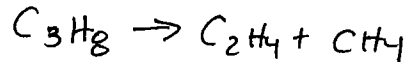


HW#9 Solutions

①

(1)

13.16



$$P = 1 \text{ bar}$$

Find conversion at ~~600~~⁶²⁵ K (A) and temperature for ~~85%~~^{85%} conversion

$$K = \frac{Y_{C_2H_4} Y_{CH_4}}{Y_{C_3H_8}} \left(\frac{P}{P^\circ} \right)^{\Delta n}$$

↓
1

Basis $n_{C_3H_8}^\circ = 1$

$$n_{C_3H_8} = 1 - \epsilon$$

$$Y_{C_3H_8} = \frac{1 - \epsilon}{1 + \epsilon}$$

$$n_{C_2H_4} = \epsilon$$

$$Y_{C_2H_4} = \frac{\epsilon}{1 + \epsilon}$$

$$n_{CH_4} = \epsilon$$

$$Y_{CH_4} = \frac{\epsilon}{1 + \epsilon}$$

$$n_T = 1 + \epsilon$$

$$K = \frac{\epsilon^2}{(1 + \epsilon)(1 + \epsilon)} = \frac{\epsilon^2}{1 + 2\epsilon + \epsilon^2}$$

$$K - K\epsilon^2 = \epsilon^2$$

$$\epsilon^2(1 + K) = K$$

$$\epsilon = \sqrt{\frac{K}{1 + K}}$$

(both parts)

K dependence on T

(2)

Substance	$\Delta G_{f,i}^{\circ} \frac{\text{J}}{\text{mol}}$	$\Delta H_{f,i}^{\circ} \frac{\text{J}}{\text{mol}}$	A_i	B_i	C_i	d_i
Ethylene	68,460	52,510	1.424	.014394	-4.392×10^{-6}	0
Methane	-50,460	-74,520	1.702	.009081	-2.164×10^{-6}	0
Propane	-24,290	-104,680	1.213	.028785	-8.824×10^{-6}	0

$$\Delta G_{298}^{\circ} = 68,460 + (-50,460) - (-24,290) = 42,290 \text{ J/mol}$$

$$\Delta H_{298}^{\circ} = 52,510 + (-74,520) - (-104,680) = 82,670 \text{ J/mol}$$

$$\Delta A = 1.913$$

$$\Delta D = 0$$

$$\Delta B = -.00531$$

$$\Delta C = 2.268 \times 10^{-6}$$

$$\therefore K_{298} = \exp\left(\frac{-\Delta G_{298}^{\circ}}{RT}\right) = \exp\left(\frac{-42,290}{(8.314)(298.15)}\right) = 3.897 \times 10^{-8}$$

$$\therefore \ln \frac{K(T)}{3.897 \times 10^{-8}} = \frac{82,670}{(8.314)(298.15)} \left(1 - \frac{1}{X}\right) + 1.913 \left(\frac{1}{X} - 1 + \ln X\right)$$

$$+ \frac{298.15}{2} (-.00531) \left(X + \frac{1}{X} - 2\right) + \frac{(2.268 \times 10^{-6})(298.15)^2}{3} \left(\frac{X^2}{2} + \frac{1}{X} - \frac{3}{2}\right)$$

$$\ln K(T) = -17.060 + 33.351 \left(1 - \frac{1}{X}\right) + 1.913 \left(\frac{1}{X} - 1 + \ln X\right) + (-.7916) \left(X + \frac{1}{X} - 2\right) + (.06720) \left(\frac{X^2}{2} + \frac{1}{X} - \frac{3}{2}\right)$$

(both parts)

A) Fractional conversion at 625 K

$$X = \frac{625}{248.15} = 2.0962$$

K(T) from
Previous:
page:

$$K = 1.525$$

$$E = \sqrt{\frac{K}{1+K}} = \boxed{.7771} = \text{fractional conversion}$$

B) want $E = .85$

$$.85 = \sqrt{\frac{K}{1+K}} \quad K = 2.604$$

Solve K(T) for T when $K = 2.604$

Trial & error yields

$$\boxed{T = 646.8 \text{ K}}$$

(2)

