

American Chemical Society



USNCO Coaching Session Local Exam Preparation Tutorial Notes: Kinetics

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11 Feb 2022

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Kinetics



- **Chemical Kinetics** – area of chemistry dealing with speeds/rates of reactions
- Rates of chemical reactions are determined by the details of the molecular collisions.
- When all else fails, remember that chemical reactions are caused by successful collisions of molecules. In order for this to happen, only certain things can affect the rate of a chemical reaction.
- Rates of reactions affected by four factors
 - concentrations of reactants
 - temperature at which reaction occurs
 - presence of a catalyst
 - surface area of solid or liquid reactants and/or catalyst
 - GASES ONLY–Pressure

Concentration Effects



- If the concentration of the reactants increase, the reaction rate will increase.
- If the concentration of the reactants increase, the products concentration will decrease. If the concentration of the reactants decrease, the products concentration will increase.
- Rate Law $R = k[A]^x[B]^y$
 - k is the rate constant; $[A]$ $[B]$ are the reactant concentrations; x & y are the order of the reactants (explained later)

**Concentration of reactants **



Rate = change in concentration /
change in time

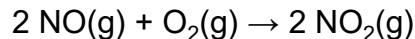
Units are M/s or M/min

We are given the conc. of a reactant and asked for the rate of the product. If reactant concentration is **decreasing**, the product must be **increasing**.

We simply look at the mole ratios and see that we have 1 mole of O₂ and 2 moles of NO₂ so the rate will be increasing by double. The answer is C.

Local 2020 #25

In a study of the reaction below, the concentration of O₂(g) is found to be decreasing by 0.042 M min⁻¹. At what rate is the concentration of nitrogen dioxide gas changing?



- (A) Increasing by 0.021 M min⁻¹
- (B) Increasing by 0.042 M min⁻¹
- (C) Increasing by 0.084 M min⁻¹**
- (D) It cannot be determined without knowing the rate law for the reaction.

Concentration of reactants



Rate = change in concentration / change in time

We are given the reaction rate and asked for the rate of decrease of a reactant. If product is increasing the reactant is decreasing.

We simply look at the mole ratios and see that we have 1 mole of CCl_4 and 3 moles of Cl_2 so the rate will be decreasing by a factor of 3. Since it asks for a disappearance rate, we will multiply instead of divide. $0.063 \times 3 = 0.19 \text{ M/min}$

The answer is D.

Local 2018 #25

Carbon tetrachloride is produced from methyl chloride and chlorine according to the following equation:



If the rate of formation of CCl_4 is measured to be 0.063 M min^{-1} , what is the rate of disappearance of Cl_2 ?

- (A) 0.021 M min^{-1} (B) 0.063 M min^{-1}
(C) 0.13 M min^{-1} **(D) 0.19 M min^{-1}**

Concentration of reactants with rate constants (k)

Elementary chemical reactions are single step reactions with a single transition state (see graph on slide 8) and no intermediates (formed in one reaction and used up in a subsequent reaction).

$$R = k [A]^x [B]^y$$

$k = Ae^{-E_a/Rt}$ (A-frequency factor, e inverse log, E_a -activation energy, R-universal gas constant, t-temp)

Rate constants (k) are not dependent on reactant or product concentrations, (although the rate of reaction is). They are only dependent on temperature.

Local 2020 #26

The rate constant for an elementary chemical reaction can be affected by which of the following?

