8

Thermodynamics

HOW OFTEN DOES THERMODYNAMICS APPEAR ON THE EXAM?

In the multiple-choice section, this topic appears in about 5 out of 75 questions. In the free-response section, this topic appears every year.

THE FIRST AND SECOND LAWS OF THERMODYNAMICS

The first law of thermodynamics says that the energy of the universe is constant. Energy can be neither created nor destroyed, so while energy can be *converted* in a chemical process, the total energy remains constant.

The second law of thermodynamics says that if a process is spontaneous in one direction, then it can't be spontaneous in the reverse direction, and that the entropy of the universe always increases during spontaneous reactions.

STATE FUNCTIONS

Enthalpy change (ΔH), entropy change (ΔS), and free-energy change (ΔG) are **state functions.** That means they all depend only on the change between the initial and final states of a system, not on the process by which the change occurs. For a chemical reaction, this means that the thermodynamic state functions are independent of reaction pathway; for instance, the addition of a catalyst to a reaction will have no effect on the overall energy or entropy change of the reaction.

STANDARD STATE CONDITIONS

When the values of thermodynamic quantities are given on the test, they are almost always given for standard state conditions. A thermodynamic quantity under standard state conditions is indicated by the little superscript circle, so the following is true under standard state conditions:

$$\Delta H = \Delta H°$$
$$\Delta S = \Delta S°$$
$$\Delta G = \Delta G°$$

Standard State Conditions

- All gases are at 1 atmosphere pressure.
- All liquids are pure.
- All solids are pure.
- All solutions are at 1-molar (1 M) concentration.
- The energy of formation of an element in its normal state is defined as zero.
- The temperature used for standard state values is almost invariably room temperature: 25°C (298 K). Standard state values can be calculated for other temperatures, however.

ENTHALPY

ENTHALPY CHANGE, ΔH

The enthalpy of a substance is a measure of the energy that is released or absorbed by the substance when bonds are broken and formed during a reaction.

The Basic Rules of Enthalpy
When bonds are *formed*, energy is *released*.
When bonds are *broken*, energy is *absorbed*.

The change in enthalpy, ΔH, that takes place over the course of a reaction can be calculated by subtracting the enthalpy of the reactants from the enthalpy of the products.

Enthalpy Change
$$\Delta H = H_{products} - H_{reactants}$$

If the products have stronger bonds than the reactants, then the products have lower enthalpy than the reactants and are more stable; in this case, energy is released by the reaction, which is **exothermic.**

If the products have weaker bonds than the reactants, then the products have higher enthalpy than the reactants and are less stable; in this case, energy is absorbed by the reaction, which is **endothermic.**

All substances like to be in the lowest possible energy state, which gives them the greatest stability. This means that, in general, exothermic processes are more likely to occur spontaneously than endothermic processes.

HEAT OF FORMATION, ΔH_f°

Heat of formation is the change in energy that takes place when one mole of a compound is formed from its component pure elements under standard state conditions. Heat of formation is almost always calculated at a temperature of 25°C (298 K).

Remember, ΔH_f° for a pure element is defined as zero.

- If ΔH_f° for a compound is negative, energy is released when the compound is formed from pure elements, and the product is *more* stable than its constituent elements. That is, the process is exothermic.

- If ΔH_f° for a compound is positive, energy is absorbed when the compound is formed from pure elements, and the product is *less* stable than its constituent elements. That is, the process is endothermic.

If the ΔH_f° values of the products and reactants are known, ΔH for a reaction can be calculated.

$$\Delta H^\circ = \Sigma\, \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants}$$

Let's find ΔH° for the reaction below.

$$2\, CH_3OH(g) + 3\, O_2(g) \rightarrow 2\, CO_2(g) + 4\, H_2O(g)$$
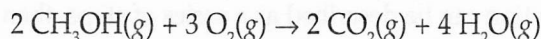
Compound	ΔH° (kJ/mol)
$CH_3OH(g)$	−201
$O_2(g)$	0
$CO_2(g)$	−394
$H_2O(g)$	−242

$\Delta H^\circ = \Sigma\, \Delta H_f^\circ \text{ products} - \Sigma\, \Delta H_f^\circ \text{ reactants}$

$\Delta H^\circ = [(2)(\Delta H_f^\circ\, CO_2) + (4)(\Delta H_f^\circ\, H_2O)] - [(2)(\Delta H_f^\circ\, CH_3OH) + (3)(\Delta H_f^\circ\, O_2)]$

$\Delta H^\circ = [(2)(-394\ kJ) + (4)(-242\ kJ)] - [(2)(-201\ kJ) + (3)(0\ kJ)]$

$\Delta H^\circ = (-1{,}756\ kJ) - (-402\ kJ)$

$\Delta H^\circ = -1{,}354\ kJ$

BOND ENERGY

Bond energy is the energy required to break a bond. Because the breaking of a bond is an endothermic process, bond energy is always a positive number. When a bond is formed, energy equal to the bond energy is released.

$$\Delta H° = \Sigma \text{ Bond energies of bonds broken} - \Sigma \text{ Bond energies of bonds formed}$$

The bonds broken will be the reactant bonds, and the bonds formed will be the product bonds. Let's find $\Delta H°$ for the reaction below.

