Heat, Work, Entropy, and Internal Energy

For an ideal gas, $E_{int} = E_{int}(T)$

$$dE_{int} = dQ - dW$$

$$\left.\frac{\partial E_{int}}{\partial T}\right|_V = \left.\frac{\partial Q}{\partial T}\right|_V + \text{no work} = nC_V$$

$$dQ\Big|_V = nC_V\,dT$$

If we hold the pressure constant,

$$dE_{int} = \underbrace{\left(\frac{\partial E_{int}}{\partial T}\right)_p}\,dT + \left(\frac{\partial E_{int}}{\partial p}\right)_T dP$$

$$= \left(\left.\frac{\partial Q}{\partial T}\right|_p - \left.\frac{\partial W}{\partial T}\right|_p\right) dT + \underbrace{\left(\frac{\partial E_{int}}{\partial p}\right)_T}\,dP$$

$$= \left(nC_p - \left.\frac{\partial W}{\partial T}\right|_p\right) dT + 0$$

$$= \left(nC_p - \left.p\frac{\partial V}{\partial T}\right|_p\right) dT$$

aside

$$\boxed{V = \frac{nRT}{p}}$$

$$= \left(nC_p - \cancel{p}\frac{nR}{\cancel{p}}\right) dT$$

$$= nC_V\,dT$$

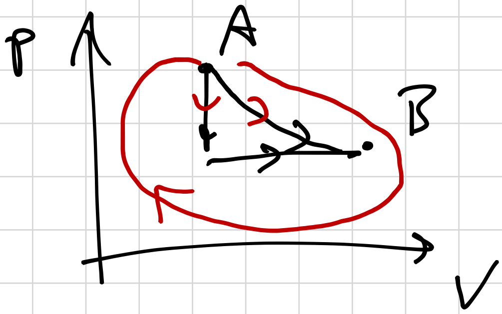
aside

$$C_p - C_V = R$$

$$C_p - R = C_V$$

Entropy changes for heat cycles

S is a state variable



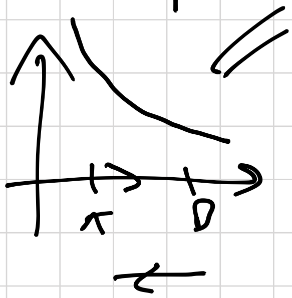
$$\oint dS = 0$$

$$\oint dE_{int} = 0$$

$$dE_{int} = T\,dS - p\,dV$$

$$\frac{dE_{int}}{T} + \frac{p\,dV}{T} = dS$$

$$\oint \frac{dE_{int}}{T} = \oint (nC_v)\frac{dT}{T} = nC_v \oint \frac{dT}{T} = 0$$

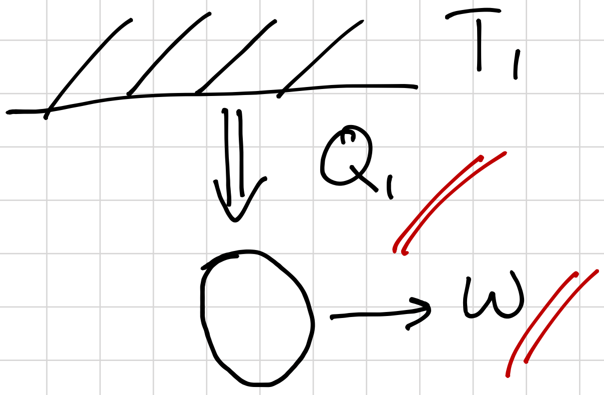


$$\oint \frac{p\,dV}{T} = \oint \frac{nR\cancel{T}}{V\cancel{T}}\,dV = nR\oint \frac{dV}{V} = 0$$

