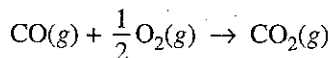


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Question 2

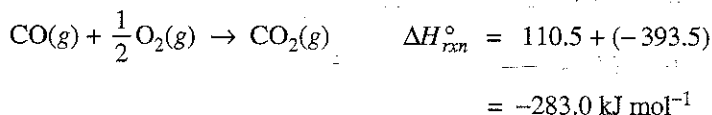


2. The combustion of carbon monoxide is represented by the equation above.

(a) Determine the value of the standard enthalpy change, $\Delta H_{\text{rxn}}^{\circ}$, for the combustion of $\text{CO}(g)$ at 298 K using the following information.



Reverse the first equation and add it to the second equation to obtain the third equation.



OR

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} \text{ of } \text{CO}_2(g) - \Delta H_f^{\circ} \text{ of } \text{CO}(g)$$

$$= -393.5 \text{ kJ mol}^{-1} - (-110.5 \text{ kJ mol}^{-1}) = -283.0 \text{ kJ mol}^{-1}$$

One point is earned for reversing the first equation.

One point is earned for the correct answer (with sign).

OR

Two points are earned for determining $\Delta H_{\text{rxn}}^{\circ}$ from the enthalpies of formation.

(If sign is incorrect, only one point is earned.)

(b) Determine the value of the standard entropy change, $\Delta S_{\text{rxn}}^{\circ}$, for the combustion of $\text{CO}(g)$ at 298 K using the information in the following table.

Substance	S_{298}° ($\text{J mol}^{-1} \text{K}^{-1}$)
CO(g)	197.7
CO ₂ (g)	213.7
O ₂ (g)	205.1

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Question 2 (continued)

$\Delta S_{rxn}^{\circ} = 213.7 \text{ J mol}^{-1} \text{ K}^{-1} - (197.7 \text{ J mol}^{-1} \text{ K}^{-1} + \frac{1}{2}(205.1 \text{ J mol}^{-1} \text{ K}^{-1}))$ $= -86.5 \text{ J mol}^{-1} \text{ K}^{-1}$	<p>One point is earned for taking one-half of S_{298}° for $\text{O}_2(\text{g})$.</p> <p>One point is earned for the answer (with sign).</p>
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- (c) Determine the standard free energy change, ΔG_{rxn}° , for the reaction at 298 K. Include units with your answer.

$\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T \Delta S_{rxn}^{\circ}$ $= -283.0 \text{ kJ mol}^{-1} - (298 \text{ K})(-0.0865 \text{ kJ mol}^{-1} \text{ K}^{-1})$ $\Delta G_{rxn}^{\circ} = -257.2 \text{ kJ mol}^{-1}$	<p>One point is earned for substituting the values from parts (a) and (b) into the equation.</p> <p>One point is earned for the answer (with sign and units).</p>
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- (d) Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.

<p>Yes, the reaction is spontaneous because the value of ΔG_{rxn}° for the reaction is negative ($-257.2 \text{ kJ mol}^{-1}$).</p>	<p>One point is earned for an answer with justification (consistent with the answer in part (c)).</p>
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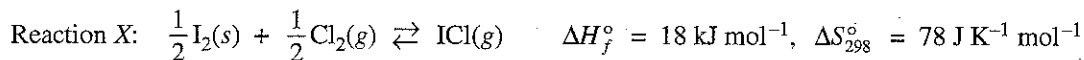
- (e) Calculate the value of the equilibrium constant, K_{eq} , for the reaction at 298 K.

$\Delta G_{rxn}^{\circ} = -RT \ln K_{eq} \Rightarrow \frac{\Delta G_{rxn}^{\circ}}{-RT} = \ln K_{eq}$ $\frac{-257,200 \text{ J mol}^{-1}}{-(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = \ln K_{eq} \Rightarrow K_{eq} = 1.28 \times 10^{45}$	<p>One point is earned for correct substitution into the equation.</p> <p>One point is earned for the answer.</p>
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Question 3

3. Answer the following questions about the thermodynamics of the reactions represented below.



(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}$ <p>Reaction is spontaneous because $\Delta G^\circ < 0$.</p>	<p>One point is earned for the correct value of ΔG°.</p> <p>One point is earned for a correct justification of spontaneity.</p>
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(b) Calculate the value of the equilibrium constant, K_{eq} , for reaction X at 25°C.

