Chemical Kinetics

DPP-5: Integrated Rate Law -1 - Solutions

"The only way to do great work is to love what you do—Steve Jobs"

PART-1: ZERO ORDER REACTIONS

TYPE-1.1: Direct Formula Based Questions

Question 1

K for a zero order reaction is 2×10^{-2} mol $L^{-1}s^{-1}$. If the concentration of the reactant after 25 s is 0.5 M, the initial concentration must have been.

Explanation

For a zero order reaction, the integrated rate law is:

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

Given:

- $k = 2 \times 10^{-2}$ mol $L^{-1}s^{-1}$
- $t = 25$ s
- $[A] = 0.5$ M (concentration after 25 s)
- $[A]_0 =?$ (initial concentration)

Substituting into the equation:

$$0.5 = [A]_0 - (2 \times 10^{-2})(25)$$
$$0.5 = [A]_0 - 0.5$$
$$[A]_0 = 0.5 + 0.5$$
$$[A]_0 = 1.0 \text{ M}$$

Approach

Zero order means the reaction proceeds at a constant rate, like a water tank draining at a steady rate. The concentration decreases linearly with time. Just rearrange the formula: initial = final + (rate × time).

Answer

Answer: (4) 1.0 M

Question 2

The rate constant of a zero order reaction is 0.2 mol $dm^{-3}h^{-1}$. If the concentration of the reactant after 30 minutes is 0.05 mol dm^{-3}. Then its initial concentration would be:

Explanation

For zero order: $[\text{A}] = [\text{A}]_0 - kt$
Given:

- $k = 0.2$ mol dm^{-3}h^{-1}
- $t = 30$ minutes $= 0.5$ h
- $[\text{A}] = 0.05$ mol dm^{-3}

Substituting:

$$0.05 = [\text{A}]_0 - (0.2)(0.5)$$
$$0.05 = [\text{A}]_0 - 0.1$$
$$[\text{A}]_0 = 0.05 + 0.1$$
$$[\text{A}]_0 = 0.15 \text{ mol dm}^{-3}$$

Approach

Convert time to hours first! 30 minutes = 0.5 hours (since k is in per hour). Then it's simple addition: you lost 0.1 mol dm^{-3} in 30 minutes, so initial = 0.05 + 0.1 = 0.15.

Answer

Answer: (2) 0.15 mol dm^{-3}

Question 3

For which of the following, the unit of rate and rate constant of the reaction are identical:

Explanation

Rate always has units: concentration/time = mol L^{-1}s^{-1}
For different orders:

- **Zero order:** Rate = k
  Units of k = mol L^{-1}s^{-1} (same as rate) ✓
- **First order:** Rate = $k[\text{A}]$
  Units of k = s^{-1} (different from rate)
- **Second order:** Rate = $k[\text{A}]^2$
  Units of k = mol^{-1} L s^{-1} (different from rate)

Only for zero order reactions, the units of rate and rate constant are identical!

Approach

Think dimensionally: Rate always has concentration/time units. For zero order, Rate = k (no concentration term), so k must have the same units as rate. For other orders, concentration terms appear, changing k's units.

Answer

Answer: (2) Zero order reaction

TYPE-1.2: Half-Life Based Questions

Question 4

Which of the following statement is not correct for the reaction whose rate is r = k (rate constant):

Explanation

When rate = k (constant), this is a zero order reaction.
Analyzing each statement:
(1) ”rate of reaction is independent of concentration of reactant”
TRUE - Zero order means rate = k, independent of [reactant]
(2) ”$t_{1/2}$ of reaction is not depends upon concentration of reactant”
FALSE - For zero order: $t_{1/2} = \frac{[A]_0}{2k}$
Half-life DEPENDS on initial concentration!
(3) ”rate constant is independent of concentration of reactant”
TRUE - k is always independent of concentration (depends on temperature)
(4) ”this is zero order reaction”
TRUE - rate = k is the definition of zero order

Approach

The trap is statement (2)! For zero order, half-life is proportional to initial concentration - higher starting concentration means longer half-life. It’s like emptying tanks: a bigger tank takes longer to drain halfway at a constant rate.

