

## The Heat (Enthalpy) of Combustion:

-An older method of calculating enthalpy changes when chemical reactions occur is via standard heats (enthalpies) of combustion ( $\Delta\hat{H}_c^\circ$ ).

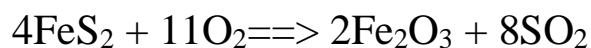
The conventions used with the standard heats of combustion are as follows:

- The compound is oxidized with oxygen or some other substance to the products  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ , and so on.
- The reference conditions are still  $25^\circ\text{C}$  and 1 atm .
- Stoichiometric quantities react completely .

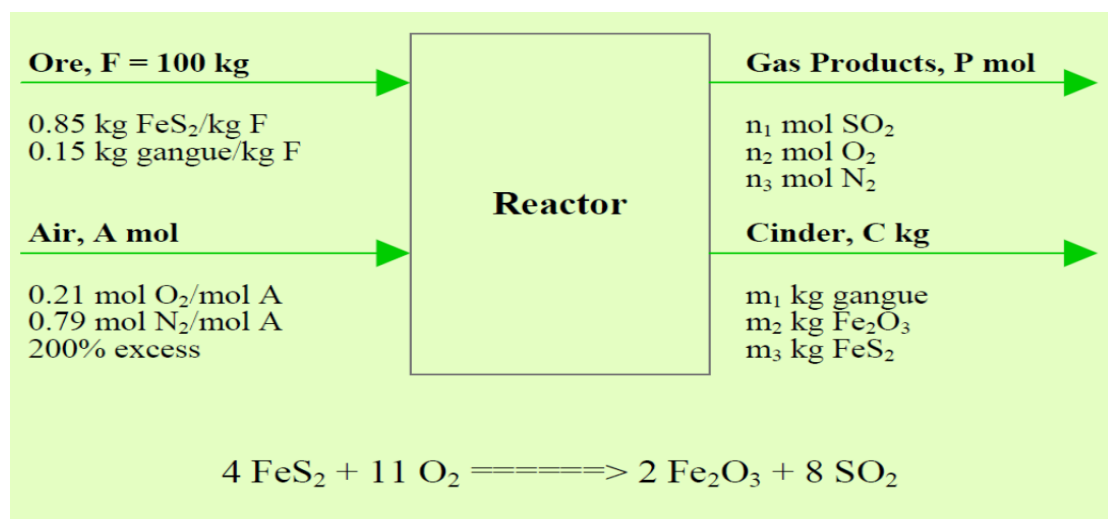
**The rationale is that if a compound has a higher heat of combustion, it can release more energy than other compounds during combustion and would be easier to incinerate.**

### Example.4.3. Roasting of Iron pyrite Ore:

An iron pyrite ore containing 85.0%  $\text{FeS}_2$  and 15.0% gangue (inert dirt, rock, etc.) is roasted with an amount equal to 200% excess air according to the reaction



in order to produce  $\text{SO}_2$ . All the gangue plus the  $\text{Fe}_2\text{O}_3$  and unreacted  $\text{FeS}_2$  end up in the solid waste product (cinder). Analysis shows the cinder contains 4.0%  $\text{FeS}_2$ . Determine the heat transfer per kilogram of ore to keep the product stream at  $25^\circ\text{C}$  if the entering stream streams are at  $25^\circ\text{C}$ . Assume that pressure is constant at 1 atm



The heat transfer required is calculated from the energy balance equation. Assuming  $\Delta K = \Delta P = W_s = 0$ , then

$$Q = \Delta H = \Sigma H_{\text{out}} - \Sigma H_{\text{in}}$$

The total enthalpy at the inlet is:

$$\Sigma H_{\text{in}} = (H_{\text{gangue}} + H_{\text{FeS}_2} + H_{\text{N}_2} + H_{\text{O}_2})_1$$

The total enthalpy at the outlet is:

$$\Sigma H_{\text{out}} = (H_{\text{SO}_2} + H_{\text{O}_2} + H_{\text{N}_2} + H_{\text{gangue}} + H_{\text{Fe}_2\text{O}_3} + H_{\text{FeS}_2})_2$$

Hence,

$$Q = (H_{\text{SO}_2} + H_{\text{O}_2} + H_{\text{N}_2} + H_{\text{gangue}} + H_{\text{Fe}_2\text{O}_3} + H_{\text{FeS}_2})_2 - (H_{\text{gangue}} + H_{\text{FeS}_2} + H_{\text{N}_2} + H_{\text{O}_2})_1$$

Since the amount of  $\text{N}_2$  and gangue are the same at the inlet and outlet and there are no changes in T and P conditions at the inlet and outlet, then

$$(H_{\text{gangue}})_1 = (H_{\text{gangue}})_2 \text{ and } (H_{\text{N}_2})_1 = (H_{\text{N}_2})_2$$

And the heat transfer equation becomes,

$$Q = (H_{\text{SO}_2} + H_{\text{O}_2} + H_{\text{Fe}_2\text{O}_3} + H_{\text{FeS}_2})_2 - (H_{\text{FeS}_2} + H_{\text{O}_2})_1$$

