1995

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, $\Delta H_f^\circ$ of propane given that $\Delta H_f^\circ$ of $H_2O(l)$ = −285.3 kJ/mol and $\Delta H_f^\circ$ 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.

1998

$$C_6H_5OH(s) + 7\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$$

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, $\Delta H^\circ_f$, at 25°C (kJ/mol) | Absolute Entropy, $S^\circ$, 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, $\Delta H^\circ_f$, of phenol in kilojoules per mole at 25°C.

(c) Calculate the value of the standard free-energy change, $\Delta G^\circ$ 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.)

# Essay Questions

1991

$$BCl_3(g) + NH_3(g) \leftrightarrows Cl_3BNH_3(s)$$

The reaction represented above is a reversible reaction.

(a) Predict the sign of the entropy change, $\Delta S$, as the reaction proceeds to the right. Explain your prediction.
(b) If the reaction spontaneously proceeds to the right, predict the sign of the enthalpy change, $\Delta H$. Explain your prediction.
(c) The direction in which the reaction spontaneously proceeds changes as the temperature is increased above a specific temperature. Explain.
(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.

1993

$$2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(l)$$

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.

1994

$$2\ H_2S(g) + SO_2(g) \rightarrow 3\ S(s) + 2\ H_2O(g)$$

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 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?

# Problems

1990

Standard Free Energies of Formation at 298 K

| Substance | $\Delta G^\circ_f$ 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 $\Delta H^\circ$ for the reaction above, using the table of average bond dissociation energies.
(b) Calculate the $\Delta S^\circ$ for the reaction at 298 K, using data from either table as needed.
(c) Calculate the value of $K_{eq}$ for the reaction at 298 K.
(d) What is the effect of an increase in temperature on the value of the equilibrium constant? Explain your answer.

1992

$$Cl_2(g) + 3\,F_2(g) \rightarrow 2\,ClF_3(g)$$

$ClF_3$ can be prepared by the reaction represented by the equation above. For $ClF_3$ the standard enthalpy of formation, $\Delta H_f^\circ$,is −163.2 kilojoules/mole and the standard free energy of formation, $\Delta G_f^\circ$, is −123.0 kilojoules/mole.

(a) Calculate the value of the equilibrium constant for the reaction at 298K.
(b) Calculate the standard entropy change, $\Delta S^\circ$, for the reaction at 298K.
(c) If $ClF_3$ were produced as a liquid rather than as a gas, how would the sign and the magnitude of $\Delta S$ for the reaction be affected? Explain.
(d) At 298K the absolute entropies of $Cl_2(g)$ and $ClF_3(g)$ are 222.96 joules per mole ·Kelvin and 281.50 joules per mole · Kelvin, respectively.
   (i) Account for the larger entropy of $ClF_3(g)$ relative to that of $Cl_2(g)$.
   (ii) Calculate the value of the absolute entropy of $F_2(g)$ at 298K.

2003

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.

$$2\,N(g) \rightarrow N_2(g)$$

Using the table of average bond energies below, determine the enthalpy change, $\Delta H$, 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.

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \qquad \Delta H^\circ = -92.2\text{ kJ}$$

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

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

(d) When $N_2(g)$ and $H_2(g)$ are placed in a sealed container at a low temperature, no measurable amount of $NH_3(g)$ is produced. Explain.

2004B

$$N_2(g) + 2\,H_2(g) \leftrightarrows N_2H_4(g) \qquad \Delta H^\circ_{298} = +95.4\text{ kJ mol}^{-1};\ \Delta S^\circ_{298} = -176\text{ J K}^{-1}\text{ mol}^{-1}$$

Answer the following questions about the reaction represented above using principles of thermodynamics.

(a) On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.

(b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.

(c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.

(d) Explain how to determine the value of the equilibrium constant, $K_{eq}$, for the reaction. (Do not do any calculations.)

(e) Predict whether the value of $K_{eq}$ for the reaction is greater than 1, equal to 1, or less than 1. Justify your prediction.

## 1995

2)

a) one point

$$C_3H_8 + 5\ O_2 \text{-->} 3\ CO_2 + 4\ H_2O$$

ignore phases (even when wrong)
multiples are OK
if balanced wrong, parts b and c should be consistent

---

b) four points

10.0 g $C_3H_8$ x (1 mol $C_3H_8$ / 44.1 g $C_3H_8$) = 0.227 mol $C_3H_8$

0.227 mol $C_3H_8$ x (5 mol $O_2$ / 1 mol $C_3H_8$) = 1.13 mol $O_2$

V = [ (1.13 mol $O_2$) (0.0821 L atm $mol^{-1}$ $K^{-1}$) (303K) ] ÷ 1.00 atm = 28.1 L $O_2$

28.1 L $O_2$ x (100 L air / 21.0 L $O_2$) = 134 L air

Note: answer must be consistent with part a

---

c) two points

[delta]$H°_{rxn}$ = [sigma] [delta]$H°_f$ (products) - [sigma] [delta]$H°_f$ (reactants)

