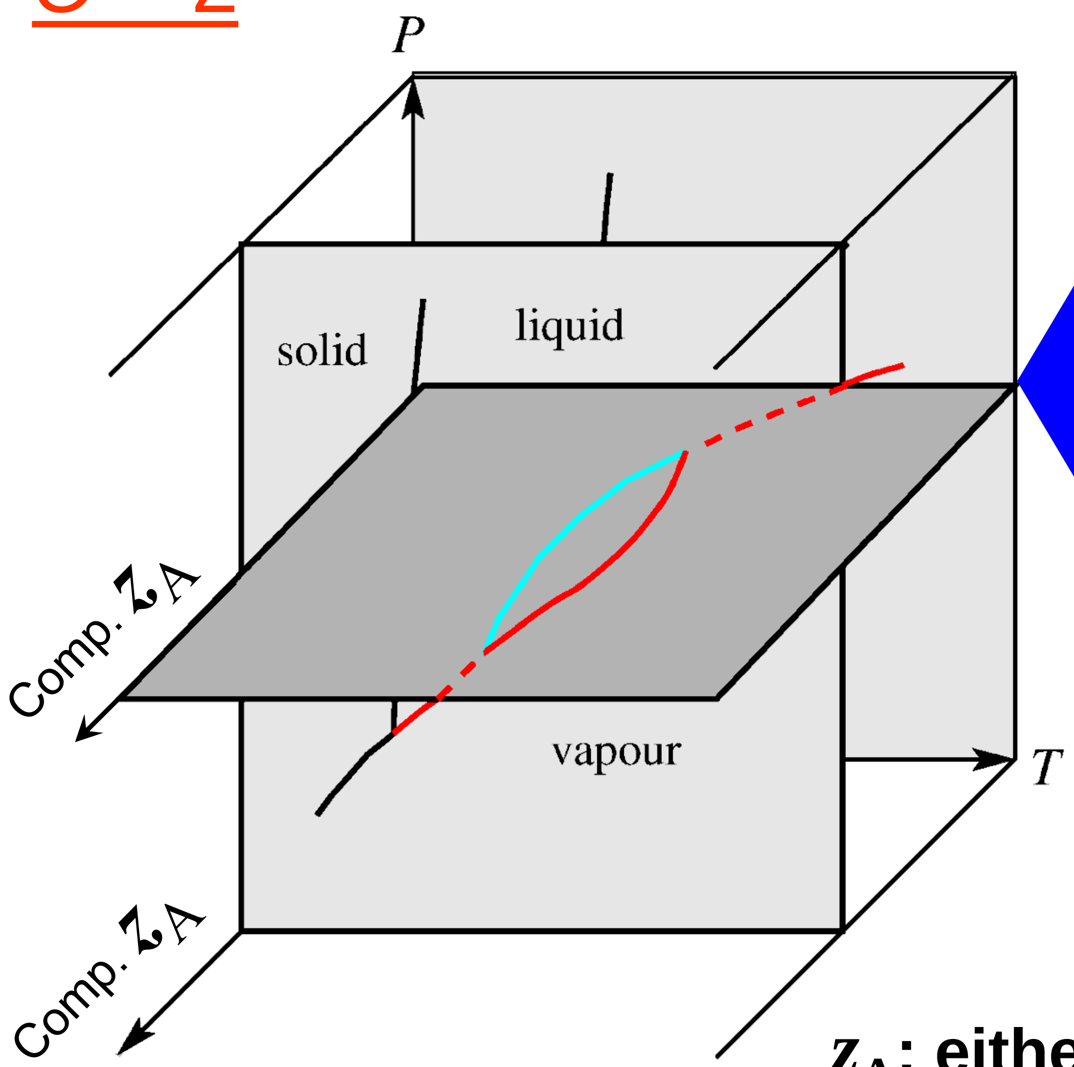
Fixed *P*

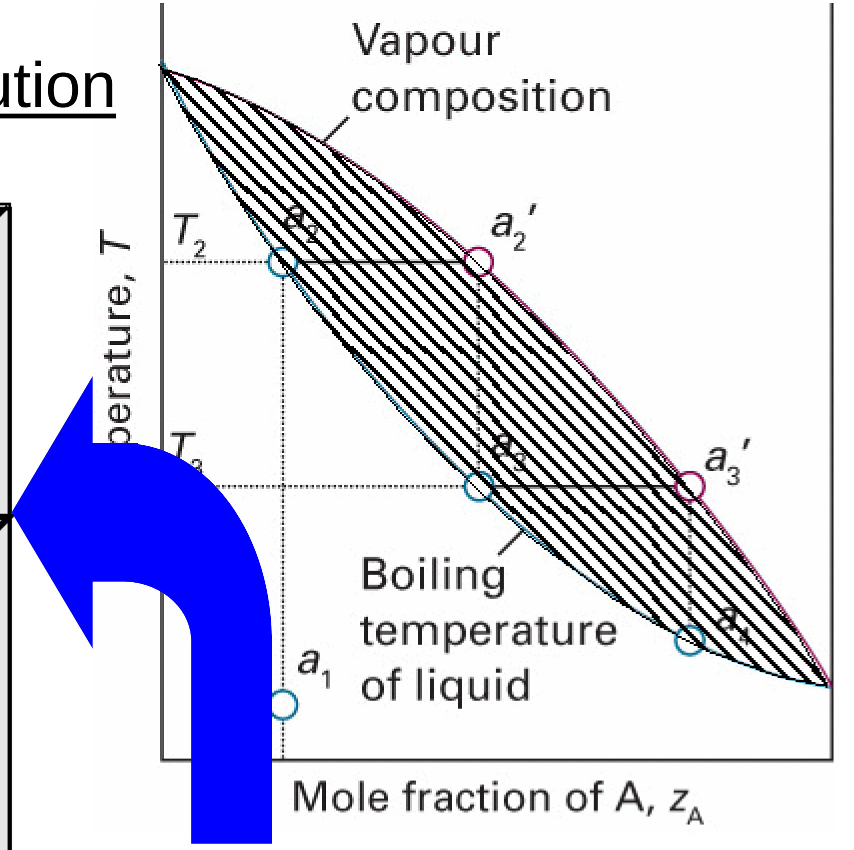
important for distillation processes

Vapour-liquid-composition (T,x) diagram

C = 2

Ideal solution



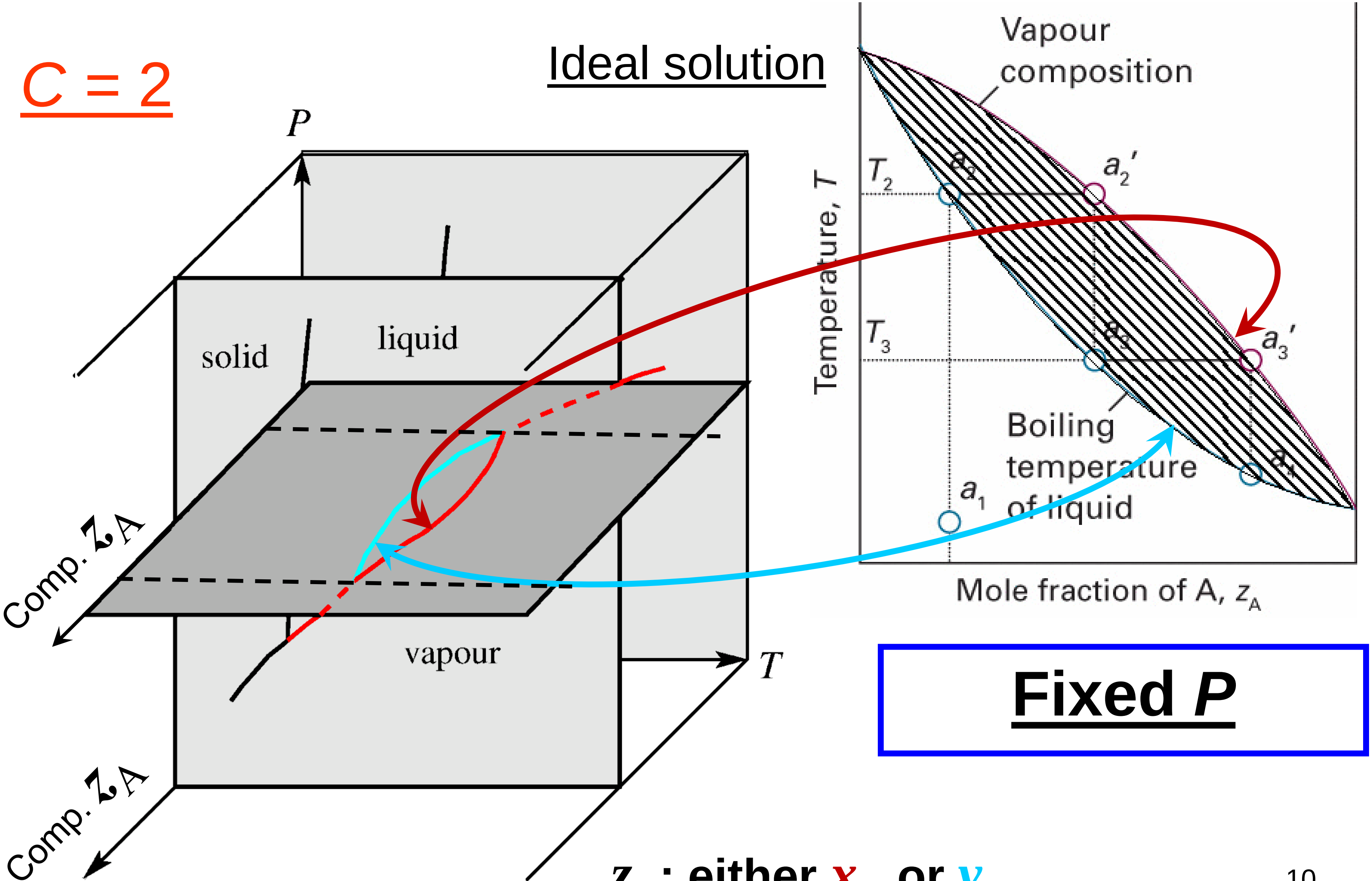


Fixed P

z_A: **either** x_A **or** y_A

Vapour-liquid-composition (T,x) diagram

C = 2



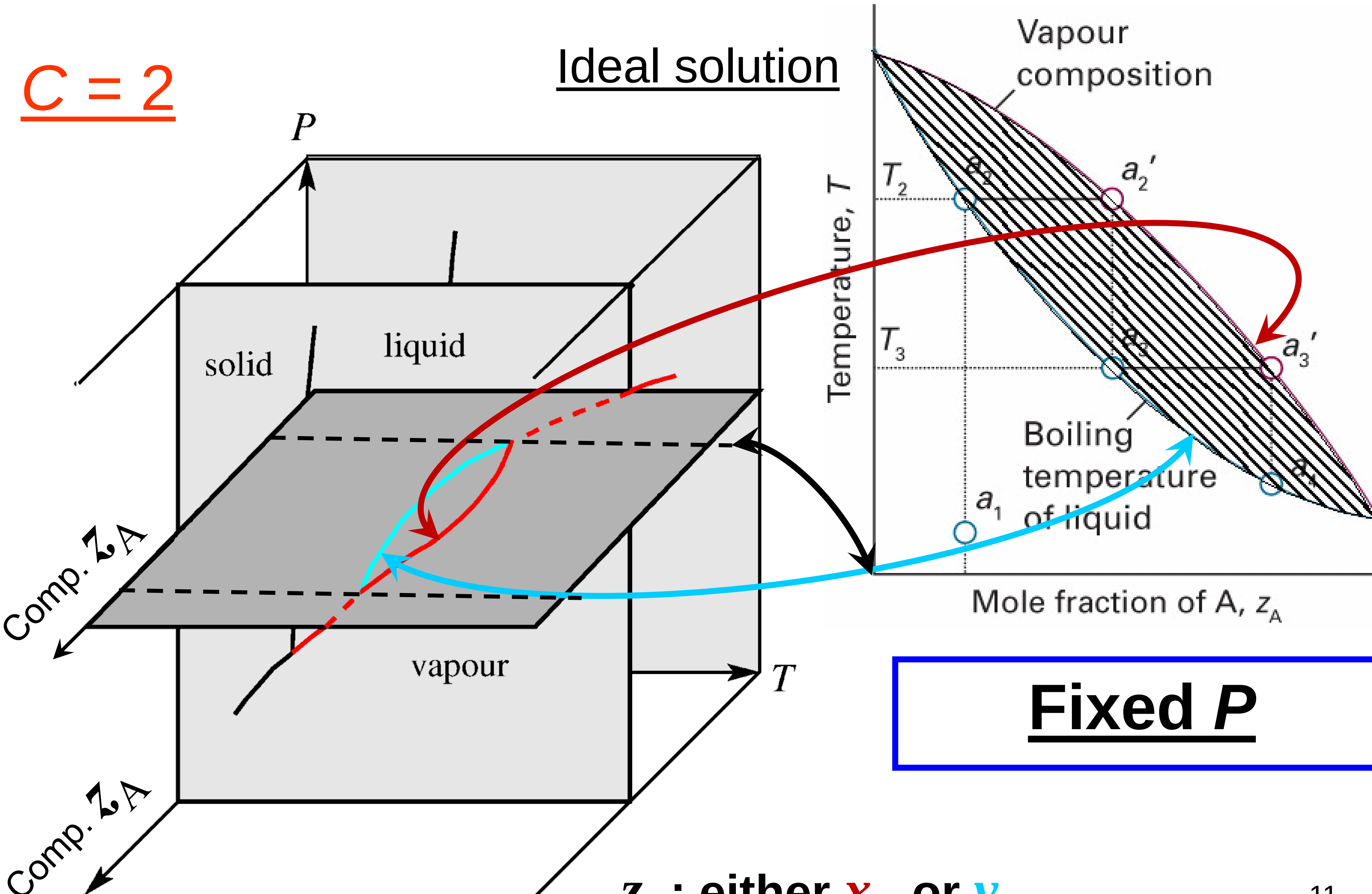
Fixed *P*

z_A: **either** x_A **or** y_A

Vapour-liquid-composition (T,x) diagram

C = 2

Ideal solution



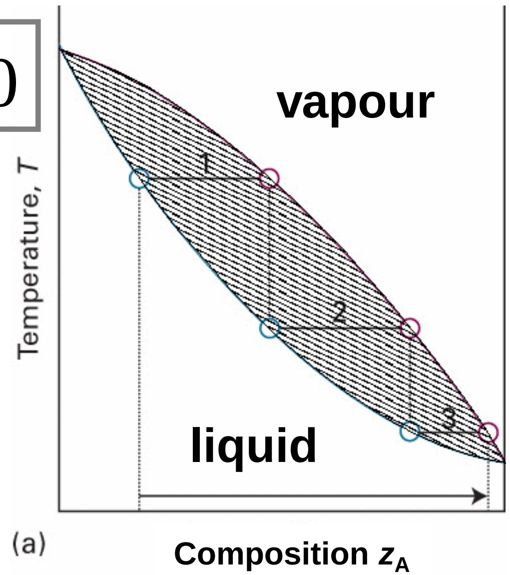
Fixed *P*

z_A: **either** x_A **or** y_A

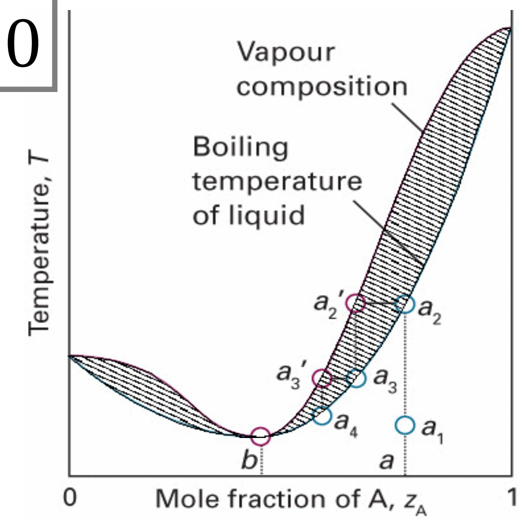
C = 2 Temperature-composition diagrams

$G^{E} = 0$

ideal solution

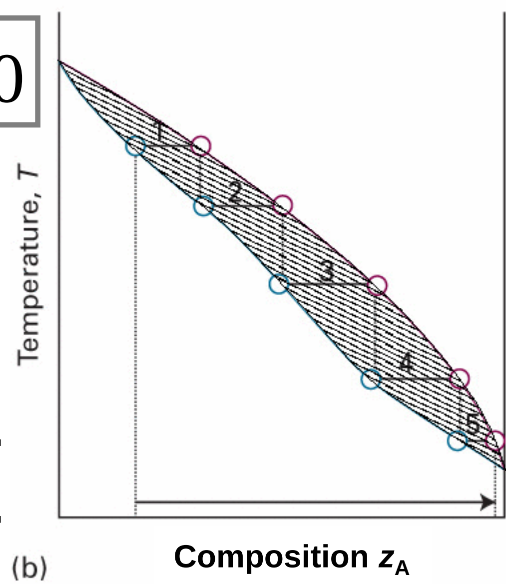


$G^{E} \gg 0$

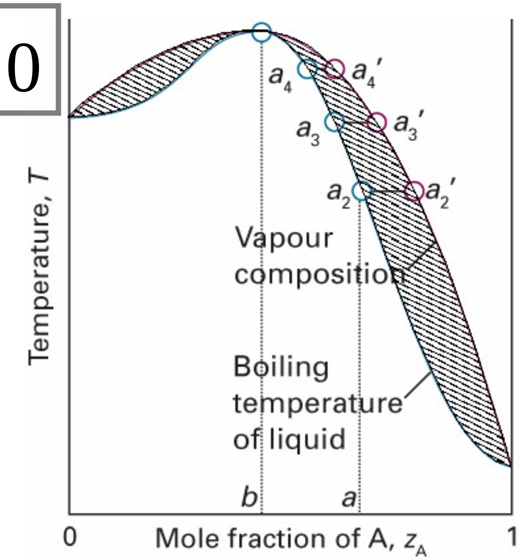


$G^{E} < 0$

non-ideal solutions

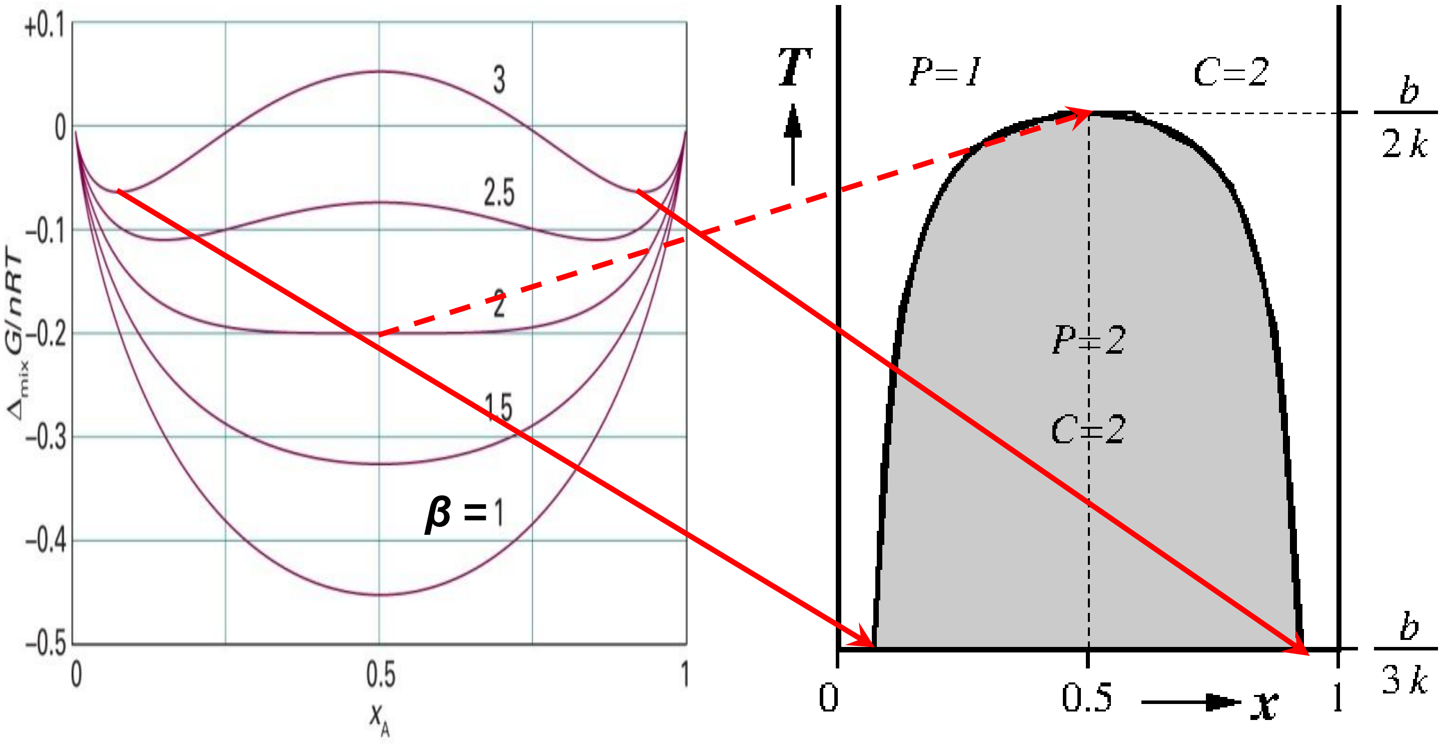


$G^{E} \ll 0$



C = 2

Liquid-liquid separation for Regular solution



$$\boxed{H^{E} = n\beta RTx_{A}x_{B}}$$

Model regular solution

$$\boxed{\beta = \frac{b}{kT}} \qquad \boxed{T = \frac{b}{\beta k}}$$

Lecture 5

- colligative properties
- liquid-gas phase diagrams
- liquid-liquid phase diagrams
- solid-liquid phase diagrams
- ternary phase diagrams

Solutions: Colligative properties

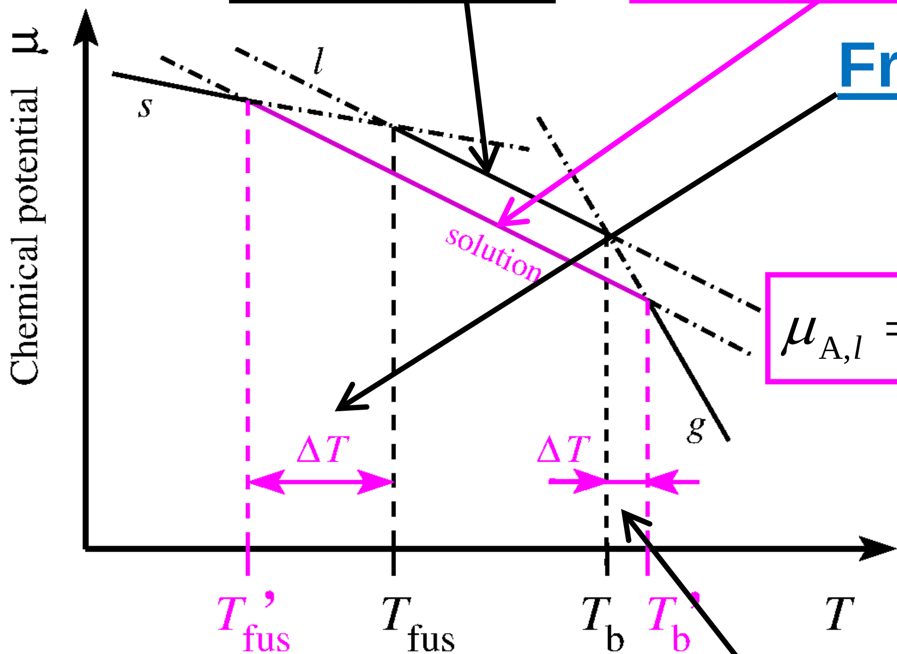
https://dullenslab.com/wp-content/uploads/2024/12/Lecture7_thermo.pdf

(or http://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html ; Lecture 5, slides 33-57)

Pure liquid A

B only present in liquid

Freezing point depression



$$\mu_{\mathrm{A},l} = \mu^*_{\mathrm{A},l} + RT\ln a_{\mathrm{A},l} \approx \mu^*_{\mathrm{A},l} + RT\ln x_{\mathrm{A},l}$$

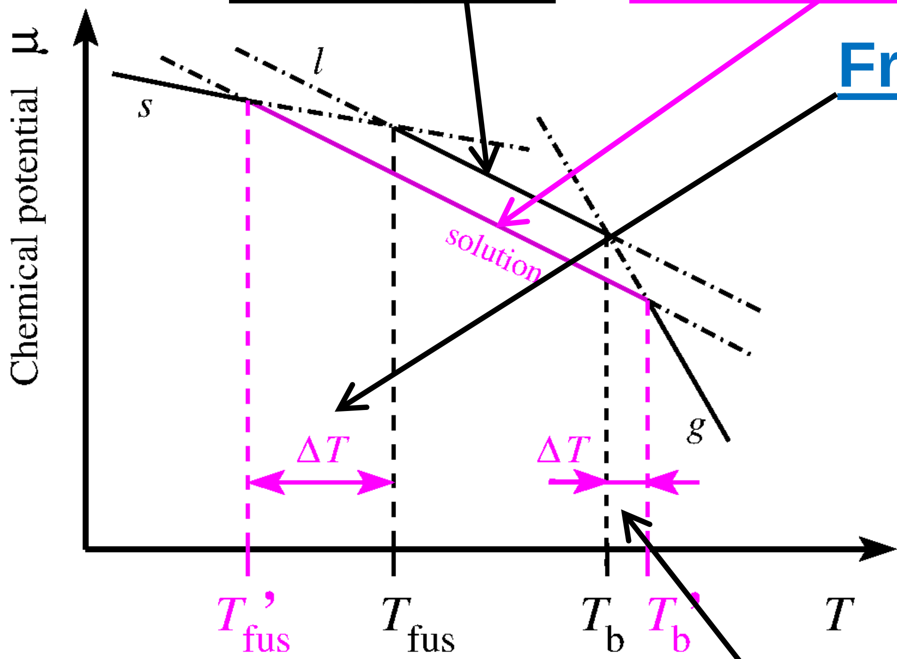
Fixed *P*

Boiling point elevation

Solutions: Colligative properties

A is the (liquid) solvent **B is the solute**

Pure liquid A **B only present in liquid**



