

CEM 882

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Lecture Notes 3

Weliky

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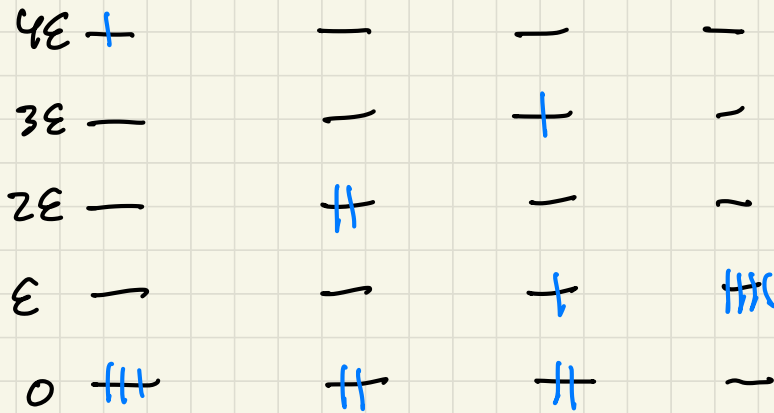
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Although the most probable and highest multiplicity distribution is with equal numbers of molecules in each state, this distribution is typically not possible because of fixed total energy. This total energy is a constraint on the distribution. We now derive the most probable distribution with this constraint.

Model system with 4 molecules,  
5 energy levels, and total energy =  $4E$



W

Overall trend is that highest multiplicity distribution has molecules distributed across more states and greater population in lower energy states

Now consider the general case of the distribution with the maximum multiplicity under fixed total energy.

Two states  $A \hat{=} B$  with  $\epsilon_A < \epsilon_B$

$$P_A + P_B = 1 \quad \text{normalization}$$

Goal is to derive expressions for  $P_A \hat{=} P_B$

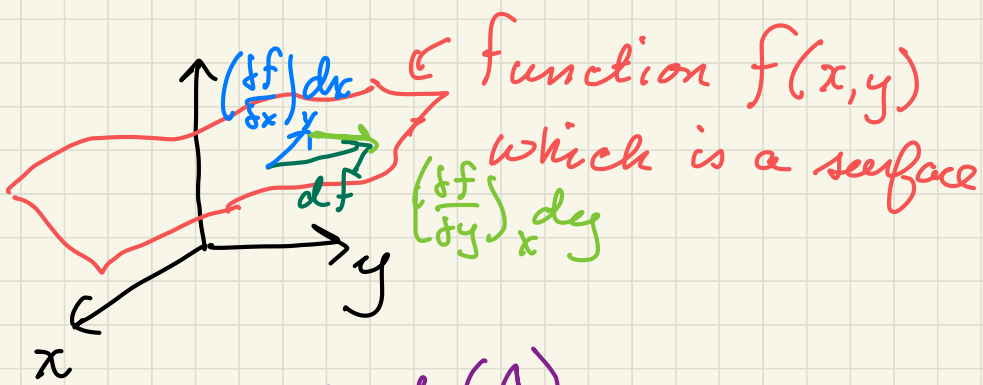
$$\langle \epsilon \rangle = P_A \epsilon_A + P_B \epsilon_B$$

average energy per molecule

$$g(P_A, P_B) = P_A + P_B = 1$$

$$\left( \frac{\partial g}{\partial P_A} \right)_{P_B} = \left( \frac{\partial g}{\partial P_B} \right)_{P_A} = 1$$

partial derivative of  $g$  with respect to  $P_A$  while keeping  $P_B$  fixed



because  $g$  is a constant (1)

$$dg = 0 = \left( \frac{\partial g}{\partial p_A} \right)_{p_B} dp_A + \left( \frac{\partial g}{\partial p_B} \right) dp_B$$

$$= dp_A + dp_B = 0$$

$$\frac{dp_B}{dp_A} = - \frac{\left( \frac{\partial g}{\partial p_A} \right)_{p_B}}{\left( \frac{\partial g}{\partial p_B} \right)_{p_A}}$$

$$h(p_A, p_B) = p_A \epsilon_A + p_B \epsilon_B$$

$$\left( \frac{\partial h}{\partial p_A} \right)_{p_B} = \epsilon_A$$

$$\left( \frac{\partial h}{\partial p_B} \right)_{p_A} = \epsilon_B$$

$$\textcircled{dh} = \left( \frac{\partial h}{\partial p_A} \right)_{p_B} dp_A + \left( \frac{\partial h}{\partial p_B} \right)_{p_A} dp_B = \epsilon_A dp_A + \epsilon_B dp_B$$

