

Thermochemistry

Energy and Matter

- Definition – the capacity to do work.
- Type of energy
 - Potential energy – energy of position
 - Kinetic energy – energy of motion
- Units of energy
 - Can be found from the formula of kinetic energy.

Energy and its units

- Kinetic energy can be calculated by the formula

$$KE = \frac{1}{2}mv^2$$

- In this formula if mass is in kilograms and velocity (speed) is in meters per second the energy will have units of $\text{kg m}^2 \text{s}^{-2}$.

Kinetic energy

- The SI units for energy are $\text{kg m}^2 \text{s}^{-2}$.
- This unit is also called the **Joule (J)**.
- Another unit that is used is the calorie (cal).
 - definition – the amount of energy needed to increase the temperature of 1 g of water by 1°C.
 - 1 cal = 4.184 J

Energy units

- All chemical processes follow the **law of conservation of energy**.
- This is a statement of observation that energy in a process is neither created nor destroyed. It can, however, be converted from one type of energy into another.

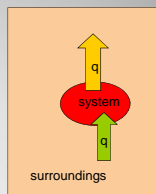
Law of Conservation of Energy

- To understand heats of reaction we must understand the difference, in thermodynamic terms, between the **system** and the **surroundings**.
 - system – in most cases we'll see it is just the chemical reaction.
 - surroundings – everything else that is not the system.

Heats of reaction

- The energy that flows into or out of a system because of a temperature difference between the system and its surroundings.

- $q < 0$ if the system loses energy (the surroundings gain energy)
- $q > 0$ if the system gains energy (the surroundings lose energy)



Heat (q)

- Before a reaction occurs the system and surroundings are at the same temperature.
- When the reaction occurs, heat flows.
- The heat of reaction is the amount of heat (q) needed to return the system to a given temperature (usually 25°C , standard thermodynamic temperature).

Heat of reaction

- A reaction is said to be exothermic if the reaction (system) gives up energy.
 - $q < 0$
 - the reaction vessel heats up
- The reaction is endothermic if the reaction absorbs energy.
 - $q > 0$
 - the reaction vessel cools down

Heats of reaction

- Extensive property – a property that depends on the amount of substance present.
- State function – a function that depends only on the difference between the initial and final values not on the path taken.
- Enthalpy allows us to determine the amount of heat lost or gained by a reaction.

Enthalpy (H)

- The relationship between the heat of a reaction and its enthalpy change is given by $\Delta H = q_p$
- q_p is the heat transferred at constant pressure.

Enthalpy Changes (ΔH)

- A thermochemical equation is the chemical equation (including phase labels) immediately followed by the enthalpy change of the reaction
 - $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}); \Delta H = -570. \text{ kJ}$
 - $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}); \Delta H = -482. \text{ kJ}$

Thermochemical Equations

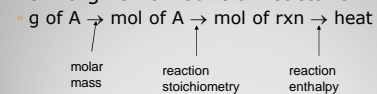
- Rules to follow

- If a chemical equation is multiplied by a factor the ΔH is multiplied by the same factor.
- If the chemical equation is reversed, the ΔH has its sign reversed.

Thermochemical equations

- In a thermochemical equation the enthalpy that is given is for one mole of the **reaction**.

- We can then use this information to calculate the amount of heat generated from a given amount of reactant.



Heats of reaction and stoichiometry

- Heat capacity and specific heat

- When a substance transfers heat, its temperature changes by some amount proportional to the amount of heat transferred.
- The proportionality constant is the **heat capacity (C)** and is dependent on the amount of material present.

$$q = C\Delta T$$

Measuring heats of reaction – Calorimetry

- Heat capacity and specific heat

- When the heat capacity is specified for 1 g of material that is called the **specific heat (s)**.
- Specific heat is defined as the amount of heat needed to increase the temperature of 1 g of a substance by 1°C.
- We can calculate the amount of heat transferred by $q = ms\Delta T$

