

Chemical Process Calculations CL204

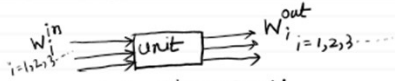
Module-5

Energy balance

Tutorials

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Energy balance
Macroscopic View.

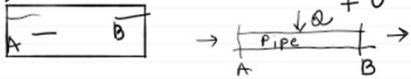


Conservation of Energy
Rate Accumulation of Energy = rate of Energy in - rate of Energy out + Source
at Steady State

$$\text{rate of energy in} - \text{rate of energy out} + \text{Source} = 0$$

Total energy = kinetic energy + Potential Energy + Mechanical Energy

Energy/unit mass $\rightarrow E = \frac{1}{2}V^2 + gh + \frac{PV}{m} + \text{internal Energy}$



at Steady State $\sum \text{energy}_A - \sum \text{energy}_B + Q = 0$

$$u + \frac{PV}{m} = \text{Enthalpy/unit mass}$$

$$u + \frac{P}{\rho} = H_i \text{ (enthalpy/unit mass)}$$

(internal + mechanical) energy

$$\rho = \text{density (kg/m}^3\text{)} = \text{Enthalpy}$$

$$E_i = \frac{1}{2}V_i^2 + gh_i + H_i$$

$$\sum W_i^{\text{in}} E_i - \sum W_i^{\text{out}} E_i + Q = 0$$

$$\frac{\text{kJ}}{\text{hr}}$$

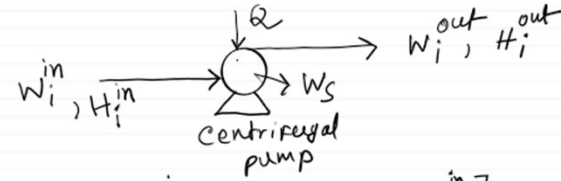
$$\text{kJ/hr}$$

$$\frac{\text{kJ}}{\text{hr}} \approx \text{Watt}$$

$$\frac{\text{kJ} \times 1000}{3600} \approx \text{kWatt}$$

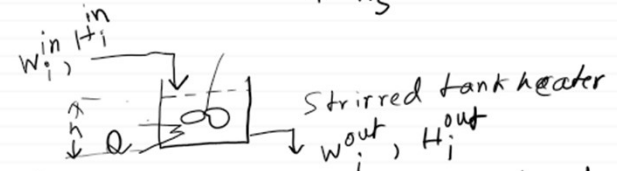
$$E = \text{kJ/kg}$$

$$W \left(\frac{\text{kg}}{\text{hr}} \right)$$



$$Q + \sum W_i^{\text{in}} [H_i^{\text{in}} + \frac{1}{2}V_i^{\text{in}} + gh_i^{\text{in}}] =$$

$$= \sum W_i^{\text{out}} [H_i^{\text{out}} + \frac{1}{2}V_i^{\text{out}} + gh_i^{\text{out}}] + W_s$$



$h \ll$

$$Q + \sum W_i^{\text{in}} H_i^{\text{in}} = \sum W_i^{\text{out}} H_i^{\text{out}}$$

in case of negligible change of mechanical Energy. $\left(\frac{PV}{m} \right) \sim \frac{P}{\rho}$

$$Q + \sum u_i^{\text{in}} W_i^{\text{in}} = \sum u_i^{\text{out}} W_i^{\text{out}}$$

internal Energy $\rightarrow u = f(T)$
 $= f(\text{incp}T)$

$$Q + \sum T_i^{\text{in}} c_{p,i}^{\text{in}} W_i^{\text{in}} = \sum T_i^{\text{out}} c_{p,i}^{\text{out}} W_i^{\text{out}}$$

Energy balance

Conservation of energy.

$$\hookrightarrow \text{Accumulation of energy} = \text{Energy in} - \text{Energy out}$$

+ Source.

