Phase Space

a)
$$V_{PS} = \int_{[E, E+\delta E]} d^3r\, d^3p = V \int d^3p$$

shell with energy in range $[E, E+\delta E]$

$$= V\, 4\pi p^2\, \delta p$$

P_{max}

Then

$\nearrow$ $P = \sqrt{2mE}$

See lecture!

$P_{max} = \sqrt{2m(E+\delta E)}$
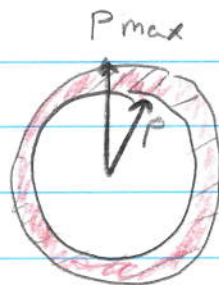
$$\delta p = P_{max} - P = \sqrt{2mE}\, (1 + \delta E/E)^{1/2} - \sqrt{2mE}$$

$$\simeq \sqrt{2mE}\left(1 + \frac{1}{2}\frac{\delta E}{E}\right) - \sqrt{2mE}$$

$$\delta p = P\,\frac{\delta E}{2E} \qquad i.e. \qquad \frac{\delta p}{P} = \frac{\delta E}{2E}$$

So

$$V_{PS} = V\, 4\pi p^3\, \frac{\delta E}{2E} = V\left[4\pi (2mE)^{3/2}\, \frac{\delta E}{2E}\right]$$

b) Then

$$\Omega(E,V) = \frac{1}{2!} \int \frac{d^3 r_1 \, d^3 p_1}{h^3} \, \frac{d^3 r_2 \, d^3 p_2}{h^3}$$

$$= \frac{V^2}{2!} \underbrace{\int_{[E, E+\delta E]} \frac{d^3 p_1 \, d^3 p_2}{h^6}}_{\text{shell volume}/h^6}$$

The momentum integral is a spherical shell in 6 dimensions
The momentum space volume is :

$$\frac{\text{Shell volume}}{h^6} = 2 \frac{\pi^{6/2}}{\Gamma(6/2)} \, p^5 \, \frac{\delta p}{h^6}$$

As before

$$\delta p = p \, \frac{\delta E}{2E}$$

So

$$p = \sqrt{2mE}$$

$$\Omega(E,V) = \frac{V^2}{2!} \, \frac{2\pi^3}{2!} \left(\frac{p}{h}\right)^6 \frac{\delta E}{2E}$$

$$\boxed{\Omega(E,V) = V^2 \, \pi^3 \left(\frac{2mE}{h^2}\right)^3 \cdot \frac{\delta E}{4E}}$$

c) Now the general case

$$\Omega(E,V) = \frac{1}{N!} \int \frac{d^3r_1 \, d^3p_1}{h^3} \cdots \frac{d^3r_N \, d^3p_N}{h^3}$$

$$= \left(\frac{V^N}{N!}\right) \int_{[E, E+\delta E]} (d^3p_1 \cdots d^3p_N) / h^{3N}$$

← coordinate space

momentum space →

shell volume / h^{3N}

So this is again a shell of dimension $3N$

$$\frac{\text{Shell volume}}{h^{3N}} = \cancel{2} \frac{\pi^{3N/2}}{\Gamma(3N/2)} \left(\frac{p}{h}\right)^{3N} \frac{\delta E}{\cancel{2}E}$$

Using $\frac{p}{h} = \left(\frac{2mE}{h^2}\right)^{1/2}$ we get:

momentum space →

$$\Omega(E,V) = \left(\frac{V^N}{N!}\right) \left(\frac{1}{\Gamma(3N/2)} \left(\frac{2\pi mE}{h^2}\right)^{3N/2}\right) \frac{\delta E}{E}$$

↗ coordinate space

d) Writing

$$N! = \left(\frac{N}{e}\right)^N, \quad \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2e}\right)^{3N/2}$$

We have

$$\Omega(E,V) = \left[e^N \left(\frac{V}{N} \right)^N \right] \left[e^{3N/2} \left(\frac{4\pi m E}{3 N h^2} \right)^{3N/2} \right] \frac{\delta E}{E}$$

