Week 7 Recitation

Chapter 5: Statistical Thermodynamics

Questions?

Section Update

- Last week sucked! So I am a bit behind, and basically lied in the email from Oct. 4th. Oops.
- Doodle poll with topics I can elaborate on in a separate GitHub submission – might also base on Assignment 5 grading results
- Plan to get Assignment 5 in by Wednesday
- Exam 1 grading is on standby, need to finalize answer key for TAs

Relationship between k_B and R

Instead of showing a derivation here, take the following to be evident:

$$\frac{PV}{NT} = k_B$$

- N is the number of gas particles in the system
- k_B is a **proportionality constant**
- Multiply both sides by Avogadro's constant to get…

$$\frac{PV}{nT} = R$$

- n is the number of moles of gas in the system
- R is also a **proportionality constant**

m/s^2 = a
N = a x kg
J = N x m
K = Kelvin
k_B = J/K
R = J/mol K

$(6.022 \times 10^{23}\ mol^{-1})(1.38064852 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}) = 8.314\ J\ mol^{-1}\ K^{-1}$

HW4 Mistakes: 6a

If Dr. Foster provides code to solve a problem, it may contain "dummy data" to prevent students from copy and pasting the code.

Dr. Foster's lists:	The textbook lists:
T = 10, 20, 30, 40	T = 0, 20, 30, 45
K = 3, 4, 5, 6	K = 0.1535, 0.1558, 0.1569, 0.1584
dH = 704 J/mol	dH = 504 J/mol

A few responded using: $\Delta_r H = -\frac{R ln(\frac{K_2}{K_1})}{\frac{1}{T_2} - \frac{1}{T_1}}$, which is close!

HW4 Mistakes: 10 and 24d

Pay careful attention to **everything** the question is asking you!

If you see words/prompts like:

- Rationalize
- Explain
- Why?

4.10: The equilibrium concentration is too low to matter – despite higher affinity for hemoglobin than oxygen, there is not enough under these conditions to outcompete the abundance of O_2.

4.24: Duplexes brings together two DNA strands – Na^+ ions stabilize this structure by neutralizing the negative backbone charge, thereby reducing repulsive interactions.

HW4 Mistakes: 24b

The actual answer is:

dG = -48.9 kJ/mol

K = 3.66e08

The question asked for these values at 25˚C, but most used textbook values at 37˚C – this was a pervasive error, so the decision was made to treat these answers:

dG = ~-40 kJ/mol

K = ~9e6

As correct!

Ch 5 Review: The Boltzmann Distribution

Recall: $\frac{3}{2}RT = \frac{1}{2}M\langle v^2 \rangle$, where $\langle v^2 \rangle$ is the mean-square velocity of all particles

Consider **two** states, 1 and 2:

- The population ratio of A and B depends on the difference between their associated energies, such that: $\frac{p_2}{p_1} = f(E_2 - E_1)$
- What function *f* allows us to predict the population ratio?

Consider **three** states:

Result:

$$\frac{p_3}{p_1} = \frac{p_3}{p_2} \times \frac{p_2}{p_1}$$

$$f(E_3 - E_1) = f(E_3 - E_2)f(E_2 - E_1)$$

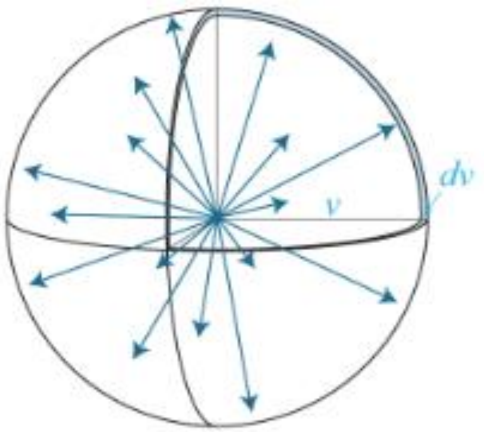
The function must be a product of functions!

Ch 5 Review: The Boltzmann Distribution

$p_i = Ne^{-\beta E_i}$, where:

- β is a reciprocal energy factor to get rid of units in the exponent [$1/k_B T$]
- N is a normalization factor – probability of all states must add to 1!

