

## SL IB Chem 1 Thermodynamics - Guided Notes

### Slide 3: Measuring Enthalpy

- Think of the burning food as your \_\_\_\_\_.
- The \_\_\_\_\_ change in the water is related to the energy given off.

### Slide 4: Enthalpy Change

- We calculate enthalpy change directly from the \_\_\_\_\_ change of a known mass of water.

### Slide 5: Enthalpy Change

### Slide 6: Specific Heat Capacity

### Slide 7: Measuring enthalpy changes

- \_\_\_\_\_ state is the state at RTP (SATP):
- $100 \text{ kPa} = 100\,000 \text{ Pa}$
- $25^\circ\text{C} = 298 \text{ K}$
- Standard \_\_\_\_\_ and specific heat capacity of water are in your data books.
- \_\_\_\_\_ of water =  $1 \text{ g/cm}^3$
- $1 \text{ g water} = 1 \text{ cm}^3$
- (Be \_\_\_\_\_ - not all liquids are the same)

### Slide 8: Example

- The student carried out a laboratory experiment to determine the enthalpy change when a sample of butan-1-ol was burned. The student found that the temperature of 175 g of water increased by  $8.0^\circ\text{C}$  when  $5.00 \times 10^{-3} \text{ mol}$  of pure butan-1-ol was burned in air and the heat produced was used to warm the water. Use the student's results to calculate a value, in  $\text{kJ mol}^{-1}$ , for the enthalpy change when one mole of butan-1-ol is burned. (The specific heat capacity of water is  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ )
- **What information from here do we need???**

### Slide 9: Example

- The student carried out a laboratory experiment to determine the enthalpy change when a sample of butan-1-ol was burned. The student found that the temperature of **175 g of water** increased by **8.0 °C** when  $5.00 \times 10^{-3}$  mol of pure butan-1-ol was burned in air and the heat produced was used to warm the water. Use the student's results to calculate a value, in  $\text{kJ mol}^{-1}$ , for the enthalpy change when one mole of butan-1-ol is burned. (The specific heat capacity of water is  **$4.18 \text{ J K}^{-1} \text{ g}^{-1}$** )
- $m = 175 \text{ g}$
- $c = 4.18 \text{ JK}^{-1}\text{g}^{-1}$
- $\Delta T = 8 \text{ K}$

### Slide 10: Example

- $5.852 / (5.00 \times 10^{-3})$
- When doing a calorimetry experiment, the heat released by an **exothermic reaction is absorbed by water**.
- $\Delta H_{\text{rxn}} = -\Delta H_{\text{water}}$

### Slide 11: Enthalpy change in solution

### Slide 12: Enthalpy change in solution

- $50.0 \text{ cm}^3$  of  $1.0 \text{ mol dm}^{-3} \text{ NaOH}_{(\text{aq})}$  is added to  $50.0 \text{ cm}^3$  of  $1.0 \text{ mol dm}^{-3} \text{ HCl}_{(\text{aq})}$  in a calorimeter. The temperature of the reaction mixture rises from  $18.0^\circ\text{C}$  to  $24.6^\circ\text{C}$ . The specific heat capacity of water is  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ . Calculate the standard molar enthalpy of \_\_\_\_\_.
- $1 \text{ cm}^3 \text{ water} = 1 \text{ g}$
- $m = 50 + 50 = 100 \text{ g}$
- $c = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$ .
- $\Delta T = 24.6 - 18.0 = 6.6 \text{ K}$
- $Q = 100 \times 4.18 \times 6.6 = 2758.8 \text{ J}$

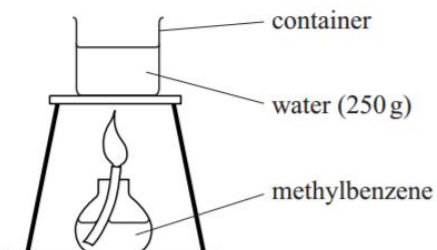
- $Q = 2.7588\text{kJ}$
- $n = C \times V = 0.05 \times 1$
- $= 0.05 \text{ mol}$
- $\Delta H_n^0 = -(q \div n)$
- $= -2.7588 / 0.05$
- $= -55.18 \text{ kJ mol}^{-1}$

### Slide 13: Theory of knowledge

- What criteria do we use in judging discrepancies between experimental and theoretical values? Which ways of knowing do we use when assessing experimental limitations and theoretical assumptions?

### Slide 14: Exam Question

An experiment was carried out to determine a value for the enthalpy of combustion of liquid methylbenzene using the apparatus shown in the diagram.



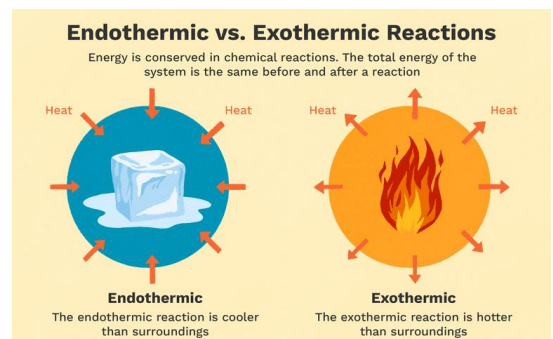
Burning 2.5 g of methylbenzene caused the temperature of 250 g of water to rise by 60 °C. Use this information to calculate a value for the enthalpy of combustion of methylbenzene,  $\text{C}_7\text{H}_8$   
 (The specific heat capacity of water is  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ . Ignore the heat capacity of the container.)

Slide 15: List all of the problems with this method.

