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

Solutions

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. **Solution:**

   $$\mathcal{P}(J=1) = \frac{g(J)e^{-\epsilon_{\rm rot}/(k_{\rm B}T)}}{q_{\rm rot}(T)} = \frac{(2J+1)\,e^{-BJ(J+1)/(k_{\rm B}T)}}{k_{\rm B}T/B} = \frac{3\,B\,e^{-2B/(k_{\rm B}T)}}{k_{\rm B}T}.$$

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

   i. If T (in K) doubles? **Solution:** u decreases by factor of 2, so $\boxed{2.0\,\mathrm{kJ\,mol^{-1}}.}$

   ii. If R doubles? **Solution:** u decreases by factor of $2^6 = 64$, so $\boxed{0.0625\,\mathrm{kJ\,mol^{-1}}.}$

   (c) What volume in L is occupied by 2.00 mol of an ideal gas at 1.50 bar and 350.0 K? **Solution:**

   $$V = \frac{nRT}{P} = \frac{(2.00\,\mathrm{mol})(0.083145\,\mathrm{bar\,L\,K^{-1}\,mol^{-1}})}{(350.0\,\mathrm{K})(1.50\,\mathrm{bar})} = \boxed{38.8\,\mathrm{L}.}$$

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

   i. electron **Solution:** Each electron, proton, and neutron has a spin of 1/2. Any combination of an even total number of these particles is a boson, any odd number is a fermion. $\boxed{\mathbf{F}.}$

   ii. $^{2}H^{+}$ **Solution:** 1p+1n $\boxed{\mathbf{B}.}$

   iii. ^{13}C **Solution:** 6p+7n+6e $\boxed{\mathbf{F}.}$

   iv. ^{14}N **Solution:** 7p+7n+7e $\boxed{\mathbf{F}.}$

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

   (a) $\lim_{T\to 0} q_{\rm rot}(T) = \lim_{T\to 0} \sum_{J=0}^{i} nfty(2J+1)e^{-BJ(J+1)/(k_{\rm B}T)} = 1+0+0+\ldots = \boxed{1.}$

   (b) $\lim_{T\to\infty} q_{\rm rot}(T) = \lim_{T\to\infty} \frac{k_{\rm B}T}{B} = \boxed{\infty.}$

   (c) $\lim_{\omega_e\to\infty} q_{\rm vib}(T) = \lim_{\omega_e\to\infty}(1-e^{-\omega_e/(k_{\rm B}T)})^{-1} = (1-0)^{-1} = \boxed{1.}$

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

   (e) $\lim_{v\to 0} \mathcal{P}_v(v) = \lim_{v\to 0} v^2 e^{-mv^2/(2k_{\rm B}T)} = (0)(1) = \boxed{0.}$

   (f) $\lim_{v\to\infty} \mathcal{P}_v(v) = \lim_{v\to 0} v^2 e^{-mv^2/(2k_{\rm B}T)} = \lim_{v\to 0} v^2(0) = \boxed{0.}$

   (g) $\lim_{R\to 0} \mathcal{G}(R) = \lim_{R\to 0} e^{-u(R)/(k_{\rm B}T)} = \boxed{0.}$ because $\lim_{R\to 0} u(R) = \infty$.

   (h) $\lim_{T\to\infty} B_2(T) = \lim_{T\to\infty} \left(b - \frac{a}{RT}\right) = \boxed{b.}$

3. We open a small hole in one side of a container of water vapor at 373 K and connect it to a chilled tube. Only molecules with $v \approx v_Z$ leave the container through the tube.

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

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} = \left[\frac{8(1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}})(373\,\mathrm{K})}{\pi(18.0\,\mathrm{amu})(1.661 \cdot 10^{-27}\,\mathrm{kg\,amu^{-1}})}\right]^{1/2} = \boxed{662\,\mathrm{m\,s^{-1}}.}$$

(b) What is the *average* speed of the molecules exiting the tube? **Solution:** The molecules leaving are still characterized by a Maxwell-Boltzmann distribution, because the canonical distribution predicts the probability of being at a particular value of v_Z will be proportional to $v_Z^2\, e^{-mv_Z^2/(2k_BT)}$. However, the distribution of values of v_Z in the container is different from the distribution of speeds v, because

$$\langle v \rangle = \left\langle \sqrt{v_X^2 + v_Y^2 + v_Z^2} \right\rangle = \left\langle \sqrt{3v_Z^2} \right\rangle = \left\langle \sqrt{3}v_Z \right\rangle = \sqrt{3}\,\langle v_Z \rangle .$$

Recall that we can set $\langle v_X^2 \rangle = \langle v_Y^2 \rangle = \langle v_Z^2 \rangle$ because motion along each of the three axes is equivalent. Therefore,

$$\langle v_{\mathrm{exit}} \rangle = \langle v_Z \rangle = \frac{1}{\sqrt{3}}\,\langle v \rangle = \boxed{382\,\mathrm{m\,s^{-1}}.}$$

(c) If we use the speeds to determine the temperature, what is the temperature of the vapor exiting the tube? **Solution:** The speed is proportional to $\sqrt{T}$, so temperature is proportional to v^2. Therefore, if the speed decreases by a factor of $\sqrt{3}$, the apparent temperature is lower by a factor of 3:

$$T_{\mathrm{eff}} = \frac{373\,\mathrm{K}}{3} = \boxed{124\,\mathrm{K}.}$$

4. For three interacting particles, briefly show the steps and approximations used to rewrite

$$Q'_U = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-U(X_1 \ldots Z_3)/(k_BT)}\, dX_1 \ldots dZ_3$$

in terms of an integral over the single variable R. **Solution:** Begin with the approximation that the overall potential energy U is the sum of all pair potential energies u:

$$U(X_1 \ldots Z_3) \approx \sum_{\text{pairs } ij} u(R_{ij}) = u(R_{12}) + u(R_{23}) + u(R_{13})$$

$$\begin{aligned} Q'_U &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-U(X_1 \ldots Z_3)/(k_BT)}\, dX_1 \ldots dZ_3 \\ &\approx \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-[u(R_{12})+u(R_{23})+u(R_{13})]/(2k_BT)}\, dX_1 \ldots dZ_3. \end{aligned}$$

Each $dX\,dY\,dZ$ is equivalent to $4\pi R^2\,dR$, where we integrate R from 0 to ∞:

$$\begin{aligned} Q'_U &\approx (4\pi)^3 \int_0^{\infty}\int_0^{\infty}\int_0^{\infty} e^{-[u(R_{12})+u(R_{23})+u(R_{13})]/(2k_BT)} R_{12}^2\,dR_{12}\,R_{23}^2\,dR_{23}\,R_{13}^2\,dR_{13} \\ &= (4\pi)^3 \int_0^{\infty} e^{-u(R_{12})/(k_BT)} R_{12}^2\,dR_{12} \int_0^{\infty} e^{-u(R_{23})/(k_BT)} R_{23}^2\,dR_{23} \int_0^{\infty} e^{-u(R_{13})/(k_BT)} R_{13}^2\,dR_{13} \end{aligned}$$

and these three integrals are all equal, so we can just set $R_{ij} = R$:

$$= \left[(4\pi) \int_0^{\infty} e^{-u(R)/(k_BT)} R^2\,dR\right]^3 .$$