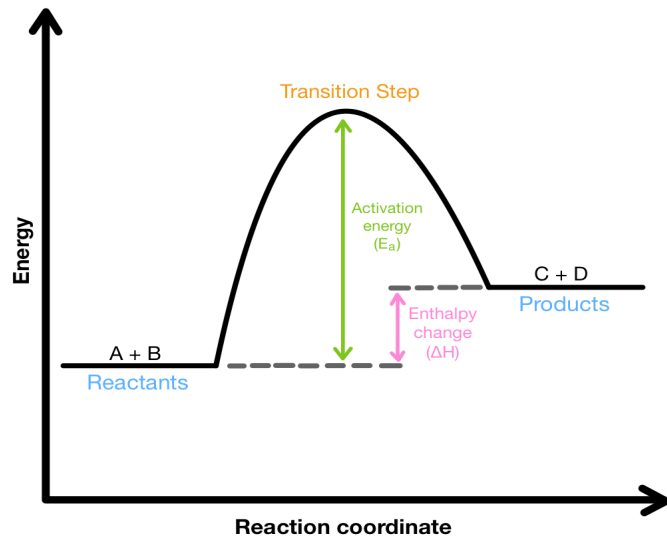
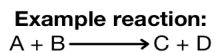
- I. Reactant concentrations
- II. Product concentrations

- (A) I only
- (B) II only
- (C) Both I and II
- (D) Neither I nor II**

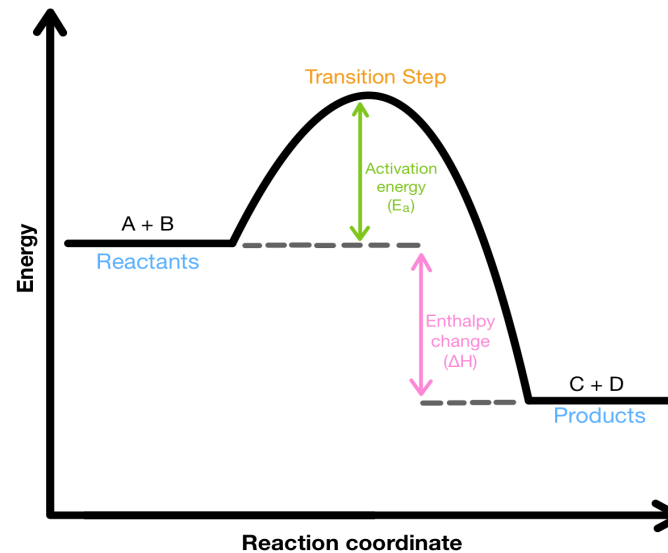
Temperatures effect

- If temperature **increases**, the reaction rate will **increase** (due to more force of collisions)
- Activation energy (E_a) is the minimum amount of energy required to initiate chemical reactions.
 - Endothermic rxns the ΔE is +; Exothermic rxns the ΔE is -
- Arrhenius equation
 - $K = Ae^{-E_a/RT}$ (K-rate constant; A-frequency factor constant)
 - $f = e^{-E_a/RT}$
 - To \uparrow f, we must \uparrow T or \downarrow E_a

Endothermic Energy Diagram



Exothermic Energy Diagram



Reaction Rates-Temperature vs. concentration



$$R = k[A]^x [B]^y$$

$$K = A e^{-E_a/RT}$$

If we change concentration of reactants or k , that will alter reaction rate. This eliminates A & B.

We can $\uparrow R$ by $\uparrow T$ or by $\downarrow E_a$

Local 2018 #28

28. In comparing two reactions, the reaction with the greater activation energy always has

(A) the slower rate.

(B) the faster rate.

(C) the rate that varies less with temperature.

(D) the rate that varies more with temperature.

Temperature effects

Pay attention to units!!

The equation below is given to you on the formulas! We can use it to solve for activation energy (E_a).

Temperature must be in K to use $R = 8.31$ J/mol K

K_2 is 26% more so $K_2 = 1.26 K_1$

$E_a = 40,721$ J/mol = 41 kJ/mol

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Local 2020 # 28

28. The rate constant of a chemical reaction increases 26% when the temperature is raised from 50 °C to 55 °C. What is the activation energy of this reaction?

(A) 1.1 kJ mol⁻¹

(B) 18 kJ mol⁻¹

(C) 41 kJ mol⁻¹

(D) 220 kJ mol⁻¹

Temperature Effects



We use the equation from the previous slide which is from the equation list.