Answer

Answer: (2) $t_{1/2}$ of reaction is not depends upon concentration of reactant
This statement is NOT correct (it’s false).

Question 5

The reaction 2X → B is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be:

Explanation

Step 1: Find rate constant k
For zero order: $t_{1/2} = \frac{[A]_0}{2k}$
Given: $[X]_0 = 0.2$ M, $t_{1/2} = 6$ h

$$6 = \frac{0.2}{2k}$$
$$12k = 0.2$$
$$k = \frac{0.2}{12} = \frac{1}{60} \text{ M h}^{-1}$$

Step 2: Find time for new conditions
Now: $[X]_0 = 0.5$ M, $[X] = 0.2$ M, $t = ?$
Using: $[X] = [X]_0 - kt$

$$0.2 = 0.5 - \frac{1}{60}t$$
$$\frac{1}{60}t = 0.5 - 0.2 = 0.3$$
$$t = 0.3 \times 60 = 18 \text{ h}$$

Approach

First use the given half-life to find k. Then use the integrated rate law for the new scenario. The concentration needs to drop by 0.3 M (from 0.5 to 0.2), and at the constant rate we found, this takes 18 hours.

Answer

Answer: (1) 18.0 h

PART-2: FIRST ORDER REACTIONS

TYPE-2.1: Direct Formula Based Questions

Question 6

If the first order reaction involves gaseous reactants and gaseous products the unit of its rate is:

Explanation

For gaseous reactions, concentration is often expressed in terms of pressure (atm, Pa, etc.).
Rate = change in concentration per unit time
For gaseous systems:

$$\text{Rate} = \frac{d[\text{Pressure}]}{dt}$$

Units = pressure/time = atm s^{-1} (or atm/s)
Note: This is independent of the order - rate always has units of concentration/time.

Approach

Rate is "how fast pressure changes" for gases. Just like speed is distance/time, rate is pressure/time. The answer is atm per second, written as atm s^{-1}.

Answer

Answer: (3) atm - s^{-1}

Question 7

The rate constant of a first order reaction is 4×10^{-3} s^{-1}. At a reactant concentration of 0.02 M, the rate of reaction would be:

Explanation

For first order: Rate = k[A]
Given:

- $k = 4 \times 10^{-3}$ s^{-1}
- $[A] = 0.02$ M

Calculating rate:

$$\begin{aligned}\text{Rate} &= k[A] \\ &= (4 \times 10^{-3})(0.02) \\ &= 8 \times 10^{-5} \text{ M s}^{-1}\end{aligned}$$

Approach

For first order, rate is directly proportional to concentration. Just multiply k by [A]. Think of it as: rate constant × concentration = rate.

Answer

Answer: (1) 8×10^{-5} **M s^{-1}**

Question 8

In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be:

Explanation

For first order: $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$
Given:

- $[A]_0 = 1.0$ M
- $[A] = 0.25$ M
- $t = 20$ min

Calculating k:

$$\begin{aligned} k &= \frac{2.303}{20} \log \frac{1.0}{0.25} \\ &= \frac{2.303}{20} \log 4 \\ &= \frac{2.303}{20} \times \log 2^2 \\ &= \frac{2.303}{20} \times 2 \log 2 \\ &= \frac{2.303}{20} \times 2 \times 0.301 \\ &= \frac{2.303 \times 0.602}{20} \\ &= \frac{1.386}{20} \\ &= 0.06931 \text{ min}^{-1} \end{aligned}$$

Approach

The concentration went from 1.0 to 0.25, which is 1/4. That's two half-lives ($1 \to 0.5 \to 0.25$). So 20 min $= 2 \times t_{1/2}$, giving $t_{1/2} = 10$ min. Then $k = 0.693/10 = 0.0693$ min^{-1}.