$$\therefore \text{Total energy, } E = \text{kinetic energy} \rightarrow \frac{1}{2}mv^2 \\ + \text{potential energy} \rightarrow mgh \\ + \text{mechanical energy} \rightarrow PV \\ + \text{internal energy} \rightarrow U(V, T) \\ \text{at constant volume} \\ U = U(T).$$

$$E = \frac{1}{2}mv^2 + mgh + PV + U$$

$$\therefore \text{Energy per unit mass (J) = (N \times m)}$$

$$= \text{specific energy} \quad \left(= \text{kg} \frac{\text{m}}{\text{s}^2} \times \text{m} \right)$$

$$\hat{E} = \frac{E}{m} \quad \left(= \text{kg} \cdot \frac{\text{m}^2}{\text{s}^2} \right)$$

$$\text{J/s} = \text{Watt} \\ = \text{W}$$

total specific energy

$$\hat{E} = \frac{1}{2}v^2 + gh + \frac{PV}{m} + \hat{U}$$

$$= \frac{1}{2}v^2 + gh + \frac{P}{\rho} + \hat{U} \quad \left(\frac{\text{m}^2}{\text{s}^2} \right) \text{ or } \frac{\text{J}}{\text{kg}}$$

Specific

$$\text{Enthalpy} = \frac{P}{\rho} + \hat{U}$$

$$= \hat{H} \cdot (\text{J/kg}) \quad [\hat{H} = \text{enthalpy (J)}]$$

$$\hat{E} = \frac{1}{2} v^2 + gh + \hat{H}$$

If the body is not moving with its axis $v=0$

and it is in reference level of elevation (ground level)

$$gh = 0$$

$$\Delta \hat{E} = \Delta \hat{H}$$

stagnant body.
h = ground level.

$$\Delta \frac{1}{2} v^2 = 0$$

$$\Delta gh = 0$$

$$\Delta H = \Delta \left(\frac{P}{\rho} \right) + \Delta \hat{U}$$

temperature is constant.

$$\Delta \hat{U} = 0$$

$$\Delta H = \Delta \left(\frac{P}{\rho} \right) \quad \text{change of mechanical energy.}$$

$$\Delta \hat{E} = \Delta \left(\frac{P}{\rho} \right)$$

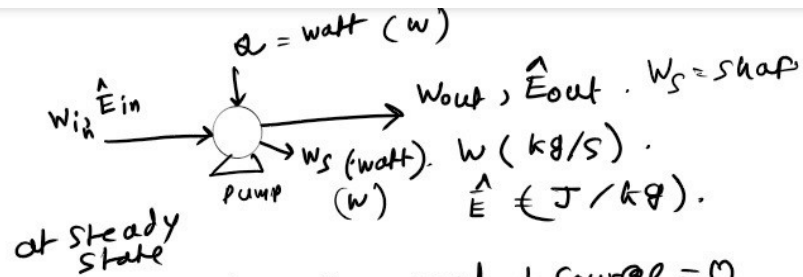


accumulation of energy.

$$\Delta \hat{E} = Q + W_s - \Delta \left(\hat{H} + \frac{1}{2} v^2 + gh \right)$$

at steady state when no energy accumulation. $\Delta \hat{E} = 0$.

$$\Delta \left(\hat{H} + \frac{1}{2} v^2 + gh \right) = Q + W_s$$



at steady state
 \therefore Energy in - Energy out + source = 0
 (watt) watt watt

$$\Rightarrow W_{in} \hat{E}_{in} - W_{out} \hat{E}_{out} + Q - W_s$$

$\frac{\text{kg}}{\text{s}} \times \frac{\text{J}}{\text{kg}} = (\text{Watt})$ watt

$$\frac{W_{in} \hat{E}_{in}}{\text{total inlet energy}} + \overset{\text{shaft work}}{\underset{\text{(the work is done by the pump)}}{Q}} = \frac{W_s + W_{out} \hat{E}_{out}}{\text{total outlet energy}}$$

