First order reaction:— If the total change in concentration of reacting species with respect to time experimently is equal to one then the reaction is said to be first order reaction.

i.e $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

Calculation of rate constant 'K' in first order reaction by integration method:—

	A →	B
Initial moles $t=0$	a	0
Final $t = t$ sec	$(a-x)$	x

According to rate law the rate of chemical reaction is directly proportional to the left concentration of reacting species.

$$\frac{dx}{dt} \propto (a-x)$$

$$\frac{dx}{(a-x)} \propto dt$$

$$\text{or} \quad \frac{dx}{a-x} = K \cdot dt \quad \text{—— I}$$

Where K is constant called rate constant.

Integrate both sides we have

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

$$-\ln(a-x) = kt + c \text{ ———— } II$$

Where 'c' is Constant Called Integration Const.

At equilibrium, $t=0$, then $x=0$

then equation II will be:

$$-\ln a = c \text{ ———— } III$$

Now we put the value of 'c' from eqn III to eqn II we have

$$-\ln a-x = kt - \ln a$$

or $K = \frac{1}{t} \ln \frac{a}{(a-x)}$

or $\boxed{k = \frac{2.303}{t} \log \frac{a}{(a-x)}}$

This is known as Kinetic equation for 1st order reaction.

During titration if volume at zero time, infinite time or angle of rotation of optically active compounds are given then the above kinetic equation can be used in this way also.

<u>Case I</u> V at zero time & given time is given then

$$K = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

<u>Case II</u> If volume at infinite time & volume at a given time is given then

$$K = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

<u>Case III</u> If volume at zero time, at a fix-time and at infinite time all three are given then:

$$K = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

Case IV If degree of rotation is given at zero time, infinite time & given time, then

$$K = \frac{2.303}{t}\log\frac{r_\infty - r_0}{r_\infty - r_t}$$

r_0, r_f & r_t can be used as volume only as mentioned above.

Integrated Rate equation for 1st order gas phase reaction:→

$$A(g) \longrightarrow B(g) + C(g)$$

Pressure at initial time (in atm)	P_0	0	0
Pressure at final time (t) (in atm)	$(P_0 - p)$	p	p

Total pressure of the reaction mixture:-

$$P_T = P_0 - \cancel{p} + \cancel{p} + p$$

$$P_T = P_0 + p$$

$$p = P_T - P_0$$

Pressure of A after time t, $P_A = P_0' - p$

$$= P_0 - (P_T - P_0)$$

$$= 2P_0 - P_T$$

By the first order rate equation $K = \frac{2.303}{t} \log \frac{A_0}{A_t}$

$$\boxed{K = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_T}}$$

Where K = rate constant

t = time

P_0 = Initial pressure of A

P_T = Total pressure of gaseous mixture.