First Page: Useful information and equations:

Law I \[ \Delta U = q + w \]
\[ U = U(T, V) \]
\[ dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \]

Law II: \[ dS = \frac{q_{rev}}{T} \]
\[ S = S(T, V) \]
\[ dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \]

Comb I, II:
\[ dU = T dS - P dV \]
\[ H = U + PV; \quad A = U - TS \]
\[ G = H - TS; \quad dG = -SdT + VdP \]

Thermodynamic Equation of State
\[ \left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P \]
\[ \left( \frac{\partial S}{\partial T} \right)_P = C_P; \quad \left( \frac{\partial S}{\partial V} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P \]
\[ \mu_A = \mu_A^o + RT \ln \frac{P_A}{P_o} \]

Dalton's Law
\[ P_A = \chi_A P; \quad P = \sum_A P_A; \quad G = \sum_i n_i \mu_i \]

\[ \Delta G_{mix} = RT \sum n_i \ln \left( \frac{P_i}{P_o} \right) \]

Integral Identity:
\[ \Delta Z = \int_{z_i}^{z_f} \left( \frac{\partial Z}{\partial y} \right)_x dx \]

Cyclic rule:
\[ \left( \frac{dy}{dz} \right)_x \left( \frac{dz}{dx} \right)_y = \left( \frac{dz}{dx} \right)_y \left( \frac{dy}{dz} \right)_x \]

Chain Rules:
\[ \frac{d(zy)}{dx} = z \frac{d(y)}{dx} + y \frac{d(z)}{dx} \]
\[ \frac{dx}{dz} = \frac{dy}{dz} \frac{dx}{dy}, \quad \left( \frac{\partial x}{\partial z} \right)_a \left( \frac{\partial y}{\partial z} \right)_a = \left( \frac{\partial x}{\partial y} \right)_a \]

Thermal expansion and compression coefficient
\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]
\[ \kappa = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

vdW Gas EoS:
\[ P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]

Reaction Info
\[ \Delta H_{rxn}^o = \sum_i v_i \Delta H_f^o (i) \]
\[ \Delta S_{rxn}^o = \sum_i v_i S_f^o (i) \]
\[ d\ell_i = n_i - n_i^{init} = v_i dX \]
\[ \Delta C_{P,rxn} = \sum_i v_i C_{P,m} (i) \]
\[ \Delta H_{rxn}^o = \Delta H_{rxn}^o dX \]
\[ \Delta G_{rxn} = \Delta G_{rxn}^o + RT \ln Q_P = RT \ln \frac{Q_P}{K_P} \]
\[ Q_P = \prod_{i=1}^{N} \left( \frac{P_i}{P_o} \right)^{v_i} \] @ Eq
\[ Q_P = \prod_{i=1}^{N} \left( \frac{P_i}{P_o} \right)^{v_i} \]
\[ K_P = \left( \frac{P}{P_o} \right)^{\Delta v} \]
\[ \Delta H_{rxn}^o dX = \Delta H_{rxn}^o \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

Van’t Hoff Eqn:
\[ \ln \left( \frac{K_P(T_2)}{K_P(T_1)} \right) = - \frac{\Delta H_{rxn}^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

Gas Constant:
\[ R = 8.314 \text{ J/mol K} \]
\[ R = 0.082 \text{ L-atm/mol K} \]
\[ R \cdot 298.15 = 2.48 \text{ kJ/mol} \]
\[ 1 \text{ bar} = 10^5 \text{ Pa} \]
\[ T(K) = T(C) + 273.15 \]

Show your work throughout; clearly show what equations you are using, and always show units for computed quantities.
Q1) (30 pts) Consider the dissociation of baking soda, CaH$_2$CO$_3$($s$) at elevated temperatures. The reaction is: CaH$_2$CO$_3$($s$) ⇄ CaO($s$) + H$_2$O($g$) + CO$_2$($g$). The solid CaH$_2$CO$_3$($s$) was placed in an evacuated chamber and allowed to come to equilibrium. At the equilibrium there was still some solid reactant and some solid CaO($s$). The total pressure (due to the reaction) at 400K and 500K was measured: $P(400K) = 0.17$ bar and $P(500K) = 1.4$ bar. Assume that H$_2$O($g$) and CO$_2$($g$) behave as ideal gasses and that CaH$_2$CO$_3$($s$) and CaO($s$) behave as solids. Each part is worth 6 points.

a) Compute the thermodynamic equilibrium constant, $K_p(T)$, for this reaction at the two temperatures, 400 and 500K.

\[
K_p(T) = e^{\frac{\Delta G_{rxn}(T)}{RT}} = \frac{P_{H_2O} \cdot P_{CO_2}}{P_{CO_2}^2}; P_{H_2O} = P_{CO_2} \quad \text{and} \quad P_{\text{Total}} = P_{H_2O} + P_{CO_2} = \frac{1}{2} P_{CO_2}
\]

\[
K_p(400) = \left( \frac{0.17}{2} \right)^2 = 0.0072 \quad \text{and} \quad K_p(500) = \left( \frac{1.4}{2} \right)^2 = \frac{1}{2}
\]

b) Compute the reaction Gibbs energies, $\Delta G_{rxn}(T)$, for this reaction at these two temperatures.

