**Chemistry 410B** **Exam 2** **Fall 2016**

# NAME:

**Instructions:**

1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

**Other notes:**

- **The first portion of the exam (problem 1) is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. **40 points.**

   (a) Write an expression (in terms of $B$ and $T$) for the probability of finding a diatomic molecule in the $J = 1$ rotational state at temperature $T$ if $k_{\mathrm{B}}T \gg B$.

   (b) If the interaction energy for two rotating dipoles is initially $4.0\,\mathrm{kJ\,mol^{-1}}$, what is the new interaction energy if we

      i. double the temperature (in K)?

      ii. double the distance between the dipoles?

   (c) What volume in L is occupied by $2.00\,\mathrm{mol}$ of an ideal gas at $1.50\,\mathrm{bar}$ and $350.0\,\mathrm{K}$?

   (d) Identify each of the following particles as a boson (**B**) or a fermion (**F**):

      i. electron

      ii. $^{2}H^{+}$ (deuterium nucleus)

      iii. $^{13}C$ neutral atom

      iv. $^{14}N$ neutral atom

2. Evaluate the following limiting values. If a numerical answer is not possible, give the simplest algebraic expression.

   (a) $\lim_{T \to 0} q_{\mathrm{rot}}(T)$

   (b) $\lim_{T \to \infty} q_{\mathrm{rot}}(T)$

   (c) $\lim_{\omega_e \to \infty} q_{\mathrm{vib}}(T)$

   (d) $\lim_{u(R) \to 0} Q'_U(T, V)$ (assume $N$ particles)

   (e) $\lim_{v \to 0} \mathcal{P}_v(v)$

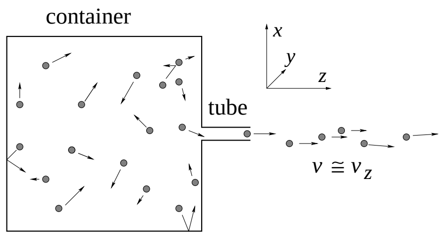
   (f) $\lim_{v \to \infty} \mathcal{P}_v(v)$

   (a) $\lim_{R \to 0} \mathcal{G}(R)$

   (h) $\lim_{T \to \infty} B_2(T)$

3. Water vapor at 373 K occupies a container. We open a small hole in one side of the container, in the $+Z$ direction, connected to a tube so that only molecules moving principally along the $Z$ axis (i.e., $v \approx v_Z$) can exit.

   (a) What is the *average* speed of the molecules in the container?




   (b) What is the *average* speed of the molecules exiting the tube?

   (c) If we use the speeds to determine the temperature, what is the temperature of the vapor exiting the tube?

4. In solving for the configuration integral of a non-ideal gas, we replaced an integral of $3N$ dimensions by a one-dimensional integral. For the special case of three interacting particles, this approximation can be shown without any fancy manipulation of the volume element. Briefly, write the steps and list any approximations necessary to rewrite

$$Q'_U = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-U(X_1 \ldots Z_3)/(k_B T)}\, dX_1 \ldots dZ_3$$

in terms of an integral over the single variable $R$.

## Fundamental Constants

| | | |
|---|---|---|
| Avogadro's number | $\mathcal{N}_A$ | $6.0221367 \cdot 10^{23}$ mol$^{-1}$ |
| Bohr radius | $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ | $5.29177249 \cdot 10^{-11}$ m |
| Boltzmann constant | $k_\mathrm{B}$ | $1.380658 \cdot 10^{-23}$ J K$^{-1}$ |
| electron rest mass | $m_e$ | $9.1093897 \cdot 10^{-31}$ kg |
| fundamental charge | $e$ | $1.6021773 \cdot 10^{-19}$ C |
| permittivity factor | $4\pi\epsilon_0$ | $1.113 \cdot 10^{-10}$ C$^2$ J$^{-1}$ m$^{-1}$ |
| gas constant | $R$ | 8.314510 J K$^{-1}$ mol$^{-1}$ |
| | $R$ | 0.08314510 L bar K$^{-1}$ mol$^{-1}$ |
| | $R$ | 0.08206 L atm K$^{-1}$ mol$^{-1}$ |
| hartree | $E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$ | $4.35980 \cdot 10^{-18}$ J |
| Planck's constant | $h$ | $6.6260755 \cdot 10^{-34}$ J s |
| | $\hbar$ | $1.05457266 \cdot 10^{-34}$ J s |
| proton rest mass | $m_p$ | $1.6726231 \cdot 10^{-27}$ kg |
| neutron rest mass | $m_n$ | $1.6749286 \cdot 10^{-27}$ kg |
| speed of light | $c$ | $2.99792458 \cdot 10^{8}$ m s$^{-1}$ |

