



# **Equilibrium pt.2 acids and bases**

## Exercise #2

What is the pH of a solution of 0.50M of ammonium hypochlorite ( $\text{NH}_4\text{ClO}$ ) ?

$$K_{\text{a NH}_4^+} = 5.70 \times 10^{-10}$$

$$K_{\text{b ClO}^-} = 3.45 \times 10^{-7}$$



# Reaction Kinetics

# Class Goals

- Understand what is the rate of a reaction
- Understand the models that explain the rate of reaction
- Understand what can affect the rate of reaction

### 3.5. Kinetic study

Every adsorption process may follow one or their combination from different patterns such as chemical reaction, diffusion control and mass transfer. Analysis of experimental data at various time make possible to calculate the kinetic parameters, (helpful for the prediction of adsorption rate) and take some information for designing and modeling the adsorption processes. The modeling of the kinetics of present removal studies was investigated by evaluation and analysis of the removal rate to various conventional models like the Lagergren pseudo-first-order model (Eq. (12)) [39], Ho's pseudo-second-order model (Eq. (13)) [40], and the Elovich model (Eq. (14)) [41].

$$q = q_e(1 - e^{-k_1 t}) \quad (12)$$

$$q = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \quad (13)$$

$$q = \frac{1}{\beta \ln(1 + \alpha \beta t)} \quad (14)$$

**Table 3**

Kinetic parameters of MG adsorption onto ZnO-NP-AC conditions: 0.005 g adsorbent over 5–30 mg/L at optima conditions of other variables.

Parameter values: concentration dye (ppm)							
Models	Parameters	5	10	15	20	25	30
First order kinetic model: $\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t$	$k_1$	0.09811	0.0889	0.0847	0.0735	0.0647	0.0534
	$q_e$ (cal)	13.225	26.78	43.0427	65.1628	98.333	125.661
	$R^2$	0.9349	0.8976	0.8793	0.888	0.9145	0.8912
Second-order kinetic model: $t/q_t = 1/k_2 q_e^2 + (1/q_e)t$	$k_2 \times 10^2$	0.0282	0.0133	0.0082	0.0052	0.0031	0.0025
	$q_e$ (cal)	50	100	149.254	196.078	243.902	277.78
	$R^2$	0.9996	0.9996	0.9997	0.9993	0.9984	0.9969
	$H$	70.4225	133.33	181.82	200	185.185	196.078
Intraparticle diffusion $q_t = K_{id} t^{1/2} + C$	$K_{dif}$	3.473	7.496	12.21	16.928	22.629	26.486
	$C$	32.421	61.891	87.596	109.29	121	137.35
	$R^2$	0.6871	0.6833	0.7051	0.7178	0.7941	0.7772
Elovich $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$	$\beta$	0.2008	0.0927	0.0572	0.0416	0.0319	0.0273
	$R^2$	0.8656	0.8673	0.886	0.8882	0.9329	0.9139

concentrations and its efficiency for fitting and prediction of experimental data improves at higher MG concentrations [42]. The initial adsorption rates can be calculated from the pseudo-second-order model by the following equation:

$$h_{0,2} = k_2 q_e^2 \quad (15)$$

and the results are shown in Tables 3–6. The result notice that the initial adsorption rate increases with elevating the initial MG concentration and maximum value was obtained at maximum concentration. The initial increase in  $h_{0,2}$  probably attributed to enhance in the mass transport driving force emerged from higher ratio of MG molecules to reactive vacant adsorbent sites. At higher concentrations due to apparent MG dimerization [43,44] and difficult diffusion of large dimers in small adsorbent pores that cause to kinetic parameters worsened.

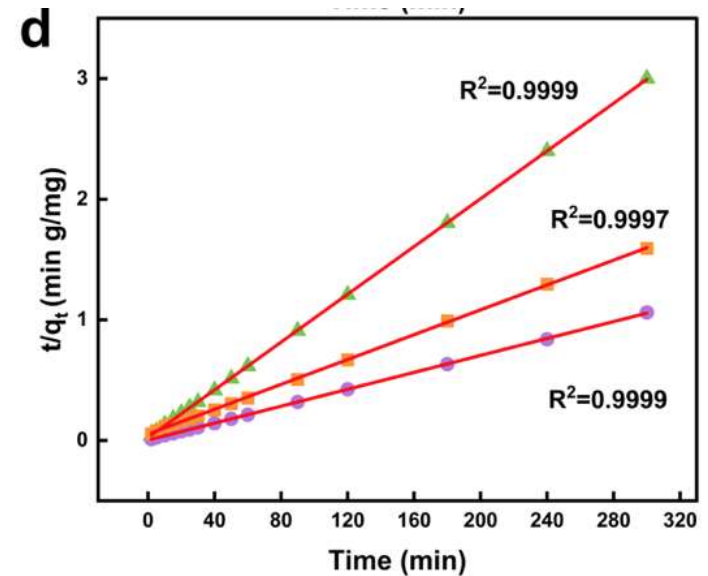
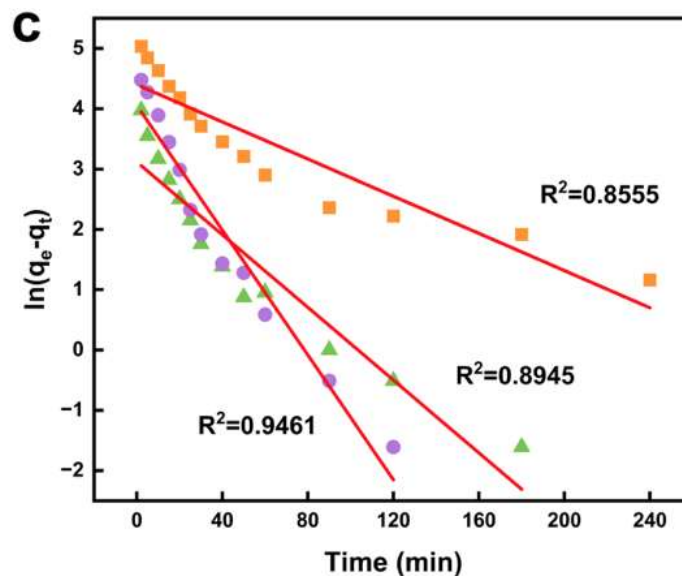
The slope and the intercepts of show the plots of  $\log(q_e - q_t)$  versus  $t$  used for calculation of  $k_1$  and  $q_e$  value and the numerical value of these parameters is shown in Tables 3–6. The difference between the  $q_{e,calc}$  to the experimental data ( $q_{e,exp}$ ) and low  $R^2$  values (Tables 3–6) for the Lagergren model at different



### 3.3.3 Adsorption kinetics

To further investigate the adsorption mechanism, the kinetics of the process was analyzed. Fig. 4a and b plot the evolution of removal efficiency with time for Fe<sub>3</sub>C-MCA (a) and Ag-Fe<sub>3</sub>C-MCA (b), tested with three different concentration of MG (200 mg/L, 100 mg/L and 50 mg/L). Both composites present fast adsorption capacity for MG; it is clear that the adsorption capacity increases rapidly during the first 30 min, and then increases slowly reaching adsorption equilibrium in approx. 60 min. The same fast behavior with removal efficiency > 90% below 30 min was found for other

magnetic composite  
time, the adsorption  
adsorbent, as report  
Pseudo-first-order  
to describe the proc  
Ag-Fe<sub>3</sub>C-MCA are



# Kinetics

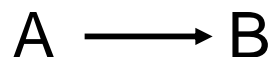
Studies the **rate** at which a chemical process occurs.

Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).

# Chemical Kinetics

Kinetics – how fast does a reaction proceed?

**Reaction rate** is the change in the concentration of a reactant or a product with time ( $M/s$ ).



$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$  = change in concentration of A over time period  $\Delta t$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$  = change in concentration of B over time period  $\Delta t$



# Chemical Kinetics

Kinetics – how fast does a reaction proceed?

