Thermodynamics Practice Exam Key

Note: All problems included in this practice exam are drawn from problems used in previous semesters. Exams typically include 7 or 8 problems that are a mixture of qualitative problems calling for written explanations and quantitative problems that involve calculations and, in some cases, written explanations.

On the following pages are problems that consider the thermodynamics of chemical or biochemical systems. 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 a question, then move on to another question; working on a new question may suggest an approach to a question 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 and that work is relevant to the question.

Problem	Points	Maximum	Problem	Points	Maximum
1		11	5		16
2		11	6		19
3		11	7		16
4		16	Total		100

A few constants and thermodynamics values are given here; other information is included within individual problems.

- density (d) of water is 1.00 g/mL
- specific heat (S) of water is 4.184 J/g $\bullet$ °C
- the gas constant (R) is 8.314 J/mol$_{\mathrm{rxn}}$ $\bullet$ K
- Faraday's constant (F) is 96,485 J/V $\bullet$ mol e$^-$

substance	ΔH_f^o (kJ/mol$_{\mathrm{rxn}}$)	ΔS^o (J/K $\bullet$ mol$_{\mathrm{rxn}}$)	ΔG_f^o (kJ/mol$_{\mathrm{rxn}}$)
$CO_2(g)$	−393.5	213.6	−394.4
$CO(g)$	−110.5	197.9	−137.3
$CH_4(g)$	−74.85	186.2	−50.8
$C_6H_{12}O_6(s)$	−1274.5	212.1	−910.56
$H^+(aq)$	0	0	0
$H_2(g)$	0	131.0	0
$H_2O(g)$	−241.8	188.7	−228.6
$H_2O(l)$	−285.8	69.9	−237.1
$O_2(g)$	0	205.0	0
$OH^-(aq)$	−229.94	−10.5	−157.3

Problem 1. In a blast furnace for producing iron from iron ore, the following sequence of reactions takes place: Fe_2O_3 *(s)* $\rightarrow$ Fe_3O_4 *(s)* $\rightarrow$ FeO *(s)* $\rightarrow$ Fe *(s)*. Shown below is a plot of ΔG as a function of temperature for the last step in this sequence of reactions

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$
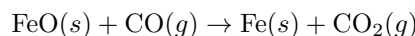
Based on this plot, predict the sign for ΔH and for ΔS, and explain the reason for your predictions in 1–2 sentences.
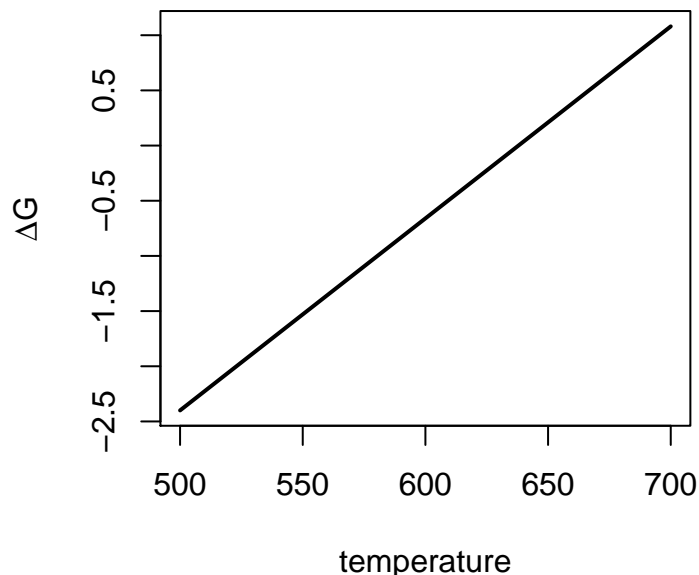
From the plot, we see that the reaction is favorable ($\Delta G < 0$) at temperatures below $\approx$ 640 K and unfavorable ($\Delta G > 0$) at temperatures above $\approx$ 640 K; given the relationship $\Delta G = \Delta H - T\Delta S$, this requires that ΔH is negative and that ΔS is negative.

Problem 2. The reaction $A \rightarrow B$ has a standard state free energy, ΔG^o, of 10 kJ/mol$_{rxn}$ and a free energy, ΔG, of 0 kJ/mol$_{rxn}$. Which of the following statements about the system is correct:

- ~~Some A will react with B until equilibrium is reached.~~

- ~~Some B will react with A until equilibrium is reached.~~

- **The system is at equilibrium and contains more A than B.**

- ~~The system is at equilibrium and contains more B than A.~~

- ~~There is insufficient information to reach a conclusion.~~

Circle the statement that is correct and, in 2–3 sentences, convince me that you are right. Should you choose the last option, then explain what additional information you need to arrive at a conclusion.

Because ΔG is zero, we know that the system is at equilibrium, eliminating the first two options as possible answers. Because ΔG^o is positive, we know that the equilibrium constant is less than one—recall that $\Delta G^o = -RT\ln K$ and that the natural log of a number less than one is negative, which makes ΔG^o positive— and at equilibrium there are more reactants than there are products; thus, the third option is correct.

