Chem 260 – First Exam Key

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 _____/10   Problem 2 _____/16   Problem 3 _____/14   Problem 4 _____/12

Problem 5 _____/12   Problem 6 _____/12   Problem 7 _____/12   Problem 8 _____/12

Total_____

A few constants and thermodynamics values are given here:

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

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

species	ΔH^o_f (kJ/mol$_{rxn}$)	ΔG^o_f (kJ/mol$_{rxn}$)	S^o (J/mol$_{rxn}$·K)
C(s, graphite)	0	0	5.74
CO_2(g)	-393.5	-394.4	213.7
C_6H_6(l)	49.028	124.50	172.8
C_8H_{18}(l)	-208.45	16.40	466.73
H_2(g)	0	0	130.684
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^o (V)
Fe^{2+}(aq) + 2e$^-$ → Fe(s)	-0.409
Fe^{3+}(aq) + 3e$^-$ → Fe(s)	-0.036
Fe^{3+}(aq) + e$^-$ → Fe^{2+}(aq)	0.770

Problem 1. A student is asked to determine the concentration of aspirin in tablets of St. Joseph's aspirin, obtaining values of 79.3 mg, 81.8 mg, 78.4 mg, 81.3 mg and 80.1 mg. The tablets are known to contain 80.0 mg of aspirin. Does the student's data show evidence of indeterminate and/or determinate errors? As part of you answer be sure to define each type of error and to state your evidence for that error's presence or absence.

Determinate errors are errors in accuracy, are of similar magnitude for each trial and lead to results that are always too large or always too small. Indeterminate errors are errors in precision, are random in nature and lead to results that are both too large and too small. For this data the results are both smaller and larger than the true value; thus, the data show evidence of indeterminate errors only.

Problem 2. Imagine you are caught in a rainstorm and that your clothes absorb 1.00 L of water, H_2O. The temperature is 20^oC and remains constant during the time it takes the water to evaporate. Knowing that ΔH^o for the evaporation of water is $+44$ kJ/mol$_{rxn}$, how much heat is needed to effect the evaporation of this water?

The heat, q, needed to evaporate the water is

$$\Delta H^o = +44\frac{kJ}{mol_{rxn}} = \frac{q}{n_{LR}} \times \frac{\nu_{LR}}{mol_{rxn}} = \frac{q}{1000\,ml \times \dfrac{1.00\,g}{ml} \times \dfrac{1\,mol}{18.02\,g}} \times \frac{1\,mol}{mol_{rxn}}$$

Solving for q gives a result of $+2442$ kJ of thermal energy. Note that this equation relates the enthalpy of a reaction to the amount of thermal energy released or absorbed during a specific instance of the reaction.

Suppose you are a cold-blooded animal and cannot regulate your body's temperature by producing heat from metabolism. Assuming a body weight of 60.0 kg and assuming that the specific heat of the body is that of water, what will be the change in your body's temperature upon evaporating this water? If you don't have an answer for the first part of this problem, then assume the answer is X.

The energy needed to evaporate the water is $+2442$ kJ; thus, the energy the body must lose is -2442 kJ (that is, $-q_{rxn} = q_{body}$). The change in the body's temperature is given by

$$q = -2442\ kJ = mS\Delta T = (60.0 \times 10^3\ g)(4.184 \times 10^{-3}\ kJ/g \bullet {}^oC)\Delta T$$
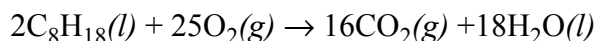
Solving for the change in temperature gives

$$\Delta T = -9.73^oC$$

Problem 3. There is a growing interest in using H_2 as a fuel for automobiles. In a H_2-powered vehicle, energy comes from the following combustion reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
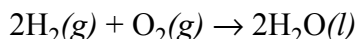
while in a traditional automobile the energy comes from the combustion of *n*-octane

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

Which automobile can supply the greatest amount of energy per gram of fuel and what is its value?

