

### Introduction

**Thermochemistry:** the study of the **energy changes** that accompany physical or chemical changes in matter

#### Types of energy:

**$E_p$**  (potential energy) the energy of an object due to its **position/composition**

**$E_k$**  (kinetic energy) the energy of an object due to its **motion**

**Thermal energy ( $E_{th}$ ):** the **total quantity of  $E_k$  and  $E_p$**  in a substance; depends on how fast the particles are moving: more energy = more speed = more  $E_{th}$

**Heat:** the transfer of  $E_{th}$  **from a warm object to a cool object**

**Temperature:** measure of the **average  $E_k$**  of the particles in a substance

**Law of Conservation of Energy:** energy **cannot be created or destroyed**, only converted from one form to another

**Note:** Temperature  $\neq E_{th}$ ! A cup of water at 90°C has a higher temperature than a bathtub of water at 40°C, but the water has more  $E_{th}$  since it has more molecules

### System/Surroundings and Reactions

**System:** the group of **reactants and products** being studied

**Surroundings:** all the matter that is **not** a part of the system

#### Types of systems:

### System/Surroundings and Reactions (cont)

**Open system** both energy and matter are allowed to enter and leave freely

**Closed system** energy can enter and leave the system, but matter cannot

**Isolated system** neither matter are allowed to leave the system (complete isolation is **impossible**)

#### Types of reactions:

**Endothermic** energy from the surroundings is **absorbed** by the system

**Exothermic** energy from the system is **released** into the surroundings

### Specific Heat Capacity and Calorimetry

**Specific heat capacity:** the amount of energy required to **raise the temperature** of 1 g of a substance **by 1°C** (measured in  $J/g^\circ C$ ); depends on **type** and **form** of substance

**Calorimetry:** the experimental process of measuring the  **$\Delta E_{th}$**  in a **chemical or physical** change

**Calorimeter:** device used to **measure  $\Delta E_{th}$**

#### Types of calorimeters:

**Polystyrene (styrofoam)** Reasonably accurate and inexpensive

**Bomb** More precise, used for reactions that involve gases

**Flame** Used for combustion reactions

### Calorimetry Calculations

#### 4 assumptions when performing calorimetry calculations:

1. Any thermal energy transferred from the calorimeter to the outside environment is negligible

3. All dilute, aqueous solutions have the same density as water ( $D = 1.00 \text{ g/mL}$ )

2. Any thermal energy absorbed by the calorimeter itself is negligible

4. All dilute, aqueous solutions have the same specific heat capacity as water ( $c = 4.18 \text{ J/g}^\circ C$ )

#### Calorimetry formula:

$$Q = mc\Delta T$$

**m** = mass of the substance (g)

**c** = specific heat capacity of the substance ( $J/g^\circ C$ )

**$\Delta T$**  = temperature change experienced by the system;  $\Delta T = T_{final} - T_{initial}$  ( $^\circ C$ )

**Q** = total amount of  $E_{th}$  absorbed/released by a chemical system (J)

Value of **Q** has two parts:

The **number**: how much energy is involved  
The **sign**: the direction of the energy transfer (important to show, **even if it is positive!**)

Because of the law of conservation of energy, the total thermal energy of the system and the surroundings remain constant:

$$Q_{system} + Q_{surroundings} = 0$$

$$Q_{system} = -Q_{surroundings}$$



By **NescafeAbusive32**  
(nescafeabusive32)

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### Enthalpy Change ( $\Delta H$ )

*Enthalpy* (H): the total amount of  $E_{th}$  in a system; **not directly measurable**

Must measure **enthalpy change ( $\Delta H$ )** by measuring the  $\Delta T$  in the **surroundings**

*Enthalpy change* ( $\Delta H$ ): the energy **released to/absorbed from the surroundings** during a chemical/physical change; can be measured **using calorimetry data**

As long as pressure is constant, the enthalpy change of a chemical system is equal to the **flow of thermal energy in or out of the system**

Enthalpy change formula:

$$\Delta H = |Q_{system}|$$

$$\Delta H = \pm |Q_{surroundings}|$$

If  $\Delta H > 0$ , the reaction is **endothermic**      If  $\Delta H < 0$ , the reaction is **exothermic**

If there is **more than one substance** making up the surroundings (i.e. **bomb/flame calorimeters**), then

$$Q_{surroundings} = \sum Q_{substances}$$

### Molar Enthalpy Change ( $\Delta H_x$ )

*Molar enthalpy change* ( $\Delta H_x$ ): the enthalpy change **associated with** a physical/chemical change involving **1 mol of a substance** (J/mol)

$x$  = **type of change** (vaporization, neutralization, combustion, etc.)

