

1. Function of state: function which depends on state of system and not on how it reached that state.

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

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

$$= \int_{T_1}^{T_2} \frac{C dT}{T} \quad \left[C_x = \left(\frac{dq_{rev}}{dT} \right)_x \right]$$

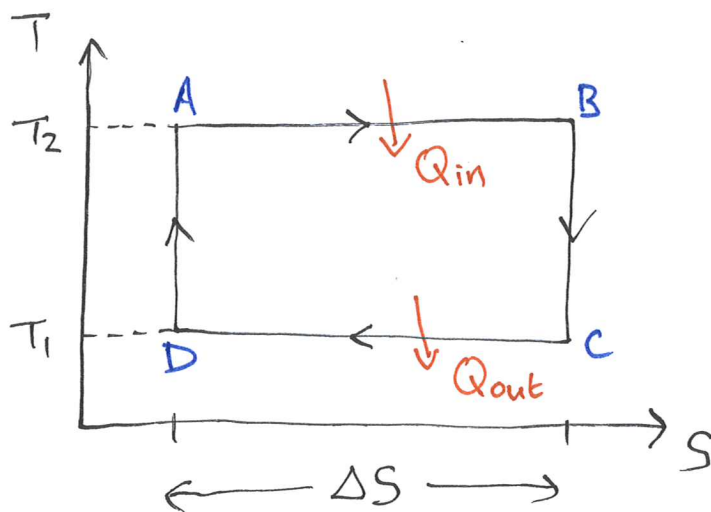
$$= C \ln(T_2/T_1) \text{ providing } C \text{ is indep. of } T.$$

2.

Thermal efficiency

$$\eta = \frac{\text{Work done}}{\text{Heat absorbed}}$$

$$= \frac{W}{Q_{in}}$$



A → B Isothermal, heat Q_{in} absorbed

B → C Adiabatic

C → D Isothermal, heat Q_{out} expelled

D → A Adiabatic

First Law of Thermodynamics

$$W = Q_{in} - Q_{out}$$

$$\rightarrow \eta = \frac{Q_{in} - Q_{out}}{Q_{in}}$$

Carnot cycle is reversible

$$\rightarrow Q_{in} = T_2 \Delta S$$

$$Q_{out} = T_1 \Delta S$$

$$\rightarrow \eta = \frac{T_2 - T_1}{T_2}$$

$$= \frac{1 - T_1/T_2}{1} \quad [\text{nb. in lectures } T_1 > T_2 \rightarrow \eta = 1 - T_2/T_1]$$

Steam engine :

$$T_1 \approx 300\text{K}, \quad T_2 \approx 800\text{K}$$

$$\rightarrow \underline{\eta \approx 63\%} \quad [\text{reduced in practice by friction}]$$

3. Helmholtz $F = U - TS$
 Gibbs $G = U - TS + pV$

Fundamental eq. $dU = TdS - pdV$

$\rightarrow dF = -SdT - pdV$ — ①

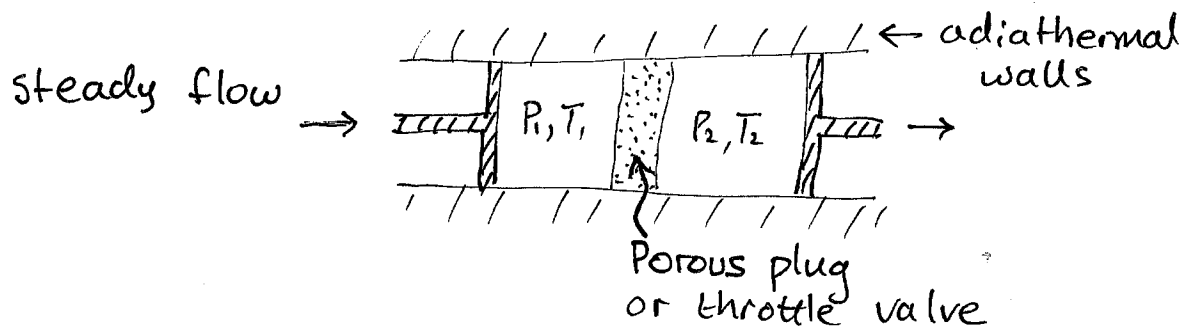
$dG = -SdT + Vdp$ — ②

From ① $-S = \left(\frac{\partial F}{\partial T}\right)_V$ and $-P = \left(\frac{\partial F}{\partial V}\right)_T$

