Chem 260 – First Exam

On the following pages are seven problems covering material in thermodynamics. Read each problem carefully and think about how best to approach the problem before you begin work. If you aren't sure how to begin a problem, then move on; working on a new problem may stimulate an idea that helps you solve the more troublesome one. For problems requiring a written response, be sure that your answer directly and clearly answers the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

Problem 1 _____/12   Problem 2 _____/18   Problem 3 _____/12

Problem 4 _____/14   Problem 5 _____/15   Problem 6 _____/14   Problem 7 _____/15

Total_____

A few constants and thermodynamics values are given here:

$$d_{H_2O} = 1.00 \text{ g/mL} \qquad S_{H_2O} = 4.184 \text{ J/g·°C}$$

$$R = 8.314 \text{ J/mol}_{rxn}·K \qquad F = 96,485 \text{ J/V·mol e}^-$$

species	$\Delta H^°_f$ (kJ/mol$_{rxn}$)	$\Delta G^°_f$ (kJ/mol$_{rxn}$)	$S^°$ (J/mol$_{rxn}$·K)
$CO_2(g)$	-393.5	-394.4	213.7
$C_4H_8(g, \text{ 1-butene})$	-20.5	-0.63	215.6
$C_6H_{12}O_6(s)$	-1273.0	-910.4	212.1
$O_2(g)$	0	0	205.0
$H_2O(g)$	-241.8	-228.6	188.2
$H_2O(l)$	-285.8	-237.1	69.9

Reduction Reaction	$E^°$ (V)
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.409
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	-0.036
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.770
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.8272
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	-0.401
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.229

Problem 1. Imagine you are holding a large, unstretched rubber band in your hands. With a quick movement you stretch the rubber band and touch it to your forehead, noting that the rubber band is warm. Based on this information, predict the signs for ΔG, ΔH and ΔS for the stretching of the rubber band, which we can represent as:

unstretched rubber band → stretched rubber band
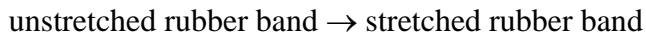
In each case indicate if the thermodynamic parameter is positive, negative or unknown and, for each, briefly explain your reasoning in one sentence.

Answer. Because it becomes warm we know that stretching a rubber band is an exothermic process; thus, the sign for ΔH is negative. Since the reverse process occurs naturally, we know that the sign for ΔG for stretching a rubber band is positive. If a process is unfavorable but is exothermic, then ΔS must be negative. If ΔS were positive the process would be favorable at all temperatures.

Problem 2. Suppose you placed a six-pack of your favorite beverage in an insulated cooler. Each can is made from 38.5 g of aluminum and contains 354.8 mL of your favorite beverage. Assume that the specific heat of your favorite beverage is equal to that of water, but that its density is 0.993 g/mL. The specific heat of Al is 0.902 J/g·°C To cool the drinks from 22.8°C to 0°C, what is the minimum amount of ice, in grams, that you need to add to the cooler? The ΔH^o for melting ice is 6.00 kJ/mol$_{rxn}$.

Answer. Begin by calculating the total amount of heat you need to remove from the cans and the beverage to produce a ΔT of -22.8°C; for one can this is

q = (38.5 g Al)(0.902 J/g·°C)(-22.8°C) + (354.8 mL)(0.993 g/mL)(4.184 J/g·°C)(-22.8°C)

$$q = -34{,}400 \text{ J}$$

The total heat lost by the six cans, therefore, is -206406 J, or -206.4 kJ. This heat flows into the ice, which absorbs 206.4 kJ. Since each mole of ice requires 6.00 kJ of heat for the reacttion

$$H_2O(s) \rightarrow H_2O(l)$$
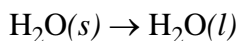
the total moles of ice needed is

$$\Delta H^o = (q_{ice}/n \text{ moles ice}) \times (1 \text{ mol ice/mol}_{rxn})$$

$$6.00 \text{ kJ/mol}_{rxn} = (206.4 \text{ kJ}/n) \times (1 \text{ mol ice/mol}_{rxn})$$

Solving for n gives 34.4 moles of $H_2O(s)$, or 619.9 g of ice. Thus, you must add a minimum of 620 g of ice to cool the six cans of your favorite beverage.

Problem 3. Isomers are molecules with the same elemental composition but with a different arrangements of the atoms. Three of the six isomers of C_4H_8 are *cis*-butene, *trans*-butene and 1-butene. Each isomer undergoes the same combustion reaction

$$C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$$
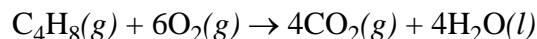
but the standard state enthalpy changes for combustion, as shown below, are different.

cis-butene	-2687.5 kJ/mol$_{rxn}$
trans-butene	-2684.2 kJ/mol$_{rxn}$
1-butene	-2696.7 kJ/mol$_{rxn}$

Draw an energy diagram, using the axes shown to the right, for the reaction

<center><i>cis</i>-butene → <i>trans</i>-butene</center>
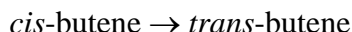
Clearly show on your diagram the transition that is equivalent to the reaction's change in enthalpy and state its value below.

Answer. The arrow shows the change in enthalpy, which is equal to the difference in the combustion enthalpies, or <u>-3.3 kJ/mol$_{rxn}$</u>.


cis → *trans*

Knowing that the ΔH_f^o for 1-butene is -20.5 kJ/mol$_{rxn}$, what is the standard state heat of formation for *trans*-butene?