Measuring heats of reaction – Calorimetry

- Calculate the amount of heat needed to increase the temperature of 250.0 g of water from 25.0°C to 80.0°C.

$$q = ms\Delta T = (250.0 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(80.0 \text{ }^\circ\text{C} - 25.0 \text{ }^\circ\text{C}) = 5.75 \times 10^4 \text{ J}$$

Example

- Calorimetry – the process of measuring heat transfer during a chemical reaction.
- Can be measured at constant pressure using a **coffee-cup calorimeter**.
- A coffee-cup calorimeter is two nested Styrofoam® cups acting as an insulated container. The reaction takes place in the cup and the temperature change of the water is measured to determine the heat of reaction.

Measuring heats of reaction – Calorimetry

- Some things to remember
 - the heat transferred by the reaction is the same as the heat transferred by the surroundings with the opposite sign
 - to get the thermochemical equation we must take into account the amount of material used.

Measuring heats of reaction – Calorimetry

- 0.150 g of Magnesium metal is added to 36.74 g of excess hydrochloric acid solution. The temperature of the solution increased from 23.6°C to 41.7°C. What is the molar enthalpy change for the single replacement reaction of magnesium with hydrochloric acid? Assume the specific heat of the solution is the same as that of water.

Example

- Find $q_{\text{calorimeter}}$

$$q_{\text{cal}} = ms\Delta T$$

$$= (36.74 \text{ g})(4.184 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1})(41.7^\circ\text{C} - 23.6^\circ\text{C})$$

$$= 2782.33 \text{ J}$$
- Find q_{rxn}

$$q_{\text{rxn}} = -q_{\text{cal}} = -2782.33 \text{ J}$$

Answer

- Now the molar enthalpy can be determined.

$$\Delta H = \frac{q_{\text{rxn}}}{n_{\text{Mg}}} = \frac{-2782.33 \text{ J}}{(0.15 \text{ g Mg}) \left(\frac{1 \text{ mol Mg}}{24.3050 \text{ g Mg}} \right) \left(\frac{1 \text{ mol rxn}}{1 \text{ mol Mg}} \right)} = -4.508 \times 10^5 \text{ J/mol rxn}$$

$$= -451 \text{ kJ/mol rxn}$$

- The thermochemical equation is $\text{Mg} + 2 \text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$; $\Delta H = -451 \text{ kJ}$

Answer

- Hess's Law is a direct consequence of the fact that enthalpies are state functions.
- Hess's Law states that it is possible to determine the enthalpy change of a reaction by adding the enthalpy changes of a series of reactions that add to give the overall reaction.

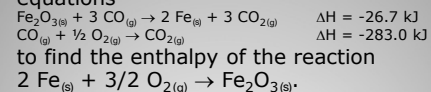
Rxn 1	ΔH_1
Rxn 2	ΔH_2
Rxn 3	ΔH_3

Rxn	ΔH_4
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$$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$$

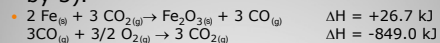
Hess's Law of Summation

- Use the following thermochemical equations



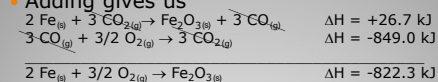
Example

- We can see that we need to reverse the first equation (and change the sign on the enthalpy) and multiply the second equation by 3 (and multiply the enthalpy by 3).



Answer

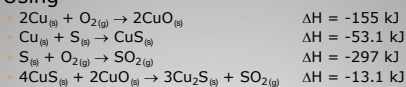
- Adding gives us



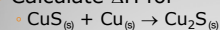
- The enthalpy of the reaction is -822.3 kJ.

Answer

- Using

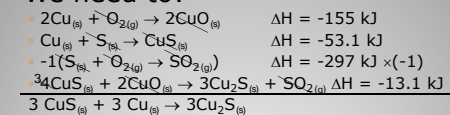


- Calculate ΔH for



Problem

- We need to:



- Divide by 3

- $\text{CuS}_{(s)} + \text{Cu}_{(s)} \rightarrow \text{Cu}_2\text{S}_{(s)}$ What we are looking for
- Now we add the enthalpies the same way.

