

Chem 260 – First Exam [Key](#)

On the following pages are problems covering material in thermodynamics. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer one question, then move on to another question; working on a new question may suggest an approach to the one that is more troublesome. If a question requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

Problem 1 ____/11 Problem 2 ____/11 Problem 3 ____/11

Problem 4 ____/16 Problem 5 ____/16 Problem 6 ____/19 Problem 7 ____/16

Total_____

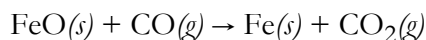
A few constants and thermodynamics values are given here:

$$d_{\text{H}_2\text{O}} = 1.00 \text{ g/mL} \quad S_{\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot^\circ\text{C}$$

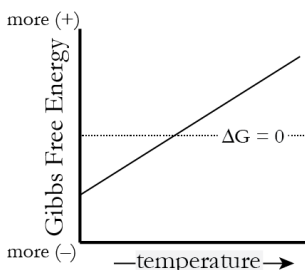
$$R = 8.314 \text{ J/mol}_{\text{rxn}}\cdot\text{K} \quad F = 96,485 \text{ J/V}\cdot\text{mol e}^-$$

species	ΔH°_f (kJ/mol _{rxn})	ΔG°_f (kJ/mol _{rxn})	S° (J/mol _{rxn} •K)
CO ₂ (g)	−393.5	−394.4	213.6
CO(g)	−110.5	−137.3	197.9
CH ₄ (g)	−74.85	−50.8	186.2
C ₆ H ₁₂ O ₆ (s)	−1274.5	−910.56	212.1
H ⁺ (aq)	0	0	0
H ₂ (g)	0	0	131.0
H ₂ O(g)	−241.8	−228.6	188.7
H ₂ O(l)	−285.8	−237.1	69.9
O ₂ (g)	0	0	205.0
OH [−] (aq)	−229/94	−157.3	−10.5

Problem 1. In a blast furnace for producing iron from iron ore, the following sequence of reactions takes place: $\text{Fe}_2\text{O}_3(s) \rightarrow \text{Fe}_3\text{O}_4(s) \rightarrow \text{FeO}(s) \rightarrow \text{Fe}(s)$. Shown below is a plot of ΔG° vs. temperature for the last step in this sequence of reactions



Based on this plot, predict the sign for ΔH and for ΔS , and explain the reason for your predictions in 1–2 sentences.



From the plot we see that the reaction shifts from being favorable ($\Delta G < 0$) to unfavorable ($\Delta G > 0$) at higher temperatures; given the relationship $\Delta G = \Delta H + T\Delta S$, this requires that ΔH be negative and that ΔS be negative.

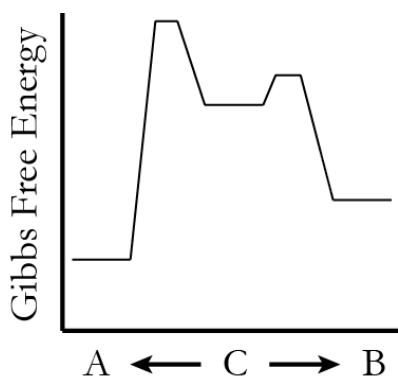
Problem 2. The heat of formation for $\text{NO}(g)$ is $+90.25 \text{ kJ/mol}_{\text{rxn}}$ and the heat of atom combination for $\text{NO}(g)$ is $-631.62 \text{ kJ/mol}_{\text{rxn}}$. In no more than 2–3 sentences, explain why the magnitudes and the signs of these two enthalpy values are so different from each other.



Because a formation reaction involves both bond breaking (endothermic) and bond formation (exothermic) and an atom combination reaction involves bond formation only, the heat of formation for any species is always more positive (less negative) than its heat of atom combination. The heat of atom combination always is negative, but the sign of a heat of formation reaction depends on the relative strengths of the bonds in the reactants and the bonds in the products.

Problem 3. Using the axes below, draw a reaction energy diagram that is consistent with the following description of a chemical system.

