FROM CARNOT Cycle

$$\text{exact differential} = \frac{dq_{rev}}{T} = \text{state function}$$

$$\oint \frac{dq_{rev}}{T} = 0 \qquad \text{FROM CARNOT'S CYCLE}$$

DEFINITION

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

$$\boxed{\Delta S = \int \frac{dq_{rev}}{T}}$$

CALCULATIONS OF ΔS

a) ADIABATIC PROCESS $dq_{rev} = 0$

$$\Rightarrow \quad \Delta S = 0$$

b) ISOTHERMAL EXPANSION OR COMPRESSION

$$\Delta U = 0 = q + w$$

$$q_{rev} = -w_{rev} = nRT\ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T}\int dq_{rev}$$

$$\boxed{\Delta S_{ISOTHERMAL} = \frac{q_{rev}}{T}}$$

$$\Delta S_{ISOT} = nR\ln\left(\frac{V_f}{V_i}\right)$$

c) Reversible change in T at const V

$$\Delta S = \int_{T_i}^{T_f} \frac{dq_{rev}}{T'} = \int_{T_i}^{T_f} \frac{C_v(T')}{T'}\,dT'$$

FOR CONSTANT $\overline{C}_V$

$$C_V = n\overline{C}_V$$

$$\Delta S = n\overline{C}_V \int_{T_i}^{T_f} \frac{dT'}{T'}$$

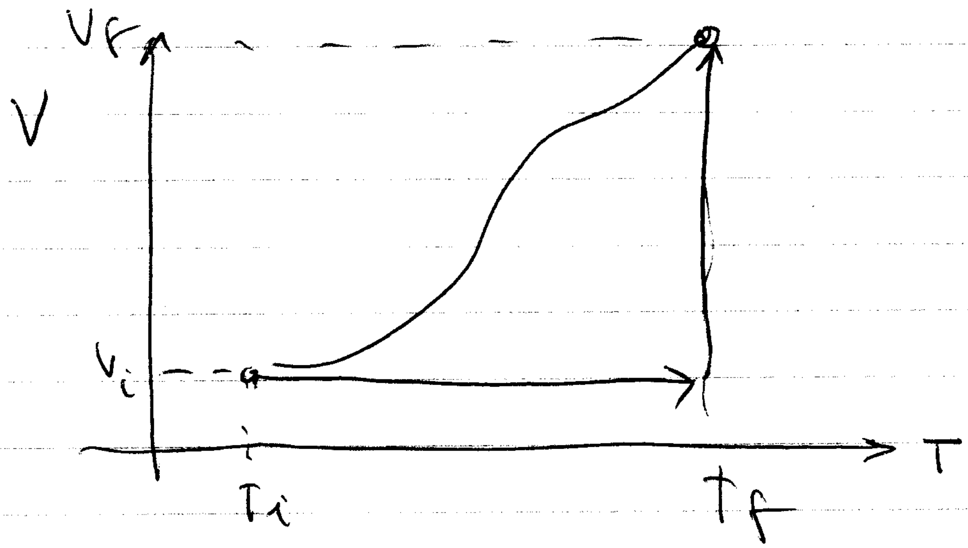
$$\boxed{\Delta S = n\overline{C}_V \ln\left(\frac{T_f}{T_i}\right)}$$

CONSTANT V

d) CONSTANT PRESSURE REVERSIBLE PROCESS

$$\boxed{\Delta S = n\overline{C}_p \ln\left(\frac{T_f}{T_i}\right)}$$

CONSTANT P



$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) + n\bar{C}_V \ln\left(\frac{T_f}{T_i}\right)$$

4) Phase Transition occurn at CONSTANT T and P

$$\Delta S_{pt} = \frac{q_{tran}}{T_{tran}} = \frac{\Delta H_{tran}}{T_{tran}}$$

Vaporization

$$\boxed{\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p(T')\,dT'}{T'} \qquad \text{AT CONSTANT } P$$

SINCE WE HAVE AN ABSOLUTE TEMPERATURE

WE CAN CALCULATE ABSOLUTE ENTROPIES

$$\Delta S = S^{\circ}(T_f) - S^{\circ}(0)$$

$$= \int_{0}^{T_f} \frac{C_p^{solid}(T')\,dT'}{T'} + \frac{\Delta H^{\circ}_{fus}}{T_{fus}}$$

$$+ \int_{T_f}^{T_{vap}} \frac{C_p^{liq}(T')\,dT'}{T'} + \frac{\Delta H^{\circ}_{vap}}{T_{vap}}$$

$$+ \int_{T_{vap}}^{T} \frac{C_p^{gas}(T')\,dT'}{T'}$$

3th LAW

The ENTROPY OF A PURE, PERFECT CRYSTALLINE SUBSTANCE (ELEMENT OR COMPOUND) is ZERO AT ZERO KELVIN.

a) $S_m^{gas} > S_m^{liq} > S_m^{sol}$

b) The molar entropy increases with SIZE of a molecule.

