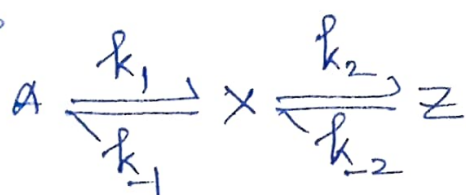


① A situation where the ratio of rate constants is not the equilibrium constant.

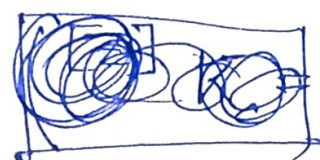
Let us consider the reaction as follows



All the rate constants are assumed to be first order

If the system is at complete equilibrium,

$$\left(\frac{[X]}{[A]}\right)_{eq} = \frac{k_1}{k_{-1}} \text{ and } \left(\frac{[Z]}{[X]}\right)_{eq} = \frac{k_2}{k_{-2}}$$

and  $\frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} = \left(\frac{[X]}{[A]}\right)_{eq} \left(\frac{[Z]}{[X]}\right)_{eq}$

$$= \left(\frac{[Z]}{[A]}\right)_{eq} = K_c$$

Again, let us consider two limiting situations:

① At the very beginning of the reaction before any X and Z have accumulated,

$$-\frac{d[A]}{dt} = k_1[A] \quad \left[\begin{array}{l} \text{Assuming} \\ A \xrightarrow{k_1} \bullet \text{ (No X is formed initially)} \end{array} \right]$$

above said

Since the ~~A → Z~~ reaction is a kind of opposing reaction, wherever you start either from A or Z, finally the reaction relaxes to the equilibrium condition, where A, X and Z will be in equilibrium.

don't need to write in exam!!!

② Therefore, if one starts with pure Z ~~and measures~~, $-\frac{d[Z]}{dt} = k_{-2}[Z]$

Since, we compute @ rates of consumptions of ~~the~~ the reactant A and product Z at the very beginning not at the equilibrium condition,

$$-\frac{d[A]}{dt} \neq -\frac{d[Z]}{dt}$$

$$\therefore k_1[A] \neq k_{-2}[Z]$$

That means

~~$$\frac{k_1}{k_{-2}} \neq \frac{[Z]}{[A]}$$~~

Remember

$$K_c = \left(\frac{[Z]}{[A]} \right)_{eq}$$

$$\neq \frac{[Z]}{[A]}$$

$$\neq K_c \left[\frac{[Z]}{[A]} \right]_{eq}$$

Applying the steady state approximation,

$$\frac{d[X]}{dt} = k_1[A] - (k_{-1} + k_2)[X] + k_{-2}[Z]$$

$$\stackrel{=0}{\text{therefore}}, [X] = \frac{k_1[A] + k_{-2}[Z]}{k_{-1} + k_2} \quad \text{--- eq. x}$$

The net rate of consumption of A is

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X] \quad \text{--- eq. } v_A$$

Introduction of the expression for $[X]$ (see eq. x) in the (eq. y) gives

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X]$$

$$= k_1[A] - k_{-1} \frac{k_1[A] + k_{-2}[Z]}{k_{-1} + k_2}$$

$$= k_1[A] - \frac{k_{-1}k_1[A] + k_{-1}k_{-2}[Z]}{k_{-1} + k_2}$$

$$= \frac{k_1[A](k_{-1} + k_2) - k_{-1}k_1[A] - k_{-1}k_{-2}[Z]}{k_{-1} + k_2}$$

$$= \frac{k_1k_{-1}[A] + k_1k_2[A] - k_{-1}k_1[A] - k_{-1}k_{-2}[Z]}{k_{-1} + k_2}$$

$$-\frac{d[A]}{dt} = \frac{k_1k_2[A]}{k_{-1} + k_2} - \frac{k_{-1}k_{-2}[Z]}{k_{-1} + k_2}$$

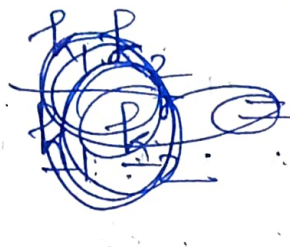
1. The first term is \rightarrow
~~the rate of the reaction~~
~~from left to right and~~
 the rate constant is $\frac{k_1k_2}{k_{-1} + k_2}$.

[Why is the first term called the rate of the reaction from left to right?]

Ans: If you consider only the first term, $-\frac{d[A]}{dt} \propto [A] \rightarrow$ that means the reaction of $A \rightarrow Z$.

Similarly, the rate constant from right to left is $\frac{k_1 k_2}{k_{-1} + k_{-2}}$.

The ratio of the two rate constants

 $\frac{k_1 k_2}{(k_{-1} + k_{-2})} \times \frac{(k_{-1} + k_{-2})}{k_{-1} k_{-2}} = \frac{k_1 k_2}{k_{-1} k_{-2}}$

is equal to the equilibrium constant.