Heterogeneous Phase Equilibria

Equilibrium

- **Thermal** - *T* same in the whole system

- **Mechanical** - *p* same in the whole system

- **Chemical** - amount of substance of individual components is constant, dG = 0, **chemical potentials** of all components in all phases are the same

Condition of phase coexistence :
Phases have the same ***G***
Transition between phases $\Delta G = 0$

Chemical Potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j}$$

Chemical potential = changes in *G* caused by changing composition n_i

Differences in chemical potential lead to chemical reactions, diffusion,….

Chemical potential of every component in all coexisting phases is the SAME.

Gibbs' Phase Rule

Phase (P) = homogeneous part of a system separated by a physical interface where the properties and structure change discontinuously, states of matter (s, l, g), modifications (Ice I - XII, He I and II)

P = 1: mixture of gases, solution
P = 2: liquid + sat. g, sat. solution + solid
P = 3: liquid + sat. g + sat. solution + solid

Component (C) = chemically independent constituents of the system
C = the minimum number of independent species necessary to define the composition of all phases of the system, $CaCO_3$, CO_2, CaO

Degrees of freedom (F) = intensive variables p, T, c
F = the number of intensive variables which are independent of each other, can change without changing P

Gibbs' Phase Rule

- Each phase requires C-1 data on composition (molar fractions x_i) plus T and p to define its state,

  total P(C-1) + 2 state **variables**

- Each component follows P-1 equilibrium conditions $\mu(\alpha) = \mu(\beta)$ equal chemical potentials of a component in P phases

  total C(P-1) **conditions**

- Number of degrees of freedom is number of **variables** minus number of **conditions**

  F = P(C-1) + 2 - C(P-1)

- **F = C - P + 2**

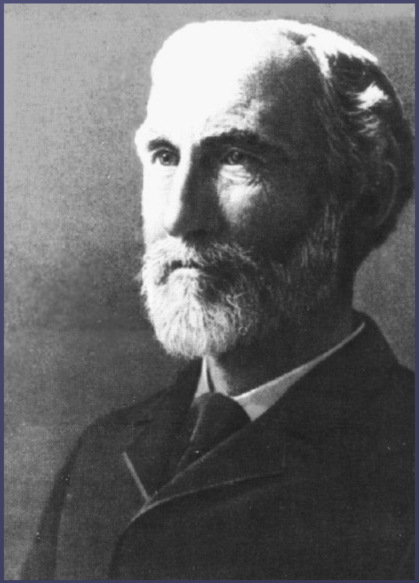
Gibbs' Phase Rule

P + F = C + 2

Number of phases (P)
Degrees of freedom (F)
Number of components (C)

For C = 1

P = 1	F = 2	plane
P = 2	F = 1	line
P = 3	F = 0	triple point



J. Willard Gibbs
(1839-1903)

Phase Diagrams

Phase diagram = graphic information about the state of a system

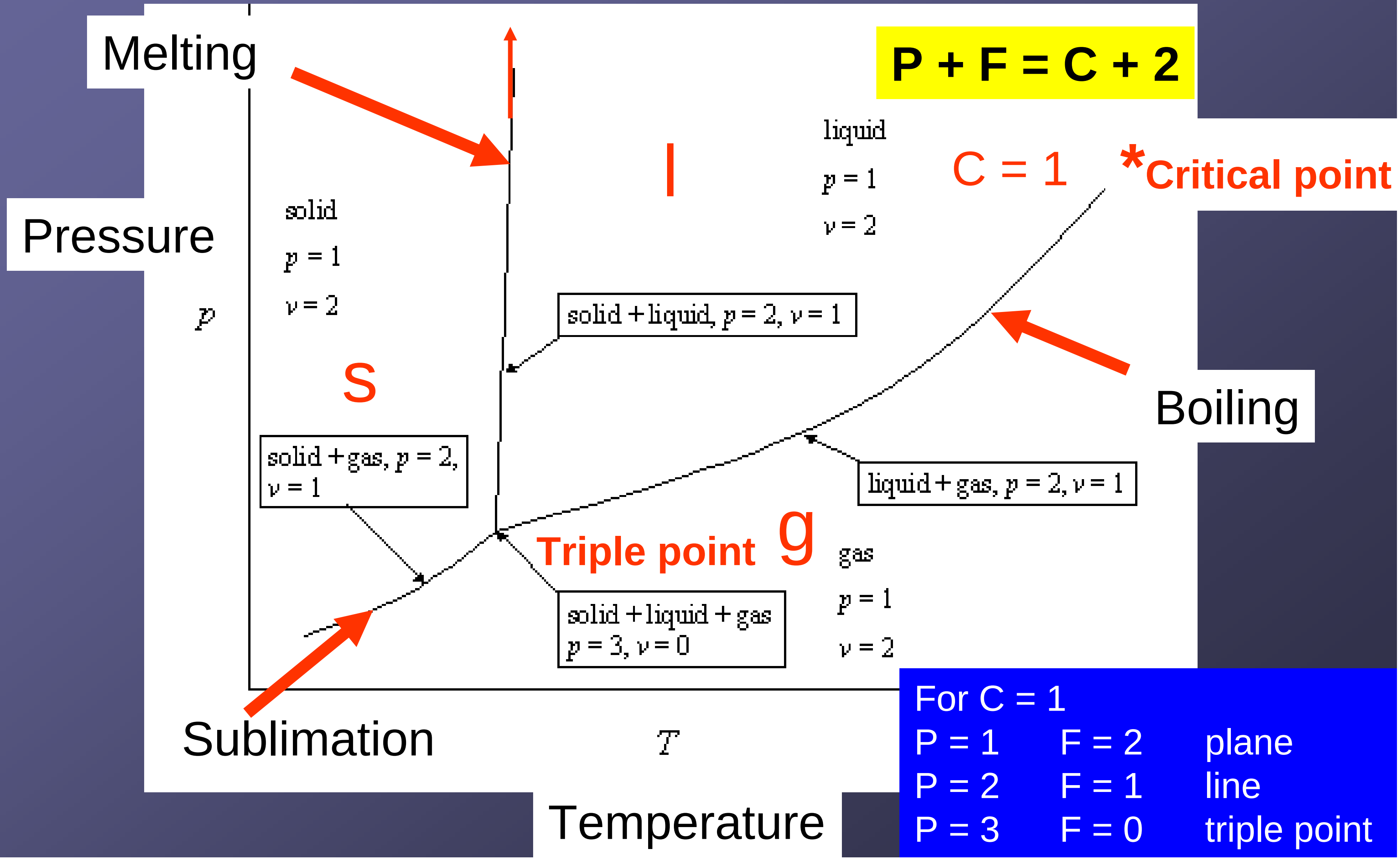
Variables – p, T, C – 1 data on composition
(for more than 1 component in the system, the corresponding phase diagram is more than 3-dimensional)

Cuts thru a phase diagram – some variables kept constant:

p = const.	isobaric diagram
T = const.	isothermic diagram
c = const.	isoconcentration diagram

p-T Phase Diagram for One-Component System

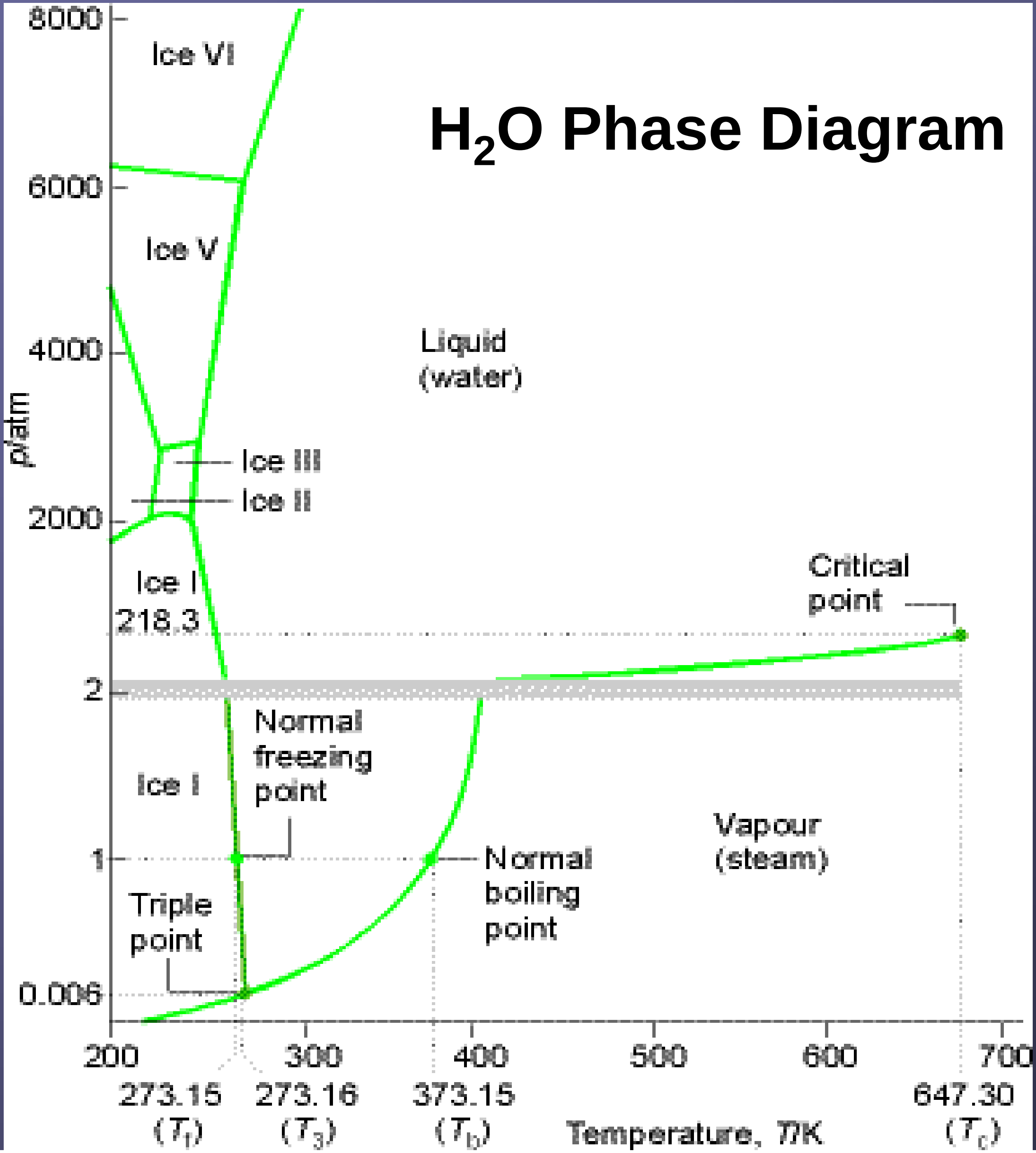
P + F = C + 2



For C = 1

P = 1	F = 2	plane
P = 2	F = 1	line
P = 3	F = 0	triple point

H_2O Phase Diagram



Clausius-Clapeyron Equation

Clapeyron equation for a phase change

$$\frac{dp}{dT} = \frac{\Delta H_m}{T\Delta V_m}$$

for l-g equilibrium – boiling:
1) $V_m(g) >> V_m(l)$, than $\Delta V_m = V_m(g)$
2) $V_m(g)$ from state eq. of id. gas

$$V_m(g) = \frac{RT}{p}$$

Differencial Clausius-Clapeyron eq.

$$\frac{d\ln p}{dT} = \frac{\Delta H_m}{RT^2}$$

Integrated Clausius-Clapeyron eq.

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Water Vapor Tension

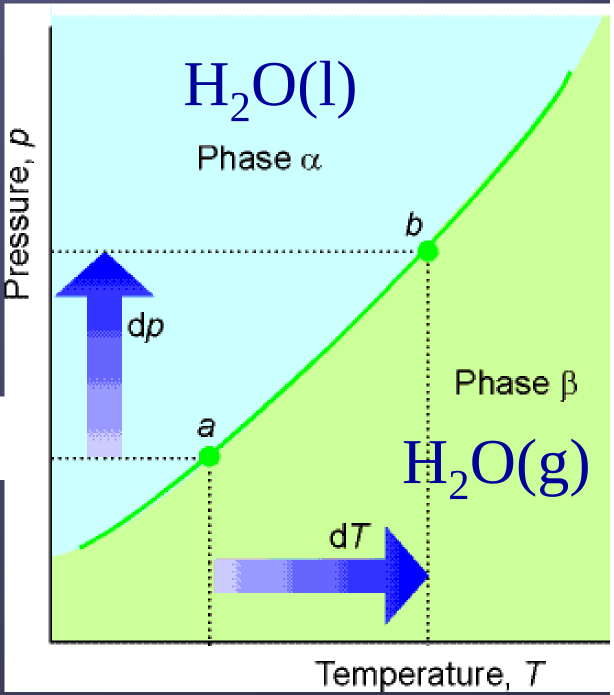
$H_2O(l) \leftrightarrows H_2O(g)$ $\Delta H^0_{výp} = 40.66\ \mathrm{kJ\ mol^{-1}}$

$K_p = P_{H2O}$

van’t Hoff eq.

$$\ln\frac{K_2}{K_1} = \ln\frac{p_T}{p_{\mathrm{var}}} = \ln p_T = \frac{\Delta H^0_{výp}}{R}\left(\frac{1}{T_{\mathrm{var}}} - \frac{1}{T}\right)$$

$P_{\mathrm{var}} = 1\ \mathrm{atm}$



Clausius-Clapeyron eq.

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Water Vapor Tension

$$\ln\frac{K_2}{K_1}=\ln\frac{p_T}{p_{\mathrm{var}}}=\ln p_T=\frac{\Delta H^0_{v\acute{y}p}}{R}\left(\frac{1}{T_{\mathrm{var}}}-\frac{1}{T}\right)$$