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$
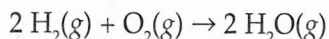
Bond	Bond Energy (kJ/mol)
H–H	436
O=O	499
O–H	463

$\Delta H° = \Sigma$ Bond energies of bonds broken $- \Sigma$ Bond energies of bonds formed
$\Delta H° = [(2)(H–H) + (1)(O=O)] – [(4)(O–H)]$
$\Delta H° = [(2)(436 \text{ kJ}) + (1)(499 \text{ kJ})] – [(4)(463 \text{ kJ})]$
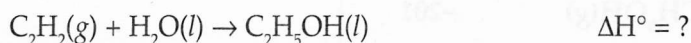$\Delta H° = (1,371 \text{ kJ}) – (1,852 \text{ kJ})$
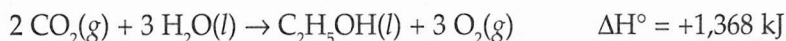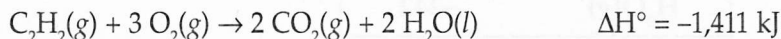$\Delta H° = –481 \text{ kJ}$

HESS'S LAW

Hess's law says that if a reaction can be described as a series of steps, then ΔH for the overall reaction is simply the sum of the ΔH values for all the steps.

For example, let's say you wanted to calculate the enthalpy change for the following reaction:

$$C_2H_2(g) + H_2O(l) \rightarrow C_2H_5OH(l) \qquad\qquad \Delta H° = ?$$

And let's say that you know the enthalpy changes for the following two reactions:

$$C_2H_2(g) + 3 O_2(g) \rightarrow 2 CO_2(g) + 2 H_2O(l) \qquad \Delta H° = –1,411 \text{ kJ}$$

$$2 CO_2(g) + 3 H_2O(l) \rightarrow C_2H_5OH(l) + 3 O_2(g) \qquad \Delta H° = +1,368 \text{ kJ}$$

If you add the two reactions whose enthalpy changes you know (as though they were simultaneous equations) and cancel the substances that appear on both sides, you'll get the reaction that you're looking for. This means that you can add the enthalpy changes for the reactions that you know to get the enthalpy change that you're looking for.

$$–1,411 \text{ kJ} + 1,368 \text{ kJ} = –43 \text{ kJ}$$

HEAT CAPACITY AND SPECIFIC HEAT

Heat capacity, C_p, is a measure of how much the temperature of an object is raised when it absorbs heat.

Heat Capacity
$$C_p = \frac{\Delta H}{\Delta T}$$
C_p = heat capacity ΔH = heat added (J or cal) ΔT = temperature change (K or °C)

An object with a large heat capacity can absorb a lot of heat without undergoing much of a change in temperature, whereas an object with a small heat capacity shows a large increase in temperature even if only a small amount of heat is absorbed.

Specific heat is the amount of heat required to raise the temperature of one gram of a substance one degree Celsius.

Specific Heat
$$q = mc\Delta T$$
q = heat added (J or cal) m = mass of the substance (g or kg) c = specific heat ΔT = temperature change (K or °C)

ENTROPY

The entropy, S, of a system is a measure of the randomness or disorder of the system; the greater the disorder of a system, the greater its entropy. Because zero entropy is defined as a solid crystal at 0 K, all substances that we encounter will have some positive value for entropy. Standard entropies, $S°$, are calculated at 25°C (298 K).

You should be familiar with several simple rules concerning entropies.

- Liquids have higher entropy values than solids.
- Gases have higher entropy values than liquids.
- Particles in solution have higher entropy values than solids.
- Two moles of a substance have higher entropy value than one mole.

ENTROPY CHANGE, $\Delta S°$

The standard entropy change, $\Delta S°$, that has taken place at the completion of a reaction is the difference between the standard entropies of the products and the standard entropies of the reactants.

$$\Delta S° = \Sigma\ S°_{products} - \Sigma\ S°_{reactants}$$

GIBBS FREE ENERGY

The **Gibbs free energy**, or simply free energy, G, of a process is a measure of the spontaneity of the process.

For a given reaction

- if ΔG is negative, the reaction is spontaneous

- if ΔG is positive, the reaction is not spontaneous

- if $\Delta G = 0$, the reaction is at equilibrium

FREE ENERGY CHANGE, ΔG

The standard free energy change, ΔG, for a reaction can be calculated from the standard free energies of formation, ΔG_f°, of its products and reactants in the same way that ΔS° was calculated.

$$\Delta G^\circ = \Sigma\ \Delta G_{f\ products}^\circ - \Sigma\ \Delta G_{f\ reactants}^\circ$$

ΔG, ΔH, AND ΔS

In general, nature likes to move toward two different and seemingly contradictory states—low energy and high disorder, so spontaneous processes must result in decreasing enthalpy or increasing entropy or both.

There is an important equation that relates spontaneity (ΔG), enthalpy (ΔH), and entropy (ΔS) to one another.

$$\Delta G^o = \Delta H^\circ - T\Delta S^\circ$$
T = absolute temperature (K)

The chart below shows how different values of enthalpy and entropy affect spontaneity.

ΔH	ΔS	T	ΔG	
−	+	Low	−	Always spontaneous
		High	−	
+	−	Low	+	Never spontaneous
		High	+	
+	+	Low	+	Not spontaneous at low temperature
		High	−	Spontaneous at high temperature
−	−	Low	−	Spontaneous at low temperature
		High	+	Not spontaneous at high temperature

You should note that at low temperature, enthalpy is dominant, while at high temperature, entropy is dominant.

ΔG AND $\Delta G°$

The standard free energy change, $\Delta G°$, gives the spontaneity of a reaction when all the concentrations of reactants and products are in their standard state concentrations (at 1 molar). The free energy change, and thus the spontaneity, of a reaction will be different from the standard free energy change if the initial concentrations of reactants and products are not 1 molar.

