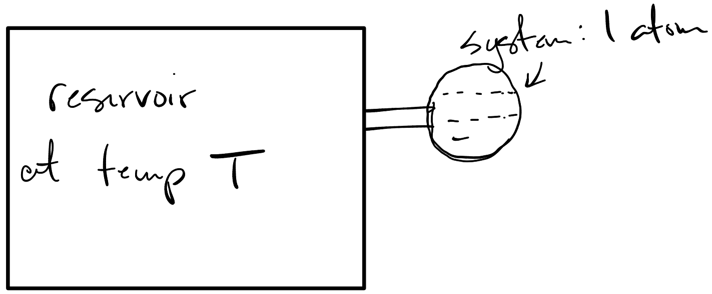
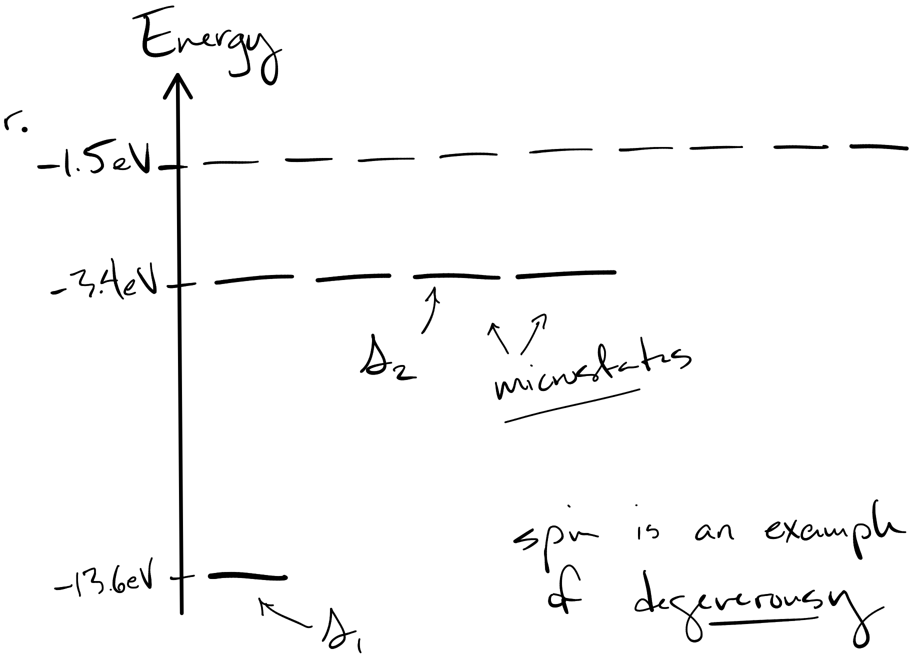
Chapter 6 - Boltzmann Statistics

System of an atom in contact w/ a reservoir.





spin is an example of degeneracy

all of these states are equally probable

states: s_1 & s_2

probabilities: $P(s_1)$ & $P(s_2)$

energies: $E(s_1)$ & $E(s_2)$

multiplicities: $\Omega_R(s_1)$ & $\Omega_R(s_2)$

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

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

$$\Omega_R(s_1) = e^{\ln(\Omega_R(s_1))} = e^{S_R(s_1)/k_B}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)/k_B}}{e^{S_R(s_1)/k_B}}$$

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

very small compared to dU

literally 0

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

$$dU_R = T\,dS_R$$

$$dE = -T\,dS_R$$

energy of the system

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

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

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

$$\frac{p(s_2)}{p(s_1)} = \frac{e^{-E(s_2)/k_B T}}{e^{-E(s_1)/k_B T}}$$

$$\frac{p(s_2)}{e^{-E(s_2)/k_B T}} = \frac{p(s_1)}{e^{-E(s_1)/k_B T}} = \frac{1}{Z} \Rightarrow \boxed{p(s) = \frac{1}{Z} e^{-E(s)/k_B T}}$$

$Z \rightarrow$ par<u>tition</u> <u>function</u>

How do we calculate Z?

$$\underbrace{\sum_s p(s) = 1}_{\text{now probability works!}} = \sum_s \frac{1}{Z} e^{-E(s)/k_B T} = \frac{1}{Z} \sum_s e^{-E(s)/k_B T} = 1$$

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

An example: probability of finding a H in its first excited state $T = 5800K$

Sun's atmosphere

from the ground state to the first excited state 10.2 eV

eV → energy of one electron accelerated from rest by a potential of 1 V.

$$\Delta K = q\Delta V = 1.6\cdot10^{-19}\,C\cdot 1V = 1.6\cdot10^{-19}\,J$$

$$1\,eV = 1.6\cdot10^{-19}\,J$$

$$\frac{P(s_2)}{P(s_1)} = e^{-[E_2-E_1]/k_BT}$$

$$k_BT = 1.38\cdot10^{-23}\frac{J}{K}\cdot 5800\,K$$

$$k_B = \left[\frac{eV}{K}\right] = 1.38\cdot10^{-23}\frac{\cancel{J}}{K}\cdot\frac{1\,eV}{1.6\cdot10^{-19}\,\cancel{J}}$$

$$= 0.8625\cdot10^{-4}$$

$$= 8.625\cdot10^{-5}\,eV/K$$

$$k_BT = 8.625\cdot10^{-5}\frac{eV}{K}\cdot 5800K = 0.5\,eV$$

$$\frac{P(s_2)}{P(s_1)} = e^{-10.2eV/0.5eV} = e^{-20.4}$$

$$= 1.4\cdot10^{-9}$$

$\times 4$ ← degenerate states

$5.5 \cdot 10^9$

Problem 6.6 + 6.12