$$\oint dS = \oint \frac{dE_{ind}}{T} + \oint p\,dV = 0$$

$\Rightarrow$ S is a state variable

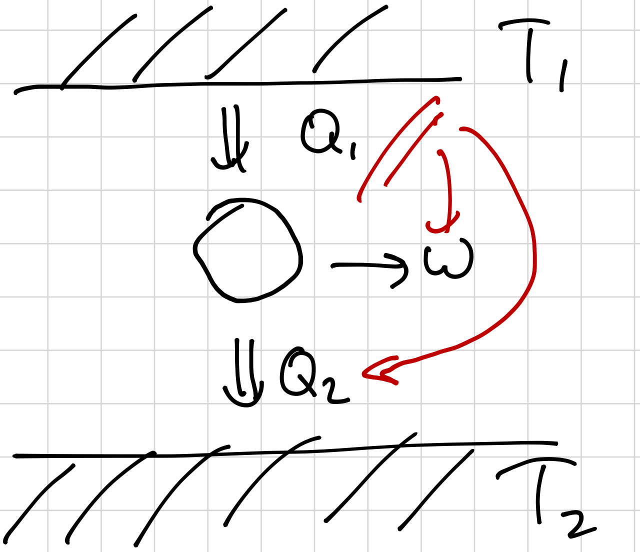
Heat engines



$$\Delta S = -\frac{|Q_1|}{T_1} < 0$$

forbidden by the 2nd law of thermodynamics

$$|Q_1| = |W|$$



$$\Delta S = -\frac{|Q_1|}{T_1} + \frac{Q_2}{T_2} \geq 0$$

$$\frac{Q_2}{T_2} \geq \frac{|Q_1|}{T_1}$$

$$\frac{Q_2}{|Q_1|} \geq \frac{T_2}{T_1} \rightarrow -\frac{Q_2}{|Q_1|} \leq -\frac{T_2}{T_1}$$

$$\underset{\substack{\uparrow \\ \text{efficiency} \\ \text{of} \\ \text{any} \\ \text{engine}}}{\varepsilon} = \frac{W}{|Q_1|} = \frac{|Q_1| - Q_2}{|Q_1|}$$

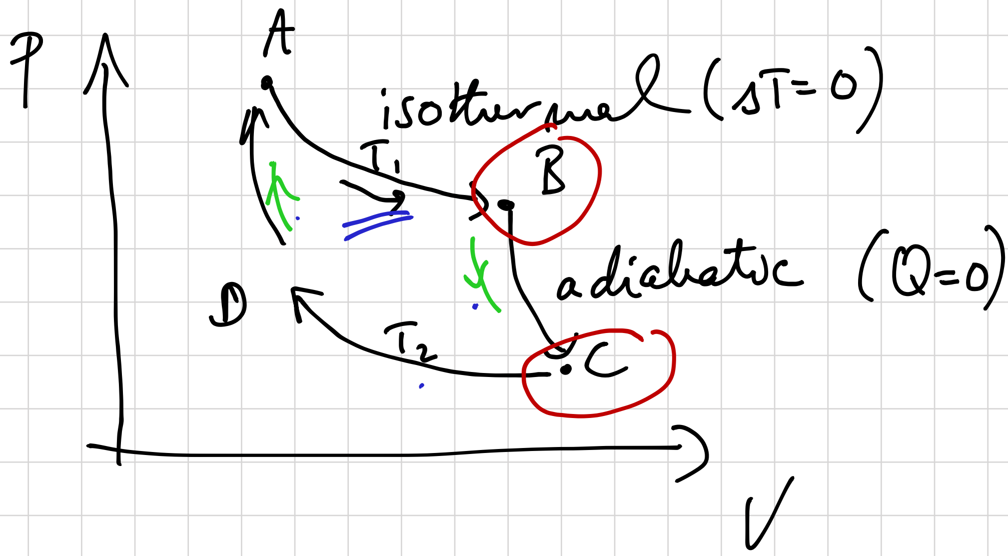
$$= 1 - \frac{Q_2}{|Q_1|} \leq \underbrace{1 - \frac{T_2}{T_1}}_{} < 1$$

2^{nd} of thermo. $\Rightarrow$ bound on efficiency

Best possible engine

$$\varepsilon = 1 - \frac{T_2}{T_1}$$

Carnot cycle / engine



Isothermal: $\Delta T=0$, $\Delta E_{int}=0$

$$W_{AB}=\int_A^B p\,dV = \int_{V_A}^{V_B} \frac{nRT_1}{V}\,dV = nRT_1 \log\frac{V_B}{V_A} > 0$$

ΔE_{int}: $Q-W=0$

$Q_{AB}=W_{AB}$

$$W_{CD}=nRT_2\log\frac{V_D}{V_C} < 0$$

$Q_{CD}=W_{CD}$ $\Leftarrow$

Adiabatic : $Q=0$, $\Rightarrow$ $\Delta E_{int}=0$

$$pV^\gamma = p_0 V_0^\gamma$$

$$W_{BC}=\int_B^C p\,dV = p_B V_B^\gamma \int_B^C \frac{dV}{V^\gamma} = p_B V_B^\gamma \times$$