The standard free energy change, $\Delta G°$, can be related to ΔG for other conditions by the following equations:

$$\Delta G = \Delta G° + RT \ln Q$$
$$\text{or}$$
$$\Delta G = \Delta G° + 2.303RT \log Q$$

$\Delta G° =$ standard free energy change (J)
$\Delta G =$ free energy change under given initial conditions (J)
$R \quad =$ the gas constant, 8.31 J/mol-K
$T \quad =$ absolute temperature (K)
$Q \quad =$ the reaction quotient for the given initial conditions

STANDARD FREE ENERGY CHANGE AND THE EQUILIBRIUM CONSTANT

Let's look at the equation relating ΔG and $\Delta G°$.

$$\Delta G = \Delta G° + RT \ln Q$$
$$\text{At equilibrium, } \Delta G = 0 \text{ and } Q = K.$$

Knowing this, we can derive an equation relating the standard free energy change, $\Delta G°$, and the equilibrium constant, K.

$$\Delta G° = -RT \ln K$$
$$\text{or}$$
$$\Delta G° = -2.303RT \log K$$

$\Delta G° =$ the gas constant, 8.31 J/mol-K
$T \quad =$ absolute temperature (K)
$K \quad =$ the equilibrium constant

Notice that if $\Delta G°$ is negative, K must be greater than 1, and products will be favored at equilibrium. Alternatively, if $\Delta G°$ is positive, K must be less than 1, and reactants will be favored at equilibrium.
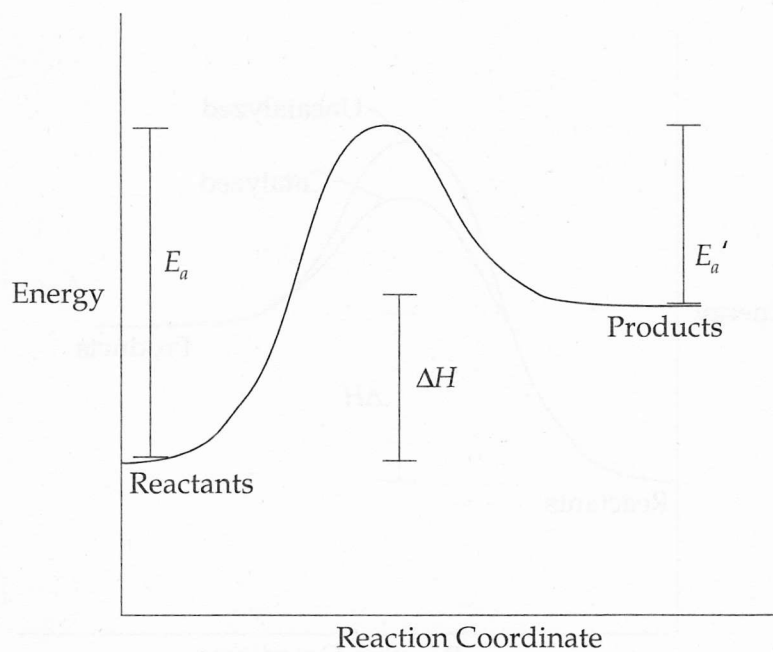
ENERGY DIAGRAMS
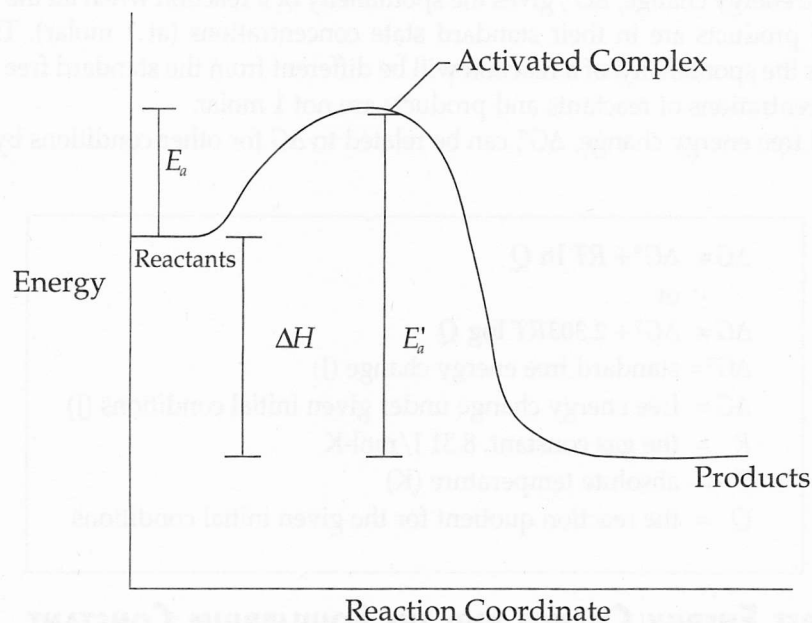
EXOTHERMIC REACTION

The diagram above shows the energy change that takes place during an exothermic reaction. The reactants start with a certain amount of energy (read the graph from left to right). For the reaction to proceed, the reactants must have enough energy to reach the transition state, where they are part of an activated complex. This is the highest point on the graph above. The amount of energy needed to reach this point is called the **activation energy, E_a**. At this point, all reactant bonds have been broken, but no product bonds have been formed, so this is the point in the reaction with the highest energy and lowest stability. The energy needed for the reverse reaction is shown as line E_a'.

Moving to the right past the activated complex, product bonds start to form, and we eventually reach the energy level of the products.

This diagram represents an exothermic reaction, so the products are at a lower energy level than the reactants and ΔH is negative.

The diagram below shows an endothermic reaction.

