

ENERGY BALANCE

The first law of thermodynamics demands that energy be neither created nor destroyed. The following is a systematic energy balance performed for each unit of the process. The datum temperature for calculation is taken as 25 °C. The units are as depicted in the flow sheet.

Data available:

C_p = Specific Heat.

T = Temperature, °K.

$C_{p, \text{Hydrogen (g)}} = 6.62 + (0.00081 \times T)$, cal/mol.°K.

$C_{p, \text{Carbon Monoxide (g)}} = 6.60 + (0.0012 \times T)$, cal/mol.°K.

$C_{p, \text{Isobutylene (g)}} = 3.834 + (6.698 \times 10^{-2} \times T) - (2.607 \times 10^{-5} \times T^2)$, cal/mol.°K.

$C_{p, \text{Valeraldehyde (l)}} = (1.1205 \times 10^5) + (2.5778 \times 10^2 \times T)$, J/kmol.°K.

$C_{p, \text{Isoamyl alcohol (l)}} = (-5.3777 \times 10^4) + (8.8342 \times 10^2 \times T)$, J/kmol.°K.

ΔH_f^0 = Standard Heat of formation, kJ/mol.

$\Delta H_{f, \text{Valeraldehyde}}^0 = -227.80$ kJ/mol.

$\Delta H_{f, \text{Isoamyl alcohol}}^0 = -302.10$ kJ/mol.

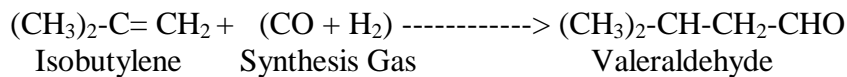
$\Delta H_{f, \text{Isobutylene}}^0 = -16.91$ kJ/mol.

$\Delta H_{f, \text{Hydrogen}}^0 = 0.00$ kJ/mol.

$\Delta H_{f, \text{Carbon Monoxide}}^0 = -110.53$ kJ/mol.

5.1 ENERGY BALANCE AROUND THE OXO REACTOR:

Reaction:



Pressure = 250 atmospheres.

Temperature = 170°C to 175°C.

$$\Delta H_{\text{reaction}}^0 = \Delta H_{f, \text{product}}^0 - \Delta H_{f, \text{reactants}}^0$$

$$\Delta H_{\text{reaction}}^0 = \Delta H_{f, \text{Valeraldehyde}}^0 - \Delta H_{f, \text{Isobutylene}}^0 - \Delta H_{f, \text{Carbon Monoxide}}^0 - \Delta H_{f, \text{Hydrogen}}^0$$

$$\text{i.e., } \Delta H_{\text{reaction}}^0 = -227.80 - (-16.91) - (-110.53) - 0 = \underline{-100.36} \text{ kJ/mol.}$$

$$C_{p, \text{Hydrogen (g)}} = 6.62 + (0.00081 \times T)$$
, cal/mol.°K.

$$\begin{aligned} C_{p, \text{Hydrogen (g)}} &= 6.62 + (0.00081 \times 448.15) = \underline{6.9830} \text{ cal/mol.}^{\circ}\text{K} \\ &= \underline{29.2169} \text{ J/mol.}^{\circ}\text{K} \end{aligned}$$

$$C_{p, \text{ Carbon Monoxide (g)}} = 6.60 + (0.0012 \times T), \text{ cal/mol.}^{\circ}\text{K}.$$

$$C_{p, \text{ Carbon Monoxide (g)}} = 6.60 + (0.0012 \times 448.15) = \underline{7.1378} \text{ cal/mol.}^{\circ}\text{K}$$

$$= \underline{29.8646} \text{ J/mol.}^{\circ}\text{K}$$

$$C_{p, \text{ Isobutylene (g)}} = 3.834 + (6.698 \times 10^{-2} \times T) - (2.607 \times 10^{-5} \times T^2), \text{ cal/mol.}^{\circ}\text{K}.$$

$$C_{p, \text{ Isobutylene (g)}} = 3.834 + (6.698 \times 10^{-2} \times 448.15) - (2.607 \times 10^{-5} \times 448.15^2)$$

