CHEM1612 Worksheet 5: Kinetics and Mechanisms

Model 1: Elementary Steps

In worksheet 10, you studied the rate law. The rate law shows us how the rate of a reaction is effected by the concentration of the reactants and you worked out the rate law from experimental measurements.

Most reactions occur at the molecular level through a sequence of one of more events called **elementary steps**. Only two types of elementary step are important:

- a unimolecular step: a bond breaks in a molecule
- a bimolecular step: two molecules collide leading to one or more bonds being broken or made.

Critical thinking questions

1. An example of a unimolecular step is the decomposition of bromine: $Br_2(g) \rightarrow Br(g) + Br(g)$
   (a) If the number of Br_2 molecules is *doubled*, what will happen to the rate?
   (b) If $[Br_2(g)]$ is *doubled*, what will happen to the rate?
   (c) What is the rate law for this step? (Is the rate proportional to $[Br_2(g)]$, $[Br_2(g)]^2$ or $[Br_2(g)]^3$?)

2. An example of a bimolecular step is the reaction between H and Br_2: $H(g) + Br_2(g) \rightarrow HBr(g) + Br(g)$
   (a) If the number of Br_2 molecules is *doubled*, what will happen to the number of collisions that occur between H and Br_2?
   (b) If the number of H atoms is *doubled*, what will happen to the number of collision that occur between H and Br_2?
   (c) If the rate is proportional to the number of collisions, what is the rate law for this step?

3. An example of a bimolecular step is the reaction of NO with itself: $NO(g) + NO(g) \rightarrow N_2O_2(g)$
   (a) If the number of NO molecules is *doubled*, what will happen to the number of collisions that occur between NO molecules?
   (b) If the rate is proportional to the number of collisions, what is the rate law for this step?

Model 2: A Multi-Step Mechanism

Because each step in a mechanism is either a unimolecular or bimolecular step, you can write the rate law down as you did in Model 1:

- a unimolecular step involves only one molecule so the rate is proportional to its concentration:

  rate = $k_1[Br_2(g)]$

- a bimolecular step involves two molecules colliding so the rate is proportional to the concentration of each:

  rate = $k_2[H(g)][Br_2(g)]$

  rate = $k_3[NO(g)][NO(g)] = k_3[NO(g)]^2$

Each rate constant is different: some elementary steps have high values of k and are fast and some elementary steps have low values of k and are slow. For a reaction involving more than one step, the overall rate is determined by the slowest or *rate determining step*.

We cannot see how the molecules react. When trying to work out the mechanism of a reaction, the process is to (i) propose what it might look like, (ii) work out by the rate law for this guess and (iii) compare this rate law with that determined experimentally. The experimental rate law will only involve the concentration of chemicals that can be varied experimentally, so will only involve reactants. **No intermediates should appear in the rate law.**

Critical thinking questions

1. The reaction between NO_2 and O_3 is proposed to proceed through 3 steps:

$NO_2 + O_3 \rightarrow NO_3 + O_2$ — k_1; slow

$NO_3 + O_2 \rightarrow NO_2 + O_3$ — k_2; fast

$NO_3 + NO_2 \rightarrow N_2O_5$ — k_3; fast

(a) Which is the rate determining step?

(b) What is the rate law for the reaction?

2. The conversion of ozone to molecular oxygen in the upper atmosphere is proposed to proceed via 2 steps:

$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ — fast equilibrium

$O + O_3 \rightarrow 2O_2$ — k_2; slow

(a) Which is the rate determining step?

(b) What is the rate law for this step?

(c) If the first step is very fast compared to the second, it will have time to reach equilibrium. What is the equilibrium constant in terms of $[O_3]$, $[O_2]$ and $[O]$?

equilibrium constant = K = ———

(d) Using your answer to (c), what is [O]?

(e) Substitute your answer to (d) into your rate law from (b) to obtain a rate law that does not involve any intermediates.

(f) If the first step is at equilibrium, what are the relative rates of the forward and backward reaction?

(g) By first writing down the rate laws for the forward and backward reactions in the first step, find a relationship between the rate constants k_1 and k_{-1} and the equilibrium constant K.

3. The reaction between NO and O_2 gives NO_2. By varying [NO] and $[O_2]$, the rate law has been found to be:

rate = $k[NO]^2[O_2]$

It is proposed that the reaction proceeds through 2 steps:

$NO(g) + NO(g) \rightleftharpoons N_2O_2$ — fast equilibrium

$N_2O_2(g) + O_2 \rightarrow 2NO_2(g)$ — k_2; slow

Is this mechanism consistent with the experimental rate law?