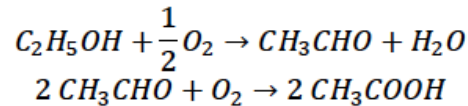


**Sample: Chemistry - Chemical Engineering**

We are designing a reactor that produces a target of 1200 kmol of acetaldehyde,  $\text{CH}_3\text{CHO}$ , per hour from ethanol and air. At the operating conditions, two reactions will occur; the first results in the desired product, but the second consumes the desired product, creating an undesired byproduct of acetic acid:



Preliminary R&D data indicate that if we use a new catalyst, a feed ratio of 5.7 moles ethanol per mole of oxygen, and run the reactor at 300 °C and 1.5 atm, we can expect a 25% conversion of ethanol and an acetaldehyde selectivity of 0.6. One proposed block diagram has pure ethanol vapor and air (79 mol%  $\text{N}_2$ , the rest oxygen) at 300 °C and 1.5 atm being fed to the system, and a stream of vapor exiting at the same pressure.

- If it is desired to maintain the temperature at 300 °C, how much energy needs to be added or removed from the system? [4 points]
- If energy needs to be added, saturated steam at 10 bar is available to condense (but we want to keep the temperature the same). If energy needs to be removed, cooling water at 25°C is available (but we want to keep its temperature below 50°C). What mass flow rate of steam or cooling water would meet the need for this system? [2 points]

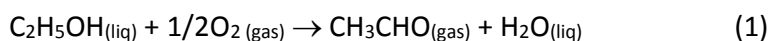
**Solution**

Calculations of  $\Delta H$ :

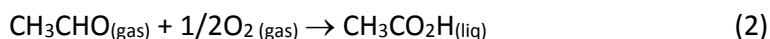
Table values for standard enthalpies:

$$\Delta H^{298}(\text{C}_2\text{H}_5\text{OH}_{(\text{liq})}) = -277.6 \text{ kJ/mol}; \Delta H^{298}(\text{CH}_3\text{CHO}_{(\text{gas})}) = -166.0 \text{ kJ/mol};$$

$$\Delta H^{298}(\text{H}_2\text{O}_{(\text{liq})}) = -286.0 \text{ kJ/mol}; \Delta H^{298}(\text{CH}_3\text{CO}_2\text{H}_{(\text{liq})}) = -484.1 \text{ kJ/mol}$$



$$\Delta H_{(1)}^{298} = \Delta H^{298}(\text{H}_2\text{O}_{(\text{liq})}) + \Delta H^{298}(\text{CH}_3\text{CHO}_{(\text{gas})}) - \Delta H^{298}(\text{C}_2\text{H}_5\text{OH}_{(\text{liq})}) = -286.0 - 166.0 + 277.6 = -174.4 \text{ kJ/mol}$$



$$\Delta H_{(2)}^{298} = \Delta H^{298}(\text{CH}_3\text{CO}_2\text{H}_{(\text{liq})}) - \Delta H^{298}(\text{CH}_3\text{CHO}_{(\text{gas})}) = -484.1 + 166.0 = -318.1 \text{ kJ/mol}$$

The equations for temperature dependence of  $\Delta H$ :

$$\Delta H_1^{573} = \Delta H_1^{298} + \int_{298}^{573} \Delta c_p(1) dT + \Delta H_{vap}(\text{H}_2\text{O}) - \Delta H_{vap}(\text{C}_2\text{H}_5\text{OH})$$



$$\Delta H_2^{573} = \Delta H_2^{298} + \int_{298}^{573} \Delta c_p(2)dT + \Delta H_{vap}(CH_3CO_2H)$$

We found the next values for heat capacity ( $c_p$ ) and enthalpy of vaporization ( $\Delta H_{vap}$ ) for substances on the Internet. The average value of heat capacity in a predetermined range was used:

$$c_p(H_2O_{(liq)}) = 76 \text{ J/mol}\cdot\text{K}; c_p(H_2O_{(gas)})^{373-573} = 31.5 \text{ J/mol}\cdot\text{K}$$

$$c_p(C_2H_5OH_{(liq)}) = 121.9 \text{ J/mol}\cdot\text{K}; c_p(C_2H_5OH_{(gas)})^{350-573} = 35.7 \text{ J/mol}\cdot\text{K}$$

$$c_p(CH_3CO_2H_{(liq)}) = 123.4 \text{ J/mol}\cdot\text{K}; c_p(CH_3CO_2H_{(gas)})^{391-573} = 92.0 \text{ J/mol}\cdot\text{K}$$

$$c_p(CH_3CHO_{(gas)})^{298-573} = 69.4 \text{ J/mol}\cdot\text{K}; c_p(O_2(gas))^{298-573} = 30.6 \text{ J/mol}\cdot\text{K}$$

$$\Delta H_{vap}(H_2O) = 40.7 \text{ kJ/mol}\cdot\text{K}; \Delta H_{vap}(C_2H_5OH) = 38.6 \text{ kJ/mol}\cdot\text{K}; \Delta H_{vap}(CH_3CO_2H) = 23.7 \text{ kJ/mol}$$

$c_p$  changes considerably due to the phase transitions, so we have to split the integral into parts where  $c_p$  of each compound is approximately constant.