Compound C can react to form compound A and/or compound B. The formation of compound A from compound C is known to release more free energy than the formation of compound B from compound C, yet only compound B is recovered from the reaction mixture.



Note that the energy level for compound C is shown and that the x-axis indicates the reaction's two possible directions. In no more than 2–3 sentences, explain your reason(s) for drawing your reaction energy diagram.

Because the formation of A releases more free energy than the formation of B, we know that the absolute free energy of A is less than that for B. Because compound B, which is the less thermodynamically favorable product, is the reaction's only product, its formation must have a lower energy barrier than does the formation of A.

Problem 4. Suppose you are sitting around a campfire on a chilly, late February evening when the temperature is -5°C , and you find your favorite hot beverage—even though it is in an insulated container—has cooled to a lukewarm 18°C . To reheat your beverage you grab the fire tongs, place a 0.189 kg chunk of iron into the fire until its temperature reaches 800°C , remove the container's cap, plunge the chunk of iron into your beverage, and then reseal the cap. Assuming you have 0.500 L of your beverage and assuming no heat is lost to the environment, what final temperature will your beverage reach? The specific heat of iron is $0.450\text{ J/g}\cdot^{\circ}\text{C}$; you may assume the specific heat and the density of the beverage are the same as water.

We assume that all the energy released by the chunk of iron as it cools from 800°C to T_f is absorbed by the beverage as it warms from 18°C to T_f ; thus

$$q_{\text{Fe}} = -q_{\text{bev}}$$

$$m_{\text{Fe}}S_{\text{Fe}}(T_f - 800^{\circ}\text{C}) = -m_{\text{bev}}S_{\text{bev}}(T_f - 18^{\circ}\text{C})$$

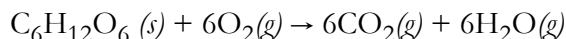
$$(189\text{ g})(0.450\text{ J/g}\cdot^{\circ}\text{C})(T_f - 800^{\circ}\text{C}) = -(500\text{ mL})(1.00\text{ g/mL})(4.184\text{ J/g}\cdot^{\circ}\text{C})(T_f - 18^{\circ}\text{C})$$

$$85.05\text{ J}\times T_f - 68,040\text{ J} = -2092\text{ J}\times T_f + 37,656\text{ J}$$

$$2177\text{ J}\times T_f = 105,196$$

$$T_f = 48.6^{\circ}\text{C}$$

Problem 5. As you may know, the energy content of foods is reported in Calories (with a capital “C”). What you may not know is a Calorie is just another way of reporting the enthalpy of a combustion reaction using units of Cal/g instead of $\text{kJ/mol}_{\text{rxn}}$. For example, the combustion reaction for glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is



Mary Poppins sang “A teaspoon of sugar helps the medicine go down.” Given that one Calorie is equivalent to one kilocalorie, that one calorie (with a little “c”) is equivalent to 4.184 J , and that a teaspoon of sugar has 4.0 g of glucose, how many Calories help the medicine go down?

First, we need to find ΔH for the combustion of glucose, which is

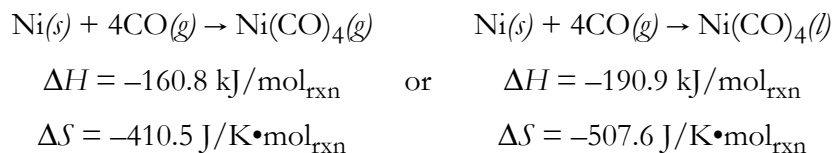
$$\Delta H = \{(6)(-393.5) + (6)(-241.8)\} - \{(1)(-1274.5) + (6)(0)\} = -2537\text{ kJ/mol}_{\text{rxn}}$$

and then use this result to convert the mass of glucose (G) into Calories

$$\begin{aligned} (4.0\text{ g G}) \times (-2537\text{ kJ/mol}_{\text{rxn}}) \times (1\text{ mol}_{\text{rxn}}/\text{mol G}) \times (1\text{ mol G}/180.2\text{ g G}) \\ \times (1000\text{ J/kJ}) \times (1\text{ cal}/4.184\text{ J/g}\cdot^{\circ}\text{C}) \times (1\text{ Cal}/1000\text{ cal}) = -13\text{ Cal} \end{aligned}$$

Thus, 13 Calories help the medicine go down.

