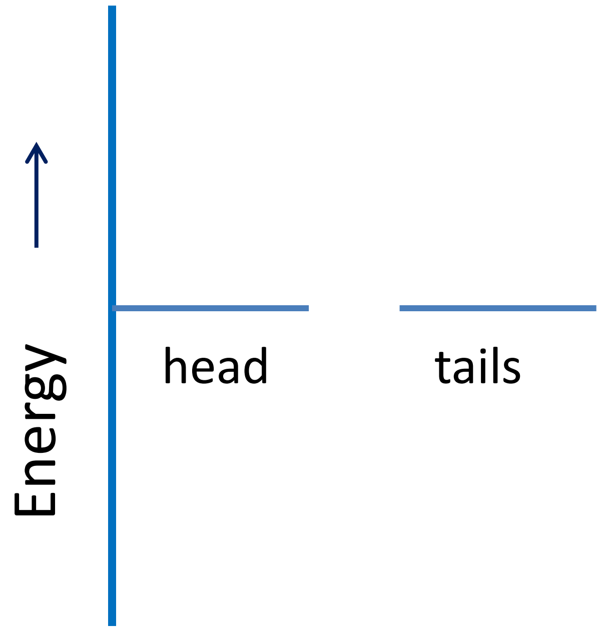
Thermodynamics tutorhour 7

Statistical Thermodynamics

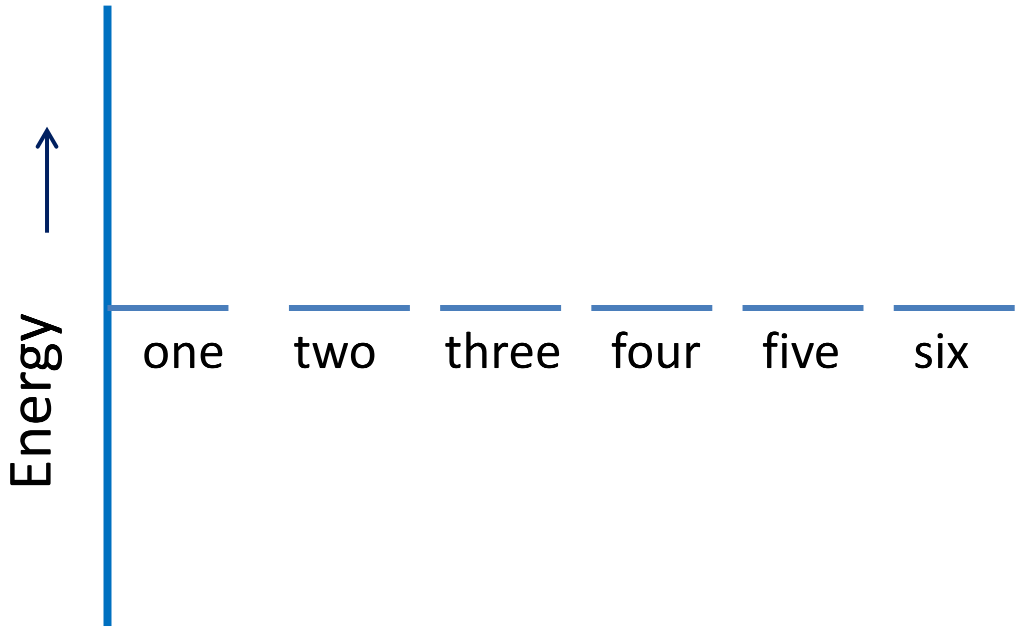
At equal energy levels

Head or tails?



