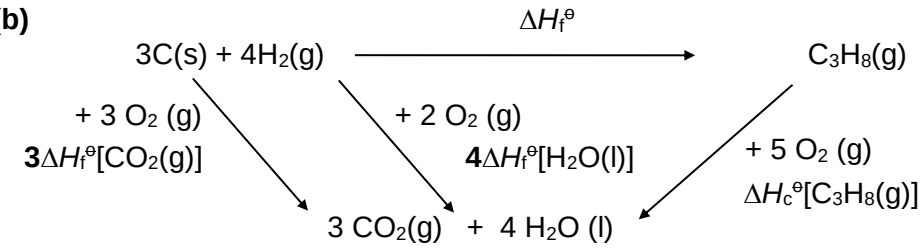
Tutorial 5a Chemical Energetics 1: Suggested Solutions to Practice Questions

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.

(b)



By Hess' Law, $\Delta H_f^\ominus [C_3H_8(g)] = 3\,\Delta H_f^\ominus [CO_2(g)] + 4\,\Delta H_f^\ominus [H_2O(l)] - \Delta H_c^\ominus [C_3H_8(g)]$

$= \mathbf{-104\ kJ\ mol^{-1}}$

(c) Total amount of propane and butane present = 5.60 / 22.7 = 0.2467 mol
Let the amt of propane be x mol, then amt of butane is (0.2467 – x) mol.

q = n(–ΔH) where n is the no of mol of compound burnt (reactant)

total q = $x\,(-\Delta H_c^\ominus [C_3H_8(g)]) + (0.2467 - x)(-\Delta H_c^\ominus [C_4H_{10}(g)]) = +654$ kJ

$\Rightarrow x\,(2220) + (0.2467 - x)(2877) = +654$ kJ

$\Rightarrow$ x = amt of propane = 0.08486 mol

amt of butane = 0.2467 – 0.08486 = 0.1618 mol

By Avogadro's law,
% composition of propane = (0.08486 / 0.2467) x 100 = **34.4%**
% composition of butane = (0.1618 / 0.2467) x 100 = **65.6%**

12 (a) (i) $K_2CO_3(s) + 2HCl(aq) \longrightarrow 2KCl(aq) + CO_2(g) + H_2O(l)$

(ii) q = 30.0 x 4.18 x 5.20 = +652.1 J (or heat produced by rxn = 652.1 J)
Molar mass of K_2CO_3 = 2(39.1) + 12.0 + 3(16.0) = 138.2 g mol^{-1}
Amt of K_2CO_3 = 2.76 / 138.2 = 0.01997 mol
Amt of HC*l* = 30.0/1000 x 2 = 0.0600 mol; hence, HC*l* is in excess.

$\therefore$ Enthalpy change of reaction, ΔH_1 = –652.1/0.01997
= –32650 J mol^{-1}
= **–32.7 kJ mol^{-1}**

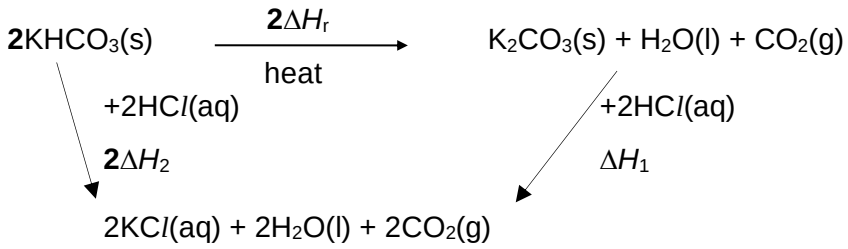
(iii) Amt of HC*l* = 30.0/1000 x 2 = 0.0600 mol.
Since HC*l* is in excess, its concentration need not be specified accurately.

(b) (i) $KHCO_3(s) + HCl(aq) \longrightarrow KCl(aq) + CO_2(g) + H_2O(l)$

(ii) q = 30.0 x 4.18 x (–3.70) = –464 J (or heat absorbed by rxn = 464 J)
Molar mass of $KHCO_3$ = 39.1 + 1.0 + 12.0 + 3(16.0) = 100.1 g mol^{-1}
Amt of $KHCO_3$ = 2.00 / 100.1 = 0.01998 mol
Amt of HC*l* = 30.0 / 1000 x 2 = 0.0600 mol; hence, HC*l* is in excess.

