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موازنة الطاقة

م. د. د. علي عبد الرحمن

Energy and Energy Balances
Dr: Ali Abdul Rahman AL-ezzi

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CHAPTER ONE (1)

This chapter illustrates the fundamental theory of energy balance without reactions. The concept of energy conservation as expressed by an energy balance equation is essential to chemical engineering calculations. Similar to material balances studied in previous chapters, a balance of energy is important to solving many problems. The chapter begins with definitions of the first law of thermodynamics, each term in the first law, and application for closed and open systems. Next, the three forms of energy, that is, kinetic, potential, and internal, are explained. Mechanical energy balance and Bernoulli's equations are also covered in this chapter. The following items outline the principal learning objectives of this chapter.

Learning Objectives

1. Calculate energy balance for closed and open systems (Section 1.1).
2. Write mechanical energy balance for a non reacting system (Section 1.2).
3. Use Bernoulli's equation to solve mechanical energy problems involving flowing fluids with no work input/output (Section 1.3).
4. Use heat capacities to calculate enthalpy changes (Section 1.4).
5. Use latent heats within energy balances for systems involving phase changes (Section 1.5).
6. Use psychrometric charts (Section 1.6).

1.1 Energy Balance for Closed and Open Systems

A **system** is an object or a collection of objects that an analysis is carried out on. The system has a definite boundary, called the system boundary, which is chosen and specified at the beginning of the analysis. Once a

system is defined, through the choice of a system boundary, everything external to it is called the surroundings. All energy and material that are transferred out of the system enter the surroundings, and vice versa. **An isolated system** is a system that does not exchange heat, work, or material with the surroundings. A **closed system** is a system in which heat and work are exchanged across its boundary, but material is not. **An open system** can exchange heat, work, and material with the surroundings.

1.1.1 Forms of Energy: The First Law of Thermodynamics

Energy is often categorized as kinetic energy, potential energy, and internal energy. The first law of thermodynamics is a statement of energy conservation. Although energy cannot be created or destroyed, it can be converted from one form to another. Energy can also be transferred from one point to another or from one body to another one. Energy transfer can occur by flow of heat, by transport of mass, or by performance of work [1]. The general energy balance for a thermodynamic process can be expressed in words as the accumulation of energy in a system equals the input of energy into the system minus the output of energy from the system.

1.1.2 Energy Balance for a Closed System

Energy can cross the boundaries of a closed system in the form of heat and work (Figure1.1). The energy balance of a system is used to determine the amount of energy that flows into or out of each process unit, calculate the net energy requirement for the process, and assess ways of reducing energy requirements in order to improve process profitability and efficiency [2]. The energy balance for a closed system takes the form

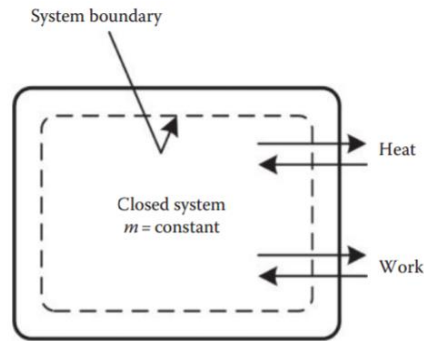


FIGURE1.1 Energy balance for a closed system.

$$Q - W = \Delta U + \Delta KE + \Delta PE \dots\dots\dots (1.1)$$

where heat (Q), work (W), internal energy (U), kinetic energy (KE), and potential energy (PE) are defined as follows.

Heat is the energy that flows due to a temperature difference between the system and its surroundings and always flows from regions at high temperatures to regions at low temperatures. By convention, heat is defined to be positive if it flows to a system (i.e., gained). For systems with no significant heat exchange with the surroundings, $Q = 0$. Such a system is said to be *adiabatic*. The absence of any heat transfer can be due to perfect thermal insulation or the fact that the system and surroundings are at the same temperature. **Work** is the energy that flows in response to any driving force (e.g., applied force, torque) other than temperature, and is defined as positive if it flows from the system (i.e., work done by the system). In chemical processes, work may, for instance, come from pumps, compressors, moving pistons, and moving turbines. Heat or work only refers to energy that is being transferred to or from the system. If there is no motion along the system boundary, then $W=0$. **Internal Energy** is all the energy associated with a system that does not fall under the earlier definitions of kinetic or potential energy. More

specifically, internal energy is the energy due to all molecular, atomic, and subatomic motions, and interactions. Usually, the complexity of these various contributions means that no simple analytical expression is available from which internal energy can be readily calculated. An *isothermal* system is one where the temperature does not change with time and in space. This does not mean that no heat crosses the boundaries. **Kinetic Energy** is associated with directed motion of the system. Translation refers to straight line motion. If the system is not accelerating, then $\Delta KE=0$. **Potential Energy** of a system is due to the position of the system in a potential field. There are various forms of potential energy, but only gravitational potential energy will be considered in this course. If the system is not experiencing a displacement in the direction of the gravitational field, then $\Delta PE=0$.

