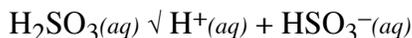


Thermodynamics, ΔH , ΔS , ΔG

page 1

1970

Consider the first ionization of sulfurous acid:



Certain related thermodynamic data are provided below:

	$\text{H}_2\text{SO}_3(\text{aq})$	$\text{H}^+(\text{aq})$	$\text{HSO}_3^-(\text{aq})$
H_f° kcal/mole	-145.5	0	-151.9
S° cal/mole K	56	0	26

- Calculate the value of ΔG° at 25°C for the ionization reaction.
- Calculate the value of K at 25°C for the ionization reaction.
- Account for the signs of ΔS° and ΔH° for the ionization reaction in terms of the molecules and ions present.

Answer:

- $$\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$= [-151.9] - [-145.5] \text{ kcal} = -14.4 \text{ kcal}$$

$$\Delta S = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$= (26 - 56) \text{ cal} = -30 \text{ cal/K}$$

$$\Delta G^\circ = \Delta H - T\Delta S = -14400 - (298)(-30) \text{ cal}$$

$$= -5.46 \text{ kcal}$$
- $K = e^{-\Delta G/RT} = e^{-(-5460/(1.9872)(298))} = 10100$
-

1971

Given the following data for graphite and diamond at 298K.

$$S^\circ(\text{diamond}) = 0.58 \text{ cal/mole deg}$$

$$S^\circ(\text{graphite}) = 1.37 \text{ cal/mole deg}$$

$$\Delta H_f^\circ \text{ CO}_2(\text{from graphite}) = -94.48 \text{ kilocalories/mole}$$

$$\Delta H_f^\circ \text{ CO}_2(\text{from diamond}) = -94.03 \text{ kilocalories/mole}$$

Consider the change: $\text{C}(\text{graphite}) = \text{C}(\text{diamond})$ at 298K and 1 atmosphere.

- What are the values of ΔS° and ΔH° for the conversion of graphite to diamond.
- Perform a calculation to show whether it is thermodynamically feasible to produce diamond from graphite at 298K and 1 atmosphere.
- For the reaction, calculate the equilibrium constant K_{eq} at 298K

Answer:

- $$\Delta S^\circ = S^\circ(\text{dia.}) - S^\circ(\text{graph.}) = (0.58 - 1.37) \text{ cal/K}$$

$$= -0.79 \text{ cal/K}$$

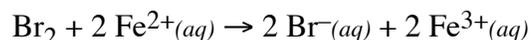


- $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -450 - (298)(-0.79) \text{ cal}$$

$$= -223.52 \text{ cal/mol}; \text{ a } \Delta G^\circ < 0 \text{ indicates feasible conditions}$$
- $$K_{\text{eq}} = e^{-\Delta G/RT} = e^{-(-223.52/(1.9872)(298))}$$

$$= -0.686$$

1972



For the reaction above, the following data are available:



	S° , cal/mole °C	
$\text{Br}_2(\text{l})$	58.6	$\text{Fe}^{2+}(\text{aq})$ -27.1
$\text{Br}^-(\text{aq})$	19.6	$\text{Fe}^{3+}(\text{aq})$ -70.1

- Determine ΔS°
- Determine ΔG°
- Determine ΔH°

Answer:

- $$\Delta S^\circ = \sum S^\circ_{\text{prod.}} - \sum S^\circ_{\text{reactants}}$$

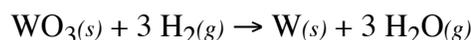
$$= [(19.6)(2) + (-70.1)(2)] - [58.6 + (-27.1)(2)] \text{ cal}$$

$$= -105.4 \text{ cal} = -441 \text{ J/K}$$
- $$E^\circ_{\text{cell}} = [+1.07 + (-0.77)] \text{ v} = 0.30 \text{ v}$$

$$\Delta G^\circ = -n\mathfrak{F}E^\circ = -(2)(96500)(0.30\text{v}) = -57900 \text{ J/mol}$$
- $$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = 57900 + 298(-441) \text{ J}$$

$$= -73.5 \text{ kJ/mol}$$

1974



Tungsten is obtained commercially by the reduction of WO_3 with hydrogen according to the equation above. The following data related to this reaction are available:

	$\text{WO}_3(\text{s})$	$\text{H}_2\text{O}(\text{g})$
ΔH_f° (kilocalories/mole)	-200.84	-57.8
ΔG_f° (kilocalories/mole)	-182.47	-54.6

- What is the value of the equilibrium constant for the system represented above?
- Calculate ΔS° at 25°C for the reaction indicated

Thermodynamics, ΔH , ΔS , ΔG

by the equation above.

- (c) Find the temperature at which the reaction mixture is in equilibrium at 1 atmosphere.

Answer:

$$(a) \Delta G^\circ = [3(-54.6) + 0] - [-182.47 + 0] = 18.7 \text{ kcal}$$

$$K_{eq} = e^{-\Delta G/RT} = e^{-(18700/(1.9872)(298))} = 1.93 \times 10^{-8}$$

$$(b) \Delta H^\circ = [3(-57.8) + 0] - [-200.84 + 0] = 27.44 \text{ kcal}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{27440 - 18670}{298} = 29.2 \text{ cal/mol}\cdot\text{K}$$

$$(c) \Delta G = 0; \text{ assume } K = \left(\frac{P_{H_2O}}{P_{H_2}} \right)^3 = 1 \text{ at equilibrium}$$

$$T = \Delta H / \Delta S = 27440 / 29.2 = 938\text{K}$$

1975 B



A rate expression for the reaction above is:

$$-\frac{d[\text{O}_2]}{dt} = k[\text{NO}]^2[\text{O}_2]$$

	ΔH_f° kcal/mole	S° cal/(mole)(K)	ΔG_f° kcal/mole
NO(g)	21.60	50.34	20.72
O ₂ (g)	0	49.00	0
NO ₂ (g)	8.09	57.47	12.39

- (a) For the reaction above, find the rate constant at 25°C if the initial rate, as defined by the equation above, is 28 moles per liter-second when the concentration of nitric oxide is 0.20 mole per liter and the concentration of oxygen is 0.10 mole per liter.
- (b) Calculate the equilibrium constant for the reaction at 25°C.

