Example 13.5 The water-gas-shift reaction

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
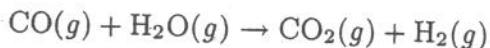
is carried out under the different sets of conditions described below. Calculate the fraction of steam reacted in each case. Assume the mixture behaves as an ideal gas.

(a) The reactants consist of 1 mol of H_2O vapor and 1 mol of CO. The temperature is 1100 K and the pressure is 1 bar.

(b) Same as (a) except that the pressure is 10 bar.

(c) Same as (a) except that 2 mol of N_2 is included in the reactants.

(d) The reactants are 2 mol of H_2O and 1 mol of CO. Other conditions are the same as in (a).

(e) The reactants are 1 mol of H_2O and 2 mol of CO. Other conditions are the same as in (a).

(f) The initial mixture consists of 1 mol of H_2O, 1 mol of CO, and 1 mol of CO_2. Other conditions are the same as in (a).

(g) Same as (a) except that the temperature is 1650 K.

(a) First K need to be calculated at 1100 K

$$\Delta H_0^\circ = -393509 + 0 - (-110525) - (-241818) = -41161$$

$$\Delta G_0^\circ = -394359 + 0 - (-137169) - (-228572) = -28618 \; \frac{J}{mol}$$

$$K_0 = \exp\left(-\frac{\Delta G^\circ}{RT_0}\right) = \exp\left(\frac{28618}{(8.314)(298.15)}\right) = 103\,260.84$$

assume ΔH° constant

$$\ln\left(\frac{K}{103260.84}\right) = \frac{41161}{8.314}\left(\frac{1}{1100} - \frac{1}{298.15}\right)$$

$$\Rightarrow K = 0.6$$

$$K \left(\frac{P}{P^0} \right)^{-\nu} = \prod_i (y_i)^{\nu_i} \qquad \left(\begin{array}{l} \text{ideal gas.} \\ \text{assumption} \end{array} \right)$$

$p = 1 \text{ bar}, \quad P_0 = 1 \text{ bar} \quad \text{\&} \quad \nu = 1 + 1 - 1 - 1 = 0,$

$$\Rightarrow \quad 0.6 = \frac{y_{H_2} \, y_{CO_2}}{y_{CO} \, y_{H_2O}} \qquad (1)$$

$$y_i = \frac{n_i}{n} = \frac{n_{io} + \nu_i \varepsilon}{n_0 + \gamma \varepsilon}$$

at equilibrium $\quad y_i = \dfrac{n_{io} + \nu_i \varepsilon_e}{n_0 + \gamma \varepsilon_e}$

$$y_{H_2} = \frac{\varepsilon_e}{2} \qquad\qquad y_{CO_2} = \frac{\varepsilon_e}{2}$$

$$y_{CO} = \frac{1 - \varepsilon_e}{2} \qquad\qquad y_{H_2O} = \frac{1 - \varepsilon_e}{2}$$

substitute in equation (1) above

$$0.6 = \frac{\left(\frac{\varepsilon_e}{2} \right) \left(\frac{\varepsilon_e}{2} \right)}{\left(\frac{1 - \varepsilon_e}{2} \right) \left(\frac{1 - \varepsilon_e}{2} \right)} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2}$$

$$0.6 \, (\varepsilon_e^2 - 2\varepsilon_e + 1) = \varepsilon_e^2$$

$$0.4 \cdot \varepsilon_e^2 + 1.2 \, \varepsilon_e - 0.6 = 0$$

$$\varepsilon_e = \frac{-1.2 + \sqrt{1.2^2 + 4(0.4)(0.6)}}{0.8} = 0.44$$

$$X_{steam} = \text{fraction reacted} = \frac{(n_{H_2O})_o - H_2O}{(n_{H_2O})_o}$$

$$X_{steam} = \frac{1 - ((n_{H_2O})_o - \varepsilon_e)}{1} = 0.44$$

$$44\% \text{ reacts at equilibrium.}$$

(b) $P = 10$ bar

$$K \left(\frac{P}{P^o}\right)^{-\nu} = \prod_i (y_i)^{\nu_i}$$

since $\nu = 0$ $\Rightarrow$ $K = \prod_i (y_i)^{\nu_i}$

solution is exactly similar to (a)

(c)   2 moles N_2 added (inert gas)

$$K \left(\frac{P}{P^o}\right)^{-\nu} = \prod_i (y_i)^{\nu_i}$$

$$0.6 = \frac{y_{H_2} \, y_{CO_2}}{y_{CO} \, y_{H_2O}}$$

$$y_{H_2} = \frac{\varepsilon_e}{4} \qquad y_{CO_2} = \frac{\varepsilon_e}{4}$$

$$y_{CO} = \frac{1 - \varepsilon_e}{4} \qquad y_{H_2O} = \frac{1 - \varepsilon_e}{4}$$

$$\Rightarrow \quad 0.6 = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2}$$

$$\Rightarrow \quad \text{result similar to (a)}$$

(d)   2 mole H_2O & 1 mol CO initially

$$0.6 = \frac{y_{H_2} \, y_{CO_2}}{y_{CO} \, y_{H_2O}}$$

$$y_{CO} = \frac{1 - \varepsilon_e}{3} \qquad y_{H_2O} = \frac{2 - \varepsilon_e}{3}$$

$$y_{CO_2} = \frac{\varepsilon_e}{3} \qquad y_{H_2} = \frac{\varepsilon_e}{3}$$

$$\Rightarrow \quad 0.6 = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)(2 - \varepsilon_e)}$$

$$\Rightarrow \quad 0.4 \, \varepsilon_e^2 + 1.8 \varepsilon_e - 1.2 = 0 \quad \Rightarrow \quad \varepsilon_e = 0.59$$

$$X_{steam} = \frac{n_{o\,H_2O} - (n_{o\,H_2O} - \varepsilon_e)}{n_{o\,H_2O}} = 0.295$$

(e) 1 mole H_2O

$$0.6 = \dfrac{\dfrac{\varepsilon_e}{3} \quad \dfrac{\varepsilon_e}{3}}{\dfrac{(2-\varepsilon_e)}{3} \quad \dfrac{(1-\varepsilon_e)}{3}}$$

$$\Rightarrow \varepsilon_e = 0.59$$

$$X_{Stem} = \frac{n_{0\,H_2O} - (n_{0\,H_2O} - \varepsilon_e)}{n_{0\,H_2O}} = 0.59$$

(f) $0.6 = \dfrac{y_{H_2}\, y_{CO_2}}{y_{CO}\, y_{H_2O}} = \dfrac{\varepsilon_e(1+\varepsilon_e)}{(1-\varepsilon_e)^2}$

$$0.4\,\varepsilon_e^2 + 2.2\,\varepsilon_e - 0.6 = 0$$

$$\Rightarrow \varepsilon_e = 0.26$$

$$X_{Stem} = \frac{n_{0\,H_2O} - (n_{0\,H_2O} - \varepsilon_e)}{n_{0\,H_2O}} = 0.26$$

(g) $\ln\left(\dfrac{k}{103260.84}\right) = \dfrac{41161}{8.314}\left(\dfrac{1}{1650} - \dfrac{1}{298.15}\right)$

$$\Rightarrow k = 0.13$$

$$\Rightarrow 0.13 = \frac{\varepsilon_e^2}{(1-\varepsilon_e)^2} \Rightarrow \varepsilon_e = 0.27 \Rightarrow X = 0.27$$