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.
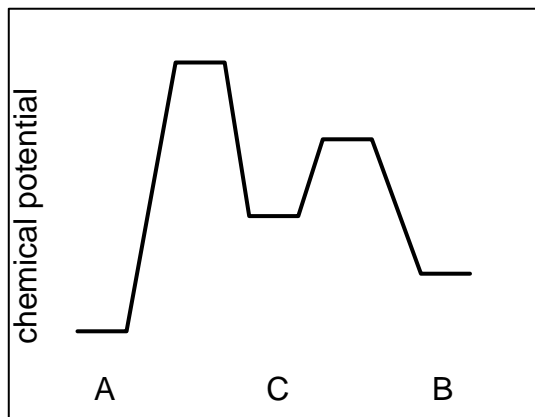
Because the formation of A releases more free energy than the formation of B, we know that the absolute free energy of A is less than that for B; thus, it is lower on the y-axis. Because compound B is the only product—even though it is less thermodynamically favorablethan compound A—its formation must have a smaller energy barrier than does compound 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 J/g°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_{final} is absorbed by the beverage as it warms from 18°C to T_{final}; thus

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

$$m_{Fe}S_{Fe}(T_{final} - 800^{o}C) = -m_{bev}S_{bev}(T_{final} - 18^{o}C)$$

$$(189 \; g)(0.450 \; J/g^{o}C)(T_{final} - 800^{o}C) = -(500 \; mL)(1.00 \; g/mL)(4.184 \; J/g^{o}C)(T_{final} - 18^{o}C)$$

$$85.05 \; J/^{o}C \times T_{final} - 68,040 \; J = -2092 \; J/^{o}C \times T_{final} + 37,656 \; J$$

$$2177 \; J/^{o}C \times T_{final} = 105,696 \; J$$

$$T_{final} = 48.3^{o}C$$

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 kJ/mol$_{\text{rxn}}$. For example, the combustion reaction for glucose, $C_6H_{12}O_6$, is

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$$
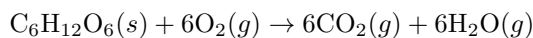
Mary Poppins sang "A teaspoon of sugar helps the medicine go down." Given that one Calorie is equivalent to one kilocalorie, that one calorie (with a little "c") is equivalent to 4.184 J, and that a teaspoon of sugar has 4.0 g of glucose, how many Calories help the medicine go down?

*First, we need to calculate ΔH^o for the combustion of glucose, which, using the data from the exam's cover sheet, is*

$$\Delta H^o = [(6)(-393.5) + (6)(-241.8)] - [(1)(-1274.5) + (6)(0)] = -2537 \ kJ/mol_{rxn}$$

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

$$4.0 \ g \ glu \times \frac{-2537 \ kJ}{mol_{rxn}} \times \frac{mol_{rxn}}{mol \ glu} \times \frac{mol \ glu}{180.2 \ g \ glu} \times \frac{1000 \ J}{kJ} \times \frac{1 \ cal}{4.184 \ J/g^o C} \times \frac{1 \ Cal}{1000 \ cal} = -13 \ Cal$$

Thus, 13 Calories help the medicine go down.

Problem 6. One of the most common batteries uses the following redox reaction

$$2Zn(s) + 3MnO_2(s) \rightarrow Mn_3O_4(s) + 2ZnO(s)$$
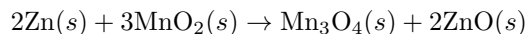
Given that a fresh battery has a potential, E, of +1.54 V, how much free energy is available for useful work if 0.500 g of Zn reacts completely and if the efficiency of converting energy to useful work is 75%?

$$\Delta G^o = -nF\Delta E^o = \frac{-4 \ mol \ e^-}{mol_{rxn}} \times \frac{96,485 J}{V \bullet mole^-} \times 1.54 \ V = -594,300 \ J/mol_{rxn}$$

$$0.500 \ g \ Zn \times \frac{1 \ mol \ Zn}{65.3 \ g \ Zn} \times \frac{mol_{rxn}}{2 \ mol \ Zn} \times \frac{-594,300 \ J}{mol_{rxn}} \times \frac{1 \ kJ}{1000 \ J} \times 0.75 = -1.7 \ kJ$$

Problem 7. 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 carbon monoxide, CO, to form $Ni(CO)_4$, which is isolated and converted back to pure Ni. Depending on the temperature, the reaction is one or the other of these two reactions

reaction	ΔH (kJ/mol$_{rxn}$)	ΔS (J/K • mol$_{rxn}$)
Ni*(s)* + 4CO*(g)* → Ni(CO)$_4$*(g)*	−160.8	−410.5
Ni*(s)* + 4CO*(g)* → Ni(CO)$_4$*(l)*	−190.9	−507.6

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 both favorable and 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 that the reaction is favorable only below a critical temperature, so let's start by calculating this upper boundary for the temperature; thus

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

$$T_{crit} = 392 \ K$$

Then, we note that the ΔG vs. T curves for Ni(CO)$_4$(g) and for Ni(CO)$_4$(l) must cross as they do not have the same value for ΔS. 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}, which is

$$\Delta H_{Ni(CO)4(g)} - T_{cross}\Delta S_{Ni(CO)4(g)} = \Delta H_{Ni(CO)4(l)} - T_{cross}\Delta S_{Ni(CO)4(l)}$$

$$-160.8 \ kJ/mol_{rxn} + 0.4105 \ kJ/K \ mol_{rxn} \times T_{cross} = -190.9 \ kJ/mol_{rxn} + 0.5076 \ kJ/K \ mol_{rxn} \times T_{cross}$$

$$30.1 \ kJ/mol_{rxn} = 0.0971 \ kJ/K \ mol_{rxn} \times T_{cross}$$

$$T_{cross} = 310 \ K$$

Thus, we recover Ni(CO)$_4$(g) when 310 K ≤ T ≤ 392 K.