4.1 Gibbs phase rule - general discussion

Before introducing and discussing Gibbs phase rule we will repeat some basic terms related to equilibrium conditions:

- For an isolated system we have S to be at maximum, i.e. $dS = 0$.
- For thermal and mechanical equilibrium we have $T' = T'' = T''' = \cdots$ and $p' = p'' = p''' = \cdots$.
- For chemical equilibrium we have $\mu' = \mu'' = \mu''' = \cdots$. So the chemical potential inside a specimen is constant independent from locus, number of phases, etc.

We now define some basic terms:

- Phase (=P): homogeneous area of the system
- Chemical species (=S)
- Component (=C): independent chemical species, i.e. the number of S minus the number of additional conditions R, i.e. $C = S - R$
- DOF (=F): number of independent variables that can be selected freely without changing the number of phases. These "engineering parameters" are the parameters which can be adjusted to modify the system.

To find Gibbs phase rule we have to calculate several numbers:

1. Number of variables = Number of phases (P, "$\alpha, \beta, \gamma, \cdots$") $\times$ (Number of independent mole fractions and their T and p (i.e. $C - 1 + 2$)) $= P \times (C + 1)$. Here we have used that a state of a phase with C independent components needs $C - 1$ mole fractions to be specified.
2. Number of equilibrium conditions $= (C + 2) \times (P - 1)$
   $T^\alpha = T^\beta = T^\gamma = \cdots$
   $p^\alpha = p^\beta = p^\gamma = \cdots$
   $\mu(A)^\alpha = \mu(A)^\beta = \mu(A)^\gamma = \cdots$
   $\mu(B)^\alpha = \mu(B)^\beta = \mu(B)^\gamma = \cdots$
   i.e. we have $(P - 1)$ equilibrium conditions in $C + 2$ equations.
3. F = Number of variables $-$ Number of equilibrium conditions,
   i.e. $F = C - P + 2$ or: $P + F = C + 2$ which is the famous Gibbs phase rule.

Some examples for the phase rule:

- Saturated solution of a salt:
  - $F = 1 = 1 - 2 + 2$: We have pure salt and saturated solution of water as 2 phases, $C = S - 2 = 1$ two restrictions due to charge neutrality $[Na^+] = [Cl^-]$ and saturation condition. Thus T is variable.
  - $F = 0 = 1 - 3 + 2$: We have pure salt, a saturated solution of water, and ice as 3 phases, $C = S - 2 = 1$ two restrictions: charge neutrality $[Na^+] = [Cl^-]$ and saturation condition. Thus this condition can only be fulfilled at one temperature which is below -20°C. Thus above this temperature salt will melt snow/ice completely. This explains why snow melts in winter when salting a street.
- Pure compound: $P + F = 3$
  $P = 3$ implies $F = 0$, i.e. there is only one point in the phase diagram (the triple point), $P = 2$ implies $F = 1$, i.e. a line in the phase diagram, $P = 1$ implies $F = 2$, i.e. an area in the phase diagram.
- We now discuss a binary mixture of water and ether. Is it possible to have $F = 0$? Since $P + F = 4$ we need $P = 4$: 1) solid ice (without ether), 2) liquid water (with low amount of ether), 3) ether (with low amount of water, 4) gas phase (ether).