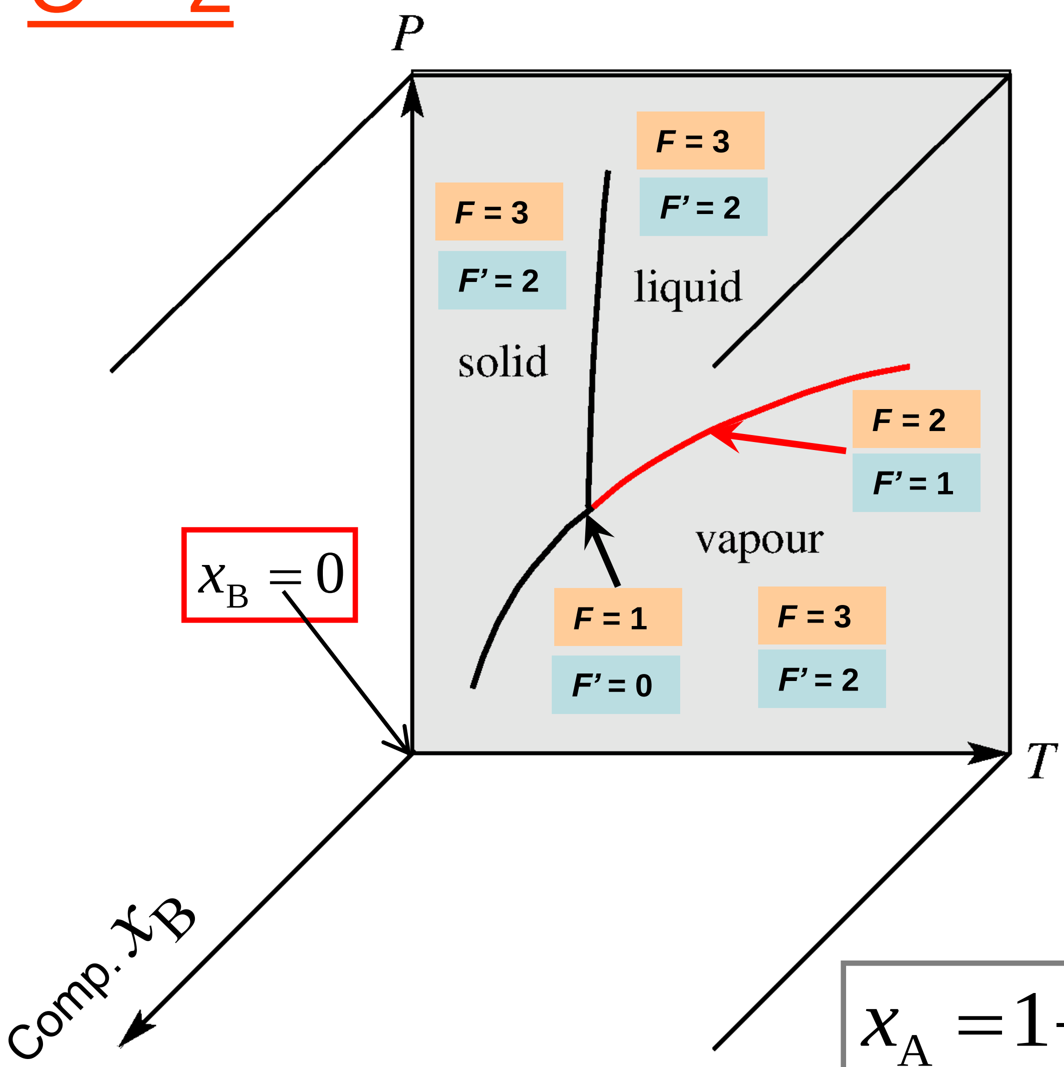
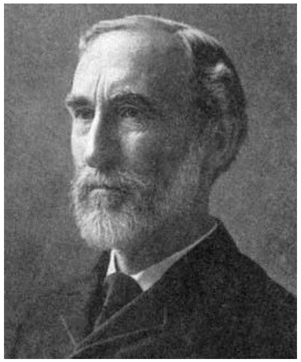
Phase diagrams of multicomponent systems

C = 2

P,T,x diagram of a binary sytem





Gibbs phase rule

$$F = C - P + 2$$

$$F' = C - P + 2 - 1$$

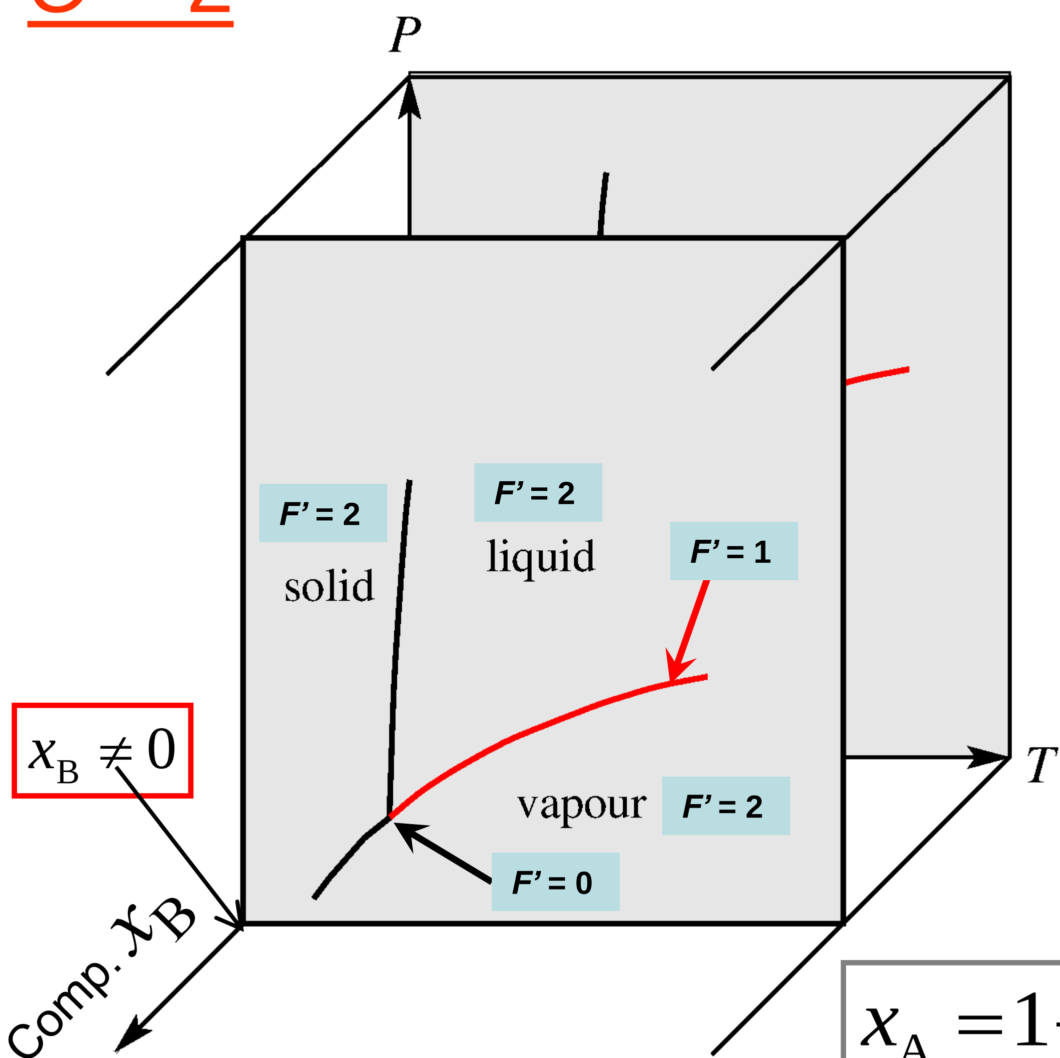
(if x is considered fixed)

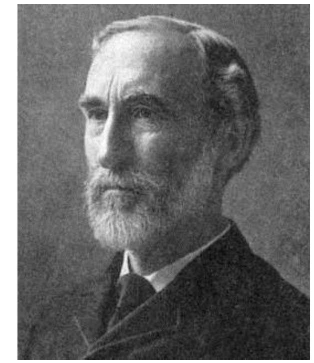
$$x_A = 1 - x_B$$

Vapour-liquid-composition diagram

P, T, x diagram of a binary sytem

C = 2





Gibbs phase rule

$$F = C - P + 2$$

$$F' = C - P + 2 - 1$$

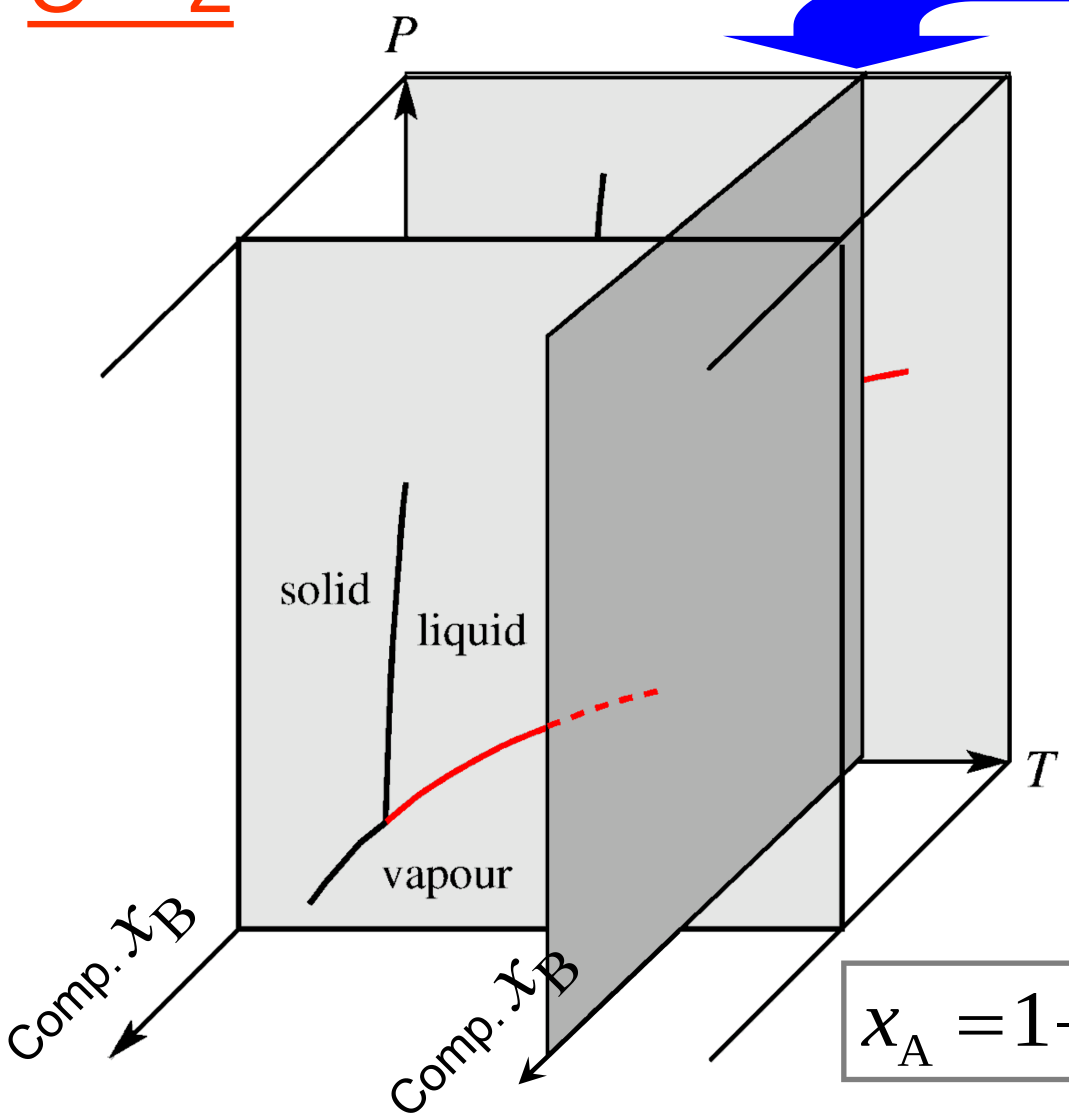
(x is fixed)