If we compare the $(1/T_1 - 1/T_2)$ we have:

$$(1/323.15 - 1/333.15) = 9.29 \times 10^{-5} \text{ (50-60}^\circ\text{C)}$$

$$(1/333.15 - 1/343.15) = 8.75 \times 10^{-5} \text{ (60-70}^\circ\text{C)}$$

The rate is less for 60-70 so A is the answer.

Local 2019 # 27

The rate of a reaction is 2.3 times faster at 60 °C than it is at 50 °C. By what factor will the rate increase on going from 60 °C to 70 °C?

- (A) By less than a factor of 2.3**
- (B) By a factor of 2.3
- (C) By more than a factor of 2.3
- (D) The rate increase cannot be determined from the information given.

Rate Law and Order of Reactants



- $R = k[A]^x [B]^y$
- In elementary reactions, the order is equal to the number of moles (coefficients in balanced equations)
 - Elementary reactions are those that have a single step with a single transition state with no intermediates!
- In reactions that are not elementary, the order can only be determined by experiment data. We usually use the initial concentrations as compared to the reaction rate (examples follow).

Determining Molecularity

TABLE 14.4 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	Rate = $k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

Reaction	Rate Law
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	Rate = $k[NO]^2[O_2]$
$2NO(g) + 2H_2(g) \rightarrow 2N_2(g) + 2H_2O(g)$	Rate = $k[NO]^2[H_2]$
$2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$	Rate = $k[ICl][H_2]$
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	Rate = $k[N_2O_5]$
$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$	Rate = $k[NO_2][F_2]$
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$	Rate = $k[H_2O_2]$
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	Rate = $k[H_2][Br_2]^{\frac{1}{2}}$
$O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$	Rate = $k[O_3][Cl]$



Method Of Initial Rates Summary

The effects of doubling one initial concentration:

- For *zero-order* reactions, *no effect* on rate.
- For *first-order* reactions, the rate *doubles*.
- For *second-order* reactions, the rate *quadruples*.
- For *third-order* reactions, the rate increases *eightfold*.

The value of k for the reaction can be calculated.

Reaction mechanisms–Orders

Not an elementary reaction so we can't use # of moles for reaction order!

$$R = k[A]^x [B]^y$$

Reaction mechanism is the sequence of steps by which a reaction proceeds.

The slow step is the rate determining step (RDS)

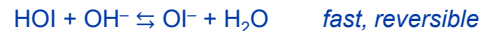
We can focus on the first 2 reactions because they have all of the substances we are looking for.

Fast equilibrium reactions we can assume **rate forward = rate reverse** due to Pre-equilibrium Approximation (PEA)

Transitions can be used to substitute

Local 2020 #30

30. The following mechanism is proposed for the oxidation of I⁻ by OCl⁻ in aqueous solution:



What reaction orders for OCl⁻, I⁻, and OH⁻ are consistent with this mechanism?

	<u>Order in OCl⁻</u>	<u>Order in I⁻</u>	<u>Order in OH⁻</u>
(A)	1	1	1
(B)	1	1	0
(C)	1	0	0
(D)	1	1	-1

Reaction Mechanism–Rate Law



PEA determines that the 1st step rate forward (k_1) = rate reverse (k_{-1}) so we can set them equal to each other
 $R(\text{forward}) = R(\text{reverse})$.

$$k_1 [\text{NO}] [\text{Br}_2] = k_{-1} [\text{NOBr}_2]$$

Step 2-Rate determining step (RDS) is the slow reaction (k_2)

NOBr_2 is an intermediate so we can solve for it in step 1 and substitute its value into step 2.

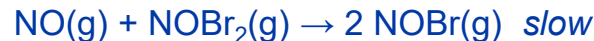
$$R = k[\text{NO}]^2 [\text{Br}_2]$$

Local 2018 #29

The formation of NOBr ,



is studied, and the following mechanism is proposed:



What rate law is predicted by this mechanism?