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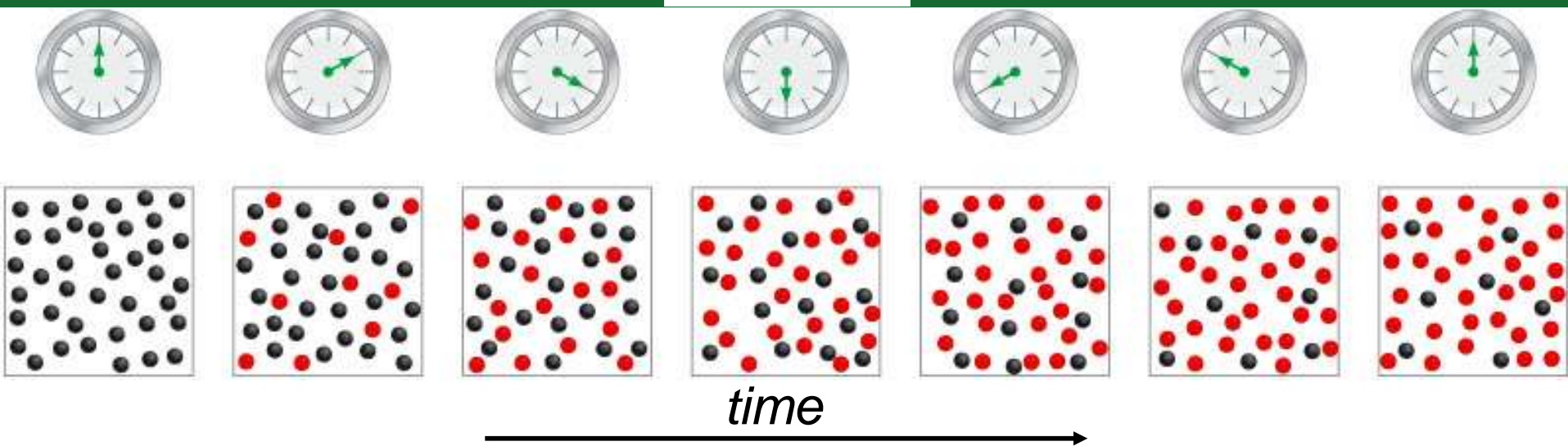
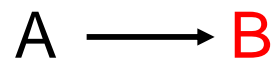
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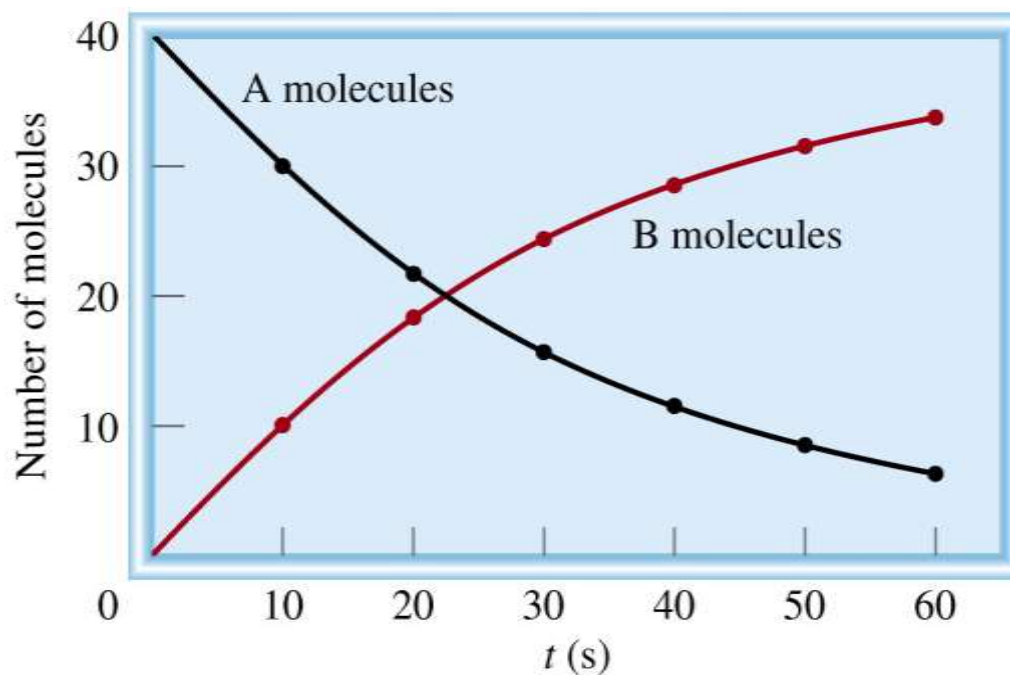
$\Delta[B]$  = change in concentration of B over time period  $\Delta t$

Because  $[A]$  decreases with time,  $\Delta[A]$  is negative.



$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



# Rate and Stoichiometry



Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

# Rate and Stoichiometry



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$$\text{rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

Reactants (decrease)

Products (increase)

# Rate and Stoichiometry

Write the general rate expression for the following reaction:



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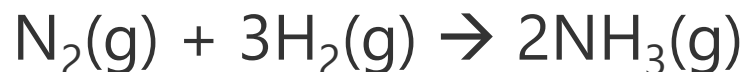
$$\text{rate} = -\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$





# Rate and Stoichiometry

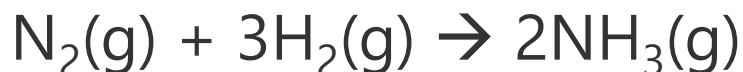
For the reaction



If the hydrogen disappearing rate is  $0.074 \text{ Ms}^{-1}$ ,  
what is the rate of ammonia production?

# Rate and Stoichiometry

For the reaction



If the hydrogen loss rate is  $0.074 \text{ Ms}^{-1}$ , what is the rate of ammonia production?

$$\begin{aligned}\text{Rate of reaction} &= -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} \\ \frac{d[\text{NH}_3]}{dt} &= -\frac{2}{3} \frac{d[\text{H}_2]}{dt} \\ &= \frac{2}{3} (0.074) \\ &= 0.0493\end{aligned}$$

# Rate and Stoichiometry

For the reaction:

YOU !



If the nitrogen oxide ( $\text{NO}_2$ ) rate is  $0.52 \text{ Ms}^{-1}$ , what is the rate of oxygen production?

$1.04 \text{ Ms}^{-1}$

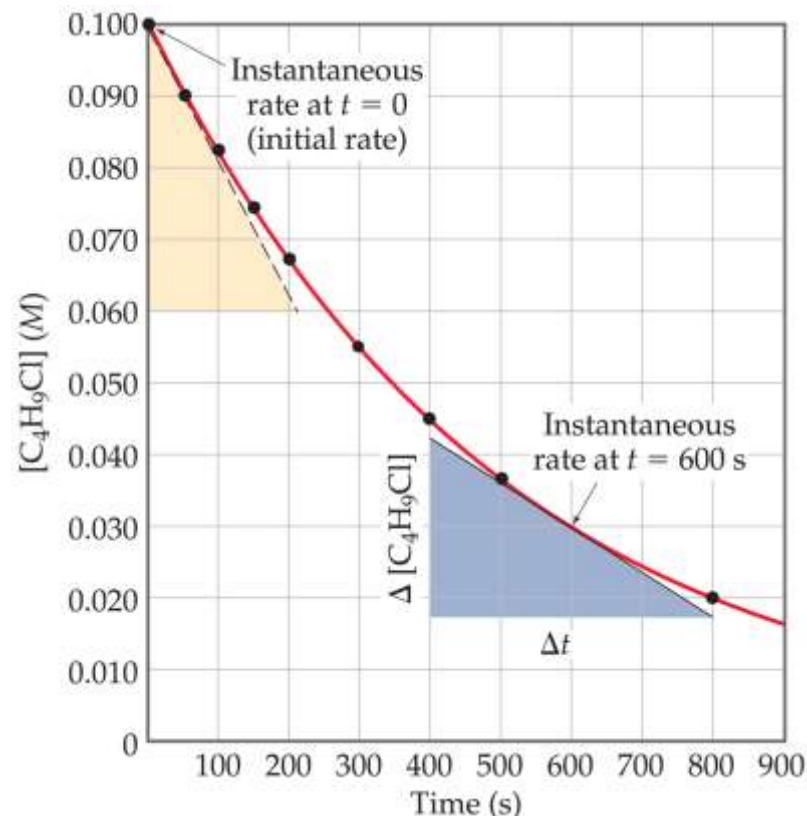
# Example of Reaction Rate



A **plot of concentration vs. time** for this reaction yields a curve.

