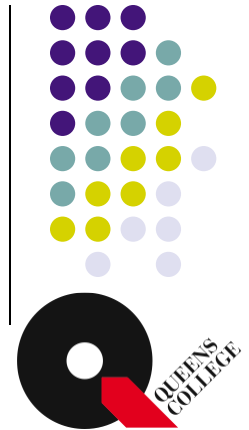# Chap. 3. <u>The Second Law</u>

↑ **Law of Spontaneity, world gets more random**

Kelvin - No process can transform heat completely into work

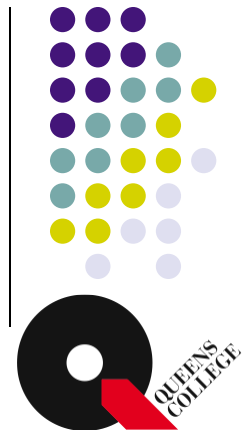# Chap. 3. <u>The Second Law</u>

↑ **Law of Spontaneity, world gets more random**

Kelvin - **No process can transform heat completely into work**

The entropy of an isolated system increases in the course of a spontaneous change.

S - **Entropy, the degree of randomness**

- **State function, completely specified by thermodynamic variables**

- **Unit: Energy/temperature (K)**

- **Thermodynamic definition:** $TdS = dq_{rev}$

Chap. 3. <u>The Second Law</u>

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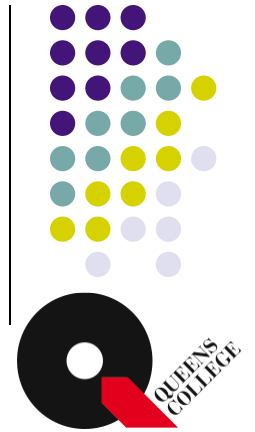$$\Delta S = S_f - S_i = \int_i^f \frac{dq_{rev}}{T}$$
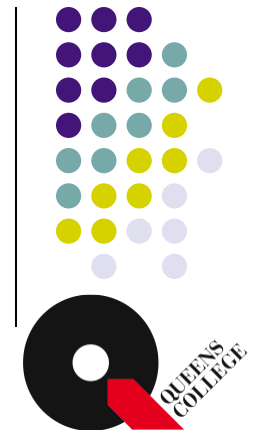
For surroundings, $dS_{sur} = \dfrac{dq_{sur}}{T_{sur}}$

because $dq_{sur} = dq_{sur,rev}$

The above relation holds even for finite amount of heat

$\longrightarrow \quad \Delta S_{sur} = \dfrac{q_{sur}}{T_{sur}}$

For surroundings, $dS_{sur} = \dfrac{dq_{sur}}{T_{sur}}$

because $dq_{sur} = dq_{sur,rev}$

The above relation holds even for finite amount of heat $\longrightarrow \Delta S_{sur} = \dfrac{q_{sur}}{T_{sur}}$

For adiabatic process, $\Delta S_{ad} = 0$

For surroundings, $dS_{sur} = \dfrac{dq_{sur}}{T_{sur}}$

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The above relation holds even for finite amount of heat $\longrightarrow$ $\Delta S_{sur} = \dfrac{q_{sur}}{T_{sur}}$
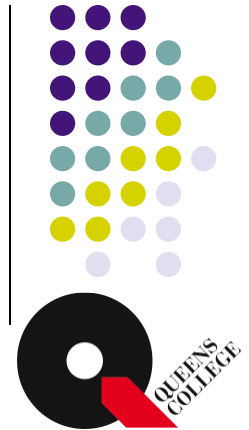
For adiabatic process, $\Delta S_{ad} = 0$
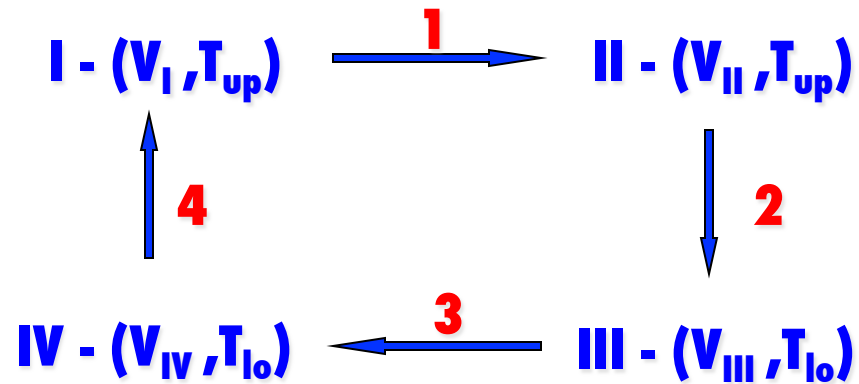
Isothermal expansion of an ideal gas

$$dU = 0 = dq_{rev} - pdV \longrightarrow dq_{rev} = pdV = \frac{nRT}{V}dV$$

$$\longrightarrow dS = \frac{dq_{rev}}{T} = \frac{nR}{V}dV$$

$$\longrightarrow \Delta S = \int_{V_i}^{V_f} dS = nR \int_{V_i}^{V_f} \frac{1}{V}dV = nR\ln\left(\frac{V_f}{V_i}\right)$$
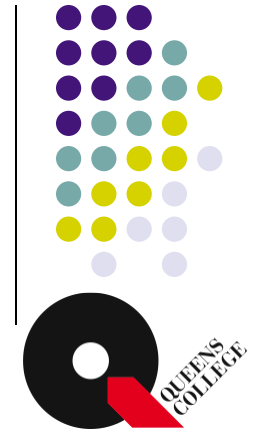
Carnot Cycle (Ideal Gas)

I - (V_I, T_{up}) $\xrightarrow{\text{1}}$ II - (V_{II}, T_{up})

