The relation between reactant concentration and time

First order reaction: → is a reaction whose rate depends on the reactants concentration raised to the first power.

☒ In a first order reaction of the type

A⟶ product

The rate = $\frac{\Delta[A]}{\Delta t}$ from the rate Law rate = K$[A]$

Units of K:- K = $\frac{rate}{[A]} = \frac{M/S}{M}$ = 1/S or S^{-1}

☒ Combining the first two equations for the rate.

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

$ln\frac{[A]t}{[A]0} = -Kt$ $[A]t$:Is the concentration of A at any time"t" .

$[A]_0$: Is the concentration of A at time "t" = 0

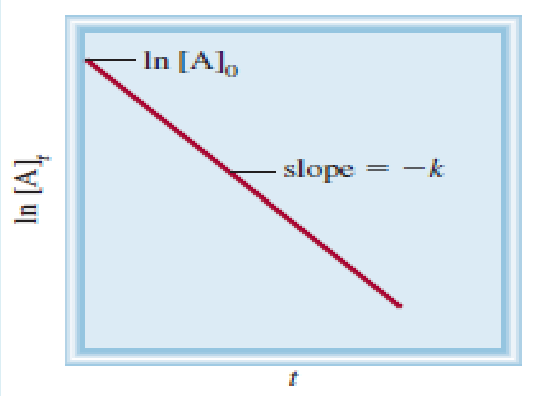
The above equation can be rearranged as follows:

$$ln[A]_t = -Kt + ln[A]_0$$

$$[A]t = [A]_0 e^{-kt}$$

For a first-order reaction

- If we plot $ln[A]t$ versus time, we obtain a straight line with a slope equal to –K
- A(y) intercept equal to $ln[A]0$



There are many first-order reactions for example:

- The decomposition of ethane to methyl radicals.

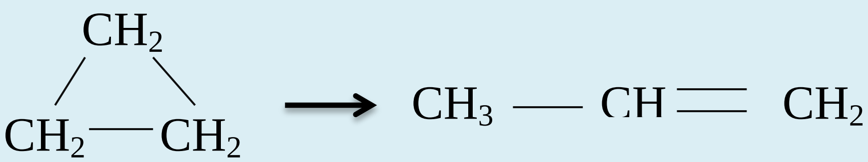
$$C_2H_6 \rightarrow 2CH_3$$

- The decomposition of N_2O_5

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

Example

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 * 10^{-4}\ s^{-1}$ at 500°C.



(a) If the initial concentration of cyclopropane was 0.25 *M*, what is the concentration after 8.8 min?
(b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 *M* to 0.15 *M*?
(c) How long (in minutes) will it take to convert 74 percent of the starting material?

Solution

(a) In applying Equation, we note that because *k* is given in units of s^{-1}, we must first convert 8.8 min to seconds:
8.8min * 60 s = 528 s
We write:-