Answer

Answer: (4) 0.06931 min^{-1}

Question 9

In the biologically-catalysed oxidation of ethanol, the concentration of ethanol decreases in a first order reaction from 800 mol dm^{-3} to 50 mol dm^{-3} in 2×10^4 s. The rate constant (s^{-1}) of the reaction is:

Explanation

For first order: $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$
Given:

- $[A]_0 = 800$ mol dm^{-3}
- $[A] = 50$ mol dm^{-3}
- $t = 2 \times 10^4$ s

Calculating k:

$$\begin{aligned} k &= \frac{2.303}{2 \times 10^4} \log \frac{800}{50} \\ &= \frac{2.303}{2 \times 10^4} \log 16 \\ &= \frac{2.303}{2 \times 10^4} \times \log 2^4 \\ &= \frac{2.303}{2 \times 10^4} \times 4 \log 2 \\ &= \frac{2.303}{2 \times 10^4} \times 4 \times 0.301 \\ &= \frac{2.303 \times 1.204}{2 \times 10^4} \\ &= \frac{2.773}{2 \times 10^4} \\ &= 1.38 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

Approach

800 to 50 is dividing by 16 (which is 2^4). That's 4 half-lives! So 2×10^4 s $= 4 \times t_{1/2}$, giving $t_{1/2} = 5000$ s. Then $k = 0.693/5000 \approx 1.4 \times 10^{-4}$ s^{-1}.

Answer

Answer: (B) 1.38×10^{-4}

Question 10

For a given reaction of first order it takes 20 minute for the concentration to drop from 1 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be:

Explanation

For first order reactions, the time taken for the same **fractional** change is always constant.
First interval: 1.0 M → 0.6 M
Fraction remaining $= \frac{0.6}{1.0} = 0.6$
Time = 20 min
Second interval: 0.6 M → 0.36 M
Fraction remaining $= \frac{0.36}{0.6} = 0.6$
Since the fraction remaining is the same (0.6 in both cases), the time required is also the same!
Time = 20 min

Approach

First order reactions have a special property: the time for a concentration to drop by the same *factor* is constant. Both intervals involve a drop to 60% of the starting value ($1.0 \times 0.6 = 0.6$, and $0.6 \times 0.6 = 0.36$). Same factor = same time!

Answer

Answer: (3) Equal to 20 min

Question 11

In the first order reaction, 75% of the reactant disappeared in 1.388 h. Calculate the rate constant of the reaction:

Explanation

If 75% disappeared, then 25% remains.
Let $[A]_0 = 100$, then $[A] = 25$
For first order: $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$
Given: $t = 1.388$ h $= 1.388 \times 3600$ s $= 4996.8$ s ≈ 5000 s

$$\begin{aligned} k &= \frac{2.303}{5000} \log \frac{100}{25} \\ &= \frac{2.303}{5000} \log 4 \\ &= \frac{2.303}{5000} \times 2 \log 2 \\ &= \frac{2.303 \times 0.602}{5000} \\ &= \frac{1.386}{5000} \\ &= 2.772 \times 10^{-4} \text{ s}^{-1} \\ &\approx 2.8 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

Approach

75% gone means 25% left, which is 1/4. That's exactly 2 half-lives (100% → 50% → 25%). So 1.388 h $= 2t_{1/2}$, giving $t_{1/2} = 0.694$ h. Converting: $k = 0.693/2500 \text{ s} \approx 2.8 \times 10^{-4} \text{ s}^{-1}$.

Answer

Answer: (2) 2.8×10^{-4} **s**$^{-1}$

Question 12

A first order reaction is carried out with an initial concentration of 10 mol per litre and 80% of the reactant changes into the product. Now if the same reaction is carried out with an initial concentration of 5 mol per litre for the same period the percentage of the reactant changing to the product is.

