Chemistry 304 - Problem Set 4

Due November 17, 2017

Questions 1–5 must be answered online using the link found in the Assessment area on the course Connect website. They are repeated below so you can work on them in advance of entering the solutions online. The variables in the questions will be substituted with randomly chosen values in the online environment. Each online question can be attempted 3 times but each attempt will generate a new set of random values. Questions 6–11, and optionally the bonus question, must be handed-in at the beginning of the lecture on the due date given above. Both the online and written parts of the problem set need to be completed.

Note: Spectroscopic values are often expressed in units of wavenumbers, cm^{-1}. If $\tilde{\nu}$ and $\tilde{B}$ are the harmonic frequency and rotational constant expressed in wavenumbers, respectively then $\Theta_{vib} = h\nu/k = hc\tilde{\nu}/k$ and $\Theta_{rot} = B/k = \tilde{B}hc/k$, in which $c = 2.998 \times 10^8\,\mathrm{m\,s^{-1}}$ is the speed of light.

1. Using expressions derived from statistical mechanics, determine the value of ΔH, in kJ, for the irreversible expansion and heating of 3 mol of oxygen gas from an initial volume of 1 L and temperature 25 °C to a final volume of V L and temperature T °C. Treat the gas as non-interacting with $\tilde{\nu} = 1580\,\mathrm{cm}^{-1}$ and $\tilde{B} = 1.43\,\mathrm{cm}^{-1}$.

2. Using expressions derived from statistical mechanics, determine the value of ΔS, in $\mathrm{J\,K^{-1}}$, for the irreversible expansion and heating of 3 mol of chlorine gas from an initial volume of 1 L and temperature 25 °C to a final volume of V L and temperature T °C. Treat the gas as non-interacting with $\tilde{\nu} = 559.7\,\mathrm{cm}^{-1}$ and $\tilde{B} = 0.2439\,\mathrm{cm}^{-1}$.

3. In a gaseous sample containing 5 mol of HCl at T °C and 1 bar, how many moles of molecules are in the $J = 3$ rotational state? Treat the gas as non-interacting with $\tilde{B} = 10.593\,\mathrm{cm}^{-1}$.

4. In a gaseous sample containing 4 mol of ClF at T K and 1 bar, how many moles of molecules are in the first excited vibrational state? Treat the gas as non-interacting with $\Theta_{vib} = 1132\,\mathrm{K}$.

5. Treating the gas as non-interacting with $\tilde{\nu} = 325.3\,\mathrm{cm}^{-1}$ and $\tilde{B} = 0.0821\,\mathrm{cm}^{-1}$, estimate the value of $C_{V,m}/R$ for Br_2 at T °C.

6. Calculate the value of kT when $T = 25$ °C. Using online or printed resources, find approximate estimates for the energy barriers for i) single bond rotation, for example methyl rotations in ethane, ii) hydrogen bond formation, and iii) carbon-carbon single bond cleavage. What is the physical significance of the value of kT? Use your calculated value of kT to describe the ease with which each of the three listed chemical processes will occur at room temperature.

7. Consider the contributions of translational motion to the partition function for a system of non-interacting, identical particles. The classical translational energy is

$$\epsilon_{trans} = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2) = \frac{m}{2}v^2 \ .$$

Using a classical mechanical approach and treating the velocity components v_x, v_y, and v_z or the speed v as continuous variables, the contribution of the translational states to the partition function is

$$
\begin{aligned}
q_{trans} &= \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \exp\left[-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)\right] \\
&= 4\pi \int_0^{\infty} v^2 dv \exp\left[-\frac{m}{2kT}v^2\right] \\
&= \frac{4\pi}{m}\sqrt{\frac{2}{m}} \int_0^{\infty} \sqrt{\epsilon_{trans}}\, d\epsilon_{trans} \exp\left[-\frac{\epsilon_{trans}}{kT}\right] \\
&= \left(\frac{2\pi kT}{m}\right)^{3/2} ,
\end{aligned}
$$

in which the integration is expressed in terms of Cartesian velocity components in the first case, in spherical polar variables of velocity (yielding only the speed v dependence) in the second case, and in terms of the translational energy in the third case. Using these expressions one can form three probability distributions as

$$
\begin{aligned}
p(v_x, v_y, v_z) &= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)} , \\
p(v) &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{m}{2kT}v^2} , \\
p(\epsilon_{trans}) &= \frac{2}{\sqrt{\pi} kT}\sqrt{\frac{\epsilon_{trans}}{kT}} e^{-\frac{\epsilon_{trans}}{kT}} ,
\end{aligned}
$$

where $p(v_x, v_y, v_z)$ is the probability for finding a particle with its velocity components equal to v_x, v_y, and v_z, $p(v)$ is the probability for finding a particle with speed v, and $p(\epsilon_{trans})$ is the probability for finding a particle with translational energy ϵ_{trans}. These are three different forms of the famous Maxwell-Boltzmann distribution for a system at equilibrium.