The slope of a line tangent to the curve at any point is the **instantaneous rate** at that time.

$$\frac{d[A]}{dt}$$

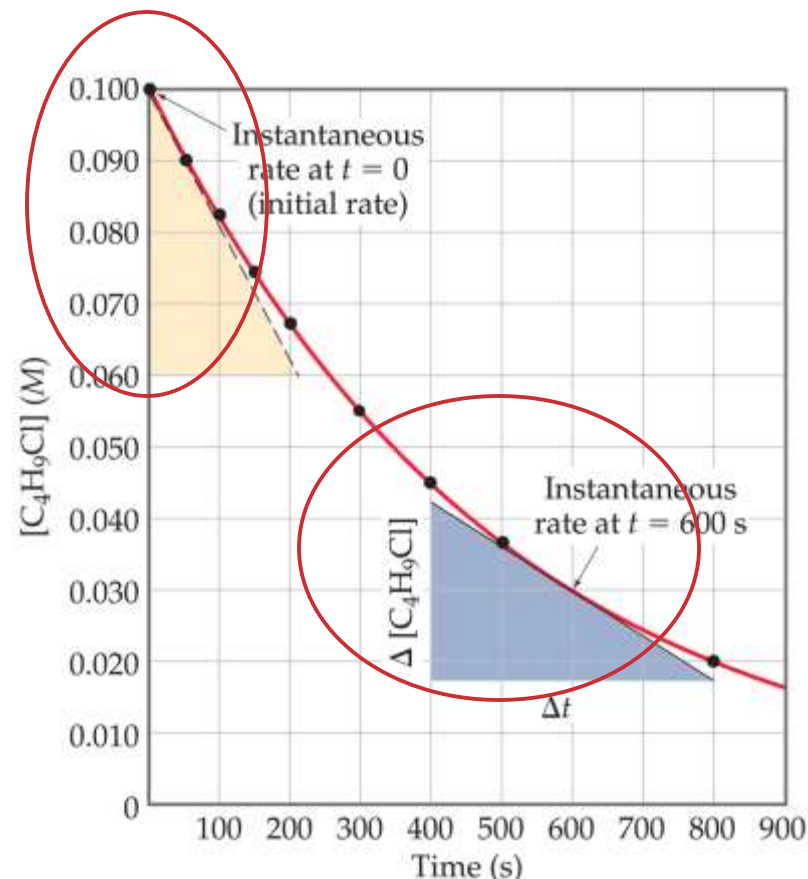


# Example of Reaction Rate



The reaction slows down with time because the concentration of the reactants decreases.

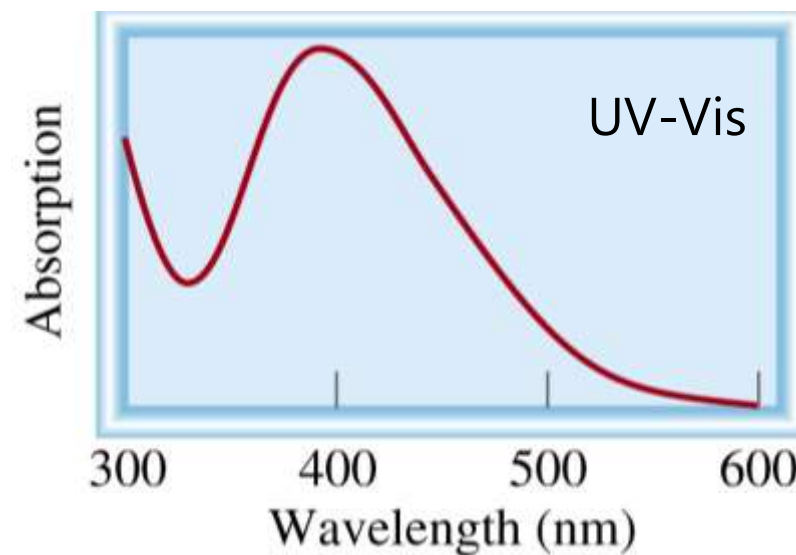
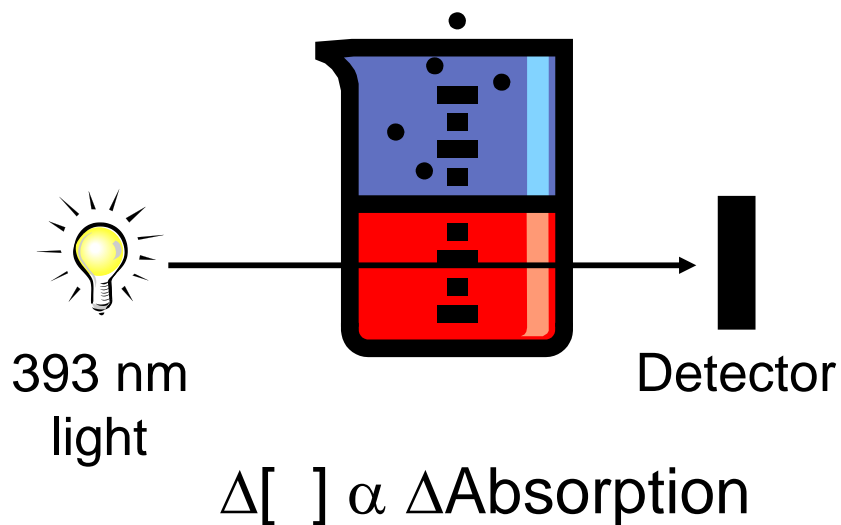
$$\text{Rate} = \frac{-d[\text{C}_4\text{H}_9\text{Cl}]}{dt} = \frac{d[\text{C}_4\text{H}_9\text{OH}]}{dt}$$



