Chemistry 410B Exam 4 Spring 2012
Solutions

1. **40 points.**

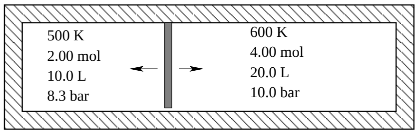
   (a) Predict the standard molar entropy of I(g) at 573 K and 1.00 bar. **Solution:** We want the mass of one iodine atom, 126.904 amu, and let's use SI units for pressure and mass:

$$\begin{aligned} S_m &= R\left\{\frac{5}{2}+\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{RT}{\mathcal{N}_A P}\right]\right\} \\ &= R\left\{\frac{5}{2}+\ln\left[\left(\frac{2\pi(126.904\,\mathrm{amu})(1.661\cdot10^{-27}\,\mathrm{kg\,amu^{-1}})(1.381\cdot10^{-23}\,\mathrm{J\,K^{-1}})(573\,\mathrm{K})}{(6.626\cdot10^{-34}\,\mathrm{J\,s})^2}\right)^{3/2}\right.\right. \\ &\times \left.\left.\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(573\,\mathrm{K})}{(6.022\cdot10^{23}\,\mathrm{mol^{-1}})(1.00\,\mathrm{bar})(10^5\,\mathrm{Pa\,bar^{-1}})}\right]\right\} = R\left\{\frac{5}{2}+\ln\left[2.92\cdot10^8\right]\right\} = 22.0R \\ &= \boxed{183\,\mathrm{J\,K^{-1}\,mol^{-1}}.} \end{aligned}$$

   (b) Calculate the entropy change when we heat calcium chloride from 298 K to 323 K, if the heat capacity remains a constant 72.59 $\mathrm{J\,K^{-1}\,mol^{-1}}$. **Solution:**

$$\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) = (72.59\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\left(\frac{323}{298}\right) = \boxed{5.85\,\mathrm{J\,K^{-1}\,mol^{-1}}.}$$

   (c) The container shown below separates an ideal gas into two compartments with a movable, thermally conducting wall between them. The conditions in each compartment are labeled.



   Solution: The pressure is initially greater on the right, so the wall will move to the left to equalize the forces, at which point the pressures become equal. At the same time, heat will flow from the higher temperature right side to the left across the wall until the temperatures are equal. The correct choices are $\boxed{\text{ii, iv, vi, and vii.}}$

2. Repeat the reversible, isothermal expansion of 1.00 mol of an ideal gas from 2.48 L at 10.00 bar and 298 K to a final pressure of 1.00 bar, but this time set the final pressure P_2 to 0.100 bar. Calculate the following parameters. **Solution:**

   (a) $V_2 = nRT/P_2 = (1.00\,\mathrm{mol})(0.083145\,\mathrm{bar\,L\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})/(0.100\,\mathrm{bar}) = \boxed{248\,\mathrm{L}.}$

   (b) $\Delta E = 0$ because the energy of an ideal gas depends only on the temperature and number of moles, and here neither value changes.

   (c) $w = -nRT\ln(V_2/V_1) = -(1.00\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})\ln(248/2.48) = \boxed{-11.4\,\mathrm{kJ}.}$

(d) $\Delta S = nR\ln(V_2/V_1) = (1.00\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln(248/2.48) = \boxed{38.3\,\mathrm{J\,K^{-1}}.}$

(e) $\Delta F = \Delta(E - TS) = \Delta E - T\Delta S = 0 - (298\,\mathrm{K})(38.3\,\mathrm{J\,K^{-1}}) = \boxed{-11.4\,\mathrm{kJ}.}$