Energy $\quad$ E_a

$E_a{}'$

Products

ΔH

Reactants
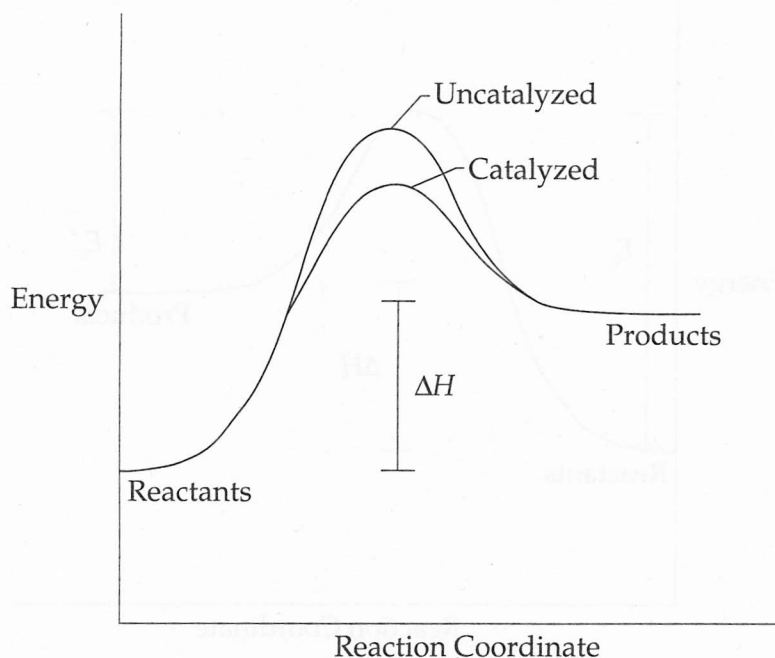
Reaction Coordinate

ENDOTHERMIC REACTION

In this diagram, the energy of the products is greater than the energy of the reactants, so ΔH is positive.
    Reaction diagrams can be read in both directions, so the reverse reaction for an exothermic reaction is endothermic and vice versa.

CATALYSTS AND ENERGY DIAGRAMS

A catalyst speeds up a reaction by providing the reactants with an alternate pathway that has a lower activation energy, as shown in the diagram above.

Notice that the only difference between the catalyzed reaction and the uncatalyzed reaction is that the energy of the activated complex is lower for the catalyzed reaction. A catalyst lowers the activation energy, but it has no effect on the energy of the reactants, the energy of the products, or ΔH for the reaction.

Also note that a catalyst lowers the activation energy for both the forward and the reverse reaction, so it has no effect on the equilibrium conditions.

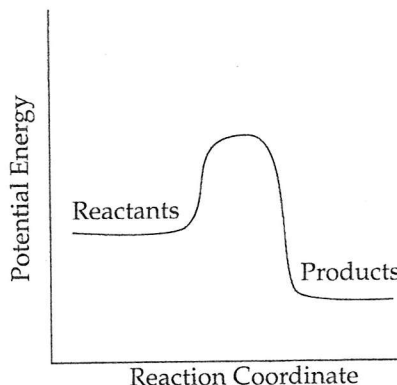# CHAPTER 8 QUESTIONS

MULTIPLE-CHOICE QUESTIONS

Questions 1–4

    (A) Free energy change (ΔG)
    (B) Entropy change (ΔS)
    (C) Heat of vaporization
    (D) Heat of fusion
    (E) Heat capacity

1. If this has a negative value for a process, then the process occurs spontaneously.

2. This is a measure of how the disorder of a system is changing.

3. This is the energy given off when a substance condenses.

4. This is the energy taken in by a substance when it melts.

5. $2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$
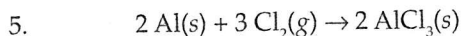
The reaction above is not spontaneous under standard conditions, but becomes spontaneous as the temperature decreases toward absolute zero. Which of the following is true at standard conditions?

    (A) ΔS and ΔH are both negative.
    (B) ΔS and ΔH are both positive.
    (C) ΔS is negative, and ΔH is positive.
    (D) ΔS is positive, and ΔH is negative.
    (E) ΔS and ΔH are both equal to zero.

6.

Which of the following is true of the reaction shown in the diagram above?

    (A) The reaction is endothermic because the reactants are at a higher energy level than the products.
    (B) The reaction is endothermic because the reactants are at a lower energy level than the products.
    (C) The reaction is exothermic because the reactants are at a higher energy level than the products.
    (D) The reaction is exothermic because the reactants are at a lower energy level than the products.
    (E) The reaction is endothermic because the reactants are at the same energy level as the products.

7.
$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$
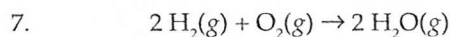
Based on the information given in the table below, what is $\Delta H°$ for the above reaction?

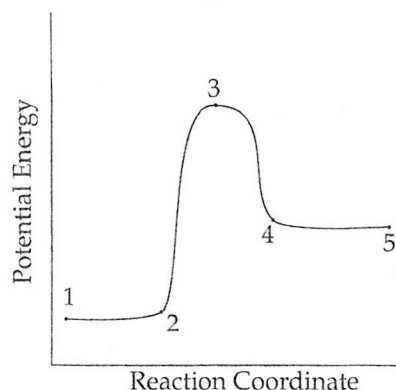| Bond	Average bond energy (kJ/mol)
H–H	500
O=O	500
O–H	500

(A) −2,000 kJ
(B) −1,500 kJ
(C) −500 kJ
(D) +1,000 kJ
(E) +2,000 kJ

8. Which of the following is true of a reaction that is spontaneous at 298 K but becomes nonspontaneous at a higher temperature?

