CH1011 Tutorial 5 Answers

1. The variation in initial rate of reaction of nitrogen dioxide with fluorine is given in the following table. What is the overall order of the reaction? Write out a general rate law for this reaction.

Experiment	Initial $[NO_2]$	Initial $[F_2]$	Initial rate
1	0.10	0.10	0.005
2	0.20	0.10	0.010
3	0.10	0.20	0.010

Compare experiment 1 & 2 here $[F_2]$ is constant as $[NO_2]$ doubles the rate doubles therefore the order wrt $[NO_2]$ is 1.
Compare experiment 1 & 3 here $[NO_2]$ is constant as $[F_2]$ doubles the rate doubles therefore the order wrt $[F_2]$ is 1.
The overall order of the reaction is 2.
rate = $k[NO_2][F_2]$

2. Dinitrogen pentoxide (N_2O_5) decomposes by a uni-molecular first order process. If the rate constant is $5.00 \times 10^{-4}\ s^{-1}$ how long will it take (s) for an initial concentration of N_2O_5 of 0.0400 mol dm^{-3} to fall to a value of 0.0200 mol dm^{-3}?

Rate = $k[N_2O_5]$

$t_{1/m} = \ln(m) / k$
$t_{1/2} = \ln(2) / k \quad \Rightarrow \quad t_{1/2} = 0.6932 / 5.00 \times 10^{-4}\ s^{-1} = 1386\ s$
$[N_2O_5] = 0.04 \Rightarrow 0.02$ the concentration has halved therefore this is one half-life.

The time taken is therefore 1.39×10^3 seconds.

3. What is the difference between a **heterogeneous** and a **homogeneous** catalyst? Give an example of a catalyst and explain why it is used.

A heterogeneous catalyst is a catalyst which exists in a different phase to the substrate being catalysed.
A homogeneous catalyst operates in the same phase as the catalysed substrate.
An example of a heterogeneous catalyst is Pd/C which catalyses the hydrogenation of double bonds in unsaturated hydrocarbons eg. Vegetable oil → Margarine

4. Using the nuclide $^{232}_{90}Th$ illustrate the processes of alpha decay and with the nuclide ^{14}C the process of beta decay.

$^{232}_{90}Th \rightarrow {}^{228}_{88}Ra + {}^{4}_{2}He$

$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$

5. Enzymes function as biological catalysts. Describe the function of a typical enzyme including the enzyme-substrate complex, active site, turnover rate.

Nitrogenase is a metalloenzyme, it is a 2 protein enzyme that catalyses the reduction of N_2. One of the proteins in nitrogenase contains the Fe-Mo cofactor (a non-protein, needed for activity).

N_2 (O) + $8H^+ + 6e^- \rightarrow 2NH_4^+$ (-III) ambient T and p

The enzyme catalyses the cleavage of the triple bond in N_2 (bond E 945 kJ/mol). The enzyme coordinates through the cofactor to the N_2 and weakens the bond thereby lowering the activation barrier (by stabilising the TS) for bond cleavage to 200 kJ/mol allowing the reduction to occur. It is the metallic part of the enzyme that is the active site that coordinates to the N_2 molecule and forms the enzyme-substrate complex (nitrogenase = enzyme, N_2 = substrate). It is the transformation from the ES complex to the products that is rate limiting, slow step in the reaction (according to Michaelis-Menton kinetics). The reaction is slow with a low turnover (1 mol N_2 s^{-1}/ mol Mo) but it does occur at a sufficient rate to provide a valuable and often limiting nutrient for micro-organisms that operate using this enzyme to provide N. The turnover rate is the number of catalysed events at the active site per second.

The function of nitrogenase is pH, T and pressure dependent, these conditions influencing the turnover rate.

6. Stable isotope measurements are used in many areas of the biological and earth sciences. Explain the difference between **kinetic fractionation** and **equilibrium fraction** as it applies to stable isotope ratios. Illustrate your answer using $\delta^{18}O$ ratios.

$$\delta\,^{18}O = \left(\frac{^{18}O/^{16}O_{sample} - ^{18}O/^{16}O_{standard}}{^{18}O/^{16}O_{standard}} \right) \text{x}10^3\ ‰$$

The stable isotopes of oxygen are ^{18}O 0.20% ^{16}O 99.76%

The reference standard used in stable isotope measurements ($\delta^{18}O$) is SMOW : Standard Mean Oceanic Water.

Equilibrium fractionation and kinetic fractionation are physico-chemical mechanisms that alter the background isotope ratio.

1) *Equilibrium fractionation*. In this mechanism for altering the ratios exchange reactions occur which re-distribute isotopes. In a chemical reaction the isotopes re-distribute to generate the lowest ΔG_{rxn}

$\Delta G_{rxn} = -RT\ln K$ T is a major factor influencing K

$$½CO^{16}{}_2 + H_2O^{18} \leftrightarrows ½CO^{18}{}_2 + H_2O^{16}$$

2) *Kinetic fractionation* - Lighter isotopes have weaker bonds and react faster. This means for instance that a molecule of $H_2{}^{18}O$ will react more slowly than a molecule of $H_2{}^{16}O$.