Entropy and isothermal expansion:

$V_i \Rightarrow V_f$, $T = const$

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

$$\Delta S = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T}$$

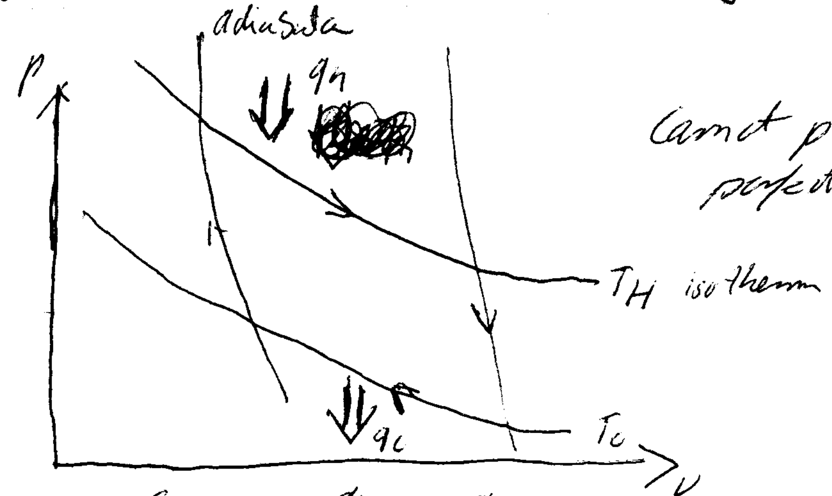
$$q_{rev} = -w_{rev} = nRT \ln \frac{V_f}{V_i} \Rightarrow \Delta S = nR \ln \frac{V_f}{V_i}$$

pressure change: $p_i \to p_f \Rightarrow \Delta S = nR \ln \frac{p_i}{p_f}$

Entropy is a state function $\Leftrightarrow \oint \frac{dq_{rev}}{T} = 0$

Proof:

1.



Carnot process, perfect gas

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

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

2. efficiency ε

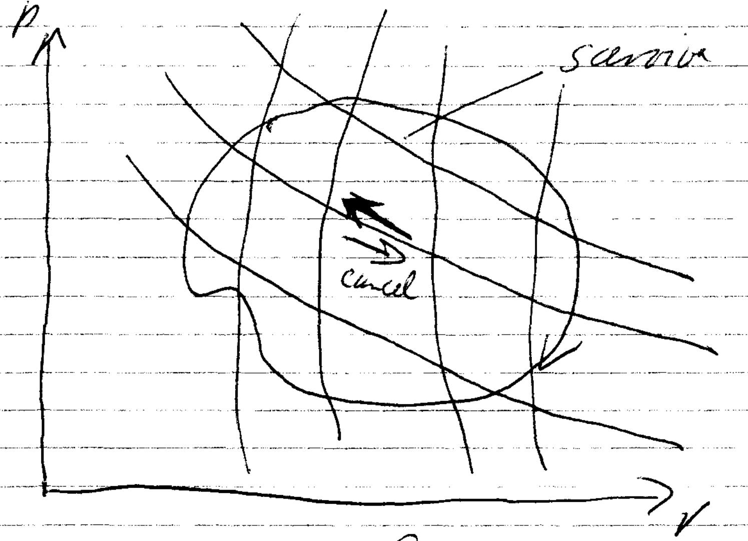
$$\varepsilon = \frac{|W|}{q_h} = \frac{\text{work performed}}{\text{heat absorbed}}$$

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

$$\varepsilon_{rev} = 1 - \frac{T_H}{T_C}$$

All reversible engines have the same efficiency regardless of their construction (otherwise it would be possible to run an engine by just cooling a reservoir)

3.



$$\Rightarrow \oint dS = 0$$

Clausius inequality

system in thermal and mechanical contact with its surroundings at the same temperature T

$$dS + dS_{sur} \geq 0$$

$$dS_{sur} = -\frac{dq_{sur}}{T} = \frac{dq}{T}$$

$$\Rightarrow \boxed{dS \geq \frac{dq}{T}}$$ signpost of spontaneous change

isolated system $dq = 0 \Rightarrow dS \geq 0$

irreversible spontaneous cooling

energy transfer from a hot source (T_h) to a cold sink (T_c)

entropy decrease in hot source : $-\frac{|dq|}{T_H}$

entropy increase in cold sink : $+\frac{|dq|}{T_c}$

$$\Rightarrow dS = |dq|\left(\frac{1}{T_c} - \frac{1}{T_h}\right) \geq 0$$

$\Rightarrow$ spontaneous change

Entropy of phase transitions at the transition temperature:

at the transition temperature any transfer of heat is reversible because 2 phases in the system are in equilibrium