Answer:

$$(a) k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{28}{(0.20)^2(0.10)} = 7000 \text{ mol}^{-2}\text{L}^2\text{sec}^{-1}$$

$$(b) \Delta G = [2(12.39)] - [2(20.72) + 0] = -16.66 \text{ kcal}$$

$$K_{eq} = e^{-\Delta G/RT} = e^{-(-16660/(1.9872)(298))} = 1.65 \times 10^{12}$$

1975 D



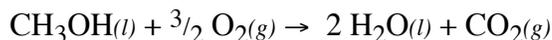
For the reaction above, ΔH° , ΔG° , and ΔS° are all negative. Which of the substances would predominate in an equilibrium mixture of copper, sulfur, and copper(I) sulfide at 298K? Explain how you drew your conclusion about the predominant

Thermodynamics, ΔH , ΔS , ΔG

substance present at equilibrium. Why must a mixture of copper and sulfur be heated in order to produce copper(I) sulfide?

Answer: Copper(I) sulfide. The forward reaction involves bond formation and is, therefore, exothermic ($\Delta H < 0$). The forward reaction produces 1 molecule from 3 atoms and, therefore, decreases in entropy ($\Delta S < 0$). But since ΔG is < 0 and $\Delta G = \Delta H - T\Delta S$, this reaction is spontaneous at low temperatures. This mixture must be heated because both reactants are solids and they react only when the copper atoms and sulfur atoms collide, an infrequent occurrence in the solid state.

1977 B



The value of ΔS° for the reaction is -19.3 cal/mol-degree at 25°C .

	ΔH_f° kcal/mole at 25°C	S° cal/mole-degree at 25°C
$\text{CH}_3\text{OH}(l)$	-57.0	30.3
$\text{H}_2\text{O}(l)$	-68.3	16.7
$\text{CO}_2(g)$	-94.0	51.1

- Calculate ΔG° for the complete combustion of methanol shown above at 25°C .
- Calculate the value for the equilibrium constant for this reaction at 25°C .
- Calculate the standard absolute entropy, S° , per mole of $\text{O}_2(g)$.

Answer:

- $$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$= [2(-68.3) + (-94.0)] - [-57.0] = -173.6 \text{ kcal}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -173.6 + (298)(0.0193) \text{ kcal}$$

$$= -167.8 \text{ kcal}$$
- $$K_{\text{eq}} = e^{-\Delta G/RT} = e^{-(-167800)/(1.9872)(298)}$$

$$= 1.15 \times 10^{123}$$
- $$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$-19.3 = [2(16.7) + 51.1] - [30.3 + \frac{3}{2} X]$$

$$X = 49.0 \text{ cal/mol K}$$

Thermodynamics, ΔH , ΔS , ΔG

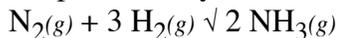
page 4

1978 B

When 1.000 gram of propane gas, C_3H_8 , is burned at $25^\circ C$ and 1.00 atmosphere, $H_2O(l)$ and $CO_2(g)$ are formed with the evolution of 12.03 kilocalories.

<u>Substance</u>	<u>Standard Entropy</u> cal/deg mole
$N_2(g)$	45.8
$H_2(g)$	31.2
$NH_3(g)$	46.0

Ammonia can be produced by the following reaction:



The Gibbs free energy of formation ΔG_f° of $NH_3(g)$ is -3.94 kilocalories per mole.

- (a) Calculate the value for ΔH° for the reaction above at $298K$.
- (b) Can the yield of ammonia be increased by raising the temperature? Explain.
- (c) What is the equilibrium constant for the reaction above at $298K$?
- (d) If 235 milliliters of H_2 gas measured at $25^\circ C$ and 570 millimeters Hg were completely converted to ammonia and the ammonia were dissolved in sufficient water to make 0.5000 liter of solution, what would be the molarity of the resulting solution?

Answer:

- (a) $\Delta S^\circ = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)}$
 $= [2(46.0)] - [45.8 + 3(31.2)] = -47.4 \text{ cal/K}$
 $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = -7.88 + (298)(-0.0474) \text{ kcal}$
 $= -22.0 \text{ kcal}$
- (b) No, since $\Delta H^\circ > 0$, an increase in T shifts equilibrium to left and decreases equilibrium yield of NH_3 .
- (c) $K_{eq} = e^{-\Delta G/RT} = e^{-(-7880)/(1.9872)(298)} = 6.01 \times 10^5$
- (d) $n = \frac{P \cdot V}{R \cdot T} = \frac{(570)(235)}{(62400)(298)} = 0.00720 \text{ mol } H_2$
 $0.00720 \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} \times \frac{1}{0.500 \text{ L}} =$
 $= 0.00960 \text{ M } NH_3$

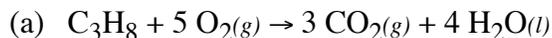
1979 B

<u>Compound</u>	<u>ΔH_f°</u> (kilocalories/mole)	<u>S°</u> (calories/mole K)
$H_2O(l)$	-68.3	16.7
$CO_2(g)$	-94.1	51.1
$O_2(g)$	0.0	49.0
C_3H_8	?	64.5

Thermodynamics, ΔH , ΔS , ΔG

- Write a balanced equation for the combustion reaction.
- Calculate the molar enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$, of propane.
- Calculate the standard molar enthalpy of formation, ΔH_f° , of propane gas.
- Calculate the entropy change, $\Delta S^\circ_{\text{comb}}$, for the reaction and account for the sign $\Delta S^\circ_{\text{comb}}$.