$\therefore$ Enthalpy change of reaction, ΔH_2 = –(–464.0 /0.01998)
= +23220 J mol^{-1}
= **+23.2 kJ mol^{-1}**

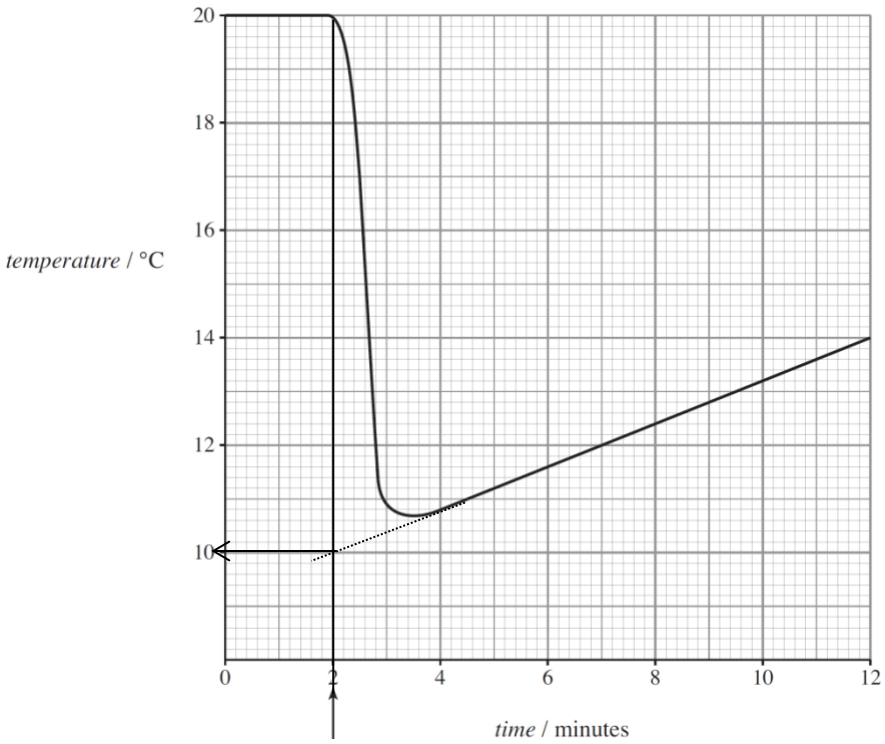
(c)



By Hess' Law,
2ΔH_r = $2\Delta H_2 - \Delta H_1$ = +79.1 kJ mol^{-1}
$\therefore$ Enthalpy change for the decomposition of 1 mole $KHCO_3$ = **+39.6 kJ mol^{-1}** (to 3 sf)

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

(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, ΔT = (10.0 – 20.0) °C = −10.0 °C
q = 50 × 4.18 × –10.0 = −2090 J (or heat absorbed by reaction = 2090 J)

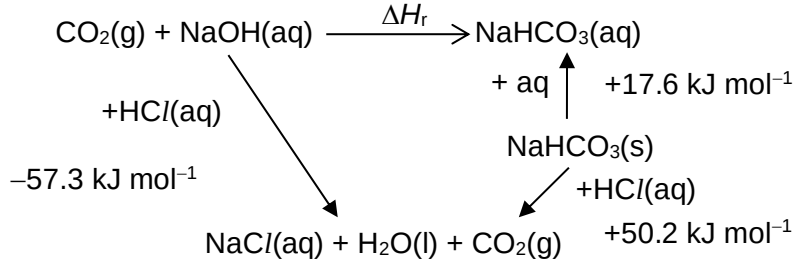
Note: ΔT in K is the same as ΔT in °C

Amt of $NaHCO_3$ = 3.50 / 84.0 = 0.04167 mol
Limiting reagent = $NaHCO_3$ since amt of HCl = 0.05 mol

Enthalpy change of reaction = –(–2.090 kJ) / 0.04167 = **+ 50.2 kJ mol^{-1}**

Assumption made
- **<u>Heat gain</u>** from the surroundings is accounted for from the extrapolation of the graph.
- Heat capacity of the cup/calorimeter is negligible.

