8.5 Enthalpy calculations with phase changes

The state of a system can be changed, for example, by increasing its temperature or changing its composition. Properties of the system whose change depends only on the initial and final states of the system but not on the manner used to realize the change from the initial to the final state are referred to as state properties [4].

Phase changes, such as evaporation and melting, are accompanied by relatively large changes in internal energy and enthalpy, as bonds between molecules are broken and reformed. Heat transferred to or from a system, causing change of phase **at constant temperature and pressure**, is known as **latent heat**. The types of latent heats are latent heat of vaporization, which is the heat required to vaporize a liquid; latent heat of fusion, which is the heat required to melt a solid; and latent heat of sublimation, which is the heat required to directly vaporize a solid. Heat is released during condensation, and heat is required to vaporize a liquid or melt a solid. Table A.1 reports these two latent heats for substances at their normal melting and boiling points (i.e., at a pressure of 1 atm). Sensible heat refers to heat that must be transferred to raise or lower the temperature of a substance without change in phase as defined earlier. The quantity of sensible heat required to produce a temperature change in a system can be determined from the appropriate form of the first law of thermodynamics. The heat capacity at constant pressure, C_P, for most incompressible liquids and solids is equal; $C_P \approx C_v$ and for ideal gases, $C_P = C_v + R$.

Example 8.18 Enthalpy of phase change

Problem

Steam at a rate of 100 kg/h is used to heat a stream of gas flowing on the tube side of a heat exchanger. The steam enters the shell side of the heat exchanger as saturated vapor at 10 bar of 90% quality, and exits as saturated liquid water at 10 bar. Calculate the rate of heat transfer to the gas side.

Solution

Known quantities: Inlet (10 bar, 90% quality) and exit (10 bar, saturated water) steam conditions.

Find: The change in enthalpy transport rate.

Assumption: No change in potential and kinetic energy, no shaft work.

Analysis: Use the general energy balance equation for an open system around the heat exchanger. The simplified energy balance is obtained as follows.

Energy balance for an open system is

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

After including the assumptions, the equation is reduced to

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

Setting enthalpy transport rate ($\dot{H}$) in terms of specific enthalpy *h*,

$$\Delta \dot{H} = \dot{m}_s (h_2 - h_1) = Q$$

The change in specific enthalpy of steam is

$$\Delta h_s = h_{s,2} - h_{s,1}$$

The inlet steam specific enthalpy ($h_{s,1}$) of saturated vapor at 10 bar and 90% quality is

$$h_{s,1}\big|_{10\text{ bar},\, x=0.9} = h_f + x h_{fg} = 762.6 + 0.9 \times 213.6 = 2574.84\text{ kJ/kg}$$

The exit steam specific enthalpy at 10 bar, saturated water is

$$h_{s,2}\big|_{10\text{ bar, sat'd water}} = 762.6\text{ kJ/kg}$$

Substituting the values of specific enthalpies of steam,

$$\Delta h_s = h_{s,2} - h_{s,1} = 762.6 - 2574.84 = -1812.24\text{ kJ/kg}$$

The rate of heat transfer from condensed steam to gas stream is

$$Q = m_s \Delta h_s = 100\,\frac{\text{kg}}{\text{h}}\left(-1812.24\,\frac{\text{kJ}}{\text{kg}}\right)\frac{\text{h}}{3600\text{ s}} = -50.34\text{ kJ/s}$$

The sign of *Q* value is negative; that is, heat is transferred from the condensed steam to gas stream.

8.5.1 Energy balance for open systems with multiple inputs and multiple outputs

The general energy balance for an open system is

$$Q - \dot{W}_s = \Delta \dot{H} + \Delta KE + \Delta PE \qquad (8.25)$$

The change in the rate of enthalpy for multiple streams is

$$\Delta \dot{H} = \sum \dot{H}_{\text{out}} - \sum \dot{H}_{\text{in}} \qquad (8.26)$$

Setting enthalpy transport rate ($\dot{H}$) in terms of specific enthalpy *h*,

$$\Delta \dot{H} = \sum \dot{m}_{\text{out}} h_{\text{out}} - \sum \dot{m}_{\text{in}} h_{\text{in}} \qquad (8.27)$$

Example 8.19 Enthalpy change of mixtures and phase change

Problem

Thousand kilomoles per hour of a liquid mixture of 70 mol% acetone and 30 mol% benzene is heated from 10°C to 50°C in a shell-and-tube heat exchanger using steam as the heating medium. The steam enters the heat exchanger in the shell as a saturated vapor at 16 bar of 90% quality, and exits as saturated liquid water at 16 bar. Calculate the mass flow rate of the inlet steam required for this purpose.

Solution

Known quantities: Inlet mixture flow rate and composition, inlet and exit temperature, steam inlet and outlet conditions. Find: The mass flow rate of inlet steam.

Assumptions: The boiler is adiabatic, no shaft work, no change in kinetic and potential energy, inlet and exit pipe is at the same diameter and level.

