

2nd Order Kinetics

Chemical Kinetics-Lecture 3

2nd Order Reaction

- **Case I** : Single Reactant type : $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$

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

$$\Rightarrow k = \frac{\text{Rate}}{[\text{A}]^2} = \frac{\text{mol} \cdot \text{L}^{-1} \cdot \text{time}^{-1}}{(\text{mol} \cdot \text{L}^{-1})^2} = \text{L} \cdot \text{mol}^{-1} \cdot \text{time}^{-1} = \text{M}^{-1} \cdot \text{t}^{-1}$$

Derivation of Integrated Equation

$$\text{rate} = -\frac{d(a_0 - x)}{dt} = k(a_0 - x)^2$$

$$\frac{dx}{dt} = k(a_0 - x)^2 \quad \Rightarrow \quad \frac{dx}{(a_0 - x)^2} = k dt$$

Integrating both the sides, we have

$$\int \frac{dx}{(a_0 - x)^2} = \int k dt \quad \Rightarrow \quad \frac{1}{(a_0 - x)} = kt + C_0$$

$C_0 = \text{Integration Constant}$

When $t = 0$; $x = 0$, So we get $C_0 = \frac{1}{a_0}$

Substituting the value of C_0 , we have

$$\frac{1}{(a_0 - x)} = kt + \frac{1}{a_0} \quad \Rightarrow \quad kt = \frac{1}{a_t} - \frac{1}{a_0}$$

$$k = \frac{1}{t} \left(\frac{1}{a_t} - \frac{1}{a_0} \right) \quad \text{Integrated 2nd Order Equation}$$

Half Life Period($t_{0.5}$)

When $t = 0$, $a_t = a_0/2$, Then from the 2nd order integrated equation we have

$$k = \frac{1}{t_{0.5}} \left(\frac{1}{a_0/2} - \frac{1}{a_0} \right) \quad \Rightarrow \quad t_{0.5} = \frac{1}{ka_0} \quad t_{0.5} \propto \frac{1}{a_0}$$

2nd order Reaction is inversely proportional to the initial(starting) concentration of the reactant($1/a_0$)
Each $t_{0.5}$ is the double of the previous $t_{0.5}$.

Comparison with 1st Order Reaction

- For 1st 50% completion, suppose 2nd order reaction takes $t_{0.5}$ (let us call this initial half life period).
- For the next 25%, it takes $2t_{0.5}$ and for the next 12.5%, it takes $4t_{0.5}$ and so on.
- Hence for 87.5% completion, a total of $7t_{0.5}$ is required. Note that $t_{0.5}$ here is the initial half life period. ($1t_{0.5} + 2t_{0.5} + 4t_{0.5}$)
- For first order reaction only 3 $t_{0.5}$ are required for 87.5% completion, as $t_{0.5}$ is independent of the starting concentration of the reactant.

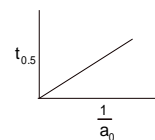
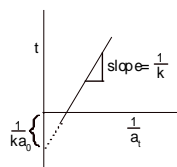
- So a 2nd order reaction slows down more and more as the concentration decreases with time.
- So Reactant concentration vs. time graph for 2nd reaction lies above that of 1st order graph.



Graphs for 2nd Order Reaction

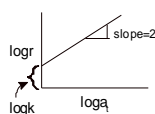
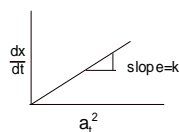
$$t = \frac{1}{k} \left(\frac{1}{a_t} - \frac{1}{a_0} \right)$$

$$t_{0.5} = \frac{1}{ka_0}$$



$$\frac{dx}{dt} = ka_t^2$$

$$\log r = \log k + 2 \log a_t$$



• Cases-II: Two Reactant type : H₂ + I₂ → 2HI

- In this case, if the initial concentration of both the reactants are same, then the kinetics derivation will be exactly same as the previous case.
- When the two concentrations are different then, the integrated equation will be different.

