

	SCH 4U1 UNIT 3: ENERGY AND RATES OF CHEMICA	AL REACTIONS
DAY(S)	TOPIC/EXPECTATION	HOMEWORK
1	TOPIC 1 : Introduction to Thermochemistry, Energy in a Molecule	Read 5.1 p.291 # 1,2,4,5,8
1	TOPIC 2: Calorimetry – define (nested cup, bomb); calculations $q=mc\Delta T$; $qsys= - qsurr$, specific heat capacity; molar enthalpy; assumptions made in calorimetry cal'ns (p. 309) Heat transfer and enthalpy changes.	Read 5.2 p. 297 # 1 -3 p. 301 # 1 - 4 <u>Extra Practice Worksheet</u> <u>Enthalpy (Calorimetry)</u> <u>Problems</u> <u>Worksheet+Answers.docx</u>
2	 TOPIC 3: Compare heat produced through physical, chemical and nuclear reactions TOPIC 4: Representing Enthalpy Changes (thermochemical. Eq'ns) - 4 different methods 	<mark>p. 304 #1- 4</mark>
2	TOPIC 5 : Bond Dissociation TOPIC 6 : Hess's Law + standard heat of formation	Read 5.3 p. 312 # 1- 4 p. 313 # 1b, 2b, 4, 7-9, 12-13 Read 5.4 and 5.5 p. 317 # 1-3; p 318 # 1-8 p. 323 # 1-2, p. 324 # 1-10
3	Present and future Energy Sources-5.6 (summarize) TOPIC 7: Rates of Reactions - definition; graphing Measuring rates of reactions	Read 5.6 & 6.1 p. 330 1-7 p. 350 # 1; p. 352 # 1 p. 356 # 1-2; p. 360 # 1-2
3	TOPIC 8: Factors Affecting Reaction Rates	Read 6.2 p. 365 # 3,4 <u>Extra Practice Worksheets</u> <u>Factors Affecting Reaction</u> <u>Rates Worksheets</u>
3	TOPIC 9: Rate Law and determining the order of a reaction	Read 6.5 p. 380 # 1-5 p. 382 # 1-4
4	TOPIC 10: Collision Theory and Rate of Reaction: activation energy, potential energy graphs	Read 6.3 p. 372 #1- 2 <u>Extra Practice Worksheets</u> Potential Energy Graphs with AC <u>Potential Energy Graphs with AC</u> <u>Key</u>

UNIT 3: ENERGY & RATES IN CHEMICAL REACTIONS

4	TOPIC 11 & 12: Explaining factors affecting rate of reaction using the collision theory; reaction mechanisms	Read 6.6p. 386 # 1 -3; p 387 #1-9Extra Practice WorksheetsReaction MechanismsPractice Worksheets.pdfReaction MechanismsWorksheets Answer Key.pdf
5	Review/TEST	p. 407 #30, 33, 34,37,38,40,43-56,79, 80,88

356 This is like an He holds everything endothermic in and gets reaction. hotter. You little This is like an He releases all @\$!?* his heat on exothermic ~010+/1 his reaction. surroundings.

TOPIC 1: INTRODUCTION TO THERMOCHEMISTRY

Thermochemistry is the study of **ENERGY CHANGES** that accompany **PHYSICAL** or **CHEMICAL** changes of matter. There are always 2 environments affected in an energy change:

- 1. The chemical system (*chemical reaction*)
- 2. The surroundings (all the matter that is not part of the chemical system)

Three different types of systems exist. A system is *the chemical system* and *its surroundings*. **Open system** - a system which allows both matter and energy to leave **Closed system** - a system which prevents the movement of matter. e.g. calorimeter **solated system** - a system where careful measurements of mass and temperature changes are made.

DEFINITIONS

- 1. Energy: the ability to do work, measured in kJ where 1 kJ = 1000 J and 4.184 J = 1 cal
- 2. Kinetic Energy E_K the energy of motion, mathematically $E_{K} = \frac{1}{2} \text{ mv}^{2}$
- Potential Energy E_P energy of position or stored energy E_P = mgh; this energy increases if two objects which attract each other are pulled apart or if two objects which repel each other are pushed together)
- 4. **Chemical Energy** the **potential energy in chemical bonds**, aka as chemical potential energy
- 5. **Thermal Properties** physical properties of a substance that enable it to absorb heat without **chemically changing** e.g. heat capacity, specific heat capacity, molar heat capacity
- Specific Heat Capacity (c) the amount of energy needed to raise the temperature of 1 g or 1 kg of a substance by 1°C - measured in J/g °C or in kJ/kg °C.

