Chemistry 410B **Exam 4** **Fall 2016**

Solutions

1. **40 points.**

   (a) Write the symbol (*not* the mathematical formula) that we use for each of the following parameters:

      i. **example:** Gibbs free energy: $\boxed{G}$

      ii. heat capacity at constant pressure: $\boxed{C_P}$

      iii. isothermal compressibility: $\boxed{\kappa_T}$

      iv. chemical potential: $\boxed{\mu}$

      v. heat: $\boxed{q}$

   (b) During an irreversible isothermal expansion of an ideal gas, 255 J of work is done.

      i. What is ΔE for the process? **Solution:** For an ideal gas, ΔE depends only on T and n. Since both of those are constant here, $\Delta E = \boxed{0.}$

      ii. What is q? **Solution:** $\Delta E = q + w$, and since $w = -255\,\text{J}$, $q = \boxed{+255\,\text{J.}}$

   (c) Estimate the molar heat capacity at constant pressure (in SI units) of hexabromoethane (C_2Br_6), assuming that all of the vibrational motions contribute completely. **Solution:** If we assume full equipartition, then

   $$N_{\text{ep}} = 3(\text{trans}){+}3(\text{rot}){+}2{\times}(3{\cdot}8{-}6)(\text{vib}) = 42 \qquad C_{Vm} = \tfrac{1}{2}N_{\text{ep}}R = 21R \qquad C_{Pm} = 22R = \boxed{183\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}.}$$

   (d) What is the work (in kJ) done by the process illustrated in this graph? **Solution:** The work is the integrated area under the P vs. V curve, in this case the area of a triangle ($3\,\text{L} \times 3\,\text{bar}/2 = 4.5\,\text{bar}\,\text{L}$) plus a rectangle ($3\,\text{L} \times 1\,\text{bar} = 3\,\text{bar}\,\text{L}$) to get a total of $7.5\,\text{bar}\,\text{L}$, or we could integrate the straight line with formula $P = -V + 5$ from $V = 1$ to 4:

   $$w = -\int_{V_1}^{V_2} P\,dV = -\int_{1\,\text{L}}^{4\,\text{L}} (-V+5)\,dV = \left(-\frac{V^2}{2} + 5V\right)\Bigg|_1^4$$
   $$= -\frac{(16-1)}{2} + 5(4-1) = -7.5\,\text{bar}\,\text{L} = -750\,\text{J} = -0.75\,\text{kJ}.$$

   The "work done" is normally given as the magnitude of the work, so the proper answer is $\boxed{0.75\,\text{kJ,}}$ but with the minus sign is okay too.

2. Define the adiabatic coefficient of thermal expansion α_S to be $\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{S,n}$. Simplify the expression $\kappa_T C_P/(TV\alpha)$ to get a function of only α and α_S: **Solution:** The first three steps below are consolidating the terms. The step after the Maxwell relation is the toughest to figure out, but it's motivated by recognizing that if we could combine $\left(\frac{\partial V}{\partial P}\right)_T$ and $\left(\frac{\partial P}{\partial T}\right)_S$ to eliminate the ∂P, then we would get the right partial derivative for the α's:

$$\frac{\kappa_T C_P}{TV\alpha} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T T\left(\frac{\partial S}{\partial T}\right)_P}{(TV)\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P}$$

$$= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P \qquad \text{reciprocal rule}$$

$$= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial S}{\partial V}\right)_P \qquad \text{chain rule}$$

$$= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S \qquad \text{Maxwell relation}$$

$$= -\frac{1}{V}\left[\left(\frac{\partial V}{\partial T}\right)_S - \left(\frac{\partial V}{\partial T}\right)_P\right] \qquad \text{that other identity}$$

$$= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S = \boxed{\alpha - \alpha_S.}$$