$$= \underline{28.6152} \text{ cal/mol.}^{\circ}\text{K} = \underline{119.7260} \text{ J/mol.}^{\circ}\text{K}$$

$$C_{p, \text{ Valeraldehyde (l)}} = (1.1205 \times 10^5) + (2.5778 \times 10^2 \times T), \text{ J/kmol.}^{\circ}\text{K}.$$

$$C_{p, \text{ Valeraldehyde (l)}} = (1.1205 \times 10^5) + (2.5778 \times 10^2 \times 448.15)$$

$$= \underline{227.5741 \times 10^3} \text{ J/kmol}^{\circ}\text{K} = \underline{227.5741} \text{ J/mol.}^{\circ}\text{K}$$

$$= \underline{54.3915} \text{ cal/mol.}^{\circ}\text{K}.$$

$$C_{p, \text{ Isoamyl alcohol (l)}} = (-5.3777 \times 10^4) + (8.8342 \times 10^2 \times T), \text{ J/kmol.}^{\circ}\text{K}.$$

$$C_{p, \text{ Isoamyl alcohol (l)}} = (-5.3777 \times 10^4) + (8.8342 \times 10^2 \times 448.15)$$

$$= \underline{342.1277 \times 10^3} \text{ J/kmol}^{\circ}\text{K} = \underline{342.1277} \text{ J/mol.}^{\circ}\text{K}$$

$$= \underline{81.7705} \text{ cal/mol.}^{\circ}\text{K}.$$

$$\Delta C_p = C_{p, \text{ product}} - C_{p, \text{ reactants}}$$

$$\Delta C_p = C_{p, \text{ Valeraldehyde}} - (C_{p, \text{ Isobutylene}} + C_{p, \text{ Carbon Monoxide}} + C_{p, \text{ Hydrogen}})$$

$$\Delta C_p = 227.5741 - (119.7260 + 29.8646 + 29.2169)$$

$$\Delta C_p = \underline{48.7666} \text{ J/mol.}^{\circ}\text{K}$$

Now we know that,

$$\Delta H_{\text{reaction, T}} = \Delta H_{\text{reaction}}^{\circ} + (\Delta C_p \times (T - 298.15))$$

$$\Delta H_{\text{reaction, T}} = (-100.36 \times 10^3) + (48.7666 \times (448.15 - 298.15))$$

$$\Delta H_{\text{reaction, T}} = \underline{-93045.01} \text{ J/mol}$$

$$\text{Hence, } \Delta H_{\text{reaction, T, act}} = (-93045.01 \text{ J/mol}) \times (44.9045 \times 10^3 \text{ mol})$$

$$= \underline{-4.1781 \times 10^9} \text{ J} = \underline{-4.1781 \times 10^6} \text{ kJ}$$

Taking the datum temperature to be $25^{\circ}\text{C} = 298.15^{\circ}\text{K}$. Further it is assumed that the reactants are entering the reactor at $25^{\circ}\text{C} = 298.15^{\circ}\text{K}$

Thus, $\Sigma H_{in} = 0.0$

Now, $\Sigma H_{out} = \Sigma (m \times C_p \times \Delta T)$

$$\Delta T = T - 298.15 = 448.15 - 298.15 = \underline{150^0 \text{ K}}$$

$$\begin{aligned} \Sigma H_{out} &= (44.9045 \times 10^3 \times 54.3915 \times 150)_{\text{val.}} + (11.2261 \times 10^3 \times 81.7705 \times 150)_{\text{alc.}} \\ &\quad + (2.9543 \times 10^3 \times 28.6152 \times 150)_{\text{IB}} + (2.9543 \times 10^3 \times 7.1378 \times 150)_{\text{CO}} \\ &\quad + (3.5451 \times 10^3 \times 6.9830 \times 150)_{\text{H}_2} \end{aligned}$$

$$\Sigma H_{out} = (366.3635 \times 10^6) + (137.6946 \times 10^6) + (12.6807 \times 10^6) + (3.1631 \times 10^6) \\ + (3.7133 \times 10^6)$$

$$\Sigma H_{out} = \underline{523.6152 \times 10^6 \text{ cal}} = \underline{2094.4608 \times 10^6 \text{ J}} = \underline{2.0945 \times 10^6 \text{ kJ}}$$