$Q =$ power of pump
 (the energy is done on the pump)

$$\hat{U} = \hat{U}(T) \text{ at constant volume}$$

$$\hat{U} = \int_{T_1}^{T_2} c_v dT \quad c_v = \frac{\text{J kg}^{-1} \text{K}^{-1}}{\text{J kmol}^{-1} \text{K}^{-1}}$$

$$\underline{c_p - c_v = R}$$

$$c_v = c_p - R$$

$$c_p = \frac{5}{2} R$$

$$\therefore c_v = \frac{5}{2} R - R$$

$$\underline{c_v = \frac{3}{2} R}$$

real gases

$$\Delta H = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} \left[\hat{V} - T \left(\frac{\partial \hat{V}}{\partial T} \right)_P \right] dP$$
$$= \left(\frac{dH}{dT} \right)_P dT + \left(\frac{dH}{dP} \right)_T dP$$

at constant pressure $dP=0$

$$\Delta H = \int_{T_1}^{T_2} c_p dT$$

$$c_p = a + bT + cT^2$$

$$= a + bT$$

a, b, c are constant

$$c_p - \text{J/(kg)(K)}$$

$$\text{J/kg(}^\circ\text{C)}$$

$$\text{BTU/(lb)(}^\circ\text{F)}$$

$$\text{BTU/(lb-mol)(}^\circ\text{F)}$$

$$\Delta H = \Delta \hat{U} + \Delta \frac{P}{V}$$

$\Delta \hat{U} = \Delta \hat{U}$
 mechanical energy = 0

$$\Delta T_k = \frac{\Delta T_o R}{1.8}$$

$$T_{oR} = T_{oF} + 460$$

A frictionless piston expanded from 0.1 m^3 to 0.2 m^3 at 300 K and with ideal gas.

Initial pressure of piston was 200 kPa . Find work done.

$$\Delta \left(\frac{1}{2} v^2 + gh + \frac{P}{\rho} \right) + Q + W_s = 0$$

$v = 0$, $h = 0$,
isothermal process. $\Delta \hat{U} = 0$.

$$Q = 0$$

$$\dot{E}_{in} - E_{out} - W_s = 0$$

$$E_{out} - E_{in} = -W_s$$

$$\begin{aligned} \therefore W_s &= E_{in} - E_{out} \quad p = \text{constant} = 200 \text{ kPa} \\ &= \bar{P} V_{in} - \bar{P} V_{out} = 200 \times 10^3 \text{ Pa} \\ &= 200 (V_{in} - V_{out}) \\ &= 200 (0.1 - 0.2) \times 10^3 \text{ J} \\ &= -0.1 \times 200 \times 10^3 \text{ J} \\ &= \underline{\underline{-20 \text{ kJ}}} \end{aligned}$$

ideal gas

$$PV = nRT$$

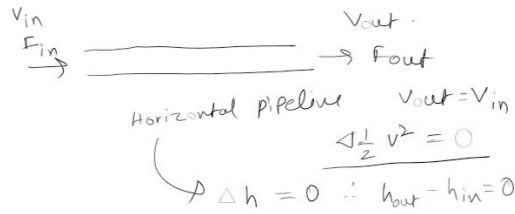
$$n = \frac{PV}{RT} = \frac{200 \times 0.1^3}{300 \text{ K} \times 8.314} = 0.00802 \text{ kmol}$$

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W = -nRT \ln \frac{V_2}{V_1}$$

at constant P , and T .

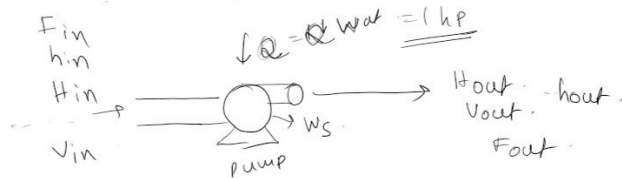
$$W = -0.00802 \times 8.314 \times 300 \times \ln 2 = \underline{\underline{-13.86 \text{ kJ}}}$$



$$\Delta \frac{1}{2} v^2 = 0; \Delta \text{potential energy} = 0$$

$$\Delta H = \dots$$

$$H_{in} - H_{out} = 0 \text{ at steady state.}$$



$$-F_{in} \left[h_{in} + H_{in} + \frac{1}{2} v_{in}^2 \right] + Q$$

$$-F_{in} \left[h_{in} + H_{in} + \frac{1}{2} v_{in}^2 \right] + Q$$

inlet

$$= W_s + F_{out} \left[h_{out} + H_{out} + \frac{1}{2} v_{out}^2 \right]$$

$$\text{if } \begin{cases} h_{in} = h_{out} \\ v_{out} = v_{in} \end{cases} \begin{cases} \Delta \text{potential} = 0 \\ \Delta \text{kinetic} = 0 \end{cases}$$