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

freezing, condensing $\Rightarrow$ exothermic $\Rightarrow \Delta_{trs} H < 0$
$\Rightarrow \Delta S < 0 \Leftrightarrow$ system becomes more ~~ordered~~ ordered

melting, vaporizing $\Rightarrow$ endothermic $\Rightarrow \Delta_{trs} H > 0$
$\Rightarrow \Delta S > 0 \Leftrightarrow$ system becomes more disordered

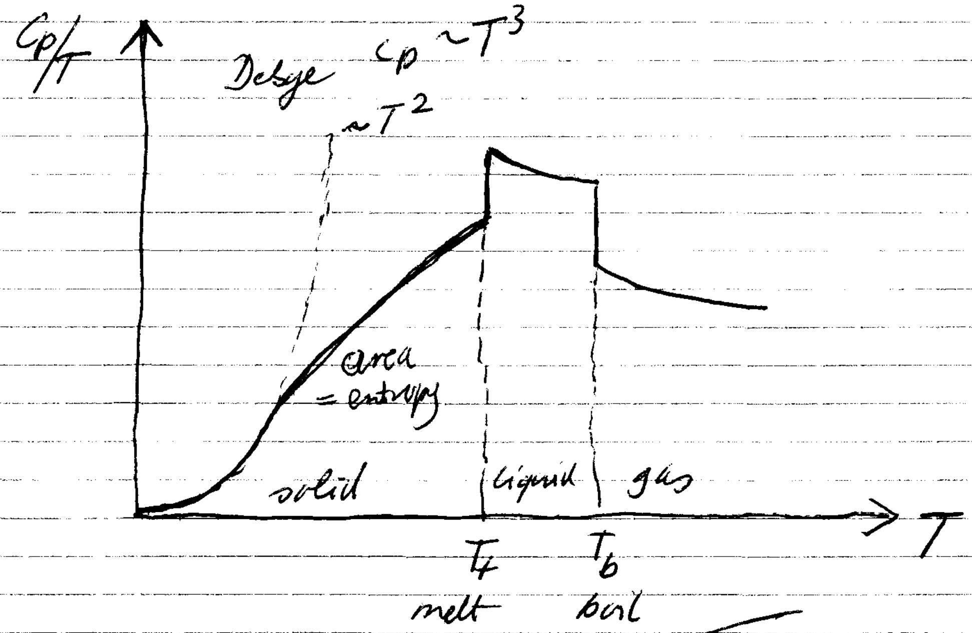
Trouton's rule

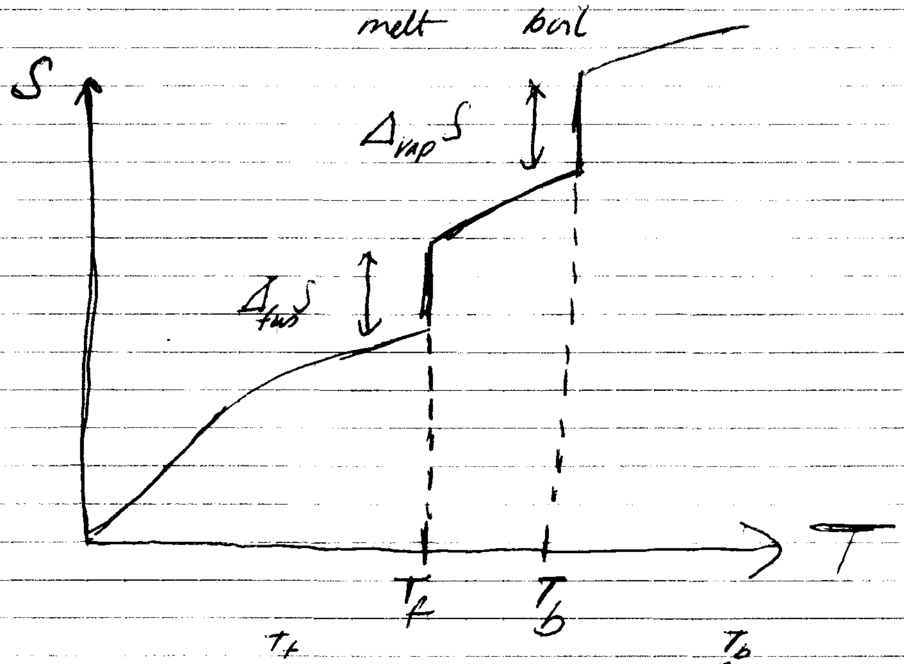
A wide range of liquids give approximately the same standard entropy of vaporization $\approx 85 \frac{J}{K\,mol}$

$\Leftrightarrow$ comparable amount of disorder is generated when any liquid evaporates and becomes a gas

(water has a larger entropy of vaporization arising from hydrogen bonding)

Calorimetry and the measurement of entropy:





$$S(T) = \underbrace{S(0)}_{=0} + \int_0^{T_f} \frac{C_p(s)\,dT}{T} + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)\,dT}{T} + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_p(g)\,dT}{T}$$