$\uparrow$ 4 $\qquad\qquad$ 2 $\downarrow$

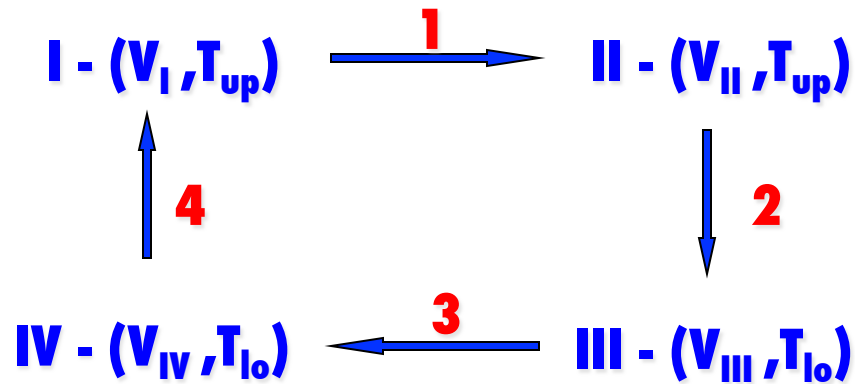IV - (V_{IV}, T_{lo}) $\xleftarrow{\text{3}}$ III - (V_{III}, T_{lo})

Fig. 3.6 (with different notations)

1,3 - Reversible and isothermal processes

2,4 - Reversible and adiabatic processes

Carnot Cycle (Ideal Gas)
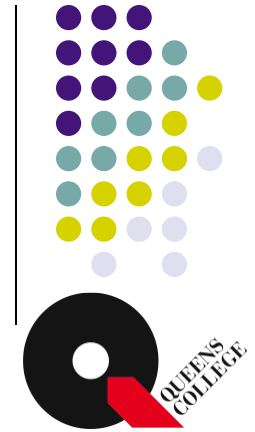
I - (V_I , T_{up}) $\xrightarrow{\textbf{1}}$ II - (V_{II} , T_{up})

$\uparrow$ **4** $\downarrow$ **2**

IV - (V_{IV} , T_{lo}) $\xleftarrow{\textbf{3}}$ III - (V_{III} , T_{lo})

Fig. 3.6 (with different notations)

1,3 - Reversible and isothermal processes

2,4 - Reversible and adiabatic processes
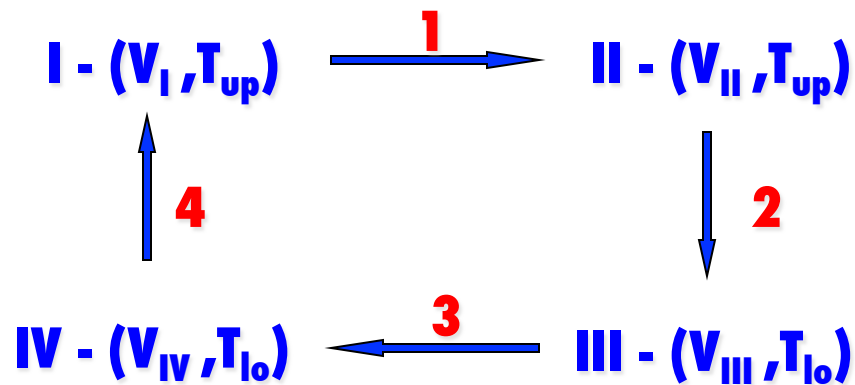
$$\Delta S_1 = nR \ln\left(\frac{V_{II}}{V_I}\right) \quad \textbf{and} \quad \Delta S_3 = nR \ln\left(\frac{V_{IV}}{V_{III}}\right)$$

$$\Delta S_2 = \Delta S_4 = 0$$

Carnot Cycle (Ideal Gas)

I - (V_I, T_{up}) $\xrightarrow{\;\;1\;\;}$ II - (V_{II}, T_{up})

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Fig. 3.6 (with different notations)

1,3 - Reversible and isothermal processes
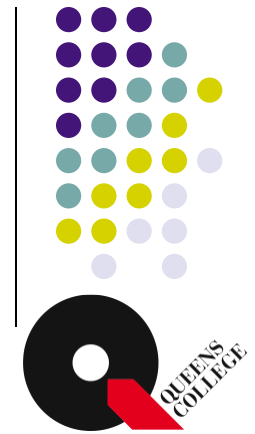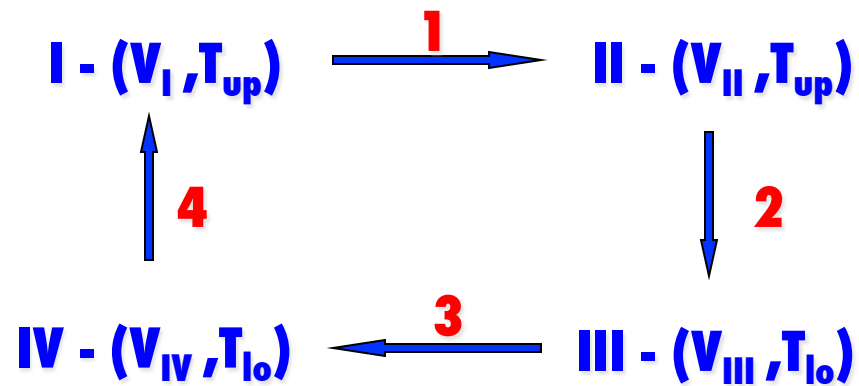
2,4 - Reversible and adiabatic processes

$$\Delta S_1 = nR\ln\left(\frac{V_{II}}{V_I}\right) \quad \text{and} \quad \Delta S_3 = nR\ln\left(\frac{V_{IV}}{V_{III}}\right)$$
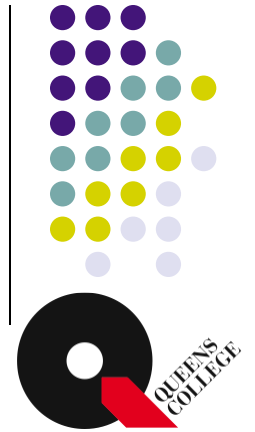
$$\Delta S_2 = \Delta S_4 = 0$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = nR\ln\left(\frac{V_{II}V_{IV}}{V_I V_{III}}\right)$$

Carnot Cycle (Ideal Gas)

$$\text{I} - (V_I, T_{up}) \xrightarrow{\ \ 1\ \ } \text{II} - (V_{II}, T_{up})$$

Fig. 3.6 (with different notations)

$$\text{IV} - (V_{IV}, T_{lo}) \xleftarrow{\ \ 3\ \ } \text{III} - (V_{III}, T_{lo})$$

(4 — left vertical arrow, 2 — right vertical arrow)

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = nR \ln \left(\frac{V_{II} V_{IV}}{V_I V_{III}} \right)$$