-2,220.1 kJ = [ 4 (-285.3kJ) + 3 (-393.5 kJ)] - [5 (0 kJ) + [delta]$H°_f$ ($C_3H_8$)]

-2,220.1 kJ = -1,141.2 kJ - 1,180.5 kJ - [delta]$H°_f$ ($C_3H_8$)

-2,220.1 kJ = -2,321.7 kJ - [delta]$H°_f$ ($C_3H_8$)

-101.6 kJ = [delta]$H°_f$ ($C_3H_8$)

answer should be consistent with part a
1 point deducted if negative sign missing from answer
1 point deducted if -2,220.1 kJ substituted for [delta]$H°_f$ ($C_3H_8$)
no points earned if coefficients are inconsistent and not set equal to [delta]H°

d) two points

30.0 g $C_3H_8$ x (1 mol $C_3H_8$ / 44.1 g $C_3H_8$) x (2,220.1 kJ / 1 mol $C_3H_8$) = 1.51 x $10^3$ kJ

1.51 x $10^3$ kJ = 1.51 x $10^6$ J = (8,000 g) (4.18 J $g^{-1}$ $K^{-1}$) ([delta]T)

45.1 K (or °C) = [delta]T

must correctly substitute into q = m$C_p$[delta]T for 1 point
1 point earned if q value wrong but [delta]T consistent

## 1998

a) $2.000\ g \times \frac{1\ mol}{94.113\ g} = 0.02125$ mol phenol — 1 point

Heat released per mole $= \frac{64.98\ kJ}{0.02125\ mol} = 3{,}058\ kJ\ mol^{-1}$

Or, $\Delta H_{comb} = -3058$ kJ mol$^{-1}$ — 1 point

*Units not necessary*

b) $\Delta H_{comb} = -3058$ kJ mol$^{-1}$ — 1 point

-3058 kJ = [6(-395.5) + 3(-285.85)] – [$\Delta H_f^o$ (phenol)] — 1 point

$\Delta H_f^o$ (phenol) = -161 kJ — 1 point

*One point earned for correct sign of heat of combustion, one point for correct use of moles / coefficients, and one point for correct substitution*

*c)* $\Delta S^o$ = [3(69.91) + 6(213.6)] [7(205.0) + 144.0] = -87.67 *J/K* — *1 point*

$\Delta G^o = \Delta H^o - T\Delta S^o$ = 3058 kJ – (298 K)(-0.08767 kJ K$^{-1}$) = -3032 kJ — 1 point

*Units not necessary; no penalty if correct except for wrong $\Delta H_{comb}$ for part a*

d) moles gas = 9 × [moles from part a] = 9 (0.02125 mol) = 0.1913 moles gas

$$P = \frac{nRT}{V} = \frac{(0.1913\ mol)(0.0821\ L\ atm\ mol^{-1}\ K^{-1})(383\ K)}{10.0\ L} = 0.601\ atm$$ — 1 point

## 1991

a) two points

ΔS will be negative. The system becomes more ordered as two gases form a solid.

---

b) two points

ΔH must be negative. For the reaction to be spontaneous, ΔG must be negative, so ΔH must be more negative than -TΔS is positive.

---

c) two points

As T increases, -TΔS increases. Since ΔS is negative, the positive -TΔS term will eventually exceed ΔH (which is negative), making ΔG positive. (In the absence of this, ΔG = ΔH - TΔS and general discussion of the effect of T and ΔS gets 1 point.)

---

d) two points

The equilibrium constant is 1. The system is at equilibrium at this temperature with an equal tendancy to go in either direction.

OR

$\Delta G = 0$ at equilibrium so $K = 1$ in $\Delta G = -RT \ln K$

(In the absence of these, $\Delta G = -RT \ln K$ gets 1 point).

**1993**

8) average = 4.5

a) one point

[delta]S < 0

The number of moles of gaseous products is less than the number of moles of gaseous reactant

OR

a liquid is formed from gaseous reactants.

---

b) one point

[delta]G < 0

[delta]G becomes less negative as the temperature is increased since [delta]S < 0 and [delta]G = [delta]H - T[delta]S. The term - T[delta]S adds a positive number to [delta]H.

---

c) one point

[delta]H < 0

The bond energy of the reactants is less than the bond energy of the products.

---

d) one point

The reaction has a high activation energy

OR

is kinetically slow,

OR

a specific neuton of the needs for a catalyst or spark.

