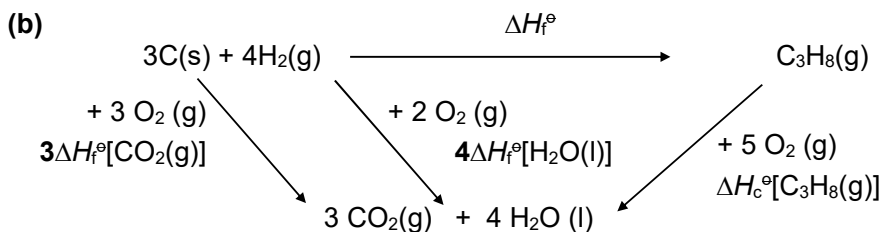


Tutorial 5a Chemical Energetics 1: Suggested Solutions to Practice Questions

- 11 (a) Hess' Law states that the enthalpy change of a reaction is determined by the initial and final states of the system and is *independent* of the pathways taken.

It allows one to calculate ΔH_r of a reaction that is difficult or impossible to perform in the laboratory.



By Hess' Law,
$$\Delta H_f^\circ [\text{C}_3\text{H}_8\text{(g)}] = 3 \Delta H_f^\circ [\text{CO}_2\text{(g)}] + 4 \Delta H_f^\circ [\text{H}_2\text{O(l)}] - \Delta H_c^\circ [\text{C}_3\text{H}_8\text{(g)}]$$
$$= -104 \text{ kJ mol}^{-1}$$

- (c) Total amount of propane and butane present = $5.60 / 22.7 = 0.2467 \text{ mol}$
Let the amt of propane be $x \text{ mol}$, then amt of butane is $(0.2467 - x) \text{ mol}$.

(Note: Use $\Delta H = -\frac{q}{n_A} \times a$, $q = n(-\Delta H) / a$)

$$\text{total } q = x(-\Delta H_c^\circ [\text{C}_3\text{H}_8\text{(g)}]) + (0.2467 - x)(-\Delta H_c^\circ [\text{C}_4\text{H}_{10}\text{(g)}]) = +654 \text{ kJ}$$

$$\Rightarrow x(2220) + (0.2467 - x)(2877) = +654 \text{ kJ}$$

$$\Rightarrow x = \text{amt of propane} = 0.08486 \text{ mol}$$

$$\text{amt of butane} = 0.2467 - 0.08486 = 0.1618 \text{ mol}$$

By Avogadro's law,

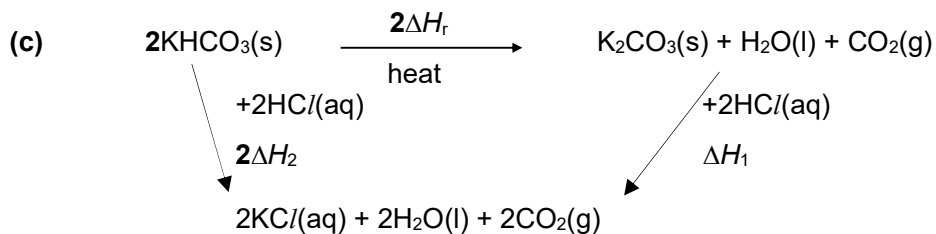
$$\% \text{ composition of propane} = (0.08486 / 0.2467) \times 100 = \mathbf{34.4\%}$$

$$\% \text{ composition of butane} = (0.1618 / 0.2467) \times 100 = \mathbf{65.6\%}$$