Now

$$\Sigma H_{in} + \Delta H_{\text{reaction, T, act}} = \Sigma H_{out} + (m_w \times C_{pw} \times \Delta T_w)$$

Where m_w = mass flow rate of water, kg/s

Assuming that the cooling water is available at $\underline{25^0\text{C}} = \underline{298.15^0\text{K}}$ and that is to be heated to $\underline{40^0\text{C}} = \underline{313.15^0\text{K}}$

$$\Delta T_w = 40 - 25 = 15^0\text{C}$$

$$\Sigma H_{in} + \Delta H_{\text{reaction, T, act}} = \Sigma H_{out} + (m_w \times C_{pw} \times \Delta T_w)$$

$$\text{i.e., } 0 + (4.1781 \times 10^6) = (2.0945 \times 10^6) + (m_w \times 4.187 \times \Delta T_w)$$

$$\Rightarrow m_w = (4.1781 - 2.9045) \times 10^6 / (4.187 \times 15) = \underline{33175.7026 \text{ kg/hr.}} = \underline{9.2155 \text{ kg/s}}$$

5.2 Energy Balance around the Separator/Decobaltiser:

$$\Sigma H_{in} = \underline{2.0945 \times 10^6 \text{ kJ}}$$

$$\text{Temperature} = 180^0\text{C} = 453.15^0\text{K}$$

$$\Sigma H_{\text{vent gas}} = \Sigma (m \times C_p \times \Delta T)$$

It is assumed that the reactants leave the separator at $\underline{25^0\text{C}} = \underline{298.15^0\text{K}}$

$$\Delta T = 453.15 - 298.15 = \underline{155^0\text{K}}$$

$$C_{p, \text{Hydrogen}} (\text{g}) = 6.62 + (0.00081 \times T), \text{ cal/mol.}^0\text{K.}$$

$$\begin{aligned} C_{p, \text{Hydrogen}} (\text{g}) &= 6.62 + (0.00081 \times 453.15) = \underline{6.9871 \text{ cal/mol.}^0\text{K}} \\ &= \underline{29.2340 \text{ J/mol.}^0\text{K}} \end{aligned}$$

$$C_{p, \text{Carbon Monoxide}} (\text{g}) = 6.60 + (0.0012 \times T), \text{ cal/mol.}^0\text{K.}$$

$$C_{p, \text{Carbon Monoxide}} (\text{g}) = 6.60 + (0.0012 \times 453.15) = \underline{7.1438 \text{ cal/mol.}^0\text{K}}$$

$$= \underline{29.8897 \text{ J/mol.}^0\text{K}}$$

$$C_{p, \text{ Isobutylene (g)}} = 3.834 + (6.698 \times 10^{-2} \times T) - (2.607 \times 10^{-5} \times T^2), \text{ cal/mol.}^0\text{K.}$$

$$C_{p, \text{ Isobutylene (g)}} = 3.834 + (6.698 \times 10^{-2} \times 453.15) - (2.607 \times 10^{-5} \times 453.15^2) \\ = \underline{28.3827 \text{ cal/mol.}^0\text{K}} = \underline{118.7532 \text{ J/mol.}^0\text{K}}$$

$$\Sigma H_{\text{vent gas}} = \Sigma (m \times C_p \times \Delta T)$$

$$\Sigma H_{\text{vent gas}} = (2.9543 \times 10^3 \times 28.3827 \times 155)_{\text{IB}} + (2.9543 \times 10^3 \times 7.1438 \times 155)_{\text{CO}} \\ + (3.5451 \times 10^3 \times 6.9871 \times 155)_{\text{H}_2}$$

$$\Sigma H_{\text{vent gas}} = (12.9969 \times 10^6) + (3.2713 \times 10^6) + (3.8394 \times 10^6) = \underline{20.1076 \times 10^6 \text{ cal}}$$

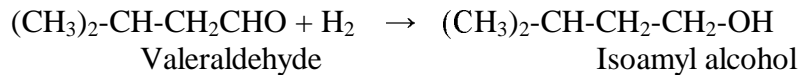
$$\Sigma H_{\text{vent gas}} = \underline{84.1302 \times 10^6 \text{ J}} = \underline{84.1302 \times 10^3 \text{ kJ}}$$

$$\Sigma H_{\text{out}} = \Sigma H_{\text{in}} - \Sigma H_{\text{vent gas}}$$

$$\Sigma H_{\text{out}} = (2.0945 \times 10^6) - (84.1302 \times 10^3) = \underline{2.0104 \times 10^6 \text{ kJ}}$$

5.3 Energy Balance around the Hydrogenation Reactor:

Reaction:



Pressure = 100 atmospheres.