Taking the log of this expression, and dropping the $\delta E/E$ term, we have

$$S = k \ln \Omega$$

$$S = k \left[\frac{5N}{2} + N \ln \frac{V}{N} + N \ln \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right]$$

The term: $\left(\frac{4\pi m E}{N h^2} \right)^{3/2} = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} = \left(\frac{1}{\lambda_{th}^2} \right)^{3/2} = \frac{1}{\lambda_{th}^3}$

where we used $\frac{E}{N} = \frac{3}{2} kT$

So finally

$$S = N k \left[\ln \left(\frac{V_N}{\lambda_{th}^3} \right) + \frac{5}{2} \right]$$

we will derive this in other ways as the course progresses. Here we have derived it from the microcanonical ensemble. Later we will derive it from the canonical ensemble.

Entropy Changes of Ideal Gas

(☆) $$S = Nk \ln V + \frac{3}{2} Nk \ln E + const$$

a) $PV = NkT$, so for P const, $\dfrac{V_1}{V_2} = \dfrac{T_1}{T_2} = \dfrac{E_1}{E_2}$

Since $E = \frac{3}{2} NkT \propto T$.

So

$$\Delta S = S_2 - S_1$$

$$= Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{E_2}{E_1}$$

$$= Nk \ln \frac{T_2}{T_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

$$\boxed{\Delta S = \frac{5}{2} Nk \ln \frac{T_2}{T_1}}$$

b) $$\Delta S = S_2 - S_1$$

$$= Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{E_2}{E_1} \qquad now \qquad PV = NkT$$

constant volum

$$P \propto T \propto E$$

So

$$\Delta S = \frac{3}{2} Nk \ln \left(\frac{P_2}{P_1} \right)$$

c) Now for an adiabatic expansion

$$TV^{\gamma - 1} = const$$

this is for a MAIG

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$ where $\gamma = \frac{5}{3}$

or

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{2/3}$$

$$\frac{E_2}{E_1} = \frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{-2/3}$$

So

$$\Delta S = Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

(i)
$$= Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \left(\frac{V_2}{V_1} \right)^{-2/3} = 0$$

(ii) The coordinate space volume is getting bigger, but the momentum space volume is getting smaller as the temperature drops. We have $EV^{3/2} = const$ during the adiab expansion of a MAIG.

Ball and Lake

a) $\quad Q = C(T - T_B^0)$

b) $\quad \Delta S = \int_{T_B^0}^{T} \dfrac{C\,dT_B}{T_B}$

(i) $\quad \Delta S = C \ln \dfrac{T}{T_B^0}$

(ii) Now

$$\Delta S = C \ln \dfrac{T}{T_B^0} = -C \ln \dfrac{T_B^0}{T} = C \ln \left(1 - \dfrac{T - T_B^0}{T}\right)$$

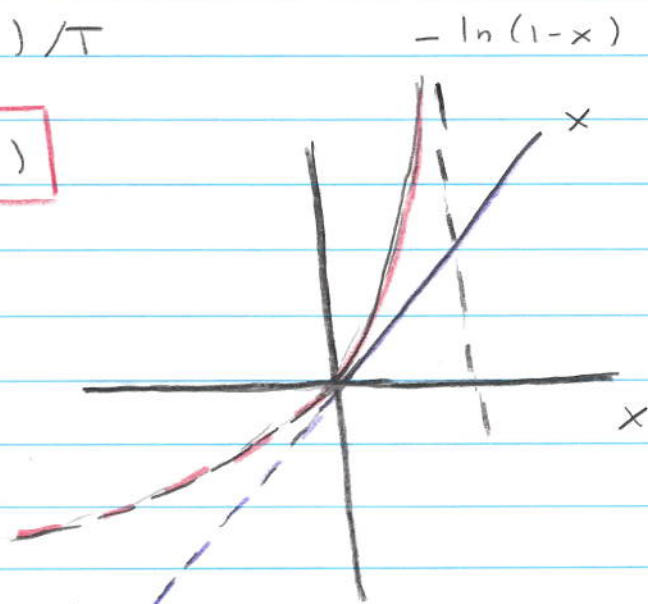$$\dfrac{Q}{T} = \dfrac{C(T - T_B^0)}{T}$$