$$ln[A]_t = -Kt + ln[A]_0$$

$$= - (6.7 * 10^{-4}\ s^{-1})(528\ s) + \ln(0.25)$$

$$= -1.74$$

$$[A]_t = e^{-1.74} = 0.18\ M$$

(b) Using Equation

$$ln\frac{0.15M}{0.25M} = -(6.7*10^{-4}\ s^{-1})t$$

$T = 7.6 * 10^2\ s * 1min / 60\ s$
$= 13min$

(c) From Equation

$$ln\frac{0.26M}{1.00M} = -(6.7*10^{-4}\ s^{-1})t$$

$t = 2.0 * 10^3\ s * 1\ min/60\ s = 33min$

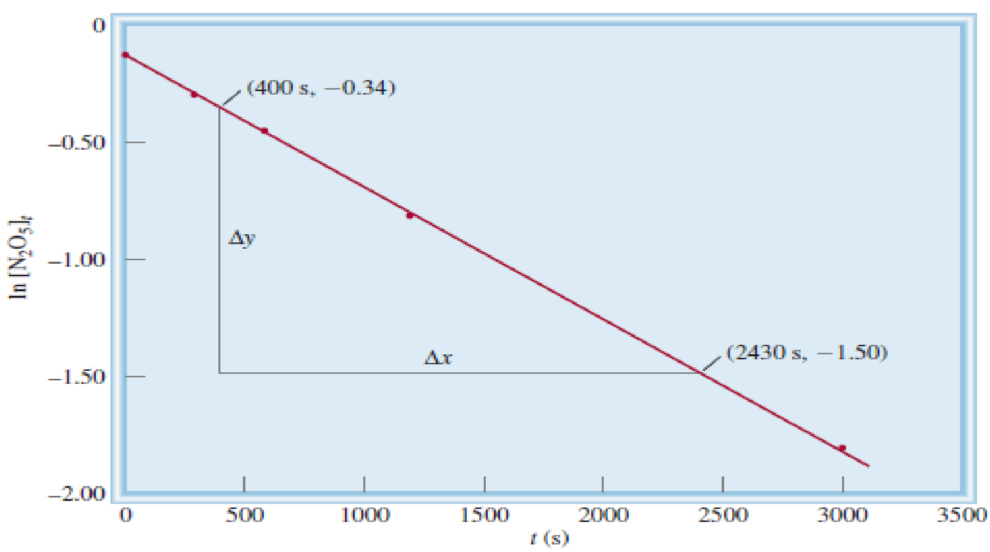
☒ Determination graphically the order and rate constant of the decomposition of nitrogen pentoxide in carbon tetrachloride (CCl_4) solvent at 49°C.

$$2N_2O_5 \longrightarrow 4NO_{2\,(g)} + O_{2(g)}$$

- The following table shows the variation of N_2O_5 concentration with time, and the corresponding lnN_2O_5 values.

t (s)	$[N_2O_5]$ (M)	ln $[N_2O_5]$
0	0.91	−0.094
300	0.75	−0.29
600	0.64	−0.45
1200	0.44	−0.82
3000	0.16	−1.83

- We plot lnN_2O_5 versus t, the fact that the points lie on a straight line shows that the rate law is first order.
- We determine the rate constant from the slop.
  - Slope = $\frac{\Delta y}{\Delta t} = \frac{-1.5-(-0.34)}{(2430-400)S} = -5.7 * 10^{-4} S^{-1}$
- Slope = -K
  - $K = 5.7 * 10^{-4}\ S^{-1}$



Example

The reaction ($2A \rightarrow B$) is first order in A with a rate constant of 2.8 * 10^{-2} S^{-1} at 80°C. How long will it take for A to decrease from 0.88M to 0.14M?

Solution

$\ln[A]t = -Kt + \ln[A]_0$ $\quad\quad$ $[A]_0 = 0.88M$

$[A]t = 0.14M$

$Kt = \ln[A]_0 - \ln[A]t$

$$t = \frac{\ln[A]_0 - \ln[A]t}{K} = \frac{\ln\frac{[A]_0}{[A]t}}{K} = \frac{\ln\frac{0.88}{0.14}}{2.8*10^{-2}S^{-1}} = 66\ S$$

Reaction half-life

The half-life $t_{1/2}$: → is the time required for the concentration of a reactant to decrease to half of its initial concentration.

The expression of $t_{1/2}$:

