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Year 12 Chemistry ATAR:

Equilibrium

Collision frequency, reaction rates

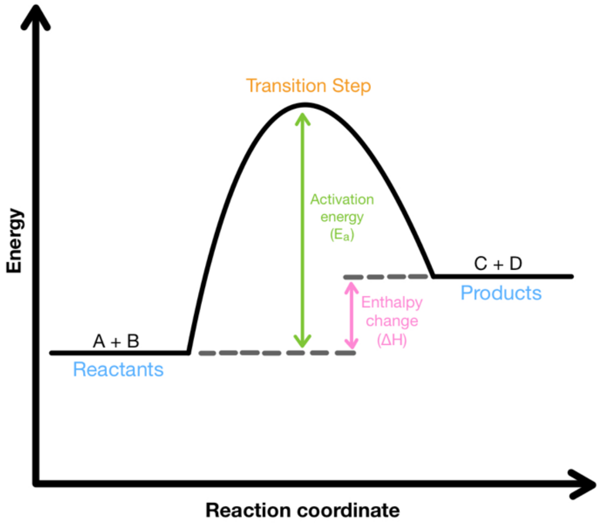
Intro to equilibrium

Name: ____________________

EQUILIBRIUM PRETEXT

YEAR 11 REACTION RATES / COLLISION THEORY REVIEW

Concept Terminology:



Transition State/Activated complex

Definition:

- State when reactants are forming products

Key points:

- Highest potential energy state for reacting system
- Highly Unstable
- Exists temporarily

Activation Energy

Definition:

- Minimum energy required for a collision between reacting particles to result in a reaction

Key points:

- Different values for forward and reverse reaction
- Smaller the activation energy the more spontaneous the reaction

Enthalpy

Definition:

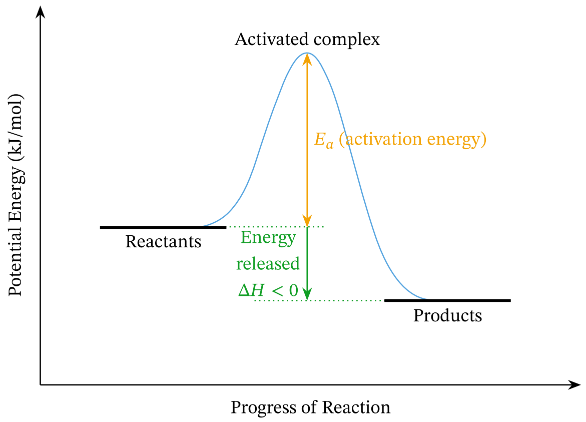
- Total amount of energy possessed by a substance: Both chemical potential and kinetic energy
- ΔH (change in enthalpy) = enthalpy of products – enthalpy of reactants
- Measured in kJ/mol

Energy Profile Diagrams

Exothermic Reactions

Definition:

- Type of reaction in which heat flows out to surroundings. E.g. combustion, acid + base reaction
- Resulting in chemical potential energy being converted to E_k in the system; increase in E_k of system results in an increase in temperature (Since temperature is $\propto$ avg. E_k)
- Since heat is lost to surroundings, final enthalpy is less than initial enthalpy, thus change in enthalpy is negative.
- ∴ $\Delta H<0$ kJ/mol



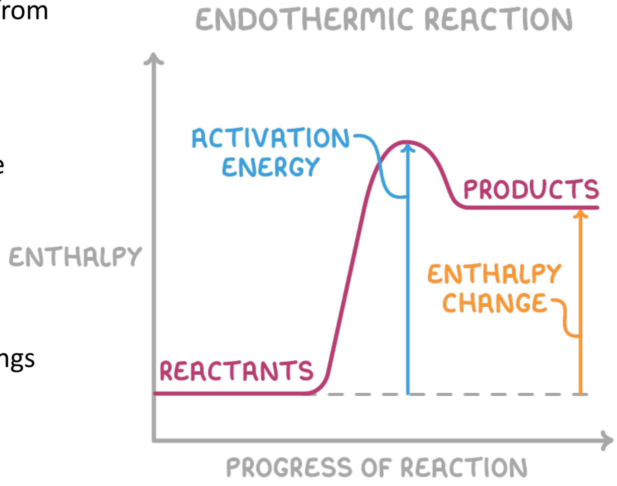
For FULL marks when drawing enthalpy diagram:

1) Label axes
2) List Reactants and Products on either end
3) Label E_a
4) Label ΔH
5) Ensure appropriate scale (dependant on question)

