1 Write an equation to represent the following enthalpy changes.

(a) Second ionisation energy of calcium

(b) Standard enthalpy change of formation of NaNO₃(s)

(c) Standard enthalpy change of hydration of Na⁺

(d) Bond energy of I–I

(e) Standard enthalpy change of atomisation of bromine

2 State the enthalpy change represented by the following equations.

(a) HNO₃(aq) + KOH(aq) → KNO₃(aq) + H₂O(l)

(b) S⁻(g) + e⁻ → S²⁻(g)

(c) CO(g) + ½O₂(g) → CO₂(g)

(d) Al³⁺(g) + 3F⁻(g) → AlF₃(s)

(e) Na₂SO₄(s) + aq → 2Na⁺(aq) + SO₄²⁻(aq)
3 (a) When 2.76 g (0.020 mol) of potassium carbonate was added to 30.0 cm$^3$ of approximately 2 mol dm$^{-3}$ hydrochloric acid, the temperature rose by 5.2 °C.

(i) Write an equation for this reaction.

(ii) Calculate the enthalpy change of this reaction per mole of potassium carbonate. Assume that the specific heat capacities of all solutions are 4.2 J g$^{-1}$K$^{-1}$ and that all solutions have a density of 1.0 g cm$^{-3}$.

(iii) Explain why the concentration of hydrochloric acid need only be approximately 2 mol dm$^{-3}$.

(b) When 2.00 g (0.020 mol) of potassium hydrogencarbonate was added to 30.0 cm$^3$ of the same hydrochloric acid, the temperature fell by 3.7 °C.

(i) Write an equation for this reaction.

(ii) Calculate the enthalpy change of this reaction per mole of potassium hydrogencarbonate.

(c) When potassium hydrogencarbonate is heated, it decomposes into potassium carbonate, water and carbon dioxide. By applying Hess’ law and using your results in (a)(ii) and (b)(ii), calculate the enthalpy change for the thermal decomposition of 1 mole of potassium hydrogencarbonate.
1 Nitroglycerine ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$) is a flammable and explosive oil. It undergoes combustion to give $\text{CO}_2(\text{g})$, $\text{NO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ as products. Using the data below, construct an energy cycle to calculate the enthalpy change of combustion of nitroglycerine.

- Enthalpy change of combustion of $\text{C}(\text{s})$ = $-394 \text{ kJ mol}^{-1}$
- Enthalpy change of combustion of $\text{H}_2(\text{g})$ = $-242 \text{ kJ mol}^{-1}$
- Enthalpy change of formation of $\text{NO}_2(\text{g})$ = $+34 \text{ kJ mol}^{-1}$
- Enthalpy change of formation of $\text{C}_3\text{H}_5\text{N}_3\text{O}_9(\text{l})$ = $-354 \text{ kJ mol}^{-1}$

Enthalpy change of combustion of nitroglycerine ____________

2 Use of the Data Booklet is relevant to this question.

The $\text{C}_1$–$\text{C}_2$ double bond in Vitamin C may be reduced using hydrogen gas, under suitable conditions, according to the equation below.

\[
\begin{align*}
\text{HO-C-C-O-C-OO} + \text{H}_2(\text{g}) & \rightarrow \text{HO-C-C-O-C-OO} \\
\text{Vitamin C} & \rightarrow \text{Vitamin C}
\end{align*}
\]

Calculate the enthalpy change of this reaction, showing your working clearly.
5 Chemical Energetics and Thermodynamics – Class Exercise 3 20 min
Lattice Energy, Born–Haber Cycle and Enthalpy Changes of Hydration and Solution

1 *Use of the Data Booklet is relevant to this question.*

(a) Construct a Born–Haber cycle to calculate the lattice energy of beryllium oxide.

\[
\begin{align*}
\text{Enthalpy change of formation of beryllium oxide} &= -609 \text{ kJ mol}^{-1} \\
\text{Enthalpy change of atomisation of beryllium} &= +324 \text{ kJ mol}^{-1} \\
\text{First electron affinity of oxygen} &= -141 \text{ kJ mol}^{-1} \\
\text{Second electron affinity of oxygen} &= +798 \text{ kJ mol}^{-1}
\end{align*}
\]

(b) The theoretical lattice energy of beryllium oxide is –4432 kJ mol\(^{-1}\). Suggest a reason why this value is different from your answer in (a).