3. A sample of I_2 gas ($\omega_e = 214.5\,\mathrm{cm^{-1}}$, $B_e = 0.0559\,\mathrm{cm^{-1}}$) initially has distinct temperatures for vibration $T_{\mathrm{vib}} = 653\,\mathrm{K}$, rotation $T_{\mathrm{rot}} = 437\,\mathrm{K}$, and translation $T_{\mathrm{trans}} = 298\,\mathrm{K}$. We isolate the sample and wait until the temperatures are equal for all degrees of freedom. What is the final temperature? **Solution:** The total energy of the isolated sample is conserved, but the second law will distribute that energy among the different degrees of freedom to equalize the temperatures, because this will maximize the entropy of the sample. We need to know how the energy and temperature are related in ewach degree of freedom, therefore. The equipartition principle provides a good starting point, because it should apply as long as the thermal energy k_BT is signifiacntly greater than the excitation energies of each degree of freedom. We can assume that to be true for translations in any macroscopic system. To check if this applies to the rotational and vibrational energies, we compare the values of k_BT ($304\,\mathrm{cm^{-1}}$and $454\,\mathrm{cm^{-1}}$, respectively) to B_e and ω_e. The condition $k_BT \gg B_e$ is satisfied, and $k_BT > \omega_e$ but only by about 50%. Assuming equipartition holds, we can calculate the energy in each degree of freedom, sum these to calculate the total energy in the sample, and then divide that by the total number of equipartition degrees of freedom to estimate the final temperature. For a diatomic, $N_{\mathrm{ep,trans}} = 3$, $N_{\mathrm{ep,rot}} = 2$, and $N_{\mathrm{ep,vib}} = 2$. Because we don't know the amount of material, the following are calculated as quantities per mole:

$$
\begin{aligned}
E_{\mathrm{trans}} &= \frac{3}{2}RT = \frac{3}{2}(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K}) = 3.717\,\mathrm{kJ\,mol^{-1}} \\
E_{\mathrm{rot}} &= RT = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(437\,\mathrm{K}) = 3.633\,\mathrm{kJ\,mol^{-1}} \\
E_{\mathrm{vib}} &= RT = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(653\,\mathrm{K}) = 5.429\,\mathrm{kJ\,mol^{-1}} \\
E_{\mathrm{tot}} &= E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{vib}} = 12.779\,\mathrm{kJ\,mol^{-1}} = N_{\mathrm{ep}}\left(\frac{1}{2}RT_f\right) \\
N_{\mathrm{ep}} &= N_{\mathrm{ep,trans}} + N_{\mathrm{ep,rot}} + N_{\mathrm{ep,vib}} = 7 \\
T_f &= \frac{E_{\mathrm{tot}}}{7R/2} = \frac{12779\,\mathrm{J\,mol^{-1}}}{7(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})/2} = \boxed{479\,\mathrm{K}.}
\end{aligned}
$$

Because the thermal energy in vibration is not much larger than ω_e, a more accurate answer would be obtained by using the exact expression for the average energy of a harmonic oscillator: but in fact this yields an answer only slightly different: 437 K.

4. Plot T vs S of the three expansions described in the text, starting from the point (T_1, S_1). **Solution:** (a) For the reversible isothermal process, T is constant, and $\Delta S = nRln(V_2/V_1) = +19.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$. (b) For the irreversible isothermal process, the initial and final states are the same as for the reversible isothermal expansion, but the middle of the curve is not the same. The heat flow q is the area under this curve, because $q = \int dq = \int T\,dS$. As with the reversible case, $\Delta E = 0$ because n and T are the same at the beginning and end of the expansion. From the first law of thermodynamics, that result requires that $q = -w$. However, we know that $|w_{\mathrm{irr}}| < |w_{\mathrm{rev}}|$, so therefore

$|q_{\text{irr}}| < |q_{\text{rev}}|$. In these specific cases, $w_{\text{rev}} = -5.71\,\text{kJ}$ and $w_{\text{irr}} = -2.33\,\text{kJ}$. The curve must therefore have the same endpoints but an area of $2.33\,\text{kJ}$, 41% the area under the curve for (a). (c) For the reversible adiabatic process, S is constant, and $T_2 = 119\,\text{K}$.