$\Delta G^\circ = -RT \ln K_{eq} \Rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT}$ $\ln K_{eq} = -\frac{(-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.019$ $K_{eq} = e^{2.019} = (7.5314) = 8$	<p>One point is earned for the correct answer.</p>
--	--

(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

$\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \Rightarrow \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ <p>Since ΔH° is positive, an increase in T will cause $-\Delta H^\circ/RT$ to become a smaller negative number, therefore K_{eq} will increase.</p> <p>OR</p> <p>The reaction is endothermic ($\Delta H = +18 \text{ kJ mol}^{-1}$); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of K_{eq}.</p>	<p>One point is earned for the correct choice with a correct explanation.</p>
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Question 3 (continued)

- (d) Explain why the standard entropy change is greater for reaction *Y* than for reaction *X*.

<p>Both reaction <i>X</i> and reaction <i>Y</i> have solid iodine as a reactant, but the second reactant in reaction <i>X</i> is chlorine gas whereas the second reactant in reaction <i>Y</i> is liquid bromine. Liquids have lower entropies than gases, thus in reaction <i>Y</i> the reactants are more ordered (and have lower entropies) than in reaction <i>X</i>. The products of both reaction <i>X</i> and reaction <i>Y</i> have about the same disorder, so the <u>change</u> in entropy from reactants to products is greater in reaction <i>Y</i> than in reaction <i>X</i>.</p>	<p>One point is earned for a correct explanation.</p>
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- (e) Above what temperature will the value of the equilibrium constant for reaction *Y* be greater than 1.0? Justify your answer with calculations.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $K_{eq} = 1 \text{ when } \Delta G^\circ = 0 \Rightarrow T\Delta S^\circ = \Delta H^\circ \Rightarrow$ $T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1}\text{K}^{-1}} = 330 \text{ K}$ <p>So when $T > 330 \text{ K}$, $\Delta G^\circ < 0 \text{ kJ mol}^{-1} \Rightarrow K_{eq} > 1.0$</p>	<p>One point is earned for $\Delta G^\circ = 0$.</p> <p>One point is earned for the correct temperature.</p>
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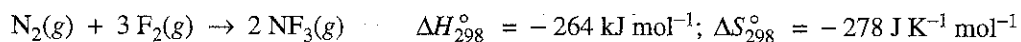
- (f) For the vaporization of solid iodine, $\text{I}_2(s) \rightarrow \text{I}_2(g)$, the value of ΔH_{298}° is 62 kJ mol^{-1} . Using this information, calculate the value of ΔH_{298}° for the reaction represented below.



$\begin{array}{l} \text{I}_2(s) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad \Delta H_{298}^\circ = 2 \times 18 \text{ kJ mol}^{-1} \\ \text{I}_2(g) \rightleftharpoons \text{I}_2(s) \quad \Delta H_{298}^\circ = -62 \text{ kJ mol}^{-1} \\ \hline \text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad \Delta H_{298}^\circ = -26 \text{ kJ mol}^{-1} \end{array}$	<p>One point is earned for ΔH_{298}° of either the first or second equation.</p> <p>One point is earned for the correct sum of the ΔH_{298}° values.</p>
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Question 2



The following questions relate to the synthesis reaction represented by the chemical equation in the box above.

- (a) Calculate the value of the standard free energy change, ΔG_{298}° , for the reaction.

$\begin{aligned} \Delta G_{298}^{\circ} &= \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ} \\ &= -264 \text{ kJ mol}^{-1} - (298 \text{ K})(-0.278 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ &= -181 \text{ kJ mol}^{-1} \end{aligned}$	<p>One point is earned for correct substitution.</p> <p>One point is earned for the value of ΔG_{298}° (including kJ or J).</p>
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- (b) Determine the temperature at which the equilibrium constant, K_{eq} , for the reaction is equal to 1.00. (Assume that ΔH° and ΔS° are independent of temperature.)

<p>When $K_{eq} = 1$, then $\Delta G_T^{\circ} = -RT \ln(1) = 0$</p> <p>If $\Delta G_T^{\circ} = 0$, then $0 = \Delta H^{\circ} - T\Delta S^{\circ} \Rightarrow$</p> $T = \frac{\Delta H_{298}^{\circ}}{\Delta S_{298}^{\circ}}$ $T = \frac{-264 \text{ kJ mol}^{-1}}{-0.278 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 950. \text{ K}$	<p>One point is earned for indicating that if $K_{eq} = 1$, then $\Delta G_T^{\circ} = 0$.</p> <p>One point is earned for the answer (including the unit K).</p>
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- (c) Calculate the standard enthalpy change, ΔH° , that occurs when a 0.256 mol sample of $\text{NF}_3(\text{g})$ is formed from $\text{N}_2(\text{g})$ and $\text{F}_2(\text{g})$ at 1.00 atm and 298 K.