Explanation

For first order reactions, the **percentage** of reactant converted in a given time is **independent** of initial concentration.
This is because the rate constant k depends only on temperature, not on concentration.
Case 1:

- $[A]_0 = 10$ mol/L
- 80% reacts in time t

Case 2:

- $[A]_0 = 5$ mol/L
- Same time t
- Same temperature (same k)

Since k and t are the same, the same percentage (80%) will react!

Approach

First order reactions don't care about absolute concentration - they only care about the fraction remaining. It's like saying "half of whatever you start with" decays in one half-life. Same time, same percentage conversion, regardless of how much you started with!

Answer

Answer: (2) 80

Question 13

A substance 'A' decomposes in solution following the first order kinetics. Flask I contains 1 L of 1M solution of A and flask II contains 100 ml of 0.6 M solution. After 8 hr, the concentration of A in flask I becomes 0.25 M, what will be the time for concentration of A in flask II to become 0.3 M.

Explanation

Step 1: Find k from Flask I data
Flask I: $[A]_0 = 1$ M, $[A] = 0.25$ M, $t = 8$ h

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{8}\log\frac{1}{0.25}$$

$$k = \frac{2.303}{8}\log 4 = \frac{2.303}{8}\times 2\log 2 = \frac{2.303\times 0.602}{8} = \frac{1.386}{8}$$

Step 2: Use k to find time for Flask II
Flask II: $[A]_0 = 0.6$ M, $[A] = 0.3$ M, $t = ?$

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{1.386/8}\log\frac{0.6}{0.3}$$

$$t = \frac{2.303\times 8}{1.386}\log 2 = \frac{2.303\times 8}{1.386}\times 0.301$$

$$t = \frac{2.303\times 8\times 0.301}{1.386} = \frac{5.547}{1.386} = 4.0 \text{ h}$$

Actually, notice: Flask I goes from 1 to 0.25 (factor of 4) in 8 h, which is 2 half-lives (8 h $= 2t_{1/2}$, so $t_{1/2} = 4$ h).
Flask II goes from 0.6 to 0.3 (factor of 2) = exactly 1 half-life = 4 h.

Approach

Flask I: $1 \rightarrow 0.25$ is dividing by 4, which is 2 half-lives in 8 hours. So one half-life = 4 hours. Flask II: $0.6 \rightarrow 0.3$ is dividing by 2, which is exactly 1 half-life = 4 hours!

Answer

Answer: (3) 4.0 hr

Question 14

A reaction is of first order. After 100 minutes 75 gm of the reactant A are decomposed when 100 gm are taken initially, calculate the time required when 150 gm of the reactant A are decomposed, the initial weight taken is 200 gm:

Explanation

Case 1:

- Initial = 100 g, Decomposed = 75 g, Remaining = 25 g
- Fraction remaining = 25/100 = 1/4
- Time = 100 min

Case 2:

- Initial = 200 g, Decomposed = 150 g, Remaining = 50 g
- Fraction remaining = 50/200 = 1/4
- Time = ?

Since both cases have the same fraction remaining (1/4), and the rate constant k is the same (same reaction, same temperature), the time required is the same!
Time = 100 minutes

Approach

Both scenarios end up with 1/4 of the starting amount remaining (75% decomposed). For first order, same fraction = same time. It's like saying "two half-lives" - doesn't matter if you started with 100 g or 200 g!

Answer

Answer: (1) 100 minutes

Question 15

In a first order reaction the a/(a - x) was found to be 8 after 10 minute. The rate constant is:

Explanation

For first order: $k = \frac{2.303}{t} \log \frac{a}{a-x}$
Given:

- $\frac{a}{a-x} = 8$
- $t = 10$ min

Substituting:

$$\begin{aligned} k &= \frac{2.303}{10} \log 8 \\ &= \frac{2.303}{10} \log 2^3 \\ &= \frac{2.303}{10} \times 3 \log 2 \\ &= \frac{2.303 \times 3 \log 2}{10} \end{aligned}$$

Approach

Just substitute directly into the formula. Since $8 = 2^3$, we get $\log 8 = 3 \log 2$. Simple substitution!

