Brett Anderson
1/15/2003

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                    ┌─────────────────────┐
                    │  Chemical Kinetics  │
                    └─────────────────────┘
            ┌────────────────┐   ┌────────────────┐
            │  Macroscopic   │   │ Submicroscopic │
            └────────────────┘   └────────────────┘
            ┌────────────────┐   ┌─────────────────────┐
            │ Rate of Reactions │ │ Reaction Mechanisms │
            └────────────────┘   └─────────────────────┘
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                    ┌────────────────────────────┐
                    │ Rates of chemical reactions │
                    └────────────────────────────┘

   ┌──────────────┐  ┌──────────────┐      ┌──────────────┐
   │ Expressions of│  │ Techniques for│     │Factors affecting│
   │rate of reaction│ │following a reaction│ │reaction rates │
   └──────────────┘  └──────────────┘      └──────────────┘

        ┌─────────────────────────────┐
        │ Concentration-time graphs   │
        │ in estimating instantaneous │
        │ rates of reaction           │
        └─────────────────────────────┘

  ┌────────────┐ ┌──────────────┐ ┌─────────────┐      ┌──────────┐
  │Surface area│ │Concentration │ │ Temperature │      │ Catalysis│
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                                         ┌────────────────────┐
                                         │ Homogeneous and    │
                                         │ heterogeneous      │
                                         │ catalysis          │
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        ┌────────────┐ ┌────────────┐ ┌────────────┐
        │ Boltzmann  │ │ Activation │ │ Energy     │
        │ distribution│ │ energy    │ │ profiles   │
        │ of molecular│ └────────────┘ └────────────┘
        │ energies   │
        └────────────┘

  ┌────────────┐      ┌─────────────────┐ ┌──────────────┐
  │ Collision  │      │ Explanation of  │ │ Catalysts    │
  │ theory     │      │ temperature     │ │ provide      │
  └────────────┘      │ effect in terms of│ │ alternative │
                      │ the proportion of│ │ reaction     │
                      │ molecules having │ │ pathways     │
                      │ minimum energy   │ └──────────────┘
                      │ to react         │
                      └─────────────────┘
                                              ┌──────────────┐
                                              │ Application  │
                                              │ of catalysis │
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Arrhenius Eq.

Order of Rxn

Half-life

(26)

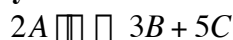**Reaction Rates and Stoichiometry**

Rate of Reaction = $\dfrac{\Delta[\ ]}{\Delta t}$ (The rate is negative for reactant loss and positive for appearance)

Instantaneous Rate:

Rate at a specific point in time. Tangent to a rate curve.

Initial Rate: Instantaneous rate at t=0.

Stoichiometry:

$$2A \longrightarrow 3B + 5C$$

$$Rate = -\frac{\Delta[A]}{2\Delta t} = +\frac{\Delta[B]}{3\Delta t} = +\frac{\Delta[C]}{5\Delta t}$$

Reaction Conditions and Rate

1	Nature of Reactants	Solids → Rate depends on surface area
		Gases → Most reactive
		Liquids → Less reactive than gases
2	Concentration of Reactants	*Concentration ∝ Rate*
3	Temperature	*Temperature ∝ Rate*
4	Catalysts	Accelerate rate by decreasing activation energy.

Further Catalysis:

Chemical Catalysts: lower the energy pathway from reactants to products and form different activated complexes. There are more effective collisions because more molecules will have the necessary Activation Energy (The activation energy is lowered). This is expressed by the equation $Rate = Ae^{\left(\frac{-E_A}{RT}\right)}$. If E_A is lowered, the rate must increase.

1. **Catalysts** do not affect all reactions.
2. **Autocatalysis**: Reaction product is a catalyst.
3. **Promoter**: Species increasing catalyst's power.
4. **Inhibitor**: Species decreasing catalyst's power (Preservatives)
5. **Enzyme**: Catalyst in living things (Enable a substrate that must fit into an active site)
6. **Surface catalyst**: attracts reactants and keeps them close to surface for reaction.
7. **Homogenous** Catalyst: Same state as reactants (ex: NO_2)
8. **Heterogenous** Catalyst: Different physical state (compared to reactants). Work through adsorbtion. An example of heterogenous catalysis is the Haber Process, which uses iron to catalyze the reaction $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$.

Collision Theory:

$$Rate \propto \frac{Collisions}{Time}$$

Effective Collision: Collision that produces an actual reaction (Small number of effective collisions compared to total number of collisions)

Why?

    i. Steric Factor: Correct orientation needed for reaction.

    ii. Energy Factor: A certain amount of energy is needed to break bonds.

Nature of Reactants: How fall will a species give up electrons.

Surface Area: More surface area, more collisions, more effective collisions.

Concentration: $Rate \propto Concentration \Rightarrow \dfrac{1}{Time} \propto Concentration$

    Greater Concentration → More collisions → More effective collisions

    It follows that increasing pressure increases the rate: Increasing the pressure pushes molecules together → More frequent collisions → React more rapidly.