$0.256 \text{ mol NF}_3(\text{g}) \times \frac{-264 \text{ kJ}}{2.00 \text{ mol NF}_3(\text{g})} = -33.8 \text{ kJ}$	<p>One point is earned for multiplying ΔH_{298}° by the number of moles of NF_3 formed.</p> <p>One point is earned for recognizing that 2.00 mol of NF_3 are produced for the reaction as it is written.</p> <p>One point is earned for the answer (including kJ or J).</p>
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Question 2 (continued)

The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and energy released by bond formation in the products.

- (d) How many bonds are formed when two molecules of NF_3 are produced according to the equation in the box above?

There are six N–F bonds formed.	One point is earned for the correct answer.
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- (e) Use both the information in the box above and the table of average bond enthalpies below to calculate the average enthalpy of the F–F bond.

Bond	Average Bond Enthalpy (kJ mol ⁻¹)
N≡N	946
N–F	272
F–F	?

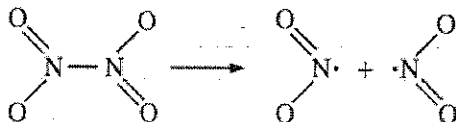
$\begin{aligned} \Delta H_{298}^{\circ} &= \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}} = -264 \text{ kJ mol}^{-1} \\ &= [\text{BE}_{\text{N}\equiv\text{N}} + (3 \times \text{BE}_{\text{F-F}})] - (6 \times \text{BE}_{\text{N-F}}) \\ &= [946 \text{ kJ mol}^{-1} + (3 \times \text{BE}_{\text{F-F}})] - 6(272 \text{ kJ mol}^{-1}) \\ &= -264 \text{ kJ mol}^{-1} \\ \Rightarrow 3 \text{ mol BE}_{\text{F-F}} &= (-264 - 946 + 1,632) \text{ kJ mol}^{-1} \\ \Rightarrow \text{BE}_{\text{F-F}} &= 141 \text{ kJ mol}^{-1} \end{aligned}$	<p>One point is earned for the correct number of bonds in all three compounds multiplied by the average bond enthalpies.</p> <p>One point is earned for the answer (including kJ or J).</p> <p><u>Note:</u> A total of one point is earned if an incorrect number of bonds is substituted in a correct equation and the answer is reasonable (i.e., positive).</p>
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Question 6

Use principles of thermodynamics to answer the following questions.

- (a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



- (i) Predict the sign of ΔH° for the reaction. Justify your answer.

Bonds are broken when NO_2 molecules form from N_2O_4 molecules. Energy must be absorbed to break bonds, so the reaction is endothermic and the sign of ΔH° is positive.

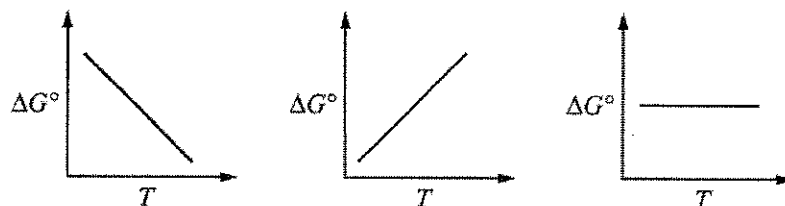
One point is earned for the correct sign and a correct explanation.

- (ii) Predict the sign of ΔS° for the reaction. Justify your answer.

There are two gaseous product molecules for each gaseous reactant molecule, so the product has more entropy than the reactant. The entropy increases as the reaction proceeds, so the sign of ΔS° is positive.

One point is earned for the correct sign and a correct explanation.

- (b) One of the diagrams below best represents the relationship between ΔG° and temperature for the reaction given in part (a). Assume that ΔH° and ΔS° are independent of temperature.



Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The leftmost graph should be circled.

ΔS° is positive, so as T increases, $T\Delta S^\circ$ becomes a larger positive number. At higher temperatures, you are subtracting larger positive numbers from ΔH° to get ΔG° , so ΔG° decreases with increasing temperature.

One point is earned for the correct graph selection.

One point is earned for the explanation.

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Question 6 (continued)

(c) A reaction mixture of N_2O_4 and NO_2 is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of N_2O_4 decreases.

