Quiz 2
(Solutions)

$$CO + H_2O \longrightarrow CO_2 + H_2$$ [water-gas shift reaction]

Mechanism:

a) $CO + S \underset{}{\overset{K_1}{\rightleftharpoons}} CO \cdot S$

b) $H_2O + S \overset{K_2}{\rightleftharpoons} H_2O \cdot S$

(c) $H_2O \cdot S + S \overset{K_3}{\rightleftharpoons} OH \cdot S + H \cdot S$

(d) $OH \cdot S + CO \cdot S \overset{K_4}{\rightleftharpoons} CO_2 \cdot S + H \cdot S$

(e) $CO_2 \cdot S \overset{K_5}{\rightleftharpoons} CO_2 + S$

(f) $2H \cdot S \overset{K_6}{\rightleftharpoons} H_2 + 2S$

(a) Equation (d) is irreversible rate determining step and all other steps are in quasi-equillibrium ($r \equiv 0$) $\quad OH \cdot S + CO \cdot S \xrightarrow{k_4} CO_2 \cdot S + H \cdot S$

$$\theta_{CO} = K_1 P_{CO} \theta_v \quad \text{— (4)}$$

$$\theta_{H_2O} = K_2 P_{H_2O} \theta_v \quad \text{— (4)}$$

$$\theta_{CO_2} = K_5^{-1} P_{CO_2} \theta_v \quad \text{— (4)}$$

$$\theta_H = K_6^{-1/2} P_{H_2}^{1/2} \theta_v \quad \text{— (5)}$$

$$\left\{ \begin{aligned} r_6 &= k_6 \theta_H^2 - k_{-6} P_{H_2} \theta_v^2 \\ r_6 &= k_6 \left[\theta_H^2 - \frac{P_{H_2} \theta_v^2}{K_6} \right] \\ r_6 &= 0 \\ K_6 \theta_H^2 &= P_{H_2} \theta_v^2 \\ \theta_H &= K_6^{-1/2} P_{H_2}^{1/2} \theta_v \end{aligned} \right.$$

$$\theta_H \theta_{OH} = K_3 \theta_{H_2O} \theta_v \quad \text{— (4)}$$

$$\left. \begin{aligned} \theta_{OH} &= \frac{K_3 K_2 P_{H_2O} \theta_v^{\cancel{2}}}{K_6^{-1/2} P_{H_2}^{1/2} \cancel{\theta_v}} \\ \theta_{OH} &= \frac{K_3 K_2 P_{H_2O} \theta_v}{K_6^{-1/2} P_{H_2}^{1/2}} \end{aligned} \right\} \text{(9)}$$

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

$$\therefore \boxed{\theta_{CO} + \theta_H + \theta_v = 1} \quad \text{— (2)}$$

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

$$\boxed{\theta_v = \frac{1}{K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} + 1}} \quad \text{— (2)}$$

$$r^+ = -k_4^+ \theta_{OH} \theta_{CO}$$

$$r^+ = -k_4^+ K_1 K_6^{1/2} K_3 K_2 \frac{P_{H_2O} P_{CO} \theta_v^2}{P_{H_2}^{1/2}}$$

$$r^+ = -K_1 K_2 K_3 k_4^+ K_6^{1/2} \frac{P_{H_2O} P_{CO}}{P_{H_2}^{1/2}} \theta_v^2$$

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

$$\theta_{CO} = K_1 P_{CO} \theta_v \quad \text{— } 6$$

$$\theta_{H_2O} = K_2 P_{H_2O} \theta_v \quad \text{— } 6$$

$$\theta_{CO_2} \theta_H = K_4 \theta_{OH} \theta_{CO} \quad \text{— } 6$$

$$\theta_H = K_6^{-1/2} P_{H_2}^{1/2} \theta_v \quad \text{— } 6$$

$$\theta_{CO_2} = K_5^{-1} P_{CO_2} \theta_v \quad \text{— } 6$$

$$r = -k_3^+ \theta_{H_2O} \theta_v$$

$$r = -k_3^+ K_2 P_{H_2O} \theta_v^2$$

$$r = -k_3^+ K_2 P_{H_2O} \left(\frac{1}{K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} + 1} \right)^2$$

— 6

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

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

'α_{CO}' is order w.r.t CO

$$\alpha_{CO} = P_{CO} \frac{\partial}{\partial P_{CO}} \left[\ln \left(k_4^+ K_1 K_2 K_3 K_6^{1/2} \right) + \ln P_{H_2O} + \ln P_{CO} - \frac{1}{2} \ln P_{H_2} - 2 \ln \left(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} \right) \right]$$

$$\alpha_{CO} = P_{CO} \left[0 + 0 + \frac{1}{P_{CO}} - 0 - \frac{2 [K_1]}{1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2}} \right]$$

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

— 6

$$\alpha_{CO} = 1 - 2 P_{CO} K_1 \theta_v$$

$$\boxed{\alpha_{CO} = 1 - 2 \theta_{CO}}$$

→ 3 [From $\theta_{CO} = K_1 P_{CO} \theta_v$]

Also, $\boxed{\alpha_{H_2} = P_{H_2} \frac{\partial \ln r}{\partial P_{H_2}}}$ —— (a)

$$\alpha_{H_2} = P_{H_2} \frac{\partial}{\partial P_{H_2}} \left[\ln \left(k_4^{+} K_1 K_2 K_3 K_6^{1/2} \right) + \ln P_{H_2O} + \ln P_{CO} - \frac{1}{2} \ln P_{H_2} - 2 \ln \left(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} \right) \right]$$

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

(6) ←

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

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

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

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

$$\boxed{\alpha_{H_2} = -\frac{1}{2} - \theta_H}$$ —— (3)

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

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

$$\alpha_{CO} = P_{CO} \frac{\partial}{\partial P_{CO}} \left[\ln k_3^{+} + \ln K_2 + \ln H_2O - 2 \ln \left(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} \right) \right]$$

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

$$\alpha_{CO} = P_{CO} \; -2 K_1 \theta_v$$

$$\boxed{\alpha_{CO} = -2 K_1 P_{CO} \theta_v = -2 \theta_{CO}}$$

Similarly, $\alpha_{H_2} = P_{H_2} \frac{\partial \ln (r)}{\partial P_{H_2}}$

$$\alpha_{H_2} = P_{H_2} \frac{\partial}{\partial P_{H_2}} \left(\ln k_3^{+} K_2 + \ln H_2O - 2 \ln \left(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} \right) \right]$$

$$\boxed{\alpha_{H_2} = P_{H_2} \frac{(-\cancel{2} K_6^{-1/2}) \frac{1}{\cancel{2}} P_{H_2}^{-1/2}}{\left(1 + K_1 P_{CO} + K_6^{-1/2} P_{H_2}^{1/2} \right)} = -K_6^{-1/2} P_{H_2}^{1/2} \theta_v = -\theta_H}$$

$\therefore$ 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 $\theta_{CO} \simeq 0.2$. The order w.r.t H_2 is negative and can be -0.6, if $\theta_{H_2} \simeq 0.1$.

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

$\alpha_{H_2} = -\theta_H$

Here, this seems inconsistent as θ_{CO} can never be negative to get order 0.6 w.r.t CO.