Carnot Cycle (Ideal Gas)

$$I - (V_I, T_{up})$$ $\xrightarrow{\ 1\ }$ $$II - (V_{II}, T_{up})$$

$\uparrow 4$ $\qquad\qquad\qquad\qquad\qquad \downarrow 2$

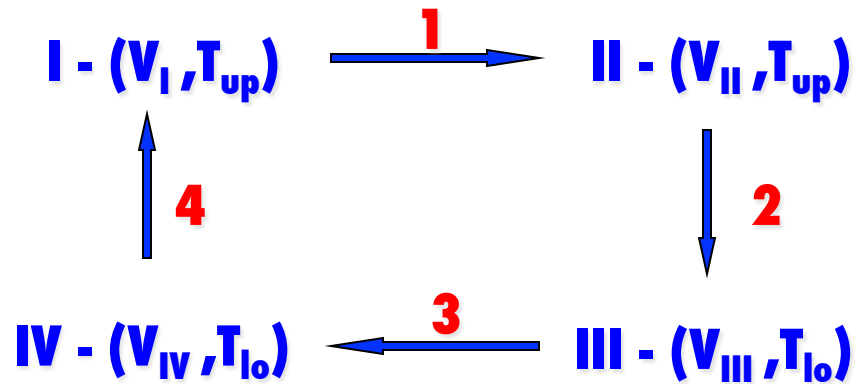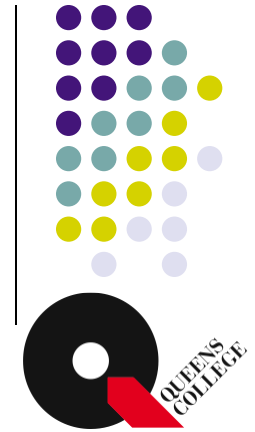$$IV - (V_{IV}, T_{lo})$$ $\xleftarrow{\ 3\ }$ $$III - (V_{III}, T_{lo})$$

Fig. 3.6 (with different notations)

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = nR \ln\left(\frac{V_{II}V_{IV}}{V_I V_{III}}\right)$$

$$\frac{V_{II}}{V_{III}} = \left(\frac{T_{lo}}{T_{up}}\right)^c$$ **and** $$\frac{V_{IV}}{V_I} = \left(\frac{T_{up}}{T_{lo}}\right)^c$$ **, where** $$c = \frac{C_V}{nR}$$

See further information 2.1 (page 69)

Carnot Cycle (Ideal Gas)

$$I - (V_I, T_{up}) \xrightarrow{\quad 1 \quad} II - (V_{II}, T_{up})$$

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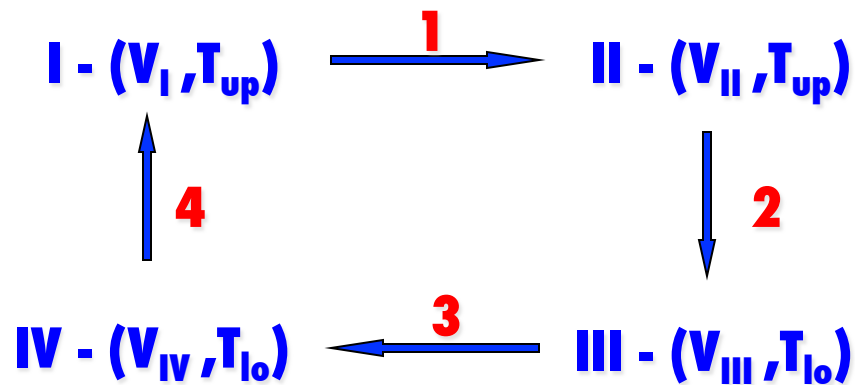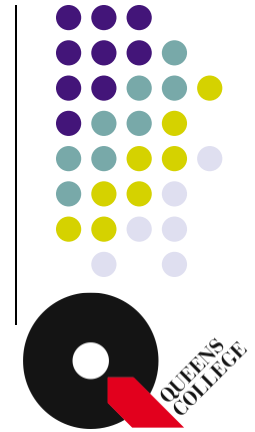
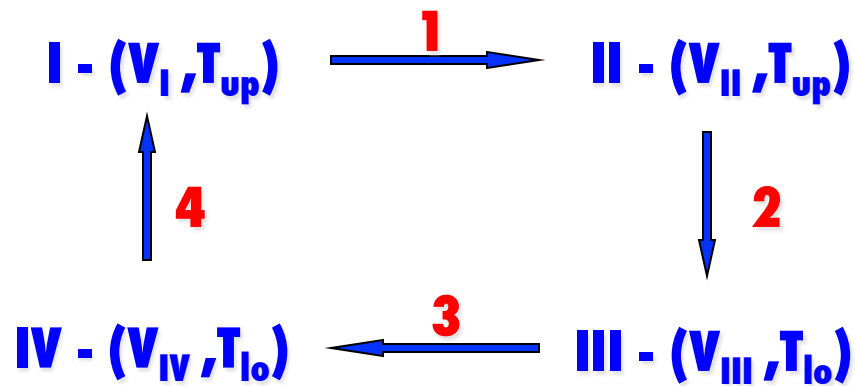**Fig. 3.6 (with different notations)**

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = nR \ln \left(\frac{V_{II} V_{IV}}{V_I V_{III}} \right)$$

$$\frac{V_{II}}{V_{III}} = \left(\frac{T_{lo}}{T_{up}} \right)^c \quad \textbf{and} \quad \frac{V_{IV}}{V_I} = \left(\frac{T_{up}}{T_{lo}} \right)^c \textbf{, where} \quad c = \frac{C_V}{nR}$$

See further information 2.1 (page 69)

$$\longrightarrow \quad \Delta S = nR \ln \left(\frac{T_{lo}}{T_{up}} \frac{T_{up}}{T_{lo}} \right)^c = nR \ln 1 = 0$$

Carnot Cycle (Ideal Gas)

I - (V_I, T_{up}) $\xrightarrow{\textbf{1}}$ II - (V_{II}, T_{up})

4 $\uparrow$ $\downarrow$ **2**

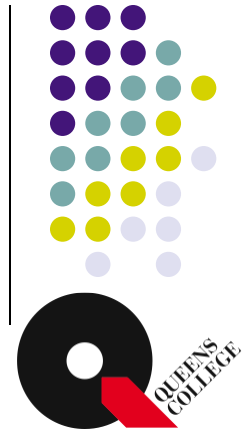IV - (V_{IV}, T_{lo}) $\xleftarrow{\textbf{3}}$ III - (V_{III}, T_{lo})

