

Republic of Iraq

Ministry of Higher Education

and Scientific Research

Al-Mustaqbal University College

Chemical Engineering and Petroleum Industries Department



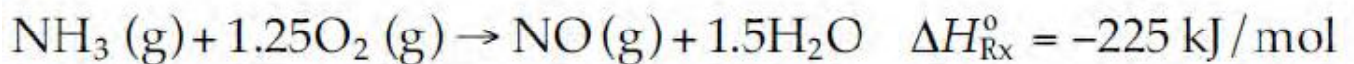
Subject: Energy and Energy Balances

2nd Class

Lecture eight

Example 1. Oxidation of Ammonia

Hundred moles per minute of ammonia (NH₃) and 200 mol/min of oxygen (O₂) at 25°C are fed into a continuous reactor in which ammonia is completely consumed. The product gas emerges at 300°C. Calculate the rate at which heat must be transferred to or from the reactor to maintain the reactor temperature at 300°C. The standard heat of reaction for the gas phase oxidation of ammonia is

**Solution**

Known quantities: Inlet molar flow rates, inlet temperature, exit temperature.

Find: Rate of heat transferred from or to the reactor.

Analysis: Use the first law of thermodynamics for an open system.

Basis: 100 mol/min of NH₃

Reference: 25°C and 1 atm

Using the first law of thermodynamics for an open system,

$$Q - W_s = \Delta \dot{H} + \Delta KE + \Delta PE$$

Since there is no shaft work in the process, no moving parts, no change in elevation between inlet and exit stream, and no change in velocity of inlet and exit streams, the general energy balance equation is reduced to

$$Q = \Delta \dot{H}$$

Using the extent of reaction or heat of reaction method,

$$Q = \Delta \dot{H} = \dot{\xi} \Delta H_{\text{Rx}}^{\circ} + \sum_{\text{out}} \dot{n}_i h_i - \sum_{\text{in}} \dot{n}_i h_i$$

Material balance (Extent of reaction method)

$$\dot{n}_{\text{NH}_3} = 100 - \xi$$

$$\dot{n}_{\text{O}_2} = 200 - 1.25\xi$$

$$\dot{n}_{\text{NO}} = 0.0 + \xi$$

$$\dot{n}_{\text{H}_2\text{O}} = 0.0 + 1.5\xi$$

Because of complete conversion of ammonia ($f=1$), no ammonia exits in the reactor exit stream; $\dot{n}_{\text{NH}_3} = 0$

$$0.0 = 100 - \xi \Rightarrow \xi = 100 \text{ mol}$$

Substituting the values of the extent of reaction in the material balance equation will give the following molar flow rate of exit stream components:

$$\dot{n}_{\text{NH}_3} = 0.0 \text{ mol/min}, \quad \dot{n}_{\text{O}_2} = 75 \text{ mol/min}, \quad \dot{n}_{\text{NO}} = 100 \text{ mol/min}, \quad \dot{n}_{\text{H}_2\text{O}} = 150 \text{ mol/min}$$

Energy balance (Heat of reaction method)

Reference temperature: 25°C

$$Q = \Delta \dot{H} = \xi \Delta H_{\text{Rx}}^{\circ} + \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

Heat capacities of components involved in the process $C_{p,i}$ (J/mol.C) are

$$C_{pO_2} = 29.1 + 0.01158T - 0.6076 \times 10^{-5}T^2$$

$$C_{pNO} = 29.5 + 0.008188T - 0.2925 \times 10^{-5}T^2$$

$$C_{pH_2O} = 33.46 + 0.00688T + 0.7604 \times 10^{-5}T^2$$

Substitute known values:

$$Q = \Delta \dot{H} = 100(-225 \text{ kJ/mol}) + \frac{\text{kJ}}{1000 \text{ J}}$$

$$\times \left[75 \int_{25^\circ\text{C}}^{300^\circ\text{C}} C_{pO_2} dT + 100 \int_{25}^{300} C_{pNO} dT + 150 \int_{25}^{300} C_{pH_2O} dT \right]_{\text{out}}$$

$$- \frac{\text{kJ}}{1000 \text{ J}} \left[100 \int_{25}^{25} C_{pNH_3} dT + 200 \int_{25}^{25} C_{pO_2} dT \right]_{\text{in}}$$

The change in sensible heat is in the units of J/mol, so it should be divided by 1000 to convert to the units of kJ/mol to be added to heat of reaction. Accordingly, the heat transfer rate is