The reaction is endothermic. For endothermic reactions, increasing the temperature drives the reaction to the right. This increases the equilibrium concentration of NO_2 and decreases the equilibrium concentration of N_2O_4 .	One point is earned for the correct explanation.
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(ii) The value of K_{eq} at 25°C is 5.0×10^{-3} . Will the value of K_{eq} at 100°C be greater than, less than, or equal to this value?

Because the reaction is endothermic, at higher temperatures the reaction goes further to the right. This means that the value of K_{eq} at 100°C will be greater than the value of K_{eq} at 25°C .	One point is earned for the correct choice. (No explanation required.)
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(d) Using the value of K_{eq} at 25°C given in part (c)(ii), predict whether the value of ΔH° is expected to be greater than, less than, or equal to the value of $T\Delta S^\circ$. Explain.

K_{eq} at 25°C is less than 1, hence ΔG° must be positive. And in order for ΔG° to be positive, ΔH° must be greater than $T\Delta S^\circ$.	One point is earned for the correct prediction. One point is earned for the explanation.
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Question 5 (8 points)

Reaction	Equation	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
X	$\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$	+131 kJ mol ⁻¹	+134 J mol ⁻¹ K ⁻¹	+91 kJ mol ⁻¹
Y	$\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$	+41 kJ mol ⁻¹	+42 J mol ⁻¹ K ⁻¹	+29 kJ mol ⁻¹
Z	$2 \text{CO}(g) \rightleftharpoons \text{C}(s) + \text{CO}_2(g)$?	?	?

Answer the following questions using the information related to reactions X, Y, and Z in the table above.

- (a) For reaction X, write the expression for the equilibrium constant, K_p .

$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$	One point is earned for the correct expression.
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- (b) For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.

<p>K_p will increase.</p> <p>If the temperature is increased for an endothermic reaction ($\Delta H_{298}^{\circ} = +131 \text{ kJ mol}^{-1}$), then by Le Chatelier's principle the reaction will shift toward products, thereby absorbing energy. With greater concentrations of products at equilibrium, the value of K_p will increase.</p> <p>OR</p> <p>Because $\Delta G^{\circ} = -RT \ln K_p = \Delta H_{298}^{\circ} - T \Delta S_{298}^{\circ}$,</p> <p>then $\ln K_p = -\frac{\Delta H_{298}^{\circ}}{RT} + \frac{\Delta S_{298}^{\circ}}{R}$.</p> <p>An increase in T for a positive ΔH_{298}° results in an increase in $\ln K_p$ and thus an increase in K_p.</p>	<p>One point is earned for the correct answer with appropriate justification.</p>
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Question 5 (continued)

(c) For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.

K_p for reaction Y is less than 1.

For reaction Y, $\Delta G_{298}^{\circ} = +29 \text{ kJ mol}^{-1}$, a positive number.

Because $\Delta G^{\circ} = -RT \ln K$ and ΔG° is positive, then $\ln K_p$ must be negative. This is true when K_p is less than 1.

OR

A positive ΔG° results in a nonspontaneous reaction under standard conditions. This favors reactants over products as equilibrium is approached starting from standard conditions, resulting in a K_p less than 1.

One point is earned for the correct answer with appropriate justification.

(d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

The total bond energy of the reactants is larger.

Reaction Y is endothermic ($\Delta H_{298}^{\circ} = +41 \text{ kJ mol}^{-1} > 0$), so there is a net input of energy as the reaction occurs. Thus, the total energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.

One point is earned for the correct answer with appropriate explanation.

(e) Is the following statement true or false? Justify your answer.

“On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur.”

The statement is false.

Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs.

One point is earned for the correct answer with appropriate justification.

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Question 5 (continued)

(f) Consider reaction Z at 298 K.

(i) Is ΔS° for the reaction positive, negative, or zero? Justify your answer.

<p>ΔS° for reaction Z is negative. In reaction Z, two moles of gas with relatively high entropy are converted into one mole of solid and one mole of gas, a net loss of one mole of gas and thus a net loss in entropy.</p> <p>OR</p> <p>Reaction Z can be obtained by reversing reactions X and Y and adding them together. Thus ΔS° for reaction Z is the sum of two negative numbers and must itself be negative.</p>	<p>One point is earned for the correct answer with an appropriate justification.</p>
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(ii) Determine the value of ΔH° for the reaction.