From Table F.1,

$$(\hat{H}_f^\circ)_{\text{FeS}_2} = -177.9 \text{ kJ/mol}$$

$$(\hat{H}_f^\circ)_{\text{Fe}_2\text{O}_3} = -822.156 \text{ kJ/mol}$$

$$(\hat{H}_f^\circ)_{\text{SO}_2} = -296.90 \text{ kJ/mol}$$

$$(\hat{H}_f^\circ)_{\text{O}_2} = 0.00 \text{ kJ/mol}$$

These are the specific enthalpies at 25°C. The actual enthalpy at the given temperature condition is:

$$\hat{H} = \hat{H}_f^\circ + \int_{T_R}^T C_P dT$$

Since the actual temperature is also at 25°C, then

$$\hat{H} = \hat{H}_f^\circ$$

The total enthalpy of each component at the inlet and outlet is determined as:

$$H = n\hat{H} = n\hat{H}_f^\circ$$

The molar amount of each component can be obtained thru material balances.

From excess air information:

$$\text{Total O}_2 \text{ in} = 5.8437 \text{ kmol}$$

$$\text{Total N}_2 \text{ in} = 21.983 \text{ kmol}$$

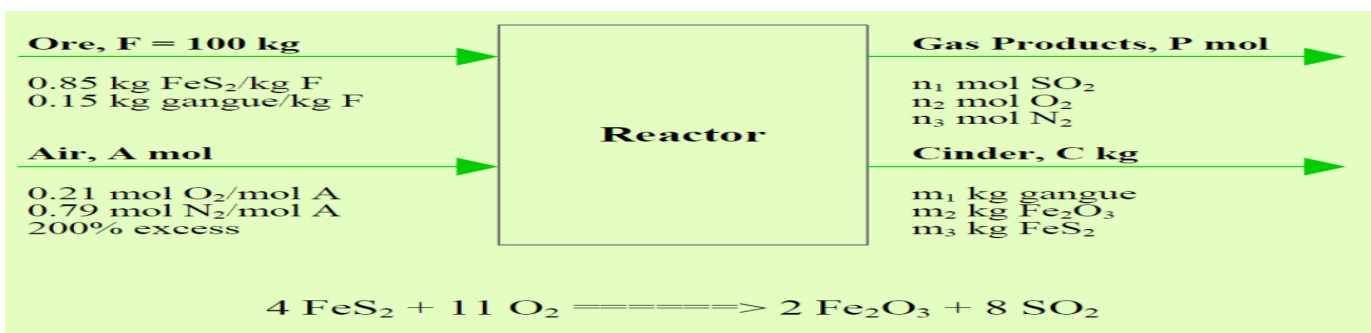
$$\text{Gangue Balance: } m_1 = 15.0 \text{ kg}$$

$$\text{N}_2 \text{ Balance: } n_3 = 21.983 \text{ kmol}$$

$$\text{S Balance (kmol)} \quad 2(85.0/120.0) = n_1 + (m_3/120.0)(2)$$

$$\text{Fe Balance (kmol)} \quad (85.0/120.0) = (m_2/159.02)2 + (m_3/120.0)$$

$$\text{O}_2 \text{ Balance (kmol)} \quad 5.8437 = n_2 + n_1 + (m_2/159.02)(1.5)$$



Also,

$$m_3/(15.0 + m_2 + m_3) = 0.04$$

Solving the last 4 equations simultaneously,

$$\text{Fe}_2\text{O}_3: \quad m_2 = 54.63 \text{ kg} \implies 0.342 \text{ kmol}$$

$$\text{FeS}_2: \quad m_3 = 2.90 \text{ kg} \implies 0.0242 \text{ kmol}$$

$$\text{SO}_2: \quad n_1 = 1.368 \text{ kmol}$$

$$\text{O}_2: \quad n_2 = 3.938 \text{ kmol}$$

Solving for the total enthalpy of the inlet:

$$\Sigma H_{\text{in}} = (85.0/120.0 \text{ kmol})(-177.9 \text{ kJ/mol})(1000 \text{ mol/kmol}) \\ + (5.8437)(0)$$

$$\Sigma H_{\text{in}} = - \mathbf{126,007 \text{ kJ}}$$

Solving for the total enthalpy of the outlet:

$$\Sigma H_{\text{out}} = (1.368)(-296.90)(1000) + (0.0242)(-177.90)(1000) \\ + (1.368)(-296.90)(1000)$$

$$\Sigma H_{\text{out}} = - \mathbf{691,641 \text{ kJ}}$$

Solving for Q:

$$Q = - 691,641 - ( - 126,007) = - \mathbf{565,634 \text{ kJ}} \text{ per 100 kg of ore}$$

Per kg of ore:

$$Q = - 5,656 \text{ kJ per kg of ore}$$

The negative sign indicates that heat must be removed during the process in order to maintain the temperature at 25°C.

### Example.4.3.

Methane is oxidised with air to produce formaldehyde as per the following equation:  $\text{CH}_4(\text{g}) + \text{O}_2 \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{g})$   $\Delta H_R^\circ = -283.094 \frac{\text{kJ}}{\text{mol}}$

100 mol of methane are fed to the reactor at 311k, air is used 50% excess and supplied at 373 k. If the percent conversion is 60, calculate the heat that must be removed for the product stream to be at 478k.

