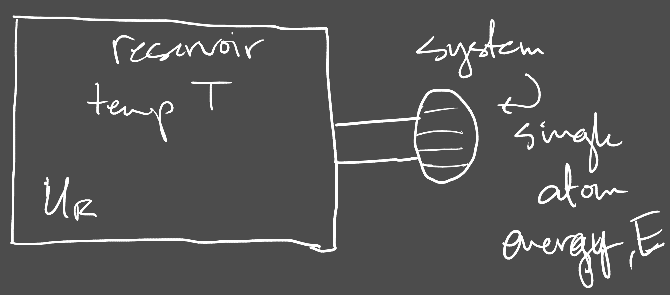
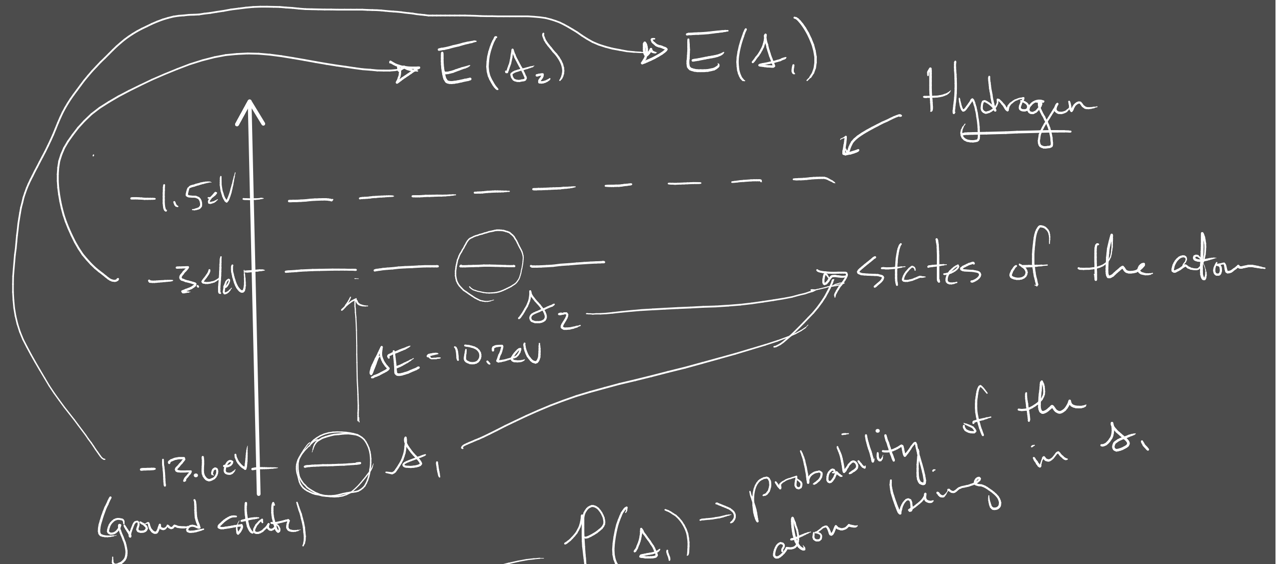
Chapter 6 - Boltzmann Statistics

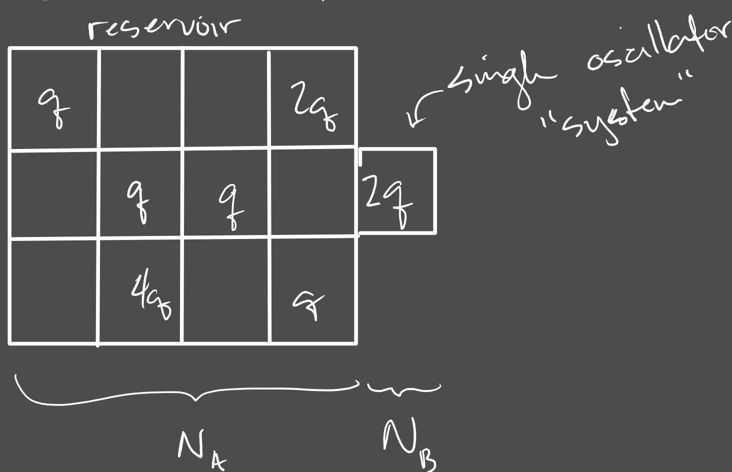




$P(s_1) \rightarrow$ probability of the atom being in s_1

> The probability of finding the atom in any particular state is proportion to the number microstates that are accessible to the reservoir.