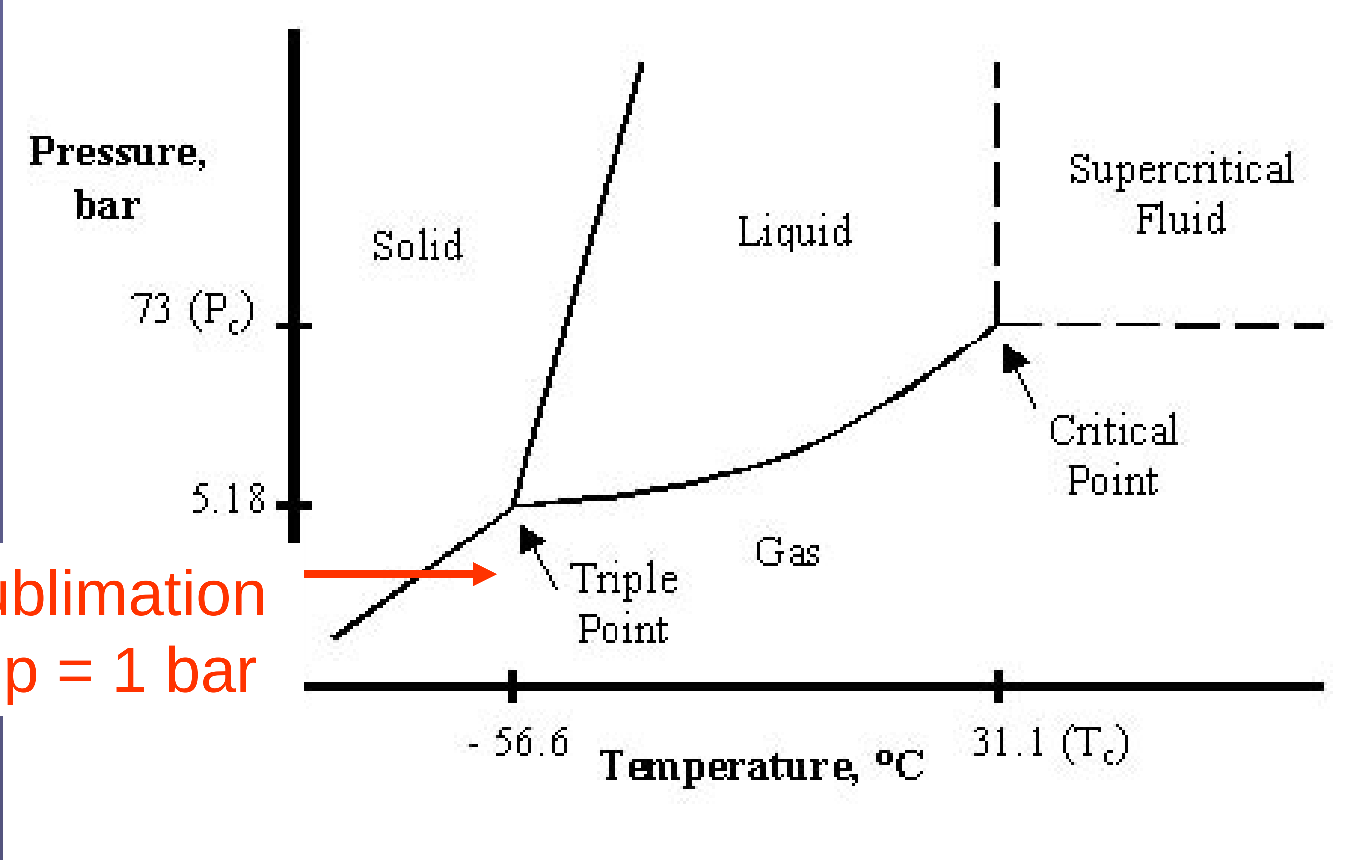
$$\ln P_T=\frac{40660\,Jmol^{-1}}{8.315\,JK^{-1}mol^{-1}}\left(\frac{1}{373\,K}-\frac{1}{323\,K}\right)=-2.03$$

$$P_{323}=e^{-2.03}=0.131\,atm$$

Tension of saturated water vapor at 50 °C = 323 K

CO$_2$ Phase Diagram

Dry Ice



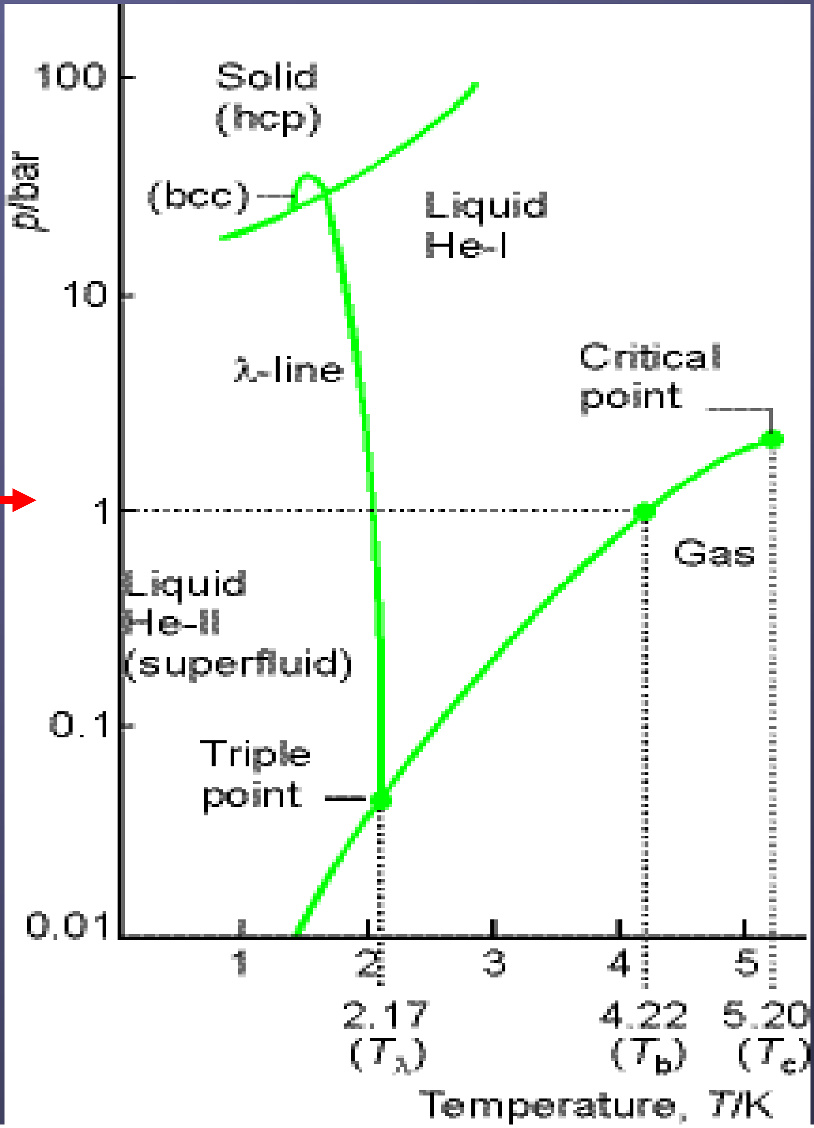
Sublimation at p = 1 bar

Phase Diagram for carbon dioxide.

He Phase Diagram

He cannot be solidified at normal atmospheric pressure

He does not have triple point of g-l-s phase coexistence



Two-Component Phase Diagram

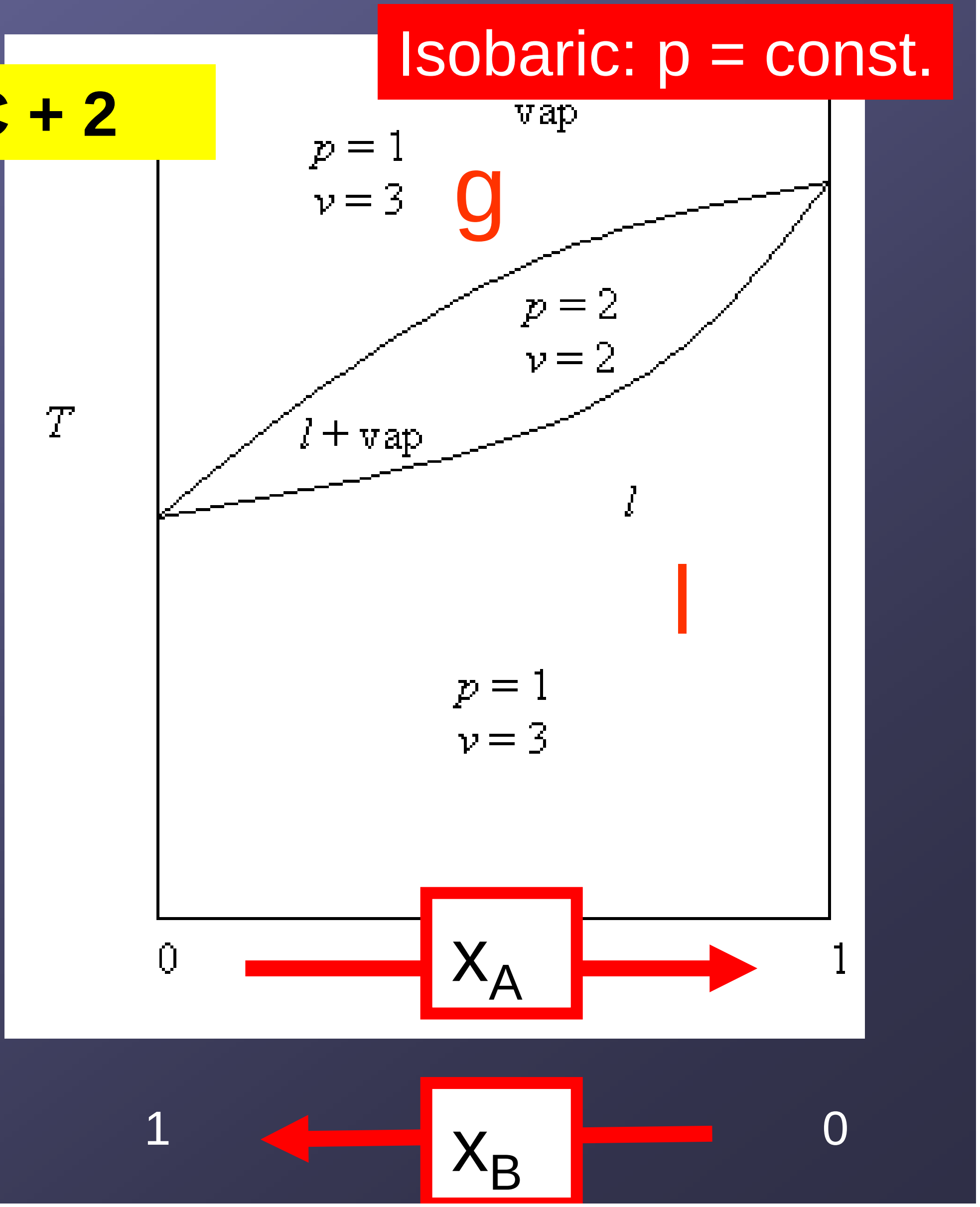
C = 2, P + F = 4
F = 4 – P
Minimum one phase present
P = 1

F_{max} = 3 (T, p, x)
3-dimensional diagram

F = 2
Isothermal T = const.
p is a function of x

Isobaric: p = const.
T is a function of x

P + F = C + 2


Isobaric: p = const.

Mixture of Two Liquids

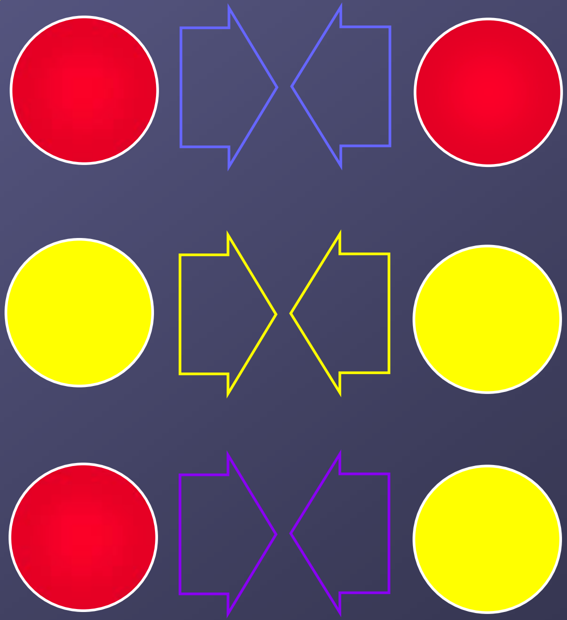
Ideal mixture of 2 liquids:

vdW interactions **A-A**, **B-B** and **A**-**B** are similar

e.g. hexane-heptane

Chemically similar compounds

$\Delta H_{sol} = 0$ $\Delta V_{sol} = 0$



Nonideal mixture:

vdW interactions **A-A**, **B-B** are different (stronger or weaker) then **A**-**B**

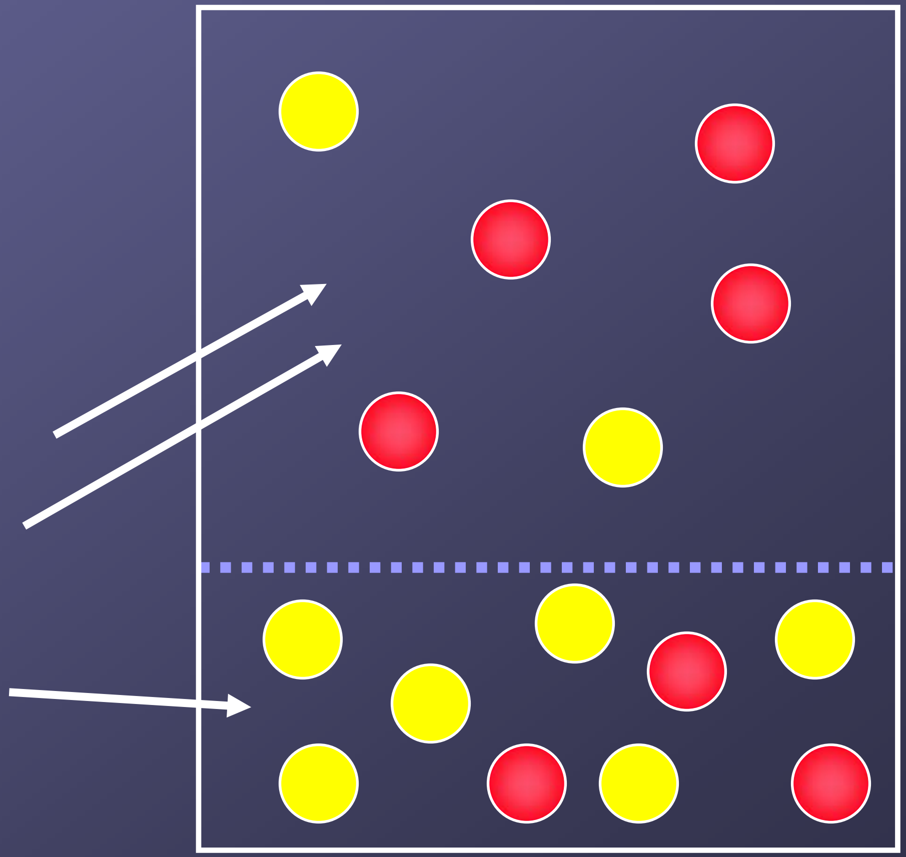
$\Delta H_{sol} \neq 0$ $\Delta V_{sol} \neq 0$

Equilibrium $l \leftrightarrow g$ in a Mixture of 2 Liquids

- Both phases
  are mixtures of **A** and **B**.

- y_A, y_B molar fractions in g
- p_A, p_B partial press. in g

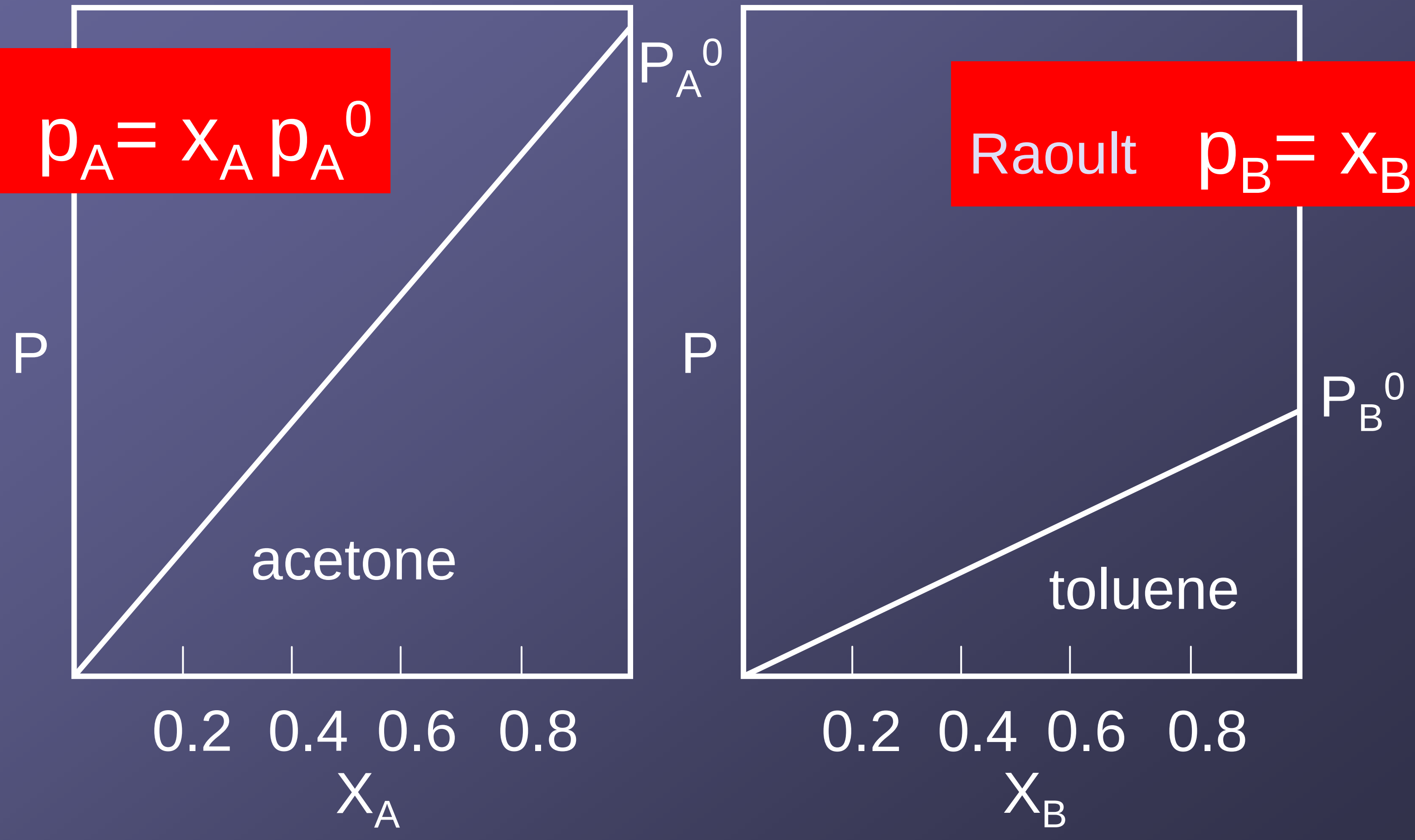
- x_A, x_B molar fractions in l



Vapor Pressure and Liquid Phase Composition

More volatile component
= higher vapor pressure

Isothermal: T = const.