$$x_A = 1 - x_B$$

Vapour-liquid-composition (P,x) diagram

C = 2

Fixed *T*



Gibbs phase rule

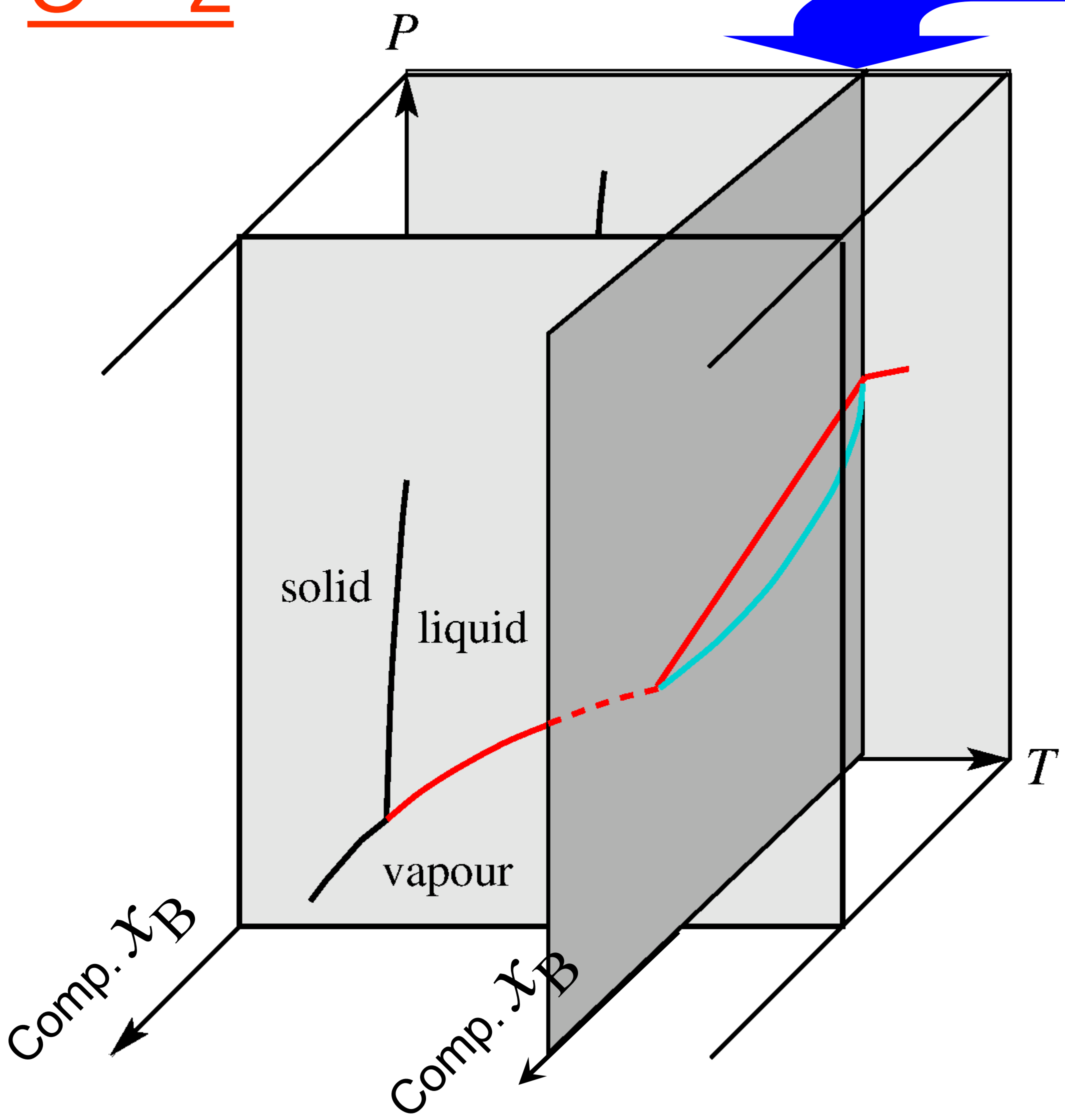
$$F = C - P + 2$$

$$x_A = 1 - x_B$$

Vapour-liquid-composition (P,x) diagram

$C = 2$

Fixed *T*



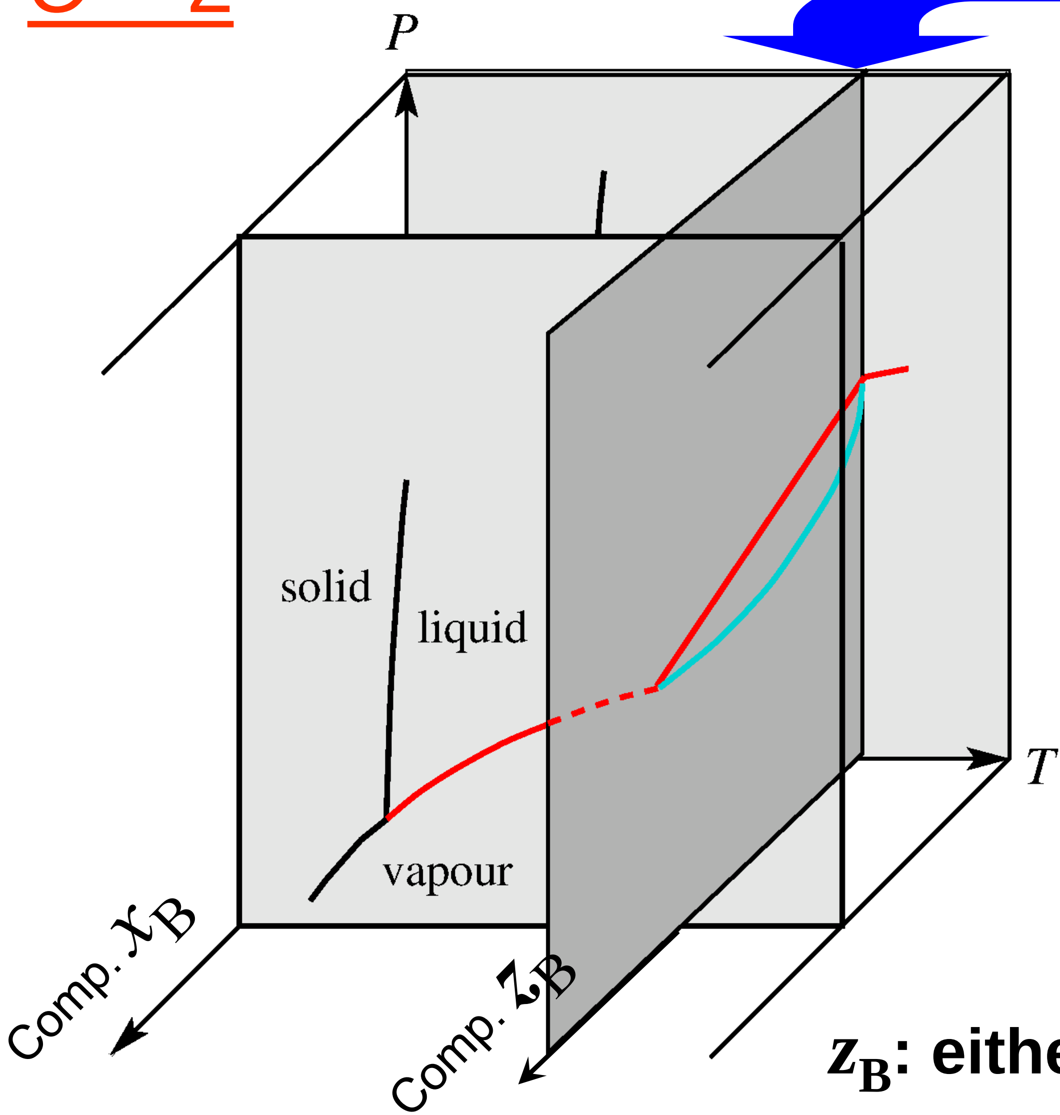
Gibbs phase rule

$$F = C - P + 2$$

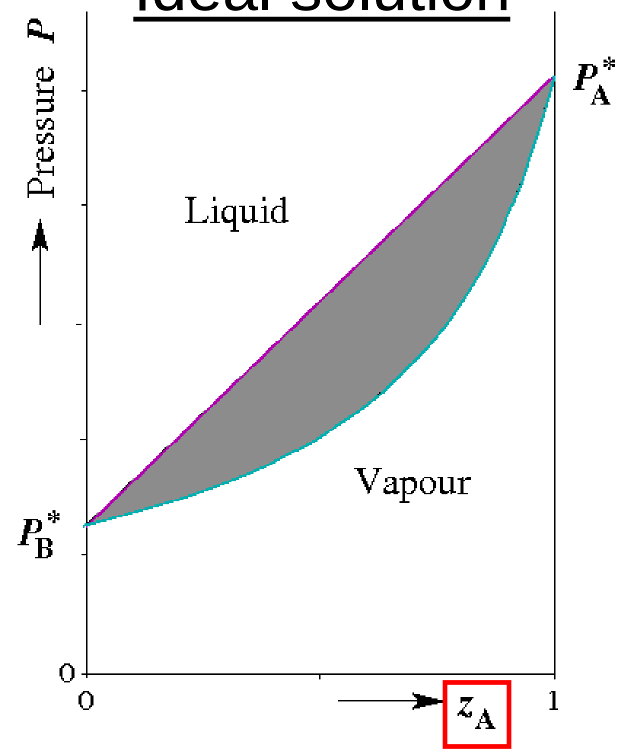
Vapour-liquid-composition (P,x) diagram

C = 2

Fixed *T*



Ideal solution

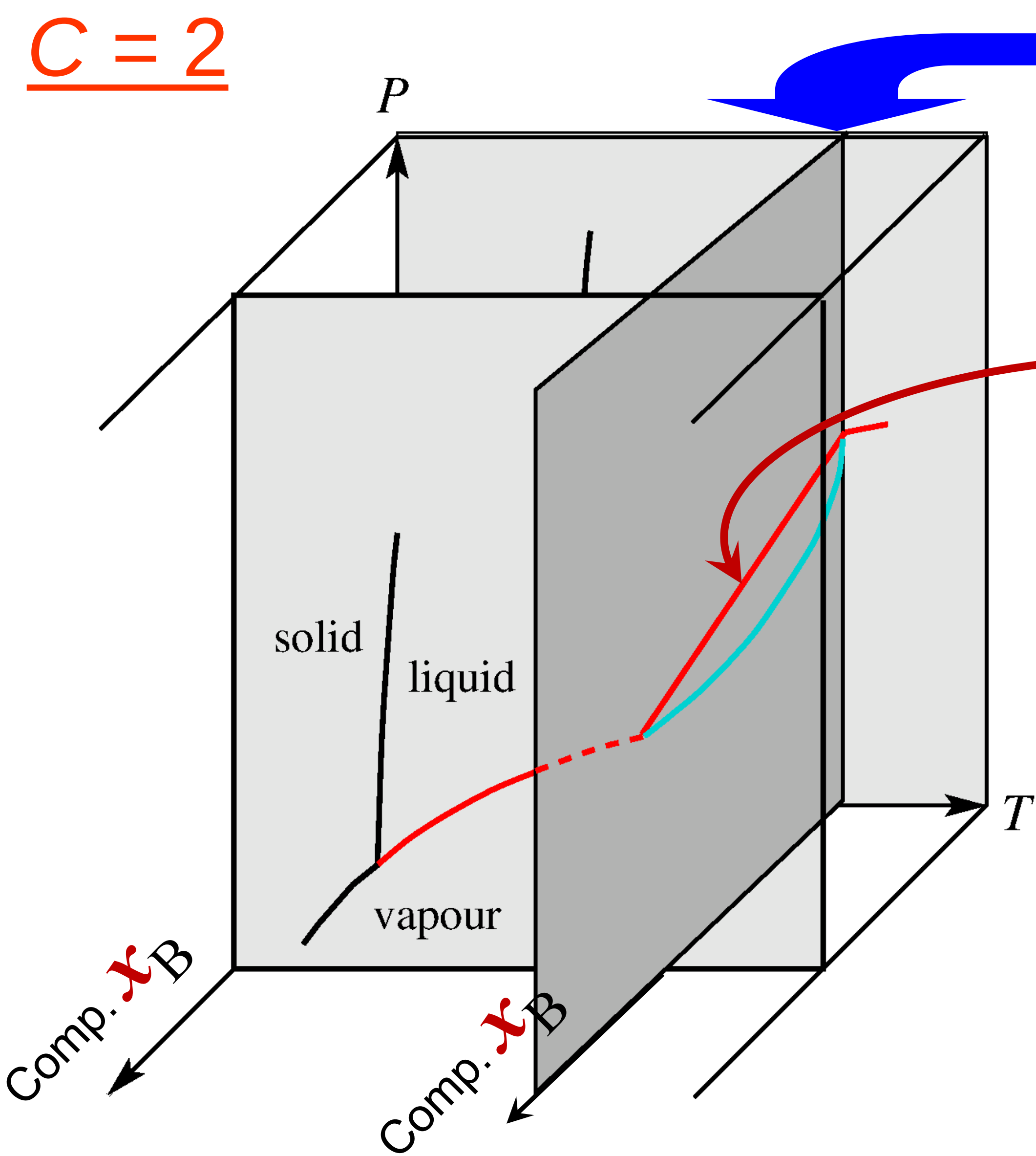


z_B: either x_B or y_B

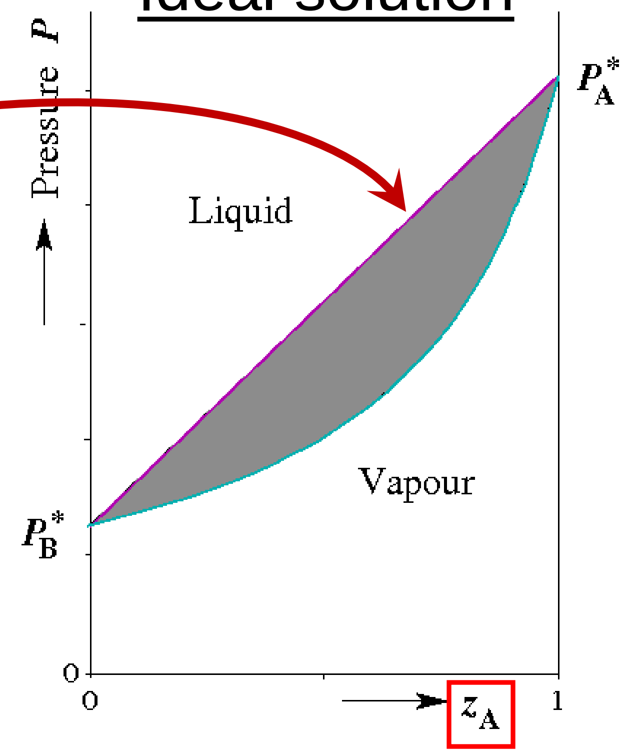
Vapour-liquid-composition (P,x) diagram

C = 2

Fixed T



Ideal solution

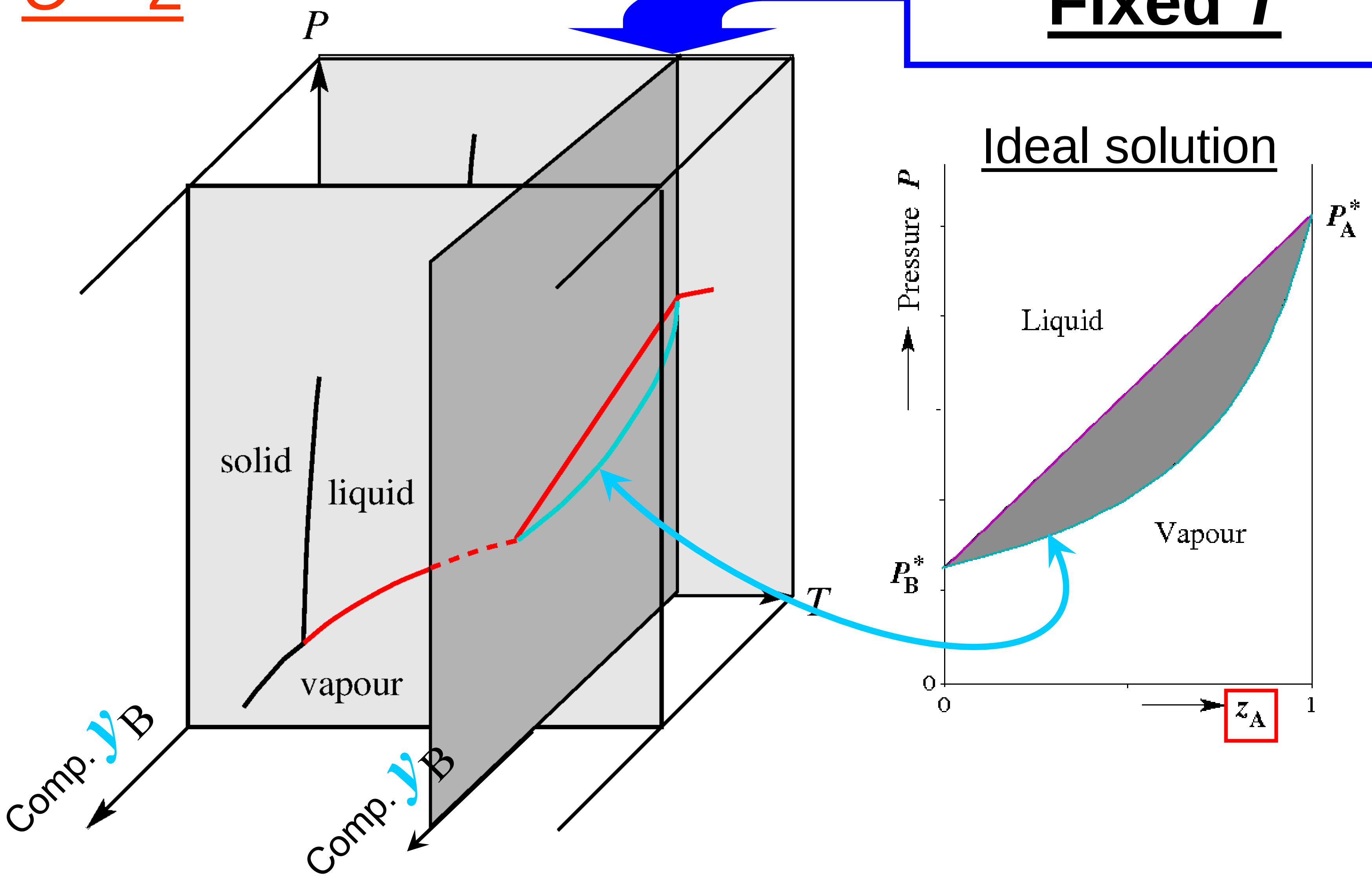


Vapour-liquid-composition (P,x) diagram

C = 2

Fixed *T*

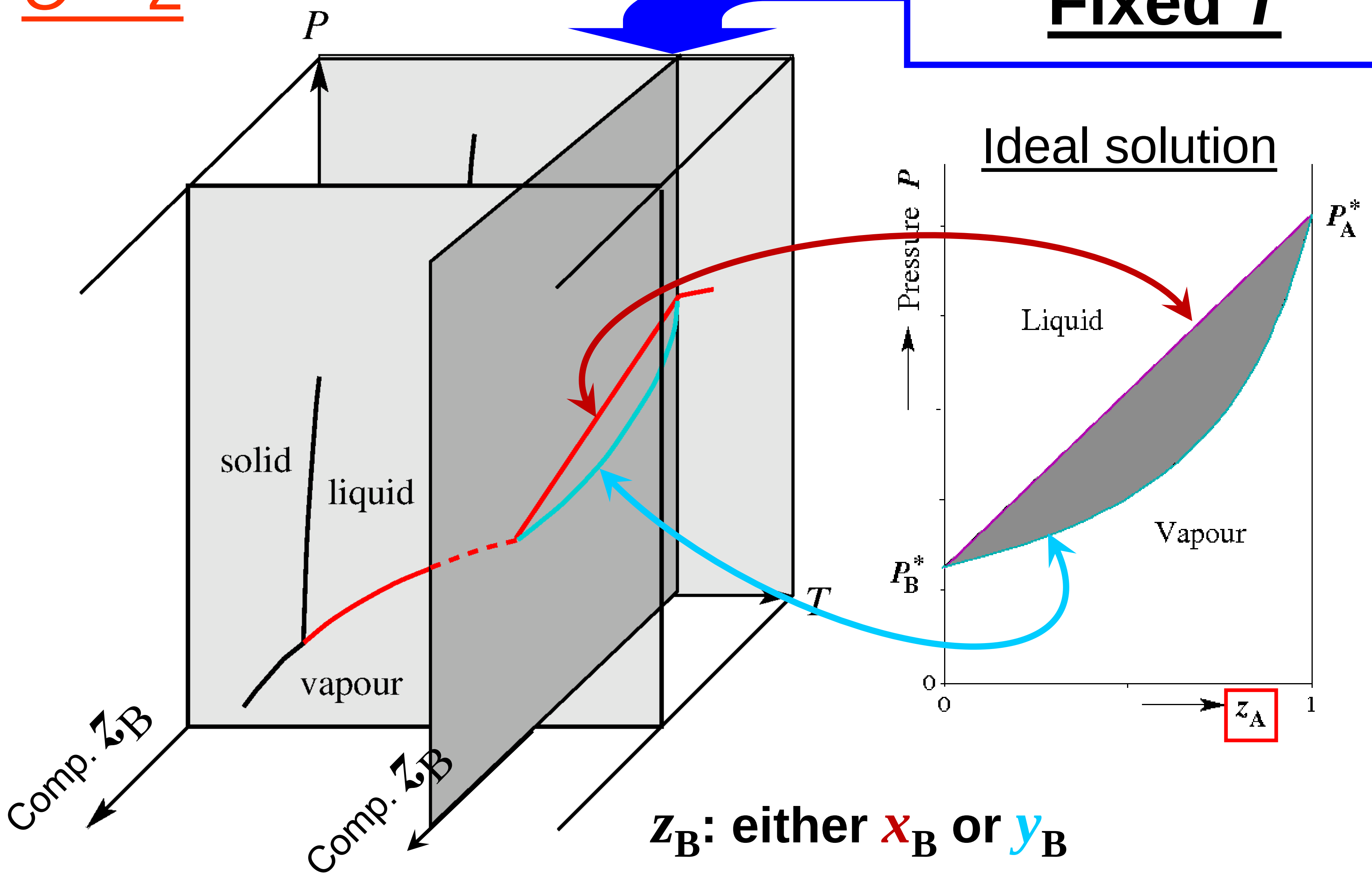
Ideal solution



Vapour-liquid-composition (P,x) diagram

C = 2

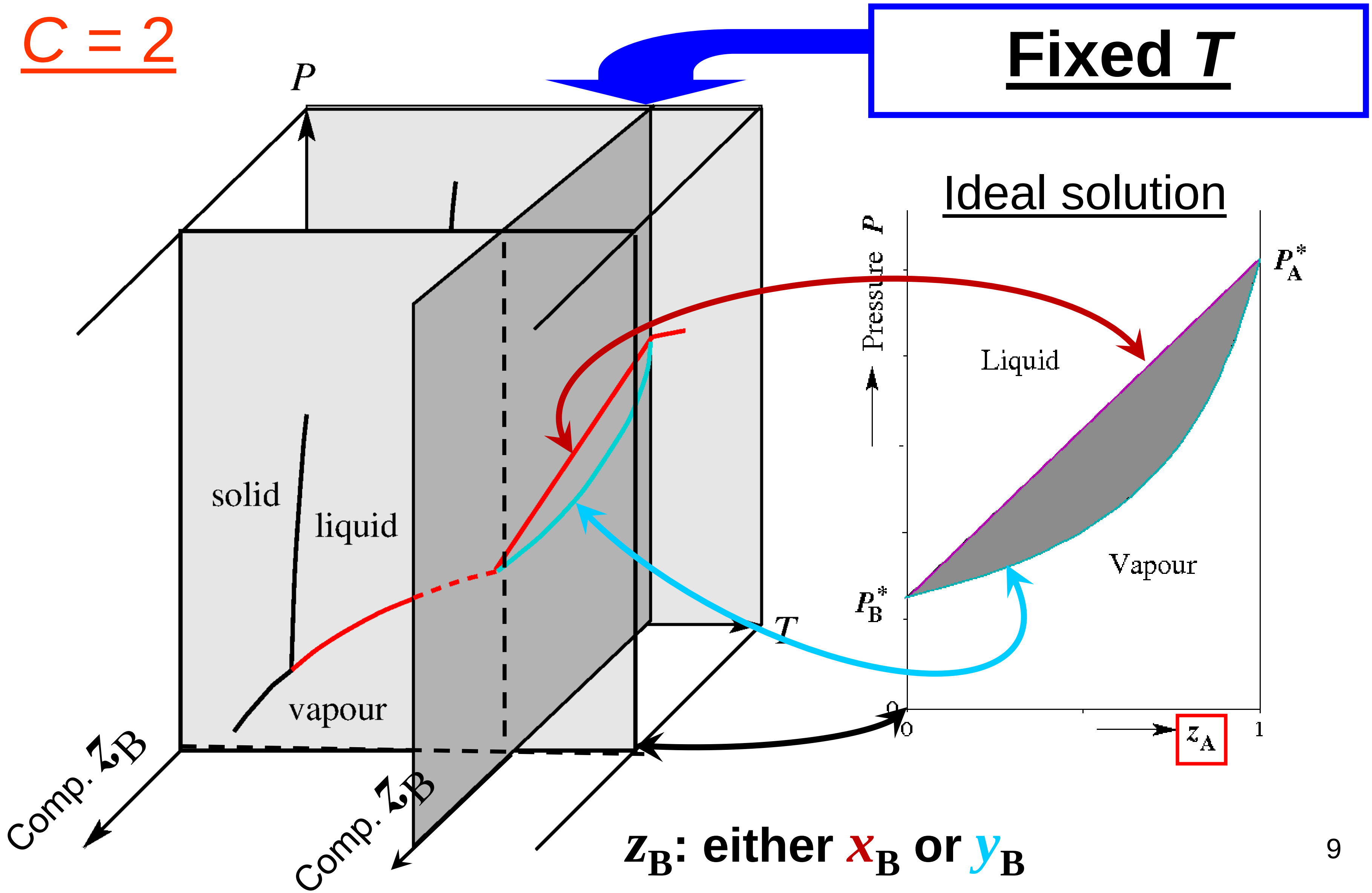
Fixed *T*



z_B: either x_B or y_B

Vapour-liquid-composition (P,x) diagram

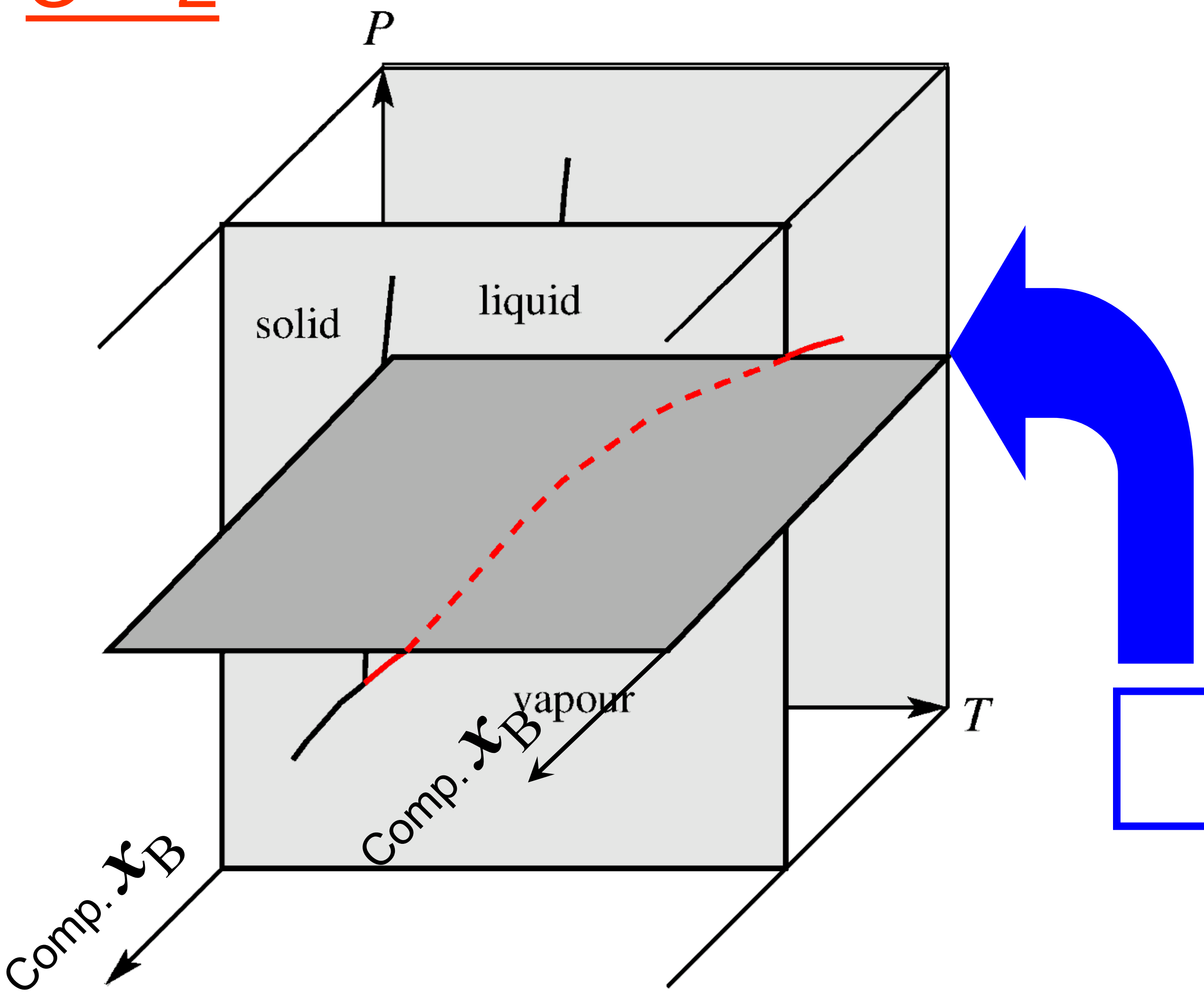
C = 2



z_B: either x_B or y_B

Vapour-liquid-composition (T,x) diagram

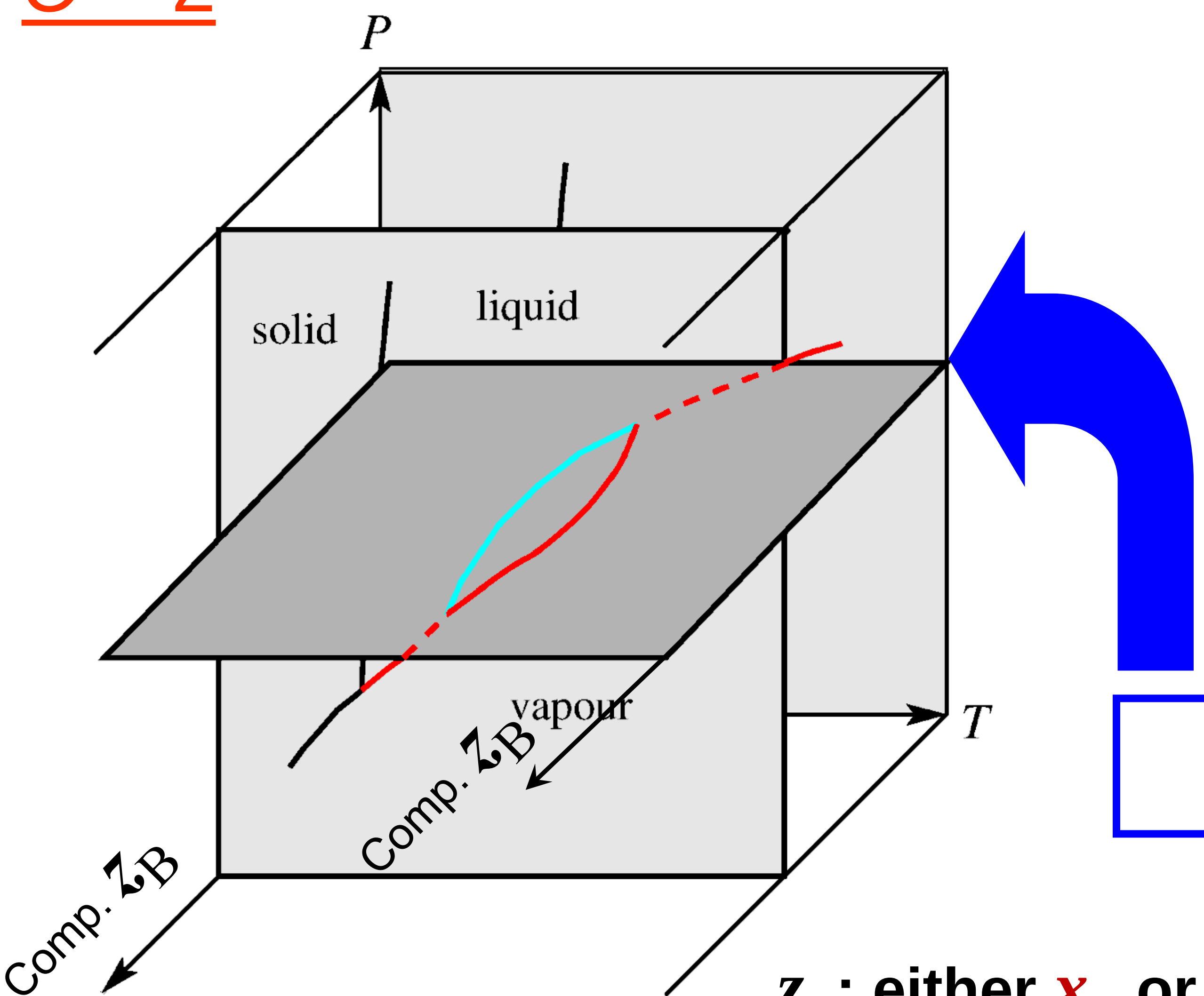
C = 2



Fixed *P*