Freezing point depression

$$\Delta T \approx \frac{R T^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}$$

(Ideal solution and $x_B << 1$)

$$\Delta T \approx \frac{R T^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H^{*}_{\mathrm{m,A}}} x_{\mathrm{B}}$$

Boiling point elevation

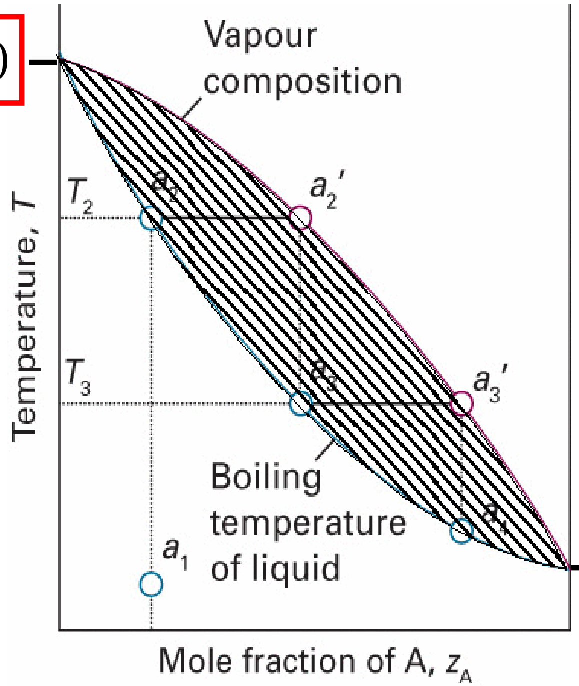
Fixed *P*

C = 2 *T*-*x* diagrams: Boiling point elevation

A is the (liquid) solvent **B is the solute**

Ideal solution

$T^*_{\mathrm{B,vap}}(P)$



$T^*_{\mathrm{A,vap}}(P)$

$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$

B: non volatile ➡ $P_B^* \approx 0$

was a condition for the simple expression for **boiling point elevation**

(together with $\boxed{a_i = x_i}$)

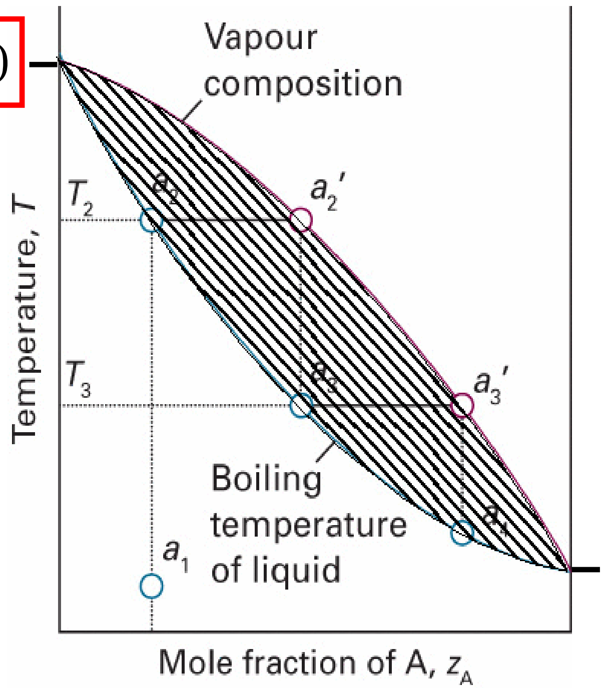
(Ideal solution)

Fixed *P*

C = 2 *T*-*x* diagrams: Boiling point elevation

Ideal solution

$T^*_{\mathrm{B,vap}}(P)$

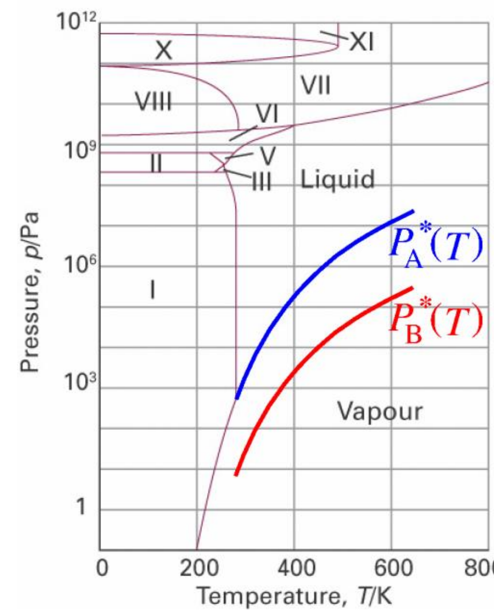


$T^*_{\mathrm{A,vap}}(P)$

$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

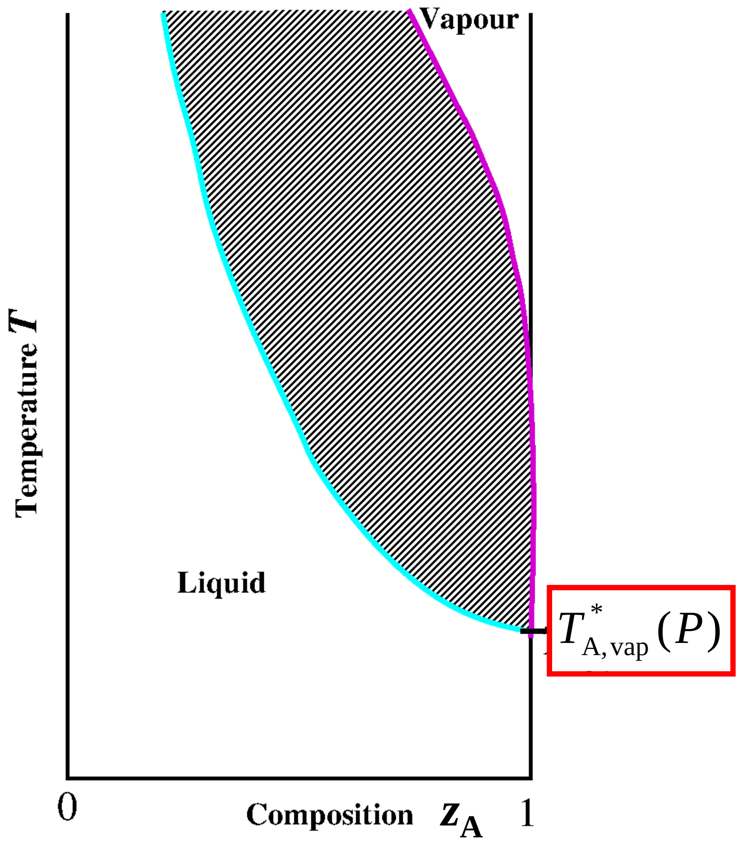
$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$

B: non volatile → $P_B^* \approx 0$



Fixed *P*

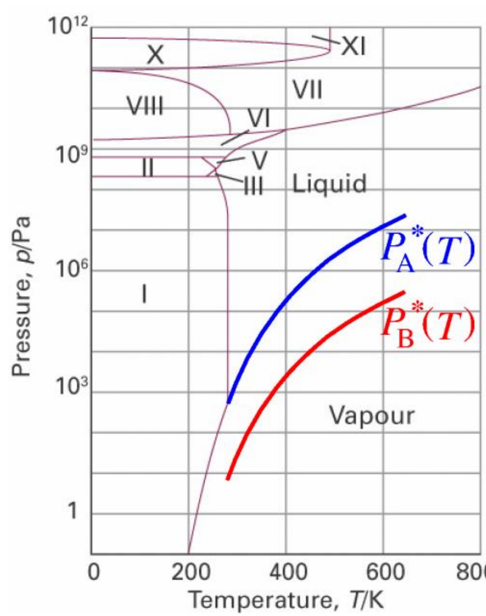
C = 2 *T*-*x* diagrams: Boiling point elevation



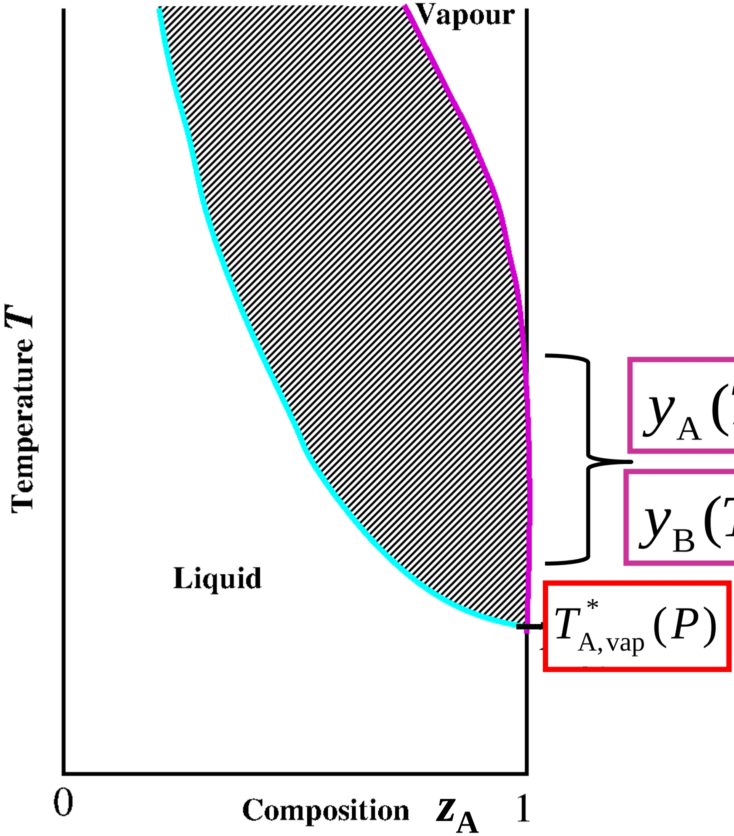
B: non volatile → $P^*_B \approx 0$

$T^*_{B,vap}(P) >> T^*_{A,vap}(P)$

Fixed *P*



C = 2 *T*-*x* diagrams: Boiling point elevation



B: non volatile $\Rightarrow$ $\boxed{P^*_{\mathrm{B}} \approx 0}$

$$\boxed{y_{\mathrm{A}}(T) = \frac{P^*_{\mathrm{A}}(T)\left[P - P^*_{\mathrm{B}}(T)\right]}{P\left[P^*_{\mathrm{A}}(T) - P^*_{\mathrm{B}}(T)\right]} \approx 1}$$

$$\boxed{y_{\mathrm{A}}(T) \approx 1}$$

$$\boxed{y_{\mathrm{B}}(T) \approx 0}$$

Fixed *P*

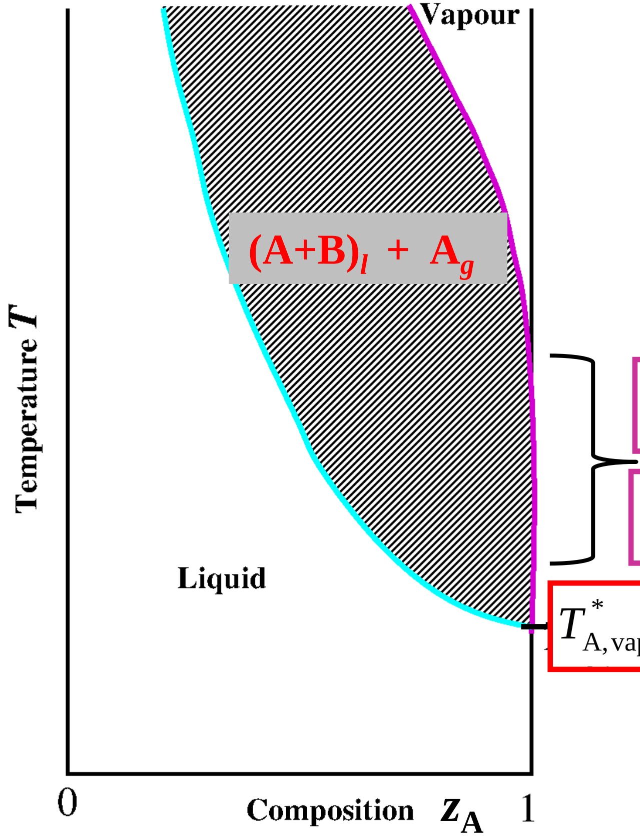
C = 2 *T*-*x* diagrams: Boiling point elevation

