# Ideal Gas:

**2D**

$$Z_1 = \int \frac{d^2r\, d^2p}{h^2}\, e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{A}{\lambda_{th}^2}} \qquad \frac{1}{\lambda_{th}^2} \equiv 2\pi \frac{m k_B T}{h^2}$$

**1D**

$$Z_1 = \int \frac{dr\, dp}{h}\, e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{L}{\lambda_{th}}} \qquad \frac{1}{\lambda_{th}} \equiv \frac{\sqrt{2\pi m k_B T}}{h}$$

So $\quad Z_1 \equiv L^d / \lambda_{th}^d$

$$Z_{TOT} = \frac{1}{N!} Z_1^N \simeq \left(\frac{e Z_1}{N}\right)^N$$

So

$$F = -kT \ln Z_{TOT} = -kTN\left[\ln \frac{Z_1}{N} + 1\right]$$

$$= -kTN\left[-\ln(N/Z_1) + 1\right]$$

So

$$\boxed{F = -kTN\left[-\ln(n\lambda_{th}^{d}) + 1\right]}$$

where $d = 1, 2, 3$ for dimensions $1, 2, 3$

$$S = -\frac{\partial F}{\partial T}$$

Now $\lambda_{th} = \dfrac{h}{\sqrt{2\pi m k T}} = c\,T^{-1/2}$. Then

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + NkT\frac{\partial}{\partial T}\left(-\ln n\lambda_{th}^{d}\right)$$

Now

$$\ln n\lambda_{th}^{d} = \ln(T^{-d/2}) + \text{const} \qquad \frac{\partial}{\partial T}\ln n\lambda_{th}^{d} = \frac{-d}{2T}$$

So

$$\boxed{S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + \frac{NkT\,d}{2T}}$$

or

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + \frac{d+2}{2}\right] \quad \text{with } d = 1, 2, 3$$

The Energy

$$F = E - TS \qquad E = F + TS$$

So

$$E = -kTN\left[-\ln(n\lambda^d) + 1\right] + TNk\left[-\ln(n\lambda_{th}^d) + \frac{d+2}{2}\right]$$

$$\boxed{E = NkT\frac{d}{2}}$$

So finally we need the pressure

$$F = -kTN\left[-\ln\left(\frac{N}{V_d}\lambda_{th}^d\right) + 1\right]$$

Where $V_d = L, A, V = L^d$ in d-dimensions

$$p = -\left(\frac{\partial F}{\partial V_d}\right)_T = kTN\frac{\partial}{\partial V_d}\left(\ln V_d + \text{const}\right)$$

$$\boxed{p = \frac{kTN}{V_d}}$$

## Degeneracy

$$Z_{TOT} = \frac{Z_1^N}{N!} \simeq \left(\frac{eZ_1}{N}\right)^N$$

where

$$Z_1 = Z_{trans} Z_{atom}$$

So

$$E = -\frac{\partial}{\partial \beta} \log Z_{TOT}$$

$$= N \left[ -\frac{\partial}{\partial \beta} \left( \log \left( \frac{eZ_{trans}}{N} \right) + \log Z_{atom} \right]$$

Where

$$Z_{trans} = \int \frac{d^3 r \, d^3 p}{h^3} e^{-p^2/2mkT} = \frac{V}{\lambda_{th}^3} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$Z_{atom} = \sum e^{-\varepsilon_{int}/kT} = g_1 + g_2 e^{-\beta\Delta}$$

So

internal energy

$$E = N(\varepsilon_{trans} + \varepsilon_{atom})$$

$$\varepsilon_{trans} = -\frac{\partial}{\partial \beta} \ln Z_{trans} = -\frac{\partial}{\partial \beta} \ln \beta^{-3/2} = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2} kT \checkmark$$

Similarly

$$\varepsilon_{atom} = -\frac{\partial}{\partial \beta} \ln Z_{atom} = \frac{g_2 \Delta e^{-\beta\Delta}}{g_1 + g_2 e^{-\beta\Delta}}$$

Finally we need to compute $C_V$.
We use

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial E}{\partial \beta}\frac{\partial \beta}{\partial T} = -k\beta^2 \left(\frac{\partial E}{\partial \beta}\right)_V$$

So

$$C_V = \frac{\partial}{\partial T}\left(\frac{3}{2}NkT + \frac{N g_2 \Delta e^{-\beta\Delta}}{(g_1 + g_2 e^{-\beta\Delta})}\right)$$

$$= \frac{3}{2}Nk + -k\beta^2 \frac{\partial}{\partial \beta} \frac{\Delta N g_2 e^{-\beta\Delta}}{(g_1 + g_2 e^{-\beta\Delta})}$$

$$= \frac{3}{2}Nk - k\beta^2 \frac{\partial}{\partial \beta} \frac{\Delta N g_2}{g_1 e^{\beta\Delta} + g_2}$$