Chance(tails) = ½ = 0.500

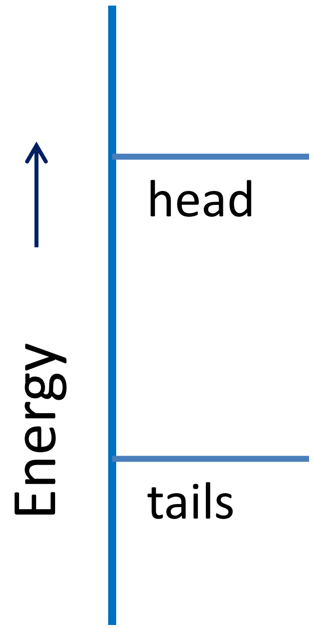
dice



Chance(six) = 1/6 = 0.167

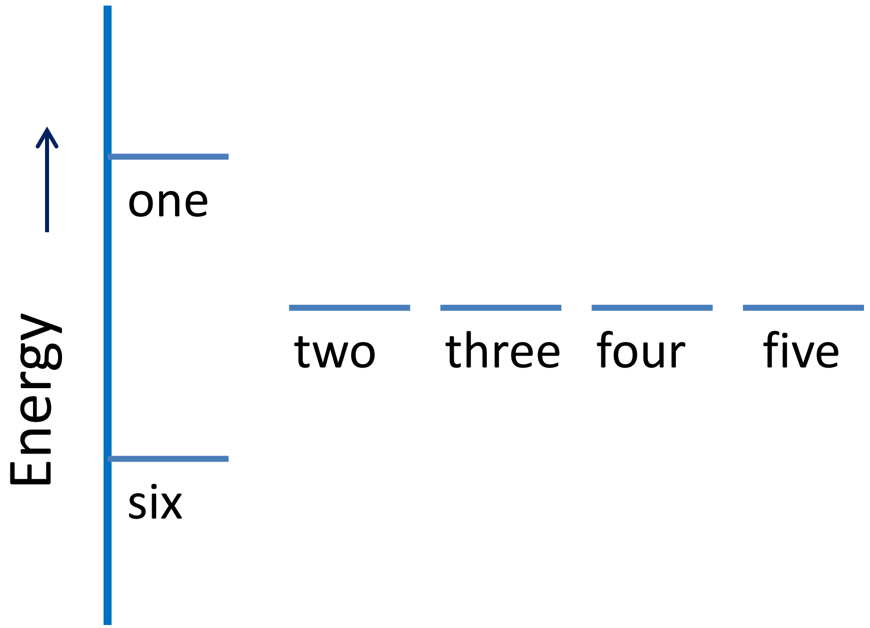
At different energy levels

Lucky coin



Chance(tails) = ????

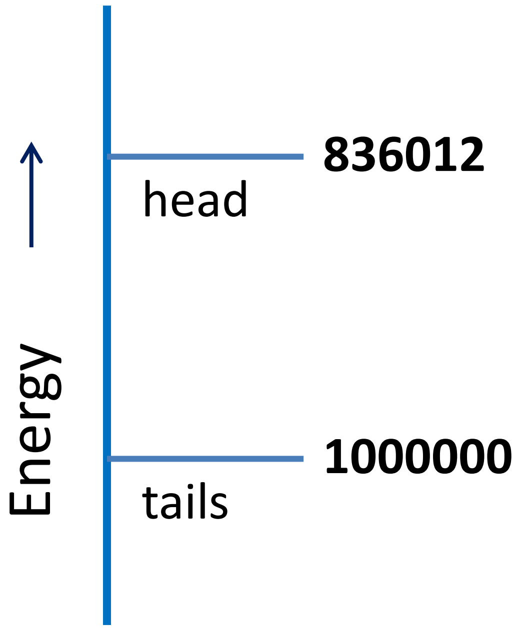
Loaded dice



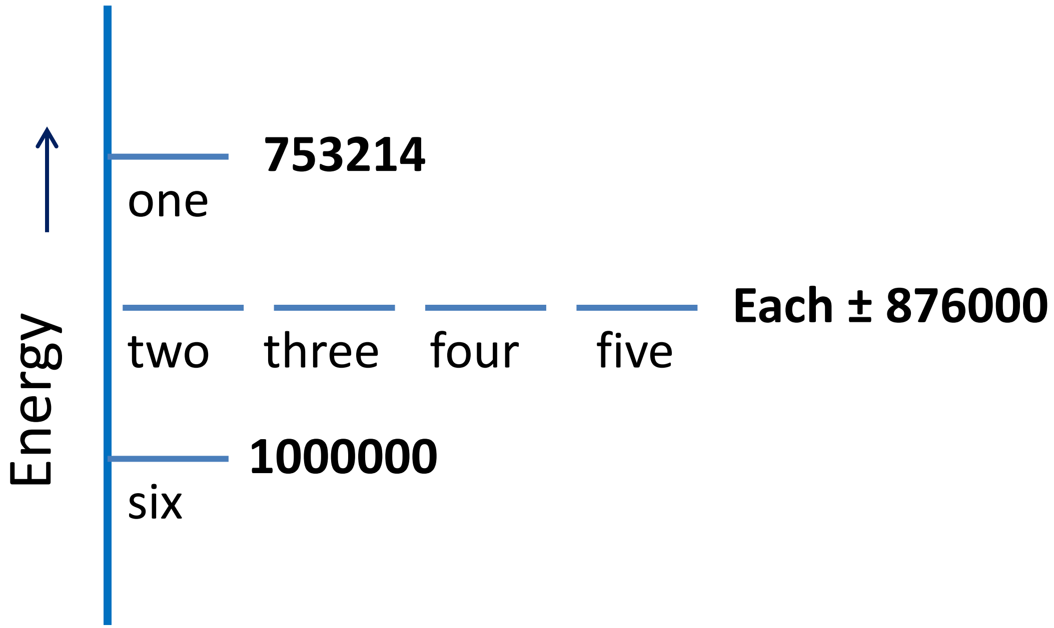
Chance(six) = ????