B: non volatile → $P_B^* \approx 0$

$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]} \approx 1$$

$y_A(T) \approx 1$

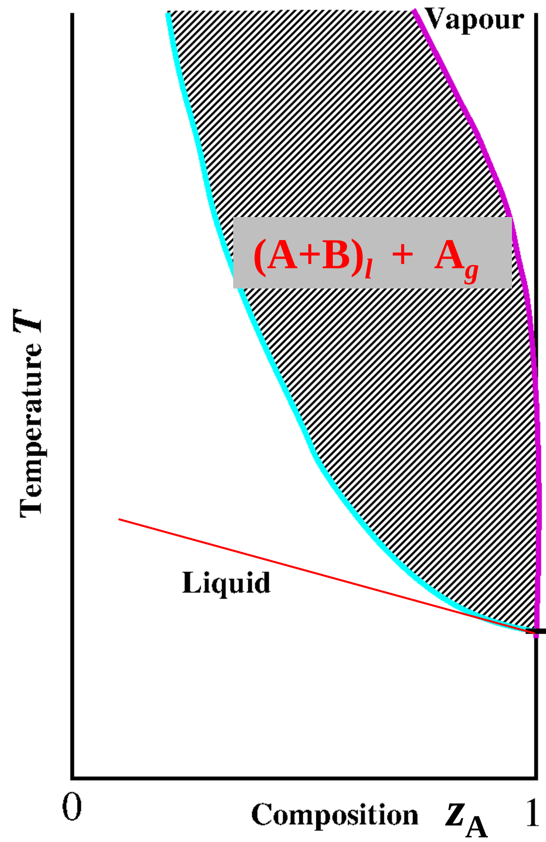
$y_B(T) \approx 0$



$T^*_{A,vap}(P)$

Fixed *P*

C = 2 *T*-*x* diagrams: Boiling point elevation



$$T^*_{A,vap}(P)$$

$$y_A(T) \approx 1$$

$$y_B(T) \approx 0$$

B: non volatile → $P_B^* \approx 0$

$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

$$x_A(T) \approx \frac{P}{P_A^*(T)}$$

Boiling point elevation

$$\Delta T \approx \frac{RT_A^{*2}}{\Delta_{vap}H_A} x_B = \frac{RT_A^{*2}}{\Delta_{vap}H_A}(1 - x_A)$$

(A: solvent, B: solute)

Fixed *P*

C = 2 *T*-*x* diagrams: Colligative properties

Similar colligative properties (ideal solutions and x_B<<1):

Boiling point elevation

$$\Delta T = \frac{RT^{*2}_{A,vap}}{\Delta_{vap}H_A} x_B \qquad \boxed{(P_B \approx 0)}$$

Freezing point depression

$$\Delta T = \frac{RT^{*2}_{A,fus}}{\Delta_{fus}H_A} x_B \qquad \boxed{(x_{B,s} \approx 0)}$$

Exercise 18

Osmosis

$$\Pi = [B]RT$$

Solubility

Exercise 20

(cf. Exercise 16)

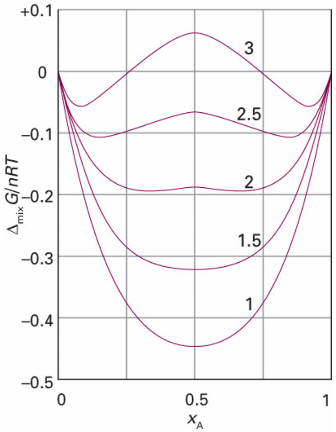
$$\ln x_B = \frac{\Delta_{fus}H_B}{R}\left[\frac{1}{T_{B,fus}} - \frac{1}{T}\right]$$

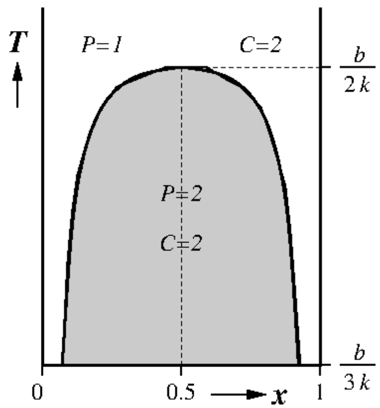
A is the solvent and B is the solute

C = 2 Liquid-liquid separation (oiling out)

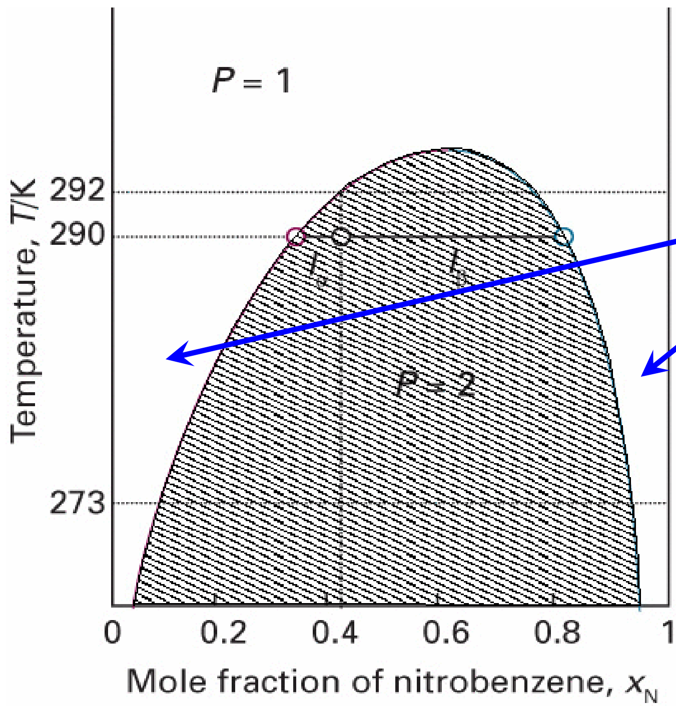
Extreme case of non-ideality

C = 2 Liquid-liquid separation (oiling out)





(Exercise 17)



Nitrobenzene/hexane

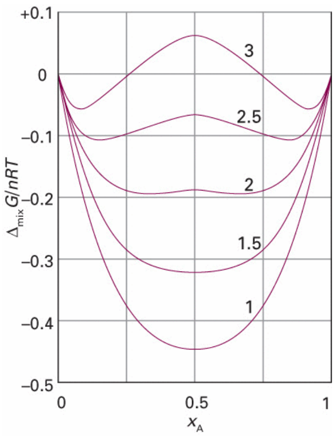
Partial miscibility of liquids

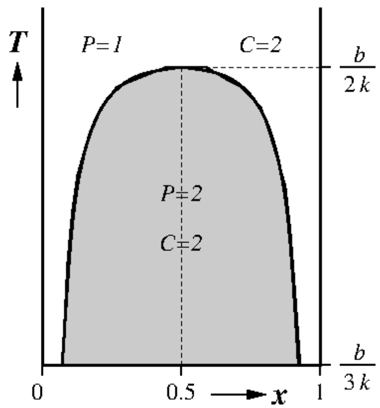
$$G^{E} = nRT\beta x_{A} x_{B}$$

$$T = \frac{b}{\beta k}$$

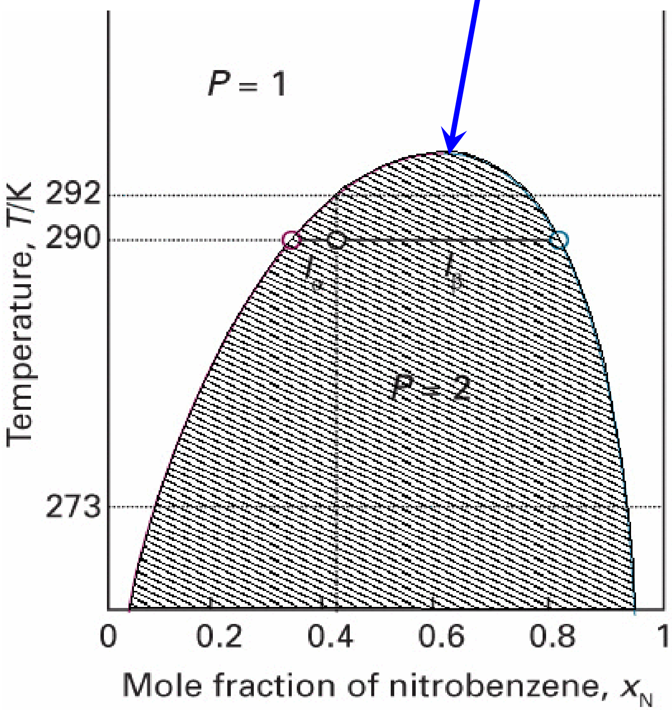
Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

C = 2 Liquid-liquid separation (oiling out)





Upper Critical (Solution) Temperature



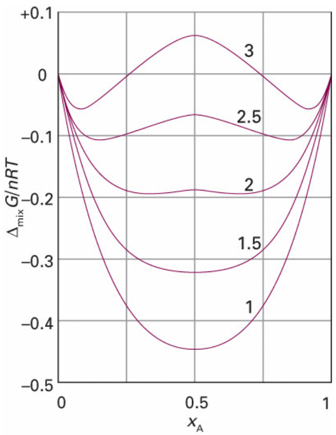
Nitrobenzene/hexane

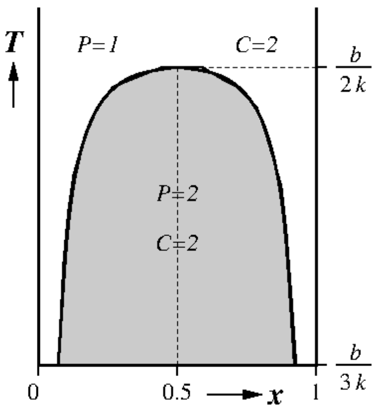
$$\boxed{G^{E} = nRT\beta x_A x_B}$$

$$\boxed{T = \frac{b}{\beta k}}$$

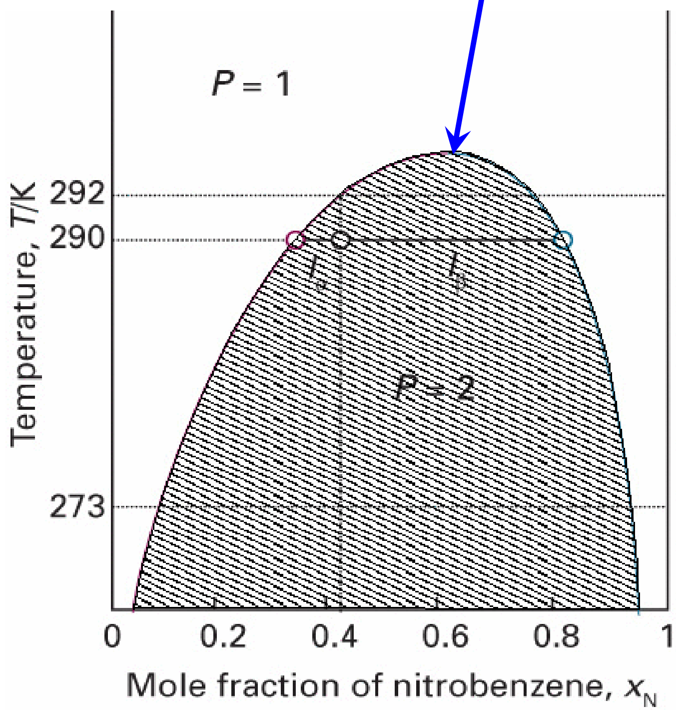
Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 Liquid-liquid separation (oiling out)

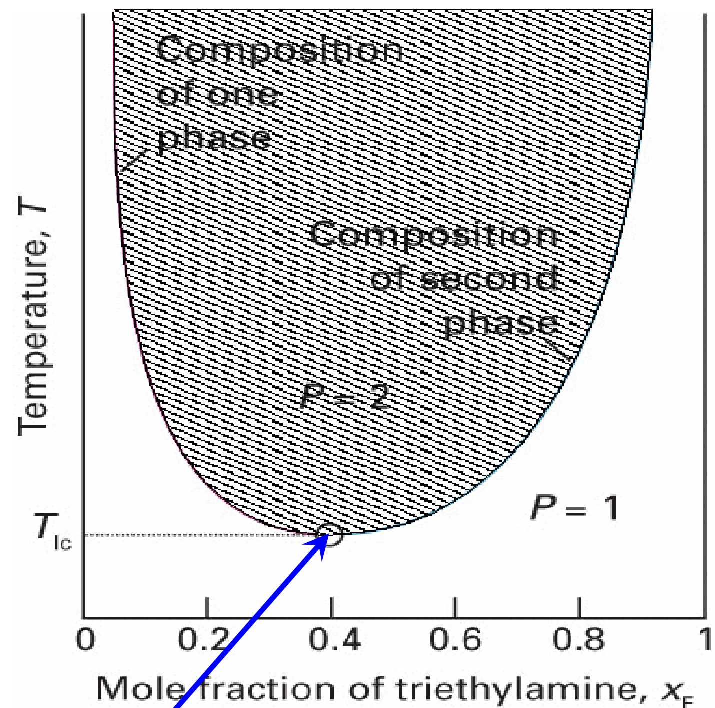




Upper Critical (Solution) Temperature



Nitrobenzene/hexane



H_2O / triethylamine

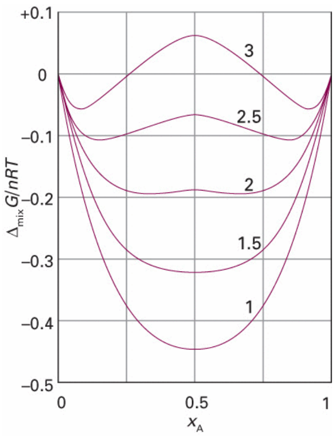
Lower Critical (Solution) Temperature

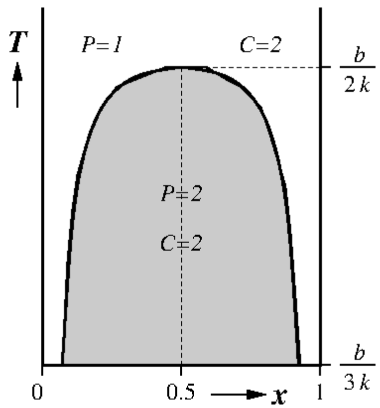
$$\boxed{G^E = nRT\beta x_A x_B}$$

$$\boxed{T = \frac{b}{\beta k}}$$

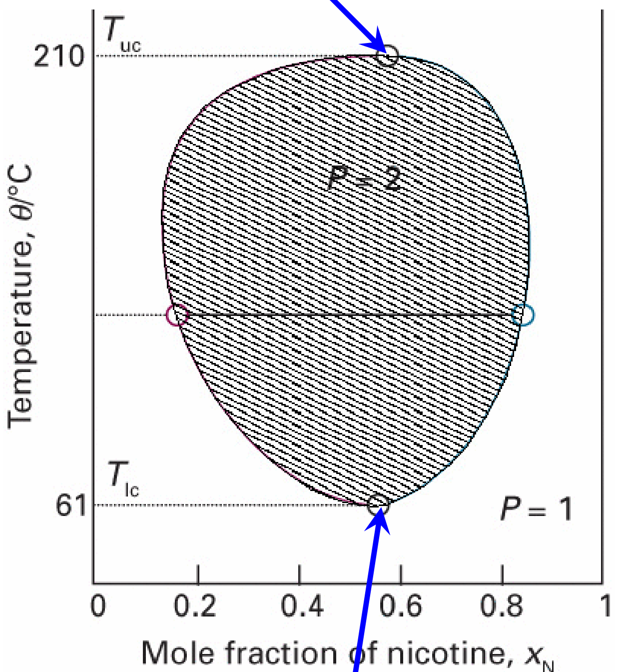
Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 Liquid-liquid separation (oiling out)