(A) $\Delta S°$ and $\Delta H°$ are both negative.
(B) $\Delta S°$ and $\Delta H°$ are both positive.
(C) $\Delta S°$ is negative, and $\Delta H°$ is positive.
(D) $\Delta S°$ is positive, and $\Delta H°$ is negative.
(E) $\Delta S°$ and $\Delta H°$ are both equal to zero.

9. Which of the following will be true when a pure substance in liquid phase freezes spontaneously?

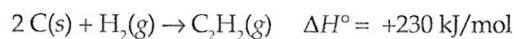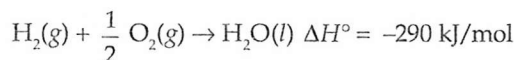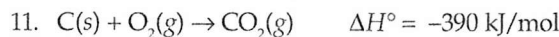(A) ΔG, ΔH, and ΔS are all positive.
(B) ΔG, ΔH, and ΔS are all negative.
(C) ΔG and ΔH are negative, but ΔS is positive.
(D) ΔG and ΔS are negative, but ΔH is positive.
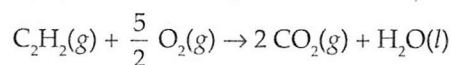(E) ΔS and ΔH are negative, but ΔG is positive.

10.

Reaction Coordinate

Which point on the graph shown above corresponds to activated complex or transition state?

(A) 1
(B) 2
(C) 3
(D) 4
(E) 5

11. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H° = -390$ kJ/mol

$H_2(g) + \dfrac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta H° = -290$ kJ/mol

$2 C(s) + H_2(g) \rightarrow C_2H_2(g)$ $\quad \Delta H° = +230$ kJ/mol

Based on the information given above, what is $\Delta H°$ for the following reaction?

$$C_2H_2(g) + \dfrac{5}{2} O_2(g) \rightarrow 2 CO_2(g) + H_2O(l)$$

(A) −1,300 kJ
(B) −1,070 kJ
(C) −840 kJ
(D) −780 kJ
(E) −680 kJ

12. If an endothermic reaction is spontaneous at 298 K, which of the following must be true for the reaction?

    I. ΔG is greater than zero.
    II. ΔH is greater than zero.
    III. ΔS is greater than zero.

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

13. The addition of a catalyst will have which of the following effects on a chemical reaction?

    I. The enthalpy change will decrease.
    II. The entropy change will decrease.
    III. The activation energy will decrease.

(A) I only
(B) II only
(C) III only
(D) I and II only
(E) II and III only

14. $C(s) + 2\,H_2(g) \rightarrow CH_4(g)$ $\Delta H° = x$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = y$

$H_2(g) + \dfrac{1}{2}\,O_2(g) \rightarrow H_2O(l)$ $\Delta H° = z$

Based on the information given above, what is $\Delta H°$ for the following reaction?

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$

(A) $x + y + z$
(B) $x + y - z$
(C) $z + y - 2x$
(D) $2z + y - x$
(E) $2z + y - 2x$

15. For which of the following processes will ΔS be positive?

    I. $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
    II. $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$
    III. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(A) I only
(B) II only
(C) I and II only
(D) I and III only
(E) I, II, and III

16. In which of the following reactions is entropy increasing?

(A) $2\,SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g)$
(B) $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$
(C) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$
(D) $2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$
(E) $2\,H_2S(g) + 3\,O_2(g) \rightarrow 2\,H_2O(g) + 2\,SO_2(g)$

17. When pure sodium is placed in an atmosphere of chlorine gas, the following spontaneous reaction occurs.

$2\,Na(s) + Cl_2(g) \rightarrow 2\,NaCl(s)$

Which of the following statements is true about the reaction?

    I. $\Delta S > 0$
    II. $\Delta H < 0$
    III. $\Delta G > 0$

(A) I only
(B) II only
(C) I and II only
(D) II and III only
(E) I, II, and III

18. $H_2(g) + F_2(g) \rightarrow 2 \, HF(g)$
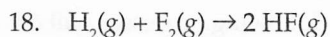
Gaseous hydrogen and fluorine combine in the reaction above to form hydrogen fluoride with an enthalpy change of –540 kJ. What is the value of the heat of formation of $HF(g)$?
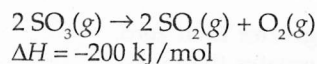
(A) –1,080 kJ/mol
(B) –540 kJ/mol
(C) –270 kJ/mol
(D) 270 kJ/mol
(E) 540 kJ/mol

19. $H_2O(s) \rightarrow H_2O(l)$
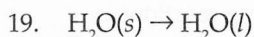
Which of the following is true of the reaction shown above at room temperature?

I. ΔG is greater than zero.
II. ΔH is greater than zero.
III. ΔS is greater than zero.

(A) II only
(B) III only
(C) I and II only
(D) I and III only
(E) II and III only
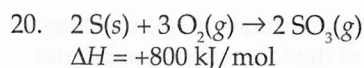
20. $2 \, S(s) + 3 \, O_2(g) \rightarrow 2 \, SO_3(g)$
$\Delta H = +800 \text{ kJ/mol}$

$2 \, SO_3(g) \rightarrow 2 \, SO_2(g) + O_2(g)$
$\Delta H = –200 \text{ kJ/mol}$

Based on the information given above, what is ΔH for the following reaction?

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
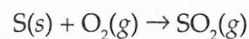
(A) 300 kJ
(B) 500 kJ
(C) 600 kJ
(D) 1,000 kJ
(E) 1,200 kJ

PROBLEMS

1.