<u>Standard States</u> $P = 1$ bar
$T = 298.15K$

In contrast with $\Delta H_f^{\circ}[\text{elements}] \equiv 0$,

WE CAN CALCULATE ABSOLUTE ENTROPIES OF FORMATION, S_f°

FOR AN IDEAL GAS ~~AT~~ WITH $P^{\circ} = 1\,bar$ AS REFERENCE

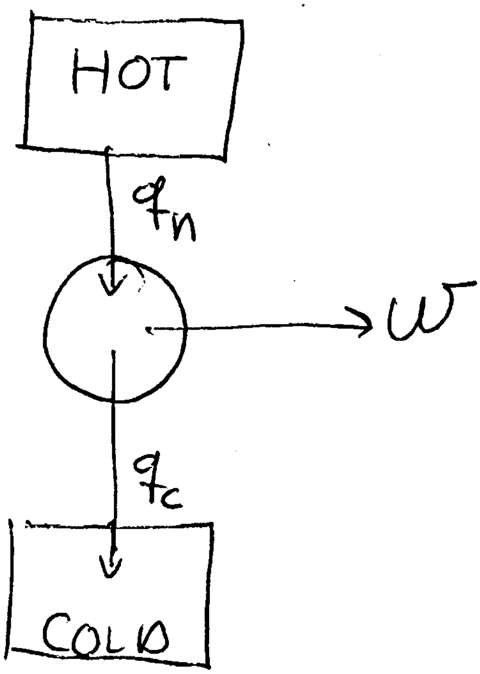
$$dS = C_p^{IG} \frac{dT}{T}$$

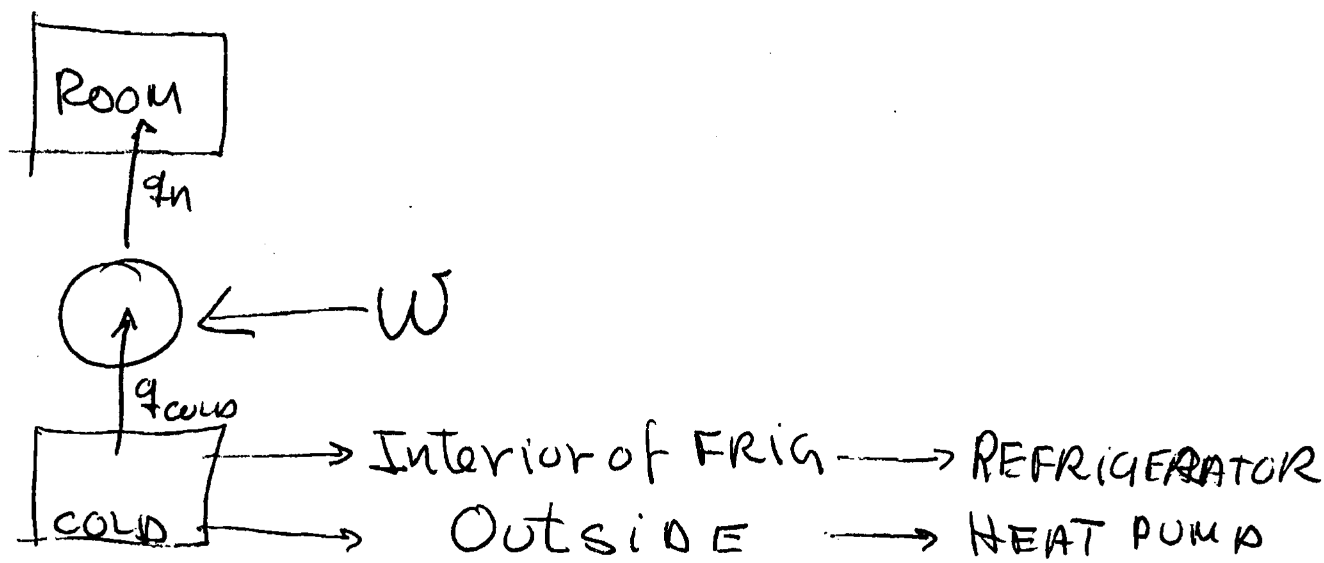
$$\boxed{S_m(P) = S_m^{\circ} - R \ln\left(\frac{P}{bar}\right)}$$