$$\Delta H = \int_{T_1}^{T_2} (a + bT + cT^2) dT$$

$$= \left[aT + \frac{b}{2} T^2 + \frac{c}{3} T^3 \right]_{T_1}^{T_2}$$

$k \rightarrow c \rightarrow \frac{1}{3} \rightarrow \circ R$

$$k = \circ c + 273 \cdot 15$$

$$= T \circ c + 273 \cdot 15$$

$$\circ c = \frac{F - 32}{9}$$

$$\rightarrow c = \frac{F - 32}{1.8} + \frac{9}{5}$$

$$= \frac{T \cdot F - 32}{1.8} + 273 \cdot 15$$

$$\circ R = \circ T + 460$$

$$\circ R - 460 = \circ T$$

$$TK = \frac{\circ T \circ R - 460 - 32}{1.8} + \underline{\underline{273 \cdot 15}}$$

Heat transfer

$$Q = U A \Delta T \quad (\text{watt}) \text{ W.}$$

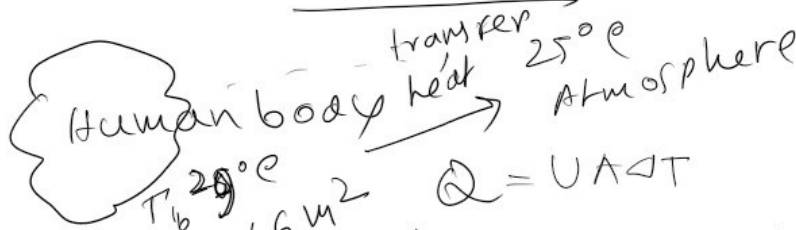
U = heat transfer coefficient overall $(\text{W}/(\text{m}^2)(^\circ\text{C}))$

A = surface area, m^2

$\Delta T = ^\circ\text{C}$ or K

$$\frac{\text{W}}{(\text{m}^2)(\text{K})}$$

$$\Delta^\circ\text{C} = \Delta\text{K}$$



$$A_b = 1.6 \text{ m}^2$$

$$U = 7 \text{ W}/(\text{m}^2)(^\circ\text{C})$$

$$Q = U A \Delta T$$

$$= 7 \times 1.6 \times (25 - 29)$$

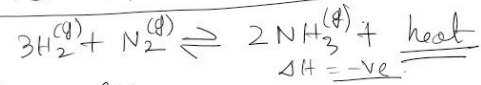
$$= \underline{\underline{-44.8 \text{ watt (W)}}}$$

-ve sign heat is done by the system

Energy balance with chemical reaction

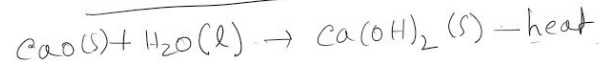
Exothermic reaction.

heat is removed from the process.



Endothermic reaction

heat is absorbed by the system



endothermic reaction

$$\Delta H = +ve$$

heat of reaction

$$\Delta H = 627 \text{ kJ/mol glucose}$$

To produce 10 mol of glucose

627 x 10 kJ energy must be required.

$$= 6270 \text{ kJ}$$

exothermic reaction

$$\Delta H = -600 \text{ kJ/mol.}$$

$$10 \text{ mol total heat} = \underline{600 \times 10 \text{ kJ}}$$

$$= 6000 \text{ kJ}$$

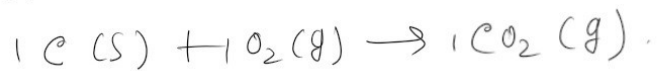
cooling will be required.

heat of reaction is equivalent to enthalpy.

