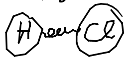
$$P(s) = \frac{1}{Z} e^{-E_s/kT} = \frac{1}{Z} e^{-\beta E_s} \qquad \beta = \frac{1}{kT}$$

$\omega_0 = 5.4\times10^{14}/s$

e.g. HCl atom 

$$E_n = (n+\tfrac{1}{2})\hbar\omega_0 = 0.35\,eV(n+\tfrac{1}{2})$$

$$E_0 = 0.18\,eV$$

$$E_1 = 0.53\,eV$$

$$\frac{P(n=0)}{P(n=1)} = \frac{\frac{1}{Z}e^{-E_0/kT}}{\frac{1}{Z}e^{-E_1/kT}} = e^{(E_1-E_0)/kT}$$

300K $\quad kT = \frac{1}{40}\,eV$

$$\frac{P_0}{P_1} = e^{(0.35eV)\cdot 40} = 1{,}200{,}000$$

HCl doesn't vibrate much at R.T.

When $kT \sim E_1 - E_0 = 0.35\,eV$

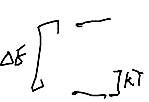
$$\rightarrow T = \frac{.35\,eV}{8.6\times10^{-5}\,eV/K} = 4000K$$

At 4000K, $\frac{P_0}{P_1} = e = 2.7$

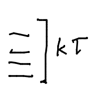
Two energy scales

ΔE: gap between energy microstates

kT: thermal energy



$kT \ll \Delta E$, very unlikely to be at higher energy level



$kT \gg \Delta E$, higher energy levels will be well-populated → much more likely

Average Energy

$$\bar{E} = \sum_s P_s E_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s}$$

$$= \frac{1}{Z} \sum_s \left(-\frac{\partial}{\partial \beta} e^{-\beta E_s} \right)$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s}$$

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \frac{1}{k^2 T} \frac{\partial Z}{\partial T}$$

(see HW 10 for more fun!)

If N particles

each with same energy states

Then occupancy of state s is

N° $$n_s = N \frac{1}{Z} e^{-\beta E_s}$$

If s is a microstate

Degeneracy means that are multiple

microstates with same energy

$$\begin{pmatrix} \#\text{ with} \\ \text{energy } E \end{pmatrix} = \begin{pmatrix} n(E) \\ \#\text{ of particles} \\ \text{in a microstate} \\ \text{w/ energy } E \end{pmatrix} \times \begin{pmatrix} \#\text{ of states} \\ \text{with energy} \\ E \\ g(E) \end{pmatrix}$$

$\frac{1}{Z}e^{-\beta}$ $\frac{1}{Z}e^{-\beta}$ $\frac{1}{Z}e^{-\beta}$ $E=1$

$\frac{1}{Z}e^{-\beta 0}$ $E=0$

$$\bar{E} = \frac{1}{N}\sum_{\substack{s \\ \text{states}}} E_s n_s = \frac{1}{N}\sum_{E} E\, n(E)\, g(E)$$

if levels really close ~~together~~ $\equiv$

$$\bar{E} = \frac{1}{N}\int E\, n(E) \boxed{\frac{dg(E)}{dE}}\, dE$$

$D(E)$ density of states

$\#$ $D(E)\,dE$

\# of microstates

with energy between E & $E+dE$