- A + B → Products
- time=0 a₀ b₀
- time=t (a₀-x) (b₀-x)

$$\frac{dx}{dt} = k(a_0 - x)^i (b_0 - x)^j$$

$$\Rightarrow \frac{dx}{(a_0 - x)(b_0 - x)} = k dt$$

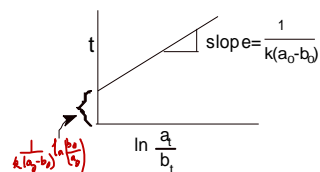
$$\Rightarrow \int \frac{dx}{(a_0 - x)(b_0 - x)} = \int k dt$$

On integration, we get (steps omitted)

$$k = \frac{1}{t(a_0 - b_0)} \ln \frac{b_0(a_0 - x)}{a_0(b_0 - x)} = \frac{1}{t(a_0 - b_0)} \ln \frac{b_0 a_t}{a_0 b_t}$$

$$\Rightarrow t = \frac{1}{k(a_0 - b_0)} \ln \left(\frac{b_0}{a_0} \right) + \frac{1}{k(a_0 - b_0)} \ln \left(\frac{a_t}{b_t} \right)$$

- N.B: Half life period (t_{0.5}) for such cases cannot be determined, as the time required for a₀ to be halved is not the same as the time for b₀ to be halved.



- **Integration Steps:**

$$\int \frac{dx}{(a_0-x)(b_0-x)} = \int \frac{A(b_0-x) + B(a_0-x)}{(a_0-x)(b_0-x)} dx = \frac{1}{(a_0-b_0)} \int \left(\frac{1}{b_0-x} - \frac{1}{a_0-x} \right) dx$$

$$\int k dt = \frac{1}{(a_0-b_0)} \int \left(\frac{1}{b_0-x} - \frac{1}{a_0-x} \right) dx$$

$$\Rightarrow kt = \frac{1}{(a_0-b_0)} [-\ln(b_0-x) + \ln(a_0-x)] + C_0$$

When $t=0, x=0$, Hence $C_0 = \frac{1}{(a_0-b_0)} \ln \frac{b_0}{a_0}$ Substituting the value of C_0 .

$$\Rightarrow t = \frac{1}{k(a_0-b_0)} \ln \left(\frac{b_0}{a_0} \right) + \frac{1}{k(a_0-b_0)} \ln \left(\frac{a_t}{b_t} \right)$$

- SAQ: Look to the following reaction: $3A \rightarrow 4B + C$

The rate constant for the reaction is $2.0 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$ and the initial concentration of A is 0.02M. Then find the rate of reaction w.r.t to disappearance of A. Also find the rate of reaction w.r.t formation of B.

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$$-\frac{d[A]}{dt} = k[A]^2 = 2 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1} \times (0.02 \text{ M})^2 = 8 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$$

$$-\frac{1}{3} \frac{d[A]}{dt} = +\frac{1}{4} \frac{d[B]}{dt} = +\frac{d[C]}{dt}$$

$$\Rightarrow +\frac{d[B]}{dt} = -\frac{4}{3} \frac{d[A]}{dt} = \frac{4}{3} \times 8 \times 10^{-6} \text{ M} \cdot \text{s}^{-1} = 10.67 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$$

Examples of 2nd Order Reactions

- $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
- $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$
- $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$
- Alkaline Hydrolysis of Esters (saponification of ester)
- $\text{RCOOR}' + \text{NaOH} \rightarrow \text{RCOONa} + \text{R}'\text{OH}$

- SAQ: If a flask that initially contains 0.056 M NO_2 is heated at 300°C to form NO and O_2 . what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Rate constant of the reaction is $0.54 \text{ M}^{-1} \cdot \text{s}^{-1}$.