- 12 (a) (i) $\text{K}_2\text{CO}_3\text{(s)} + 2\text{HCl(aq)} \longrightarrow 2\text{KCl(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$
- (ii) $q = 30.0 \times 4.18 \times 5.20 = +652.1 \text{ J}$ (or heat produced by rxn = 652.1 J)
Molar mass of $\text{K}_2\text{CO}_3 = 2(39.1) + 12.0 + 3(16.0) = 138.2 \text{ g mol}^{-1}$
Amt of $\text{K}_2\text{CO}_3 = 2.76 / 138.2 = 0.01997 \text{ mol}$
Amt of $\text{HCl} = 30.0/1000 \times 2 = 0.0600 \text{ mol}$; hence, HCl is in excess.
 $\therefore$ Enthalpy change of reaction, $\Delta H_1 = -652.1/0.01997$
 $= -32650 \text{ J mol}^{-1}$
 $= \mathbf{-32.7 \text{ kJ mol}^{-1}}$

- (iii) Amt of $\text{HCl} = 30.0/1000 \times 2 = 0.0600 \text{ mol}$.
Since HCl is in excess, its concentration need not be specified accurately.

- (b) (i) $\text{KHCO}_3\text{(s)} + \text{HCl(aq)} \longrightarrow \text{KCl(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$
- (ii) $q = 30.0 \times 4.18 \times (-3.70) = -464 \text{ J}$ (or heat absorbed by rxn = 464 J)
Molar mass of $\text{KHCO}_3 = 39.1 + 1.0 + 12.0 + 3(16.0) = 100.1 \text{ g mol}^{-1}$
Amt of $\text{KHCO}_3 = 2.00 / 100.1 = 0.01998 \text{ mol}$
Amt of $\text{HCl} = 30.0 / 1000 \times 2 = 0.0600 \text{ mol}$; hence, HCl is in excess.
 $\therefore$ Enthalpy change of reaction, $\Delta H_2 = -(-464.0 / 0.01998)$
 $= +23220 \text{ J mol}^{-1}$
 $= \mathbf{+23.2 \text{ kJ mol}^{-1}}$



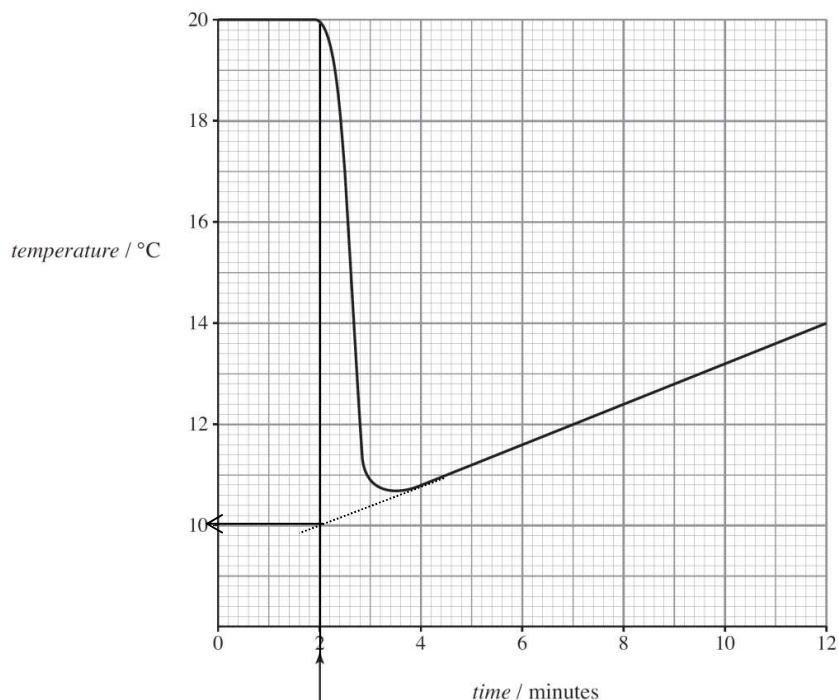
By Hess' Law,

$$2\Delta H_r = 2\Delta H_2 - \Delta H_1 = +79.1 \text{ kJ mol}^{-1}$$

$\therefore$ Enthalpy change for the decomposition of 1 mole $\text{KHCO}_3 = +39.6 \text{ kJ mol}^{-1}$ (to 3 sf)

13 (a) Standard enthalpy change of neutralisation is the energy change when an acid and a base react to form one mole of water at 298 K and 1 bar.

