STATISTICAL MOLECULAR THERMODYNAMICS

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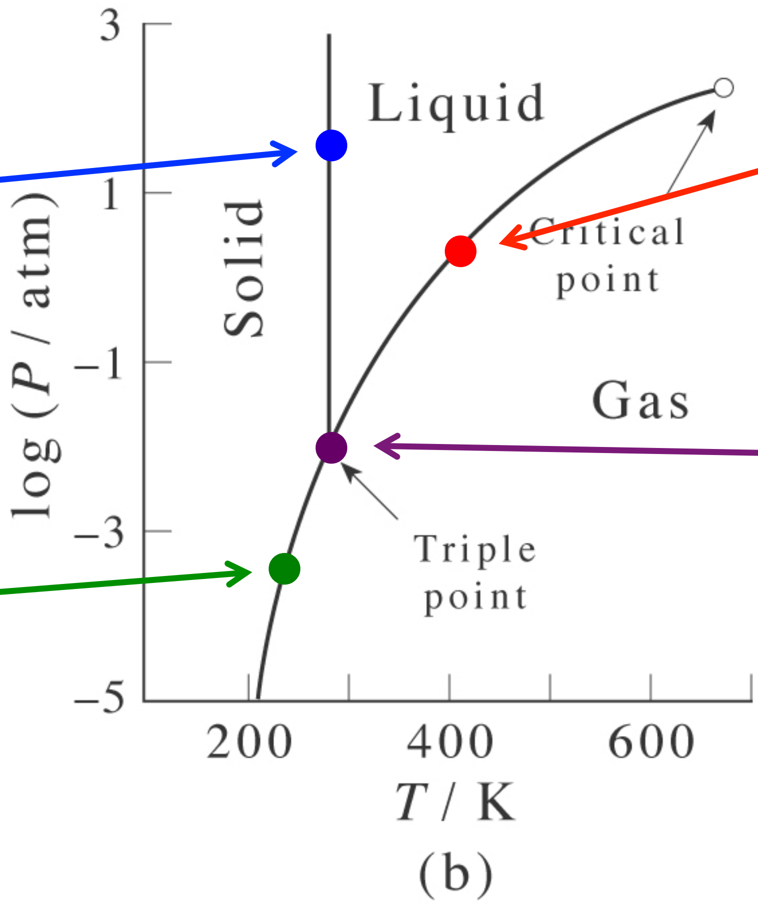
Video 10.3

Multicomponent/Multiphase Equilibria

CHEMICAL POTENTIALS AT EQUILIBRIUM

At equilibrium the chemical potential (the partial molar free energy) of each component has the same value in each phase (in contact with all the others) in which the component appears.



$\mu_j^{solid} = \mu_j^{liq}$

$\mu_j^{liq} = \mu_j^{gas}$

solution vapor

$\mu_j^{solid} = \mu_j^{liq} = \mu_j^{gas}$

$\mu_j^{solid} = \mu_j^{gas}$

note phase diagram depends *on other* $n_{i\neq j}$ *value(s)*

PHASE TRANSFER GENERALIZATION

Consider the transfer of *dn* moles of component *j* from the solution to the vapor at constant *T* and *P*:

$$\boxed{G_j^{total} = G_j^{solution} + G_j^{vapor}}$$

$$dG_j^{total} = dG_j^{sol} + dG_j^{vap} = \left(\frac{dG^{sol}}{dn_j^{sol}}\right)_{T,P,n_{i\neq j}} dn_j^{sol} + \left(\frac{dG^{vap}}{dn_j^{vap}}\right)_{T,P,n_{i\neq j}} dn_j^{vap}$$

$$= \mu_j^{sol} dn_j^{sol} + \mu_j^{vap} dn_j^{vap}$$

$$= \left(\mu_j^{vap} - \mu_j^{sol}\right) dn_j^{vap}$$ (mass balance)

Transfer occurs spontaneously when ⇨

$$dG_j^{total} < 0$$

$$dn_j^{vap} < 0, \quad dn_j^{vap} > 0$$

$$\mu_j^{vap} > \mu_j^{sol}, \quad \mu_j^{vap} < \mu_j^{sol}$$

CHEMICAL POTENTIAL IN SOLUTION

$\mu_j^{vap} = \mu_j^{sol}$ This equation holds for each component (and is general for any two phases in which j is found).

Therefore, if we know the chemical potential of each component in the vapor phase, we can get the chemical potential of that component in the solution. And, if the vapor pressure is low enough we can assume ideal behavior:

$$\mu_j^{vap} - \mu_j^{vap,\circ}(T) = RT \ln \frac{P_j}{P_j^\circ}$$

1 bar

cf. Lecture 8.7, slide 1

⇓

$$\mu_j^{vap} = \mu_j^{vap,\circ}(T) + RT \ln P_j = \mu_j^{sol}$$

Self-assessment

How does the chemical potential of the pure liquid, μ^*, relate to the standard-state potential, μ°, of the pure gas?

Self-assessment Explained

$$\mu_j^*(l) = \mu_j^*(v) = \mu_j^\circ(T) + RT\ln\frac{P_j^*}{P_j^\circ} = \mu_j^\circ(T) + RT\ln P_j^*$$

$$\mu_j^*(l) = \mu_j^\circ(T) + RT\ln P_j^*$$

Convenient Expression for μ_j^{sol}

$$\mu_j^*(l) = \mu_j^*(v) = \mu_j^\circ(T) + RT\ln P_j^*$$

$*$ denotes pure j

$$\begin{array}{rl} & \mu_j^{sol} = \mu_j^\circ(T) + RT\ln P_j \\ - & \mu_j^*(l) = \mu_j^\circ(T) + RT\ln P_j^* \\ \hline \end{array}$$

subtract these two eqs

$$\mu_j^{sol} - \mu_j^*(l) = RT\ln P_j - RT\ln P_j^*$$

$$\boxed{\mu_j^{sol} = \mu_j^*(l) + RT\ln\frac{P_j}{P_j^*}}$$

Next: Ideal Solutions