1.1.2.1 Kinetic Energy

Kinetic energy is the energy carried by a moving system because of its velocity. The kinetic energy KE of a moving object of mass m , traveling with speed v , is given by

$$KE = \frac{1}{2} \dot{m} v^2 \Rightarrow \left(\frac{\text{kg}}{\text{s}} \right) \left(\frac{\text{m}}{\text{s}} \right)^2 \left| \frac{\text{N}}{\text{kg m/s}^2} \right| \left| \frac{\text{J}}{\text{N} \cdot \text{m}} \right| \left| \frac{\text{W}}{\text{J/s}} \right| = \text{W} \quad \dots\dots\dots (1.2)$$

KE has units of energy, \dot{m} has units of mass flow rate (mass/time), and v has units of velocity (length/time).

Example 1.1 Kinetic Energy Calculations

Water flows from a large lake into a process unit through a 0.02 m inside diameter pipe at a rate of 2.0 m³ /h. calculate the change in kinetic energy for this stream in joules per second.

Solution

Known quantities: Pipe diameter (0.02 m), water volumetric flow rate ($2.0 \text{ m}^3/\text{h}$), density of water (1000 kg/m^3).

Find: Change in kinetic energy

Analysis: First, calculate the mass flow rate from the density and volumetric flow rate, and, next, determine the velocity as the volumetric flow rate divided by the pipe inner cross-sectional area. The rate of change in kinetic energy is calculated by

$$\Delta KE = \frac{1}{2} \dot{m} \Delta v^2 = \frac{1}{2} \dot{m} (v_2^2 - v_1^2) \quad \dots\dots\dots (1.3)$$

The mass flow rate, \dot{m} , is the density (ρ) multiplied by volumetric flow rate (\dot{V}):

$$\dot{m} = \rho \dot{V} = \frac{1000 \text{ kg}}{\text{m}^3} \left| \frac{2 \text{ m}^3}{\text{h}} \right| \left| \frac{\text{h}}{3600 \text{ s}} \right| = 0.56 \text{ kg/s}$$

The water exit velocity (v_2) is calculated from the volumetric flow rate (\dot{V}) divided by pipe inner cross-sectional area of the exit of the pipe (A). The surface of the lake being large, the water surface can be assumed to be almost stagnant. Accordingly, the initial velocity is negligible ($v_1=0$):

$$v_2 = \frac{\dot{V}}{A = \frac{\pi D^2}{4}} = \left(\frac{2.00 \frac{\text{m}^3}{\text{h}} \left| \frac{\text{h}}{3600 \text{ s}} \right|}{\frac{3.14 \times (0.02 \text{ m})^2}{4}} \right) = 1.77 \text{ m/s}$$

Substituting the values of mass flow rate and velocities in the kinetic energy equation,

$$\Delta KE = \frac{1}{2} \dot{m}(v_2^2 - v_1^2) = \frac{1}{2} \left(0.56 \frac{\text{kg}}{\text{s}} \right) \left(\left(1.77 \frac{\text{m}}{\text{s}} \right)^2 - 0 \right) \left(\frac{1 \text{ N}}{\frac{\text{kg m}}{\text{s}^2}} \right) \\ \times \left(\frac{1 \text{ J}}{1 \text{ N m}} \right) = 0.88 \text{ J/s}$$

1.1.2.2 Potential Energy

Potential energy is the energy due to the position of the system in a potential field (e.g., earth's gravitational field, $g=9.81 \text{ m/s}^2$). The gravitational potential energy (ΔPE) of an object of mass m at an elevation z in a gravitational field, relative to its gravitational potential energy at a reference elevation z_0 , is given by

$$\Delta PE = mg(z - z_0) \Rightarrow m(\text{kg})g(\text{m/s}^2)\Delta z(\text{m}) = \text{N} \cdot \text{m} = \text{J} \quad \dots\dots\dots (1.4)$$

To calculate the change in the rate of potential energy (ΔPE), often, the earth's surface is used as the reference, assigning $z_0=0$:

$$\Delta PE = \dot{m}g(z - z_0) \quad \dots\dots\dots (1.5)$$

The unit of the change in transport rate of potential energy is obtained as follows:

$$\Delta PE = \dot{m}(\text{kg/s})g(\text{m/s}^2)\Delta z(\text{m}) = \text{N} \cdot \text{m/s} = \text{J/s} = \text{W} \quad \dots\dots\dots (1.6)$$

Example 1.2 Potential Energy Calculation

Water is pumped at a rate of 10.0 kg/s from a point 200.0 m below the earth's surface to a point 100.0 m above the ground level. Calculate the rate of change in potential energy.