So define $x \equiv (T - T_B^0)/T$

$$\boxed{\Delta S = -C \ln(1 - x)}$$

$$\boxed{\dfrac{Q}{T} = C x}$$

So $\quad \Delta S > \dfrac{Q}{T}$

as is clear from graph

iii) For small x

$$-\ln(1-x) \simeq -\left(-x - \frac{(-x)^2}{2}\right)$$

$$\simeq x + \frac{x^2}{2}$$

So

$$\Delta S \simeq C\,\frac{\Delta T}{T} + \frac{C}{2}\left(\frac{\Delta T}{T}\right)^2 = \frac{Q}{T} + \frac{C\,\Delta T^2}{2T^2} > \frac{Q}{T}$$

$$\frac{Q}{T} = C\,\frac{\Delta T}{T}$$

Heating Water

a) We have one steps, $T_o = 0°C = 273K$
and $T_1 = 100°C = 373K$.

The specific heat of one mole of H_2O, is the mass of 1 mol M_{ml} times $C_m = 4180 \, J/k \cdot kg$

The molar mass is

$$M_{m\ell} = 18 \, N_A m_p = 18 \, g$$

↑ two hydrogen $1+1 + 16$ ← oxygen

So $C = 18g \, C_m = 75.2 \, J/°K$

Then from the previous problem

$$\Delta S_{uni} = \Delta S_{water} + \Delta S_{res} = C \ln \frac{T_1}{T_o} - C \frac{(T_1 - T_o)}{T_o}$$

$$= 3.3 \, J/°K$$

b) In two steps $T_o \equiv 0°C$, $T_1 = 50°C$, $T_2 = 100°C$

combine

$$\Delta S = C \left[\ln \frac{T_1}{T_o} - C \frac{(T_1 - T_o)}{T_1} + \ln \frac{T_2}{T_1} - C \frac{(T_2 - T_1)}{T_2} \right]$$

Step 1   step 2

So

$$\Delta S_{uni} = C \left[\ln \frac{T_2}{T_0} - \sum_{i=1}^{2} \frac{\Delta T_i}{T_i} \right] = 1.75 \text{ J/}^\circ\text{K}$$

with $\Delta T_i = T_i - T_{i-1}$. We note this can be written:

$$\Delta S_{uni} = \Delta S_{sys} - \sum_i \frac{Q_i}{T_i}$$

c) For four steps we have $T_0 = 0^\circ C$, $T_1 = 25^\circ C$, $T_2 = 50^\circ C$, $T_3 = 75^\circ C$, $T_4 = 100^\circ C$

$$\Delta S_{univ} = \Delta S_{sys} - \sum_{i=1}^{4} Q_i / T_i$$

$$= C \left[\ln \left(\frac{T_4}{T_0} \right) - \sum_{i=1}^{4} \frac{\Delta T_i}{T_i} \right] = 0.9 \text{ J/}^\circ\text{K}$$

d) To make a reversible process we must take the number of steps very large

$$\Delta S_{univ} = C \left[\ln \left(\frac{T_N}{T_0} \right) - \sum_{i=1}^{N} \frac{\Delta T_i}{T_i} \right]$$

In the limit, the sum is replaced by an integral

$$\sum_i \frac{\Delta T_i}{T_i} \simeq \int_{T_0}^{T_N} \frac{dT}{T} = \ln\left(\frac{T_N}{T_0}\right)$$

And then

$$\Delta S_{univ} = C\left[\ln\left(\frac{T_N}{T_0}\right) - \ln\left(\frac{T_N}{T_0}\right)\right] = 0$$