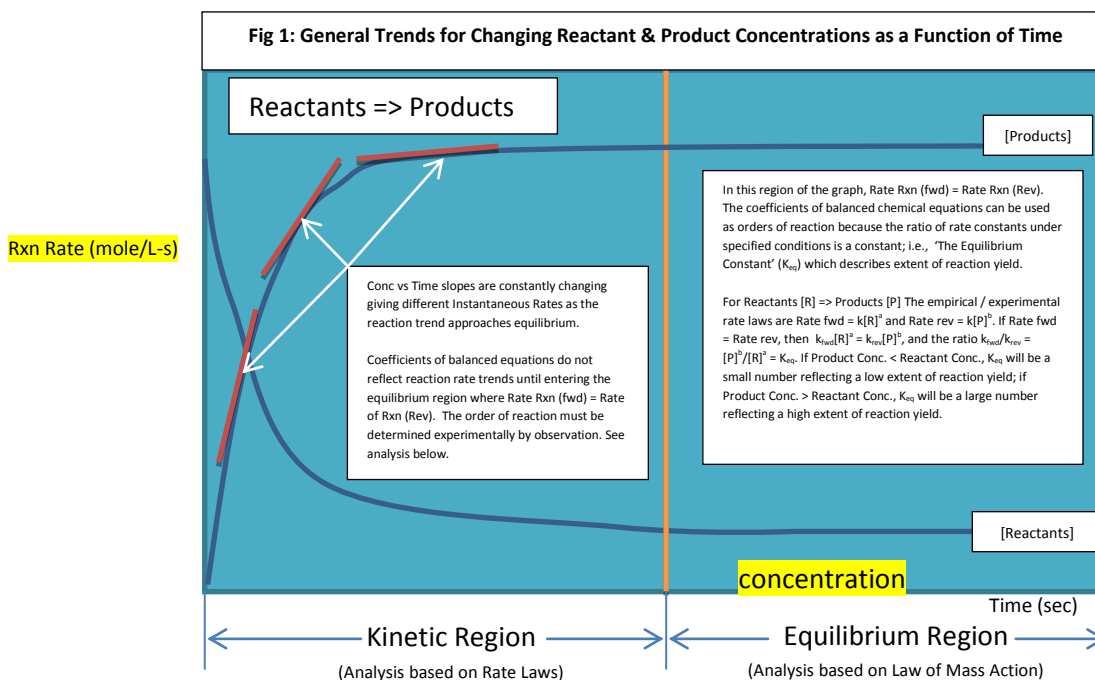


## ORDER OF REACTION – RATE TRENDS

The 'order of reaction' is a reflection of a reaction's rate trend from initiation until reaching equilibrium. The order of reaction can be whole numbers, fractions or negative numbers. However, most texts will give Kinetics problems that use positive whole numbers. Visualize a simple decomposition reaction  $A \Rightarrow \text{Products}$ . Mentally think of the reactant at time  $t = 0$  being like a horse in the starting gate ready to run a race. At that moment before the starting gate opens, there is no product and 100% reactant. Now, open the gate (mentally) and let the horse/reaction run. You would expect the concentration of reactant to decrease with respect to time while the concentration of product increases with time. (See figure 1)

Fundamentally, the numerical rate of product formation and reactant consumption will steadily change until reaching a dynamic equilibrium, much like the running horse reaching its maximum speed. The difference is the horse accelerates to its max speed, but a chemical reaction's speed decreases until the equilibrium is reached. The fastest kinetic rate of a chemical reaction is right at initiation at at time  $t$  just barely after time  $t = 0$ . Since the issue is 'rate of reaction' then identifying the rate at any given point between start and reaching equilibrium would be calculation of the instantaneous rate of reaction. Now, instantaneous rate of reaction at a given point is mathematically the tangent line to the selected point. As time increases the tangent line on the product growth trend changes from vertical (slope = 1) at  $t \sim 0$  seconds to horizontal (slope = 0) at time reaching equilibrium. Now, some reactions go faster than others from zero time to equilibrium time. The rate trends demonstrated as a function of changing concentration of reactant is the order of reaction. Since reactions differ on rates to reaching equilibrium, the order of the reaction cannot be determined theoretically, but must be done experimentally by physically measuring the changes in concentration of one of the reaction components as a function of time. From the observed rate trend, an order of reaction is assigned. This can be illustrated graphically on a plot of Rate vs Concentration of Reactant. (See Table 1 & figure 2).