Endothermic Reactions:

Definition:

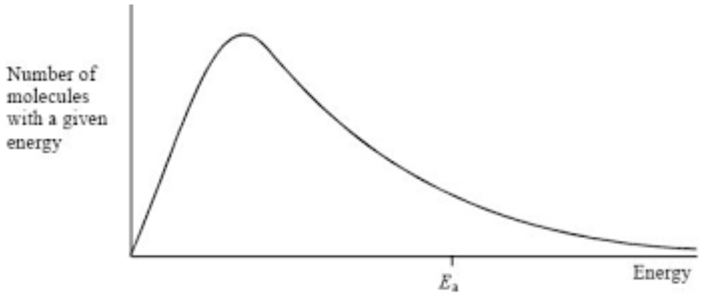
- Type of reaction in which heat flows into system from surrounding
- Results in E_k converted to E_p; decrease in E_k of surroundings results in a decrease in temperature
- (Since temperature is $\propto$ avg. E_k)
- Positive enthalpy: since enthalpy of products > enthalpy of reactants; heat was lost by surroundings
- ∴ $\Delta H>0$ kJ/mol



Maxwell Boltzmann Diagram

Definition:

- Shows range of kinetic energies possessed by particles in a substance at a specific temperature



For FULL marks when drawing enthalpy diagram:

1) Label axes
2) Ensure graph starts at (0,0)
3) Never touches x-axis as energy approaches infinity

Collision Theory Reaction Rates

To occur:

1) Particles must collide
2) Particles must collide with sufficient energy
    - Disrupt existing bonds and overcome E_a (Ek > E_a)
3) Particles must collide with the correct orientation
    - Larger and more complex structures have smaller reaction site hence slower reaction rate

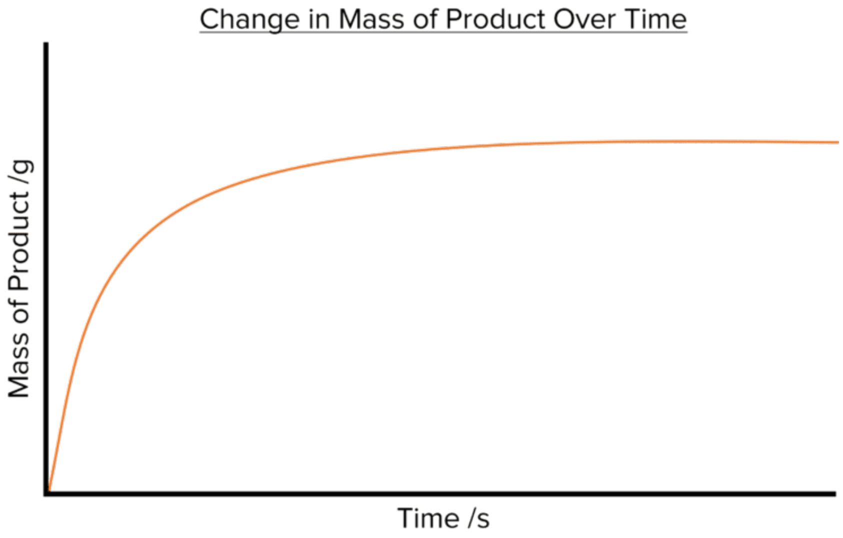
Rate

Definition: Successful collision between reactant particles per unit time

Measurable Factors

1) Change in mass by reactants/products – solid to gas
2) Colour intensity – increase in concentration of a colour substance
3) Solution concentration – how concentration changes as reaction progresses
4) Gas pressure – concentration of gas
5) pH – increase in concentration of acidic/basic substance
6) Volume liquid/gas – state changes

Reaction rate graphs



Common WACE Question:

Q. Explain shape of graph

- Gradient of graph represents rate of reaction
- Initially only reactants added to reacting vessel therefore [products] initially = 0M
- As [reactants] is initially high, frequency of collisions and hence frequency of successful collisions is high therefore high reaction rate initially represented by steep gradient
- As [reactants] decreases as it turns to products less frequent collisions occur and hence reaction rate decreases therefore gradient becomes less steep
- Eventually one or more of the reactants is fully consumed and reaction is complete, graph now flat. OR reaction reaches an equilibrium

Factors affecting rate of reaction

Increases frequency of collisions	*Increases proportion of successful collisions*
Concentration	Catalyst
Increasing State of Subdivision	Temperature (part of column 1 as well)
Pressure	