Answer:



(b) $\Delta H^\circ_{\text{comb}} = \frac{-12.03 \text{ kcal}}{1.000 \text{ g}} \times \frac{44.10 \text{ g}}{1 \text{ mol}} = -530.5 \text{ kcal/mol}$ 1981 D

(c) $\Delta H^\circ_{\text{comb}} = 3\Delta H_f^\circ \text{CO}_2 + 4\Delta H_f^\circ \text{H}_2\text{O} - \Delta H_f^\circ \text{C}_3\text{H}_8$
 $-530.8 \text{ kcal} = [3(-94.1) + 4(-68.3) - X] \text{ kcal}$
 $\Delta H^\circ_{\text{comb}} = -25.0 \text{ kcal/mol}$

(d) $\Delta S^\circ_{\text{comb}} = [3S^\circ \text{CO}_2 + 4S^\circ \text{H}_2\text{O}] - [S^\circ \text{C}_3\text{H}_8 + 5S^\circ \text{O}_2]$
 $= [3(51.1) + 4(16.7)] - [64.5 + 5(49.0)]$
 $= -89.4 \text{ cal/mol.K}$

Entropy decreases due to loss of highly disordered gaseous species upon combustion.

1980 D

- State the physical significance of entropy.
- From each of the following pairs of substances, choose the one expected to have the greater absolute entropy. Explain your choice in each case. Assume 1 mole of each substance.
 - $\text{Pb}(s)$ or $\text{C}(\text{graphite})$ at the same temperature and pressure.
 - $\text{He}(g)$ at 1 atmosphere or $\text{He}(g)$ at 0.05 atmosphere, both at the same temperature.
 - $\text{H}_2\text{O}(l)$ or $\text{CH}_3\text{CH}_2\text{OH}(l)$ at the same temperature and pressure.
 - $\text{Mg}(s)$ at 0°C or $\text{Mg}(s)$ at 150°C both at the same pressure.

Answer:

- Entropy is a measure of randomness, disorder, etc. in a system.
- (1) Pb has greater molar entropy, Pb, with metallic bonding, forms soft crystals with high amplitudes of vibration; graphite has stronger (covalent) bonds, is more rigid, and thus is more ordered.
 (2) $\text{He}(g)$ at 0.05 atmosphere has greater molar

entropy. At lower pressure (greater volume) He atoms have more space in which to move and are so more random.

- $\text{CH}_3\text{CH}_2\text{OH}$ has greater molar entropy. Ethanol molecules have more atoms and thus more vibrations; water exhibits stronger hydrogen bonding.
- $\text{Mg}(s)$ at 150°C has greater molar entropy. At the higher temperature the atoms have more kinetic energy and vibrate faster and, thus, show greater randomness.



For the reaction above, $\Delta H^\circ = +22.1$ kilocalories per mole at 25°C

- Does the tendency of reactions to proceed to a state of minimum energy favor the formation of the products of this reaction? Explain
- Does the tendency of reactions to proceed to a state of maximum entropy favor the formation of the products of this reaction? Explain.
- State whether an increase in temperature drives this reaction to the right, to the left, or has no effect. Explain.
- State whether a decrease in the volume of the system at constant temperature drives this reaction to the right, to the left or has no effect. Explain?

Answer:

- No, since reaction is endothermic, the products must be at higher energy than the reactants. **OR**
 $\ln K_P = -\Delta H/RT + \text{constant}$; if $\Delta H > 0$, $\ln K_P$ is less than if $\Delta H < 0$. **OR**
 $\Delta G = \Delta H - T\Delta S$. Low free energy ($\Delta G \leq 0$) is not favored by $\Delta H > 0$.
- Yes, $\Delta S > 0$ since 1 mol gas yields 2 mol gas, which means increased disorder. **OR**
 At equilibrium $\Delta H = T\Delta S$ and a positive ΔH means a positive ΔS .
- Application of heat favors more products. Predictable from LeChatelier's principle. **OR**
 $T\Delta S$ term here increases as T is increased resulting in a more negative ΔG .
- Reduction of volume favors more reactants. Predictable from LeChatelier's principle. Increased

Thermodynamics, ΔH , ΔS , ΔG

pressure is reduced by 2 gas molecules combining to give 1 molecule.

1983 B



	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
CO(g)	-110.5	-137.3	+197.9
CH ₃ OH(l)	-238.6	-166.2	+126.8

The data in the table above were determined at 25°C.

- Calculate ΔG° for the reaction above at 25°C.
- Calculate K_{eq} for the reaction above at 25°C.
- Calculate ΔS° for the reaction above at 25°C.
- In the table above, there are no data for H₂. What are the values of ΔH_f° , ΔG_f° , and of the absolute entropy, S° , for H₂ at 25°C?

Answer:

- $$\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$$

$$= -166.2 - [-137.3 + 2(0)] = -28.9 \text{ kJ/mol}$$
- $$K_{eq} = e^{-\Delta G^\circ/RT} = e^{-(-28900)/(8.3143)(298)} = 1.16 \times 10^5$$
- $$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-128100 - (-28900) \text{ J}}{298 \text{ K}}$$

$$= -333 \text{ J/K}$$
- Both the standard enthalpy of formation and the standard free energy of formation of elements = 0.