3. Let's estimate the temperature change associated with a meteor entering the atmosphere. A column of air in the upper atmosphere has initial conditions $P_1 = 1.0 \cdot 10^3\,\mathrm{Pa}$ and $T_1 = 200\,\mathrm{K}$. A meteor with mass $m_\mathrm{M} = 1.0 \cdot 10^3$ kg and cross-section area $A = 1.0\,\mathrm{m}^2$ enters at a constant speed $v_\mathrm{M} = 15\,\mathrm{km\,s^{-1}}$ and adiabatically compresses the air column to new pressure P_2:

$$P_2 = \frac{F}{A} \approx \frac{m_\mathrm{M} v_\mathrm{M}}{A\Delta t} = \frac{1.5 \cdot 10^7\,\mathrm{Pa \cdot s}}{\Delta t},$$

where p is the meteor's momentum and Δt is the time we wait for the pressure to build up. Calculate the final temperature T_2 after 1.0 s. Let $C_{Pm} = 7R/2$. **Solution:**

$$\left(\frac{T_2}{T_1}\right)^{-C_{Vm}/R} = \left(\frac{P_2}{P_1}\right)^{-C_{Vm}/C_{Pm}}$$

$$\left(\frac{T_2}{T_1}\right) = \left[\left(\frac{P_2}{P_1}\right)^{-C_{Vm}/C_{Pm}}\right]^{-R/C_{Vm}} = \left(\frac{P_2}{P_1}\right)^{R/C_{Pm}}$$

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{R/C_{Pm}} = T_1\left(\frac{(1.5 \cdot 10^7\,\mathrm{Pa \cdot s})/\Delta t}{P_1}\right)^{R/C_{Pm}} = (200\,\mathrm{K})\left[\frac{1.5 \cdot 10^7\,\mathrm{Pa \cdot s}}{(1.0\,\mathrm{s})(1.0 \cdot 10^3\,\mathrm{Pa})}\right]^{R/(7R/2)}$$

$$= (200\,\mathrm{K})\left[1.5 \cdot 10^4\right]^{2/7} = (200\,\mathrm{K})(15.6) = \boxed{3100\,\mathrm{K.}}$$

4. In our derivation of the Joule-Thomson coefficient, we obtained the following expression for α:

$$\alpha = \frac{1}{V}\frac{\frac{V}{T} + \frac{nRT}{P}\frac{n}{V}\left(\frac{\partial B_2}{\partial T}\right)_P}{1 + \frac{nRT}{P}\frac{n}{V^2}B_2}. \approx \frac{\frac{V_m}{T} + \left(\frac{\partial B_2}{\partial T}\right)_P}{V_m + B_2}.$$

Your final expressions for each of the parts below should depend on some combination of the temperature, the molar volume, and/or one or two of the van der Waals coefficients. If you get the ideal gas result, you've approximated too much.

(a) Rewrite this last form of the equation in terms of the van der Waals coefficients.

$$\left(\frac{\partial B_2}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(b - \frac{a}{RT}\right) = \frac{a}{RT^2}$$

$$\alpha \approx \frac{\frac{V_m}{T} + \frac{a}{RT^2}}{V_m + b - \frac{a}{RT}}$$

(b) Find an expression for α in the limit of high temperature.

$$\lim_{T\to\infty} \alpha = \lim_{T\to\infty}\left(\frac{V_m + \frac{a}{RT}}{TV_m + Tb - \frac{a}{R}}\right) = \frac{V_m}{TV_m + Tb} = \frac{1}{T}\left(\frac{V_m}{V_m + b}\right).$$

(c) Find an expression for α in the limit of low temperature.

$$\lim_{T\to 0} \alpha = \lim_{T\to 0}\left(\frac{V_m + \frac{a}{RT}}{TV_m + Tb - \frac{a}{R}}\right) = \lim_{T\to 0}\left(\frac{V_m + \frac{a}{RT}}{-\frac{a}{R}}\right) = \lim_{T\to 0}\left(\frac{\frac{a}{RT}}{-\frac{a}{R}}\right) = -\frac{1}{T}.$$