Lecture 8

Tuesday, October 1, 2024 09:57

Topic 3A: Entropy Continued

The Second Law: heat does not flow spontaneously from a cool object to a hotter object.

$\Delta S_{tot} \geq 0$ for a spontaneous process

$\Delta S + \Delta S_{sur}$

Mathematical definitions

Statistical (Boltzmann): $S = k_B \ln \Omega$

Ω : number of microstates

Thermodynamic: $dS = \dfrac{dq_{rev}}{T}$

$$\Delta S = \frac{q_{rev}}{T}$$

Practice Problem :

Calculate the entropy change of a sample of perfect gas when it expands isothermally from a volume V_i to a volume V_f.

Solution : isothermal process, $\Delta T = 0$

$\Delta U = C_v \Delta T$; $\Delta U = 0$

$$\Delta U = q + w$$

$$\Delta U = q_{rev} + \underbrace{w_{rev}}_{\text{reversible}}$$

$$0 = q_{rev} + w_{rev}$$

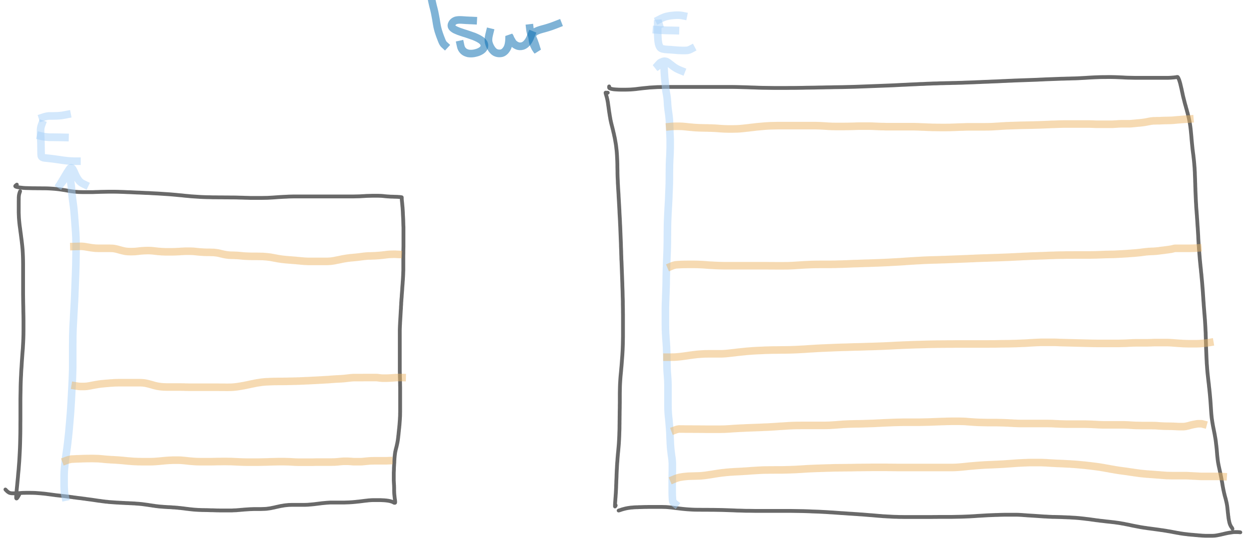
$$q_{rev} = - w_{rev}$$

$$w_{rev} = -nRT \ln \frac{V_f}{V_i}$$

$$q_{rev} = + nRT \ln \frac{V_f}{V_i}$$

$$\boxed{\Delta S = \frac{q_{rev}}{T} = +nR\ln\frac{V_f}{V_i}}$$

$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}}$$ for the surroundings



smaller V   larger V

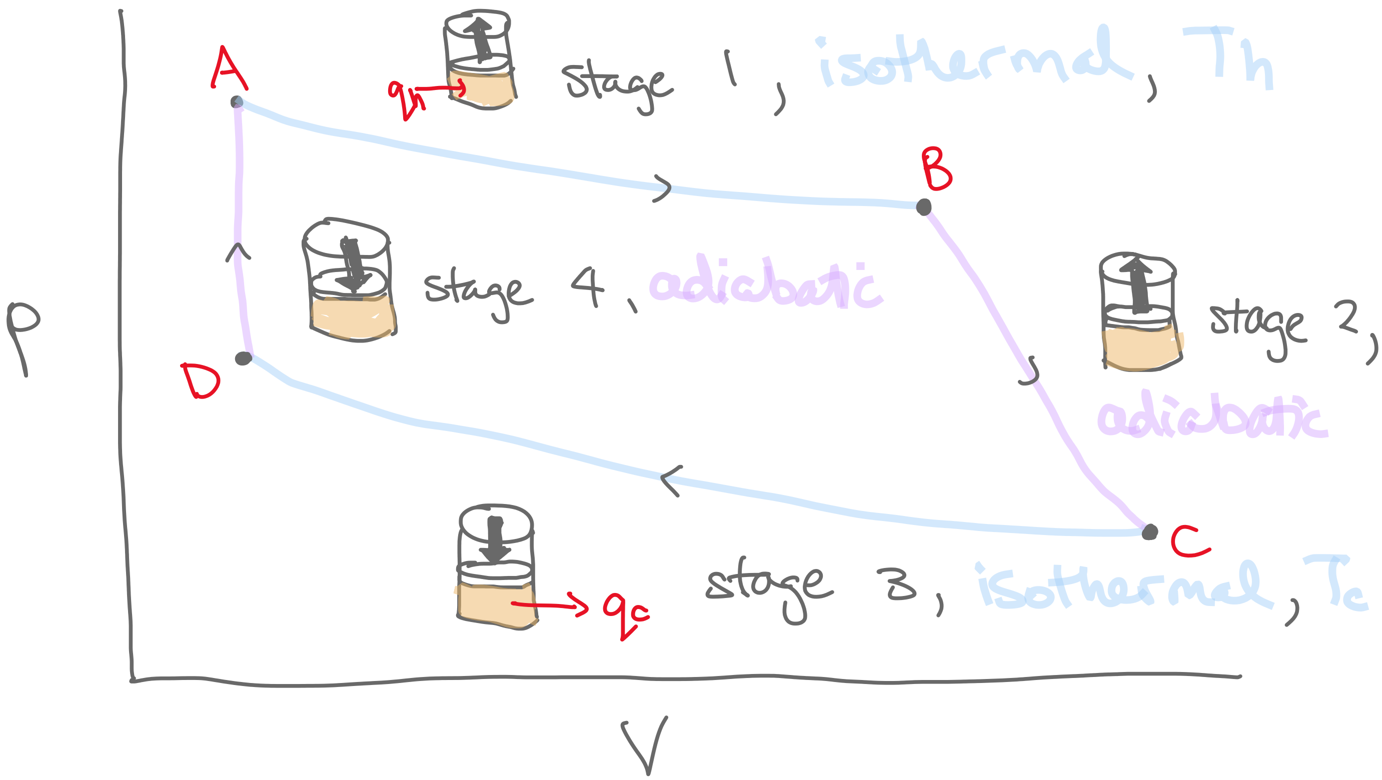
$$E = \frac{n^2 h^2}{8 m l^2}$$

The Carnot Cycle

We need to show that

$$\oint dS = \oint \frac{dq_{rev}}{T} = 0$$

integration around a closed path



Stages 2 and 4 : $q = 0$

$$\oint dS = \underbrace{\frac{q_h}{T_h}}_{\text{positive}} + \underbrace{\frac{q_c}{T_c}}_{\text{negative}}$$