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

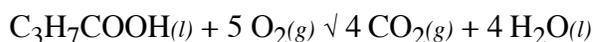
$$-333 \text{ J/K} = 126.8 \text{ J/K} - 197.9 \text{ J/K} - 2 S^\circ_{\text{H}_2}$$

$$S^\circ_{\text{H}_2} = 131 \text{ J/mol.K}$$

1984 B

Substance	Standard Heat of Formation, ΔH_f° , in kJ mol ⁻¹	Absolute Entropy, S° , in J mol ⁻¹ K ⁻¹
C(s)	0.00	5.69
CO ₂ (g)	-393.5	213.6
H ₂ (g)	0.00	130.6
H ₂ O(l)	-285.85	69.91
O ₂ (g)	0.00	205.0
C ₃ H ₇ COOH(l)	?	226.3

The enthalpy change for the combustion of butyric acid at 25°C, $\Delta H^\circ_{\text{comb}}$, is -2,183.5 kilojoules per mole. The combustion reaction is



Thermodynamics, ΔH , ΔS , ΔG

page 7

- From the above data, calculate the standard heat of formation, ΔH_f° , for butyric acid.
- Write a correctly balanced equation for the formation of butyric acid from its elements.
- Calculate the standard entropy change, ΔS_f° , for the formation of butyric acid at 25°C. The entropy change, ΔS° , for the combustion reaction above is -117.1 J K^{-1} at 25°C.
- Calculate the standard free energy of formation, ΔG_f° , for butyric acid at 25°C.

$\Delta T < 0$ since the more rapidly moving molecules leave the liquid first. The liquid remaining is cooler.

Answer:

- $$\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$
$$= [4(393.5) + 4(205.85) - 2183.5] \text{ kJ} = -533.8 \text{ kJ}$$
- $$4 \text{ C}(s) + 4 \text{ H}_2(g) + \text{O}_2(g) \rightarrow \text{C}_3\text{H}_7\text{COOH}(l)$$
- $$\Delta S_f^\circ(\text{butyric acid}) = S^\circ(\text{butyric acid}) - [4 S^\circ(\text{C}) + 4 S^\circ(\text{H}_2) + S^\circ(\text{O}_2)]$$
$$= 226.3 - [4(5.69) + 4(130.6) + 205] = -523.9 \text{ J/K}$$
- $$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ = 533.8 - (298)(-0.5239) \text{ kJ}$$
$$= -377.7 \text{ kJ}$$

1985 D

- When liquid water is introduced into an evacuated vessel at 25°C, some of the water vaporizes. Predict how the enthalpy, entropy, free energy, and temperature change in the system during this process. Explain the basis for each of your predictions.
- When a large amount of ammonium chloride is added to water at 25°C, some of it dissolves and the temperature of the system decreases. Predict how the enthalpy, entropy, and free energy change in the system during this process. Explain the basis for each of your predictions.
- If the temperature of the aqueous ammonium chloride system in part (b) were to be increased to 30°C, predict how the solubility of the ammonium chloride would be affected. Explain the basis for each of your predictions.

Answer:

- $\Delta H > 0$ since heat is required to change liquid water to vapor
 $\Delta S > 0$ since randomness increases when a liquid changes to vapor.
 $\Delta G < 0$ since the evaporation takes place in this situation.

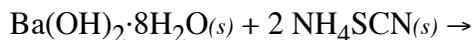
Thermodynamics, ΔH , ΔS , ΔG

- (b) $\Delta H > 0$. The system after dissolving has a lower temperature and so the change is endothermic.

$\Delta S > 0$, since the solution is less ordered than the separate substances are.

$\Delta G < 0$. The solution occurred and so is spontaneous.

- (c) Solubility increases. The added heat available pushes the endothermic process toward more dissolving.



- (a) Indicate how the enthalpy, the entropy, and the free energy of this system change as the reaction occurs. Explain your predictions.

1986 D

The first ionization energy of sodium is +496 kilojoules per mole, yet the standard heat of formation of sodium chloride from its elements in their standard state is -411 kilojoules per mole.

- (a) Name the factors that determine the magnitude of the standard heat of formation of solid sodium chloride. Indicate whether each factor makes the reaction for the formation of sodium chloride from its elements more or less exothermic.
- (b) Name the factors that determine whether the reaction that occurs when such a salt dissolves in water is exothermic or endothermic and discuss the effect of each factor on the solubility.

Answer:

- (a) heat of sublimation of sodium : endothermic
first ionization energy of sodium: endothermic
heat of dissociation of Cl_2 : endothermic
electron affinity of chlorine: exothermic
lattice energy of NaCl : exothermic
- (b) lattice energy of NaCl : endothermic to solution
hydration energy of the ions: exothermic
solvent expansion is endothermic. **OR**
increased exothermicity is associated with increased solubility.

1987 D

When crystals of barium hydroxide, $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, are mixed with crystals of ammonium thiocyanate, NH_4SCN , at room temperature in an open beaker, the mixture liquefies, the temperature drops dramatically, and the odor of ammonia is detected. The reaction that occurs is the following:

Thermodynamics, ΔH , ΔS , ΔG

- (b) If the beaker in which the reaction is taking place is put on a block of wet wood, the water on the wood immediately freezes and the beaker adheres to the wood. Yet the water inside the beaker, formed as the reaction proceeds, does not freeze even though the temperature of the reaction mixture drops to -15°C . Explain these observations.

Answer

- (a) The enthalpy increases ($\Delta H > 0$) since the reaction absorbs heat as in shown by the decrease in temperature.

The entropy increases ($\Delta S > 0$) since solid reactants are converted to gases and liquids, which have a much higher degree of disorder.

The free energy decreases ($\Delta G < 0$) as is shown by the fact that the reaction is spontaneous.

- (b) The water on the wood froze because the endothermic reaction lowered the temperature below the freezing point of water.

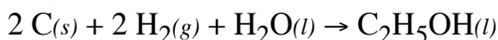
The solution in the beaker did not freeze because the presence of ions and dissolved gases lowered the freezing point of the solution below -15°C . The freezing point depression is given by the equation $\Delta T = K_f m$ where m = the molality of the solution and K_f = the molal freezing point constant for water.