$$t = \frac{1}{K} ln \frac{[A]_0}{[A]_t}$$

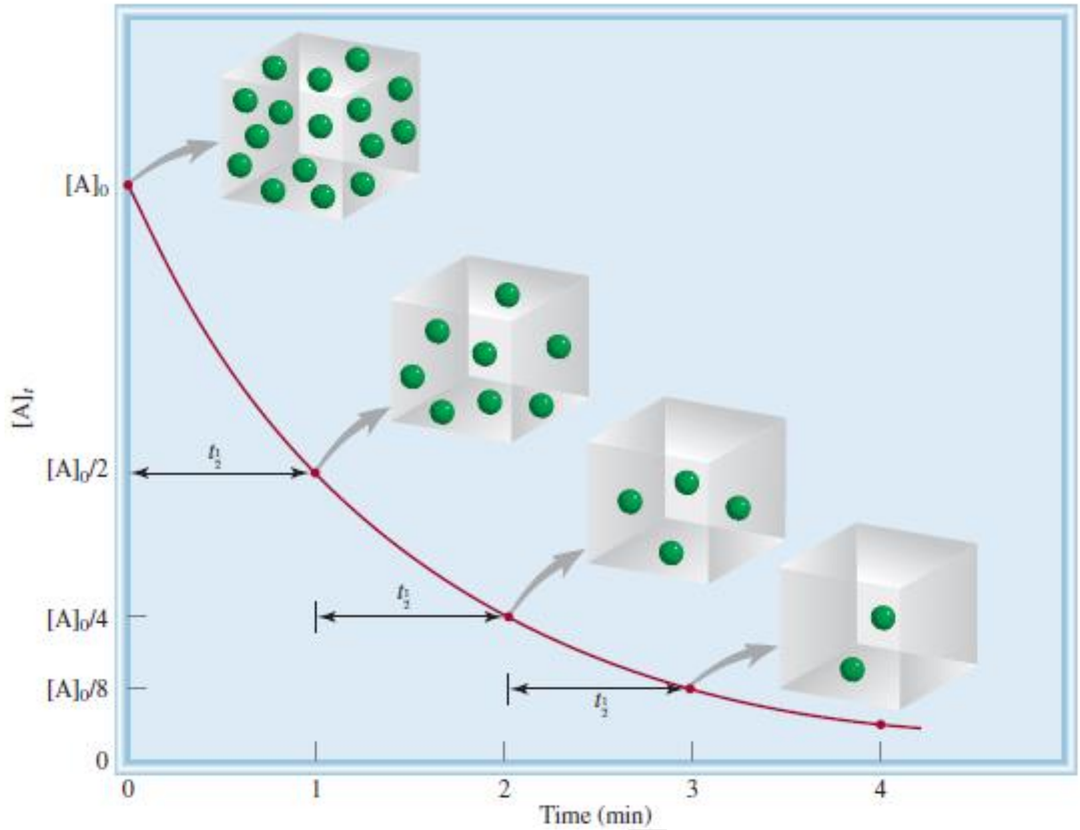
When $t = t_{1/2}$, $[A]_t = \frac{[A]_0}{2}$

$$t_{1/2} = \frac{1}{K} ln \frac{[A]_0}{\frac{[A]_0}{2}}$$

$$t_{1/2} = \frac{1}{K} ln2 = \frac{0.693}{K}$$

Note that

- ☒ The half-life of a first- order reaction is independent on the initial concentration of the reactant.
- ☒ Measuring the half-life of a reaction is one way to determine the rate constant of a first-order reaction.



A plot of $[A]_t$ versus time for the first-order reaction(A→ products). The half-life of the reaction is 1 min. After the elapse of each half-life, the concentration of A is halved.

Example

What is the half-life of N_2O_5, If it decomposes with a rate constant of $5.7*10^{-4}S^{-1}$?!

Solution

$$t_{1/2} = \frac{ln2}{K} = \frac{0.693}{5.7*10^{-4}S^{-1}} = 1200\ S = 20\ min.$$

Example

The decomposition of ethane (C_2H_6) to methyl radicals is a first order reaction with a rate constant of $5.36*10^{-4}\ S^{-1}$ at 700°C, Calculate $t_{1\backslash 2}$.

$$C_2H_6 \longrightarrow 2CH_{3(g)}$$

Solution

$$t_{1/2} = \frac{ln2}{K} = \frac{0.693}{5.36*10^{-4}S^{-1}} = 1.29 * 10^3 S = 21.5\ min.$$

Second-order reaction

Second-order reaction: → is a reaction whose rate depends on the concentration of one reactant raised to the second power.

: → is a reaction whose rate depends on the concentrations of two different reactants each raised to the first power.

☒ The simpler type involves only one kind of reactant molecule

A→ product

Rate = $\frac{-\Delta[A]}{\Delta t}$ rate law = $K[A]^2$

Unites of K:-

$$K = Rate/[A]^2 = \frac{M/S}{M^2} = \frac{1}{S.M} = M^{-1}S^{-1}$$

Another type of second-order reaction:

A+B→ product

The rate Law : Rate = $K[A][B]$

☒ The reaction is first order in A and first order in B, So it has a second order overall reaction.

