Thermodynamics

There always seems to be at least one free response question that involves thermodynamics. These types of question also show up in the multiple choice questions.

- $\Delta G$, $\Delta S$, and $\Delta H$. Know what each of this is, the units associated with each and how to calculate each.
- Calculate all of the functions using Hess’ law
- Use $\Delta G = \Delta H - T\Delta S$
- Know the meaning of the signs of all three functions
- $\Delta G = \Delta G^\circ + RT \ln(Q)$
- $\Delta G = -RT \ln(K)$
- $\Delta G = -nF\varepsilon$
- $\log K = nF/0.0592$
- Lower enthalpy and higher entropy favored in the universe
- Draw energy diagrams for exothermic and endothermic reactions.
- What does it mean when $\Delta G$ is 0? At equilibrium.
- Bond energies: be able to calculate this (reactants – products or break – make)
- Calorimetry. Be able to do calculations involving $q = m \Delta Ts$
The tables above contain information for determining thermodynamic properties of the reaction below:

\[
\text{C}_2\text{H}_5\text{Cl}(g) + \text{Cl}_2(g) \rightarrow \text{C}_2\text{H}_4\text{Cl}_2(g) + \text{HCl}(g)
\]

(a) Calculate the \(\Delta H^\circ\) for the reaction above, using the table of average bond dissociation energies.

(b) Calculate the \(\Delta S^\circ\) for the reaction at 298 K, using data from either table as needed.

(c) Calculate the value of \(K_{eq}\) for the reaction at 298 K.

(d) What is the effect of an increase in temperature on the value of the equilibrium constant? Explain your answer.
#2:

$$\text{BCl}_3(g) + \text{NH}_3(g) \rightleftharpoons \text{Cl}_3\text{BNH}_3(s)$$

The reaction represented above is a reversible reaction.

(a) Predict the sign of the entropy change, $\Delta S$, as the reaction proceeds to the right. Explain your prediction.

(b) If the reaction spontaneously proceeds to the right, predict the sign of the enthalpy change, $\Delta H$. Explain your prediction.

(c) The direction in which the reaction spontaneously proceeds changes as the temperature is increased above a specific temperature. Explain.

#3:

$$\text{Cl}_2(g) + 3 \text{F}_2(g) \rightarrow 2 \text{ClF}_3(g)$$

ClF$_3$ can be prepared by the reaction represented by the equation above. For ClF$_3$ the standard enthalpy of formation, $\Delta H_f^\circ$, is $-163.2$ kilojoules/mole and the standard free energy of formation, $\Delta G_f^\circ$, is $-123.0$ kilojoules/mole.

(a) Calculate the value of the equilibrium constant for the reaction at 298K.

(b) Calculate the standard entropy change, $\Delta S^\circ$, for the reaction at 298K.

(c) If ClF$_3$ were produced as a liquid rather than as a gas, how would the sign and the magnitude of $\Delta S$ for the reaction be affected? Explain.

(d) At 298K the absolute entropies of Cl$_2$(g) and ClF$_3$(g) are 222.96 joules per mole–Kelvin and 281.50 joules per mole–Kelvin, respectively.

(i) Account for the larger entropy of ClF$_3$(g) relative to that of Cl$_2$(g).

(ii) Calculate the value of the absolute entropy of F$_2$(g) at 298K.

#4:

$$2 \text{C}_4\text{H}_{10}(g) + 13 \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 10 \text{H}_2\text{O}(l)$$

The reaction represented above is spontaneous at 25°C. Assume that all reactants and products are in their standard state.

(a) Predict the sign of $\Delta S^\circ$ for the reaction and justify your prediction.

(b) What is the sign of $\Delta G^\circ$ for the reaction? How would the sign and magnitude of $\Delta G^\circ$ be affected by an increase in temperature to 50°C? Explain your answer.

(c) What must be the sign of $\Delta H^\circ$ for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products?

(d) When the reactants are place together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.
#5:

\[ 2 \text{H}_2\text{S}(g) + \text{SO}_2(g) \rightarrow 3 \text{S}(s) + 2 \text{H}_2\text{O}(g) \]

At 298 K, the standard enthalpy change, \(\Delta H^\circ\), for the reaction represented above is \(-145\) kilojoules.

(a) Predict the sign of the standard entropy change, \(\Delta S^\circ\), for the reaction. Explain the basis for your prediction.

(b) At 298 K, the forward reaction \(i.e.,\) toward the right) is spontaneous. What change, if any, would occur in the value of \(\Delta G^\circ\) for this reaction as the temperature is increased? Explain your reasoning using thermodynamic principles.

(c) What change, if any, would occur in the value of the equilibrium constant, \(K_{eq}\), for the situation described in (b)? Explain your reasoning.

(d) The absolute temperature at which the forward reaction becomes nonspontaneous can be predicted. Write the equation that is used to make the prediction. Why does this equation predict only an approximate value for the temperature?

#6:

Propane, \(\text{C}_3\text{H}_8\), is a hydrocarbon that is commonly used as fuel for cooking.

(a) Write a balanced equation for the complete combustion of propane gas, which yields \(\text{CO}_2(g)\) and \(\text{H}_2\text{O}(l)\).

