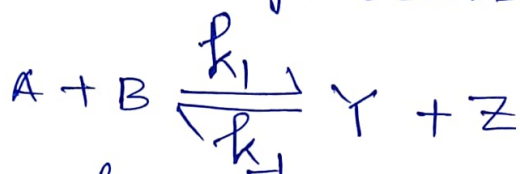① Few important points on "Microscopic. Reversibility and Detailed Balance"

For an elementary reaction the equilibrium constant must be the ratio of the rate constants in the forward and reverse directions.

Consider the process

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y + Z$$

The rate of the forward direction
$(A + B \longrightarrow Y + Z)$ is

$$v_1 = k_1 [A][B]$$

and for the reverse direction $(Y + Z \rightarrow A + B)$ is

$$v_{-1} = k_{-1} [Y][Z]$$

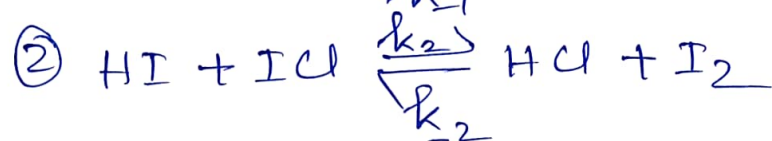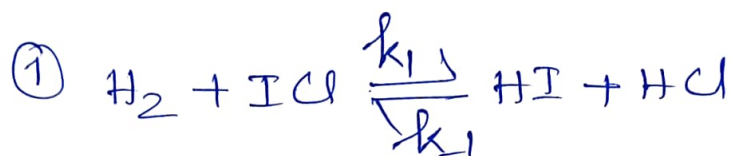If the system is at equilibrium, these rates are equal; hence,

$$v_1 = v_{-1}$$

$$k_1 \Big([A][B] \Big)_{eq} = k_{-1} \Big([Y][Z] \Big)_{eq}$$

$$\frac{k_1}{k_{-1}} = \left(\frac{[Y][Z]}{[A][B]} \right)_{eq} = K_c \Rightarrow \text{Equilibrium constant}$$

[ ]$_{eq} \rightarrow$ stands for equilibrium concentration.
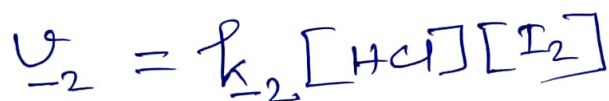
@ for example, consider the reaction.

$$H_2 + 2ICl \rightleftharpoons I_2 + 2HCl.$$

At equilibrium the processes are occurring at equal rates in the forward and reverse directions:

① $H_2 + ICl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HI + HCl$

② $HI + ICl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCl + I_2$

~~At equilibrium~~, The rates of the reactions involved in step ① are

$v_1 = k_1 [H_2][ICl]$ ⟹ $H_2 + ICl \xrightarrow{k_1} HI + HCl$

$v_{-1} = k_{-1}[HI][HCl]$ ⟹ $HI + HCl \xrightarrow{k_{-1}} H_2 + ICl$

Similarly, for the step ②, the rates are
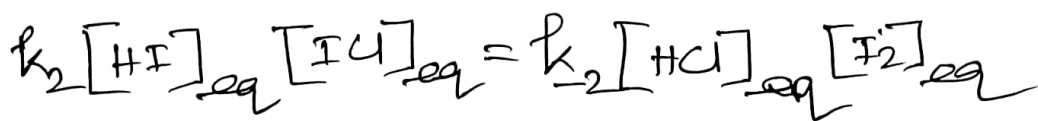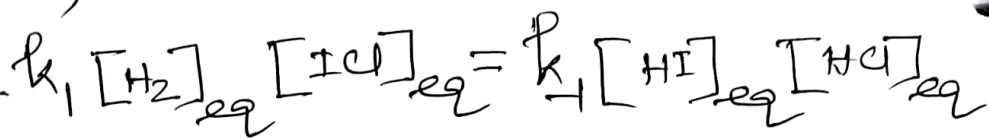
$v_2 = k_2[HI][ICl]$

$v_{-2} = k_{-2}[HCl][I_2]$

⟶ Put this statement here.