(c)



ΔH_r = –57.3 – (50.2) + (17.6) = **– 89.9 kJ mol^{-1}**

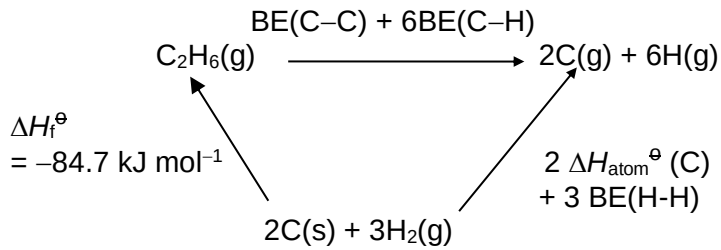
(d) HCN is a **weak acid** and energy is **required** to ionise it to produce one mole of H^+ ions before neutralisation.
NH_3 is a **weak base** and energy is **required** to ionise it to produce one mole of OH^- ions before neutralisation can take place.
Enthalpy of ionisation of the weak acid and 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 <u>average</u> energy absorbed when <u>1 mole of C–H bonds</u> of methane are broken in the <u>gaseous</u> state.

$CH_4(g) \rightarrow C(g) + 4H(g)$ $\quad \Delta H = 4$ BE(C–H)

Note that this is also ΔH_{atom} [$CH_4(g)$]

(b)(i) <u>Method 1</u>: Constructing energy cycles and using Hess' Law



Draw similar energy cycles for C_2H_4 and C_2H_2.

BE(C–C) + 6BE(C–H) = $-\Delta H_f^{\ominus}$ + 2 $\Delta H_{atom}^{\ominus}$ (C)+ 3 BE(H–H)
BE(C–C) = –(–84.7) + 2(+715) + 3(436) – 6(410)
BE(C–C) in C_2H_6 = **+ 363 kJ mol^{-1}**

<u>Method 2:</u>
$\Delta H_f^{\ominus}$ = energy consumed in bond breaking + energy released in bond formation
–84.7 = 2 $\Delta H_{atom}^{\ominus}$ (C)+ 3 BE(H–H) – [BE(C–C) + 6 BE(C–H)]
BE(C–C) in C_2H_6 = **+ 363 kJ mol^{-1}**

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

<u>Comments:</u>
- Since bond energies are a reflection of the bond strengths,
  Bond strength: C≡C > C=C > C–C
- Bond energy of C=C is not twice that of C–C ⇒ π-bond is weaker than a σ-bond.

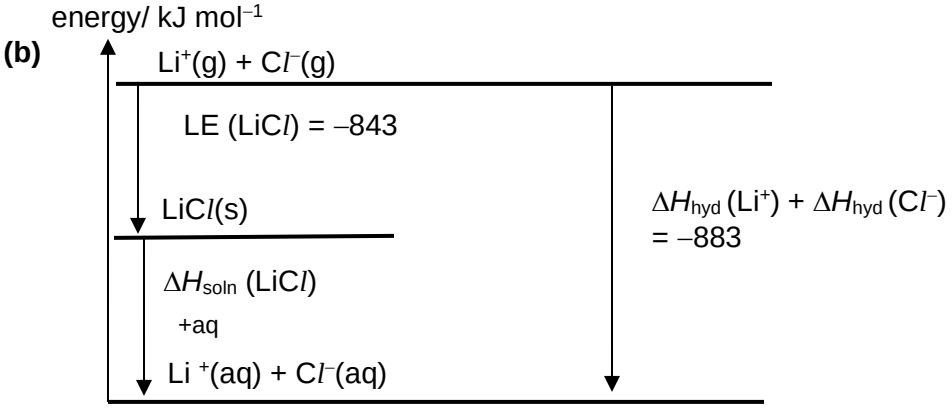
(b)(ii) The C–C bond energy found in the Data Booklet is an **average value** and not specific for the C–C bond in ethane.

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** ($\Sigma\Delta H_{hyd}$) due to the formation of ion-dipole interactions between the gaseous ions and water.

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

(b)

