The Advanced Placement Examination in Chemistry

Part II - Free Response Questions & Answers 1970 to 2005

Thermodynamics

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Compiled for the Macintosh and PC by:

Harvey Gendreau
Framingham High School
115 "A" Street
Framingham, MA 01701-4195
508-620-4963
419-735-4782 (fax)

508-877-8723 (home office)
www.apchemistry.com
hgendrea@framingham.k12.ma.us
hgendreau@rcn.com

Requests for copies of these questions and answers as e-mail attachments for either the Macintosh or the PC (MS-Office files) should be sent to:
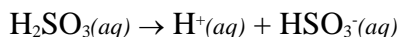
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1970

Consider the first ionization of sulfurous acid:

$$H_2SO_3(aq) \rightarrow H^+(aq) + HSO_3^-(aq)$$

Certain related thermodynamic data are provided below:

	$H_2SO_3(aq)$	$H^+(aq)$	$HSO_3^-(aq)$
$H_f°$ kcal/mole	-145.5	0	-151.9
$S°$ cal/mole K	56	0	26

(a) Calculate the value of $\Delta G°$ at 25°C for the ionization reaction.

(b) Calculate the value of K at 25°C for the ionization reaction.

(c) Account for the signs of $\Delta S°$ and $\Delta H°$ for the ionization reaction in terms of the molecules and ions present.

Answer:

(a) $\Delta H = \Re \Delta H_{\overline{f}(products\ )} - \Re \Delta H_{\overline{f}\ (reac\tan ts\ )}$

= [-159.9] - [-145.5] kcal = -14.4 kcal

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

= (26 - 56) cal = -30 cal/K

$\Delta G° = \Delta H - T\Delta S = -14400 - (298)(-30)$ cal

= -5.46 kcal

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

(c)

1971

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

$$S°(\text{diamond}) = \quad 0.58 \text{ cal/mole deg}$$
$$S°(\text{graphite}) = \quad 1.37 \text{ cal/mole deg}$$
$$\Delta H_f° \ CO_2(\text{from graphite}) = -94.48 \text{ kilocalories/mole}$$
$$\Delta H_f° \ CO_2(\text{from diamond}) = -94.03 \text{ kilocalories/mole}$$

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

(a) What are the values of $\Delta S°$ and $\Delta H°$ for the conversion of graphite to diamond.

(b) Perform a calculation to show whether it is thermodynamically feasible to produce diamond from graphite at 298K and 1 atmosphere.

(c) For the reaction, calculate the equilibrium constant K_{eq} at 298K

Answer:

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

= -0.79 cal/K

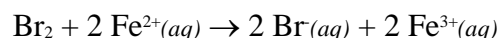| $CO_2 \rightarrow C(\text{dia.}) + O_2$	$\Delta H = + 94.03$ kcal/mol
$\underline{C(\text{graph.}) + O_2 \rightarrow CO_2}$	$\underline{\Delta H = - 94.48 \text{ kcal/mol}}$
$C(\text{graph.}) \rightarrow C(\text{dia.})$	$\Delta H = \quad -0.45$ kcal/mol

(b) $\Delta G° = \Delta H° - T\Delta S° = -450 - (298)(-0.79)$ cal

= -223.52 cal/mol; a $\Delta G° < 0$ indicates feasible conditions

(c) $K_{eq} = e^{-\Delta G/RT} = e^{-(-223.52/(1.9872)(298))} = -0.686$

1972

$$Br_2 + 2\ Fe^{2+}(aq) \rightarrow 2\ Br^-(aq) + 2\ Fe^{3+}(aq)$$

For the reaction above, the following data are available:

$2\ Br^-(aq) \rightarrow Br_2(l) + 2e-$	E° =	-1.07 volts
$\underline{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e-}$	E° =	-0.77 volts

S°, cal/mole °C			
$Br_2(l)$	58.6	$Fe^{2+}(aq)$	-27.1
$Br^-(aq)$	19.6	$Fe^{3+}(aq)$	-70.1

(a) Determine $\Delta S°$

(b) Determine $\Delta G°$

(c) Determine $\Delta H°$

Answer:

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

= [(19.6)(2)+(-70.1)(2)]-[58.6+(-27.1)(2)] cal

= -105.4 cal = -441 J/K

(b) $E°_{cell} = [+1.07 + (-0.77)]$ v = 0.30 v

$\Delta G° = -n\Im E° = -(2)(96500)(0.30v) = -57900$ J/mol

(c) $\Delta H° = \Delta G° + T\Delta S° = 57900 + 298(-441)$ J

= -73.5 kJ/mol

1974

$$WO_3(s) + 3\ H_2(g) \rightarrow W(s) + 3\ H_2O(g)$$
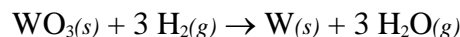
Tungsten is obtained commercially by the reduction of WO_3 with hydrogen according to the equation above. The following data related to this reaction are available:

	$WO_3(s)$	$H_2O(g)$
$\Delta H_f°$ (kilocalories/mole)	-200.84	-57.8
$\Delta G_f°$ (kilocalories/mole)	-182.47	-54.6

(a) What is the value of the equilibrium constant for the system represented above?

(b) Calculate $\Delta S°$ at 25°C for the reaction indicated by the equation above.

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

Answer:

(a) $\Delta G° = [3(-54.6) + 0] - [-182.47 + 0] = 18.7$ kcal

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

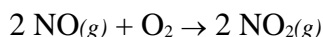(b) $\Delta H° = [3(-57.8) + 0] - [-200.84 + 0] = 27.44$ kcal

$$\Delta S_- = \frac{\Delta H_- - \Delta G_-}{T} = \frac{27440 - 18670}{298} = 29.2 \, ^{cal}/_{mol\_K}$$

$\Delta G = 0$; assume $K = \dfrac{P_{H_2O}^3}{P_{H_2}} = 1$ at equilibrium

(c)

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

1975 B

$$2 \, NO_{(g)} + O_2 \rightarrow 2 \, NO_{2(g)}$$

A rate expression for the reaction above is:

$$-\frac{d[O_2]}{dt} = k[NO]^2[O_2]$$

	$\Delta H_f°$ kcal/mole	$S°$ cal/(mole)(K)	$\Delta G_f°$ 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.