# How I monitor a reaction ?

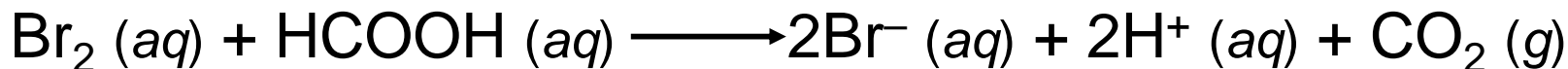


*time*

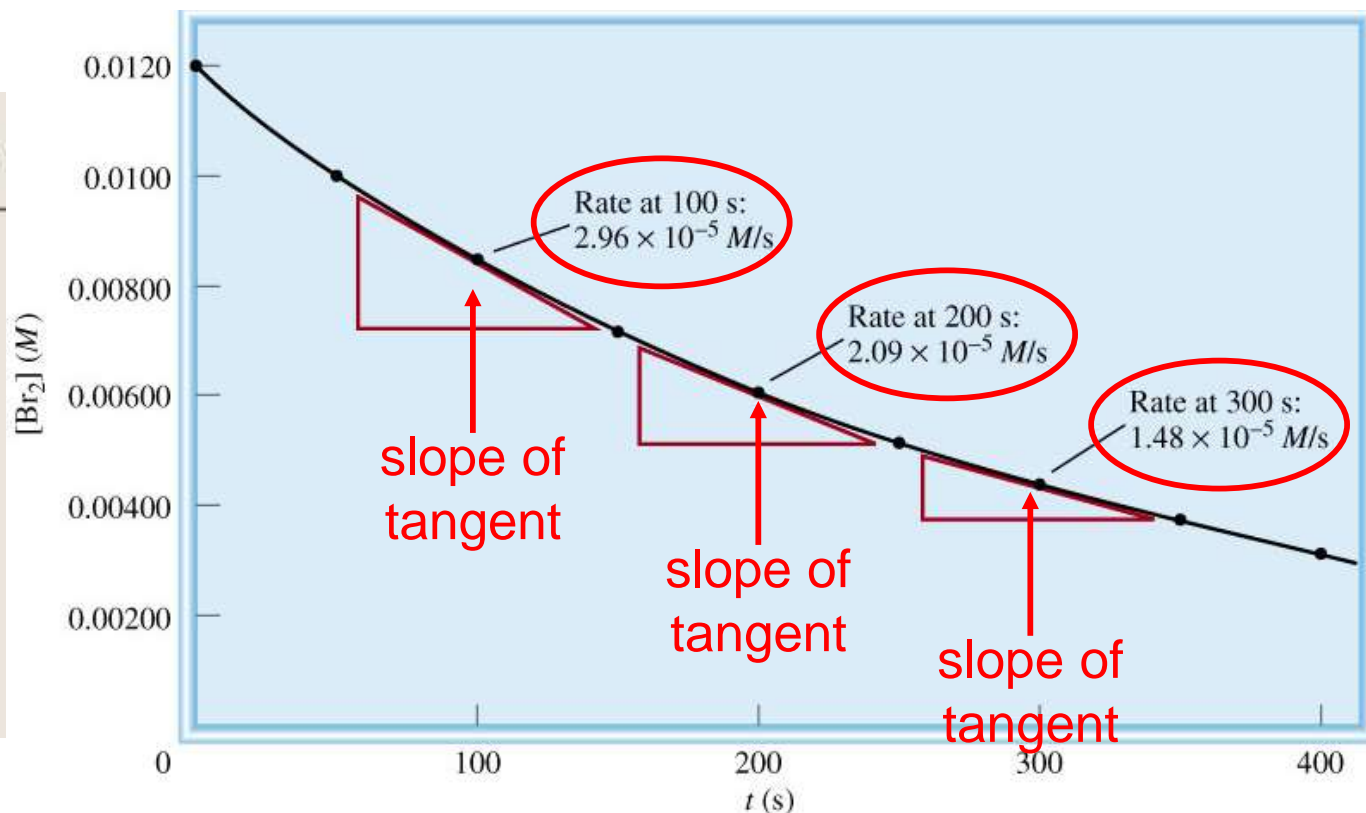




# How I monitor a reaction ?



Time (s)	[Br <sub>2</sub> ] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



The instantaneous rate changes with time: how we can compare one reaction with another? **RATE LAW** and **Constant**

# Rate Law

Each reaction has its own equation that expresses its **rate as a function of the initial concentrations** of the reactants.

This is called its **Rate Law**

# Rate Law

The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.


$$v = k [A]^m [B]^n \dots$$

- [A], [B]: reactant concentrations
  - The exponents  $m$  and  $n$ : **reaction order**
  - The constant  $k$ : **rate constant**
  - The **overall reaction order** is the sum of the reaction order:  $m + n$

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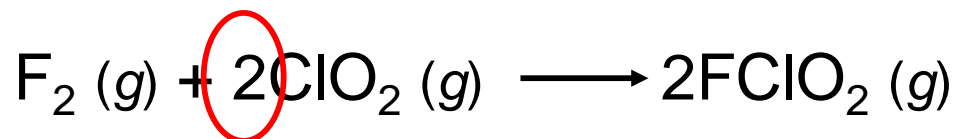
- [A], [B]: reactant concentrations
  - The exponents  $m$  and  $n$ : **reaction order**



"how much this particular reagent affect the total reaction speed"

# Rate Law

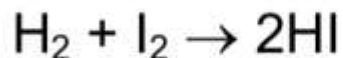
- Rate laws, rate constants, and orders are **determined experimentally**.
- Reaction order is **always** defined in terms of **reactant** (not product) concentrations.
- The order of a reactant is **NOT** generally related to its stoichiometric coefficient in a balanced chemical equation.



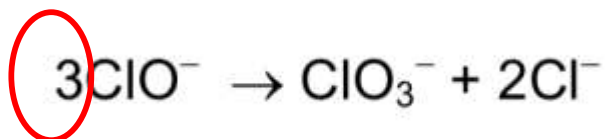
$$v = k [\text{F}_2][\text{ClO}_2]^1$$

# Rate Law Expressions

Reactions with **simple rate laws**:

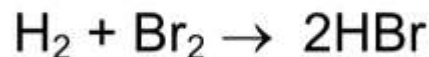


$$v = k [\text{H}_2][\text{I}_2].$$



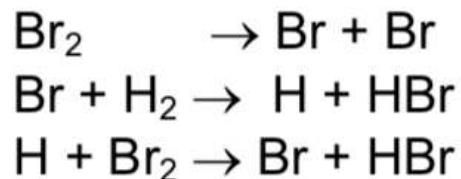
$$v = k [\text{ClO}^-]^2$$

Reactions with **complex rate laws**∗:



$$v = \frac{[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}]/[\text{Br}_2]}$$

∗ imply multi-step reactions (sequence of elementary steps)



Rate of reaction is  
linked to the  
mechanism (later)



# Rate Law Expressions

Reactant **order** reflects **molecularity**:

# of molecules involved in reaction

To determine the reactant order, we measure the rate at different starting concentrations.

# Rate Law Order

Different experiments with different initial concentrations

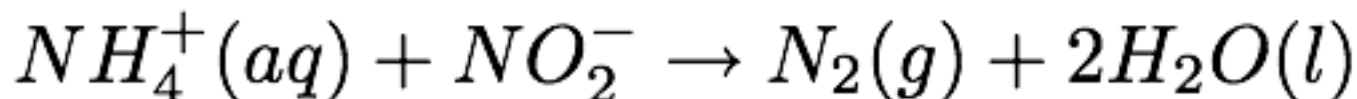
[A] (M)	Initial Rate (M , s)
0.10	0.025
0.20	0.025
0.40	0.025

The reaction rate is **not affected** by the initial amount of the reagent: it DOESN'T depend on it!!!  
It's constant!

$$\text{rate} = k[A]^0 \longrightarrow \text{rate} = k$$

# Rate Law Order

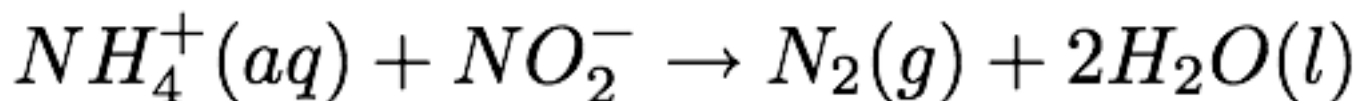
Experiment Number	Initial $\text{NH}_4^+$ Concentration (M)	Initial $\text{NO}_2^-$ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4 \times 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.0600	0.200	$32.3 \times 10^{-7}$
5	0.200	0.0202	$10.8 \times 10^{-7}$
6	0.200	0.0404	$21.6 \times 10^{-7}$
7	0.200	0.0606	$32.4 \times 10^{-7}$
8	0.200	0.0808	$43.3 \times 10^{-7}$



Compare Experiments 1 and 2:  
when  $[\text{NH}_4^+]$  **doubles**, the initial rate **doubles**.

# Rate Law Order

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Likewise, compare Experiments 5 and 6:  
when  $[\text{NO}_2^-]$  doubles, the initial rate doubles.

# Rate Law Order

$$\text{rate} \propto [\text{NH}_4^+]^1$$

$$\text{rate} \propto [\text{NO}_2^-]^1$$

$$\text{rate} \propto [\text{NH}_4^+] [\text{NO}_2^-]$$

$$\text{rate} = k [\text{NH}_4^+] [\text{NO}_2^-] \quad \text{rate law}$$

*First-order* in  $[\text{NH}_4^+]$

*First-order* in  $[\text{NO}_2^-]$

The overall reaction order: *second-order overall*.