2 The following data relates to the energy changes which occur when magnesium hydroxide, Mg(OH)\(_2\), and barium hydroxide, Ba(OH)\(_2\), dissolve in water.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy change of hydration of metal ion / kJ mol(^{-1})</td>
<td>-1890</td>
<td>-1360</td>
</tr>
<tr>
<td>Lattice energy of metallic hydroxide / kJ mol(^{-1})</td>
<td>-2995</td>
<td>-1768</td>
</tr>
<tr>
<td>Enthalpy change of solution of metallic hydroxide / kJ mol(^{-1})</td>
<td>x</td>
<td>-512</td>
</tr>
</tbody>
</table>

(a) Explain why the hydration energy of a metal ion is exothermic.

(b) With the aid of suitable energy cycles and the data provided above, calculate the enthalpy change of hydration of OH\(^-\) and hence determine a value for x, the enthalpy change of solution of Mg(OH)\(_2\).
5 Chemical Energetics and Thermodynamics – Class Exercise 4

Entropy and Gibbs Free Energy

1 The following data was given for carbon disulfide, CS₂.

<table>
<thead>
<tr>
<th>At 25 °C</th>
<th>ΔH°/ kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS₂(ℓ)</td>
<td>+89.70</td>
</tr>
<tr>
<td>CS₂(g)</td>
<td>+117.36</td>
</tr>
</tbody>
</table>

The standard entropy change of vaporisation is given as +86.50 J K⁻¹ mol⁻¹.

Calculate ΔG° for the conversion of liquid CS₂ to gaseous CS₂ and hence deduce which state of carbon disulfide is more stable at room temperature.

2 Describe and explain how the entropy of each of the following systems will change during the stated process. Assume the pressure of each system remains constant throughout the process.

(a) 1 mol of Ne(g) at 298K is added to 1 mol of O₂(g) at 298K.

(b) 1 mol of Mg(s) reacts with O₂(g) according to the following equation.

\[ \text{Mg}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{MgO}(s) \]
5  Chemical Energetics and Thermodynamics – Class Exercise 1
Suggested Answers

1(a)  \[
Ca^+(g) \rightarrow Ca^{2+}(g) + e
\]
(b)  \[
\text{Na}(s) + \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{NaNO}_3(s)
\]
(c)  \[
\text{Na}^+(g) + \text{aq} \rightarrow \text{Na}^+(\text{aq})
\]
(d)  \[
\text{I}_2(g) \rightarrow 2\text{I}(g)
\]
(e)  \[
\frac{1}{2} \text{Br}_2(l) \rightarrow \text{Br}(g)
\]

2(a)  \[
\Delta H_{\text{neut}}
\]
(b)  \[
2^{\text{nd}} \text{ electron affinity of S}
\]
(c)  \[
\Delta H_c \text{ of CO}
\]
(d)  \[
\text{Lattice energy of } \text{AlF}_3
\]
(e)  \[
\Delta H_{\text{sol}} \text{ of } \text{Na}_2\text{SO}_4
\]

3(a)(i)  \[
\text{K}_2\text{CO}_3(s) + 2\text{HCl}(aq) \rightarrow 2\text{KCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)
\]
(a)(ii)  \[
\text{Heat absorbed} = mc\Delta T = 30.0 \times 4.2 \times 5.2 = 655.2 \text{ J}
\]
\[
\Delta H_r = -\frac{655.2}{0.020} = -3.28 \times 10^4 \text{ J mol}^{-1} = -32.8 \text{ kJ mol}^{-1}
\]
(a)(iii) Since \text{K}_2\text{CO}_3 is the limiting reagent, and \text{HCl} is used in excess, there is no need for the concentration / amount of \text{HCl} added to be exact.