(b) Calculate the volume of air at 30°C and 1.00 atmosphere that is needed to burn completely 10.0 grams of propane. Assume that air is 21.0 percent \(\text{O}_2\) by volume.

(c) The heat of combustion of propane is \(-2,220.1\) kJ/mol. Calculate the heat of formation, \(\Delta H_f^\circ\), of propane given that \(\Delta H_f^\circ\) of \(\text{H}_2\text{O}(l) = -285.3\) kJ/mol and \(\Delta H_f^\circ\) of \(\text{CO}_2(g) = -393.5\) kJ/mol.

(d) Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kilograms of water (specific heat = 4.18 J/g°C), calculate the increase in temperature of water.
#7
Lead iodide is a dense, golden yellow, slightly soluble solid. At 25°C, lead iodide dissolves in water forming a system represented by the following equation.

\[
PbI_2(s) \rightarrow Pb^{2+} + 2 I^- \quad \Delta H = +46.5 \text{ kilojoules}
\]

(a) How does the entropy of the system \( \text{PbI}_2(s) + \text{H}_2\text{O}(l) \) change as \( \text{PbI}_2(s) \) dissolves in water at 25°C? Explain.

(b) If the temperature of the system were lowered from 25°C to 15°C, what would be the effect on the value of \( K_{sp} \)? Explain.

(c) If additional solid \( \text{PbI}_2 \) were added to the system at equilibrium, what would be the effect on the concentration of \( I^- \) in the solution? Explain.

(d) At equilibrium, \( \Delta G = 0 \). What is the initial effect on the value of \( \Delta G \) of adding a small amount of \( \text{Pb(NO}_3)_2 \) to the system at equilibrium? Explain.

#8

\[
C(s) + CO_2(g) \rightleftharpoons 2CO(g)
\]

Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a) Predict the sign for the change in entropy, \( \Delta S \), for the reaction. Justify your prediction.

(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, \( \Delta H \), for the reaction. Justify your predictions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>% CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>60</td>
</tr>
<tr>
<td>850</td>
<td>94</td>
</tr>
</tbody>
</table>

(c) Draw the energy diagram below that accurately depicts this reaction. Clearly indicate \( \Delta H \) for the reaction on the graph.

(d) If the initial amount of \( C(s) \) were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer.
#1 Answer:
(a) \( \Delta H = \text{energy of bonds broken} - \text{energy of bonds formed} \)
\[
\text{C}_2\text{H}_5\text{Cl} + \text{Cl}_2 / \text{C}_2\text{H}_4\text{Cl}_2 + \text{HCl}
\]
\[
\Delta H = (2794 + 243) - (2757 + 431) \text{ kJ} = -151 \text{ kJ}
\]
**OR**
\[
\text{CH} + \text{Cl}–\text{Cl} \rightarrow \text{C}–\text{Cl} + \text{HCl} \quad \text{(representing the changes)}
\]
\[
\Delta H = (414) + 243) - (377 + 431) = -151 \text{ kJ}
\]
(b) \( \Delta G = \sum \Delta G^\circ(\text{products }) - \sum \Delta G^\circ(\text{reactants }) \)
\[
= [-80.3 + (-95.3)] - [-60.5 + 0] = -115 \text{ kJ}
\]
\[
\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-151 - (-115) \text{kJ}}{298 \text{K}} = -0.120 \text{kJ/K}
\]
(c) \( K_{eq} = e^{-\Delta G/RT} = e^{(-115100/(8.3143)(298))} = 1.50 \times 10^{20} \)
(d) \( K_{eq} \) will decrease with an increase in \( T \) because the reverse (endothermic) reaction will be favored with the addition of heat. **OR**
\( \Delta G \) will be less negative with an increase in temperature (from \( \Delta G = \Delta H - T\Delta S \)), which will cause \( K_{eq} \) to decrease.

#2 Answer:
(a) Because a mixture of 2 gases produces a single pure solid, there is an extremely large decrease in entropy, \( \therefore \Delta S < 0 \), i.e. the sign of \( \Delta S \) is negative.
(b) In order for a spontaneous change to occur in the right direction, the enthalpy change must overcome the entropy change which favors the reactants (left), since nature favors a lower enthalpy, then the reaction must be exothermic to the right, \( \therefore \Delta H < 0 \).
(c) \( \Delta G = \Delta H - T\Delta S \), the reaction will change direction when the sign of \( \Delta G \) changes, since \( \Delta H < 0 \) and \( \Delta S < 0 \), then at low temperatures the sign of \( \Delta G \) is negative and spontaneous to the right. At some higher \( T \), \( \Delta H = T\Delta S \) and \( \Delta G = 0 \), thereafter, any higher temperature will see \( \Delta G \) as positive and spontaneous in the left direction.
(d) At equilibrium, \( K = e^{-\Delta G/RT} \), where \( \Delta G = 0 \), \( K = e^0 = 1 \)
**#3 Answer:**

(a) \( K_{eq} = e^{-\Delta G/RT} = e^{-(–246000/(8.3143)(298))} = 1.32 \times 10^{43} \)

(b) \( \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{[–326400 - (–246000)]}{298K} = -270 \text{J/K} \)

(c) \( \Delta S \) is a larger negative number. ClF\(_3\)(l) is more ordered (less disordered) than ClF\(_3\)(g).