Upper Critical (Solution) Temperature



H_2O / nicotine

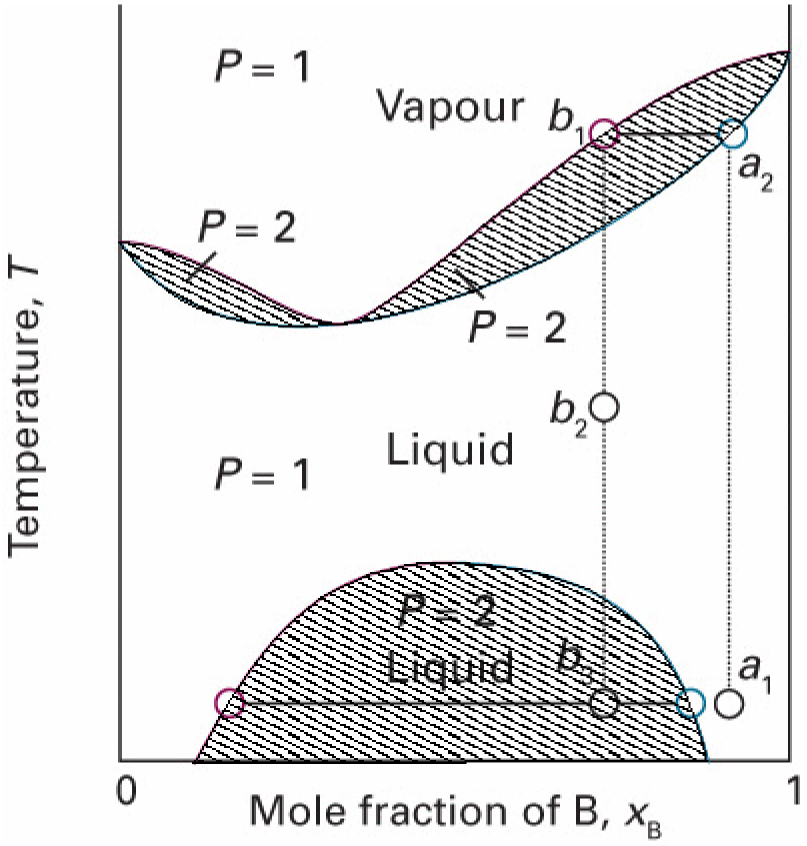
Lower Critical (Solution) Temperature

$$\boxed{G^{E} = nRT\beta x_A x_B}$$

$$\boxed{T = \frac{b}{\beta k}}$$

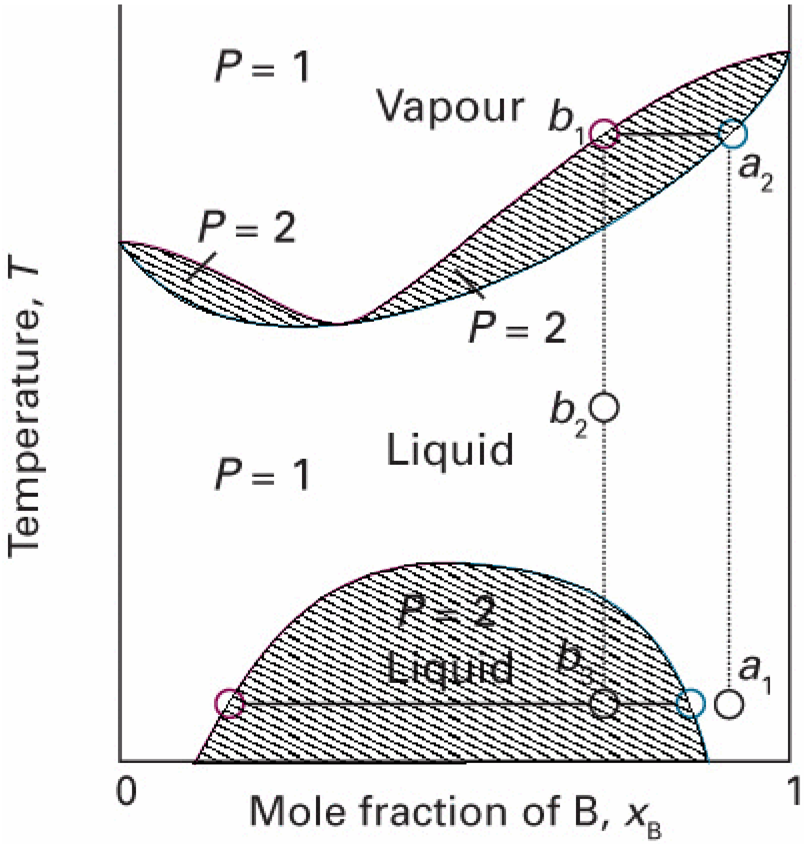
Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

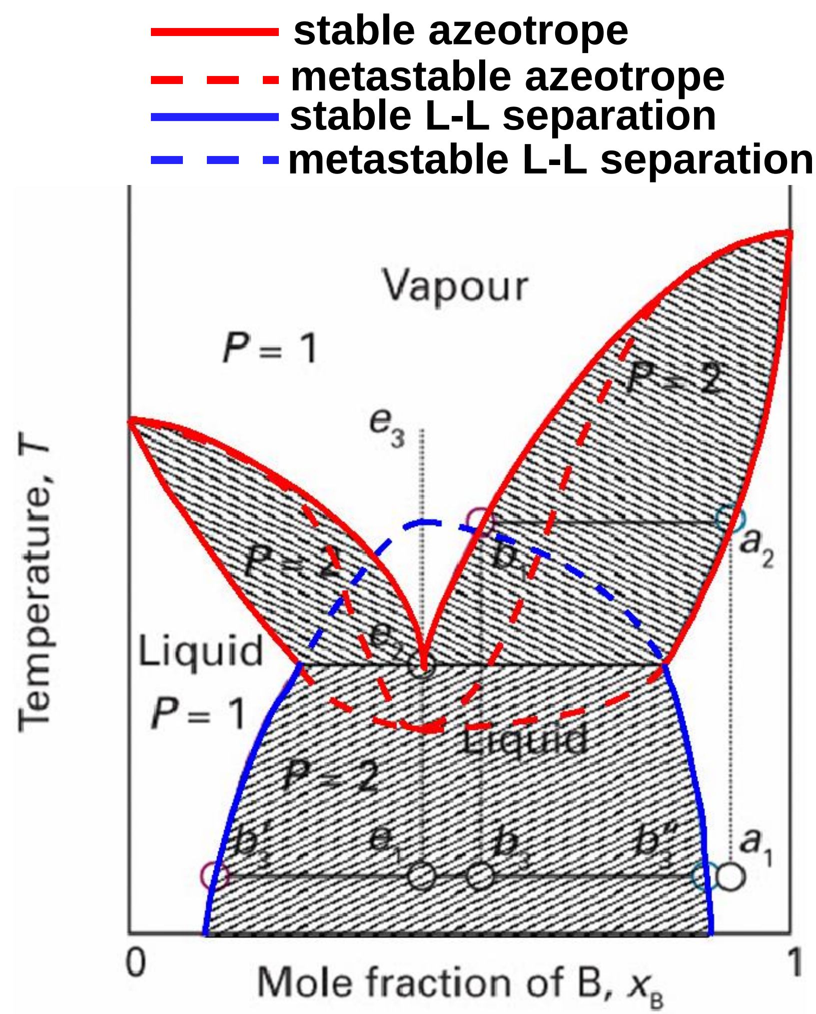
C = 2 L-L separation in liquid-gas phase diagram



Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

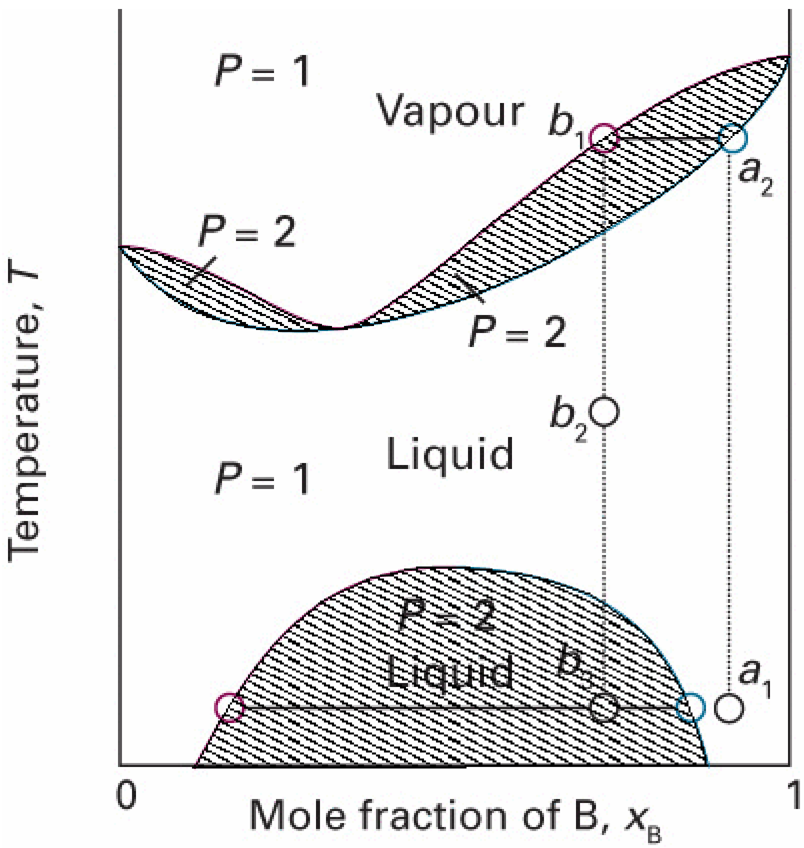
C = 2 L-L separation in liquid-gas phase diagram

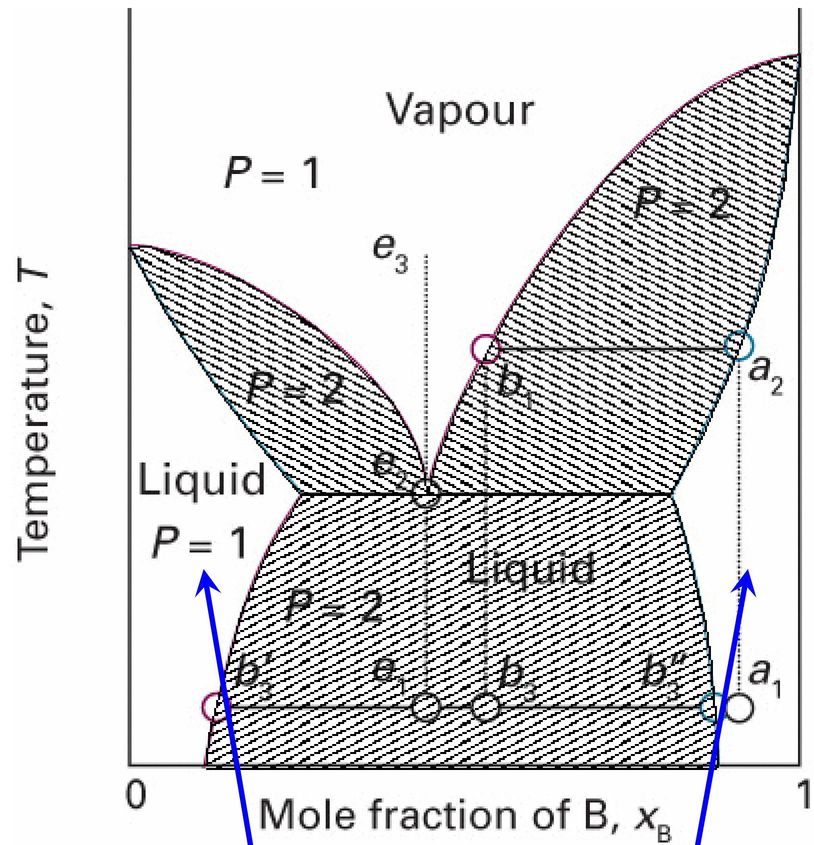




Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 L-L separation in liquid-gas phase diagram

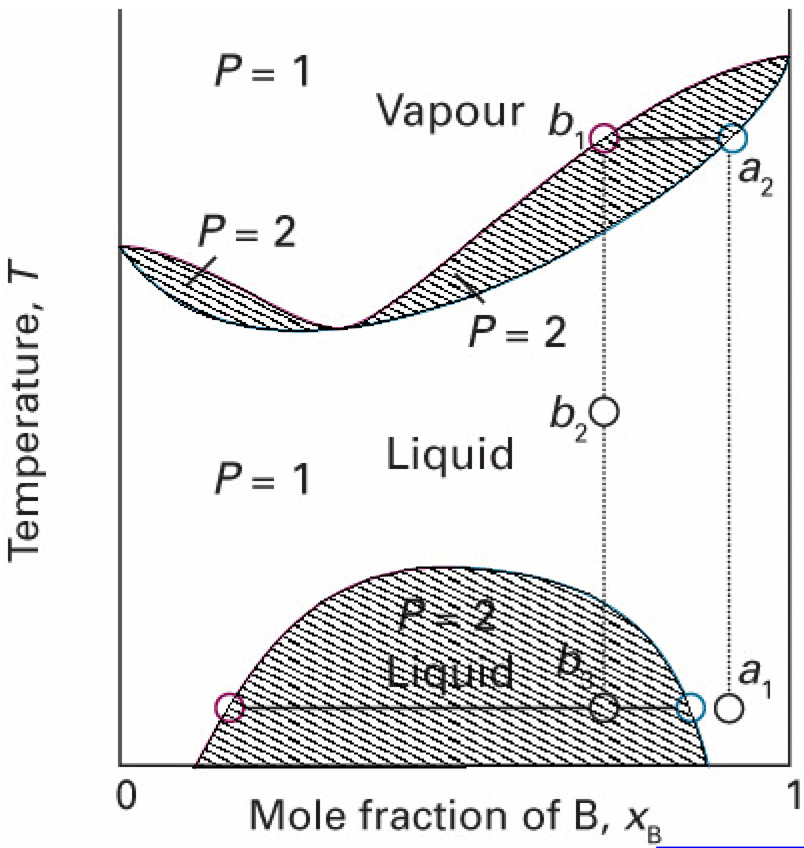


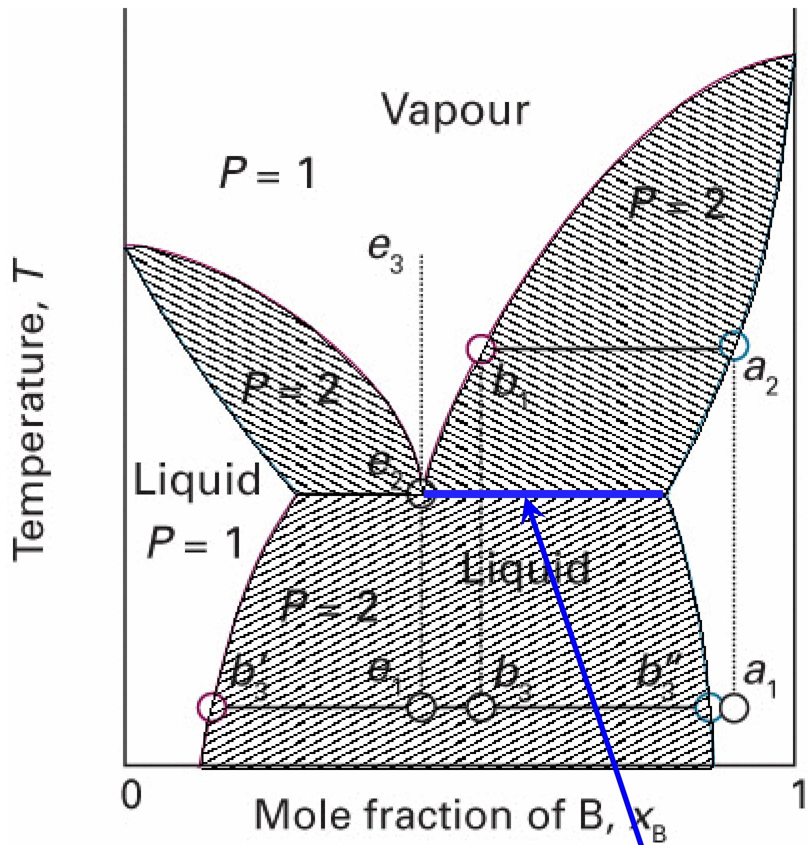


Partial miscibility of liquids

Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 L-L separation in liquid-gas phase diagram



