Chemistry 410B — Exam 4 — Spring 2009
Solutions

1. **40 points.**

   (a) Write a **single** thermodynamic parameter equal to each of the following:

   i. $\frac{nRT}{V}$ for ideal gas $\boxed{P}$

   ii. $\left(\frac{\partial H}{\partial P}\right)_{S,n}$ $\boxed{V}$

   iii. $\left(\frac{\partial H}{\partial T}\right)_{P,n}$ $\boxed{C_P}$

   iv. $F+TS$ $\boxed{E}$

   (b) Rank the following gas-phase compounds (by letter) in order of **increasing** molar heat capacity C_{Pm} (from lowest value on the left, to highest value on the right).
   (A) C_3H_8 (B) HCCH (C) C_3H_7I (D) H_2CO
   Solution: If $C_P = C_V + nR = (\frac{1}{2}N_{\mathrm{ep}}+1)nR$, we only need to know N_{ep}. B,D<A,C because A and C have more atoms and more vibrations. B<D because B is linear and has only 2 rotational degrees of freedom, while C has 3. A<C because the C-I bond has vibrational modes that contribute more to C_P. $\boxed{\text{B<D<A<C}}$.

   (c) A leak in a container allows an ideal gas to escape irreversibly and isothermally at constant pressure. For each of the following parameters, **circle** any that stay unchanged during this process, put a **square** around any that decrease, and **underline** any that increase.

   $\boxed{S}$ $\quad \boxed{n}$ $\quad \boxed{V}$ $\quad \boxed{E}$

   S_{tot} $\quad T$ $\quad \boxed{H}$ $\quad \mu$

   (d) If $\Omega = AV^N$, find $\Delta S = S(V_2) - S(V_1)$ when $V_2 = 2V_1$ and $N = \mathcal{N}_A$. **Solution:**

$$\Delta S = k_B\left(\ln A(2V)^N - \ln AV_1^N\right) = k_B\left(\ln A + N\ln(2V_1) - \ln A - N\ln V_1\right)$$
$$= k_B\left(\ln A + N\ln(2V_1) - \ln A - N\ln V_1\right) = k_B\mathcal{N}_A \ln\left(\frac{2V_1}{V_1}\right) = \boxed{R\ln 2}$$

2. (a) Find an expression for $\left(\frac{\partial P}{\partial T}\right)_{F,n}$ of any material in terms of any of α, C_P, C_V, or the compressibilities κ.

$$\left(\frac{\partial P}{\partial T}\right)_{F,n} = -\left(\frac{\partial P}{\partial F}\right)_{T,n}\left(\frac{\partial F}{\partial T}\right)_{P,n} = \left(\frac{\partial P}{-S\partial T - P\partial V + \mu\partial n}\right)_{T,n}\left(\frac{-S\partial T - P\partial V + \mu\partial n}{\partial T}\right)_{P,n}$$
$$= -\frac{1}{P}\left(\frac{\partial P}{\partial V}\right)_{T,n}(-P)\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{1}{V\kappa_T}\right)(V\alpha) = \boxed{\frac{\alpha}{\kappa_T}}.$$

   (b) Evaluate the expression for an ideal gas.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial nRT/P}{\partial T}\right)_P = \frac{nR}{PV} = \frac{1}{T}$$
$$\kappa_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial nRT/P}{\partial P}\right)_T = \frac{nRT}{P^2V} = \frac{1}{P}$$
$$\left(\frac{\partial P}{\partial T}\right)_{F,n} = \frac{\alpha}{\kappa_T} = \frac{P}{T}.$$

3. We start from 0.100 mol of a monatomic ideal gas at a volume of 5.00 L at 298 K. Find the final pressure if we want to change the volume adiabatically to bring the gas to a final temperature of 410 K. **Solution:**

$$\frac{V_2}{V_1} = \left(\frac{P_2}{P_1}\right)^{-C_V/(C_V+nR)} = \left(\frac{P_2}{P_1}\right)^{-C_V/C_P} = \frac{nRT_2/P_2}{nRT_1/P_1} = \frac{T_2}{T_1}\frac{P_1}{P_2}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{1-C_V/C_P} \qquad \frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{(C_P-C_V)/C_P}$$

$$P_2 = P_1\left(\frac{T_2}{T_1}\right)^{C_P/(C_P-C_V)} = (0.496)\left(\frac{410}{298}\right)^{(5/2)} = \boxed{1.10\,\mathrm{bar}}$$

4. Define the "work capacities" B_T and B_S, as $B_T = \left(\frac{\partial w}{\partial P}\right)_T$ and $B_S = \left(\frac{\partial w}{\partial P}\right)_S$. Find an expression for B_T in terms of B_S.

$$B_T = \left(\frac{-P\partial V}{\partial P}\right)_T = \left(\frac{\partial F}{\partial P}\right)_T \qquad B_S = \left(\frac{-P\partial V}{\partial P}\right)_S = \left(\frac{\partial E}{\partial P}\right)_T$$

$$\begin{aligned}
B_T &= \left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial(E-TS)}{\partial P}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \\
&= \left(\frac{\partial E}{\partial P}\right)_S + \left(\frac{\partial E}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \\
&= B_S + \left(\frac{T\partial S - P\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \\
&= B_S + \left[T - P\left(\frac{\partial V}{\partial S}\right)_P\right]\left(\frac{\partial S}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T = B_S - P\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T \\
&= B_S + P\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial V}{\partial T}\right)_P = B_S + P\,(V\alpha)\left(\frac{T}{C_P}\right)(V\alpha) \\
&= B_S + \frac{PT\,(V\alpha)^2}{C_P}
\end{aligned}$$