$1 : q_1 = q_{up}, w_1 = -q_{up}$

$2 : q_2 = 0, w_2 = -w_{ad}$
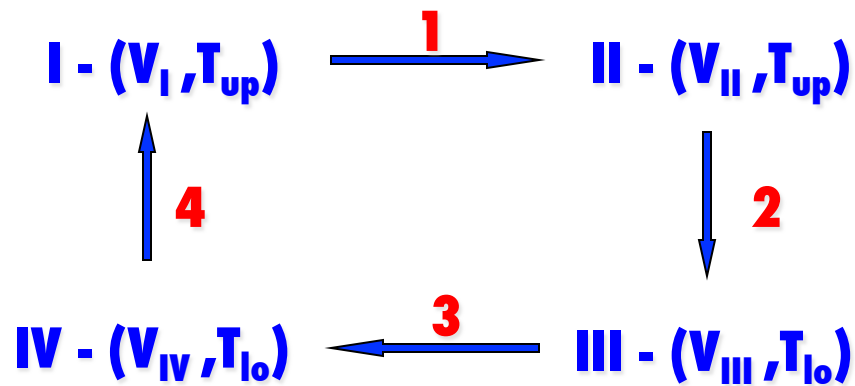
$3 : q_3 = -q_{lo}, w_3 = q_{lo}$

$4 : q_4 = 0, w_4 = w_{ad}$

$$\Delta S = 0 = S_1 + S_3 = \frac{q_{up}}{T_{up}} - \frac{q_{lo}}{T_{lo}} \longrightarrow \frac{q_{up}}{q_{lo}} = \frac{T_{up}}{T_{lo}}$$

Carnot Cycle (Ideal Gas)

I - (V_I, T_{up}) $\xrightarrow{\text{1}}$ II - (V_{II}, T_{up})

$\uparrow$ 4

$\downarrow$ 2

IV - (V_{IV}, T_{lo}) $\xleftarrow{\text{3}}$ III - (V_{III}, T_{lo})

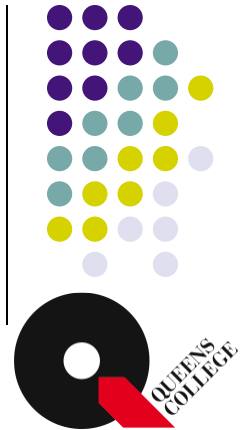$1 : q_1 = q_{up}, w_1 = -q_{up}$

$2 : q_2 = 0, w_2 = -w_{ad}$

$3 : q_3 = -q_{lo}, w_3 = q_{lo}$

$4 : q_4 = 0, w_4 = w_{ad}$

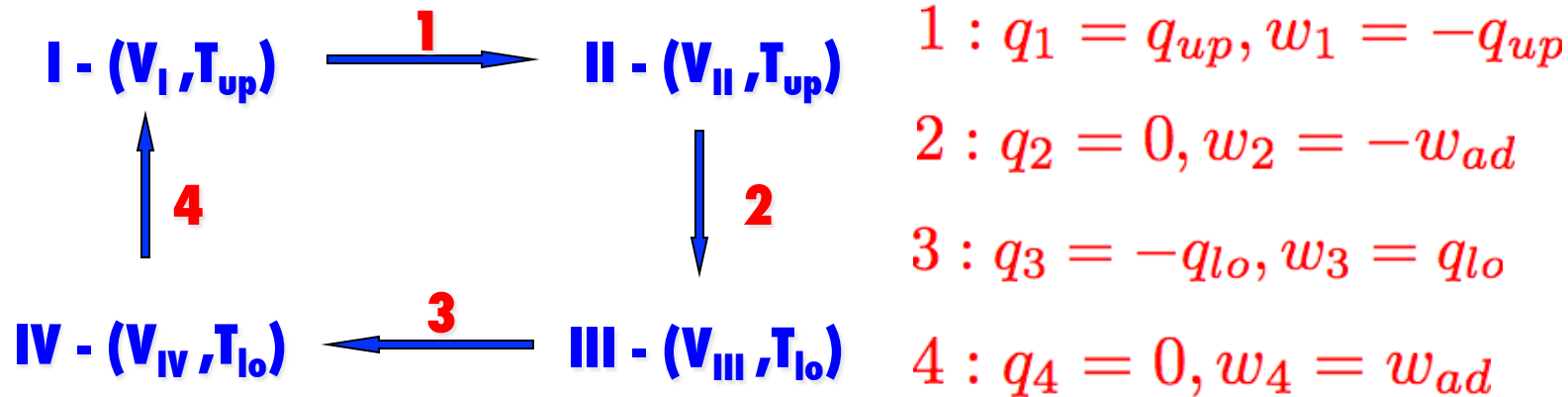$$\Delta S = 0 = S_1 + S_3 = \frac{q_{up}}{T_{up}} - \frac{q_{lo}}{T_{lo}} \xrightarrow{\hspace{1cm}} \frac{q_{up}}{q_{lo}} = \frac{T_{up}}{T_{lo}}$$

$$q = q_{up} - q_{lo}$$

$$w = w_1 + w_2 + w_3 + w_4 = -q_{up} + q_{lo} = -q$$
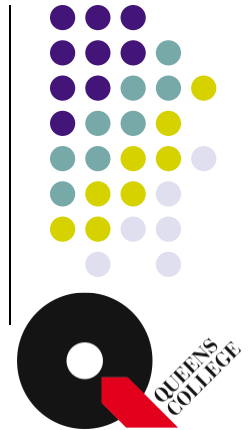
Carnot Cycle (Ideal Gas)

I - (V_I, T_{up}) $\xrightarrow{\ 1\ }$ II - (V_{II}, T_{up})

$\uparrow 4$ $\qquad\qquad\qquad\downarrow 2$

IV - (V_{IV}, T_{lo}) $\xleftarrow{\ 3\ }$ III - (V_{III}, T_{lo})