a) Submit a single graph with $p(\epsilon_{trans})$ plotted as a function of ϵ_{trans} for i) $kT = 1$ and ii) $kT = 5$ with the x-axis varying from 0 to 15, and the y-axis from 0 to 0.5. With an "X" mark the value of the average particle energy ($\bar{\epsilon}_{trans} = 3kT/2$) for each curve.

b) Why does $\bar{\epsilon}_{trans} = 3kT/2$ not correspond to the peak of the distribution? Do most particles in a system have an energy equal to $\bar{\epsilon}_{trans} = 3kT/2$?

c) How does the shape of the probability distribution change as temperature is increased? How does the width of the distribution compare with the average energy? What does this imply about the fluctuations of *particle* energies? How is this different from the fluctuations of the total energy of the system?

8. In addition to carrying charge, electrons are also small magnets, possessing a magnetic moment proportional to their spin quantum number. When placed in an external magnetic field, B, these magnetic moments align and produce a bulk magnetization, M, which in the canonical ensemble is determined from

$$
M = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial B}\right)_{N,\beta} .
$$

A non-zero M means the sample has become magnetic.

Consider N electronic spins in equilibrium with a heat bath at temperature T, with the spins treated as non-interacting and distinguishable. When placed in a magnetic field, each spin is a two-level system with ground and excited state energies given by $\epsilon_{gs} = -\mu_e B/2$ and $\epsilon_{ex} = \mu_e B/2$ with μ_e is the magnetic moment of the electron. The ground and excited states correspond to the $m_s = 1/2$ an $m_s = -1/2$ spin states, that is spins aligned and anti-aligned with the magnetic field, respectively. The energy gap between the states is $\mu_e B$ and increases as the strength of the magnetic field increases.

a) Derive the following expressions for the probabilities for the spins to be in the ground and excited states, the magnetic moment, and the magnetic contributions to the average internal energy, heat capacity at constant volume, and entropy:

$$\begin{aligned}
p_{gs} &= \frac{1}{1+e^{-\frac{\mu_e B}{kT}}} \\
p_{ex} &= \frac{e^{-\frac{\mu_e B}{kT}}}{1+e^{-\frac{\mu_e B}{kT}}} \\
M &= \frac{N\mu_e}{2}\tanh\left(\frac{\mu_e B}{2kT}\right) \\
\overline{E}_{mag} &= -\frac{N\mu_e B}{2}\tanh\left(\frac{\mu_e B}{2kT}\right) \\
C_{V,mag} &= Nk\left(\frac{\mu_e B}{2kT}\right)^2 \operatorname{sech}^2\left(\frac{\mu_e B}{2kT}\right) \\
S_{mag} &= Nk\left\{\ln\left[2\cosh\left(\frac{\mu_e B}{2kT}\right)\right] - \frac{\mu_e B}{2kT}\tanh\left(\frac{\mu_e B}{2kT}\right)\right\}
\end{aligned}$$

Note: if necessary, please review the properties of the hyperbolic functions on Wikipedia: en.wikipedia.org/wiki/Hyperbolic_function .

b) Using the expressions from part a), submit a single graph with six curves plotted as a function of $\mu_e B/(2kT)$: i) p_{gs}, ii) p_{ex}, iii) $\overline{E}_{mag}/(N\mu_e B)$, iv) $C_{V,mag}/(Nk)$, v) $S_{mag}/(Nk)$ and vi) $M/(N\mu_e)$ all plotted with the x-axis varying from $\mu_e B/(2kT) = 0$ to $\mu_e B/(2kT) = 4$ and the y-axis from -0.55 to 1.05. Label the curves and axes.

c) Rationalize the shapes of the curves in part (b). In other words, explain why these shapes are consistent with each other and with the behaviour of the spins. In your response, be sure to discuss the limits when i) $B = 0$, and ii) $B > 0$ with both small T and large T. Under what conditions is the system the strongest magnet?

d) The magnetic field strength, B, is measured in units of Tesla, T, where $\mathrm{T} = \mathrm{N\,A^{-1}\,m^{-1}}$, and the magnetic moment for the electron is $\mu_e = 9.2848 \times 10^{-24}\,\mathrm{J\,T^{-1}}$. A large, helium-cooled, superconducting magnet generates approximately $B = 2\,\mathrm{T}$. Calculate the difference in spin populations between the ground and excited states in such a field at $T = 25\,^\circ\mathrm{C}$.

