

Unit Exam Key: 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	Average	Maximum	Problem	Average	Maximum
1	86.3	12	4	86.9	18
2	91.7	12	5	80.0	22
3	80.7	12	6	87.8	24
			Total	84.8	100

high score	scores 100–90	scores 89–80	scores ≤ 79
98	7	12	5

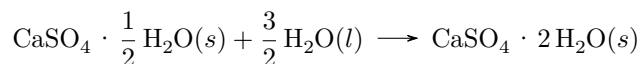
A few constants are shown below; other information is included within individual problems. A periodic table and a sheet of equations also are available.

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

Specific thermodynamic values—such as heats of formation, free energies of 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

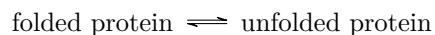
Problem 1. Perhaps when you were younger, you made a plaster cast of your hand-prints to give to your parents or grandparents. If you did, then you witnessed the following reaction between Plaster of Paris, which is $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, and water, H_2O to form gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.



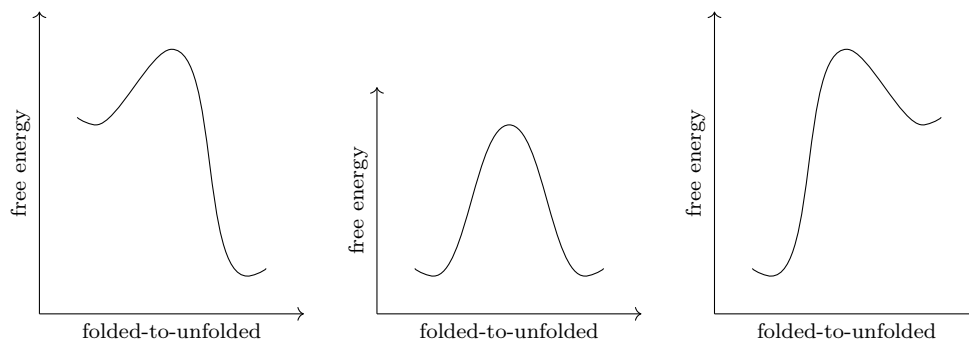
Based on the information provided above, report the sign of ΔH for this reaction. Provide your answers in the form of “ $\Delta H > 0$ ”, “ $\Delta H < 0$ ”, “ $\Delta H = 0$ ”, or “there is insufficient information to determine the sign of ΔH .” In 2–4 sentences, explain how you arrived at this choice.

Answer. We know that the reaction happens, which means that $\Delta G < 0$. We also know that the entropy change is unfavorable because liquid water is incorporated into the solid, moving from a less condensed phase to a more condensed phase, which means that $\Delta S < 0$. If a favorable reaction is not driven by a change in entropy, then it must be driven by a change in enthalpy, which requires that $\Delta H < 0$.

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



for which ΔH° is 300 kJ/mol_{rxn} and for which ΔS° is 750 J/K • mol_{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.



Answer. There are two ways to decide on the correct reaction energy diagram, both of which require determining if the reaction’s ΔG is positive, negative, or equal to 0 at 298 K. One approach is to calculate ΔG at this temperature; thus

$$\Delta G = \Delta H - T\Delta S = 300 - (298)(0.750) = 76.5 \text{ kJ/mol}_{\text{rxn}}$$

The other approach is note that the signs for ΔH° and ΔS° tell us that the unfolding reaction is favorable at higher temperatures where the favorable ΔS° wins out over the unfavorable ΔH° . What counts as “higher” is unclear, so we calculate the critical temperature, T_{crit} , which is

$$T_{\text{crit}} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{300 \text{ kJ/mol}_{\text{rxn}}}{0.750 \text{ kJ/K} \cdot \text{mol}_{\text{rxn}}} = 400 \text{ K}$$

Both approaches show that the unfolding reaction is unfavorable at 298 K, which is consistent with the reaction energy diagram on the far right, which shows $\Delta G > 0$.

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 double bond and for a carbon-carbon triple bond.

compound	formula	$\Delta H_{\text{ac}}^{\circ}$ (kJ/mol)
methane	CH_4	–1662
ethylene	$\text{H}_2\text{C}=\text{CH}_2$	–2252
acetylene	$\text{HC}\equiv\text{CH}$	–1642

Answer. An atom combination enthalpy gives the energy released when we form the chemical bonds in one mole of a compound and is a measure of bond strength as no energy is used to break any bonds; thus, the $\Delta H_{\text{ac}}^{\circ}$ for one mole of CH_4 gives the total energy for four C–H bond, or an average bond strength of

$$\frac{-1662 \text{ kJ/mol}}{4 \text{ mol C-H bonds/mol}} = -415.5 \text{ kJ/mol of C-H bonds}$$

To find the bond strength of a carbon-carbon double bond or a carbon-carbon triple bond, we subtract out the energy of the four C–H bonds in ethylene and the two C–H bonds in acetylene; thus

$$-2252 \text{ kJ/mol} - (4 \text{ mol C-H bonds})(-415.5 \text{ kJ/mol C-H bonds}) = -590 \text{ kJ/mole of C=C bonds}$$

$$-1642 \text{ kJ/mol} - (2 \text{ mol C-H bonds})(-415.5 \text{ kJ/mol C-H bonds}) = -811 \text{ kJ/mole of C}\equiv\text{C bonds}$$

The more negative the energy, the stronger the bond, which makes the triple bond in acetylene stronger than the double bond in ethylene.