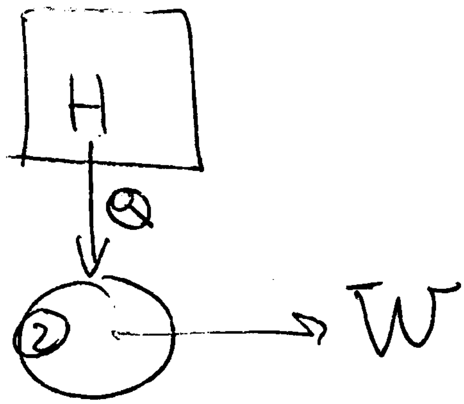
REACTIONS

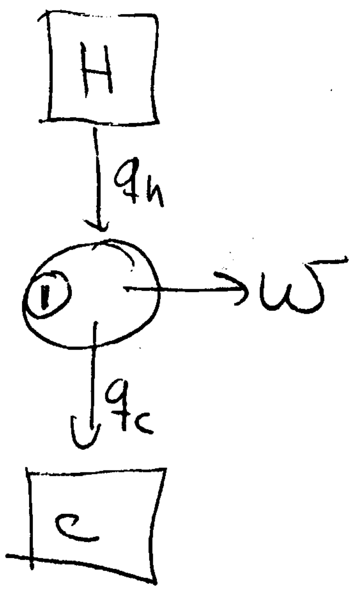
$$\Delta S^\circ_{rxn} = \sum_{\nu} \nu_i \, S^\circ_f(i) \qquad \text{AT } T = 298.15\,K$$

$$\Delta S^\circ_{rxn}(T) = \Delta S^\circ_{rxn}(298.15\,K) + \int_{298.15\,K}^{T} \frac{\Delta C^\circ_P}{T'} \, dT'$$