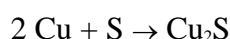(b) Calculate the equilibrium constant for the reaction at 25°C.

Answer:

(a)
$$k = \frac{rate}{[NO]^2[O_2]} = \frac{28}{(0.20)^2(0.10)}$$

$$= 7000 \, mol^{-2}L^2sec^{-1}$$

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

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

1975 D

$$2 \, Cu + S \rightarrow Cu_2S$$

For the reaction above, $\Delta H°$, $\Delta G°$, and $\Delta S°$ 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 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

$$CH_3OH_{(l)} + {}^3/_2 \, O_{2(g)} \rightarrow 2 \, H_2O_{(l)} + CO_{2(g)}$$
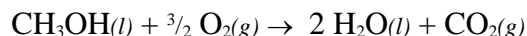
The value of $\Delta S°$ for the reaction is -19.3 cal/mol-degree at 25ΔC.

	$\Delta H_f°$ kcal/mole at 25°C	$S°$ cal/mole-degree at 25°C
$CH_3OH_{(l)}$	-57.0	30.3
$H_2O_{(l)}$	-68.3	16.7
$CO_{2(g)}$	-94.0	51.1

(a) Calculate $\Delta G°$ for the complete combustion of methanol shown above at 25°C.

(b) Calculate the value for the equilibrium constant for this reaction at 25°C.

(c) Calculate the standard absolute entropy, $S°$, per mole of $O_{2(g)}$.

Answer:

(a) $\Delta H_- = \Re \, \Delta H_{\overline{f} \, (products)} - \Re \, \Delta H_{\overline{f} (reactants)}$

$= [2(-68.3) + (-94.0)] - [-57.0] = -173.6$ kcal

$\Delta G° = \Delta H° - T\Delta S° = -173.6 + (298)(0.0193)$ kcal

$= -167.8$ kcal

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

$= 1.15 \times 10^{123}$

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

$-19.3 = [2(16.7) + 51.1] - [30.3 + {}^3/_2 \, X]$

X = 49.0 cal/mol K

1978 B

Standard Entropy

Substance	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:

$$N_2(g) + 3\ H_2(g) \to 2\ NH_3(g)$$

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

(a) Calculate the value for $\Delta H°$ for the reaction above 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°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) $\Delta S° = \Sigma S°_{(products)} - \Sigma S°_{(reactants)}$

$= [2(46.0)] - [45.8 + 3(31.2)] = -47.4$ cal/K

$\Delta H° = \Delta G° + T\Delta S° = -7.88 + (298)(-0.0474)$ kcal

$= -22.0$ kcal

(b) No, since $\Delta H° > 0$, 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) $n = \dfrac{P\_V}{R\_T} = \dfrac{(570)(235)}{(62400)(298)} = 0.00720\ mol\ H_2$

$0.00720\ mol\ H_2 \propto \dfrac{2\ mol\ NH_3}{3\ mol\ H_2} \propto \dfrac{1}{0.500\ L} =$

$= 0.00960\ M\ NH_3$

1979 B

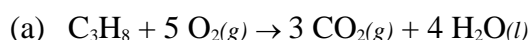| Compound	$\Delta H_f°$ (kilocalories/mole)	$S°$ (calories/mole K)
$H_2O(l)$	-68.3	16.7
$CO_2(g)$	-94.1	51.1
$O_2(g)$	0.0	49.0

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

(a) Write a balanced equation for the combustion reaction.

(b) Calculate the molar enthalpy of combustion, $\Delta H°_{comb}$, of propane.

(c) Calculate the standard molar enthalpy of formation, $\Delta H_f°$, of propane gas.

(d) Calculate the entropy change, $\Delta S°_{comb}$, for the reaction and account for the sign $\Delta S°_{comb}$.

Answer:

(a) $C_3H_8 + 5\ O_2(g) \to 3\ CO_2(g) + 4\ H_2O(l)$

(b) $\Delta H_{\_comb.} = \dfrac{-12.03\ kcal}{1.000\ g} \propto \dfrac{44.10\ g}{1\ mol} = -530.5\ kcal/mol$

(c) $\Delta H_{comb.}^- = 3\Delta H_f^- CO_2 + 4\Delta H_f^- H_2O - \Delta H_f^- C_3H_8$

-530.8 kcal = [3(-94.1) + 4(-68.3) - X] kcal

$\Delta H°_{comb.} = -25.0$ kcal/mol

(d) $\Delta S_{comb.}^- = [3\ S\_CO_2 + 4\ S\_H_2O] - [S\_C_3H_8 + 5\ S\_O_2]$

$= [3(51.1) + 4(16.7)] - [64.5 + 5(49.0)]$

$= -89.4$ cal/mol.K

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

1980 D

(a) State the physical significance of entropy.

(b) 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.

(1) $Pb(s)$ or $C(graphite)$ at the same temperature and pressure.

(2) $He(g)$ at 1 atmosphere or $He(g)$ at 0.05 atmosphere, both at the same temperature.

(3) $H_2O(l)$ or $CH_3CH_2OH(l)$ at the same temperature and pressure.

(4) $Mg(s)$ at 0°C or $Mg(s)$ at 150°C both at the same pressure.

Answer:

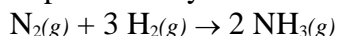(a) Entropy is a measure of randomness, disorder, etc. in a system.