☒ The above equation can be rearranged as follow:

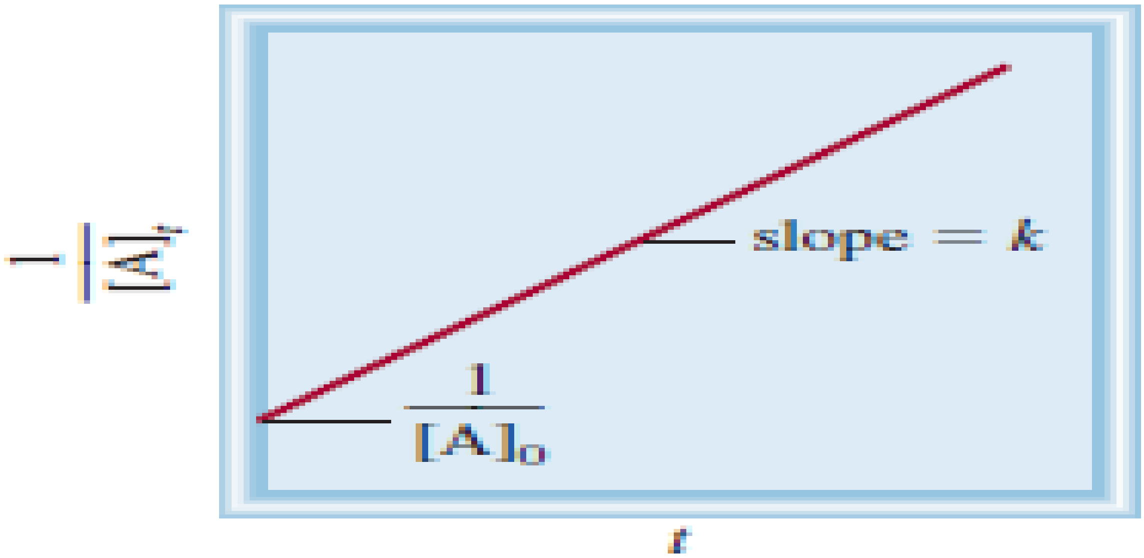
$$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$$

$[A]t$ = concentration of A at any time t.

$[A]_0$ = concentration of A at time t = 0.

☒ If we plot of $\frac{1}{[A]_t}$ versus(t) gives a straight line with slope K

☒ Intercept = $\frac{1}{[A]_0}$



- Equation for the half-life of a second-order reaction.

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

$$\frac{1}{\frac{[A]_0}{2}} = kt_{1/2} + \frac{1}{[A]^0}$$

$$t_{1/2} = \frac{1}{k[A]^0}$$

Note that

- The half-life of a second order reaction is inversely proportional to the initial reactant concentration.
- Measuring the half-life at different initial concentrations is one way to distinguish between the first order and a second order reaction.

Example

Iodine atoms combine to form molecular iodine in the gas phase.

$$I_{(g)} + I_{(g)} \rightarrow I_{2(g)}$$

This reaction follows second-order kinetics and has the high rate constant $7.0 * 10^9/M$. s at 23°C.
(a) If the initial concentration of I was 0.086 *M*, calculate the concentration after 2.0 min.
(b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 *M* and if it is 0.42 *M*.

Solution

(a) Applying Equation:

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

$$\frac{1}{[A]_t} = (7.0 * 10^9)(2.0 * 60\ ) + \frac{1}{0.086M}$$

Where $[A]_t$ is the concentration at t = 2.0 min.

Solving the equation, we get

$[A]_t = 1.2*10^{-12}M$

(b) For $[I]_0 = 0.60\ M$

$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(7.0*10^9\ /M.s)(0.60M)}$

$=2.4*10^{-10}S$

Zero order reactions

☒ Reactions whose order is zero are rare.

- For a zero order reaction

$$A \rightarrow \text{product}$$

- Rate Law is given by

$$\text{Rate} = k[A]^0 = K$$

- The above equation can be rearranged as follows:

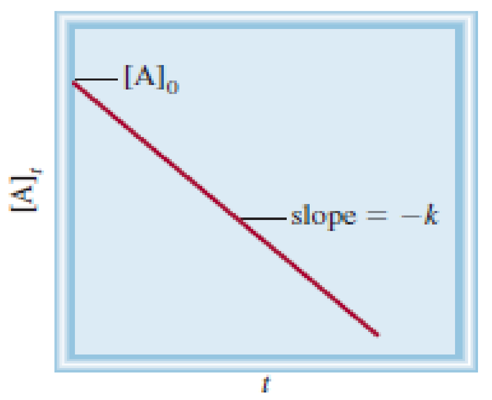
$$[A]_t = -kt + [A]_0$$

Note that

☒ The rate of a zero-order reaction is a constant, independent of a reactant concentration

☒ If we plot $[A]_t$ versus t gives a straight line with Slope = -K

☒ Intercept = $[A]_0$



☒ Half-life of a zero order reaction

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

$$t_{1/2} = \frac{[A]^0}{2K}$$

Note that

- Many of the known zero order reactions take place on a metal surface.