<p>Add the values of the negatives of ΔH_{298}° for reactions X and Y :</p> $-131 \text{ kJ mol}^{-1} + (-41 \text{ kJ mol}^{-1}) = -172 \text{ kJ mol}^{-1}$	<p>One point is earned for the correct answer.</p>
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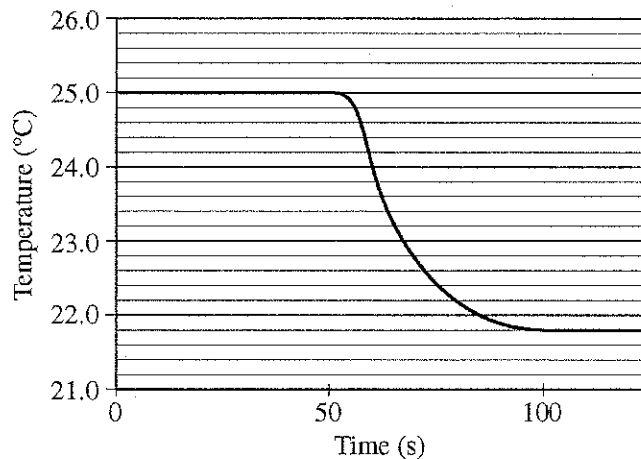
(iii) A sealed glass reaction vessel contains only $\text{CO}(g)$ and a small amount of $\text{C}(s)$. If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

<p>The pressure in the flask decreases.</p> <p>The reaction would proceed to the right, forming more $\text{C}(s)$ and $\text{CO}_2(g)$. Because two moles of $\text{CO}(g)$ would be consumed for every mole of $\text{CO}_2(g)$ that is produced, the total number of moles of gas in the flask would decrease, thereby causing the pressure in the flask to decrease.</p>	<p>One point is earned for the correct answer with an appropriate explanation.</p>
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Question 2
(10 points)

A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2 . The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C , to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.



- (a) Determine the change in temperature of the solution that results from the dissolution of the urea.

$\Delta T = 21.8 - 25.0 = -3.2$ Celsius degrees	One point is earned for the correct temperature change.
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- (b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

The process is endothermic. The decrease in temperature indicates that the process for the dissolution of urea in water requires energy.	One point is earned for the correct choice with justification.
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Question 2 (continued)

(c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is $4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.

Assuming that no heat energy is lost from the calorimeter and given that the calorimeter has a negligible heat capacity, the sum of the heat of dissolution, q_{soln} and the change in heat energy of the urea-water mixture must equal zero.

$$q_{\text{soln}} + mc\Delta T = 0 \Rightarrow q_{\text{soln}} = -mc\Delta T$$

$$m_{\text{soln}} = 5.13 \text{ g} + 91.95 \text{ g} = 97.08 \text{ g}$$

$$q_{\text{soln}} = -(97.08 \text{ g})(4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(-3.2^\circ\text{C}) = 1.3 \times 10^3 \text{ J}$$

One point is earned for the correct setup.

One point is earned for the correct numerical result for the heat of dissolution.

(ii) Calculate the molar enthalpy of solution, $\Delta H_{\text{soln}}^\circ$, of urea in kJ mol^{-1} .

$$\Delta H_{\text{soln}}^\circ = \frac{q_{\text{soln}}}{\text{mol solute}}$$

$$\text{molar mass of urea} = 4(1.0) + 2(14.0) + 12.0 + 16.0 = 60.0 \text{ g mol}^{-1}$$

$$\text{moles of urea} = 5.13 \text{ g urea} \times \frac{1 \text{ mol urea}}{60.0 \text{ g urea}} = 0.0855 \text{ mol}$$

$$\Delta H_{\text{soln}}^\circ = \frac{1.3 \times 10^3 \text{ J}}{0.0855 \text{ mol}} = 1.5 \times 10^4 \text{ J mol}^{-1} = 15 \text{ kJ mol}^{-1}$$

One point is earned for the calculation of moles of urea.

One point is earned for the correct numerical result with correct algebraic sign.

(d) Using the information in the table below, calculate the value of the molar entropy of solution, $\Delta S_{\text{soln}}^\circ$, of urea at 298 K. Include units with your answer.

	Accepted Value
$\Delta H_{\text{soln}}^\circ$ of urea	14.0 kJ mol^{-1}
$\Delta G_{\text{soln}}^\circ$ of urea	-6.9 kJ mol^{-1}

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-6.9 \text{ kJ mol}^{-1} = 14.0 \text{ kJ mol}^{-1} - (298 \text{ K})(\Delta S^\circ)$$

$$\Delta S_{\text{soln}}^\circ = 0.0701 \text{ kJ mol}^{-1} \text{ K}^{-1} = 70.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

One point is earned for the correct setup.