Standard heat of formation

(enthalpy) ΔH_f° denotes standard state
25°C & 1 atm

It refers the enthalpy change associated with the formation of 1 mol of compound from the reactants and other products at standard state.



$$\Delta H_f^\circ = \underbrace{1 \times \Delta H_{f, \text{CO}_2}^\circ}_{\text{product}} - \underbrace{1 \times \Delta H_{f, \text{C}}^\circ - 1 \times \Delta H_{f, \text{O}_2}^\circ}_{\text{reactant}} \quad [\text{Hess's Law}]$$

$$= \sum_i n_i \Delta H_{f, \text{product}}^\circ - \sum_i n_i \Delta H_{f, \text{reactant}}^\circ$$

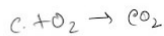
For stable element (O₂, N₂, C ...)

$$\Delta H_{f, \text{stable element}}^\circ = 0$$

$$\Delta H_f^\circ = \Delta H_{f, \text{CO}_2}^\circ - 1 \times 0 - 1 \times 0$$

$$\Delta H_f^\circ = \Delta H_{f, \text{CO}_2}^\circ = -393.51 \text{ kJ/g mol}$$

Heat of formation of reaction at standard state

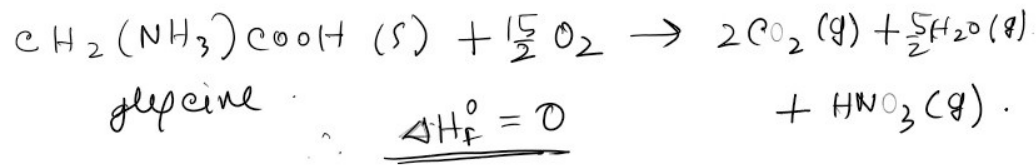


$$\Delta H = -393.51 \text{ kJ/g-mol}$$

Other than endothermic & exothermic.

$$\Delta H_f^\circ = 0$$

$$\Rightarrow \sum \Delta H_f^\circ \text{ reactant} = \sum \Delta H_f^\circ \text{ product}$$

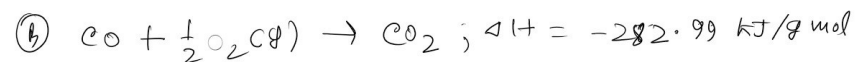
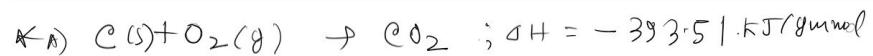


$$\sum \Delta H_f^\circ \text{ product} = \sum \Delta H_f^\circ \text{ reactant}$$

$$\begin{aligned} \therefore \sum \Delta H_f^\circ \text{ glycine} &= 2\Delta H_f^\circ \text{ CO}_2 + \frac{5}{2}\Delta H_f^\circ \text{ H}_2\text{O} \\ &= 2(-393.51) + \frac{5}{2} \times (-241.826) \\ &\quad + 1 \times (-173.23) \\ &= -1202.08 \text{ kJ/gm-mol of glycine} \end{aligned}$$

$$\therefore \frac{-1202.08}{15/2} \text{ kJ/gm-mol O}_2$$

$15/2 \rightarrow \text{O}_2$



$$\Delta H_A^0 = \cancel{\Delta H_{CO_2}^0} - 0 - 0$$

$$\Delta H_B^0 = \cancel{\Delta H_{CO_2}^0} + \Delta H_{CO}^0$$

$$\Delta H_{CO}^0 = \Delta H_A^0 - \Delta H_B^0$$

$$= -393.51 - (-282.99)$$

$$= \underline{\underline{-110.52 \text{ kJ/gmol}}}$$



$$\Delta H_{rxn}^0 = 4 \Delta H_{f,NO}^0 + 6 \times \Delta H_{H_2O}^0 - 4 \times \Delta H_{NH_3}^0$$