**1990**

3)

a) two points

[delta]H = bonds broken minus bonds formed.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_2H_5Cl$ | + | Cl-Cl | ---> | $C_2H_4Cl_2$ | + | HCl |
| [delta]H = | (2794 | + | 243) | minus | (2757 | + | 431) |

[delta]H = 3037 - 3188 = - 151 kJ $mol^{-1}$

OR

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | CH | + | Cl-Cl | ---> | C-Cl | + | HCl |
| [delta]H = | (414 | + | 243) | minus | (377 | + | 431) |

[delta]H = - 151 kJ $mol^{-1}$

---

b) four points

[delta]G = [[delta]G°$_f$ $C_2H_4Cl_2$ + [delta]G°$_f$ HCl] - [[delta]G°$_f$ $C_2H_5Cl$ + [delta]G°$_f$ $Cl_2$]

= (- 80.3 - 95.3) - (- 60.5 + 0) = - 115 kJ

[delta]G = [delta]H - T[delta]S

[delta]S = ((- 151 kJ - (- 115 kJ)) / 298 = - 0.120 kJ $mol^{-1}$ $K^{-1}$

---

c) two points

[delta]G = - RT ln K

- ln K = - 11510 / (8.314 x 298)

ln K = 46.46

K = 1.50 x $10^{20}$

---

d) one point

$K_{eq}$ will decrease with an increase in T because the reverse (endothermic) reaction will be favored with addition of heat

OR

[delta]G will be less negative with an increase in temperature (from [delta]G = [delta]H - T[delta]S) which will cause K to decrease.

**1992**

3)

a) two points [delta]G° = - RT ln K; rearranging gives ln K = [delta]G° ÷ - RT ln K = - 123,000 J ÷ - ((8.31 J/mol K) (298 K)) = 49.7 K = 3.72 x $10^{21}$

---

b) two points

[delta]G° = [delta]H° - T[delta]S°

- 246,000 J = - 326,400 J - (298) (x)

x = - 270 J / K

---

c) two points

[delta]S is a larger negative number

$ClF_3$ (liquid) is more ordered (less disordered) than $ClF_3$ (gas)

---

d) three points

i) $ClF_3$ is a more complex molecule (i.e. more atoms) with more vibrational and rotational degrees of freedom than $Cl_2$

ii) $Cl_2 + 3\ F_2 \text{--->} 2\ ClF_3$; use Hess's Law

[sigma]$S_{rxn}$ = [sigma]$S_{\text{products}}$ - [sigma]$S_{\text{reactants}}$

$-270 = [2\ (281.50)] - [222.96 + 3x]$

$x = 203\ J\ mol^{-1}\ K^{-1}$

---

## Question 7

$$N_2(g) + 2\,H_2(g) \rightleftarrows N_2H_4(g) \qquad \Delta H^\circ_{298} = +95.4 \text{ kJ mol}^{-1}\,;\ \Delta S^\circ_{298} = -176 \text{ J K}^{-1}\text{ mol}^{-1}$$

7. Answer the following questions about the reaction represented above using principles of thermodynamics.

(a) On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer.

| | |
|---|---|
| Bond energy (B.E.) of reactants is greater than bond energy of products. Reaction is endothermic, so more energy is required to break bonds of reactants than is given off when new bonds form in products: $\Delta H = \sum(\text{B.E.})_{reactants} - \sum(\text{B.E.})_{products} > 0$ | 1 point for indicating that reactants have greater bond strength<br><br>1 point for correct explanation |

(b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.

| | |
|---|---|
| Entropy change favors reactants.<br><br>Since there are three moles of reactants in gas phase compared to only one mole of products, there are more possible arrangements of reactant molecules compared to product molecules. | 1 point for indicating which, reactants or products, are favored<br><br>1 point for explanation |

(c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.

| | |
|---|---|
| Reactants are favored because $\Delta G^\circ$ for reaction is positive.<br>$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, so a positive $\Delta H^\circ$ and a negative $\Delta S^\circ$ means $\Delta G^\circ$ is always positive, independent of temperature.<br><br><u>Note:</u> Calculation of $\Delta G^\circ$ is acceptable with explanation. | 1 point for indicating which, reactants or products, are favored<br><br>1 point for explanation |

## Question 7 (cont'd.)

(d) Explain how to determine the value of the equilibrium constant, $K_{eq}$, for the reaction. (Do not do any calculations.)

| | |
|---|---|
| Solve formula $\Delta G^\circ = -RT \ln K_{eq}$ for $K_{eq}$ and plug in value of $\Delta G^\circ$ calculated in part (c), value of temperature (298 K), and value of $R$ (8.31 J mol$^{-1}$ K$^{-1}$). | 1 point for correct mathematical equation and substitution |

(e) Predict whether the value of $K_{eq}$ for the reaction is greater than 1, equal to 1, or less than 1. Justify your answer.

| | |
|---|---|
| $K_{eq}$ value is less than 1 for the reaction as written.<br><br>$\Delta G^\circ = -RT \ln K_{eq}$, and since $\Delta G^\circ$ is positive, $\ln K_{eq}$ will be a negative number which means that $K_{eq}$ is less than one.<br><br>*OR*<br><br>$\Delta H^\circ > 0$ and $S^\circ < 0$, thus $\Delta G^\circ > 0$, which means that $K_{eq} < 1$. | 1 point for the correct prediction with an explanation |