(b) (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) $He_{(g)}$ at 0.05 atmosphere has greater molar entropy. At lower pressure (greater volume) He atoms have more space in which to move are so are more random.

(3) CH_3CH_2OH has greater molar entropy. Ethanol molecules have more atoms and thus more vibrations; water exhibits stronger hydrogen bonding.

(4) $Mg_{(s)}$ 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.

1981 D

$$PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$$

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

(a) Does the tendency of reactions to proceed to a state of minimum energy favor the formation of the products of this reaction? Explain

(b) Does the tendency of reactions to proceed to a state of maximum entropy favor the formation of the products of this reaction? Explain.

(c) State whether an increase in temperature drives this reaction to the right, to the left, or has no effect. Explain.

(d) 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:

(a) No, since reaction is endothermic, the products must be at higher energy than the reactants. **OR**

$\ln K_P = -\Delta H/RT +$ 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 ($\Delta G°0$) is not favored by $\Delta H > 0$.

(b) 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.

(c) 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.

(d) Reduction of volume favors more reactants. Predictable from LeChatelier's principle. Increased pressure is reduced by 2 gas molecules combining to give 1 molecule.

1983 B

$$CO_{(g)} + 2 H_{2(g)} \rightarrow CH_3OH_{(l)} \quad \Delta H° = -128.1 \text{ kJ}$$

	$\Delta H_f°$ (kJ mol⁻¹)	$\Delta G_f°$ (kJ mol⁻¹)	S° (J mol⁻¹ K⁻¹)
$CO_{(g)}$	-110.5	-137.3	+197.9
$CH_3OH_{(l)}$	-238.6	-166.2	+126.8

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

(a) Calculate $\Delta G°$ for the reaction above at 25°C.

(b) Calculate K_{eq} for the reaction above at 25°C.

(c) Calculate $\Delta S°$ for the reaction above at 25°C.

(d) In the table above, there are no data for H_2. What are the values of $\Delta H_f°$, $\Delta G_f°$, and of the absolute entropy, S°, for H_2 at 25°C?

Answer:

(a) $\Delta G = \Re \Delta G_{\bar{f}(products)} - \Re \Delta G_{\bar{f}(reactants)}$

$= -166.2 - [-137.3 + 2(0)] = -28.9$ kJ/mol

(b) $K_{eq} = e^{-\Delta G/RT} = e^{(-28900/(8.3143)(298))} = 1.16 \times 10^5$

(c) $\Delta S = \dfrac{\Delta H - \Delta G}{T} = \dfrac{-128100 - (-28900)\text{J}}{298 \text{ K}}$

$= -333$ J/K

(d) Both the standard enthalpy of formation and the standard free energy of formation of elements = 0.

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

-333 J/K $= 126.8$ J/K $- 197.9$ J/K $- 2 S°_{H_2}$

$S°_{H_2} = 131$ J/mol.K

1984 B

Substance	Standard Heat of Formation, $\Delta H_f°$, 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
$H_2O_{(l)}$	-285.85	69.91
$O_{2(g)}$	0.00	205.0
$C_3H_7COOH_{(l)}$	?	226.3

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

$$C_3H_7COOH_{(l)} + 5\ O_{2(g)} \rightarrow 4\,CO_{2(g)} + 4\,H_2O_{(l)}$$
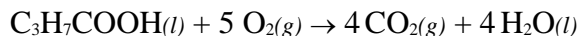
(a) From the above data, calculate the standard heat of formation, $\Delta H_f°$, for butyric acid.

(b) Write a correctly balanced equation for the formation of butyric acid from its elements.

(c) Calculate the standard entropy change, $\Delta S_f°$, for the formation of butyric acid at 25°C. The entropy change, $\Delta S°$, for the combustion reaction above is -117.1 J K^{-1} at 25°C.

(d) Calculate the standard free energy of formation, $\Delta G°_f$, for butyric acid at 25°C.

Answer:

(a) $\Delta H = \mathfrak{R}\,\Delta H_{\overline{f}(products\ )} - \mathfrak{R}\,\Delta H_{\overline{f}\,(reac\tan ts\ )}$

$= [4(393.5) + 4(205.85) - 2183.5]\ kJ = -533.8\ kJ$

(b) $4\ C_{(s)} + 4\ H_{2(g)} + O_{2(g)} \rightarrow C_3H_7COOH_{(l)}$

(c) $\Delta S°_f$ (butyric acid) $= S°$(butyric acid) - [4 $S°$(C) + 4 $S°$(H$_2$) + $S°$(O$_2$)]

$= 226.3 - [4(5.69) + 4(130.6) + 205] = -523.9\ J/K$

(d) $\Delta G°_f = \Delta H°_f - T\Delta S°_f = 533.8 - (298)(-0.5239)\ kJ$

$= -377.7\ kJ$

1985 D

(a) 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.

(b) 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.

(c) 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:

(a) $\Delta H>0$ 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.

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

(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.

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, $Ba(OH)_2 \cdot 8H_2O$, 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:

$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2\ NH_4SCN_{(s)} \rightarrow$
$$Ba^{2+} + 2\ SCN^- + 2\ NH_{3(g)} + 10\ H_2O_{(l)}$$

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

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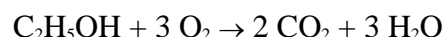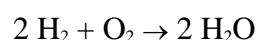
(b) The water on the wood froze because the endothermic reaction lowered the temperature below the freezing point of water.

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.
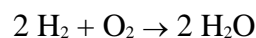
1988 B

Substance	Enthalpy of Combustion, $\Delta H°$ (kiloJoules/mol)	Absolute Entropy, $S°$ (Joules/mol-K)
$C_{(s)}$	-393.5	5.740
$H_{2(g)}$	-285.8	130.6
$C_2H_5OH_{(l)}$	-1366.7	160.7
$H_2O_{(l)}$	- -	69.91

(a) Write a separate, balanced chemical equation for the combustion of each of the following: $C_{(s)}$, $H_{2(g)}$, and $C_2H_5OH_{(l)}$. Consider the only products to be CO_2 and/or $H_2O_{(l)}$.