Temperature: More of reactants have sufficient energy to react (E_A) → (Maxwell Boltsmann Curve)

Light: Will increase rate of reaction

a) Concentration – higher concentration, more particles in a given volume, hence more collisions

b) Surface area – greater surface area, so more collisions per second can occur.

c) Temperature – higher temperature, more collisions with the required activation energy

Low temperature ———
High temperature - - - - - - -

Probability of this energy

E_a with catalyst E_a un-catalysed   Energy

) Catalyst – provides an alternative mechanism with a lower activation energy

Without catalyst

Reactants

Catalysed E_a

Uncatalysed E_a

With catalyst

Enthalpy

ΔH

Activation Energy:

Energy needed to reach an <u>activated complex</u>
Activated Complex: Intermediate state formed during a reaction.

Reaction Mechanism:

Definite sequence of bond-making and bond-breaking steps in a reaction.
Elementary step: each step in mechanism.
Unimolecular, bimolecular: Number of molecules in a certain step.
Rate Determining Step: One step in a reaction that is slower than all other.   It will determine the overall rate of reaction.
Intermediate: Species involved in a reaction mechanism; does not appear in the "overall reaction."
eggs:

$$xA + yB \xrightarrow{\;Slow\;} zC$$

$$Rate = k[A]^x[B]^y[C]^z$$

Arrhenius Equations

Arrhenius Equation: $k = e^{\frac{-E_A}{RT}}$

> e is the base of all natural logs
> E_A is the activation energy of the reaction
> R is the moral gas constant (8.3143)
> T is the absolute temperature (in Kelvin)

From this equation, a graph may be drawn to determine the activation energy and the value of A.

> Taking the natural logs of both sides of the equation gives: $\ln k = \ln A - \dfrac{E_A}{RT}$,
>
> which is in the form y=mx+b. (This formula is already in the data book)
> A is the antilog of the y-intercept.
> E_A can be determined from the slope.

Rate Graphs

ORDER OF ZERO

Concentration vs. Time

Rate of Reaction vs. Time

FIRST ORDER

Concentration vs. Time

Rate of Reaction vs. Time

SECOND ORDER

Concentration vs. Time

Rate of Reaction vs. Time
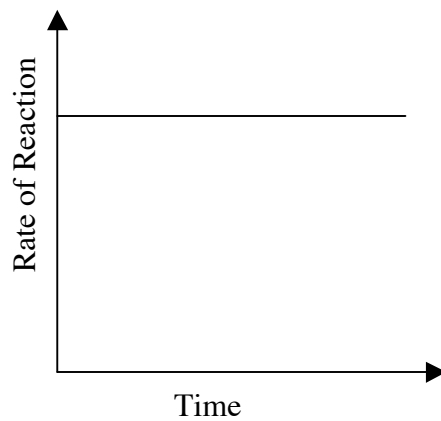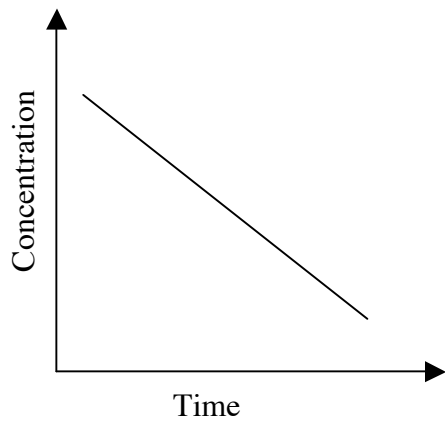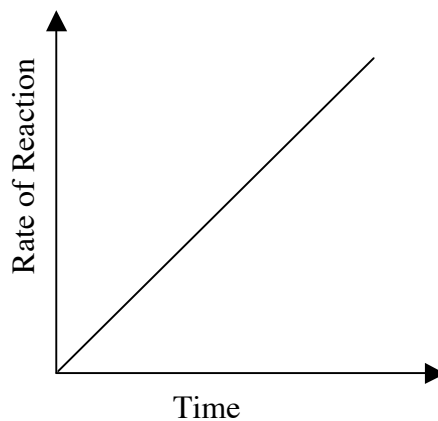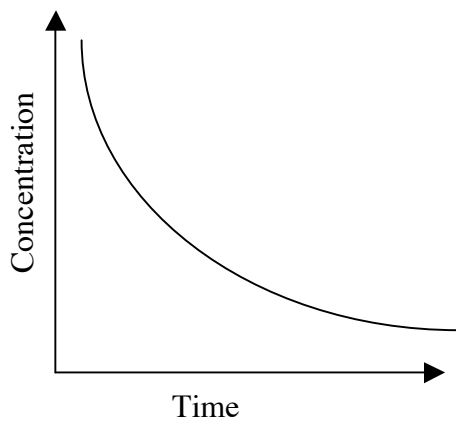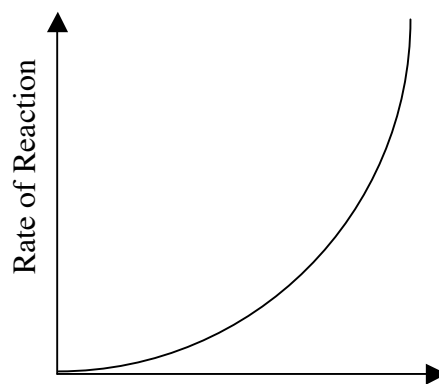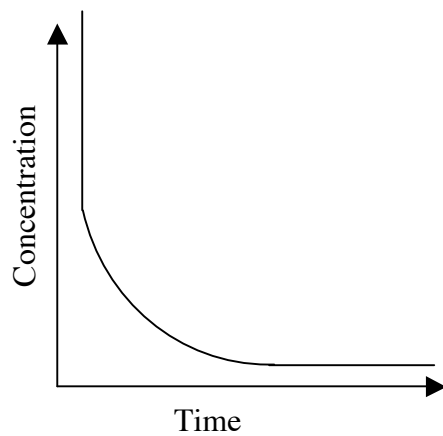
Fill in the Blank Questions