Then $\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Similarly, from ② $\rightarrow \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

Joule - Kelvin expansion:



3. cont.

$$\begin{aligned}\mu_{JK} &= \left(\frac{\partial T}{\partial P}\right)_H \\ &= - \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T \quad \text{by reciprocity} \\ &\quad \text{--- (1)}\end{aligned}$$

Enthalpy: $H = U + pV$

$$\rightarrow dH = \underbrace{T ds}_{dQ_{rev}} + V dp$$

$$\rightarrow \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q_{rev}}{\partial T}\right)_P = C_P \quad \text{--- (2)}$$

and $\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \quad \text{--- (3)}$

Sub. (2) & (3) in (1)

$$\rightarrow \mu_{JK} = \frac{-1}{C_P} \left[T \left(\frac{\partial S}{\partial P}\right)_T + V \right]$$

Maxwell

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$= \frac{-1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

$$= \frac{V}{C_P} \left[T \beta_P - 1 \right] \quad \beta_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

3. cont.

$$p(V-b) = RT - \frac{ap}{RT}$$

$$\rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2} \quad \text{--- ①}$$

$$\text{and } p = \frac{RT}{V-b + a/RT} \quad \text{--- ②}$$

Sub. ② in ①

$$\rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{V-b + a/RT}{T} + \frac{a}{RT^2}$$

$$\rightarrow \beta_p = \frac{V-b}{VT} + \frac{2a}{RT^2V}$$

$$\rightarrow \mu_{JK} = \frac{V}{C_p} \left[\frac{V-b}{V} + \frac{2a}{RTV} - 1 \right]$$

$$= \frac{1}{C_p} \left[V-b + \frac{2a}{RT} - V \right]$$

$$= \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$$

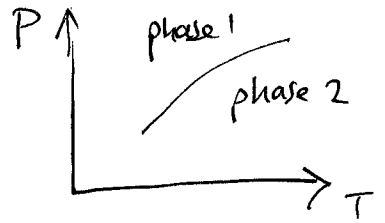
Significance is that μ_{JK} can be > 0 or < 0 depending on T . So Joule-Kelvin expansion can result in heating or cooling.
($\mu_{JK} < 0$) ($\mu_{JK} > 0$)

4. $dG = -SdT + Vdp$

Chemical potential $\mu = \frac{G}{N}$

Define $s = \frac{S}{N}$ and $v = \frac{V}{N}$.

On phase boundary $\mu_1 = \mu_2$



Take small step along phase boundary

$$\rightarrow d\mu_1 = d\mu_2$$

$$\rightarrow -s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$\rightarrow (v_2 - v_1) dp = (s_2 - s_1) dT$$

$$\rightarrow \frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

From Second Law of thermodynamics

$$dS = \frac{dQ_{rev}}{T}$$

$$\rightarrow \Delta S = \frac{L}{T} \quad \text{where } L \text{ is heat absorbed when system changes from phase 1 to phase 2}$$

$$\rightarrow \frac{dp}{dT} = \frac{L}{T \Delta v}$$

Clausius-Clapeyron eq.

Nb. If L is per unit mass, then Δv is per unit mass.

4. cont.