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$$\begin{aligned} \text{Sol}^n \quad 0.54 &= \frac{1}{3600} \left(\frac{1}{a_t} - \frac{1}{0.056} \right) \Rightarrow a_t = 5.25 \times 10^{-4} \text{ M} \\ t_{1/2} &= \frac{1}{k a_0} = \frac{1}{0.54 \times 0.056} = 33.068 \text{ s} \\ t &= \frac{1}{0.54} \left(\frac{1}{10} - \frac{1}{100} \right) = \frac{1}{0.54} \times \frac{9}{100} = 0.167 \text{ s} \end{aligned}$$

Pseudo-first order Reaction

- It was formerly called Pseudo-unimolecular reaction.
- It is truly a 2nd order reaction but it fakes to behave as first order reaction. In other words, it is virtually a 1st order reaction.
- $A + B \rightarrow \text{products}$
- This happens when one of the reactants (say B) is taken in large excess. So that [B] virtually remains constant and the rate is independent of its concentration. So we can take the order w.r.t B to be 0. $\Rightarrow \text{rate} = k[A]^1 \times [B]^0$

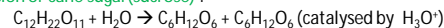
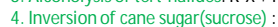
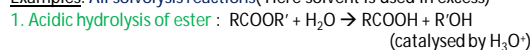
Where k = rate constant for the pseudo first order reaction.

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

And we can apply first order kinetics to this reaction.

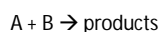
$$\Rightarrow k = \frac{1}{t} \ln \frac{a_0}{a_t}$$

Examples: All solvolysis reactions (Here solvent is used in excess)



- N.B: In reality 'k' varies with different high concentration of B. But for particular high concentration of B, 'k' remains virtually constant relative to the drastic decrease in [A].
- See the detailed kinetics of pseudo-first order reaction.

Derivation of Pseudo-first order equation from 2nd Order Kinetics



$$\text{Rate} = k'[A][B] \quad k' = 2^{\text{nd}} \text{ order rate constant}$$

$$k' = \frac{1}{t(a_0 - b_0)} \ln \frac{b_0 a_t}{a_0 b_t}$$

Assuming $b_0 \gg a_0$, we can neglect a_0 from $(a_0 - b_0)$ and substitute $b_t = b_0$ in the ln expression. So the above expression is reduced to

$$k' = -\frac{1}{tb_0} \ln \frac{a_t}{a_0}$$

$$\Rightarrow -k'b_0 = \frac{1}{t} \ln \frac{a_t}{a_0} \quad \Rightarrow -kt = \ln \frac{a_t}{a_0}$$

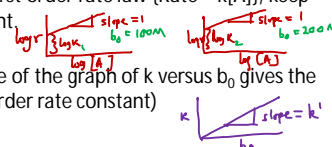
Where $k = k'b_0 = 1^{\text{st}} \text{ order rate constant}$

$$\Rightarrow k = \frac{1}{t} \ln \frac{a_0}{a_t} \quad \text{pseudo-first order equation}$$

N.B: While solving problems on pseudo-first order reaction, you must see, whether k or k' value is given. Accordingly the strategy should be made.

Determination of k' for the pseudo-first order reaction

- k' is the rate constant for the 2nd order reaction
- Note that for different high concentration of B, different ' k' ' (pseudo-first order rate constants) are obtained.
- These are obtained from the intercepts of $\log(\text{rate})$ versus $\log[A]$ for the pseudo-first order rate law $\{\text{Rate} = k[A]\}$, keep the [B] high but different.
- Since $k = k'b_0$, the slope of the graph of k versus b_0 gives the slope equals to k' (2nd order rate constant)



Half Life($t_{0.5}$) Period of Pseudo-first order Reaction

$$-k'b_0 = \frac{1}{t} \ln \frac{a_t}{a_0} \quad \text{When } t=t_{0.5}, \text{ at } = a_0/2; \text{ then we have}$$

$$k' = -\frac{1}{t_{0.5}b_0} \ln \frac{1}{2} \quad \Rightarrow \quad t_{0.5} = \frac{\ln 2}{k'b_0} = \frac{\ln 2}{k}$$

- **SAQ:** 1. If a 2nd order reaction has the rate equation $R = k[A][B]$, and the rate constant, k , is $3.67 \text{ M}^{-1} \text{ s}^{-1}$, $[A]$ is 4.5 M and $[B]$ is 99 M , what is the rate constant of its pseudo-1st-order reaction?

