Ch 23 : Phase Equilibria

A phase with a lower Gibbs energy is more stable.
It is thermodynamically favored, but kinetic factors may prevent its formation.

Phase diagram of benzene : see Fig 1.
The lines that separate the regions indicate pressures and temperatures at which two phases can co-exist at equilibrium.

For example, at all points along the line that separates the solid from the gas, (line CF) benzene exists as a solid and a gas in mutual equilibrium.

This line is called the solid-gas coexistance curve.
It specifies the vapor pressure of solid benzene as a function of its temperature.

Line FE, solid-liquid coexistance, gives the melting point of benzene as a function of pressure.

Lines intersect at the triple point.

- single-phase region : two thermodynamic degrees of freedom
- coexistance curves : one degree of freedom
- triple point : none (unique point)

phase diagram of a pure substance : $f = 3 - p$ phase rule
where p is the # of phases that coexist at equil.

Figs 2, 3 : the melting point is not so sensitive to pressure but the boiling point is.

The boiling point is defined to be the T at which the vapor pressure equals the atmospheric pressure, so going up in elevation changes the boiling point noticably.

Fig 23.4 : CO_2 goes directly from solid to gas at 1 atm.
(triple point is at $P = 5.11$ atm)

Fig 23.5, 23.6 are for water. The slope of the solid-liquid coexistance curve is negative, so the melting point decreases with increasing pressure.

Critical point: the liquid-gas coexistance curve ends abruptly at the critical point. As we approach the critical point along the l-g coexistance curve, the difference between the liquid phase and the gaseous phase becomes increasingly less distinct until any difference disappears entirely at the critical point.

Fig 23.7 and 23.8 show this merging of properties: a single fluid phase exists past the critical point.

A gas cannot be liquified no matter how high the pressure. From Fig 23.8 we see that $\Delta S_{vap} = 0$ at the critical point.

Look at Gibbs free energy. Want to know how the Gibbs energy changes as we go through a phase transition.

The change is continuous because

- the Gibbs energy of the liquid and vapor are the same when the liquid and vapor are in equilibrium with each other (at coexistance).
- $\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$ and $\Delta S_{vap} = \Delta H_{vap}/T_{vap}$.

Fig 22.7 : $G(T) - H(0)$ is a continuous and monotone decreasing function of T.

Now look at Fig 23.10a. This is a plot of $G(T)$ versus T in the vicinity of the melting point of benzene.

The dashed lines are for a supercooled liquid and a superheated solid.

For the solid phase branch, $G(T)$ decreases with slope $\left.\frac{\partial G}{\partial T}\right)_p = -S^{solid}$.

When the melting point is reached, the liquid phase has (equal or) lower Gibbs energy so it is thermodynamically favored. The slope of the liquid branch is steeper than that of the solid branch because $\left.\frac{\partial G}{\partial T}\right)_p = -S^l$ and $S^l > S^{solid}$.

$G^{solid} = G^l$ at T_{fus} and the slopes are ordered by $S^l > S^{solid}$. Therefore the Gibbs energy of the liquid phase must be lower than that of the solid phase at $T > T_{fus}$.

Dashed lines are metastable: they are not thermodynamically stable but may exist due to kinetic reasons.

Same story for Fig 23.10b (vaporization).

We can see from $G = H - TS$ why the solid phase is favored at low T whereas the gas phase is favored at high T.

At low T, the TS term is small compared to H and the solid phase has the lowest enthalpy of the three phases.

At high T, H is small compared to TS, so the gas with a large entropy is favored.

section 23-3 : Chemical Potential.

Consider a system consisting of two phases (liquid and gas) of a pure substance in equil. with each other.

$$G = G^l + G^g$$

Suppose dn moles of liquid are transferred to the vapor phase at constant T, P.

We know $\Delta G = 0$ for this process because at constant T, P $dG = 0$ for an equil. process.

We can write $dG = \left.\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left.\frac{\partial G}{\partial n^l}\right)_{T,P} dn^l$

and we also have $dn^l = -dn^g$ since $n^l + n^g = \text{constant}$

So this becomes $dG = \left[\left.\frac{\partial G^g}{\partial n^g}\right)_{T,P} - \left.\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$

We define the chemical potentials

$$\mu^g = \left.\frac{\partial G^g}{\partial n^g}\right)_{T,P} \quad ; \quad \mu^l = \left.\frac{\partial G^l}{\partial n^l}\right)_{T,P}$$

We can then rewrite the previous equation as

$$dG = (\mu^g - \mu^l)\, dn^g \qquad (\text{const } T, P)$$

At equil. we must have $dG = 0 \Longrightarrow \mu^g = \mu^l$.

In general, if two phases of a single substance are in equil. with each other, the chemical potentials of the two phases are equal.

If the two phases are not in equil., a spontaneous transfer of matter from one phase to the other will occur in the direction such that $dG < 0$.

Matter will "flow" from a higher chemical potential to a lower chemical potential, which is why the term "potential" is used.

What can we do with this concept of chemical potential? We will derive the Clapeyron and the Clausius-Clapeyron equations, which tell us some information about phases in equil.

G is extensive (proportional to system size): $G \propto n$.

For a single phase of a pure substance, we can express this proportionality as $G = n\mu(T,P) = n\bar{G}$

$$\mu \equiv \left.\frac{\partial G}{\partial n}\right)_{T,P} = \left.\frac{\partial\, n\mu(T,P)}{\partial n}\right)_{T,P} = \mu(T,P)$$

So $\mu(T,P)$ is the intensive (molar) Gibbs energy.