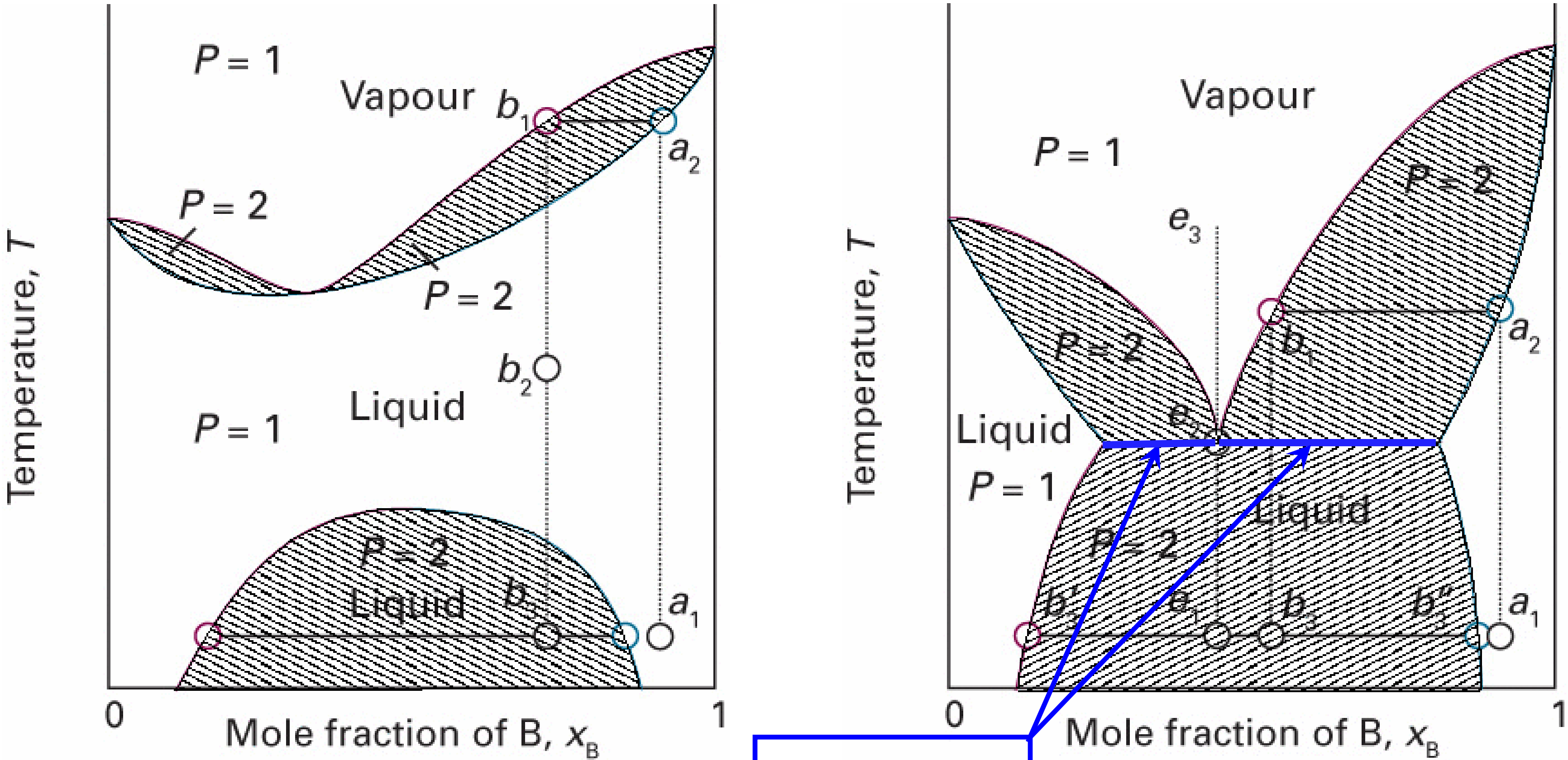


(P, x_β) ← **F = C – P + 2 = 2**

(x_β) ← **F' = C – P + 1 = 1**

P = 2

C = 2 L-L separation in liquid-gas phase diagram

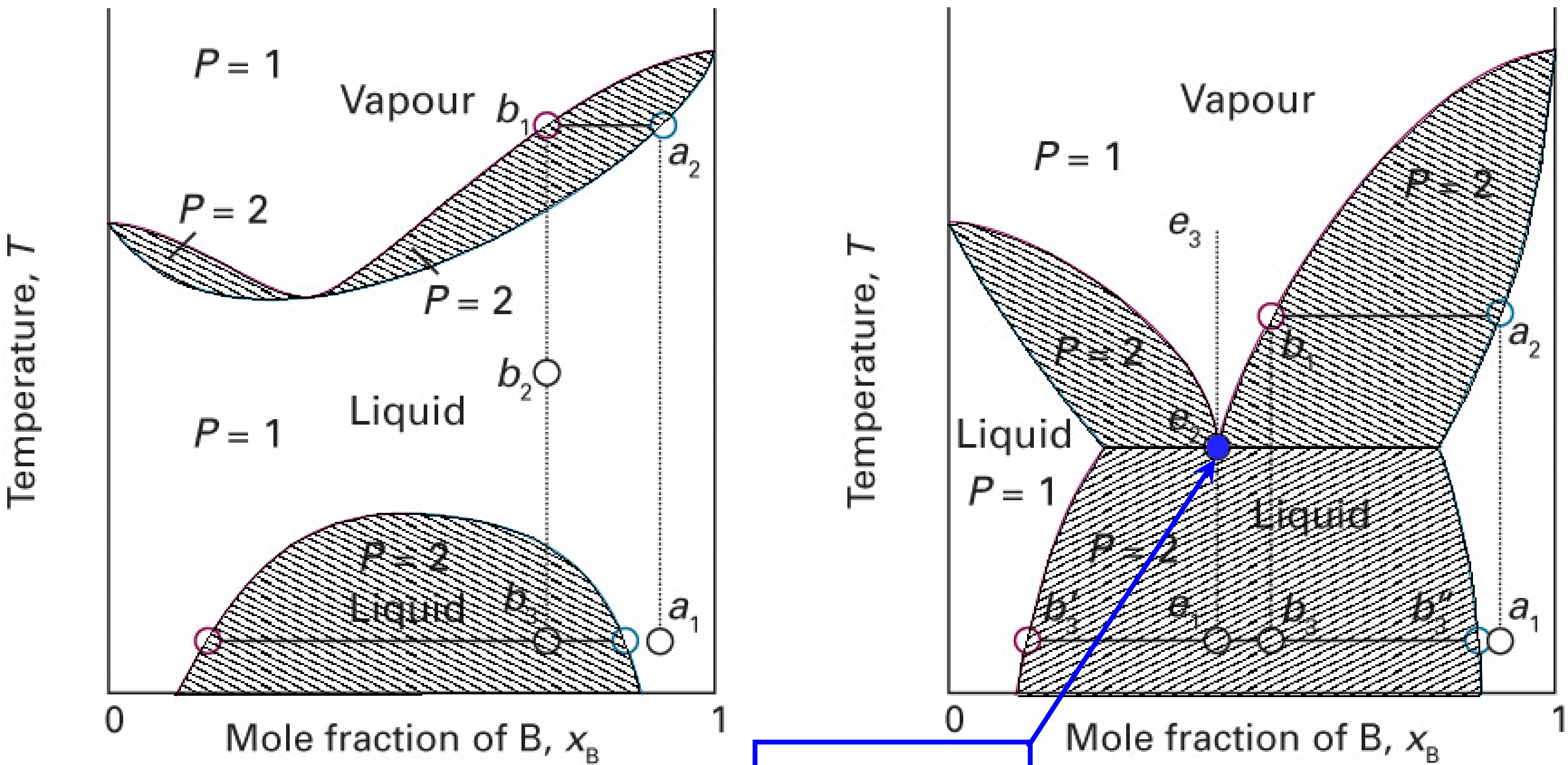


$\boxed{P = 2}$

$\boxed{F' = C - P + 1 = 1}$

Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 L-L separation in liquid-gas phase diagram



$P = 3$

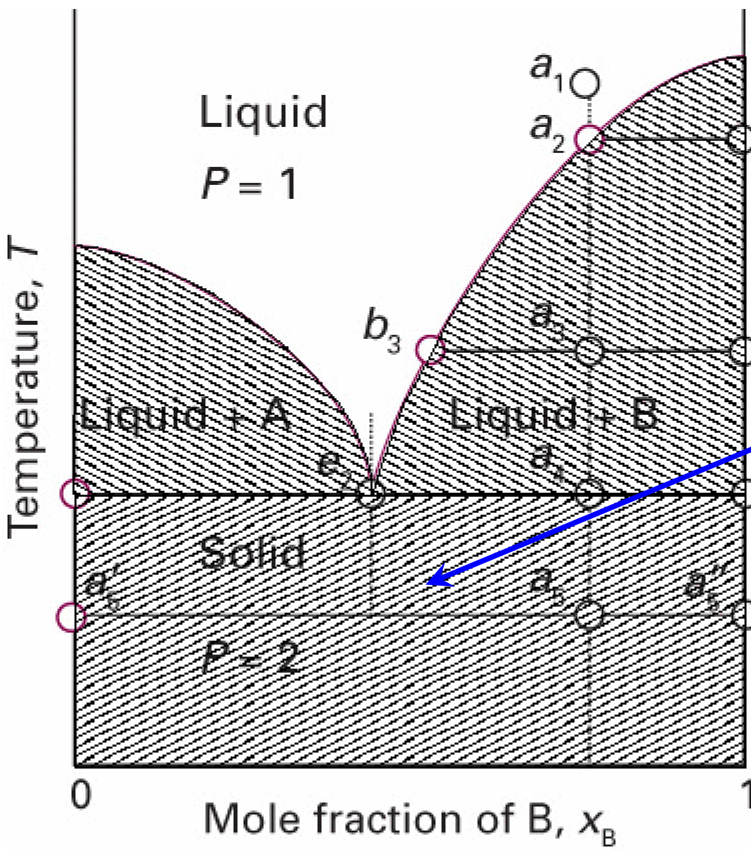
$$\boxed{F' = C - P + 1 = 0}$$

Lever rule $\cancel{n_\alpha l_\alpha = n_\beta l_\beta}$

$C = 2$ Solid-liquid phase diagram

$C = 2$ Solid-liquid phase diagram

Eutectic: A(s) and B(s) not miscible



$T_{e(utectic)}$

Completely immiscible solids

↓

$\boldsymbol{P = 2}$

↓

$\boldsymbol{F = 2}$

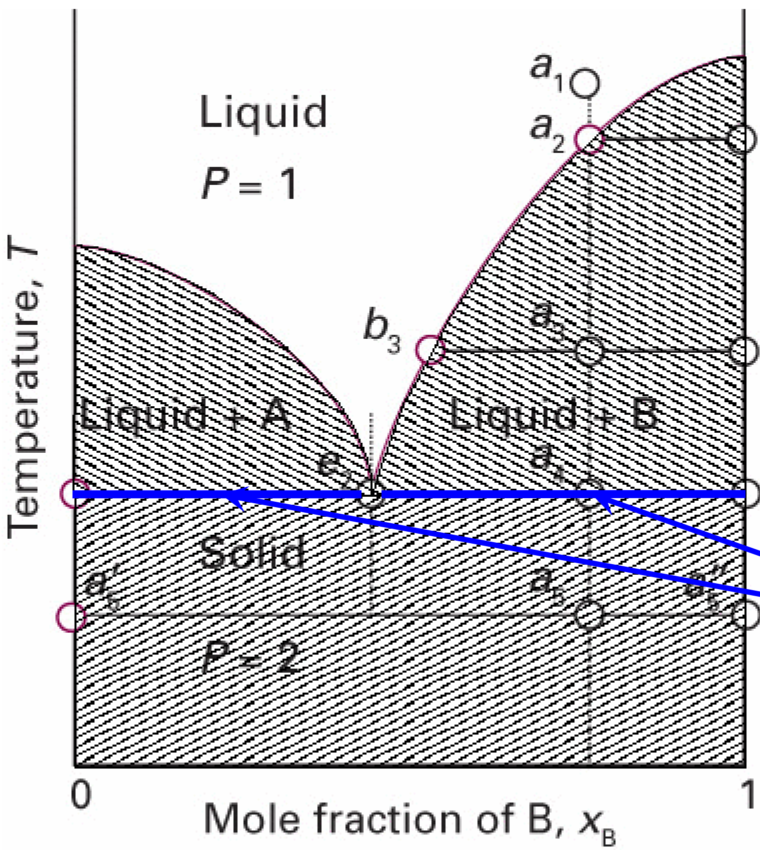
↓

(P, T)

Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 Solid-liquid phase diagram

Eutectic: A(s) and B(s) not miscible



$T_{\text{e(utectic)}}$

$\boxed{P = 2}$

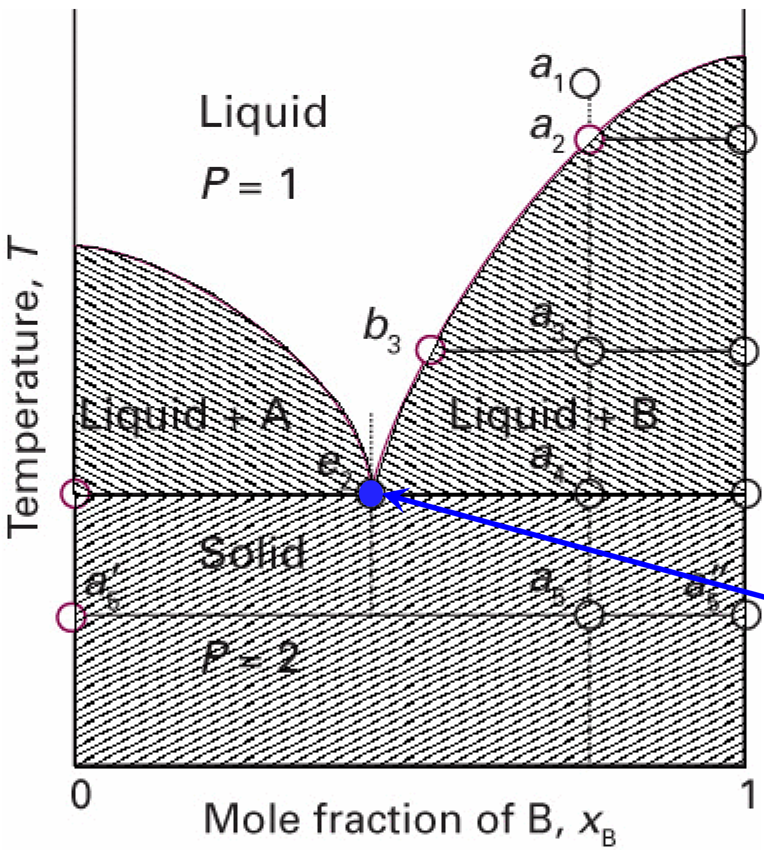
$\boxed{F = 2}$

(P, x_B)

Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

$C = 2$ Solid-liquid phase diagram

Eutectic: A(s) and B(s) not miscible



$T_{e(utectic)}$

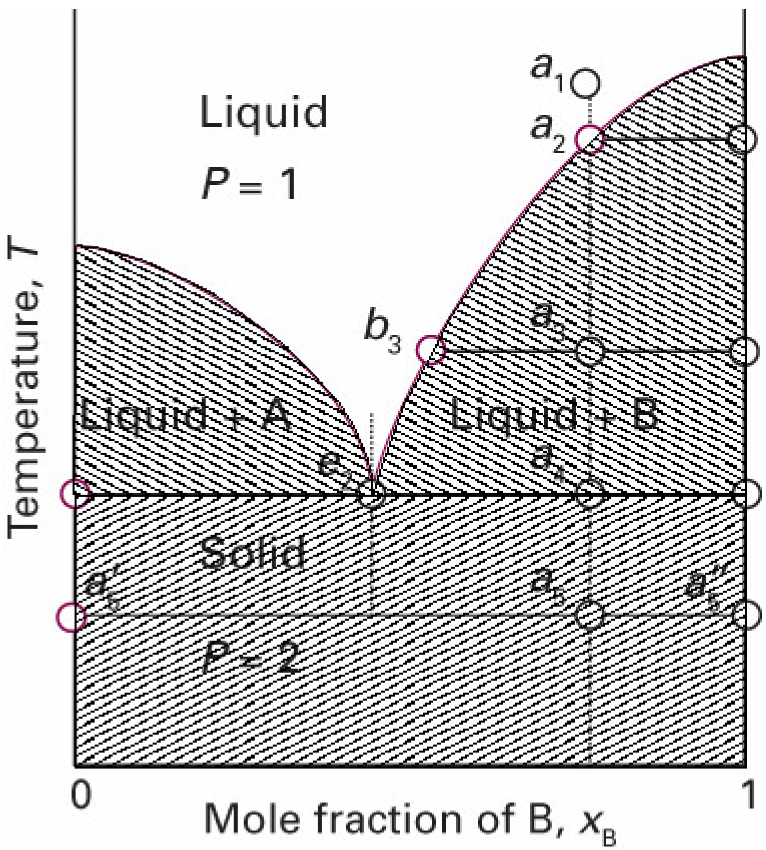
$\boxed{P = 3} \rightarrow \boxed{F = 1} \rightarrow (P)$

Exercise 18

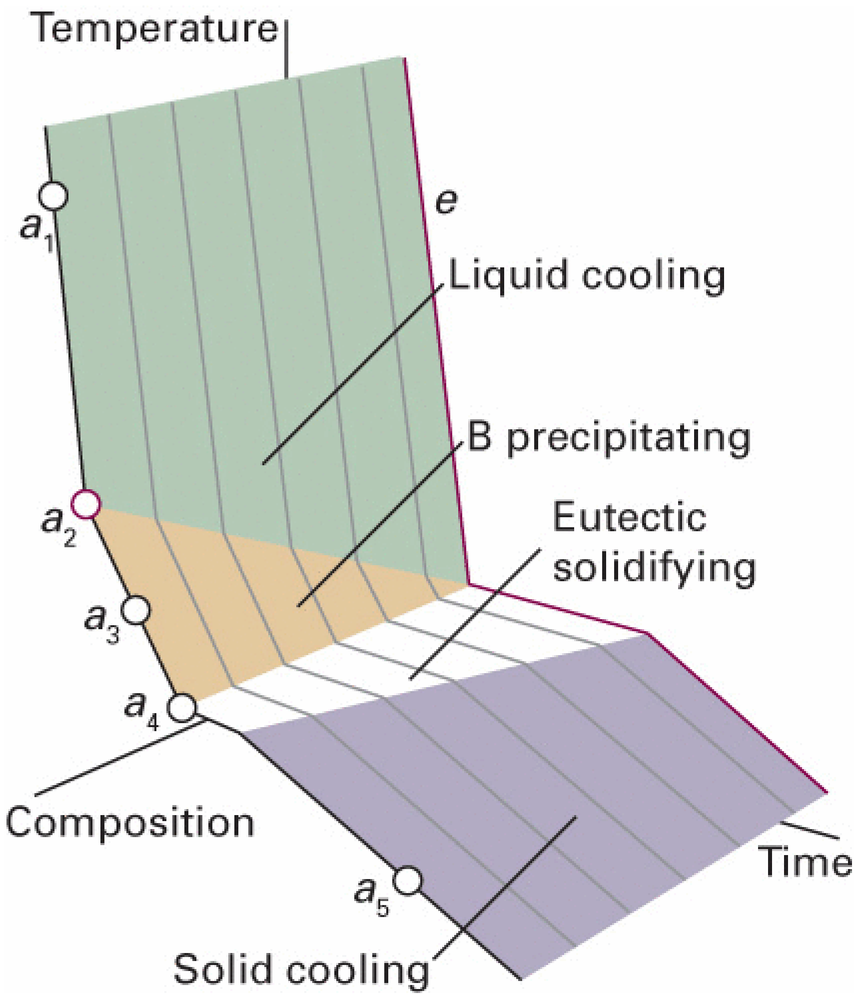
Lever rule $\cancel{\boxed{n_\alpha l_\alpha = n_\beta l_\beta}}$