Temperature = 150°C

$$\Sigma H_{\text{in}} = \underline{2.0104 \times 10^6 \text{ kJ}}$$

$$\text{Temperature} = 150^\circ\text{C} = 423.15^\circ\text{K}$$

$$\Delta H_{\text{reaction}}^0 = \Delta H_{\text{f, product}}^0 - \Delta H_{\text{f, reactants}}^0$$

$$\Delta H_{\text{reaction}}^0 = \Delta H_{\text{f, Isoamyl alcohol}}^0 - \Delta H_{\text{f, Valeraldehyde}}^0 - \Delta H_{\text{f, Hydrogen}}^0$$

$$\text{i.e., } \Delta H_{\text{reaction}}^0 = -302.1 - (-227.80) - 0 = \underline{-74.30 \text{ kJ/mol.}} = \underline{-74.30 \times 10^3 \text{ J/mol}}$$

$$C_{p, \text{ Isoamyl alcohol (l)}} = (-5.3777 \times 10^4) + (8.8342 \times 10^2 \times T), \text{ J/kmol.}^0\text{K.}$$

$$C_{p, \text{ Isoamyl alcohol (l)}} = (-5.3777 \times 10^4) + (8.8342 \times 10^2 \times 423.15) \\ = \underline{320.0422 \times 10^3 \text{ J/kmol}^0\text{K}} = \underline{320.0422 \text{ J/mol.}^0\text{K}} \\ = \underline{76.4919 \text{ cal/mol.}^0\text{K.}}$$

$$C_{p, \text{ Valeraldehyde (l)}} = (1.1205 \times 10^5) + (2.5778 \times 10^2 \times T), \text{ J/kmol} \cdot ^\circ\text{K}.$$

$$\begin{aligned} C_{p, \text{ Valeraldehyde (l)}} &= (1.1205 \times 10^5) + (2.5778 \times 10^2 \times 423.15) \\ &= \underline{221.1296 \times 10^3} \text{ J/kmol} \cdot ^\circ\text{K} = \underline{221.1296} \text{ J/mol} \cdot ^\circ\text{K} \\ &= \underline{52.8512} \text{ cal/mol} \cdot ^\circ\text{K}. \end{aligned}$$

$$C_{p, \text{ Hydrogen (g)}} = 6.62 + (0.00081 \times T), \text{ cal/mol} \cdot ^\circ\text{K}.$$

$$\begin{aligned} C_{p, \text{ Hydrogen (g)}} &= 6.62 + (0.00081 \times 423.15) = \underline{6.9628} \text{ cal/mol} \cdot ^\circ\text{K} \\ &= \underline{29.1324} \text{ J/mol} \cdot ^\circ\text{K} \end{aligned}$$

$$\Delta C_p = C_{p, \text{ product}} - C_{p, \text{ reactants}}$$

$$\Delta C_p = C_{p, \text{ Isoamyl alcohol}} - (C_{p, \text{ Valeraldehyde}} + C_{p, \text{ Hydrogen}})$$

$$\Delta C_p = 320.0422 - (221.1296 + 29.1324)$$

$$\Delta C_p = \underline{69.7802} \text{ J/mol} \cdot ^\circ\text{K}$$

Now we know that,

$$\Delta H_{\text{reaction, T}} = \Delta H_{\text{reaction}}^0 + (\Delta C_p \times (T - 298.15))$$

$$\Delta H_{\text{reaction, T}} = (-74.30 \times 10^3) + (69.7802 \times (423.15 - 298.15))$$