We are interested in enthalpy (total energy released); thus, for the combustion of H_2

$$\Delta H^\circ = [(2)(-285.8)] - [(2)(0) + (1)(0)] = -571.6 \text{ kJ/mol}_{rxn}$$

and for the combustion of *n*-octane

$$\Delta H^\circ = [(16)(-393.5) + (18)(-285.8)] - [(2)(-208.45)) + (25)(0)] = -11020 \text{ kJ/mol}_{rxn}$$

To answer the question, these must be converted to kJ/g of reactant

$$-571.6 \frac{\text{kJ}}{\text{mol}_{rxn}} \times \frac{1 \text{ mol}_{rxn}}{2 \text{ mol } H_2} \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2} = -141.8 \text{ kJ/g } H_2$$

$$-11020 \frac{\text{kJ}}{\text{mol}_{rxn}} \times \frac{1 \text{ mol}_{rxn}}{2 \text{ mol } C_8H_{18}} \times \frac{1 \text{ mol } C_8H_{18}}{114.2 \text{ g } C_8H_{18}} = -48.25 \text{ kJ/g } C_8H_{18}$$

Thus, H_2 provides more energy per gram.

Problem 4. You work for a biotech company that uses a lot of benzene and you have been given the job of finding the cheapest way of obtaining benzene for your company. A salesperson at another company offers you a great deal on a machine that she says will speed up the reaction of carbon and hydrogen to make benzene at a temperature of 500 K and under standard state conditions

$$6C(s, graphite) + 3H_2(g) \rightarrow C_6H_6(l)$$
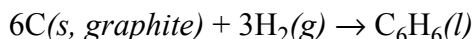
In two or three sentences, and supported with some thermodynamic information, explain to your bosses why you should or should not purchase the machine.

Speeding up a reaction is a good thing, but won't help if the reaction is not favorable at this temperature. The ΔH° and ΔS° values for this reaction are

$$\Delta H^\circ = [(1)(49.028)] - [(6)(0) + (3)(0)] = 49.028 \text{ kJ/mol}_{rxn}$$
$$\Delta S^\circ = [(1)(172.8)] - [(6)(5.74) + (3)(130.684)] = -253.692 \text{ kJ/mol}_{rxn}$$

With a positive ΔH° and a negative ΔS°, this reaction is unfavorable at all temperatures. Purchasing the machine is a poor investment since the reaction will not happen.

Problem 5. The table below gives atom combination enthalpies for several simple gas-phase hydrocarbons.

compound	ΔH°_{ac} (kJ/mol$_{rxn}$)
CH_4	-1662
$HC{\equiv}CH$	-1642
$H_2C{=}CH_2$	-2252
$H_3C\text{-}CH_3$	-2824

Using this data present a convincing argument showing that a carbon-carbon triple bond is stronger than a carbon-carbon double bond, which is stronger than a carbon-carbon single bond. The best answers to this question will provide estimates for the bond energies for each type of carbon-carbon bond.

Atom combination enthalpies represent the energy released when forming bonds. In forming methane a total of 1662 kJ/mol of energy is released when forming four C-H bonds; thus, the bond energy for a C-H bond is 415.5 kJ/mol.

If we assume that the C-H bond energy is similar for all hydrocarbons, then acetylene, with 2 C-H bonds, needs 2×415.5 or 831 kJ/mol of energy to break the C-H bonds, leaving 1662 – 831 = 831 kJ/mol to break the 1 C≡C; thus the C≡C has a bond energy of 831 kJ/mol.

In a similar manner, for ethylene the 4 C-H bonds need 4×415.5 or 1662 kJ/mol of energy to break the C-H bonds, leaving 2252 – 1662 = 590 kJ/mole to break the 1 C=C bond; thus, the C=C bond has a bond energy of 590 kJ/mol.