- **Solution:** Given k is the 2nd order rate constant; We know that Pseudo 1st order rate constant = 2nd order rate constant $\times b_0$
 $= 3.67 \text{ M}^{-1} \cdot \text{s}^{-1} \times 99 \text{ M} = 363.33 \text{ s}^{-1}$.

- **SAQ:** What is the half-life of a reaction with $[A]_0 = 109 \text{ M}$, $[B]_0 = 1 \text{ M}$, $k' = 45 \text{ M}^{-1} \text{ s}^{-1}$?

Solution: Though it is a pseudo-1st order reaction, second order rate constant is given. So,

$$\Rightarrow t_{0.5} = \frac{\ln 2}{k'b_0} = \frac{\ln 2}{45 \text{ M}^{-1} \text{ s}^{-1} \times 109 \text{ M}} = \frac{0.693}{4905 \text{ s}^{-1}} = 1.41 \times 10^{-4} \text{ s}$$

- **SAQ:** If $[A] = 55 \text{ M}$ at 39 s , $[A]_0 = 99 \text{ M}$, and $[B]_0 = 1000 \text{ M}$, what is the 2nd order reaction rate constant? Also find the pseudo-1st order rate constant.

- **Solution:**

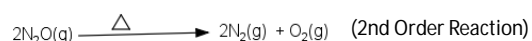
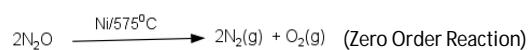
$$k' = -\frac{1}{tb_0} \ln \frac{a_t}{a_0} = -\frac{1}{39 \text{ s} \times 1000 \text{ M}} \ln \frac{55}{99} = 1.507 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{So, } k = 1.507 \times 10^{-5} \text{ M}^{-1} \cdot \text{s}^{-1} \times 1000 \text{ M} = 1.507 \times 10^{-2} \text{ s}^{-1}$$

Zero Order Reaction

- The rate remains constant throughout, although the concentration of the reactant goes on decreasing.
- It really sounds strange.
- But such a time-independent rate remains valid only in some restricted conditions and that too for a limited (small) time period.
- Therefore, we often say it to be **pseudo-zero order reaction**, as the reaction fakes to be a zero order for some limited time and thereafter the kinetics changes to non-zero order.

- Zero order reaction can happen for a single reactant reaction, if the reactant molecules are adsorbed on the surface of a hetero phase (say solid catalyst) catalyst and reaction occurs there.
- Once a reactant disappears, the product(s) is(are) expelled out the surface and new reactant molecule takes its place. Thus the concentration of the reactant remains virtually constant for some limited time.
- *During that time rate remains constant as the reactant concentration remains constant and the reaction behaves to be a zero order reaction.*
- After sometime, as the replenishment of reactant molecules does not take place at a steady rate, the reaction slows down.



Zero Order Integrated Rate equation

$$-\frac{d[A]}{dt} = \frac{dx}{dt} = k \quad \Rightarrow \quad \frac{dx}{dt} = k[A]^0$$

Unit of $k = M.t^{-1} = \text{mol.L}^{-1}.s^{-1}$ etc. (same as rate)

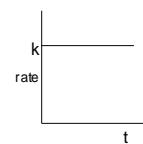
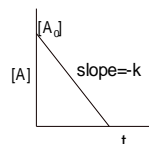
$$\frac{dx}{dt} = k \quad \Rightarrow \quad dx = k dt \quad \Rightarrow \quad \int dx = \int k dt$$

$\Rightarrow x = kt + C_0$ When $t=0, x=0$, So we get $C_0 = 0$; Thus

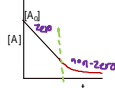
$$x = kt$$

$$\Rightarrow t = \frac{x}{k} = \frac{a_0 - a_t}{k}$$

$$\Rightarrow a_t = a_0 - kt \quad \Rightarrow [A] = [A]_0 - kt$$



- The graph looks paradoxical, as the $[A]$ or a_t decreases with time in it while in reality the $[A] = [A]_0$ remains constant as long as zero order kinetics persists.
- In fact, $[A]$ in the graph does not taken into account addition of fresh reactant to maintain it at a constant value. It shows only how $[A]$ decreases with time.
- The graph of zero order reaction is a myth and only a mathematical gimmick. $[A]$ never attains zero value.
- Actually, after a certain time, the kinetics become non-zero order and $[A]$ decreases exponentially.

