Lecture 8

Tuesday, October 3, 2023 11:32

Midterm Exam Information

October 17, MacKinnon 304

11:30 - 12:45

Cutoff: up to and including Thursday October 5 lecture

no class October 10

October 12: review

bring a non-graphing calculator

recommend writing with pen (in case of regrades)

- exam booklet provided
- equation sheet provided

Topic 3: Entropy

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

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

$$dS_{sur} = \frac{dq_{sur}}{T_{sur}}$$

$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}}$$

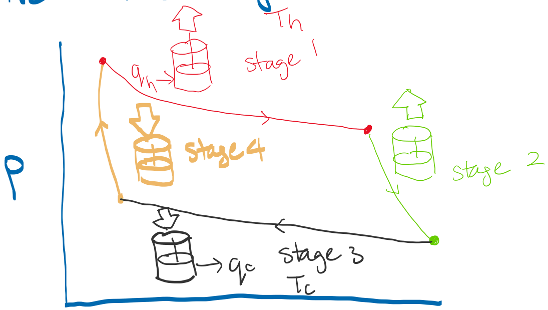
$$S = k_B \ln \Omega$$

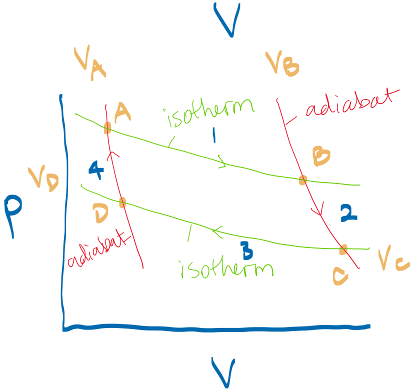
The entropy as a state function

prove:

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

The Carnot Cycle:





in stages 2 and 4: no heat flows in or out of the system; $q_{rev}=0$ therefore $\Delta S = 0$.

Stage 1: $\Delta S = \frac{q_h}{T_h}$

Stage 3: $\Delta S = \frac{q_c}{T_c}$

need to show:

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

Isothermal expansion: $\Delta T = 0$

$$\Delta U = C_V \Delta T$$

$$\Delta U = 0$$

$$\Delta U = q + w$$

$$\boxed{q = -w}$$

$$dw = -p\,dV$$

$$dw = -\frac{nRT}{V}\,dV$$

$$w = -nRT\int_{V_i}^{V_f} \frac{1}{V}\,dV$$

$$w = -nRT\ln\frac{V_f}{V_i}$$

$$\boxed{q = nRT\ln\frac{V_f}{V_i}}$$

$$q_h = nRT_h\ln\frac{V_B}{V_A}$$

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

$$V_i T_i^{\,c} = V_f T_f^{\,c} \qquad c = \frac{C_V}{nR}$$

adiabatic expansion

Stage 2: $V_B T_h^{\,c} = V_C T_c^{\,c}$

Stage 4: $V_D T_c^{\,c} = V_A T_h^{\,c}$

$\updownarrow$ multiply

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

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

$$q_h = nRT_h \boxed{\ln \frac{V_B}{V_A}} , \boxed{q_c = nRT_c \ln \frac{V_D}{V_C}}$$

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

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

$$\frac{q_h}{q_c} = \frac{nRT_h \ln \frac{V_B}{V_A}}{-nRT_c \ln \frac{V_B}{V_A}} = -\frac{T_h}{T_c}$$

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

$$\left(\begin{array}{c} \dfrac{q_h}{q_c} = -\dfrac{T_h}{T_c} \\ \\ \dfrac{q_h}{T_h} = -\dfrac{q_c}{T_c} \end{array} \right)$$

Rearrange :

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

$\therefore$ For a perfect gas, $\Delta S = 0$ in a

Carnot cycle.

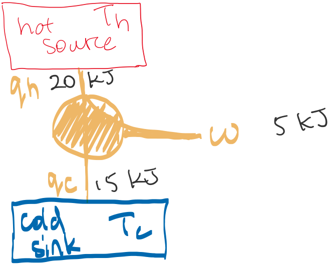
Next: need to show that $\Delta S = 0$ in a Carnot cycle regardless of the working substance.