This is where things get a bit complicated…



- Velocity is a vector: $v^2 = v \cdot v$
- Quantize and group vectors within infinitesimally small "slice"
- g_i is the degeneracy of that speed, such that:

$g_i = 4\pi v_i^2 dv$ [volume of slice]

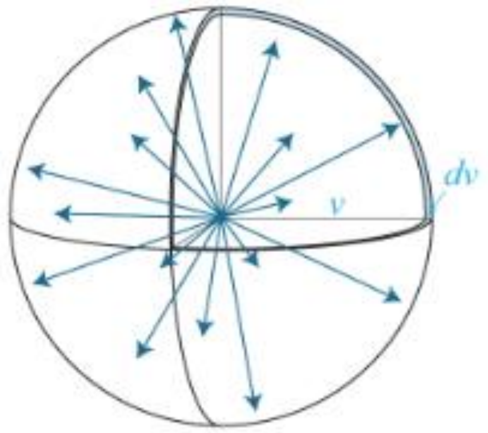
- Taking the ratio of some v_2 twice the magnitude of v_1:

$$\frac{g_2}{g_1} = \frac{4\pi v_2^2 dv}{4\pi v_1^2 dv} = \frac{v_2^2}{v_1^2} = \frac{(2v_1)^2}{v_1} = 4$$

Ch 5 Review: The Boltzmann Distribution

Recall: $p_i = Ne^{-\beta E_i}$

$p_i dv \propto 4\pi v_i^2 dv \times Ne^{-\beta E_i} = 4\pi N v_i^2 dv \times e^{-\frac{1}{2}\beta m v_i^2}$



Do a simple-ish integral (=1, dv) to determine norm:

$$N = \left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}}$$

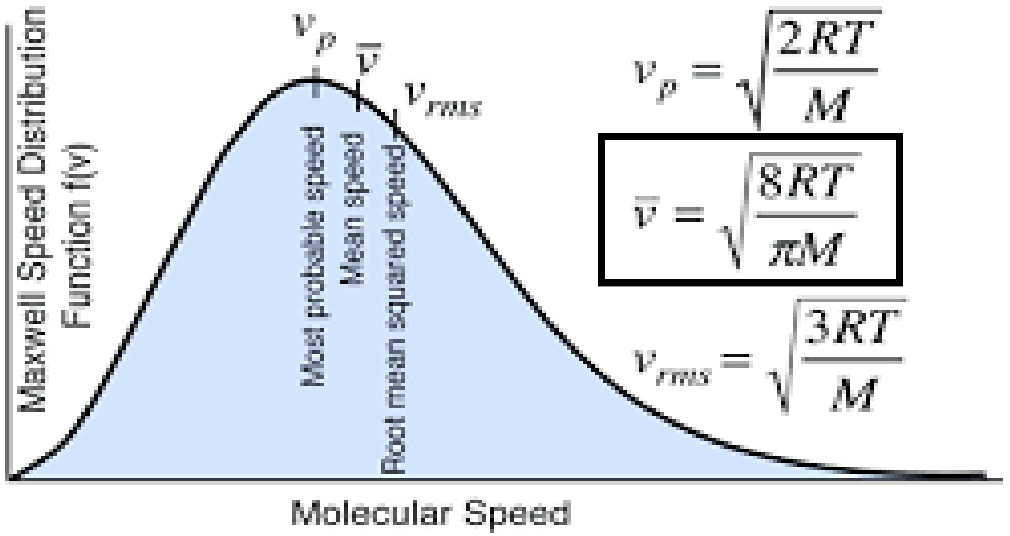
To determine β, evaluate the integral of energy (see 06-Stat-Term.pdf):

$\langle E \rangle = \frac{3}{2\beta}$, recall that $U = \frac{3}{2}RT = N_A \frac{3}{2} k_B T \therefore \beta = \frac{1}{k_B T}$, recall $R = k_B N_A$

Ch 5 Review: The Boltzmann Distribution

$$p_i = Ne^{-\beta E_i}$$

$$f(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



$$\langle v \rangle = \int_0^\infty v p(v) dv = \sqrt{\frac{2}{\pi}}\left(\frac{M}{RT}\right)^{3/2} \int_0^\infty \left[v \times v^2 \exp\left(\frac{-Mv^2}{2RT}\right)\right] dv$$

$$N = \left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} = \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}$$

Substitute and integrate (see pg. 155):

$$\langle v \rangle = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

While the assumptions made seem to limit this to translational modes, equipartition theorem states this energy is distributed across all thermally accessible modes – this relationship is generally true.

Questions?