(b) Final temperature as extrapolated on graph to time of mixing at 2 min = 10 °C
Maximum temperature fall by extrapolation = 10.0 °C



Temperature change, $\Delta T = (10.0 - 20.0) ^\circ\text{C} = -10.0 ^\circ\text{C}$

$$q = 50 \times 4.18 \times -10.0 = -2090 \text{ J (or heat absorbed by reaction} = 2090 \text{ J)}$$

Note: ΔT in K is the same as ΔT in $^\circ\text{C}$

Amt of $\text{NaHCO}_3 = 3.50 / 84.0 = 0.04167 \text{ mol}$

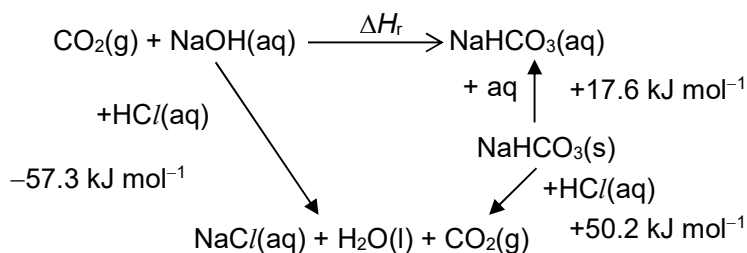
Limiting reagent = NaHCO_3 since amt of $\text{HCl} = 0.05 \text{ mol}$

$$\text{Enthalpy change of reaction} = -(-2.090 \text{ kJ}) / 0.04167 = + 50.2 \text{ kJ mol}^{-1}$$

Assumption made

- Heat gain from the surroundings is accounted for from the extrapolation of the graph.
- Heat capacity of the cup/calorimeter is negligible.

(c)



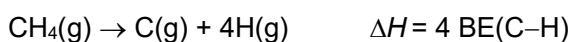
$$\Delta H_r = -57.3 - (50.2) + (17.6) = -89.9 \text{ kJ mol}^{-1}$$

(d) 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.

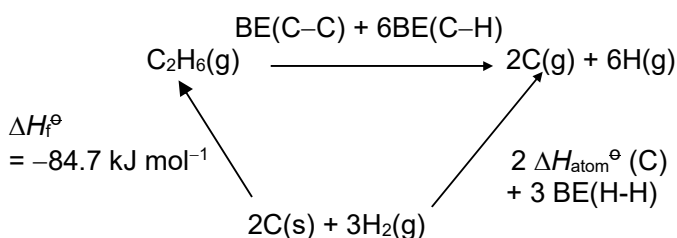
Enthalpy of ionisation of the weak acid and weak base are **endothermic** and that resulted in a **less exothermic** enthalpy change of neutralisation of the weak acid–weak base as compared to that of a strong acid–strong base.

14 (a) The bond energy of a C–H bond is the average energy absorbed when 1 mole of C–H bonds of methane are broken in the gaseous state.



Note that this is also $\Delta H_{\text{atom}} [\text{CH}_4(\text{g})]$

(b)(i) Method 1: Constructing energy cycles and using Hess' Law



Draw similar energy cycles for C_2H_4 and C_2H_2 .

$$\begin{array}{ll}
 \text{BE}(\text{C}-\text{C}) + 6\text{BE}(\text{C}-\text{H}) & = -\Delta H_f^\ominus + 2 \Delta H_{\text{atom}}^\ominus (\text{C}) + 3 \text{BE}(\text{H}-\text{H}) \\
 \text{BE}(\text{C}-\text{C}) & = -(-84.7) + 2(+715) + 3(436) - 6(410) \\
 \text{BE}(\text{C}-\text{C}) \text{ in } \text{C}_2\text{H}_6 & = +363 \text{ kJ mol}^{-1}
 \end{array}$$