## Unit Conversions

| | K | cm$^{-1}$ | kJ mol$^{-1}$ | kcal mol$^{-1}$ | erg | kJ |
|---|---|---|---|---|---|---|
| kHz = | $4.799 \cdot 10^{-8}$ | $3.336 \cdot 10^{-8}$ | $3.990 \cdot 10^{-10}$ | $9.537 \cdot 10^{-11}$ | $6.626 \cdot 10^{-24}$ | $6.626 \cdot 10^{-34}$ |
| MHz = | $4.799 \cdot 10^{-5}$ | $3.336 \cdot 10^{-5}$ | $3.990 \cdot 10^{-7}$ | $9.537 \cdot 10^{-8}$ | $6.626 \cdot 10^{-21}$ | $6.626 \cdot 10^{-31}$ |
| GHz = | $4.799 \cdot 10^{-2}$ | $3.336 \cdot 10^{-2}$ | $3.990 \cdot 10^{-4}$ | $9.537 \cdot 10^{-5}$ | $6.626 \cdot 10^{-18}$ | $6.626 \cdot 10^{-28}$ |
| K = | 1 | 0.6950 | $8.314 \cdot 10^{-3}$ | $1.987 \cdot 10^{-3}$ | $1.381 \cdot 10^{-16}$ | $1.381 \cdot 10^{-26}$ |
| cm$^{-1}$ = | 1.4388 | 1 | $1.196 \cdot 10^{-2}$ | $2.859 \cdot 10^{-3}$ | $1.986 \cdot 10^{-16}$ | $1.986 \cdot 10^{-26}$ |
| kJ mol$^{-1}$ = | $1.203 \cdot 10^{2}$ | 83.59 | 1 | 0.2390 | $1.661 \cdot 10^{-14}$ | $1.661 \cdot 10^{-24}$ |
| kcal mol$^{-1}$ = | $5.032 \cdot 10^{2}$ | $3.498 \cdot 10^{2}$ | 4.184 | 1 | $6.948 \cdot 10^{-14}$ | $6.948 \cdot 10^{-24}$ |
| eV = | $1.160 \cdot 10^{4}$ | $8.066 \cdot 10^{3}$ | 96.49 | 23.06 | $1.602 \cdot 10^{-12}$ | $1.602 \cdot 10^{-22}$ |
| hartree = | $3.158 \cdot 10^{5}$ | $2.195 \cdot 10^{5}$ | $2.625 \cdot 10^{3}$ | $6.275 \cdot 10^{2}$ | $4.360 \cdot 10^{-11}$ | $4.360 \cdot 10^{-21}$ |
| erg = | $7.243 \cdot 10^{15}$ | $5.034 \cdot 10^{15}$ | $6.022 \cdot 10^{13}$ | $1.439 \cdot 10^{13}$ | 1 | $10^{-10}$ |
| J = | $7.243 \cdot 10^{22}$ | $5.034 \cdot 10^{22}$ | $6.022 \cdot 10^{20}$ | $1.439 \cdot 10^{20}$ | $10^{7}$ | $10^{-3}$ |
| dm$^3$ bar = | $7.243 \cdot 10^{24}$ | $5.034 \cdot 10^{24}$ | $6.022 \cdot 10^{22}$ | $1.439 \cdot 10^{22}$ | $1.000 \cdot 10^{9}$ | 0.1000 |
| kJ = | $7.243 \cdot 10^{25}$ | $5.034 \cdot 10^{25}$ | $6.022 \cdot 10^{23}$ | $1.439 \cdot 10^{23}$ | $10^{10}$ | 1 |