Vapour-liquid-composition (T,x) diagram

C = 2



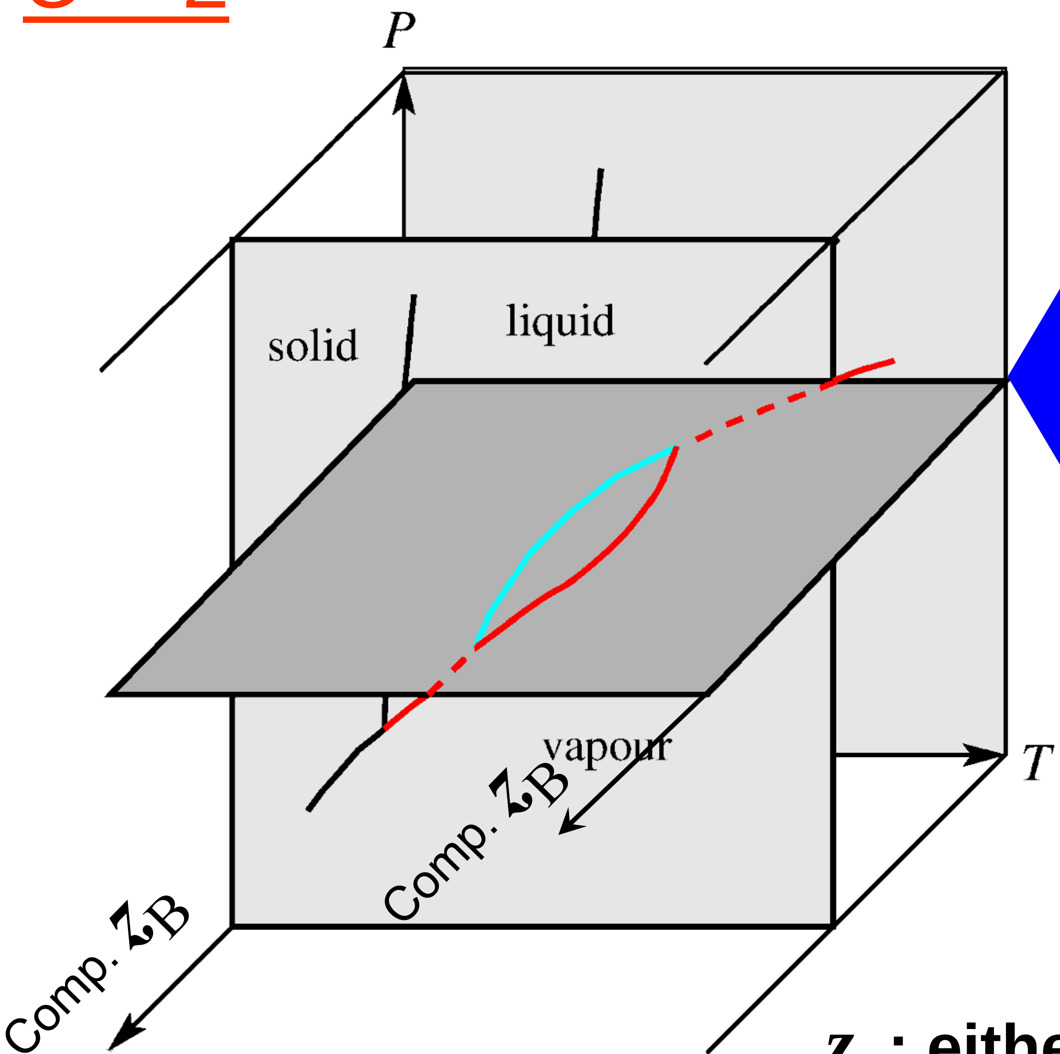
Fixed *P*

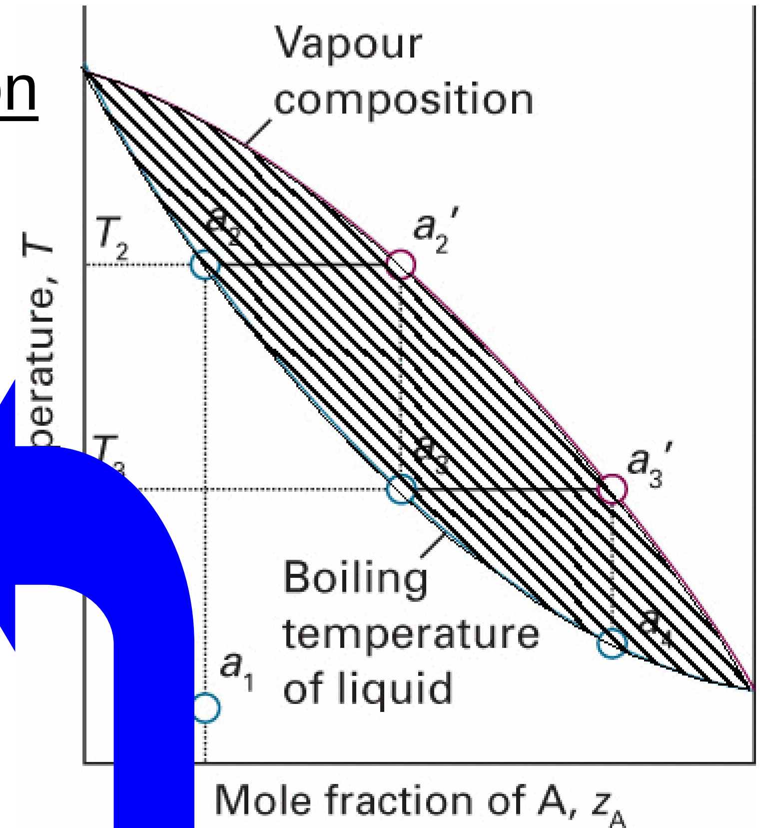
z_B: either x_B or y_B

Vapour-liquid-composition (T,x) diagram

C = 2

Ideal solution





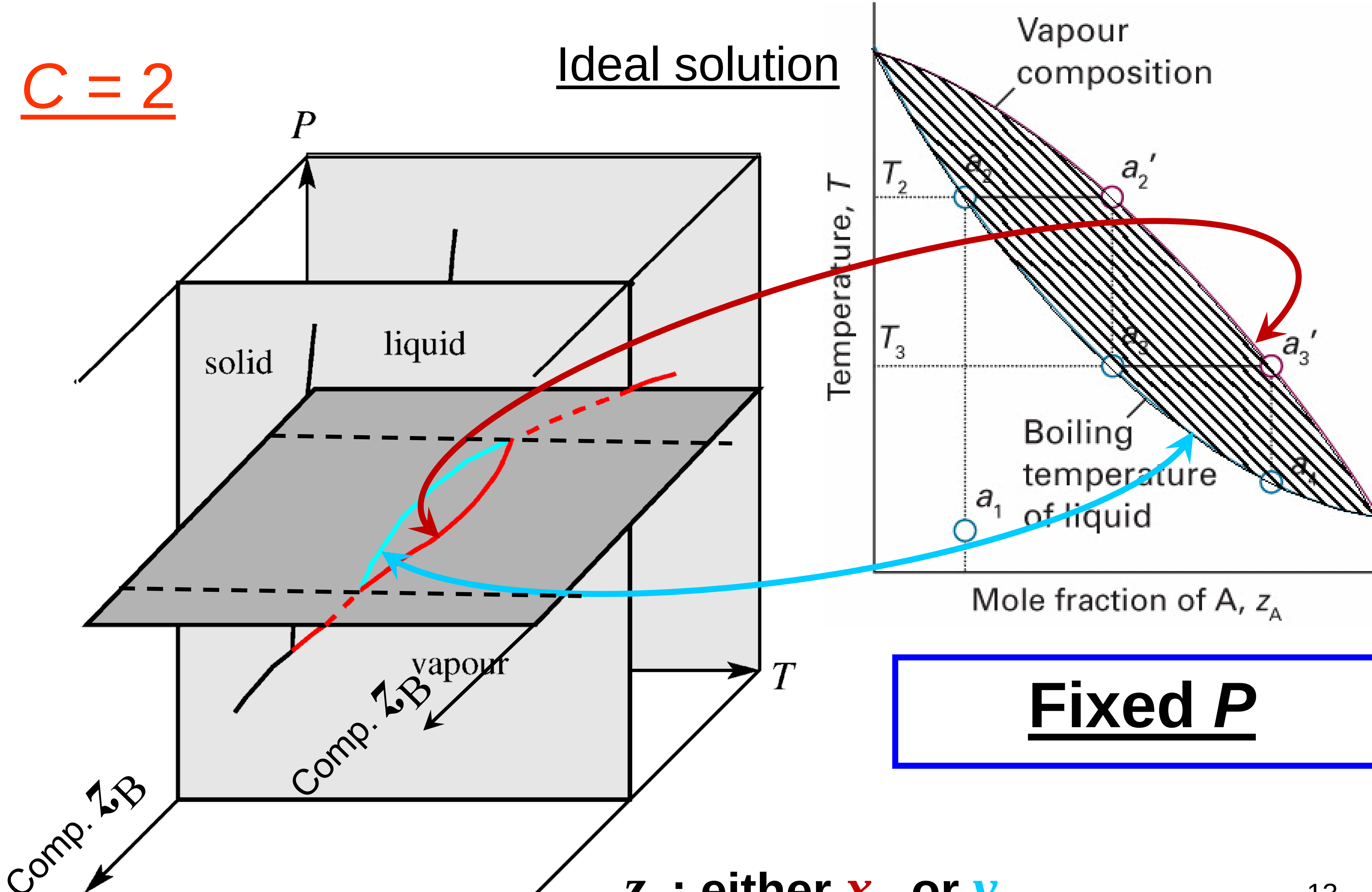
Fixed *P*

z_B: **either x_B or y_B**

Vapour-liquid-composition (T,x) diagram

C = 2

Ideal solution

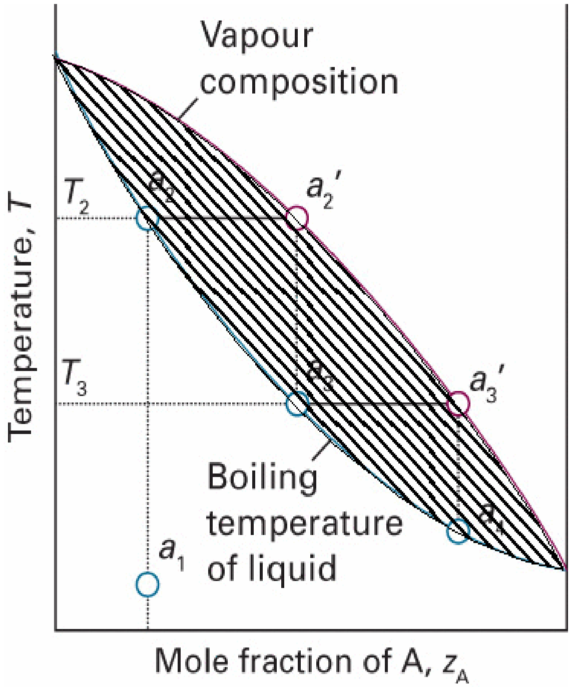


Fixed *P*

z_B: either x_B or y_B

C = 2 Temperature-composition diagrams

Ideal solution



Fixed *P*

$$P(x_A) = x_A P_A^* + (1 - x_A) P_B^*$$

$$P(y_A) = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) y_A}$$

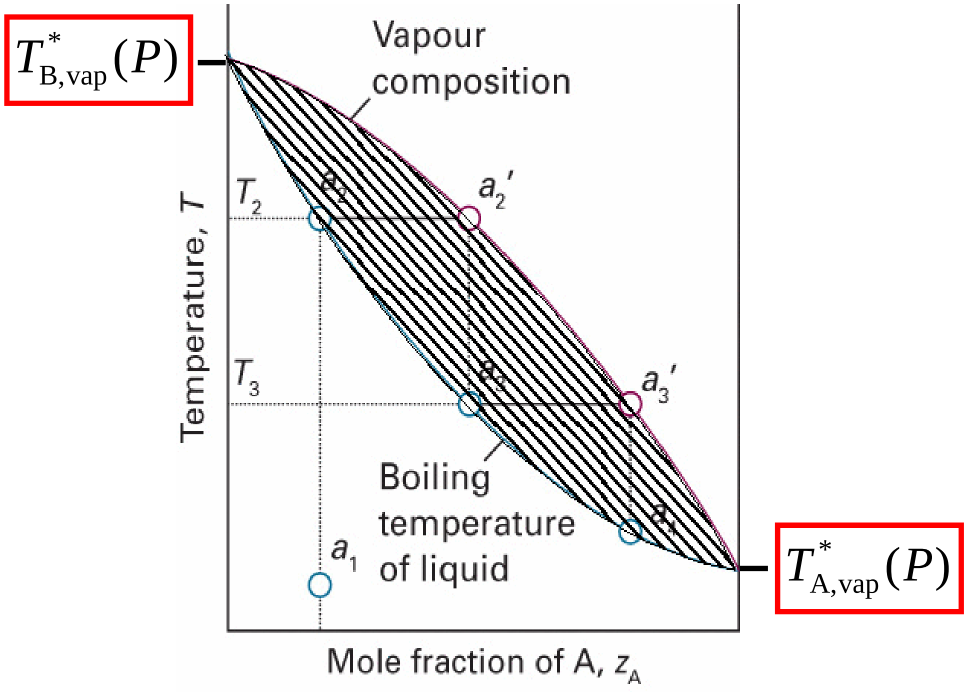
$$x_A(T) = \frac{P - P_B^*(T)}{P_A^*(T) - P_B^*(T)}$$

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

$C = 2$ Temperature-composition diagrams

$$P(x_A) = x_A P_A^* + (1 - x_A) P_B^*$$

Ideal solution



$$P(y_A) = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) y_A}$$

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

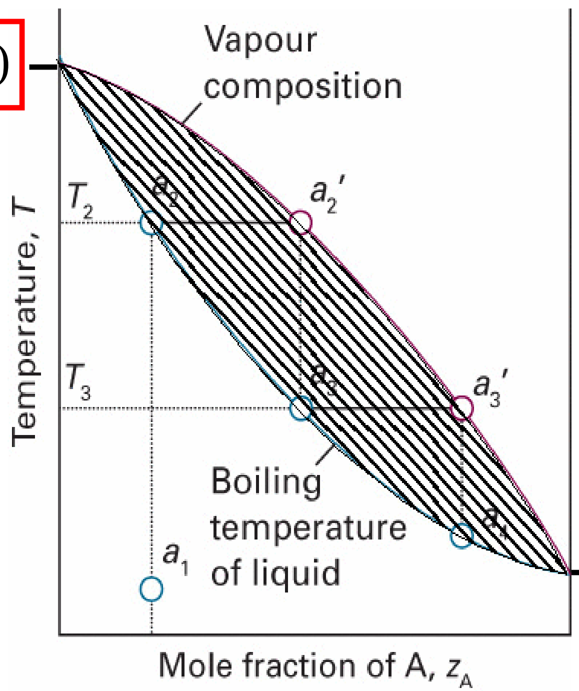
$$y_A(T) = \frac{P_A^*(T)\left[P - P_B^*(T)\right]}{P\left[P_A^*(T) - P_B^*(T)\right]}$$