# Order of Reactions

- A reaction is **zero order** if the change in concentration of that reactant produces no effect.
- A reaction is **1<sup>st</sup> order** if doubling the concentration causes the rate to double.
- A reaction is **2<sup>nd</sup> order** if doubling the concentration causes a quadruple increase in rate.
  - **3<sup>rd</sup> order**...doubling concentration leads to  $2^3$  (or 8 times) the rate.
  - extremely rare.



# Exercise

**TABLE 13.2**

**Rate Data for the Reaction Between  $F_2$  and  $ClO_2$**

$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)
1. 0.10	0.010	$1.2 \times 10^{-3}$
2. 0.10	0.040	$4.8 \times 10^{-3}$
3. 0.20	0.010	$2.4 \times 10^{-3}$

Determine x and y in the rate law  $\text{Rate} = k [F_2]^x [ClO_2]^y$

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The rate **doubles**

Therefore, **x = 1**

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**Quadruple**  $[ClO_2]$  with  $[F_2]$  held constant:

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The rate **quadruples**

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The rate law is

$$\text{Rate} = k [F_2]^1 [ClO_2]^1$$

# Exercise

Determine the rate law and calculate the rate constant:

Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial Rate (M/s)
1	0.08	0.034	$2.2 \times 10^{-4}$
2	0.08	0.017	$1.1 \times 10^{-4}$
3	0.16	0.017	$2.2 \times 10^{-4}$

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**Double  $[\text{I}^-]$ , rate doubles**

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**Double  $[\text{I}^-]$ , rate doubles**

**Double  $[\text{S}_2\text{O}_8^{2-}]$ , rate doubles**

$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/S}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08 \text{ M}^{-1}\cdot\text{s}^{-1}$$

# Rate Laws

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k [A]$	$\ln[A] = \ln[A]_0 - kt$
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rate = v =

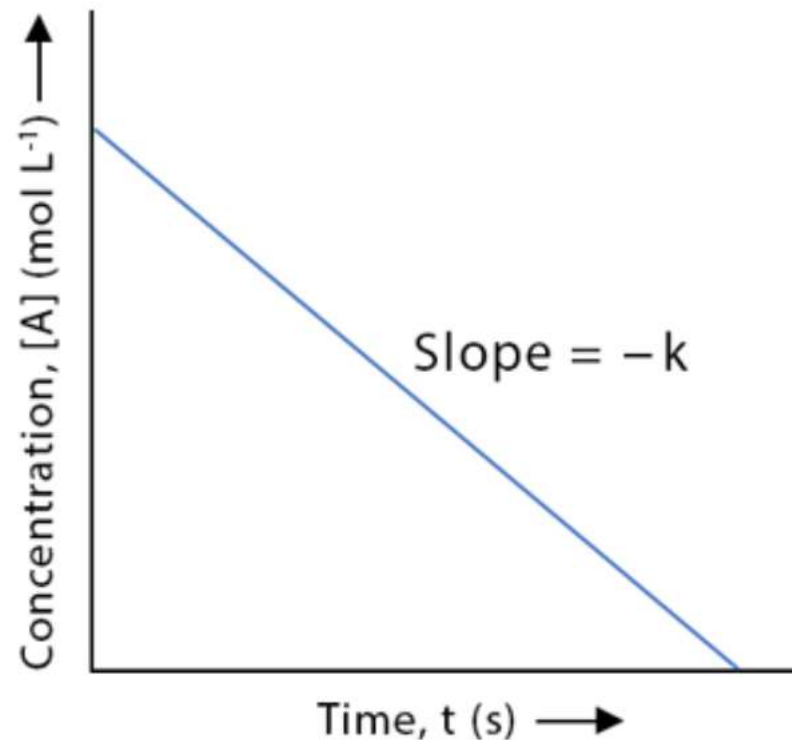
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To get info from the graphs !!!

# Rate Law Order

[A] (M)	Initial Rate (M , s)
0.10	0.025
0.20	0.025
0.40	0.025



$$[A] = [A]_0 - kt$$

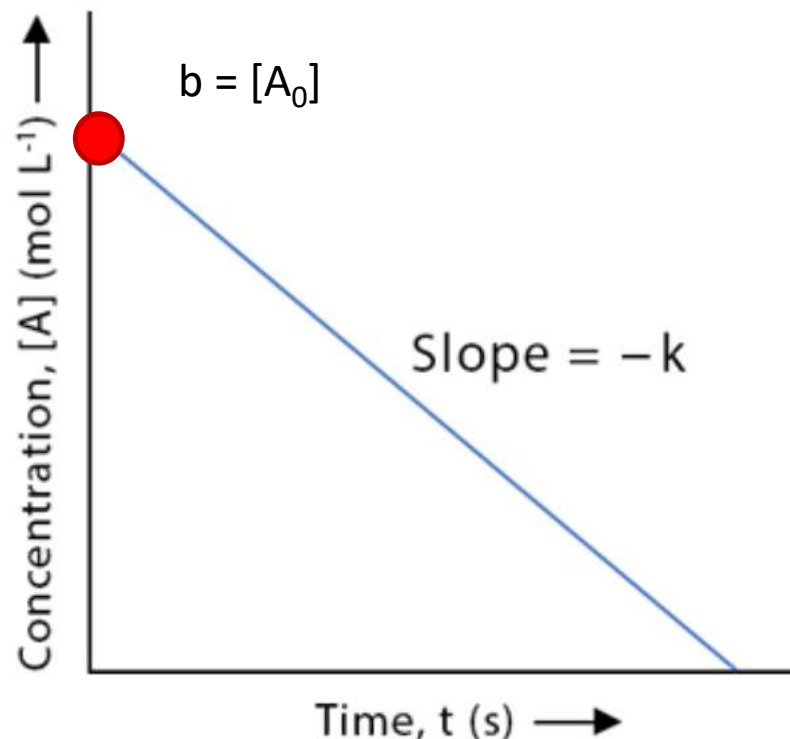
$$Y = b - mX$$

# Rate Law Order

[A] (M)	Initial Rate (M , s)
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If the graph of the concentration with time is a straight line, the kinetics of the reaction is zero-order