Substance	Absolute Entropy, S° (J/mol-K)	Molecular Weight
$C_6H_{12}O_6$ (s)	212.13	180
O_2 (g)	205	32
CO_2 (g)	213.6	44
H_2O (l)	69.9	18

Energy is released when glucose is oxidized in the following reaction, which is a metabolism reaction that takes place in the body.
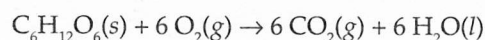
$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$$

The standard enthalpy change, $\Delta H°$, for the reaction is –2,801 kJ at 298 K.

(a)   Calculate the standard entropy change, $\Delta S°$, for the oxidation of glucose.

(b)   Calculate the standard free energy change, $\Delta G°$, for the reaction at 298 K.

(c)   What is the value of K_{eq} for the reaction?

(d)   How much energy is given off by the oxidation of 1.00 gram of glucose?

2.

Bond	Average Bond Dissociation Energy (kJ/mol)
C–H	415
O=O	495
C=O	799
O–H	463

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$
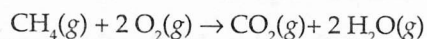
The standard free energy change, $\Delta G°$, for the reaction above is –801 kJ at 298 K.

(a)   Use the table of bond dissociation energies to find $\Delta H°$ for the reaction above.

(b)   What is the value of K_{eq} for the reaction?

(c)   What is the value of $\Delta S°$ for the reaction at 298 K?

(d)   Give an explanation for the size of the entropy change found in (c).

3.
$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

The heat of formation, ΔH_f°, of $NH_3(g)$ is – 46.2 kJ/mol. The free energy of formation, ΔG_f°, of $NH_3(g)$ is –16.7 kJ/mol.

(a)   What are the values of ΔH° and ΔG° for the reaction?

(b)   What is the value of the entropy change, ΔS°, for the reaction above at 298 K?

(c)   As the temperature is increased, what is the effect on ΔG for the reaction? How does this affect the spontaneity of the reaction?

(d)   At what temperature can N_2, H_2, and NH_3 gases be maintained together in equilibrium, each with a partial pressure of 1 atm?

Essays

4.
$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$$

The reaction above proceeds spontaneously from standard conditions at 298 K.

(a)   Predict the sign of the entropy change, ΔS°, for the reaction. Explain.

(b)   How would the value of ΔS° for the reaction change if the product of the reaction was $H_2O(g)$?

(c)   What is the sign of ΔG° at 298 K? Explain.

(d)   What is the sign of ΔH° at 298 K? Explain.

5.
$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$

The reaction above is spontaneous at 298 K, and the heat of reaction, ΔH°, is –178 kJ.

(a)   Predict the sign of the entropy change, ΔS°, for the reaction. Explain.

(b)   What is the sign of ΔG° at 298 K? Explain.

(c)   What change, if any, occurs to the value of ΔG° as the temperature is increased from 298 K?

(d)   As the reaction takes place in a closed container, what changes will occur in the concentration of CO_2 and the temperature?

6.
$$H_2O(l) \rightleftharpoons H_2O(g)$$

At 298 K, the value of the equilibrium constant, K, for the reaction above is 0.036.

(a)   What is the sign of ΔS° for the reaction above at 298 K?

(b)   What is the sign of ΔH° for the reaction above at 298 K?

(c)   What is the sign of ΔG° for the reaction above at 298 K?

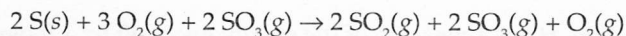(d)   At approximately what temperature will ΔG for the reaction be equal to zero?
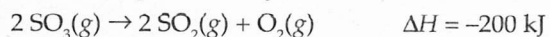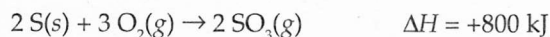
CHAPTER 8 ANSWERS AND EXPLANATIONS
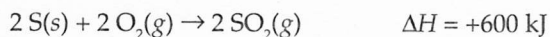
MULTIPLE-CHOICE QUESTIONS

1. **A** A negative value for ΔG means that the process is spontaneous. A positive value for ΔG means that the process is nonspontaneous.

2. **B** Entropy is a measure of the disorder of a system. A positive value for ΔS means that a system has become more disordered. A negative value for ΔS means that a system has become more orderly.

3. **C** The heat of vaporization is the heat given off when a substance condenses. It is also the heat that must be put into a substance to make it vaporize.

4. **D** The heat of fusion is the heat that must be put into a substance to melt it. It is also the heat given off when a substance freezes.

   By the way, choice (E), heat capacity, is a measure of how much heat must be added to a given object to raise its temperature 1°C.

5. **A** Remember $\Delta G = \Delta H - T\Delta S$.

   If the reaction is spontaneous only when the temperature is very low, then ΔG is only negative when T is very small. This can only happen when ΔH is negative (which favors spontaneity) and ΔS is negative (which favors nonspontaneity). A very small value for T will eliminate the influence of ΔS.

6. **C** In an exothermic reaction, energy is given off as the products are created because the products have less potential energy than the reactants.

7. **C** The bond energy is the energy that must be put into a bond to break it. First let's figure out how much energy must be put into the reactants to break their bonds.

   To break 2 moles of H–H bonds, it takes (2)(500) kJ = 1,000 kJ

   To break 1 mole of O=O bonds, it takes 500 kJ.

   So to break up the reactants, it takes +1,500 kJ.

   Energy is given off when a bond is formed; that's the negative of the bond energy. Now let's see how much energy is given off when 2 moles of H_2O are formed.