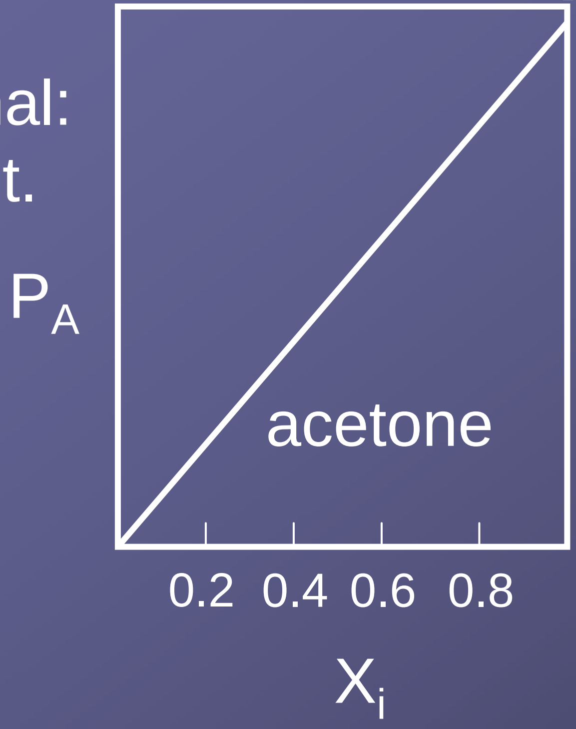
Raoult $p_A = x_A\, p_A^0$

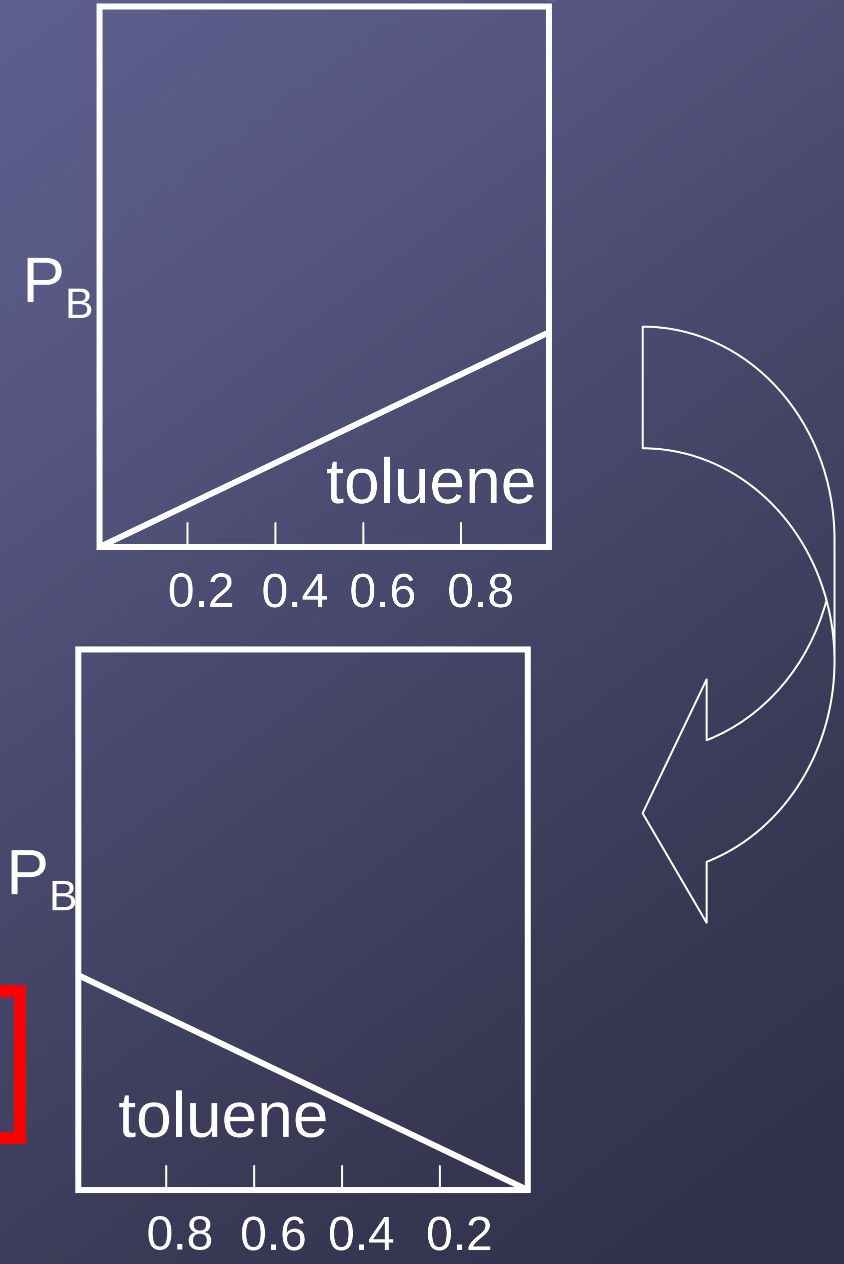
Raoult $p_B = x_B\, p_B^0$

A mixture of 2 liquids: acetone and toluene

Vapor Pressure and Liquid Phase Composition

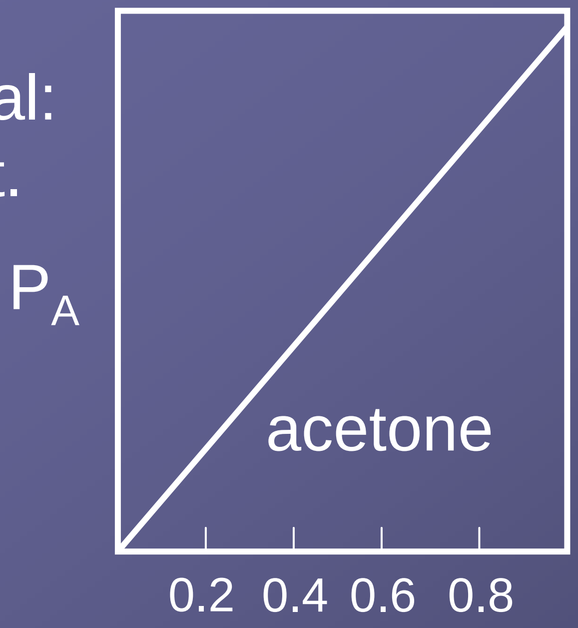
Isothermal:
T = const.

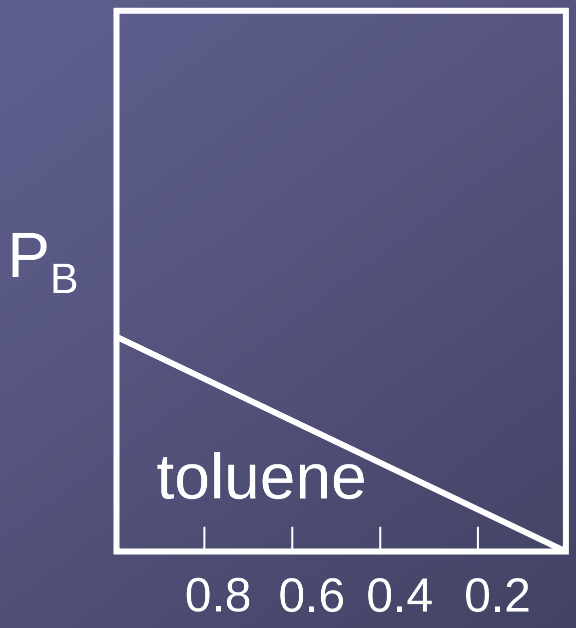




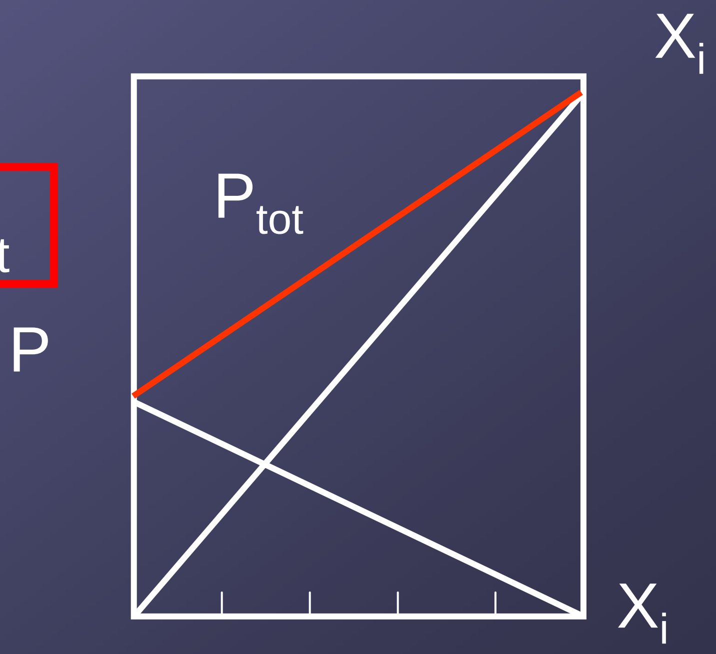
$$\boxed{X_{acetone} + X_{toluene} = 1}$$

Isothermal:
T = const.



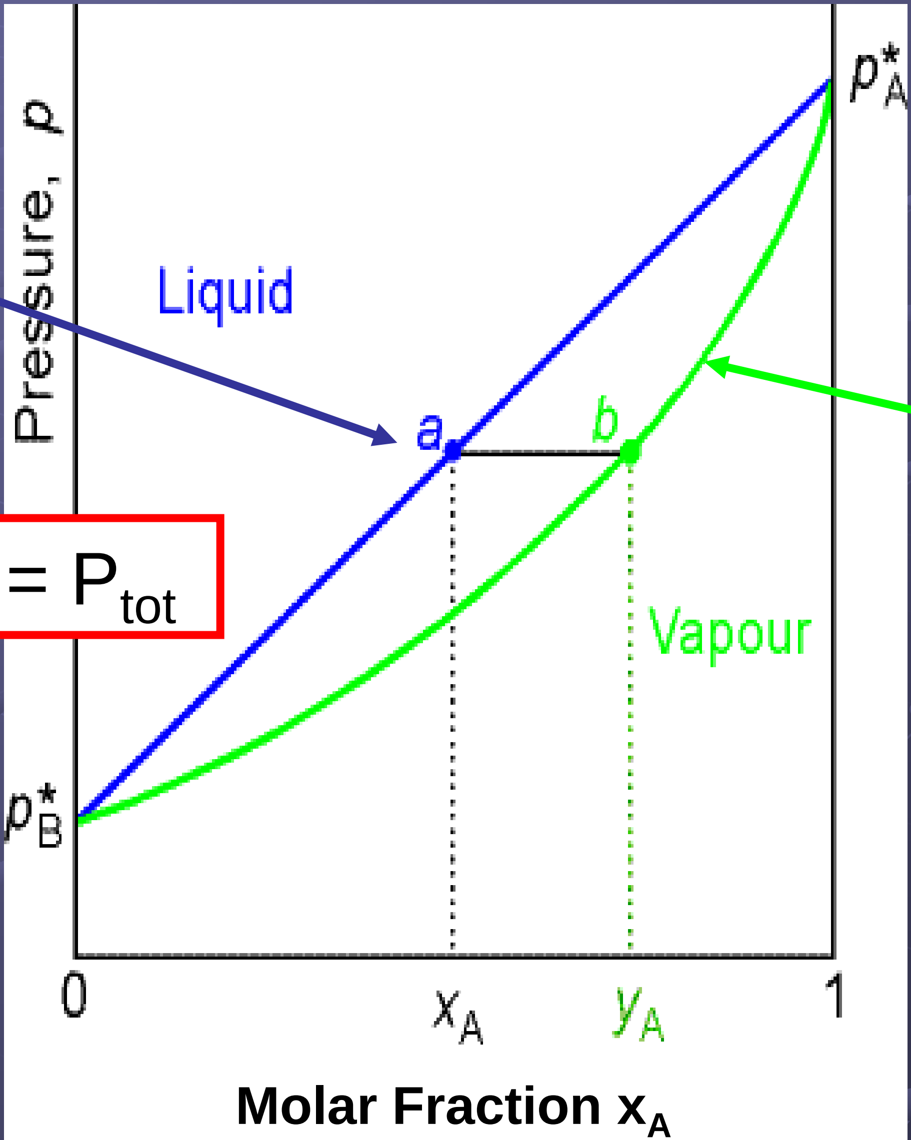


$$\boxed{P_{acetone} + P_{toluene} = P_{tot}}$$



Two-Component Phase Diagram

Vapor pressure as a function of liquid phase composition

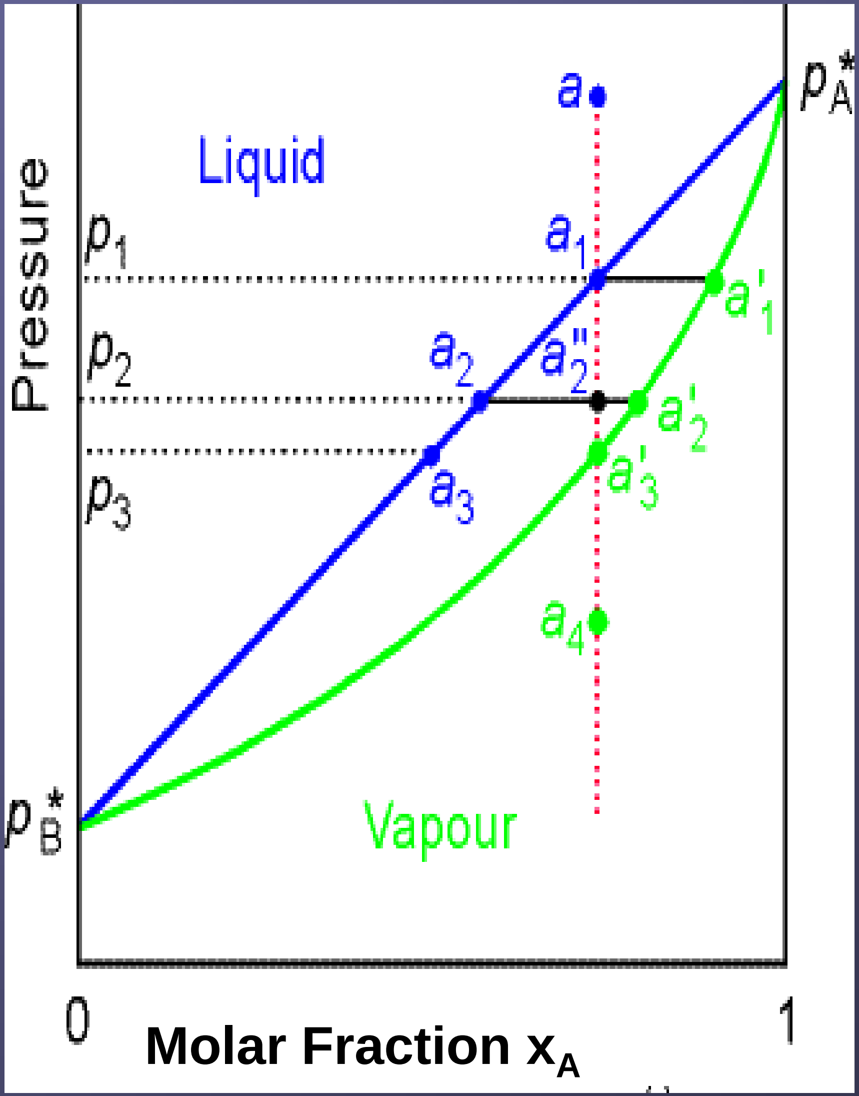


Vapor pressure as a function of gas phase composition

$$\boxed{P_{acetone} + P_{toluene} = P_{tot}}$$

Isothermal:
T = const.