Solution

Known quantities: Water mass flow rate (10.0 kg/s), initial location of water below the earth's surface (−200.0 m), and final location of water above the earth's surface (100 m).

Find: The rate of change in potential energy.

Analysis: Use the definition of potential energy.

Taking the surface of the earth as a reference, the distance below the earth's surface is negative ($z_1 = -200.0$) and above the surface is positive ($z_2 = 100$):

$$\Delta PE = \dot{m}g(z_2 - z_1)$$

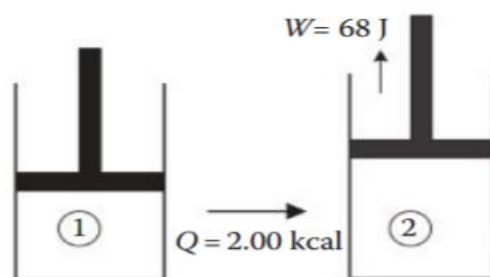
Substituting the values of the mass flow rate, gravitational acceleration, and change in inlet and exit pipe elevation from the surface of the earth,

$$\Delta PE = \left(10.0 \frac{\text{kg}}{\text{s}}\right) \times \left(9.81 \frac{\text{m}}{\text{s}^2}\right) \times (100.0 - (-200.0)) \text{ m} \left| \frac{\text{J}}{\text{kg} \cdot \text{m}^2 / \text{s}^2} \right. = 29,430 \text{ J/s}$$

The rate of change in potential energy $\Delta PE = 29.43 \text{ kW}$

Example 1.3 Internal Energy Calculation

A cylinder fitted with a movable piston is filled with gas. An amount of 2.00 kcal of heat is transferred to the gas to raise the gas temperature 100°C higher. The gas does 68 J of work in moving the piston to its new equilibrium position. Calculate the change in internal energy of the system (Example Figure 1.3.1).



EXAMPLE FIGURE 1.3.1 Heat added to a cylinder fitted with a piston.

Solution

Known quantities: The difference in gas temperature (100°C), work done by the system (+68 J), and heat added to the system (+2.00 kcal).

Find: Change in internal energy.

Analysis: Use the energy balance equation for a closed system.

System: Gas in the system, closed system

$$\Delta U + \Delta KE + \Delta PE = Q - W$$

Assumption: No change in kinetic and potential energy; accordingly, both are set to zero. The equation is reduced to

$$\Delta U = Q - W$$

Substitute the values of Q and W to calculate the change in internal energy (make sure units are consistent). The heat is added to the system (positive value) and the work is done by the system (positive value as well):

$$\Delta U = (2.0 \text{ kcal}) \left[\frac{1000 \text{ cal}}{\text{kcal}} \frac{1 \text{ J}}{0.239 \text{ cal}} \right] - 68 \text{ J} = 8300 \text{ J}$$

The change in internal energy $\Delta U = 8.30 \text{ kJ}$. The specific enthalpy ($h = H/m$) can be calculated using the following equation:

$$H = u + Pv \quad \dots\dots\dots (1.7)$$

Substituting the values of specific internal energy ($u = U/m$), pressure (P), and specific volume (v) in the earlier equations gives the specific enthalpy h.

Example 1.4 Enthalpy from Internal Energy

The specific internal energy of helium at 25°C and 1 atm is 3.80 kJ/mol, and the specific molar volume under the same conditions is 25 L/mol. Calculate the specific enthalpy of helium at this temperature and pressure, and the rate at which enthalpy is transported by a stream with a molar flow rate of 250 kmol/h.

Solution

Known quantities: Internal energy, pressure, temperature, molar volume, molar flow.

Find: Specific molar enthalpy (h), rate of enthalpy transport (H).