Answer

Answer: (1) $\frac{(2.303 \times 3 \log 2)}{10}$

TYPE-2.2: Half-Life Based Questions

Question 16

For a first order reaction A → products, the rate of reaction at [A] = 0.2 M is 1×10^{-2} mol $L^{-1}min^{-1}$. The half life period for the reaction is:

Explanation

Step 1: Find k
For first order: Rate = $k[A]$

$$1 \times 10^{-2} = k(0.2)$$
$$k = \frac{1 \times 10^{-2}}{0.2} = \frac{0.01}{0.2} = 0.05\ \text{min}^{-1}$$

Step 2: Find $t_{1/2}$
For first order: $t_{1/2} = \frac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{0.05}$$
$$= 13.86\ \text{min}$$
$$\approx 14\ \text{min}$$

Approach

First find k from the rate equation, then plug into the half-life formula. Rate/[A] gives you k, then 0.693/k gives you half-life.

Answer

Answer: (4) 14 min

Question 17

A first order reaction has a half life period of 69.3 s. At 0.10 mol L^{-1} reactant concentration, the rate will be:

Explanation

Step 1: Find k from half-life

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01\ \text{s}^{-1} = 10^{-2}\ \text{s}^{-1}$$

Step 2: Find rate
For first order: Rate = $k[A]$

$$\text{Rate} = (10^{-2})(0.10)$$
$$= 10^{-3}\ \text{M s}^{-1}$$

Approach

Half-life gives you k (just 0.693 divided by half-life). Then multiply k by concentration to get rate. Two simple steps!

Answer

Answer: (2) 10^{-3} **M s**$^{-1}$

Question 18

The rate of a first order reaction is 0.04 mole litre^{-1} s^{-1} at 10 minutes and 0.03 mol litre^{-1} s^{-1} at 20 minutes after initiation. Find the half life of the reaction.

Explanation

For first order: Rate $= k[\text{A}]$
At $t = 10$ min: Rate$_1 = k[\text{A}]_1 = 0.04$
At $t = 20$ min: Rate$_2 = k[\text{A}]_2 = 0.03$
Taking ratio:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{A}]_1}{k[\text{A}]_2} = \frac{[\text{A}]_1}{[\text{A}]_2} = \frac{0.04}{0.03} = \frac{4}{3}$$

So in 10 minutes (from $t = 10$ to $t = 20$), concentration decreased by factor of 4/3.
Using first order equation:

$$k = \frac{2.303}{10}\log\frac{4}{3} = \frac{2.303}{10} \times 0.125 = 0.0288 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0288} = 24 \text{ min}$$

Approach

The ratio of rates equals the ratio of concentrations (since k is constant). From rate ratio, find how concentration changed, then use that to find k, then find half-life.

Answer

Answer: 24 min

Question 19

The half life for the first order reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ is 24 hrs at 30°C. Starting with 10 g of N_2O_5, how many grams of N_2O_5 will remain after a period of 96 hours?

Explanation

Number of half-lives $= \frac{\text{Total time}}{t_{1/2}} = \frac{96}{24} = 4$
After each half-life, the amount is halved:

$$\begin{aligned} \text{After 0 half-lives (0 h):} &\quad 10 \text{ g} \\ \text{After 1 half-life (24 h):} &\quad 5 \text{ g} \\ \text{After 2 half-lives (48 h):} &\quad 2.5 \text{ g} \\ \text{After 3 half-lives (72 h):} &\quad 1.25 \text{ g} \\ \text{After 4 half-lives (96 h):} &\quad 0.625 \text{ g} \end{aligned}$$

Alternatively: Amount remaining = Initial $\times (1/2)^n$

$$= 10 \times \left(\frac{1}{2}\right)^4 = 10 \times \frac{1}{16} = 0.625 \text{ g}$$

Approach

96 hours = 4 half-lives (since each is 24 h). After 4 halvings: $10 \to 5 \to 2.5 \to 1.25 \to 0.625$ g. Or use the formula: $10 \times (1/2)^4 = 10/16 = 0.625$ g.

