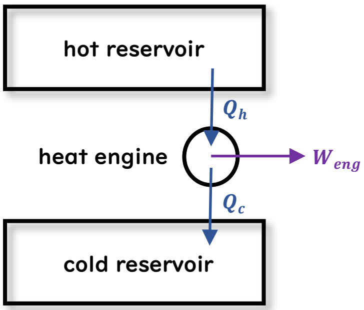
The Second Law of Thermodynamics

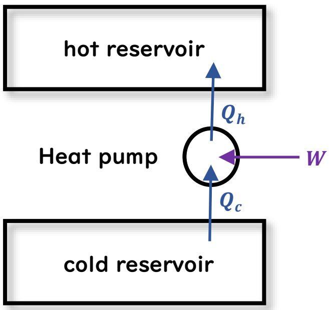
Heat Engine



thermal efficiency

$$\boxed{\eta = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}}$$

Heat pump/Refrigerator



coefficient of performance (COP)

for heat pump:

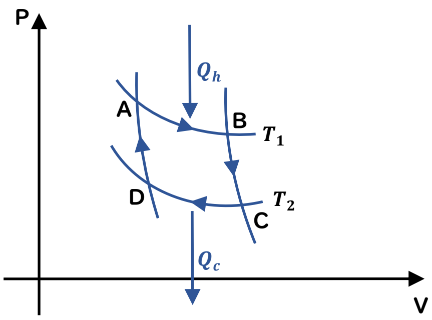
$$\boxed{COP = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}}$$

for refrigerator:

$$\boxed{COP = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}}$$

then $COP_{HP} = COP_R + 1$

Carnot Cycle



A→B, C→D: isothermal

B→C, D→A: adiabatic

process A→B: isothermal expansion

$$\Delta U = 0 \Rightarrow Q_h = -W_{AB} = \int_{V_A}^{V_B} P dV = RT_1 \frac{V_B}{V_A}$$

process B→C: adiabatic expansion

$$\Delta Q = 0 \Rightarrow \Delta U = W_{BC} = C_V(T_2 - T_1)$$

process C→D: isothermal compression

$$\Delta U = 0 \Rightarrow Q_C = -W_{CD} = \int_{V_C}^{V_D} P dV = RT_1 \frac{V_D}{V_C}$$

process D→A: adiabatic compression

$$\Delta Q = 0 \Rightarrow \Delta U = W_{CD} = C_V(T_1 - T_2)$$

$$\eta = \frac{|W|}{Q} = \frac{W_{AB} + W_{CD}}{Q_h + Q_c} = 1 - \frac{T_2}{T_1} \frac{\ln\left(\frac{V_C}{V_D}\right)}{\ln\left(\frac{V_B}{V_A}\right)} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \boxed{\eta = 1 - \frac{T_2}{T_1}}$$

Entropy

for any reversible process

$$\oint \frac{\delta Q}{T} = 0$$

define state function of entropy:

$$\boxed{dS = \frac{\delta Q}{T}}$$

The second law of thermodynamics: the entropy of an isolated system will only increase

Clausius Inequality

for reversible process: $\eta_R = 1 - T_1/T_2$

for irreversible process: $\eta_I = 1 + Q_C/Q_h$

according to Carnot theorem: $\eta_I < \eta_R$

therefore, for a number of irreversible processes:

$$\boxed{\left(\sum \frac{\delta Q}{T}\right)_{I+R} < 0}$$

Calculation of ΔS

- isothermal process: $\Delta U = 0$

  $$\Delta S = \int dS = \int \frac{dQ}{T} = \int \frac{-dW}{T} = \frac{1}{T}\left(nRT \ln \frac{V_2}{V_1}\right) = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

- isochoric process: $\Delta V = 0$

  $$\Delta S = \int dS = \int \frac{dQ}{T} = \int \frac{dU}{T} = \int \frac{C_V dT}{T} = C_V \ln \frac{T_2}{T_1}$$

- isobaric process: $\Delta P = 0$

  $$\Delta S = \int dS = \int \frac{dQ}{T} = \int \frac{C_P dT}{T} = C_P \ln \frac{T_2}{T_1}$$

- adiabatic process: $\Delta S = 0$ (equilibrium everywhere)

$$Q = \int T dS$$

for $T - S$ diagram, the area below (surrounded by) the curve represents heat Q

The third law of thermodynamics

$S^{*}(perfect\ crystal, 0K) = 0J/K$

for entropy S of temperature T

$S_T = S_0 + \int_0^T \frac{C_P dT}{T} = C_P d \ln T$