   2 moles of H_2O molecules contain 4 moles of O–H bonds, so (4)(–500) kJ = –2,000 kJ are given off.

   So the value of $\Delta H°$ for the reaction is

   (–2,000 kJ, the energy given off) + (1,500 kJ, the energy put in) = –500 kJ.

8. **A** Remember, $\Delta G = \Delta H - T\Delta S$. If the reaction is spontaneous at standard temperature but becomes nonspontaneous at higher temperatures, then ΔG is negative only at lower temperatures. This can only happen when ΔH is negative (which favors spontaneity) and ΔS is negative (which favors nonspontaneity). As the value of T increases, the influence of ΔS increases, eventually making the reaction nonspontaneous.

9. **B** The process is spontaneous, so ΔG must be negative. The intermolecular forces become stronger and the substance moves to a lower energy level when it freezes, so ΔH must be negative. The substance becomes more orderly when it freezes, so ΔS must be negative.

10. **C** Point 3 represents the activated complex, which is the point of highest energy. This point is the transition state between the reactants and the products.

11. **A** The equations given on top give the heats of formation of all the reactants and products (remember, the heat of formation of O_2, an element in its most stable form, is zero).

$\Delta H°$ for a reaction = ($\Delta H°$ for the products) − ($\Delta H°$ for the reactants).

First, the products:

From CO_2, we get (2)(−390 kJ) = −780 kJ

From H_2O, we get −290 kJ

So $\Delta H°$ for the products = (−780 kJ) + (−290 kJ) = −1,070 kJ

Now the reactants:

From C_2H_2, we get +230 kJ. The heat of formation of O_2 is defined as zero, so that's it for the reactants.

$\Delta H°$ for the reaction = (−1,070 kJ) − (+230 kJ) = −1,300 kJ.

12. **D** The reaction is spontaneous, so ΔG must be less than zero, so (I) is not true. The reaction is endothermic, so ΔH must be greater than zero; therefore, (II) is true.

The only way that an endothermic reaction can be spontaneous is if the entropy is increasing, so ΔS is greater than zero, and (III) is true.

13. **C** The addition of a catalyst speeds up a reaction by lowering the activation energy. A catalyst has no effect on the entropy or enthalpy change of a reaction.

14. **D** The equations given above the question give the heats of formation of all the reactants and products (remember, the heat of formation of O_2, an element in its most stable form, is zero).

$\Delta H°$ for a reaction = ($\Delta H°$ for the products) − ($\Delta H°$ for the reactants).

First, the products:

From 2 H_2O, we get 2z

From CO_2, we get y

So $\Delta H°$ for the products = 2z + y

Now the reactants:

From CH_4, we get x. The heat of formation of O_2 is defined to be zero, so that's it for the reactants.

$\Delta H°$ for the reaction = (2z + y) − (x) = 2z + y − x.

15. **D** In (I), NaCl goes from a solid to aqueous particles. Aqueous particles are more disorderly than a solid, so ΔS will be positive.

In (II), we go from 3 moles of gas to 2 moles of gas. Fewer moles and less gas means less entropy, so ΔS will be negative.

In (III), we go from a solid to a solid and a gas. More moles and the production of more gas means increasing entropy, so ΔS will be positive.

16. **D** Choice (D) is the only reaction where the number of moles of gas is increasing, going from 2 moles of gas on the reactant side to 3 moles of gas on the product side. In all the other choices, the number of moles of gas either decreases or remains constant.

17. **B** In the reaction, a solid combines with a gas to produce fewer moles of solid, so the entropy change is negative and (I) is not true. The reaction is spontaneous, so the free energy change is negative and (III) is not true. For a reaction with decreasing entropy to be spontaneous, it must be exothermic. The enthalpy change is negative for an exothermic reaction and (II) is true.

18. **C** The reaction that forms 2 moles of HF(*g*) from its constituent elements has an enthalpy change of –540 kJ. The heat of formation is given by the reaction that forms 1 mole from these elements, so you can just divide –540 kJ by 2 to get –270 kJ.

19. **E** Ice melts spontaneously at room temperature, so ΔG is less than zero; therefore, (I) is not true.

In this reaction, ice melts, so heat is absorbed to break up the intermolecular forces, and ΔH is greater than zero; therefore, (II) is true.

Liquid water is less orderly than ice, so the entropy change when ice melts is positive; therefore, ΔS is greater than zero, and (III) is true.

20. **A** You can use Hess's law. Add the two reactions together, and cancel things that appear on both sides.

$$2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g) \qquad \Delta H = +800\ kJ$$
$$2\ SO_3(g) \rightarrow 2\ SO_2(g) + O_2(g) \qquad \Delta H = -200\ kJ$$

$$2\ S(s) + 3\ O_2(g) + 2\ SO_3(g) \rightarrow 2\ SO_2(g) + 2\ SO_3(g) + O_2(g)$$

This reduces to

$$2\ S(s) + 2\ O_2(g) \rightarrow 2\ SO_2(g) \qquad \Delta H = +600\ kJ$$

Now we can cut everything in half to get the equation we want.

$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H = +300\ kJ$$

PROBLEMS

1. (a) Use the entropy values in the table.

$$\Delta S° = \sum S°_{products} - \sum S°_{reactants}$$

$$\Delta S° = [(6)(213.6) + (6)(69.9)] - [(212.13) + (6)(205)] \text{ J/K}$$

$$\Delta S° = 259 \text{ J/K}$$

(b) Use the equation below. Remember that enthalpy values are given in kJ and entropy values are given in J.

$$\Delta G° = \Delta H° - T \Delta S°$$

$$\Delta G° = (-2,801 \text{ kJ}) - (298)(0.259 \text{ kJ}) = -2,880 \text{ kJ}$$

(c) Use the equation below. Remember that the gas constant is given in terms of J.

$$\log K = \frac{\Delta G°}{-2.303RT}$$

$$\log K = \frac{(-2,880,000)}{(-2.303)(8.31)(298)} = 505$$

$$K = 10^{505}$$

(d) The enthalpy change of the reaction, $H°$, is a measure of the energy given off by 1 mole of glucose.