Molar enthalpy change formula:

$$\Delta H = n\Delta H_x$$

### Representing Enthalpy Change

4 ways to represent  $\Delta H$ :

1. Thermochemical equations with <b>energy terms</b>	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O + 890.8 \text{ kJ}$
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### Representing Enthalpy Change (cont)

2. Thermochemical equations with <b><math>\Delta H</math> terms</b>	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O \quad \Delta H = -890.8 \text{ kJ}$
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3. Molar enthalpies ( <b><math>\Delta H_x</math></b> )	$\Delta H_{comb} = -890.8 \text{ kJ/mol}$
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4. Potential energy ( <b><math>E_p</math></b> ) diagrams	See an example here
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### Hess' Law

Enthalpy change ( $\Delta H$ ) is determined by **initial and final conditions** of a system; it is **independent** of the pathway

The total  $\Delta H$  of a multi-step reaction is the **sum of the  $\Delta H$  of its individual steps**

Hess's Law formula:

$$\Delta H_{reaction} = \sum \Delta H_{steps}$$

This formula can be used in cases where the **overall reaction is not feasible to be done in a calorimeter** (i.e. reaction is too slow/too fast/too violent)

Rules:

1. If a reaction is **flipped**, flip the  $\Delta H$  value's sign
2. If a reaction is **multiplied**, multiply the  $\Delta H$  value

### Standard Enthalpy of Formation ( $\Delta H^{\circ}f$ )

The standardized  $\Delta H$  when **1 mol** of a substance is formed (**synthesized**) directly from its elements to its **standard state at SATP**

The elements themselves have a  $\Delta H^{\circ}f$  of **0** (elements **cannot be synthesized**)

### Bond Energies (D) and Bond Enthalpy

#### Bond Energies

Stability of a molecule is related to the **strength of its covalent bonds**

The **strength** is determined by the **energy required to break that bond**

#### Bond Enthalpy:

$\Delta H$  for breaking a particular bond in **1 mol of a gaseous substance**

**Always positive** because energy is always required to break bonds

Used for **predicting reaction types** before the reaction is performed (**not entirely accurate**)

Formula for predicting reaction type using D and bond H:

$$\Delta H = \sum (nD_{bonds \text{ broken}}) - \sum (nD_{bonds \text{ formed}})$$

### Reaction Rates

The **speed** at which a reaction **occurs**

Can be **fast** ( $10^{-15}s$ ) or **slow** (years)

Measured by the **change** in the amount of **reactants consumed** or **products formed** at a given time interval(s)

Can be measured by **volume, mass, colour, pH, and electrical conductivity**

Often expressed as a **positive value** for convenience, regardless of what is being measured

**Average rate of reaction:** rate of a chemical reaction **between two points in time** (one time interval); calculated from the **slope of the secant** of the time interval on a **concentration-time graph**

Average rate of reaction formulas:

How fast a **reactant disappears**  $-\frac{\Delta[A]}{\Delta t}$



By **NescafeAbusive32**  
(nescafeabusive32)

[cheatography.com/nescafeabusive32/](https://cheatography.com/nescafeabusive32/)

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### Reaction Rates (cont)

How fast a **product appears**  $\Delta[B]/\Delta t$   
 $\Delta[A], \Delta[B], \Delta t = [A]_2 - [A]_1, [B]_2 - [B]_1, t_2 - t_1$

Units mol/L.s

**Instantaneous rate of reaction:** rate of a chemical reaction at a **single point in time**; calculated from the **slope of the tangent** of the time position on a **concentration-time graph**