❖ Summary of the kinetics of zero order, first order and second order reactions.

Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate $= k$	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$
1	Rate $= k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{0.693}{k}$
$2^{\dagger}$	Rate $= k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

Choose

1) ………. is a reaction whose rate depends on the reactants concentration raised to the first power.

A) Second order
B) first order
C) Third order
D) zero order

2) The unit of K in the first order reaction is……….

A) $M^{-1}.S^{-1}$
B) S^{-1}
C) M/S
D) None of them

3) ………. is the time required for the concentration of a reactant to decrease to half of its initial concentration.

A) Full time
B) part time
C) Half life time
D) None of them

4) $ln\frac{[A]_t}{[A]_0} = -kt$, this is the equation of ……….

A) first order reaction
B) zero order reaction
C) second order reaction
D) third order reaction

5) The expression of $t_{1/2}$ for the first order reaction is…….

A) $t_{1/2} = \frac{1}{K[A]^0}$
B) $t_{1/2} = \frac{[A]^0}{2K}$
C) $t_{1/2} = \frac{\ln 2}{K}$
D) None of them

6) What is the half-life of N_2O_5, If it decomposes with a rate constant of $9.5*10^{-3}$ S^{-1}?!

A) $7*10^5$

B) $7.3*10^{-5}$

C) $3.5*10^{-5}$

D) $3.5*10^{-3}$

Solution

$$t_{1/2} = \frac{\ln 2}{K} = \frac{\ln 2}{9.5*10^{-3}} = 7.29 * 10^{-5} S$$

7) ……….. is a reaction whose rate depends on the concentration of one reactant raised to the second power.

A) first order reaction

B) second order reaction

C) zero order reaction

D) third order reaction

8) ……… is the concentrations of two different reactants each raised to first power.

A) first order reaction

B) second order reaction

C) zero order reaction

D) third order reaction

9) The unit of K in the second order reaction is……….

A) S^{-1}

B) $M^{-1}S^{-1}$

C) Mole/S

D) None of them

10) Equation for the half-life of a second order reaction is …….

A) $t_{1/2} = \frac{\ln 2}{K}$

B) $t_{1/2} = \frac{1}{K[A]^0}$

C) $t_{1/2} = \frac{A}{K}$

D) None of them

11) At 25°C the rate constant for the first order decomposition of a pesticide solution is $6.4*10^{-3}$ min^{-1} , if the starting concentration of pesticide is 0.0314M what concentration remain after 62min at 25°C?!

A) $1.14*10^{-1}$M

B) 47.4M

C) $2.11*10^{-2}$M

D) $2.68*10^{-2}$M

Solution

$$A_t = A^0 e^{-kt} = 0.0314e^{-(6.4*10^{-3}*62)} = 2.11 * 10^{-2} M$$

12) A certain first order reaction (A→B) is 25% complete in 42 min at 25°C. what is the half-life of the reaction?!

A) 21 min

B) 42 min

C) 120 min

D) 101 min

Solution

$$\ln\frac{A_t}{A_0} = -Kt \qquad \ln\frac{75}{100} = -K * 42$$

$$\therefore K = 6.8 * 10^{-3} \overset{-1}{\text{min}}$$

$$t_{\frac{1}{2}} = \frac{ln2}{K}$$

$$t_{\frac{1}{2}} = \frac{ln2}{6.8 * 10^{-3}} = 101 \text{ min}$$

13) A first order reaction has a rate constant of $3*10^{-3}S^{-1}$, the time required for the reaction to be 75% complete is……..

A) 95.8 S
B) <u>462 S</u>
C) 201 S
D) 41.75 S

Solution

$$\ln\frac{A_t}{A_0} = -Kt \qquad \ln\frac{25}{100} = -3 * 10^{-3} * t$$

$$\therefore t = 462 \text{ S}$$

14) A certain first order reaction A→B is 25% complete in 42 min at 25°C, what is its rate constant?

