

Chem 260 – First Exam

On the following pages are six 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 _____/14

Problem 4 _____/19

Problem 2 _____/19

Problem 5 _____/14

Problem 3 _____/19

Problem 6 _____/ 15

Total _____

A few constants and thermodynamics values are given here:

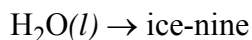
$$d_{\text{H}_2\text{O}} = 1.00 \text{ g/mL}$$

$$S_{\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot^\circ\text{C}$$

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

species	ΔH°_f (kJ/mol _{rxn})	ΔG°_f (kJ/mol _{rxn})	S° (J/mol _{rxn} ·K)
<i>C(s, graphite)</i>	0	0	5.7
<i>CO(g)</i>	-110.5	-137.2	197.7
<i>CO₂(g)</i>	-393.5	-394.4	213.7
<i>Fe(s)</i>	0	0	27.3
<i>FeO(s)</i>	-272.0	-255.0	61.0
<i>Fe₂O₃(s)</i>	-842.2	-742.2	87.4
<i>Fe₃O₄(s)</i>	-1118.4	-1015.4	146.4
<i>H₂(g)</i>	0	0	130.7
<i>H₂O(g)</i>	-241.8	-228.6	188.2
<i>H₂O(l)</i>	-285.8	-237.1	69.9
<i>Mg(s)</i>	0	0	32.7
<i>Mg(OH)₂(s)</i>	-924.5	-833.6	63.2

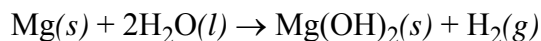
Problem 1. In Kurt Vonnegut's novel *Cat's Cradle*, a hypothetical substance known as ice-nine destroys the world. Ice-nine is described as a crystalline compound consisting of water molecules arranged differently than those in normal ice. This alternative arrangement of water molecules gives ice-nine its unique properties, one of which is that its melting point is 45.8°C. When a seed crystal of ice-nine is introduced into the ocean, the water in the ocean instantly solidifies. Based on this description, what can you say about the sign of ΔH° for the reaction



at room temperature. The possible answers are ΔH° is negative, ΔH° is positive, ΔH° is zero or there is insufficient information to determine the value of ΔH° . Clearly justify your choice in two to three sentences.

Answer. Since the reaction happens, we know that ΔG° is negative. A transition from a liquid to a crystalline solid means that ΔS° is negative. This requires that the ΔH° be negative as this is the only combination that will favor the reaction's happening. An alternative approach is to note that the reaction is favorable only below a critical temperature of 45.8°C; this implies that both ΔH° and ΔS° are negative.

Problem 2. Several companies market prepared foods that are packaged in self-heating containers. One such product consists of a pouch containing the food, which sits on top of a Styrofoam tray. On the bottom of the tray is a mesh bag containing magnesium metal. To use the device the food pouch is removed, a packet containing salt water is opened and added to the tray, and the food pouch replaced. The reaction



liberates heat, which raises the temperature of the salt water, heating the food. Suppose that a typical package contains 2.00 g of Mg and a packet containing 0.125 L of salt water with a density of 1.07 g/mL. If the initial temperature of the water is 25.0°C, what is its final temperature? You may assume that the specific heat of salt water is the same as that for deionized water.

Answer. This is a calorimetry problem. The first thing to do is to find the reaction's ΔH° , which is

$$\Delta H^\circ = [1 \times (-924.5) + 1 \times (0)] - [1 \times (0) + 2 \times (-285.8)] = -352.9 \text{ kJ/mol}_{\text{rxn}}$$

