## CH1011 Tutorial 5 Answers

2NO(g) + O<sub>2</sub>(g) → 2NO<sub>2</sub>(g)
1. For the above reaction write down expressions for the rate law in terms of the concentration dependence of nitrogen dioxide (the product).

rate =  $\frac{1}{2} d[NO_2] / dt$ 

2. Assume that the half-life for the above reaction at 300°C is 250 ms and that the reaction is first order with respect to NO and overall first order.

• How long will it take, in milliseconds, for the NO concentration to fall from an initial value of 0.130 mol dm<sup>-3</sup> to a value of 0.0325 mol dm<sup>-3</sup>?

 $t_{\frac{1}{2}} = 250 \text{ms} \qquad 0.0325 / 0.130 = 0.25$ It has fallen to <sup>1</sup>/<sub>4</sub> of the initial value. Therefore 2 half-lives have passed. 2 \* 250 ms = 500 ms

or  $t_{3/4} = \ln(4) / k$  where k is found from  $t_{1/2} = \ln 2/k \Rightarrow k = 2.77 \text{ s}^{-1}$ = 0.500 s = **500ms** 

• Calculate the activation energy,  $E_a$ , for the above reaction given that  $k = 2.4E-5 \text{ dm}^{-3}/\text{mol s}$  at 30°C and  $k = 5.3E-4 \text{ dm}^{-3}/\text{mol s}$  at 80°C.

 $E_a = -R \ln(k_2/k_1) (1/T_2 - 1/T_1)^{-1}$ = -8.314 J/mol K ln(5.3E-4 dm<sup>-3</sup>/mol s / 2.4E-5 dm<sup>-3</sup>/mol s) (1/353K - 1/303K)<sup>-1</sup> = 55 kJ / mol

3. What is an enzyme and how does an **enzyme** function as a **catalyst**? Use an example to illustrate your answer.

An enzyme is a globular protein that has been designed by an organism to catalyse a biochemical reaction that would otherwise proceed at an unacceptably slow rate for the organism to operate successfully. The globular protein is a large polypeptide synthesized from amino acids. The enzyme may either operate in solution as a colloid particle or may be bound to cellular membranes.

The enzyme functions catalytically by providing an active site that has one (or more) of three functions:

1) Bringing the reacting parts of the substrate(s) together

2) Stretching reactive bonds in the substrate by moving atoms apart

3) Providing acid catalysis by adding H<sup>+</sup>.

The substrate(s) **S** is the reactant molecule(s) that bind to the active site according to Michaelis-Menton kinetics to form the product(s) **P**.

Step 1)  $E + S \leftrightarrows ES$  [fast, reversible]

Step 2)  $ES \rightarrow E + P$  [slow, rate-determining]

An example is the molybdenum containing 2 protein enzyme nitrogenase which catalyses the reaction:  $N_2 + 8H^+ \rightarrow 2NH_{4+}$ 

This process involves stretching the N= N in the active site and protonation to form the plant useful ammonium ion. Without catalysis by nitrogenase  $E_a$  is E = 945 kJ/mol with catalysis to 200 kJ/mol

4. Using the **radionuclide** <sup>222</sup><sub>90</sub>**Rn** illustrate the processes of **alpha decay** and with the **radionuclide** <sup>210</sup>**Pb** the process of **beta decay**. In both cases assume that in the decay process only a daughter nuclide and the given decay particle are formed.

$$^{222}_{86}\text{Rn} \rightarrow ^{218}_{84}\text{Po} + ^{4}_{2}\text{He}$$
  
 $^{210}_{82}\text{Pb} \rightarrow ^{210}_{83}\text{Bi} + ^{0}_{-1}\text{e}$ 

- 5. The atmospheric testing of thermonuclear weapons had some un-intentional scientific use, it dosed the atmosphere with trace amounts of **radioactive tritium** (<sup>3</sup>**H**) an isotope of hydrogen which has a relatively short half-life (12.3yr).
  - Assuming that an iguana in atoll in the Pacific accumulated 24.10µg of on the day of the testing (based on breathing in contaminated air) and when it died it was found to have 2.53µg of tritium in the body mass how long did it take for the iguana to die?

