1 Equilibrium between Phases

vapor $\rightleftharpoons$ water $\rightleftharpoons$ ice

1.1 Isolated System

General Aspects :

- For an isolated system, at equilibrium, the entropy is maximized

- For multiple systems, we must consider the entire system's entropy as a maximized quantity.

Case 1: Isolated System

$$Q = \Delta \bar{E} + W$$
$$W = 0, Q = 0, \Delta \bar{E} = 0$$

For some fluctuation:

$$P(y) \propto \Omega(y) = e^{S(y)/k}, \quad \frac{P(y)}{P(\tilde{y})} = \frac{e^{S(y)/k}}{e^{S(\tilde{y})/k}} = e^{\Delta S/k}$$

where the relative prob is exponentially suppressed.

1.2 System in Contact with a Reservoir

Case 2: System is in contact with a reservoir at T

$$A' + A = A^{(0)}$$

where $S^{(0)}$ is maximized

$$\Delta S^{(0)} \geq 0 = \Delta S + \Delta S'$$

Heat transfer from the heat reservoir A' (which doesn't change in Tempertature) to the system A is

$$\Delta S' = -\frac{Q}{T_0}$$

In additiion, there is no work done on the system i.e. $Q = \Delta \bar{E}$ so

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{T_0 \Delta S - \Delta \bar{E}}{T_0} = \frac{\Delta(T_0 S - \bar{E})}{T_0} = \frac{-F_0}{T_0}$$

where

$$F_0 = T_0 S - \bar{E}$$

is the Helmholtz free energy of system A as it has the same temperature of the reservoir. Furthermore,

$$\Delta F_0 \leq 0$$

So the equilibrium condition requires a minimized free energy!

1.3   System in Contact with Reservoir at Constant Temperature and Pressure

Review :

- Case I: Isolated system:

$$S \text{maximum} : \Delta S \geq 0$$

- Case II: Systme is contact with reservoir: Minimized 'Helmholtz' free energy at constant temperature

$$\bar{F}_0 = \bar{E} - T_0 S$$

- Case III: System in contact with reservoir at constant T_0, P_0

$$A^{(0)} = A + A'$$

$$\implies \Delta S^{(0)} = \Delta S + \Delta' \geq 0 \quad \Delta S' = -\frac{Q}{T_0}$$

so the entropy of the system and reservoir must increase by

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0}(T_0 \Delta S - Q)$$

where

$$Q = \Delta \bar{E} + P_0 \Delta V$$

And doing some math movement, we find

$$= \frac{1}{T_0}(T_0 \Delta S - (\Delta \bar{E} + P_0 \Delta V))$$

$$= \frac{1}{T_0}(\Delta(T_0 S - (\bar{E} + P_0 V)))$$

or

$$\Delta S^{(0)} = -\frac{1}{T_0}\Delta G_0 \geq 0 \implies G_0 \leq 0$$

So the equilibrium contision is: "Gibbs free energy is minimized"

1.4   Stability of homogeneous substance

For the homogeneous substance, the Gibbs free energy is at a minimum

$$G_0 \equiv \bar{E} - T_0 S + P_0 V$$

and assume at equilibrium, subsystem A is at $\tilde{T}, \tilde{P}$.

Fix V and change T:

$$\left(\frac{\partial G_0}{\partial T}\right)_V = 0 \quad \text{for} \quad T = \tilde{T}$$

or using the definition

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V - T_0\left(\frac{\partial S}{\partial T}\right)_V = 0$$

where $T dS = d\bar{E}$ so

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \frac{1}{T}$$

Therefore

$$\frac{\partial G_0}{\partial T}\bigg|_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \left(1 - \frac{T_0}{T}\right) = 0$$

or $\tilde{T} = T$ at equilibrium.