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 $\text{F}_2^-(g) \rightarrow \text{F}(g) + \text{F}^-(g)$. It is possible to determine ΔH° for

- breaking a F–F single bond in molecular fluorine, $\text{F}_2(g) \rightarrow 2\text{F}(g)$, for which ΔH° is 156.9 kJ/mol_{rxn}
- the electron affinity of atomic fluorine, $\text{F}(g) + e^- \rightarrow \text{F}^-(g)$, for which ΔH° is –333 kJ/mol_{rxn}
- the electron affinity of molecular fluorine, $\text{F}_2(g) + e^- \rightarrow \text{F}_2^-(g)$, for which ΔH° is –290 kJ/mol_{rxn}

What is ΔH° for breaking the fluorine-fluorine bond in $\text{F}_2^-(g)$ as given in the reaction $\text{F}_2^-(g) \rightarrow \text{F}(g) + \text{F}^-(g)$? In 1–2 sentences, explain why your answer makes sense (or does not make sense if you think it is incorrect).

Answer. Adding together the following three reactions gives the overall reaction $\text{F}_2^-(g) \rightarrow \text{F}(g) + \text{F}^-(g)$.



If we add together a set of reactions, then we add together their ΔH° values to arrive at the desired value of ΔH° for the overall reaction; thus

$$\Delta H^{\circ} = 156.9 + (-333) + 290 = 113.9 \text{ kJ/mol}_{\text{rxn}}$$

Finding that ΔH° for breaking the F–F bond in F_2^- is smaller than for F_2 makes sense as F_2 is the stable form of the element fluorine.

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 H₂O(s) is 2.107 J/g°C
- specific heat of H₂O(l) is 4.184 J/g°C
- specific heat of H₂O(g) is 1.996 J/g°C
- density of soda is 0.993 g/mL
- density of H₂O(s) is 0.9 g/cm³
- density of H₂O(l) is 1.0 g/mL
- density of Al(s) is 2.7 g/cm³
- ΔH° for H₂O(s) \rightleftharpoons H₂O(l) is 6.01 kJ/mol_{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!

Answer. First, we find the amount heat that leaves the six aluminum cans when they cool from 25°C to 0°C

$$q_{\text{Al}} = mS\Delta T = (38.5 \text{ g/can})(6 \text{ cans})(0.902 \text{ J/g}^\circ\text{C})(0^\circ\text{C} - 25^\circ\text{C}) = -5209 \text{ J}$$

and the amount of heat that leaves the soda in the six cans when they cool from 25°C to 0°C

$$q_{\text{soda}} = mS\Delta T = (354.8 \text{ mL/can})(0.993 \text{ g/mL})(6 \text{ cans})(4.184 \text{ J/g}^\circ\text{C})(0^\circ\text{C} - 25^\circ\text{C}) = -221114 \text{ J}$$

The heat that the ice must absorb, therefore, is

$$q_{\text{ice}} = -(q_{\text{Al}} + q_{\text{soda}}) = -(5209 + 221114) = 226323 \text{ J}$$

or 226.323 kJ. To find the amount of ice needed, we use ΔH° for the reaction H₂O(s) \rightleftharpoons H₂O(l); thus

$$n_{\text{ice}} = \frac{q_{\text{ice}}}{\Delta H^\circ} = \frac{226.323 \text{ kJ}}{6.01 \text{ kJ/mol}_{\text{rxn}}} \times \frac{1 \text{ mol H}_2\text{O}(s)}{\text{mol}_{\text{rxn}}} = 37.7 \text{ moles of ice}$$

or, in terms of the mass of ice

$$37.7 \text{ moles of ice} \times \frac{18.02 \text{ g of ice}}{\text{mol of ice}} = 680 \text{ g of ice}$$

This mass of ice is equivalent to approximately 750 mL of water, which seems reasonable if we assume that the cooler is a perfect insulator that does not lose heat to the environment or absorb heat on its own.