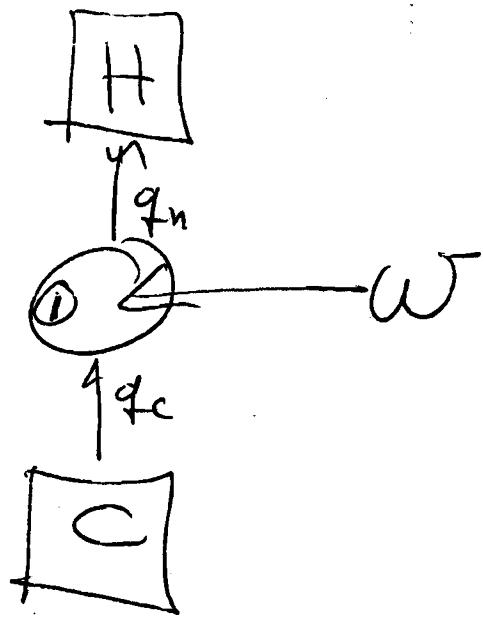

HOT
q_h
W
q_c
COLD

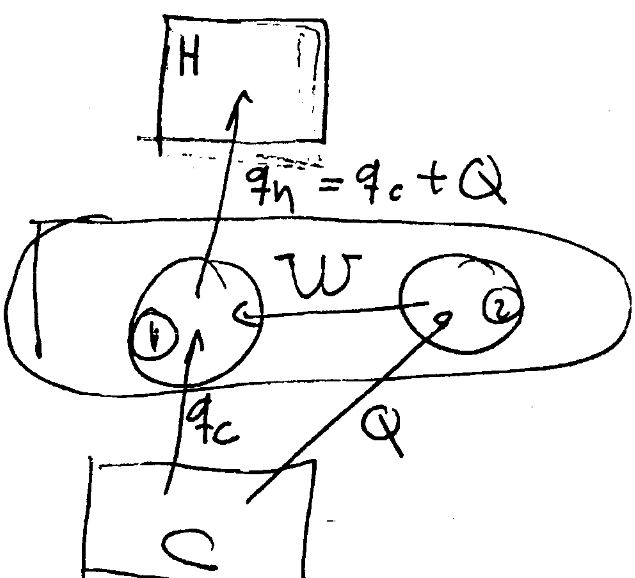

ROOM
q_h
W
q_{cold}
COLD
Interior of FRIG → REFRIGERATOR
Outside → HEAT PUMP





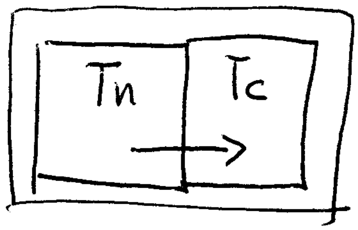
RE
AS FRIGIRATOR





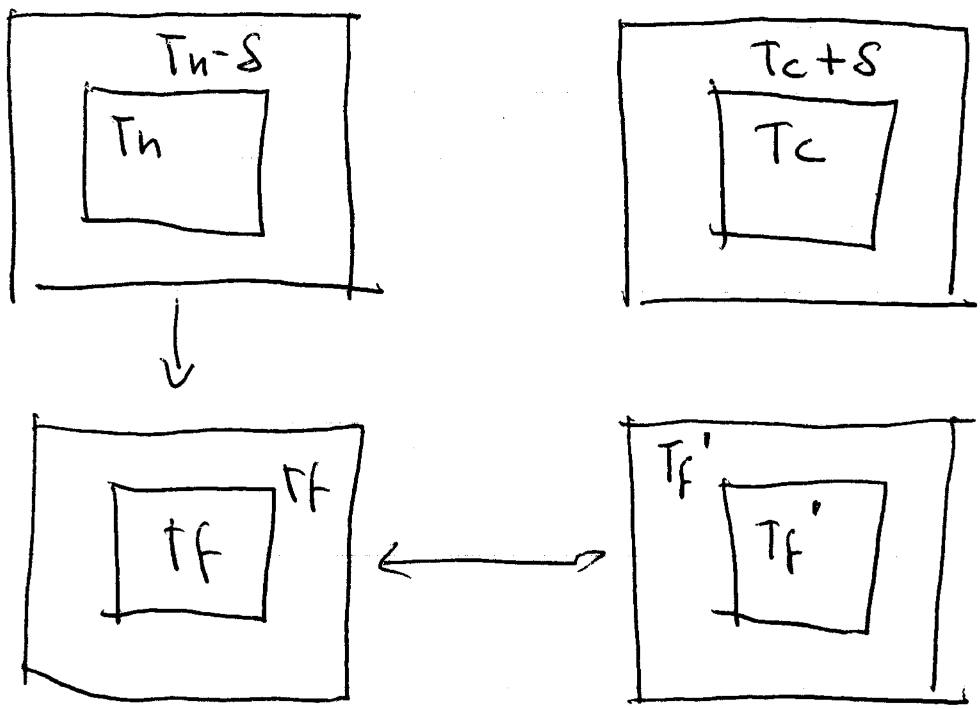
TRANSFER HEAT
FROM COLD TO HOT
WITHOUT EXTERNAL
WORK

ΔS



IRREVERSIBLE
SPONTANEOUS
PROCESS

CONSIDER AN ALTERNATIVE REVERSIBLE PATH



a) $T_f = T_f' = \dfrac{T_h + T_c}{2}$

b) $T_f > T_h > T_c > T_f'$!

$$\Delta S_h = \int \frac{dq_{rev}}{T} = \int_{T_h}^{T_f} \frac{C_p\,dT}{T} = C_p \ln\left(\frac{T_f}{T_h}\right)$$

$$\Delta S_c = C_p \ln\left(\frac{T_f'}{T_c}\right)$$

$$\Delta S = \Delta S_h + \Delta S_c = C_p \ln\left\{\frac{T_f}{T_h}\,\frac{T_f'}{T_c}\right\}$$

a) $$\frac{T_f}{T_h}\,\frac{T_f}{T_c} = \frac{1}{4}\left(1+\frac{T_c}{T_h}\right)\left(1+\frac{T_h}{T_c}\right)$$

$$= \frac{1}{4}\left\{2 + \frac{T_c}{T_h} + \frac{T_h}{T_c}\right\}$$

$$T_h = T_c + \delta$$

$$\frac{T_c}{T_h} + \frac{T_h}{T_c} = \frac{T_c}{T_c+\delta} + \frac{T_c+\delta}{T_c} = \frac{1}{1+\delta/T_c} + 1 + \frac{\delta}{T_c}$$

$$= \sum_{n=0}^{\infty} (-1)^n \left(\frac{\delta}{T_c}\right)^n + 1 + \frac{\delta}{T_c} = 2 + \sum_{n=2}^{\infty} \left(\frac{\delta}{T_c}\right)^n$$

$$\simeq 2 + \left(\frac{\delta}{T_c}\right)^2$$

$$= 2 + \frac{\left(\frac{\delta}{T_c}\right)^2}{1+\frac{\delta}{T_c}} > 2$$