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

$$2\ C_{(s)} + 2\ H_{2(g)} + H_2O_{(l)} \rightarrow C_2H_5OH_{(l)}$$

Calculate the standard enthalpy change, $\Delta H°$, for the preparation of ethanol, as shown in the reaction above.

(c) Calculate the standard entropy change, $\Delta S°$, for the reaction given in part (b).

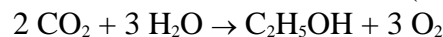(d) Calculate the value of the equilibrium constant at 25°C for the reaction represented by the equation in part (b).

Answer:

(a) $C + O_2 \rightarrow CO_2$

$2\ H_2 + O_2 \rightarrow 2\ H_2O$

$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

(b) $2\ C + 2\ O_2 \rightarrow 2\ CO_2$
$$\Delta H° = 2(-393.5) = -787.0\ kJ$$

$2\ H_2 + O_2 \rightarrow 2\ H_2O$
$$\Delta H° = 2(-285.8) = -571.6\ kJ$$

$2\ CO_2 + 3\ H_2O \rightarrow C_2H_5OH + 3\ O_2$
$$\Delta H° = -(-1366.7) = +1366.7\ kJ$$

$2\ C + 2\ H_2 + H_2O \rightarrow C_2H_5OH$ $\Delta H° = +8.1\ kJ$

OR

$\Delta H°_{comb.}\ C_{(s)} = \Delta H°_f\ CO_{2(g)}$

$\Delta H°_{comb.}\ H_{2(g)} = \Delta H°_f\ H_2O_{(l)}$
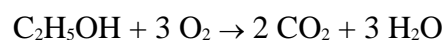
$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$
$$\Delta H° = -1366.7\ kJ$$

$\Delta H = \Re\ \Delta H_{\overline{f}(products)} - \Re\ \Delta H_{\overline{f}(reactants)}$

$= [2(-393.5) + 3(-258.8)] - [\Delta H°_f\ C_2H_5OH + 0]\ kJ$

$= -277.7\ kJ/mol$

$$2\,C + 2\,H_2 + H_2O \rightarrow C_2H_5OH$$
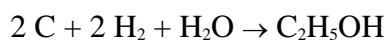
$$\Delta H = \Re\,\Delta H_{\bar{f}(products\;)} - \Re\,\Delta H_{\bar{f}(reactan ts\;)}$$

$$= [-277.7] - [0 + 0 + (-285.8)]\text{ kJ} = +8.1\text{ kJ}$$

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

$$= [160.7] - [11.5 + 261.2 + 69.9]\text{ J/mol.K}$$

$$= -181.9\text{ J/mol.K}$$

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

$$= 62300\text{ J}$$

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

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 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 head (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

$$Br_{2(l)} \rightarrow Br_{2(g)}$$
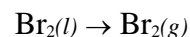
At 25°C the equilibrium constant, K_p, for the reaction above is 0.281 atmosphere.

(a) What is the $\Delta G°_{298}$ for this reaction?

(b) It takes 193 joules to vaporize 1.00 gram of $Br_{2(l)}$ at 25°C and 1.00 atmosphere pressure. What are the values of $\Delta H°_{298}$ and $\Delta S°_{298}$ for this reaction?

(c) Calculate the normal boiling point of bromine. Assume that $\Delta H°$ and $\Delta S°$ remain constant as the temperature is changed.

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

Answer:

(a) $\Delta G° = -RT\ln K$

$$= -(8.314\text{ J.mol}^{-1}\text{K}^{-1})(298\text{ K})(\ln 0.281)$$

$$= 3.14 \times 10^3\text{ J.mol}^{-1}$$

(b) $\Delta H° = (193\text{ J/g})(159.8\text{ g/mol}) = 3.084 \times 10^4\text{ J/mol}$

$$\Delta S_{\_} = \frac{\Delta H_{\_} - \Delta G_{\_}}{T} = \frac{(30840 - 3140)\text{J}}{298\text{ K}} =$$

$$= 92.9\text{ J/mol.K}$$

(c) At boiling point, $\Delta G° = 0$ and thus,

$$T = \frac{\Delta H_{\_}}{\Delta S_{\_}} = \frac{3.08 \times 10^4}{92.9} = 332\text{ K}$$

(d) vapor pressure = 0.281 atm.

1990 B

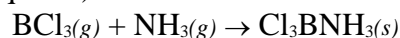Standard Free Energies of
Formation at 298 K

Thermodynamics, ΔH, ΔS, ΔG page 9

Substance	$\Delta G°_f$ 298 K, kJ mol^{-1}
$C_2H_4Cl_{2(g)}$	-80.3
$C_2H_5Cl_{(g)}$	-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.
$$C_2H_5Cl_{(g)} + Cl_{2(g)} \rightarrow C_2H_4Cl_{2(g)} + HCl_{(g)}$$
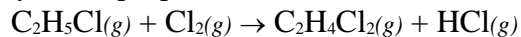
(a) Calculate the $\Delta H°$ for the reaction above, using the table of average bond dissociation energies.

(b) Calculate the $\Delta S°$ 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.

