5/27/20

Integrated rate laws

Zero-order rxn

$R = k$

The rate of reaction is independent of any concentrations

reagent X

$$\frac{\Delta[X]}{\Delta t} = -k \quad \text{(average)}$$

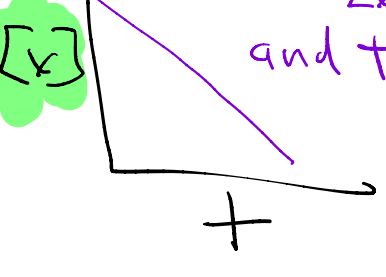
reagents disappear over time

$$\frac{d[X]}{dt} = -k$$

$$d[X] = -k\,dt$$

$$\int_{[X]_0}^{[X]_t} d[X] = \int_0^t -k\,dt$$

linear relationship between $[X]$ and t



$$[X]_t - [X]_0 = -kt$$

$$[X]_t = [X]_0 - kt$$

1st-order reaction

↳ One molecule is involved in the RLS

This the reagent that's in the RLS

$$R = -k[x]$$

$$\frac{d[x]}{dt} = -k[x]$$

$$\frac{d[x]}{[x]} = -k\,dt$$

$$\frac{1}{[x]}\,dx = -k\,dt$$

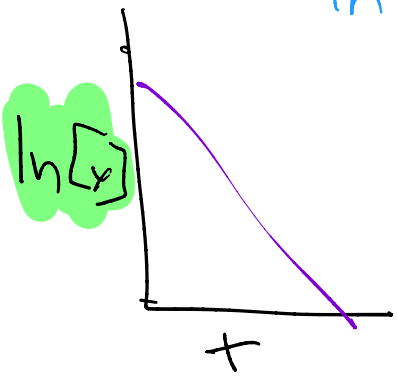
$$\int_{[x]_0}^{[x]_t} \frac{1}{[x]}\,dx = \int_0^t -k\,dt$$

$$\ln x \Big|_{[x]_0}^{[x]_t} = -kt \Big|_0^t$$

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

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

let $y = \ln[x]_t$



Second-order reaction (involving two molecules of one reagent)

$$R = -k[x]^2$$

$$\frac{d[x]}{dt} = -k[x]^2$$

$$\frac{1}{x^2}\,d[x] = -k\,dt$$

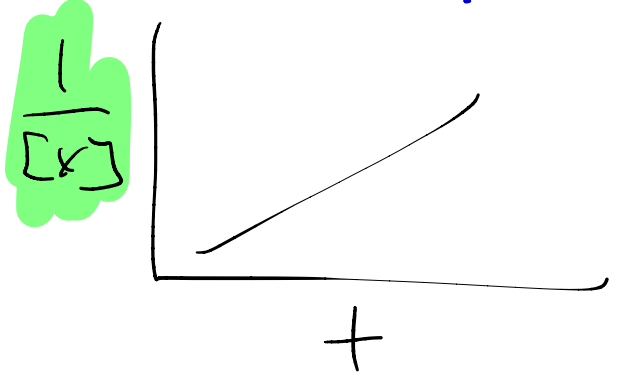
$$\int \frac{1}{x^2}\,d[x] = \int -k\,dt$$