For ethane, the 6 C-H bonds need 6×415.5 or 2493 kJ/mol of energy to break the C-H bonds, leaving 2824 – 2493 = 331 kJ/mole to break the 1 C-C bond; thus, the C-C bond has a bond energy of 331 kJ/mol.

Problem 6. Nicotinamide adenine dinucleotide, abbreviated NAD^+, is an oxidizing agent and one of the central agents for electron transfer in biological systems. The E° value for the reduction of NAD^+ to NADH

$$NAD^+ + 2e^- + H_3O^+ \rightarrow NADH + H_2O$$
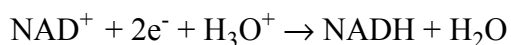
is -0.320 V. Is NAD^+ capable of oxidizing Fe^{2+} to Fe^{3+} under standard state conditions? Justify your answer with an appropriate calculation and a one sentence explanation.

The oxidation potential for $Fe^{3+} \rightarrow Fe^{2+} + e^-$ is -0.770 V. The overall potential is

$$E^\circ = E^\circ_{NAD^+/NADH} + E^\circ_{Fe^{3+}/Fe^{2+}} = \text{-0.320 V} + \text{(-0.770 V)} = \text{-1.09 V}$$

Because a negative potential is unfavorable, NAD^+ is not capable of oxidizing Fe^{3+} to Fe^{2+}.

Problem 7. The atom combination enthalpy for $CH_4(g)$ is -1662 kJ/mol$_{rxn}$ and the heat of formation for $CH_4(g)$ is -74.8 kJ/mol$_{rxn}$. In two or three sentences, explain why the $\Delta H°_f$ value for $CH_4(g)$ is smaller than its value for $\Delta H°_{ac}$.

The atom combination enthalpy for CH_4, which is for the reaction

$$C(s) + 4H(g) \rightarrow CH_4(g)$$
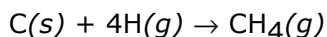
is the energy released upon forming the four C-H bonds in CH_4. The heat of formation for CH_4, which is for the reaction

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$
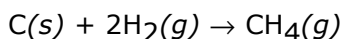
is smaller (less negative) because, in addition to the 1662 kJ/mol$_{rxn}$ energy released when making the four C-H bonds, it also includes the energy needed to first break the bonds in graphite and H_2.

Problem 8. Dissolving pentane in hexane creates a mixture, or solution, of the two liquids. To a physical chemist, an "ideal solution" has very specific thermodynamic properties. The enthalpy involved in dissolving pentane in hexane can be envisioned as occurring by the following hypothetical pathway. First, thermal energy is added to convert the pentane from a liquid into fully separated molecules; this is $\Delta H°_1$. Second, thermal energy is added to convert the hexane from a liquid into fully separated molecules; this is $\Delta H°_2$. Finally, when the fully separated molecules of hexane and pentane are allowed to come together, producing the ideal solution of pentane dissolved in hexane, energy is released; this is $\Delta H°_3$. For an ideal solution the following is true

$$\Delta H°_1 + \Delta H°_2 = -\Delta H°_3$$

Based on this information, predict the signs for $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the reaction

$$\text{pentane}(l) + \text{hexane}(l) \rightarrow \text{ideal solution of pentane in hexane}$$
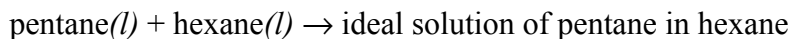
For each parameter, clearly state if the value is greater than zero, less than zero, equal to zero or that it cannot be determined, and provide a one-sentence explanation for your choice.

The reaction happens, therefore the sign of $\Delta G°$ must less than zero ($\Delta G° < 0$). The total enthalpy needed to separate the molecules of pentane and hexane is equal to the total enthalpy released upon forming the mixture; thus, $\Delta H°$ is zero ($\Delta H° = 0$). The change in entropy, therefore, must be greater than zero ($\Delta S° > 0$) for the reaction to be favorable.