- (A) Rate = $k[\text{NO}][\text{Br}_2]$ (B) Rate = $k[\text{NO}]^2 [\text{Br}_2]$
(C) Rate = $k[\text{NO}][\text{Br}_2]^2$ (D) Rate = $k[\text{NO}]^2$

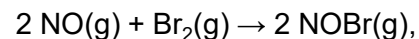
Reaction mechanisms–Intermediate



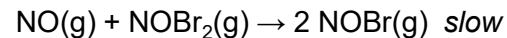
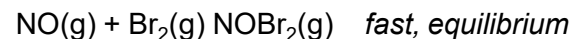
An intermediate is defined as a molecule that is formed in one step of an elementary reaction and is consumed in subsequent step.

Local 2018 #30

The formation of NOBr,



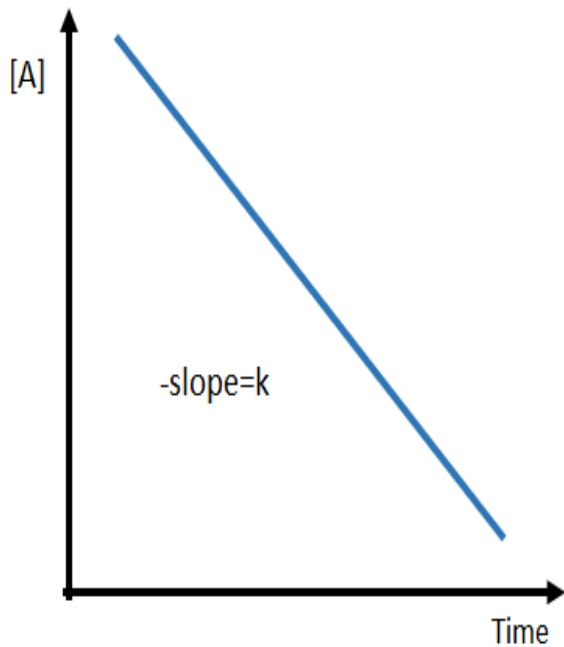
is studied, and the following mechanism is proposed:



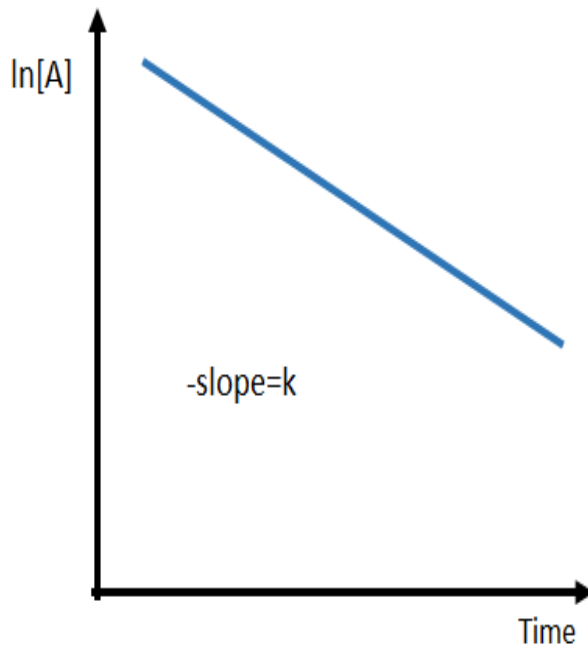
In this reaction, NOBr₂(g) is best described as

- (A) an intermediate.**
- (B) a product.
- (C) a homogeneous catalyst.
- (D) a heterogeneous catalyst