Method 2:

$$\Delta H_f^\ominus = \text{energy consumed in bond breaking} + \text{energy released in bond formation}$$

$$-84.7 = 2 \Delta H_{\text{atom}}^\ominus (\text{C}) + 3 \text{BE}(\text{H}-\text{H}) - [\text{BE}(\text{C}-\text{C}) + 6 \text{BE}(\text{C}-\text{H})]$$

$$\text{BE}(\text{C}-\text{C}) \text{ in } \text{C}_2\text{H}_6 = +363 \text{ kJ mol}^{-1}$$

Hydrocarbon	C_2H_6	C_2H_4	C_2H_2
BE(carbon-carbon) / kJ mol^{-1}	+363	+610	+819

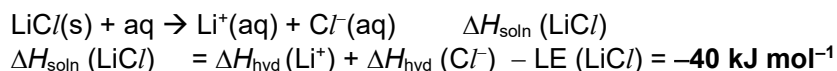
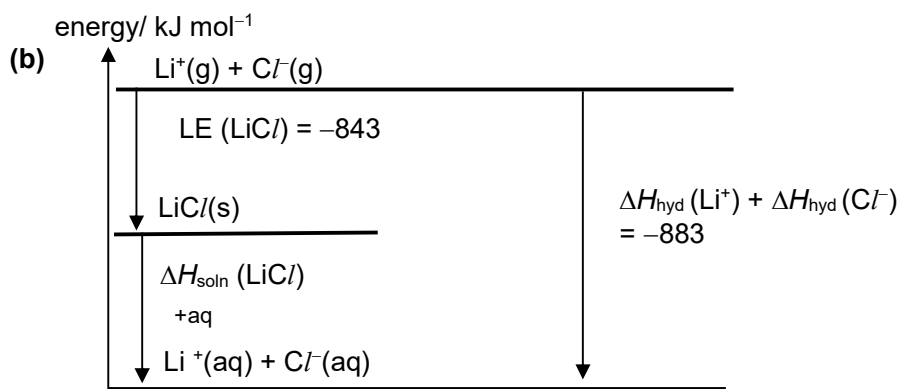
Comments:

- Since bond energies are a reflection of the bond strengths,
Bond strength: $\text{C}\equiv\text{C} > \text{C}=\text{C} > \text{C}-\text{C}$
- Bond energy of $\text{C}=\text{C}$ is not twice that of $\text{C}-\text{C} \Rightarrow \pi$ -bond is weaker than a σ -bond.

(b)(ii) The C–C bond energy found in the Data Booklet is an **average value** and not specific for the C–C bond in ethane.

- 15 (a) When an ionic solid dissolves in water, two enthalpy terms are involved.
1. The ions must be separated from the ionic lattice. The energy **required** is the lattice enthalpy ($-LE$). It is also called the lattice dissociation energy.
 2. The specific gaseous ions interact with water molecules. Energy is **released** ($\Sigma\Delta H_{\text{hyd}}$) due to the formation of ion-dipole interactions between the gaseous ions and water.

$$\Delta H_{\text{soln}}^{\ominus} = -LE + \Sigma\Delta H_{\text{hyd}}^{\ominus}$$



