**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

\( p \) = number of phases  
gas, homogeneous liquid phases, homogeneous solid phases

\( c \) = 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 \( \text{NaH}_2\text{PO}_4 \) in water --  
\[ \text{H}_2\text{PO}_4^- \xrightleftharpoons{} \text{HPO}_4^{2-} + \text{H}^+ \xrightleftharpoons{} \text{PO}_4^{3-} + \text{H}^+ \]  
Constituents: \( \text{Na}^+, \text{H}^+, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}, \text{PO}_4^{3-}, \text{H}_2\text{O} \)  
but only 2 components -- \( \text{NaH}_2\text{PO}_4 \) and \( \text{H}_2\text{O} \).

*Example 3:* start with \( \text{NaH}_2\text{PO}_4 \) and \( \text{Na}_2\text{HPO}_4 \) in water --  
Same constituents: \( \text{Na}^+, \text{H}^+, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}, \text{PO}_4^{3-}, \text{H}_2\text{O} \)  
but now 3 components -- \( \text{NaH}_2\text{PO}_4, \text{Na}_2\text{HPO}_4, \) and \( \text{H}_2\text{O} \).

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 = \( c \ p + 2 - p - c \ (p-1) \)

\( f = c - p + 2 \)

*Colby College*
\[ f' = c - p + 1 \quad \text{cst. P} \]
\[ f'' = c - p \quad \text{cst. T&P} \]

**Binary solid-liquid Equilibrium**

**Melting Point Variation with Composition**
\[ c = 2 \]
\[ p = 3 \]

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 °C at 23% wt/wt giving NaCl·2H₂O

**Add One Extensive Independent Variable for Each Phase:**
Gibbs energy is extensive:
Degrees of freedom:
\[ D = f + p \]

**Binary Solid-Liquid at constant T & P:**
Solid-liquid 2-phase region:
\[ f'' = 2 - 2 = 0 \]
\[ D'' = f'' + p = 0 + 2 = 2 \]

\[ dG = \mu_A\, dn_A + \mu_B\, dn_B \]

\[ dn_A \text{ and } dn_B: \text{totals for both phases} \]

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