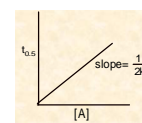


Half Life Period($t_{0.5}$) for Zero Order Reaction

- When $t=t_{0.5}, a_t=a_0/2$, So from zero order kinetics we have

$$a_t = a_0 - kt \quad \Rightarrow \quad \frac{a_0}{2} = a_0 - kt_{0.5}$$

$$\Rightarrow t_{0.5} = \frac{a_0}{2k}$$

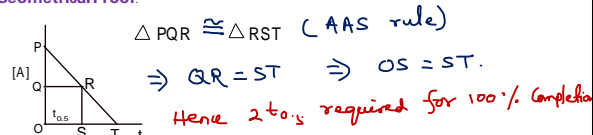


Half Life period is directly proportional to initial concentration of reactant.

Every half life period is one half of the previous half life period.

- Mathematically, two initial half life periods are required for 100% completion of the reaction, In reality, this never happens.
- $50\% = 1t_{0.5}; \quad 75\% = 1t_{0.5} + \frac{1}{2}t_{0.5}$
- $87.5\% = 1t_{0.5} + \frac{1}{2}t_{0.5} + \frac{1}{4}t_{0.5}$
- $93.75\% = 1t_{0.5} + \frac{1}{2}t_{0.5} + \frac{1}{4}t_{0.5} + \frac{1}{8}t_{0.5}$
- and this infinite series will add up to $2t_{0.5}$.

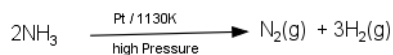
Geometrical Proof:



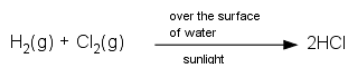
$$t = \frac{a_0 - a_t}{k} \quad \Rightarrow \quad t_{100\%} = \frac{a_0}{k} \quad \text{and} \quad t_{50\%} = \frac{a_0}{2k}$$

$$\Rightarrow \frac{t_{100\%}}{t_{50\%}} = 2 \quad \Rightarrow \quad t_{100\%} = 2t_{50\%}$$

Examples of Zero Order Reactions



Decomposition of NH_3 over the surface of Pt at high temperature and pressure



The reaction between $\text{H}_2(\text{g})$ with $\text{Cl}_2(\text{g})$ in a closed container over surface of water. As HCl formed get absorbed by water, $[\text{H}_2]$ and $[\text{Cl}_2]$ remain constant at constant pressure condition.

- Most enzyme catalyzed reactions in organisms.
- In pseudo-first order reaction, the order is zero w.r.t the reactant taken in excess.
- In some complex reactions, in which the concentration of a reactant does not appear in the rate law. It is zero order w.r.t that reactant.
- $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
- Rate = $k[\text{NO}_2]^2$

- **SAQ 1:** Using the integrated form of the rate law, determine the rate constant 'k' of a zero-order reaction if the initial concentration of substance A is 1.5 M and after 120 seconds the concentration of substance A is 0.75 M.
(Ans: $6.25 \times 10^{-3} \text{ Ms}^{-1}$)
- **SAQ 2:** Using the substance from the previous problem, what is the half-life of substance A if its original concentration is 1.2 M?
(Ans: 96 s)
- **SAQ 3:** If the original concentration is reduced to 1.0 M in the previous problem, does the half-life decrease, increase, or stay the same? If the half-life changes what is the new half-life?
(Changes, decreases, 80 sec)

- **SAQ 4:** Given are the rate constants k of three different reactions:

Reaction A: $k = 2.3 \text{ M}^{-1}\text{s}^{-1}$

Reaction B: $k = 1.8 \text{ Ms}^{-1}$

Reaction C: $k = 0.75 \text{ s}^{-1}$

Which reaction represents a zero-order reaction? (Ans.B)

