Important information is found on the insert. You may use the back for scratch work but enter **all** work to be graded in the space provided with each question. Show your work in all questions involving a calculation in order to receive credit.

1) (55 points) This question deals with the oxidation of ammonia, a reaction of great industrial importance: $4\,NH_3(g) + 7\,O_2(g) \rightarrow 4\,NO_2(g) + 6\,H_2O(l)$ [reaction 1].

    a) Calculate values of $\Delta H°$ and $\Delta S°$ of reaction 1 at 25°C.

    $\Delta H° = 6(-285.83) + 4(33.18) -7(0) - 4(-46.11) = -1397.82$ kJ $= -1397820$ J
    $\Delta S° = 6(69.91) + 4(240.06) - 7(205.138) -4(192.45) = -826.066$ J/K

    b) Interpret the value of $\Delta S°$ calculated in part (a).

    The standard entropy change is large and negative. 11 molecules combine to form 10; this reduction leads to a lowering in W. Also one of the products is in the liquid state, a state with more order and lower entropy.

    c) The standard enthalpy of vaporization of water, i.e. $\Delta H°$ for the reaction $H_2O(l) \rightarrow H_2O(g)$, is 44.012 kJ/mol at 25°C. Calculate the value of $\Delta H°$ at 25°C for the reaction: $4\,NH_3(g) + 7\,O_2(g) \rightarrow 4\,NO_2(g) + 6\,H_2O(g)$ [reaction 2].

    The net reaction is the sum of reaction 1 plus 6 times the vaporization reaction. $\Delta H(2) = \Delta H(1) + 6\Delta H(\text{vaporization}) = (-1397.92) = 6(44.012) = -1133.85$ kJ

    d) Calculate a value of the equilibrium constant for reaction 1 at 35°C.

    We shall assume that the change in S and H does not change much with temperature and use the value at 298.15 K. 35°C = 35 + 273.15 = 308.15 K
    $\Delta G°(308\,K) \approx \Delta H°(298\,K) - (308.15)\Delta S°(298\,K)$
         $= -1397820$ J $- (308.15)(-826.066) = -1397820 + 254522$
         $= -1143000$ J
$K = \exp(-\Delta G°/RT) = \exp[-(-1143000)/(8.3145)(308.15)]\ \exp(446.22)$
  $= 10^{(445.22/\ln10)} = 10^{193.79} = 10^{0.79}10^{193} = 6.2 \times 10^{193}$

2) (80 points) Reaction 1 examined in Problem 1 is also the focus of this problem. A large bomb calorimeter with a mass of 2000 Kg and a specific heat of 1.5 J/K-g is charged with 2.0 mole of ammonia, an excess of gaseous oxygen, and liquid water. The initial temperature of the calorimeter was 25ºC. The system is this problem is the contents of the sealed bomb.

a) Why was water added to the bomb?

The addition of liquid water guarantees that all water from the combustion will be produced in the liquid state.

b) A reaction between the reactants was initiated by the addition of a catalyst. Calculate the energy change of the system, ΔE_σ. [If you are unable to solve Problem 1a, assume that $\Delta H° = -200$ kJ.]

For the reaction, $\Delta n(gas) = 4 - 11 = -7$ so $\Delta pV \approx -n7RT$
$H = E + pV$ so $\Delta H = \Delta E + \Delta pV$.
$\Delta E = \Delta H - \Delta pV = n(\Delta H° + 5RT)$
2 moles of ammonia is half of 4 so n in the above equation is 0.5.
$\Delta E = (0.50)[(-1.397 \times 10^6) + (7)(8.31)(298)] = -6.898 \times 10^5$ J

c) Calculate ΔT_θ, the increase in temperature of the calorimeter.

In the bomb V is constant and there is only p-V work so $\Delta E_\sigma = q_\sigma$.
Also $q_\sigma = -q_\theta = -C_\theta \Delta T_\theta = 6.898$ x105 J.
$C_\theta = (2000000$ g$)(1.5$ J/K-g$) = 3.5 \times 10$6 J/K.
$\Delta T_\theta = (6.898 \times 10^5$ J$)/(3.5 \times 10^6$ J/K$) = 0.20$ K

d) What are the system heat and work, q_σ and w_σ, for the combustion?

There is no work as the volume is constant and there is no other type of work. Therefore by the first law, $q_\sigma = \Delta E_\sigma$.

e) Suppose that the reaction had occurred in a gas cloud in the interstellar medium. What are ΔE_σ, q_σ, and w_σ in this case?

ΔE_σ, a path independent quantity, will be the same. In the interstellar medium, there is no external force working on the system so the work is zero. There is no external heat bath so the heat is also zero.

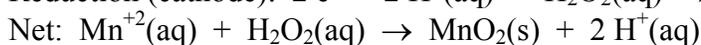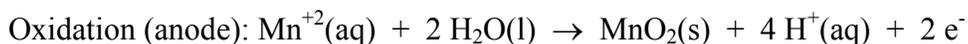f) What are ΔS_σ and ΔS_θ for the reaction?