C = 2 Solid-liquid phase diagram

Eutectic: A(s) and B(s) not miscible

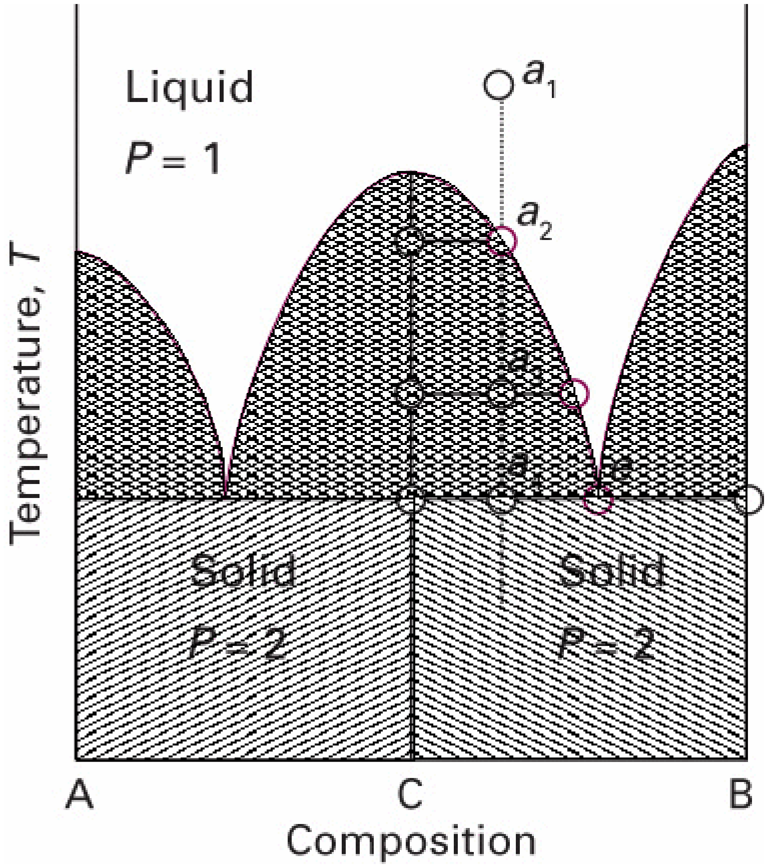


$T_{e(utectic)}$



Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 Solid-liquid phase diagram



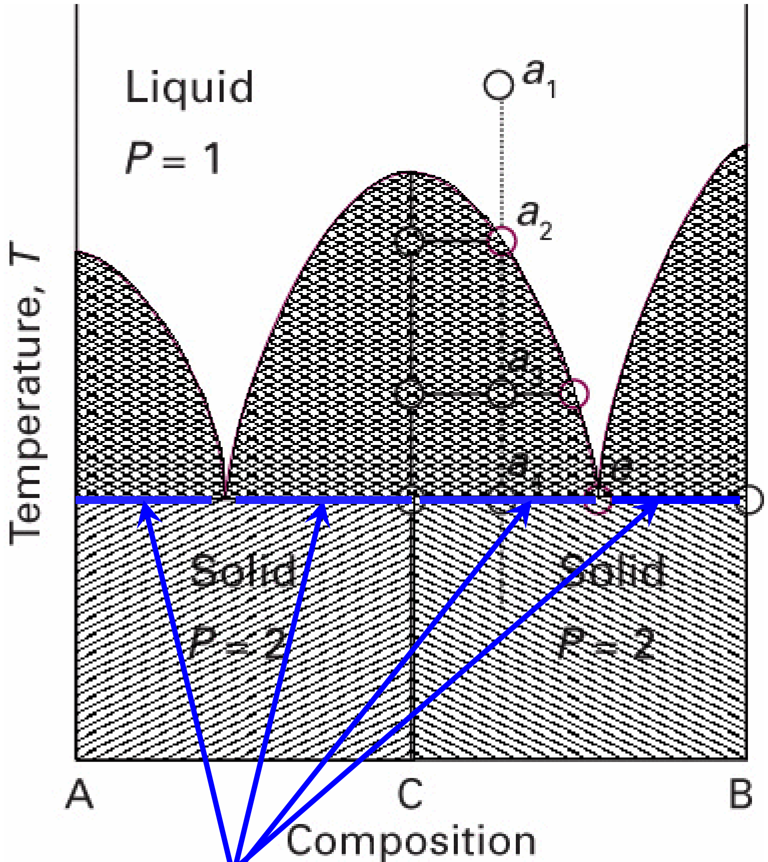
Compound

C = AB

Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

Three solid compounds: A, B and C = AB

C = 2   Solid-liquid phase diagram



$T_{e(utectic)}$

Compound

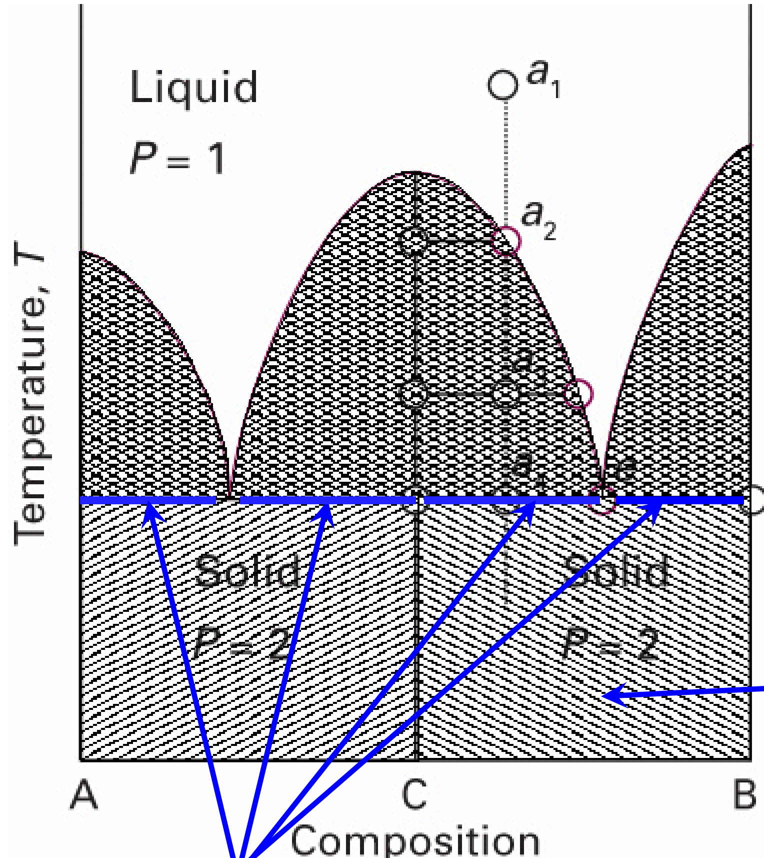
C = AB

(P, x) **F = 2** ← **P = 2**

Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

Three solid compounds: A, B and C = AB

C = 2 Solid-liquid phase diagram



$T_{e(utectic)}$

Compound

C = AB

P = 2 → **F = 2**

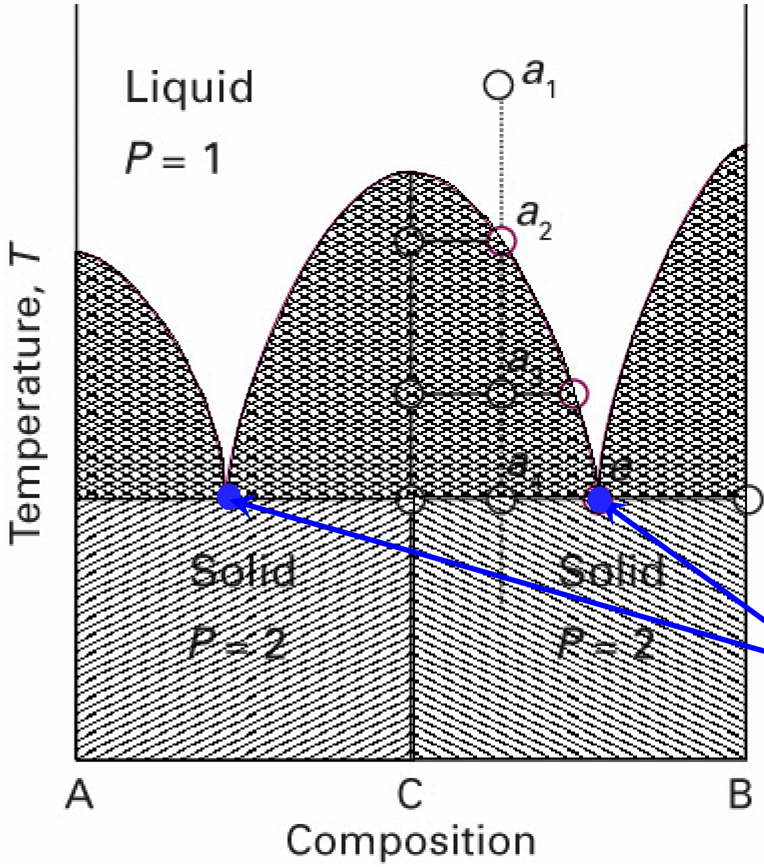
(P, T)

(P, x) **F = 2** ← **P = 2**

Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

Three solid compounds: A, B and C = AB

C = 2 Solid-liquid phase diagram



$T_{e(utectic)}$

***P* = 3**
***F* = 1**

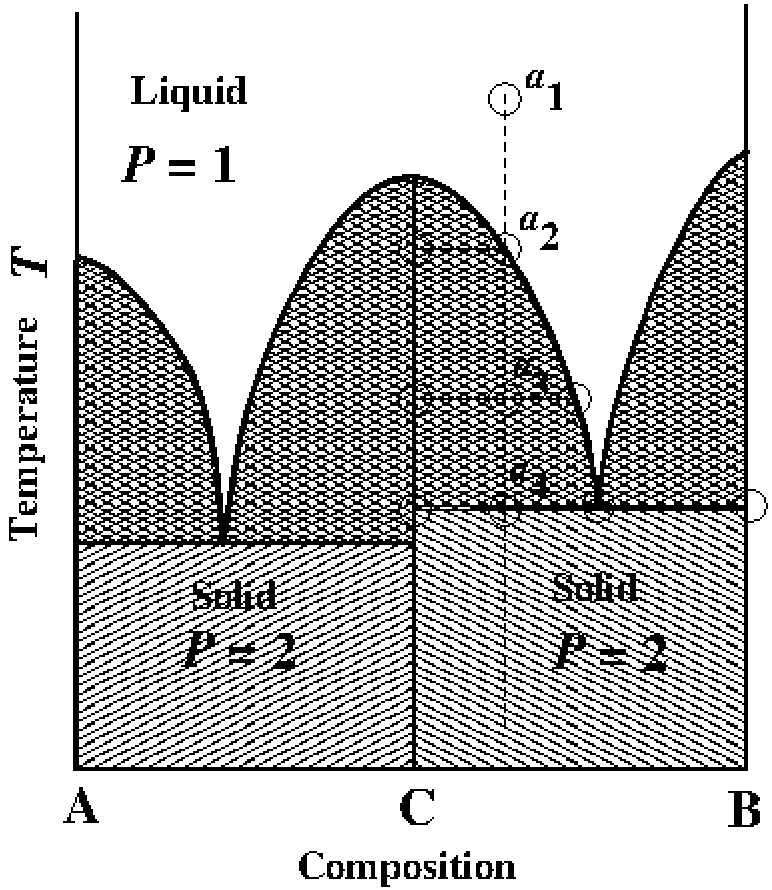
Compound

C = AB

Lever rule $\cancel{n_\alpha l_\alpha = n_\beta l_\beta}$

Three solid compounds: A, B and C = AB

C = 2   Solid-liquid phase diagram



Compound

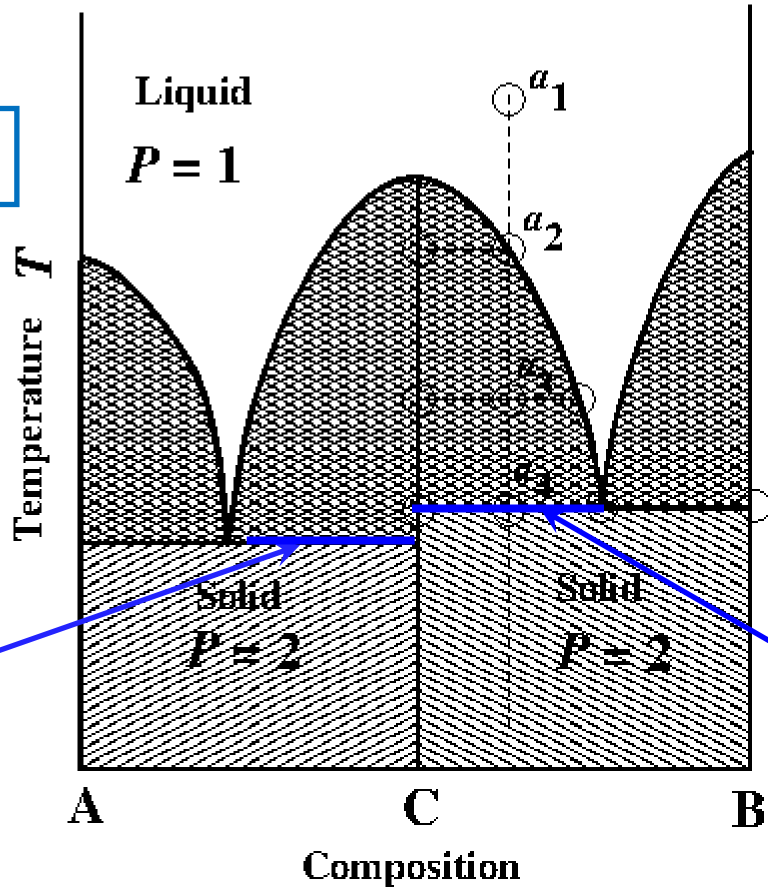
C = AB

Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

Three solid compounds: A, B and C = AB

C = 2 Solid-liquid phase diagram

Exercise 19



T_e(AC)

P = 2

T_e(CB)

P = 2

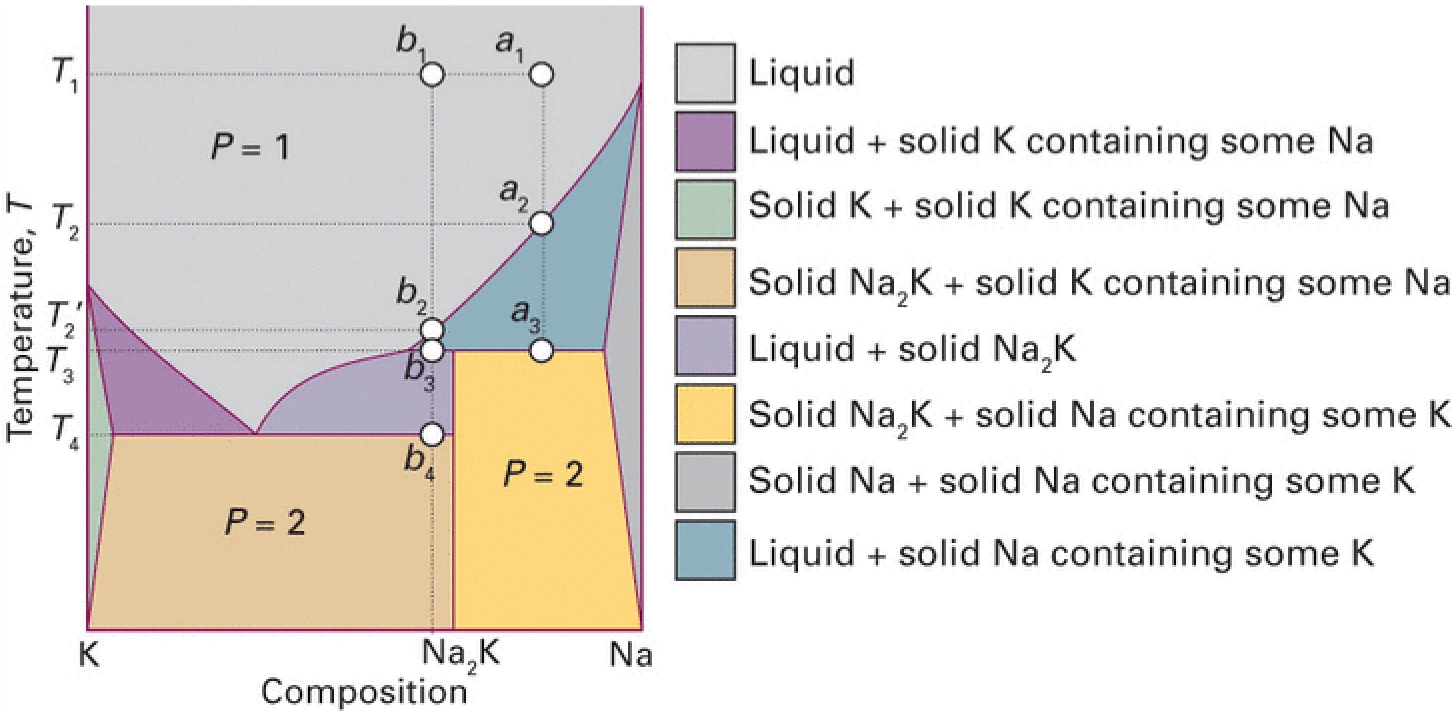
Compound

C = AB

Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

Three solid compounds: A, B and C = AB

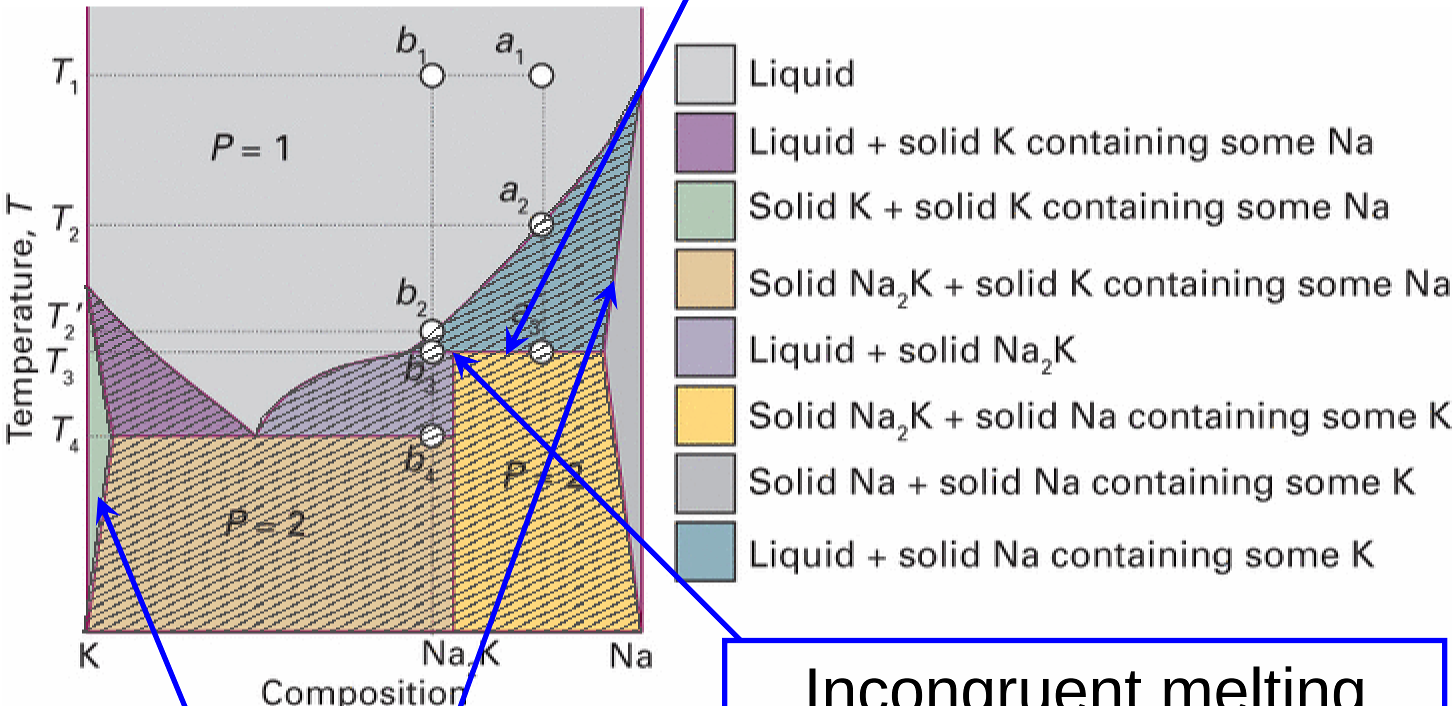
C = 2 Solid-liquid phase diagram



Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

C = 2 Solid-liquid phase diagram

peritectic



Incongruent melting

Solid solutions

Partially miscible solids

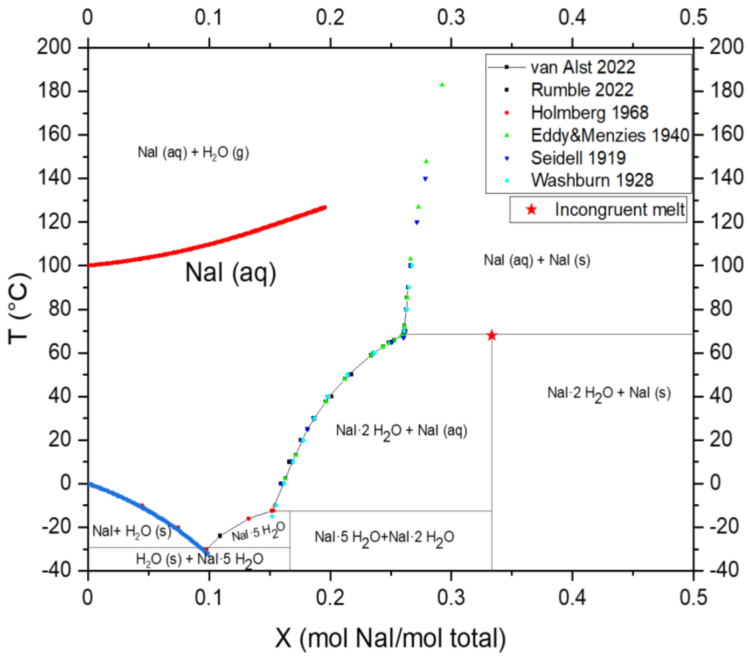
Lever rule $\boxed{n_\alpha l_\alpha = n_\beta l_\beta}$