WACE RESPONSES FOR HOW FACTORS AFFECT REACTION RATE

Increased Collision Frequency – more collisions, same proportion of successful

Concentration

Increasing the concentration of reactants **decreases the average distance** between all reacting particles resulting in an **increase in frequency of collisions** and hence **increase in frequency of successful collisions** therefore **increasing reaction rate**

State of subdivision

Increasing state of subdivision **increases surface area of reacting particles exposed for further collisions**. This **increases** the probability and **frequency of collisions**. Thus, the **frequency of successful collisions increases** and hence **rate of reaction increases**

Pressure

Volume of reaction vessel decreases. **Average distance between all reacting particles decreases** therefore **frequency of collisions increases** and hence so does **frequency of all successful collision**. This results in an **increase in reaction rate**

Increased Proportion of Successful Collisions – same amount of collisions, greater proportion successful

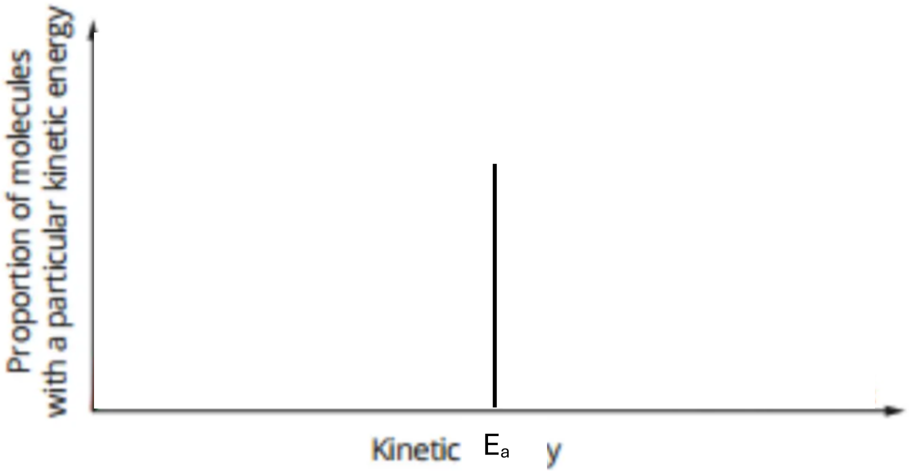
Temperature

Increasing temperature **increases the average kinetic energy of all reacting particles.** Thus, a greater **proportion** of particles have Ek>Ea, so proportion of successful collisions increases.

Since, Ek $\propto$ velocity, **velocity increases**, resulting in more collisions, hence **both frequency and proportion of successful collision increases** resulting in an increase in reaction rate

WACE Question:

Draw two different Maxwell Boltzmann distribution curves and label each curve. Describe how the curve represents that rate of reaction increases at higher temperatures



1) As temperature increases, peak of curve is lower and further to the right
2) Therefore, a greater proportion of reacting particles have Ek>Ea (shaded area of higher temperature curve > shaded area of lower temperature curve)
3) Hence proportion of successful collisions increases
4) Therefore, rate of reaction increases