Next, we find q_{rxn} ; thus

$$q_{\text{rxn}} = \Delta H^\circ \times \text{moles Mg} \times (\text{mol}_{\text{rxn}}/\text{mol Mg})$$

$$q_{\text{rxn}} = -352.9 \text{ kJ/mol}_{\text{rxn}} \times 2.00 \text{ g Mg} \times (1 \text{ mol Mg}/24.31 \text{ g Mg}) \times (1 \text{ mol}_{\text{rxn}}/\text{mol Mg})$$

$$q_{\text{rxn}} = -29.0 \text{ kJ/mol}_{\text{rxn}}$$

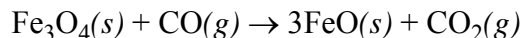
The heat lost by the reaction is gained by the salt water; thus

$$-q_{\text{rxn}} = q_{\text{water}}$$

$$29.0 \text{ kJ/mol}_{\text{rxn}} = (125 \text{ mL}) \times (1.07 \text{ g/mL}) \times 4.184 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}} \cdot \text{K} \times \Delta T$$

Solving for the change in temperature gives ΔT as 51.8°C. The final temperature, therefore, is 76.8°C.

Problem 3. Over three thousand years ago ancient metal workers first developed the technique of smelting iron ore in the presence of charcoal to obtain metallic iron. The same general process continues to find use in the modern blast furnace. The chemistry of the process is relatively simple, consisting of a series of steps in which iron ore, Fe_2O_3 , is reduced first to Fe_3O_4 , then to FeO and, finally, to Fe . The second step in the process is



Is this reaction favorable at the typical blast furnace temperature of 1000 K to 2000 K assuming standard state conditions?

Answer. The simplest approach to this problem is to begin by determining the reaction's temperature dependency. To do this, we first find the values for ΔH° and ΔS° ; thus

$$\Delta H^\circ = [3 \times (-272) + 1 \times (-393.5)] - [1 \times (-1118.4) + 1 \times (-110.5)] = 19.4 \text{ kJ/mol}_{\text{rxn}}$$

$$\Delta S^\circ = [3 \times (61) + 1 \times (213.7)] - [1 \times (146.4) + 1 \times (197.7)] = 52.6 \text{ J/mol}_{\text{rxn}} \cdot \text{K}$$

The combination of a positive ΔH° and a positive ΔS° tells us that the reaction is favorable only at higher temperatures. The critical temperature occurs when ΔG° is zero; thus

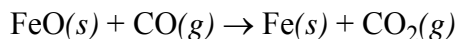
$$\Delta G^\circ = \Delta H^\circ - T_{\text{crit}} \Delta S^\circ$$

$$0 = 19.4 \text{ kJ/mol}_{\text{rxn}} - T_{\text{crit}} \times 52.6 \times 10^{-3} \text{ J/mol}_{\text{rxn}} \cdot \text{K}$$

$$T_{\text{crit}} = 369 \text{ K}$$

Since the operating temperatures of the blast furnace are greater than T_{crit} , we know that the reaction is favorable in the blast furnace.

Problem 4. The final step in the process of smelting iron is



This reaction is unfavorable under standard state conditions at a blast furnace's operating temperatures. Nevertheless, the reaction is favorable and does occur. Knowing that K_{eq} for this reaction is $P_{\text{CO}_2}/P_{\text{CO}}$, that ΔH° is $-11.0 \text{ kJ/mol}_{\text{rxn}}$ and that ΔS° is $-17.7 \text{ J/mol}_{\text{rxn}} \cdot \text{K}$, what must be true about the value of Q at 1300 K ?

Answer. If a reaction is favorable, then the value of ΔG (not ΔG°) must be negative. Since we know that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

and that ΔG° is positive, the value of Q must be less than 1 at this temperature. We can, however, be even more specific. Knowing that

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

we can find the reaction's equilibrium constant for the reaction at a temperature of 1300 K ; thus

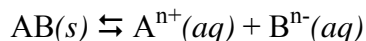
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -11.0 \text{ kJ/mol}_{\text{rxn}} - 1300 \text{ K} \times (-0.0177 \text{ kJ/mol}_{\text{rxn}} \cdot \text{K}) = 12.01 \text{ kJ/mol}_{\text{rxn}}$$

$$12.01 \text{ kJ/mol}_{\text{rxn}} = -8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}} \cdot \text{K} \times 1300 \text{ K} \times \ln K_{\text{eq}}$$

$$K_{\text{eq}} = 0.329$$

Thus, the value of Q must be less than 0.329 if the reaction is to be favorable at a temperature of 1300 K .