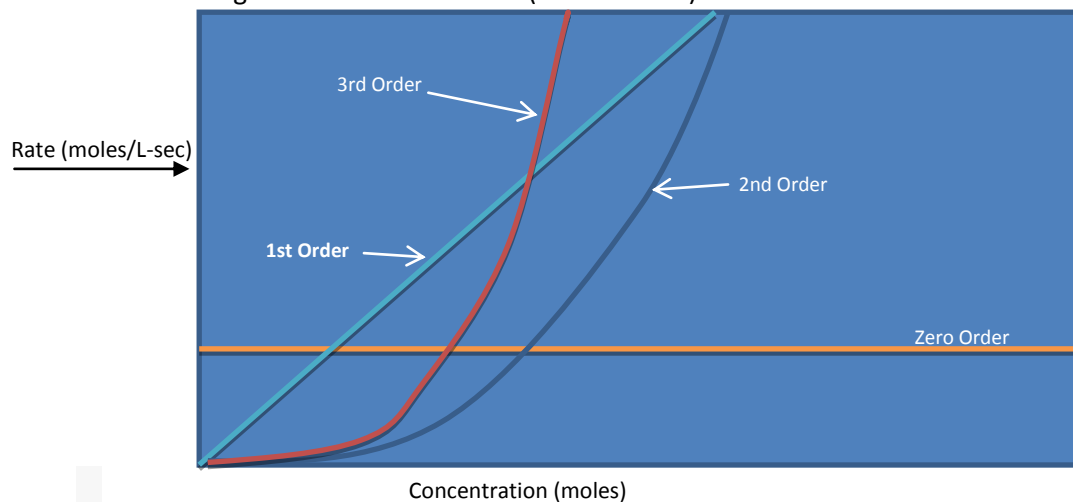


Given a simple hypothetical reaction,  $A \Rightarrow \text{Products}$ , define the empirical rate trends for zero, 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> order reactions.

The empirical rate law is  $\text{Rate} = k[A]^x$ ; Let  $x = 0, 1, 2, 3$  and note rate trends for concentrations  $[A] = a, 2a, 3a, 4a$ , etc.

TABLE 1 – Rate Trends	a (Reference Concentration)	2a	3a	4a
Rate(zero order) = $k[A]^0$ (See yellow graph below)	Rate(1) = $k(a)^0 = k$ (Reference Rate)	Rate(2a) = $k(2a)^0 = k$ (Dbl Conc => Rate Chg = 0)	Rate(3a) = $k(3a)^0 = k$ (Trpl Conc => Rate Chg = 0)	Rate(4a) = $k(4a)^0 = k$ (Quadpl Conc => Rate Chg = 0)
Rate(1 <sup>st</sup> order) = $k[A]^1$ (See light blue graph below)	Rate(1) = $k(a)^1 = ka$ (Reference Rate)	Rate(2a) = $k(2a)^1 = 2ka$ (Dbl Conc => Rate Chg = 2x)	Rate(3a) = $k(3a)^1 = 3ka$ (Trpl Conc => Rate Chg = 3x)	Rate(4a) = $k(4a)^1 = 4ka$ (Quadpl Conc => Rate Chg = 4x)
Rate(2 <sup>nd</sup> order) = $k[A]^2$ (See red graph below)	Rate(1) = $k(a)^2 = ka^2$ (Reference Rate)	Rate(2a) = $k(2a)^2 = 4ka^2$ (Dbl Conc => Rate Chg = 4x)	Rate(3a) = $k(3a)^2 = 9ka^2$ (Trpl Conc => Rate Chg = 9x)	Rate(4a) = $k(4a)^2 = 16ka^2$ (Quadpl Conc => Rate Chg = 16x)
Rate(3 <sup>rd</sup> order) = $k[A]^3$ (See red graph below)	Rate(1) = $k(a)^3 = ka^3$ (Reference Rate)	Rate(2a) = $k(2a)^3 = 8ka^3$ (Dbl Conc => Rate Chg = 8x)	Rate(3a) = $k(3a)^3 = 27ka^3$ (Trpl Conc => Rate Chg = 27x)	Rate(4a) = $k(4a)^3 = 64ka^3$ (Quadpl Conc => Rate Chg = 64x)