Answer

Answer: (2) 0.63 g

Question 20

The half-life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be:

Explanation

Number of half-lives = $\frac{60 \text{ min}}{15 \text{ min}} = 4$
After n half-lives, fraction remaining = $(1/2)^n$
After 4 half-lives:

$$\text{Fraction remaining} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

So 1/16 of the original amount remains.

Approach

60 minutes = 4 half-lives. After 4 halvings: $1 \to 1/2 \to 1/4 \to 1/8 \to 1/16$. Simple!

Answer

Answer: (3) 1/16 of the original amount

Question 21

75% of a first order reaction was found to complete in 32 min. When will 50% of the same reaction complete:

Explanation

75% complete means 25% remains = 1/4 of original
This is 2 half-lives (100% → 50% → 25%)
So: $2 \times t_{1/2} = 32$ min

$$t_{1/2} = 16 \text{ min}$$

For 50% completion = 1 half-life = 16 min

Approach

75% done = 25% left = 1/4 = two halvings. So 32 min = 2 half-lives, meaning 1 half-life = 16 min. That's also when 50% is complete!

Answer

Answer: (2) 16 min

Question 22

What is the half life of a radioactive substance if 87.5% of any given amount of the substance disintegrate in 40 minutes?

Explanation

87.5% disintegrated means 12.5% remains
12.5% = 12.5/100 = 1/8
This represents 3 half-lives:

$$100\% \rightarrow 50\% \rightarrow 25\% \rightarrow 12.5\%$$

$$(1 \rightarrow 1/2 \rightarrow 1/4 \rightarrow 1/8)$$

So: $3 \times t_{1/2} = 40$ min

$$t_{1/2} = \frac{40}{3} = 13.33 \text{ min} = 13 \text{ min } 20 \text{ sec}$$

Approach

87.5% gone = 12.5% left = 1/8. Count the halvings: $1 \rightarrow 1/2 \rightarrow 1/4 \rightarrow 1/8 = 3$ half-lives. So 40 min $= 3t_{1/2}$, giving $t_{1/2} = 40/3 = 13$ min 20 sec.

Answer

Answer: (4) 13 min 20 sec

Question 23

99% of a first order reaction was completed in 32 min. When will 99.9% of the reaction complete?

Explanation

For 99% completion:
99% done → 1% remains = 1/100
Using: $k = \frac{2.303}{t} \log \frac{100}{1} = \frac{2.303}{32} \times 2 = \frac{4.606}{32}$
For 99.9% completion:
99.9% done → 0.1% remains = 1/1000

$$t = \frac{2.303}{k} \log \frac{100}{0.1} = \frac{2.303}{4.606/32} \times \log 1000$$

$$t = \frac{2.303 \times 32}{4.606} \times 3 = \frac{32}{2} \times 3 = 48 \text{ min}$$

Alternatively: $\log(1000) = 3$ and $\log(100) = 2$
Ratio: $\frac{t_{99.9}}{t_{99}} = \frac{3}{2}$, so $t_{99.9} = 32 \times \frac{3}{2} = 48$ min

Approach

For first order, time is proportional to log(initial/final). For 99%: $\log(100/1) = 2$. For 99.9%: $\log(100/0.1) = 3$. Ratio = 3/2, so time = $32 \times 3/2 = 48$ min.