$1 : q_1 = q_{up}, w_1 = -q_{up}$

$2 : q_2 = 0, w_2 = -w_{ad}$

$3 : q_3 = -q_{lo}, w_3 = q_{lo}$

$4 : q_4 = 0, w_4 = w_{ad}$

$$\Delta S = 0 = S_1 + S_3 = \frac{q_{up}}{T_{up}} - \frac{q_{lo}}{T_{lo}} \qquad\longrightarrow\qquad \frac{q_{up}}{q_{lo}} = \frac{T_{up}}{T_{lo}}$$
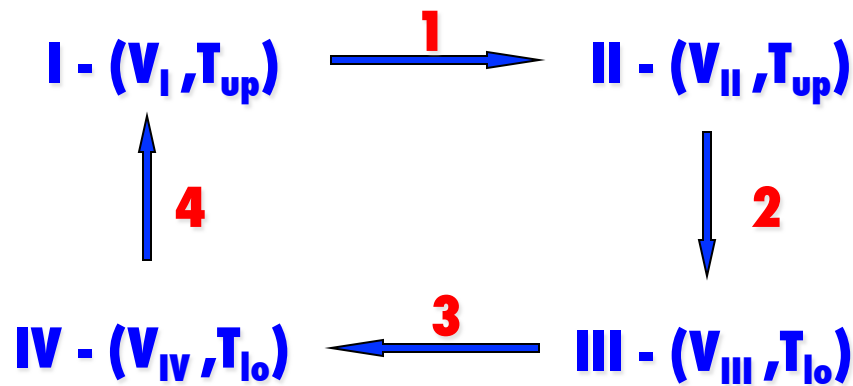
$$q = q_{up} - q_{lo}$$

$$w = w_1 + w_2 + w_3 + w_4 = -q_{up} + q_{lo} = -q$$

Efficiency: $\quad \mathcal{E} = \dfrac{-w}{q_{up}} = \dfrac{q_{up} - q_{lo}}{q_{up}} = 1 - \dfrac{q_{lo}}{q_{up}} = 1 - \dfrac{T_{lo}}{T_{up}}$

Carnot Cycle (General)

I - (V_I, T_{up}) $\xrightarrow{\text{1}}$ II - (V_{II}, T_{up})

$\uparrow$ 4   2 $\downarrow$

IV - (V_{IV}, T_{lo}) $\xleftarrow{\text{3}}$ III - (V_{III}, T_{lo})

$1 : q_1 = q_{up}$

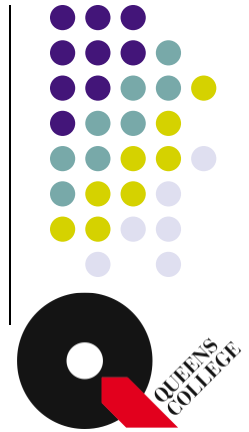$2 : q_2 = 0$

$3 : q_3 = -q_{lo}$

$4 : q_4 = 0$

$$\Delta S = S_1 + S_3 = \frac{q_{up}}{T_{up}} - \frac{q_{lo}}{T_{lo}}$$

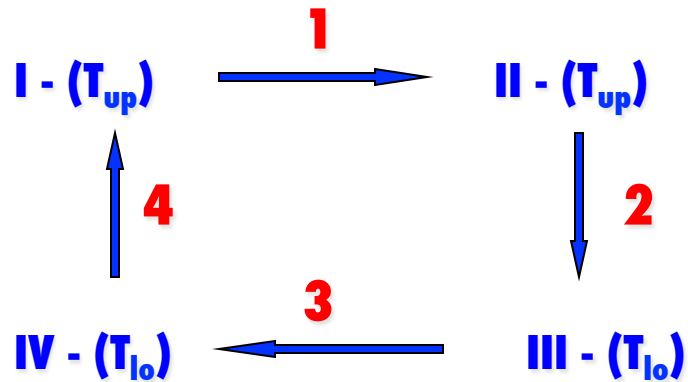$$q = q_{up} - q_{lo} \longrightarrow w = -q \quad \textbf{(First law)}$$

Efficiency: $\mathcal{E} = -\dfrac{w}{q_{up}} = \dfrac{q_{up} - q_{lo}}{q_{up}} = 1 - \dfrac{q_{lo}}{q_{up}} = ?$

If $\mathcal{E} \neq 1 - \dfrac{T_{lo}}{T_{up}} = \mathcal{E}_{id}$, then $\Delta S \neq 0 \longrightarrow$ **S is not a state function**
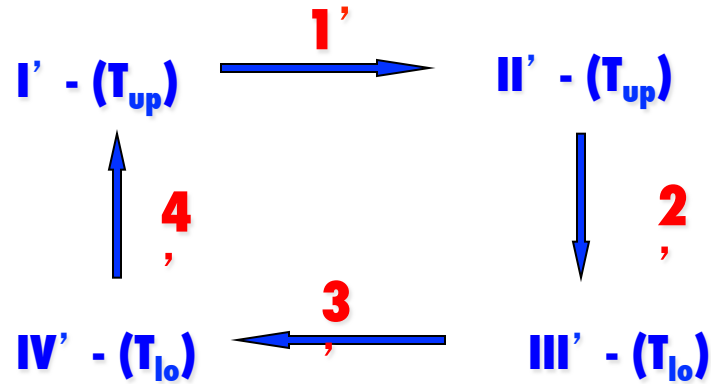
Proof that $\mathcal{E} = \mathcal{E}_{id}$