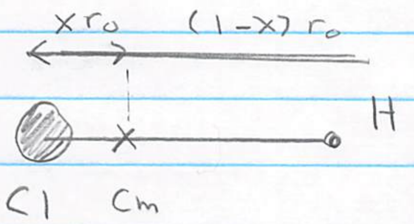
$$= \frac{3}{2}\cancel{N}k + \cancel{N}k\Delta \frac{g_2 \beta^2 g_1 e^{\beta\Delta} \Delta}{(g_1 e^{\beta\Delta} + g_2)^2}$$

$$\boxed{C_V = Nk\left[\frac{3}{2} + \frac{g_1 g_2 (\beta\Delta)^2 e^{\beta\Delta}}{(g_1 e^{\beta\Delta} + g_2)^2}\right]}$$

## HCl

a) Take $r_0 = 1\ \text{Å}$

b)




The location of the cm is at $x r_0$

$$I = m_{Cl}(x r_0)^2 + m_H (1-x)^2 r_0^2$$

Now

$$x r_0 = \frac{m_H r_0}{m_H + m_{Cl}} \qquad \text{definition of cm}$$

And $\quad x = \dfrac{m_H}{m_H + m_{Cl}} = \dfrac{m_H}{M_{TOT}} \qquad (1-x) = \dfrac{m_{Cl}}{M_{TOT}}$

$$I = M_{TOT}\, r_0^2 \left[ (1-x)x^2 + x(1-x)^2 \right]$$

$$= M_{TOT}\, r_0^2 \left[ x^2 - x^3 + x(1-2x+x^2) \right]$$

$$= M_{TOT}\, r_0^2 \left[ (1-x)x \right] = \boxed{\frac{m_H m_{Cl}}{(m_H + m_{Cl})} r_0^2 = \mu r_0^2}$$

So since $m_{Cl} \simeq 35\, m_H$ we expand

$$\frac{I}{r_0^2} = m_H \frac{1}{(1 + m_H/m_{Cl})} \simeq m_H (1 - m_H/m_{Cl} + \dots)$$

So

$$\boxed{I = m_H r_0^2 \left(1 - m_H/m_{cl} + O\left((m_H/m_{cl})^2\right)\right)}$$

c) So

$$\Delta = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2m_p r_0^2} \simeq \frac{\hbar^2}{2m_e r_0^2 (m_p/m_e)} \simeq \frac{13.6\,eV}{m_p/m_e} \left(\frac{a_0}{r_0}\right)^2$$

We used knowledge of the Bohr atom

$$\frac{\hbar^2}{2ma_0^2} = 13.6\,eV$$ where $a_0 = 0.53\,\mathring{A}$ is the Bohr radius.

Then $(a/r_0) \simeq 1/2$

$$\boxed{\Delta = \frac{13.6\,eV}{2000} \frac{1}{2^2} = 0.0017\,eV}$$

$$\frac{\Delta}{kT} = 14.7$$ for $kT = 1/40\ eV$

So

$\Delta = \hbar\omega$ $\qquad$ $$\omega = \frac{\Delta c}{\hbar c} = \frac{0.0017\,eV \times 3\times10^8\ m/s}{197\ eV \times nm}$$

$$\boxed{\omega = 400\ GHz}$$

b)

We have

$$C_v = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left(\frac{1}{Z}\frac{-\partial Z}{\partial \beta}\right) = -k_B\beta^2\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\left(\frac{-\partial Z}{\partial\beta}\right)\right)$$

see below

Note $\boxed{\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta}\frac{\partial \beta}{\partial T} = -k\beta^2\frac{\partial X}{\partial\beta}}$

this is very useful
X is anyting
$\partial X/\partial T = -k\beta^2\,\partial X/\partial\beta$

$$\frac{\partial}{\partial T}\left(\frac{1}{kT}\right)$$

Then differentiating

$$-\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\left(-\frac{\partial Z}{\partial\beta}\right)\right) = \frac{1}{Z}\left(+\frac{\partial^2 Z}{\partial\beta^2}\right) - \frac{1}{Z^2}\left(\frac{-\partial Z}{\partial\beta}\right)\left(\frac{-\partial Z}{\partial\beta}\right)$$

$$= \langle E^2\rangle - \langle E\rangle^2$$

So

$$\boxed{C_v = -k\beta^2\left[\langle E^2\rangle - \langle E\rangle^2\right]}$$

Finally,

c) Note

$$\boxed{C_v = -k\beta^2\frac{\partial}{\partial\beta}\frac{1}{Z}\left(\frac{-\partial Z}{\partial\beta}\right) = k\beta^2\frac{\partial}{\partial\beta}\frac{\partial \ln Z}{\partial\beta} = k\beta^2\partial_\beta^2\ln Z}$$