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{Moles of glucose} = \frac{(1.00 \text{ g})}{(180 \text{ g / mol})} = 0.00556 \text{ moles}$$

$$(0.00556 \text{ mol})(2,801 \text{ kJ/mol}) = 15.6 \text{ kJ}$$

2. (a) Use the relationship below.

$$\Delta H° = \sum \text{Energies of the bonds broken} - \sum \text{Energies of the bonds formed}$$

$$\Delta H° = [(4)(415) + (2)(495)] - [(2)(799) + (4)(463)] \text{ kJ}$$

$$\Delta H° = -800 \text{ kJ}$$

(b) Use the following equation. Remember that the gas constant is given in terms of J.

$$\log K = \frac{\Delta G°}{-2.303RT}$$

$$\log K = \frac{(-801,000)}{(-2.303)(8.31)(298)} = 140$$

$$K = 10^{140}$$

(c) Use $\Delta G° = \Delta H° - T\,\Delta S°$

Remember that enthalpy values are given in kJ and entropy values are given in J.

$$\Delta S° = \frac{\Delta H - \Delta G}{T} = \frac{(-800\text{ kJ}) - (-801\text{ kJ})}{(298\text{ K})}$$

$$\Delta S° = 0.003\text{ kJ/K} = 3\text{ J/K}$$

(d) $\Delta S°$ is very small, which means that the entropy change for the process is very small. This makes sense because the number of moles remains constant, the number of moles of gas remains constant, and the complexity of the molecules remains about the same.

3. (a) By definition, $\Delta H°_f$ and $\Delta G°_f$ for $N_2(g)$ and $H_2(g)$ are equal to zero.

$$\Delta H° = \sum \Delta H°_f \text{products} - \sum \Delta H°_f \text{reactants}$$

$$\Delta H° = [(2\text{ mol})(-46.2\text{ kJ/mol})] - 0 = -92.4\text{ kJ}$$

$$\Delta G° = \sum \Delta G°_f \text{products} - \sum \Delta G°_f \text{reactants}$$

$$\Delta G° = [(2\text{ mol})(-16.7\text{ kJ/mol})] - 0 = -33.4\text{ kJ}$$

(b) Use $\Delta G° = \Delta H° - T\,\Delta S°$

Remember that enthalpy values are given in kJ and entropy values are given in J.

$$\Delta S° = \frac{\Delta H - \Delta G}{T} = \frac{(-92.4\text{ kJ}) - (-33.4\text{ kJ})}{(298\text{ K})}$$

$$\Delta S° = -0.198\text{ kJ/K} = -198\text{ J/K}$$

(c) Use $\Delta G = \Delta H° - T\,\Delta S°$

From (b), $\Delta S°$ is negative, so increasing the temperature increases the value of $\Delta G°$, making the reaction less spontaneous.

(d) Use $\Delta G = \Delta H° - T\,\Delta S°$

At equilibrium, $\Delta G = 0$

$$T = \frac{\Delta H°}{\Delta S°} = \frac{(-92,400\text{ J})}{(-198\text{ J / K})} = 467\text{ K}$$

ESSAYS

4. (a) $\Delta S°$ is negative because the products are less random than the reactants. That's because gas is converted into liquid in the reaction.

    (b) The value of $\Delta S°$ would increase, becoming less negative because $H_2O(g)$ is more random than water but remaining negative because the entropy would still decrease from reactants to products.

    (c) $\Delta G°$ is negative because the reaction proceeds spontaneously.

    (d) $\Delta H°$ must be negative at 298 K. For a reaction to occur spontaneously from standard conditions, either $\Delta S°$ must be positive or $\Delta H°$ must be negative. This reaction is spontaneous although $\Delta S°$ is negative, so $\Delta H°$ must be negative.

5. (a) $\Delta S°$ is negative because the products are less random than the reactants. That's because two moles of reactants are converted to one mole of products and gas is converted into solid in the reaction.

    (b) $\Delta G°$ is negative because the reaction proceeds spontaneously.

    (c) Use $\Delta G° = \Delta H° - T \Delta S°$

    $\Delta G°$ will become less negative because as temperature is increased, the entropy change of a reaction becomes more important in determining its spontaneity. The entropy change for this reaction is negative, which discourages spontaneity, so increasing temperature will make the reaction less spontaneous, thus making $\Delta G°$ less negative.

    (d) The concentration of CO_2 will decrease as the reaction proceeds in the forward direction and the reactants are consumed. The temperature will increase as heat is given off by the exothermic reaction.

6. (a) $\Delta S°$ is positive because the product is more random than the reactant. That's because liquid is converted into gas in the reaction.

    (b) $\Delta H°$ is positive because $H_2O(g)$ is less stable than water. Energy must be put into water to overcome intermolecular forces and create water vapor.

    (c) Use $\Delta G° = -2.203RT \log K$

    If K is less than 1, $\log K$ will be negative, making $\Delta G°$ positive.

    (d) ΔG will be equal to zero at 373 K or 100°C. ΔG will be equal to zero at equilibrium. The point at which water and $H_2O(g)$ are in equilibrium is the boiling point.