(d) Entropy of ClF\(_3\) > entropy of Cl\(_2\) because

   i) 1) larger number of atoms **OR**
   2) more complex particle **OR**
   3) more degrees of freedom

   ii) \( \Delta S = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \)

   \( -270 = [2(281.5)] - [222.96 + 3(S^\circ_{F_2})] \)

   \( S^\circ_{F_2} = 203 \text{J/mol.K} \)

**#4 Answer:**

(a) \( \Delta S < 0 \). The number of moles of gaseous products is less than the number of moles of gaseous reactants. OR A liquid is formed from gaseous reactants.

(b) \( \Delta G < 0 \). \( \Delta G \) becomes less negative as the temperature is increased since \( \Delta S < 0 \) and \( \Delta G = \Delta H - T \Delta S \). The term “–T\( \Delta S \)” adds a positive number to \( \Delta H \).

(c) \( \Delta H < 0 \). The bond energy of the reactants is less than the bond energy of the products.

(d) The reaction has a high activation energy; OR is kinetically slow; OR a specific mention of the need for a catalyst or spark.

**#5 Answer:**

(a) \( \Delta S^* \) is negative (–). A high entropy mixture of two kinds of gases forms into a low entropy solid and a pure gas; 3 molecules of gas makes 2 molecules of gas, fewer gas molecules is at a lower entropy.

(b) \( \Delta G^* < 0 \) if spontaneous. \( \Delta G^* = \Delta H^* - T\Delta S^* \). Since \( \Delta S^* \) is neg. (–), as \( T \) gets larger, \(-T\Delta S^* \) will become larger than \(+145 \text{kJ} \) and the sign of \( \Delta G^* \) becomes pos. (+) and the reaction is non–spontaneous.

(c) When \(-T\Delta S^* < +145 \text{kJ} \), \( K_{eq} > 1 \),

   when \(-T\Delta S^* = +145 \text{kJ} \), \( K_{eq} = 1 \),

   when \(-T\Delta S^* > +145 \text{kJ} \), \( K_{eq} < 1 \), but \( > 0 \)

(d) \( \Delta G = 0 \) at this point, the equation is \( T = \frac{\Delta H^*}{\Delta S^*} \); this assumes that \( \Delta H \) and/or \( S \) do not change with temperature; not a perfect assumption leading to errors in the calculation.
#6 Answer:
(a) \( C_3H_8 + 5 O_2 \rightarrow 3 CO_2 + 4 H_2O \)

(b) \( 10.0 \text{ g } C_3H_8 \times \frac{1 \text{ mol } C_3H_8}{44.0 \text{ g}} \times \frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} = \)

\( = 1.14 \text{ mol } O_2 \)

\[ V_{O_2} = \frac{nRT}{P} = \frac{(1.14 \text{ mol})(0.0821 \frac{L \cdot atm}{mol \cdot K})(303K)}{1.00 \text{ atm}} \]

\( = 28.3 \text{ L } O_2 ; \frac{28.3 \text{ L}}{21.0\%} = 135 \text{ L of air} \)

(c) \( \Delta H^o_{comb} = \left[ \Delta H^o_{f(CO_2)} + \Delta H^o_{f(H_2O)} \right] - \left[ \Delta H^o_{f(C_3H_8)} + \Delta H^o_{f(O_2)} \right] \)

\( -2220.1 = [3(-393.5) + 4(-285.3)] - [X + 0] \)

\( X = \Delta H^o_{comb} = -101.7 \text{ kJ/mol} \)

(d) \( q = 30.0 \text{ g } C_3H_8 \times \frac{1 \text{ mol}}{44.0 \text{ g}} \times \frac{2220.1 \text{ kJ}}{1 \text{ mol}} = 1514 \text{ kJ} \)

\( q = (m)(C_p)(\Delta T) \)

\( 1514 \text{ kJ} = (8.00 \text{ kg})(4.18 \text{ J/g-K})(\Delta T) \)

\( \Delta T = 45.3^\circ \)

#7 Answer:
(a) Entropy increases. At the same temperature, liquids and solids have a much lower entropy than do aqueous ions. Ions in solutions have much greater “degrees of freedom and randomness”.

(b) \( K_{sp} \) value decreases. \( K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 \). As the temperature is decreased, the rate of the forward (endothermic) reaction decreases resulting in a net decrease in ion concentration which produces a smaller \( K_{sp} \) value.

(c) No effect. The addition of more solid \( \text{PbI}_2 \) does not change the concentration of the \( \text{PbI}_2 \) which is a constant (at constant temperature), therefore, neither the rate of the forward nor reverse reaction is affected and the concentration of iodide ions remains the same.

(d) \( \Delta G \) increases. Increasing the concentration of \( \text{Pb}^{2+} \) ions causes a spontaneous increase in the reverse reaction rate (a “shift left” according to LeChatlier's Principle). A reverse reaction is spontaneous when the \( \Delta G > 0 \).