Performing an experiment → frequencies

Lucky coin



Loaded dice

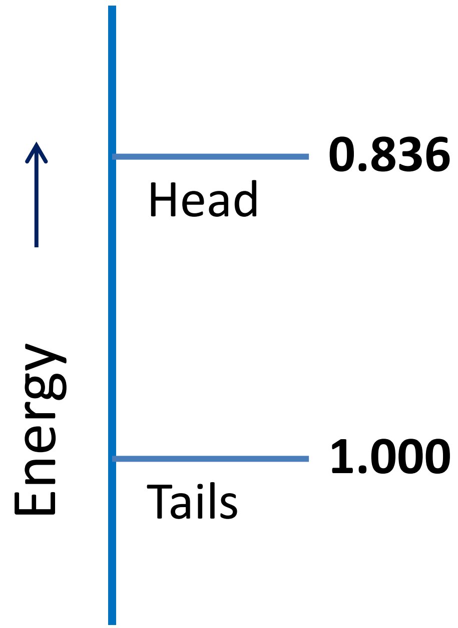


Chance(tails) = ????

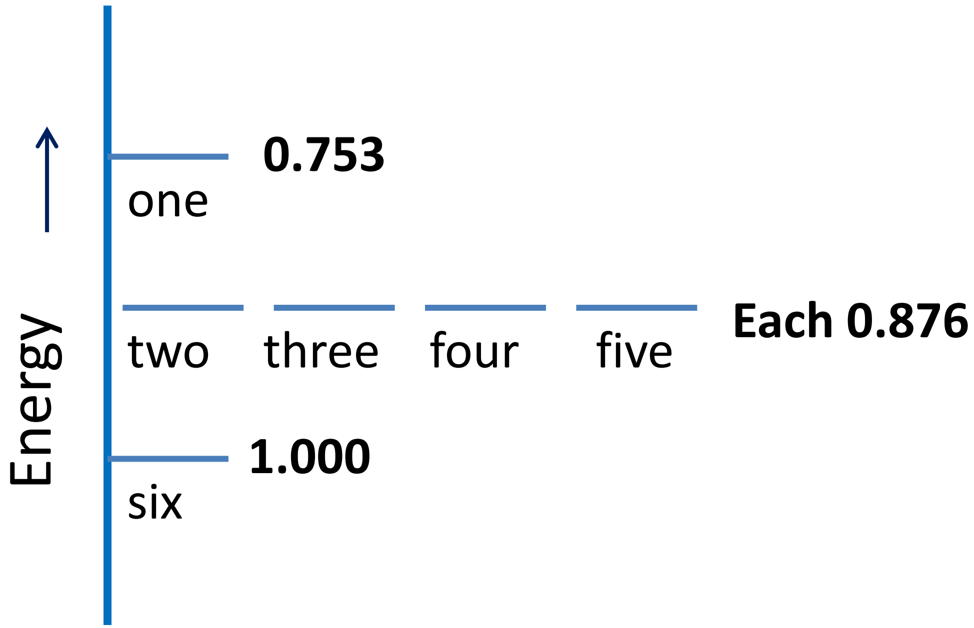
Chance(six) = ????

