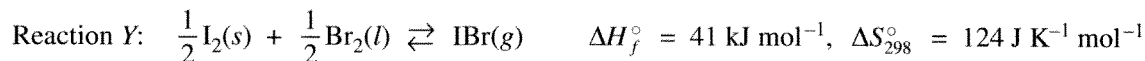


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Question 3

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.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}\end{aligned}$$

Reaction is spontaneous because $\Delta G^\circ < 0$.

One point is earned for the correct value of ΔG° .
 One point is earned for a correct justification of spontaneity.

(b) Calculate the value of the equilibrium constant, K_{eq} , for reaction X at 25°C.

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_{eq} \Rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT} \\ \ln K_{eq} &= -\frac{(-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.019 \\ K_{eq} &= e^{2.019} = (7.5314) = 8\end{aligned}$$

One point is earned for the correct answer.

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

$$\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \Rightarrow \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

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.

OR

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} .

One point is earned for the correct choice with a correct explanation.

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Question 3 (continued)

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

Both reaction *X* and reaction *Y* have solid iodine as a reactant, but the second reactant in reaction *X* is chlorine gas whereas the second reactant in reaction *Y* is liquid bromine. Liquids have lower entropies than gases, thus in reaction *Y* the reactants are more ordered (and have lower entropies) than in reaction *X*. The products of both reaction *X* and reaction *Y* have about the same disorder, so the change in entropy from reactants to products is greater in reaction *Y* than in reaction *X*.

One point is earned for a correct explanation.

(e) Above what temperature will the value of the equilibrium constant for reaction *Y* be greater than 1.0? Justify your answer with calculations.

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

$$K_{eq} = 1 \text{ when } \Delta G^\circ = 0 \Rightarrow T\Delta S^\circ = \Delta H^\circ \Rightarrow$$

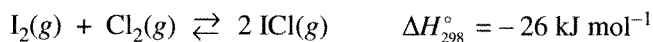
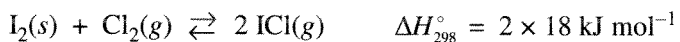
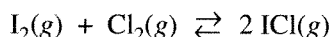
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1}\text{K}^{-1}} = 330 \text{ K}$$

$$\text{So when } T > 330 \text{ K, } \Delta G^\circ < 0 \text{ kJ mol}^{-1} \Rightarrow K_{eq} > 1.0$$

One point is earned for $\Delta G^\circ = 0$.

One point is earned for the correct temperature.

(d) For the vaporization of solid iodine, $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$, the value of ΔH_{298}° is 62 kJ mol^{-1} . Using this information, calculate the value of ΔH_{298}° for the reaction represented below.



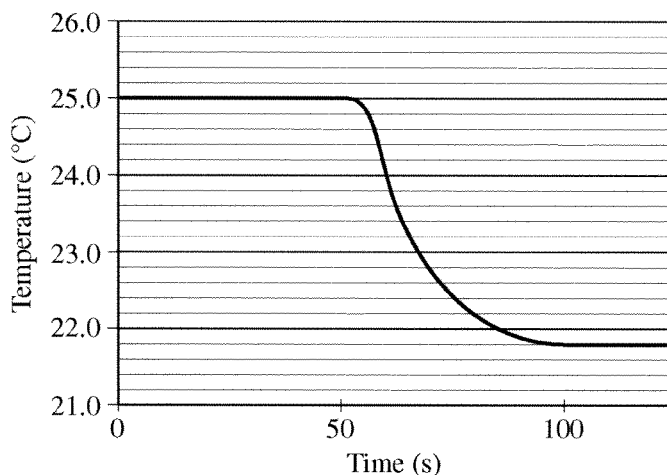
One point is earned for ΔH_{298}° of either the first or second equation.

One point is earned for the correct sum of the ΔH_{298}° values.

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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.

$$\Delta T = 21.8 - 25.0 = -3.2 \text{ Celsius degrees}$$

One point is earned for the correct temperature change.

- (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.

<p>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.</p> $q_{\text{soln}} + mc\Delta T = 0 \Rightarrow q_{\text{soln}} = -mc\Delta T$ $m_{\text{soln}} = 5.13 \text{ g} + 91.95 \text{ g} = 97.08 \text{ g}$ $q_{\text{soln}} = -(97.08 \text{ g})(4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1})(-3.2^{\circ}\text{C}) = 1.3 \times 10^3 \text{ J}$	<p>One point is earned for the correct setup.</p> <p>One point is earned for the correct numerical result for the heat of dissolution.</p>
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(ii) Calculate the molar enthalpy of solution, $\Delta H_{\text{soln}}^{\circ}$, of urea in kJ mol^{-1} .

$\Delta H_{\text{soln}}^{\circ} = \frac{q_{\text{soln}}}{\text{mol solute}}$ <p>molar mass of urea = $4(1.0) + 2(14.0) + 12.0 + 16.0 = 60.0 \text{ g mol}^{-1}$</p> <p>moles of urea = $5.13 \text{ g urea} \times \frac{1 \text{ mol urea}}{60.0 \text{ g urea}} = 0.0855 \text{ mol}$</p> $\Delta H_{\text{soln}}^{\circ} = \frac{1.3 \times 10^3 \text{ J}}{0.0855 \text{ mol}} = 1.5 \times 10^4 \text{ J mol}^{-1} = 15 \text{ kJ mol}^{-1}$	<p>One point is earned for the calculation of moles of urea.</p> <p>One point is earned for the correct numerical result with correct algebraic sign.</p>
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- (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}

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ $-6.9 \text{ kJ mol}^{-1} = 14.0 \text{ kJ mol}^{-1} - (298 \text{ K})(\Delta S^{\circ})$ $\Delta S_{\text{soln}}^{\circ} = 0.0701 \text{ kJ mol}^{-1} \text{ K}^{-1} = 70.1 \text{ J mol}^{-1} \text{ K}^{-1}$	<p>One point is earned for the correct setup.</p> <p>One point is earned for the correct numerical result with correct units.</p>
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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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