- Calorimetric Methods

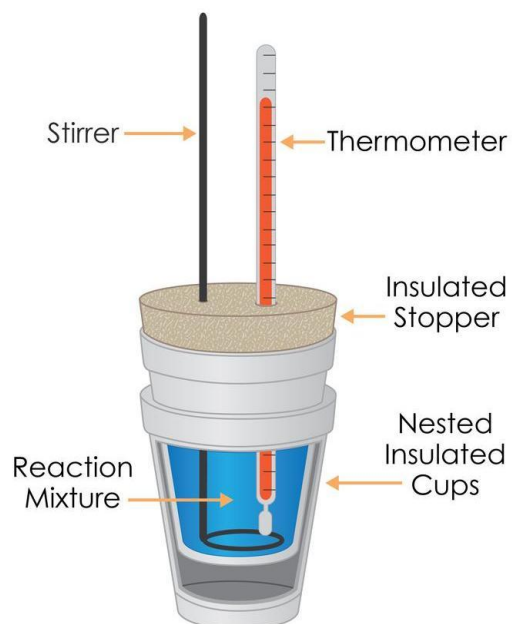
Slide 16: Experiments investigating endothermic and exothermic processes could be run numerous times to compare reliability of repetitive data and compare to theoretical values.

- Reliable data?



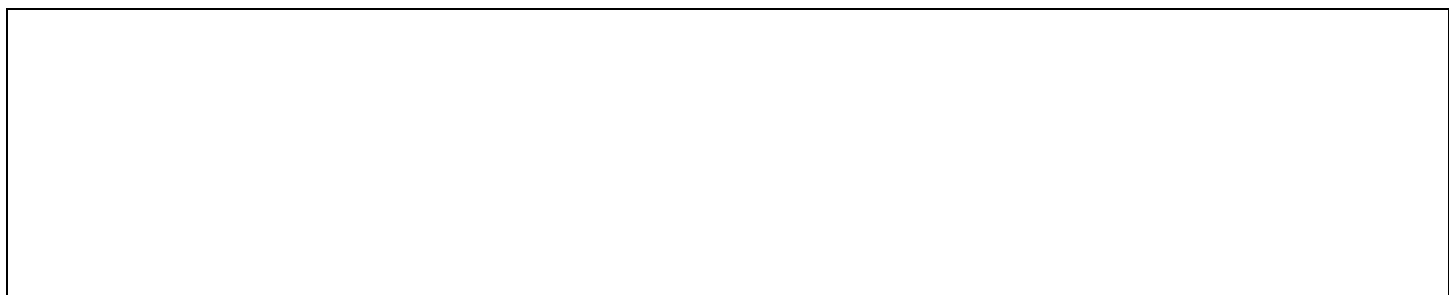
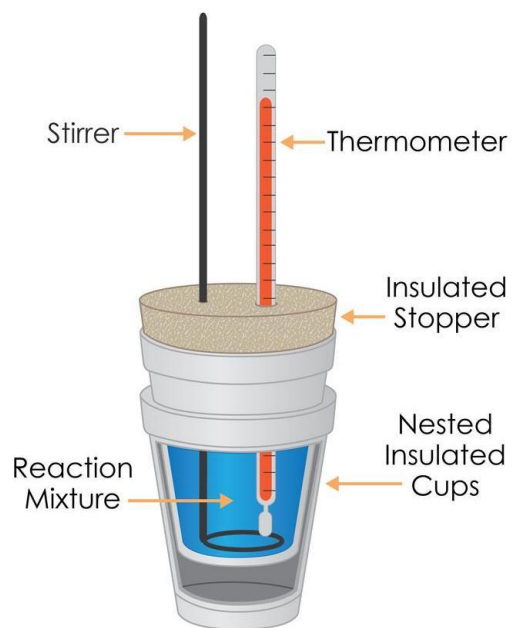
Slide 17: Heat Loss

- The \_\_\_\_\_ beaker method helps us to reduce heat loss because polystyrene is a good insulator.
- (Only for \_\_\_\_\_ in solution)



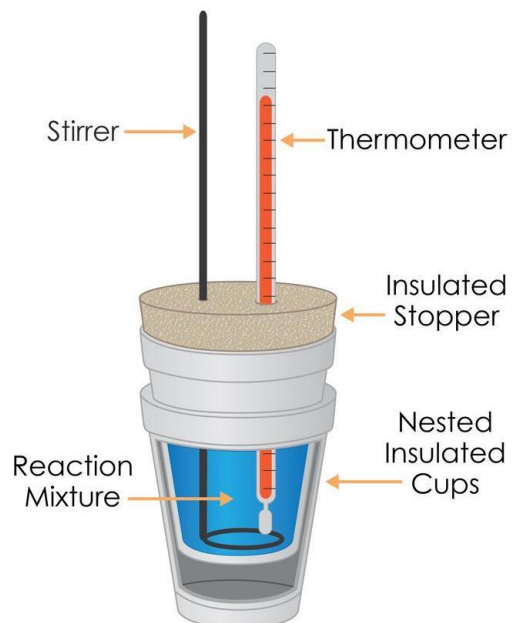
### Slide 18: Heat Loss

- Can heat loss still occur?
- How will this affect your measurement of enthalpy?



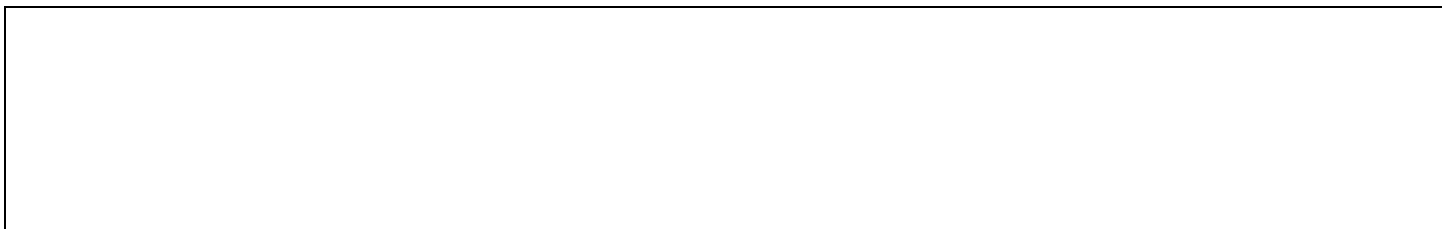
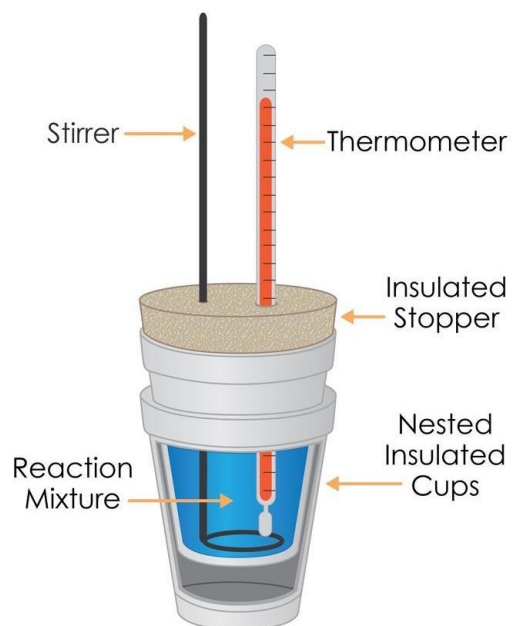
### Slide 19: Allowing for heat loss