Problem 6. Most of the nickel in the world comes from a single mine in Canada where the impact of a comet many years ago brought a deeply buried deposit of NiS to the earth's surface. To obtain pure Ni, the ore is reduced to an impure metallic Ni and purified by reacting with CO(g) to form Ni(CO)₄, which is isolated and converted back to pure Ni. Depending on the temperature, the reaction is either



The desired product is Ni(CO)₄(g) because it is easier to separate a gas from solid impurities than it is to remove a liquid from these same impurities. Using the thermodynamic values provided above, report the range of possible temperatures for which the formation of Ni(CO)₄(g) is favorable, and for which the formation of Ni(CO)₄(g) is more favorable than the formation of Ni(CO)₄(l).

First, we note that the signs of ΔH and of ΔS for Ni(CO)₄(g) indicate the reaction is favorable below a critical temperature

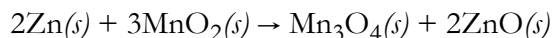
$$\Delta G = 0 = \Delta H - T_{\text{crit}}\Delta S = (-160.8 \text{ kJ/mol}_{\text{rxn}}) - T_{\text{crit}}(-0.4105 \text{ kJ/K}\cdot\text{mol}_{\text{rxn}})$$

or a T_{crit} of 392 K. Then, we note that the compound's free energy vs. temperature curves intersect at T_{cross} and that because ΔS for Ni(CO)₄(l) is more negative than ΔS for Ni(CO)₄(g), the desired product is more favorable at temperatures greater than T_{cross}

$$\begin{aligned} \Delta H_{\text{Ni(CO)}_4(g)} - T_{\text{cross}}\Delta S_{\text{Ni(CO)}_4(g)} &= \Delta H_{\text{Ni(CO)}_4(l)} - T_{\text{cross}}\Delta S_{\text{Ni(CO)}_4(l)} \\ -160.8 \text{ kJ/mol}_{\text{rxn}} + 0.4105 \text{ kJ/K}\cdot\text{mol}_{\text{rxn}} \times T_{\text{cross}} &= \\ -190.9 \text{ kJ/mol}_{\text{rxn}} + 0.5076 \text{ kJ/K}\cdot\text{mol}_{\text{rxn}} \times T_{\text{cross}} & \\ 30.1 \text{ kJ/mol}_{\text{rxn}} = 0.0971 \text{ kJ/K}\cdot\text{mol}_{\text{rxn}} \times T_{\text{cross}} & \\ T_{\text{cross}} = 310 \text{ K} & \end{aligned}$$

or a T_{cross} of 310 K. Thus, we recover Ni(CO)₄(g) when $310 \text{ K} \leq T \leq 392 \text{ K}$.

Problem 7. One of the most common batteries uses the following redox reaction



Given that a fresh battery has a potential, E , of +1.54 V, how much free energy is available for useful work if 0.500 g of Zn reacts completely and if the efficiency of converting energy to useful work is 75%?

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ = -(4 \text{ mol } e^-/\text{mol}_{\text{rxn}})(96,485 \text{ J/V}\cdot\text{mol } e^-)(1.54 \text{ V}) = -594,300 \text{ J/mol}_{\text{rxn}} \\ 0.500 \text{ g Zn} \times (1 \text{ mol Zn}/65.3 \text{ g Zn}) \times (1 \text{ mol}_{\text{rxn}}/2 \text{ mol Zn}) & \\ \times (-594,300 \text{ J/mol}_{\text{rxn}}) \times (1 \text{ kJ}/1000 \text{ J}) \times 0.75 &= -1.70 \text{ kJ} \end{aligned}$$