Chemistry 410B **Exam 3** **Fall 2016**

Solutions

1. **40 points.**

   (a) What is the probability of flipping a fair coin 6 times and getting heads 5 times? **Solution:** One way: tails appears only once, there are $2^6 = 64$ possible sequences, and there are 6 different places in the sequence for the tails to appear, so the probability is $\boxed{6/64}$ or 3/32. Or use the formula with $i = 5$ heads, $j = 1$ tails:

   $$\mathcal{P}(k=4) = \frac{N!}{2^N\, i!\, j!} = \frac{6!}{2^6(5!)(1!)} = \frac{6}{64} = \frac{3}{32} = 0.09375.$$

   (b) If the flux J is the same at all points along a channel, what is $d\rho/dt$ at any point Z_0? **Solution:** If $J(Z)$ is a constant, then

   $$\frac{d\rho}{dt} = D\frac{d^2\rho}{dZ^2} = -\frac{dJ(Z)}{d^Z} = \boxed{0.}$$

   This makes sense—if the flow rate into a position is the same as the flow away from that position, then the concentration does not change with time.

   (c) Identify the mechanism of heat transfer (conduction, convection, or radiation) in each of the following processes:

   i. Sunlight passes through the atmosphere and warms the ground. $\boxed{\text{radiation}}$

   ii. The ground warms the air directly above it. $\boxed{\text{conduction}}$

   iii. The warm air rises, raising the temperature of the upper atmosphere. $\boxed{\text{convection}}$

   (d) What is the value of the absorption coefficient ϵ for a molecule if a sample absorbs half of the light ($I = I_0/2$) at a pathlength of 1.00 cm and a concentration of $1.0 \cdot 10^{-5}$ mol/ L. **Solution:**

   $$\varepsilon = \frac{A}{Cl} = \frac{-\log_{10}\left(\frac{I}{I_0}\right)}{Cl} = \frac{-\log_{10}\frac{1}{2}}{(1.0\cdot 10^{-5}\,\mathrm{mol/\,L})(1.00\,\mathrm{cm})} = \boxed{3.0\cdot 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}.}$$

2. Calculate the diffusion constant of helium in CO_2 at 73.8 bar and 304 K. The collision cross section is roughly $32\,\text{Å}^2$. **Solution:** I think the easiest is to put everything in SI units. We also need the reduced mass μ:

   $$\mu = \frac{(4.003)(44.01)}{4.003 + 44.01}\,\mathrm{amu} = 3.67\,\mathrm{amu}$$

   $$D = \frac{\langle v_{\mathrm{AB}}\rangle}{4\rho_{\mathrm{A}}\sigma_{\mathrm{AB}}}$$

   $$v_{\mathrm{AB}} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu}} = \sqrt{\frac{8(1.381\cdot 10^{-23}\,\mathrm{J\,K^{-1}})(304\,\mathrm{K})}{\pi(3.67\,\mathrm{amu})(1.661\cdot 10^{-27}\,\mathrm{kg\,amu^{-1}})}} = 1324\,\mathrm{m\,s^{-1}}$$

   $$\rho_{\mathrm{A}} = \frac{P\mathcal{N}_A}{RT} = \frac{(73.8\cdot 10^5\,\mathrm{Pa})(6.022\cdot 10^{23}\,\mathrm{mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(304\,\mathrm{K})} = 1.76\cdot 10^{27}\,\mathrm{m^{-3}}$$

   $$D = \frac{1324\,\mathrm{m\,s^{-1}}}{4(32\cdot 10^{-20}\,\mathrm{m^2})(1.76\cdot 10^{27}\,\mathrm{m^{-3}})} = 5.9\cdot 10^{-7}\,\mathrm{m^2\,s^{-1}} = \boxed{5.9\cdot 10^{-3}\,\mathrm{cm^2\,s^{-1}}.}$$

This value is about 100 times lower than the gas-phase examples in Table 5.5, which seems reasonable, given that the density is about 100 times higher. These conditions are for supercritical CO_2, which we'll discuss in Chapter 10.

3. We start with an ideal blackbody at 10,000 K, and measure its spectrum as a function of **wavelength**. We increase the temperature to 20,000 K and measure the changes. Write + if the parameter increases, − if it decreases, and **0** if it remains unchanged. **Solution:** Higher temperature increases the energy output at all frequencies (and at all wavelengths) and shifts the peak frequency higher, so shifts the peak wavelength lower. The vibrational constant of the solid is not changed, but part of the ideality of an ideal blackbody is that the specific value of the material's vibrational constants have no direct effect on the emission. In order for the emitted energy to increase at every wavelength, the number of possible states emitting those wavelengths must be higher (because the energy per photon at a given wavelength is constant); therefore the ensemble size must increase at higher temperatures.

$\rho_{\text{rad}}(510\,\text{nm})$	+
$\rho_{\text{rad}}(1020\,\text{nm})$	+
λ_{max}	−
ensemble size Ω	+
ω_e	**0**

4. A two-state system with ground state 1 and excited state 2 and radiation field ρ_{12} is in steady state. Let $g_1 = g_2$. Find the relationship between ρ_{12} and N_2/N and fill in the table below to show how the radiation density affects the fraction of the particles in the excited state. **Solution:** If $g_1 = g_2$, then we can set $B_{12} = B_{21}$.

$$\begin{aligned}
\frac{dN_1}{dt} &= -N_1\rho_{12}B_{12} + N_2\left(A_{21} + \rho_{12}B_{21}\right) = 0 && \text{steady state} \\
\rho_{12}\left(-N_1B_{12} + N_2B_{21}\right) &= -N_2A_{21} \\
\rho_{12} &= \frac{N_2A_{21}}{N_1B_{12} - N_2B_{21}} = \frac{N_2A_{21}}{N_1B_{12} - N_2B_{12}} && B_{12} = B_{21} \\
&= \frac{N_2A_{21}}{(N-N_2)B_{12} - N_2B_{12}} = \frac{N_2A_{21}}{B_{12}\left(N - 2N_2\right)} && N = N_1 + N_2 \\
&= \left(\frac{A_{21}}{B_{12}}\right)\frac{(N_2/N)}{1 - 2(N_2/N)}.
\end{aligned}$$

N_2/N	$\rho_{12}(\nu_{12})\,/\,(A_{21}/B_{12})$
0	0
1/8	1/6
1/4	1/2
1/2	∞

The last value indicates that no matter how much radiation we shine on this system, we can never get more than half of the molecules into the excited state.