(b)(i)  \[
\text{KHCO}_3(s) + \text{HCl}(aq) \rightarrow \text{KCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)
\]
(b)(ii)  \[
\text{Heat absorbed} = mc\Delta T = 30.0 \times 4.2 \times 3.7 = 466.2 \text{ J}
\]
\[
\Delta H_r = +\frac{466.2}{0.020} = +2.33 \times 10^4 \text{ J mol}^{-1} = +23.3 \text{ kJ mol}^{-1}
\]
(c)  \[
\begin{align*}
\text{2HCl}(aq) + 2\text{KHCO}_3(s) & \quad \Delta H_r \quad \text{K}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) + 2\text{HCl}(aq) \\
2(+23.3) & \quad -32.8 \\
2\text{KCl}(aq) + 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l) & \\
\end{align*}
\]
By Hess’s Law,  \[
\Delta H_r = 2(+23.3) - (-32.8) = +79.4 \text{ kJ mol}^{-1}
\]
\[
\therefore \Delta H_f \text{ for thermal decomposition of 1 mole of } \text{KHCO}_3 = +79.4 / 2 = +39.7 \text{ kJ mol}^{-1}
\]
1. By Hess’s Law, \( \Delta H_c = \Sigma B.E. (bonds\ broken) - \Sigma B.E. (bonds\ formed) \)

\[
\begin{align*}
\Delta H_c &= \{(C=C) \times 1 + (H\text{-}H) \times 1\} - \{(C\text{-}H) \times 2\} + (C\text{-}C) \times 1 \\
&= (610 + 436) - [2(410) + 350] \\
&= 1046 - 1170 \\
&= -124\ \text{kJ mol}^{-1}
\end{align*}
\]
1(a) 

\[ \text{Be}^{2+}(g) + \text{O}^2-(g) \]

\[ 900 + 1760 \quad (\text{L.E. BeO}) \]

\[ \text{Be}(g) + \text{O}(g) \]

\[ 324 + \frac{1}{2} \times 496 \]

\[ \text{Be}(s) + \frac{1}{2} \text{O}_2(g) \]

\[ -609.4 \]

\[ \text{BeO}(s) \]

\[ \text{L.E. (BeO)} \]

\[ -609 = 324 + \frac{1}{2} (496) + 900 + 1760 + (\text{L.E. (BeO)}) + (-141) + 798 + \text{L.E. (BeO)} \]

\[ \text{L.E. (BeO)} = -4500 \text{ kJ mol}^{-1} \]

(b) The theoretical lattice energy assumes a pure ionic compound. However, BeO is an ionic compound with covalent character as Be^{2+} ion is small and highly charged and polarizes the electron cloud of O^{2-} ion to a great extent.

2(a) Energy is released when ion–dipole interaction is formed between the metal ion and (polar) water molecules during hydration.

\[ \text{M(OH)}_2(s) \xrightarrow{\Delta H_{\text{soln}}} \text{M}^{2+}(aq) + 2\text{OH}^- (aq) \]

\[ \text{LE} \]

\[ \text{M}^{2+}(g) + 2\text{OH}^-(g) \]

By Hess’s Law,

\[ \Delta H_{\text{soln}} = \Delta H_{\text{hyd}}(\text{M}^{2+}) + 2 \times \Delta H_{\text{hyd}}(\text{OH}^-) \]

For Ba(OH)_2,

\[ -512 = 1768 + (-1360) + 2 \times \Delta H_{\text{hyd}}(\text{OH}^-) \]

\[ \therefore \Delta H_{\text{hyd}}(\text{OH}^-) = -460 \text{ kJ mol}^{-1} \]

For Mg(OH)_2,

\[ x = 2995 + (-1890) + 2(-460) \]

\[ \therefore x = +185 \text{ kJ mol}^{-1} \quad \text{(units not required)} \]
1 \( \text{CS}_2(l) \rightarrow \text{CS}_2(g) \)

\[ \Delta H_{\text{vap}} = 117.36 - 89.70 = +27.66 \text{ kJ mol}^{-1} \]

At 298 K, \( \Delta G_{\text{vap}} = 27.66 - 298 (0.08650) = +1.88 \text{ kJ mol}^{-1} > 0 \) \( \therefore \) conversion is not spontaneous

Thus, liquid \( \text{CS}_2 \) is the more stable state.

2(a) When the gases are mixed at constant pressure, the volume available for each gas (O\(_2\) and Ne) is increased. There are more ways that the particles and the energy can be arranged. Hence, entropy increases \( (\Delta S > 0) \).

(b) Number of gas molecules decreases after the reaction. The number of ways that the particles and the energy can be arranged decrease. Hence, entropy decreases \( (\Delta S < 0) \).