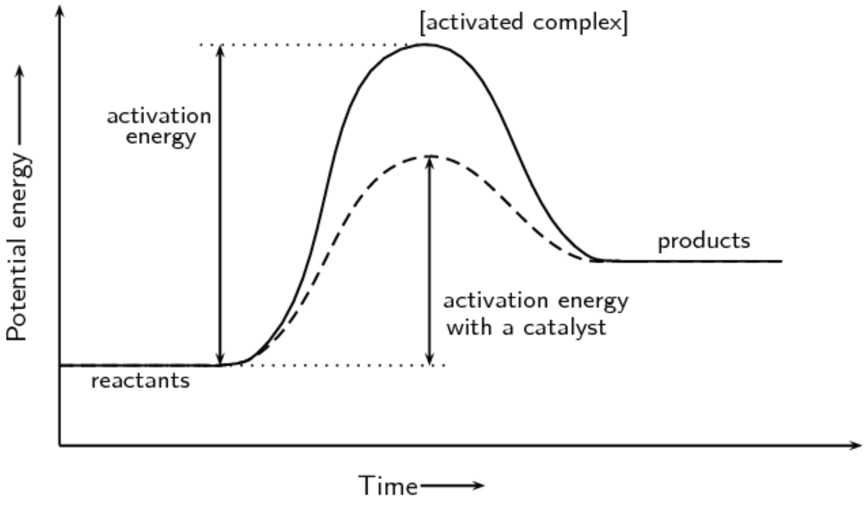
Catalyst

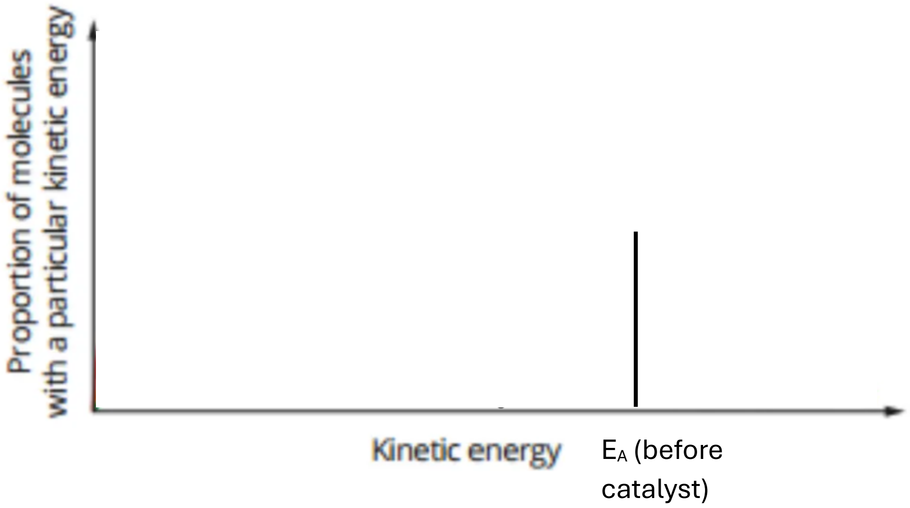
Definition:

- Chemical substance which increases the rate of reaction without being consumed in the process

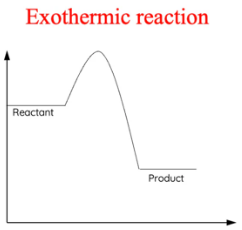
Explanation:

- Provides an alternate reaction pathway with lower activation energy. Therefore, a greater proportion of reacting particles have Ek>Ea; hence, proportion of successful collisions increases resulting in an increase in reaction rate





EQUILIBRIUM

Concept Terminology	
Open system	Matter and energy can be exchanged with the surroundings
Closed system	Only energy can be exchanged with the surroundings
Isolated system	Neither matter nor energy can be exchanged with the surroundings
Homogenous reactions	Reactants and products in same state/phase
Heterogenous reactions	Reactants and products in different states
Partial pressure	Pressure exerted by individual gas in container e.g. as if it was only gas in container The concentration of a gas
	Reversible Reactions and Dynamic Equilibrium
Reversible reaction	Reaction which occurs in both directions $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ *Key Terms*  - If forward exothermic, reverse endothermic and vice versa - Ea different value for forward and reverse - Change in enthalpy → change sign - If activation energy for both directions are similar then likely reversible - If rate of forward and reverse reaction are the same —> equilibrium - If newly formed products collide with sufficient energy, breaks bonds to reform original reactants

Reversible systems examples	*Evaporation and condensation of water* - reversible in both open and closed systems but can only reach equilibrium in closed *Saturated salt solution* - $\text{NaCl (s)} \leftrightharpoons \text{Na+ (aq)} + \text{Cl- (aq)}$ - e.g. $\text{Na+ (aq)} + \text{Cl- (aq)} \leftrightharpoons \text{NaCl (s)}$
Dynamic equilibrium	Point in which the rate of reaction for the forward and reverse reaction of a reversible reaction is equal and constant in rate. This can only occur in a closed system where matter cannot be transferred to surroundings. When system is in equilibrium all macroscopic properties such as: concentration, pressure, temperature, and colour are constant *Key points* - Forward reaction rate = Reverse reaction rate - Reversible (chem/physical) - Closed system - Does not go to completion and goes to different extents - Macroscopic properties constant (concentration, pressure, temp) - No observable change

	Le Chatelier’s Principle (LCP)
Le chatelier's principle	If an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of that change $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$ *Imposed changes* 1. Concentration (adding/removing reactants/products/dilution/evaporation) 2. Pressure (increasing/decreasing volume of container) 3. Temperature (*Kc only changed by temp)
	Prediction Answer Structure
Le Chatelier’s Principle	1. Describe imposed change 2. Forward/ reverse favored or equilibrium shift left/right + working 3. *“To partially oppose effect of that change”* 4. [reactants/products] decrease while [products/reactants] increase As reactants/products are being consumed faster than produced, and products/reactants are being produced faster than consumed … Until equilibrium is reestablished