$\approx 0$

near maximum multiplicity

$$\frac{dp_B}{dp_A} = \frac{-\left( \frac{\partial h}{\partial p_A} \right)_{p_B}}{\left( \frac{\partial h}{\partial p_B} \right)_{p_A}}$$

$$\textcircled{dS} = \left( \frac{\partial S}{\partial p_A} \right)_{p_B} dp_A + \left( \frac{\partial S}{\partial p_B} \right)_{p_A} dp_B$$

0 at maximum multiplicity (entropy  $S = k \ln \Omega$ )

$$\frac{dp_B}{dp_A} = \frac{-\left( \frac{\partial S}{\partial p_A} \right)_{p_B}}{\left( \frac{\partial S}{\partial p_B} \right)_{p_A}}$$

$$\frac{\left( \frac{\partial S}{\partial p_A} \right)_{p_B}}{\left( \frac{\partial S}{\partial p_B} \right)_{p_A}} = \frac{\left( \frac{\partial g}{\partial p_A} \right)_{p_B}}{\left( \frac{\partial g}{\partial p_B} \right)_{p_A}} = \frac{\left( \frac{\partial h}{\partial p_A} \right)_{p_B}}{\left( \frac{\partial h}{\partial p_B} \right)_{p_A}}$$

# Method of Lagrange multipliers

$$\frac{\left(\frac{\delta S}{\delta p_A}\right)_{p_B}}{2} = N \alpha \left(\frac{\delta g}{\delta p_A}\right)_{p_B} \quad (1)$$

*# of molecules*

$$\frac{\left(\frac{\delta S}{\delta p_A}\right)_{p_B}}{2} = N \beta \left(\frac{\delta h}{\delta p_A}\right)_{p_B} \quad (2)$$

$$\frac{\left(\frac{\delta S}{\delta p_B}\right)_{p_A}}{2} = N \alpha \left(\frac{\delta g}{\delta p_B}\right)_{p_A} \quad (3)$$

$$\frac{\left(\frac{\delta S}{\delta p_B}\right)_{p_A}}{2} = N \beta \left(\frac{\delta h}{\delta p_B}\right)_{p_A} \quad (4)$$

$$(1) + (2)$$

$$(3) + (4)$$

$$-\left(\frac{\partial S}{\partial P_A}\right)_{P_B} + N\alpha \left(\frac{\partial g}{\partial P_A}\right)_{P_B} + N\beta \left(\frac{\partial h}{\partial P_A}\right)_{P_B} = 0$$

$$-\left(\frac{\partial S}{\partial P_B}\right)_{P_A} + N\alpha \left(\frac{\partial g}{\partial P_B}\right)_{P_A} + N\beta \left(\frac{\partial h}{\partial P_B}\right)_{P_A} = 0$$

$N(k \ln p_A + k)$        $\uparrow$        $\epsilon_A$   
 $N(k \ln p_B + k)$        $\downarrow$        $\epsilon_B$

$$P_A = e^{-1-\alpha/k} e^{-\beta \epsilon_A/k}$$

$$P_B = e^{-1-\alpha/k} e^{-\beta \epsilon_B/k}$$

$P_A + P_B = 1$  (Normalized probability)

$$\frac{1}{e^{-1-\alpha/k}} = e^{-\beta \epsilon_A/k} + e^{-\beta \epsilon_B/k} = \mathcal{Q}$$

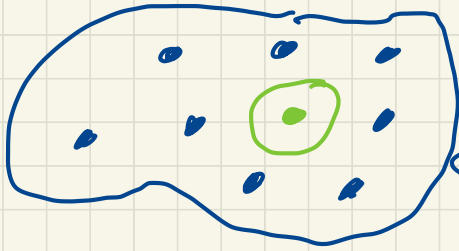
Partition function

$$\frac{P_B}{P_A} = e^{\frac{\epsilon_B - \epsilon_A}{k}}$$

$$P_A = \frac{e^{-\epsilon_A \beta/k}}{\mathcal{Q}} \qquad P_B = \frac{e^{-\epsilon_B \beta/k}}{\mathcal{Q}}$$