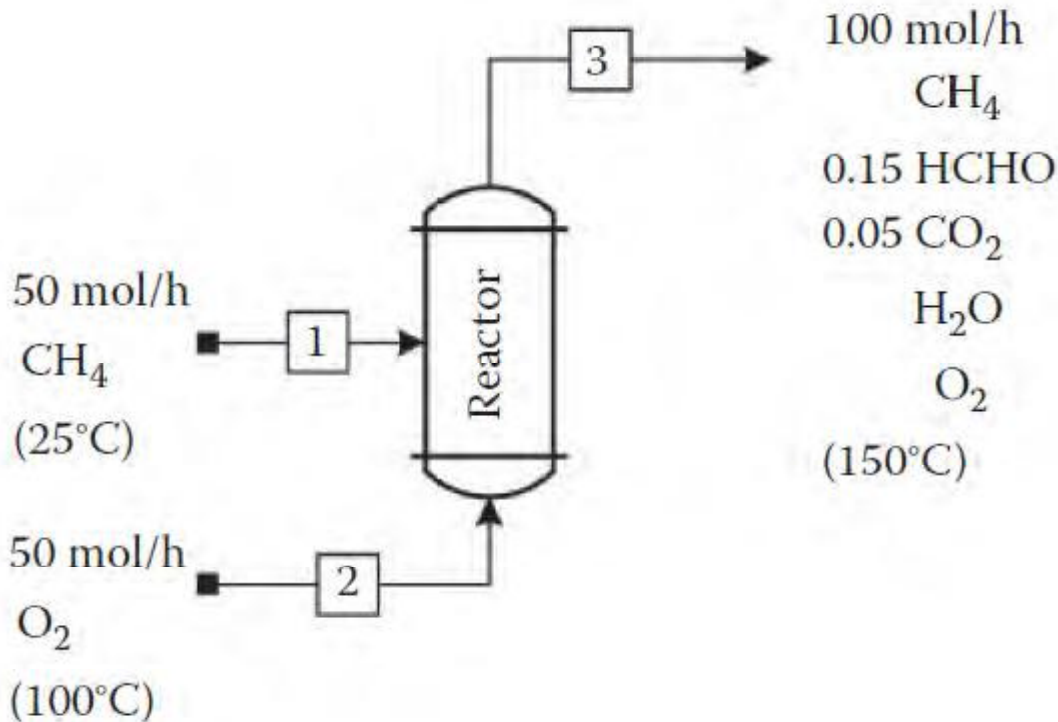
$$Q = \Delta \dot{H} = 100 \text{ mol} \left[\frac{-225 \text{ kJ}}{\text{mol}} \right] + [75(8.47) + 100(8.45) + 150(9.57)] - 0$$

$$= -19,600 \text{ kJ/min}$$

The heat released from the reaction process is $-19,600 \text{ kJ/min}$ (-326 kW).

Example 2. Production of Formaldehyde

Formaldehyde is produced in a continuous reactor by oxidizing methane with pure oxygen (Example Figure 2.9.1). Feed streams of 50 mol/h of methane and 50 mol/h of pure oxygen are fed to a continuous reactor. The exit stream molar flow rate is 100 mol/h. The mole fractions of formaldehyde and carbon dioxide are 0.15 and 0.05, respectively. Calculate the rate of heat that must be added to or removed from the reactor to maintain the reactor temperature at 150°C.



EXAMPLE FIGURE 2.9.1 Process flow sheet of the methane oxidation process.

Solution

Known quantities: Inlet and exit streams temperature and molar composition of formaldehyde and carbon dioxide.

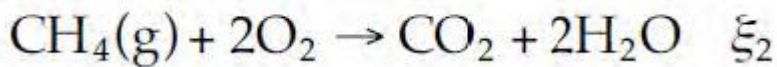
Find: Heat transfer rate from or to the system.

Analysis: Use the extent of reaction method for both material and energy balance.

Basis: 100 mol/h of the exit gas stream

Material balance:

Since carbon dioxide appears in the exit gas stream, the following reactions take place in the reactor:



To calculate the extent of reaction of the first reaction, select a component that is available only in the first reaction, which is formaldehyde in this case:

$$n_{\text{HCHO}} = n_{\text{CHHO}}^0 + \xi_1$$

$$0.15 \times 100 \text{ mol/h} = 0 + \xi_1 \Rightarrow \xi_1 = 15 \text{ mol/h}$$

The extent of the second reaction is obtained by selecting a component that is only available in the second reaction, which is in this case carbon dioxide:

$$n_{\text{CO}_2} = n_{\text{CO}_2}^0 + \xi_2$$

Substitute inlet and exit molar flow rate of carbon dioxide:

$$0.05 \times 100 \text{ mol/h} = 0 + \xi_2 \Rightarrow \xi_2 = 5 \text{ mol/h}$$