- The way in which we \_\_\_\_\_ data can affect our final results
- Use a **cooling curve** to find the **best \_\_\_\_\_** of  $\Delta T$



### Slide 20: Uncertainty

- How many uncertainties can you find for a calorimetry experiment?
- Temperature measurements
- Volume/mass of water
- Volume/mass of reactants
- How do we quantify these uncertainties?



### Slide 21: Uncertainty

- Consider a \_\_\_\_\_ experiment measuring the enthalpy change when  $1 \text{ mol dm}^{-3}$  NaOH is mixed with  $1 \text{ mol dm}^{-3}$  HCl (slide 11).
- \_\_\_\_\_: uncertainty is half the smallest division (analog) or  $0.1 \text{ }^\circ\text{C}$  (digital).
- If the \_\_\_\_\_ is measured as  $25.6 \text{ }^\circ\text{C}$ , it is written as  $T = 25.6 \pm 0.1 \text{ }^\circ\text{C}$ , meaning it could be between  $25.5$  and  $25.7 \text{ }^\circ\text{C}$ .  $\pm 0.1 \text{ }^\circ\text{C}$  is the absolute uncertainty.
- Change this into a percentage \_\_\_\_\_:
- $0.1/25.6 \times 100 = 0.39\%$

### Slide 22: Error Propagation

- To find  $\Delta T$  we take 2 \_\_\_\_\_: initial and final. Each measurement has an uncertainty.
- $\Delta T = 25.6 - 19.0 = 6.6 \text{ }^\circ\text{C}$
- When we add/subtract measurements, we ADD the absolute \_\_\_\_\_.
- $\Delta T = 6.6 \pm 0.2 \text{ }^\circ\text{C} = 6.6 \text{ }^\circ\text{C} \pm 3.03\%$
- When we multiply/divide measurements, we ADD the percentage \_\_\_\_\_.

### Slide 23: Practice

- Calculate the uncertainty when making a  $1 \text{ mol dm}^{-3}$  solution of NaOH.
- A 2 d.p. mass balance was used to weigh  $10.00\text{g}$  of solid sodium hydroxide.
- In making the standard solution, a  $250 \text{ cm}^3$  volumetric flask ( $\pm 0.12 \text{ cm}^3$ ) was used.
- Assume  $M_r(\text{NaOH}) = 39.997 \text{ g mol}^{-1}$  with no error.
- $0.01/10.00 = 0.10\%$  uncertainty
- $0.12/250.00 = 0.048\%$  uncertainty
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$

### Slide 24: Practice

- $\Delta T = 6.6 \pm 0.2 \text{ }^\circ\text{C} = 6.6 \text{ }^\circ\text{C} \pm 3.03\%$
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$
- $50.0 \text{ cm}^3$  of each solution (HCl and NaOH) were added together to the calorimeter using  $50.0 \text{ cm}^3$  graduated pipettes with an uncertainty of  $\pm 0.05 \text{ cm}^3$ .
- $0.10/100.00 = 0.10\%$  uncertainty
- Volume:  $100.0 \text{ cm}^3 \pm 0.10\%$

### Slide 25: Practice

- $\Delta T = 6.6 \pm 0.2^\circ\text{C} = 6.6^\circ\text{C} \pm 3.03\%$
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$
- Volume HCl + NaOH =  $100.0 \text{ cm}^3 \pm 0.10\%$
- $n(\text{NaOH}) = 0.0500 \text{ mol} \pm 0.25\%$
- **Calculate the % uncertainty in the number of moles of base in the reaction.**
- $1.00 \text{ mol dm}^{-3} \times 0.0500 \text{ dm}^3 = 0.0500 \text{ mol NaOH}$
- $0.15\% + 0.10\% = 0.25\%$

### Slide 26: Practice

- $\Delta T = 7.6 \pm 0.2^\circ\text{C} = 7.6^\circ\text{C} \pm 3.03\%$
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$
- Volume HCl + NaOH =  $100.0 \text{ cm}^3 \pm 0.10\%$
- $n(\text{NaOH}) = 0.0500 \text{ mol} \pm 0.25\%$
- mass of water =  $100.0 \text{ g} \pm 0.10\%$
- **Assume density of water is  $1.00 \text{ g cm}^{-3}$**
- **Calculate the % uncertainty in the volume of the reaction mixture and therefore the mass of water.**

### Slide 27: Practice

- $\Delta T = 6.6 \pm 0.2^\circ\text{C} = 6.6^\circ\text{C} \pm 3.03\%$
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$
- Volume HCl + NaOH =  $100.0 \text{ cm}^3 \pm 0.10\%$
- $n(\text{NaOH}) = 0.0500 \text{ mol} \pm 0.25\%$
- mass of water =  $100.0 \text{ g} \pm 0.10\%$

- Calculate the % uncertainty in the enthalpy change of the reaction. Assume specific heat capacity of water =  $4.18 \text{ Jg}^{-1}\text{K}^{-1}$  with no error.
- $q = mc\Delta T$
- $= 100.0(4.18)(6.6) = 2,758.8 \text{ J} \pm 3.13\%$