Fixed *P*

C = 2 Temperature-composition diagrams

Ideal solution

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



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

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

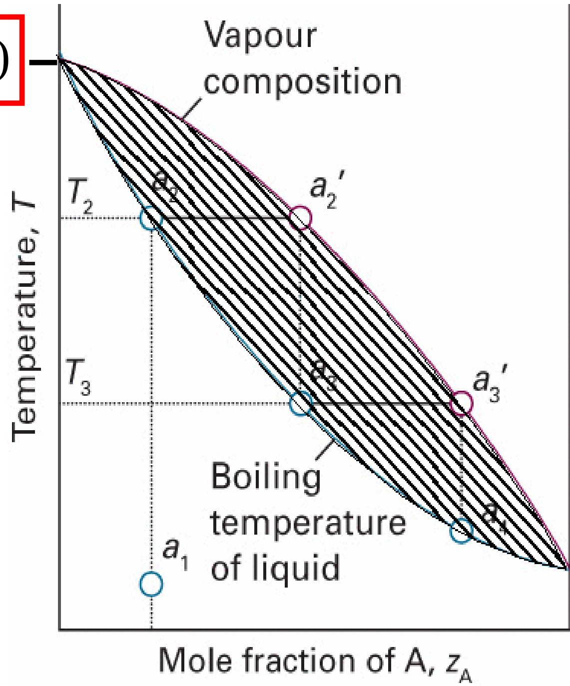
$$y_{\mathrm{A}}(T) = \frac{P^*_{\mathrm{A}}(T)\left[P - P^*_{\mathrm{B}}(T)\right]}{P\left[P^*_{\mathrm{A}}(T) - P^*_{\mathrm{B}}(T)\right]}$$

Fixed *P*

$C = 2$ Temperature-composition diagrams

Ideal solution

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



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

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

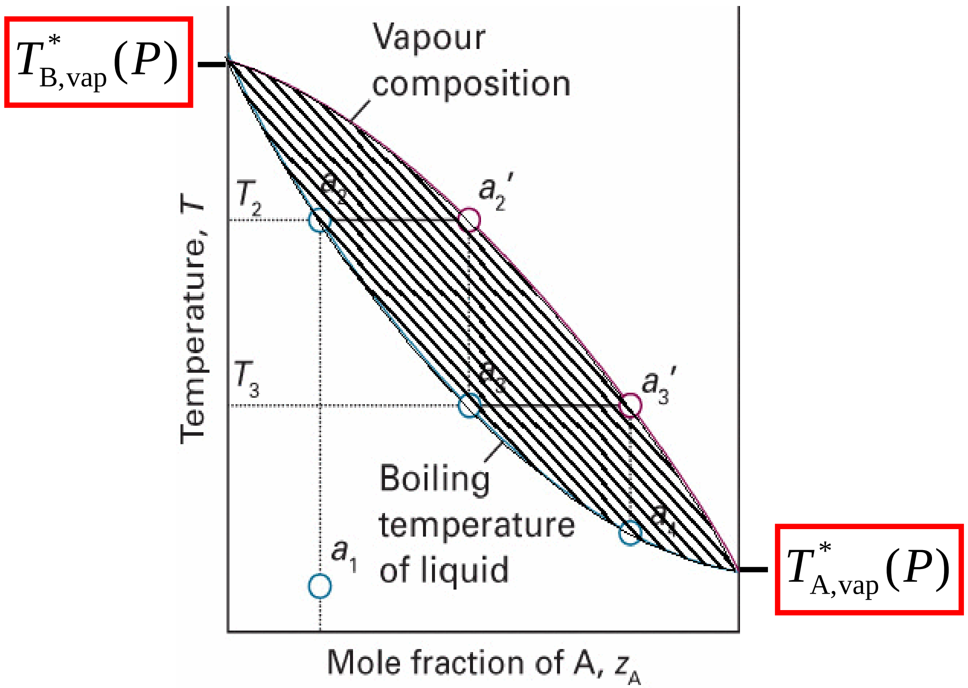
$$y_\mathrm{A}(T) = \frac{P^*_\mathrm{A}(T)\left[P - P^*_\mathrm{B}(T)\right]}{P\left[P^*_\mathrm{A}(T) - P^*_\mathrm{B}(T)\right]}$$

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

Fixed *P*

$C = 2$ Temperature-composition diagrams

Ideal solution



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

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

Fixed *P*

B: non volatile → $P_B^* \approx 0$

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

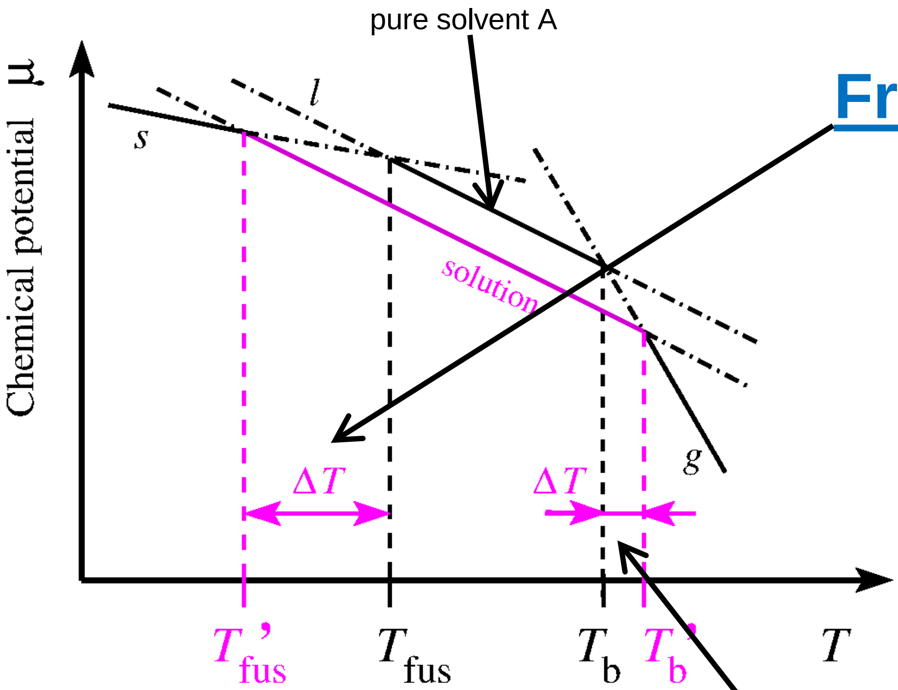
(together with $a_i = x_i$)

(Ideal solution)

Solutions: Colligative properties

Lecture 5: Thermodynamics

(http://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html)



Freezing point depression

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

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

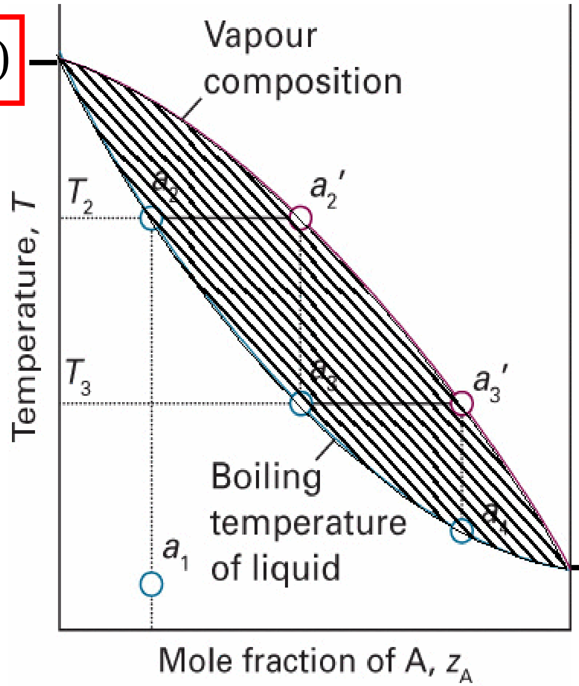
Boiling point elevation

Fixed *P*

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

Ideal solution

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



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

$$x_A(T) = \frac{P - P^*_B(T)}{P^*_A(T) - P^*_B(T)}$$

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

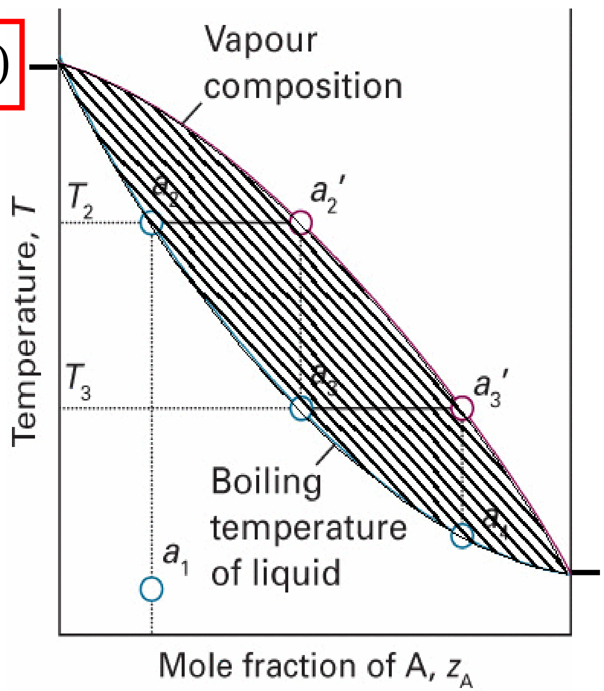
B: non volatile → $P^*_B \approx 0$

Fixed *P*

C = 2 T-x diagrams: Boiling point elevation

Ideal solution

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



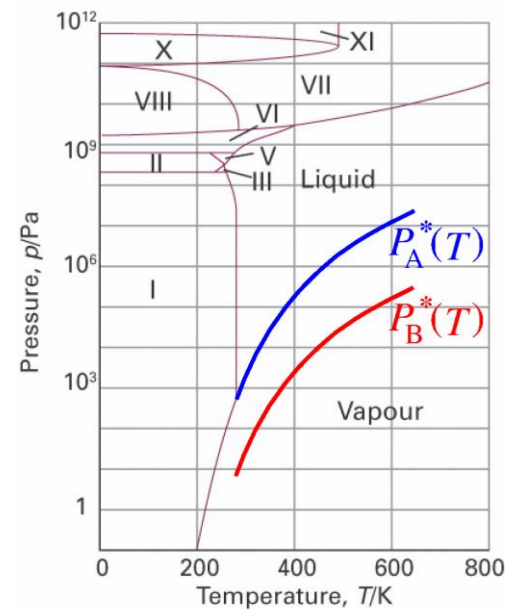
$T^*_{\mathrm{A,vap}}(P)$

Fixed *P*

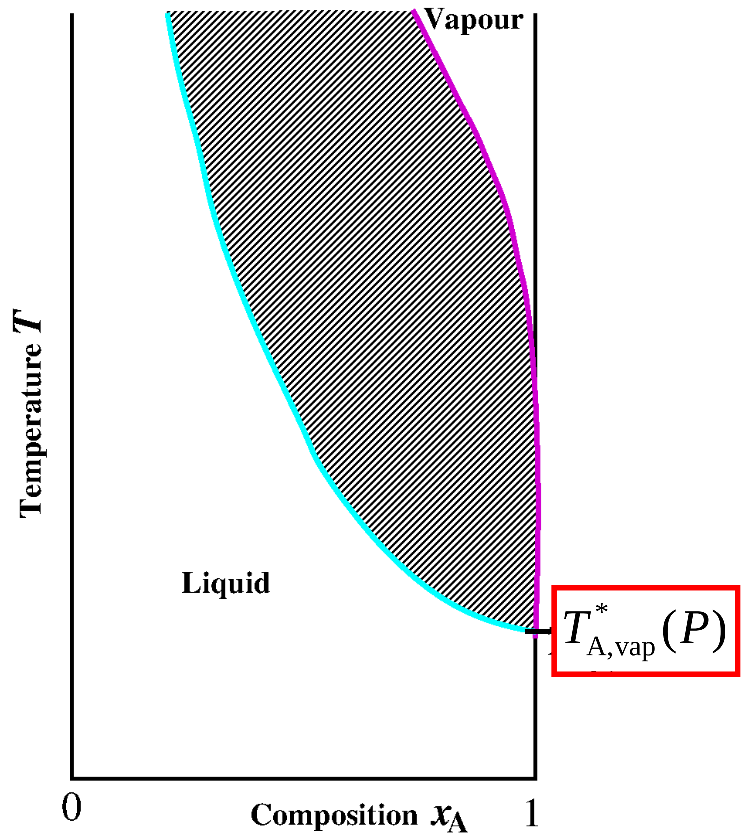
$$x_\mathrm{A}(T) = \frac{P - P^*_\mathrm{B}(T)}{P^*_\mathrm{A}(T) - P^*_\mathrm{B}(T)}$$

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

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



C = 2 T-x diagrams: Boiling point elevation

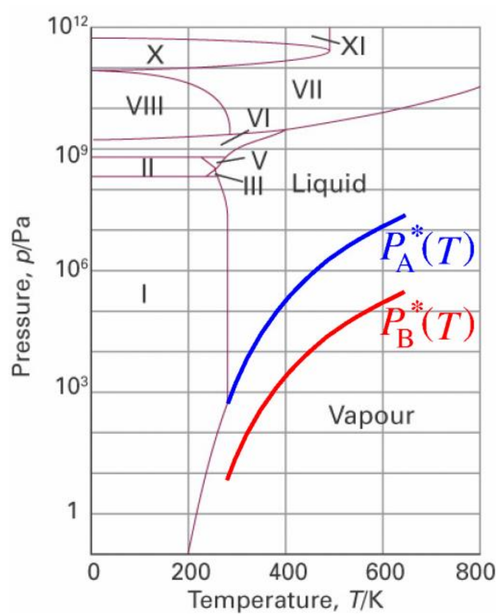


Fixed *P*

B: non volatile

$P^*_B \approx 0$

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



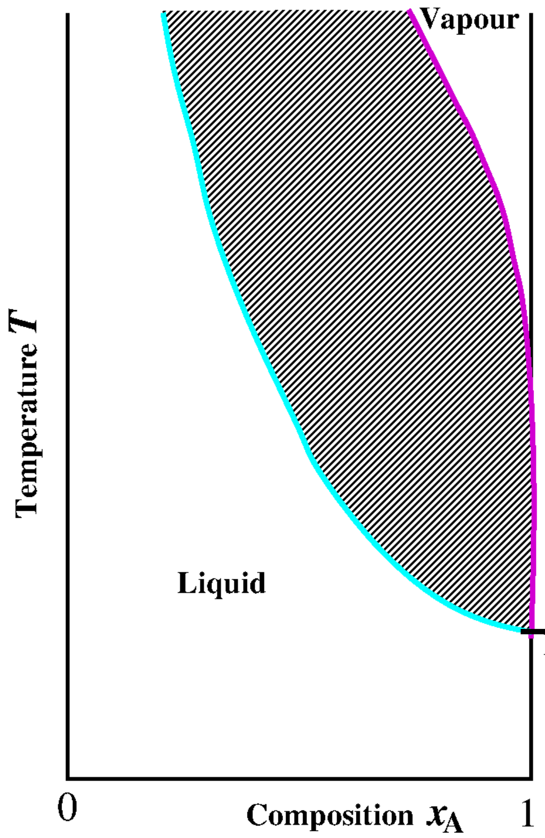
C = 2 T-x diagrams: Boiling point elevation

B: non volatile → $P_{\mathrm{B}}^{*} \approx 0$

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

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

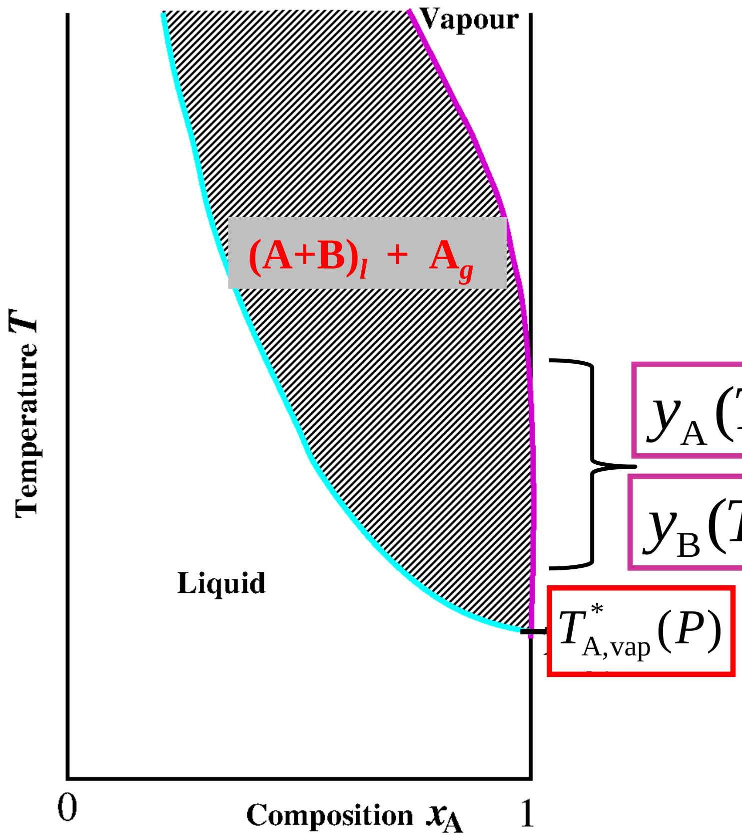
$y_{\mathrm{B}}(T) \approx 0$



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

Fixed *P*

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

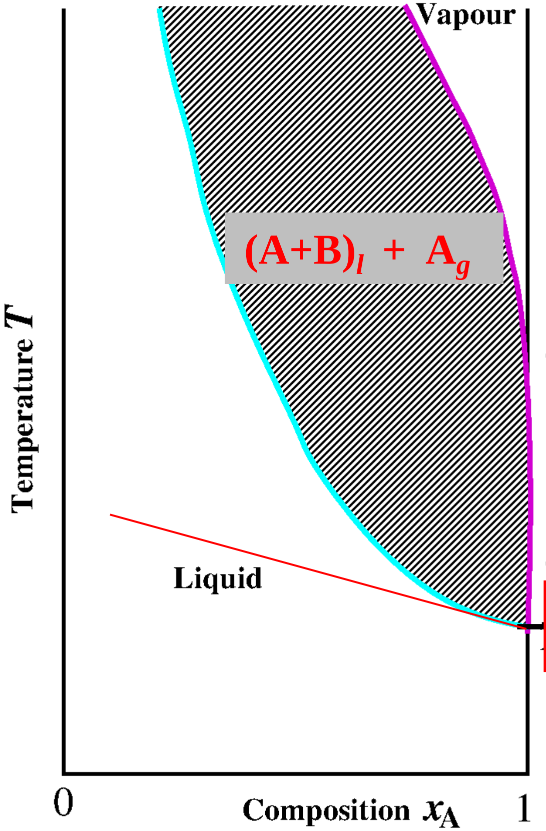


B: non volatile → $P^*_B \approx 0$

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

Fixed *P*

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



B: non volatile → $P_B^* \approx 0$

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

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

$$y_A(T) \approx 1$$

$$y_B(T) \approx 0$$

$$T_{A,vap}^*(P)$$

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

Boiling point elevation

Fixed *P*

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

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

Boiling point elevation

$$\Delta T = \frac{RT^{*2}_{\mathrm{A,vap}}}{\Delta_{\mathrm{vap}} H_{\mathrm{A}}} x_{\mathrm{B}}$$

$$\left(P_{\mathrm{B}} \approx 0\right)$$

Freezing point depression

$$\Delta T = \frac{RT^{*2}_{\mathrm{A,fus}}}{\Delta_{\mathrm{fus}} H_{\mathrm{A}}} x_{\mathrm{B}}$$

$$\left(x_{\mathrm{B},s} \approx 0\right)$$

Exercise 18

Osmosis

$$\Pi = [B]RT$$

Solubility

Exercise 19

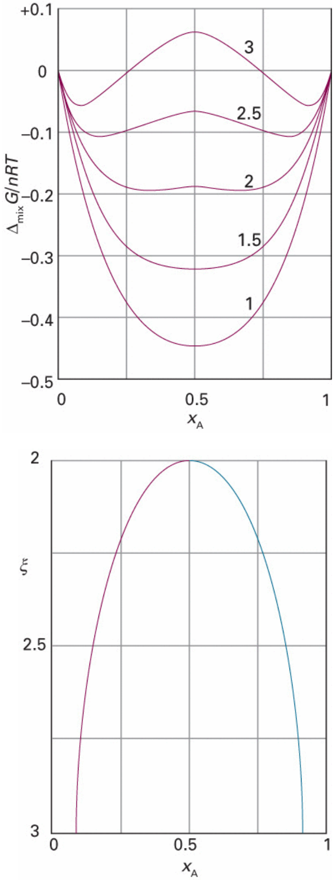
$$\ln x_{\mathrm{B}} = \frac{\Delta_{\mathrm{fus}} H_{\mathrm{B}}}{R}\left[\frac{1}{T_{\mathrm{B,fus}}} - \frac{1}{T}\right]$$

