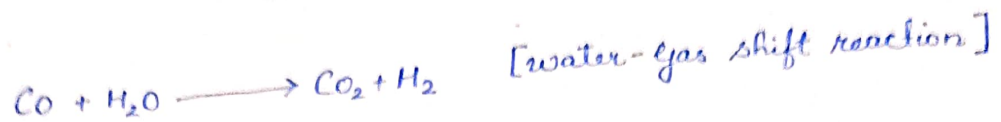
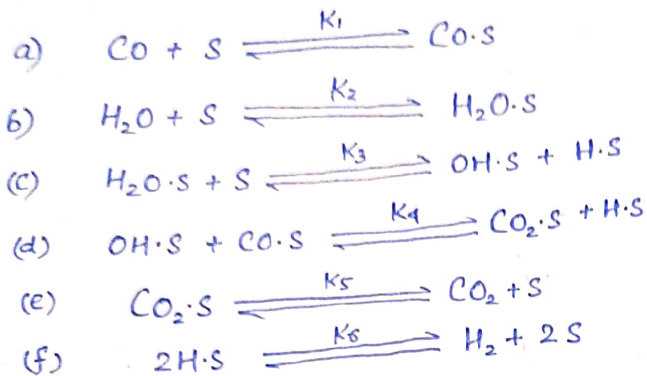


## Quiz 2 (Solutions)

(1)



Mechanism:



(a) Equation (d) is irreversible rate determining step and all other steps are in quasi-equilibrium ( $\gamma \approx 0$ )

$$\text{OH} \cdot \text{S} + \text{CO} \cdot \text{S} \xrightarrow{K_4} \text{CO}_2 \cdot \text{S} + \text{H} \cdot \text{S}$$

$$\theta_{\text{CO}} = K_1 P_{\text{CO}} \theta_{\text{V}} \quad \text{--- (4)}$$

$$\theta_{\text{H}_2\text{O}} = K_2 P_{\text{H}_2\text{O}} \theta_{\text{V}} \quad \text{--- (4)}$$

$$\theta_{\text{CO}_2} = K_5^{-1} P_{\text{CO}_2} \theta_{\text{V}} \quad \text{--- (4)}$$

$$\theta_{\text{H}} = K_6^{-1/2} P_{\text{H}_2}^{1/2} \theta_{\text{V}} \quad \text{--- (5)}$$

$$\theta_{\text{H}} \theta_{\text{OH}} = K_3 \theta_{\text{H}_2\text{O}} \theta_{\text{V}} \quad \text{--- (4)}$$

$$\left. \begin{aligned} \theta_{\text{OH}} &= \frac{K_3 K_2 P_{\text{H}_2\text{O}} \theta_{\text{V}}^2}{K_6^{-1/2} P_{\text{H}_2}^{1/2} \theta_{\text{V}}} \\ \theta_{\text{OH}} &= \frac{K_3 K_2 P_{\text{H}_2\text{O}} \theta_{\text{V}}}{K_6^{-1/2} P_{\text{H}_2}^{1/2}} \end{aligned} \right\} \quad \text{--- (9)}$$

$$\left\{ \begin{aligned} \gamma_6 &= K_6 \theta_{\text{H}}^2 - K_6 P_{\text{H}_2} \theta_{\text{V}}^2 \\ \gamma_6 &= K_6 \left[ \theta_{\text{H}}^2 - \frac{P_{\text{H}_2} \theta_{\text{V}}^2}{K_6} \right] \\ \gamma_6 &= 0 \\ K_6 \theta_{\text{H}}^2 &= P_{\text{H}_2} \theta_{\text{V}}^2 \\ \theta_{\text{H}} &= K_6^{-1/2} P_{\text{H}_2}^{1/2} \theta_{\text{V}} \end{aligned} \right.$$

Since, CO & H are in abundance, so, applying MARI approximation

$$\therefore \boxed{\theta_{\text{CO}} + \theta_{\text{H}} + \theta_{\text{V}} = 1} \quad \text{--- (2)}$$

$$K_1 P_{\text{CO}} \theta_{\text{V}} + K_6^{-1/2} P_{\text{H}_2}^{1/2} \theta_{\text{V}} + \theta_{\text{V}} = 1$$

$$\boxed{\theta_{\text{V}} = \frac{1}{K_1 P_{\text{CO}} + K_6^{-1/2} P_{\text{H}_2}^{1/2} + 1}} \quad \text{--- (2)}$$

$$\left. \begin{aligned} r^+ &= -k_4^+ \theta_{OH} \theta_{CO} \\ r^+ &= -k_4^+ k_1 k_6^{-1/2} k_3 k_2 \frac{P_{H_2O} P_{CO}}{P_{H_2}^{1/2}} \theta_V^2 \\ r^+ &= -k_1 k_2 k_3 k_4^+ k_6^{-1/2} \frac{P_{H_2O} P_{CO}}{P_{H_2}^{1/2}} \theta_V^2 \end{aligned} \right\} \rightarrow (8)$$

(b) Equation (c) is rate determining step & irreversible. All other steps are in quasi-equilibrium.