(Note: cwater= 4.184 J/g·°C or 4.184 kJ/kg·°C) Memorize this!

- 7. **Molar heat capacity (H)** energy needed to raise the temperature of **one mole** of any substance by **1° C**; unit is J/mol°C or kJ/mol°C
- Heat Capacity (C) the amount of energy needed or released to change the temperature of a substance by 1°C; unit is J/°C or kJ/°C
- Law of Conservation of Energy energy can neither be created nor destroyed but can be converted from one for to another - i.e. all the energy in the universe is constant (First Law of Thermodynamics)

- 10. **Heat-** (**q or Q**) -the **transfer of thermal energy** from a warm object to a cooler object. Measured in J or kJ.
- 11. **Temperature (T)**-a measure of the **average kinetic energy** of entities in a substance.
- 12. **Exothermic releasing energy to the surroundings**. Energy term is on *product* side of reaction.
- 13. Endothermic-absorbing energy from the surroundings. Energy term would be on the reactant side of reaction.

ENERGY IN A MOLECULE

- (I) **Kinetic Energy** 3 types: translational, rotational and vibrational
 - a) **translational:** energy associated with the movement of the entire molecule through space (in gases)
 - b) **rotational:** energy associated with the rotation of the molecule about an axis through its centre produces an end over end motion
 - c) **Vibrational:** energy associated with movement of the atoms towards and away from each other atoms bonded together are pulled towards each other by attractive forces (nucleus attracting electrons) until the repulsive forces between the two nuclei causes them to spring away from each other



(II) **Potential Energy** -energy related to the attractive forces acting **between** molecules (eg hydrogen bonding etc.) - these forces are largest in solids, large between liquid molecules and small between gas molecules. **Responsible for physical changes i**.e. change of states



- in calculations with calorimeters three assumptions are made: 1. no heat is transferred between the calorimeter and the outside environment; 2. any heat absorbed or released by the calorimeter materials, such as the container is negligible; unless otherwise stated 3. and a dilute aqueous solution is assumed to have a density (1.0g/mL or 1.0 kg/L) and specific heat capacity equal to that of pure water $(4.184 J/g) \circ C$ or $4.184 kJ/kg \circ C$ - the quantity of heat transferred when using a calorimeter can be calculated using: $\mathbf{q} = \mathbf{C} \Delta \mathbf{t}$ calorimeter **q=mc∆t** н20 or $q = (C\Delta t)_{calorimeter} + (mc\Delta t)_{H2O}$ or Note: Law of Conservation of Energy; all the energy in the universe is constant **q** system(chemical reaction/substance under analysis) = -**q** surrounding (calorimeter+ water etc.) (III) CALCULATING QUANTITIES OF HEAT (Thermal Energy) Heat is represented by the symbol, **q or Q.** It is **positive** (a reactant) when it is **endothermic** (heat absorbed), and negative (a product) when it exothermic (heat released). E.g. Burning of ethane Exothermic b/c heat produced/released $2 C_2 H_6 + 7O_2 \rightarrow 4 CO_2 + 6 H_2O + energy$ Burning ethane produces heat/energy therefore the system is **exothermic**. That means the surroundings absorbed the amount of heat given off. *Practice: Simple Heat Calculations (q)* E.g. 1. How much *heat* flows into water when 600 mL of water is heated from 20°C to 85°C? q=? q=mc∆t $= (600 \text{ q}) (4.184 \text{ J/q}^{\circ}\text{C}) (65^{\circ}\text{C})$ = 1.6 x 10⁵ J or 1.6 x 10² kJ $\Delta t = 85^{\circ}C - 20^{\circ}C = 65^{\circ}C$ V= 600 mL \rightarrow m= 600g (D=m/v) c=4.18 J/g°C



(III) CHANGE OF ENTHALPY, ΔH°

- all of the energy contained in a molecule is the enthalpy of the substance, but we cannot determine the sum of all these energies

- instead, the **change in enthalpy** can be determined from the energy changes in the surroundings (i.e. the law of conservation of energy is used - the value of enthalpy of the system equals the value transferred to the surroundings)

(chemical potential energy of the chemicals) = - (quantity of heat absorbed/lost by surroundings)



the change in enthalpy when ONE MOLE of the substance is reacted; symbol is ΔH°_{x} where x indicates the **type of reaction (units kJ/mol)**

- eg.

