RATE LAWS

- Consider the general reaction: aA + bB → products where A and B are the reactants and a and b are the coefficients

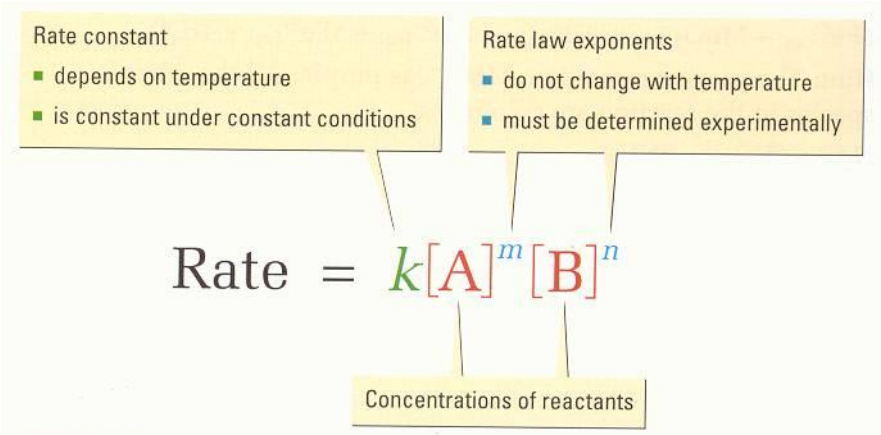


Figure 6.5 This diagram explains the components of the rate law.

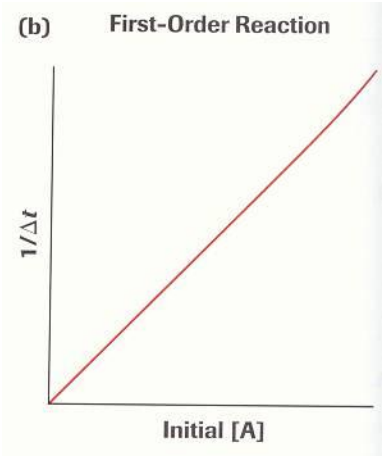
- The values of the exponents in the rate law equation establish the order of the reaction

- Look at this theoretical reaction: 2X + 2Y + 3Z → products
  - Experimental data gives us rate = k $[X]^1$ $[Y]^2$ $[Z]^0$
    - The order of reaction with respect to X is 1
    - The order of reaction with respect to Y is 2
    - The order of reaction with respect to Z is 0
    - The overall order of reaction is 3 (1 + 2 + 0)

    - Because rate α $[X]^1$:
      If initial [X] doubles; rate is multiplied by 2
      If initial [X] increases by 5, rate is multiplied by 5
    - Because rate α $[Y]^2$:
      If initial [Y] doubles; rate is multiplied by 4 (2^2)
      If initial [Y] increases by 5; rate is multiplied by 25 (5^2)
    - Because rate α $[Z]^0$:
      If initial [Z] doubles; rate is multiplied by 1 (2^0) = rate remains unchanged

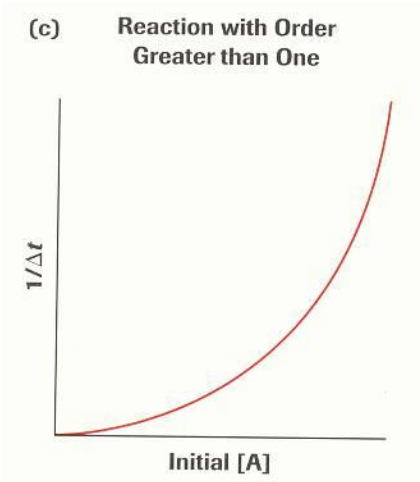
- A first order reaction has an overall order of 1
  - $2N_2O_5(g) \rightarrow 4NO_2(g) + 5O_2(g)$
    rate = $k[N_2O_5]^1$

  - $(CH_3)_3CBr(aq) + H_2O(l) \rightarrow (CH_3)_3OH(aq) + H^{+1}(aq) + Br^{-1}(aq)$
    rate = $k\,[(CH_3)_3CBr]^1[H_2O]^0$



- a second order reaction has an overall reaction order of 2
  - $2HI(g) \rightarrow H_2(g) + I_2(g)$
    rate = $k[HI]^2$

  - $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$
    Rate = $k\,[NO]^1\,[O_3]^1$



- The rate constant and exponents in a rate law can only be determined experimentally

To find the rate law:

