The Lecture Contains:

Previous Next

Effect of surfaces (curvature) on chemical equilibrium

Surface effects play an important role, especially during a phase change like condensation, evaporation, and solubilization.

Consider a liquid drop in its own vapor (Fig. 4.4).

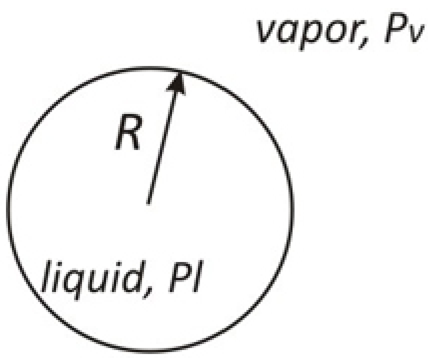

Fig 4.4:

$$R \sim 500\,\text{Å}, \Delta p = \frac{2\gamma}{R} \sim 28 atm!!$$

The equilibrium vapor pressure for flat surface depends on T and P_{total}.

A high p_l means that there is more tendency for the liquid molecules to escape to vapor phase.

Gibbs-Duhem Equation

Intensive form:

$$F = 2 - \pi + N \qquad (4.11)$$

where F is the Degrees of freedom,

If M is any molar property of a mixture the following can be written.

$$nM = M\sum_i n_i = \sum_i n_i \bar{M}_i\,; \quad \bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j} = \text{partial molar property}$$

$$d(nM) = \sum n_i d\bar{M}_i + \sum \bar{M}_i dn_i$$

$$nM = f(T, P, n_1, n_2, \dots\dots, n_l)$$

$$d(nM) = \left.\frac{\partial(nM)}{\partial T}\right|_{P,n_i} dT + \left.\frac{\partial(nM)}{\partial P}\right|_{T,n_i} dP + \sum \left.\frac{\partial(nM)}{\partial n_i}\right|_{T,P,n_j} dn_i$$

Equating the two, the generalized Gibbs-Duhem equation (a constraint) is obtained.

$$\left.\frac{\partial(nM)}{\partial T}\right|_{P,n_i} dT + \left.\frac{\partial(nM)}{\partial P}\right|_{T,n_i} dP - \sum n_i d\bar{M}_i = 0 \qquad (4.12)$$

$$nM = U, \bar{M}_i = \left.\frac{\partial U}{\partial n_i}\right|_{S,V,n_j} = \left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j}$$

$$\left.\frac{\partial U}{\partial T}\right|_{P,n_j} = -S$$

$$\left.\frac{\partial U}{\partial P}\right|_{T,n_j} = V$$

$$\therefore SdT - VdP + \sum n_i d\bar{G}_i = 0$$

$$SdT - VdP + \sum n_i d\mu_i = 0 \qquad (4.13)$$

The above equation is the Gibbs-Duhem Equation.

Previous Next

Condition for mechanical equilibrium

$$dp" - dp' = d\left\{\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right\} \qquad (4.14)$$

Condition for chemical equilibrium

$$d\mu_i' = d\mu_i^{"} = d\mu_i \qquad (4.15)$$

The Gibbs-Duhem equation for single component (for each of the phases) yields

$$\bar{s}'dT' - \bar{v}'dp' + d\mu' = 0 \qquad (4.16)$$

$$\bar{s}^{"}dT^{"} - \bar{v}^{"}dp^{"} + d" = 0 \qquad (4.17)$$

Previous Next

Condition for thermal equilibrium

$T' = T"$ (4.18)

For an isothermal system $dT = 0$. Therefore,

$\bar{v}' dp' = \bar{v}" dp"$

or $dp" = dp' + d\left(\gamma \frac{1}{r_m}\right)$

This is known as the Kelvin's Equation.

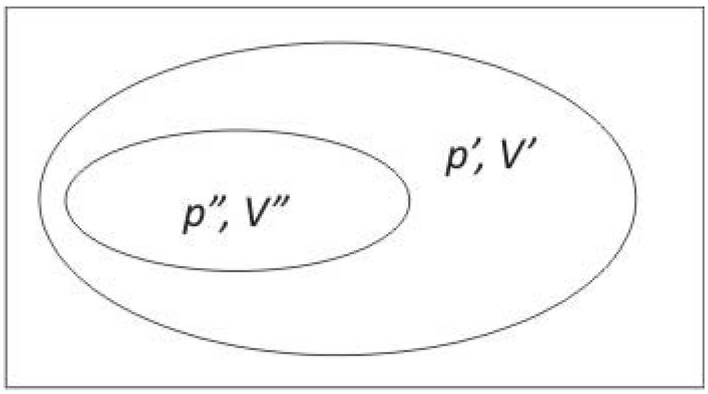

Fig. 4.5:

Consider a spherical drop of liquid in its own vapor (Fig. 4.5).

Previous Next

Notation:

$[]"$ liquid phase property

$[]'$ vapor phase property

$\frac{1}{r_m} = \frac{2}{r}$ where r is the radius of the drop

$\bar{v}" \ll \bar{v}' \approx \frac{RT}{p'}$. assuming ideal gas behaviour

$$d\left(\frac{2\gamma}{r}\right) = \frac{RT}{p'}\frac{dp'}{\bar{v}"}$$

$$\int_{r\to\infty}^{r} d\left(\frac{2\gamma}{r}\right) = \int_{p_0}^{p'} \frac{RT}{p'}\frac{dp'}{\bar{v}"}$$

$$\ln\frac{p'}{p_0} = \frac{2\gamma\bar{v}"}{rRT} \qquad (4.20)$$

where p_0 is the equilibrium vapor pressure for flat surface.

As r decreases, the equilibrium vapor pressure (p') becomes larger than p_0. This implies that in order to be in equilibrium with the liquid phase the vapor phase has to be super-saturated.

.

Module 3: "Thin Film Hydrodynamics"

Lecture 16: ""

A drop in chemical equilibrium with its surroundings

$$\ln\frac{p'}{p_0} = 2\frac{\bar{V}"\gamma}{rRT}; p' > p_0$$

As it's clear from above equation that condensation or formation of drop is possible if vapor in supersaturated state if process is kept isothermal.

This equation (Kelvin equation) tells the minimum radius of drop which would be in equilibrium with the surrounding.
However, this equilibrium is not stable equilibrium .One can easily check it by introducing a little perturbation in the equilibrium state.

Previous Next