$$= 4 \times (90.374) + 6 \times (-241.826)$$

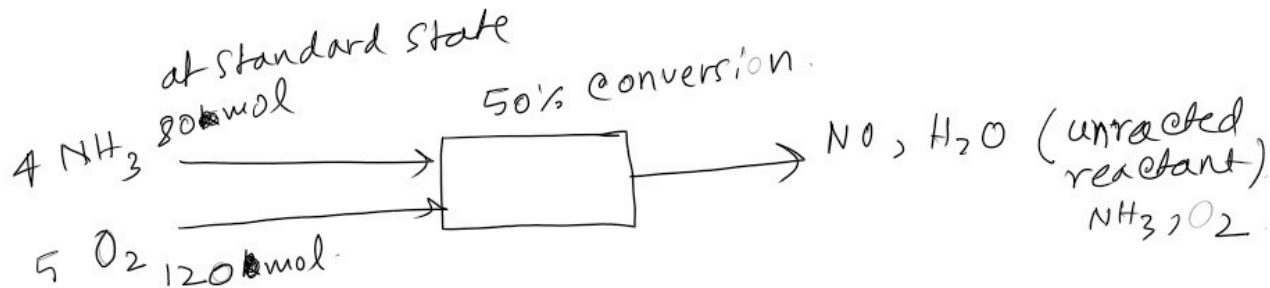
$$- 4 \times (-46.191)$$

$$\Delta H_{rxn}^0 = -904.696 \text{ kJ}$$

$$\Delta H_{rxn}^0 = \frac{-904.696 \text{ kJ/gmol } NH_3}{4}$$

$$= -226.174 \text{ kJ/gmol } NH_3$$

The heat of reaction so far calculated
for 100% conversion.



$$\xi = \frac{-x \times n_{\text{limiting reactant}}}{Q_{\text{limiting reactant}}}$$

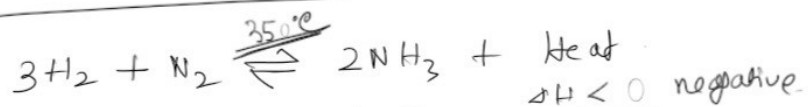
$$= -0.5 \times \frac{80}{(-4)} = 10$$

$$\therefore \Delta H_{\text{rxn}}^{\circ} = \xi \times \Delta H_{\text{rxn}}^{\circ} (\text{at } 100\%)$$

$$= 10 \times (-226.174) \text{ kJ/gmol NH}_3$$

$$= \underline{\underline{-2260.174 \text{ kJ/gmol NH}_3}}$$

If reaction is carried out at different state than standard state



$$T_{\text{reaction}} > T_{25^\circ\text{C}}$$

$$P > P_{\text{atm}}$$

$\Delta H < 0$ negative

ΔH at constant P

$$= \int_{T_1}^{T_2} c_p dT$$

ΔH at constant T

$$= \int_{P_1}^{P_2} \left[\hat{V} + T \left(\frac{\partial \hat{V}}{\partial T} \right)_P \right] dP$$

ΔH at constant pressure

$$= \int_{T_1}^{T_2} c_p dT$$

$$c_p = a + bT + cT^2$$

$$\Delta H_{\text{rxn}}(T) = \sum_i^{\text{Product}} n_i \left[H_i(T_{\text{product}}) - H_i^\circ(25^\circ) \right] - \sum_i^{\text{reactant}} n_i \left[H_i(T_{\text{reactant}}) - H_i^\circ(25^\circ) \right] + \Delta H_{\text{rxn}}^\circ(25^\circ)$$

$$H_i(T_{\text{product}}) - H_i^\circ(25^\circ) = n_i \int_{25^\circ}^{T_{\text{product}}} c_{p,i} dT + n_i \Delta H_{i, \text{phase change}}$$

neglect phase change
latent heat

$$H_i(T_{\text{reactant}}) - H_i^\circ(25^\circ) = n_i \int_{25^\circ}^{T_{\text{reactant}}} c_{p,i} dT + n_i \Delta H_{i, \text{phase change}}$$

phase change

$$\Delta H_{\text{rxn}}(T) = \sum_i^{\text{Product}} n_i \int_{25^\circ}^{T_{\text{product}}} c_{p,i} dT - \sum_i^{\text{Reactants}} n_i \int_{25^\circ}^{T_{\text{reactant}}} c_{p,i} dT + \Delta H_{\text{rxn}}^\circ$$

unknown $f(T_{\text{product}})$



1 inlet + 1.59 mol CO_2 -
 $\rightarrow 4$ " H_2 \rightarrow Limiting

Sensible heat due to $\int_{T_1}^{T_2}$ change

$$\begin{aligned} \rightarrow \text{reactant } \text{H}_2 & 4 \times \int_{25^\circ}^{100} c_{p,\text{H}_2} dT \\ & \rightarrow \text{CO}_2 \quad 1.59 \times \int_{25^\circ}^{700^\circ\text{C}} c_{p,\text{CO}_2} dT \end{aligned} \quad \left. \vphantom{\int} \right\} \text{Sensible heat}$$