Type of Molar Enthalpy	Example of Change
Solution ΔH^{o}_{sol}	$NaBr(s) \rightarrow Na^+ (aq) + Br^-(aq)$
Combustion ΔH^{o}_{comb}	$CH_4 (g) + 2 O_2 (g) \rightarrow CO_2 (g) + H_2O(I)$
Vaporization ΔH^{o}_{vap}	$CH_3OH (I) \rightarrow CH_3OH (g)$
Freezing ΔH^{o}_{fr}	$H_2O(I) \rightarrow H_2O(s)$
Neutralization ΔH^{o}_{neut}	2 NaOH (aq) + H ₂ SO ₄ (aq) \rightarrow Na ₂ SO ₄ (aq) + 2 H ₂ O (I)
Formation ΔH^{o}_{f}	$C(s) + 2 H_2(g) + \frac{1}{2} O_2(g) \rightarrow CH_3OH (I)$





e.g. 4

In an experiment, 12.5 g of naphthalene, C₁₀H₁₀, were burnt. The **calorimeter jacket** had a heat **capacity of 21.8 kJ/°C**. **2.50 L of water** was placed in the calorimeter. The temperature **rose** from **23.5°C** to **30.6 °C**. Determine the **molar enthalpy of combustion for naphthalene**.

 $\Delta H^{\circ}_{comb}=?$

 ΔH°_{sys} = - q surroundings

m_{H2O} = 2.50 kg c_{H2O}= 4.184 kJ/kg°C Δt= 30.6°C-23.5°C = 7.1°C C_{cal jacket} = 21.8 kJ/ °C

Surroundings (H₂O+Cal Jacket)

System (naphthalene C₁₀H₁₀) mn=12.5 g Mn= 130.20 g/mol $\frac{n_n\Delta H^\circ_{comb} = -[(mc\Delta t)_{H2O} + C\Delta t_{cal jacket}]}{\Delta H^\circ_{comb} = -[(mc\Delta t)_{H2O} + C\Delta t_{cal jacket}]} n_n$

 $=-[(2.50 \text{ kg})(4.184 \text{ kJ/kg}^{\circ}\text{C})(7.1^{\circ}\text{C}) + (21.8 \text{ kJ/}^{\circ}\text{C})(7.1^{\circ}\text{C})] \\ \frac{12.5 \text{ g}}{130.20 \text{ g/mol}} \\ \Delta \text{H}^{\circ}_{\text{comb}} = -2.39 \text{ x } 10^3 \text{ kJ/mol}$

e.g. 5

A 9.80 g sample of carbon was burned in a bomb calorimeter containing **3.00 L** of water at **24.0°C** in its jacket. If the heat of combustion of carbon is **-394.0 kJ/mol**, determine the **final temperature** of the water.

Tf=? Tip: Solve for ΔT first	step1 n _C ΔH° _{comb} = -(mc Δt) _{H2O}
Surroundings (H ₂ O)	$\Delta t = -\underline{n_c \Delta H^{\circ}_{comb}}{mc}$
m _{H2O} = 3.00 kg c _{H2O} = 4.184 kJ/kg°C Ti= 24.0 °C	$\Delta t = \frac{-(9.80 \text{ g})(-394.0 \text{ kJ/mol})}{(12.01 \text{ g/mol})(3.00 \text{ kg})(4.184 \text{ kJ/kg}^{\circ}C)}$
System (carbon) mc=9.80 g M _C = 12.01g/mol	$\Delta t = 25.6 \underline{1} \ ^{\circ}C$ step 2 $\Delta t = t_{\text{final}} - t_{\text{initial}}$ $t_{\text{final}} = \Delta t + t_{\text{initial}}$ $t_{\text{final}} = 25.61 \ ^{\circ}C + 24.0 \ ^{\circ}C = 49.6 \ ^{\circ}C$

TOPIC 3: PHYSICAL, CHEMICAL & NUCLEAR CHANGES

all have heats of reaction or enthalpy changes, but the <u>magnitude of the change varies</u> greatly

TYPE OF CHANGE	WHAT IS CHANGED	ENERGY IS USED TO	MAGNITUDE OF ENTHALPY CHANGE (kJ/mol)
Physical Change	Change of state or dissolving	 -energy is used to overcome or allow intermolecular forces to act -fundamental particles remain unchanged at molecular level 	10 – 10 ²
Chemical Change	<i>New substances</i> with new chemical bonds are formed	-energy changes overcome the electronic structure and chemical bonds within the particles	10 ² – 10 ⁴
Nuclear Change	<i>New atoms</i> with different number of protons or neutrons are formed	-energy changes overcome the forces between protons and neutrons in nuclei	10 ¹⁰ – 10 ¹²

TOPIC 4: REPRESENTING ENTHALPY CHANGES



For endothermic reactions, enthalpy change is written on the ____REACTANT SIDE____

For exothermic reactions, enthalpy change is written on the <u>**PRODUCT SIDE**</u>



UNIT 3: ENERGY & RATES IN CHEMICAL REACTIONS







TOPIC 6 A: HESS'S LAW of ADDITIVITY OF REACTION ENTHALPIES

Hess's Law of Summation

- often calorimetry cannot be used to determine the enthalpy changes so for any reaction that can be written in steps the ΔH^{o}_{rxn} equals the <u>sum of the enthalpies in each step leading</u> to the overall reaction.