Answer:

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

$C_2H_5Cl + Cl_2 \rightarrow C_2H_4Cl_2 + HCl$
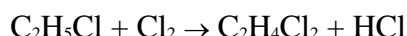
$\Delta H = (2794 + 243) - (2757 + 431)$ kJ = -151 kJ

OR

$CH + Cl-Cl \rightarrow C-Cl + HCl$ (representing the changes)

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

(b) $\Delta G = \Re \Delta G\_{(products\ )} - \Re \Delta G\_{(reactants\ )}$

$= [-80.3 + (-95.3)] - [-60.5 + 0] = -115$ kJ

$\Delta S\_ = \dfrac{\Delta H\_ - \Delta G\_}{T} = \dfrac{-151 - (-115)\,kJ}{298\,K} = -0.120\ ^{kJ}\!/_K$

(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**

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.
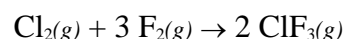
1991 D (Required)
$$BCl_{3(g)} + NH_{3(g)} \rightarrow Cl_3BNH_{3(s)}$$
The reaction represented above is a reversible reaction.

(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 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 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.

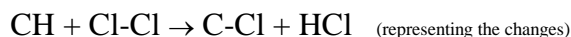(d) At equilibrium, $K = e^{-\Delta G/RT}$, where $\Delta G = 0$, $K = e° = 1$

1992 B
$$Cl_{2(g)} + 3\ F_{2(g)} \rightarrow 2\ ClF_{3(g)}$$
ClF_3 can be prepared by the reaction represented by the equation above. For ClF_3 the standard enthalpy of formation, $\Delta H_f°$, is -163.2 kilojoules/mole and the

standard free energy of formation, $\Delta G_f°$, is -123.0 kilojoules/mole.

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

(b) Calculate the standard entropy change, $\Delta S°$, 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 $Cl_{2(g)}$ 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.

Answer:

(a) $K_{eq} = e^{-\Delta G//RT} = e^{(-246000/(8.314)(298))}$

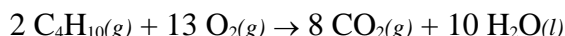 $= 1.32 \times 10^{43}$

(b) $\Delta S_\_ = \dfrac{\Delta H\_ - \Delta G\_}{T} = \dfrac{[-326400 - (-246000)]\,J}{298\,K} =$

   $= -270$ J/K

(c) ΔS 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 praticle **OR**
        3) more degrees of freedom

   (ii) $\Delta S° = \Sigma\, S°_{(products)} - \Sigma S°_{(reactants)}$

        $-270 = [2(281.5)] - [222.96 + 3(S°_{F_2})]$

        $S°_{F_2} = 203$ J/mol.K

1993 D

$$2\,C_4H_{10(g)} + 13\,O_{2(g)} \rightarrow 8\,CO_{2(g)} + 10\,H_2O_{(l)}$$

The reaction represented above is spontaneous at 25°C. Assume that all reactants and products are in their standard state.
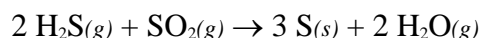
(a) Predict the sign of $\Delta S°$ for the reaction and justify your prediction.

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

(c) What must be the sign of $\Delta H°$ 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.

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

$$2\,H_2S_{(g)} + SO_{2(g)} \rightarrow 3\,S_{(s)} + 2\,H_2O_{(g)}$$

At 298 K, the standard enthalpy change, $\Delta H°$ for the reaction represented above is -145 kilojoules.

(a) Predict the sign of the standard entropy change, $\Delta S°$, 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 $\Delta G°$ 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 <u>nonspontaneous</u> 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?

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 $+145$ kJ and the sign of $\Delta G°$ becomes pos. (+) and the reaction is non-spontaneous.

(c) When $-T\Delta S° < +145$ kJ, $K_{eq} > 1$,
when $-T\Delta S° = +145$ kJ, $K_{eq} = 1$,
when $-T\Delta S° > +145$ kJ, $K_{eq} < 1$, but > 0

(d) $\Delta G = 0$ at this point, the equation is $T = \Delta H°/\Delta S°$; 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 $CO_{2(g)}$ and $H_2O_{(l)}$.

(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 kJ/mol. Calculate the heat of formation, $\Delta H_f°$, of propane given that $\Delta H_f°$ of $H_2O_{(l)} = -285.3$ kJ/mol and $\Delta H_f°$ of $CO_{2(g)} = -393.5$ 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·K), calculate the increase in temperature of water.

Answer:

(a) $C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$
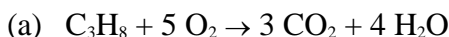
(b) 10.0 g C_3H_8 × 1 mol C_3H_8/44.0 g × 5 mol O_2/1 mol C_3H_8) = 1.14 mol O_2

$$V_{O_2} = \frac{nRT}{P} = \frac{(1.14\ \text{mol})(0.0821\frac{\text{L\_atm}}{\text{mol\_K}})(303K)}{1.00\,\text{atm}}$$

= 28.3 L O_2 ; f(28.3 L,21.0%) = 135 L of air

(c)
$$\Delta H°_{comb} = [\Delta H°_{f(CO_2)} + \Delta H°_{f(H_2O)}]$$

$$-[\Delta H°_{f(C_3H_8)} + \Delta H°_{f(O_2)}]$$

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

$X = \Delta H°_{comb}) = -101.6$ kJ/mol

(d) $q = 30.0$ g C_3H_8 × 1 mol/44.0 g × 2220.1 kJ/1 mol = 1514 kJ

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

1514 kJ = (8.00 kg)(4.184 J/g·K)(ΔT)

$\Delta T = 45.2°$

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.

    $PbI_{2(s)} \rightarrow Pb^{2+} + 2\ I^-$ $\Delta H = +46.5$ kilojoules

(a) How does the entropy of the system $PbI_{2(s)}$ + $H_2O_{(l)}$ change as $PbI_{2(s)}$ 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 $Pb(NO_3)_2$ 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. $K_{sp} = [Pb^{2+}][I^-]^2$. 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

$$C_2H_2(g) + 2\ H_2(g) \rightarrow C_2H_6(g)$$
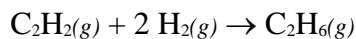
Information about the substances involved in the reaction represented above is summarized in the following tables.