So

$$Z_{TOT} = \frac{1}{N!} Z_1^N \simeq \left(\frac{e Z_1}{N}\right)^N$$

$Z_1$ is always of this form

$$\boxed{Z_1 = \sum_s \int \frac{d^3r\, d^3p}{h^3} e^{-(p^2/2m + \varepsilon^s_{int})/kT}}$$

We used that for one particle

$$E = \frac{\vec{p}^{\,2}}{2m} + \varepsilon_{int}$$

$\varepsilon_{int}$ = internal energy levels

$= \frac{\hbar^2 \ell(\ell+1)}{2I}$ in this case

$$\boxed{Z_1 = Z_{trans} Z_{int}}$$

Where

$$\boxed{Z_{trans} = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-p^2/2mT} = \frac{V}{\lambda_{th}^3} = V n_Q}$$

$$\boxed{Z_{int} = \sum_s e^{-\varepsilon_{int}\beta} = \sum_{\ell, m} e^{-\hbar^2(\ell(\ell+1)/2I)\beta}}$$

$$Z_{int} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\hbar^2(\ell(\ell+1)/2I)\beta}$$

$$= \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\beta\varepsilon_\ell} \qquad \varepsilon_\ell \equiv \frac{\ell(\ell+1)\hbar^2}{2I}$$

So

$$\log Z_{TOT} = N\left[\underbrace{\log\left(\frac{e\,Z_{trans}}{N}\right)}_{\text{this is a mono-atomic ideal gas} \equiv MAIG} + \log Z_{int}\right]$$

Now

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z_{TOT}$$

$$= N\left[\langle\varepsilon\rangle_{MAIG} + \langle\varepsilon_{rot}\rangle\right]$$

$$\boxed{\langle E\rangle = N\left[\frac{3}{2}k_B T + \langle\varepsilon_{rot}\rangle\right]}$$

Where $\langle\varepsilon_{rot}\rangle = \frac{1}{Z}\sum_{\ell}(2\ell+1)\,e^{-(\hbar^2\ell(\ell+1)/2I)\beta}\left(\frac{\hbar^2\ell(\ell+1)}{2I}\right)$

Differentiating again

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = N\left[\frac{3}{2}k_B T + \frac{\partial}{\partial T}\langle\varepsilon_{rot}\rangle\right]$$

Finally since

$$\frac{\partial}{\partial T} = -k_B\beta^2\frac{\partial}{\partial\beta}$$

We get defining $\varepsilon_\ell \equiv \ell(\ell+1)\hbar^2/2I$

$$\frac{\partial \mathcal{E}_{rot}}{\partial T} = -k\beta^2 \frac{\partial}{\partial\beta}\left[\underbrace{\frac{1}{Z}\sum_\ell (2\ell+1)\, e^{-\beta\varepsilon_\ell}\,\varepsilon_\ell}_{=\frac{1}{Z_{rot}}\left(-\frac{\partial Z_{rot}}{\partial\beta}\right)}\right]$$

So

$$\frac{\partial \mathcal{E}_{rot}}{\partial T} = k\beta^2\left[\frac{1}{Z}\sum_\ell (2\ell+1)\, e^{-\beta\varepsilon_\ell}\,\varepsilon_\ell^2 - \left(\frac{-1}{Z}\frac{\partial Z}{\partial\beta}\right)\left(\frac{-1}{Z}\frac{\partial Z}{\partial\beta}\right)\right]$$

$$\boxed{\frac{\partial \mathcal{E}_{rot}}{\partial T} = k\beta^2\left[\langle \varepsilon_{rot}^2\rangle - \langle \varepsilon_{rot}\rangle^2\right]}$$

Where

$$\beta^2\langle \varepsilon_{rot}^2\rangle \equiv \frac{1}{Z}\sum_{\ell=0}^{\infty} e^{-\beta\varepsilon_\ell}\,(\beta\varepsilon_\ell)^2\,(2\ell+1)$$

$$\beta\langle\varepsilon\rangle \equiv \frac{1}{Z}\sum_{\ell=0}^{\infty} e^{-\beta\varepsilon_\ell}\,\beta\varepsilon_\ell$$

So Finally

$$\boxed{C_V = Nk_B\left[\frac{3}{2}k_B T + \beta^2\left(\langle\varepsilon_{rot}^2\rangle - \langle\varepsilon_{rot}\rangle^2\right)\right]}$$

A graph is shown in the problem statement.

d) Looking at the graph, We see a 10% deviation from one when

$$k_B T/\Delta \sim 1$$

Or

$$k_B T \sim \Delta$$

$$T \sim \frac{0.0017eV}{\frac{0.025eV}{300°K}}$$

$$\boxed{T \sim 20.4°K}$$