Enthalpy is a **state function**

- any property that does not depend upon its history is a state function
- **enthalpy depends** only upon the **initial and final state** of the reactants and products and **NOT on the specific pathway** taken to get from the reactants to the products
- whether on can arrive at the products via either a single step or multi-step mechanism is unimportant as far as the enthalpy of reaction is concerned they should be equal

<u>**HESS'S LAW</u>** – the value of the Δ H for any reaction that can be written in steps (the target) equals the sum of the values of the Δ H for each of the individual steps.</u>

$$\Delta H^{\circ}_{target} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

$$\Delta H_{target} = \Sigma \Delta H_{steps}$$

To use Hess's law:

- the steps **may be reversed** to give the overall reaction, if so the ΔH^{o}_{f} sign changes
- if there are more or less than one mole required than **a multiple may need to be used** (i.e. ΔH^{o}_{f} is multiplied to give correct number of mole)
- items that are on the **same side** of the equation are **added**
- items that are **on opposite sides** of the equation are **crossed out as long as they are in the same state.**

e.g. 1

Carbon monoxide is often used in metallurgy to remove oxygen from metal oxides to give the free metal. This is used to obtain Fe

TARGET EQUATION - Fe₂O₃ (s) + 3 CO (g) \rightarrow 2 Fe (s) + 3 CO₂ (g) $\Delta H^{o}rxn = ?$

Use the equations below to determine the ΔH^{o}_{rxn} for the target equation.

 $\Delta H^{o}_{rxn} = -282.9 \text{ kJ/mol} \times 3$ $CO(q) + \frac{1}{2}O_2(q) \rightarrow CO_2(q)$

2 Fe (s) + 3/2 O₂ (g) \rightarrow Fe₂O₃ (s) ΔH^{o}_{f} = -1118.4 kJ/mol x-1 (flip and change sign)

3 CO(g) + $3/2^{\circ}O_{2}^{\circ}(g) \rightarrow$ **3** CO₂ (g) $\Delta H^{\circ}_{rxn} = 3 \text{ mol}(-282.9 \text{ kJ/mol}) = -848.7 \text{ kJ}$

Fe₂O₃ (s) \rightarrow **2 Fe (s)** + 3/2 O₂ (g) $\Delta H^{o}_{f} = -1 \text{ mol}$ (-1118.4 kJ/mol) = +1118.4 kJ +

 Fe_2O_3 (s) + 3 CO (g) \rightarrow 2 Fe (s) + 3 CO₂ (g) $\Delta H^{o}_{rxn} = 269.7 kJ$

e.g. 2

Ethanol (C₂H₅OH) is made industrially by the reaction of water with ethylene, (C₂H₄). Calculate the ΔH^{o}_{rxn}

Determine the target (overall) reaction: $C_2H_4(g) + H_2O(U) \rightarrow C_2H_5OH(U) \Delta H^{\sigma}_{rxn} = ?$

Given:

 $C_2H_4(g) + 3 O_2(g) \rightarrow 2 H_2O(l) + 2 CO_2(g)$ $\Delta H^{\circ}_{rxn} = -1411.1 \text{ kJ}$ $C_2H_5OH(I) + 3 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(I)$ $\Delta H^{o}_{rxn} = -1367.1 \text{ kJ x - 1 (flip sign)}$ **C**₂**H**₄(**g**) + 3. O_2 (**g**) → 2 H₂O (**I**) + 2 CO₂ (**g**) Δ H^o_{rxn} = -1411.1 kJ

1

2 CO₂ (g) + 3 H₂O (I) → C₂H₅OH (I) + 3 O₂ (g)
$$\Delta H^{o}_{rxn} = +1367.1 \text{ kJ}$$

 $C_2H_4(g) + H_2O(I) \rightarrow C_2H_5OH(I) \Delta H^{\circ}_{rxn} = -44.0 \text{ kJ}$

TOPIC 6B: HESS'S LAW & SPECIFIC ENTHALPY OF FORMATION, ΔH^{o_f}

Hess's Law

Definition – the change in enthalpy when <u>one mole of a substance is formed from its elements in</u> their natural state. (Can be found in table). One mole of any element in its natural state has a $\Delta H^{o}_{f} = 0$ kJ/mol

e.g. $O_2(g) \Delta H^o_f = 0 \text{ kJ/mol} O_2(l) \Delta H^o_f \neq 0 \text{ kJ/mol}$

e.g. The standard enthalpy of formations are found on page 320 of text.