Knowing the extent of the first and second reactions, the component molar flow rate can be found easily by performing the extent of reaction balance for each component:

$$n_{\text{CH}_4} = 50 - \xi_1 - \xi_2 = 50 - 15 - 5 = 30 \text{ mol/h}$$

$$n_{\text{H}_2\text{O}} = 0 + \xi_1 + 2\xi_2 = 15 + 2 \times 5 = 25 \text{ mol/h}$$

$$n_{\text{O}_2} = 50 - \xi_1 - 2\xi_2 = 50 - 15 - 2 \times 5 = 25 \text{ mol/h}$$

Energy balance:

Reference state: 25°C

The standard heat of reaction for both reactions is calculated from standard heats of formation as follows:

The standard heat of the first reaction, ΔHR_{rxn1} , is given by

$$\Delta H_{\text{Rx1}}^{\circ} = \Delta H_{\text{f},\text{H}_2\text{O}(\text{v})}^{\circ} + \Delta H_{\text{f},\text{HCHO}(\text{g})}^{\circ} - \Delta H_{\text{f},\text{CH}_4(\text{g})}^{\circ}$$

$$\Delta H_{\text{Rx1}}^{\circ} = (-241.83) + (-115.9) - (-74.85) = -282.88 \text{ kJ/mol}$$

The standard heat of the second reaction, ΔH_{Rx2} , is given by
Overall

$$\Delta H_{\text{Rx2}}^{\circ} = 2\Delta H_{\text{f},\text{H}_2\text{O}(\text{v})}^{\circ} + \Delta H_{\text{f},\text{CO}_2(\text{g})}^{\circ} - \Delta H_{\text{f},\text{CH}_4(\text{g})}^{\circ}$$

Overall energy balance of the reactor, no work, no moving parts, no change in elevation, hence, work, kinetic and potential energy, are neglected:

$$Q = \Delta \dot{H}$$

The rate of change in enthalpy, $\Delta \dot{H}$, is given by

$$\Delta \dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta H_{\text{Rx},j}^{\circ} + \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

Heat capacities of all components involved in the process, C_{pi} (J/mol $^{\circ}$ C), are as follows:

$$C_{\text{PCH}_4} = 34.31 + 0.05469T + 0.3661 \times 10^{-5}T^2$$

$$C_{\text{PHCHO}} = 34.28 + 0.04268T$$

$$C_{\text{PCO}_2} = 36.11 + 0.04233T - 2.887 \times 10^{-5}T^2$$

$$C_{\text{PH}_2\text{O}} = 33.46 + 0.00688T + 0.7604 \times 10^{-5}T^2$$

$$C_{\text{PO}_2} = 29.1 + 0.01158T - 0.6076 \times 10^{-5}T^2$$

In more detail, the energy balance equation is as follows:

$$Q = \dot{\xi}_1 \Delta H_{R_{x1}}^{\circ} + \dot{\xi}_2 \Delta H_{R_{x2}}^{\circ} + \left\{ \dot{n}_{\text{CH}_4} \bar{h}_{\text{CH}_4} + \dot{n}_{\text{HCHO}} \bar{h}_{\text{HCHO}} + \dot{n}_{\text{CO}_2} \bar{h}_{\text{CO}_2} + \dot{n}_{\text{H}_2\text{O}} \bar{h}_{\text{H}_2\text{O}} + \dot{n}_{\text{O}_2} \bar{h}_{\text{O}_2} \right\}_{\text{out}} - \left\{ \dot{n}_{\text{CH}_4} \bar{h}_{\text{CH}_4} + \dot{n}_{\text{O}_2} \bar{h}_{\text{O}_2} \right\}_{\text{in}}$$

Substitute known quantities:

$$Q = \Delta \dot{H} = \dot{\xi}_1 \Delta H_{R_{x1}}^{\circ} + \dot{\xi}_2 \Delta H_{R_{x2}}^{\circ} + \left\{ 30 \int_{25^{\circ}\text{C}}^{150^{\circ}\text{C}} C_{p_{\text{CH}_4}} dT + 15 \int_{25}^{150} C_{p_{\text{HCHO(g)}}} dT + 5 \int_{25}^{150} C_{p_{\text{CO}_2}} dT + 25 \int_{25}^{150} C_{p_{\text{H}_2\text{O}}} dT + 25 \int_{25}^{150} C_{p_{\text{O}_2}} dT \right\} - \left\{ 50 \int_{25}^{25} C_{p_{\text{CH}_4}} dT + 50 \int_{25}^{100} C_{p_{\text{O}_2}} dT \right\}$$

Substituting the expressions of the heat capacities and integrating,

$$Q = \{15(-282.88) + 5(-802.31)\} + \{30(4.9) + 15(4.75) + 5(4.75) + 25(4.27) + 25(3.758)\} - \{50(0) + 50(2.235)\} = -7923 \text{ kJ/h}$$

The rate of heat transfer is -7923 kJ/h (-2.2 kW).