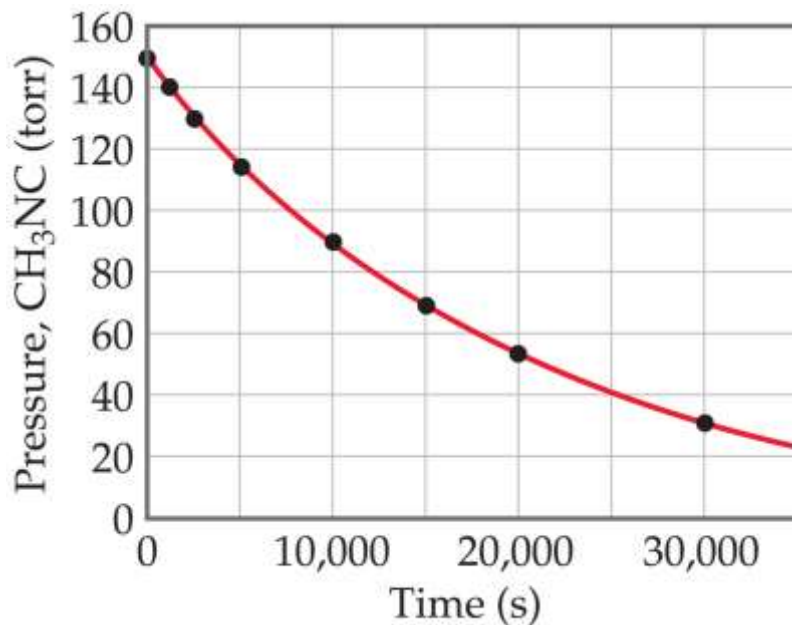
Measure units of  $k = \text{M/s}$



$$[A] = [A]_0 - kt$$

$$Y = b - mX$$

# First-Order Processes



Methyl isonitrile

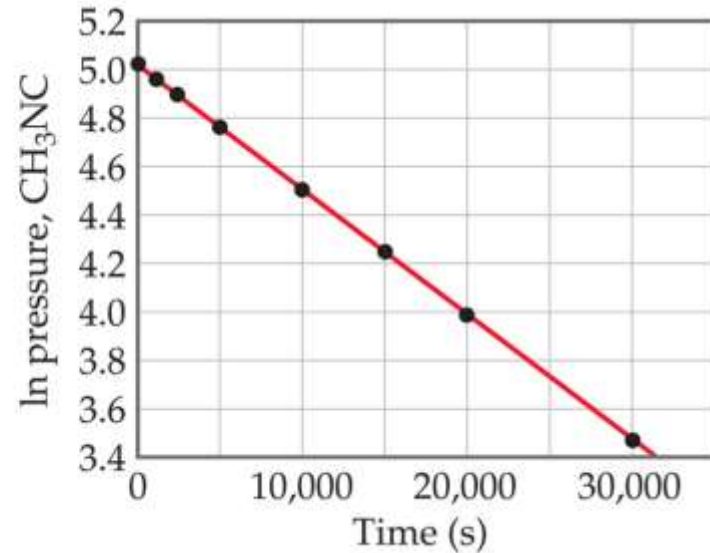
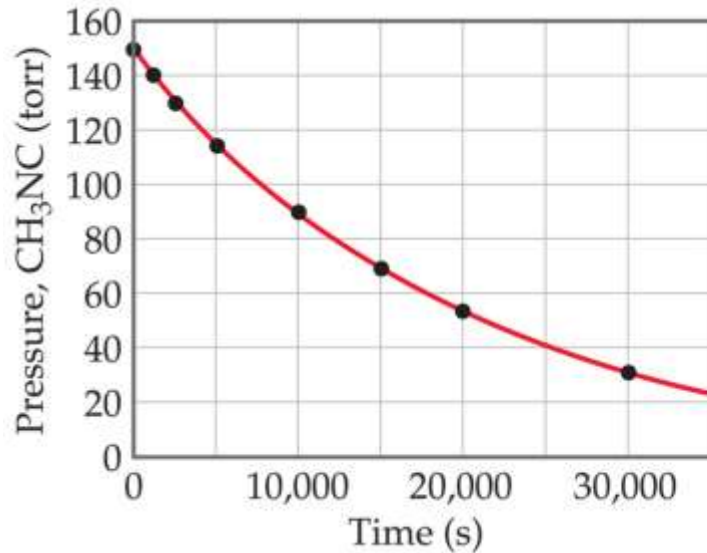


Acetonitrile

Is the rate the same for all time intervals?  
Difficult to extract information



# First-Order Processes



$$\frac{d[A]}{dt}$$

$$\ln [A]_t = -kt + \ln [A]_0$$

If I take the concentration values of A and do the logarithm and then plot → straight line !

# First-Order Processes

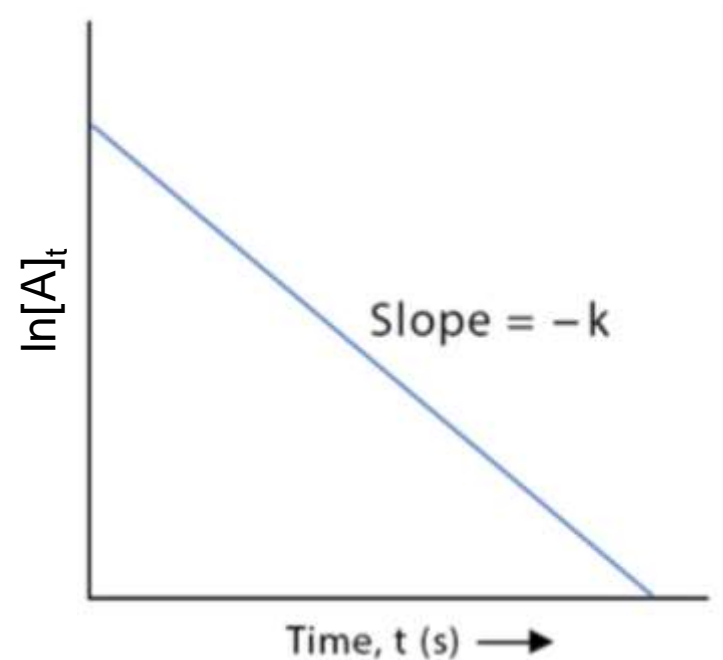
$$\ln[A]_t = -kt + \ln[A]_0$$

This equation has the general form for a straight line if you plot  $\ln[A]_t$  vs.  $t$

Slope =  $-k$

intercept  $\ln[A]_0$ .

Measure units of  $k = s^{-1}$



# Second-Order Processes

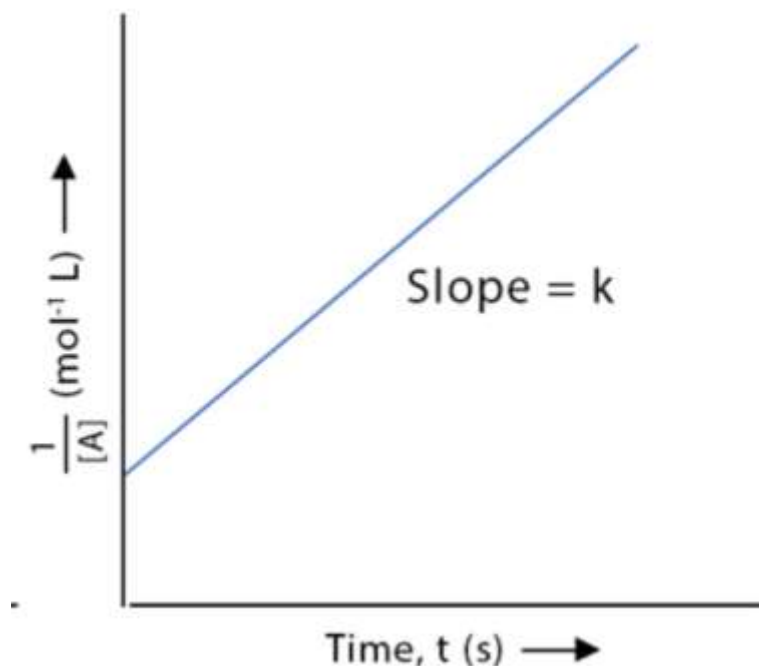
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

This equation has the general form for a straight line if you plot  $1/[A]_t$  vs.  $t$

Slope =  $-k$

intercept  $1/[A]_0$ .

Measure units of  $k = \text{M}^{-1}\text{s}^{-1}$



# Find order by graph

Zero                  first                  second

time	$\text{C}_2\text{H}_6\text{N}_2$	$\ln [\text{C}_2\text{H}_6\text{N}_2]$	$1/[\text{C}_2\text{H}_6\text{N}_2]$
0	0.36		
15	0.30		
30	0.25		
48	0.19		
72	0.13		

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0	0,36	-1,02	2,78
15	0,31	-1,17	3,23
30	0,26	-1,35	3,85
48	0,19	-1,66	5,26
72	0,13	-2,04	7,69

