Gibbs Phase Rule: f = c – p + 2

f = Intensive Degrees of freedom = variance
Number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium

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p = number of phases
gas, homogeneous liquid phases, homogeneous solid phases

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c = components
Minimum number of independent constituents
Case I. No chemical reactions: c = constituents
Example 1: start with methanol and water – **2** components

Case II With chemical reactions:
Example 2: start with NaH_2PO_4 in water --

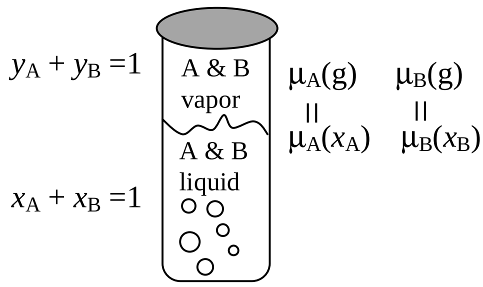
$$H_2PO_4^- \underset{\leftarrow}{\overset{K_{a2}}{\rightarrow}} HPO_4^{2-} + H^+ \underset{\leftarrow}{\overset{K_{a3}}{\rightarrow}} PO_4^{3-} + H^+$$

Constituents: Na^+, H^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_2O
but only **2** components -- NaH_2PO_4 and H_2O.

Example 3: start with NaH_2PO_4 and Na_2HPO_4 in water --
Same constituents: Na^+, H^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_2O
but now **3** components -- NaH_2PO_4, Na_2HPO_4, and H_2O.

Need to know: T, P, y_A, y_B, x_A, x_B

total intensive variables = c p + 2

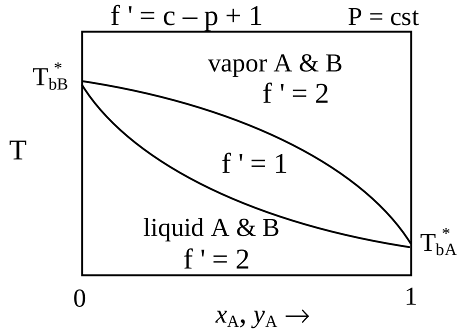


But $y_A + y_B = 1$
$x_A + x_B = 1$
Get p such equations, one for each phase:

Independent variables = c p + 2 – p

But, chemical potential is everywhere equal:
$\mu_A(x_A) = \mu_A(g)$
$\mu_B(x_B) = \mu_B(g)$
Get p–1 for each component
Get c(p–1) such equations:
Independent variables = c p + 2 – p – c(p–1)

f **= c – p + 2**



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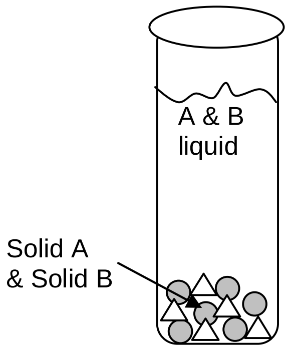
f ' = c – p + 1 cst. P
f "= c – p cst. T&P

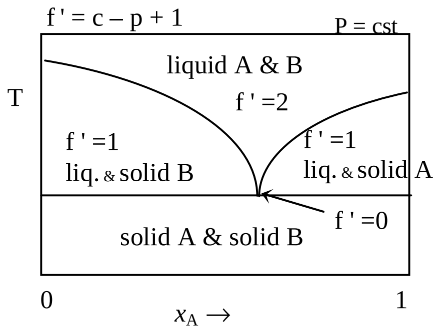
<u>Binary solid-liquid Equilibrium</u>
<u>Melting Point Variation with Composition</u>
c = 2
p = 3



liquid, pure solid A, pure solid B

Solid-liquid 2-phase region:
f ' = 2 – 2 + 1 **= 1**

Eutectic:
f ' = 2 – 3 + 1 **= 0**
invariant at cst P



For NaCl in water:
Eutectic -21.1 ^oC at 23% wt/wt giving $NaCl \cdot 2H_2O$

<u>Add One Extensive Independent Variable for Each Phase:</u>
Gibbs energy is extensive:
Degrees of freedom:

D = f + p

Binary Solid-Liquid at constant T & P:
Solid-liquid 2-phase region:
f " = 2 – 2 **= 0**
D " = f " + p = 0 + 2 = **2**

$dG = \mu_A\, dn_A + \mu_B\, dn_B$ dn_A and dn_B: totals for both phases

since: $\mu_A(s) = \mu_A(l)$, and $\mu_B(s) = \mu_B(l)$ (doesn't matter which phase)