

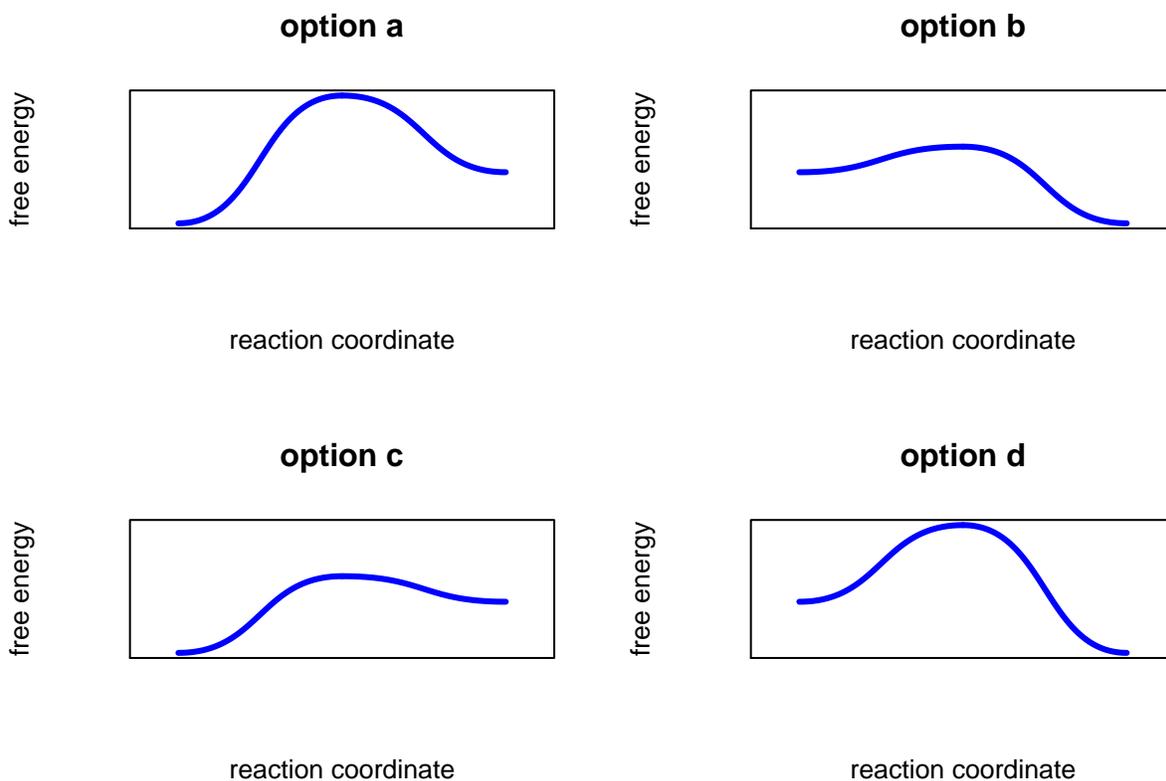
Key for Unit Exam: Thermodynamics

On the following pages are six 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 | 10.8 (83.4%) | 13 | 4 | 19.2 (79.8%) | 24 |
| 2 | 11.1 (85.8%) | 13 | 5 | 16.1 (80.6%) | 20 |
| 3 | 11.8 (91.1%) | 13 | 6 | 14.1 (83.1%) | 17 |
| | | | Total | 82.5 | 100 |

| high score | scores 100–90 | scores 89–80 | scores ≤ 79 |
|------------|---------------|--------------|------------------|
| 98 | 6 | 8 | 10 |