# Find order by graph

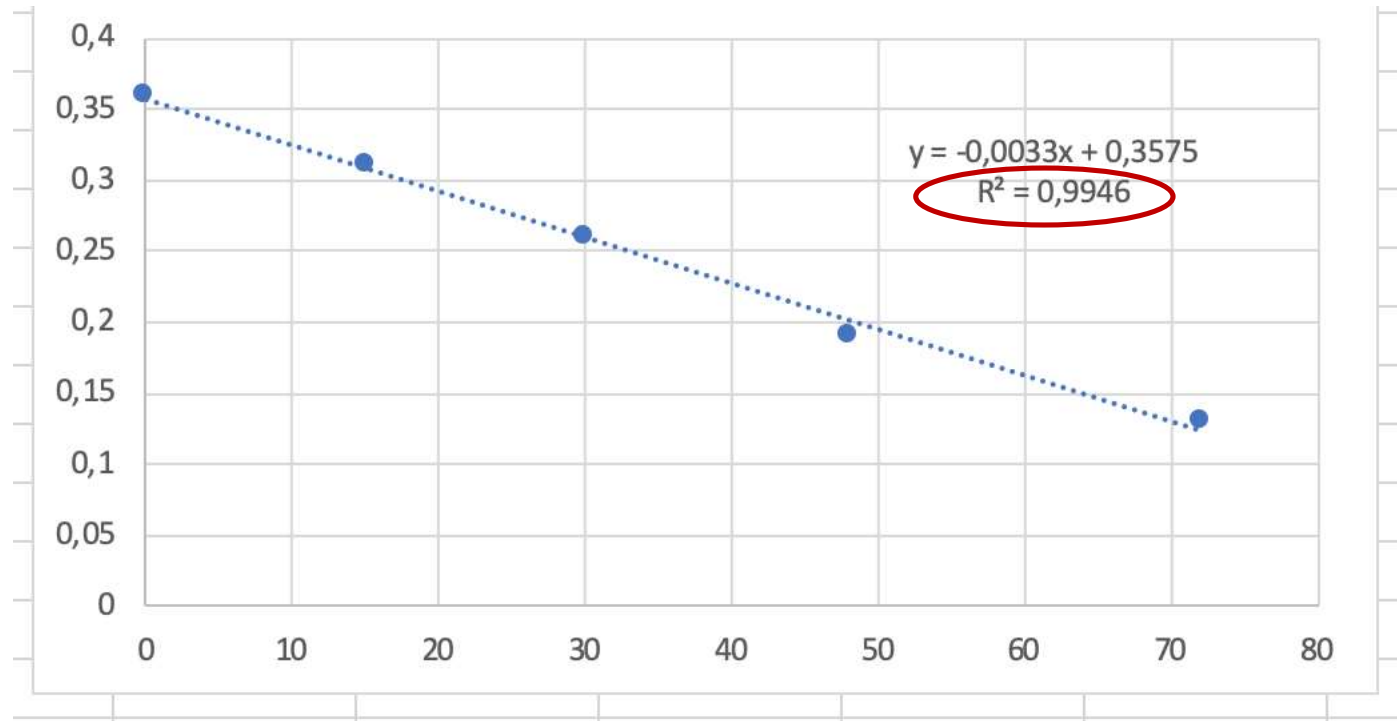
Zero

first

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Zero order graph

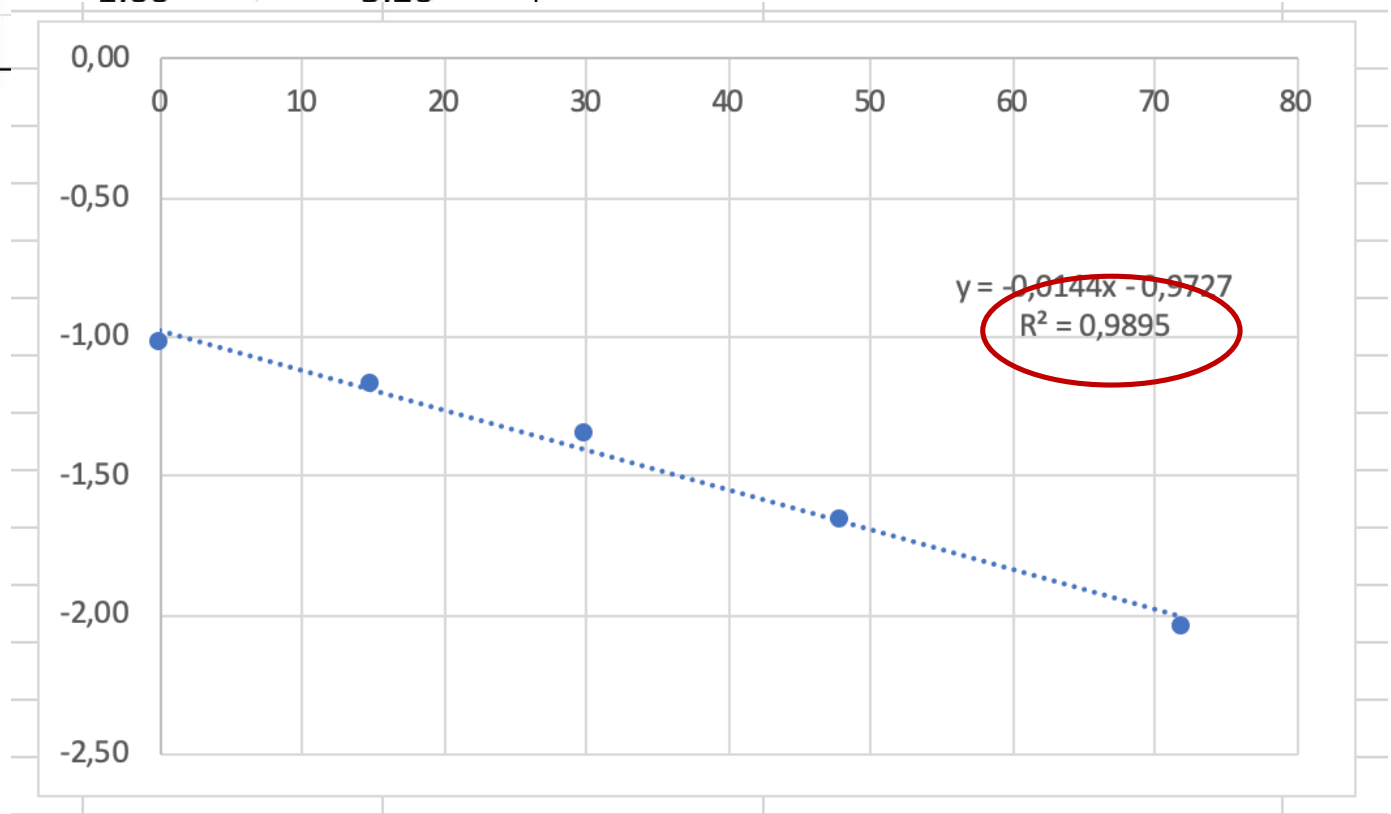


# Find order by graph

Zero **first** second

time	$C_2H_6N_2$	$\ln [C_2H_6N_2]$	$1/[C_2H_6N_2]$
0	0,36	-1,02	2,78
15	0,31	-1,17	3,23
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72	0,13		

