Lecture 13, Oct 6, 2022

Phase Change

- We assume a phase is either liquid, vapour, or solid and only deal with pure substances
- Most applications involve phase changes
  - e.g. cooling down a hot surface by blowing a fluid across the surface (surface cooling)
    - If we used air, $c_p \approx 1\text{kJ/kg K}$, but if we used water and get it to boil, the latent heat is approximately 2000kJ/kg
    - If we can get the water to boil we can carry away orders of magnitude more heat
  - Steam turbines are also an example

Two-Phase Mixtures

- e.g. getting vapour bubbles when we heat water, or water carried along in a steam pipe
- How do we define properties for such a mixed system? We have neither an incompressible liquid nor an ideal gas

Phase Transitions

- Consider if we had a tank with a liquid and a vapour
  - The molecules in the liquid are much closer together; in the vapour molecules are much further apart
  - The liquid molecules have varying energies, some with enough energy to break loose (evaporation)
  - At the same time, the vapour molecules are hitting the surface of the liquid, some with low enough energy that they are re-captured (condensation)
  - Eventually we will reach a point where the rate of evaporation equals the rate of condensation, and we have *phase equilibrium*
- At phase equilibrium, the pressure of the system is constant; we define this as the *saturation pressure* P_{sat}
  - The temperature will also be constant, defined as the *saturation temperature* T_{sat}
- If we increase the temperature, more molecules end up in the vapour at phase equilibrium ($P_{sat}, T_{sat} \uparrow$)
- The rate of evaporation is proportional to the surface area
- If we consider the energy distribution of the molecules, the molecules evaporating have a higher energy, so evaporation removes the most energetic molecules, resulting in cooling of a liquid
- To keep the temperature constant, we need to supply energy
  - This is defined as the *latent heat of evaporation*
- Consider a system with a liquid and vapour and consider an infinitesimal amount of mass δm going from liquid to vapour
  - Treat either the liquid or the vapour as an open system
  - How much is the energy change of this system?
  - Consider forcing the system to a constant temperature and pressure
  - Consider an infinitesimal δs being pushed into the system
  - The net change in internal energy (PE, KE change assumed 0) so $\mathrm{d}u = \delta q + \delta w + h\,\mathrm{d}m$
    - Enthalpy change includes flow rate
  - Entropy change is $\mathrm{d}s = \frac{\delta q}{T} + \delta \mathrm{d}m \implies \delta q = T\,\mathrm{d}s - Ts\,\mathrm{d}m$
  - If we assume reversibility $\delta w = -P\,\mathrm{d}V$
  - $\mathrm{d}U = T\mathrm{d}s - P\,\mathrm{d}V + (h - Ts)\,\mathrm{d}m$
- Energy change is due to 3 terms: heat transfer, work, and mass transfer

Definition

The Gibbs Energy $G = H - TS$ and the specific Gibbs Energy $g = \dfrac{G}{m} = h - Ts$, also known as the chemical potential

A difference in the Gibbs energy results in mass transfer

- Then energy change is $\mathrm{d}U = T\,\mathrm{d}s - P\,\mathrm{d}V + g\,\mathrm{d}m$
- g is the increase in energy of an open system per unit mass added

Important

Gibbs equation for an open system:

$$\mathrm{d}s = \frac{\mathrm{d}U}{T} + \frac{P}{T}\mathrm{d}V - \frac{g}{T}\,\mathrm{d}m$$

Phase Equilibrium

- Consider an isolated system partially filled with saturated liquid and partially filled with saturated vapour
- What is the condition for phase equilibrium?
  - Start with the state principle: $S = S(U, V, m)$
    - We have two components, the saturated vapour (subscript g) and the saturated liquid (subscript f)
  - Total entropy: $S = S_f(U_f, V_f, m_f) + S_g(U_g, V_g, m_g)$
  - At equilibrium $\mathrm{d}S = 0 \implies \mathrm{d}S_f + \mathrm{d}S_g = 0$
  - $\mathrm{d}S_f = \dfrac{\mathrm{d}U_f}{T_f} + \dfrac{P_f}{T_f}\mathrm{d}V_f - \dfrac{g_f}{T_f}\mathrm{d}m_f, \mathrm{d}S_g = \dfrac{\mathrm{d}U_g}{T_g} + \dfrac{P_g}{T_g}\mathrm{d}V_g - \dfrac{g_g}{T_g}\mathrm{d}m_g$
  - Isolated system so $\mathrm{d}U_f = -\mathrm{d}U_g, \mathrm{d}V_f = -\mathrm{d}V_g, \mathrm{d}m_f = -\mathrm{d}m_g$
  - Combining these two we get $\mathrm{d}S = \left(\dfrac{1}{T_f} - \dfrac{1}{T_g}\right)\mathrm{d}U_f + \left(\dfrac{P_f}{T_F} - \dfrac{P_g}{T_g}\right)\mathrm{d}V_f + \left(\dfrac{g_f}{T_f} - \dfrac{g_g}{T_g}\right)\mathrm{d}m_f = 0$
  - $\mathrm{d}U_f, \mathrm{d}V_f, \mathrm{d}m_f$ are all arbitrary (we never said how much the mass, volume, etc had to change), so each of the terms in the brackets are independently zero
  - Therefore the equilibrium condition is: $\begin{cases} T_f = T_g \\ P_f = P_g \\ g_f = g_g \end{cases}$
- $g_f = g_g$ is new – at equilibrium there is no exchange of gas between two phases whose chemical potentials are the same
- g, the specific Gibbs energy, drives mass exchange
  - Assume T, P are constant but $g_f > g_g$, then $\mathrm{d}S = -\dfrac{1}{T_f}(g_f - g_g)\mathrm{d}m_f > 0 \implies \mathrm{d}m_f < 0$
  - If $g_f > g_g$ then there is mass transfer from the liquid to the vapour (evaporation)
  - Conversely if $g_g < g_f$ then there is mass transfer from vapour to liquid (condensation)
- If chemical potentials are unequal, then there will be mass exchange until chemical potentials are equal