$$\Delta H_{\text{reaction, T}} = \underline{-65577.4750} \text{ J/mol}$$

$$\text{Hence, } \Delta H_{\text{reaction, T, act}} = (-65577.4750 \text{ J/mol}) \times (38.1688 \times 10^3 \text{ mol})$$

$$= \underline{-2.5030 \times 10^9} \text{ J} = \underline{-2.5030 \times 10^6} \text{ kJ}$$

$$\Delta T = T - 298.15 = 423.15 - 298.15 = \underline{125} \text{ K}$$

$$\Sigma H_{\text{out}} = \Sigma (m \times C_p \times \Delta T)$$

$$\begin{aligned} \Sigma H_{\text{out}} &= (49.3949 \times 10^3 \times 76.4919 \times 125)_{\text{alc.}} + (6.7357 \times 10^3 \times 52.8512 \times 125)_{\text{Val}} \\ &\quad + (29.1880 \times 10^3 \times 6.9628 \times 125)_{\text{H}_2} \end{aligned}$$

$$\Sigma H_{\text{out}} = (472.2887 \times 10^6) + (44.4987 \times 10^6) + (25.4738 \times 10^6) = \underline{542.2612} \text{ cal}$$

$$\Sigma H_{\text{out}} = \underline{2268.8209 \times 10^6} \text{ J} = \underline{2.2688 \times 10^6} \text{ kJ}$$

Now

$$\Sigma H_{\text{in}} + \Delta H_{\text{reaction, T, act}} = \Sigma H_{\text{out}} + (m_w \times C_{pw} \times \Delta T_w)$$

Where m_w = mass flow rate of water, kg/s

Assuming that the cooling water is available at $25^{\circ}\text{C} = 298.15^{\circ}\text{K}$ and that is to be heated to $40^{\circ}\text{C} = 313.15^{\circ}\text{K}$

$$\Delta T_w = 40 - 25 = 15^{\circ}\text{C}$$

$$\Sigma H_{\text{in}} + \Delta H_{\text{reaction, T, act}} = \Sigma H_{\text{out}} + (m_w \times C_{pw} \times \Delta T_w)$$

$$\text{i.e., } (2.0104 \times 10^6) + (2.5030 \times 10^6) = (2.2688 \times 10^6) + (m_w \times 4.187 \times \Delta T_w)$$

$$\Rightarrow m_w = (2.0104 + 2.5030 - 2.2688) \times 10^6 / (4.187 \times 15) = \underline{35739.1927} \text{ kg/hr.}$$

$$= \underline{9.9276} \text{ kg/s}$$

Thus, flow rate of water = 9.9276 kg/s

5.4 Energy Balance around the Separator:

$$\Sigma H_{\text{in}} = \underline{2.2688 \times 10^6} \text{ kJ}$$

$$\text{Temperature} = 150^{\circ}\text{C} = 423.15^{\circ}\text{K}$$

$$\Sigma H_{\text{H}_2, \text{ recycled}} = (m \times C_p \times \Delta T)$$

$$= 29.1880 \times 10^3 \times 6.9628 \times (423.15 - 298.15) = \underline{25.4038 \times 10^6} \text{ cal}$$

$$= \underline{106.2895 \times 10^6} \text{ J} = \underline{106.2895 \times 10^3} \text{ kJ}$$

$$\Sigma H_{\text{out}} = \Sigma H_{\text{in}} - \Sigma H_{\text{H}_2, \text{ recycled}}$$

$$\Sigma H_{\text{out}} = (2.2688 \times 10^6) - (106.2895 \times 10^3) = \underline{2.1625 \times 10^6} \text{ kJ}$$

5.5 Energy Balance around the Distillation Column:

$$\Sigma H_{\text{in}} = \underline{2.1625 \times 10^6} \text{ kJ}$$

$$\text{Condenser load} = Q_c = \underline{661.2158} \text{ kW}$$

$$\text{Cooling Water requirement in the condenser} = m_w = \underline{10.52} \text{ kg/s}$$

$$\text{Reboiler load} = Q_d = \underline{732.68} \text{ kW}$$

Steam is available at 1 atmosphere.

The above data is taken from the process design of condenser and reboiler.