1988 B

Substance	Enthalpy of Combustion, ΔH° (kiloJoules/mol)	Absolute Entropy, S° (Joules/mol-K)
$\text{C}_{(s)}$	-393.5	5.740
$\text{H}_{2(g)}$	-285.8	130.6
$\text{C}_2\text{H}_5\text{OH}(l)$	-1366.7	160.7
$\text{H}_2\text{O}(l)$	--	69.91

- (a) Write a separate, balanced chemical equation for the combustion of each of the following: $\text{C}_{(s)}$, $\text{H}_{2(g)}$, and $\text{C}_2\text{H}_5\text{OH}(l)$. Consider the only products to be CO_2 and/or $\text{H}_2\text{O}(l)$.

- (b) In principle, ethanol can be prepared by the following reaction:

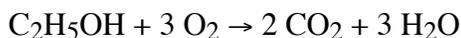
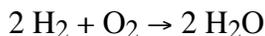


Calculate the standard enthalpy change, ΔH° , for the preparation of ethanol, as shown in the reac-

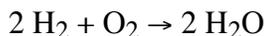
tion above.

- (c) Calculate the standard entropy change, ΔS° , for the reaction given in part (b).
- (d) Calculate the value of the equilibrium constant at 25°C for the reaction represented by the equation in part (b).

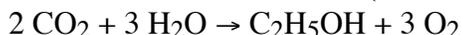
Answer:



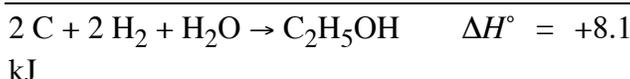
$$\Delta H^\circ = 2(-393.5) = -787.0 \text{ kJ}$$



$$\Delta H^\circ = 2(-285.8) = -571.6 \text{ kJ}$$



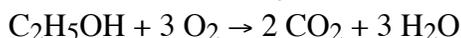
$$\Delta H^\circ = -(-1366.7) = +1366.7 \text{ kJ}$$



OR

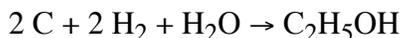
$$\Delta H^\circ_{\text{comb. C}(s)} = \Delta H^\circ_f \text{CO}_2(g)$$

$$\Delta H^\circ_{\text{comb. H}_2(g)} = \Delta H^\circ_f \text{H}_2\text{O}(l)$$



$$\Delta H^\circ = -1366.7 \text{ kJ}$$

$$\begin{aligned} \Delta H &= \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants}) \\ &= [2(-393.5) + 3(-285.8)] - [\Delta H^\circ_f \text{C}_2\text{H}_5\text{OH} + 0] \text{ kJ} \\ &= -277.7 \text{ kJ/mol} \end{aligned}$$



$$\begin{aligned} \Delta H &= \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants}) \\ &= [-277.7] - [0 + 0 + (-285.8)] \text{ kJ} = +8.1 \text{ kJ} \end{aligned}$$

- (c) $\Delta S = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$
- $$= [160.7] - [11.5 + 261.2 + 69.9] \text{ J/mol.K}$$
- $$= -181.9 \text{ J/mol.K}$$

- (d) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 8100 - (298)(-181.9) \text{ J}$
- $$= 62300 \text{ J}$$

$$K_{\text{eq}} = e^{-\Delta G^\circ/RT} = e^{-(62300)/(8.3143)(298)} = 1.2 \times 10^{-11}$$

1988 D

An experiment is to be performed to determine the standard molar enthalpy of neutralization of a strong acid by a strong base. Standard school laboratory equipment and a supply of standardized 1.00 molar HCl and standardized 1.00 molar NaOH are

Thermodynamics, ΔH , ΔS , ΔG

page 10

available.

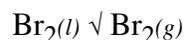
- (a) What equipment would be needed?
- (b) What measurements should be taken?
- (c) Without performing calculations, describe how the resulting data should be used to obtain the standard molar enthalpy of neutralization.

- (d) When a class of students performed this experiment, the average of the results was -55.0 kilojoules per mole. The accepted value for the standard molar enthalpy of neutralization of a strong acid by a strong base is -57.7 kilojoules per mole. Propose two likely sources of experimental error that could account for the result obtained by the class.

Answer:

- (a) Equipment needed includes a thermometer, and a container for the reaction, preferably a container that serves as a calorimeter, and volumetric glassware (graduated cylinder, pipet, etc.).
- (b) Measurements include the difference in temperatures between just before the start of the reaction and the completion of the reaction, and amounts (volume, moles) of the acid and the base.
- (c) Determination of heat (evolved or absorbed): The sum of the volumes (or masses) of the two solutions, and change in temperature and the specific heat of water are multiplied together to determine the heat of solution for the sample used. $q = (m)(c_p)(\Delta T)$.
Division of the calculated heat of neutralization by moles of water produced, or moles of H^+ , or moles of OH^- , or moles of limiting reagent.
- (d) Experimental errors: heat loss to the calorimeter wall, to air, to the thermometer; incomplete transfer of acid or base from graduated cylinder; spattering of some of the acid or base so that incomplete mixing occurred, ... Experimenter errors: dirty glassware, spilled solution, misread volume or temperature, ...

1989 B



At $25^\circ C$ the equilibrium constant, K_p , for the reaction above is 0.281 atmosphere.

- (a) What is the ΔG°_{298} for this reaction?
- (b) It takes 193 joules to vaporize 1.00 gram of $Br_2(l)$ at $25^\circ C$ and 1.00 atmosphere pressure. What are the values of ΔH°_{298} and ΔS°_{298} for this reaction?
- (c) Calculate the normal boiling point of bromine.

Thermodynamics, ΔH , ΔS , ΔG

Assume that ΔH° and ΔS° remain constant as the temperature is changed.

- (d) What is the equilibrium vapor pressure of bromine at 25°C?

Answer:
 (a) $\Delta G^\circ = -RT \ln K$
 $= -(8.314 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1})(298 \text{ K})(\ln 0.281)$
 $= 3.14 \times 10^3 \text{ J}\cdot\text{mol}^{-1}$

(b) $\Delta H^\circ = (193 \text{ J/g})(159.8 \text{ g/mol}) = 3.084 \times 10^4 \text{ J/mol}$
 $\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{(30840 - 3140) \text{ J}}{298 \text{ K}} =$
 $= 92.9 \text{ J/mol}\cdot\text{K}$

- (c) At boiling point, $\Delta G^\circ = 0$ and thus,

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.08 \times 10^4}{92.9} = 332 \text{ K}$$

- (d) vapor pressure = 0.281 atm.