A is the solvent and B is the solute

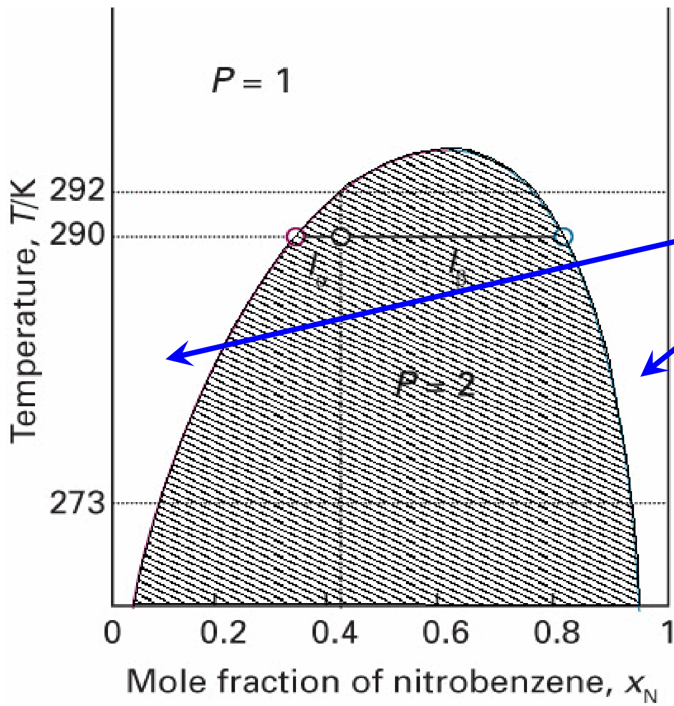
C = 2 Liquid-liquid separation (oiling out)

Extreme case of non-ideality

C = 2 Liquid-liquid separation (oiling out)



(Exercise 17)



Nitrobenzene/hexane

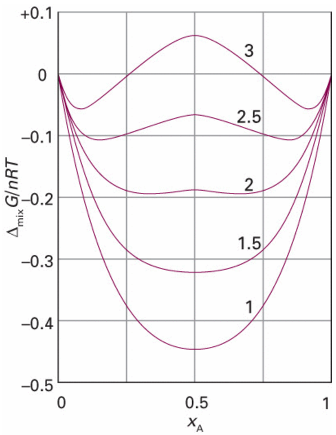
Partial miscibility of liquids

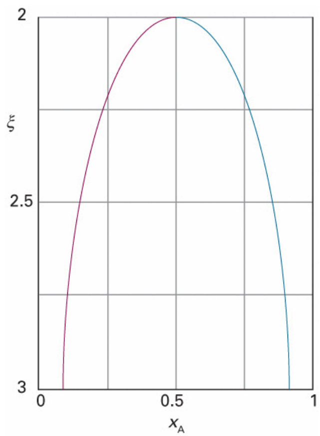
$$G^E = nRT\beta x_A x_B$$

$$\beta = \beta(T) > 0$$

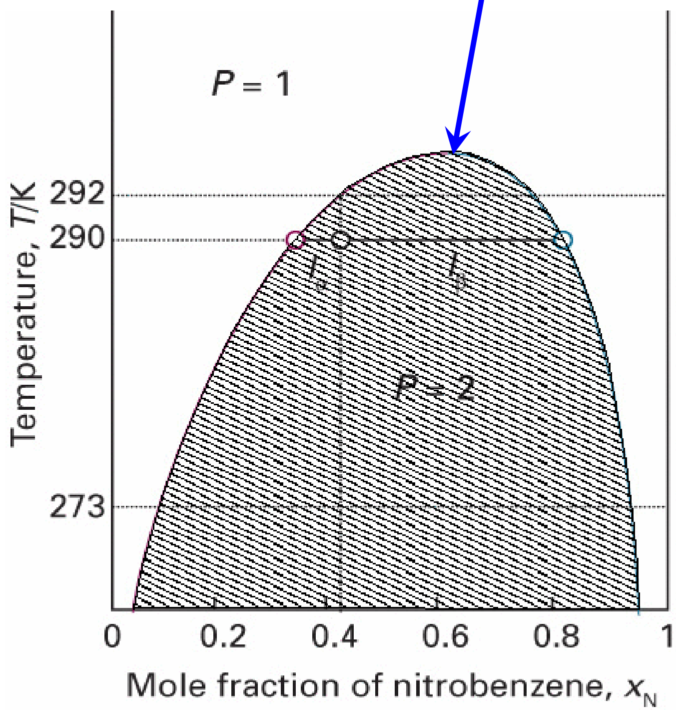
Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

C = 2 Liquid-liquid separation (oiling out)





Upper Critical (Solution) Temperature



Nitrobenzene/hexane

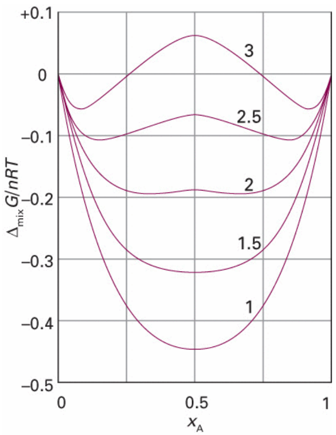
$$G^{E} = nRT\beta x_A x_B$$

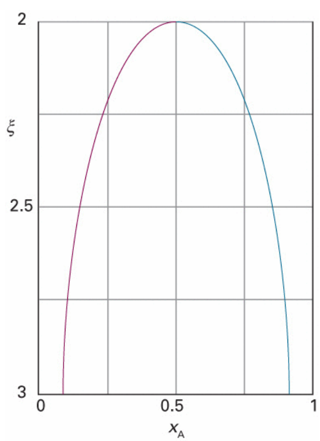
$$\beta = \beta(T) > 0$$

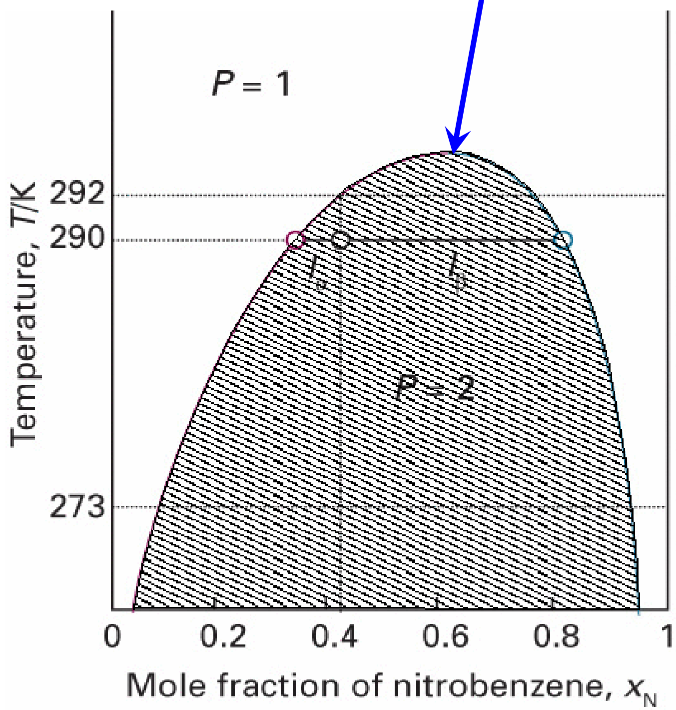
Lever rule $$n_\alpha l_\alpha = n_\beta l_\beta$$

C = 2   Liquid-liquid separation (oiling out)

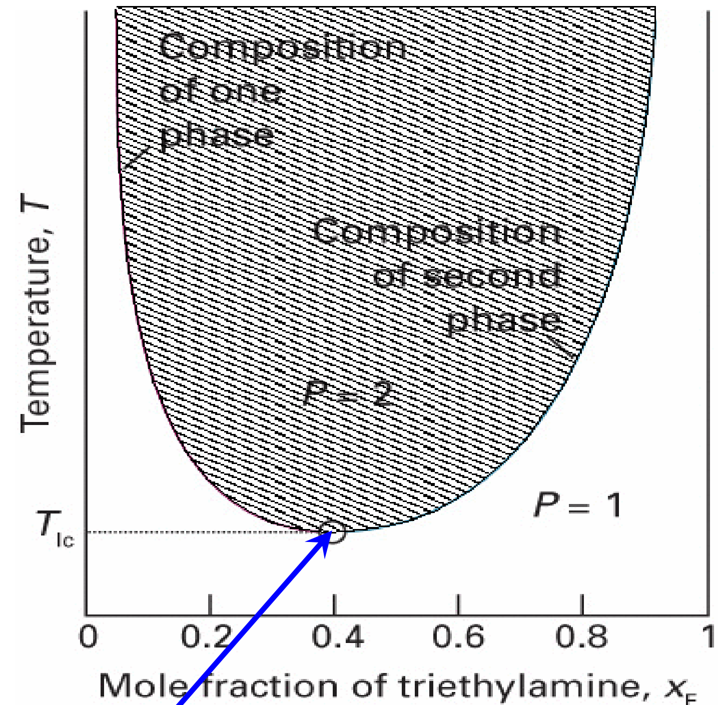
Upper Critical (Solution) Temperature







Nitrobenzene/hexane



H_2O / triethylamine

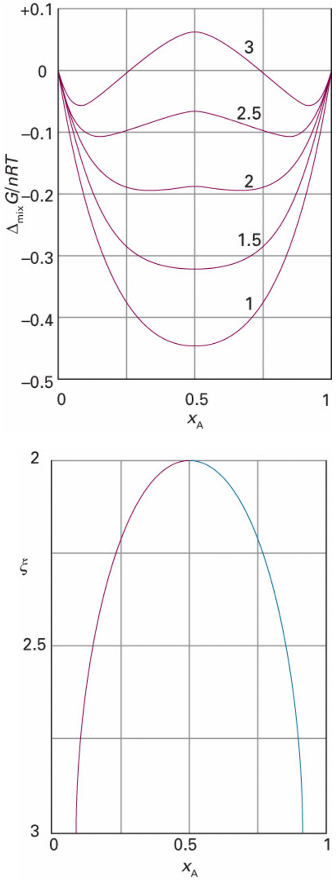
Lower Critical (Solution) Temperature

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

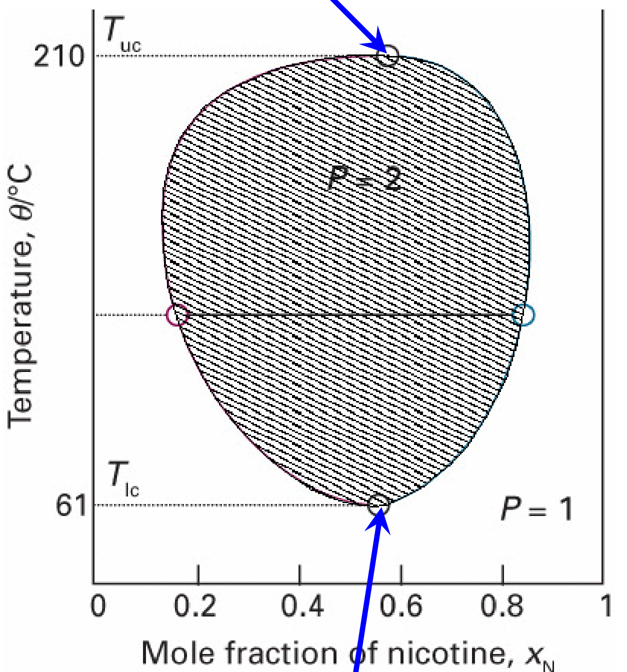
$$\beta = \beta(T) > 0$$

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

C = 2   Liquid-liquid separation (oiling out)



Upper Critical (Solution) Temperature



H_2O / nicotine

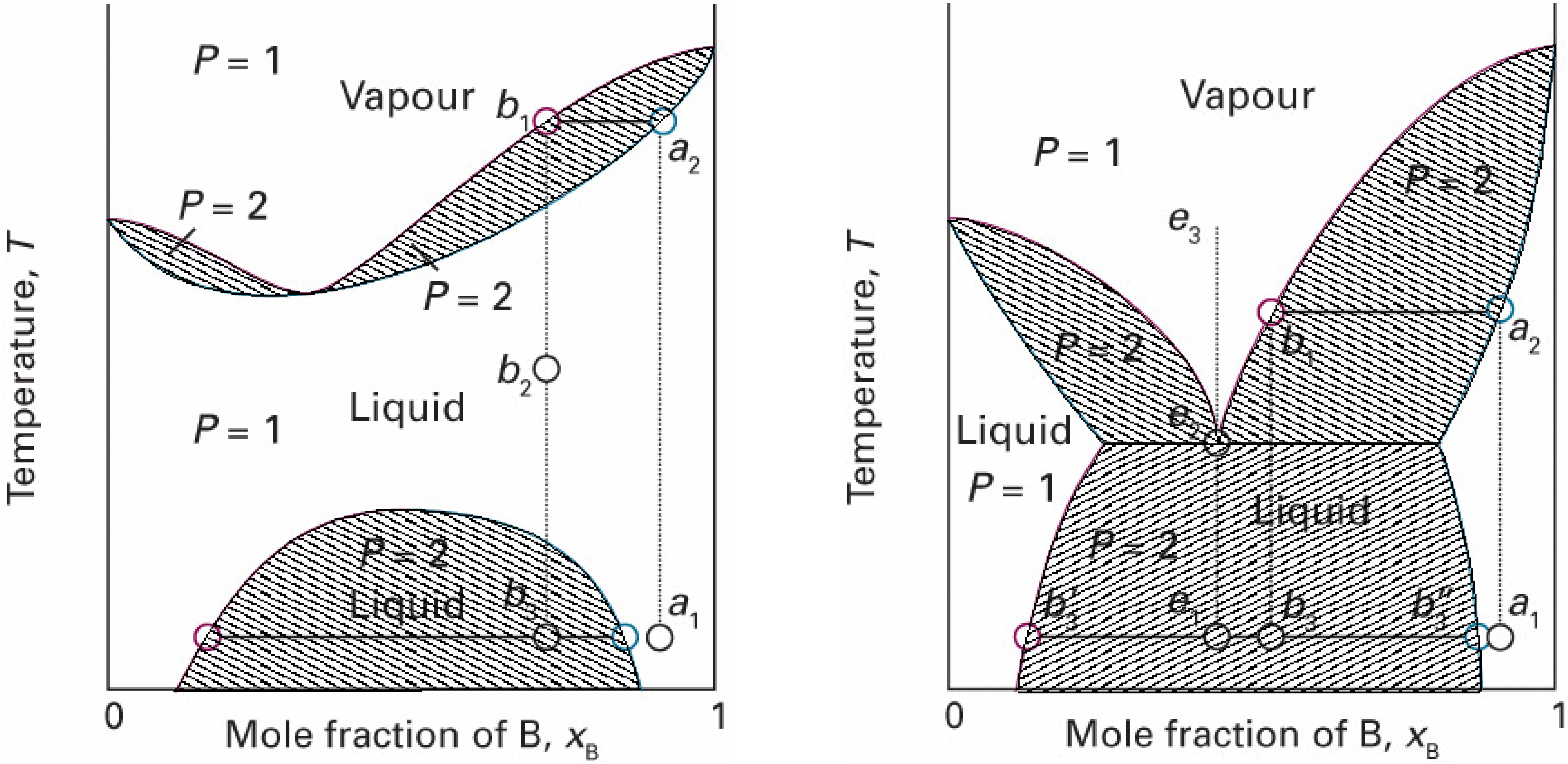
Lower Critical (Solution) Temperature

$$G^E = nRT\beta x_A x_B$$

$$\beta = \beta(T) > 0$$

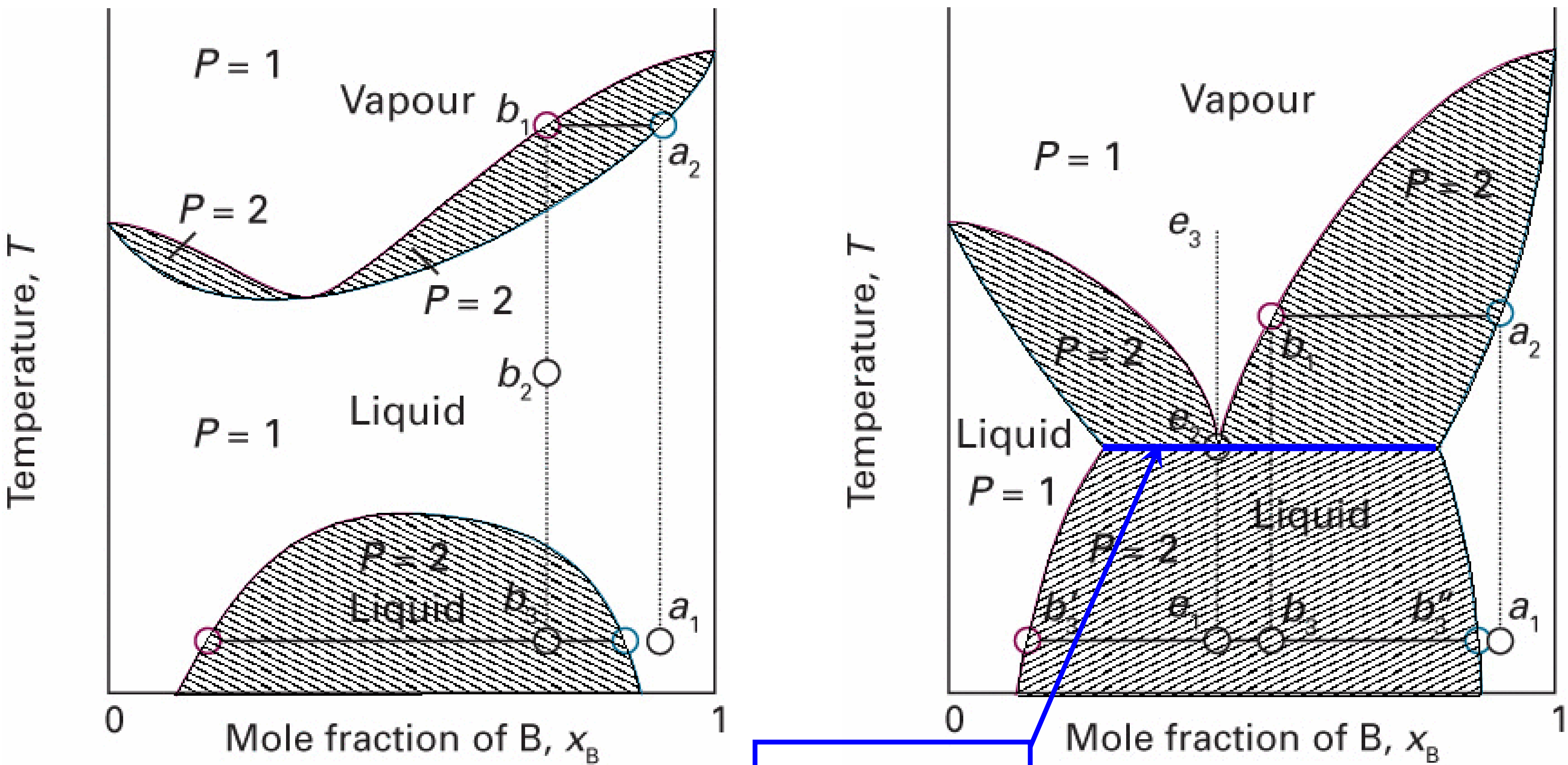
Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

