Lecture 10 (Videos)

Postulate of Thermodynamics

- *Fundamental properties* are properties that cannot be explained in simpler terms:
  - By defining them we are postulating fundamental assumptions
- Fundamental properties (postulates):
  - Mass: matter exists
  - Volume: matter takes up space
  - Energy: matter moves and interacts
  - Entropy: interactions between pieces of matter lead to equilibrium
- Other properties:
  - Time is a fundamental property, but we don't care about it since we only deal with equilibrium states which are independent of time
  - All other properties can be expressed in terms of fundamental properties (including temperature and pressure)
- Four Postulates:
  - State Postulate: All isolated systems reach a state of equilibrium; the equilibrium state of a pure, simple compressible substance is completely described by its mass, volume, and internal energy
    - $S = S(U, V, m)$
  - First Law: The change in energy of a closed system equals the net energy transferred to it in the form of work and heat
    - $Q + W = \Delta E$
  - Second Law: The entropy of an isolated system increases until equilibrium, at which point it remains constant
    - $\Delta S \geq 0$
  - Third Law: The entropy of a pure substance in equilibrium at absolute zero is zero
    - $S = 0$ at $T = 0$
- Using these fundamental properties and postulates we can develop thermodynamics as a logical system

Defining Temperature

- T can be defined in terms of fundamental properties
- Consider system A and B at different temperatures, brought together to form system C; what is the condition for C to reach thermal equilibrium?
  - The two systems have m_A, V_A, m_B, V_B fixed, so only U_A, U_B may change
  - $S_C = S_A(U_A, V_A, m_A) + S_B(U_B, V_B, m_B) \implies \mathrm{d}S_C = \frac{\partial S_A}{\partial U_A}\mathrm{d}U_A + \frac{\partial S_B}{\partial U_B}\mathrm{d}U_B$
  - At equilibrium $\mathrm{d}S_C = 0$ (entropy is constant)
  - C is isolated so $U_C = U_A + U_B = \text{const} \implies \mathrm{d}U_A = -\mathrm{d}U_B$
  - Substituting this we have $\mathrm{d}S_C = \left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\right)\mathrm{d}U_A = 0$
  - Therefore for thermal equilibrium we must have $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$ – what does this mean?

Definition

Temperature $T = \left(\frac{\partial U}{\partial S}\right)_{m,V}$

- The equilibrium condition becomes $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \implies \frac{1}{T_A} = \frac{1}{T_B} \implies T_A = T_B$
  - This satisfies our understanding of temperature since the system is at thermal equilibrium when temperatures are the same

- If $T_A > T_B$ then $\mathrm{d}S_C = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\mathrm{d}U_A > 0$ must be true; to satisfy this $\mathrm{d}U_A < 0$
  - This means energy of system A decreases while energy of B increases
  - This matches our understanding since we have heat transfer from A to B

Defining Pressure

- Consider a container with two compartments A and B separated by a locked piston, initially with different pressures; when the piston is removed the system goes to equilibrium; what is the equilibrium condition?
  - $S_C = S_A(U_A, V_A, m_A) + S_B(U_B, V_B, m_B) \implies \mathrm{d}S_C = \frac{\partial S_A}{\partial U_A}\mathrm{d}U_A + \frac{\partial S_A}{\partial V_A}\mathrm{d}V_A + \frac{\partial S_B}{\partial U_B}\mathrm{d}U_B + \frac{\partial S_B}{\partial V_B}\mathrm{d}V_B$
  - Energy and volume are constant so $\mathrm{d}U_A = -\mathrm{d}U_B, \mathrm{d}V_A = -\mathrm{d}V_B$
  - $\mathrm{d}S_C U = \left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\right)\mathrm{d}U_A + \left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right)\mathrm{d}V_A = \left(\frac{1}{T_A} - \frac{\partial 1}{\partial T_B}\right)\mathrm{d}U_A + \left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right)\mathrm{d}V_A$
  - For a system at equilibrium $T_A = T_B$ so $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$

Definition

The thermodynamic pressure P, such that $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{m,U} \implies P = T\left(\frac{\partial S}{\partial V}\right)_{m,U}$

- Substituting this back in we have $\mathrm{d}S_C = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\mathrm{d}U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\mathrm{d}V_A$
  - At equilibrium we would require $T_A = T_B, P_A = P_B$
  - If the system is not at equilibrium (assume $T_A = T_B = T$, but $P_A > P_B$), then $\mathrm{d}S_C = \left(\frac{P_A}{T} - \frac{P_B}{T}\right)\mathrm{d}V_A > 0 \implies (P_A - P_B)\mathrm{d}V_A > 0 \implies \mathrm{d}V_A > 0$
  - This means system A, at higher pressure, expands while system B contracts, which matches our understanding of pressure