One point is earned for the correct numerical result with correct units.

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Question 2 (continued)

- (e) The student repeats the experiment and this time obtains a result for ΔH_{soln}° of urea that is 11 percent below the accepted value. Calculate the value of ΔH_{soln}° that the student obtained in this second trial.

$\text{Error} = (0.11)(14.0 \text{ kJ mol}^{-1}) = 1.54 \text{ kJ mol}^{-1}$ $14.0 \text{ kJ mol}^{-1} - 1.54 \text{ kJ mol}^{-1} = 12.5 \text{ kJ mol}^{-1}$	One point is earned for the correct numerical result.
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- (f) The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at 5°C. What effect, if any, would using the cold urea instead of urea at 25°C have on the experimentally obtained value of ΔH_{soln}° ? Justify your answer.

There would be an increase in the obtained value for ΔH_{soln}° because the colder urea would have caused a larger negative temperature change.	One point is earned for the correct prediction with justification.
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2011 SCORING GUIDELINES (Form B)

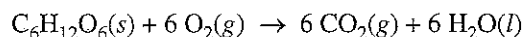
Question 3
(9 points)

Answer the following questions about glucose, $C_6H_{12}O_6$, an important biochemical energy source.

- (a) Write the empirical formula of glucose.

CH_2O	1 point is earned for the correct formula.
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In many organisms, glucose is oxidized to carbon dioxide and water, as represented by the following equation.

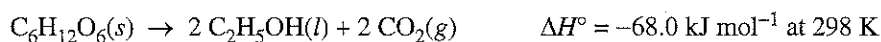


A 2.50 g sample of glucose and an excess of $O_2(g)$ were placed in a calorimeter. After the reaction was initiated and proceeded to completion, the total heat released by the reaction was calculated to be 39.0 kJ.

- (b) Calculate the value of ΔH° , in kJ mol^{-1} , for the combustion of glucose.

$2.50 \text{ g} \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.16 \text{ g } C_6H_{12}O_6} = 0.0139 \text{ mol } C_6H_{12}O_6$ $\frac{-39.0 \text{ kJ}}{0.0139 \text{ mol}} = -2,810 \text{ kJ mol}^{-1}$	1 point is earned for the correct answer.
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- (c) When oxygen is not available, glucose can be oxidized by fermentation. In that process, ethanol and carbon dioxide are produced, as represented by the following equation.



The value of the equilibrium constant, K_p , for the reaction at 298 K is 8.9×10^{39} .

- (i) Calculate the value of the standard free-energy change, ΔG° , for the reaction at 298 K. Include units with your answer.

$\Delta G^\circ = -RT \ln K$ $= -(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})(\ln 8.9 \times 10^{39})$ $= -228,000 \text{ J mol}^{-1} = -228 \text{ kJ mol}^{-1}$	1 point is earned for correct setup. 1 point is earned for correct answer.
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Question 3 (continued)

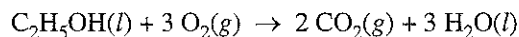
(ii) Calculate the value of the standard entropy change, ΔS° , in $\text{J K}^{-1} \text{mol}^{-1}$, for the reaction at 298 K.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$ $= \frac{(-68.0 \text{ kJ mol}^{-1}) - (-228 \text{ kJ mol}^{-1})}{298 \text{ K}}$ $= 0.537 \text{ kJ K}^{-1} \text{ mol}^{-1} = 537 \text{ J K}^{-1} \text{ mol}^{-1}$	<p>1 point is earned for the correct setup.</p> <p>1 point is earned for the correct answer.</p>
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(iii) Indicate whether the equilibrium constant for the fermentation reaction increases, decreases, or remains the same if the temperature is increased. Justify your answer.

<p>ΔH° is negative, so when the temperature increases, the equilibrium for the reaction is shifted to the left (according to Le Châtelier's principle). This means that the equilibrium constant decreases.</p>	<p>1 point is earned for the correct answer with justification.</p>
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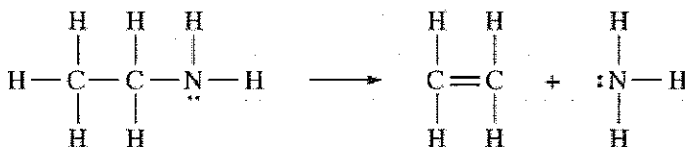
(d) Using your answer for part (b) and the information provided in part (c), calculate the value of ΔH° for the following reaction.