13.27

First find K for $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{s}) + 2\text{H}_2(\text{g})$ at 650°C

$$\Delta G_{298}^\circ = 0 + 2(0) - 1(-50,460) = 50,460 \text{ J/mol}$$

$$\Delta H_{298}^\circ = 0 + 2(0) - 1(-74,520) = 74,520 \text{ J/mol}$$

$$K_{298} = \exp\left(\frac{-50,460}{8.314(298.15)}\right) = \underline{\underline{1.443 \times 10^{-9}}}$$

$$\Delta A = 1.771 + 2(3.244) - (1.702) = 6.567$$

$$\Delta B = \frac{0.771 + 2(0.422) - (9.081)}{1000} = -7.466 \times 10^{-3}$$

$$\Delta C = \frac{0 + 0 - (-2.164)}{10^6} = 2.164 \times 10^{-6}$$

$$\Delta D = \frac{(-.867) + 2(.083) - 0}{10^{-5}} = -.701 \times 10^5$$

$$X = \frac{T}{T^*} = \frac{650 + 273.15}{298.15} = 3.096$$

Handout 14

$$\ln \frac{K_{650}}{1.443 \times 10^{-9}} = \frac{74520}{8.314(298.15)} \left(1 - \frac{1}{X}\right) + 6.567 \left(\frac{1}{X} - 1 + \ln X\right) + \frac{298.15}{2} (-0.007466) \left(X + \frac{1}{X} - 2\right) + \frac{(298.15)^2 (2.164 \times 10^{-6})}{3} \left(\frac{X^2}{2} + \frac{1}{X} - \frac{3}{2}\right) + \frac{(-.701 \times 10^5)}{2(298.15)^2} \left(\frac{1}{X^2} - \frac{2}{X} + 1\right)$$

$$K_{650} = 4.239$$

$$K = \frac{\hat{f}_c}{\hat{f}_c^0} \left(\frac{\hat{f}_{H_2}}{\hat{f}_{H_2}^0} \right)^2 \frac{\hat{f}_{CH_4}^0}{\hat{f}_{CH_4}}$$

Assume low P & pure solid phase $\Rightarrow \hat{f}_c / \hat{f}_c^0 = 1$

Assume gas phase is ideal

$$K = \frac{Y_{H_2}^2}{Y_{CH_4}} \left(\frac{P}{\text{bar}} \right) \quad (\text{A})$$

Part (A)

$$\begin{aligned} n_{CH_4} &= 1 - \epsilon & Y_{CH_4} &= \frac{1 - \epsilon}{1 + \epsilon} \\ n_{H_2} &= 2\epsilon & Y_{H_2} &= \frac{2\epsilon}{1 + \epsilon} \\ n_{\text{gas}} &= 1 + \epsilon & P &= 1 \text{ bar} \end{aligned}$$

$$4.239 = \frac{(2\epsilon)^2}{(1 - \epsilon)(1 + \epsilon)} = \frac{4\epsilon^2}{1 - \epsilon^2} \Rightarrow \epsilon = .7173$$

Fraction of methane decomposed = $\frac{1 - (1 - \epsilon)}{1} = \epsilon = .7173$

$$\begin{aligned} Y_{CH_4} &= \frac{1 - \epsilon}{1 + \epsilon} = .165 \\ Y_{H_2} &= \frac{2\epsilon}{1 + \epsilon} = .835 \end{aligned}$$

(B) Still use (A) but now inert is present

$$\begin{aligned} n_{CH_4} &= 1 - \epsilon & Y_{CH_4} &= \frac{1 - \epsilon}{2 + \epsilon} \\ n_{N_2} &= 1 & Y_{H_2} &= \frac{2\epsilon}{2 + \epsilon} \\ n_{H_2} &= 2\epsilon & Y_{N_2} &= \frac{1}{2 + \epsilon} \\ n_{\text{gas}} &= 2 + \epsilon \end{aligned}$$

$$4.239 = \frac{4\epsilon^2}{(1 - \epsilon)(2 + \epsilon)} = \frac{4\epsilon^2}{2 - \epsilon - \epsilon^2}$$

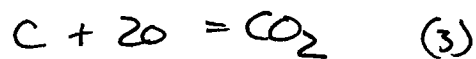
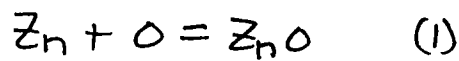
$$\epsilon = .7893$$

fraction decomposed

$$\begin{aligned} Y_{CH_4} &= .0755 \\ Y_{H_2} &= .5659 \\ Y_{N_2} &= .3585 \end{aligned}$$

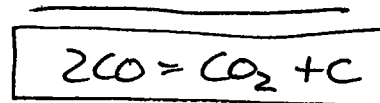
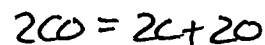
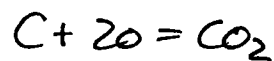
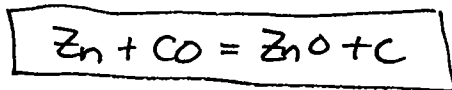
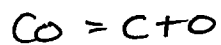
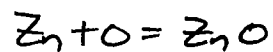
(3) (A) C, ZnO, CO, CO₂ & Zn are present.

