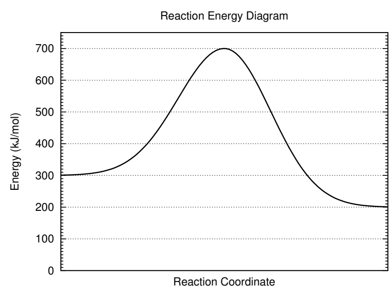
CHEM 10050 - Fundamentals of Chemistry
Sample Kinetics Problems (with solutions)

1. The following diagram shows a reaction energy diagram for a hypothetical reaction. From this diagram:
   (a) Calculate the energy change (ΔH) for this reaction.
   (b) Calculate the activation energy (E_a) for this reaction
   (c) Is this reaction endothermic or exothermic ?



2. A reaction is known to obey 1^{st} order kinetics, with k = 0.45.
   (a) Calculate the rate of this reaction if the concentration of starting material is 0.15 M.
   (b) Calculate the rate of this reaction if the concentration of starting material is 0.10 M.
3. A reaction is known to obey 2^{nd} order kinetics, with k = 0.45. Calculate the rate of this reaction if the concentration of starting material is 0.15 M.
4. Write the equilibrium constant for the following reactions.
   (a) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$
   (b) $CaCO_{3\,(solid)} + 2\,HCl_{(aq)} \rightleftharpoons CaCl_{2\,(aq)} + H_2O_{(liquid)} + CO_{2\,(gas)}$

Background Information

In general terms, the rate of a chemical reaction can be defined by:

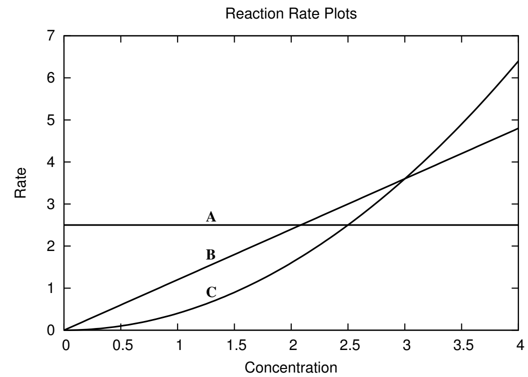
$$\text{rate} = \frac{change\ in\ concentration}{change\ in\ time} = \frac{\Delta[]}{\Delta t}$$

The previous equation is quite useful for experimental determination of rates. However, it is usually beneficial to determine if this data can be fit a theoretical model. A large number of reactions can be fit to one of the following reaction types.

Zeroth Order
Rate = k
In this case, the reaction rate does not depend on concentration, but is a constant value.
See Plot 'A'

First Order
Rate = k[A]
In this case, the reaction rate does depend on concentration. As the concentration increases, the reaction rate increases.
See Plot 'B'

Second Order
Rate = $k[A]^2$
In this case, the reaction rate is highly dependent on concentration. Small changes in concentration can have large changes on the rate of reaction.
See Plot 'C'



Answers

1. Reaction Energy Diagram

   (a) ΔH is the difference between the energy of the reactants and the energy of the products. In this example, the reaction goes from 300 $\rightarrow$ 200, which is a difference of 100. Since this is 'downhill', ΔH = -100.

   (b) The activation energy is the difference between the energy of the reactants and the energy at the 'top of the peak'. In this example, the reaction goes from 300 $\rightarrow$ 700, so E_a = +400. *(Note that E_a values are always positive).*

   (c) Since this reaction is 'downhill', it is exothermic.

2. For a 1^{st} order reaction, rate = $k[A]^1$

   (a) rate = 0.45*(0.15) = 0.068

   (b) rate = 0.45*(0.10) = 0.045 *(Note: rate is lower with lower concentrations)*

3. For a 2^{nd} order reaction, rate = $k[A]^2$ = $0.45*(0.15)^2$ = 0.010

4. Equilibrium constants: Ignore solids and pure liquids. Ratio = $\frac{Products}{Reactants}$

   (a) $K_{eq} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$

   (b) $K_{eq} = \frac{[CaCl_2][CO_2]}{[HCl]^2}$ Ignore $CaCO_3$ (solid) and H_2O (pure liquid). $[HCl]^2$ due to coefficient