1990 B

Standard Free Energies of Formation at 298 K

Substance	ΔG_f° 298 K, kJ mol ⁻¹
C ₂ H ₄ Cl ₂ (g)	-80.3
C ₂ H ₅ Cl(g)	-60.5
HCl(g)	-95.3
Cl ₂ (g)	0

Average Bond Dissociation Energies at 298 K

Bond	Energy, kJ mol ⁻¹
C-H	414
C-C	347
C-Cl	377
Cl-Cl	243
H-Cl	431

The tables above contain information for determining thermodynamic properties of the reaction below.



- (a) Calculate the ΔH° for the reaction above, using the table of average bond dissociation energies.
 (b) Calculate the ΔS° 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.

Thermodynamics, ΔH , ΔS , ΔG

page 12

Answer:

- (a) ΔH = energy of bonds broken – energy of bonds formed



$$\Delta H = (2794 + 243) - (2757 + 431) \text{ kJ} = -151 \text{ kJ}$$

OR



$$\Delta H = (414) + 243 - (377 + 431) = -151 \text{ kJ}$$

- (b) $\Delta G = \sum \Delta G^\circ(\text{products}) - \sum \Delta G^\circ(\text{reactants})$
 $= [-80.3 + (-95.3)] - [-60.5 + 0] = -115 \text{ kJ}$

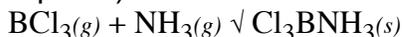
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-151 - (-115) \text{ kJ}}{298 \text{ K}} = -0.120 \text{ kJ/K}$$

- (c) $K_{\text{eq}} = e^{-\Delta G/RT} = e^{-(-115100)/(8.3143)(298)}$
 $= 1.50 \times 10^{20}$

- (d) K_{eq} will decrease with an increase in T because the reverse (endothermic) reaction will be favored with the addition of heat. **OR**

ΔG will be less negative with an increase in temperature (from $\Delta G = \Delta H - T\Delta S$), which will cause K_{eq} to decrease.

1991 D (Required)



The reaction represented above is a reversible reaction.

- (a) Predict the sign of the entropy change, ΔS , 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, ΔH . Explain your prediction.
- (c) The direction in which the reaction spontaneously proceeds changes as the temperature is increased above a specific temperature. Explain.
- (d) What is the value of the equilibrium constant at the temperature referred to in (c); that is, the specific temperature at which the direction of the spontaneous reaction changes? Explain.

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 ΔS is negative.
- (b) In order for a spontaneous change to occur in the right direction, the enthalpy change must over-

come the entropy change which favors the reactants (left), since nature favors a lower enthalpy, then the reaction must be exothermic to the right, $\therefore \Delta H < 0$.

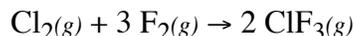
Thermodynamics, ΔH , ΔS , ΔG

- (c) $\Delta G = \Delta H - T\Delta S$, the reaction will change direction when the sign of ΔG changes, since $\Delta H < 0$ and $\Delta S < 0$, then at low temperatures the sign of ΔG 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 ΔG as positive and spontaneous in the left direction.
- (d) At equilibrium, $K = e^{-\Delta G/RT}$, where $\Delta G = 0$, $K = e^0 = 1$

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

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

1992 B



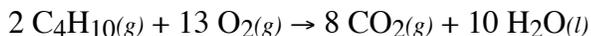
ClF_3 can be prepared by the reaction represented by the equation above. For ClF_3 the standard enthalpy of formation, ΔH_f° , is -163.2 kilojoules/mole and the standard free energy of formation, ΔG_f° , is -123.0 kilojoules/mole.

- (a) Calculate the value of the equilibrium constant for the reaction at 298K.
- (b) Calculate the standard entropy change, ΔS° , 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 ΔS for the reaction be affected? Explain.
- (d) At 298K the absolute entropies of $\text{Cl}_2(g)$ and $\text{ClF}_3(g)$ are 222.96 joules per mole-Kelvin and 281.50 joules per mole-Kelvin, respectively.
- (i) Account for the larger entropy of $\text{ClF}_3(g)$ relative to that of $\text{Cl}_2(g)$.
- (ii) Calculate the value of the absolute entropy of $\text{F}_2(g)$ at 298K.

Answer:

- (a) $K_{eq} = e^{-\Delta G/RT} = e^{-(-246000)/(8.314)(298)}$
 $= 1.32 \times 10^{43}$
- (b) $\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{[-326400 - (-246000)]\text{J}}{298\text{K}} =$
 $= -270 \text{ J/K}$
- (c) ΔS is a larger negative number. $\text{ClF}_3(l)$ is more ordered (less disordered) than $\text{ClF}_3(g)$.
- (d) Entropy of $\text{ClF}_3 >$ entropy of Cl_2 because
- (i) 1) larger number of atoms **OR**
 2) more complex particle **OR**
 3) more degrees of freedom
- (ii) $\Delta S = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$

1993 D



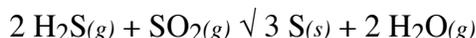
The reaction represented above is spontaneous at 25°C. Assume that all reactants and products are in their standard state.

- (a) Predict the sign of ΔS° for the reaction and justify your prediction.
- (b) What is the sign of ΔG° for the reaction? How would the sign and magnitude of ΔG° be affected by an increase in temperature to 50°C? Explain your answer.
- (c) What must be the sign of ΔH° 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 placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.

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) $\Delta G < 0$. ΔG 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 ΔH .
- (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.

1994 D



At 298 K, the standard enthalpy change, ΔH° for the reaction represented above is -145 kilojoules.