Evaluate  $\beta$  in system with total energy  $U_0$



• = molecule

• = molecule 1

⇐ reservoir ("bath")

PA (probability) that molecule 1 is in A state is proportional to multiplicity of entire system of molecules with molecule 1 in A state

$$W = W_{\text{molecule 1}} \times W_{\text{reservoir}} \quad W_r(U_0 - \epsilon_A)$$

$$PA \propto W_r(U_0 - \epsilon_A) \propto e^{\ln W_r(U_0 - \epsilon_A)}$$

*W<sub>r</sub> is function of energy*

$$PA \propto e^{\left\{ \frac{S(U_0)}{k} - \frac{\epsilon_A}{k} \left( \frac{\partial S}{\partial U} \right) \right\}}$$

*EA Taylor Series approx. when  $E_A \ll U_0$*

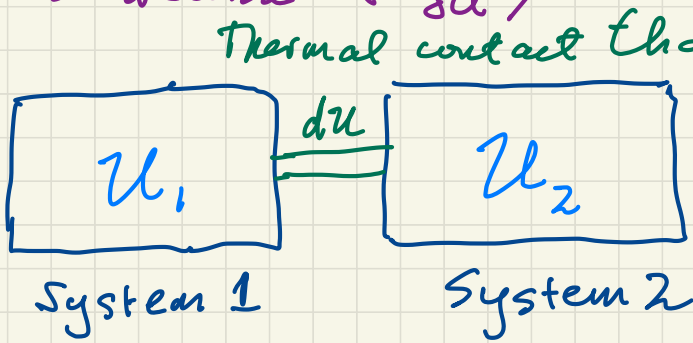
$$PB \propto e^{\left\{ \frac{S(U_0)}{k} - \frac{\epsilon_B}{k} \left( \frac{\partial S}{\partial U} \right) \right\}}$$

*total population*

$$\frac{PB}{PA} = e^{\frac{\Delta \epsilon}{k} \left( \frac{\partial S}{\partial U} \right)} \Rightarrow \beta$$

*individual molecule*

Understand  $\left(\frac{\partial S}{\partial U}\right)$



Energy ( $dU$ ) will flow in direction that increases  $S_{\text{total}}$  and  $S = k \ln \Omega$

$$S = S_1(U_1) + S_2(U_2) \quad \text{before } dU \text{ energy flow}$$

$$S = S_1(U_1 + dU) + S_2(U_2 - dU) \quad \text{after } dU \text{ energy flow}$$

$$\approx S_1(U_1) + \left(\frac{\partial S_1}{\partial U}\right)_{U=U_1} dU + S_2(U_2) - \left(\frac{\partial S_2}{\partial U}\right)_{U=U_2} dU$$

$$dS = \left(\frac{\partial S_1}{\partial U}\right)_{U=U_1} dU - \left(\frac{\partial S_2}{\partial U}\right)_{U=U_2} dU \quad \text{happens if } dS > 0$$

Energy flow continues until  $S$  is

maximum and  $dS = 0$

$$\left(\frac{\partial S_1}{\partial U}\right)_{U=U_1} = \left(\frac{\partial S_2}{\partial U}\right)_{U=U_2}$$

What is the experimental parameter that determines direction of energy flow?

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)$$

k units

$$T = \left( \frac{\partial U}{\partial S} \right)$$

## General Equations

$$Q = \sum_{j=1}^t e^{-\epsilon_j / kT}$$

sum over all states of molecule

partition function

$$P_j = \frac{e^{-\epsilon_j / kT}}{Q}$$

Boltzmann factor

normalized probability of state  $t$

$$\sum_{j=1}^t P_j = 1$$

$$\langle \epsilon \rangle = \sum_{j=1}^t P_j \epsilon_j = kT^2 \frac{\partial \ln Q}{\partial T}$$

average energy/molecule