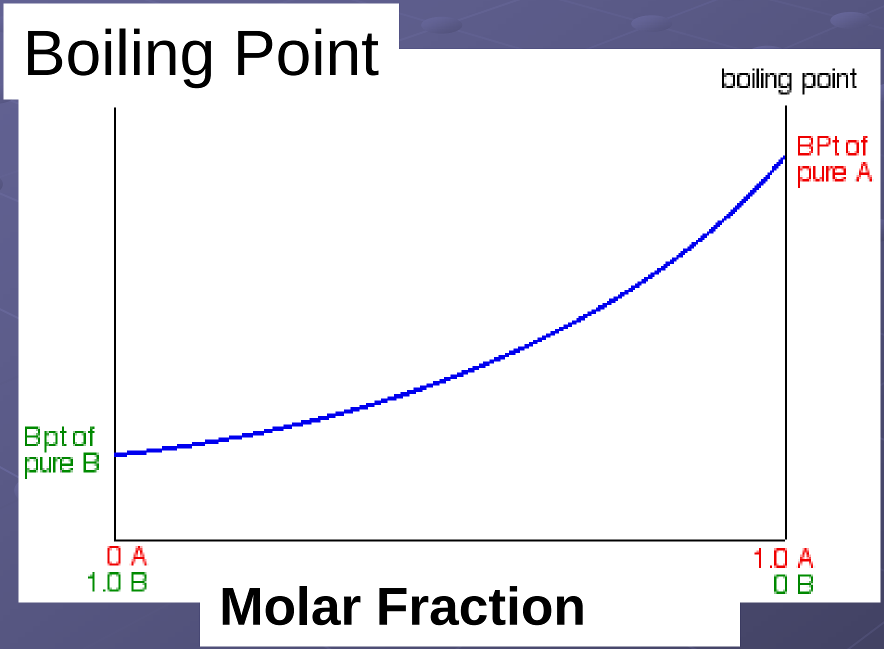
Destillation at T = const. by Decreasing Pressure

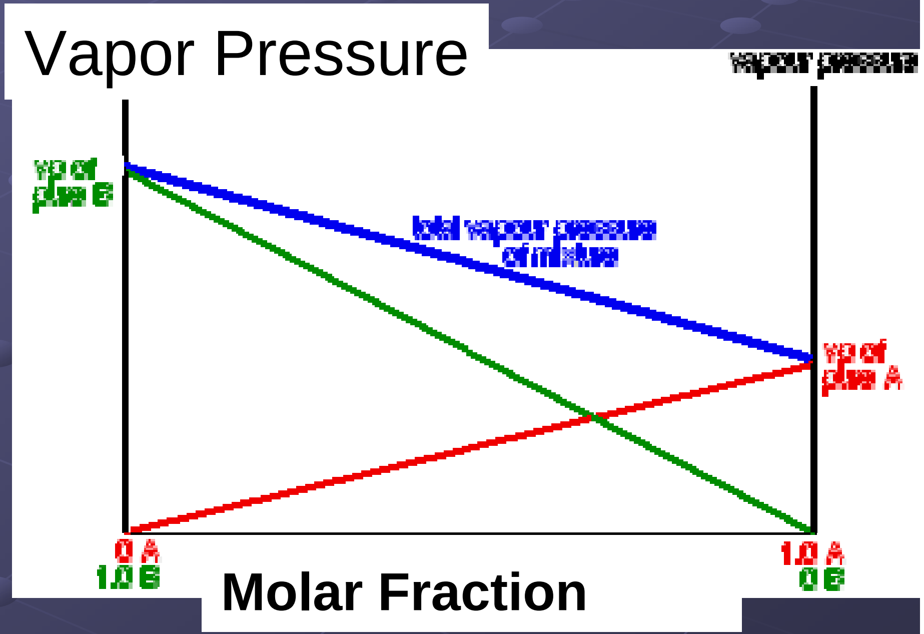


Two-Component Phase Diagram

Isobaric: p = const.

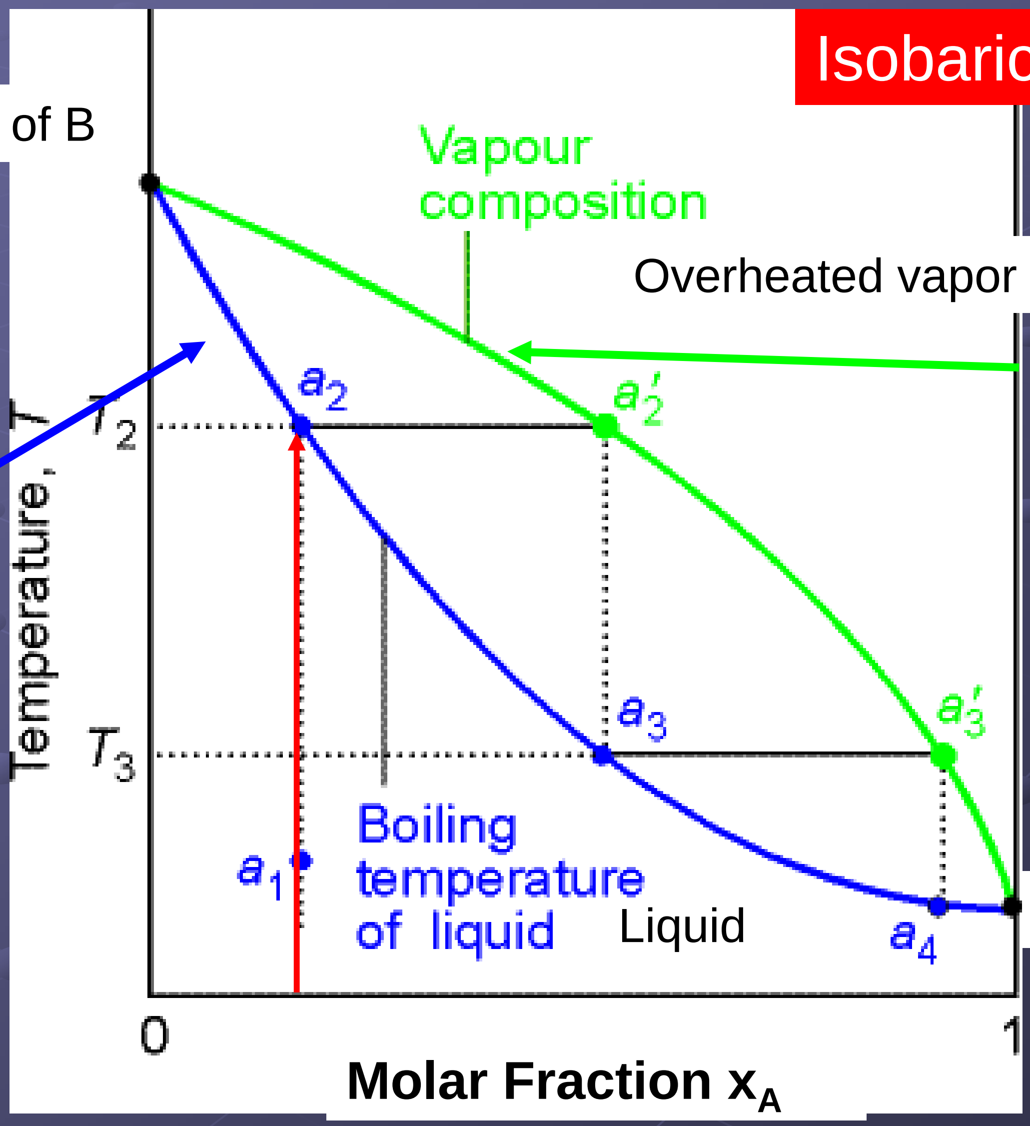
Isothermal: T = const.





More volatile component
= higher vapor pressure = lower boiling point

Destillation at p = const. by Increasing Temperature T



Isobaric: p = const.