### Collision Theory

States that chemical reactions can only occur if the reactants have the right **kinetic energy (speed)** and **orientation** to break reactant bonds and form product bonds

*Effective collision:* a collision that has **sufficient energy** and **correct orientation** of colliding particles to **start a reaction**

*Ineffective collision:* a collision where the particles rebound, **unchanged in nature**

**Activation energy** ( $E_a$ ): the **minimum energy required** for reactants to have for a collision to be effective

*Activated complex/transition state:* **unstable arrangement of atoms** containing **partially formed** and **partially broken bonds**; **maximum  $E_p$  point** in the reaction

Rate of a reaction depends on the **frequency of collisions** and the **fraction of those collisions** that are **effective**.

Rate = **frequency** of collisions x **fraction of collisions** that are **effective**

### Increasing Reaction Rates

5 factors that can increase a reaction rate: **chemical nature** of reactants, **concentration**, **surface area**, **temperature**, and **catalysts**

#### Chemical nature of reactants

For any reactant, the activation energy required depends on the **bond type** (single vs double vs triple), the **bond strength** ( $D$  value), the **number of bonds**, and the **size and shape** of the molecule(s)

#### Concentration of reactants

*Concentration* = amount of substance per unit volume (mol/L); applies only to **solutions**

$\uparrow$  [reactant] =  $\uparrow$  collisions =  $\uparrow$  rate

**Rate  $\propto$  [reactant]** - as the **concentration increases**, the **rate increases**, and vice versa

#### Surface area

*Surface area* = total area of all the surfaces of a **solid** figure

$\uparrow$  SA =  $\uparrow$  collisions =  $\uparrow$  rate

**Rate  $\propto$  SA** - as the **surface area increases**, the **rate increases**, and vice versa

#### Temperature of system

$\uparrow$  T =  $\uparrow$  collisions +  $\uparrow$  fraction of effective collisions =  $\uparrow$  rate

**Rate  $\propto$  T** - as the **temperature increases**, the **rate increases**, and vice versa

#### Catalyst

*Catalyst* = substance that **increases the rate** of a reaction **without itself being consumed** in the reaction; provide an **alternate pathway** for the reaction with a **lower  $E_a$**

### Increasing Reaction Rates (cont)

$\downarrow$   $E_a$  =  $\uparrow$  fraction of effective collisions =  $\uparrow$  rate

**Rate  $\propto 1/E_a$**  - as the **catalyzed activation energy decreases**, the **rate increases**, and vice versa

### Rate Law

**Mathematical relationship** between the **reaction rate** and the **concentration** of reactants; needs **experimental data**

**Formula:** Rate =  $k[A]^a[B]^b[C]^c$

$[A]/[B]/[C]$  = concentration of **reactants** (only **reactants** are relevant);  $k$  = rate constant

### Orders of Reaction

*Order of reaction:* the exponent used to describe the relationship between the **[i] of a reactant** and the **rate of reaction**; tells us **how quickly the rate will increase** when [conc] increases

Zero order Rate =  $k[A]^0$ ; slope is **flat**; rate is not affected by [A]

First order Rate =  $k[A]^1$ ; slope is an **increasing straight** line; rate  $\propto$  [A]

Second order Rate =  $k[A]^2$ ; slope is an **increasing curve**; rate  $\propto$  [A]<sup>2</sup>

*Total order of reaction* = the **sum** of the exponents in the rate law equation

The only accurate data for concentration and rate is the **initial rate**, because as soon as the reaction starts, products are formed and the **reverse reaction starts**, making any rate measured after  $t = 0$  affected by the products.



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### Reaction Mechanisms

Chemical reactions usually occur as a **sequence of elementary steps** that, when added, result in the **overall reaction**

Mechanism is dependent on the slowest elementary step - the **rate-determining step**

*Elementary step* = a single molecular event in the reaction mechanism

**3 criteria for a proposed reaction mechanism:**

The elementary steps must **add up to the overall reaction**

The elementary steps must **be physically reasonable** - there should not be more than 2 reactants

The rate-determining step must **be consistent with the rate law equation**



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