3rd Order Kinetics

- $3\text{A} \rightarrow \text{products}; \quad 2\text{A} + \text{B} \rightarrow \text{products}$
 $r \propto [\text{A}]^3 \Rightarrow r = k[\text{A}]^3 \quad r \propto [\text{A}]^2[\text{B}]^1 \Rightarrow r = k[\text{A}]^2[\text{B}]^1$

$$\Rightarrow k = \frac{r}{[\text{concentration}]^3} = \frac{\text{M} \cdot \text{s}^{-1}}{\text{M}^3} = \text{M}^{-2} \text{s}^{-1} = \text{L}^2 \text{mol}^{-2} \cdot \text{s}^{-1}$$

$$\frac{dx}{dt} = k(a_0 - x)^3 \quad \text{Differential Rate Equation}$$

Integrated Rate Equation

$$\frac{dx}{dt} = k(a_0 - x)^3 \quad \Rightarrow \frac{dx}{(a_0 - x)^3} = k dt$$

$$\Rightarrow \int \frac{dx}{(a_0 - x)^3} = \int k dt \quad \Rightarrow \frac{1}{2(a_0 - x)^2} = kt + C_0$$

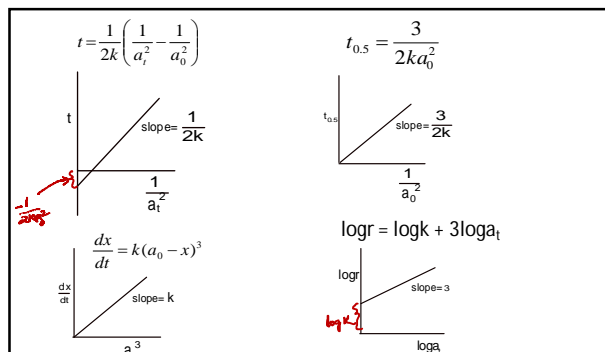
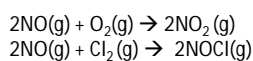
When $t=0, x=0$, So we get $C_0 = \frac{1}{2a_0^2}$ Substituting the value of C_0 ,

$$\Rightarrow \frac{1}{2a_t^2} = kt + \frac{1}{2a_0^2} \quad \Rightarrow k = \frac{1}{2t} \left(\frac{1}{a_t^2} - \frac{1}{a_0^2} \right)$$

- Half Life Period($t_{0.5}$): when $t=t_{0.5}$, $a_t=a_0/2$, so we have

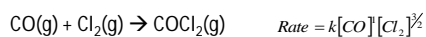
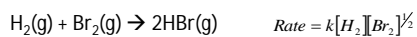
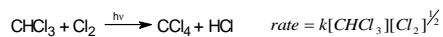
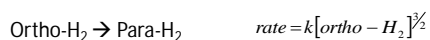
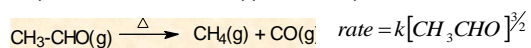
$$t_{0.5} = \frac{3}{2ka_0^2} \quad t_{0.5} \propto \frac{1}{a_0^2}$$

Examples



Fractional Order Reaction

- Examples: (Fractional order appear in complex reactions)



Negative Order Reaction

- This also occurs in some complex reactions.
- $2\text{O}_3 \rightarrow 3\text{O}_2$ (Decomposition of ozone)

$$\text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} = k[\text{O}_3]^2 \times [\text{O}_2]^{-1}$$

The reaction is **-1 order** w.r.t O_2 and **2nd order** w.r.t O_3 .
The rate decreases with increase in $[\text{O}_2]$

Note that in this case we cannot say overall order=1. In complex reactions, overall order is not determined.

- General Expression for Integrated Rate Equation (Except 1st order)

$$k = \frac{1}{(n-1)t} \left(\frac{1}{a_t^{n-1}} - \frac{1}{a_0^{n-1}} \right) \quad n = \text{order of reaction}$$

General Relationship for Half Life period($t_{0.5}$)

$$t_{0.5} \propto \frac{1}{a_0^{n-1}}$$

General Expression for the Unit of Rate constant(k)

$$\text{M}^{1-n} \text{s}^{-1} \quad ; \quad \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$