# 07 Chemical Energetics I

**Set B** **Answer key**

## A Multiple choice

4 MARKS

**1** **C** RbBr −647, CsBr −619, SrS −2779, BaS −2643 [1]

Lattice energy $\propto \frac{q_+q_-}{r_+ + r_-}$ (ionic radii from the Data Booklet)

Charges: the product of charges is +1 × −1 = −1 for RbBr and CsBr, and +2 × −2 = −4 for SrS and BaS. SrS and BaS will have higher LE than RbBr and CsBr.

Ionic radii: $Cs^+$ has a larger $r_+$ than $Rb^+$. Since $Br^-$ is a common anion, RbBr will have a higher LE than CsBr. $Ba^{2+}$ is bigger than $Sr^{2+}$. Since $S^{2-}$ is a common anion, SrS will have a larger LE.

**2** **C** formation of gaseous $O^{2-}$ ion from gaseous $O^-$ ion [1]

The second electron affinity is always positive (endothermic), because energy is required to overcome the electrostatic repulsion between the incoming electron and the singly negatively charged anion.

**A** Neutralisation is an exothermic reaction.

**B** Formation of $CO_2$ gas is the same as combustion of solid carbon (graphite), which is an exothermic reaction.

**D** This reaction is exothermic, as a solid ionic compound is formed from gaseous ions (i.e. lattice energy).

**3** **D** The $I^-$ ion is more polarisable than the $Br^-$ ion. [1]

Theoretical lattice energy is calculated using |lattice energy| $\propto \frac{|q_+q_-|}{r_+ + r_-}$, which assumes a 100% ionic nature.

The discrepancy between the experimental and theoretical lattice energies shows the presence of covalent character in the bonding in the silver halides, which arises due to substantial polarisation of the anion by the cation.

Since the anionic radius increases down the Group, the polarisability of the anion increases, causing a greater degree of covalency and hence a greater deviation of the experimental from the theoretical value.

**4** **B** s − q − p − r [1]

A possible method to solve this question without an energy cycle is to use the algebraic method.

| | enthalpy change / kJ mol$^{-1}$ |
|---|---|
| $Ba(s) + O_2(g) \rightarrow BaO_2(s)$ | s |
| $BaO_2(s) \rightarrow Ba^{2+}(g) + O_2^{2-}(g)$ | −q |
| $Ba^{2+}(g) + 2e^- \rightarrow Ba(g)$ | −p |
| $Ba(g) \rightarrow Ba(s)$ | −r |
| $O_2(g) + 2e^- \rightarrow O_2^{2-}(g)$ | s − q − p − r |

## B Structured questions

29 MARKS

**5** **(a)** Standard enthalpy change of formation of $B_2O_3(s)$ [1]

**(b)** Energy cycle: $2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$ ($\Delta H_f$). With $3O_2(g)$ added, both sides give $B_2O_3(s) + 3H_2O(l)$: directly by −1273 + 3 × (−242), or through $B_2H_6(g)$ by −2035. [1]

Using Hess' Law, $\Delta H_f(B_2H_6)$ = −1273 + 3 × (−242) − (−2035) [1]

= **+36 kJ mol$^{-1}$** [1]

**6** **(a)**

| step | ΔH / kJ mol$^{-1}$ |
|---|---|
| $Li(s) + \frac{1}{2}H_2(g) \rightarrow LiH(s)$ | −90.5 |
| $Li(s) \rightarrow Li(g)$ | +159.5 |
| $\frac{1}{2}H_2(g) \rightarrow H(g)$ | ½(+436) |
| $Li(g) \rightarrow Li^+(g) + e^-$ | +519 |
| $H(g) + e^- \rightarrow H^-(g)$ | −73 |
| $Li^+(g) + H^-(g) \rightarrow LiH(s)$ | LE |

Using Hess' Law, −90.5 = +159.5 + ½(+436) + 519 + (−73.0) + LE [1]

LE = **−914 kJ mol$^{-1}$** [1]

NOTE The relevant data from the Data Booklet are the 1st IE of Li (+519 kJ mol$^{-1}$) and the BE of $H_2$ (+436 kJ mol$^{-1}$).

**(b)** $4LiH(s) + AlCl_3(s) \rightarrow LiAlH_4(s) + 3LiCl(s)$ [1]

$\Delta H_r = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$

$-276 = [\Delta H_f + 3(-408.5)] - [4(-90.5) + (-704)]$ [1]

$\Delta H_f$ = **−116.5 kJ mol$^{-1}$** [1]

**7**

Energy cycle: $Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$ directly ($2\Delta H_f$), or by $Br_2(l) \rightarrow Br_2(g)$, then $Br_2(g) + 3F_2(g) \rightarrow 2Br(g) + 6F(g)$, then $2Br(g) + 6F(g) \rightarrow 2BrF_3(g)$, then $2BrF_3(g) \rightarrow 2BrF_3(l)$. [1]

$2\Delta H_f(BrF_3) = \Delta H_{vap}(Br_2) + BE(Br–Br) + 3BE(F–F) – 6BE(Br–F) – 2\Delta H_{vap}(BrF_3)$

