Class 2

Method of initial rates

→ measure rates when different concentrations of reactants are mixed, immediately after the reaction starts.

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2 + 2H_2O(l)$$

Expt	$[NH_4^+]_0$	$[NO_2^-]_0$	Rates
1	0.1 M	0.005 M	$1.35 * 10^{-7}$ ($mol\,L^{-1}s^{-1}$)
2	0.1 M	0.01 M	$2.70 * 10^{-7}$ "
3	0.2 M	0.01 M	$5.4 * 10^{-7}$

$$\text{rate} = -\frac{d[NH_4^+]}{dt} = k[NH_4^+]^n[NO_2^-]^m$$

$n = 1$ & $m = 1$ $\quad \boxed{\text{rate} = k[NH_4^+][NO_2^-]}$

Integrated rate laws

$$-\frac{d[A]}{dt} = k[A]^n$$ is a

differential equation.

we wish to find the value of

$[A]$ at time $t = t$

We need to <u>integrate</u>

0th order

rate $-\dfrac{d[A]}{dt} = k[A]^0 = k$

Enzyme kinetics

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

$$-[A] + [A]_0 = k(t-0) = kt$$

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

Half life of a reaction:

Time $t = t_{1/2}$ when $[A] = \dfrac{[A]_0}{2}$

$\dfrac{[A]_0}{2} = -k t_{1/2} + [A]_0 \Rightarrow$ $\underline{t_{1/2} = [A]_0/2k}$

1st order

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

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

$$-\ln[A] + \ln[A]_0 = kt$$

$$\boxed{\ln[A] = -kt + \ln[A]_0} \quad \text{or} \quad \boxed{\ln\frac{[A]_0}{[A]} = kt}$$

at $t = t_{1/2}$; $[A] = \frac{[A_0]}{2}$

$$\ln\frac{[A_0]}{[A_0]/2} = kt_{1/2} \quad : \quad \ln 2 = kt_{1/2}$$

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

Second order

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

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t k\,dt$$

$$+\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad \text{or} \quad \boxed{\frac{1}{[A]} = \frac{1}{[A]_0} + kt}$$

when $t = t_{1/2}$; $[A] = \frac{[A]_0}{2}$

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt \Rightarrow \boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

Newtons Law of Cooling

$$-\frac{dT}{dt} = k\Delta T = kT - kT_{env.}$$

the rate of cooling is proportional to the temperature difference

$$-\int \frac{d\Delta T}{dt} = \int k\,\Delta t$$

$$-\int \frac{d\Delta T}{\Delta T} = \int k\,dt \qquad \Delta T(t) = \underbrace{\Delta T(0)}_{\text{diff at time } 0} e^{-kt}$$

Compound interest

$$A = P\left(1 + \frac{r}{n}\right)^{nt}$$

A accumulated value (including principal P)

r annual interest rate

n is the compounding frequency
(eg. 1 time per year)

t is time

\$1500 at 4% compounded annually
over 20 years

$t = 20,\ r = 0.04,\ n = 1$

$A = \$\,3286.68$ cents

If the compounding is instantaneous
(continuous compounding)

$$P(t) = P_0 e^{rt}$$

$P_0 = \$1{,}500$

$r = 4\% = 0.04$

$t = 20$ years

$P(20 \text{ years}) = \$3338.31$

$\$1{,}800$ in 40 years at 10% annually is $\$100{,}000$.