Note that a reaction does not have a mass, a specific heat, or a change in temperature; thus you can never calculate q_{rxn} using the equation $q = mS\Delta T$. Instead, in a calorimetry experiment we measure the amount of heat gained or lost by an object that does have a mass, a specific heat, and a change in temperature and use that to calculate q_{rxn} . A reaction does have a ΔH and that, too, can be used to calculate q_{rxn} if we know the moles of the reaction's limiting reagent. This what we have done here where the cans of soda are the object absorbing heat and the moles of ice melting is the limiting reagent.

Problem 6. At several points in the Chem 130 lab we explore the oxidation-reduction chemistry of metals, learning, for example, that although $\text{Al}(s)$ and $\text{Zn}(s)$ dissolve in 1 M HCl at 298 K, $\text{Cu}(s)$ 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	ΔH° (kJ/mol _{rxn})	ΔS° (J/K • mol _{rxn})
$\text{Al}(s) + 3\text{H}^+(aq) \longrightarrow \text{Al}^{3+}(aq) + \frac{3}{2}\text{H}_2(g)$	-531	-154
$\text{Cu}(s) + 2\text{H}^+(aq) \longrightarrow \text{Cu}^{2+}(aq) + \text{H}_2(g)$	+65	-2.1
$\text{Zn}(s) + 2\text{H}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$	-153	-23.1

reduction reaction	E° (V)
$\text{Cu}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Cu}(s)$	+0.340 V
$2\text{H}^+(aq) + 2\text{e}^- \longrightarrow \text{H}_2(g)$	+0.000 V
$\text{Zn}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Zn}(s)$	-0.762 V
$\text{Al}^{3+}(aq) + 3\text{e}^- \longrightarrow \text{Al}(s)$	-1.66 V

Although $\text{Cu}(s)$ 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.

Answer. The simplest approach is to note that since $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, neither enthalpy nor entropy can drive the reaction; thus, the reaction will not happen at any temperature. You also can calculate ΔG° at 0 K and at one other temperature and show that it is not possible for ΔG° to be anything but positive.

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

Answer. The simplest approach here is to calculate ΔG° for each reaction at 400 K; thus

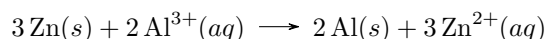
$$\Delta G_{\text{Al}}^\circ = \Delta H^\circ - T\Delta S^\circ = -531 \text{ kJ/mol}_{\text{rxn}} - (400 \text{ K})(-0.154 \text{ kJ/mol}_{\text{rxn}}) = -469.4 \text{ kJ/mol}_{\text{rxn}}$$

$$\Delta G_{\text{Zn}}^\circ = \Delta H^\circ - T\Delta S^\circ = -153 \text{ kJ/mol}_{\text{rxn}} - (400 \text{ K})(-0.0231 \text{ kJ/mol}_{\text{rxn}}) = -143.8 \text{ kJ/mol}_{\text{rxn}}$$

As ΔG° for Al is more negative than ΔG° for Zn, the oxidation reaction for Al is more favorable.

Another approach, which is a more involved calculation and requires a more careful interpretation, is to find T_{cross} , which is 2890 K. As the oxidation of Al has the more negative ΔS , and thus the more positive slope when plotting ΔG° vs T , below 2890 K the oxidation of Al is the more favorable reaction as it will have the more negative ΔG° .

What is the value for ΔG° and for E° for the following reaction at 298 K?



Answer. You can start with calculating either ΔG° or E° , and then calculate the other using the relationship $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. It is a bit quicker to begin with E° ; thus

$$E^\circ = E_{\text{Al}^{3+}/\text{Al}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -1.66 - (-0.762) = -0.898 \text{ V}$$

and, with six electrons transferred from Zn^{2+} to Al^{3+} , we have

$$\Delta G^\circ = -nFE^\circ = -(6)(96.458)(-0.900) = 519.9 \text{ kJ/mol}_{\text{rxn}}$$

To begin with a calculation for ΔG° , we first use the values for ΔH° and for ΔS° to calculate ΔG° at 298 K, arriving at values of -485.1 kJ/mol_{rxn} and -146.1 kJ/mol_{rxn} for the reactions of Al and for Zn, respectively. We then combine them, taking stoichiometry into account, to arrive at

$$\Delta G^\circ = 3 \times \Delta G_{\text{Zn}}^\circ + 2 \times (-\Delta G_{\text{Al}}^\circ) = (3)(-146.1) + (2)(485.1) = 531.9 \text{ kJ/mol}_{\text{rxn}}$$

$$E^{\circ} = \frac{\Delta G^{\circ}}{-nF} = \frac{531.9}{(-6)(96.458)} = -0.919 \text{ V}$$

Although not identical, the two approaches yield very similar results. Any differences reflect the uncertainty in the sources used to construct the two data tables.

Note that the signs for ΔG° and for E° found here are consistent with the conclusion from the previous question; that is, it is easier to oxidize Al than it is to oxidize Zn.