### Slide 28: Practice

- $\Delta T = 7.6 \pm 0.2^\circ\text{C} = 7.6^\circ\text{C} \pm 3.03\%$
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$
- Volume HCl + NaOH =  $100.00 \text{ cm}^3 \pm 0.10\%$
- $n(\text{NaOH}) = 0.0500 \text{ mol} \pm 0.25\%$
- mass of water =  $100.00 \text{ g} \pm 0.10\%$
- $\Delta H = 2758.8 \text{ J} \pm 3.13\%$
- Calculate the % uncertainty in the enthalpy change per mole of the reaction.
- $2758.8 \text{ J} / 0.0500 \text{ mol} = 55,176 \text{ J mol}^{-1} \pm 3.38\%$

### Slide 29: Practice

- $\Delta T = 7.6 \pm 0.2^\circ\text{C} = 7.6^\circ\text{C} \pm 3.03\%$
- $[\text{NaOH}] = 1.00 \text{ mol dm}^{-3} \pm 0.15\%$
- Volume HCl + NaOH =  $100.00 \text{ cm}^3 \pm 0.10\%$
- $n(\text{NaOH}) = 0.0500 \text{ mol} \pm 0.25\%$
- mass of water =  $100.00 \text{ g} \pm 0.10\%$
- $\Delta H = 2758.8 \text{ J} \pm 3.13\%$
- $\Delta H^\circ = -55.18 \text{ kJ} \pm 3.38\%$
- Therefore there is an uncertainty of 1.87kJ in the calculation.

### Slide 30: Practice

- Consider an experiment measuring the molar enthalpy change involved in dissolving anhydrous copper sulfate in water.
- Anhydrous copper sulfate is added to a dry calorimeter, and 25.0 cm<sup>3</sup> of distilled water is added. The temperature change is measured while the solution is stirred. The initial temperature was 26.1°C ± 0.1 °C and the final temperature was 57.9 °C ± 0.1 °C.
- Complete a full error analysis and calculate an absolute uncertainty for the standard molar enthalpy change for the reaction.
- Assume: 7.98 g of anhydrous copper sulphate
- 2 d.p. mass balance
- 25.0 cm<sup>3</sup> ± 0.06 cm<sup>3</sup> pipette

### Slide 31: Practical

- This unit, we will do a \_\_\_\_\_ practical.
- **You will be \_\_\_\_\_ to**
- **plan and carry out a \_\_\_\_\_ method**
- **evaluate sources of error in your method, apparatus and \_\_\_\_\_ technique.**
- **carry out \_\_\_\_\_ error analysis on your results.**

### Slide 32: Extrapolating graphs

### Slide 34: Energy vs. Heat

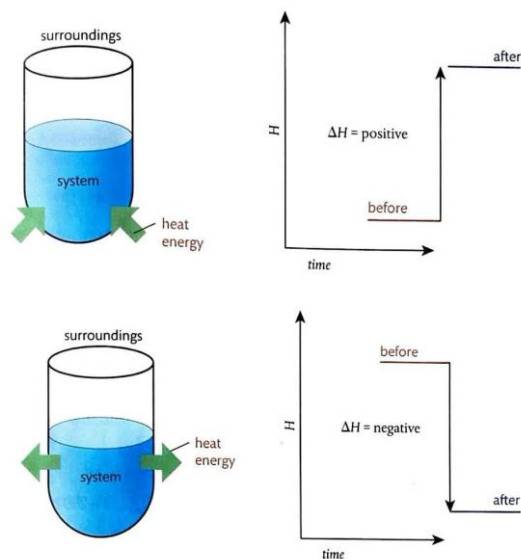
- Energy is the ability to do work and \_\_\_\_\_:
- Heat
- Light
- Sound
- Electricity
- Chemical energy
- Heat is a mode of energy transfer as a result of \_\_\_\_\_ differences
- Produces an increase in average kinetic energy of \_\_\_\_\_
- Causes an increase in disorder of \_\_\_\_\_
- **Energy \_\_\_\_\_/released during chemical rxns**

### Slide 35: System vs. Surroundings

- When studying energy transfer, it is important to define the **system** and its \_\_\_\_\_.
- **Area of interest**
- \_\_\_\_\_ **else in the universe**
- Most chemical reactions happen in **open systems** (able to exchange energy and matter with \_\_\_\_\_)
- Closed systems can exchange energy but not matter with the \_\_\_\_\_.
- \_\_\_\_\_, **TOTAL energy doesn't change during a reaction.**

### Slide 36: Enthalpy

- The heat \_\_\_\_\_ of a system (H)
- Changes in \_\_\_\_\_ ( $\Delta H$ ) are positive when heat is added to a system
- Changes in enthalpy are negative when heat is released from the system to the \_\_\_\_\_.



### Slide 37: Endothermic vs. Exothermic Rxns

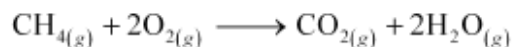
- $\Delta H < 0$
- $\Delta H > 0$

### Slide 38: Standard Enthalpy Changes

- $\Delta H^\ominus$ : \_\_\_\_\_ enthalpy change
- "Standard" means measured under the following \_\_\_\_\_:
- 100kPa
- 1 mol dm<sup>-3</sup> \_\_\_\_\_ for all solutions
- All \_\_\_\_\_ in their standard states
- Pure form of a substance under standard \_\_\_\_\_ of 298 K (25 °C) and 100 kPa

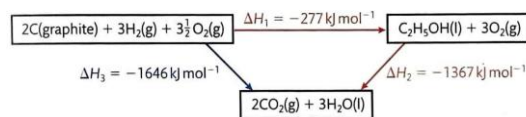
### Slide 39: Thermochemical Equations

- $\Delta H^\ominus$  is used to describe enthalpy changes in chemical \_\_\_\_\_.
- $\Delta H^\ominus = -890 \text{ kJ mol}^{-1}$
- $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + 6\text{O}_2(\text{g})$
- $\Delta H^\ominus = +2802.5 \text{ kJ mol}^{-1}$
- $\Delta H < 0$ , exothermic
- $\Delta H > 0$ , endothermic