Problem 5. Consider the following generic reaction for the solubility of a sparingly soluble ionic salt



for which the equilibrium constant is

$$K = [A^{n+}][B^{n-}]$$

Most sparingly soluble ionic salts are more soluble at higher temperatures, but in a few cases solubility decreases at higher temperatures. In two to four sentences, offer a valid thermodynamic explanation for this difference in the effect of temperature on solubility.

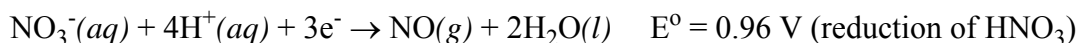
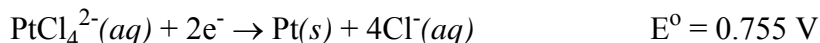
Answer. It is important to remember that the favorability of a reaction does not provide information about the reaction's equilibrium position; that is, the relative amounts of products and reactants. Favorability is given by the sign and magnitude of ΔG . The more negative the value of ΔG , the more greater the driving force for the reaction and the greater the change in free energy as the reaction occurs. The reaction's composition at equilibrium is given by the equilibrium constant, K_{eq} . The relationship of K_{eq} and temperature is determined by the sign of ΔH°

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

When ΔH° is negative (exothermic reaction), the equilibrium constant becomes smaller at higher temperatures and when ΔH° is positive (endothermic reaction), the equilibrium constant becomes larger at higher temperatures.

The more soluble a compound, the greater the concentration of dissolved ions and the larger the value of K . For most sparingly soluble salts, therefore, we can conclude that the dissolution reaction is endothermic; however, in a few cases, the dissolution reaction is exothermic.

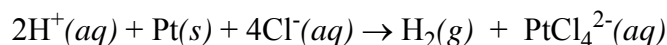
Problem 6. In 800 AD the Islamic alchemist Jabir Ibn Hayyan discovered that metals, such as gold, that could not be dissolved in HCl or HNO₃ could sometimes be dissolved in a mixture of the two acids. This mixture eventually was called *aqua regia* or “royal water.” Given the following standard-state reduction potentials:



explain why Pt can be dissolved in *aqua regia* but not in HCl or in HNO₃. Be sure your answer is clear and easy to follow! Support your answer with relevant calculations. Assume that standard state conditions apply.

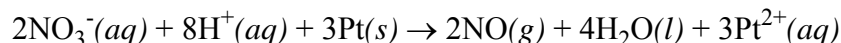
Answer. To explain these observations we need to determine the redox reaction that is (or might) occur and find the potential. Because we know that $\Delta G^\circ = -nFE^\circ$ we know that a positive E° corresponds to a negative ΔG° and a favorable reaction.

For the reaction of Pt(s) and HCl, the reaction and potential are



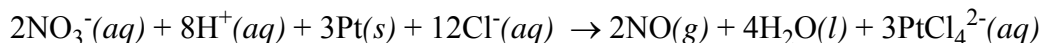
$$E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (-0.755 \text{ V}) + (0.00 \text{ V}) = -0.755 \text{ V}$$

For the reaction of Pt(s) with HNO₃, the reaction and potential are



$$E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (-1.188 \text{ V}) + (0.96 \text{ V}) = -0.228 \text{ V}$$

For the reaction of Pt(s) with HCl and HNO₃, the reaction and potential are



$$E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (-0.755 \text{ V}) + (0.96 \text{ V}) = +0.205 \text{ V}$$

Only the reaction with HCl and HNO₃ provides a positive potential and a favorable reaction.