Unit Exam: Thermodynamics

On the following pages are problems that consider the thermodynamics of chemical or biochemical systems. Read each problem carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer a problem, then move on to another; working on a new problem may suggest an approach to the one that is more troublesome. If a problem 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		12	4		18
2		12	5		22
3		12	6		24
			Total		100

A few constants are shown below; other information is included within individual problems. A periodic table and a sheet of equations also are available.

- the gas constant (R) is 8.314 $\text{J/mol}_{\text{rxn}} \bullet \text{K}$
- Faraday's constant (F) is 96,485 $\text{J/V} \bullet \text{mol e}^-$
- room temperature is 25°C or 298 K

Specific thermodynamic values—such as heats of formation, free energies or formation, and entropies—and other potentially useful information are embedded within individual problems.

Part A: Problems Requiring a Short Written Response and, perhaps, a Short Calculation

Problem 1. Perhaps when you were younger, you made a plaster cast of your hand-prints to give to your parents or grandparents. If you did, then you witnessed the following reaction between Plaster of Paris, which is $CaSO_4 \cdot \frac{1}{2}\,H_2O$, and water, H_2O to form gypsum, $CaSO_4 \cdot 2\,H_2O$.

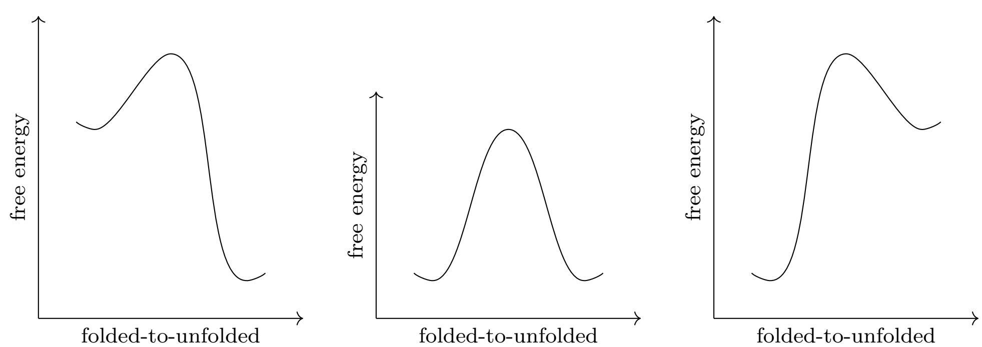
$$CaSO_4 \cdot \frac{1}{2}\,H_2O(s) + \frac{3}{2}\,H_2O(l) \longrightarrow CaSO_4 \cdot 2\,H_2O(s)$$

Based on the information provided above, report the sign of ΔH for this reaction. Provide your answers in the form of "$\Delta H > 0$", "$\Delta H < 0$", "$\Delta H = 0$", or "there is insufficient information to determine the sign of ΔH." In 2–4 sentences, explain how you arrived at this choice.

Problem 2. Proteins are one of the important classes of biomolecules. For a protein to function correctly, it must fold itself into a particular three-dimensional geometry. Whether you find a particular protein in its folded or its unfolded state depends on the system's temperature. Shown below are three possible reaction energy diagrams for the unfolding of a hypothetical protein

$$\text{folded protein} \rightleftharpoons \text{unfolded protein}$$

for which ΔH° is 300 kJ/mol$_{\text{rxn}}$ and for which ΔS° is 750 J/K • mol$_{\text{rxn}}$. Circle the reaction energy diagram that corresponds to this protein's unfolding reaction at room temperature (298 K). In 2–4 sentences, explain how you arrived at this choice.