 $k = \ln 2 / t_{2}^{1/2} = \ln 2 / 12.3 = 5.635 \text{ x } 10^{-2} \text{ y-1}$ 

 $t = (\ln No - \ln N)/k$ 

 $= (\ln 24.10 - \ln 2.53) / 5.635 \times 10^{-2} \text{ y-1}$ 

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= 40.0 \text{ y}
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(obviously died of old age!)

6. What differentiates stable isotopes from radioisotopes.Why are stable isotopes of oxygen useful in paleoclimatology?

Stable isotopes are those that have no natural decay process – they are at the end of a decay series. Radioisotopes are those that decay naturally either by  $\alpha$ , $\beta$ , ( $\gamma$  or positron decay).

The stable isotopes of oxygen are <sup>18</sup>O 0.20% <sup>16</sup>O 99.76% The reference standard used in stable isotope measurements ( $\delta^{18}$ O) is SMOW : Standard Mean Oceanic Water. Isotope enrichments ( $\delta$ ) are given in ppt (%)

In paleoclimatology the fractionation of oxygen occurs due to physical and chemical (equilibrium) effects as a result of the mass differences between  $H_{2O}^{18}$  and  $H_{2O}^{16}$ .

*Physical processes*: for H<sub>2</sub>O the processes of evaporation, condensation and freezing can alter the balance of heavy water to light water molecules. eg. H<sub>2</sub>O<sup>18</sup> heavier water  $p_{vap} \downarrow H_2O^{16}$  lighter water  $p_{vap} \uparrow Equilibrium fractionation$ . In this mechanism for altering the ratios exchange reactions occur which redistribute isotopes. In a chemical reaction the isotopes re-distribute to generate the lowest  $\Delta G_{rxn}$ 

 $\Delta G_{\text{rxn}} = -\text{RTlnK} \quad \text{T is a major factor influencing K} \\ \frac{1}{2}\text{CO}^{16}2 + \text{H}_2\text{O}^{18} \quad \leftrightarrows \quad \frac{1}{2}\text{CO}^{18}2 + \text{H}_2\text{O}^{16}$ 

In the earth's climate the oceans are coupled with the landmasses (ice sheets or lakes) through the atmosphere.

We obtain the isotope fraction factor  $\alpha$  by measuring the isotope ratios of seawater  $R_A$  and for a sample of ice  $R_B$ . R = (heavy isotope / light isotope)

$$\alpha = ({^{18}O}/{^{16}O})$$
ice / ( ${^{18}O}/{^{16}O}$ )sea

We can measure the del values ( $\delta$ ) for both reservoirs (oceans, ice) using the following formula:

$$\delta = \left(\frac{\boldsymbol{R}_{sample} - \boldsymbol{R}_{standard}}{\boldsymbol{R}_{standard}}\right) \times 10^3 \%$$

$$10^3 \ln \alpha \approx \frac{A}{T^2} + B = \delta_{\rm A} - \delta_{\rm B}$$

As the worlds oceans are in contact with the polar ice through the atmosphere which has a temperature T then it is possible (with the constants A, B known) to determine the temperature  $\mathbf{T}$  at which a particular exchange event occurred – back to 220kyr in the case of ice cores from the Antarctic.

- Currently the  $\delta^{18}$ O in seawater at present is 0‰.
- Ice which forms inland has -ve values for δ<sup>18</sup>O (≈ -20 to -60‰) due to depletion in <sup>18</sup>O; the heavier water H<sub>2</sub><sup>18</sup>O is removed by precipitation close to the point of vaporisation of water leaving the lighter H<sub>2</sub><sup>16</sup>O to precipitate further away as snow which compacts to form ice.
- During the ice age oceans were left isotopically heavy  $\delta^{18}O + 5\%$  as nearly  $\frac{1}{3}$  of the land area of the Earth was covered in ice locking up a huge amount of  $\delta^{16}O$ .

The construction of paleoclimates therefore makes use of the exchange temperature between the reservoirs and relies on available evidence for the isotope ratios in the ancient ice cores and sea.(from planktonic foram deposits – calcareous shells).