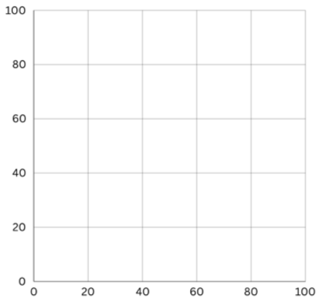
WACE QUESTION TYPE: *Predict* change to equilibrium system (Predict ∴ use LCP)

Applying LCP

Consider the Haber Process: $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ $\Delta H<0$

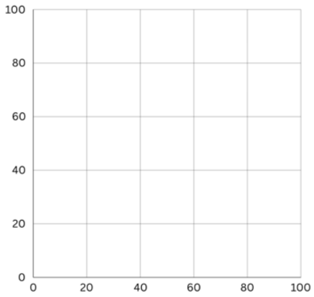
Concentration Change: (HCl added)

- Adding HCl reacts with NH3 resulting in a decrease in [NH3].
- System partially opposes this change by favoring the forward reaction to increase the [NH3].
- As forward reaction is favored, [reactants] decreases, while [NH3] increases, until [ ] remain constant, and equilibrium is re-established



Temperature Change: (System heated up)

- The temperature increases
- The system partially opposes this change by favoring the reverse endothermic reaction in order to decrease the temperature by absorbing energy (changing heat to potential energy)
- As the reverse reaction is favored, [products] decreases, while [reactants] increases, until [ ] remains constant, and equilibrium is re-established



Pressure Change: (Volume is decreased: Note dilutions use same explanation)

- Partial pressures of all gases increase. [ ] of all reacting particles increases
- The system partially opposes this change by favoring the forward reaction to create 2 moles of gas rather than 4 on the right-hand side, to decrease the total pressure
- Since the forward reaction is favored, [reactants] decreases while [products] increase, until [ ] remains constant, and equilibrium is re-established.

Note:

-> Adding solid does not affect position of equilibrium – e.g. saturated solution

-> Adding catalyst does not affect position of equilibrium – total RR increases

-> Adding an inert gas does not affect position of equilibrium (assuming container has fixed volume) – e.g. adding Neon to Haber Process

Apply

Consider the following system in equilibrium: $N_2 (g) + 2O_2 (g) \rightleftharpoons 2NO_2 (g)$ $\Delta H>0$

Predict the changes to the system when the following changes are imposed…

N_2 is removed from the system

The system is heated

The volume of the system is increased – container is increased in size

WACE QUESTION TYPE: *Explain* how position of equilibrium system is affected

(Explain ∴ use Collision Theory)

Collision Frequency Answer Structure:

1. Describe imposed change
2. Describe how reaction rate is affected, using CF
3. State whether FRR or RRR is favoured – (FRR>RRR or RRR>FRR)
4. "Thus, more products/reactants are being used than produced, and more reactants/products are being produced than used" state [ ] change
5. "FRR gradually increases/decreases, while RRR gradually decreases/increases"
6. "This continues until FRR and RRR are equal (equilibrium re-established); and the concentrations are then constant"

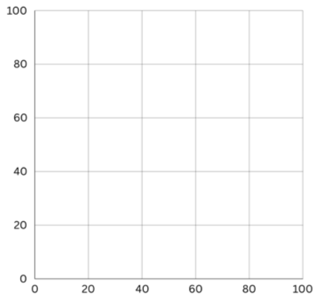
Consider the Haber Process: $N2(g) + 3H2(g) \rightleftharpoons 2NH3\ (g)$ $\Delta H<0$

Concentration Change: (more N2 added)

- [N2] increases
- CF between N2 and H2 molecules increases, resulting in an increase in the rate of forward reaction. Rate of reverse reaction stays the same.
- The rate of the forward reaction is now higher than the reverse reaction (FRR > RRR)
- Thus, more NH3 is produced than used, and more reactants are used than produced. Which results in an increase in [products] and a decrease in [reactants].
- FRR gradually decreases, while RRR gradually increases
- This continues until FRR and RRR are equal (equilibrium re-established); and the concentrations are then constant

Temperature Change: (heated up)