Aside: In an MRI scan, proton spins are aligned rather than electron spins. The proton magnetic moment is about 650 times smaller than the electron's, and even in magnetic fields of several Tesla, the difference in ground and excited state spin populations is only a few parts per million. The entire MRI image is obtained with just this slight difference in spin populations.

9. Assume a molecule has only **three** possible internal states: a ground state of energy 0 and two excited states of equal energy ε (i.e., a doubly degenerate excited state of energy ε). Consider a collection of N such molecules to be non-interacting at equilibrium with volume V. Treat the molecules as distinguishable (assume any factors due to indistinguishability have been taken into account by the translational part of the partition function which you can ignore in this question). All quantities in this problem are assumed to be those associated only with the internal states.
   a) At 27 °C, 50% of the molecules are found to be in the ground state. Calculate the value of the partition function q and the **molar** Helmholtz free energy, in $\mathrm{J\,mol^{-1}}$, at this temperature.
   b) Determine the energy ε, in J, of the two excited states.
   c) Calculate the fraction of molecules in each state at: i) $T = 0\,\mathrm{K}$, ii) $T = 27\,°\mathrm{C}$, and iii) very large T.

10. In this question, mean field theory will be used to derive the van der Waals equation. Consider a gas of *interacting*, indistinguishable particles. In principle, the potential energy from these interactions depends upon the positions of the particles so detailed structural information is needed to describe it. This is a difficult problem. However, we can take a much simpler, albeit approximate, approach by treating the interactions with a one-body energy term. The physical argument goes as follows. The interaction (potential) energies in principle will vary among microstates. However, we expect fluctuations to be small. Let's replace the exact potential U_i in the partition function with its average value (that is, the "mean field") ϵ_{MF} divided among the particles, and assume each particle has the *same* contribution regardless of its position. In other words, rather than considering the particles as interacting with each other (via a potential that depends upon particle positions) we treat them as interacting with the mean field (which is independent of particle positions and other particles). In this way, ϵ_{MF} becomes a one-body energy term that can be included in the usual *non-interacting* partition function as an additional energy contribution. That is, the interacting system is approximated by the non-interacting partition function with a one-body energy term approximating the particle interactions.

    With this mean-field approximation, the energy of our particles becomes

    $$\epsilon = \epsilon_{ideal} + \epsilon_{MF} \ ,$$

    in which ϵ_{ideal} is the energy of a particle in an ideal gas. Since these energy contributions are independent, the particle partition function is

    $$q = q_{ideal} q_{MF} \ .$$

    Normally, q_{ideal} would be the product of partition functions for translation, vibration, rotation, etc. but because the volume dependence will be important, let's write $q_{ideal} = c(T)V$ where $c(T)$ includes all the constants and temperature dependencies arising from vibrations and rotations, and where the volume factor in the translational partition function has been explicitly accounted for. The remaining part of the translational partition function in included in $c(T)$. In the present case though, we imagine the particles each occupy some volume b, so the "effective volume" of our system is $V - Nb$. In other words, take $q_{ideal} = c(T)(V - Nb)$. We don't know the value of ϵ_{MF} but physical arguments suggest it must vary with the average distance between particles, which in turn varies with density, N/V. So, let's suppose a linear dependence and write $\epsilon_{MF} = -aN/V$ with a some unknown constant. A minus sign is included here because it is anticipated ϵ_{MF} will be negative (attractive interaction) so this will make a a positive number. This one energy is the same for each particle so $q_{MF} = \exp(-\beta\epsilon_{MF}) = \exp(a\beta N/V)$.

a) Derive the expression for the average pressure and show the system obeys the van der Waals equation of state. Note: as defined b is the volume *per particle* not *per mole of particles* as usually tabulated. Similarly, as defined a is *per particle* not *per mole squared* as usually tabulated. So, write Nb as nb, and aN^2 as an^2 if you want to use a and b as the usually tabulated molar values.