At equilibrium, $v_1 = v_{-1}$

and $v_2 = v_{-2}$

Remember the concentrations are equilibrium concentrations ~~at the~~ when ~~the~~ $v_1 = v_{-1}$ & $v_2 = v_{-2}$

③ Therefore,

$$k_1 [H_2]_{eq} [ICl]_{eq} = k_1 [HI]_{eq} [HCl]_{eq}$$

$$k_2 [HI]_{eq} [ICl]_{eq} = k_2 [HCl]_{eq} [I_2]_{eq}$$

$$\frac{k_1}{k_1} = \left(\frac{[HI][HCl]}{[H_2][ICl]}\right)_{eq} = K_1 \left(\begin{array}{c}\text{equili} \\ \text{-brium} \\ \text{constant} \\ \text{for the} \\ \text{step ①}\end{array}\right)$$

$$\frac{k_2}{k_2} = \left(\frac{[HCl][I_2]}{[HI][ICl]}\right)_{eq}$$

$$= K_2 \left(\begin{array}{c}\text{Equilibrium constant} \\ \text{for the step ②}\end{array}\right)$$

The product of these two equilibri-um constant is

$$K_1 K_2 = \frac{k_1}{k_1} \times \frac{k_2}{k_2} = \left(\frac{[HI][HCl]}{[H_2][ICl]}\right)_{eq}$$

$$\times \left(\frac{[HCl][I_2]}{[HI][ICl]}\right)_{eq}$$

$$= \left(\frac{[I_2][HCl]^2}{[H_2][ICl]^2}\right)_{eq} = K_c$$

A) K_c is the equilibrium constant for the overall reaction.

$$H_2 + 2ICl \rightleftharpoons I_2 + 2HCl$$

$$K_c = \frac{[I_2]_{eq} [HCl]^2_{eq}}{[H_2]_{eq} [ICl]^2_{eq}}$$
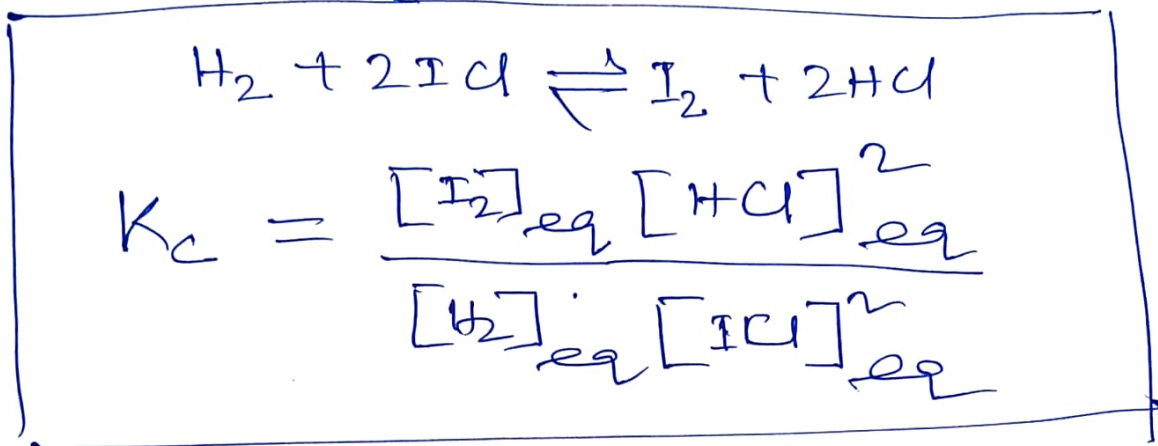
In summary, for any mechanism, involving any number of elementary and consecutive steps, the overall equilibrium constant is the product of the equilibrium constants for the individual steps and is the product of the rate constants for the reactions in the forward direction divided by the product of those for the reverse reactions!

$$K_c = K_1 K_2 K_3 \cdots = \frac{k_1 k_2 k_3 \cdots}{k_{-1} k_{-2} k_{-3} \cdots}$$

1) If a reaction occurs by a composite mechanism, and we measure a rate coefficient k_1 for the overall reaction from left to right and also measure a rate coefficient k_{-1} for the overall

⑤ reaction from right to left, at the same temperature, the ratio k_1/k_{-1} is not necessarily the equilibrium constant for the overall reaction.

(ii) The reason is that rate laws for composite reactions change with experimental conditions, such as reactant concentrations; and the rate coefficients also change.

(iii) ~~long~~ The ratio of the rate coefficients k_1 and k_{-1} that apply when the system is at equilibrium is equal to the equilibrium constant, but rate coefficients determined away from the ~~the~~ equilibrium are not necessarily the same as those at equilibrium, and their ratio is not necessarily equal to K_c.

When the rates are not in equili...

$$v_1 \neq v_{-1}$$

$$v_2 \neq v_{-2}$$