Probability with uneven energy levels

Lucky coin



Loaded dice



$$\text{Chance(tails)} = \frac{\mathbf{1.000}}{\mathbf{1.000 + 0.836}}$$

$$\text{Chance(tails)} = \mathbf{0.54 > 0.500}$$

$$\text{Chance(six)} = \frac{\mathbf{1.000}}{\mathbf{1.000 + 4 \times 0.876 + 0.753}}$$

$$\text{Chance(six)} = \mathbf{0.235 > 0.167}$$

System of particles: Boltzmann factor

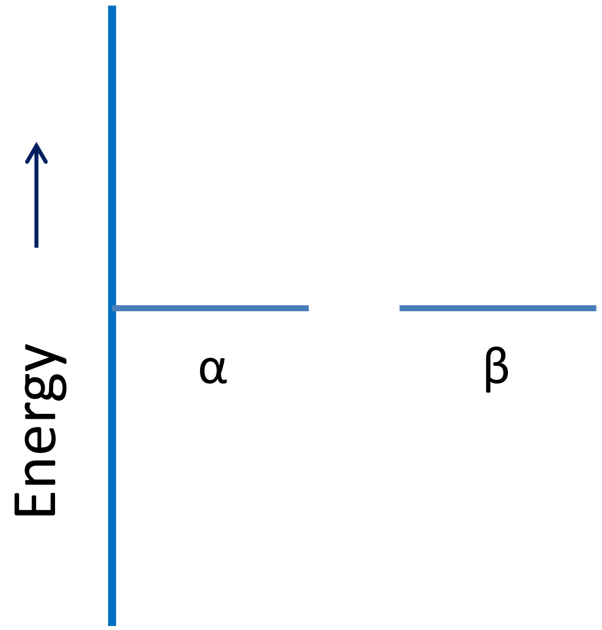
$$\exp \frac{-\varepsilon_i}{kT}$$

Checklist of key equations: $\frac{n_i}{N} = \frac{\exp \frac{-\varepsilon_i}{kT}}{q}$ with $q = \sum_i \exp \frac{-\varepsilon_i}{kT}$

Equation for calculating the fraction of particles (p_i) present at energy level ε_i:

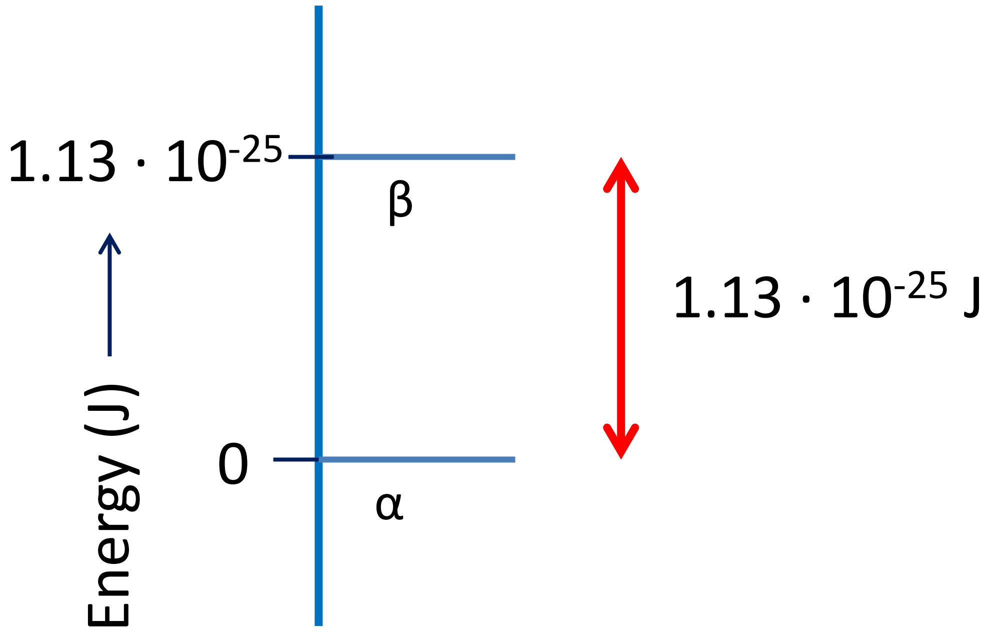
$$p_i = \frac{n_i}{N} = \frac{\exp \frac{-\varepsilon_i}{kT}}{q} = \frac{\exp \frac{-\varepsilon_i}{kT}}{\sum_i \exp \frac{-\varepsilon_i}{kT}}$$

