Lecture Notes BB: Chemical Kinetics I

Distributed on Monday, April 10, 2000

1. Definition of the rate

reaction rate = (change in concentration)/ (change in time)

A+B --> C+D

$$\text{rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

units for the rate are (concentration)/time = (moles/liter)/sec = M/s

Consider the reaction:

$2\ NO_2(g) + F_2(g)$ ---> $2\ NO_2F\ (g)$

Which of the following is correct?

a) $\text{rate} = -\frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{d[F_2]}{dt} = \frac{1}{2}\frac{d[NO_2F]}{dt}$ b) $\text{rate} = -\frac{d[NO_2]}{dt} = -\frac{1}{2}\frac{d[F_2]}{dt} = \frac{d[NO_2F]}{dt}$

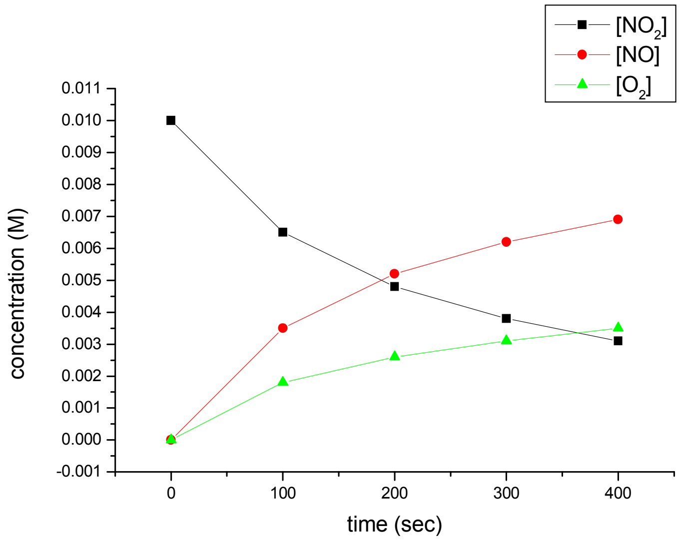
In general:

2. Initial rate

Consider the reaction: $2NO_2(g) \text{--->} 2NO(g) + O_2(g)$

The following table shows the concentration of the above species for an experiment that starts with 0.01M NO_2.

time (s)	$[NO_2]$	[NO]	$[O_2]$
0	0.0100	0	0
100	0.0065	0.0035	0.0018
200	0.0048	0.0052	0.0026
300	0.0038	0.0062	0.0031
400	0.0031	0.0069	0.0035



What is the initial rate of the reaction?

What is the rate 300-400 seconds into the reaction?

3. Definition of the order of a reaction

A + B --> C + D

When you change the concentration of a reactant, you change the rate of the reaction according to:

rate = $k [A]^m [B]^n$

The reaction is m^{th} order in [A] and n^{th} order in [B]. The reaction has a total order of (m+n)

Another experiment is performed on the reaction from page 2: $2NO_2(g) \text{ ---> } 2NO(g) + O_2(g)$
The data is shown below. What is the order of the reaction in $[NO_2]$?

time (s)	$[NO_2]$	[NO]	$[O_2]$
0	0.0050	0	0
100	0.0041	0.00087	0.0017

Concept test: If changing the concentration of a reactant, [A], has no effect on the rate of a reaction, what is the order of the reaction in [A].

a) -1 b) 0 c) 1/2 d) 1

Consider the following reaction: $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$

You do five experiments, measuring the initial rate for a variety of initial concentrations.

initial concentrations	[CO](M)	$[NO_2]$(M)	Initial rate (M/hr)
a	5.1×10^{-4}	3.5×10^{-5}	3.4×10^{-8}
b	5.1×10^{-4}	7.0×10^{-5}	6.8×10^{-8}
c	5.1×10^{-4}	1.8×10^{-5}	1.7×10^{-8}
d	10.2×10^{-4}	3.5×10^{-5}	6.8×10^{-8}
e	15.3×10^{-4}	3.5×10^{-5}	10.2×10^{-8}

a) Derive the rate expression.

b) What is the order of the reaction?

c) Calculate the rate constant

d) Calculate the rate for the following conditions

initial concentrations	[CO](M)	[NO_2](M)	Initial rate (M/hr)
	$1.4x10^{-4}$	$2.1x10^{-5}$	

Concept:

For the reaction A(g) + B(g) --> AB(g), the rate is 0.20 M/s when [A] = [B] = 1.0 M. The reaction is first order in B and second order in A. What is the rate when [A] = 2.0M and [B] = 3.0M.

a) 1.2M/s b) 2.4 M/s c) 3.6M/s

4. Integrated rate laws:

First order reaction: N_2O_4 --> 2 NO_2

Concept test: The half life for the radioactive decay of ^{32}P is 14 days. You start with 1.000g of ^{32}P. How many grams are left after 3*14 = 42 days.

a) 0.100g b) 0.125g c) 0.25g d) 0.333g

Second order reaction: $2\ NO_2 \rightarrow 2\ NO + O_2$

For the simple decomposition reaction: AB(g) --> A(g) + B(g), the rate = k[AB]^2. If it takes 5 minutes for [AB] to reach one-third of its initial concentration of 1.5M, what is k (assume you can ignore the reverse reaction)?