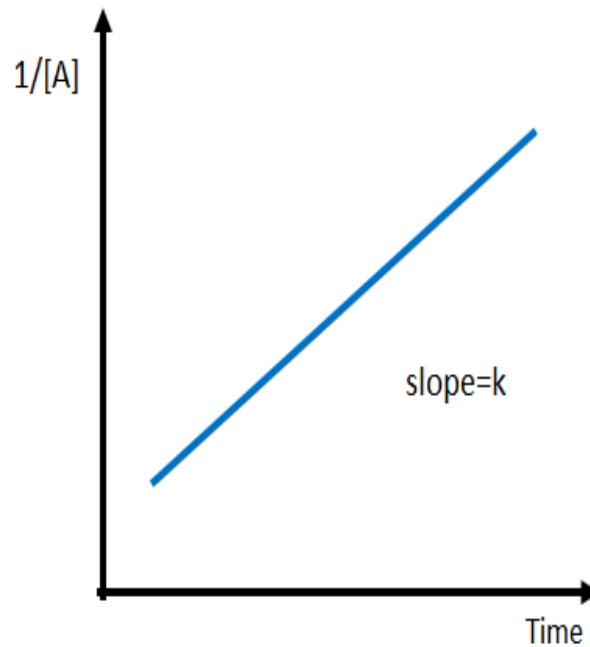
Concentration vs. Time Graph



Zeroth-order Reaction



First-order Reaction

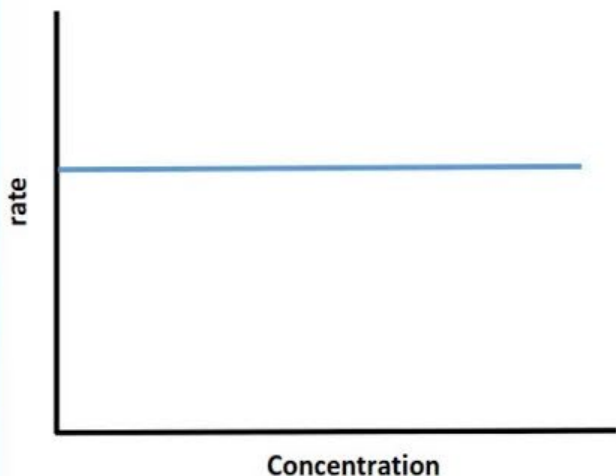


Second-order Reaction

Graphs of reaction kinetics

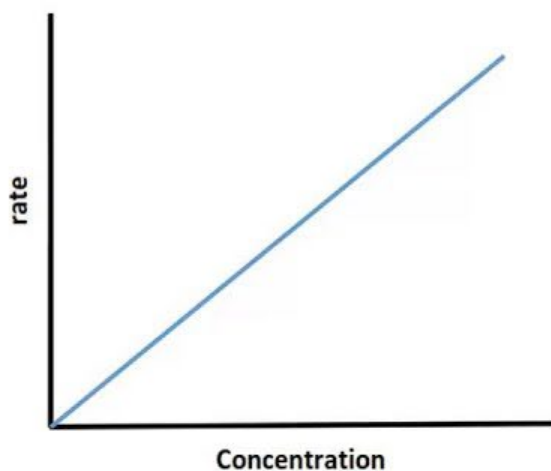
rate vs concentration (for reactant A)

Zero order



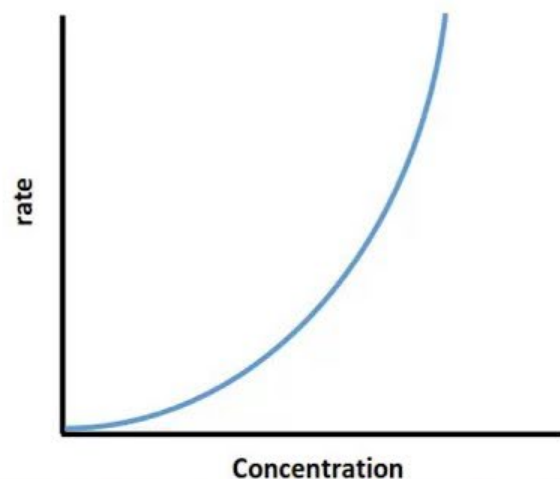
$$\text{rate} = k$$

First order



$$\text{rate} = k[A]$$

Second order



$$\text{rate} = k[A]^2$$

gradient is proportional
to concentration

Rate Law with Graphs

When $[B] \gg [A]$, $1/[A]$ is linear in both plots. This is typical of a graph of a 2nd order reaction where $1/[A]$ vs. time.