$$\begin{aligned} \text{Product } \text{H}_2 & 1.6 \times \int_{25^\circ}^{500} c_{p,\text{H}_2} dT \\ \text{CO}_2 & 0.9 \times \int_{25^\circ}^{500} c_{p,\text{CO}_2} dT \\ \text{CH}_4 & 0.6 \times \int_{25}^{500} c_{p,\text{CH}_4} dT \\ \text{H}_2\text{O} & 1.2 \times \int_{25}^{500} c_{p,\text{H}_2\text{O}} dT \end{aligned} \quad \left. \vphantom{\int} \right\} \text{Sensible heat}$$

$$\Delta H_{rxn} = \sum \text{Sensible heat}_{\text{product}}$$

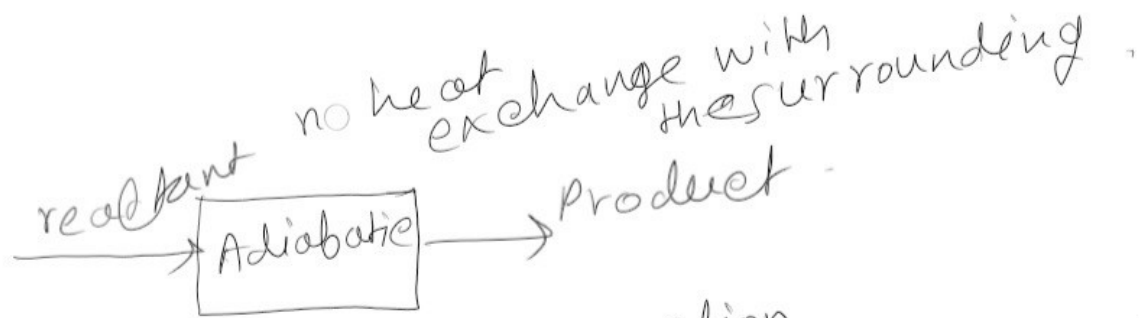
$$- \sum \text{Sensible heat}_{\text{reactant}}$$

$$+ \Delta H^\circ$$

$$= 75.3 - 54.955 + (-99.161)$$

$$= \underline{\underline{-78.85 \text{ kJ / gmol of CO}_2}}$$

adiabatic system.

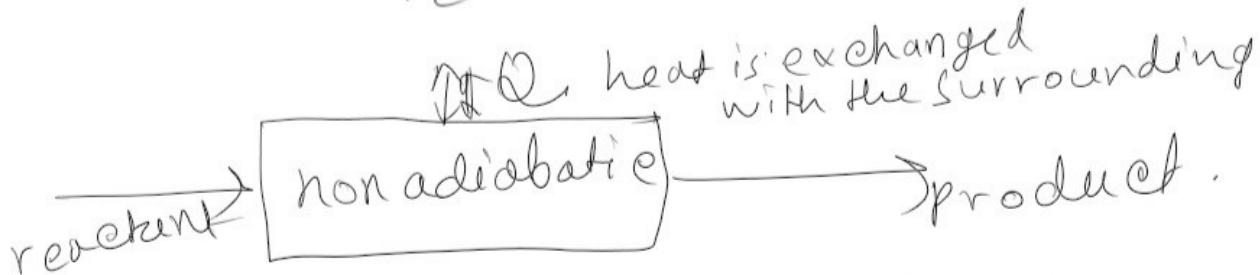


exothermic reaction

reactor temperature \uparrow \rightarrow accident melting of reactor.

endothermic reaction

reactor temperature \downarrow stop reaction.



T of reactor is controlled by cooling or heating.

$$Q + \frac{X_A F_A^{in}}{-U_A} \left[- \sum U_i H_i^{out} \right] = \sum_i^{reactant} F_i^{in} \int_{T_{in}}^{T_{out}} c_{p,i} dT$$

$$= \sum F_i^{in} \left[H(T_{out}) - H(T_{in}) \right]$$

For adiabatic system $Q = 0$.