Substance	$S°$ (J/mol·K)	$\Delta H°_f$ (kJ/mol)
$C_2H_2(g)$	200.9	226.7
$H_2(g)$	130.7	0
$C_2H_6(g)$	- - - -	-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, $\Delta S°$, 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, $\Delta G°$, for the reaction. What does the sign of $\Delta G°$ 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 C≡C bond energy in C_2H_2 in kilojoules per mole.

Answer:

(a) -232.7 J/K = $S°_{(C2H6)}$ - [2(130.7) + 200.9] J/K

$S°_{(C2H6)}$ = 229.6 J/K

(b) $\Delta H° = \Sigma \Delta H_{\hat{a}}°_{(products)} - \Sigma \Delta H_{\hat{a}}°_{(reactants)}$

= -84.7 kJ - [226.7 + 2(0)] kJ = -311.4 kJ

$\Delta G° = \Delta H° - T\Delta S°$

= -311.4 kJ - (298K)(-0.2327 kJ/K) = -242.1 kJ

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

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

= 2.74×10^{42}

(d) $\Delta H°$ = bond energy of products - bond energy of reactants

-311.4 kJ = [(2)(436) + $E_{c≡c}$ + (2)(414)] - [347 + (6)(414)] kJ

$E_{c≡c}$ = 820 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.

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

(a) What is the sign of $\Delta S°$ for the reaction? Explain.

(b) What change, if any, will occur in $\Delta G°$ for the reaction as the temperature is increased? Explain your reasoning in terms of thermodynamic principles.

(c) 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.

(d) 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.
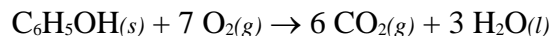
Answer:

(a) The sign of $\Delta S°$ 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.

(b) $\Delta G° = \Delta H° - T\Delta S°$. Both $\Delta S°$ and $\Delta H°$ are (+). As temperature increases, at some point the sign of $\Delta G°$ will change from (+) to (-), when the system will become spontaneous.

(c) 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.

(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.

Thermodynamics, ΔH, ΔS, ΔG

1998 B

$$C_6H_5OH_{(s)} + 7\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 3\ H_2O_{(l)}$$

When a 2.000-gram sample of pure phenol, $C_6H_5OH_{(s)}$, 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, $\Delta H°_{\hat{a}}$; at 25°C (kJ/mol)	Absolute Entropy, $S°$, at 25°C (J/mol·K)
$C_{(graphite)}$	0.00	5.69
$CO_{2(g)}$	-393.5	213.6
$H_{2(g)}$	0.00	130.6
$H_2O_{(l)}$	-285.85	69.91
$O_{2(g)}$	0.00	205.0
$C_6H_5OH_{(s)}$	?	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, $\Delta H°_{\hat{a}}$, of phenol in kilojoules per mole at 25°C.

(c) Calculate the value of the standard free-energy change, $\Delta G°$, 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) $\Delta H_{comb} = \dfrac{kJ}{\frac{mass}{molar\,mass}} = \dfrac{64.98\,kJ}{2.000\,g \Big/ 94.113\,{}^{g}\!/_{mol}} = -3058\,kJ$

(b) $\Delta H_{comb} = \Sigma\Delta H°_{\hat{a}}(products) - \Sigma\Delta H°_{\hat{a}}(reactants)$

  -3058 kJ/mol = [(6)(-393.5)+(3)(-285.85)]-[X+0]

  = -161 kJ

(c) $\Delta S° = \Sigma S°(products) - \Sigma S°(reactants)$

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

  = -87.67 J

  $\Delta G° = \Delta H° - T\Delta S° = -3058 - (298)(-0.08767)$ kJ

  = -3032 kJ

(d) $2.000\ g\ phenol\ \infty\ \dfrac{1\ mol\ phenol}{94.113\ g}\ \infty\ \dfrac{7\ mol\ O_2}{1\ mol\ phenol} =$

= 0.1488 mol O_2
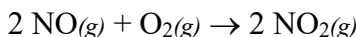
mol of gaseous product $= \frac{6}{7}(0.1489) + \frac{3}{7}(0.1489)$

= 0.1913 mol of gas

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

= 0.601 atm (or 457 mm Hg, or 60.9 kPa)

2001 B

$$2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$$

$$\Delta H° = -114.1\ kJ,\ \Delta S° = -146.5\ J\ K^{-1}$$

The reaction represented above is one that contributes significantly to the formation of photochemical smog.

(a) Calculate the quantity of heat released when 73.1 g of $NO_{(g)}$ is converted to $NO_{2(g)}$.

(b) For the reaction at 25°C, the value of the standard free-energy change, $\Delta G°$, is -70.4 kJ.

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

  (ii) Indicate whether the value of $\Delta G°$ would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.

(c) Use the data in the table below to calculate the value of the standard molar entropy, $S°$, for $O_{2(g)}$ at 25°C.

	Standard Molar Entropy, $S°$ ($J\ K^{-1}\ mol^{-1}$)
$NO_{(g)}$	210.8
$NO_{2(g)}$	240.1

(d) Use the data in the table below to calculate the bond energy, in $kJ\ mol^{-1}$, of the nitrogen-oxygen bond in NO_2. Assume that the bonds in the NO_2 molecule are equivalent (*i.e.*, they have the same energy).

	Bond Energy ($kJ\ mol^{-1}$)
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in O_2	495
Nitrogen-oxygen bond in NO_2	?

Thermodynamics, ΔH, ΔS, ΔG

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Answer:

(a) $73.1 \text{ g} \times \dfrac{1 \text{ mol NO}}{30.007 \text{ g}} \times \dfrac{114.1 \text{ kJ}}{2 \text{ mol NO}} = 139 \text{ kJ}$

(b) (i) $K_{eq} = e^{-\Delta G/RT} = e^{-(-70400/(8.31)(298))} = 2.22\times10^{12}$

(ii) less negative; $\Delta G° = \Delta H° - T\Delta S°$; as temperature increases, $-T\Delta S°$ becomes a larger positive value causing an increase in $\Delta G°$ (less negative).