Problem 3. The table below gives heats of atom combination for three simple gas-phase hydrocarbons. In 2–4 sentences use this data to present a convincing argument that a carbon-carbon triple bond is stronger than a carbon-carbon double bond. You may assume that a carbon-hydrogen bond has the same bond strength in all four compounds. The most complete answer will provide estimates for the bond energy of a carbon-carbon single bond and for a carbon-carbon double bond.

compound	formula	$\Delta H^\circ_{\text{ac}}$ (kJ/mol)
methane	CH_4	−1662
ethylene	$H_2C{=}CH_2$	−2252
acetylene	$HC{\equiv}CH$	−1642

Part B: Problems Requiring a Longer Calculation and, perhaps, a Short Written Response

Problem 4. It is not easy to measure the change in the standard state enthalpy for some reactions because one of the reactants is not sufficiently stable. Such is the case for the reaction $F_2^-(g) \longrightarrow F(g) + F^-(g)$. It is possible to determine ΔH° for

- breaking a F−F single bond in molecular fluorine, $F_2(g) \longrightarrow 2\,F(g)$, for which ΔH° is 156.9 $\text{kJ/mol}_{\text{rxn}}$
- the electron affinity of atomic fluorine, $F(g) + e^- \longrightarrow F^-(g)$, for which ΔH° is –333 $\text{kJ/mol}_{\text{rxn}}$
- the electron affinity of molecular fluorine, $F_2(g) + e^- \longrightarrow F_2^-(g)$, for which ΔH° is –290 $\text{kJ/mol}_{\text{rxn}}$

What is ΔH° for breaking the fluorine-fluorine bond in $F_2^-(g)$ as given in the reaction $F_2^-(g) \longrightarrow F(g) + F^-(g)$? In 1–2 sentences, explain why your answer makes sense (or does not make sense if you think it is incorrect).

Problem 5. Suppose you are preparing for a picnic lunch and that you need to ensure your drinks remain sufficiently cold. You place a six-pack of your favorite soda in a perfectly insulated container. Each can is made from 38.5 grams of aluminum and each can contains 354.8 mL of soda. What is the minimum amount of ice in grams needed to cool the soda from 25°C to 0°C? You will need some, but not all of the following information to arrive at an answer:

- specific heat of $Al(s)$ is 0.902 J/g°C
- specific heat of soda is 4.184 J/g°C
- specific heat of $H_2O(s)$ is 2.107 J/g°C
- specific heat of $H_2O(l)$ is 4.184 J/g°C
- specific heat of $H_2O(g)$ is 1.996 J/g°C
- density of soda is 0.993 g/mL
- density of $H_2O(s)$ is 0.9 g/cm^3
- density of $H_2O(l)$ is 1.0 g/mL
- density of $Al(s)$ is 2.7 g/cm^3
- ΔH° for $H_2O(s) \rightleftharpoons H_2O(l)$ is 6.01 kJ/mol$_{\text{rxn}}$

In 1–2 sentences, explain why your answer makes sense (or does not make sense if you think it is incorrect). There is a lot of empty real estate here, so be sure to circle your final answer for the grams of ice so that it is easy for me to find!

Problem 6. At several points in the Chem 130 lab we explore the oxidation-reduction chemistry of metals, learning, for example, that although Al(s) and Zn(s) dissolve in 1 M HCl at 298 K, Cu(s) does not. Use the data in the two tables below to answer the questions that follow. *There are several ways to approach these questions, each of which leads to the same conclusion.*

oxidation-reduction reaction	$\Delta H°$ (kJ/mol$_{rxn}$)	$\Delta S°$ (J/K • mol$_{rxn}$)
$Al(s) + 3\,H^+(aq) \longrightarrow Al^{3+}(aq) + \frac{3}{2}\,H_2(g)$	−531	−154
$Cu(s) + 2\,H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$	+65	−2.1
$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$	−153	−23.1

reduction reaction	$E°$ (V)
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.340 V
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	+0.000 V
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	–0.762 V
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	–1.66 V

Although Cu(s) will not dissolve in 1 M HCl at 298K, can it dissolve in 1 M HCl at a temperature other than 298 K? If yes, what are the limitations on temperature? Be sure to justify your answer.

Which of the other metals—Al(s) or Zn(s)—has the more favorable oxidation reaction with 1 M HCl at 400 K? Be sure to justify your answer.

What is the value for $\Delta G°$ and for $E°$ for the following reaction at 298 K?

$$3\,Zn(s) + 2\,Al^{3+}(aq) \longrightarrow 2\,Al(s) + 3\,Zn^{2+}(aq)$$