$$\sum U_i H_i^{out} = \sum U_i H_i^0 + \sum U_i \int_{25^{\circ}}^{T_{out}} c_p dT$$

$$= \Delta H_{rxn}^0 + \sum U_i \int_{25^{\circ}}^{T_{out}} c_p dT$$

$$\Rightarrow Q + \left[\Delta H_{rxn} + \sum_{\substack{\text{All} \\ \text{inlet}}} U_i \int_{25^{\circ}}^{T_{out}} c_{p,i} dT \right] \left[\frac{X_A F_A^{in}}{-U_A} \right] [-T]$$

$$= \sum_{\substack{\text{all} \\ \text{inlet}}} F_i^{in} \int_{T_{in}}^{T_{out}} c_{p,i} dT$$

One hundred gram moles of CO at 300°C are burned with 100 g mol of O₂ which is at 100°C; the exit gases leave at 400°C. What is the heat transfer to or from the system in kilojoules?



$$Q = 0$$

$$\Delta H_{\text{rxn}} = \Delta H_{\text{rxn}}^{\circ} + \sum \text{sensible heat of product}$$

$$+ \sum \text{sensible heat of reactant}$$

10 gm mol CO.
convert
 $\frac{\Delta H_{\text{rxn}}}{2} \times 10 \text{ kJ}$

$$= \Delta H_{\text{rxn}}^{\circ} + \int_{25^{\circ}}^{400} C_{p,\text{CO}_2} 100 \, dT - \int_{25}^{100} C_{p,\text{O}_2} dT$$

$$\frac{a + bT + cT^2}{dT} - \int_{25}^{300} 100 C_{p,\text{CO}} dT$$

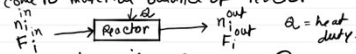
J / (gm mol)(°C)

J / (gm)(°C) × MW;

10⁻³ × kJ

Energy balance in Unit process
(Chemical reactor)
↳ Macroscopic view.

First come to material balance of reactor



$$F_i^{out} = F_i^{in} + \xi \nu_i \quad \text{--- (i)}$$

$$F_i^{out} = F_i^{in} + \frac{\nu_A F_A^{in}}{(-\nu_A)} \nu_i \quad \text{--- (ii)}$$

A = Limiting reactant
 $\xi = \frac{\nu_A F_A^{in}}{(-\nu_A)} = f(x_A)$

F_A^{in} = molar flow rate of limiting reactant in the reactor inlet.

x_A = conversion of limiting reactant
 ν_A = Stoichiometric coefficient of limiting reactant.

Energy balance.

$$Q + \sum F_i^{in} H_i^{in}(T_F, P_F) = \sum F_i^{out} H_i^{out}(T_{out}, P_{out}) \quad \text{--- (iii)}$$

Q + total rate of heat in = total rate of heat out.

T_F, P_F = Feed temperature & pressure
 T_{out}, P_{out} = outlet temperature & pressure.

replace equation (i) (F_i^{out}) in equation (iii)

$$Q + \sum F_i^{in} H_i^{in} = \sum \left[F_i^{in} + \frac{\nu_A F_A^{in}}{(-\nu_A)} \nu_i \right] H_i^{out}$$

$$Q - \sum \frac{\nu_A F_A^{in}}{(-\nu_A)} \nu_i H_i^{out} = \sum F_i^{in} (H_i^{out} - H_i^{in})$$

$$Q + \frac{\nu_A F_A^{in}}{(-\nu_A)} \left[\sum \nu_i H_i^{out} \right] = \sum F_i^{in} (H_i^{out} - H_i^{in}) \quad \text{--- (iv)}$$

In case of ideal solution

$$Q + \frac{\nu_A F_A^{in}}{(-\nu_A)} \left[\sum \nu_i H_i^{out} \right] = \sum F_i^{in} \int_{T_F}^{T_{out}} c_p dT$$

$$Q + \frac{\nu_A F_A^{in}}{(-\nu_A)} \left[\sum \nu_i H_i^{out} \right] = \sum F_i^{in} \int_{T_F}^{T_{out}} c_p dT \quad \text{--- (v)}$$

in case of adiabatic operation

$$Q = 0$$

$$\Delta H = \int_{T_1}^{T_2} c_p dT$$

$$H_i^{out} - H_i^{in} = \int_{T_F}^{T_{out}} c_p dT$$

References

- Himmelblau, D.M., Riggs, J.B., Basic Principles and Calculation in chemical engineering, Prentice Hall.