Carnot cycle A with $\mathcal{E}$

$$I - (T_{up}) \xrightarrow{\;1\;} II - (T_{up})$$

4 ↑   ↓ **2**

$$IV - (T_{lo}) \xleftarrow{\;3\;} III - (T_{lo})$$

Carnot cycle B with $\mathcal{E}'$

$$I' - (T_{up}) \xrightarrow{\;1'\;} II' - (T_{up})$$

4' ↑   ↓ **2'**

$$IV' - (T_{lo}) \xleftarrow{\;3'\;} III' - (T_{lo})$$

Assume that $\mathcal{E} > \mathcal{E}'$

Then, $1 - \dfrac{q_{lo}}{q_{up}} > 1 - \dfrac{q'_{lo}}{q'_{up}}$

Proof that $\mathcal{E} = \mathcal{E}_{id}$

Carnot cycle A with $\mathcal{E}$ **Carnot cycle B with** $\mathcal{E}'$
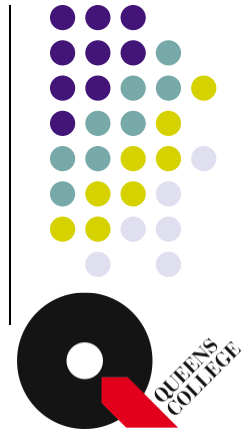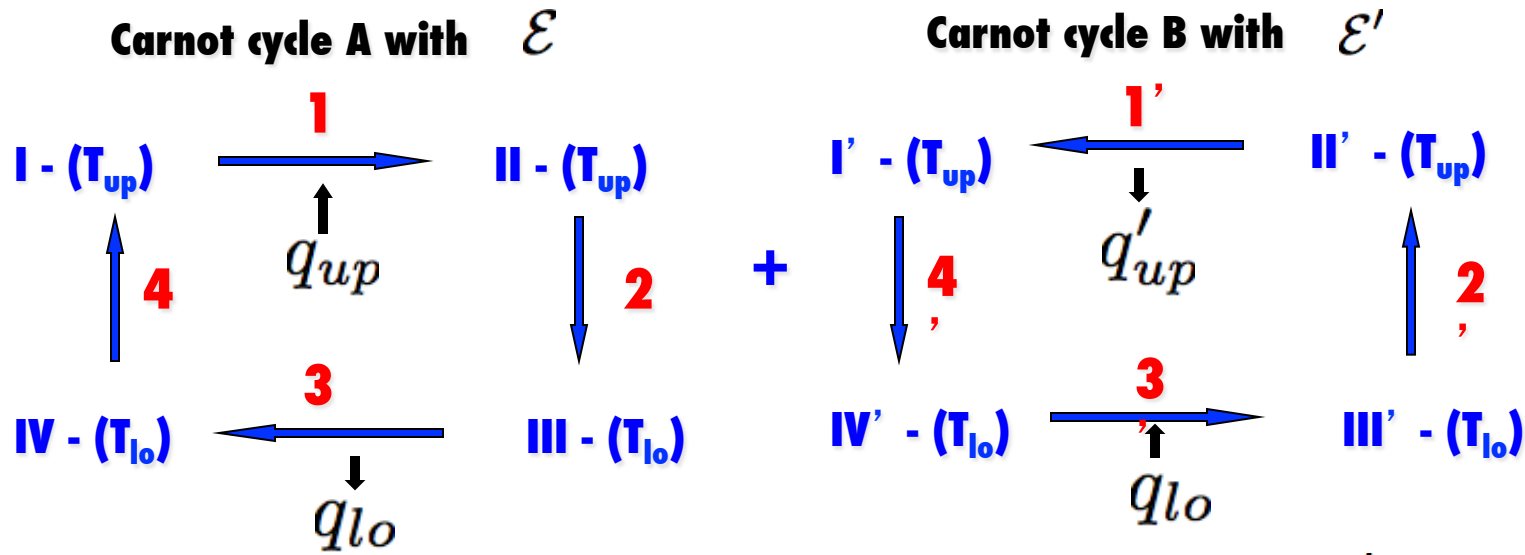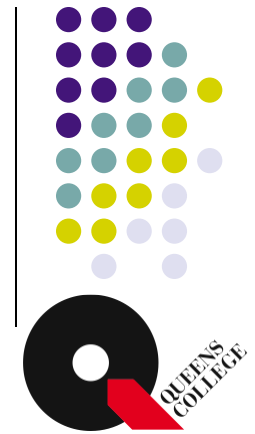

Assume that $\mathcal{E} > \mathcal{E}'$ Then, $1 - \dfrac{q_{lo}}{q_{up}} > 1 - \dfrac{q'_{lo}}{q'_{up}}$
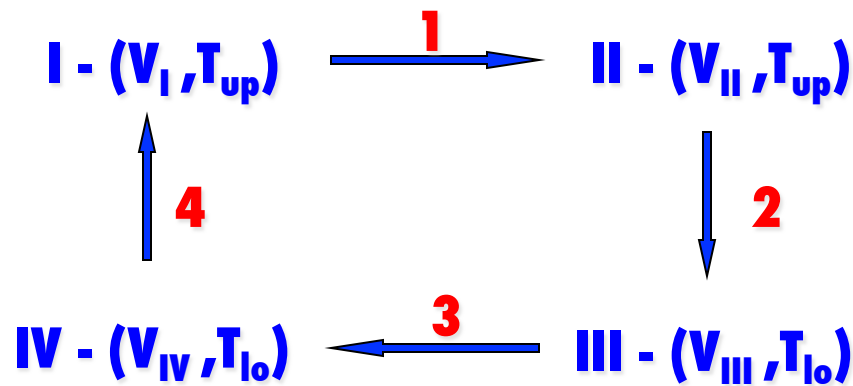
Combine A and reverse of B, and assume $q_{lo} = q'_{lo}$

Then, $q_{up} > q'_{up}$ ⟶ $w - w' = -q_{up} + q'_{up} < 0$

Complete conversion of heat $q_{up} - q'_{up}$ into work $-w + w'$

This contradicts the second law by Kelvin! ⟶ $\mathcal{E} = \mathcal{E}'$

Carnot Cycle (General)

I - (V_I, T_{up}) →[1] II - (V_{II}, T_{up})

↑[4]   ↓[2]

IV - (V_{IV}, T_{lo}) ←[3] III - (V_{III}, T_{lo})

$1 : q_1 = q_{up}$
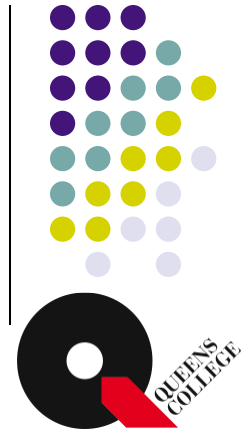
$2 : q_2 = 0$

$3 : q_3 = -q_{lo}$

$4 : q_4 = 0$

Efficiency: $\mathcal{E} = -\dfrac{w}{q_u p} = \dfrac{q_{up} - q_{lo}}{q_{up}} = 1 - \dfrac{q_{lo}}{q_{up}} = \mathcal{E}_{id} = 1 - \dfrac{T_{lo}}{T_{up}}$

$$\Delta S = S_1 + S_3 = \frac{q_{up}}{T_{up}} - \frac{q_{lo}}{T_{lo}} = \frac{q_{up}}{T_{lo}} \left(\frac{T_{lo}}{T_{up}} - \frac{q_{lo}}{q_{up}} \right) = 0$$

Any cycle can be considered as the sum of infinitesimal Carnot cycles (Fig. 3.9) → $\displaystyle\oint \frac{dq_{rev}}{T} = \sum_{Carnot,i} \Delta S_i = 0$

S defined such that $dS = \dfrac{dq_{rev}}{T}$ is a state function.