2nd order reactions have a rate law of:

29. An irreversible reaction, $A + B \rightarrow$ products, is studied under conditions where $[B] \gg [A]$. When $[B] = 0.10 \text{ M}$, a plot of $1/[A]$ vs. time is linear. When $[B] = 0.30 \text{ M}$, the plot of $1/[A]$ vs. time is indistinguishable from the first plot within experimental error. What is the rate law for this reaction?

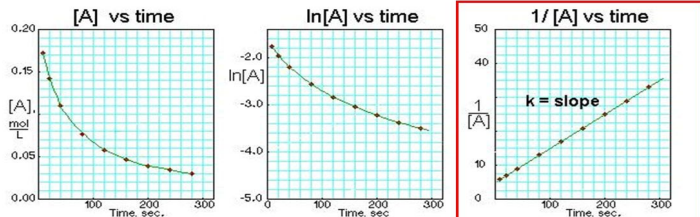
(A) Rate = $k[A][B]$
 $k[A]^2$

(B) Rate =

(C) Rate = $k[A]^2 [B]$
 $k[A][B]^2$

(D) Rate =

Integrated Rate Laws $\text{Rate} = k[A]^2$



Zero Order

First Order

Second Order

The graph that is linear indicates the order of the reaction with respect to A.

Rate Law with Graphs



Local 2018 #27

27. For an irreversible reaction $A \rightarrow$ products, the graph of $1/[A]$ as a function of time is linear. What is the reaction order in A?

(A) Zeroth-order

(B) First-order

(C) Second-order

(D) The order in A cannot be determined based on the information given.

Reaction rate—Orders of reaction

Row 1 to 2:

[A] increase by a factor of 3

[B] increase by a factor of 2

Rate increase by a factor of 12

The only combination that works is D:

$$3^1 \times 2^2 = 12$$

It works for Row 2 and 3 too!

25. The following data were collected for the reaction of A and B:

[A] ₀ (M)	Initial rate (M/s)	[B] ₀ (M)
0.20	600	0.20
0.40	7200	0.60
0.80		28800

What is the order of the reaction with respect to A and B?

- (A) 0th order in A, 2nd order in B
- (B) 1st order in A, 1st order in B
- (C) 2nd order in A, 1st order in B
- (D) 1st order in A, 2nd order in B**

Catalyst Effects



Inhibitors work opposite catalysts!
The increase the time to reach equilibrium, but it does not shift equilibrium to the reactants. (Not II)

Inhibitors can however bind to the enzyme and block the active site. (I is correct)

Local 2019 # 28

How may an enzyme inhibitor decrease the rate of a reaction catalyzed by the enzyme?

- I. The inhibitor may bind to the enzyme and block the active site.
- II. The inhibitor may shift the equilibrium of the reaction toward the starting materials.

(A) I only

(B) II only

**(C) Both I and II
nor II**

(D) Neither I

Catalyst effects

Adding a catalyst will not shift the equilibrium, so the forward and reverse rates will increase at the same rate to the same degree. Catalysts just make reaching equilibrium faster.

The y axis shows rate and x shows time; both forward and reverse rxns will show the same rate increase, therefore, the answer is A.

Local 2020 #29

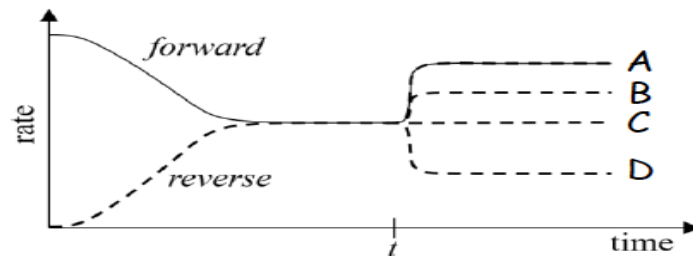
The graph below shows the forward and reverse rates for a reaction as a function of time. At time t , a catalyst is added to the system, and the forward reaction rate is observed to change as indicated by the solid curve. Which dashed curve best indicates how the reverse reaction rate changes?