Nuclear spin H-atom: α and β



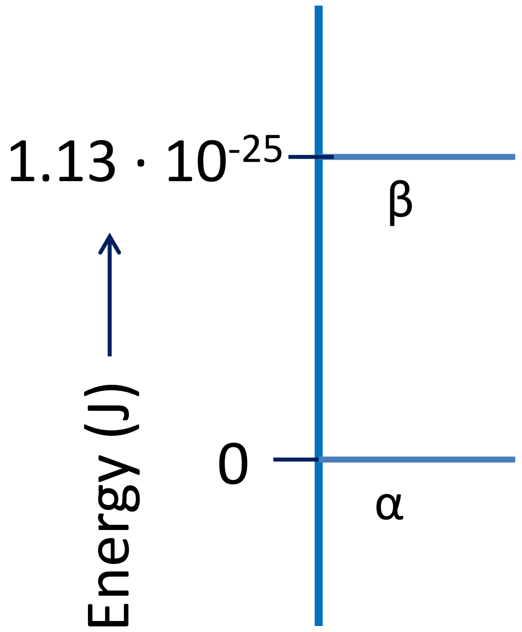
Nuclear spin α and β in a strong magnetic field

<u>At T = 50 K and B = 4 Tesla</u>



Nuclear spin α and β in a strong magnetic field

<u>At T = 50 K and B = 4 Tesla</u>



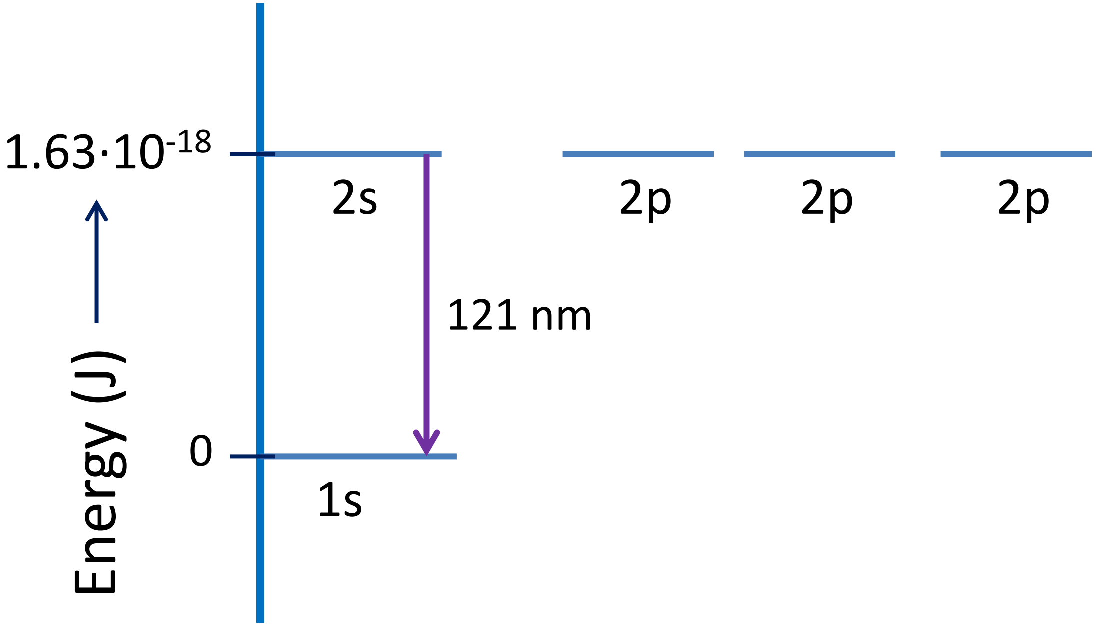
$$\exp\frac{-\varepsilon_i}{kT} = 0.99984$$

$$\exp\frac{-\varepsilon_i}{kT} = 1.00000$$

$$\text{Chance}(\boldsymbol{\beta}) = \frac{\mathbf{0.99984}}{\mathbf{1.00000 + 0.99984}} = \mathbf{0.49996}$$

simplified H atom (only 2 energy levels)