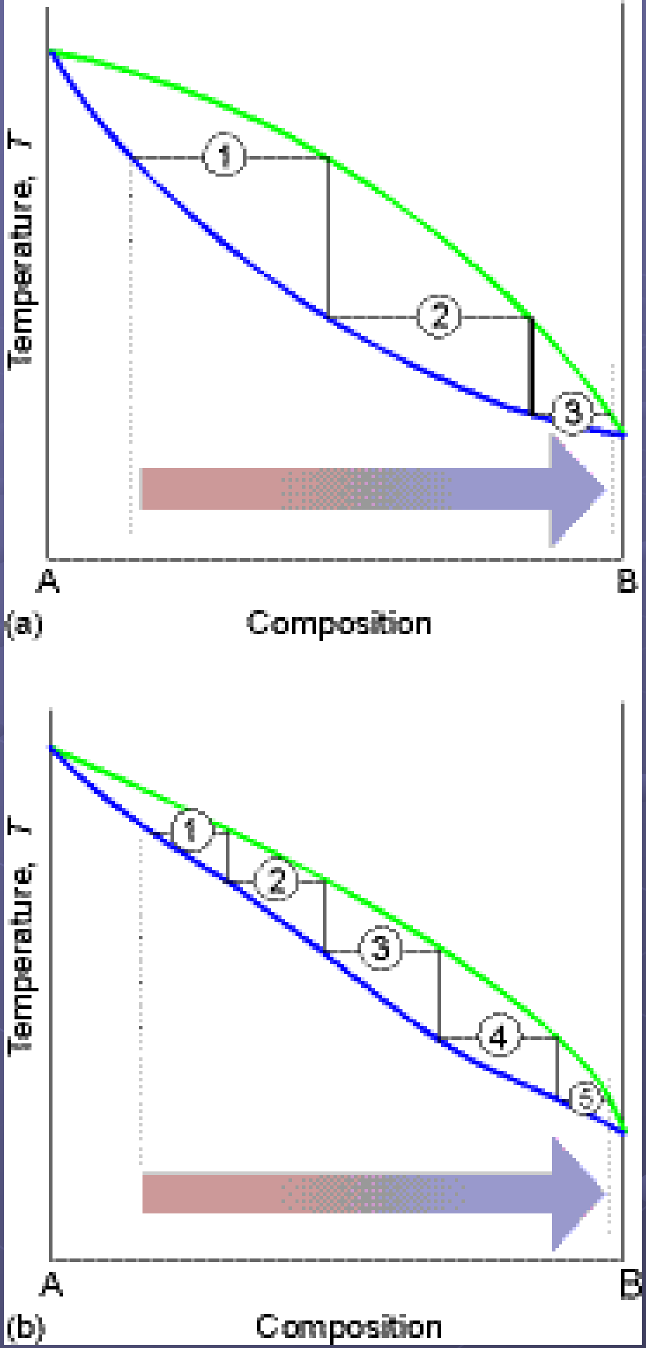
Boiling Pont of B

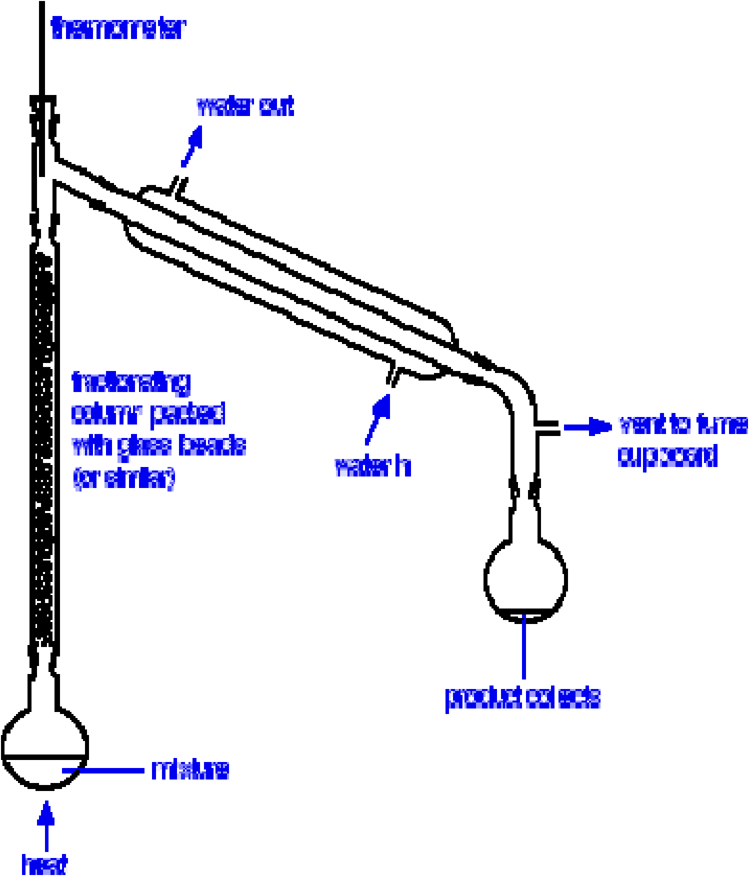
Gas Phase Composition

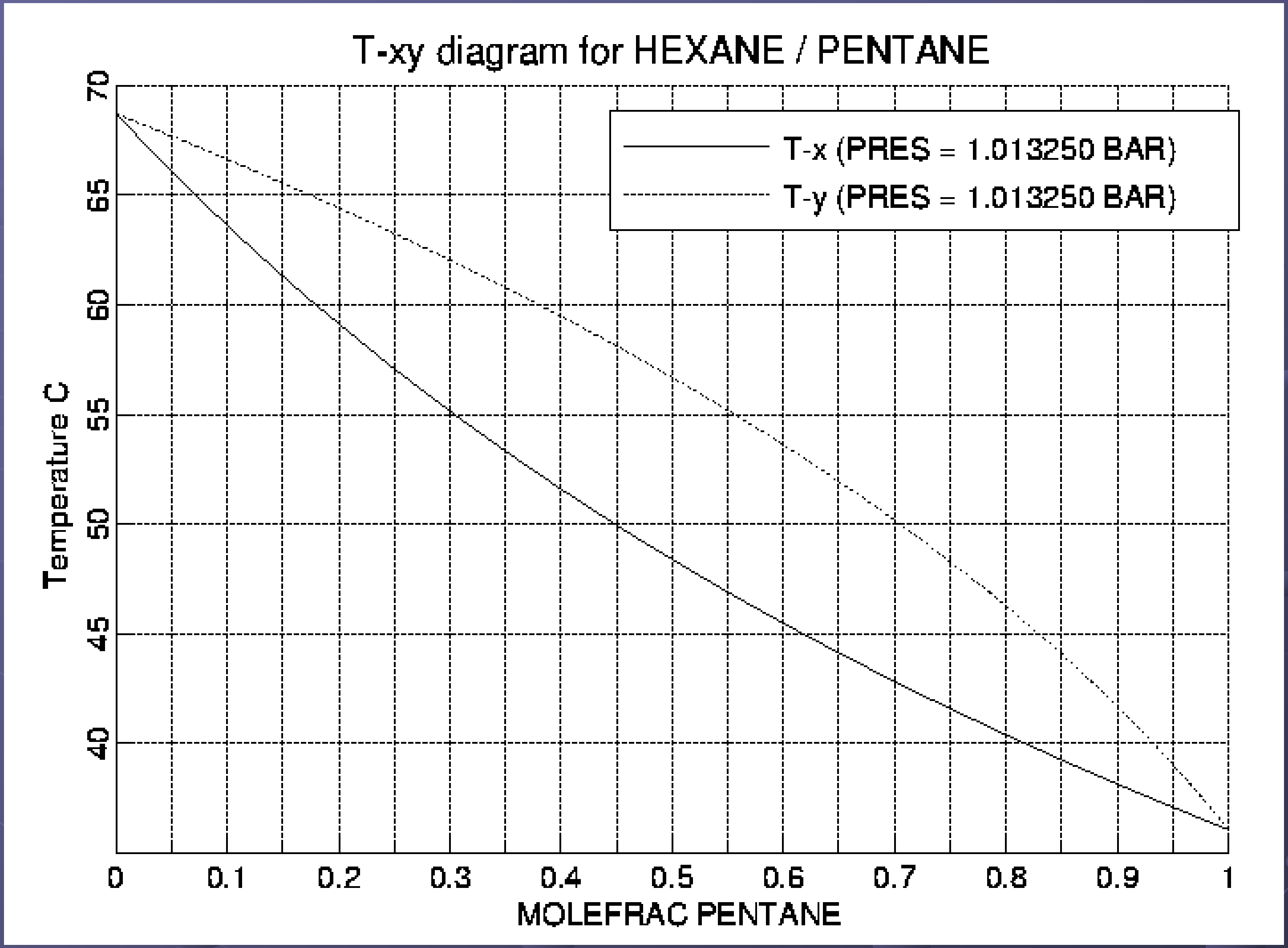
Boiling Pont of A

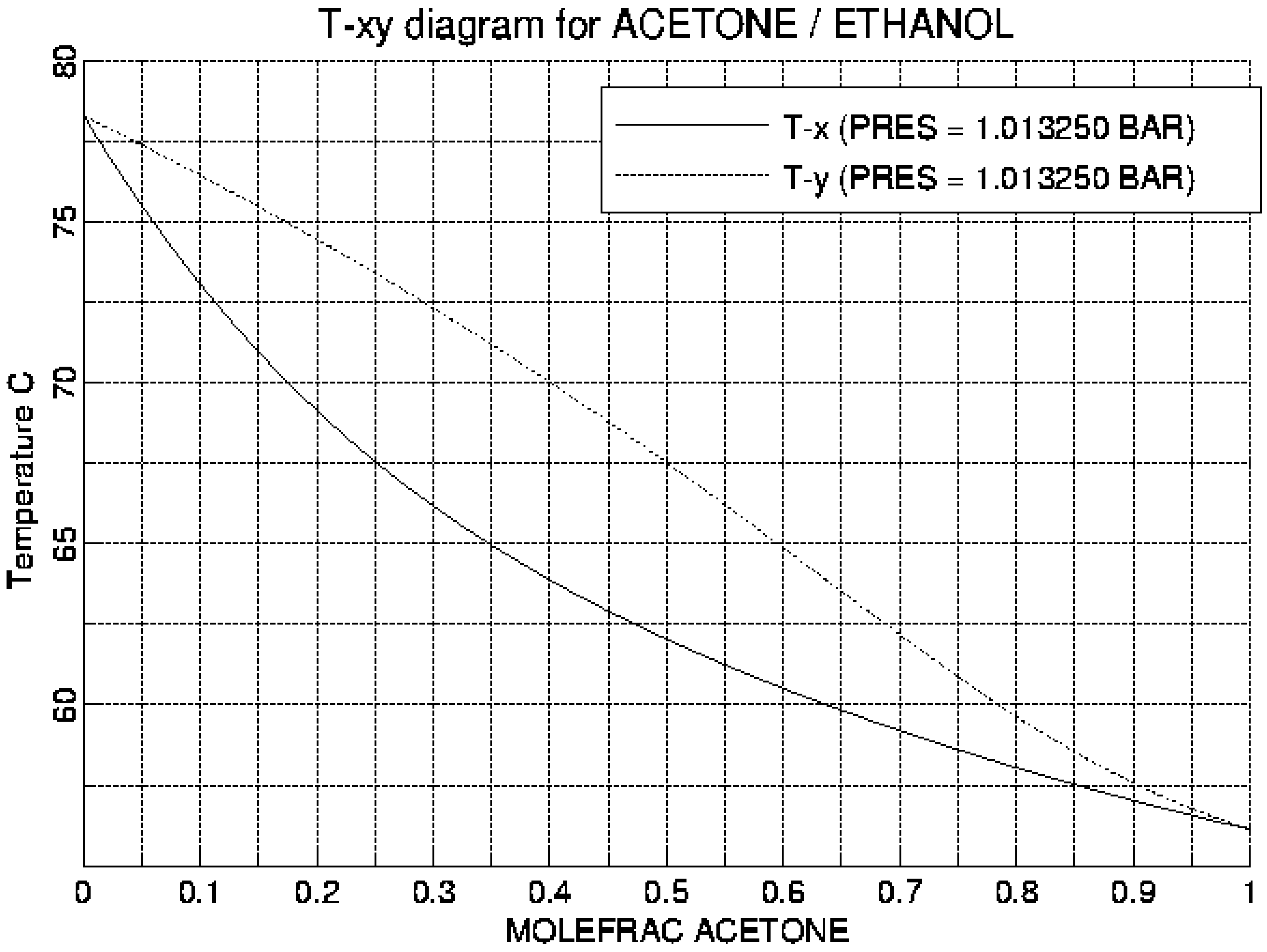
Boiling point as a function of liquid phase composition

Fractional distillation

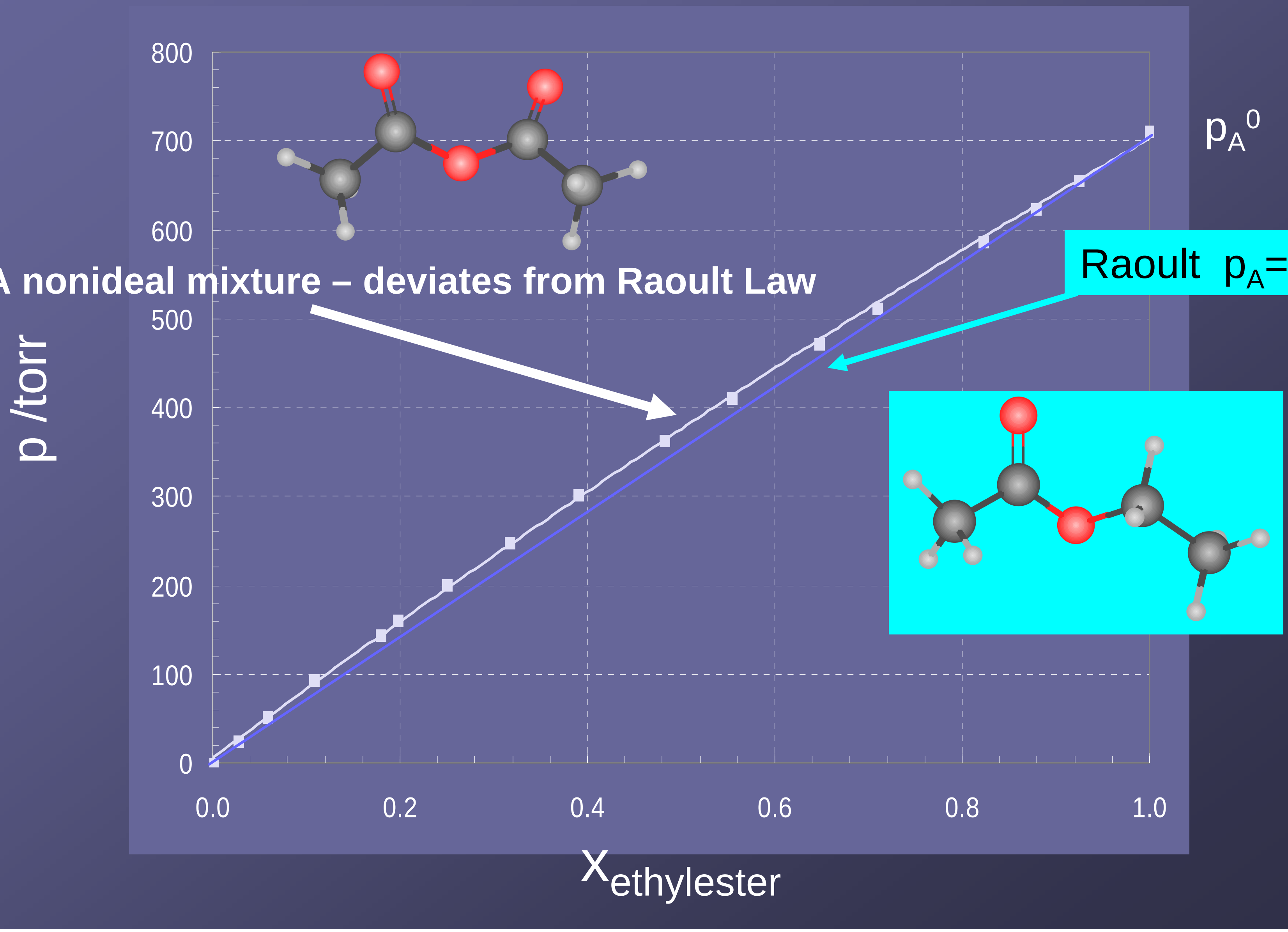





T-xy diagram for HEXANE / PENTANE
T-x (PRES = 1.013250 BAR)
T-y (PRES = 1.013250 BAR)
Temperature C
70
65
60
55
50
45
40
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLEFRAC PENTANE


T-xy diagram for ACETONE / ETHANOL
T-x (PRES = 1.013250 BAR)
T-y (PRES = 1.013250 BAR)
Temperature C
80
75
70
65
60
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLEFRAC ACETONE

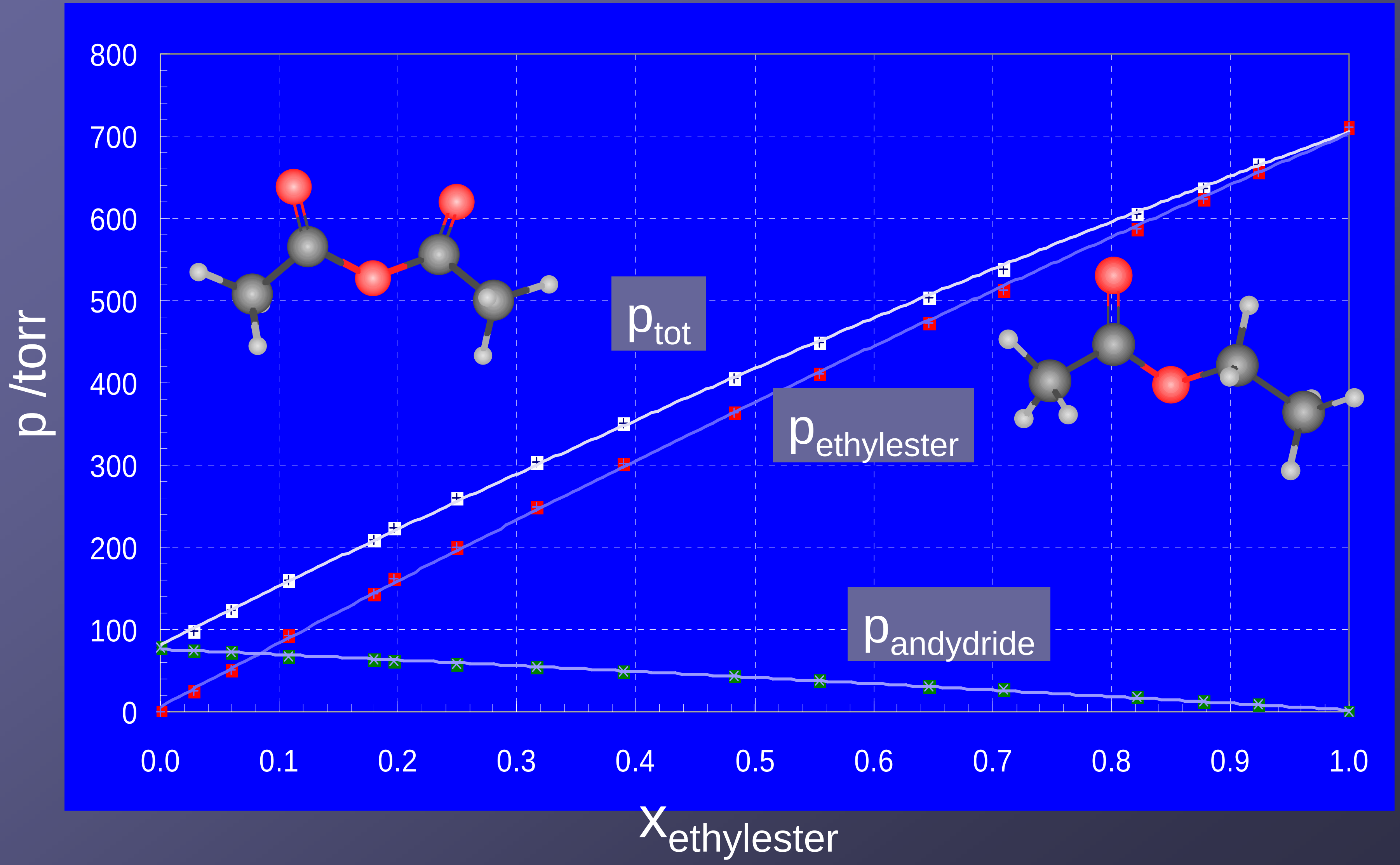
Vapor Pressure in Ethylester of Acetic Acid and Acetic Anhydride



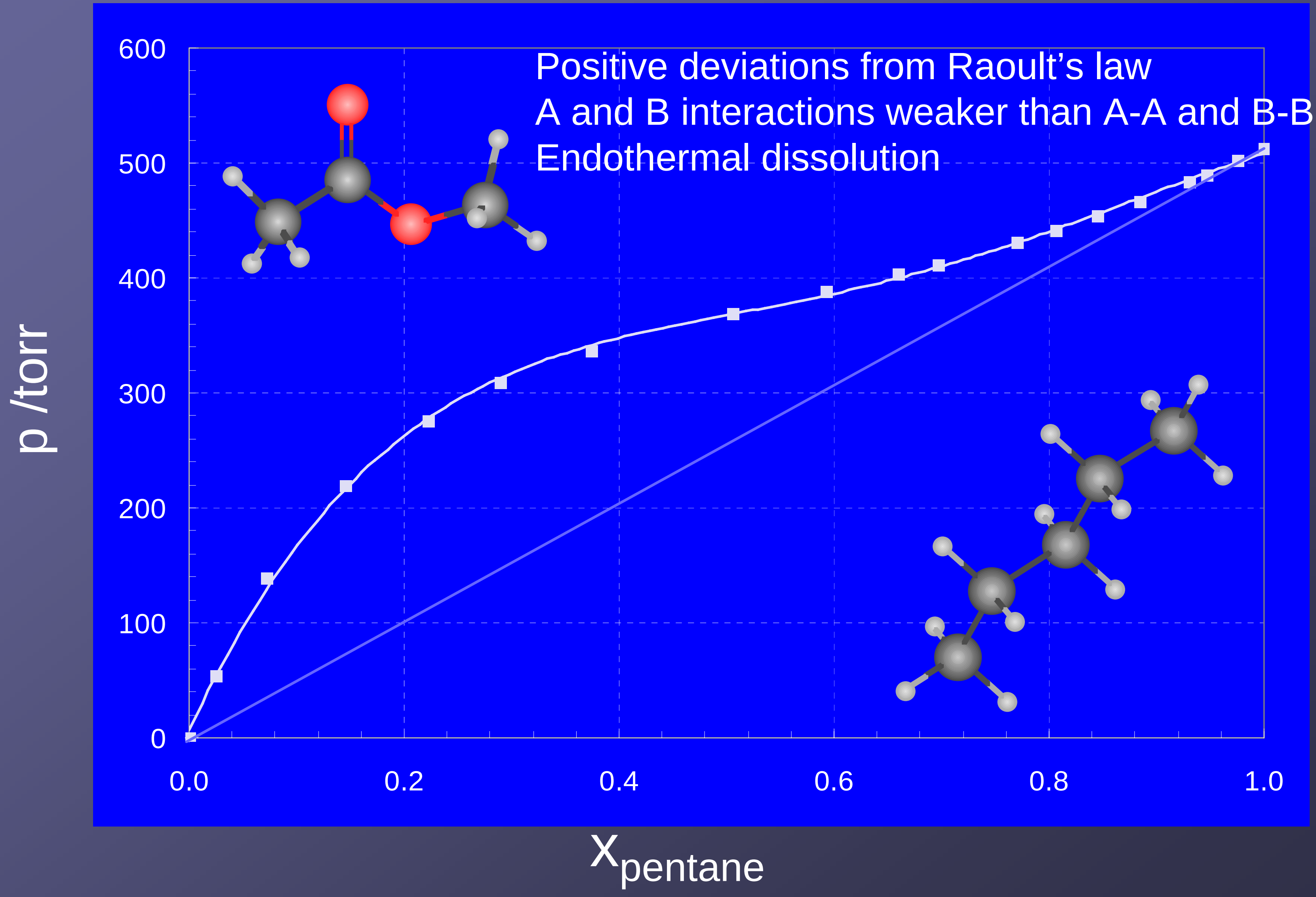
A nonideal mixture – deviates from Raoult Law