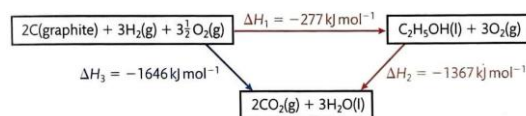
#### Slide 40: Hess's Law

- \_\_\_\_\_ enthalpy changes of a reaction are not measured directly.
- The  $\Delta H$  of a rxn is \_\_\_\_\_ from the known enthalpy changes of other reactions.
- \_\_\_\_\_ route (red arrows): elements combined to form ethanol, which is burned.
- \_\_\_\_\_ route (blue arrow): elements burned separately



#### Slide 41: Hess's Law

- **Clockwise Route:**

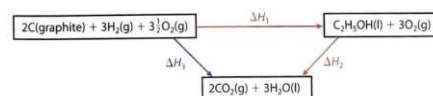


$$\Delta H_1 + \Delta H_2 = -277 + -1367 = -1644 \text{ kJ mol}^{-1}$$

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

#### Slide 42: Hess's Law

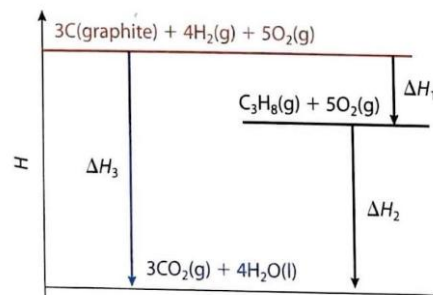
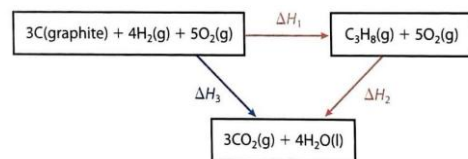
- For the Law of \_\_\_\_\_ of Energy to be followed,  $\Delta H_1 + \Delta H_2$  must be the same as  $\Delta H_3$ , since both correspond to the combustion of 2 moles of carbon and 3 moles of hydrogen.
- \_\_\_\_\_ of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes.



#### Slide 43: Using Hess's Law

- An energy level diagram can be used to show the

- \_\_\_\_\_ between different reactions.
- Even though  $\Delta H_1$  can't be measured directly, it can be \_\_\_\_\_ from the  $\Delta H_c$  of carbon, hydrogen, and propane.

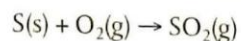


#### Slide 44: Using Hess's Law-Example

##### Worked example



Calculate the standard enthalpy change,  $\Delta H^\ominus$ , for the reaction:



## Slide 45: Using Hess's Law-Example

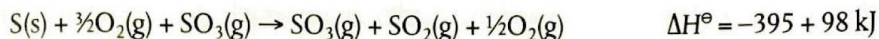
Reaction 1 starts from the required starting point:



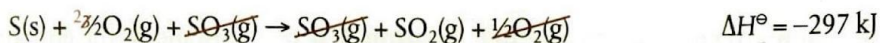
Reaction 2 relates  $\text{SO}_3(\text{g})$  to  $\text{SO}_2(\text{g})$ . To finish with the required product, we reverse the chemical change and the sign of enthalpy change:



We can now combine these equations:



Simplifying:



## Slide 46: You Try!

- Calculate the enthalpy change,  $\Delta H^\ominus$ , for the reaction
- $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
- From the information below:
- $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\ominus = -394 \text{ kJ}$
- $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\ominus = -283 \text{ kJ}$
- Calculate the enthalpy change,  $\Delta H^\ominus$ , for the reaction
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
- From the information below:
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) \quad \Delta H^\ominus = +180.5 \text{ kJ}$
- $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) \quad \Delta H^\ominus = +66.4 \text{ kJ}$

## Slide 47: More Hess's Law Problems

- Calculate the enthalpy change,  $\Delta H^\ominus$ , for the dimerization of nitrogen dioxide

- $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$
- From the information below:
- $\frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$   $\Delta H^\ominus = +33.2\text{kJ mol}^{-1}$
- $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$   $\Delta H^\ominus = +9.16\text{kJ mol}^{-1}$
- You can also multiply/divide standard enthalpy changes to get to the final equation.
- $2[\text{NO}_2(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g})]$   $\Delta H^\ominus = 2(-33.2\text{kJ mol}^{-1})$
- $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$   $\Delta H^\ominus = +9.16\text{kJ mol}^{-1}$
- $2\text{NO}_2(\text{g}) + \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) + \text{N}_2\text{O}_4(\text{g})$   $\Delta H^\ominus = -57.24\text{kJ mol}^{-1}$

### Slide 48: You Try!

- The thermochemical equations for three related reactions are shown. Determine  $\Delta H_3$
- $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   $\Delta H_1 = -283\text{kJ mol}^{-1}$
- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$   $\Delta H_2 = -572\text{kJ mol}^{-1}$
- $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$   $\Delta H_3 = ?$

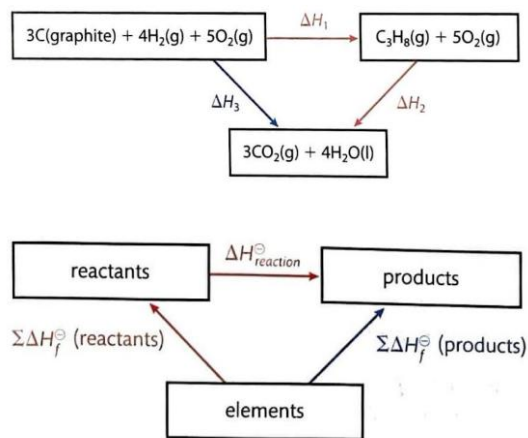
### Slide 49: Enthalpy of Formation

- **Standard Enthalpy of \_\_\_\_\_** ( $\Delta H_f^\ominus$ ): the enthalpy change that occurs when **one mole** of the substance is formed from its elements in their **standard states**.
- Gives a measure of the \_\_\_\_\_ of a substance relative to its elements
- Can be used to calculate the enthalpy change of **all reactions** (\_\_\_\_\_ or real)
- Standard Enthalpy of \_\_\_\_\_ of Ethanol:
- $2\text{C}(\text{_____}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$   $\Delta H = -278\text{kJ mol}^{-1}$
- **One mole** of product formed, so sometimes **fractional** \_\_\_\_\_ used in the equation
- **Note:**  $\Delta H_f^\ominus$  for pure \_\_\_\_\_ are **ZERO**