Answer

Answer: (4) 48 min

Question 24

In the case of first order reaction, the ratio of time required for 99.9% completion to 50% completion is:

Explanation

For 50% completion: 50% remains = 1/2

$$t_{50} = \frac{2.303}{k} \log \frac{1}{0.5} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} = t_{1/2}$$

For 99.9% completion: 0.1% remains = 0.001 = 1/1000

$$t_{99.9} = \frac{2.303}{k} \log \frac{1}{0.001} = \frac{2.303}{k} \log 1000 = \frac{2.303}{k} \times 3$$

Ratio:

$$\frac{t_{99.9}}{t_{50}} = \frac{2.303 \times 3/k}{0.693/k} = \frac{6.909}{0.693} \approx 10$$

Actually, more precisely: $\frac{2.303\times3}{2.303\times\log 2} = \frac{3}{0.301} = 9.97 \approx 10$

Approach

50% completion = 1 half-life. 99.9% completion requires going to 0.1% remaining = $1/1000 = (1/2)^{10}$ approximately, which is about 10 half-lives. Ratio 10.

Answer

Answer: (3) 10

Question 25

The expression which gives 1/4 th life of Ist order reaction is:

Explanation

For 1/4 life: 1/4 of reactant is consumed, so 3/4 remains.
Using first order integrated law:

$$t_{1/4} = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Where $[A] = \frac{3}{4}[A]_0$

$$t_{1/4} = \frac{2.303}{k} \log \frac{[A]_0}{(3/4)[A]_0}$$

$$t_{1/4} = \frac{2.303}{k} \log \frac{4}{3}$$

Approach

1/4 life means 1/4 reacted and 3/4 left. So initial/remaining = 1/(3/4) = 4/3. Plug into the formula: (2.303/k) log(4/3).

Answer

Answer: (4) $\frac{2.303}{K} \log \frac{4}{3}$

Question 26

For a first order reaction A → P, $t_{1/2}$ (half-life) is 10 days. The time required for 1/4 th conversion of A (in days) is: (ln 2 = 0.693, ln 3 = 1.1)

Explanation

For 1/4 conversion: 1/4 reacted, 3/4 remains

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{k}\log\frac{1}{3/4} = \frac{2.303}{k}\log\frac{4}{3}$$

We know: $t_{1/2} = \frac{0.693}{k} = 10$ days
So: $k = \frac{0.693}{10} = 0.0693\ \text{day}^{-1}$

$$t = \frac{2.303}{0.0693}\log\frac{4}{3}$$

$$\log\frac{4}{3} = \log 4 - \log 3 = 2\log 2 - \log 3 = 2(0.301) - 0.477 = 0.602 - 0.477 = 0.125$$

$$t = \frac{2.303}{0.0693} \times 0.125 = 33.24 \times 0.125 = 4.155 \approx 4.1 \text{ days}$$

Approach

Find k from half-life first. Then use the 1/4 life formula. With the given values, it works out to about 4.1 days.

Answer

Answer: (3) 4.1

Question 27

Which is incorrect:

Explanation

Analyzing each statement:
(1) "Half life of a first order reaction is independent of initial concentration"
TRUE - For first order: $t_{1/2} = 0.693/k$ (no concentration term)
(2) "Rate of reaction is constant for first order reaction"
FALSE - Rate $= k[A]$, which changes as [A] changes over time!
(3) "Unit of K for second order reaction is mol^{-1} L s^{-1}"
TRUE - Correct units for second order
(4) "Half life of zero order is proportional to initial concentration"
TRUE - For zero order: $t_{1/2} = [A]_0/(2k)$ (proportional to $[A]_0$)

Approach

Statement (2) is the trap! For first order, the RATE decreases as reactant is consumed (Rate = k[A]). It's the rate CONSTANT k that stays constant, not the rate itself!

Answer

Answer: (2) Rate of reaction is constant for first order reaction
This statement is INCORRECT.