Exercise 20

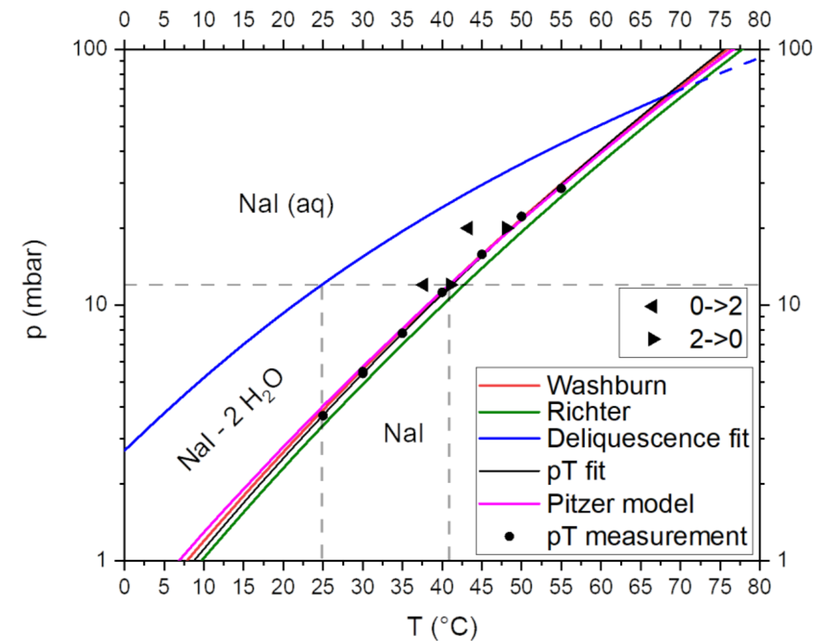
C = 2   Solid-liquid phase diagram

Salt-hydrate NaI·nH$_2$O

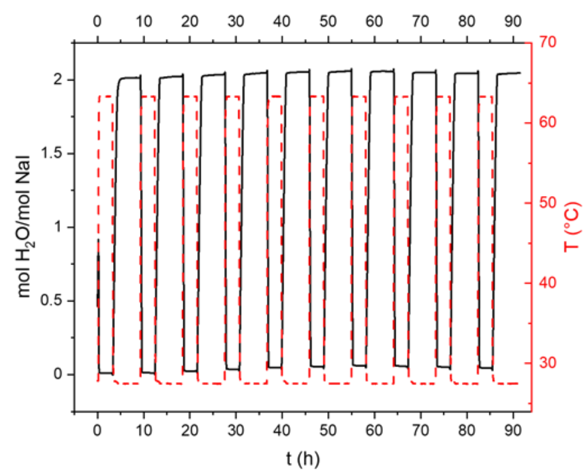
Solubility diagram



P,T- diagram

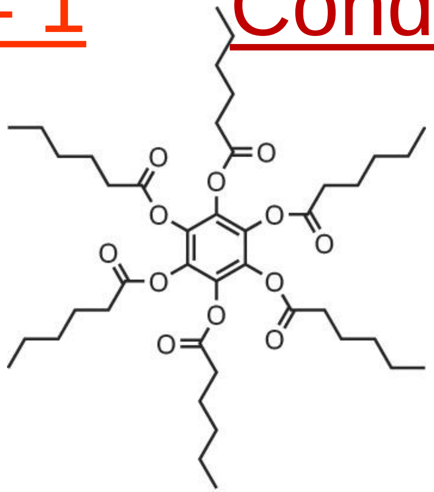


dehydration-hydration cycles of the salt-hydrate can serve as a heat battery
56 kJ/mol
1.48 GJ/m³



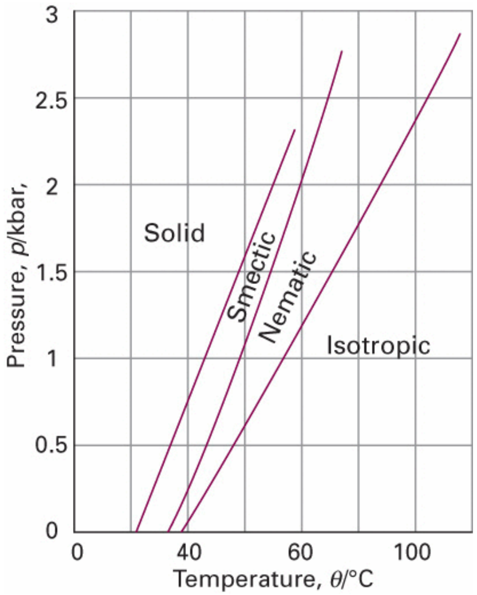
Exercise 20

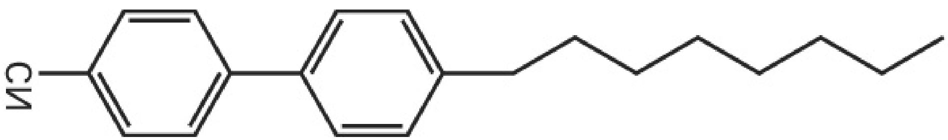
C = 1 Condensed matter phase diagrams

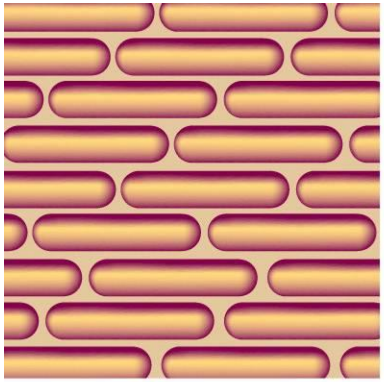


Liquid crystals

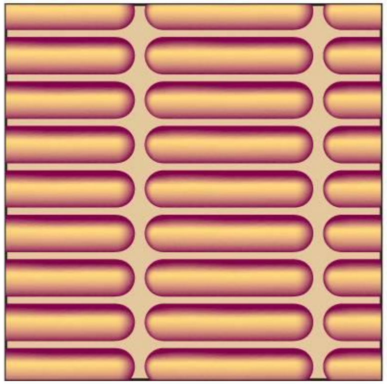
(mesophase)



