Expression of rate Constant for Second Order reaction

(1) When the Concentration of both the reactants are same :-

$$2A \longrightarrow \text{Product}$$

initial concentration	'a' mole/L	0
Concentration after time 't' sec.	$(a-x)$	x

The rate of reaction $\frac{dx}{dt} = K(a-x)^2$

where K = rate constant of 2nd order reaction.

or $\frac{dx}{(a-x)^2} = K \cdot dt$

taking Intigration on both sides –

$$\int \frac{dx}{(a-x)^2} = K \int dt$$

or $\frac{1}{(a-x)} = Kt + I$ ——— (1)

Where, I = Intigration Constant

When $t = 0$, $x = 0$

putting these value in eqn — (1)

$$\frac{1}{a} = I$$

putting the value of 'I' in eqn — (1) we get,

$$\frac{1}{(a-x)} = Kt + 1/a$$

or, $$Kt = \frac{1}{(a-x)} - \frac{1}{a}$$

or $$Kt = \frac{a-a+x}{a(a-x)} = \frac{x}{a(a-x)}$$

∴ $$\boxed{K = \frac{1}{t} \times \frac{x}{a(a-x)}} \quad \text{—— (2)}$$

eqⁿ – (2) is the expression of rate constant of 2nd order reaction.

(2) When the concentration of both the reactants are differents :-

$$A + B \longrightarrow \text{Product}$$

	A	B	Product
Initial Concn.	a mole/L	b mole/L	0
after time 't' sec.	$(a-x)$ mole/L	$(b-x)$ mole/L	

The rate of reaction —

$$\frac{dx}{dt} = K(a-x)(b-x)$$

or $$\frac{dx}{(a-x)(b-x)} = K\,dt$$

taking integration on both sides —

$$\int \frac{dx}{(a-x)(b-x)} = k\int dt$$

or $$\frac{1}{(a-b)} \int \left[\frac{1}{(b-x)} - \frac{1}{(a-x)} \right] dx = kt + I \quad \text{——— (1)}$$

where, I = Integration Constant.

or $$\frac{1}{(a-b)} \int \frac{dx}{(b-x)} - \frac{dx}{(a-x)} = kt + I$$

or $$\frac{1}{(a-b)} \left[-\ln(b-x) - \{ \ln(a-x) \} \right] = kt + I$$

or $$\frac{1}{(a-b)} \left[\ln(a-x) - \ln(b-x) \right. = kt + I$$

or $$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = kt + I \quad \text{——— (2)}$$

When $t = 0$ $x = 0$

$$I = \frac{1}{(a-b)} \ln \frac{a}{b}$$

putting the value of I in eqn (2) we get

$$\frac{1}{(a-b)} \ln \left\{ \frac{a-x}{b-x} \right\} = kt + \frac{1}{(a-b)} \ln \frac{a}{b}$$

or $$\frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} - \ln \frac{a}{b} \right. = kt$$

or $$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} \Big/ \frac{a}{b} = kt$$

or $$Kt = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

or $$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad \text{--- (3)}$$

Eqn – (3) is the expression of rate constant when the Concentration of both the reactants are different.

from
Dr. A. K. Gupta,
Chemistry