Perfect gas: $pV = RT$ ($V = \text{vol. of 1 mole}$)

$$\begin{aligned} \frac{\text{Vol. of 1 kg}}{\text{Specific vol.}} &= \frac{V}{M_A} & (M_A = \text{molecular mass} \\ &= \frac{RT}{M_A P} & = 0.018 \text{ kg for water}) \end{aligned}$$

In Clausius - Clapeyron eq. $\Delta V = V_{\text{vap}} - V_{\text{liq}}$

$$\begin{aligned} &\approx V_{\text{vap}} \\ &\approx \frac{RT}{M_A P} \end{aligned}$$

$$\rightarrow \frac{dp}{dT} = \frac{M_A L P}{R T^2}$$

Integrate:

$$\int_{P_0}^P \frac{dp}{P} = \frac{M_A L}{R} \int_{T_0}^T \frac{dT}{T^2} \quad (\text{assume } L \text{ is indep. of } T)$$

$$\rightarrow \ln\left(\frac{P}{P_0}\right) = -\frac{M_A L}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

When $P_0 = 1 \text{ atm}$, $T_0 = 373 \text{ K}$.

If $P = 2 \text{ atm}$ then

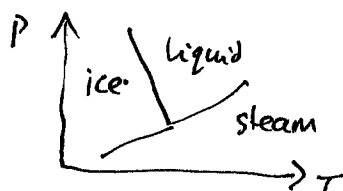
$$\ln 2 = -\frac{M_A L}{R} \left(\frac{1}{T} - \frac{1}{373 \text{ K}}\right)$$

$$= -\frac{0.018 \times 2.272 \times 10^6}{8.314} \left(\frac{1}{T} - \frac{1}{373 \text{ K}}\right)$$

$$\rightarrow \underline{T = 394 \text{ K}}$$

When ice melts the specific vol. decreases, so $\Delta V < 0$.

Hence, $\frac{dp}{dT} < 0$



5. Photon flux = $\frac{1}{4} n c$ (kinetic theory)

→ Energy flux = $\frac{1}{4} u c$ ($u = AT^4$)

= $\frac{\sigma T^4}{4}$ Stefan's Law

where

$\sigma = \frac{1}{4} A c = \frac{\pi^2 k_B^4}{60 h^3 c^2}$ Stefan-Boltzmann const.

Fundamental eq. $dU = T ds - p dV$

→ $u = Ts - p$ ($s =$ entropy density)

From kinetic theory $p = \frac{1}{3} n m c^2$

= $\frac{1}{3} u$ for photons ($\epsilon = mc^2$)

→ $s = \frac{4}{3} \frac{u}{T}$

= $\frac{4}{3} AT^3$

= $\frac{16}{3} \frac{\sigma}{c} T^3$

Adiabatic expansion: $ds = 0$

→ $dU = -p dV$

→ $V du + u dV = -\frac{1}{3} u dV$ ($U = uV, p = \frac{1}{3} u$)

→ $\frac{du}{u} = -\frac{4}{3} \frac{dV}{V}$

Integrate:

$\ln(u/u_i) = -\frac{4}{3} \ln(V/V_i)$

→ $4 \ln(T/T_i) = -\frac{4}{3} \ln(V/V_i)$ ($u = AT^4$)

→ $\frac{T}{T_i} = \left(\frac{V_i}{V}\right)^{1/3}$

So if $V = \alpha V_i$ then $T = T_i / \alpha^{1/3}$

Wien's Law: $\lambda_{\max} T = \text{const.}$

→ $\frac{\lambda_{\max}^{\text{Sun}}}{\lambda_{\max}^{\text{Nstar}}} = \frac{T^{\text{Nstar}}}{T^{\text{Sun}}} \rightarrow T^{\text{Nstar}} = \frac{510}{350} \times 5700 \text{ K}$
 = 8306 K

$$6. \quad F = -k_B T \ln Z$$

Fundamental eq. including chemical potential is

$$dU = TdS - pdV + \mu dN$$

$$\rightarrow dF = -SdT - pdV + \mu dN \quad (F = U - TS)$$

$$\rightarrow \mu = \left(\frac{\partial F}{\partial N} \right)_{T, V}$$

Given $Z = \frac{(Vz)^N}{N!}$ for ideal gas

$$\rightarrow F = -k_B T N \ln(Vz) + k_B T \ln(N!)$$

Stirling's formula: $\ln N! = N \ln N - N$

$$\rightarrow F = -k_B T N \ln(Vz) + k_B T N \ln N - k_B T N$$

$$\rightarrow \left(\frac{\partial F}{\partial N} \right)_{T, V} = -k_B T \ln(Vz) + k_B T \ln N + \cancel{k_B T} - \cancel{k_B T}$$

$$\rightarrow \mu = k_B T \ln \left(\frac{N}{V} \frac{1}{z} \right)$$

7.