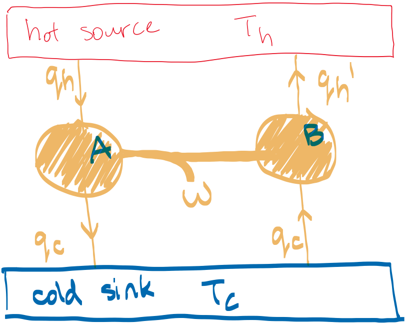
$$\eta = \frac{\text{work performed}}{\text{heat absorbed from hot source}}$$

$$\eta = \frac{|w|}{|q_h|}$$ efficiency

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

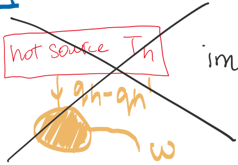
$$\boxed{\eta = 1 - \frac{T_c}{T_h}}$$





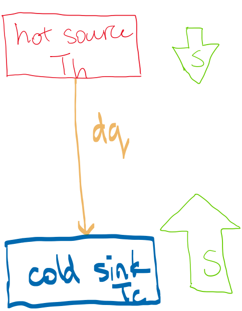
assume that these two Carnot engines have different η; i.e. A is more efficient than B

equivalent to :



impossible

Therefore, all Carnot engines must have the same efficiency regardless of the working substance.



$$dS = -\frac{|dq|}{T_h}$$

$$dS = +\frac{|dq|}{T_c}$$

Topic 3B : Entropy changes accompanying specific processes

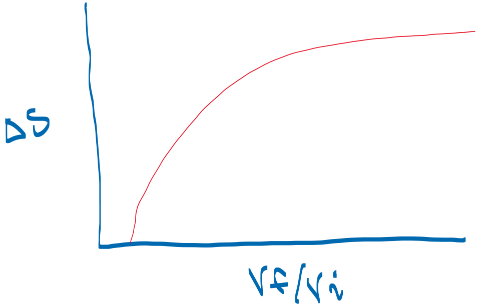
$$\Delta S_{tot} = \Delta S + \Delta S_{sur}$$

$\Delta S_{tot} = 0$ at equilibrium

$\Delta S_{tot} > 0$: spontaneous, irreversible

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

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



phase transitions

$$q = \Delta_{trs} H$$

$$\boxed{\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}}$$

Heating:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T}$$

constant pressure:

$$dq_{rev} = dH$$

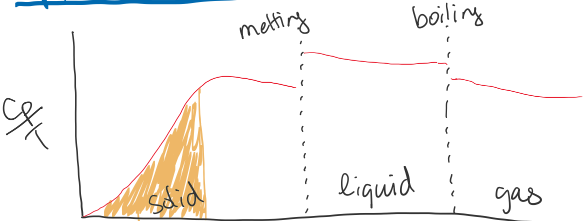
$$dH = \boxed{C_p\, dT}$$

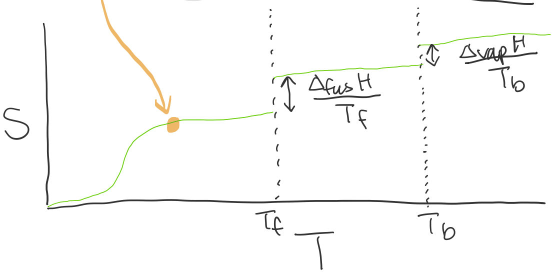
$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} C_p \frac{1}{T}\, dT$$

$C_p \approx$ constant over a small T range

$$\boxed{S(T_f) = S(T_i) + C_p \ln \frac{T_f}{T_i}}$$

Topic 3C: The measurement of Entropy





$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T')}{T'}\,dT'$$

$$+ \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(l,T')}{T'}\,dT'$$

$$+ \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}(g,T')}{T'}\,dT'$$

The Third Law of Thermodynamics:

At $T=0$, $S=0$.

$$(S = k_B \ln \underset{\underset{1}{\uparrow}}{\Omega})$$