Raoult $p_A = x_A\, p_A^0$

Total Vapor Pressure in Ethylester of Acetic Acid and Acetic Anhydride

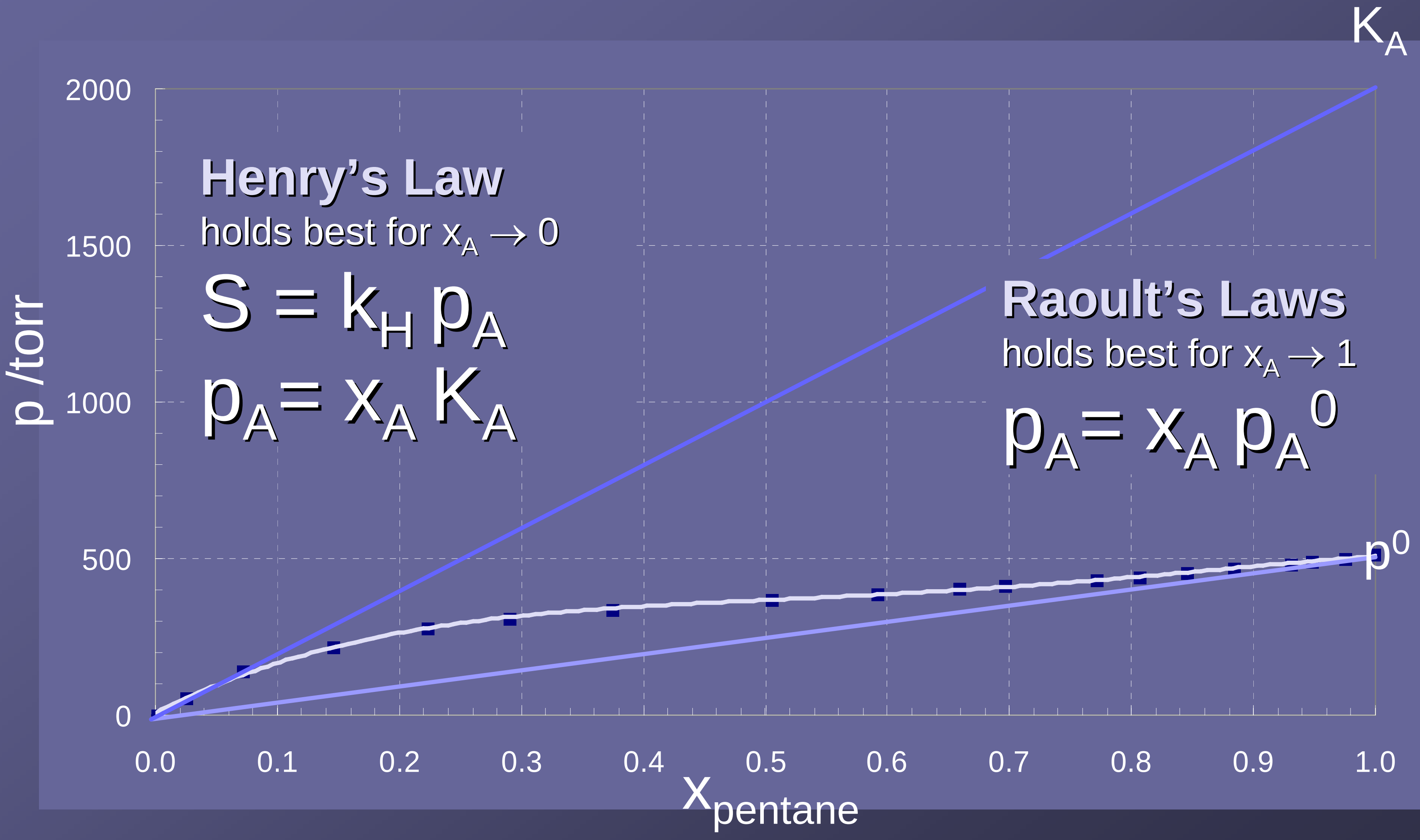


n-Pentane and Methylester of Acetic Acid



Positive deviations from Raoult's law
A and B interactions weaker than A-A and B-B
Endothermal dissolution

Raoult's and Henry's Laws



Henry's Law

holds best for $x_A \to 0$

$$S = k_H\, p_A$$

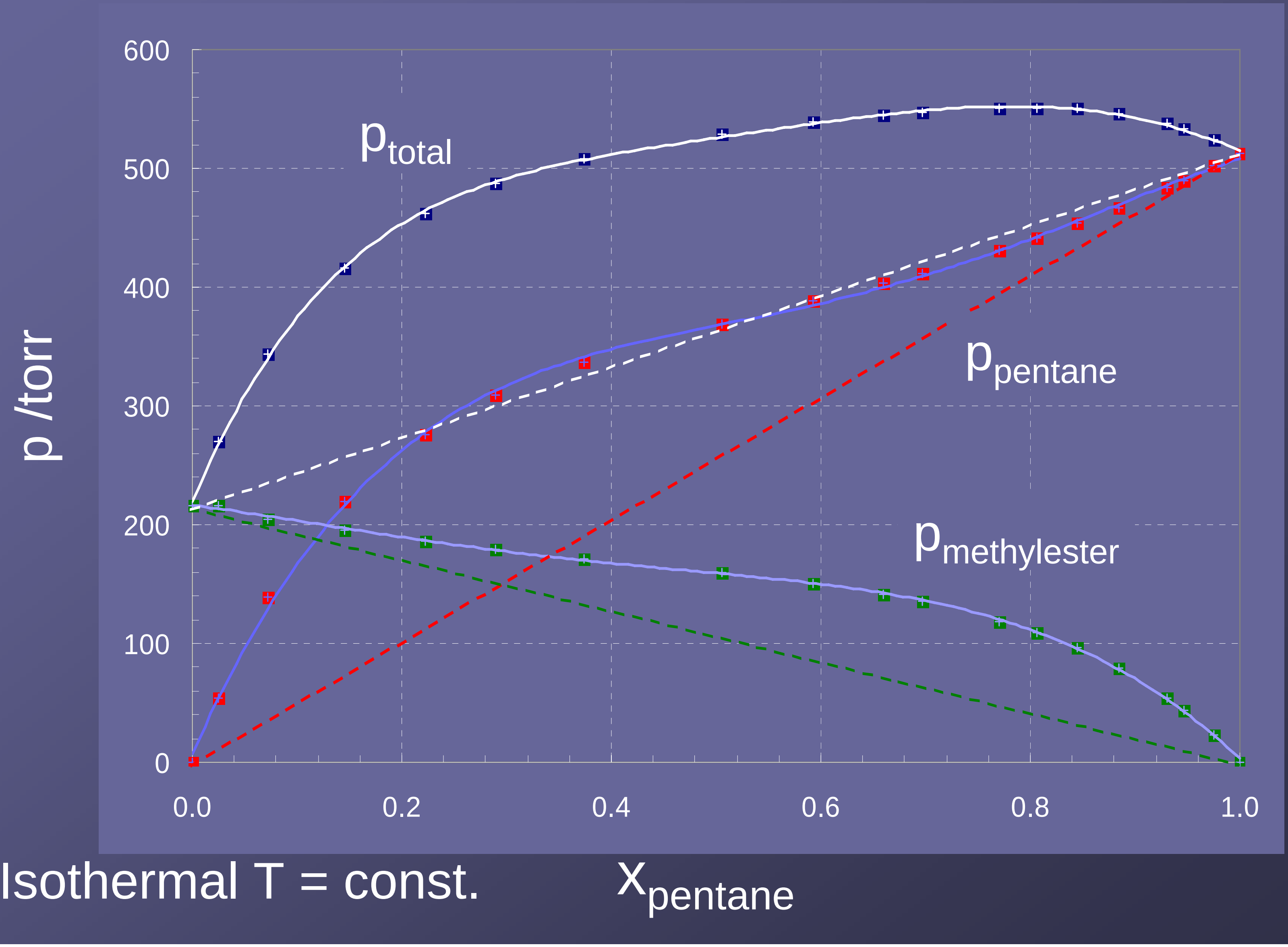
$$p_A = x_A\, K_A$$

Raoult's Laws

holds best for $x_A \to 1$

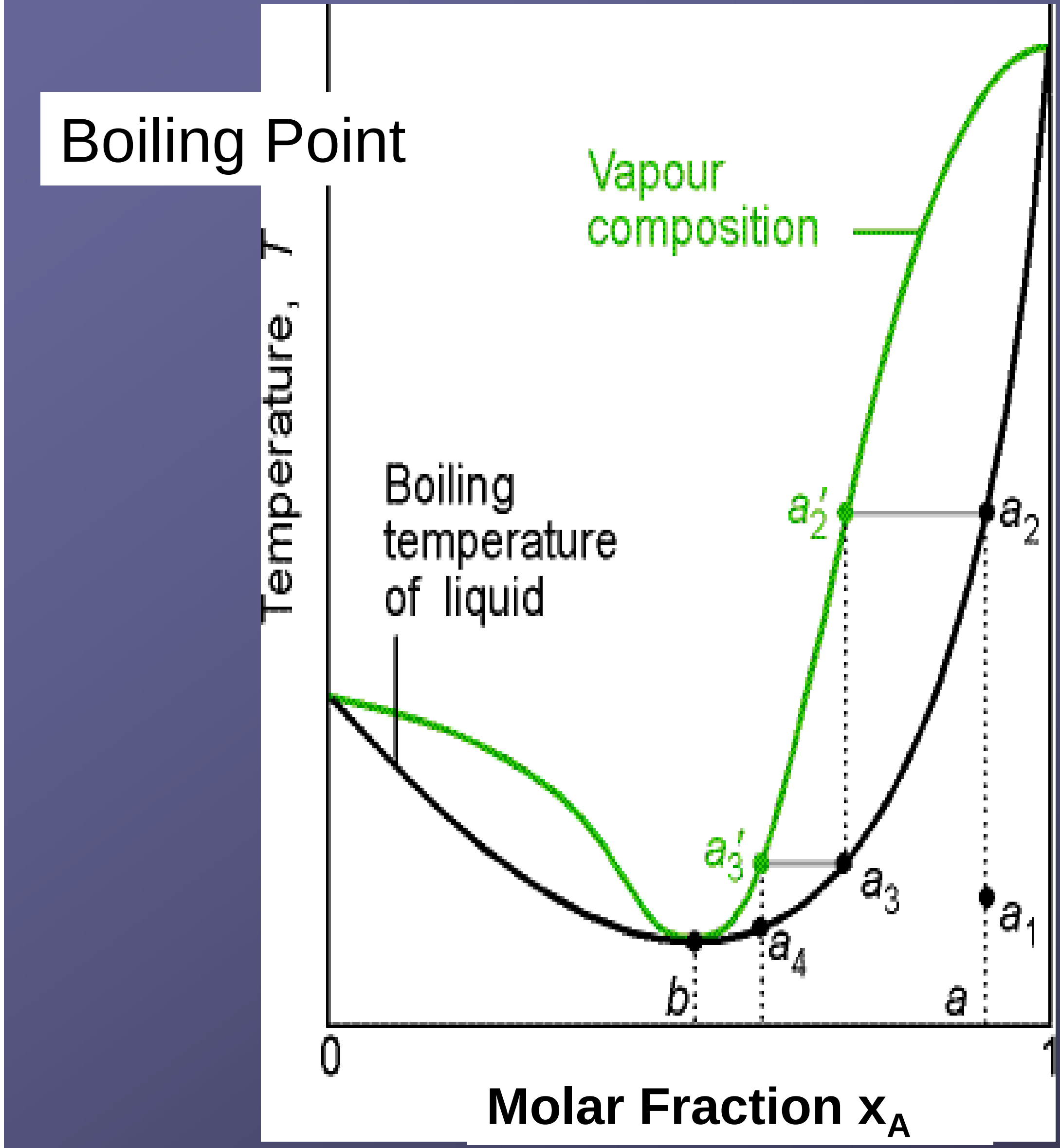
$$p_A = x_A\, p_A^0$$

n-Pentane and Methylester of Acetic Acid



Isothermal T = const.

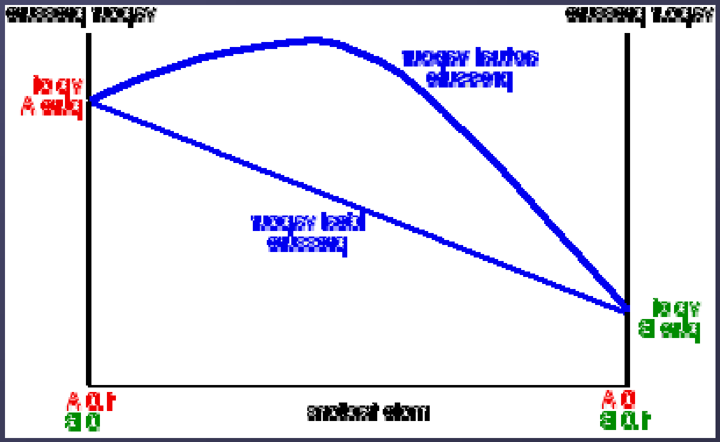
Azeotropic Mixture with Min. T_{boil} (Max. p)


Boiling Point

Molar Fraction x_A

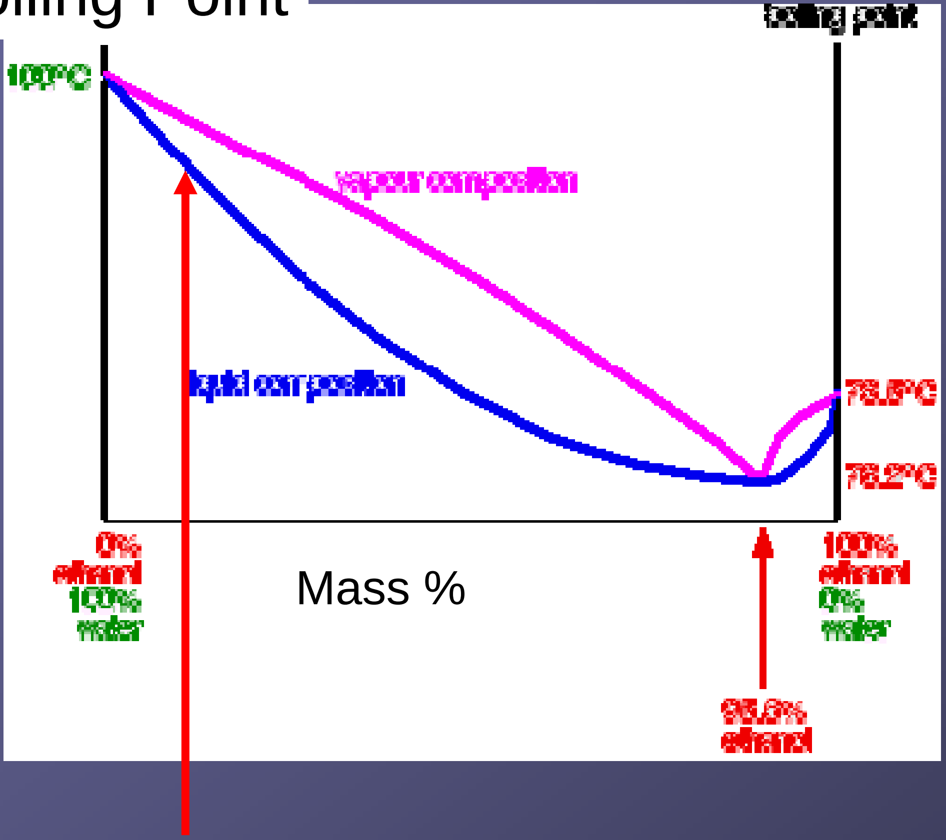
Ethanol – Water

Positive deviations from Raoult’s law A and B interactions weaker than A-A and B-B, a mixture evaporates more easily than pure components
Endothermal dissolution