Fig 2 - Kinetic Rate Trends (Order of Rxn) as a Function of Concentration



Example Problem:

In a study of the reaction  $2\text{NO}(g) + \text{O}_2(g) \Rightarrow 2\text{NO}_2(g)$  the following data were obtained for selected concentrations of  $\text{NO}(g)$  and  $\text{O}_2(g)$ :

Experiment	$[\text{NO}(g)]_{\text{initial}}$ (mole/L)	$[\text{O}_2(g)]_{\text{initial}}$ (mole/L)	Initial Rxn Rate (mol/L-s)
1	0.0125	0.0253	0.0281
2	0.0250	0.0253	0.1120
3	0.0125	0.0506	0.0561

Determine the experimental rate law and the reaction's rate constant.

Solution:

Hold one component at constant concentration and vary the concentration of the other. Then note change of rate as function of changing concentration. Compare to standard rate trends for match assign numerical order of reaction. Insert numerical orders of reaction into rate law, solve for k. Substitute concentration values for any one of the experiments to obtain the rate constant. The rate constant (k) will be the same for all experiments.

Order of Rxn as a function of changing NO(g) concentration while holding O<sub>2</sub>(g) concentration constant. (Comparing Exps 1 & 2)

Experiment		[NO(g)] <sub>initial</sub> (mole/L)		[O <sub>2</sub> (g)] <sub>initial</sub> (mole/L)	Initial Rxn Rate (mol/L-s)
1	Dbl Conc →	0.0125	Held constant →	0.0253	0.0281
2		0.0250		0.0253	0.1120
3		0.0125		0.0506	0.0561

Reaction Rate increases 4x  
=> 2<sup>nd</sup> order with respect  
to NO(g)

Rate Trend for 2<sup>nd</sup> order rxns = 1, 4, 9, 16 (See table 1)

Order of Rxn as a function of changing O<sub>2</sub>(g) concentration while holding NO(g) concentration constant. (Comparing Exps 1 & 3)

Experiment		[NO(g)] <sub>initial</sub> (mole/L)		[O <sub>2</sub> (g)] <sub>initial</sub> (mole/L)	Initial Rxn Rate (mol/L-s)
1	Held constant →	0.0125	Dbl Conc →	0.0253	0.0281
2		0.0250		0.0253	0.1120
3		0.0125	0.0506	0.0561	

Reaction Rate Doubles  
Dbl'g conc. => 1st order  
with respect to O<sub>2</sub>(g)

Inserting numerical order of reaction values => Rate = k[NO(g)]<sup>2</sup>[O<sub>2</sub>(g)] and solving for k:

$$k = \frac{\text{Rate}}{[\text{NO}(\text{g})]^2[\text{O}_2(\text{g})]}$$

$$k_1 = \frac{0.0281 \text{ mol/L-s}}{[0.0125 \text{ mol/L}]^2[0.0253 \text{ mol/L}]} = 7108 \text{ L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1} = 7100 \text{ L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$$

$$k_2 = \frac{0.1120 \text{ mol/L-s}}{[0.0250 \text{ mol/L}]^2[0.0253 \text{ mol/L}]} = 7083 \text{ L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1} = 7100 \text{ L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$$

$$k_3 = \frac{0.0561 \text{ mol/L-s}}{[0.0125 \text{ mol/L}]^2[0.0506 \text{ mol/L}]} = 7095 \text{ L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1} = 7100 \text{ L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$$

**Numerical Rate Law =>** Rate = 7100 L · mol<sup>-2</sup> · s<sup>-1</sup> [NO(g)]<sup>2</sup> [O<sub>2</sub>(g)]