Answers

$$\begin{aligned} \Delta H_{rxn} &= (-155 \text{ kJ}) + (-53.1 \text{ kJ}) - (-297 \text{ kJ}) + (-13.1 \text{ kJ}) \\ &= 75.8 \text{ kJ} = 76 \text{ kJ} \end{aligned}$$

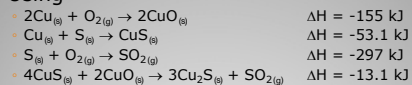
$$\Delta H_{rxn} = \frac{76 \text{ kJ}}{3} = 25 \text{ kJ}$$

Answers

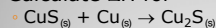
- This method is related to the mathematical way of balancing equations
- First assign a generic multiplier to each equation (a, b, c, etc.).
- Set up mathematical equations for each compound in the system.
- This should be fully specified so no need to pick a solution.

Alternative method

- Using

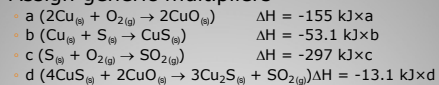


- Calculate ΔH for

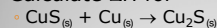


Alternative method

- Assign generic multipliers

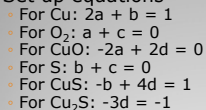


- Calculate ΔH for

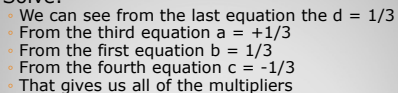


Alternative method

- Set up equations



- Solve:



Alternative method

- Now we plug in the numbers

$$\Delta H = (-155 \text{ kJ}) \times a + (-53.1 \text{ kJ}) \times b + (-297 \text{ kJ}) \times c + (-13.1 \text{ kJ}) \times d$$

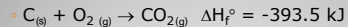
$$= (-155 \text{ kJ}) \times \left(\frac{1}{3}\right) + (-53.1 \text{ kJ}) \times \left(\frac{1}{3}\right) + (-297 \text{ kJ}) \times \left(-\frac{1}{3}\right) + (-13.1 \text{ kJ}) \times \left(\frac{1}{3}\right)$$

$$= 25.2666666 \text{ kJ} = 25 \text{ kJ}$$

- This is the same as we got before.

Alternative method

- The **standard enthalpy of formation** is the enthalpy change that accompanies the formation of **1 mole** of a substance from its elements in their standard states.



- Standard enthalpies of formation can be used to calculate the enthalpy change of reactions and are tabulated in your book.

Standard Enthalpies of Formation (ΔH_f°)

- We can think about a reaction in terms of the formation reactions and Hess's Law.

- When we do this we get the following result: $\Delta H_{\text{rxn}} = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$

- The "n"s in this equation are the stoichiometric coefficients from the chemical equation.

Heats of reaction from ΔH_f° 's

- Calculate ΔH for
- $2 \text{H}_2\text{O}_2(l) \rightarrow 2 \text{H}_2\text{O}(l) + \text{O}_2(g)$

Example

- Find enthalpies from table:

Substance	ΔH_f°
H_2O_2	-187.8 kJ
H_2O	-285.8 kJ
O_2	0.00 kJ

Answer - $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$

- Calculate ΔH_{rxn}

$$\Delta H_{\text{rxn}} = \left[\left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol rxn}} \right) \left(\frac{-285.8 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \right) + \left(\frac{1 \text{ mol O}_2}{1 \text{ mol rxn}} \right) \left(\frac{0.00 \text{ kJ}}{1 \text{ mol O}_2} \right) \right] - \left[\left(\frac{2 \text{ mol H}_2\text{O}_2}{1 \text{ mol rxn}} \right) \left(\frac{-187.8 \text{ kJ}}{1 \text{ mol H}_2\text{O}_2} \right) \right]$$

$$= -196.0 \frac{\text{kJ}}{\text{mol rxn}}$$

Answer - $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$