Azeotropic Mixture with Min. T_{boil} (Max. p)

Boiling Point

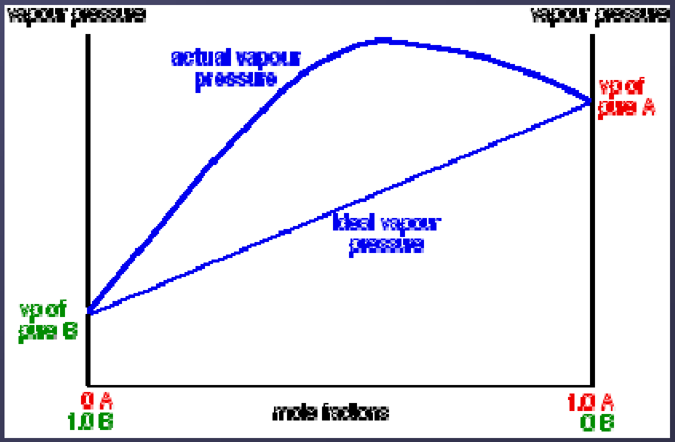


Ethanol – Water

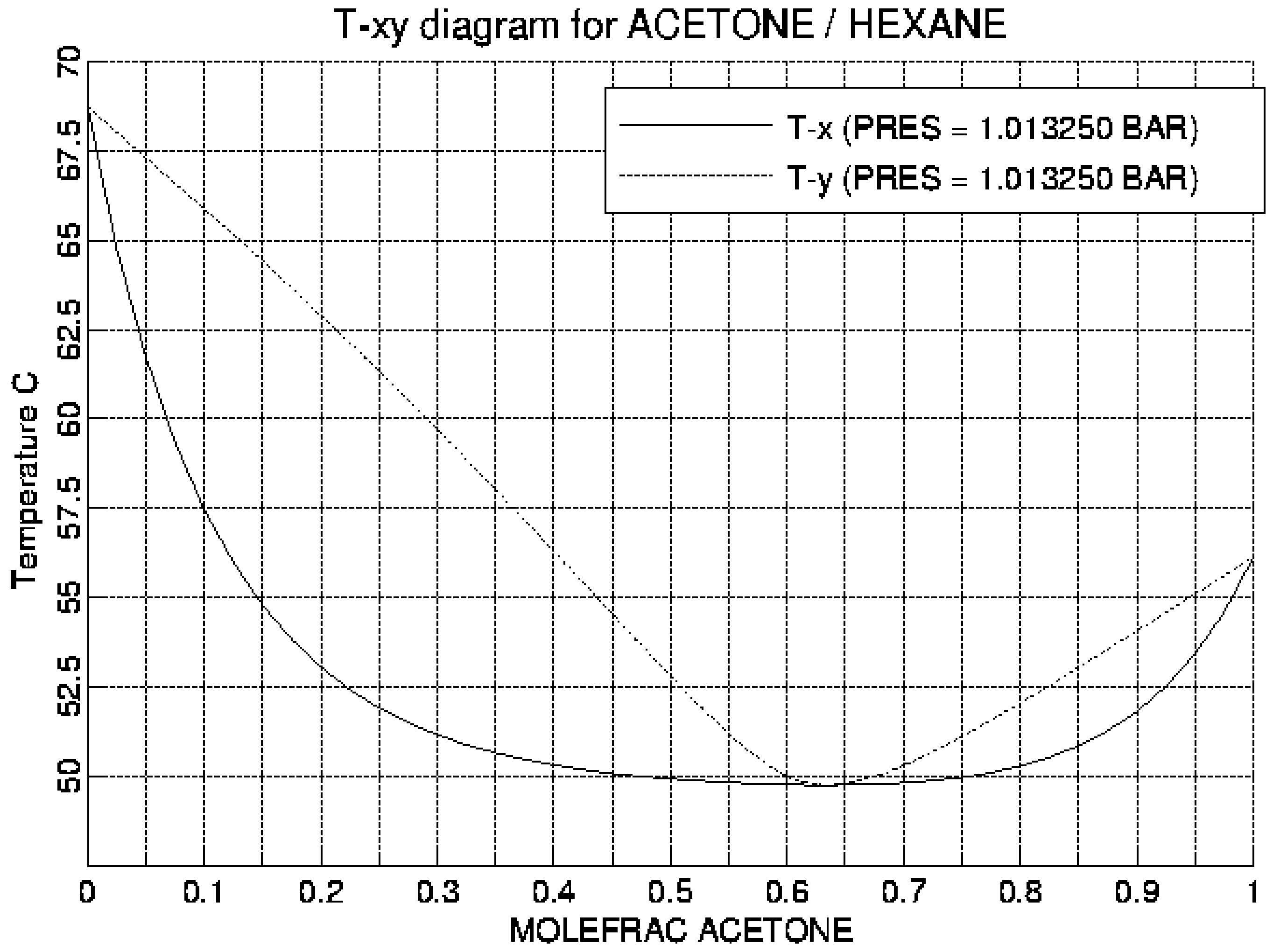
w = 95.6% x = 0.895

Positive deviations from Raoult's law A and B interactions weaker than A-A and B-B, a mixture evaporates more easily than pure components

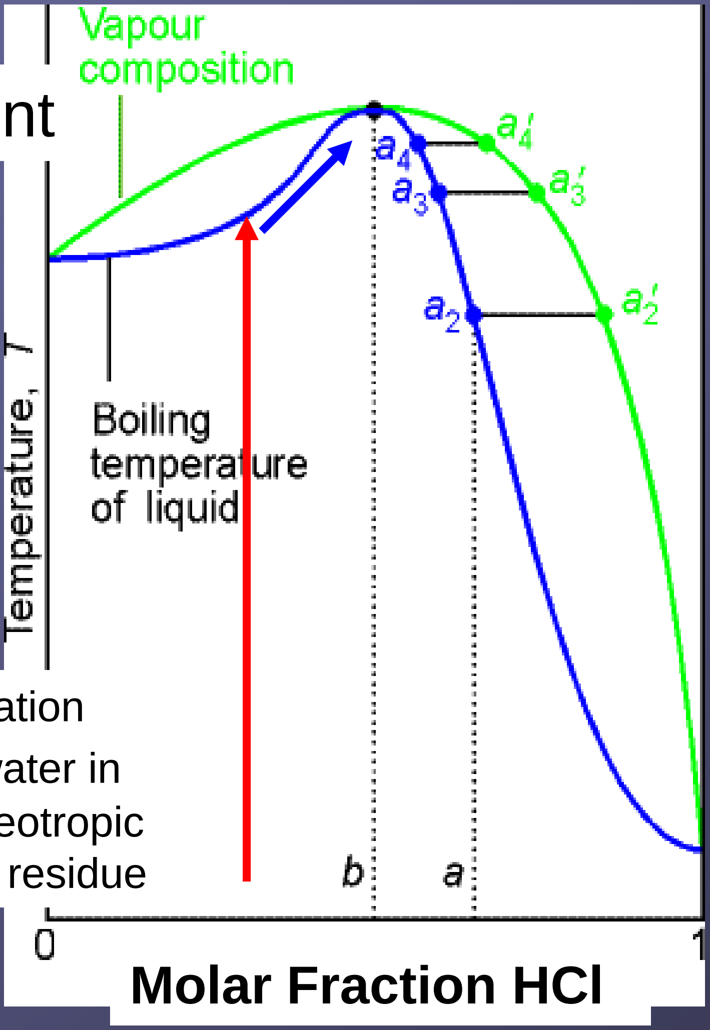
Endothermal dissolution



Fractional distillation provides ethanol with max. 95.6% in distillate and pure water as a residue


T-xy diagram for ACETONE / HEXANE
T-x (PRES = 1.013250 BAR)
T-y (PRES = 1.013250 BAR)
Temperature C
70
67.5
65
62.5
60
57.5
55
52.5
50
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLEFRAC ACETONE

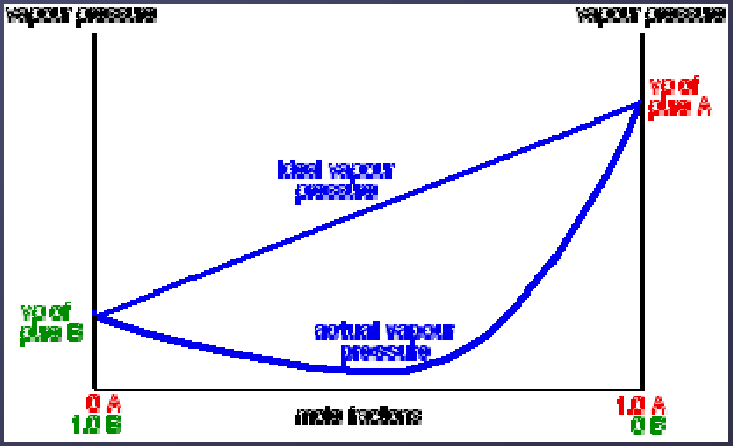
Azeotropic Mixture with Max. T_{boil} (Min. p)

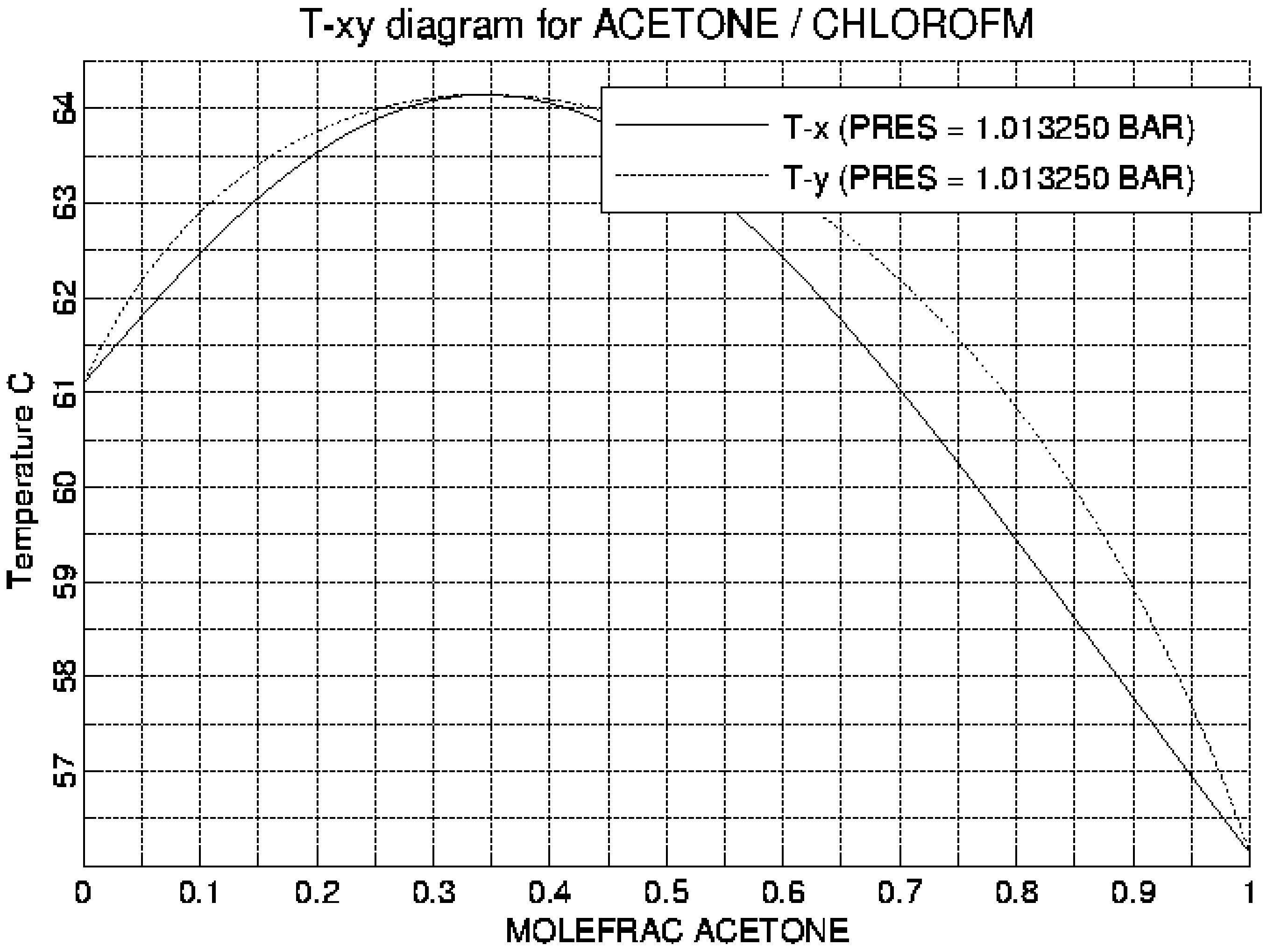


Fractional distillation provides pure water in distillate and azeotropic HCl 20.2% as a residue

HCl – Water
108.584 °C
20.222 % HCl

Negative deviations from Raoult’s law, A and B interactions stronger than A-A and B-B
Exothermal dissolution

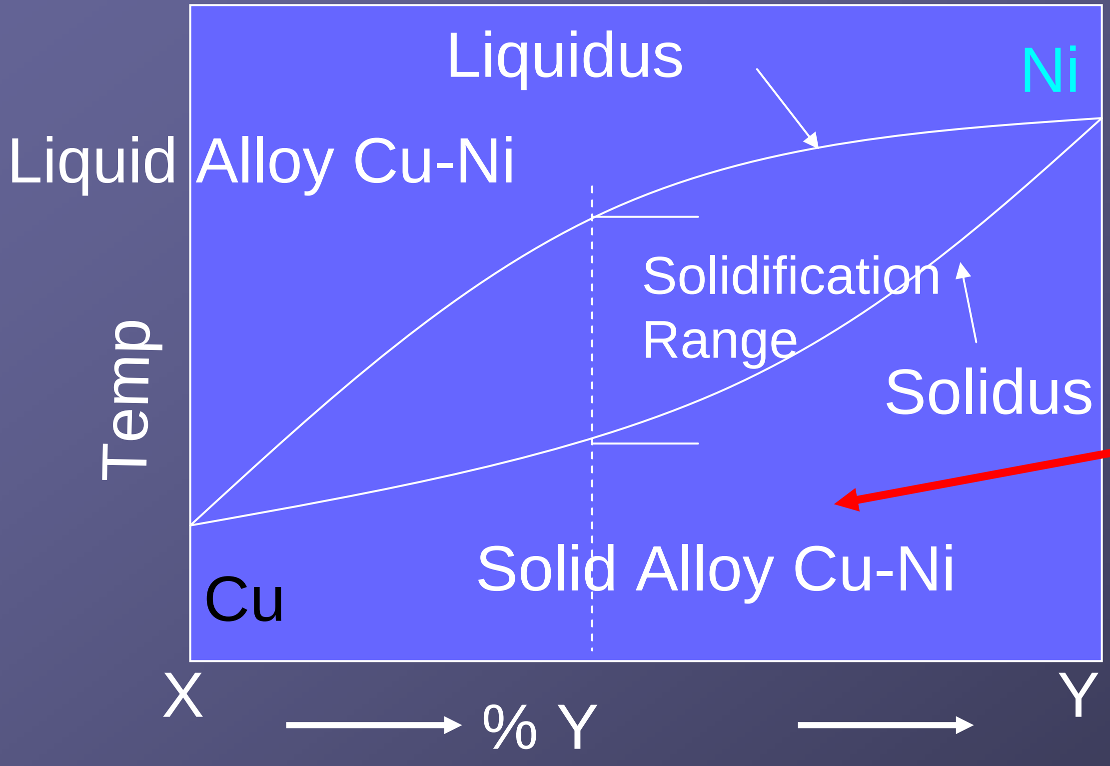


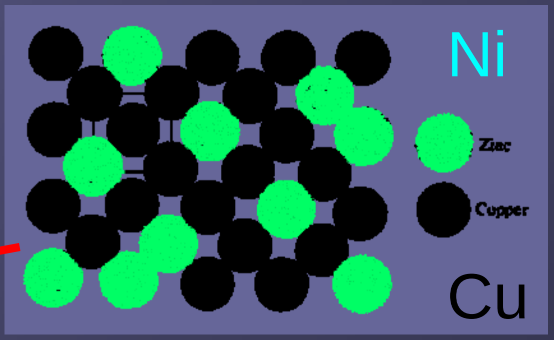

T-xy diagram for ACETONE / CHLOROFM
T-x (PRES = 1.013250 BAR)
T-y (PRES = 1.013250 BAR)
Temperature C
64
63
62
61
60
59
58
57
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLEFRAC ACETONE