Calculating Entropy Changes

- In terms of intensive properties $\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v, \frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u$
- $s = s(u, v) \implies \mathrm{d}s = \left(\frac{\partial s}{\partial u}\right)_v \mathrm{d}u + \frac{\partial s}{\partial v}u\mathrm{d}v = \frac{1}{T}\mathrm{d}u + \frac{P}{T}\mathrm{d}v$

Important

The Gibbs Equation: $\mathrm{d}s = \frac{1}{T}\mathrm{d}u + \frac{P}{T}\mathrm{d}v$

Alternative form: $\mathrm{d}s = \frac{\mathrm{d}h}{T} - \frac{v}{T}\mathrm{d}P$

- This gives us the change in entropy as a function of things we can easily measure
- For an impressible substance, $\mathrm{d}v = 0 \implies \mathrm{d}s = \frac{1}{T}\mathrm{d}u$ and $c_p = c_p = c$ and $\mathrm{d}u = c(T)\mathrm{d}T$, so $\mathrm{d}s = c(T)\frac{\mathrm{d}T}{T}$
  - $\Delta s = s_2 - s_1 = \int_{T_1}^{T_2} c(T)\frac{\mathrm{d}T}{T}$

  - $\Delta s = c_{avg} \ln \frac{T_2}{T_1}$
  - Notice $\Delta s = c_{avg}(\ln T_2 - \ln T_1)$, compare to $\Delta u = c_{avg}(T_2 - T_1)$
- For an ideal gas $\mathrm{d}u = c_v(T)\mathrm{d}T$ and $\frac{P}{T} = \frac{R}{v} \implies \mathrm{d}s = \frac{c_v(T)}{T}\mathrm{d}T + R\frac{\mathrm{d}v}{v}$
  - $\Delta s = \int_{T_1}^{T_2} c_v(T)\frac{\mathrm{d}T}{T} + \int_{v_1}^{v_2} R\frac{dv}{v}$
  - Assume constant c_v, then $\Delta s = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$
  - This gives $\Delta s = \Delta s(T, v)$
  - From the ideal gas equation $\frac{T_2}{T_1} = \frac{P_2}{P_1}\frac{v_2}{v_1}$ so $\Delta s = c_v \ln \frac{P_2}{P_1} + (c_v + R) \ln \frac{V_2}{V_1}$
  - This gives $\Delta s = \Delta s(P, v) = c_v \ln \frac{P_2}{P_1} + c_p \ln \frac{v_2}{v_1}$
  - For $\Delta s(P, T)$: $T\mathrm{d}s = \mathrm{d}u + P\mathrm{d}v$, $h = u + Pv \implies \mathrm{d}h = \mathrm{d}u + P\mathrm{d}v + v\mathrm{d}P \implies \mathrm{d}u + P\mathrm{d}v = \mathrm{d}h - v\mathrm{d}P \implies T\mathrm{d}s = \mathrm{d}h - v\mathrm{d}P$
    - Alternative form of the Gibbs equation: $\mathrm{d}s + \frac{\mathrm{d}h}{T} - \frac{v}{T}\mathrm{d}P$
  - For an ideal gas $\mathrm{d}h = c_p(T)\mathrm{d}T$ and $\frac{v}{T} = \frac{R}{P}$ so $\mathrm{d}s = \frac{c_p(T)}{T}\mathrm{d}T - R\frac{\mathrm{d}P}{P}$
    - $\Delta s(P, T) = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$

Summary

For constant specific heat, for an ideal gas:

- $\Delta s(T, v) = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$
- $\Delta s(P, v) = c_v \ln \frac{P_2}{P_1} + c_p \ln \frac{v_2}{v_1}$
- $\Delta s(P, T) = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$

For an incompressible substance, $\Delta s = c_{avg} \ln \frac{T_2}{T_1}$

- For variable specific heat, consider $\int_{T_1}^{T_2} c_p(T)\frac{\mathrm{d}T}{T} = \int_{T_{ref}}^{T_2} c_p(T)\frac{\mathrm{d}T}{T} - \int_{T_{ref}}^{T_1} c_p(T)\frac{\mathrm{d}T}{T}$
- Define $s^0(T_0) = \int_{T_{ref}}^{T_0} c_p(T)\frac{\mathrm{d}T}{T}$, so that we can instead use $s^0(T_2) - s^0(T_1)$ instead of $c_v \ln \frac{T_2}{T_1}$ whenever specific heat is nonconstant
  - Air tables list these values of s^0
  - Usually $s^0 = 0$ at $T_{ref} = 0\mathrm{K}$

Important

When c_p is nonconstant, instead of $c_p \ln \frac{T_2}{T_1}$, use $s^0(T_2) - s^0(T_1)$