(c) $\Delta S° = \Delta S°(\text{products}) - \Delta S°(\text{reactants})$

$-146.5 = [(2)(240.1)] - [(210.8)(2) + \Delta S°_{oxygen}]$ J/K

$\Delta S°_{oxygen} = +205.1 \text{ J/K}$

(d) $2 \text{ NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2 \text{ NO}_{2(g)} + 114.1 \text{ kJ}$

$\Delta H = $ enthalpy of bonds broken – enthalpy of bonds formed

$-114.1 = [(607)(2) + 495] - 2X$

$X = 912 \text{ kJ} / 2 \text{ N=O bonds}$

$456 \text{ kJ} = $ bond energy for N=O bond

2002 D Required (repeated in lab procedures)

A student is asked to determine the molar enthalpy of neutralization, ΔH_{neut}, for the reaction represented above. The student combines equal volumes of 1.0 M HCl and 1.0 M NaOH in an open polystyrene cup calorimeter. The heat released by the reaction is determined by using the equation $q = mc\Delta T$.

Assume the following.

- Both solutions are at the same temperature before they are combined.
- The densities of all the solutions are the same as that of water.
- Any heat lost to the calorimeter or to the air is negligible.
- The specific heat capacity of the combined solutions is the same as that of water.

(a) Give appropriate units for each of the terms in the equation $q = mc\Delta T$.

(b) List the measurements that must be made in order to obtain the value of q.

(c) Explain how to calculate each of the following.

(i) The number of moles of water formed during the experiment

(ii) The value of the molar enthalpy of neutraliza-

tion, ΔH_{neut}, for the reaction between HCl$_{(aq)}$ and NaOH$_{(aq)}$

(d) The student repeats the experiment with the same equal volumes as before, but this time uses 2.0 M HCl and 2.0 M NaOH.

(i) Indicate whether the value of q increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

(ii) Indicate whether the value of the molar enthalpy of neutralization, ΔH_{neut}, increases, decreases, or stays the same when compared to the first experiment. Justify your prediction.

(e) Suppose that a significant amount of heat were lost to the air during the experiment. What effect would this have on the calculated value of the molar enthalpy of neutralization, ΔH_{neut}? Justify your answer.

Answer:

(a) q in J, m in grams, C in J/g°C, T in °C

(b) mass or volume of each solution

starting temperature of each reagent

ending temperature of mixture

(c) (i) both are 1 M acid and base and react on a 1:1 basis

$\text{volume} \times \dfrac{1 \text{ mol HCl}}{1000 \text{ mL}} \times \dfrac{1 \text{ mol H}^+}{1 \text{ mol HCl}} = \text{mol of H}^+$

$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

(ii) $\dfrac{\text{joules released}}{\text{mol H}_2\text{O produced}}$

(d) (i) increases. Twice as much water is produced so it is twice the energy released in the same volume of solution

(ii) same. $\dfrac{\text{twice energy}}{\text{twice mol water}} = $ same result

(e) smaller. heat lost to the air gives a smaller amount of temperature change in the solution, which leads to a smaller measured heat release
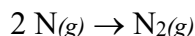
2003 D

Answer the following questions that relate to the chemistry of nitrogen.

(a) Two nitrogen atoms combine to form a nitrogen

molecule, as represented by the following equation.

$$2 \text{ N}_{(g)} \rightarrow \text{N}_{2(g)}$$

Using the table of average bond energies below, determine the enthalpy change, ΔH, for the reaction.

Bond	Average Bond Energy $(kJ \ mol^{-1})$
N–N	160
N=N	420
N≡N	950

(b) The reaction between nitrogen and hydrogen to form ammonia is represented below.

$$\text{N}_{2(g)} + 3 \text{ H}_{2(g)} \rightarrow 2 \text{ NH}_{3(g)} \qquad \Delta H° = -92.2 \text{ kJ}$$

Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Justify your answer.

(c) The value of $\Delta G°$ for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.

(d) When $\text{N}_{2(g)}$ and $\text{H}_{2(g)}$ are placed in a sealed container at a low temperature, no measurable amount of $\text{NH}_{3(g)}$ is produced. Explain.

Answer:

(a) a triple bond is formed, an exothermic process

$\Delta H = -950 \text{ kJ mol}^{-1}$

(b) (–); the mixture of gases (high entropy) is converted into a pure gas (low entropy) and the 4 molecules of gas is reduced to 2, a smaller number of possible microstates is available

(c) $\Delta G° = \Delta H° - T\Delta S°$; enthalpy favors spontaneity ($\Delta H < 0$), negative entropy change does not favor spontaneity. Entropy factor becomes more significant as temperature increases. At high temperatures the $T\Delta S$ factor becomes larger in magnitude than ΔH and the reaction is no longer spontaneous ($\Delta G > 0$).

(d) at low temperatures, the kinetic energy of the molecules is low and very few molecules have enough activation energy

2004 B (repeated in stoichiometry)

$$2 \text{ Fe}_{(s)} + \tfrac{3}{2} \text{ O}_{2(g)} \rightarrow \text{Fe}_2\text{O}_{3(s)} \quad \Delta H_f° = -824 \text{ kJ mol}^{-1}$$
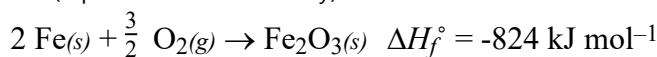
Iron reacts with oxygen to produce iron(III) oxide as represented above. A 75.0 g sample of $\text{Fe}_{(s)}$ is mixed with 11.5 L of $\text{O}_{2(g)}$ at 2.66 atm and 298 K.