Data :

Component	$C_{\text{pm}}^\circ$ (311 – 298 K)	$C_{\text{pm}}^\circ$ (478 – 298 K)
CH <sub>4</sub>	36.044	40.193
N <sub>2</sub>	–	29.2866
O <sub>2</sub>	–	30.0821
HCHO	–	41.2902
H <sub>2</sub> O	–	34.2396

$$C_{\text{pm}}^\circ \text{ for air (373 – 298 K)} = 29.2908 \text{ kJ/(kmol}\cdot\text{K)}$$

**Solution : Basis :** 100 mol of methane fed to the reactor



$$\Delta H_R^\circ = -283.094 \text{ kJ/mol} = -283094 \text{ J/mol}$$

From the reaction : 1 kmol CH<sub>4</sub>  $\equiv$  1 kmol O<sub>2</sub>. Therefore,

$$\begin{aligned} \text{Theoretical O}_2 \text{ requirement} \\ \text{for 100 kmol CH}_4 &= \frac{1}{1} \times 100 = 100 \text{ mol} \end{aligned}$$

**Given :** Air is used 50% in excess of theoretical requirement. We know that % excess air = % excess O<sub>2</sub>. Therefore, % excess O<sub>2</sub> = 50.

$$\text{O}_2 \text{ in the supplied air} = 100 \left( 1 + \frac{50}{100} \right) = 150 \text{ mol}$$

$$\text{Air supplied} = 150 \times \frac{100}{21} = 714.3 \text{ mol}$$

$$\text{N}_2 \text{ in the supplied air} = 714.3 - 150 = 564.3 \text{ mol}$$

Given : Conversion of  $\text{CH}_4 = 60$

$$\text{CH}_4 \text{ reacted} = 0.60 \times 100 = 60 \text{ mol}$$

$$\text{HCHO produced from } 60 \text{ kmol CH}_4 \text{ reacted} = \frac{1}{1} \times 60 = 60 \text{ mol}$$

Similarly,  $\text{H}_2\text{O produced} = \frac{1}{1} \times 60 = 60 \text{ mol}$

$$\text{O}_2 \text{ reacted} = \frac{1}{1} \times 60 = 60 \text{ mol}$$

$$\text{O}_2 \text{ unreacted} = \text{O}_2 \text{ in air} - \text{O}_2 \text{ reacted} = 150 - 60 = 90 \text{ mol}$$

$$\Delta H_R^\circ \text{ for } 60 \text{ mol CH}_4 \text{ reacted} = 60 \times (-283094) = -16985640 \text{ J}$$

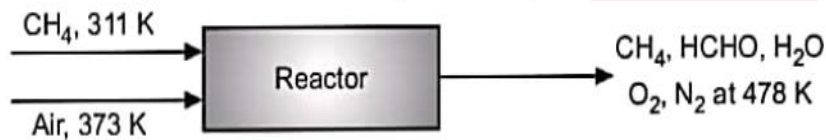


Fig. Ex 6.57

Enthalpy of reactants  $\Sigma H_R$  over 298 K (25°C).

$$\begin{aligned} \Sigma H_R &= n_{\text{CH}_4} \cdot C_{p,m_{\text{CH}_4}}^\circ (T_1 - T_0) + n_{\text{air}} \cdot C_{p,m_{\text{air}}}^\circ (T_1' - T_0) \\ &= 100 \times 36.044 \times (311 - 298) + 714.3 \times 29.2908 \times (373 - 298) \\ &= 1616038.6 \text{ J} \end{aligned}$$

$\Sigma H_p$  = Enthalpy of products over 298 K (25°C)

$$\begin{aligned} \Sigma H_p &= [n_{\text{CH}_4} \cdot C_{p,m_{\text{CH}_4}}^\circ + n_{\text{N}_2} \cdot C_{p,m_{\text{N}_2}}^\circ + n_{\text{O}_2} \cdot C_{p,m_{\text{O}_2}}^\circ \\ &\quad + n_{\text{HCHO}} \cdot C_{p,m_{\text{HCHO}}}^\circ + n_{\text{H}_2\text{O}} \cdot C_{p,m_{\text{H}_2\text{O}}}^\circ] \times (T_2 - T_0) \\ &= [40 \times 40.193 + 564.3 \times 29.2866 + 90 \times 30.0821 \\ &\quad + 60 \times 41.2902 + 60 \times 34.2396] \times (478 - 298) \\ &= 4567198.6 \text{ J} \end{aligned}$$

$\Delta H$  = Net enthalpy change = Heat to be removed

$$\begin{aligned} &= \Sigma H_p + \Sigma \Delta H_R^\circ - \Sigma H_R \\ &= 4567198.6 + (-16985640) - 1616038.6 \\ &= -14034480 \text{ J} \\ &= -14034.48 \text{ kJ} \end{aligned}$$

Heat to be removed = 14034.48 kJ

... Ans.