### Slide 50: Helpful Hints

- For \_\_\_\_\_ reactions, **add**  $\Delta H_1$  and  $\Delta H_2$  to get  $\Delta H_3$
- For \_\_\_\_\_ reactions, **subtract**  $\Delta H_f(\text{reactants})$  from  $\Delta H_f(\text{products})$

- $\Delta H^{\ominus}_{\text{rxn}} = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$



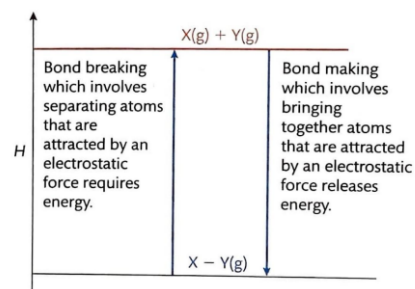
### Slide 51: Example Problem

- Calculate the enthalpy change for the reaction:
- $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
- $\Delta H^{\ominus}_{\text{rxn}} = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$
- $= 3(-394) + 4(-286) - (-105)$
- $= -2221 \text{ kJ mol}^{-1}$

### Slide 52: Bond Enthalpies

- Breaking bonds is endothermic
- Making bonds is exothermic
- Energy is needed to separate atoms previously bonded
- Energy is released when bonds are formed
- Chemical reactions involve **bond making** and **bond breaking**. If more energy is released than absorbed, the reaction will be **overall exothermic**

- $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g}) \quad \Delta H^{\ominus} = +242 \text{ kJ mol}^{-1}$
- $\text{H}(\text{g}) + \text{H}(\text{g}) \rightarrow \text{H}_2(\text{g}) \quad \Delta H^{\ominus} = -436 \text{ kJ mol}^{-1}$



### Slide 53: Bond Enthalpies

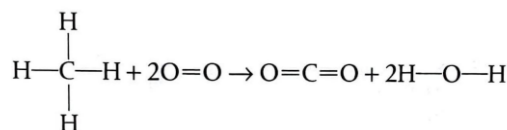
- Average bond enthalpy:** the energy needed to break one mole of bonds in **gaseous molecules** under standard conditions, averaged over **similar compounds**

- Multiple bonds generally have **higher bond \_\_\_\_\_** and **shorter bond lengths** compared to single bonds

Bond	E(X-Y) / kJ mol <sup>-1</sup>	Bond length / 10 <sup>-9</sup> m
H-H	+436	0.074
C-C	+347	0.154
C=C	+614	0.134
C-H	+414	0.108
O-O	+498	0.121
O-H	+463	0.097
C=O	+804	0.122
Cl-Cl	+242	0.199

### Slide 54: Bond Enthalpies

- $\Delta H^{\ominus}_{\text{rxn}} = \sum \Delta H^{\ominus}(\text{bonds broken}) - \sum \Delta H^{\ominus}(\text{bonds formed})$
- Example: Combustion of Methane
- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- $\Delta H^{\ominus} = +2652 - 3460$
- $= -808 \text{ kJ mol}^{-1}$

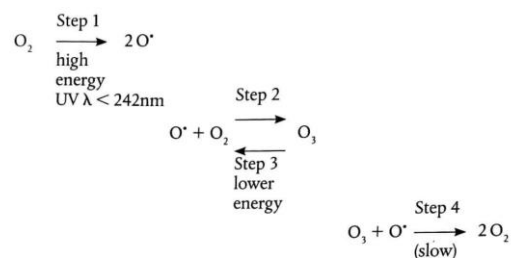


### Slide 55: Ozone Depletion

- Bond order of ozone:  $3/2 = 1.5$
- Bond order of oxygen: 2
- Oxygen has stronger bonds than ozone, which break under lower energy/longer \_\_\_\_\_ of light

### Slide 56: The Chapman Cycle

- Ozone is \_\_\_\_\_ at a **steady state** if the rate of formation of ozone is balanced by its rate of removal
- \_\_\_\_\_ free radicals are formed when oxygen is broken with UV light
- Formation of ozone is \_\_\_\_\_ because bonds are formed
- Formation of oxygen from ozone and free radicals is also \_\_\_\_\_



### Slide 57: Example Problem

- The bond energy in ozone is  $363 \text{ kJ mol}^{-1}$ . Calculate the wavelength of UV radiation needed to break the bond.
- $L \times E_{\text{photon}} = 363,000 \text{ J}$
- $E_{\text{photon}} = 363,000 \text{ J} / 6.02 \times 10^{23} = 6.03 \times 10^{-19} \text{ J}$
- $E = hf$ ,
- $c = \lambda f$  so  $f = c/\lambda$
- $E = hc/\lambda$  or
- $\lambda = ch/E$
- $\lambda = 3.00 \times 10^8 \text{ ms}^{-1} (6.63 \times 10^{-34} \text{ Js}) / 6.03 \times 10^{-19} \text{ J}$
- $= 3.30 \times 10^{-7} \text{ m} = 330 \text{ nm}$
- Avogadro's Number!

### Slide 58: You Try!

- Use the Data Booklet to calculate the minimum wavelength of radiation needed to break the O=O double bond in  $\text{O}_2$ .