<u>At T = 50000 K</u>



$$\exp\frac{-\varepsilon_i}{kT} = 0.094$$

$$\exp\frac{-\varepsilon_i}{kT} = 1.000$$

$$\text{Chance}(\mathbf{1s}) = \frac{\mathbf{1.000}}{\mathbf{1.000 + 4 \times 0.094}} = \mathbf{0.727}$$

Particle system: Boltzmann factor

In this presentation:

$$p_i = \frac{n_i}{N} = \frac{\exp \frac{-\varepsilon_i}{kT}}{q} \qquad q = \sum_i \exp \frac{-\varepsilon_i}{kT}$$

Partition function:

This summation is hard to calculate in real systems

Follow-up session: tips and tricks (January 8th):
8.30 – 9.15 tutorhour

tutors	rooms
Ade Hoekstra	HG00.308
Els Heijmen	HG00.068
André Steenbergen	HG01.028
Martin Waals	HG00.086

Answers

Question 1

a) $E = \frac{hc}{\lambda} = hc\bar{\nu} = 6.626 \cdot 10^{-34} \cdot 3.0 \cdot 10^{8} \cdot 1.00 \cdot 10^{2} = 1.988 \cdot 10^{-23}$ J

b) $q = \sum_i \exp \frac{-\varepsilon_i}{kT} = 3 \cdot 1 + 1 \cdot e^{\frac{-3500 \cdot 1.988 \cdot 10^{-23}}{1.38 \cdot 10^{-23} \cdot 1900}} + 3 \cdot e^{\frac{-4700 \cdot 1.988 \cdot 10^{-23}}{1.38 \cdot 10^{-23} \cdot 1900}} = 3.155$

c) $(3 \cdot 1/3.155) \cdot 100 =$ 95.1% on level n = 0

$(e^{\frac{-3500 \cdot 1.988 \cdot 10^{-23}}{1.38 \cdot 10^{-23} \cdot 1900}}/3.155) \cdot 100 =$ 2.23 % on level n = 1

$(3 \cdot e^{\frac{-4700 \cdot 1.988 \cdot 10^{-23}}{1.38 \cdot 10^{-23} \cdot 1900}}/3.155) \cdot 100 =$ 2.69 % on level n = 2

d) $(0.0223 \cdot 1.988 \cdot 10^{-23} \cdot 3500 + 0.0269 \cdot 1.988 \cdot 10^{-23} \cdot 4700) = 4.065 \cdot 10^{-21}$ J

per mole it becomes: $4.065 \cdot 10^{-21} \cdot 6.022 \cdot 10^{23} =$ 2.45 kJ/mol

Question 2

$$\frac{p_1}{p_0} = \frac{1}{2}$$

$$p_1 = \frac{n_1}{N} = \frac{e^{\frac{-\varepsilon_1}{kT}}}{q}$$

$$p_0 = \frac{n_0}{N} = \frac{e^{\frac{-\varepsilon_0}{kT}}}{q} = \frac{1}{q}$$

$$\frac{p_1}{p_0} = \frac{e^{\frac{-\varepsilon_1}{kT}}}{q} \cdot \frac{q}{1} = e^{\frac{-\varepsilon_1}{kT}}$$

$$\frac{1}{2} = e^{\frac{-\varepsilon_1}{kT}}$$

$$\mathrm{k}T ln \frac{1}{2} = -\varepsilon_1$$

$$T = \frac{-\varepsilon_1}{\mathrm{k} ln \frac{1}{2}} = 623\ \mathrm{K}$$

Question 3

$$\frac{p_1}{p_0} = \frac{15}{85} = 0.1765$$

$$\frac{p_1}{p_0} = \frac{2 \cdot e^{\frac{-\varepsilon_1}{kT}}}{q} \cdot \frac{q}{1} = 2 \cdot e^{\frac{-\varepsilon_1}{kT}}$$

$$\frac{-\varepsilon_1}{\mathrm{k}T} = \ln(\frac{0.1765}{2})$$

$$\varepsilon_1 = -\mathrm{k}T \ln\left(\frac{0.1765}{2}\right) = 7.136 \cdot 10^{-21}\mathrm{J}$$

$$\frac{7.136 \cdot 10^{-21}}{1.60 \cdot 10^{-19}} = 0.045 \text{ eV}$$