Chemistry 410B **Exam 2** **Spring 2012**

Solutions

1. **40 points.**

   (a) Find the average collision energy **in kJ mol^{-1}** of a 0.100 mol sample of an ideal gas at 0.831 bar and a volume of 4.00 L. **Solution:** The collision energy depends only on T, and we can get T from the ideal gas law.

$$\begin{aligned} T &= \frac{PV}{nR} = \frac{(0.831\,\mathrm{bar})(4.00\,\mathrm{L})}{(0.100\,\mathrm{mol})(0.083145\,\mathrm{bar\,L\,K^{-1}\,mol^{-1}})} = 400\,\mathrm{K} \\ \langle E_{\mathrm{AB}} \rangle &= \frac{3k_BT}{2} = \frac{3(1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}})(400\,\mathrm{K})}{2} \\ &= 8.29 \cdot 10^{-21}\,\mathrm{J}(6.022 \cdot 10^{20}\,\mathrm{kJ\,mol^{-1}/\,J}) = \boxed{4.99\,\mathrm{kJ\,mol^{-1}}.} \end{aligned}$$

   (b) Given the following values for the van der Waals coefficients, which one of these gases should have the lowest molar volume at 0.20 bar and 298 K?

molecule	a (L^2 bar/ mol^2)	b (L/ mol)
Fluoromethane	4.692	0.05264
Methanol	9.649	0.06702
Ethane	5.562	0.0638
Cyanogen	7.769	0.06901
Propane	8.779	0.08445
Sulfur dioxide	6.803	0.05636
Silane	4.377	0.05786

   Solution: The smallest molar volume is for $\boxed{\text{methanol,}}$ because it has the largest value of a among a set of molecules with similar or larger b values. The a coefficient is proportional to the well-depth of the attractive potential, so larger a values mean the molecules stick to each other more, lowering the molar volume. The value of b works in the opposite direction, so larger b means a larger molar volume. However, by checking the second virial coefficient $B_2 = b - a/(RT)$ for any of these molecules, we would find that the $a/(RT)$ term is the dominant non-ideality at this temperature.

   (c) The maximum emission from a blackbody at 770 K (about 500 C) is at a wavelength of about 6600 nm. What will be the wavelength for the most intense emission when we increase the temperature to 1540 K? **Solution:** The frequency of the blackbody radiation profile shifts in proportion to the temperature, so the $\lambda = c/\nu$ shifts as $1/T$. If T doubles, the wavelength of peak emission is cut in half: $\boxed{3300\,\mathrm{nm}.}$

   (d) Estimate the value of ln(1000!). **Solution:** For this we use Stirling's approximation, $\ln N! \approx N \ln N - N = (1000)\ln(1000) - (1000) = \boxed{5907.}$

2. The energy and degeneracy of a particle in a two-dimensional box are

$$\epsilon = \epsilon_0 n^2 \qquad\qquad g = g_0 n.$$

Use the integral approximation to find an expression for the partition function of this system. **Solution:** We can set up the partition function using the canonical distribution and jump right in:

$$\begin{aligned} q &= \sum_{n=0}^{\infty} g(n)\, e^{-\epsilon(n)/(k_BT)} \approx \int_0^\infty g(n)\, e^{-\epsilon(n)/(k_BT)}\, dn \\ &= \int_0^\infty g_0 n\, e^{-\epsilon_0 n^2/(k_BT)}\, dn = \frac{g_0}{2}\int_0^\infty g_0 n\, e^{-\epsilon_0 n^2/(k_BT)}\, d(n^2) \quad = -\frac{g_0}{2}\left(\frac{k_BT}{\epsilon_0}\right) e^{-\epsilon_0 n^2/(k_BT)}\Big|_0^\infty \\ &= -\frac{g_0}{2}\left(\frac{k_BT}{\epsilon_0}\right)(0-1) = \boxed{\frac{g_0 k_B T}{2\epsilon_0}.} \end{aligned}$$

3. (a) Find an exact expression in terms of N for the probability that in N flips of a coin, the result is tails every time *except once*. **Solution:** For this problem, we use the *discrete* probability distribution, $\mathcal{P}(k)$, for the case where $i = N-1$ and $j = 1$:

$$\mathcal{P}(k) = \frac{N!}{2^N i! j!} = \frac{N!}{2^N (N-1)!1!} = \frac{1}{2^N}\frac{N!}{(N-1)!} = \frac{1}{2^N}N = \boxed{\frac{N}{2^N}.}$$

   (b) Compare your result to the approximate solution for the case $N = 10$. **Solution:** For $N = 10$ and $i = N-1$ and $j = 1$, we have $k = i - j = 8$, so the exact solution is $10/2^{10} = \boxed{0.0098,}$ while the approximation yields

$$\mathcal{P}(k) \approx \sqrt{\frac{2}{10\pi}} e^{-8^2/(20)} = \boxed{0.010.}$$

4. Estimate how low the pressure (in bar) must be if a square patch of surface 10.0 nm on a side is to suffer on average fewer than one collision per hour when the temperature is 298 K. Assume the chief contaminant is air, and that its molecules have an average speed $\langle v \rangle$ of 650 $\mathrm{m\,s^{-1}}$ and collision cross section of 37 $\mathring{\mathrm{A}}^2$. (The surface is stationary, so you should use $\langle v \rangle$ instead of $\langle v_{\mathrm{AA}} \rangle$.) **Solution:** First, notice that the relevant area is not the collision cross section of the gas-phase molecules, but the much larger area of the surface patch, $A = (10\,\mathrm{nm})^2 = 10^4\,\mathring{\mathrm{A}}^2$. Because the surface is so large, the likelihood of a molecule striking the surface depends very little on the size of the molecule. We next set $\gamma_{\max} = 1/(3600\,\mathrm{s}) = 2.78 \cdot 10^{-4}\,\mathrm{s^{-1}}$. Then, because the collision frequency is proportional to density, we write γ max in terms of the maximum number density $\rho_{\max}$. From $\rho_{\max}$ in turn, we can find the maximum pressure:

$$\gamma_{\max} = \rho_{\max} A \langle v \rangle = \frac{P_{\max}\mathcal{N}_A}{RT} A \langle v \rangle$$

$$P_{\max} = \frac{\gamma_{\max} RT}{\mathcal{N}_A A \langle v \rangle} = \frac{(2.78\cdot 10^{-4}\,\mathrm{s^{-1}})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{(6.022\cdot 10^{23}\,\mathrm{mol^{-1}})(10\,\mathrm{nm})^2(650\,\mathrm{m\,s^{-1}})} = 1.76\cdot 10^{-11}\mathrm{Pa} = \boxed{1.76\cdot 10^{-16}\,\mathrm{bar.}}$$