 $H_{2 (g)} + \frac{1}{2} O_{2 (g)} \rightarrow H_{2}O_{(v)} \quad \Delta H^{o}{}_{f} = -241.8 \text{ kJ/mol} \qquad H_{2 (g)} + \frac{1}{2} O_{2 (g)} \rightarrow H_{2}O_{(l)} \quad \Delta H^{o}{}_{f} = -285.8 \text{ kJ/mol}$

USING HESS'S LAW & ΔH^{o}_{f}

Hess's Law can be used with ΔH^{o}_{f} for any reaction.

$$aA + bB \rightarrow cC + dD$$

then:

$$\Delta H^{o}_{reaction} = \Sigma n \Delta H^{o}_{f(products)} - \Sigma n \Delta H^{o}_{f(reactants)}$$

e.g. 1

a) Acetone (C₃H₆O), is a common organic solvent, determine the heat of combustion using enthalpy of formation data when it undergoes *complete combustion*.

 $C_{3}H_{6}O(I) + 4 O_{2}(g) \rightarrow 3 CO_{2}(g) + 3 H_{2}O(I) \Delta H^{\circ}_{comb} = ?$

 $\Delta H^{o}_{reaction} = \Sigma n \Delta H^{o}_{f(products)} - \Sigma n \Delta H^{o}_{f(reactants)}$

=[$3 \text{ mol}\Delta H^{o}_{fC02} + 3 \text{ mol} \Delta H^{o}_{fH20}$] – [1 mol}\Delta H^{o}_{fC3H60} + 4 mol}\Delta H^{o}_{f02}]

=[3 mol(-393.5 kJ/mol) + 3 mol(-285.8 kJ/mol)] – [1 mol(-248.1 kJ/mol) + 4 mol(0 kJ/mol)] products reactants

= [-2037.9 kJ] – [-248.1 kJ]

 $\Delta H^{\circ}_{comb} = -1789.8 \text{ kJ}$ exothermic rxn

UNIT 3: ENERGY & RATES IN CHEMICAL REACTIONS



TOPIC 7: RATES OF CHEMICAL REACTIONS

Reaction Rates

Chemical kinetics – the study of how to make reaction speed up or slow down i.e. study of reaction rate

<u>Rate of Reaction</u> – the speed at which a reactant is consumed or a product is formed relative to time.

Measuring the Rate of a Reaction

as a reaction progresses the concentration of the *reactants decrease and products increase* this change in concentration is relative to time

rate = $-\underline{\Delta[R]}$ or $+\underline{\Delta[P]}$ Unit: mol/Ls Δt

reaction rate changes with time (time frame is required – s, min, h, a, etc.);

rate is normally determined with respect to the *disappearance of reactants* i.e. $r = rate = -\Delta[R]$ Δt

rate of reactants disappearing is negative; if the rate is determined using appearance of products, then the rate is positive

this rate can be expressed relative to the reactants disappearing, or products appearing – measured quantities can be pH (pH meter), ion formation (conductivity apparatus), colour change (spectrophotometer), gas formation (volume or pressure gauges), mass, etc.

Ex. 1

During the combustion of methane, CH₄, the concentration of methane was measured at various time intervals with the following results being obtained:

Time	[CH4]	$CH_4 (g) + 2 O_2(g) \rightarrow CO_2 (g) + 2 H_2O (I)$	
<u>(s)</u>	<u>(mol/L)</u>		
(10)	2.40	r = rate = - <u>Δ[CH₄]_</u> =- <u>(0.60 <mark>M</mark>-2.40 <mark>M)</mark></u>	() - ()
20	1.20	Δt (40-10)s	
30	0.80		$t_1 - t_1 S$
40	0.60	=0.060 mol/Ls	
\smile			

Determine the rate of loss of methane during this time period.









TOPIC 9: DETERMINING EXPONENTS OF THE RATE LAW EXPRESSION

Determining Rate Law /Reaction Order from Experimental Data Method 1 Method 2 Reaction Order Tips

Eg.1

3.