Figure to Accompany Problem 1

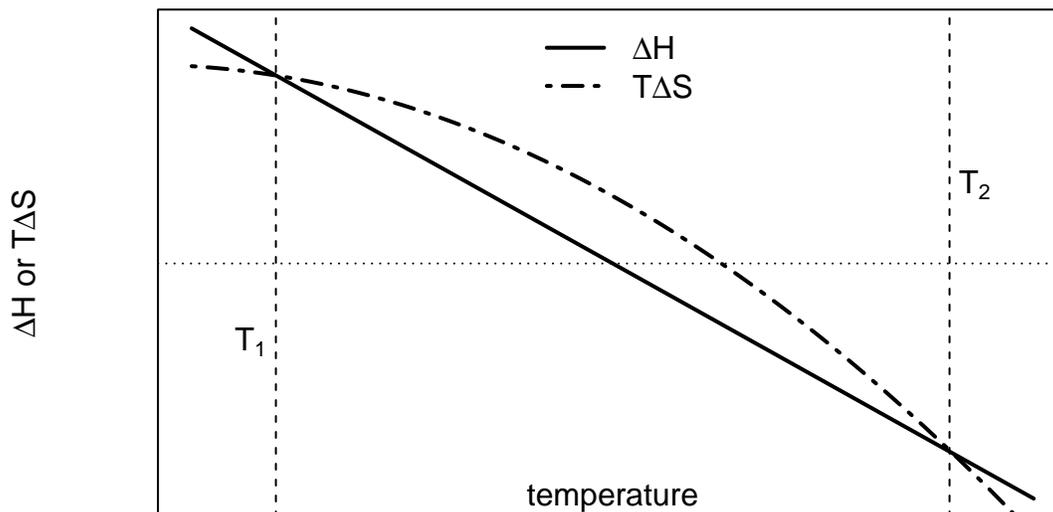


Part A: Three Problems With Short Written Answers and/or With Short Calculations

Problem 1. A supersaturated solution exists when more of a solid is dissolved in solution than is thermodynamically allowed. A supersaturated solution may remain stable for some time, but if a particle of dust falls into the solution, solid will rapidly precipitate. The figure on the exam's cover sheet shows four reaction energy diagrams. Although unmarked, the y -axis has the same scale in all four diagrams. One of the diagrams shows the supersaturated solution before the dust particle falls into the solution and one shows the supersaturated solution immediately after the dust particle falls into the solution. Fill in the blanks in the statement below and provide a 1–2 sentence explanation of your reasoning.

- Diagram **D** shows the system before the dust particle falls into the solution.
- Diagram **B** shows the system immediately after the dust particle falls into the solution.
- Let's first characterize the four reaction energy diagrams. Options A and C show $\Delta G^\circ > 0$, which means they correspond to a system where the reaction is thermodynamically unfavorable; Options B and D show $\Delta G^\circ < 0$, which means they correspond to a system where the reaction is thermodynamically favorable. Options A and D have large energy barriers and Options B and C have small energy barriers. We know that adding dust allows precipitation to occur, so it must be one of Option B or D. We also know that the original system has more solid dissolved than is thermodynamically allowed, which means it must "want" to precipitate but can't, which is the case for Option D where $\Delta G^\circ < 0$ and there is a larger energy barrier than the other option of B.

Problem 2. The folding of a protein from its unfolded state (unfolded \rightarrow folded) depends on its values for ΔH° and $T\Delta S^\circ$. The figure below shows how ΔH° and $T\Delta S^\circ$ for a typical protein change as a function of temperature. Note that the curves cross each other at temperatures T_1 and T_2 . The horizontal dotted line shows where the values of ΔH° and $T\Delta S^\circ$ are zero.



For what temperatures is protein folding favorable? The possible answers are (a) for all $T < T_1$, (b) for all $T > T_1$, (c) for all $T_1 < T < T_2$, (d) for all $T < T_2$, (e) for all $T > T_2$, (f) for all temperatures, and (g) at no temperatures. Enter your choice in the blank below and provide a 1–3 sentence explanation of your reasoning.

- Option **C** describes the temperatures for which protein folding is favorable.
- We know that $\Delta G = \Delta H - T\Delta S$. Regardless of the signs of ΔH or ΔS , as long as $T\Delta S$ is more positive than ΔH , then ΔG must be negative. As we increase temperature, this first becomes true at T_1 and remains true until we reach T_2 .

Problem 3. Consider the following set of molecules or ions:



Arrange these species in order of their entropy, placing the species with the largest entropy on the left and the species with the smallest entropy on the right. Assume you have one mole of each species. Explain how you arrived at this order in 2–3 sentences.

- I meant to include $\text{H}_2\text{O}_2(l)$ instead of $\text{H}_2\text{O}(l)$ as water's extensive hydrogen bonding complicates thinking about its entropy. In considering responses, I ignored $\text{H}_2\text{O}(l)$. At a minimum, we expect that gases have a greater entropy than liquids, which we expect have a greater entropy than solids because gases have more ways to store energy in motion than do liquids, and liquids have more ways to store energy than solids; thus, the order should place gases on the left side and solids on the right side. When comparing gases or solids, we look for relative number of bonds as more bonds allow for more ways to store energy in modes other than translational motion; thus, we expect $\text{SO}_2(g)$ has a greater entropy than $\text{N}_2(g)$, and that $\text{Fe}_2\text{O}_3(s)$ has a greater entropy than $\text{FeO}(s)$. The final order is



Part B: Three Problems With More Involved Calculations

Problem 4. Copper has two common oxide ores: CuO and Cu_2O . Given the following thermodynamic data

| species | ΔH_f° (kJ/mol _{rxn}) | ΔG_f° (kJ/mol _{rxn}) | S° (J/K • mol _{rxn}) |
|--------------------------|---|---|---------------------------------------|
| $\text{Cu}(s)$ | 0 | 0 | 33.3 |
| $\text{CuO}(s)$ | -155.2 | -127.2 | 43.5 |
| $\text{Cu}_2\text{O}(s)$ | -168.6 | -146.0 | 93.1 |
| $\text{O}_2(s)$ | 0 | 0 | 205 |

and assuming that each species is in its standard state and that the greatest expense in extracting $\text{Cu}(s)$ from an ore is the energy needed to heat the oxide, which ore will you choose? The reactions of interest are



Clearly state the oxide you will use and any restrictions you must place on temperature so your reaction is thermodynamically favorable. In addition to your calculations, explain the reason for your decision in 2–4 sentences.