First order graph

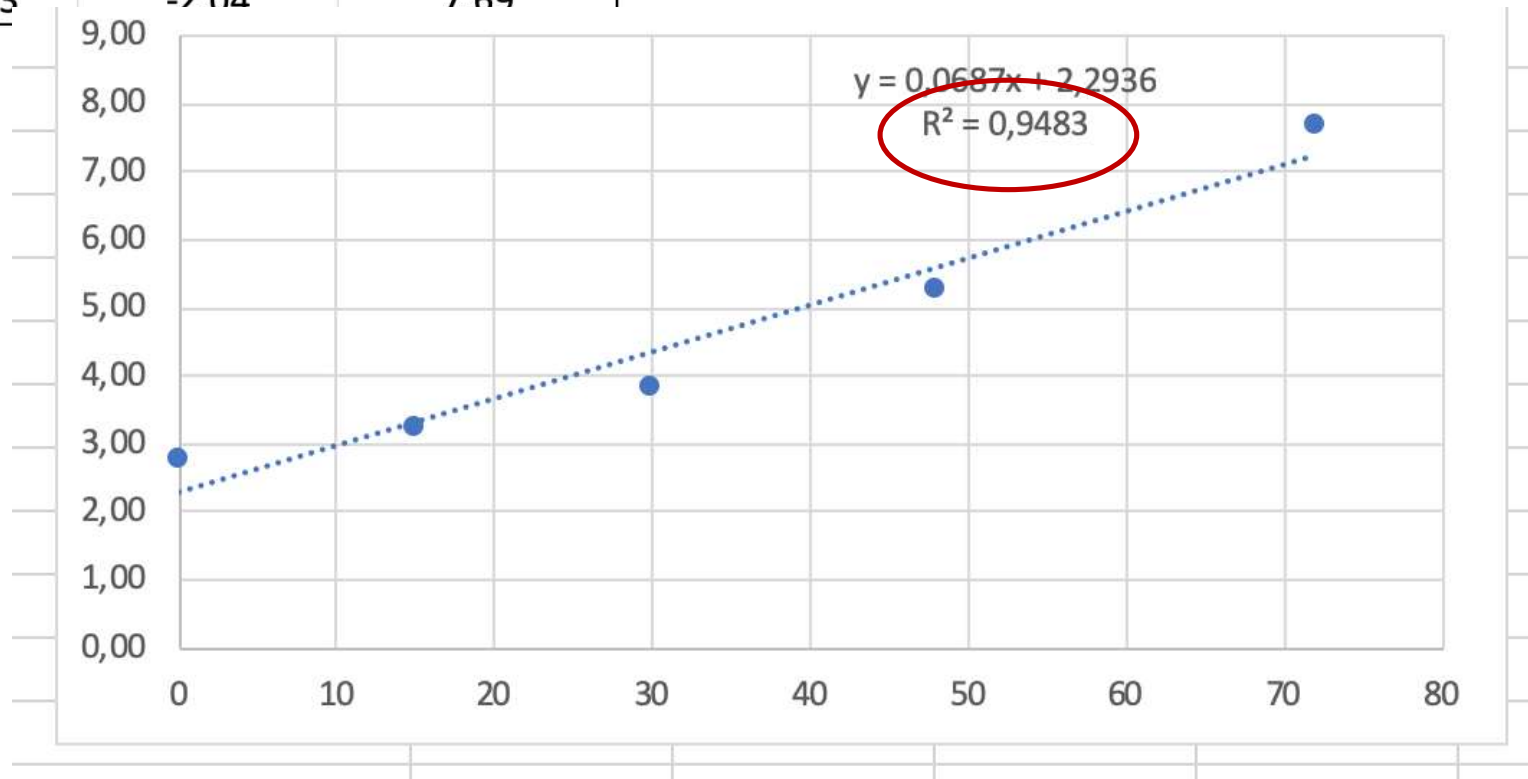


# Find order by graph

Zero      first      **second**

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Second order graph



# Exercise

The reaction  $2A \longrightarrow B$  is first order with a rate constant of  $2.8 \times 10^{-2} \text{ s}^{-1}$  at  $80^{\circ}\text{C}$ . How long will it take for A to decrease from  $0.88 \text{ M}$  to  $0.14 \text{ M}$ ?



# Exercise

The reaction  $2A \longrightarrow B$  is first order with a rate constant of  $2.8 \times 10^{-2} \text{ s}^{-1}$  at  $80^\circ\text{C}$ . How long will it take for A to decrease from  $0.88 \text{ M}$  to  $0.14 \text{ M}$ ?

$$[A]_0 = 0.88 \text{ M}$$

$$[A]_t = 0.14 \text{ M}$$

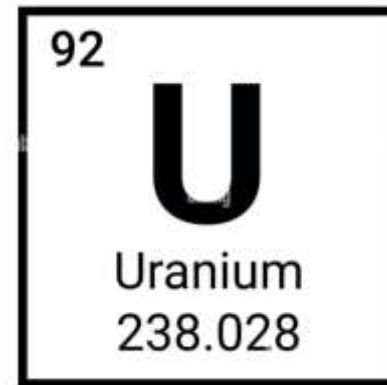
$$\ln[A]_t = \ln[A]_0 - kt$$

$$kt = \ln[A]_0 - \ln[A]$$

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88 \cancel{\text{M}}}{0.14 \cancel{\text{M}}}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$

# Half-Life time

- **Half-life** is the time taken for the concentration of a reactant to drop to half its original value.
- Important also for radioactive isotope decay:

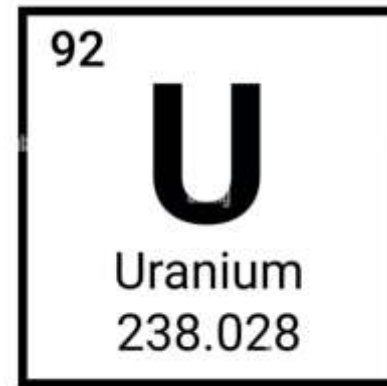


# Half-Life time

- **Half-life** is the time taken for the concentration of a reactant to drop to half its original value.
- Important also for radioactive isotope decay:



$$t_{1/2} = 22 \text{ min}$$



$$t_{1/2} = 4.5 \text{ billion years}$$

# Half-Life time

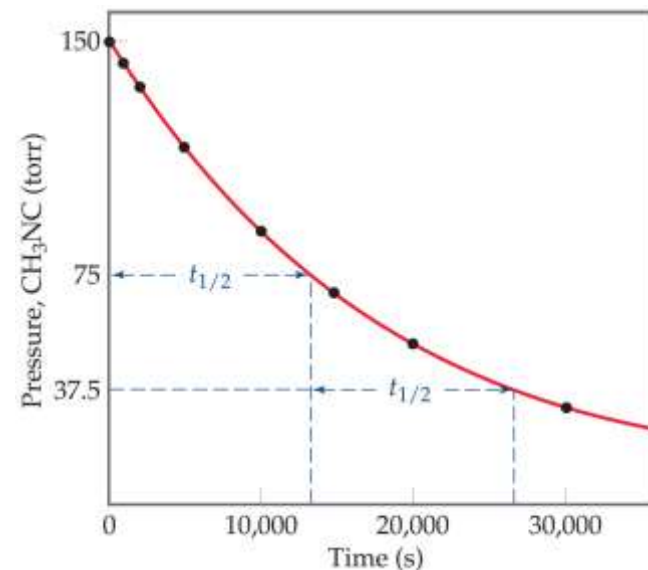
How to find it: substitute into the integrated rate laws

$$[A]_t = \frac{1}{2}[A]_0$$

Zeroth order reaction  $t_{1/2} = \frac{[A]_0}{2k}$

First order reaction  $t_{1/2} = \frac{\ln 2}{k}$

Second order reaction  $t_{1/2} = \frac{1}{k[A]_0}$



**NOTE:** For a first-order process, the half-life does not depend on  $[A]_0$ .

# Rate Laws

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# Half-Life time

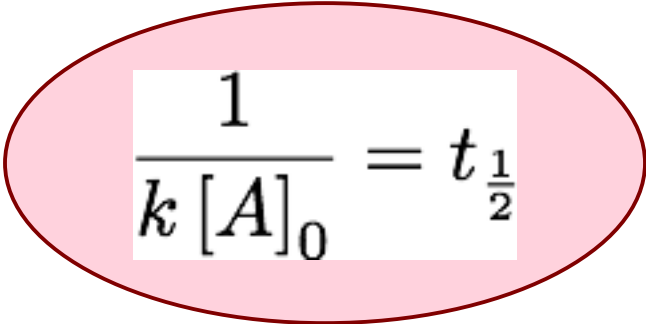
For a **second-order** process, set  
 $[A]_t = 0.5 [A]_0$ :

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$$

$$\frac{1}{0.5 [A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{\frac{1}{2}}$$


$$\frac{1}{k [A]_0} = t_{\frac{1}{2}}$$

# Half-Life time

What is the half-life of  $\text{N}_2\text{O}_5$  if it decomposes with a rate constant of  $5.7 \times 10^{-4} \text{ s}^{-1}$ ?

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How do you know decomposition is first order?

hint: units of  $k$

# Summary of the Kinetics

Order	Rate Law	Concentration-Time	
		Equation	Half-Life
0	rate = $k$	$[A] - [A]_0 = -kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] - \ln[A]_0 = -kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{1/2} = \frac{1}{k[A]_0}$

# Factors that Affect the Reaction Rate

1. **Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often
2. **Concentrations of reactants:** As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.
3. **Catalysts**
  - Speed up reactions by lowering *activation energy*
4. **Surface area of a solid reactant**
  - More area for reactants to be in contact
5. **Pressure of gaseous reactants or products**
  - Increased number of collisions