b) Show that the internal energy and heat capacity are given by

$$U = \overline{E} = \overline{E}_{ideal} - \frac{an^2}{V} \quad \text{and} \quad C_V = C_{V,ideal} \ ,$$

where $\overline{E}_{ideal}$ and $C_{V,ideal}$ are the internal energy and heat capacity for the ideal gas, respectively. Show that the first relation is consistent with $(\partial U/\partial V)_{T,n_i} = an^2/V^2$, a relation derived from thermodynamics. Give a physical argument to explain why the van der Waals gas (an interacting system) could have the same C_V as the ideal gas (a non-interacting system).

11. The expressions for the contributions to $\overline{E}$ derived in class for translational, rotational, and vibrational motions are all functions of temperature only. This means $(\partial U/\partial V)_T = 0$, the ideal gas value, from which it follows that $C_{P,m} = C_{V,m} + R$. So, even for real gases, the molar heat capacities at constant V and constant P should differ by R, provided the non-interacting assumption is good. As well, all the expressions derived in class suggest it is natural to divide heat capacities by R when comparing them. In the table below are listed measured values of $C_{P,m}$ and $C_{V,m}$ at 298 K and 1 atm (in units of $\mathrm{J\,K^{-1}\,mol^{-1}}$) for several chemical species.

a) Calculate $C_{P,m}/R$, $C_{V,m}/R$, and $(C_{P,m} - C_{V,m})/R$ and enter these values in the appropriately labelled columns.

Species	$C_{P,m}$	$C_{V,m}$	$C_{P,m}/R$	$C_{V,m}/R$	$(C_{P,m} - C_{V,m})/R$	$C_{V,vib,m}^{exact}/R$	$C_{V,vib,m}^{cl}/R$
He	20.79	12.47					
H_2	28.83	20.45					
Cl_2	33.94	25.33					
CH_4	35.64	27.00					
H_2O	33.59	25.26					
C_3H_8	73.79	65.30					
SF_6	97.00	88.23					

b) The deviation of $(C_{P,m} - C_{V,m})/R$ from unity is a measure of non-ideal behaviour. Rationalize the trends seen in these values from the Table.

c) Assuming the classical limit for translation and rotation, the experimental value of $C_{V,m}/R$ should be equal to $(C^{cl}_{V,trans,m} + C^{cl}_{V,rot,m} + C^{exact}_{V,vib,m})/R$. For each chemical species in the Table, calculate $C^{exact}_{V,vib,m}/R$ from the measured heat capacities, and record the results in the column labelled $C^{exact}_{V,vib,m}/R$. In addition, in the column labelled $C^{cl}_{V,vib,m}/R$ record the vibrational contribution to the heat capacity expected in the classical limit. Rationalize the trends in these values. Are any of the vibrational contributions close to their classical limits?

Bonus Question

This question, for bonus marks, is optional.

Consider a gas in equilibrium with the surface of a solid. Some of the molecules will be adsorbed onto the surface, depending upon the gas pressure. A simple statistical model accounting for this treats the surface as a two-dimensional lattice of M sites, each of which could be unoccupied or occupied by at most one of the molecules of the gas. Let the partition function of an unoccupied site be 1 and of an occupied site be $q(T)$. Assuming the adsorbed molecules do not interact with each other, the partition function of N molecules adsorbed onto M sites is

$$Q(N, M, T) = \frac{M!}{N!(M-N)!}[q(T)]^N \ .$$

The binomial coefficient prefactor accounts for the number of ways of distributing N molecules among M sites. By using the fact the adsorbed molecules are in equilibrium with the gas phase molecules (considered to be an ideal gas), show that the fractional coverage, $\theta = N/M$, as a function of the gas pressure can be expressed as

$$\theta = \frac{\alpha P}{1 + \alpha P} \ ,$$

and derive an expression for α. The fractional coverage as a function of pressure (at fixed temperature) is called an adsorption isotherm, and this model gives the so-called Langmuir adsorption isotherm.

Hint: since the molecules on the surface and in the gas are in equilibrium, their chemical potentials must be equal, and chemical potentials can be evaluated from the partition function. Write the particle partition function for an ideal gas as $q_{ideal} = c(T)V$ *(using the same arguments presented in Question 10). The use of Stirling's approximation,* $\ln N! \approx N \ln N - N$*, may also be required.*