- This problem is similar to the worksheet on SO_3 in that we are considering two possible reactions and trying to decide which is more favorable as a function of temperature. As we did on that worksheet, we begin by looking at each reaction's T_{crit} to see if that is sufficient to make a decision. To do this we need to calculate each reaction's ΔH° and ΔS° : these are 620.8 kJ/mol_{rxn} and 0.3692 J/K • mol_{rxn} for CuO and 337.2 kJ/mol_{rxn} and 0.1520 J/K • mol_{rxn} for Cu_2O . Given the signs for ΔH° and ΔS° , both reactions are favorable at $T > T_{\text{crit}}$. As T_{crit} is 1680 K for CuO and 2220 K for Cu_2O , we will choose to use CuO . Note that there is no need to consider T_{cross} ; if you do, you will find that at 1310 K CuO becomes more favorable than Cu_2O even though neither is favorable at this temperature. This will guide you to CuO as the proper choice, but still required calculating its T_{crit} . Note that we cannot simply calculate ΔG as we are not interested in its value at any arbitrary temperature, nor is ΔH by itself useful as it is free energy that matters if we want to know that a reaction can happen.

Problem 5. One way to determine the specific heat of a metal is to measure the mass of ice that melts when a sample of the metal at a high temperature cools to the temperature of ice. For example, the following data was determined in one experiment:

mass of metal: 4.35 g

initial temperature of metal: 95.7°C

final temperature of metal and ice: 0°C

mass of liquid water collected: 0.316 g

It will help to know that the heat of formation for $\text{H}_2\text{O}(l)$ is $-285.8 \text{ kJ/mol}_{\text{rxn}}$ and the heat of formation of $\text{H}_2\text{O}(s)$ is $-291.9 \text{ kJ/mol}_{\text{rxn}}$. What is the specific heat of the metal?

- We know that $q_{\text{metal}} = -q_{\text{ice}}$. We also know that $q_{\text{metal}} = mS\Delta T$ as it loses heat through cooling. We also know that there is no temperature change when ice melts, which means we cannot find q_{ice} using $mS\Delta T$. We do know, however, that $\Delta H_{\text{rxn}}^{\circ} = q_{\text{rxn}}/n_{LR} \times \nu_{LR}/\text{mol}_{\text{rxn}}$. We have heats of formation for liquid and solid water, so we can find ΔH° for the melting of ice



which is $6.1 \text{ kJ/mol}_{\text{rxn}}$. This gives

$$(4.35 \text{ g}) \times S \times (0^{\circ}\text{C} - 95.7^{\circ}\text{C}) = -(6100 \text{ J}) \times (0.315 \text{ gH}_2\text{O}(s)/18.02 \text{ g/mol})$$

Solving for S gives its value as $0.257 \text{ J/g} \cdot ^{\circ}\text{C}$.

Problem 6. Consider the following set of standard state reduction reactions and potentials for the halogens

| halogen | reduction reaction | E° (V) |
|----------|--|-----------------|
| fluorine | $\text{F}_2(g) + 2e^{-} \longrightarrow 2\text{F}^{-}(aq)$ | +2.87 |
| chlorine | $\text{Cl}_2(g) + 2e^{-} \longrightarrow 2\text{Cl}^{-}(aq)$ | +1.36 |
| bromine | $\text{Br}_2(l) + 2e^{-} \longrightarrow 2\text{Br}^{-}(aq)$ | +1.07 |
| iodine | $\text{I}_2(s) + 2e^{-} \longrightarrow 2\text{I}^{-}(aq)$ | +0.53 |

Identify the oxidation-reduction reaction between an elemental form of a halogen, such as $\text{Br}_2(l)$, and an anionic form of a halogen, such as $\text{I}^{-}(aq)$, that is the most favorable and determine its value for ΔG° ? Clearly identify the reaction by writing it in the general form of $\text{X}_2 + 2\text{Y}^{-} \longrightarrow 2\text{X}^{-} + \text{Y}_2$. In addition to your calculations, explain the reason for your decision in 1-2 sentences.

- The most favorable oxidation-reduction reaction is the one with the most positive value for E_{rxn}° . This reaction will combine the reaction with the most positive E° for reduction, which is for $\text{F}_2(g)$, with the oxidation reaction that has the least negative E° for oxidation, which is for $\text{I}^{-}(aq)$; thus, the reaction is



for which we have $E_{\text{rxn}}^{\circ} = +2.87 + (-0.53) = 2.34 \text{ V}$. A total of 2 electrons are transferred from 2I^{-} to the F_2 , which gives ΔG° as

$$\Delta G^{\circ} = -nFE_{\text{rxn}}^{\circ} = -2 \times 96458 \times 2.34 = -451500 \text{ J}$$

or $-451.5 \text{ kJ/mol}_{\text{rxn}}$.