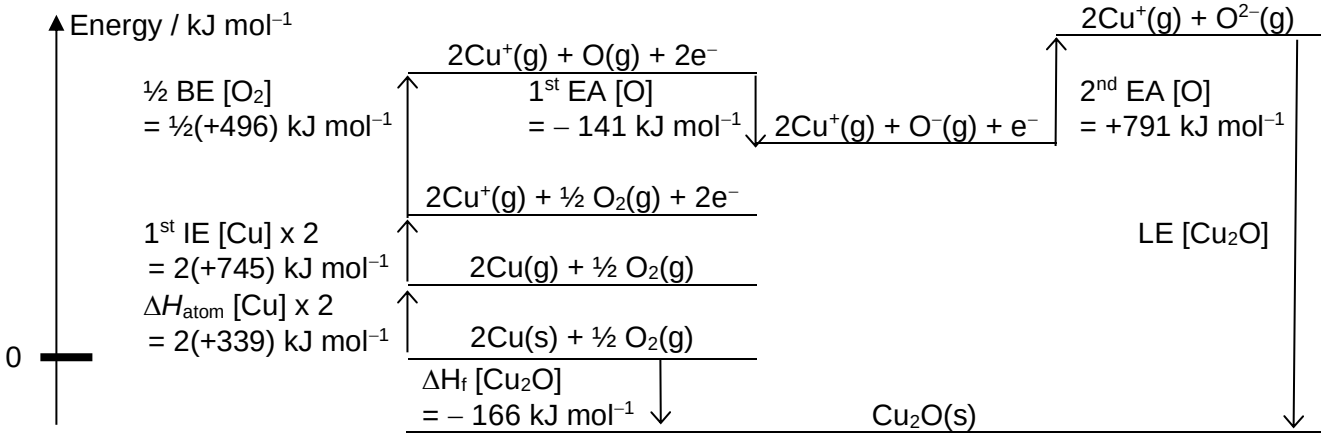


$LiCl(s) + aq \rightarrow Li^+(aq) + Cl^-(aq)$ $\quad \Delta H_{soln}$ (LiCl)

ΔH_{soln} (LiCl) $= \Delta H_{hyd}(Li^+) + \Delta H_{hyd}(Cl^-) - LE$ (LiCl) = **–40 kJ mol^{-1}**

(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.

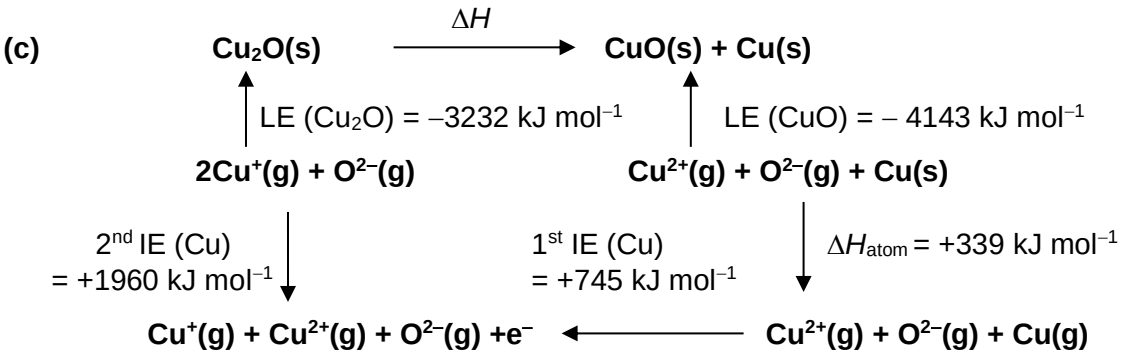
16 (a)



Lattice energy of Cu_2O = –3232 = **–3230 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.

(c)



ΔH = **–35 kJ mol^{-1}**

(d) q = 60.0 x 4.18 x 8.9 = +2232 J
Heat produced by reaction = 2232 J

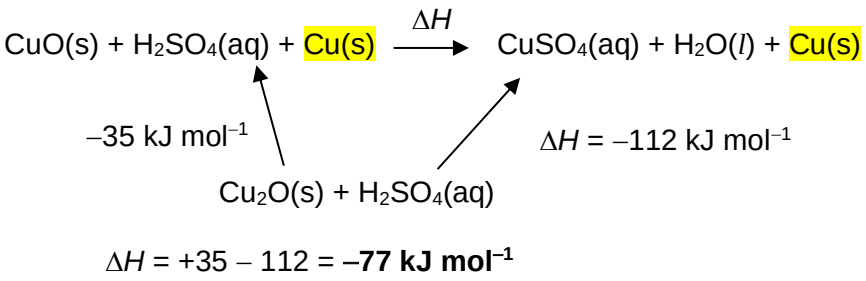
Amt of Cu_2O (s) = 2.86 / (2 x 63.5 + 16.0) = 0.0200 mol
Cu_2O is the limiting reagent since amt of $H_2SO_4 \approx 2 \times 60 \times 10^{-3}$ = 0.12 mol

$Cu_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(s) + Cu(s) + H_2O(l)$

Enthalpy change of reaction = – 2232 / 0.0200 = **–112 kJ mol^{-1}**

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

(e)



ΔH = +35 – 112 = **–77 kJ mol^{-1}**