\[
\Delta G_{rxn}(T) = -RT \ln K_p; \Delta G_{rxn}(400) = -2.48 \cdot \frac{4}{2.98} \ln(0.0072) = 16.7 \text{kJ/mol}
\]

\[
\Delta G_{rxn}(500) = -2.48 \cdot \frac{5}{2.98} \ln(\frac{1}{2}) = 2.9 \text{kJ/mol}
\]

c) Compute the standard reaction enthalpy, $\Delta H_{rxn}^o$, for this reaction assuming that it is independent of temperature over this range.

\[
T_o = 500; \quad T = 400K
\]

\[
\ln \frac{K_p(T)}{K_p(T_o)} = -\frac{\Delta H_{rxn}^o}{RT_o} \left( \frac{T_o}{T} - 1 \right); \quad \text{or} \quad \ln \frac{0.0072}{0.5} = \frac{\Delta H_{rxn}^o}{2.48 \cdot \frac{5}{3}} \left( \frac{5}{4} - 1 \right)
\]

\[
\Delta H_{rxn}^o = 71 \text{kJ/mol}
\]

d) Compute the standard reaction entropy for this reaction, $\Delta S_{rxn}^o$, assuming that the entropy is independent of temperature over this range.

\[
\Delta G_{rxn}(T) = \Delta H_{rxn}^o - T \Delta S_{rxn}^o; \quad 2.9 = 71 - 500 \Delta S_{rxn}^o \quad \Rightarrow \quad \Delta S_{rxn}^o = 135 \text{J/K}
\]

e) What is the standard reaction Gibbs energy for this reaction, $\Delta G_{rxn}^o$, at the standard temperature, 298.15K?

\[
\Delta G_{rxn}(T) = \Delta H_{rxn}^o - T \Delta S_{rxn}^o
\]

\[
\Delta G_{rxn}^o = (71,000 - 300 \cdot 135) \text{J/mol} = 30 \text{kJ/mol}
\]
Q2) a) (25 pts) Given the heats of formation of the following substances,

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f^o$ kJ/mol</th>
<th>$C_p^o$ J/mol-K</th>
<th>$S^o$ J/mol-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 (g)$</td>
<td>0.0</td>
<td>29.4</td>
<td>205.2</td>
</tr>
<tr>
<td>$CO_2 (g)$</td>
<td>-393.5</td>
<td>37.1</td>
<td>213.8</td>
</tr>
<tr>
<td>$H_2O (g)$</td>
<td>-136.3</td>
<td>43.1</td>
<td>188.8</td>
</tr>
<tr>
<td>$C_6H_{12}O_6 (s)$</td>
<td>-1273.0</td>
<td>219.2</td>
<td>209.2</td>
</tr>
</tbody>
</table>

compute the following quantities for the reaction: burning glucose (sugar), which has the following balanced reaction: $C_6H_{12}O_6 (s) + 6O_2 (g) \rightarrow 6CO_2 (g) + 6H_2O (g)$. Each of the first 3 parts is worth 6 points; part d) is worth 7 points.

a) What is the standard enthalpy of this reaction as written at 298K, $\Delta H_{rxn}^o (298K)$?

$$\Delta H_{rxn}^o = 6\left( -393 - 136 - \left( \frac{-1273}{6} \right) \right) = -1900kJ / mol$$

b) What is the standard Reaction entropy of this reaction (as written)?

$$\Delta S_{rxn}^o = 6\left( 213.8 + 188.8 - \left( 205.2 + \frac{209}{6} \right) \right) = 975J / K$$

c) What is the standard Gibbs Energy of this reaction?

$$\Delta G_{rxn}^o = \Delta H_{rxn}^o - T\Delta S_{rxn}^o$$
$$\Delta G_{rxn}^o = \left( -1900 \cdot 10^3 - 298 \cdot 975 \right) J / mol = -2,200kJ / mol$$

d) Assuming that the reaction heat capacity is independent of temperature how much larger (or smaller) do you expect the reaction entropy to be at 600K than it is at 298K?

$$\Delta C_p = 6\left( 37 + 43 - \left( 29.4 + \frac{319}{6} \right) \right) = 85J / K$$
$$\Delta S = \int_{T=300}^{600} \frac{\Delta C_p}{T} dT = \Delta C_p \ln \frac{600}{300} = 84.6 \cdot 0.7 = 60J / K$$

This is about a 5% change; not a lot.
Q3) (25 pts) Part a) is worth 10 points; part b) 15; and part c) is 5 points, extra credit.

