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

Let us consider the reaction as follows

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Z$$

All the rate constants are assumed to be first order

If the system is at complete equilibrium,

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

and

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

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

Again, let us consider two limiting situations:

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

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

[Assuming $A \xrightarrow{k_1}$ (No X is formed initially)]

Since the ~~A~~ above said reaction is a kind of opposing reaction, wherever ~~you~~ we 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!!!

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Therefore, if one starts with pure Z ~~and measures~~

$$-\frac{d[Z]}{dt} = k_{-2}[Z]$$

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

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

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

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

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

Remember

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

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

Applying the steady state approximation,

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

$$=0$$

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

The net rate of consumption of A is $-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X]$

— eq. $v_A$

Introduction of the expression for [X] (see eq. X) in the (eq. VA) gives

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

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

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

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

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

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

The first term is the rate of the reaction from left to right and the rate constant is $\frac{k_1 k_2}{k_{-1} + k_2}$.

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

Ans: If you consider only the first term, $-\frac{d[A]}{dt} \propto [A]$ → 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.