| | | | |
|---|---|---|---|
| **distance** | 1 Å = | $10^{-10}$ m | |
| **mass** | 1 amu = | $1.66054 \cdot 10^{-27}$ kg | |
| **energy** | 1 J = | 1 kg m$^2$ s$^{-2}$ | = $10^{7}$ erg |
| **force** | 1 N = | 1 kg m s$^{-2}$ | = $10^{5}$ dyn |
| **electrostatic charge** | 1 C = | 1 A s | = $2.9979 \cdot 10^{9}$ esu |
| | 1 D = | $3.3357 \cdot 10^{-30}$ C m | = $1 \cdot 10^{-18}$ esu cm |
| **magnetic field strength** | 1 T = | 1 kg s$^{-2}$ A$^{-1}$ | = $10^{4}$ gauss |
| **pressure** | 1 Pa = | 1 N m$^{-2}$ | = 1 kg m$^{-1}$ s$^{-2}$ |
| | 1 bar = | $10^{5}$ Pa | = 0.98692 atm |

| | |
|---|---|
| entropy | $S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -N k_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$ |
| temperature | $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$ |
| Stirling's approx. | $\ln N! \approx N \ln N - N$ |
| canonical dist. | $\mathcal{P}(\epsilon) = \frac{g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}}{q(T)}$ |
| Maxwell-Boltzmann | $\mathcal{P}_v(v) = 4\pi \left(\frac{m}{2\pi k_{\text{B}} T}\right)^{3/2} v^2 e^{-mv^2/(2k_{\text{B}}T)}$ |
| | $\langle v \rangle = \sqrt{\frac{8 k_{\text{B}} T}{\pi m}}$ |
| partition func.s | $q(T) = \sum_\epsilon g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}$ |
| | $q_{\text{trans}}(T,V) = \left(\frac{8\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$ |
| | $Q_K(T,V) = \frac{1}{N!} \left(\frac{8\pi m k_{\text{B}} T}{h^2}\right)^{3N/2} V^N$ |
| | $Q_U(T,V) = \left(\frac{1}{V}\right)^N \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{-U(X_1,\ldots,Z_N)/(k_{\text{B}}T)} \, dX_1 \ldots dZ_N$ |
| | $Q_{\text{trans}}(T,V) = Q_K(T) Q_U(T,V) = \frac{1}{N!} \left(\frac{8\pi m k_{\text{B}} T}{h^2}\right)^{3N/2} Q'_U(T,V)$ |
| ideal gas | $PV = nRT$ |
| | $E_{\text{vib}} = \omega_e v \qquad E_{\text{rot}} = B_v J(J+1) \qquad g_{\text{rot}} = 2J+1$ |
| | $q_{\text{rot}} \approx \frac{k_{\text{B}} T}{B} \qquad q_{\text{vib}} \approx \frac{1}{1 - e^{-\omega_e/(k_{\text{B}}T)}}$ |
| equipartition | $E = \frac{1}{2} N_{\text{ep}} N k_{\text{B}} T = \frac{1}{2} N_{\text{ep}} nRT$ |
| virial/van der Waals | $P = RT\left[V_m^{-1} + B_2(T) V_m^{-2}\right] \qquad RT = \left(P + \frac{a}{V_m^2}\right)(V_m - b)$ |
| | $B_2(T) = -\mathcal{N}_A \frac{1}{2} \mathcal{I}(\beta) \equiv -2\pi \mathcal{N}_A \int_0^{V^{1/3}} (e^{-u(R)/(k_{\text{B}}T)} - 1) R^2 dR$ |
| | $a \approx \frac{16\pi \mathcal{N}_A^2 \epsilon R_{\text{LJ}}^3}{9} \qquad b \approx \frac{2\mathcal{N}_A \pi R_{\text{LJ}}^3}{3}$ |