Looking at the second derivative

$$\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V = \left(\frac{\partial^2 \bar{E}}{\partial T^2}\right)_V \left(1 - \frac{T_0}{T}\right) + \left(\frac{\partial \bar{E}}{\partial T}\right)_V \left(\frac{T_0}{T^2}\right) = 0$$

$$= \left(\frac{\partial \bar{E}}{\partial T}\right)_V \left(\frac{T_0}{T^2}\right) = 0$$

where

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V \geq 0$$

Worksheet

1.

$$\left(\frac{\partial G_0}{\partial V}\right)_T = \left(\frac{\partial \bar{E}}{\partial V}\right)_T - T_0 \left(\frac{\partial S}{\partial V}\right)_T + P_0 = 0$$

and from the fundamental relation

$$T \frac{\partial S}{\partial V} = \frac{\partial \bar{E}}{\partial V} + \bar{P}$$

we have (using $T = T_0$)

$$\left(\frac{\partial G_0}{\partial V}\right)_T = \frac{\partial \bar{E}}{\partial V} - \frac{T_0}{T}\left(\frac{\partial E}{\partial V} + \bar{P}\right) + P_0 = 0$$

$$= P_0 - \bar{P} = 0 \implies P_0 = \bar{P}$$

2. For the stability condition; the second derivative of G_0 must be positive

$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = \left(\frac{\partial^2 \bar{E}}{\partial V^2}\right)_T - T_0 \left(\frac{\partial^2 S}{\partial V^2}\right)_T + 0 \geq 0$$

and again

$$T \frac{\partial^2 S}{\partial V^2} = \frac{\partial^2 \bar{E}}{\partial V^2} + \frac{\partial \bar{P}}{\partial V}$$

so

$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = -\left(\frac{\partial \bar{P}}{\partial V}\right) \geq 0 \implies \kappa = -\left(\frac{\partial \bar{P}}{\partial V}\right) \geq 0$$

where κ is the compressibility of the system.

1.4.1   Equilibrium between Phases

Consider a single component system consisting of two phases 1, 2, e.g., liquid & gas, liquid & solid.
    For certain equilibrium, phases can co-exist; the G_0 must still be a minimum

- Assume:

$$n_1 = \# \text{ of moles in phase 1}$$
$$n_2 = \# \text{ of moles in phase 2}$$
$$g_1 : \text{Gibbs free energy per more of phase 1}$$
$$g_2 : \text{Gibbs free energy per more of phase 2}$$

- At T, P

$$G = n_1 g_1 + n_2 g_2 \quad n_1 + n_2 = n$$
$$G = (n - n_2) g_1 + n_2 g_2$$

So at equilibrium G is a a minimum

$$dG = -g_1 dn_2 + g_2 dn_2$$
$$= (g_2 - g_1) dn_2 = 0 \implies g_1(T, P) = g_2(T, P)$$

or a phase equilibrium line on the $T - P$ diagram.
    At a point B on the line,

$$g_1(T + dT, P + dP) = g_2(T + dT, P + dP)$$

or

$$dg_i = \left(\frac{\partial g_i}{\partial T} \right)_P dT + \left(\frac{\partial g_i}{\partial P} \right)_T dP$$

So using the fundamental relation (where the lower case is the per molar quantity)

$$dg = d(\epsilon - Ts + Pv) = -s dT + v dP$$

And at the equilibrium point B

$$dg_1 = dg_2 = \implies -s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

or rewritten as

$$(s_2 - s_1) dT = (v_2 - s_1) dP \implies \frac{dP}{dT} = \frac{\Delta s}{\Delta s}$$

We can see that dP/dT is the slope of the line on the $T - P$ diagram AKA the 'Clausius-Clapeyron equation'. Using the definition $\Delta S = Q/T$ or latent heat of transformation from phase 1 to phase 2, $L_{12} = T \Delta S$:

$$\frac{dP}{dT} = \frac{Q}{T \Delta V} = \frac{L_{12}}{T \Delta V}$$

Simple Phase Transformation: Solid $\rightarrow$ Liquid:

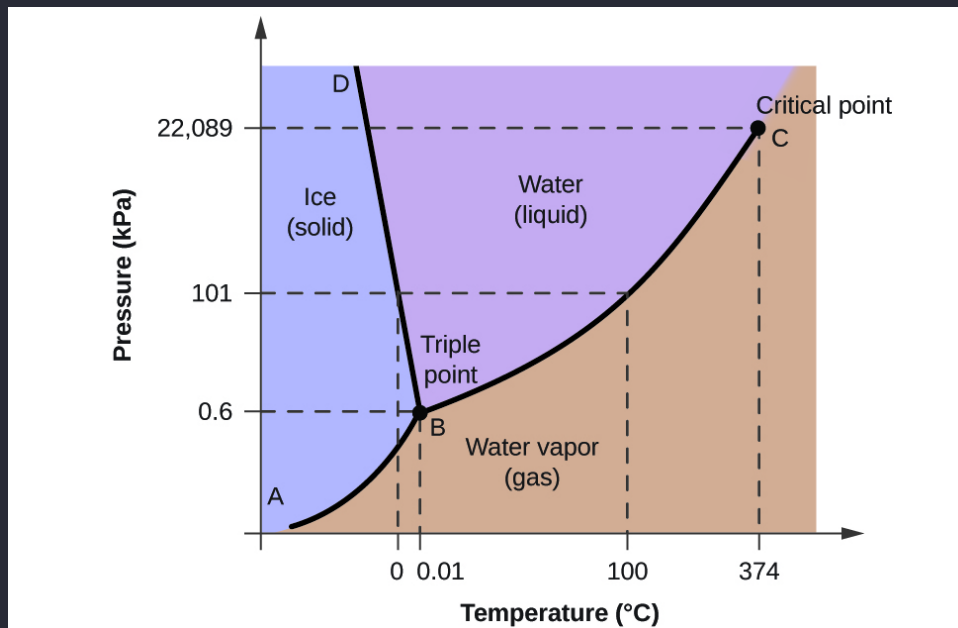- Entropy $\uparrow$ increases

- Absorb heat

Figure 1.1: Phase diagram of water

Worksheet

- For a phase diagram similar to water, as melt from Solid to Liquid, the pressure decrease, so the material expands.

- Using the CC equation

$$dP = \frac{L_{12}}{T\Delta V}dT$$

$$\implies \Delta P = \int L_{12}\frac{dT}{T\Delta V} = \frac{L_{12}}{\Delta V}\ln\frac{T_2}{T_1}$$

As an ideal gas $pv = RT \implies v = RT/p$ so

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{pl_{12}}{RT^2}$$

$$\frac{1}{p}dp = \frac{l_{12}}{RT^2}dT$$

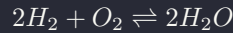integrating both sides

$$\ln p = -\frac{l_{12}}{RT} + C$$

or

$$p = p_0 e^{-l_{12}/RT}$$

So pressure increases very very rapidly with T.

1.5   Chemical Equilibrium: systems with several components

E.g.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

"Chemical potential", systems with several components:

Consider a system with $\bar{E}, V$, m different kinds of components (e.g. molecules), and N_i number of each type:

$$S = S(E, V, N_1, N_2, \ldots, N_m)$$

The number N_i can change due to chemical reactions.

For general infinitesimal process

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{j\neq i}} dN_i$$

where

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \frac{\partial S}{\partial V} = \frac{P}{T}$$

and a new quantity

$$\mu_i = -T\left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{j\neq i}}$$

or the "chemical potential" per molecule of of the ith species. So we can rewrite to

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_i^m \frac{\mu_i}{T}dN_i$$

Other forms   We can also express μ_i in different forms by moving stuff around:

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

or

$$\implies \mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

In terms of the Helmholtz free energy

$$F = E - TS \implies dF = d(E - TS)$$

or

$$\implies \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

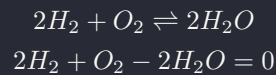And in terms of the Gibbs free energy

$$d(E - TS + pV) = dG$$

so

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

If there is only 1 species of a molecule then

$$G = G(T, p, N) = Ng'(T, p) \implies \mu = g'(T, p)$$

1.6 General conditions for chemical equilibrium

For m different molecules labels $B_1, B_2, \ldots, B_m$: e.g.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
$$2H_2 + O_2 - 2H_2O = 0$$

and $b_1, b_2, \ldots, b_m$ are the stoichiometric coefficients so

$$\sum b_i B_i = 0$$

So for the water example $m = 3$:

$$B_1 = H_2, \quad B_2 = O_2, \quad B_3 = H_2O$$
$$b_1 = 2, \quad b_2 = 1, \quad b_3 = -2$$

For N_i number of B_i molecules

$$dN_i = \lambda b_i$$

where λ is a constant.

- For an isolated system, the entropy S is maximized

$$dS = 0$$
$$V = \text{constant} \implies dV = 0$$
$$\bar{E} = \text{constant} \implies dE = 0$$

so from the previous lecture

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dN_i \implies \sum \frac{\mu_i}{T}dN_i = 0$$

or

$$\sum_{i=1}^{m} \mu_i b_i = 0$$

So if we measure the μ_1, μ_2, μ_3 for the water example, we can determine the equilibrium condition

$$\sum b_i \mu_i = 0 = 2\mu_1 + \mu_2 - 2\mu_3$$