Questions:
1. The rate of a reaction is expressed as the change in concentration of a reactant or product per unit of _____.
2. _____ of Chemical Reactions can be affected by several factors.
3. A substance that reduces a reaction rate is called a _____ catalyst or inhibitor.
4. The rate law for a reaction (can, cannot) be determined from the balanced chemical equation for a reaction.
5. If a plot of [A] versus time gives a straight line, then the reaction is _____ order in A, the slope of the line is –k and the y-intercept is $[A]_o$.
6. If a plot of ln[A] versus time gives a straight line, then the reaction is _____ order in A, the slope of the line is –k and the y-intercept is $\ln[A]_o$.
7. The most common type of elementary reaction involves the collision of two molecules, ions or atoms. Such a reaction is called a _____ reaction.
8. A _____ catalyst is one that is in the same physical state as the reactants.
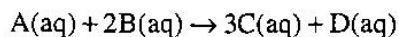9. A catalyst has no effect on the net _____ change in a reaction.

Answers
1. Time
2. Rates
3. Negative
4. Cannot
5. 0
6. 1
7. Bimolecular
8. Homongenous
9. Energy

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Past IB Exam Questions
(Questions with answers)

The following data were obtained for the reaction between A and B:

$$A(aq) + 2B(aq) \rightarrow 3C(aq) + D(aq)$$

Experiment	Initial concentration of Reactants ($mol\,dm^{-3}$)		Initial Rate of Reaction ($mol\,dm^{-3}\,hr^{-1}$)
	A	B	
1	0.200	0.200	0.50
2	0.400	0.200	2.00
3	0.400	0.800	8.00

(a)   Give the order with respect to A.   [1]

   The order with respect to A is 2.

(b)   Give the order with respect to B.   [1]

   The order with respect to B is 1.

(c)   Write the rate expression for this reaction.   [1]

   Rate=k $[A]^2$ $[B]^1$

(d)   Using the data from the first experiment, calculate the value of the rate constant and give its units.   [1]

$$Rate = k[A]^2[B]$$

$$0.5mol\,dm^{-3}\,hr^{-1} = k[0.2mol\,dm^{-3}]^2[0.2mol\,dm^{-3}]$$

$$k = 62.5 \ mol^{-2} \ dm^6 \ hr^{-1}$$

(Questions without answers)

(a)   The rate constant, k, for any reaction is related to the activation energy, E_a, by the Arrhenius equation.

    (i)   Explain the meaning of the terms: *rate constant* and *activation energy*.   [4]

    (ii)   A particular reaction is found to be second order overall. Specify the units for both the rate of reaction and the rate constant.   [2]

(b)   Rates of reactions depend on temperature.

    (i)   Using the same sets of axes, draw **two** clearly labelled curves to show the distribution of energies of the molecules of a fixed mass of gas at different temperatures, T_1 and T_2 where T_2 is the higher temperature.   [4]

    (ii)   With reference to the curves in (i) explain why an increase in temperature increases the rate of a gaseous reaction.   [2]

    (iii) Explain briefly how a catalyst can increase the rate of a chemical reaction.   [2]

(c)   The rate constant, k, was determined for the decomposition of hydrogen iodide at various temperatures. The results giving $\ln k$ for a range of temperatures are given below.

Temperature T/K	$\ln k$	T^{-1} / K^{-1}
550	−15.6	1.82×10^{-3}
600	−12.2	1.67×10^{-3}
650	−9.4	1.54×10^{-3}
700	−7	1.43×10^{-3}
750	−4.9	1.33×10^{-3}

    (i)   Plot a graph of $\ln k$ against T^{-1}.
    (Take the $\ln k$ axis from −20 to 0 and the T^{-1} axis from 1.2×10^{-3} to $1.9 \times 10^{-3} \, K^{-1}$)   [4

    (ii)   Calculate the gradient (slope) of your graph and use it to determine a value for the activation energy, E_a, stating its units.   [

    (iii) Without obtaining the actual value, state **two** different ways in which the value of A in the Arrhenius equation could be determined.   [