Key points of the last lecture

- Heats of formation
- Bond Energies
- Experimental measurement of $\Delta H$
Key points of this lecture

- Introduce the concept of entropy
- Carnot cycle
- S is a state function!
- Efficiency of a Carnot engine
Entropy

\[ \Delta U = q + w \]

The first law describes the equivalence of work and heat and we learnt that reversible reactions maximize work.

But, we haven’t learnt anything about the “natural direction” of a particular process.
The second law of thermodynamics does the following:

- Puts restrictions on the useful conversion of heat into work
- Follows from the observation of a directionality to natural or spontaneous processes
- Provides rules for
  1. determining the direction of spontaneous change
  2. determining the equilibrium state of a system

Introduce a new state function called entropy, $S$

$$dS = \frac{dq_{rev}}{T}$$
Carnot Cycle

The Carnot cycle consists of four processes:

1. Isothermal expansion (from state a to state b) at constant temperature $T_{hot}$.
2. Adiabatic expansion (from state b to state c) where no heat is exchanged with the surroundings.
3. Isothermal compression (from state c to state d) at constant temperature $T_{cold}$.
4. Adiabatic compression (from state d to state a) where no heat is exchanged with the surroundings.

The cycle starts and ends at the same state (a to a), with the highest pressure at state a and the lowest pressure at state d. The cycle is reversible and represents the most efficient possible heat engine.
Step 1: Isothermal expansion from $V_a$ to $V_b$ at $T_{\text{hot}}$

$$\Delta U_1 = 0$$

$$w_1 = -\int_{V_a}^{V_b} PdV = -\int_{V_a}^{V_b} \frac{nRT_{\text{hot}}}{V} dV = -nRT_{\text{hot}} \ln \left(\frac{V_b}{V_a}\right)$$

$$q_1 = -w_1 = nRT_{\text{hot}} \ln \left(\frac{V_b}{V_a}\right)$$
Step 2: Adiabatic expansion from $V_b$ to $V_c$

\[ q_2 = 0 \]

\[ \Delta U_2 = w_2 \]

\[ \Delta U_2 = w_2 = C_v (T_{cold} - T_{hot}) \]

\[
\int_{T_{hot}}^{T_{cold}} C_v dT = -\int_{V_b}^{V_c} \frac{nRT}{V} dV
\]

\[ C_v \ln \left( \frac{T_{cold}}{T_{hot}} \right) = nR \ln \left( \frac{V_b}{V_c} \right) \]
Step 3: Isothermal compression from $V_c$ to $V_d$ at $T_{\text{cold}}$

\[ \Delta U_3 = 0 \]

\[ w_3 = -\int_{V_c}^{V_d} P \, dV = -\int_{V_c}^{V_d} \frac{nRT_{\text{cold}}}{V} \, dV = -nRT_{\text{cold}} \ln \left( \frac{V_d}{V_c} \right) \]

\[ q_3 = -w_3 = nRT_{\text{cold}} \ln \left( \frac{V_d}{V_c} \right) \]
Step 4: Adiabatic compression from \( V_d \) to \( V_a \)

\[
q_4 = 0
\]

\[
\Delta U_4 = w_4
\]

\[
\Delta U_4 = w_4 = C_v (T_{hot} - T_{cold})
\]

\[
\int_{T_{cold}}^{T_{hot}} C_v dT = - \int_{V_d}^{V_a} \frac{nRT}{V} dV
\]

\[
C_v \ln \left( \frac{T_{hot}}{T_{cold}} \right) = nR \ln \left( \frac{V_d}{V_a} \right)
\]
Relating the ratios of the volumes

\[ C_v \ln \left( \frac{T_{\text{hot}}}{T_{\text{cold}}} \right) = nR \ln \left( \frac{V_d}{V_a} \right) = nR \ln \left( \frac{V_c}{V_b} \right) \]

\[ \left( \frac{V_d}{V_a} \right) = \left( \frac{V_c}{V_b} \right) = \left( \frac{V_d}{V_c} \right) = \left( \frac{V_a}{V_b} \right) \]

Finding the total change in heat during the cycle

\[ q_{\text{total}} = q_1 + q_2 + q_3 + q_4 \]

\[ = nRT_{\text{hot}} \ln \left( \frac{V_b}{V_a} \right) + 0 + nRT_{\text{cold}} \ln \left( \frac{V_d}{V_c} \right) \]

\[ = nR \left( T_{\text{hot}} - T_{\text{cold}} \right) \ln \left( \frac{V_b}{V_a} \right) \]
Finding the total change in work during the cycle

\[ w_{\text{total}} = w_1 + w_2 + w_3 + w_4 \]

\[ = -nRT_{\text{hot}} \ln \left( \frac{V_b}{V_a} \right) + C_v \left( T_{\text{cold}} - T_{\text{hot}} \right) - nRT_{\text{cold}} \ln \left( \frac{V_d}{V_c} \right) + C_v \left( T_{\text{hot}} - T_{\text{cold}} \right) \]

\[ = -nR \left( T_{\text{hot}} - T_{\text{cold}} \right) \ln \left( \frac{V_b}{V_a} \right) \]

Finding the total change in internal energy during the cycle

\[ \Delta U = q_{\text{total}} + w_{\text{total}} = 0 \]
Finding the total change in entropy during the cycle

\[
\Delta S = \sum_i \frac{q_i}{T_i} = \frac{q_1}{T_{hot}} + \frac{q_2}{T_2} + \frac{q_3}{T_{cold}} + \frac{q_4}{T_4}
\]

\[
= \frac{nRT_{hot}}{T_{hot}} \ln \left( \frac{V_b}{V_a} \right) + 0 + \frac{nRT_{cold}}{T_{cold}} \ln \left( \frac{V_d}{V_c} \right) + 0
\]

\[
= nR \ln \left( \frac{V_b}{V_a} \right) - nR \ln \left( \frac{V_b}{V_a} \right)
\]

\[
= 0
\]

Entropy is also a state function!
Efficiency of a Carnot engine

\[
\text{efficiency} = \varepsilon = \frac{|w_{\text{total}}|}{q_{\text{total}}}
\]

\[
\varepsilon = \frac{|w_1 + w_2 + w_3 + w_4|}{q_1 + q_2 + q_3 + q_4} = \frac{|w_1 + w_2 + w_3 + w_4|}{q_1 + q_3}
\]
\[
\varepsilon = \left| \frac{w_1 + w_2 + w_3 + w_4}{q_1 + q_2 + q_3 + q_4} \right| = \left| \frac{w_1 + w_2 + w_3 + w_4}{q_1 + q_3} \right|
\]

Since \( q_3 \) is discharged at a lower temperature it escapes into the environment and is lost.

\[
\varepsilon = \left| \frac{W_{total}}{q_1} \right|
\]

\[
\varepsilon = 1 - \frac{T_{cold}}{T_{hot}}
\]
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