- (a) Predict the sign of the standard entropy change, ΔS° , 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 ΔG° 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

Thermodynamics, ΔH , ΔS , ΔG

- (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?
- (a) $\text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}$

Answer:

- (a) ΔS° 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) $\Delta G^\circ < 0$ if spontaneous. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Since ΔS° is neg. (-), as T gets larger, $-T\Delta S^\circ$ will become larger than +145 kJ and the sign of ΔG° becomes pos. (+) and the reaction is non-spontaneous.
- (c) When $-T\Delta S^\circ < +145 \text{ kJ}$, $K_{eq} > 1$,
when $-T\Delta S^\circ = +145 \text{ kJ}$, $K_{eq} = 1$,
when $-T\Delta S^\circ > +145 \text{ kJ}$, $K_{eq} < 1$, but > 0
- (d) $\Delta G = 0$ at this point, the equation is $T = \frac{\Delta H^\circ}{\Delta S^\circ}$;
this assumes that ΔH and/or S do not change with temperature; not a perfect assumption leading to errors in the calculation.

1995 B

Propane, C_3H_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 O_2 by volume.
- (c) The heat of combustion of propane is $-2,220.1 \text{ kJ/mol}$. Calculate the heat of formation, ΔH_f° , of propane given that ΔH_f° of $\text{H}_2\text{O}(l) = -285.3 \text{ kJ/mol}$ and ΔH_f° of $\text{CO}_2(g) = -393.5 \text{ kJ/mol}$.
- (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 = $4.18 \text{ J/g}\cdot\text{K}$), calculate the increase in temperature of water.

Answer:

Thermodynamics, ΔH , ΔS , ΔG

page 16

$$(b) 10.0 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol C}_3\text{H}_8}{44.0 \text{ g}} \times \frac{5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_8} = 1.14 \text{ mol O}_2$$

$$V_{\text{O}_2} = \frac{nRT}{P} = \frac{(1.14 \text{ mol}) \left(0.0821 \frac{\text{L atm}}{\text{mol K}} \right) (303 \text{ K})}{1.00 \text{ atm}}$$

$$= 28.3 \text{ L O}_2 ; \frac{28.3 \text{ L}}{21.0\%} = 135 \text{ L of air}$$

$$(c) \Delta H_{\text{comb}}^{\circ} = \left[\Delta H_{f(\text{CO}_2)}^{\circ} + \Delta H_{f(\text{H}_2\text{O})}^{\circ} \right] - \left[\Delta H_{f(\text{C}_3\text{H}_8)}^{\circ} + \Delta H_{f(\text{O}_2)}^{\circ} \right]$$

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

$$X = \Delta H_{\text{comb}}^{\circ} = -101.6 \text{ kJ/mol}$$

$$(d) q = 30.0 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol}}{44.0 \text{ g}} \times \frac{2220.1 \text{ kJ}}{1 \text{ mol}} = 1514 \text{ kJ}$$

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

$$1514 \text{ kJ} = (8.00 \text{ kg})(4.184 \text{ J/g}\cdot\text{K})(\Delta T)$$

$$\Delta T = 45.2^{\circ}$$

1995 D (repeated in the solid, liquid, solutions section)

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.



- (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 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 ΔG of adding a small amount of $\text{Pb}(\text{NO}_3)_2$ to the system at equilibrium? Explain.

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 PbI_2 does not change the concentration of the 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) ΔG increases. Increasing the concentration of Pb^{2+} ions causes a spontaneous increase in the reverse reaction rate (a "shift left" according to LeChatelier's Principle). A reverse reaction is spontaneous when the $\Delta G > 0$.

1996 B



Information about the substances involved in the reaction represented above is summarized in the following tables.

Substance	S° (J/mol·K)	ΔH_f° (kJ/mol)
$\text{C}_2\text{H}_2(g)$	200.9	226.7
$\text{H}_2(g)$	130.7	0
$\text{C}_2\text{H}_6(g)$	—	-84.7

Bond	Bond Energy (kJ/mol)
C-C	347
C=C	611
C-H	414
H-H	436

- (a) If the value of the standard entropy change, ΔS° , for the reaction is -232.7 joules per mole·Kelvin, calculate the standard molar entropy, S° , of C_2H_6 gas.
- (b) Calculate the value of the standard free-energy change, ΔG° , for the reaction. What does the sign of ΔG° indicate about the reaction above?
- (c) Calculate the value of the equilibrium constant, K , for the reaction at 298 K .
- (d) Calculate the value of the $\text{C}\equiv\text{C}$ bond energy in C_2H_2 in kilojoules per mole.

Thermodynamics, ΔH , ΔS , ΔG

page 17

Answer:

$$(a) -232.7 \text{ J/K} = S^\circ_{(\text{C}_2\text{H}_6)} - [2(130.7) + 200.9] \text{ J/K}$$

$$S^\circ_{(\text{C}_2\text{H}_6)} = 229.6 \text{ J/K}$$

$$(b) \Delta H^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

$$= -84.7 \text{ kJ} - [226.7 + 2(0)] \text{ kJ} = -311.4 \text{ kJ}$$

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

$$= -311.4 \text{ kJ} - (298\text{K})(-0.2327 \text{ kJ/K}) = -242.1 \text{ kJ}$$

A $\Delta G^\circ < 0$ (a negative ΔG°) indicates a spontaneous forward reaction.

$$(c) K_{eq} = e^{-\Delta G/RT} = e^{-(-242100)/(8.314)(298)}$$

$$= 2.74 \times 10^{42}$$

$$(d) \Delta H^\circ = \text{bond energy of products} - \text{bond energy of reactants}$$

$$-311.4 \text{ kJ} = [(2)(436) + E_{\text{C}=\text{C}} + (2)(414)] - [347 + (6)(414)] \text{ kJ}$$

$$E_{\text{C}=\text{C}} = 820 \text{ kJ}$$

1997 D

For the gaseous equilibrium represented below, it is observed that greater amounts of PCl_3 and Cl_2 are produced as the temperature is increased.