### Slide 59: Additional Higher Level

### Slide 60: Some Useful Definitions

- **First** \_\_\_\_\_ **Energy:** the minimum energy required to remove one mole of electrons from one mole of gaseous atoms.
- **Electron Affinity:** the enthalpy change when one mole of gaseous \_\_\_\_\_ is added to one mole of gaseous atoms.
- **Lattice Enthalpy:** the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard \_\_\_\_\_.
- $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-(\text{g}) \quad \Delta H_{\text{i}}^{\ominus} = +496 \text{ kJ mol}^{-1}$
- $\text{Cl(g)} + \text{e}^-(\text{g}) \rightarrow \text{Cl}^-(\text{g}) \quad \Delta H_{\text{e}}^{\ominus} = -349 \text{ kJ mol}^{-1}$
- $\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \quad \Delta H_{\text{lat}}^{\ominus} = +790 \text{ kJ mol}^{-1}$

## Slide 61: Lattice Enthalpies

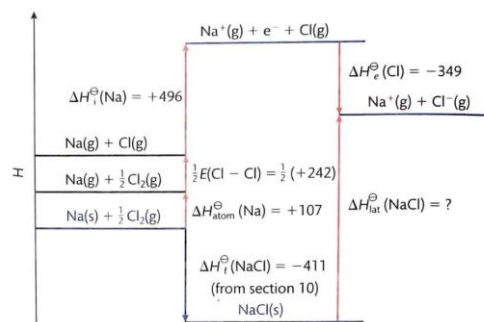
- Gaseous ions coming together to form an ionic lattice is an **exothermic process**, but lattice enthalpies express the reverse \_\_\_\_\_ process (breaking apart a solid ionic lattice into its gaseous ions) .
- Experimental lattice enthalpies can't be determined \_\_\_\_\_.
- The **Born-Haber Cycle** (based on Hess's Law) is used.
- Shows the enthalpy change for the \_\_\_\_\_ of a solid ion from its gaseous elements through several steps. Final enthalpy shown will be  $-\Delta H_{\text{lat}}^{\ominus}$

## Slide 62: Born-Haber Cycle

Step	$\Delta H^{\ominus} / \text{kJ mol}^{-1}$
Sodium is atomized to form one mole of gaseous ions: $\text{Na(s)} \rightarrow \text{Na(g)}$ The corresponding enthalpy change is known as the enthalpy change of atomization.	$\Delta H_{\text{atom}}^{\ominus}(\text{Na}) = +107$
One mole of chlorine atoms is formed as $\frac{1}{2}$ mole of Cl—Cl bonds break: $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$ $E =$ bond enthalpy, page 233 Enthalpy of atomization of chlorine	$\frac{1}{2}E(\text{Cl—Cl}) = \frac{1}{2}(+242)$
One electron is removed from the outer shell of the gaseous sodium atom: $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$ Ionization energy of sodium	$\Delta H_{\text{i}}^{\ominus}(\text{Na}) = +496$
One electron is added to the outer shell of the gaseous chlorine atom: $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$ Electron affinity of chlorine	$\Delta H_{\text{e}}^{\ominus}(\text{Cl}) = -349$
The gaseous ions come together to form one mole of solid sodium chloride: $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(s)}$ – Lattice enthalpy of sodium chloride	$-\Delta H_{\text{lat}}^{\ominus} = ???$

## Slide 63: Born-Haber Cycle

- \_\_\_\_\_ of one mole of NaCl from its elements in their **standard states**
- The \_\_\_\_\_ of one mole of NaCl from its gaseous ions (shown as  $-\Delta H_{\text{lat}}^{\ominus}$ )
- $\Delta H_{\text{f}}^{\ominus}(\text{NaCl}) = \Delta H_{\text{atom}}^{\ominus}(\text{Na}) + \Delta H_{\text{i}}^{\ominus}(\text{Na}) + \frac{1}{2}E(\text{Cl—Cl}) + \Delta H_{\text{e}}^{\ominus}(\text{Cl}) - \Delta H_{\text{lat}}^{\ominus}(\text{NaCl})$
- $-411 = +107 + 496 + \frac{1}{2}(+242) - 349 - \Delta H_{\text{lat}}^{\ominus}(\text{NaCl})$
- $\Delta H_{\text{lat}}^{\ominus}(\text{NaCl}) = +786 \text{ kJ mol}^{-1}$



### Slide 64: You Try!

- Write an equation to represent the lattice energy of magnesium oxide ( $\Delta H_f^\ominus \text{MgO} = -602 \text{ kJ mol}^{-1}$ ,  $\Delta H_a^\ominus \text{Mg(s)} = +148 \text{ kJ mol}^{-1}$ , second ionization energy of Mg:  $+1451 \text{ kJ mol}^{-1}$ )
- Write an equation to represent the second electron affinity of oxygen and comment on the relative values of the first and second values given in the Data Booklet
- Construct a Born-Haber cycle for magnesium oxide.
- Calculate the lattice energy of magnesium oxide.

### Slide 65: Theoretical Lattice Enthalpies

- Lattice enthalpies can also be calculated from the **ionic model** (assumes only interactions are due to \_\_\_\_\_ forces between ions).
- Energy needed to \_\_\_\_\_ ions depends on
- Ionic charges
- Ionic radius
- Increase in ionic charge increases \_\_\_\_\_ between ions
- Increase in ionic radius decreases \_\_\_\_\_ between ions

### Slide 66: Theoretical Lattice Enthalpies

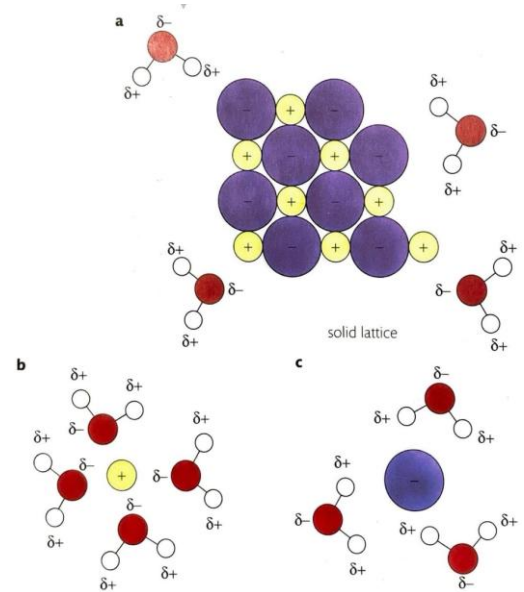
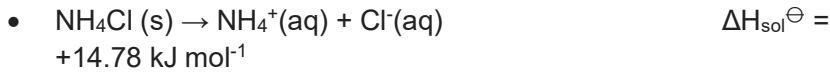
	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
Li <sup>+</sup>	1049	864	820	764
Na <sup>+</sup>	930	790	754	705
K <sup>+</sup>	829	720	691	650
Rb <sup>+</sup>	795	695	668	632
Cs <sup>+</sup>	759	670	647	613

	$\Delta H_{\text{lattice}}^\ominus$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{lattice}}^\ominus$ (kJ mol <sup>-1</sup> )	Explanation of difference
NaCl	1049	MgCl <sub>2</sub> 2540	MgCl <sub>2</sub> has more than double the lattice enthalpy of NaCl as Mg <sup>2+</sup> has double the charge of Na <sup>+</sup> and a smaller ionic radius.
CaF <sub>2</sub>	2651	CaO 3401	CaO has higher lattice enthalpy than CaF <sub>2</sub> as O <sup>2-</sup> has double the charge of F <sup>-</sup> . The value is less than double as O <sup>2-</sup> has a larger ionic radius than F <sup>-</sup> .