Question 28

The decomposition of N_2O_5 occurs as $2N_2O_5 \rightarrow 4NO_2 + O_2$, and follows first order kinetics; hence:

Explanation

Molecularity vs Order:
Molecularity = number of molecules in elementary step = 2 (from stoichiometry)
BUT the reaction follows first order kinetics (given)
This means it's NOT an elementary reaction - it's a complex reaction that happens to be first order overall.
For first order reactions:

$$t_{1/2} = \frac{0.693}{k}$$

This is **independent** of initial concentration a.
We can write: $t_{1/2} \propto a^0$ (independent of a)
Statements:

- (1) Bimolecular - TRUE (2 molecules in stoichiometry)
- (2) Unimolecular - FALSE
- (3) $t_{1/2} \propto a^0$ - TRUE (independent of a)
- (4) $t_{1/2} \propto a^2$ - FALSE

Approach

First order half-life doesn't depend on concentration, so $t_{1/2} \propto a^0$ (anything to power 0 = 1, meaning no dependence). It's constant!

Answer

Answer: (3) $t_{1/2} \propto a^0$

Question 29

An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? ($\log_{10}2 = 0.3$)

Explanation

For first order: $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$
For $t_{1/8}$: [A] = $[A]_0/8$

$$t_{1/8} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/8} = \frac{2.303}{k} \log 8 = \frac{2.303}{k} \times 3 \log 2$$

For $t_{1/10}$: [A] = $[A]_0/10$

$$t_{1/10} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/10} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \times 1$$

Ratio:

$$\frac{t_{1/8}}{t_{1/10}} = \frac{3 \log 2}{1} = 3 \times 0.3 = 0.9$$

$$\frac{t_{1/8}}{t_{1/10}} \times 10 = 0.9 \times 10 = 9$$

Approach

Time is proportional to log(1/fraction). For 1/8: log 8 = 3 log 2. For 1/10: log 10 = 1. Ratio = 3 log 2 / 1 = 3(0.3) = 0.9. Multiply by 10 → 9.

Answer

Answer: 9

Question 30

In the following first order reactions, A + Reagent → Product, B + Reagent → Product. Calculate the ratio of K_1/K_2, when 50% of B has been reacted, 94% of A has been reacted:

Explanation

Both reactions occur for the same time t.
For reaction A: 94% reacted → 6% remains = 0.06

$$t = \frac{2.303}{K_1}\log\frac{1}{0.06} = \frac{2.303}{K_1}\log 16.67$$

For reaction B: 50% reacted → 50% remains = 0.5

$$t = \frac{2.303}{K_2}\log\frac{1}{0.5} = \frac{2.303}{K_2}\log 2$$

Since both occur in same time:

$$\frac{2.303}{K_1}\log 16.67 = \frac{2.303}{K_2}\log 2$$

$$\frac{K_1}{K_2} = \frac{\log 16.67}{\log 2} = \frac{\log(100/6)}{\log 2}$$

$$= \frac{\log 100 - \log 6}{\log 2} = \frac{2 - 0.778}{0.301} = \frac{1.222}{0.301} \approx 4.06$$

Approach

Same time, different conversions means different rate constants. The faster reaction (A, which is 94% done) has a larger k. Calculate using the ratio of log terms.

Answer

Answer: (1) 4.06

Question 31

Decomposition of X exhibits a rate constant of 0.05 g/year. How many years are required for the decomposition of 5 g of X into 2.5 g?

Explanation

The units of k suggest this is a **zero order** reaction (k has units of concentration/time).
For zero order: $[A] = [A]_0 - kt$
Given:

- $k = 0.05$ g/year
- $[A]_0 = 5$ g
- $[A] = 2.5$ g

Substituting:

$$2.5 = 5 - 0.05t$$
$$0.05t = 5 - 2.5 = 2.5$$
$$t = \frac{2.5}{0.05} = 50 \text{ years}$$

Approach

The unit of k (g/year) tells you it's zero order! Just use $[A] = [A]_0$ - kt. You need to lose 2.5 g at 0.05 g/year → takes 50 years.

Answer

Answer: (4) 50