EG3029 Chemical Thermodynamics

Second Law of Thermodynamics

General Remarks

- First Law: Energy is conserved during a process
- But there are open questions:
  - In which direction is a process running naturally?
  - How efficient can a process be?
  - ...
  - ...and why do we need to reject heat from heat engines?

Photo: Arturo Ramos

Statements of Second Law

- Statement 1: No apparatus can operate in such a way that its *only effect* (in systems and surroundings) is to convert heat absorbed by a system *completely* into work done by the system.
- Statement 2: No process is possible which consists *solely* in the transfer of heat from one temperature level to a higher one.

Heat Engines

- Production of power from heat is an important task for engineers
- Heat often delivered from combustion
- Challenge: Generation of mechanical power with high efficiency
- Thermal efficiency:

$$\boxed{\eta = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}}$$

Carnot Engines

- Carnot-engine cycle: reversible process defines highest possible efficiency

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$

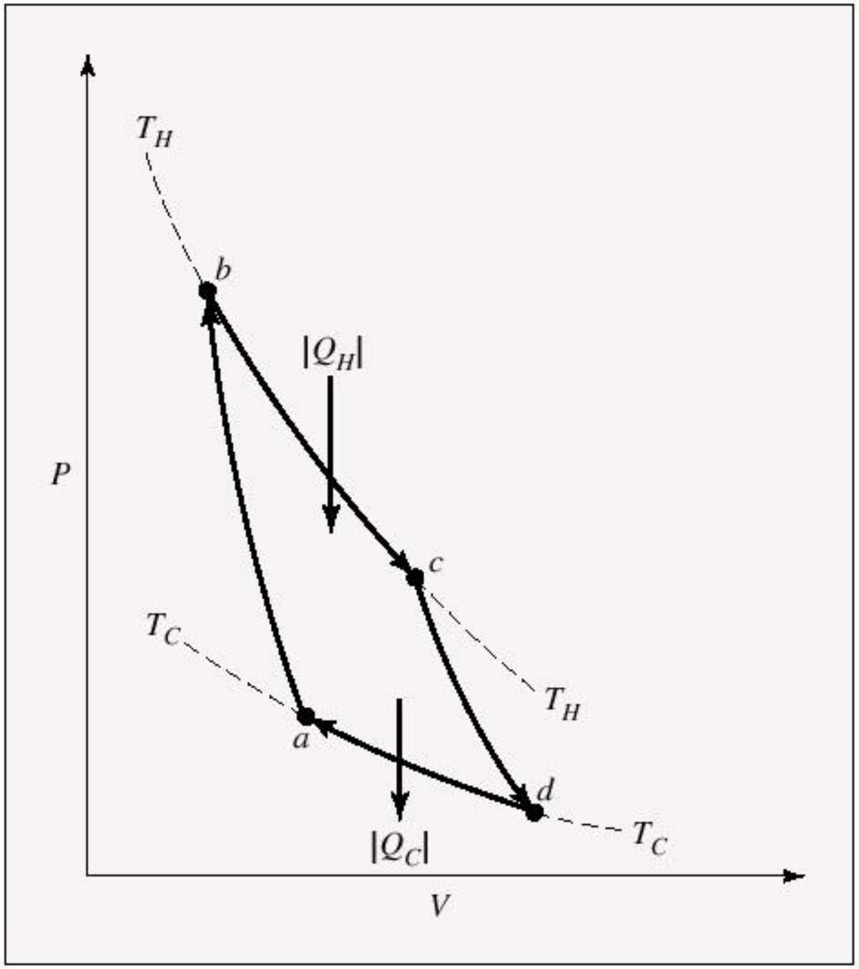
  - Step 1: Reversible adiabatic process ($T_C \rightarrow T_H$)
  - Step 2: Reversible isothermal process @ T_H
  - Step 3: Reversible adiabatic process ($T_H \rightarrow T_C$)
  - Step 4: Reversible isothermal process @ T_C

Carnot Engines

- Carnot-engine cycle: ideal gas process

$$\left|Q_H\right| = RT_H \cdot \ln \frac{V_c}{V_b}$$

$$\left|Q_C\right| = RT_C \cdot \ln \frac{V_d}{V_a}$$



Entropy

- Every body contains entropy
- Heat transfer always goes along with entropy transfer

$$\frac{transfered\,heat}{transfered\,entropy} = temperature$$

$$\frac{dQ}{dS} = T$$

- Work is not associated with entropy
- Entropy can be produced but not consumed

$$\Delta S_{total} \geq 0$$

Entropy
Ideal Gas

- Mechanically reversible process of closed system

$$\boxed{dU = dQ_{rev} - PdV}$$

- Applying the definition of entropy and enthalpy yields:

$$\boxed{\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_p^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0}}$$

relates properties only → independent of process

Exergy

- The amount of heat that can be converted to work is limited
- Max. work to be gained in ideal reversible process

$$\boxed{W_{\max} = Q_H \left(1 - \frac{T_0}{T_H}\right) = B}$$

- Exergetic efficiency is a better measure of process performance than thermal efficiency

$$\boxed{\eta_B = \frac{work\ output}{ideal\ work = exergy}}$$