Clausius Inequality: $dS \geq \dfrac{dq}{T}$

Clausius Inequality: $dS \geq \dfrac{dq}{T}$

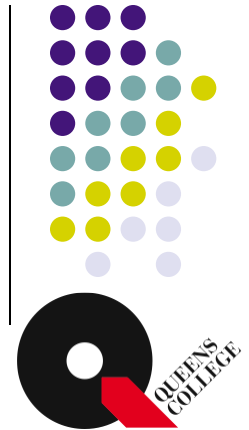(i) $-dW_{rev} \geq -dW$ **System does maximum work for reversible process.**

(ii)

Consider a change of system through a reversible process

$$dU = dq_{rev} + dW_{rev} \qquad (1)$$

The same change can happen through another process.
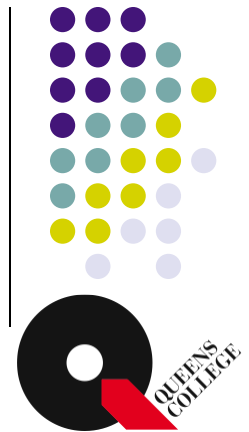
$$dU = dq + dW \qquad (2)$$

Clausius Inequality: $dS \geq \dfrac{dq}{T}$

(i) $\quad -dW_{rev} \geq -dW$ **System does maximum work for reversible process.**

(ii)

Consider a change of system through a reversible process   **(1)**

$$dU = dq_{rev} + dW_{rev} \qquad (1)$$

The same change can happen through another process.

$$dU = dq + dW \qquad (2)$$

(1)=(2) $\longrightarrow$ $dq_{rev} + dW_{rev} = dq + dW$

$$\longrightarrow \quad TdS - dq = dW - dW_{rev} \geq 0$$

$\uparrow$

(i)

For adiabatic process $\quad dS \geq 0$

Entropy change due to phase transition

Normal transition temperature: temperature at which two phases are in equilibrium at 1 atm.

Heat transfer during phase transition is reversible $\longrightarrow$ $\Delta_{trs}S = \dfrac{\Delta q}{T_{trs}} = \dfrac{\Delta_{trs}H}{T_{trs}}$

Constant pressure

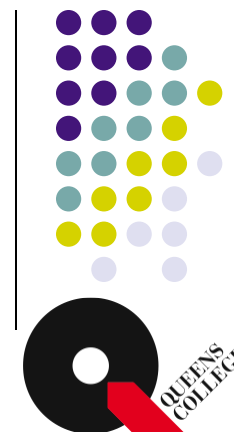## Entropy change due to heating

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

Constant pressure

If C_p is independent of temperature
$$= C_p \ln\left(\frac{T_f}{T_i}\right)$$

Entropy of a gas

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

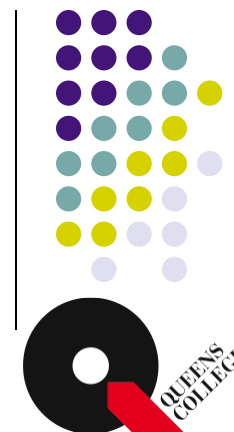$$+ \quad \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_p(g)}{T}dT$$

$$C_p(s) \propto T^3 \text{ as } T \to 0 \qquad \textbf{(Debye extrapolation)}$$

Nernst heat theorem

$\Delta S \to 0$ as $\Delta T \to 0$ for perfect crystalline substances

Third law of thermodynamics

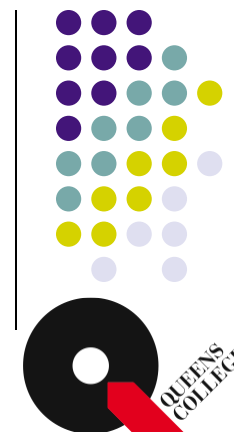For perfect crystalline substances, $S = 0$ at $T = 0$.

Standard (third law) entropy

$S^{\ominus}(T)$ - the entropy in the standard state under the   assumption that S=0 at T=0.

Entropy of reaction for $\sum_i \nu_i M_i \rightarrow \sum_f \nu_f M_f$

$$\Delta_r S^{\ominus} = \sum_f \nu_f S_m^{\ominus}(f) - \sum_i \nu_i S_m^{\ominus}(i)$$

Standard of entropies of ions are defined such that $S^{\ominus}(H^+, \mathrm{aq}) = 0$

Helmholtz free energy

Determines the spontaneous (free) process at constant volume

$$A = U - TS$$

$$dS \geq \frac{dq}{T} \quad \longrightarrow \quad (dA)_{T,V} = dq - TdS \leq 0$$
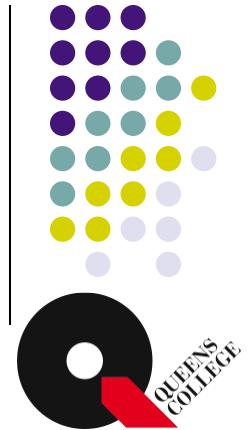
(no non-expansion work)

Gibbs free energy

Determines the spontaneous (free) process at constant process

$$G = H - TS = U + pV - TS$$

$$dS \geq \frac{dq}{T} \quad \longrightarrow \quad (dG)_{T,p} = dq - TdS \leq 0$$

(no non-expansion work)

$$(dG)_{T,p} = (dU)_{T,p} + pdV - TdS = dq - pdV + pdV - TdS$$

Helmholtz free energy

Determines the spontaneous (free) process at constant volume

$$A = U - TS$$

$$dS \geq \frac{dq}{T} \longrightarrow (dA)_{T,V} = dq - TdS \leq 0$$

(no non-expansion work)

$$-(dA)_T = -dW - dq + TdS \geq -dW$$

Maximum work system can do in isothermal situation

Gibbs free energy

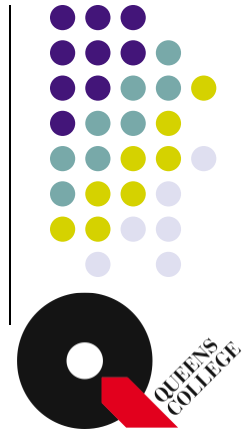**Determines the spontaneous (free) process at constant process**

$$G = H - TS = U + pV - TS$$

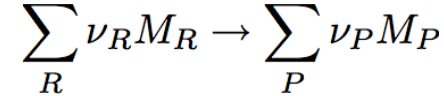$$dS \geq \frac{dq}{T} \longrightarrow (dG)_{T,p} = dq - TdS \leq 0$$