$$\begin{aligned} \theta_{CO} &= k_1 P_{CO} \theta_V \quad \text{--- (6)} \\ \theta_{H_2O} &= k_2 P_{H_2O} \theta_V \quad \text{--- (6)} \\ \theta_{CO_2} \theta_H &= k_4 \theta_{OH} \theta_{CO} \quad \text{--- (6)} \\ \theta_H &= K_6^{-1/2} P_{H_2}^{1/2} \theta_V \quad \text{--- (6)} \\ \theta_{CO_2} &= K_5^{-1} P_{CO_2} \theta_V \quad \text{--- (6)} \end{aligned}$$

$$\left. \begin{aligned} r &= -k_3^+ \theta_{H_2O} \theta_V \\ r &= -k_3^+ k_2 P_{H_2O} \theta_V^2 \\ r &= -k_3^+ k_2 P_{H_2O} \left( \frac{1}{k_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} + 1} \right)^2 \end{aligned} \right\} \text{--- (6)}$$

(c) For Part (a) of question where equation - (d) is rate determining & irreversible

$$\boxed{\alpha_{CO} = P_{CO} \frac{\partial \ln r}{\partial P_{CO}}} \quad \text{--- (2)}$$

$\alpha_{CO}$  is order w.r.t CO

$$\left. \begin{aligned} \alpha_{CO} &= P_{CO} \frac{\partial}{\partial P_{CO}} \left[ \ln \left( k_4^+ k_1 k_2 k_3 k_6^{-1/2} \right) + \ln P_{H_2O} + \ln P_{CO} - \frac{1}{2} \ln P_{H_2} - \right. \\ &\quad \left. 2 \ln (1 + k_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}) \right] \\ \alpha_{CO} &= P_{CO} \left[ 0 + 0 + \frac{1}{P_{CO}} - 0 - \frac{2 [K_1]}{1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}} \right] \\ \alpha_{CO} &= 1 - \frac{2 P_{CO} K_1}{(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2})} \end{aligned} \right\} \text{--- (6)}$$

$$\left. \begin{aligned} \alpha_{CO} &= 1 - 2 P_{CO} K_1 \theta_V \\ \boxed{\alpha_{CO} = 1 - 2 \theta_{CO}} \end{aligned} \right\} \rightarrow (3) \quad \text{[From } \theta_{CO} = k_1 P_{CO} \theta_V \text{]}$$

Also,

$$\alpha_{H_2} = P_{H_2} \frac{\partial \ln \gamma}{\partial P_{H_2}}$$

(2)

3

$$\alpha_{H_2} = P_{H_2} \frac{\partial}{\partial P_{H_2}} \left[ \ln (K_1^+ K_1 K_2 K_3 K_6^{1/2}) + \ln P_{H_2O} + \ln P_{CO} - \frac{1}{2} \ln P_{H_2} - 2 \ln (1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}) \right]$$

$$\alpha_{H_2} = P_{H_2} \frac{\partial}{\partial P_{H_2}} \left[ -\frac{1}{2} \ln P_{H_2} - 2 \ln (1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}) \right]$$

$$\alpha_{H_2} = P_{H_2} \left[ -\frac{1}{2} P_{H_2} - 2 \left( \frac{1/2 P_{H_2}^{-1/2} K_6^{-1/2}}{1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}} \right) \right]$$

6

$$\alpha_{H_2} = \frac{-P_{H_2}}{2 P_{H_2}} - 2 \frac{1/2 P_{H_2}^{1/2} K_6^{-1/2}}{1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}}$$

$$\alpha_{H_2} = -\frac{1}{2} - \frac{K_6^{-1/2} P_{H_2}^{1/2}}{(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2})}$$

$$\alpha_{H_2} = -\frac{1}{2} - \frac{K_6^{-1/2} P_{H_2}^{1/2} \Theta_V}{1}$$

$$\alpha_{H_2} = -\frac{1}{2} - \Theta_H$$

3

For Part (b) of question where equation (c) is rate determining & irreversible

$$\alpha_{CO} = P_{CO} \frac{\partial \ln \gamma}{\partial P_{CO}}$$

$$\alpha_{CO} = P_{CO} \frac{\partial}{\partial P_{CO}} \left[ \ln K_3^+ + \ln K_2 + \ln P_{H_2O} - 2 \ln (1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}) \right]$$

$$\alpha_{CO} = P_{CO} \frac{(-2 K_1)}{(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2})}$$

$$\alpha_{CO} = P_{CO} - 2 K_1 \Theta_V$$

$$\alpha_{CO} = -2 K_1 P_{CO} \Theta_V = -2 \Theta_{CO}$$

Similarly,

$$\alpha_{H_2} = P_{H_2} \frac{\partial \ln \gamma}{\partial P_{H_2}}$$

$$\alpha_{H_2} = P_{H_2} \frac{\partial}{\partial P_{H_2}} \left[ \ln K_3^+ K_2 + \ln P_{H_2O} - 2 \ln (1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}) \right]$$

$$\alpha_{H_2} = P_{H_2} \frac{(-2 K_6^{-1/2})}{2} \frac{1}{(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2})} = -K_6^{-1/2} P_{H_2}^{1/2} \Theta_V = -\Theta_H$$

∴ For Part (a):  $\alpha_{CO} = 1 - 2\theta_{CO}$

$$\alpha_{H_2} = -\frac{1}{2} - \theta_H$$

This seems consistent w.r.t experimental value since  $\theta_{CO} < 1$ .  
Therefore, order can be 0.6 if  $\theta_{CO} \approx 0.2$ . The order w.r.t  $H_2$  is negative and can be -0.6, if  $\theta_{H_2} \approx 0.1$ .

For Part (b):  $\alpha_{CO} = -2\theta_{CO}$

$$\alpha_{H_2} = -\theta_H$$

Here, this seems inconsistent as  $\theta_{CO}$  can never be negative. To get order 0.6 w.r.t CO.