$$\int_{V_B}^{V_C} V^{-\gamma}\, dV = \frac{p_B V_B^{\gamma}}{1-\gamma} V^{1-\gamma}\Big|_{V_B}^{V_C} = \frac{p_B V_B^{\gamma}}{1-\gamma}\left(V_C^{1-\gamma} - V_B^{1-\gamma}\right)$$

$$= \frac{p_B \cancel{V_B^{\gamma}}}{1-\gamma}\, \cancel{V_B^{1-\gamma}} \left(\frac{V_c^{1-\gamma}}{V_b^{1-\gamma}} - 1\right)$$

$$= \frac{p_B V_B}{1-\gamma}\left(\left(\frac{V_c}{V_b}\right)^{1-\gamma} - 1\right)$$

$$W_{BC} = \frac{p_B V_B}{1-\gamma}\left[\left(\frac{V_c}{V_B}\right)^{1-\gamma} - 1\right]$$

$$W_{DA} = \frac{p_D V_D}{1-\gamma}\left[\left(\frac{V_A}{V_D}\right)^{1-\gamma} - 1\right]$$

$$p_B V_B^{\gamma} = p_c V_c^{\gamma} \qquad p = \frac{nRT}{V}$$

$$\frac{\cancel{nR}T_1}{V_B} V_B^{\gamma} = \frac{\cancel{nR}T_2}{V_c} V_c^{\gamma}$$

$$T_1 V_B^{\gamma-1} = T_2 V_c^{\gamma-1}$$

$$\frac{V_B^{\gamma-1}}{V_c^{\gamma-1}} = \frac{T_2}{T_1} = \left(\frac{V_c}{V_B}\right)^{1-\gamma}$$

$$\begin{cases} W_{BC} = \dfrac{p_B V_B}{1-\gamma}\left[\dfrac{T_2}{T_1}-1\right] & p_B V_B = nRT_1 \\[2ex] W_{DA} = \dfrac{p_D V_D}{1-\gamma}\left[\dfrac{T_1}{T_2}-1\right] & p_D V_D = nRT_2 \end{cases}$$

$$\begin{cases} W_{BC} = \dfrac{nRT_1}{1-\gamma}\left(\dfrac{T_2}{T_1}-1\right) \\[2ex] W_{DA} = \dfrac{nRT_2}{1-\gamma}\left(\dfrac{T_1}{T_2}-1\right) \end{cases}$$

$$W_{adiabatic} = W_{BC} + W_{DA} = \frac{nR}{1-\gamma}\left(\cancel{T_2}-\cancel{T_1}\right)$$

$$+ \frac{nR}{1-\gamma}\left(\cancel{T_1}-\cancel{T_2}\right)$$

$$= 0$$

$$W_{BC} = -\Delta E_{int}^{BC} = -nC_v(T_2-T_1)$$

$$W_{DA} = -nC_v(T_1-T_2)$$

$$\overline{\overline{W_{BC}+W_{DA}}} = 0$$

Total work

$$W = W_{AB} + W_{CD} = nRT_1 \log\frac{V_B}{V_A} + nRT_2 \log\frac{V_D}{V_C}$$

$$\frac{T_2}{T_1} = \left(\frac{V_C}{V_B}\right)^{1-\gamma} = \left(\frac{V_D}{V_A}\right)^{1-\gamma}$$

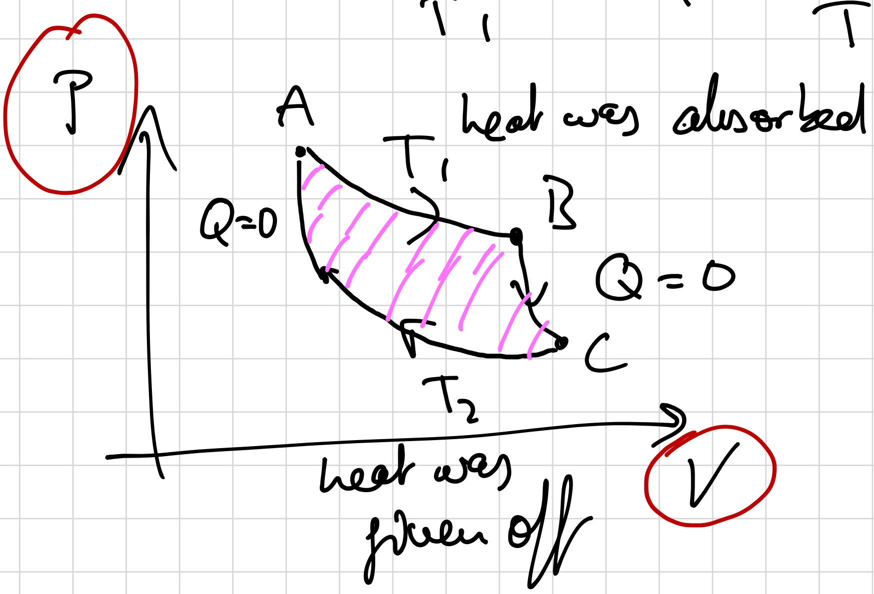
$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \Leftrightarrow \frac{V_C}{V_D} = \frac{V_B}{V_A}$$