$2(–301) = 31 + 193 + 3(158) – 6BE(Br–F) – 2(44)$ [1]

$6BE(Br–F) = 1212$

$BE(Br–F) = 1212 \div 6 =$ **+202 kJ mol$^{-1}$** [1]

**8**

| step | **ΔH / kJ mol$^{-1}$** |
|---|---|
| $2Ca(s) + Si(s) + 2O_2(g) \rightarrow Ca_2SiO_4(s)$ | $\Delta H_f[Ca_2SiO_4] = –2306$ |
| $2Ca(s) \rightarrow 2Ca(g)$ | 2(+121) |
| $2Ca(g) \rightarrow 2Ca^{2+}(g) + 4e^–$ | 2 × (1st IE[Ca] + 2nd IE[Ca]) |
| $Si(s) + 2O_2(g) + 4e^– \rightarrow SiO_4^{4–}(g)$ | +13872 |
| $2Ca^{2+}(g) + SiO_4^{4–}(g) \rightarrow Ca_2SiO_4(s)$ | $LE[Ca_2SiO_4]$ |

Using Hess' Law, $–2306 = 2(+121) + 2(+590 + 1150) + 13872 + LE[Ca_2SiO_4]$ [2]

$LE[Ca_2SiO_4] =$ **–19900 kJ mol$^{-1}$** (3 s.f.) [1]

**9** **(a)**

Enthalpy change of neutralisation is the enthalpy change when an amount of acid or alkali is neutralised to form 1 mole of water, the reaction being carried out using dilute aqueous solutions. [1]

**(b)**

HCN is a weak acid and energy is required to ionise it to produce one mole of $H^+$ ions before neutralisation. $NH_3$ is a weak base and energy is required to ionise it to produce one mole of $OH^–$ ions before neutralisation can take place. [1]

The ionisation of the weak acid is endothermic, which results in a less exothermic enthalpy change of neutralisation for the weak acid–weak base than for the strong acid–strong base. [1]

**10** **(a)**

$S(s) + O_2(g) \rightarrow SO_2(g)$ [1]

**(b)**

$q = –mc\Delta T$

$q = –(150)(4.18)(39.7 – 29.8)$

$q = –6207$ J [1]

Amount of S = $0.76 \div 32.1 = 0.02368$ mol

$$\Delta H_c = \frac{-6207}{0.02368} = -262\,000 \text{ J mol}^{-1}$$

$\Delta H_c =$ **–262 kJ mol$^{-1}$** [1]

**(c)**

$S(s) + O_2(g) \rightarrow SO_2(g)$ represents $\Delta H_f(SO_2)$, and also $\Delta H_c(S)$.

$\Delta H_r = [\Delta H_f(SO_2) + (-285.8)] - (-20.6)$

$-562 = [\Delta H_f(SO_2) + (-285.8)] - (-20.6)$ [1]

$\Delta H_c(S) = \Delta H_f(SO_2) =$ **$-297$ kJ mol$^{-1}$** [1]

**(d)**

In (b), the heat lost to the surroundings was not accounted for *or* the experiment was not 100% efficient *or* the sulfur sample from the volcano was not pure. [1]

**11** **(a)**

| step | **ΔH / kJ mol$^{-1}$** |
|---|---|
| $2Cu(s) + \frac{1}{2}O_2(g) \rightarrow Cu_2O(s)$ | $\Delta H_f[Cu_2O] = -166$ |
| $2Cu(s) \rightarrow 2Cu(g)$ | $\Delta H_{atom}[Cu] \times 2 = 2(+339)$ |
| $2Cu(g) \rightarrow 2Cu^+(g) + 2e^-$ | 1st IE[Cu] × 2 = 2(+745) |
| $\frac{1}{2}O_2(g) \rightarrow O(g)$ | $\frac{1}{2}BE[O_2] = \frac{1}{2}(+496)$ |
| $O(g) + e^- \rightarrow O^-(g)$ | 1st EA[O] = −141 |
| $O^-(g) + e^- \rightarrow O^{2-}(g)$ | 2nd EA[O] = +791 |
| $2Cu^+(g) + O^{2-}(g) \rightarrow Cu_2O(s)$ | $LE[Cu_2O]$ |

By Hess' Law, $-166 = 2(+339) + 2(+745) + \frac{1}{2}(+496) + (-141) + (+791) + LE[Cu_2O]$ [2]

Lattice energy of copper(I) oxide, $LE[Cu_2O] =$ **$-3232$ kJ mol$^{-1}$** [1]

**(b)**

The LE of CuO is more exothermic ($-4143$ kJ mol$^{-1}$), so stronger ionic bonds are formed. [1]

For CuO, the higher charge of $Cu^{2+}$ compared with $Cu^+$ gives a larger $q_+$, and the smaller cationic radius ($r_+$), as the electron cloud is attracted more strongly to the nucleus, gives a smaller interionic distance ($r_+ + r_-$). [1]