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



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

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



P = 3

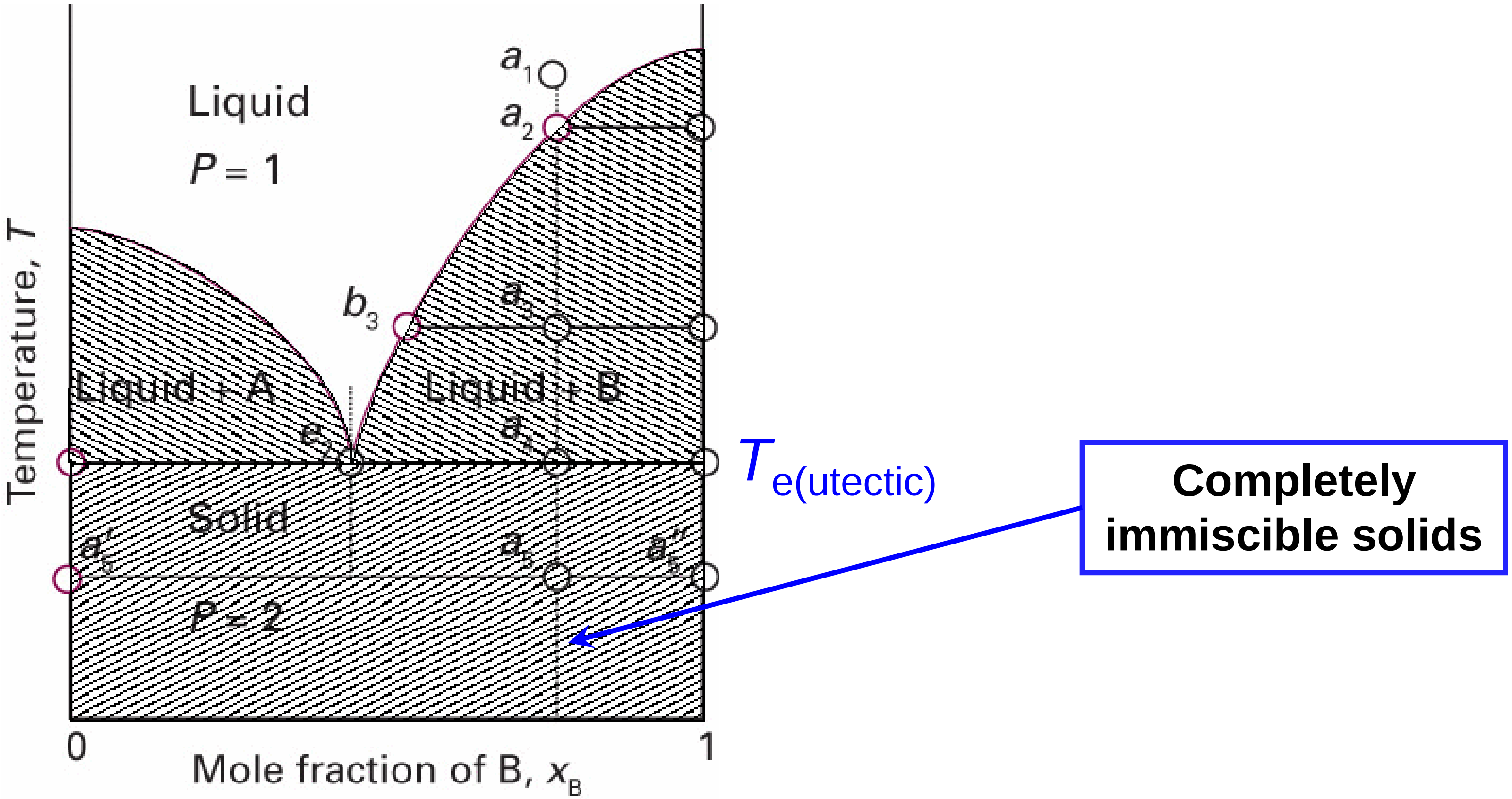
$F' = C - P + 1$

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

C = 2 Solid-liquid phase diagram

C = 2 Solid-liquid phase diagram

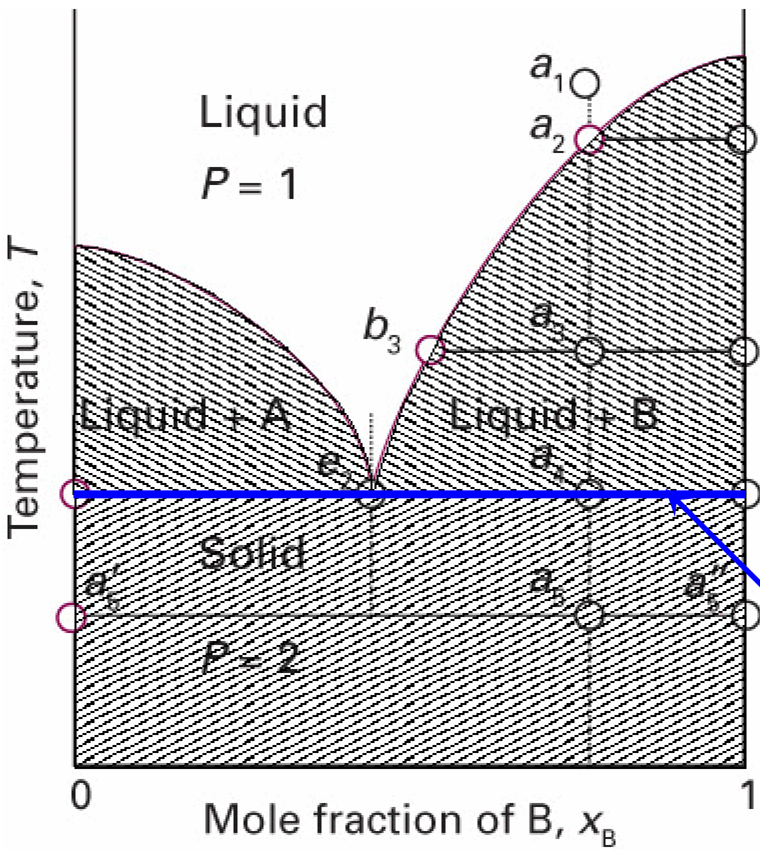
Eutectic: A(s) and B(s) not miscible



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

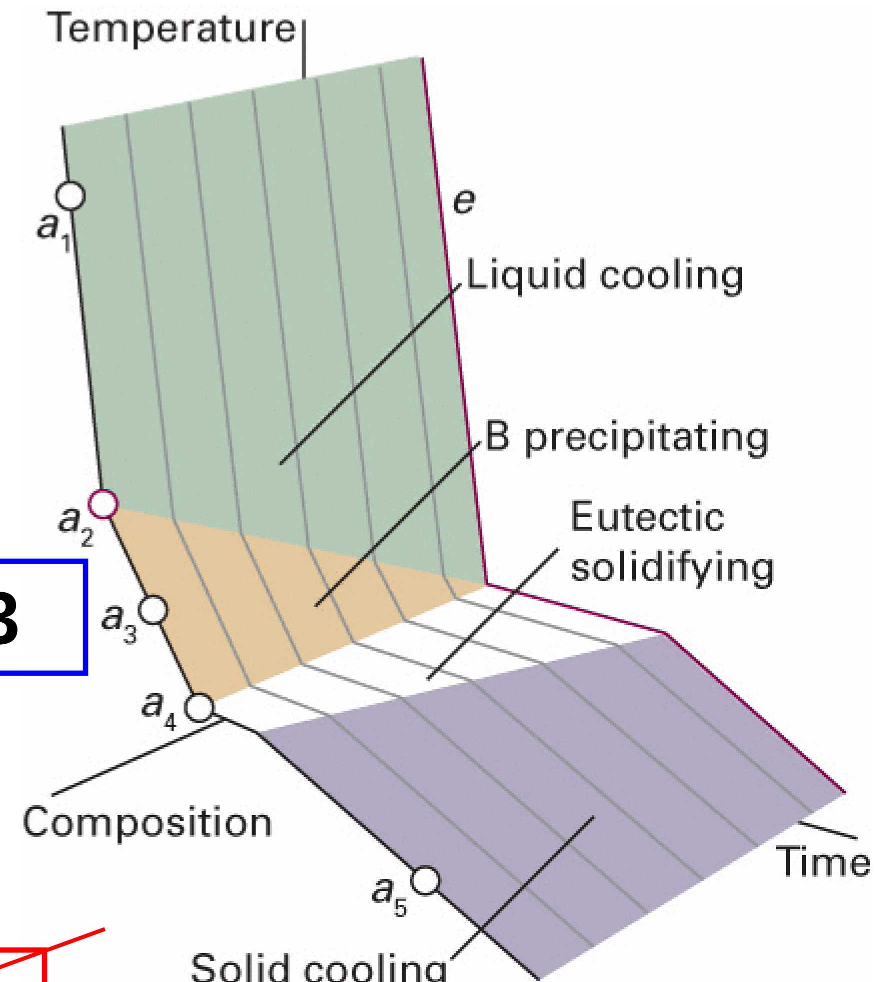
C = 2 Solid-liquid phase diagram

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



$T_{e(utectic)}$

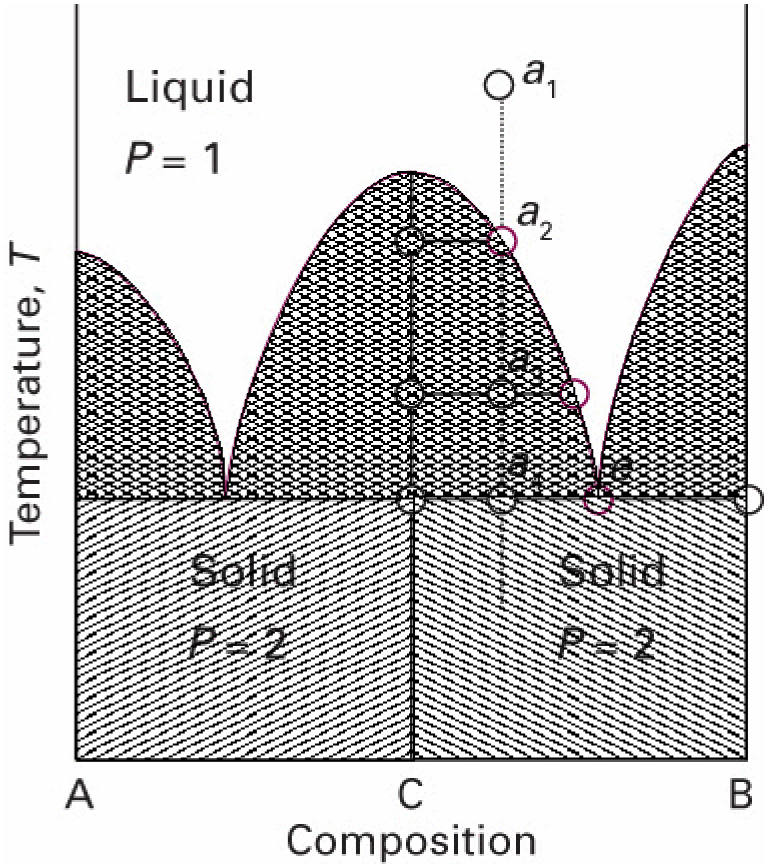
P = 3



Exercise 18

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

C = 2 Solid-liquid phase diagram



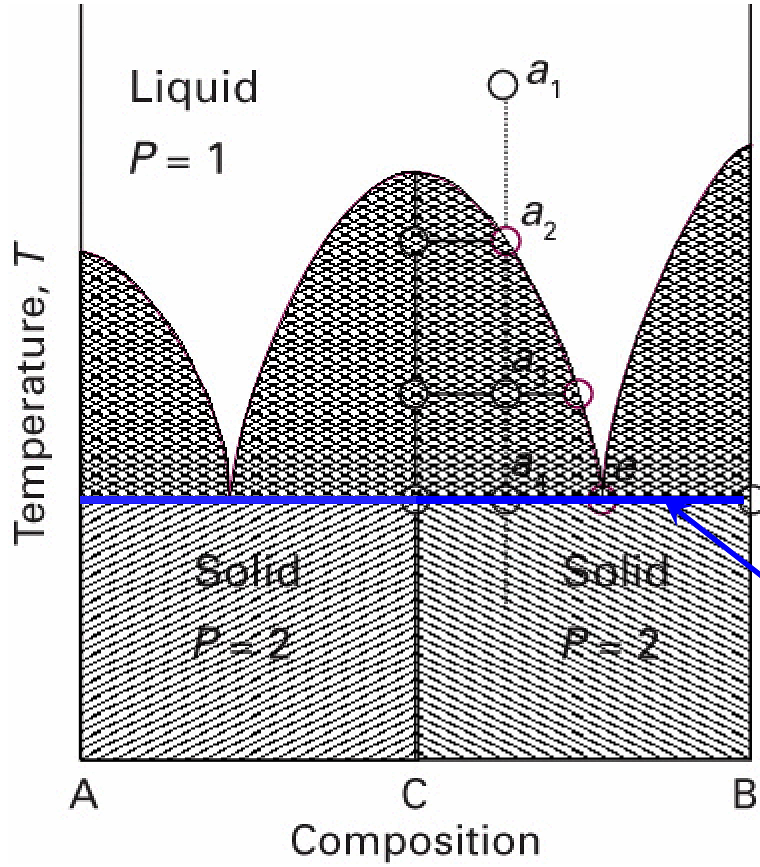
Compound

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



$T_{e(utectic)}$

$P = 5$

$F = -2$

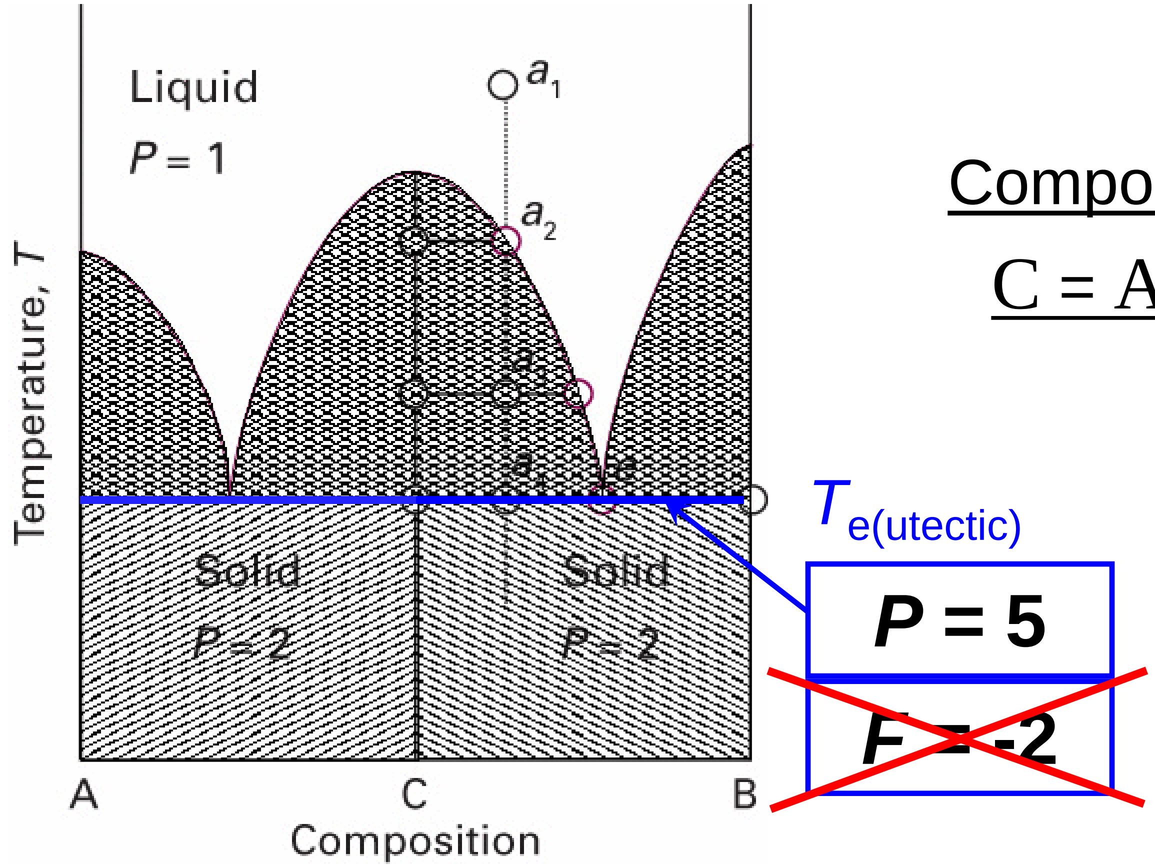
Compound

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



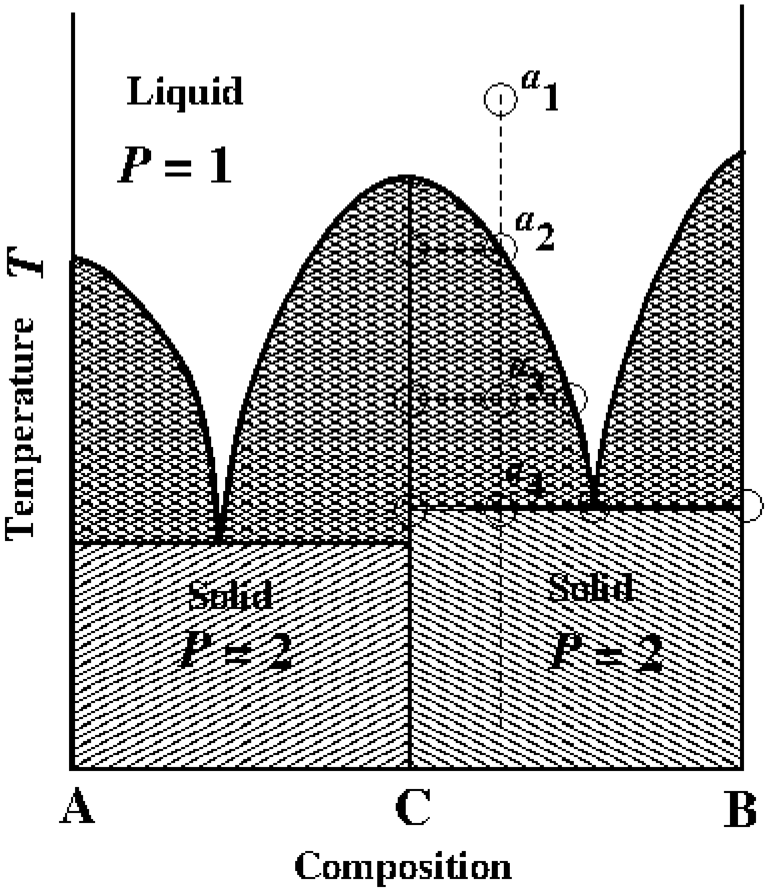
Compound

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



Compound

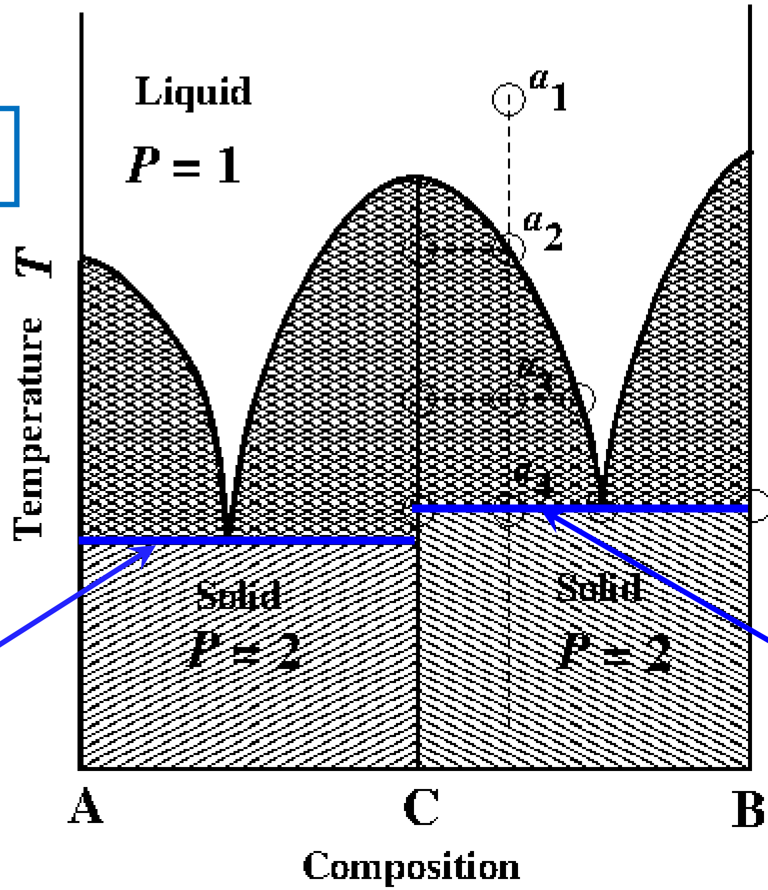
C = AB

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

Three solid compounds: A, B and C = AB

C = 2 Solid-liquid phase diagram

Exercise 20



T_e(AC)

***P* = 3**

T_e(CB)