Analysis: Use energy balance for an open system around the heat exchanger. Energy balance for an open system is given by

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

After including the assumptions, the equation is reduced to

$$\Delta\dot{H} = 0$$

Since the system is of multiple inputs and multiple outputs, the change in enthalpy around the heat exchanger is

$$\Delta\dot{H} = 0 = \sum \dot{H}_{\text{out}} - \sum \dot{H}_{\text{in}}$$

Setting the enthalpy transport rate ($\dot{H}$) in terms of specific enthalpy *h*,

$$\Delta\dot{H} = 0 = \sum \dot{m}_{\text{out}} h_{\text{out}} - \sum \dot{m}_{\text{in}} h_{\text{in}}$$

In more detail,

$$\Delta\dot{H} = 0 = \left\{\dot{m}_{\text{s,out}} h_{\text{s,out}} + \dot{m}_{\text{a,out}} h_{\text{a,out}} + \dot{m}_{\text{b,out}} h_{\text{b,out}}\right\} - \left\{\dot{m}_{\text{s,in}} h_{\text{s,in}} + \dot{m}_{\text{a,in}} h_{\text{a,in}} + \dot{m}_{\text{b,in}} h_{\text{b,in}}\right\}$$

where

$m_{\text{s,in}}$, $m_{\text{s,out}}$ are the inlet and exit mass flow rates of steam which are equal
$\dot{m}_{\text{a,in}}$, $\dot{m}_{\text{a,out}}$ are the inlet and exit mass flow rates of acetone
$\dot{m}_{\text{b,in}}$, $\dot{m}_{\text{b,out}}$ are the inlet and exit mass flow rates of benzene

Rearranging the earlier equation,

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$$\Delta \dot{H} = 0 = \dot{m}_s\left(h_{s,out} - h_{s,in}\right) + \dot{m}_a\left(h_{a,out} - h_{a,in}\right) + \dot{m}_b\left(h_{b,out} - h_{b,in}\right)$$

where

$\dot{m}_a = \dot{m}_{a,in} = \dot{m}_{a,out}$ is the mass flow rate of acetone
$\dot{m}_b = \dot{m}_{b,in} = \dot{m}_{b,out}$ is the mass flow rate of benzene

Since the mixture contains 70% acetone and 30% benzene, the mixture mass flow rate and change of mixture enthalpy can be written as

$$m_{mix} = 0.7\dot{m}_a + 0.3\dot{m}_b$$

The change in mixture specific enthalpy is given by

$$\Delta h_{mix} = 0.7\Delta h_a + 0.3\Delta h_b$$

The change in the specific enthalpy of steam, Δh_s, is given by

$$\Delta h_s = h_{s,2} - h_{s,1}$$

The inlet steam specific enthalpy ($h_{s,1}$) of saturated vapor at 16 bar and 90% quality is

$$h_{s,1}\big|_{16\text{ bar},\, x=0.9} = h_f + xh_{fg} = 858.6 + 0.9 \times 1933.2 = 2598.5\text{ kJ/kg}$$

The exit steam specific enthalpy at 16 bar, saturated water is

$$h_{s,2}\big|_{16\text{ bar, sat'd water}} = 858.6\text{ kJ/kg}$$

Substituting the values of the specific enthalpies of steam,

$$\Delta h_s = h_{s,2} - h_{s,1} = 858.6 - 2598.5 = -1740\text{ kJ/kg}$$

The change in specific enthalpy of acetone and benzene mixture, Δh_{mix}, is given by

$$\Delta h_{mix} = 0.7\Delta h_a + 0.3\Delta h_b = \int_{10^\circ C}^{50^\circ C} C_{P,mix}\, dT$$

The specific heat capacity of the mixture is given by

$$C_{P,mix} = \sum y_i C_{Pi} = 0.7C_{P,acetone} + 0.3C_{P,benzene}$$

The heat capacity at constant pressure as a function of temperature:

$$\text{Acetone (liquid): } C_{Pa}\left(\frac{\text{J}}{\text{mol}\,^\circ\text{C}}\right) = 123 + 0.186T$$

$$\text{Benzene (liquid): } C_{Pb}\left(\frac{\text{J}}{\text{mol}\,^\circ\text{C}}\right) = 126.5 + 0.234T$$

Substitute the heat capacities of acetone and benzene:

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$$C_{P,\mathrm{mix}} = \{0.7(123) + 0.3(126.5)\} + \{0.7(0.186) + 0.3(0.234)\}T$$

Rearranging,

$$C_{P,\mathrm{mix}} = 124 + 0.20T$$

Substituting the mixture heat capacity,

$$\Delta h_{\mathrm{mix}} = \int_{10^\circ\mathrm{C}}^{50^\circ\mathrm{C}} C_{P,\mathrm{mix}}\,\mathrm{d}T = \int_{10^\circ\mathrm{C}}^{50^\circ\mathrm{C}} (124 + 0.20T)\,\mathrm{d}T$$

Integrating,

$$\Delta h_{\mathrm{mix}} = \int_{10^\circ\mathrm{C}}^{50^\circ\mathrm{C}} (124 + 0.20T)\,\mathrm{d}T = \left(124T + 0.20T^2\right)\Big|_{10}^{50}$$

The change in enthalpy of the acetone-benzene mixture, Δh_{mix}, is given by

$$\Delta h_{\mathrm{mix}} = 124(50 - 10) + \frac{0.20}{2}\left(50^2 - 10^2\right) = 5200\ \mathrm{J/mol}$$

Substituting the values of change in steam enthalpy and mixture enthalpy,

$$0 = \dot{m}_s \Delta h_s + \dot{m}_{\mathrm{mix}} \Delta h_{\mathrm{mix}}$$

$$= \dot{m}_s\left(-1740\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) + 1000\ \frac{\mathrm{kmol}}{\mathrm{h}}\left(\frac{1000\ \mathrm{mol}}{\mathrm{kmol}}\right)\left(5200\ \frac{\mathrm{J}}{\mathrm{mol}}\left|\frac{\mathrm{kJ}}{1000\ \mathrm{J}}\right.\right)$$

Solving for $\dot{m}_s$, $\dot{m}_s\left(1740\ \frac{\mathrm{kJ}}{\mathrm{kg}}\right) = \left(5.20 \times 10^6\ \mathrm{kJ/h}\right)$.

The rounded value of the steam mass flow rate is $\dot{m}_s$ =2990 kg/h.

The amount of steam required for heating the acetone-benzene mixture is 2990 kg/h.