To determine the exponents in the rate law expression, a reaction must be performed in which various concentrations of reactants are used.

For example: to determine the rate law expression for the reaction A + B \rightarrow AB Experimental data might be: Find the rate law expression for this reaction given the data.

Trial	Initial [] [A]	(mol/L) [B]	Initial Rate of Formation of Products (mol/Ls)
1	<mark>0.1</mark>	0.1 🗖	0.20
2	<mark>0.2</mark>	0.1	0.40
3 const	_{ant} 🔽 0.3	<mark>0.1</mark>	0.60
4	0.3	0.2	2.40
5	0.3	0.3	5.40

1. Compare factor difference for [] and rate for one reactant.

For [A] pick trial 1 and 2 because [] it changes and the other reactant(s) stay constant.

[A] how the rate changes $\frac{1}{1} \frac{1}{2} = \frac{0.2 \text{ mol/L}}{1} = 2$ Trial 2 => 0.40 mol/Ls = 2 Trial 1 0.20 mol/Ls Trial 1 0.1 mol/L 2. Equate the 2 values calculated: 2^m =2 : m=1 Or $m \ln 2 = \ln 2$ m =ln2 = 1 ln2 Repeat for any other reactants how the rate changes [B] <u>Trial 4</u> => 0.2 mol/L = 2 <u>Trial 4</u> => 2.40 mol/Ls = 40.1 mol/L Trial 3 0.60 mol/Ls Trial 3 2ⁿ =4; n=2









At the higher temperature (T₂) there are more particles with Eょ≥ E₂ ,therefore more effective collisions.

(Regardless of T, the minimum E_{κ} needed for an effective collision E_a is the same.)

So far, the reactant molecules must:

1		2	E _k ≥ E _a	

The third factor is Collision Geometry (Steric Effect) A molecule possessing the Ea associated with a given reaction does not necessarily react when it undergoes a collision. $C_2H_4 + HCI -- \rightarrow$ Reaction occurs! lots of no attraction, no rxn Pure covalent bond Ъ No Reaction! Non-polar bond Extra repulsion No attraction for the H of the HCl, so no rxn eg. H₂O(I) + HCI (aq) ----> H₃O⁺(aq) + CI⁻(aq) A $\frac{5^{4}}{H} - \frac{5^{4}}{C_{1}} + \frac{5^{4}}{H} - \frac{5^{4}}{C_{1}} + \frac{5^{4}}{H} - \frac{5^{4}}{C_{1}} + \frac{5^{4}}{H} +$ In B, even though the molecules have energies greater than E_a, there is no reaction because: incorrect collision geometry.



Bonds are breaking at the same time as they are forming

When a collision occurs, the total Ek decreases (reactant molecules slow down, and stop at point of collision) and the total E_P increases, formation of new bonds. (Law of Conservation of Energy)





e.g.





A simple reaction consists of one elementary step, a complex reaction consists of a number of steps and each step involves one collision. Reaction mechanisms are theories as to how the product is produced from the reactants. These steps

cannot be observed. Different reaction mechanisms can be proposed but they must be based on scientific fact. Based on overall rate law expression.



Reaction Profile for a multistep reaction like: Exothermic Energy Diagram: Activation Energy, Transition States and Enthalpy Change

e.g. #1

 $4 \text{HBr} + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 2 \text{Br}_2$

The proposed reaction mechanism for the reaction:

 $HBr + O_2 \rightarrow HOOBr - bimolecular$

HOOBr + HBr \rightarrow 2 HOBr-bimolecular

 $HOBr + HBr \rightarrow H_2O + Br_2$ -bimolecular

 $HOBr + HBr \rightarrow H_2O + Br_2$ -bimolecular

HOOBr, HOBr are intermediates

$H_2 + 2 |C| \rightarrow I_2 + 2 |HC|$ e.g. # 2







Reaction Progress

proposed rxn mechanism:

 $H_2(g) + 2ICI(g) \rightarrow HCI(g) + HI(g)$ HCl (g) + HI (g) \rightarrow l₂(g) + 2HCl (g)

$$H_2 + 2 ICI \rightarrow I_2 + 2 HCI$$

Which step is the rate determining step?

Step 1 since it is the slowest step, has the largest E_a value.

Consider: 2NO + O₂ ----> 2NO₂

The proposed reaction mechanism is: $2 \text{ NO} + \text{O}_2 \rightarrow \text{N}_2\text{O}_4$ - trimolecular $N_2\text{O}_4 \rightarrow 2 \text{ NO}_2$ - unimolecular

N₂O₄ is the *intermediate*

- it is produced in the first step and used up in the second step

- it is very short lived

The rate determining step is the slowest step in the reaction mechanism!