***P* = 3**

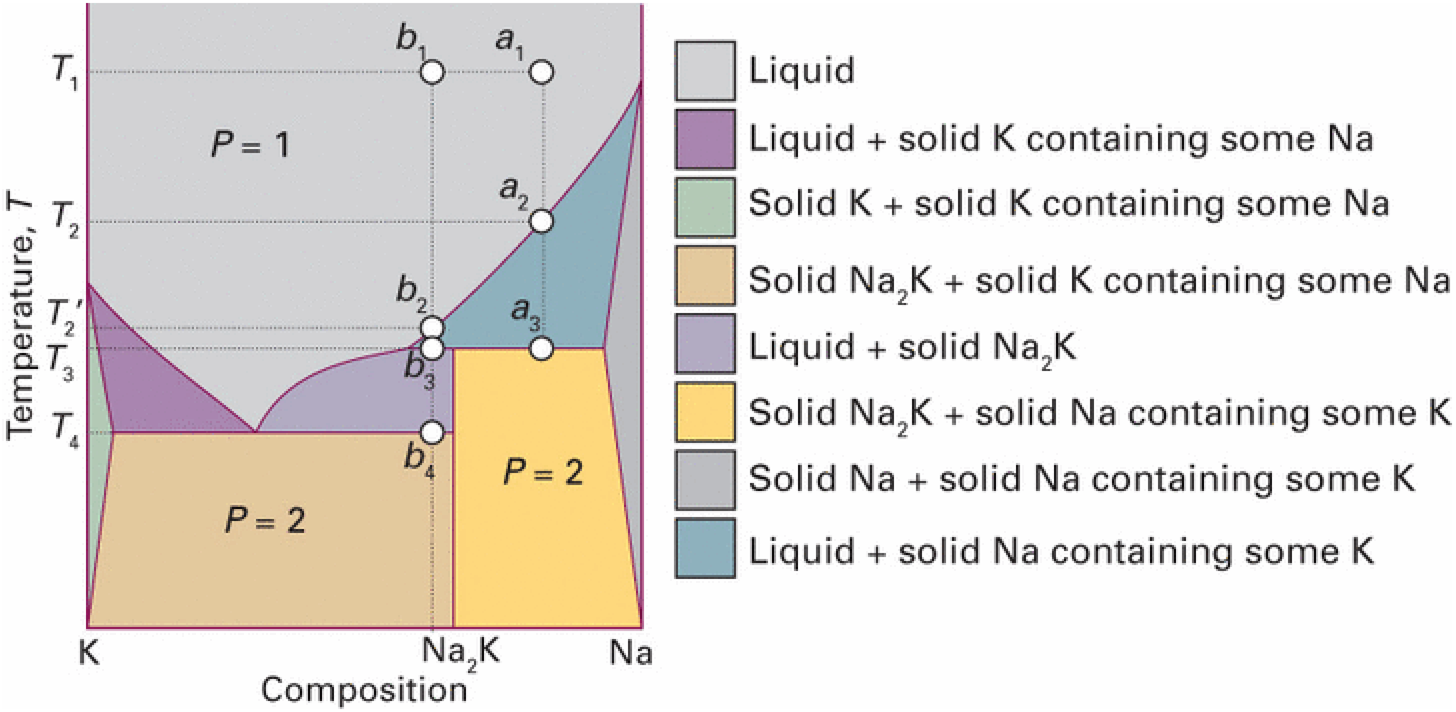
Compound

C = AB

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

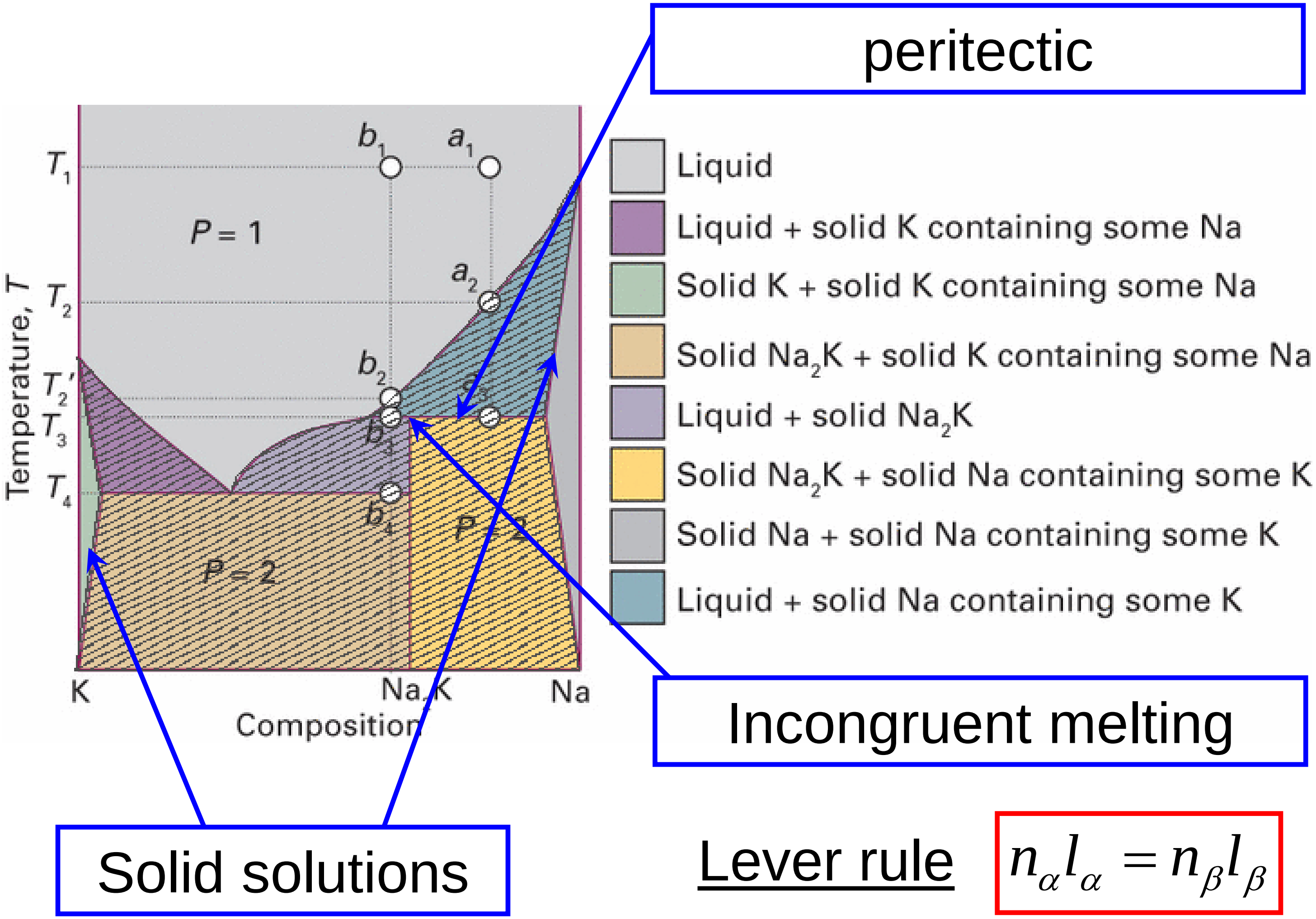
Three solid compounds: A, B and C = AB

C = 2   Solid-liquid phase diagram



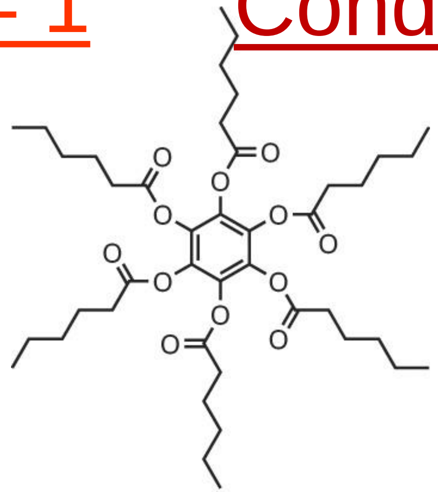
Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

C = 2 Solid-liquid phase diagram



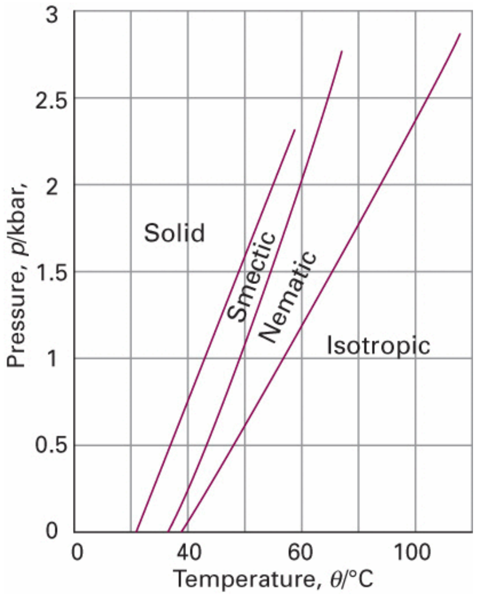
Lever rule $n_\alpha l_\alpha = n_\beta l_\beta$

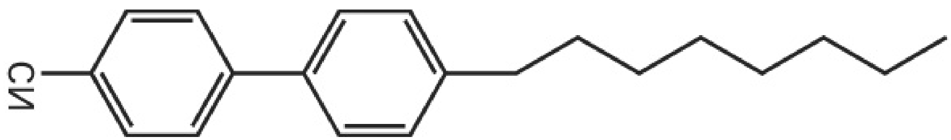
C = 1 Condensed matter phase diagrams

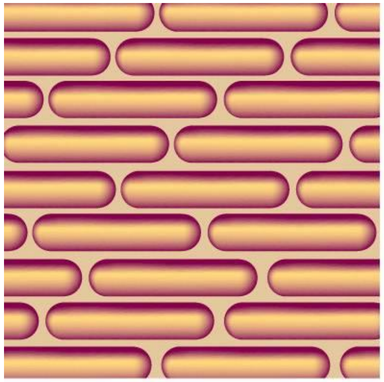


Liquid crystals

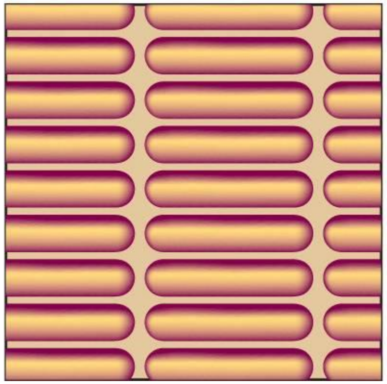
(mesophase)