## Slide 67: Enthalpies of Solution ( $\Delta H_{sol}^{\ominus}$ )

- The enthalpy change when one mole of a solute is dissolved in a solvent to infinite dilution under standard \_\_\_\_\_.

- Ions separated from the lattice and \_\_\_\_\_ by water molecules are **hydrated**.



## Slide 68: Hydration Enthalpy ( $\Delta H_{hyd}^{\ominus}$ )

- The enthalpy change when one mole of gaseous ions is dissolved to form an \_\_\_\_\_ dilute solution of one mole of aqueous ions under standard conditions.
- \_\_\_\_\_ of hydration **cannot be measured directly** since both positive and negative ions are present in solution.
- $\text{H}^+(\text{g}) \rightarrow \text{H}^+(\text{aq})$   $\Delta H_{hyd}^{\ominus} = -1130 \text{ kJ mol}^{-1}$
- Hydration is an \_\_\_\_\_ **process** since there is a force of attraction between ions and polar water molecules.

## Slide 69: Hydration Enthalpy

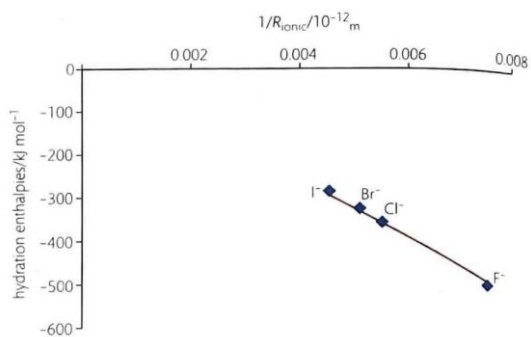
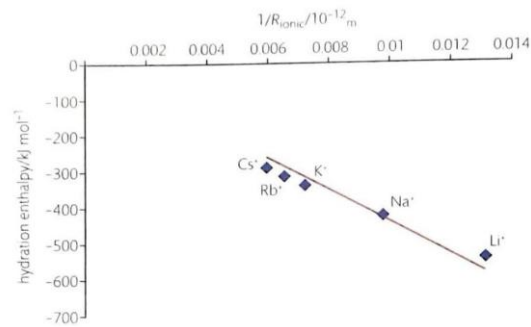
- Values get **less** \_\_\_\_\_ as the ionic radius increases down a group
- Hydration enthalpies are \_\_\_\_\_ **inversely proportional to the ionic radii**.
- Values get **more** \_\_\_\_\_ as the ionic charge increases across period 3

Cations	$\Delta H_{hyd}^{\ominus} / \text{kJ mol}^{-1}$	Anions	$\Delta H_{hyd}^{\ominus} / \text{kJ mol}^{-1}$
$\text{Li}^+$	-538	$\text{F}^-$	-504
$\text{Na}^+$	-424	$\text{Cl}^-$	-359
$\text{K}^+$	-340	$\text{Br}^-$	-328
$\text{Rb}^+$	-315	$\text{I}^-$	-287

Cations	$\Delta H_{hyd}^{\ominus} / \text{kJ mol}^{-1}$
$\text{Na}^+$	-424
$\text{Mg}^{2+}$	-1963
$\text{Al}^{3+}$	-4741

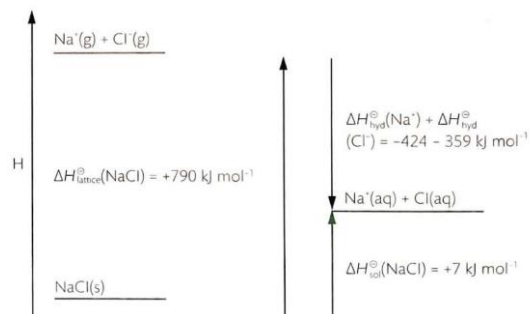
## Slide 70: Hydration Enthalpy

- Hydration \_\_\_\_\_ **decrease** as ionic radius **increases**



### Slide 71: Relationship between $\Delta H_{\text{hyd}}^{\ominus}$ , $\Delta H_{\text{sol}}^{\ominus}$ , and $\Delta H_{\text{lat}}^{\ominus}$

- $\Delta H_{\text{sol}}^{\ominus}(\text{NaCl}) = \Delta H_{\text{lat}}^{\ominus}(\text{NaCl}) + \Delta H_{\text{hyd}}^{\ominus}(\text{Na}^+) + \Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^-)$
- $\Delta H_{\text{sol}}^{\ominus}(\text{NaCl}) = +790 - 424 - 359$
- $\Delta H_{\text{sol}}^{\ominus}(\text{NaCl}) = +7 \text{ kJ mol}^{-1}$
- $\Delta H_{\text{sol}}^{\ominus}(\text{NaCl})$  reported in the Data Booklet is  $+3.88 \text{ kJ mol}^{-1}$ . This is due to problems calculating small numbers from differences in large numbers.



### Slide 72: You Try!

- Use an energy cycle to calculate the enthalpy of solution of potassium chloride ( $\Delta H_{\text{hyd}}^{\ominus}(\text{K}^+)$ :  $-340 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{hyd}}^{\ominus}(\text{Cl}^-)$ :  $-359 \text{ kJ mol}^{-1}$ )
- Calculate the % inaccuracy of your value by comparing with the theoretical value of  $\Delta H_{\text{sol}}^{\ominus} \text{ KCl}$  ( $+17.22 \text{ kJ mol}^{-1}$ ) and comment on the disagreement between the two values.