$\Delta S_\sigma = (\Delta S°)/2$
The thermal bath is huge so from its perspective the process is reversible.
$\Delta S_\theta = q_\theta/T = (6.898 \times 10^5$ J$)/(298$ K$) = 2.32 \times 10^3$ J/K.

3) (50 points) A chemist wishes to study the thermodynamics of the oxidation of the manganese(II) cation to solid manganese(IV) oxide by hydrogen peroxide in acidified water. To this end, she constructs an electrochemical cell and runs the cell at 25ºC.

a) Obtain a balanced, net ionic equation for the overall reaction.

Oxidation (anode): $Mn^{+2}(aq) + 2 H_2O(l) \rightarrow MnO_2(s) + 4 H^+(aq) + 2 e^-$
Reduction (cathode): $2 e^- + 2 H^+(aq) + H_2O_2(aq) \rightarrow 2 H_2O(l)$
Net: $Mn^{+2}(aq) + H_2O_2(aq) \rightarrow MnO_2(s) + 2 H^+(aq)$

b) Sketch an electrochemical cell suitable for the study. Label all constituents, e.g. the chemical species in the electrolyte, and components. Place the anode on the left and the cathode on the right. Write the half reaction under each cell.
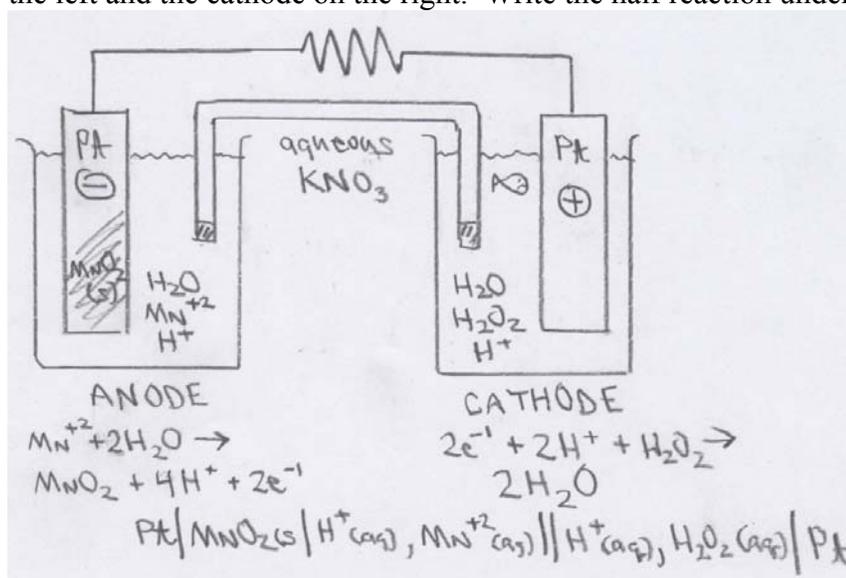
c) Calculate the standard cell potential and ΔG° for the reaction.

$E^\circ = E^\circ(\text{cathode}) + E^\circ(\text{anode}) = E_R^\circ(H_2O_2/H_2O) - E_R^\circ(MnO_2/Mn^{+2}) = 1.77-1.23 = 0.54$ V
$\Delta G^\circ = -nFE^\circ = -(2 \text{ mole})(96485 \text{ C/mole})(0.54 \text{ V}) = -104$ kJ

d) Propose concentrations for all the species that would affect the potential of the cell that you sketched in part (b) and calculate the reversible potential of the cell.

$E = E^\circ - (0.0592/2)\log_{10}([H^+]^2/[Mn^{+2}])$

4) (15 points) Edit the following half truths so that each statement becomes correct. (Changes are shown in bold red.)

a) $\Delta H = $ q **for constant pressure and only p-V work**

b) $\Delta S = $ q/T **for reversible processes**

c) **Δ**E = q + w (The first law relates energy changes, not E, to q and w.

INSERT, THIRD MIDTERM EXAMINATION

I) Useful Constants and Conversion Factors
- A) $R = 8.31451$ J/K-mole $= 0.082058$ L-atm/K-mole
- B) $k_B = 1.381 \times 10^{-23}$ J/K-molecule
- C) $N_A = 6.022 \times 10^{23}$ molecules/mole
- D) $F = 96485$ C/mole
- E) $RT ln(10)/F = 0.059$ V/mole at 298.15 K
- F) 1 L-atm $= 101.325$ J
- G) 47'th Bernoulli number $= 0$

II) Selected Thermodynamic Data at 298.15 K

Substance	$NH_3(g)$	$O_2(g)$	$NO_2(g)$	$H_2O(l)$
ΔH_f° (kJ/mole)	-46.11		33.18	-285.830
S° (J/K-mole)	192.45	205.138	240.06	69.91

III) Standard Half-Cell **Reduction** Potentials at 25.00ºC in Acidic Aqueous Solution

Pairs of Reagents	E° (V)
$MnO_2(s)/Mn^{+2}(aq)$	1.23
$MnO_4^-(aq)/Mn^{+2}(aq)$	1.51
$H_2O_2(aq)/H_2O(l)$	1.77
$O_2(g)/H_2O_2(aq)$	0.682