$$-\frac{1}{x}\Big|_0^t = -kt\Big|_0^t$$

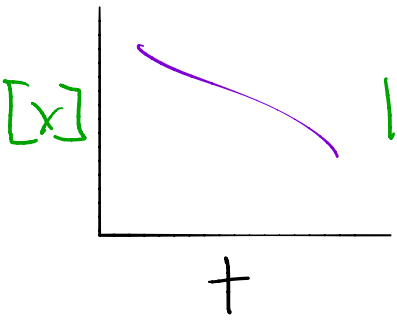
$$\frac{1}{x_t} - \frac{1}{x_0} = kt$$

$$\frac{1}{x_t} = \frac{1}{x_0} + kt$$

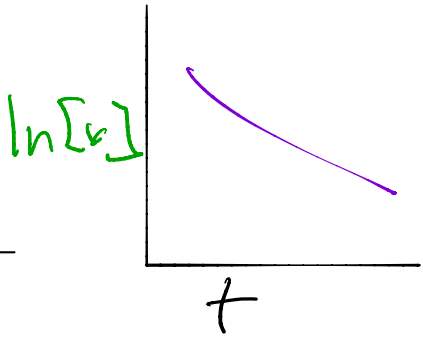
let $y = 1/x_t$



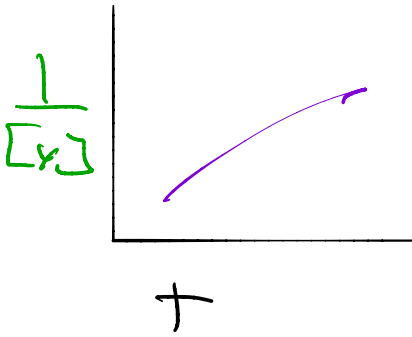
0 - order



1st - order

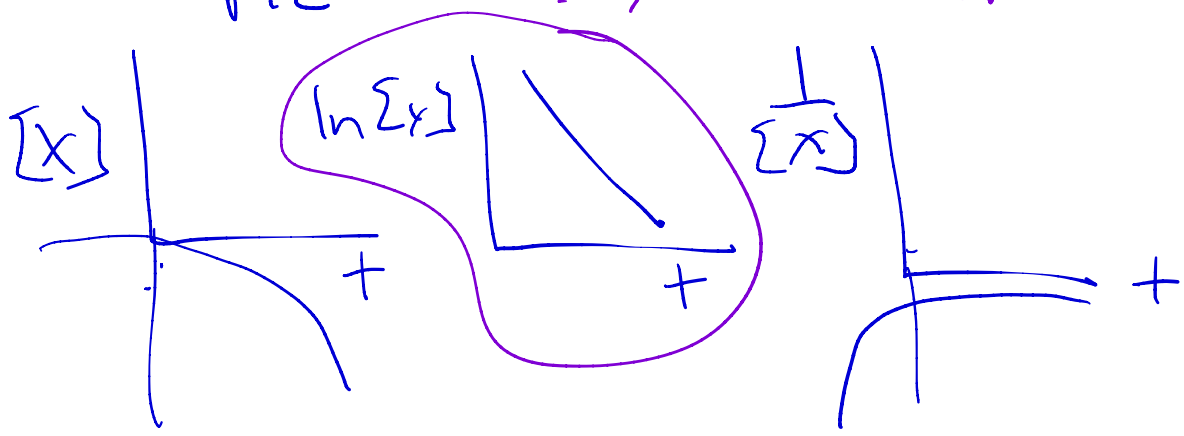


2nd - order



Any one reagent only has a single reaction order. If three graphs are prepared; [x] vs t; ln[x] vs t; $\frac{1}{[x]}$ vs t; only one graph will be linear, and that graph confirms the order of that reagent in the reaction.

Example → 1st - order



In the integrated rate law method, if there are multiple reagents, the dependency on one reagent can be established by keeping the concentrations of the other reagents large by comparison. This will make the change in the concentrations of the other reagents small, so any effect on reaction rate will only be due to the reagent being targeted.

$$2A + 3B \rightarrow 1C + 4D$$

reactants disappearing → rate → negative

products appearing → rate → positive

$$\text{rate} = -\frac{1}{1}\frac{\Delta[C]}{\Delta t} = \frac{1}{4}\frac{\Delta[D]}{\Delta t} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$$

$$= -\frac{1}{3}\frac{\Delta[B]}{\Delta t}$$

Bases → Most common definition

→ Base reacts with H^+

$$H_3N: + H^+ \rightleftharpoons H_4N^{\oplus}$$

ammonia — ammonium

→ Assume aqueous conditions

$$H_3N_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_4N^{\oplus}_{(aq)} + OH^-_{(aq)}$$

$$K_B = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

base dissociation constant

$$K_B = \frac{[HB^+][OH^-]}{[B]}$$

(if the base is neutral)

$$K_B = \frac{[HB][OH^-]}{[B^-]}$$

(if the base is an anion)

$$K_a \cdot K_B = \frac{[H^+][A^-]}{[HA]} \cdot \frac{[HB][OH^-]}{[B^-]}$$

If HA/HB and A/B are conjugates

$$= [H^+][OH^-] = K_w$$

Здравствуйте

नमस्कार