(A) A

(B) B

(C) C

(D) D



Half-life



The time required for a reactant to reach half its original concentration is called the half-life of a reactant and is designated by the symbol $t_{1/2}$.

- 1st order reaction
 - $\ln[A_0/A] = kt$
 - All nuclear decays are 1st order!
 - In a first-order reaction, the concentration of reactant decays exponentially with time. To verify that a reaction is first order, plot the natural logarithm of its concentration against time and expect a straight line; the slope of the straight line is $-k$.

Half life of 1st Order Rxns

1st order integrated Rate Law can be changed to: $[A] = [A]_0 e^{-kt}$ or $\ln(1/2) = -kt$

$$\ln(1/2) = -k(4.1 \text{ min}); k = 0.17 \text{ min}^{-1}$$

Plug k back in the equation to solve for t but this time we will put 0.7 instead of $1/2$ because we want to know how long to lose 30%.

$$\ln(0.7) = -0.17 \text{ min}^{-1} (t); t = 2.1 \text{ min}$$

Order	Rate Law	Integrated Rate Law	Half-Life
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$0.693/k$
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$1/(k[A]_0)$

Local 2020 #27

27. Sulfuryl chloride (SO_2Cl_2) decomposes via first-order kinetics. The half-life is 4.1 minutes at a certain temperature. How long does it take for 30% of the SO_2Cl_2 in a sample to decompose at this temperature?

- (A) 0.6 min
- (B) 2.1 min**
- (C) 2.5 min
- (D) 7.1 min

Half-life—1st Order Reaction

1st Order $\frac{1}{2}$ life reaction



0.900 mole N_2O initially; 0.640 mol N_2O after 42 min. (71.1% remains)

(To find $\frac{1}{2}$ life) $\ln [\text{A}] = -kt + \ln [\text{A}]_0$; $\ln [0.711] = -k(42 \text{ min})$;
 $k = 0.00812$

Plug back in same equation this time with the 90%

$\ln [0.9 \times 0.1] = -[0.00812] t + \ln [0.9]$; $t = 283.87 \text{ min}$

Order	Rate Law	Integrated Rate Law	Half-Life
0	Rate = k	$[\text{A}]_t = -kt + [\text{A}]_0$	$\frac{[\text{A}]_0}{2k}$
1	Rate = $k[\text{A}]$	$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$	$0.693/k$
2	Rate = $k[\text{A}]^2$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$	$1/(k[\text{A}]_0)$

Local 2019 #26

A sample of 0.900 mol N_2O is placed in a sealed container, where it decomposes irreversibly to N_2 and O_2 in a first-order reaction. After 42.0 min, 0.640 mol N_2O remains. How long will it take for the reaction to be 90.0% complete?

- (A) 13.0 min
- (B) 85.4 min
- (C) 131 min
- (D) 284 min**

Half-Life with 1st Order Reactions

Nuclear decay must be first order!

Solve for k first!

$$\ln[A_0/A] = kt$$

$$\ln[0.5] = k (8.02\text{d})$$

$$K = 0.086$$

$$[A] = [A_0]e^{-kt}$$

$$[A] = [5\text{mg}] e^{-(.086 \times 6.01)}$$

$$[A] = 2.97 \text{ mg}$$

Local 2018 #26

Iodine-131 decays with a half-life of 8.02 d. In a sample initially containing 5.00 mg of ^{131}I , what mass remains after 6.01 d?

(A) 1.13 mg (B) 1.87 mg

(C) 2.97 mg (D) 3.13 mg