$$W = nRT_1 \log\frac{V_B}{V_A} + nRT_2 \log\frac{V_A}{V_B}$$

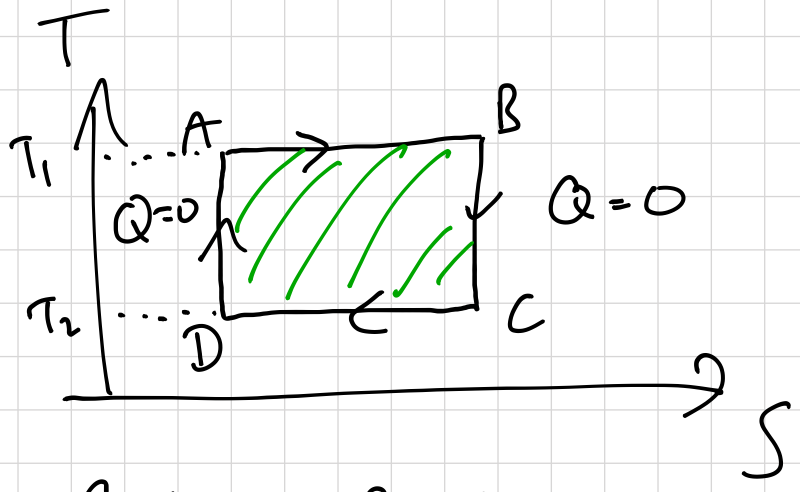
$$= nR(T_1 - T_2)\log\frac{V_B}{V_A}$$

$$\varepsilon = \frac{W}{|Q_1|} = \frac{\cancel{n}R(T_1-T_2)\cancel{\log\frac{V_B}{V_A}}}{\cancel{n}RT_1\cancel{\log\frac{V_B}{V_A}}}$$

$$= \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$



$$W = \int_A^B p\,dV + \int_B^C p\,dV + \int_C^D p\,dV + \int_D^A p\,dV$$



$$Q = \oint dQ = \oint T\,dS$$

$$= (T_1 - T_2)\,\Delta S$$

$$dE_{int} = T\,dS - p\,dV$$

$$dS = \frac{dE_{int}}{T} + \frac{p}{T}\,dV$$

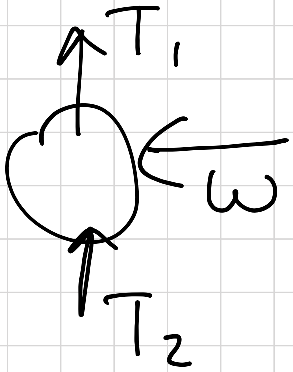
$$= nC_v\frac{dT}{T} + \frac{nR}{V}\,dV$$

$$\Delta S = \underbrace{\int_{T_1}^{T_1} nC_v\frac{dT}{T}}_{0} + \int_{V_A}^{V_B}\frac{nR}{V}\,dV$$

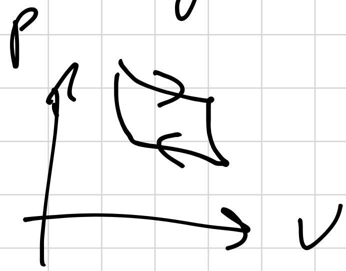
$$= nR\log\frac{V_B}{V_A}$$

$$Q = (T_1 - T_2)\,nR\log\frac{V_B}{V_A}$$

Refrigerator



usual Carnot cycle:



refrigerator:

$$\varepsilon_{\text{refrigerator}} = \frac{|Q_2|}{W}$$

$$= \frac{\left| nRT_2 \log \frac{V_D}{V_C} \right|}{nR(T_1 - T_2) \log \frac{V_B}{V_A}}$$

$$= \frac{\cancel{nR}\, T_2 \cancel{\log \frac{V_B}{V_A}}}{\cancel{nR}\,(T_1 - T_2) \cancel{\log V_B / V_A}}$$

$$= \frac{T_2}{T_1 - T_2} = \frac{1}{\frac{T_1}{T_2} - 1}$$