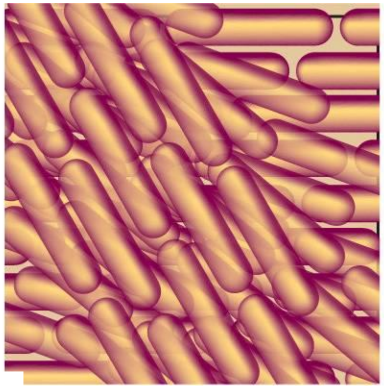




nematic



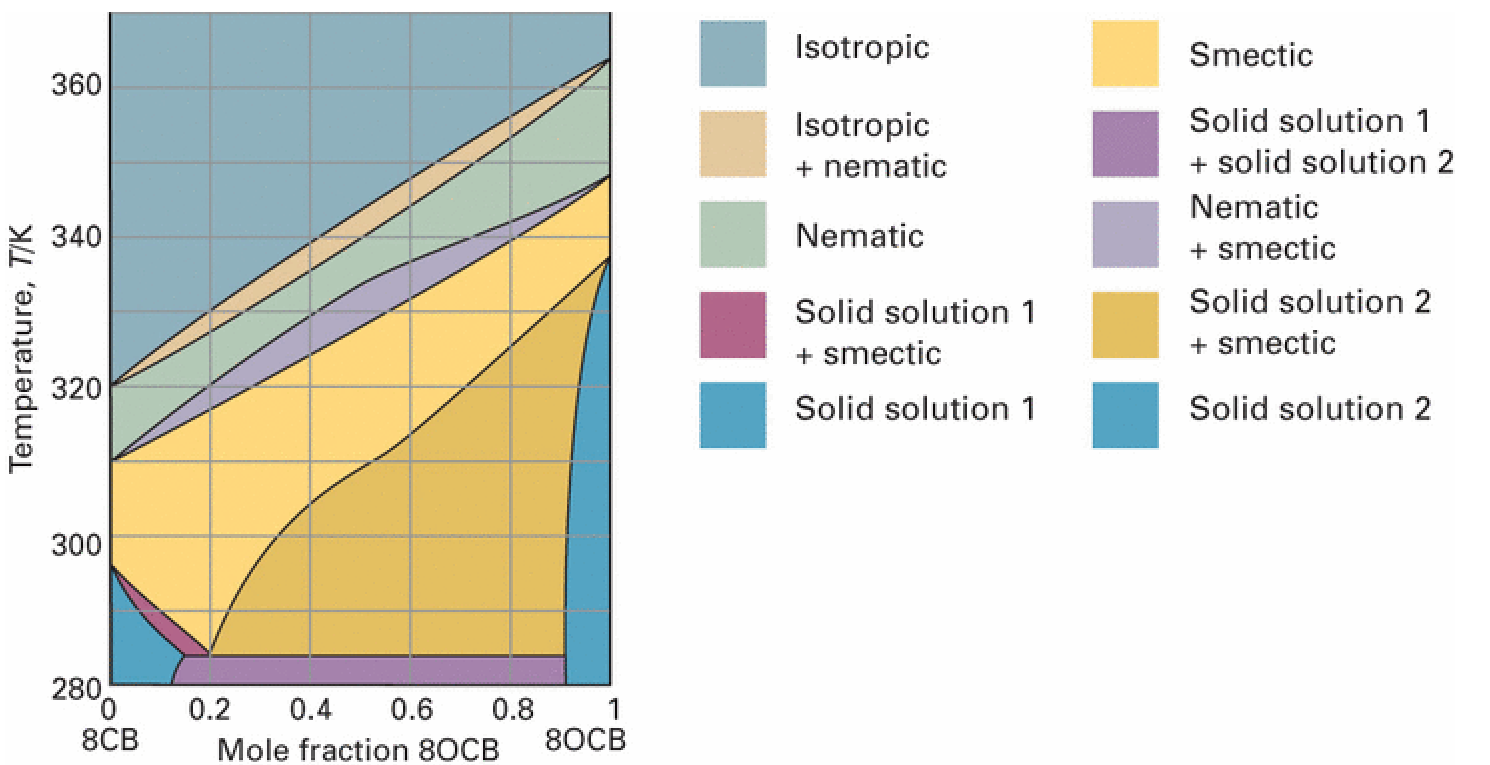
smectic



cholesteric

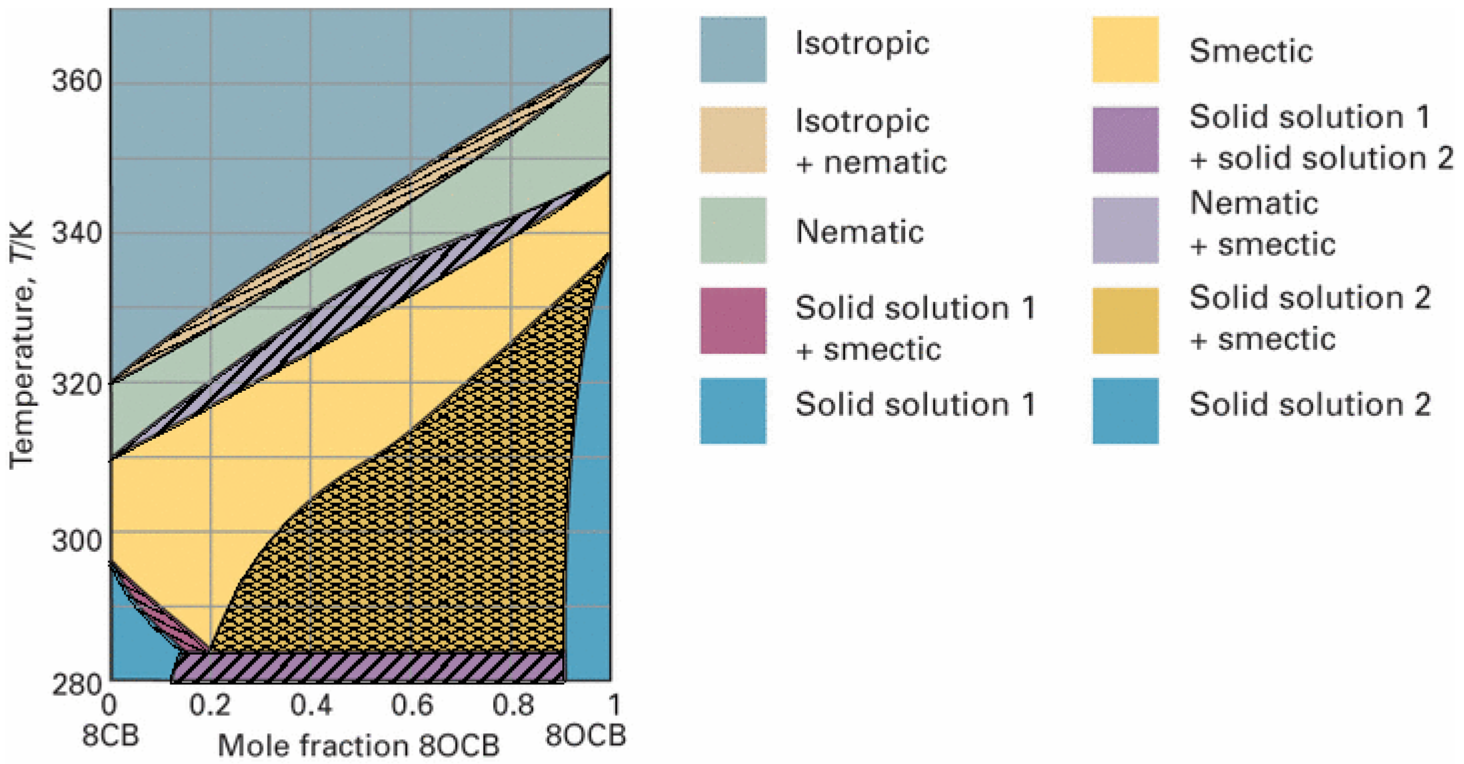
C = 2 Condensed matter phase diagrams

Liquid crystals



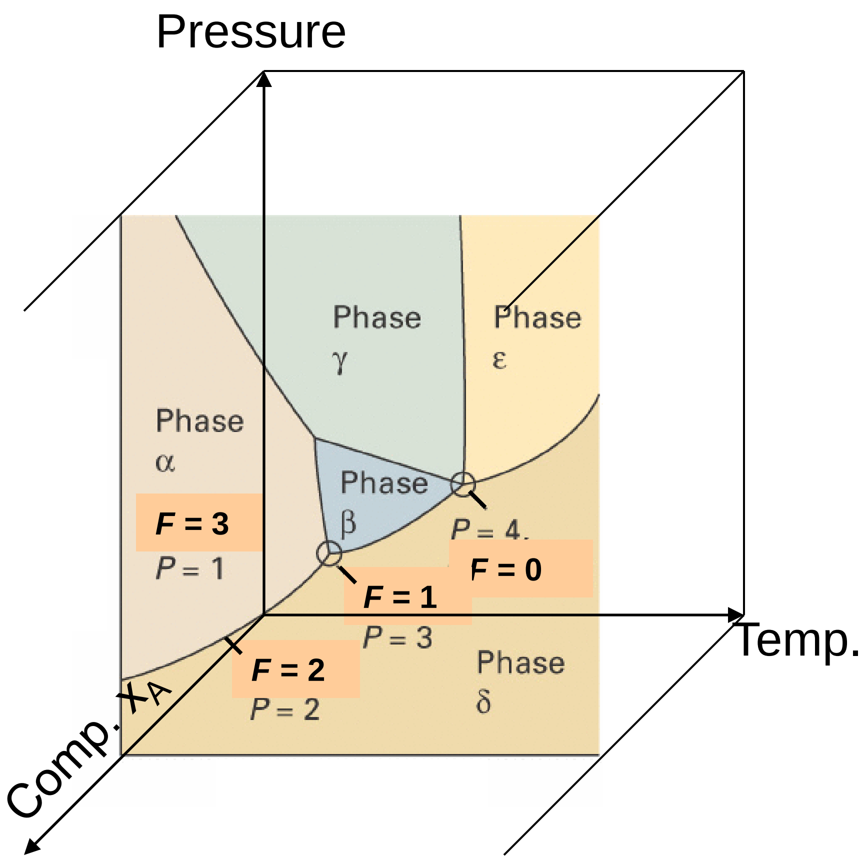
C = 2 Condensed matter phase diagrams

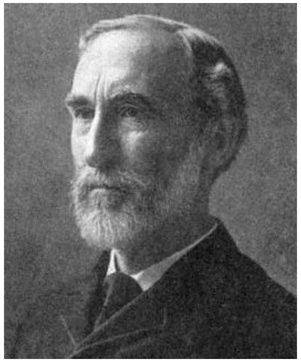
Liquid crystals



Ternary phase diagrams

C = 2 Binary phase diagrams

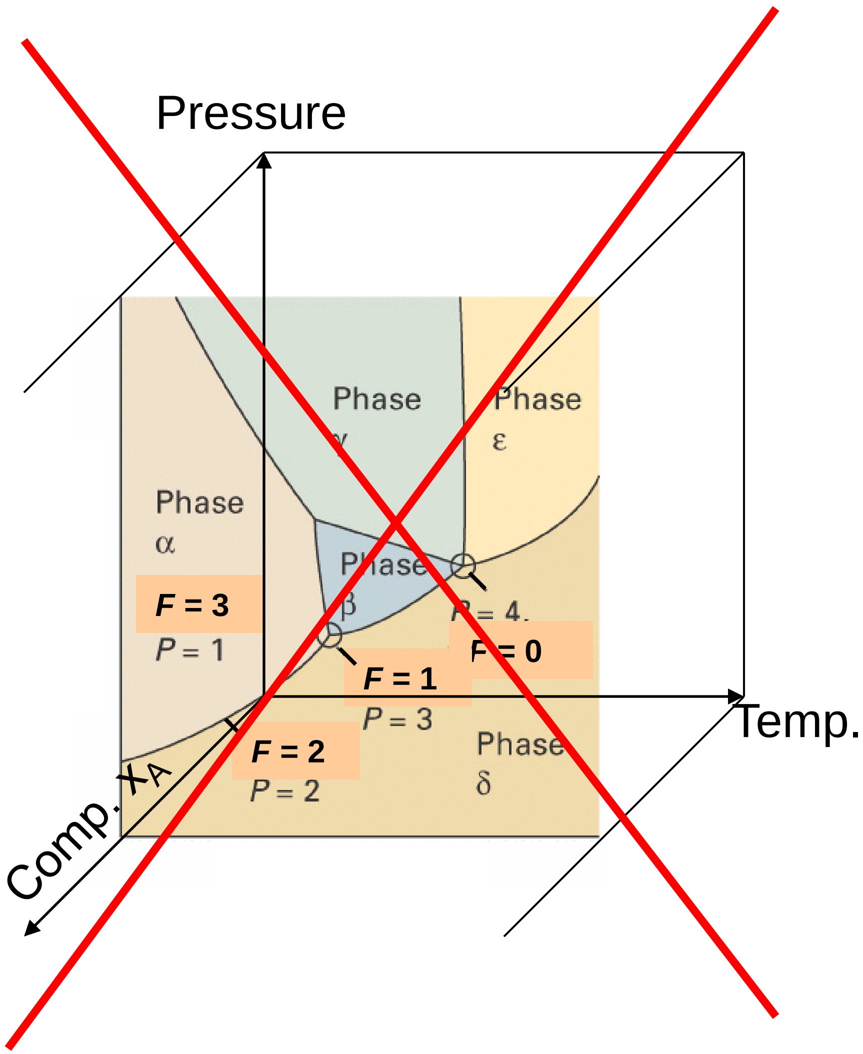


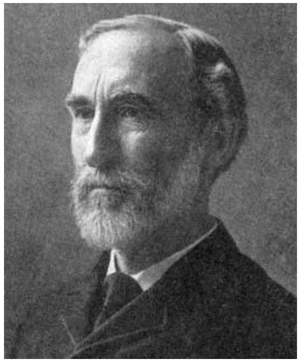


Gibbs phase rule

$$F = C - P + 2$$

C = 3   Ternary phase diagrams





Gibbs phase rule

$$F = C - P + 2$$

C = 3 Ternary phase diagrams

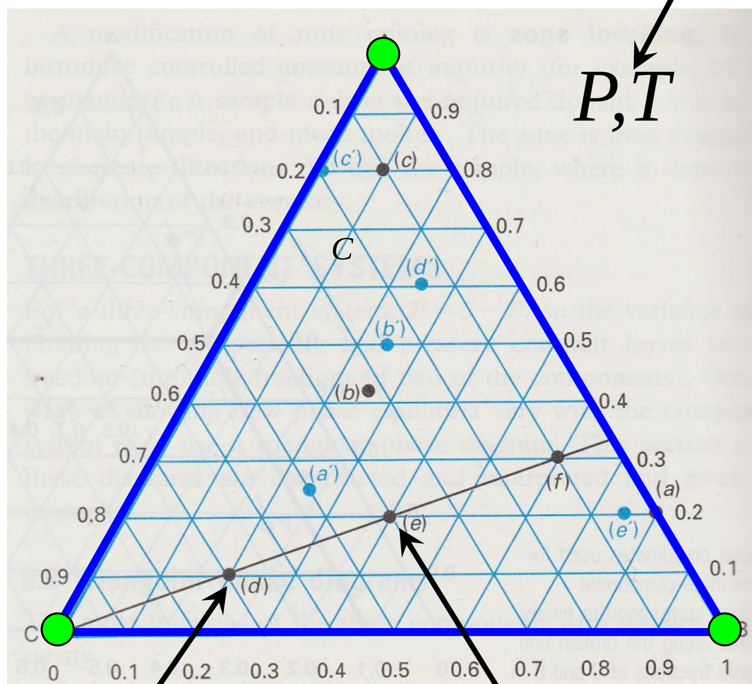
$F = 3 - P + 2$

$F'' = 3 - P$

$F'' = 2 - P$

C = 2

P, T fixed



$F'' = 1 - P$

C = 1

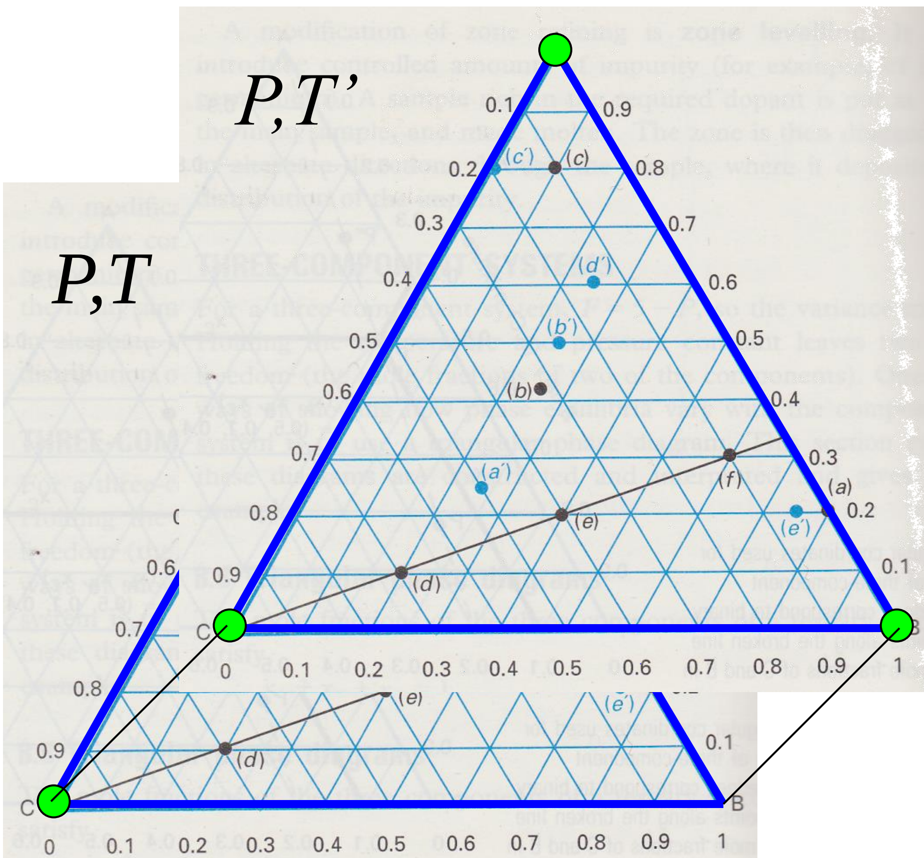
$$(x_A, x_B, x_C) = (0.1, 0.2, 0.7)$$

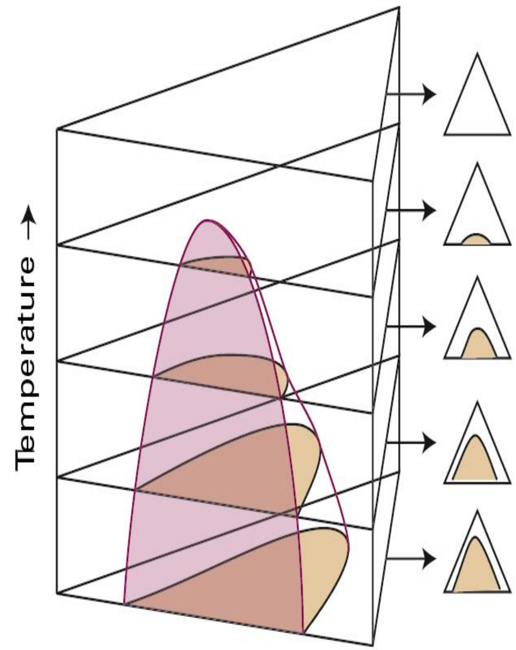
$$(x_A, x_B, x_C) = (0.2, 0.4, 0.4)$$

C = 3 Ternary phase diagrams

$F = 3 - P + 2$

$F'' = 3 - P$

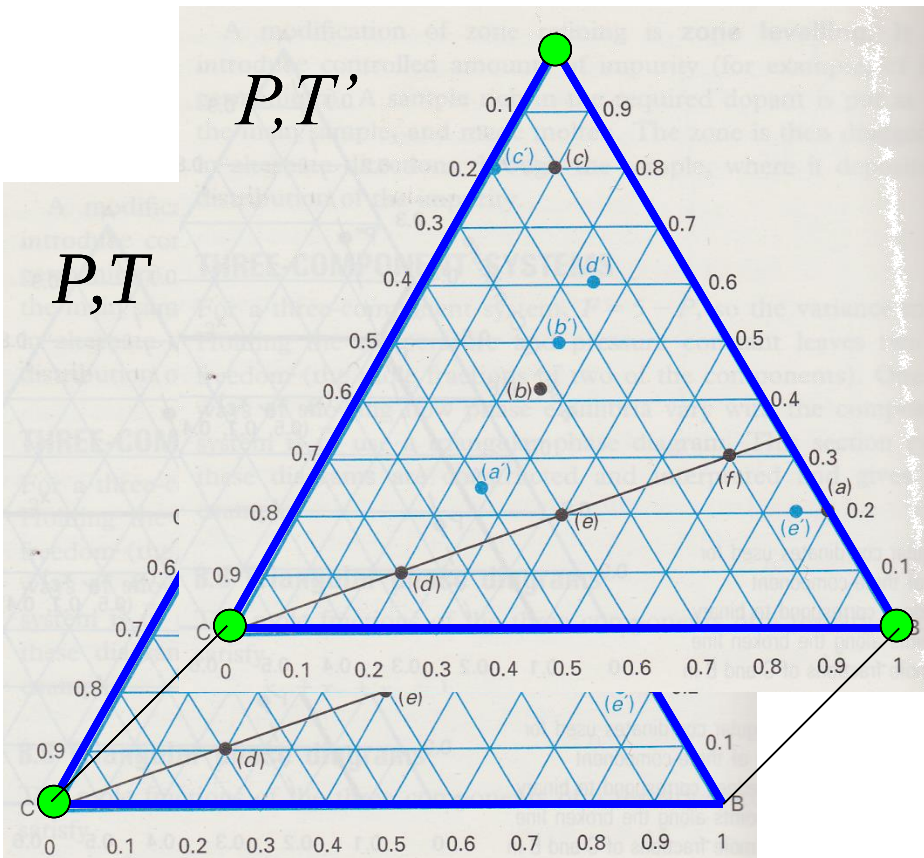


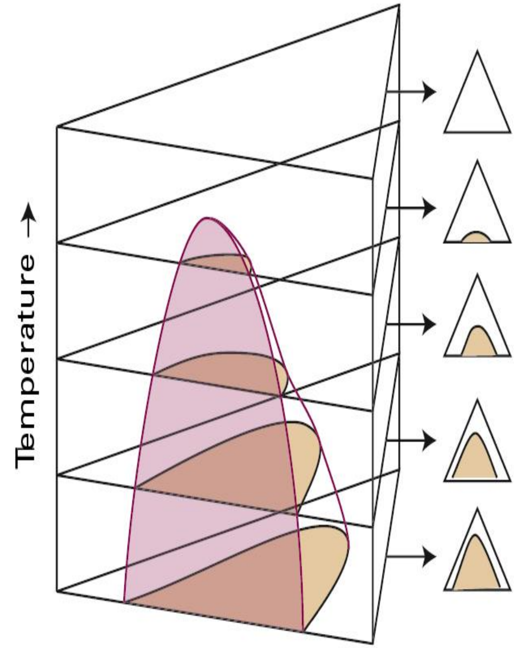


C = 3   Ternary phase diagrams

$F = 3 - P + 2$

$F'' = 3 - P$

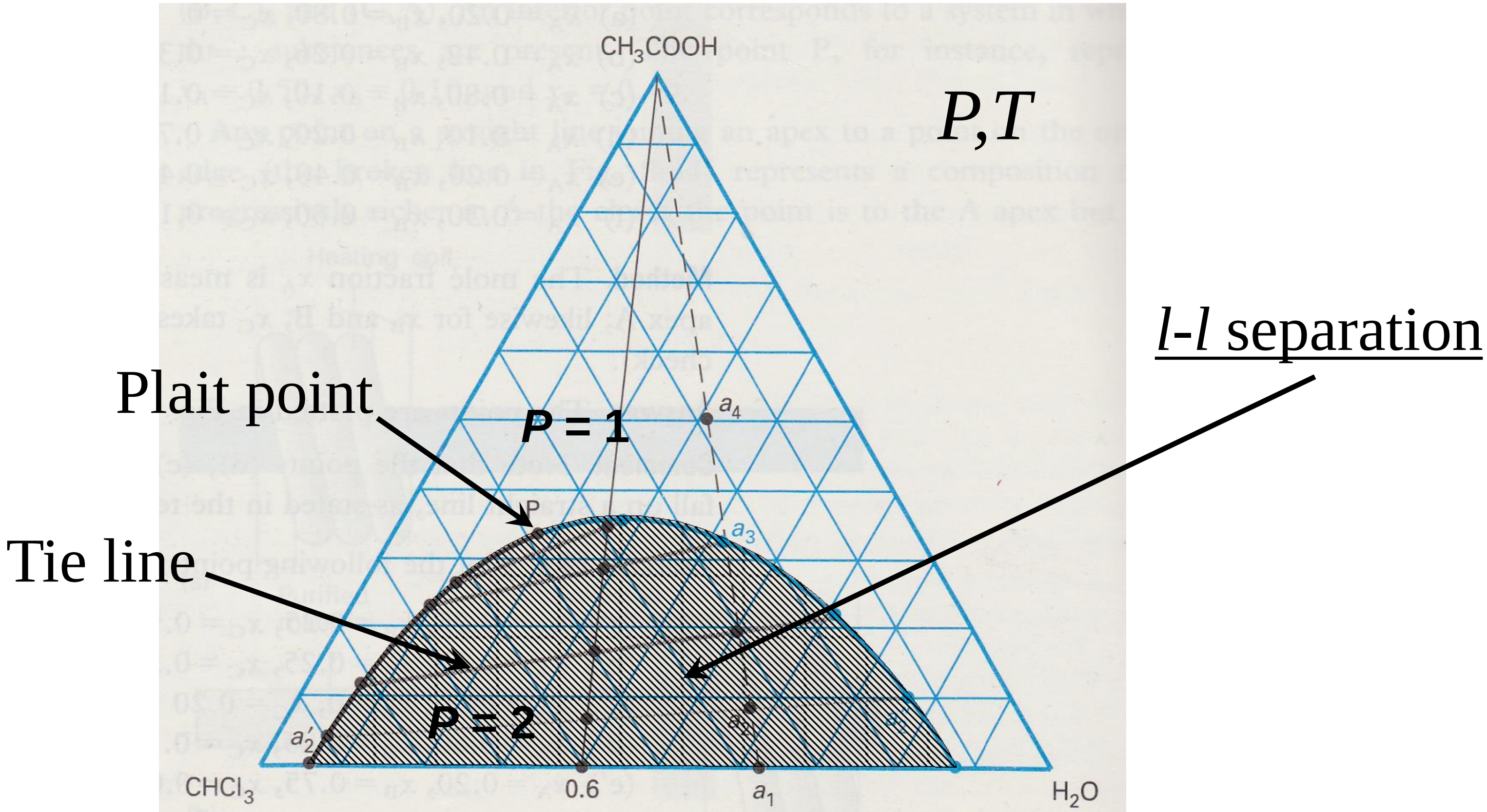




Exercise 21

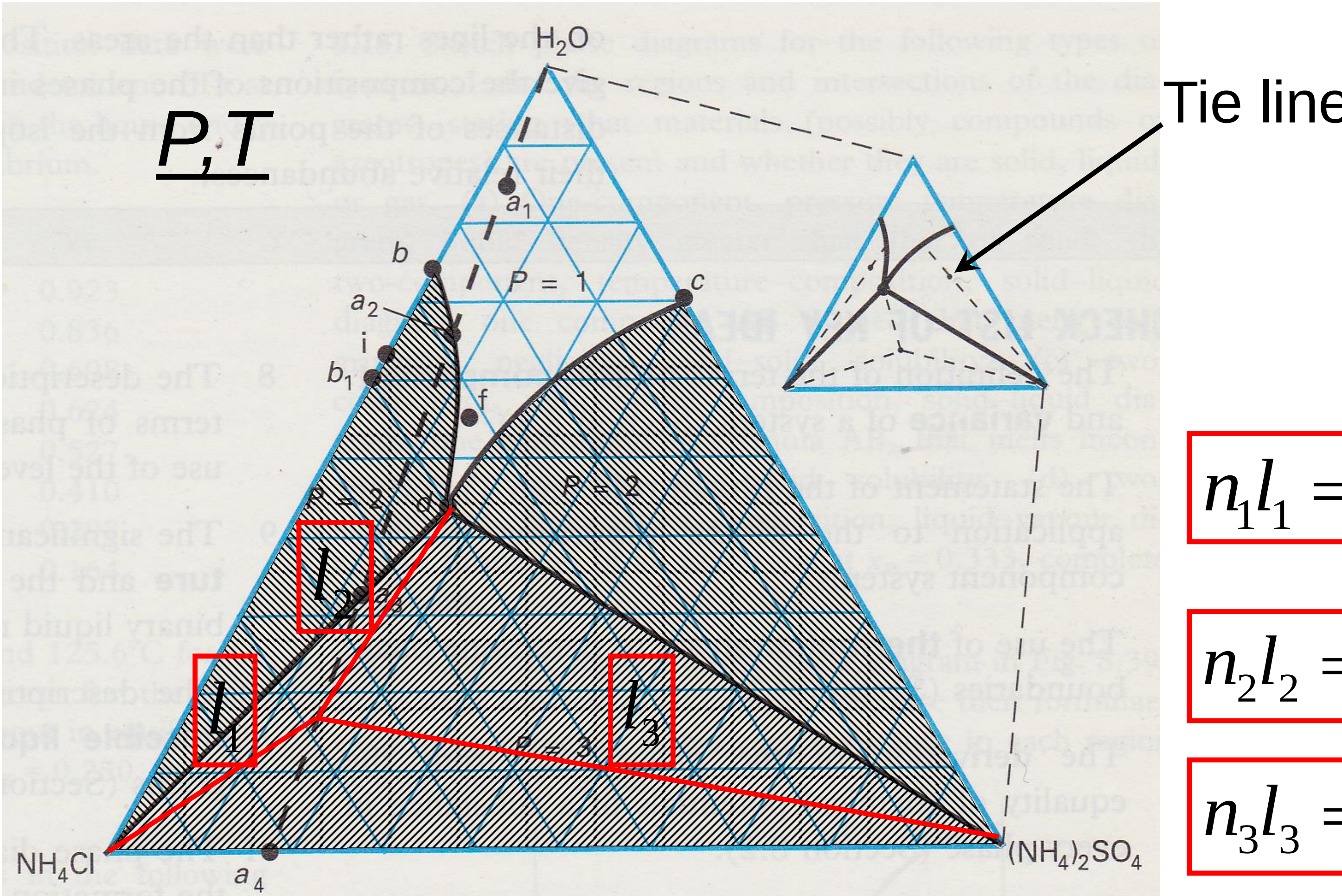
C = 3 Ternary phase diagrams

$F'' = 3 - P$



($CHCl_3$, CH_3COOH, H_2O)

C = 3 Ternary phase diagrams



$$n_1 l_1 = n_2 l_2$$

$$n_2 l_2 = n_3 l_3$$

$$n_3 l_3 = n_1 l_1$$

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