(no non-expansion work)

$$-(dG)_{T,P} = -dq + pdV - dW_e - pdV + TdS \geq -dW_e$$

Maximum non-expansion work system can do in isothermal and isobaric situation

Standard Gibbs energy of reaction $\qquad \displaystyle\sum_R \nu_R M_R \rightarrow \sum_P \nu_P M_P$

$$\Delta_r G^\ominus = \sum_P \nu_P \Delta_f G_P^\ominus - \sum_R \nu_R \Delta_f G_R^\ominus$$
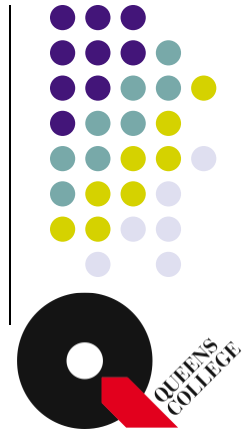
Standard Gibbs energy of formation

The standard Gibbs energy of formation for ions are defined such that

$$\Delta_f G^\ominus(H^+, \mathrm{aq}) = 0$$

zero standard Gibbs energy of formation at all temperature

Fundamental equation

closed system, no non-expansion work, reversible change

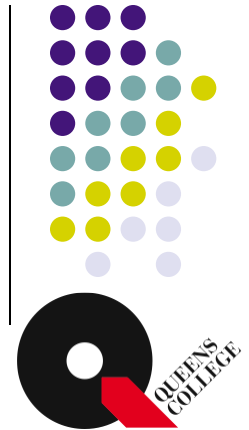$$dU = dq_{rev} + dW_{rev,exp} = \underline{TdS - pdV}$$

↑

valid even for irreversible change

Assume $U = U(S,V)$ ⟶ $dU = \left(\dfrac{\partial U}{\partial S}\right)_V dS + \left(\dfrac{\partial U}{\partial V}\right)_S dV$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \textbf{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Assume that $T = T(S,V)$ **and** $p = p(S,V)$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$dA = d(U - TS) = TdS - pdV - TdS - SdT = -SdT - pdV$$

$$dH = d(U + pV) = TdS - pdV + pdV + Vdp = TdS + Vdp$$

$$dG = d(H - TS) = TdS + Vdp - TdS - SdT = -SdT + Vdp$$

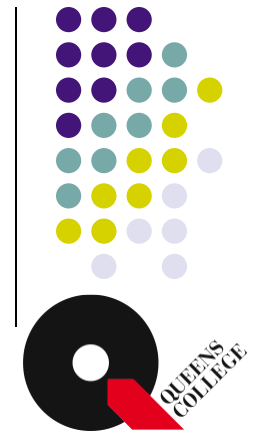$$dA = d(U - TS) = TdS - pdV - TdS - SdT = -SdT - pdV \quad \textbf{(2)}$$

$$dH = d(U + pV) = TdS - pdV + pdV + Vdp = TdS + Vdp \quad \textbf{(3)}$$

$$dG = d(H - TS) = TdS + Vdp - TdS - SdT = -SdT + Vdp \quad \textbf{(4)}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \textbf{(2')}$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \left(\frac{\partial H}{\partial p}\right)_S = V \qquad \textbf{(3')}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \textbf{(4')}$$

$$dA = d(U - TS) = TdS - pdV - TdS - SdT = -SdT - pdV \quad \textbf{(2)}$$

$$dH = d(U + pV) = TdS - pdV + pdV + Vdp = TdS + Vdp \quad \textbf{(3)}$$

$$dG = d(H - TS) = TdS + Vdp - TdS - SdT = -SdT + Vdp \quad \textbf{(4)}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \textbf{(2')}$$
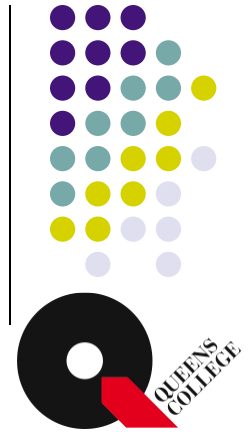
$$\left(\frac{\partial H}{\partial S}\right)_p = T, \left(\frac{\partial H}{\partial p}\right)_S = V \qquad \textbf{(3')}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \textbf{(4')}$$

$$\textbf{(2')} \longrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial^2 A}{\partial V \partial T}$$

$$\textbf{(3')} \longrightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad \frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}$$

$$\textbf{(4')} \longrightarrow \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \qquad \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T}$$
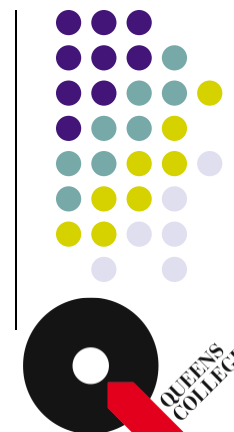
Gibbs-Helmholtz equation

$$G = H - TS$$

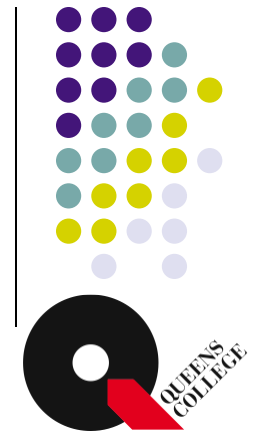$$\Rightarrow \quad \frac{H - G}{T} = S = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$\Rightarrow \quad \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{H}{T^2}$$

$$\Rightarrow \quad \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{H}{T^2}$$

$$\Rightarrow \quad \frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2}$$

Important equation for understanding phase transition

At constant temperature,

$$dG = V\,dp$$

$$\longrightarrow \quad G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m\,dp$$

Molar Gibbs energy   Molar volume

For liquids or solids, V_m is insensitive to pressure change

$$G_m(p_f) \approx G_m(p_i) + V_m \int_{p_i}^{p_f} dp = G_m(p_i) + (p_f - p_i)V_m$$

For an ideal gas,

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} \frac{RT}{p}\,dp = G_m(p_i) + RT\ln\left(\frac{p_f}{p_i}\right)$$

$$G_m(p) = G_m^{\ominus} + RT\ln\left(\frac{p}{p^{\ominus}}\right) \qquad \textbf{When} \qquad p_i = p^{\ominus}$$