PREDICTING THE RATE LAW

This can only be done for an elementary process. rate= k [R]^x, where x is the coefficient

E.g. 1. For the elementary process: NOCI + CI ----> NO + Cl₂

if [NOCI] doubles-rate doubles, since order is 1

if [CI] doubles-rate doubles, since order is 1

E.g. 2. For the elementary process: $2NO_2 - - - > O_2 + 2NO$; rate = k [NO₂]²

The exponents in the rate law for an elementary process are to the coefficients of the reactants in the chemical equations for that elementary process.

Since the **slowest step is the rate-determining step**, the <u>rate law for the overall reaction</u> is <u>directly</u> related to the <u>rate law of the rate-determining step</u>.

E.g. 3 Given the reaction 2 NO₂Cl -> 2 NO₂ + Cl₂, the proposed reaction mechanism is :

 $\begin{array}{ccc} NO_2CI \rightarrow NO_2 + CI & (slow) \\ NO_2CI + CI \rightarrow 2 NO_2 + CI_2 & (fast) \end{array}$

What would the rate law be? rate= k [NO₂CI]¹

What is the intermediate? CI

```
E.g. 4 Given the following proposed mechanism
               A + B \rightarrow C + D
               D+G \rightarrow E+F
               F \rightarrow H + G
                                           G
Determine the overall reaction: A + B \rightarrow C + E + H
What are the intermediates? D, F
Is there a catalyst? G
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Success Criteria Unit 3: Energy Changes and Rates of Reaction

I can	Yes	No	Notes/Text
Define the terms kinetic energy, potential energy, specific heat capacity, heat capacity, temperature, thermal energy and calorimetry			
List the assumptions made in calorimetry			
Compare energy changes that are involved in physical, chemical and nuclear reactions			
Calculate heat and energy changes in matter using calorimetry and $q=mc\Delta t$ or $q=C\Delta t$			
Calculate energy transfer in a system, enthalpy change $\Delta H_{system} = \pm q_{surroundings}$			
Calculate molar enthalpies = $n\Delta H_{rxn}$			
Calculate ΔH using bond dissociation energies			
Illustrate enthalpy changes using graphing, and balanced thermochemical equations including the difference between exo- and endo-thermic reactions			
Calculate enthalpy change using Hess's Law of additivity, $H_{target} = \Sigma \Delta H_{reactions}$			
Calculate enthalpy change using Hess's Law and standard enthalpies of formation and draw the resulting potential energy graph			
State and explain the factors that affect the rates of reactions – e.g. surface area, complexity of reactants, concentration etc.			
Explain using collision theory and Maxwell-Boltzmann graphs the effects of temperature and catalyst on a rate of reaction			
Define activation energy			
State the rate for either reactants or products in a chemical reaction given the rate of one entity			
Calculate the Rate Law Expression from experimental data including the rate law constant and its units			
Define reaction mechanism, elementary process/step and rate-determining step			
Determine the rate-determining step and state the reaction mechanism given a potential energy graph with the required information			

SCH 4U1 – UNIT 3: ENERGY & RATES OF CHEMICAL REACTIONS REVIEW

Test Breakdown: K - /25 I - /25 C - /10 A - /10

Definitions to know:

Energy	Temperature	Standard state	Potential energy	Heat
Kinetic energy	Enthalpy	Standard heat of formation	Endothermic	Rate
Exothermic	Bond energy	Elementary step	Unimolecular	Bimolecular
Trimolecular	Activation Energy	Specific heat capacity	Reaction mechanism	Intermediate
Activated	Collision theory	Rate determining step		
complex	-			

- 1. A sample of water with a mass of 210.5 g undergoes a temperature change from 40.83 °C to 98.73 °C. What is the heat change in kilojoules?
- 2. When 1.75 g of CaCl₂ dissolves in 125 g of water in a nested cup calorimeter, the temperature increased by 2.44 °C. What is the heat change per mole of CaCl₂ dissolved? Assume that the water absorbs all the heat.