$$Z = \sum_j e^{-\beta E_j}$$

$$P_j = \frac{e^{-\beta E_j}}{Z}$$

$$U = \sum_j P_j E_j$$

$$= - \frac{\partial \ln Z}{\partial \beta} \quad \text{as req'd}$$

$$S = -k_B \sum_j P_j \ln P_j$$

$$= -k_B \sum_j P_j (-\beta E_j - \ln Z)$$

$$= \frac{U}{T} + k_B \ln Z \quad \text{as req'd} \quad \left(\sum_j P_j = 1 \right)$$

$$F = U - TS = \underline{-k_B T \ln Z}$$

Single harmonic oscillator:

$$E_j = (j + \frac{1}{2}) \hbar \omega$$

$$\rightarrow Z = \sum_{j=0}^{\infty} e^{-\beta (j + \frac{1}{2}) \hbar \omega}$$

$$= e^{-\frac{\beta \hbar \omega}{2}} \sum_{j=0}^{\infty} r^j \quad (r = e^{-\beta \hbar \omega})$$

$$= \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}}$$

3N uncoupled harmonic oscillators

$$Z(3N) = Z^{3N}$$

$$\rightarrow F = -3N k_B \ln Z$$

$$= -3N k_B T \times \frac{-\hbar \omega}{2 k_B T} + 3N k_B T \ln(1 - e^{-\beta \hbar \omega})$$

$$= \underline{\frac{3}{2} N \hbar \omega + 3N k_B T \ln(1 - e^{-\beta \hbar \omega})}$$

7. cont.

$$\begin{aligned}
 U &= -3N \frac{\partial \ln Z}{\partial \beta} && (Z(3N) = Z^{3N}) \\
 &= -\frac{3N}{Z} \frac{\partial Z}{\partial \beta} \\
 &= -3N \frac{(1 - e^{-\beta h \omega})}{e^{-\beta h \omega / 2}} \left[\frac{-h \omega e^{-\beta h \omega / 2} e^{-\beta h \omega}}{(1 - e^{-\beta h \omega})^2} - \frac{h \omega}{2} \frac{e^{-\beta h \omega / 2}}{(1 - e^{-\beta h \omega})} \right] \\
 &= 3N h \omega \left[\frac{e^{-\beta h \omega}}{1 - e^{-\beta h \omega}} + \frac{1}{2} \right] \\
 &= 3N h \omega \left[\frac{1}{e^{\beta h \omega} - 1} + \frac{1}{2} \right]
 \end{aligned}$$

Heat capacity

$$\begin{aligned}
 C &= \frac{dU}{dT} \\
 &= -\frac{1}{k_B T^2} \frac{\partial U}{\partial \beta} && (d\beta = -\frac{1}{k_B T^2} dT) \\
 &= -\frac{3N h \omega}{k_B T^2} \times \frac{-h \omega e^{+\beta h \omega}}{(e^{\beta h \omega} - 1)^2} \\
 &= 3N k_B (\beta h \omega)^2 \frac{e^{\beta h \omega}}{(e^{\beta h \omega} - 1)^2}
 \end{aligned}$$

a) $T \rightarrow \infty$ $e^{\beta h \omega} \approx 1 - \beta h \omega$

$$\begin{aligned}
 C &\rightarrow 3N k_B (\beta h \omega)^2 \times \frac{1}{(\beta h \omega)^2} \\
 &\rightarrow 3N k_B
 \end{aligned}$$

b) $T \rightarrow 0$ $e^{\beta h \omega} - 1 \approx e^{\beta h \omega}$

$$\begin{aligned}
 C &\rightarrow 3N k_B (\beta h \omega)^2 e^{-\beta h \omega} \\
 &\rightarrow 0
 \end{aligned}$$