- What is the sign of ΔS° for the reaction? Explain.
- What change, if any, will occur in ΔG° for the reaction as the temperature is increased? Explain your reasoning in terms of thermodynamic principles.
- If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of Cl_2 ? Explain.
- If the volume of the reaction mixture is decreased at constant temperature to half the original volume, what will happen to the number of moles of Cl_2 in the reaction vessel? Explain.

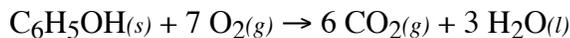
Answer:

- The sign of ΔS° is (+). There is an increase in the number of gas molecules as well as a change from a pure gas to a mixture of gases.
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Both ΔS° and ΔH° are (+). As temperature increases, at some point the sign of ΔG° will change from (+) to (-), when the system will become spontaneous.
- There will be no change in the partial pressure of the chlorine. Without a volume or temperature change, the pressure is independent of the other gases that are present.

Thermodynamics, ΔH , ΔS , ΔG

- (d) The number of moles of Cl_2 will decrease. The decrease in volume will result in an increase in pressure and, according to LeChatelier's Principle, the equilibrium system will shift to the left (the side with fewer gas molecules) to reduce this increase in pressure. This will cause a decrease in the number of moles of products and an increase in the number of moles of reactant.

1998 B



When a 2.000-gram sample of pure phenol, $\text{C}_6\text{H}_5\text{OH}(s)$, is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, ΔH_f° ; at 25°C (kJ/mol)	Absolute Entropy, S° , at 25°C (J/mol·K)
$\text{C}(\text{graphite})$	0.00	5.69
$\text{CO}_2(g)$	-393.5	213.6
$\text{H}_2(g)$	0.00	130.6
$\text{H}_2\text{O}(l)$	-285.85	69.91
$\text{O}_2(g)$	0.00	205.0
$\text{C}_6\text{H}_5\text{OH}(s)$?	144.0

- (a) Calculate the molar heat of combustion of phenol in kilojoules per mole at 25°C.
- (b) Calculate the standard heat of formation, ΔH_f° , of phenol in kilojoules per mole at 25°C.
- (c) Calculate the value of the standard free-energy change, ΔG° , for the combustion of phenol at 25°C.
- (d) If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to 110.°C. (Assume no oxygen remains unreacted and that all products are gaseous.)

Answer

$$(a) \Delta H_{\text{comb}} = \frac{\text{kJ}}{\frac{\text{mass}}{\text{molar mass}}} = \frac{64.98 \text{ kJ}}{\frac{2.000 \text{ g}}{94.113 \frac{\text{g}}{\text{mol}}}} = -3058 \text{ kJ}$$

$$(b) \Delta H_{\text{comb}} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$-3058 \text{ kJ/mol} = [(6)(-393.5) + (3)(-285.85)] - [X + 0]$$

$$= -161 \text{ kJ}$$

$$(c) \Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$= [(6)(213.6) + (3)(69.91)] - [144.0 + (7)(205.0)]$$

$$= -87.67 \text{ J}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -3058 - (298)(-0.08767) \text{ kJ}$$

$$= -3032 \text{ kJ}$$

$$(d) 2.000 \text{ g phenol} \times \frac{1 \text{ mol phenol}}{94.113 \text{ g}} \times \frac{7 \text{ mol O}_2}{1 \text{ mol phenol}} =$$

$$= 0.1488 \text{ mol O}_2$$

mol of gaseous product =

$$\frac{6}{7}(0.1489) + \frac{3}{7}(0.1489)$$

$$= 0.1913 \text{ mol of gas}$$

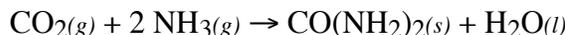
$$P = \frac{nRT}{V} = \frac{(0.1913 \text{ mol}) \left(0.08205 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (383 \text{ K})}{10.0 \text{ L}}$$

$$= 0.601 \text{ atm (or 457 mm Hg, or 60.9 kPa)}$$

1999 D (Required)

Answer the following question in terms of thermodynamic principles and concepts of kinetic molecular theory.

- (a) Consider the reaction represented below, which is spontaneous at 298 K.



$$\Delta H^\circ_{298} = -134 \text{ kJ}$$

- (i) For the reaction, indicate whether the standard entropy change, ΔS°_{298} , is positive, negative, or zero. Justify your answer.
- (ii) Which factor, the change in enthalpy, ΔH°_{298} , or the change in entropy, ΔS°_{298} , provides the principle driving force for the reaction at 298 K? Explain.
- (iii) For the reaction, how is the value of the standard free energy change, ΔG° , affected by an increase in temperature? Explain.
- (b) Some reactions that are predicted by their sign of ΔG° to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.

- (i) Account for this apparent contradiction.

- (ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on ΔG° for the reaction? Explain.

Answer

Thermodynamics, ΔH , ΔS , ΔG

- (a) (i) ΔS° is negative because (1) three molecules of reactant make two molecules of product (a decrease in entropy) and (2) two different gases make a solid and a liquid (both with smaller entropies).
- (ii) natural tendency to maximize entropy and since this reaction decreases entropy and is spontaneous ($-\Delta G^\circ$), then ΔH° must be negative to overcome the entropy change and drive this reaction.
- (iii) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; a T increase the value of $-T\Delta S^\circ$ increases and the value of $-\Delta G^\circ$ becomes a smaller negative number (i.e., moves toward zero).
- (b) (i) the sign of ΔG° (thermodynamics) does not account for activation energy (kinetics); a large activation energy would effectively prevent a reaction even though there is a favorable free energy change.
- (ii) a catalyst changes neither the ΔH° nor the ΔS° for a reaction, therefore, it will have no effect on the ΔG° .