Stage 1 : $\boxed{q_h = nRT_h \ln \frac{V_B}{V_A}}$

Stage 3 : $q_c = nRT_c \ln \frac{V_D}{V_C}$

$$\boxed{V_i T_i^{c} = V_f T_f^{c}, \quad c = \frac{C_{V,m}}{R}}$$

For an adiabatic expansion

Stage 2: $V_B T_h^c = V_C T_c^c$

Stage 4: $V_D T_c^c = V_A T_h^c$

multiply

$$V_B V_D \cancel{T_h^c} \cancel{T_c^c} = V_C V_A \cancel{T_c^c} \cancel{T_h^c}$$

$$\boxed{\frac{V_D}{V_C} = \frac{V_A}{V_B}}$$

$$q_c = nRT_c \ln \frac{V_D}{V_C} = nRT_c \ln \frac{V_A}{V_B}$$

$$\boxed{q_c = -nRT_c \ln \frac{V_B}{V_A}}$$

$$\frac{q_h}{q_c} = \frac{\cancel{n}RT_h \cancel{\ln \frac{V_B}{V_A}}}{-\cancel{n}RT_c \cancel{\ln \frac{V_B}{V_A}}} = -\frac{T_h}{T_c}$$

$$\frac{q_h}{\ } = -\frac{q_c}{\ }$$

$$T_h - \quad T_c$$

$$\boxed{\frac{q_h}{T_h} + \frac{q_c}{T_c} = 0}$$

$$\boxed{\therefore \oint dS = 0}$$

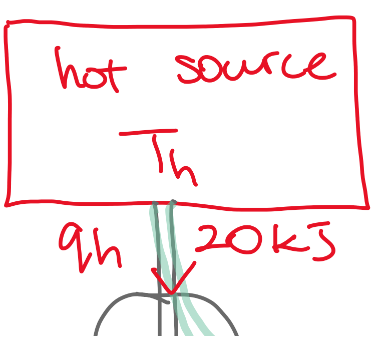
Efficiency η

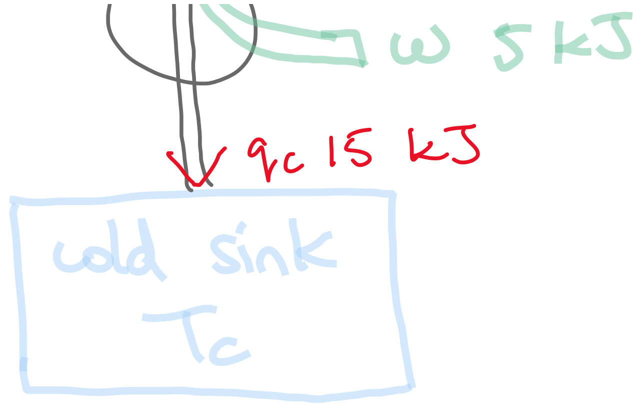
$$\eta = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{|q_h|}$$

$$\eta = \frac{|q_h| - |q_c|}{|q_h|} = 1 - \frac{|q_c|}{|q_h|}$$

$$\boxed{\eta = 1 - \frac{T_c}{T_h}}$$

$$1 - \frac{15}{20} = 25\%$$





A certain power station operates with superheated steam at 573K and discharges the waste heat into the environment at 293 K. What is the theoretical efficiency?

$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{293}{573} \approx 48.9\%$$