$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -2,810 \text{ kJ mol}^{-1}$ $2 \text{C}_2\text{H}_5\text{OH}(l) + 2 \text{CO}_2(g) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) \quad \Delta H^\circ = 68.0 \text{ kJ mol}^{-1}$	<p>1 point is earned for the correct setup.</p>
<hr style="border: 0.5px solid black;"/> <p>$2 \text{C}_2\text{H}_5\text{OH}(l) + 6 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -2,740 \text{ kJ mol}^{-1}$, thus ΔH° for the reaction as written in (d) is $-1,370 \text{ kJ mol}^{-1}$.</p>	<p>1 point is earned for the correct answer.</p>

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Question 3
(9 points)



A sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, S° , in $\text{J}/(\text{mol}\cdot\text{K})$ at 298 K
$\text{CH}_3\text{CH}_2\text{NH}_2(\text{g})$	284.9
$\text{CH}_2\text{CH}_2(\text{g})$	219.3
$\text{NH}_3(\text{g})$	192.8

- (a) Using the data in the table above, calculate the value, in $\text{J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$, of the standard entropy change, ΔS° , for the reaction at 298 K.

$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$ $\Delta S^\circ_{\text{rxn}} = [(219.3 + 192.8) - 284.9] \text{ J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$ $= 127.2 \text{ J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$	1 point is earned for the correct ΔS° .
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- (b) Using the data in the table below, calculate the value, in $\text{kJ}/\text{mol}_{\text{rxn}}$, of the standard enthalpy change, ΔH° , for the reaction at 298 K.

Bond	C–C	C = C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

$\Delta H^\circ = \text{enthalpy of bonds broken} - \text{enthalpy of bonds formed}$ $\Delta H^\circ = [5(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}}) + 2(\Delta H_{\text{N-H}})] -$ $[4(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C=C}}) + 3(\Delta H_{\text{N-H}})]$ $= [5(413) + 293 + 348 + 2(391)] - [4(413) + 614 + 3(391)] = 49 \text{ kJ}/\text{mol}_{\text{rxn}}$ <p style="text-align: center;">OR</p> $\Delta H^\circ = [(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}})] - [(\Delta H_{\text{C=C}}) + (\Delta H_{\text{N-H}})]$ $= [413 + 293 + 348] \text{ kJ}/\text{mol} - [614 + 391] \text{ kJ}/\text{mol} = 49 \text{ kJ}/\text{mol}_{\text{rxn}}$	<p>1 point is earned for the correct bond count and use of values from table.</p> <p>1 point is earned for the correct setup in terms of bonds broken minus bonds formed and calculated ΔH°.</p>
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Question 3 (continued)

- (c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

The temperature of the contents should decrease because the reaction is endothermic, as indicated by the positive ΔH° .	1 point is earned for the correct choice with explanation.
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An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $\text{CH}_3\text{CH}_2\text{NH}_2$ is found to be 3.60×10^{-4} mol/L.

- (d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.

$\ln[A]_t - \ln[A]_o = -kt$ $\ln\left(3.60 \times 10^{-4} \text{ mol/L}\right) - \ln\left(\frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}}\right) = -k(20.0 \text{ min})$ $-7.929 - (-6.053) = -k(20.0 \text{ min})$ $k = 9.38 \times 10^{-2} \text{ min}^{-1}$	<p>1 point is earned for the initial concentration of $\text{CH}_3\text{CH}_2\text{NH}_2$.</p> <p>1 point is earned for the correct setup of the first order integrated rate law equation.</p> <p>1 point is earned for the calculated result with unit.</p>
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- (e) Calculate the initial rate, in $M \text{ min}^{-1}$, of the reaction at 773 K.

$\text{initial rate} = k[\text{CH}_3\text{CH}_2\text{NH}_2] = (9.38 \times 10^{-2} \text{ min}^{-1})\left(\frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}}\right)$ $= 2.20 \times 10^{-4} M \text{ min}^{-1}$	1 point is earned for the calculated result.
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- (f) If $\frac{1}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

The plot would produce a curve; had the reaction been second order the plot would have been a straight line. A plot of $\ln[\text{CH}_3\text{CH}_2\text{NH}_2]$ vs. t would have yielded a straight line.	1 point is earned for the correct choice with explanation.
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Question 5
(8 points)

Process	ΔH° (kJ/mol _{rxn})
$\text{Br}_2(l) \rightarrow \text{Br}_2(g)$	30.91
$\text{I}_2(s) \rightarrow \text{I}_2(g)$	62.44

At 298 K and 1 atm, the standard state of Br_2 is a liquid, whereas the standard state of I_2 is a solid. The enthalpy changes for the formation of $\text{Br}_2(g)$ and $\text{I}_2(g)$ from these elemental forms at 298 K and 1 atm are given in the table above.