- 3. 5.50 g of sodium hydroxide is dissolved in 175 mL of water. Using a nested cup calorimeter, the temperature change of the water is measured to be 2.10 °C. Write the thermochemical equation for this process?
- 4. Use bond energies to estimate the heat of reaction, ΔH° , for: CH₄(g) + 2 Cl₂(g) \rightarrow CH₂Cl₂(g) + 2 HCl (g)
- 5. From the following enthalpies of reactions determine the ΔH^{0} for: 2 HCl (g) + F₂ (g) \rightarrow 2 HF (l) + Cl₂ (g)

4 HCl (g) + O ₂ (g) \rightarrow 2 H ₂ O (l) + 2 Cl ₂ (g)	$\Delta H^{o} = -148.4 \text{ kJ}$
$\frac{1}{2}$ H ₂ (g) + $\frac{1}{2}$ F ₂ (g) \rightarrow HF (l)	$\Delta H^{o} = -600.0 \text{ kJ}$
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	$\Delta H^{o} = -258.5 \text{ kJ}$

- 6. Given equations (1) and (2), calculate the enthalpy change for equation (3). (1) Pb (s) + PbO₂ (s) + 2 SO₃ (g) \rightarrow 2 PbSO₄ (s) $\Delta H^{\circ} = -775 \text{ kJ}$ (2) SO₃ (g) + H₂O (l) \rightarrow H₂SO₄ (aq) $\Delta H^{\circ} = -133 \text{ kJ}$ (3) Pb (s) + PbO₂ (s) + 2 H₂SO₄ (aq) \rightarrow 2 PbSO₄(s) + 2 H₂O (l) $\Delta H^{\circ} = ?$
- 7. Given: $H_2(g) + Br_2(l) \rightarrow 2 HBr(g) \quad \Delta H^\circ = -72.8 \text{ kJ}$ Calculate the amount of energy absorbed or released when 15.0 g of HBr(g) is formed.

- 8. The standard heat of combustion of ethanol is -1372 kJ/mol ethanol. How much heat is released when 20.0 g sample burns?
- 9. Given the following thermochemical equation: $2 P(s) + 3 Br_2(l) \rightarrow 2 PBr_3(s) \Delta H^\circ = 153 kJ$ How much energy must be added to allow the production of 7.12 g of PBr₃?
- 10. a) The ΔH^{o}_{f} of Mg(NO₃)₂ is -875.0 kJ/mol. Use this value and the heats of formation on page 799 to calculate the ΔH^{o} for the equation below:

 $2 \text{ HNO}_{3 (l)} + \text{Mg(OH)}_{2 (s)} \rightarrow \text{Mg(NO}_{3})_2 + 2 \text{ H}_2\text{O}_{(l)}$ b) Graph this reaction including the activation energy of 150 kJ. Label all axes, reactants, products, enthalpy and type of reaction (exo- or endo-thermic).

11. For the reaction: $H_2O_2(aq) + 2 H^+(aq) + 3 I^{-1} \rightarrow I_3^{-1}(aq) + 2 H_2O(l)$, the following rate data were measured. Determine the rate law, the constant and the rate for the last trial.

Trial	Initial [H ₂ O ₂]	Initial [I ⁻¹]	Initial rate of formation of I_3^{-1} (aq)
	(mol/L)	(mol/L)	(mol/Ls)
1	0.100	0.100	1.15 x 10 ⁻⁴
2	0.100	0.200	2.30 x 10 ⁻⁴
3	0.200	0.100	2.30 x 10 ⁻⁴
4	0.200	0.200	4.60 x 10 ⁻⁴
5	0.300	0.300	?

12. The rate law for the reaction $2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$ is $\text{rate} = \text{k} [\text{NO}]^2[\text{O}_2].$ At 25 °C, k = 7.1 x 10⁹ L² mol⁻²s⁻¹.

- a) What is the overall order for this reaction?
- b) Is the activation energy for this reaction high or low? Explain.
- c) If the temperature is increased, what will happen to the value of k?
- d) If the concentration of NO is doubled, what will happen to the reaction rate?
- e) If the concentrations of both NO and O_2 are doubled, how will the reaction rate change?
- f) Which will cause the rate to increase more: doubling [NO] or tripling [O₂]?
- g) What is the rate of reaction when [NO] = 0.0010 mol/L and $[O_2] = 0.034 \text{ mol/L}$?
- 13. For the reaction: $2 \text{ NO}(g) + H_2(g) \rightarrow N_2(g) + 2 H_2 O(l)$, the rate law is rate = k [NO]²[H₂]. Does the following proposed mechanism agree with this rate law? Explain your answer.

14. Using a Maxwell-Boltzmann curve, explain each of the following:

a) the effect of temperature on the rate of a reaction.

b) using a negative catalyst on the rate of a reaction.

UNIT 3: ENERGY & RATES IN CHEMICAL REACTIONS

- 15. List and explain the five factors that affect the rate of a reaction.
- 16. Using an enthalpy graph, describe the difference between an activated complex and a reaction intermediate.