Gr. 12 Energy Changes and Rates of Reaction Cheat Sheet

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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 ≠ 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°C); depends on **type** and **form** of substance

Calorimetry: the experimental process of measuring the **ΔE_{th}** in a **chemical or physical** change

Calorimeter: device used to **measure ΔE_{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
2. Any thermal energy absorbed by the calorimeter itself is negligible
3. All dilute, aqueous solutions have the same density as water (D = 1.00 g/mL)
4. All dilute, aqueous solutions have the same specific heat capacity as water (c = 4.18 J/g°C)

Calorimetry formula:

$$Q = mc\Delta T$$

m = mass of the substance (g)

c = specific heat capacity of the substance (J/g°C)

ΔT = temperature change experienced by the system; $\Delta T = T_{final} - T_{initial}$ (°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:

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

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Enthalpy Change (ΔH)

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

Must measure **enthalpy change (ΔH)** by measuring the **ΔT** in the **surroundings**

Enthalpy change (ΔH): 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 ΔH > 0, the reaction is **endothermic**	If ΔH < 0, the reaction is **exothermic**

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

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

Molar Enthalpy Change (ΔHx)

Molar enthalpy change (ΔH_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 ΔH:

1. Thermochemical equations with **energy terms**	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O +$ **890.8 kJ**

Representing Enthalpy Change (cont)

2. Thermochemical equations with **ΔH terms**	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ **ΔH = -890.8 kJ**
3. Molar enthalpies **(ΔH_x)**	ΔH_{comb} = -890.8 kJ/mol
4. Potential energy **(E_p)** diagrams	See an example here

Hess' Law

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

The total ΔH of a multi-step reaction is the **sum of the ΔH** of its **individual steps**

Hess's Law formula:

$$\Delta H_{reaction} = \Sigma\,\Delta H_{steps}$$

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 ΔH value's sign

2. If a reaction is **multiplied**, multiply the ΔH value

Standard Enthalpy of Formation (ΔH°f)

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

The elements themselves have a $\Delta H°_f$ 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:

ΔH 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:

$$\Delta H = \Sigma\,(nD_{bonds\ broken}) - \Sigma\,(nD_{bonds\ formed})$$

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**	$-\Delta[A]/\Delta t$

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 int 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**

↑ [reactant] = ↑ collisions = ↑ rate

Rate α [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

↑ SA = ↑ collisions = ↑ rate

Rate α SA - as the **surface area increases**, the **rate increases**, and vice versa

Temperature of system

↑ T = ↑ collisions + ↑ fraction of effective collisions = ↑ rate

Rate α 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)

↓ E_a = ↑ fraction of effective collisions = ↑ rate

Rate α $^1/E_a$ - 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 α [A]
Second order	Rate = $k[A]^2$; slope is an **increasing curve**; rate α $[A]^2$

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.

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**