Formation Reactions :



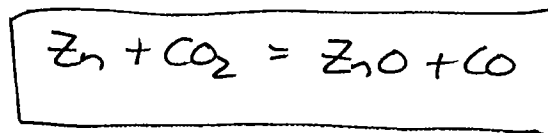
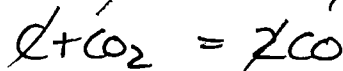
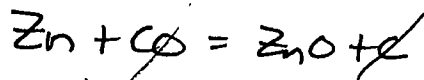
Now eliminate O but not C or Zn

Eliminate O using (2) :



Reaction 2

Reaction (1) can be obtained by combining
Above two reactions



Reaction (1)

BASIS: 1 mol of starting mixture

B)

$$n_{CO} = .5 + \epsilon_1 - 2\epsilon_2$$

$$n_{Zn} = .25 - \epsilon_1$$

$$n_{CO_2} = .25 - \epsilon_1 + \epsilon_2$$

$$n_C = \epsilon_2$$

$$n_{ZnO} = \epsilon_1$$

$$n_{gas} = n_{CO} + n_{Zn} + n_{CO_2} = 1 - \epsilon_1 - \epsilon_2$$

$$\therefore Y_{CO} = \frac{.5 + \epsilon_1 - 2\epsilon_2}{1 - \epsilon_1 - \epsilon_2}$$

$$Y_{Zn} = \frac{.25 - \epsilon_1}{1 - \epsilon_1 - \epsilon_2}$$

$$Y_{CO_2} = \frac{.25 - \epsilon_1 + \epsilon_2}{1 - \epsilon_1 - \epsilon_2}$$

Equilibrium : $\hat{f}_{ZnO} / f_{ZnO}^o \approx 1$

$$\hat{f}_C / f_C^o \approx 1$$

$$K_1 = \frac{Y_{CO}}{Y_{Zn} Y_{CO_2}} (P/atm)$$

$$K_2 = \frac{Y_{CO_2}}{Y_{CO}^2} (P/atm)$$

or

$$26 = \frac{(.5 + \epsilon_1 - 2\epsilon_2)(1 - \epsilon_1 - \epsilon_2)}{(.25 - \epsilon_1)(.25 - \epsilon_1 + \epsilon_2)} (P/atm)$$

$$.004 = \frac{(.25 - \epsilon_1 + \epsilon_2)(1 - \epsilon_1 - \epsilon_2)}{(.5 + \epsilon_1 - 2\epsilon_2)^2} (P/atm)$$



Now set $\frac{P}{\text{atm}} = 25$

and solve for ϵ_1 & ϵ_2 by trial & error

Result:

$$\begin{aligned} \epsilon_2 &= .046 \\ \epsilon_1 &= .238 \end{aligned}$$

$$\begin{aligned} \therefore n_c &= .046 \\ n_{\text{zno}} &= .238 \end{aligned}$$

$$Y_{\text{co}} = .9022$$

$$Y_{\text{zn}} = .0168$$

$$Y_{\text{co}_2} = .0810$$

(C) in order to form no C $\epsilon_2 \leq 0$. Highest pressure that will still yield no C is given by $\epsilon_2 = 0$. Set $\epsilon_2 = 0$ in equations and solve for 2 unknowns ϵ_1 & (P/atm)

$$26 = \frac{(5 + \epsilon_1)(1 - \epsilon_1)}{(25 - \epsilon_1)^2 (P/\text{atm})} \quad .004 = \frac{(25 - \epsilon_1)(1 - \epsilon_1)}{(5 + \epsilon_1)^2 (P/\text{atm})}$$

Divide first by second: $6500 = \frac{(5 + \epsilon_1)^3}{(25 - \epsilon_1)^3}$

or $18.66 = \frac{5 + \epsilon_1}{25 - \epsilon_1}$ which yields $\epsilon_1 = .212$

Substitution of ϵ_1 into either equation above yields

$$P = 14.9 \text{ atm}$$