- (a) Explain why ΔH° for the formation of $\text{I}_2(g)$ from $\text{I}_2(s)$ is larger than ΔH° for the formation of $\text{Br}_2(g)$ from $\text{Br}_2(l)$. In your explanation identify the type of particle interactions involved and a reason for the difference in magnitude of those interactions.

<p>Two reasons may be given. The first reason is that London dispersion forces, the only intermolecular forces involved for both of these nonpolar molecules, will be stronger in I_2 because of its greater number of electrons and larger size. The second reason is that since ΔH of sublimation is approximately ΔH of fusion plus ΔH of vaporization, $\text{I}_2(g)$ should have a larger ΔH° of formation since it involves sublimation, whereas $\text{Br}_2(g)$ formation involves only vaporization.</p>	<p>1 point is earned for identifying London dispersion forces.</p> <p>1 point is earned for either of the following: explaining the reason for the greater LDFs in I_2</p> <p>OR</p> <p>stating that the enthalpy change from solid to gas is greater than the enthalpy change from liquid to gas.</p>
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- (b) Predict which of the two processes shown in the table has the greater change in entropy. Justify your prediction.

<p>$\text{I}_2(s) \rightarrow \text{I}_2(g)$ should have the greater change in entropy. The sublimation of I_2 may be thought of as a combination of fusion and vaporization. The conversion from solid to liquid would involve an increase in entropy, as would the conversion from liquid to gas. Br_2 is only undergoing the liquid to gas conversion and so will undergo a smaller entropy increase.</p>	<p>1 point is earned for the correct choice with a correct explanation.</p>
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Question 5 (continued)

- (c) $I_2(s)$ and $Br_2(l)$ can react to form the compound $IBr(l)$. Predict which would have the greater molar enthalpy of vaporization, $IBr(l)$ or $Br_2(l)$. Justify your prediction.

$IBr(l)$. Two reasons may be given. First, IBr is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, IBr should have stronger London dispersion forces because of the greater number of electrons in the larger IBr molecule.

1 point is earned for the correct choice with either or both of the acceptable reasons.

An experiment is performed to compare the solubilities of $I_2(s)$ in different solvents, water and hexane (C_6H_{14}). A student adds 2 mL of H_2O and 2 mL of C_6H_{14} to a test tube. Because H_2O and C_6H_{14} are immiscible, two layers are observed in the test tube. The student drops a small, purple crystal of $I_2(s)$ into the test tube, which is then corked and inverted several times. The C_6H_{14} layer becomes light purple, while the H_2O layer remains virtually colorless.

- (d) Explain why the hexane layer is light purple while the water layer is virtually colorless. Your explanation should reference the relative strengths of interactions between molecules of I_2 and the solvents H_2O and C_6H_{14} , and the reasons for the differences.

The hexane layer is purple because most of the I_2 is dissolved in it. The entrance of the I_2 into water requires disruption of the hydrogen bonds in water, which are much stronger than the London dispersion forces in hexane. Meanwhile, the London dispersion forces between I_2 and hexane would be stronger than the London dispersion forces between I_2 and water. (Water and I_2 can also interact through a dipole-induced dipole force, but this attraction is insufficient to overcome the other differences noted above.)

1 point is earned for recognizing from the experimental observations that the iodine dissolved in the hexane.

1 point is earned for a correct explanation referencing the differences between water and hexane in their interactions with I_2 .

- (e) The student then adds a small crystal of $KI(s)$ to the test tube. The test tube is corked and inverted several times. The I^- ion reacts with I_2 to form the I_3^- ion, a linear species.

- (i) In the box below, draw the complete Lewis electron-dot diagram for the I_3^- ion.



1 point is earned for a correct Lewis diagram.

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Question 5 (continued)

(ii) In which layer, water or hexane, would the concentration of I_3^- be higher? Explain.

I_3^- would be more soluble in water because of the ion-dipole interactions that would occur between the ions and the polar water molecules. No such interactions are possible in the nonpolar hexane.

1 point is earned for the correct choice and explanation.