- The temperature increases
- Average Ek of all reacting particles increases, thus, more particles have Ek > Ea. Greater proportion of collisions are successful.
- Average particle velocity increases, thus, total CF increases.
- Thus, total reaction rates increase (both FRR and RRR), however RRR reaction increases more. This is due to the reverse reaction being an endothermic reaction, thus has a higher Ea.
- As reverse reaction is at a greater rate, more products are used than produced, and more reactants are produced than used. This results in [products] decreasing, and [reactants] increasing
- RRR gradually decreases whilst FRR gradually increases
- This continues until FRR and RRR are equal (equilibrium re-established); and the concentrations are then constant



Pressure Change (Volume of beaker is increased)

- Volume of system is increased; this decreases the partial pressures of all the gases in the system
- CF between all reacting particles decreases, thus total reaction rate decreases
- However, as the reactants have 4 moles of gas compared to products – 2 moles of gas, there is a greater decrease in the CF of reactants. Thus, FRR decreases more than the rate of the reverse reaction does, thus RRR>FRR
- Thus, products are being used faster than produced, and reactants are being produced faster than used, which results in a decrease in [products] and an increase in [reactants]
- RRR gradually decreases, while FRR gradually increases
- This continues until FRR and RRR are equal (equilibrium re-established); and the concentrations are then constant

Apply

Consider the following system in equilibrium: $N_2 (g) + 2O_2 (g) \rightleftharpoons 2NO_2 (g)$ $\Delta H>0$

Explain the changes to the system when the following changes are imposed…

NO_2 is added to the system

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The system is cooled

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The volume of the system is decreased – container is decreased in size

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Equilibrium Constant (Kc)

Definition:

- Constant for chemical reaction at fixed temperature. Expresses the relationship between products and reactants of a reaction at equilibrium – is there more products or reactants present at equilibrium
- E.g. strength of acids

$$aW + bX \leftrightharpoons cY + dZ$$

$$Kc = \frac{[\text{Products}]^{\wedge}\ \text{coefficient}}{[\text{Reactants}]^{\wedge}\ \text{coefficient}}$$

$$Kc = \frac{[Y]^{c}\,[Z\}^{d}}{[W]^{a}\,[X\}^{b}}$$

NOTE: Kc values are only affected by changes in temperature

Only gases (g) and solutions (aq) are included in an equilibrium constant expression

	OCEAN ACIDIFICATION
Equations	Absorption of CO_2 from atmosphere a) $CO_2 (g) \rightleftharpoons CO_2 (aq)$ Creates carbonic acid (a weak diprotic acid) Increase in $[H^+]$, Decreases in pH b. $CO_2 (aq) + H_2O (l) \rightleftharpoons H_2CO_3 (aq)$ c. $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ d. $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ Usually CO_3^{2-} used in CALCIFICATION. Use of carbonate ions to form protective coverings (exoskeletons) of $CaCO_3$ shells. $Ca^{2+} (aq) + CO_3^{2-} \rightleftharpoons CaCO_3 (s)$ Increase in H^+ reduces CO_3^{2-} available known as DECALCIFICATION. Impairs organisms' ability to build and maintain carbonate structures. $H^+ + CO_2^- \rightleftharpoons HCO_3^-$ Process: $[CO_2(g)]$ increases, therefore equation 1 shifts to the right and hence $[CO_2 (aq)]$ increases $[CO_2 (aq)]$ increases, therefore equation 2 shifts to the right and hence $[H_2CO_3]$ increases $[H_2CO_3]$ increases, therefore equation 3 shifts to the right and hence $[H_3O^+]$ and $[HCO_3^-]$ increases. Whilst the moles of both H_3O^+ and HCO_3^- increases by equal amounts as there is a significantly lower $[H_3O^+]$ present in ocean compared to $[HCO_3^-]$, proportional increase in $[H_3O^+]>[HCO_3^-]$ Therefore equation 4 shifts left and $[CO_3^{2-}]$ decreases Hence equation 5 shifts right resulting in a decreasing in amount of $CaCO_3 (s)$

Impacts	1. Food Chains 2. Prevent krill eggs hatching at low pH 3. No krill means no food for planktons which are at the bottom of the food chain Social and environmental impacts - Food chain - Coast protection - Tourism
Kyoto protocol	WHAT - An international agreement negotiated in 1997 to extend the United Nations Framework Convention on Climate Change (UNFCCC). Commitment signed in 2008-2012 by 192 countries. WHY - To aim to reduce collective emissions by at least 5% from 1990 levels ACHIEVEMENTS i) Simulation of national policies ii) Creation of an international market for carbon iii) Developed trading emission schemes RESTRICTIONS I) Modest emission reduction limits II) Lack of measures to achieve greater reduction III) Absence of penalties for not achieving goals