A gas in a box contains a type of molecule that will dimerize (like NO that can form $N_2O_4$). The gas is called A and the reaction is $2A \rightleftharpoons B$, where B is the dimer or $A_2$ molecule. The equilibrium constant is $K_c = 10$. [Notice: This is $K_c$ not $K_P$.] The system is at equilibrium with an external pressure, $P_f$, and at a fixed temperature, $T_f$.

a) Assume that the system began with 1.2M A (and no B). What is the concentration of A, $C_A$, and of B, $C_B$, when the system is in equilibrium.

$c_A^0 = 1.2M; \quad c_B^0 = 0M$;

c_A = c_A^0 - 2x; \quad c_B = x; \quad c_A + 2c_B = c_A^0 = 1.2; \quad c_B = \frac{c_A^0 - c_A}{2}$

$K_c = \frac{c_B}{c_A^2} = \frac{1 - 1.2 - c_A}{c_A^2}$

$2K_c c_A^2 = 1.2 + c_A = 0$

$c_A = -1 + \sqrt{1 + 8 \cdot 1.2 K_c} = \frac{\sqrt{100} - 1}{40} = 0.2M$

$c_B = \frac{1}{2} (c_A^0 - c_A) = \frac{1}{2} (1.2 - 0.2) = 0.5M$

b) The pressure is now reduced to $\frac{1}{2}$ of its original value, $P_f = \frac{1}{2} P_f$, and the temperature does not change. Show, using the Ideal Gas Equation of State, that the new volume will be double that of the original volume if there is no $2A \rightleftharpoons B$ reaction.

$P_f V_f = nRT = P_f V_f$

$\frac{P_f V_f}{P_f V_f} = 1; \quad \frac{V_f}{V_f} = \frac{P_f}{P_f} = \frac{1}{2} P_f = 2$

$V_f = 2V_f$

c) Now consider the same process as part a), where $P_f = \frac{1}{2} P_f$, and the $2A \rightleftharpoons B$ reaction is allowed to proceed. Circle your choice: Qualitatively, the new volume will be:

i) twice the original  
ii) larger than twice the original \(\Leftarrow\) The best answer  
iii) smaller than twice the original

Explain in words, why the chemical reaction impacts the new volume.

As the pressure is lowered, the volume increases; this allows the equilibrium to shift to make more molecules, so $n_{total}$ goes up; so some dimmers are consumed to make monomers. If $n_{total}$ increases, then the volume must increase (at fixed P and T).
Q4) (20 points) a) and e) are 3 points each; b) and d) are 4 points each; c) is 6 points.

a) Begin with the identity (from the combined first and second laws) \( dH = TdS + VdP \), and derive the partial derivative \( \left( \frac{\partial S}{\partial T} \right)_P \) expressed as a function of \( P, V, T \) and heat capacities \( C_p \) and/or \( C_V \). You may use the identity: \( \left( \frac{\partial H}{\partial T} \right)_P = C_p \)

\[
dH = TdS + VdP
\]

\[
\left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P + V \left( \frac{\partial P}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P
\]

because \( \left( \frac{\partial P}{\partial T} \right)_P = 0 \)

\[ C_p = T \left( \frac{\partial S}{\partial T} \right)_P \]

b) The partial derivative \( \left( \frac{\partial S}{\partial V} \right)_P \) implies that the entropy (S) is a function of Volume or \( V \) and Pressure or \( P \).

c) From \( \left( \frac{\partial S}{\partial V} \right)_P \) you can calculate the change in the Entropy (S) for a process in which the Volume (V) is changing and the Pressure (P) is held constant.

d) From the identity: \( \left( \frac{\partial S}{\partial P} \right)_V = \left( \frac{\partial S}{\partial T} \right)_V \left( \frac{\partial T}{\partial P} \right)_V \), evaluate \( \left( \frac{\partial S}{\partial P} \right)_V \) for the ideal gas equation of state, in terms of \( P, V, T \) and Heat Capacities \( C_p \) and/or \( C_V \)

\[
\left( \frac{\partial S}{\partial P} \right)_V = \left( \frac{\partial S}{\partial T} \right)_V \left( \frac{\partial T}{\partial P} \right)_V = C_V \frac{T}{P} = \frac{C_V}{P}
\]

\[
\left( \frac{\partial T}{\partial P} \right)_V = \frac{1}{nR} \left( \frac{\partial PV}{\partial P} \right)_V = \frac{V}{nR} = \frac{T}{P}
\]

e) Using the chain rule and the Maxwell relations (see first page): Express \( \left( \frac{\partial S}{\partial V} \right)_P \) in terms of \( P, V \) and \( T \) (including partial derivatives thereof as needed) and Heat Capacities \( C_p \) and/or \( C_V \). Your answer is applicable to any substance.

\[
\left( \frac{\partial S}{\partial V} \right)_P = \left( \frac{\partial S}{\partial T} \right)_P \left( \frac{\partial T}{\partial V} \right)_P = C_p \frac{\partial T}{T \beta} = \frac{C_p}{TV \beta}
\]
This page is blank. Use it for additional computations.

Histogram of exam grades:

average = 68.73
s.d. = 13.73