Chemistry 4000/5000/7000 Fall 2021
Assignment 1

Due: September 29th

Neatly handwritten assignments are welcome. You can hand in a paper assignment or email me a good-quality picture or scan of your pages. In an ideal world, your assignment would be sent as a single file.

Detailed solutions or answers are required. Little to no credit will be given for answers presented without your detailed reasoning. However, do look at the number of marks assigned to a question. As a rough rule of thumb, a 10-mark question might require about a page of math, or two to three substantial paragraphs.

If you want to use a computer algebra system for some parts of this assignment, that is fine. In this case, make sure to provide a pdf of your worksheet along with written parts of your assignment. Also, please use simplification functions of the computer algebra system to provide the simplest expression possible.

1. NMR of spin-$\frac{1}{2}$ nuclei (such as the ^{1}H nucleus) is a simple example of a two-level system. The energies of the two spin states are given by

$$\epsilon_{\pm\frac{1}{2}} = \mp\frac{1}{2}\hbar\gamma B_z,$$

where γ is the magnetogyric ratio of the nucleus and B_z is the field strength of the NMR magnet. For clarity: a nucleus whose spin is aligned with the field ($m_s = +\frac{1}{2}$) has the lower (negative) energy. For a proton, $\gamma = 2.67522 \times 10^8\,\mathrm{T^{-1}s^{-1}}$. The UofL's 700 MHz NMR has a field strength of 16.4 T. [The tesla (T) is the SI unit of magnetic field strength.] At 25 °C, by how much does the probability that the proton is to be found in the lower energy spin state exceed $\frac{1}{2}$? In other words, calculate $P(\epsilon_+) - \frac{1}{2}$. [7 marks]

Note: The sample magnetization detected in NMR is due to the difference in population between the two spin states. You will find this difference surprisingly small, so small that it is difficult to evaluate it directly using a calculator. Use the following Taylor expansion to approximate the exponentials:

$$e^x \approx 1 + x$$

for small values of x.

2. In section 2.5 of the textbook, I worked out the average speed. The standard deviation of the speed is

$$\sigma_u = \sqrt{\overline{u^2} - \overline{u}^2}.$$

The quantity under the square root is the average of u^2 minus the average of u, squared. These are not the same thing.

   (a) Work out an equation for the standard deviation of the molecular speed. You can use $\bar{u}$ from the textbook. [10 marks]

   Useful integral:

$$\int_0^\infty x^4 e^{-x^2} dx = 3\sqrt{\pi}/8$$

   (b) The coefficient of variation (CV) is the ratio of the standard deviation to the average. In this case,

$$\mathrm{CV} = \sigma_u/\bar{u}.$$

   Work out an equation for the CV. [2 marks]

3. As an intermediate result in deriving the equations of simple collision theory, we found that each molecule of A undergoes $Z_A = \sigma\bar{u}_{\mathrm{rel}}L[\mathrm{B}]$ collisions per second with molecules of B.[1] The mean free path is the distance travelled between collisions. This is the number of metres travelled per second relative to the B molecules divided by the number of collisions per second, i.e.

$$l_{\mathrm{free}} = \bar{u}_{\mathrm{rel}}/Z_A.$$

[1] We actually had u_A rather than u_{rel} and made the substitution for the relative velocity later, but we could have made this replacement at this stage. Also, the formula in the book has n_B/V instead of [B].

The average time between collisions is just the inverse of the collision frequency: $\tau_{\text{coll}} = 1/Z_A$. Calculate the average time between collisions and the mean free path for molecules of $^{35}Cl_2$ colliding with ^{40}Ar atoms if the argon pressure is 0.50 bar at 25 °C. Make sure to use isotopic masses and not averaged molar masses. Also, indicate the sources you used for any necessary data. [10 marks]

Hint: Ideal gas law!

I don't care about the format of the citations, provided they are clear. Reputable web sites are OK here.

4. Carefully read the section of the text discussing velocity selection using rotating discs. Suppose that we want to design a velocity selector that will be able to select speeds in the range 100–800 $\text{m}\,\text{s}^{-1}$. The beam will pass through the disks at a distance of 3.5 cm from the centre. We have a motor that can operate reliably at rotational speeds up to 400 Hz. The disks should not be thinner than 0.1 mm for mechanical stability. The disks should not be mounted more than 10 cm from each other, and they should be at least 1 cm apart. Provide a full set of design parameters for this velocity selector: number of slits, distance between discs, thickness of discs and width of slits. [8 marks]