A) <u>$6.8*10^{-3}$ min^{-1}</u>
B) $8.3*10^{-3}$ min^{-1}
C) $3.3*10^{-2}$ min^{-1}
D) 11 min^{-1}

Solution

$$\ln\frac{A_t}{A_0} = -Kt \qquad \ln\frac{75}{100} = -K * 42 \qquad K= 6.8*10^{-3}\text{min}^{-1}$$

15) The isomerization of cyclopropane to form propene

is a first-order reaction. At 760 K, 15% of a sample of cyclopropane changes to propene in 6.8 min. What is the half-life of cyclopropane at 760 K?

A) 3.4×10^{-2} min

B) 2.5 min

C) 23 min

D) 29 min

Solution

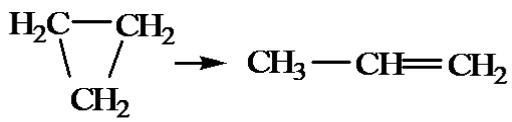
$$\ln \frac{A_t}{A_0} = -Kt$$

$$\ln \frac{85}{100} = -K * 6.8$$

K= $23.8*10^{-3}$ min^{-1}

$t_{1\backslash 2} = \frac{\ln 2}{k} = \frac{\ln 2}{23.8*10^{-3}} = 29\ min$

16) The isomerization of cyclopropane to form propene



is a first-order reaction. At 760 K, 85% of a sample of cyclopropane changes to propene in 79.0 min. Determine the rate constant for this reaction at 760 K.

A) 3.66×10^{-2} min^{-1}

C) 2.06×10^{-3} min^{-1}

B) 2.40×10^{-2} min^{-1}

D) 2.42 min^{-1}

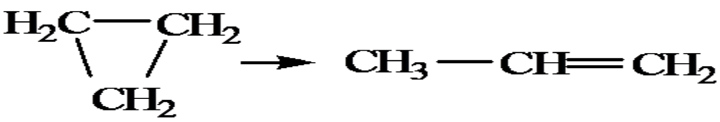
Solution

$$\ln\frac{A_t}{A_0} = -Kt$$

$$\ln\frac{15}{100} = -K * 79$$

K = $2.4 * 10^{-2}$min^{-1}

17) The isomerization of cyclopropane to propene follows first-order kinetics. At 700 K, the rate constant for this reaction is $6.2 \times 10^{-4} min^{-1}$. How many minutes are required for 10.0% of a sample of cyclopropane to isomerize to propene?



A) 16,100 min
B) <u>170 min</u>
C) 1,120 min
D) 1.43×10^{-3} min

Solution

$$\ln\frac{A_t}{A_0} = -Kt$$

$$\ln\frac{90}{100} = -t * 6.2 * 10^{-4}$$

t= 169.6 = 170 min

18) At 700 K, the rate constant for the following reaction is 6.2×10^{-4} min^{-1}. How many minutes are required for 20% of a sample of cyclopropane to isomerize to propene?

C_3H_6 (cyclopropane) → C_3H_6 (propene)

A) 1,120 min
B) 3710 min
C) <u>360 min</u>
D) 280 min

Solution

$$\ln\frac{A_t}{A_0} = -Kt$$

$$\ln\frac{80}{100} = -t * 6.2 * 10^{-4}$$

t= 359.5 = 360 min

19) A first-order reaction has a rate constant of 7.5×10^{-3} /s. The time required for the reaction to be 60% complete is

A) 3.8×10^{-3} s
B) 6.9×10^{-3} s.
C) 68 s
D) 120 s

Solution

$$\ln \frac{A_t}{A_0} = -Kt$$

$$\ln \frac{40}{100} = -t * 7.5 * 10^{-3}$$

t= 122 S

20) The first-order reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is 10% complete in 80. min. How long would it take for the reaction to be 95% complete?

A) 1.8 min
B) 104 min
C) 530 min
D) 2300 min

Solution

$$\ln \frac{A_t}{A_0} = -Kt$$

$$\ln \frac{90}{100} = -k * 80$$

$K = 1.3 * 10^{-3}\ min^{-1}$

$$\ln \frac{5}{100} = -1.3 * 10^{-3} * t$$

t = 2304 min

21) A certain reaction A → *products* is second order in A. If this reaction is 85% complete in 12 minutes, how long would it take for the reaction to be 15% complete?