Einstein solid



when the atom is in state s_1 it has energy $E(s_1)$ and the reservoir has $\Omega_R(s_1)$

atom $\rightarrow s_2 \rightarrow E(s_2) \longrightarrow$ reservoir $\Omega_R(s_2)$

$E(s_2) > E(s_1)$ then $\Omega_R(s_1) > \Omega_R(s_2)$

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{\ln \Omega_R(s_2)}}{e^{\ln \Omega_R(s_1)}} = \frac{e^{S_R(s_2)/k_B}}{e^{S_R(s_1)/k_B}} = e^{[S_R(s_2) - S_R(s_1)]/k_B}.$$

$$dS_R = \frac{1}{T}\left(dU_R + \underbrace{P\,dV_R}_{dV_R \ll dU_R} - \mu\, \cancel{dN_R}^{\,0}\right)$$

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}\underbrace{\left[U_R(s_2) - U_R(s_1)\right]}_{-[E(s_2) - E(s_1)]}$$

$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2) - E(s_1)]/k_BT}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/k_BT}}{e^{-E(s_1)/k_BT}}$$

Boltzmann factor

$$\frac{P(s_2)}{e^{-E(s_2)/k_BT}} = \frac{P(s_1)}{e^{-E(s_1)/k_BT}} = \frac{1}{Z}$$

$$\boxed{P(s) = \frac{1}{Z} e^{-E(s)/k_BT}}$$

$Z \rightarrow$ partition function

$$\sum_s P(s) = 1 = \sum_s \frac{1}{Z} e^{-E(s)/k_BT} = \frac{1}{Z} \sum_s e^{-E(s)/k_BT}$$

over all state

$$Z = \sum_s e^{-E(s)/k_BT}$$

What is the probability of a H atom being in the first excited state, relative to the ground state, in sun's atmosphere, where T = 5800K.

$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2) - E(s_1)]/k_BT} = e^{-10.2\,eV/0.5\,eV} = e^{-20.4} = 1.4 \cdot 10^{-9}$$

$\times 4$ degeneracy

$\boxed{5.5 \cdot 10^{-9}}$ $\times 10^9$ H's

eV $\rightarrow$ energy

$\Delta K = -\Delta U = -q\Delta V = 1.6 \cdot 10^{-19} C \cdot 1V = 1.6 \cdot 10^{-19} J$

$1 eV = 1.6 \cdot 10^{-19} J$

$k_BT = 1.38 \cdot 10^{-23} \cdot 5800\,K$

$k_BT = 8 \cdot 10^{-20} J \cdot \frac{1 eV}{1.6 \cdot 10^{-19} J} = 0.5\,eV$

expect 5.5 of them to be in 1st excited state

6.2

$$P(E) = \frac{1}{Z} e^{-F/k_B T}$$

$$F = E - TS$$

"entropy" $\rightsquigarrow k_B \ln(\underbrace{\text{degeneracy}}_{d(E)})$

earlier $P(s) = \frac{1}{Z} e^{-E(s)/k_B T}$

$P(s) \propto \Omega_R$

$e^{\ln \Omega_R} = e^{S}$

$$P(E) = d(E) \cdot P(s)$$

$$= d(E) \cdot \frac{1}{Z} e^{-E(s)/k_B T}$$

$$= e^{\ln d(E)} \cdot \frac{1}{Z} \cdot e^{-E(s)/k_B T}$$

$$= \frac{1}{Z} e^{\ln d(E) - E(s)/k_B T}$$

$$= \frac{1}{Z} e^{-[E(s) - T \underbrace{k_B \ln(d(E))}_{S}]/k_B T}$$

$$\rightarrow P(E) = \frac{1}{Z} e^{-F/k_B T}$$