1. Determine the exponents for each reactant
   (if there is more than one reactant, you must determine one exponent at a time by making sure the other [reactant] doesn't change)

eg1) $2N_2O_5(g) \rightarrow 4NO_2(g) + 5O_2(g)$

Experiment	Initial $[N_2O_5]$ (mol/L)	Initial rate (mo/L*s)
1	0.01	$4.8*10^{-6}$
2	0.02	$9.6*10^{-6}$
3	0.03	$1.5*10^{-5}$

General rate law: rate = $k[N_2O_5]^m$

$\frac{rate2}{rate1} = \frac{\cancel{k}[0.02]^m}{\cancel{k}[0.01]^m} = \frac{9.6*10^{-6}}{4.8*10^{-6}}$ $\quad 2^m = 2 \quad$ therefore m = 1

rate = $k[N_2O_5]^1$

eg2) $2ClO_2(aq) + 2OH^{-1}(aq) \rightarrow ClO_3^{-1}(aq) + ClO_2^{-1}(aq) + H_2O(l)$

Experiment	Initial $[ClO_2]$ (mol/L)	Initial $[OH^{-1}]$ (mol/L)	Initial Rate (mol/L*s)
1	0.015	0.025	$1.3*10^{-3}$
2	0.015	0.05	$2.6*10^{-3}$
3	0.045	0.025	$1.16*10^{-2}$

General rate law: rate = $k[ClO_2]^m [OH^{-1}]^n$

$\frac{Rate2}{Rate1} = \frac{\cancel{k[0.015]^m} [0.05]^n}{\cancel{k[0.015]^m} [0.025]^n} = \frac{2.6*10^{-3}}{1.3*10^{-3}}$ $\quad 2^n = 2 \quad$ n = 1

$\frac{Rate3}{Rate1} = \frac{k[0.045]^m \cancel{[0.025]^n}}{k[0.015]^m \cancel{[0.025]^n}} = \frac{1.16*10^{-2}}{1.3*10^{-3}}$ $\quad 3^m = 9 \quad$ m = 2

rate = $k[ClO_2]^2 [OH^{-1}]^1$

2. Find the value of the rate constant by substituting data from any of the experiments into the rate law equation.

Eg1) rate = $k[N_2O_5]^1$, sub in exp. #1 in exp #1

$4.8*10^{-6} = k[0.01]^1 [0.025]^1$

$k = 4.8*10^{-4}\ s^{-1}$

rate = $4.8*10^{-4}\ s^{-1}\ [N_2O_5]^1$

Eg2) rate = $k[ClO_2]^2 [OH^{-1}]^1$, sub

$1.3*10^{-3} = k[0.015]^2$

$k = 231\ L^2/mol^2*s$

rate = $231\ L^2/mol^2*s\ [ClO_2]^2\ [OH^{-1}]^1$

The following data was obtained for the reaction: $(CH_3)_3CBr + OH^{-1} \rightarrow (CH_3)_3COH + Br^{-1}$ at 55°C. What is the rate law of this reaction? What is the value of the rate constant at this temperature?

$[(CH_3)_3CBr]$	$[OH^{-1}]$	Initial Rate of Reaction mol/L*s
0.1	0.1	0.001
0.2	0.1	0.002
0.3	0.1	0.003
0.1	0.2	0.001
0.1	0.3	0.001

The formation of small amounts of nitric oxide, NO_2, in automobile engines is the first step in the formation of smog. Nitric acid is readily oxidized to nitrogen dioxide by the reaction: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$. The following data was collected in a study of the rate of this reaction. What is the rate law and value of the rate constant?

[NO]	$[O_2]$	Rate of Formation of NO_2
0.001	0.001	7.1
0.001	0.004	28.4
0.003	0.004	255.6

What is the rate law for this reaction? Determine the value of the rate constant.

[OCl]	$[I^{-1}]$	Rate of Formation of Cl^{-1}
0.0017	0.0017	0.000175
0.0034	0.0017	0.00035
0.0017	0.0034	0.00035

At a certain temperature, the following data was collected for the reaction: $2ICl + H_2 \rightarrow I_2 + 2HCl$. Determine the overall rate law for this reaction.

[ICl]	$[H_2]$	Rate of Formation of I_2
0.1	0.1	0.0015
0.2	0.1	0.003
0.1	0.05	0.00075

Calculate the overall rate law for a reaction given the following data:

[A]	[B]	Rate of Formation
0.1	0.1	0.2
0.2	0.1	0.4
0.3	0.1	0.6
0.3	0.2	2.40
0.3	0.3	5.40