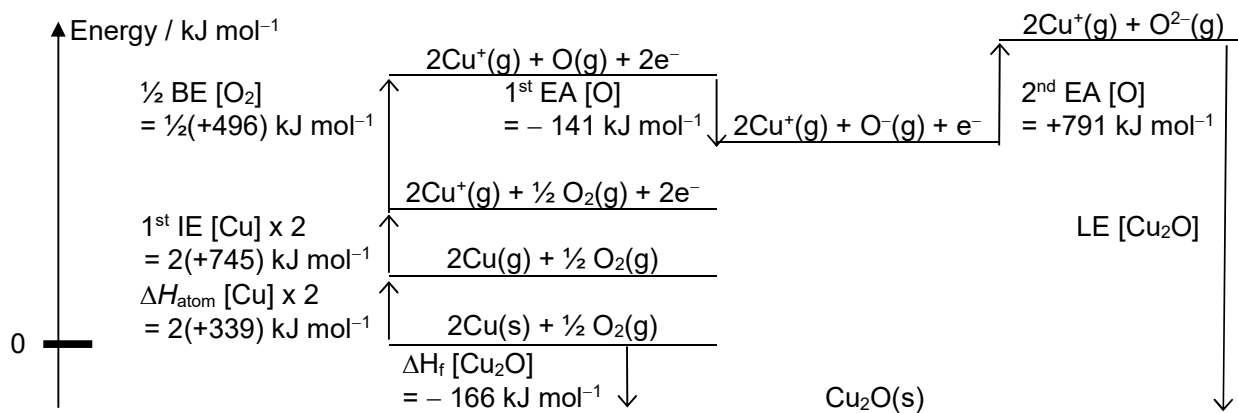
- (c) Li^+ has a **smaller radius** and a **higher charge density** than K^+ .

Since $|LE|$ is inversely proportional to interionic distance, the lattice energy of LiCl is slightly more exothermic than that of KCl .

However, since the magnitude of hydration energy is proportional to charge density, Li^+ will have a much more exothermic hydration enthalpy compared to K^+ .

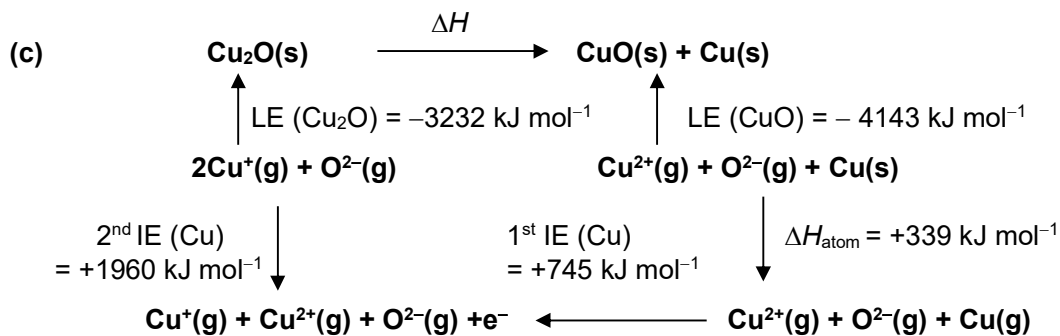
Therefore, the enthalpy change of solution of LiCl is more exothermic than that of KCl .

- 16 (a)



$$\text{Lattice energy of Cu}_2\text{O} = -3232 = -3230 \text{ kJ mol}^{-1}$$

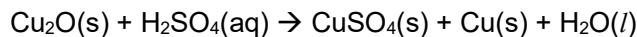
- (b) The experimental lattice energy of CuO is expected to deviate more from the theoretical value compared to that of Cu_2O . Cu^{2+} has a higher charge but smaller size than Cu^+ , hence Cu^{2+} has a higher charge density and greater polarizing power than Cu^+ , leading to greater covalent character in CuO than in Cu_2O . The greater covalent character in CuO led to the greater deviation.



$$\Delta H = -35 \text{ kJ mol}^{-1}$$

(d) $q = 60.0 \times 4.18 \times 8.9 = +2232 \text{ J}$
Heat produced by reaction = 2232 J

Amt of $\text{Cu}_2\text{O (s)} = 2.86 / (2 \times 63.5 + 16.0) = 0.0200 \text{ mol}$
 Cu_2O is the limiting reagent since amt of $\text{H}_2\text{SO}_4 \approx 2 \times 60 \times 10^{-3} = 0.12 \text{ mol}$



Enthalpy change of reaction = $-2232 / 0.0200 = -112 \text{ kJ mol}^{-1}$

Assuming no heat loss, specific heat capacity of solution = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$
Density of solution = density of water = 1.00 g cm^{-3}