Two Components Miscible Both in (l) and (s)

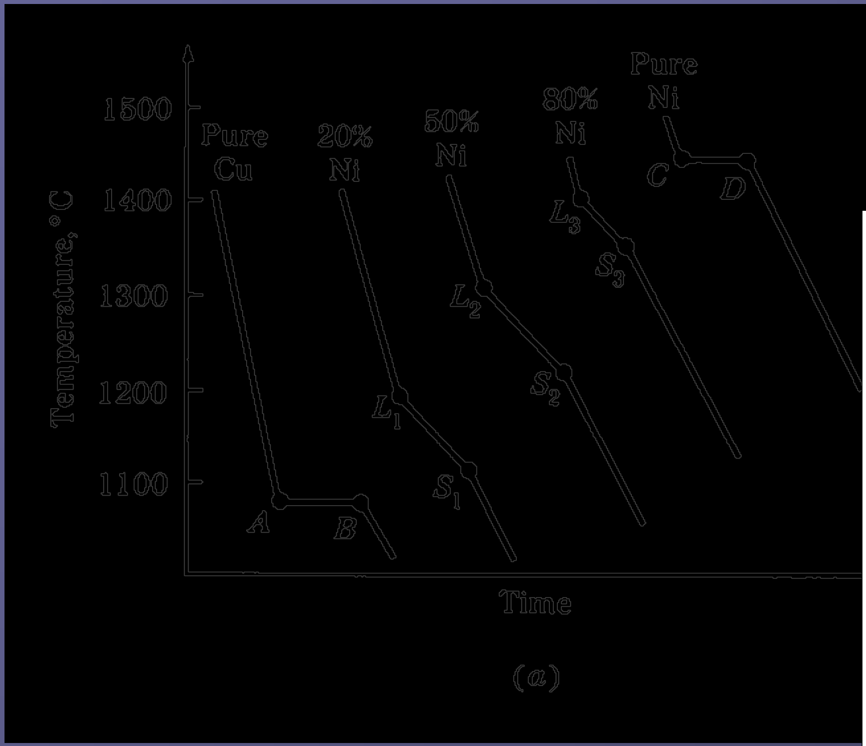
Isobaric: p = const.

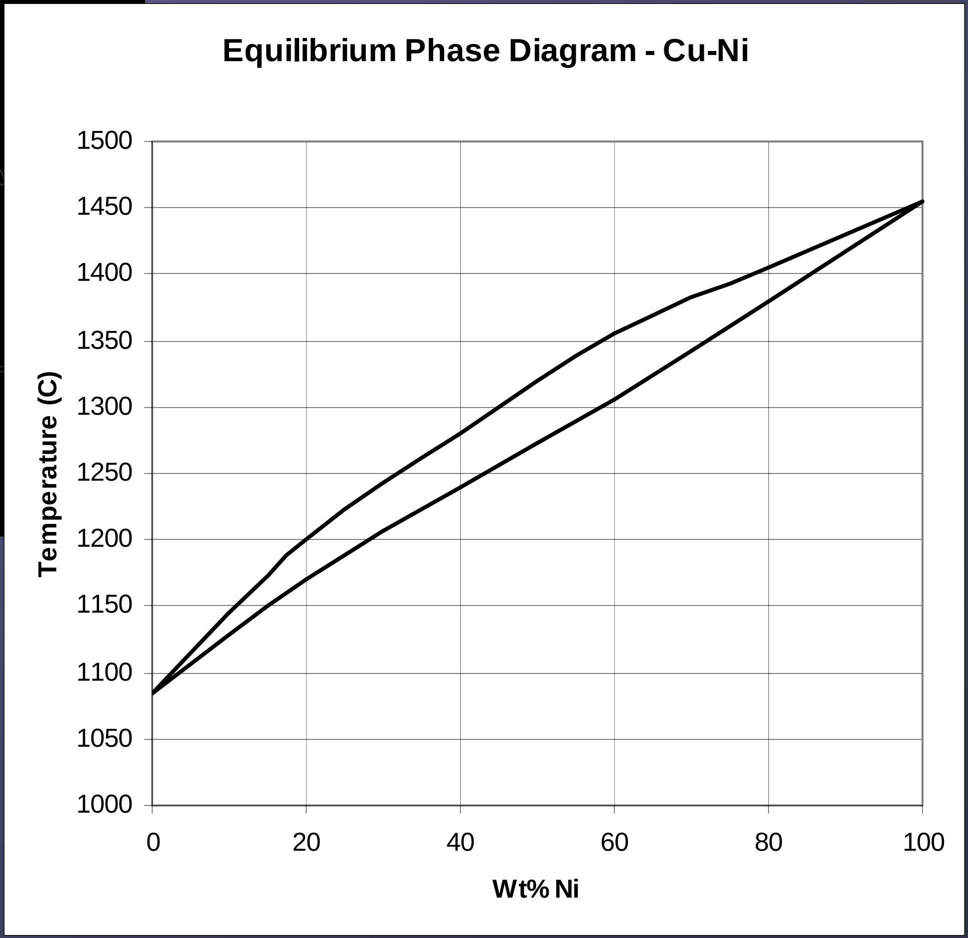
Substitutional Alloy Cu-Ni





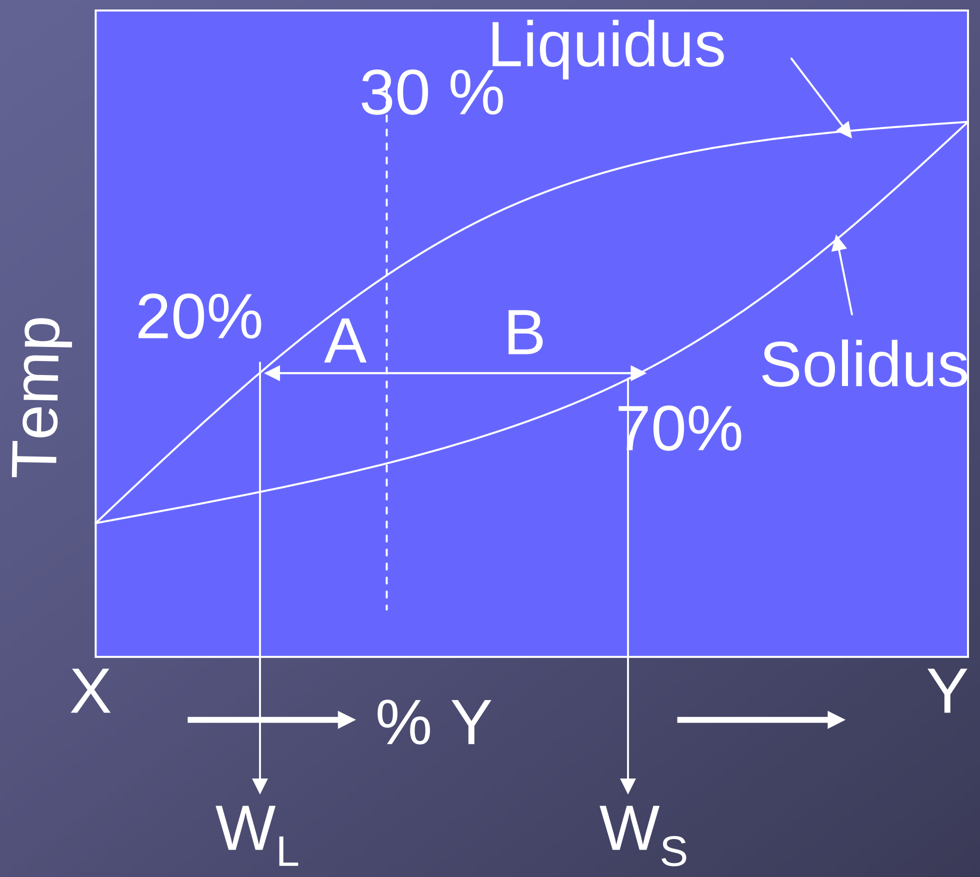
Solidification Curves of Cu-Ni Alloy





Lever Rule

Mass ratio of liquid and solid phase



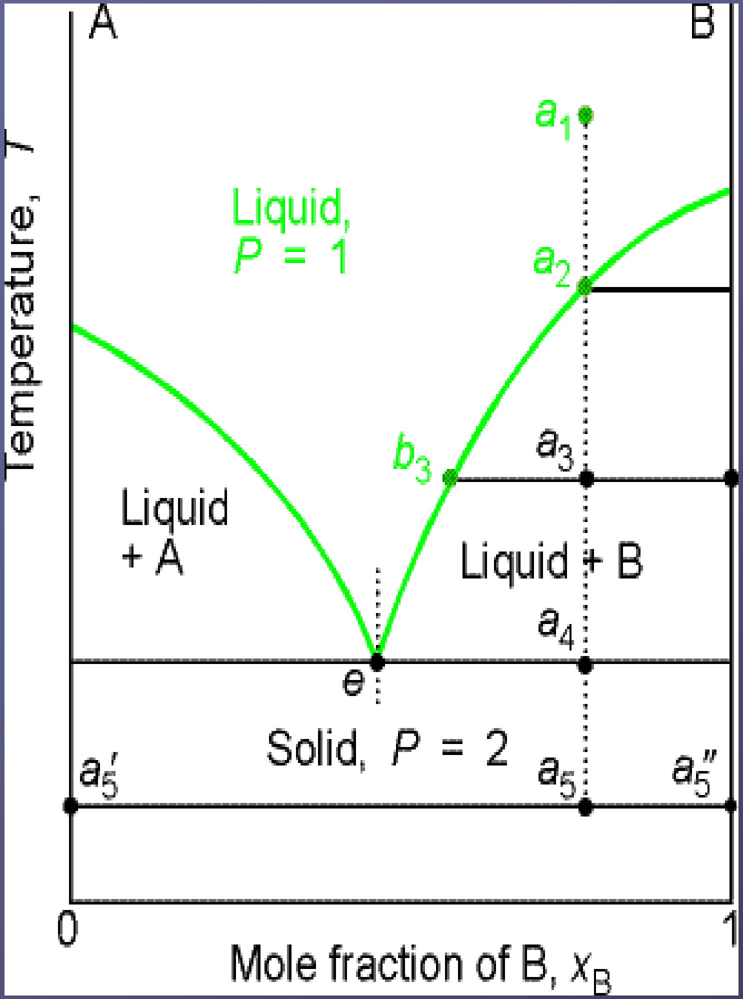
W_S = A / (A + B)

$$\%W_S = \frac{30-20}{70-20} * 100$$

W_L = B / (A + B)

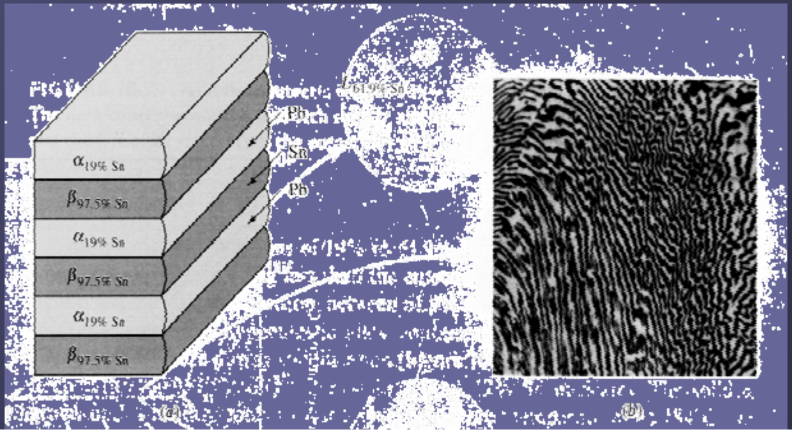
$$\%W_L = \frac{70-30}{70-20} * 100$$

Two Components Miscible in (l) and Immiscible in (s)

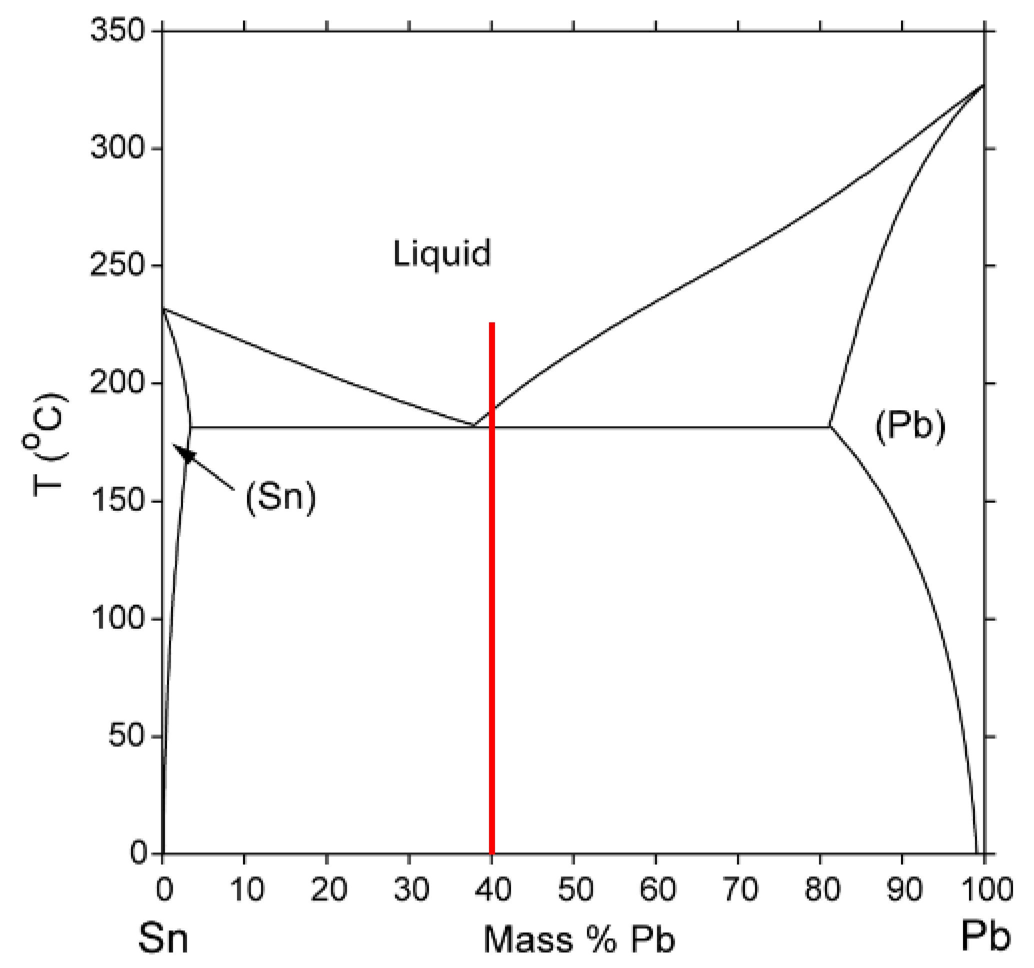


Eutectic
At eutectic composition, the mixture melts at the lowest temperature directly to a liquid

Pb-Sn solder (Pb 38%) melts at 183 °C
tin 232 °C and lead 327 °C



Pb-Sn Solder



Pb-Sn solder

(Pb 38%) melts at 183 °C

tin 232 °C

lead 327 °C