Answer. Using the same logic as above, the ΔH for the reaction is +12.5 kJ/mol$_{rxn}$. We also can arrive at this value using heats of formation; thus

$$\Delta H = (-20.5 \text{ kJ/mol}_{rxn}) - (\Delta H^o{}_{f,trans}) = +12.5 \text{ kJ/mol}_{rxn}$$

Solving gives <u>$\Delta H^o{}_{f,trans}$ as -33.0 kJ/mol$_{rxn}$</u>.

Problem 4. The conversion of inorganic carbon, in the form of CO_2, to organic carbon in the form of glucose, $C_6H_{12}O_6$, is important in many biological systems. The net reaction is:

$$CO_2(g) + H_2O(l) \rightarrow (1/6)C_6H_{12}O_6(s) + O_2(g)$$
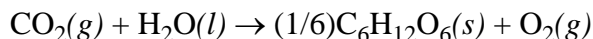
Under standard state conditions and at 298 K this reaction is unfavorable. Is there a temperature at which this reaction becomes favorable under standard state conditions, and, if so, what is that temperature? Clearly justify your response with appropriate calculation(s) and a one sentence explanation.

Answer. The values of ΔH^o and ΔS^o are:

$$\Delta H^o = [(1/6)(-1273) + (1)(0)] - [(1)(-393.5) + (1)(-285.8)] = 467.1 \text{ kJ/mol}_{rxn}$$

$$\Delta S = [(1/6)(212.1) + (1)(205)] - [(1)(213.7) + (1)(69.9)] = -43.25 \text{ J/mol}_{rxn} \cdot K$$

With a positive ΔH^o and a negative ΔS^o <u>the reaction is unfavorable for all temperatures</u>. There is no need to calculate a T_{crit} for this reaction.
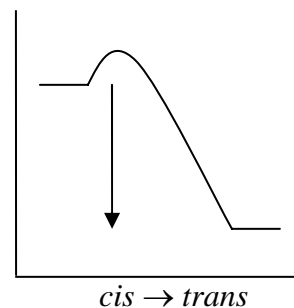
Problem 5. The reaction quotient for the reaction in problem 4 is

$$Q = P_{O_2}/P_{CO_2}$$

where P_{O_2} and P_{CO_2} are the partial pressures of O_2 and CO_2. At a temperature of 298 K, what is the largest or smallest possible value for the reaction quotient if the conversion of CO_2 to $C_6H_{12}O_6$ is to be favorable? Report your answer as "Q must be greater than…" or "Q must be less than…"

Answer. The standard state free energy change for the reaction is:

$$\Delta G^o = [(1/6)(-910.4) + (1)(0)] - [(1)(-394.4) + (1)(-237.1)] = 479.8 \text{ kJ/mol}_{rxn}$$

Knowing that $\Delta G = \Delta G^o + RT\ln Q$, we set ΔG to zero and solve for Q

$$0 = 479.8 \text{ kJ/mol}_{rxn} + (8.314 \times 10^{-3} \text{ kJ/mol}_{rxn} \cdot K)(298 \text{ K})\ln Q$$
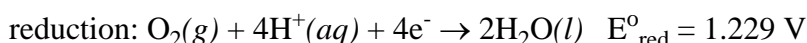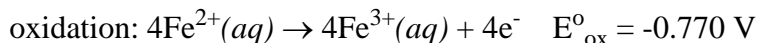
obtaining a value of 7.86×10^{-85}. Thus, <u>Q must be smaller than 7.86×10^{-85}</u> for the reaction to be favorable.

Problem 6. The autotrophic bacterium *Ferrobacillus ferrooxidans* uses the oxidation of Fe^{2+} to Fe^{3+} by oxygen

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l)$$
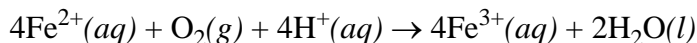
as a source of free energy. What is ΔG^o for this reaction at 298 K?

Answer. The reaction consists of an oxidation and a reduction reaction with potentials of

$$\text{oxidation: } 4Fe^{2+}(aq) \rightarrow 4Fe^{3+}(aq) + 4e^- \quad E^o_{ox} = -0.770 \text{ V}$$
$$\text{reduction: } O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^o_{red} = 1.229 \text{ V}$$

Adding the two reactions gives the overall reaction, so adding the two potentials gives E^o, which is 0.459 V. <u>The standard state free energy, as shown below, is -177.1 kJ/mol$_{rxn}$</u>.

$$\Delta G^o = -nFE^o = -(4 \text{ mol } e^-)(96,485 \text{ J/V} \cdot \text{mol } e^-)(0.459 \text{ V})(1 \text{ kJ/1000 J}) = -177.1 \text{ kJ/mol}_{rxn}$$

Problem 7. The bacterium *Ferrobacillus ferrooxidans* uses the free energy from the reaction in Problem 6 to drive the synthesis of glucose under standard state conditions, as shown by the reaction in problem 4. How many moles of Fe^{2+} are needed to synthesize 1.0 mole of glucose? Assume a temperature of 298 K.

Answer. From Problem 5 we know that the synthesis of 1/6 of a mole of glucose requires 479.8 kJ of free energy; synthesizing 1 mole, therefore, requires 2878.8 kJ of free energy. From Problem 6, the oxidation of Fe^{2+} releases 177.1 kJ of free energy per mol$_{rxn}$; thus

$$2878.8 \text{ kJ} \times (1 \text{ mol}_{rxn}/177.1 \text{ kJ}) \times (4 \text{ mol } Fe^{2+}/\text{mol}_{rxn}) = 65.0 \text{ moles of } Fe^{2+}$$

Thus, for every mole of glucose <u>the bacterium needs 65.0 moles of Fe^{2+}</u>, assuming, of course, that the efficiency of converting energy is 100%.