A) 110 s

B) 27 s

C) 62 s

D) 22 s

Solution

$$\frac{1}{A_t} - \frac{1}{A_0} = Kt$$

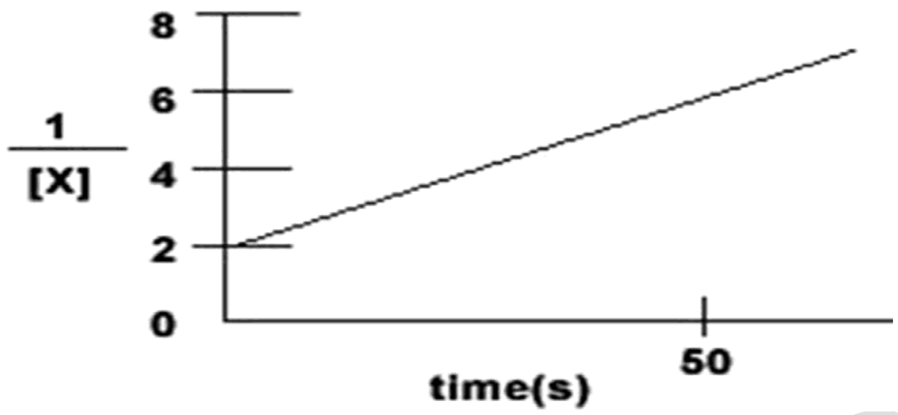
$$\frac{1}{85} - \frac{1}{100} = K * 12$$

$$k = 4.7 * 10^{-3} m^{-1} S^{-1}$$

$$\frac{1}{85} - \frac{1}{100} = 4.7 * 10^{-3} m^{-1} S^{-1}$$

t = 22 S

22) For the reaction X + Y → Z, the reaction rate is found to depend only upon the concentration of X. A plot of 1/X verses time gives a straight line.



What is the rate law for this reaction?

A) rate = k [X]

B) rate = k $[X]^2$

C) rate = k [X][Y]

D) rate = k $[X]^2$[Y]

23) The reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ is suspected to be second order in NO_2. Which of the following kinetic plots would be the most useful to confirm whether or not the reaction is second order?

A) a plot of $[NO_2]^{-1}$ vs. t

B) a plot of ln $[NO_2]$ vs. t

C) a plot of $[NO_2]$ vs. t

D) a plot of ln $[NO_2]^{-1}$ vs. t

24) The thermal decomposition of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$, is a second-order reaction. The following data were obtained at 518°C.

time, s	Pressure CH_3CHO, mmHg
0	364
42	330
105	290
720	132

Calculate the rate constant for the decomposition of acetaldehyde from the above data.

A) 2.2×10^{-3}/s

B) 0.70 mmHg/s

C) 2.2×10^{-3}/mmHg·s

D) 6.7×10^{-6}/mmHg·s

25) The thermal decomposition of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$, is a second-order reaction. The following data were obtained at 518°C.

time, s	Pressure CH_3CHO, mmHg
0	364
42	330
105	290
720	132

Based on the data given, what is the half-life for the disappearance of acetaldehyde?

A) 1.5×10^{5} s

B) 410 s

C) 5.4×10^{7} s

D) 520 s

26) For the chemical reaction A → B + C, a plot of $[A]_t$ versus time is found to give a straight line with a negative slope. What is the order of reaction with respect to A?

A) zeroth
B) first
C) second
D) Such a plot cannot reveal the order of the reaction

27) For the chemical reaction A → C, a plot of $1/[A]_t$ versus time was found to give a straight line with a positive slope. What is the order of reaction?

A) zeroth
B) first
C) second
D) Such a plot cannot reveal the order of the reaction.

28) The graphs below all refer to the same reaction. What is the order of this reaction?

A) zeroth order
B) first order
C) second order
D) unable to predict

29) For what order reaction does the half-life get longer as the initial concentration increases?

A) zeroth order

B) first order

C) second order

D) none of them because half-life is always independent of the initial concentration

30) For a second order reaction, the half-life is equal to

A) $t_{1/2} = 0.693/k$

B) $t_{1/2} = k/0.693$

C) $t_{1/2} = 1/k[A]_o$.

D) $t_{1/2} = k$.

31) Which one of the following changes would alter the rate constant (k) for the reaction 2A + B → *products*?

A) increasing the concentration of A

B) increasing the concentration of B

C) increasing the temperature

D) measuring k again after the reaction has run for a while