$$\int_{298}^{573} \Delta c_p(1)dT = \int_{298}^{351} \Delta c_{p1}(1)dT + \int_{351}^{373} \Delta c_{p2}(1)dT + \int_{373}^{573} \Delta c_{p3}(1)dT$$

$$\int_{298}^{351} \Delta c_{p1}(1)dT = \left[ c_p(H_2O_{(liq)}) + c_p(CH_3CHO_{(gas)}) - \frac{1}{2}c_p(O_2(gas)) - c_p(C_2H_5OH_{(liq)}) \right] \Delta T_1$$

$$\int_{351}^{373} \Delta c_{p2}(1)dT = \left[ c_p(H_2O_{(liq)}) + c_p(CH_3CHO_{(gas)}) - \frac{1}{2}c_p(O_2(gas)) - c_p(C_2H_5OH_{(gas)}) \right] \Delta T_2$$

$$\int_{373}^{573} \Delta c_{p3}(1)dT = \left[ c_p(H_2O_{(gas)}) + c_p(CH_3CHO_{(gas)}) - \frac{1}{2}c_p(O_2(gas)) - c_p(C_2H_5OH_{(gas)}) \right] \Delta T_3$$

Summing the expressions of these three integrals we obtain the following equation:

$$\int_{298}^{573} \Delta c_p(1)dT = c_p(H_2O_{(liq)})(\Delta T_1 + \Delta T_2) + c_p(H_2O_{(gas)})\Delta T_3 + c_p(CH_3CHO_{(gas)})\Delta T_{sum} - \frac{1}{2}c_p(O_2(gas))\Delta T_{sum} - c_p(C_2H_5OH_{(liq)})\Delta T_1 - c_p(C_2H_5OH_{(gas)})(\Delta T_2 + \Delta T_3), \text{ where } \Delta T_i \text{ is temperature difference corresponding to the interval, } \Delta T_{sum} \text{ - total temperature difference.}$$

In such manner we can obtain the equation below:



$$\int_{298}^{573} \Delta c_p(2) dT = c_p(CH_3CO_2H_{(liq)})(T_b - 298) + c_p(CH_3CO_2H_{(gas)})(573 - T_b) -$$

$$- \left[ c_p(CH_3CHO_{(gas)}) + \frac{1}{2} c_p(O_2_{(gas)}) \right] \Delta T_{sum}, \text{ where } T_b \text{ is boiling point of acetic acid.}$$

$$\int_{298}^{573} \Delta c_p(1) dT = 76 \cdot (373 - 298) + 31.5 \cdot (573 - 373) + 69.4 \cdot (573 - 298) - \frac{1}{2} \cdot 30.6 \cdot (573 - 298) -$$

$$121.9 \cdot (351 - 298) - 35.7 \cdot (573 - 351) = 12,491 \text{ J/mol} = 12.5 \text{ kJ/mol}$$

$$\int_{298}^{573} \Delta c_p(2) dT = 123.4 \cdot (391 - 298) + 92 \cdot (573 - 391) - (69.4 + 0.5 \cdot 30.6)(573 - 298) =$$

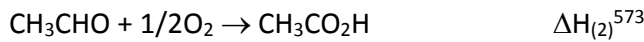
$$= 4,928 \text{ J/mol} = 4.9 \text{ kJ/mol}$$

Shifting the value of integral into equation we can obtain enthalpy of the reactions:

$$\Delta H_{(1)}^{573} = -174.4 + 12.5 + 40.7 - 38.6 = -159.8 \text{ kJ/mol}$$

$$\Delta H_{(2)}^{573} = -318.1 + 4.9 + 23.7 = -289.5 \text{ kJ/mol}$$

For getting correct energy in process of formation of the acetic acid remember that acetaldehyde needed for reaction (2) is produced in the reaction (1).



$$\Delta H_{(12)}^{573} = -159.8 - 289.5 = -449.3 \text{ kJ/mol}$$

Let us calculate the total enthalpy  $\Delta H_{(t)}^{573}$  of processes considering the contribution of each one.

$$\Delta H_{(t)}^{573} = 0.6 \cdot \Delta H_{(1)}^{573} + 0.4 \cdot \Delta H_{(12)}^{573} = 0.6 \cdot (-159.8) + 0.4 \cdot (-449.3) = -275.5 \text{ kJ/mol}$$

**Enthalpy value is negative, so we need to remove heat from the reactor.**

Using proportion we can calculate the total energy, required to form a 1200 mol product:

$$0.6 \text{ mol} \quad - \quad -275.5 \text{ kJ/mol}$$

$$1200 \cdot 10^3 \text{ mol} \quad - \quad Q$$

$$Q = 551 \cdot 10^6 \text{ kJ} = 551 \cdot 10^9 \text{ J}$$

Now we can get the amount of cooling water.  $\Delta T = 50 - 25 = 25 \text{ K}$



$Q = n c_p(\text{H}_2\text{O}) \Delta T$ ,  $n = m/M$  – amount of substance of water.

$m(\text{H}_2\text{O}) = Q * M(\text{H}_2\text{O}) / (c_p(\text{H}_2\text{O}) \Delta T) = 551 * 10^9 * 0.018 / (76 * 25) = \mathbf{5,220,000 \text{ kg of cooling water}}$