(a) Calculate the number of moles of each of the following before the reaction occurs.

(i) $\text{Fe}_{(s)}$

(ii) $\text{O}_{2(g)}$

(b) Identify the limiting reactant when the mixture is heated to produce Fe_2O_3. Support your answer with calculations.

(c) Calculate the number of moles of Fe_2O_3 produced when the reaction proceeds to completion.

(d) The standard free energy of formation, $\Delta G_f°$ of Fe_2O_3 is –740. kJ mol^{-1} at 298 K.

(i) Calculate the standard entropy of formation $\Delta S_f°$ of Fe_2O_3 at 298 K. Include units with your answer.

(ii) Which is more responsible for the spontaneity of the formation reaction at 298K, the standard enthalpy or the standard entropy?

The reaction represented below also produces iron(III) oxide. The value of $\Delta H°$ for the reaction is –280 kJ per mol.

$$2 \text{ FeO}_{(s)} + \tfrac{1}{2} \text{ O}_{2(g)} \rightarrow \text{Fe}_2\text{O}_{3(s)}$$
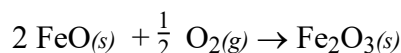
(e) Calculate the standard enthalpy of formation, $\Delta H_f°$ of $\text{FeO}_{(s)}$.

Answer:

(a) (i) $75.0 \text{ g Fe} \times \dfrac{1 \text{ mol}}{55.85 \text{ g}} = 1.34 \text{ mol Fe}$

(ii) $PV = nRT$, $n = \dfrac{PV}{RT}$

$\dfrac{(2.66 \text{ atm})(11.5 \text{ L})}{(0.0821 \frac{\text{L atm}}{\text{mol K}})(298 \text{ K})} = 1.25 \text{ mol O}_2$

(b) Fe; $1.34 \text{ mol Fe} \times \dfrac{\frac{3}{2} \text{ mol O}_2}{2 \text{ mol Fe}} = 1.01 \text{ mol O}_2$

excess O_2, limiting reagent is Fe

(c) $1.34 \text{ mol Fe} \times \dfrac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} = 0.671 \text{ mol Fe}_2\text{O}_3$

(d) (i) $\Delta G_f° = \Delta H_f° - T\Delta S_f°$

$-740 \text{ kJ mol}^{-1} = -824 \text{ kJ mol}^{-1} - (298 \text{ K})(\Delta S_f°)$
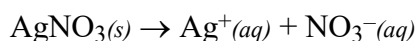
$\Delta S_f° = 0.282 \text{ kJ mol}^{-1} \text{ K}^{-1}$

(ii) standard enthalpy; entropy decreases (a non-spontaneous process) so a large change in enthalpy (exothermic) is need to make this reaction spontaneous

(e) $\Delta H = \Sigma\Delta H_{f(products)} - \Sigma\Delta H_{f(reactants)}$

–280 kJ mol^{-1} = –824 kJ mol^{-1} – [2(ΔH_f° FeO) – $^1/_2(0)$]

= -272 kJ mol^{-1}

2005 D [repeated in electrochem]

$$AgNO_{3(s)} \rightarrow Ag^+{}_{(aq)} + NO_3{}^-{}_{(aq)}$$

The dissolving of $AgNO_{3(s)}$ in pure water is represented by the equation above..

(a) Is ΔG for the dissolving of $AgNO_{3(s)}$ positive, negative, or zero? Justify your answer.

(b) Is ΔS for the dissolving of $AgNO_{3(s)}$ positive, negative, or zero? Justify your answer.

(c) The solubility of $AgNO_{3(s)}$ increases with increasing temperature.

   (i) What is the sign of ΔH for the dissolving process? Justify your answer.

   (ii) Is the answer you gave in part (a) consistent with your answers to parts (b) and (c) (i)? Explain.

The compound NaI dissolves in pure water according to the equation $NaI_{(s)} \rightarrow Na^+{}_{(aq)} + I^-{}_{(aq)}$. Some of the information in the table of standard reduction potentials given below may be useful in answering the questions that follow.

Half-reaction	E° (V)
$O_{2(g)} + 4\ H^+ + 4\ e\text{-} \rightarrow 2\ H_2O_{(l)}$	1.23
$I_{2(s)} + 2\ e\text{-} \rightarrow 2\ I^-$	0.53

$2\ H_2O_{(l)} + 2\ e\text{-} \rightarrow H_{2(g)} + 2\ OH^-$	-0.83
$Na^+ + e\text{-} \rightarrow Na_{(s)}$	-2.71

(d) An electric current is applied to a 1.0 M NaI solution.

(i) Write the balanced oxidation half reaction for the reaction that takes place.

(ii) Write the balanced reduction half-reaction for the reaction that takes place.

(iii) Which reaction takes place at the anode, the oxidation reaction or the reduction reaction?

(iv) All electrolysis reactions have the same sign for ΔG°. Is the sign positive or negative? Justify your answer.

Answer:

(a) sign of ΔG = (–); since the dissolving of silver nitrate is spontaneous, then $\Delta G < 0$

(b) sign of ΔS = (+); an increase in entropy occurs when a solid becomes aqueous and the products contain more particles than the reactants.

(c) (i) sign of ΔH = (+); an endothermic process will be favored when the temperature is increased.

(ii) yes; $\Delta G = \Delta H - T\Delta S$, as the temperature increases the $-T\Delta S$ term will increase, keeping ΔG negative.

(d) (i) $2\ I^- \rightarrow I_{2(s)} + 2\ e\text{-}$

(ii) $2\ H_2O_{(l)} + 2\ e\text{-} \rightarrow H_{2(g)} + 2\ OH^-$

(iii) anode = oxidation

(iv) sign ΔG° = (+); by definition, an electrolysis is a non-spontaneous process and requires the input of energy to get it to proceed.