First go after the variation of equil P with T.

$$\mu^\alpha(T,P) = \mu^\beta(T,P) \quad \text{equil. between phases } \alpha, \beta.$$

Take the total derivative on both sides:

$$\left.\frac{\partial \mu^\alpha}{\partial P}\right)_T dP + \left.\frac{\partial \mu^\alpha}{\partial T}\right)_P dT = \left.\frac{\partial \mu^\beta}{\partial P}\right)_T dP + \left.\frac{\partial \mu^\beta}{\partial T}\right)_P dT$$

Now, $dG = V\,dP - S\,dT$ so that $\left.\frac{\partial G}{\partial P}\right)_T = V$; $\left.\frac{\partial G}{\partial T}\right)_P = -S$

there we have $\left.\frac{\partial \mu}{\partial P}\right)_T = \left.\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$ molar volume

and $\left.\frac{\partial \mu}{\partial T}\right)_P = \left.\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$ - molar entropy

This gives $\bar{V}^\alpha dP - \bar{S}^\alpha dT = \bar{V}^\beta dP - \bar{S}^\beta dT$

Solve for dP/dT: $$\frac{dP}{dT} = \frac{\bar{S}^\beta - \bar{S}^\alpha}{\bar{V}^\beta - \bar{V}^\alpha} = \frac{\Delta \bar{S}_{transition}}{\Delta \bar{V}_{transition}}$$

For two phases in equil., $\Delta S_{transition} = \frac{\Delta H_{transition}}{T}$, giving

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{transition}}{T\,\Delta \bar{V}_{transition}} \qquad \text{Clapeyron Equation}$$

It relates the slope of the 2-phase coexistance line in a phase diagram with the values of $\Delta \bar{H}_{transition}$ and $\Delta \bar{V}_{transition}$ for a transition between these phases.

ex ΔH_{fusion} of benzene at its melting point (1 atm) of 278.7 K is $\Delta \bar{H}_{fus} = 9.95$ kJ/mol, and $\Delta \bar{V}_{fus} = 10.3$ cm^3/mol

Thus $\frac{dP}{dT} = \frac{9950 \text{ J/mol}}{(278.7\text{K})(10.3 \text{ cm}^3/\text{mol})} = 34.2 \text{ atm K}^{-1}$.

$\Longrightarrow \frac{dT}{dP} = 0.0292 \text{ K atm}^{-1}$. Says the melting point of benzene increases by 0.0292 K per atm of pressure.

This is true only at 1 atm because derivatives only give local information.

But if we assume $\Delta \bar{H}_{fus}$ and $\Delta \bar{V}_{fus}$ are independent of pressure, we would predict that the melting point of benzene at 1000 atm is 29.2 K higher than at 1 atm, which is 307.9 K. The experimental value is 306.4 K, so we're not far off.

See Fig 23.2 → curve is not perfectly straight.

ex We know $\Delta \bar{V}_{fus} < 0$ for water.

This automatically means the slope of the solid-liquid coexistance curve in the P-T phase diagram is negative.

Now go after the Clausius-Clapeyron equation which gives the vapor pressure as a function of temperature.

For a liquid-gas or solid-gas transition, $\Delta\bar{V}_{transition}$ will depend on the temperature, so we can't extrapolate with the Clapeyron equation the way we did for the solid → liquid benzene case.

For liquid-vapor, Clapeyron says $\frac{dP}{dT} = \frac{\Delta\bar{H}_{vap}}{T(\bar{V}^g - \bar{V}^l)}$

assume $\bar{V}^g \gg \bar{V}^l$ and $\bar{V}^g \approx RT/P$ (ideal gas)

get $\frac{dP}{dT} = \frac{\Delta\bar{H}_{vap}}{T(RT/P)} \Longrightarrow \frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_{vap}}{RT^2}$

$$\Longrightarrow \frac{d\ln P}{dT} = \frac{\Delta\bar{H}_{vap}}{RT^2}$$ Clausius-Clapeyron Equation

If we still assume $\Delta\bar{H}_{vap}$ is constant (independent of T) we can integrate with respect to T, giving

$$\ln P_2/P_1 = -\frac{\Delta\bar{H}_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This is useful for calculating the vapor pressure at some temperature given $\Delta\bar{H}_{vap}$ and the vapor pressure at some other temperature.

ex benzene boils at 353.2 K at 1 atm pressure, and $\Delta\bar{H}_{vap} = 30.8$ kJ/mol. Vapor pressure at 373.2 K?

$P_1 = 1\,atm = 760$ torr. $T_1 = 353.2\,K$; $T_2 = 373.2\,K$

$$\ln P_2/760 = -\frac{30800\ J/mol}{8.314\ JK^{-1}mol^{-1}}\left(\frac{1}{373.2K} - \frac{1}{353.2K}\right)$$

$$= 0.5621$$

$\Rightarrow P_2/760 = 1.754 \Rightarrow P_2 = 1333$ torr $= 1.754$ atm

The experimental value is actually 1360 torr.

What have we really done? If we perform indefinite integration assuming $\Delta\bar{H}_{vap}$ is constant, we get

$$\ln P = -\frac{\Delta\bar{H}_{vap}}{RT} + \text{constant}$$

so if we plot ln P (log of vapor pressure) versus $1/T$, we get a straight line with slope $-\frac{\Delta\bar{H}_{vap}}{R}$

Fig 23.13