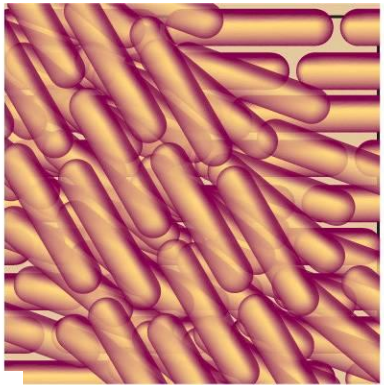




nematic



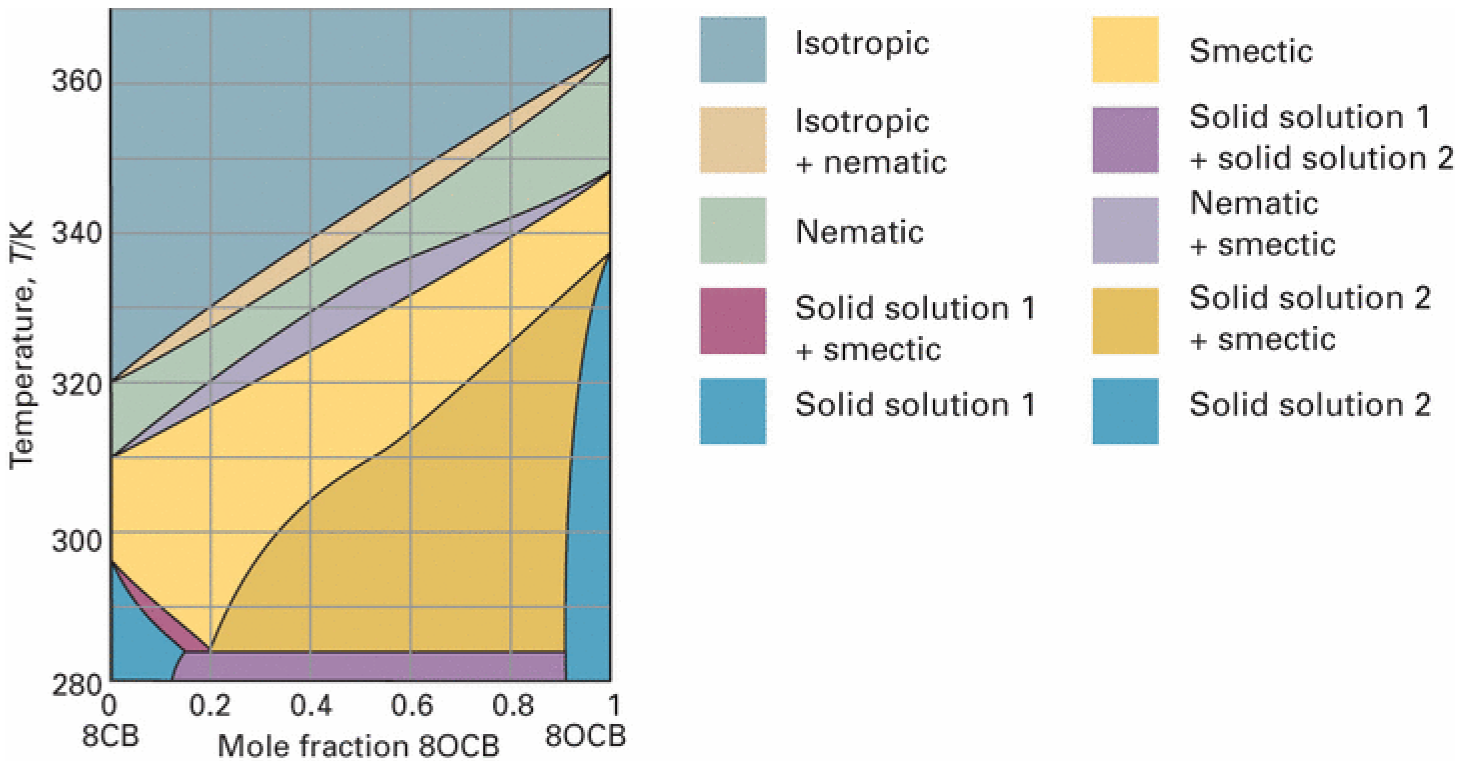
smectic



cholesteric

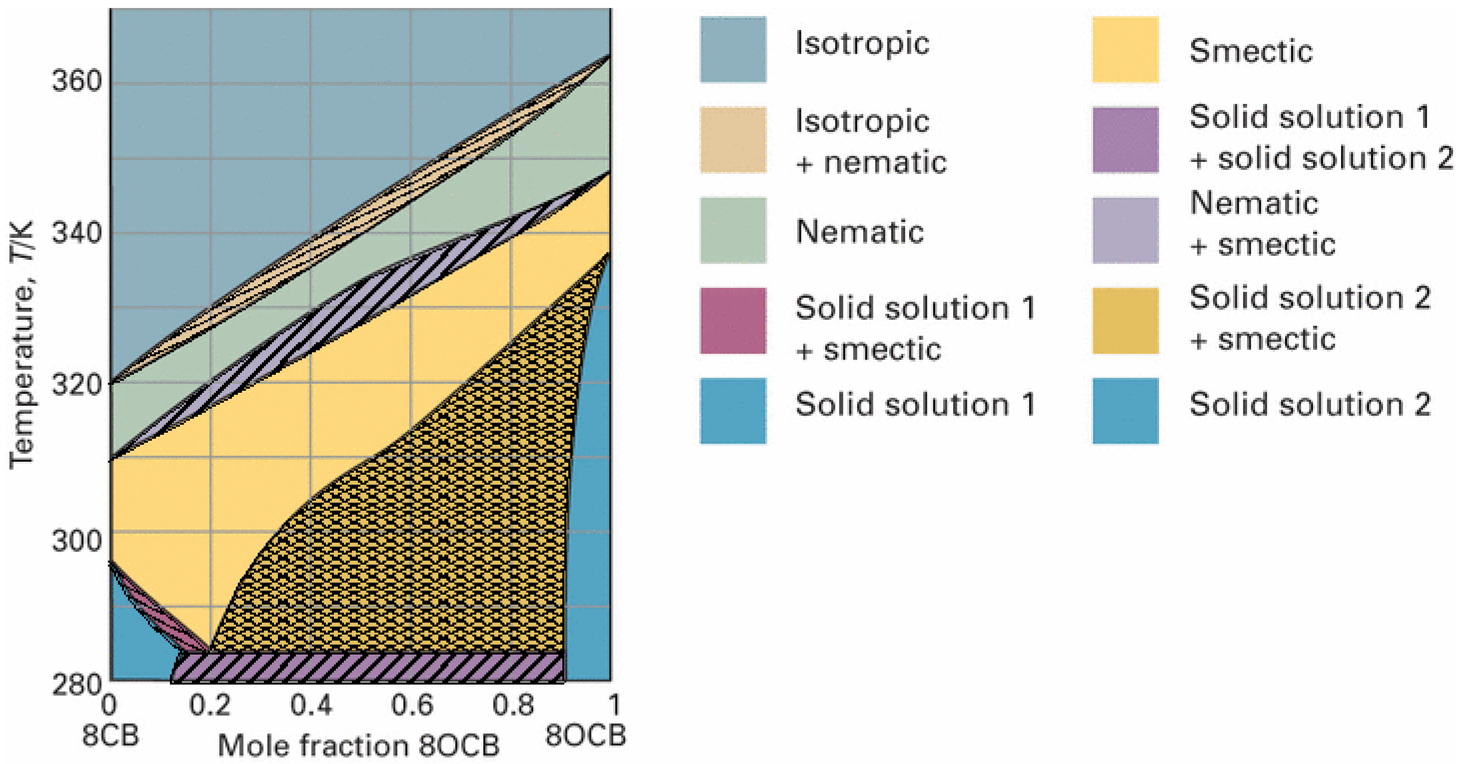
C = 2 Condensed matter phase diagrams

Liquid crystals



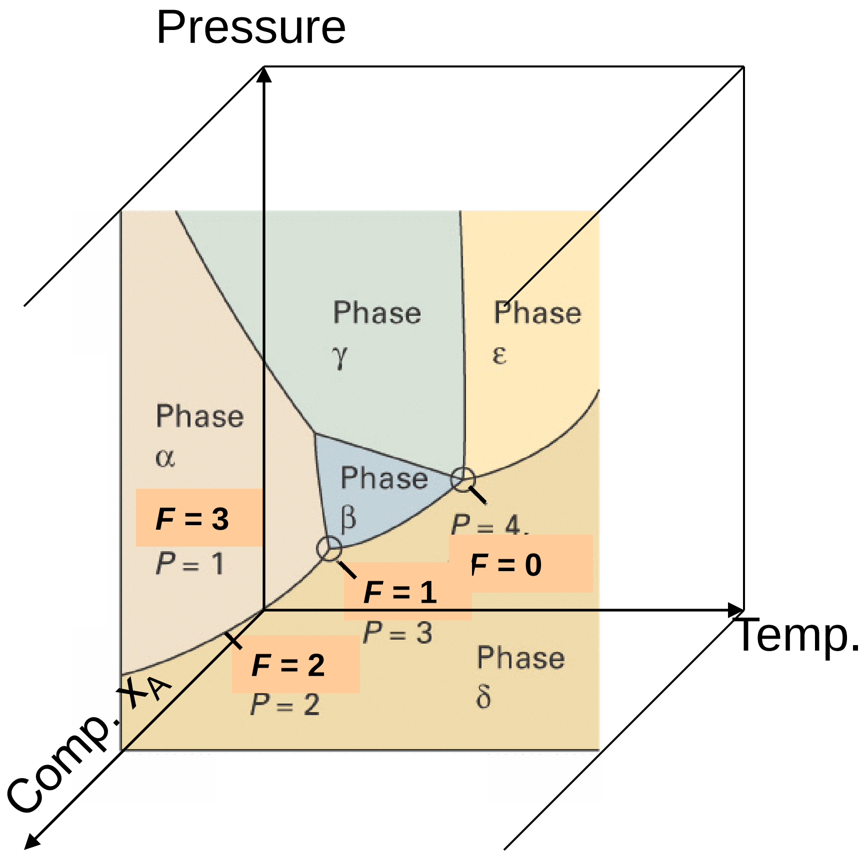
C = 2 Condensed matter phase diagrams

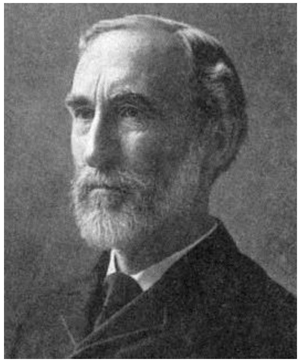
Liquid crystals



Ternary phase diagrams

C = 2 Binary phase diagrams

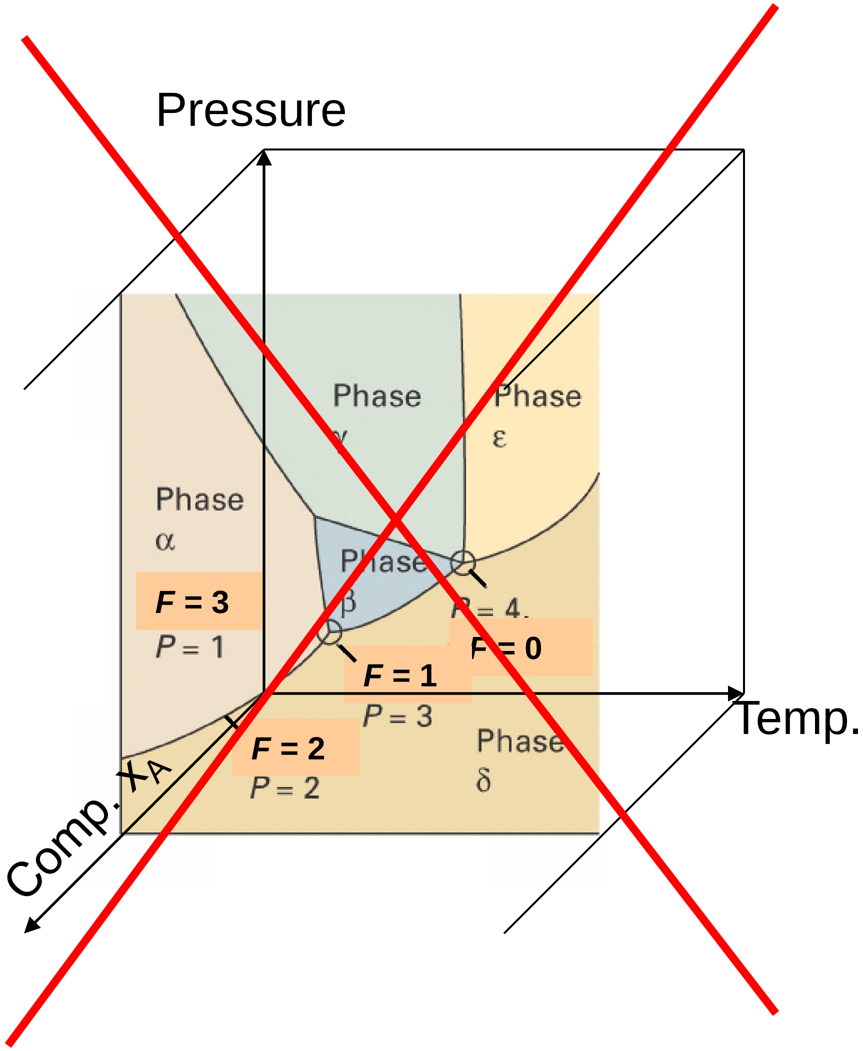


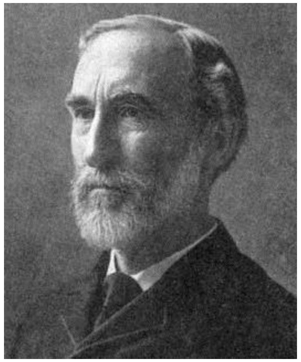


Gibbs phase rule

$$\boxed{F = C - P + 2}$$

C = 3 Ternary phase diagrams





Gibbs phase rule

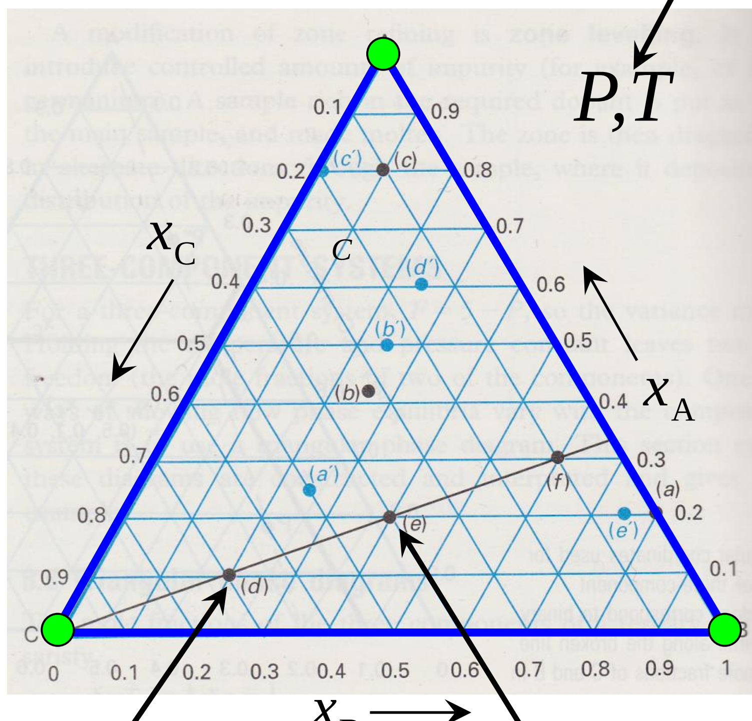
$$\boxed{F = C - P + 2}$$

$C = 3$ Ternary phase diagrams

$F = 3 - P + 2$

$F'' = 3 - P$

P, T fixed



C = 2

$F'' = 2 - P$

C = 1

$F'' = 1 - P$

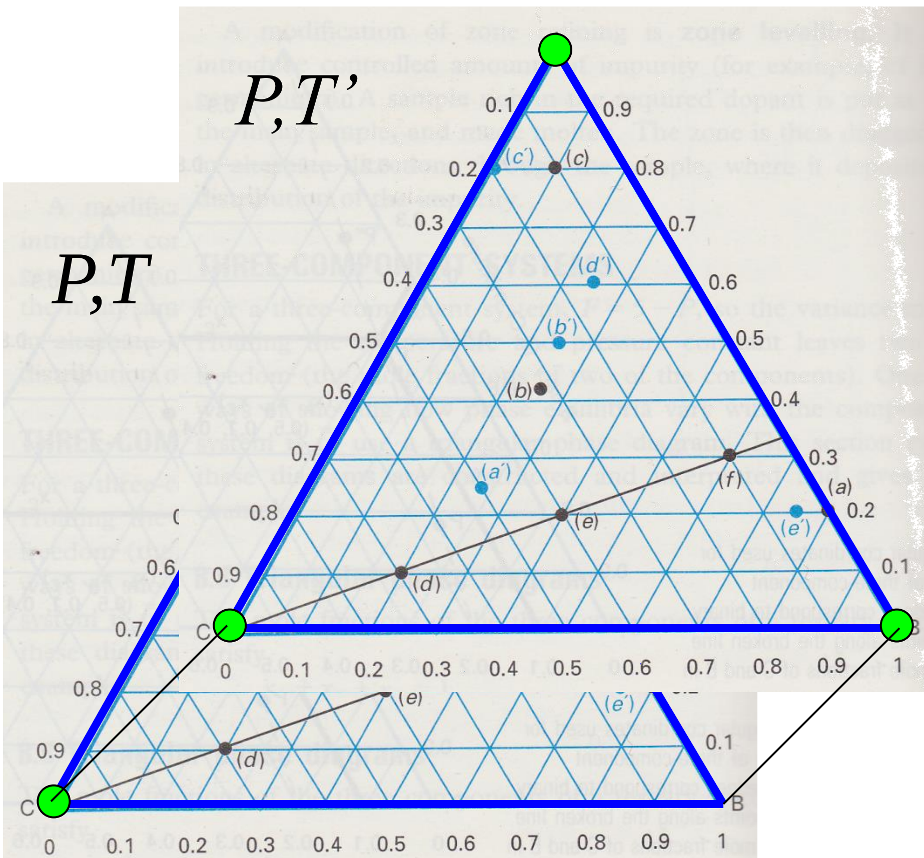
$(x_A, x_B, x_C) = (0.1, 0.2, 0.7)$

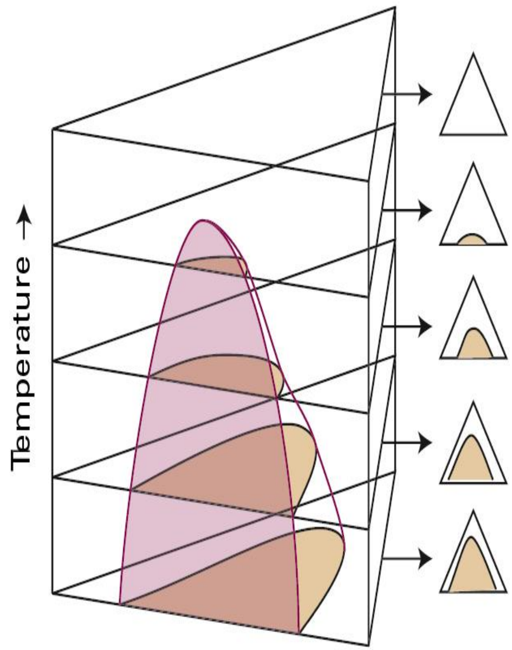
$(x_A, x_B, x_C) = (0.2, 0.4, 0.4)$

C = 3 Ternary phase diagrams

$F = 3 - P + 2$

$F'' = 3 - P$

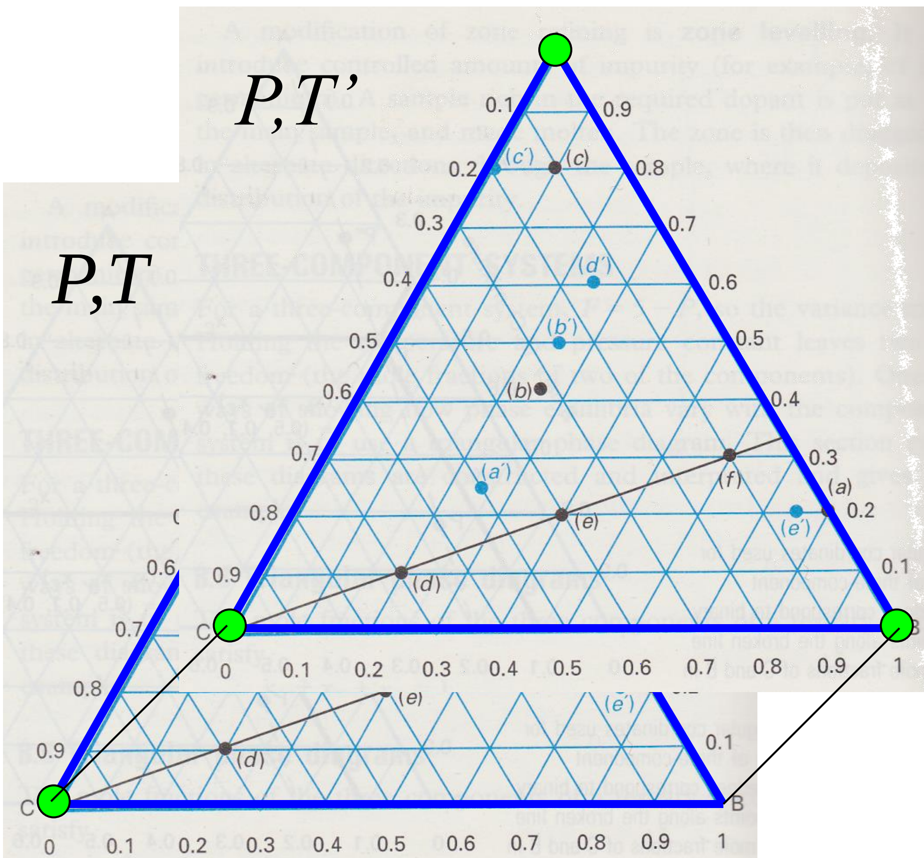


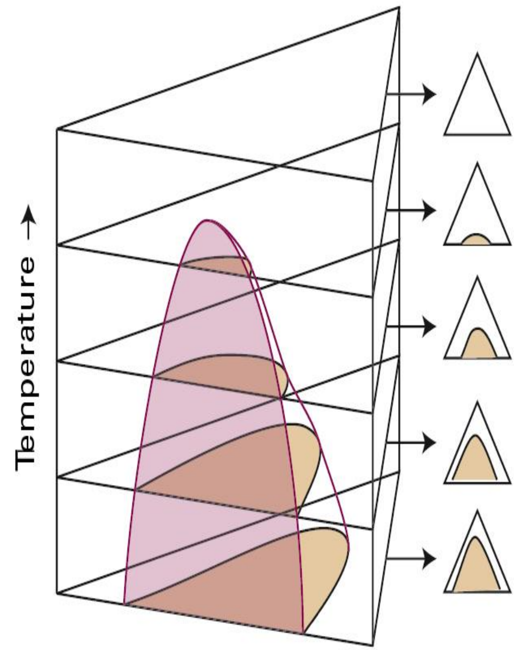


C = 3 Ternary phase diagrams

F = 3 – P + 2

F” = 3 – P

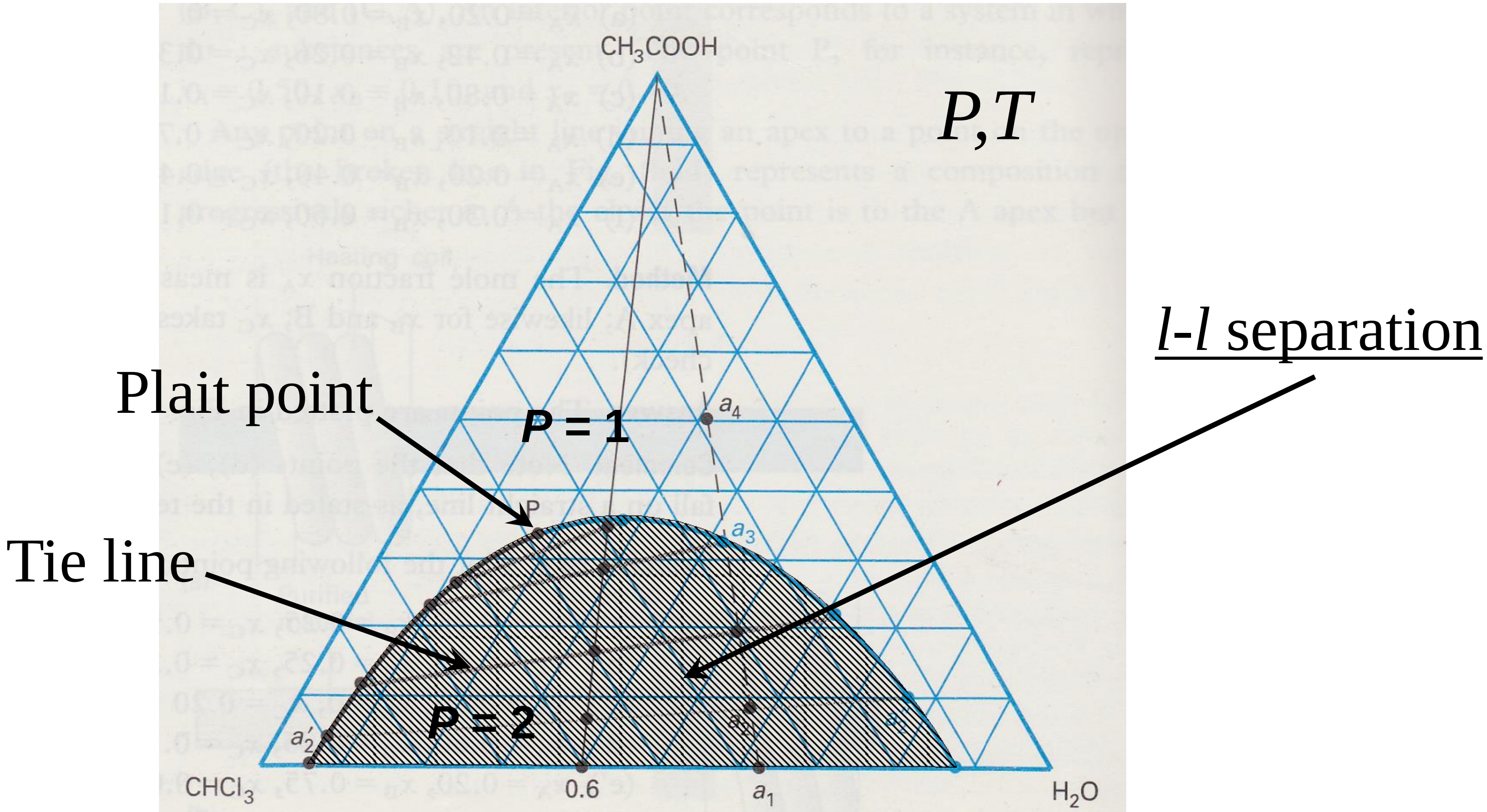




Exercise 21

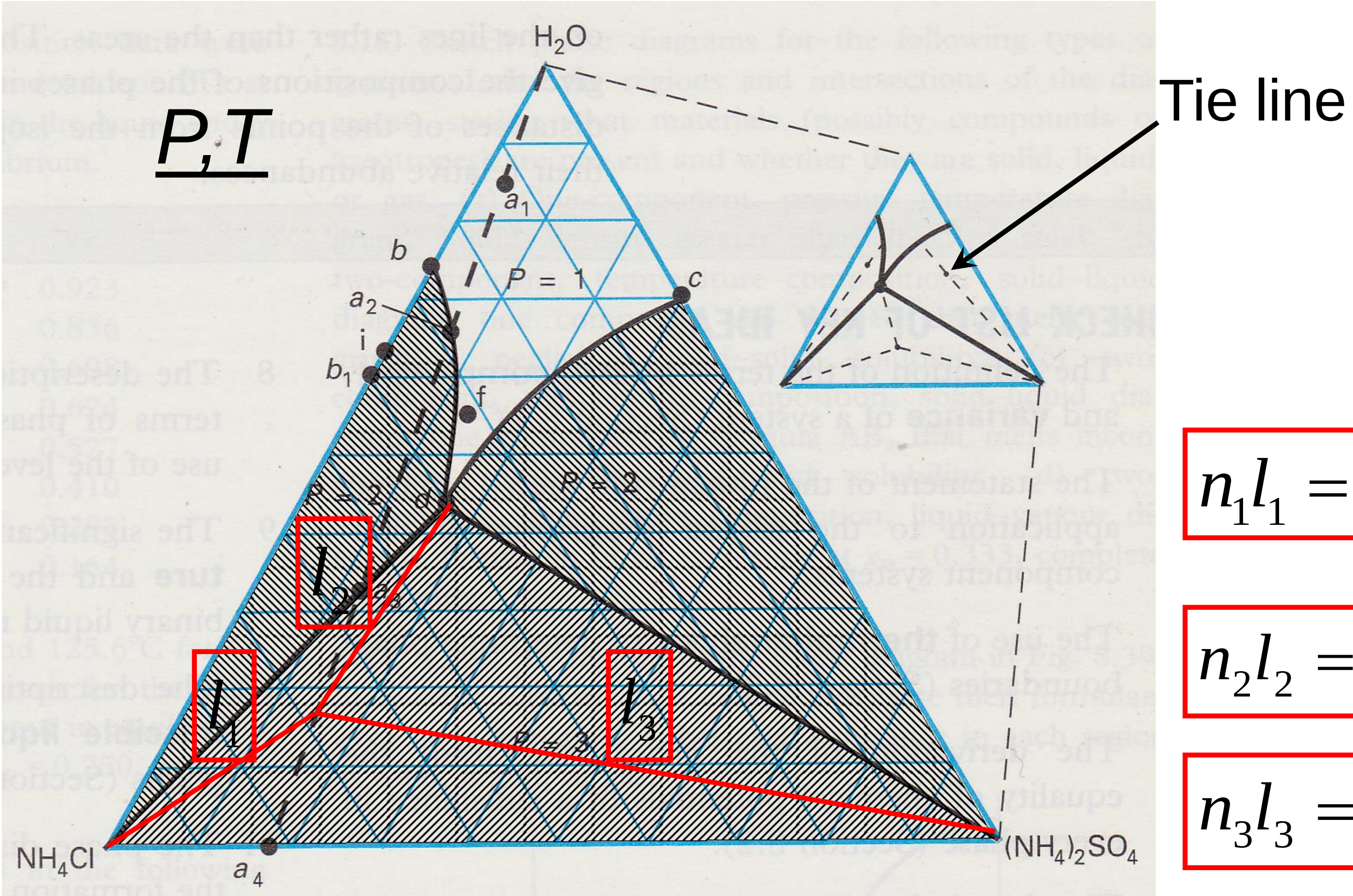
C = 3   Ternary phase diagrams

$F'' = 3 - P$



(CHCl$_3$, CH$_3$COOH, H$_2$O)

C = 3 Ternary phase diagrams



$$n_1 l_1 = n_2 l_2$$

$$n_2 l_2 = n_3 l_3$$

$$n_3 l_3 = n_1 l_1$$

$((NH_4)_2SO_4, NH_4Cl, H_2O)$