Analysis: Follow the specific enthalpy definition. The specific enthalpy of helium is given by

$$h = u + Pv$$

Substituting the values of specific internal energy, pressure (P), and specific volume (v) in the earlier equations,

$$\begin{aligned} h &= \left(3800 \frac{\text{J}}{\text{mol}} \right) + (1 \text{ atm}) \left(25 \frac{\text{L}}{\text{mol}} \right) \left[\frac{1 \text{ m}^3}{1000 \text{ L}} \frac{1.01325 \times 10^5 \frac{\text{N}}{\text{m}^2}}{1 \text{ atm}} \frac{\text{J}}{\text{N} \cdot \text{m}} \right] \\ &= 6333 \text{ J/mol} \end{aligned}$$

The enthalpy transport rate (H) is calculated by multiplying the molar flow rate (n) with the specific molar enthalpy (h):

$$H = n \times h$$

Substitute the values of molar flow rate (n) and specific enthalpy (h) to find the enthalpy transport rate (H):

$$\dot{H} = \left(250 \frac{\text{kmol}}{\text{h}} \right) \times \left(6333 \frac{\text{J}}{\text{mol}} \right) \left[\frac{1000 \text{ mol}}{\text{kmol}} \frac{\text{kJ}}{1000 \text{ J}} \right] = 1.58 \times 10^6 \text{ kJ/h}$$

1.1.3 Energy Balance for an Open System

In open systems, material crosses the system boundary as the process occurs (e.g., continuous process at steady state). In an open system, work must be

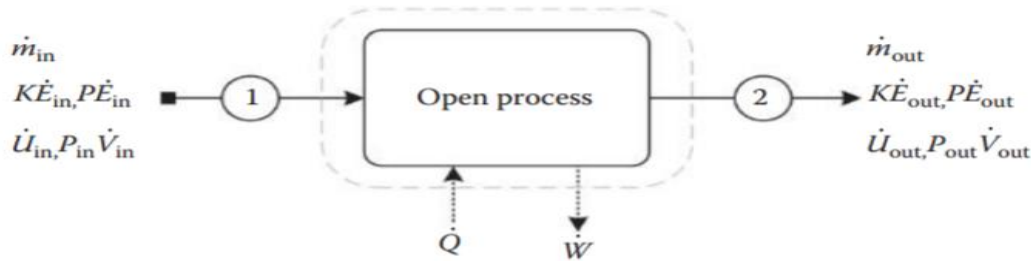


FIGURE 1.2 Energy balance for an open system.

done on the system to push input fluid streams at a pressure P_{in} into the system, and work is done on the surroundings to push output fluid streams at a pressure P_{out} out of the system, as shown in the schematic diagram in Figure 8.2 [3].

Net rate of work done by the system is

$$\dot{W}_f = \dot{W}_{out} - \dot{W}_{in} = P_{out} \dot{V}_{out} - P_{in} \dot{V}_{in} \quad \dots\dots\dots (1.8)$$

For several input and output streams,

$$\dot{W}_f = \sum_{output} P_j \dot{V}_j - \sum_{input} P_j \dot{V}_j \quad \dots\dots\dots (1.9)$$

The total rate of work (\dot{W}) done by a system on its surroundings is divided into two parts:

$$\dot{W} = \dot{W}_s + \dot{W}_f \quad \dots\dots\dots (1.10)$$

where shaft work (\dot{W}_s) is the rate of work done by the fluid on a moving part within the system (e.g., piston, turbine, and rotor), and flow work (\dot{W}_f) is the rate of work done by the fluid at the system outlet minus the rate of work done on the fluid at the system inlet. The general balance

equation for an open continuous system (Figure 1.2) under steady state in the absence of generation/consumption term is

$$\text{Energy input} = \dot{U}_{\text{in}} + K\dot{E}_{,\text{in}} + P\dot{E}_{,\text{in}} + P_{\text{in}}\dot{V}_{\text{in}} \quad \dots\dots\dots (1.11)$$

$$\text{Energy output} = \dot{U}_{\text{out}} + K\dot{E}_{,\text{out}} + P\dot{E}_{,\text{out}} + P_{\text{out}}\dot{V}_{\text{out}} \quad \dots\dots\dots (1.12)$$

$$\text{Energy transferred} = \dot{Q} - \dot{W}_s \quad \dots\dots\dots (1.13)$$

Under steady state, the accumulation term is set to zero and the following equation is valid:

$$\text{Energy input} = \text{Energy output}$$

$$\dot{Q} - \dot{W}_s = \Delta\dot{U} + \Delta K\dot{E} + \Delta P\dot{E} + \Delta(P\dot{V}) \quad \dots\dots\dots (1.14)$$

Enthalpy (H) is the sum of the internal energy (U) of fluid volume added to the system plus the flow work (PV) performed on the system in order to push the fluid in/out of the system:

$$H = U + PV \quad \dots\dots\dots (1.15)$$

The change in enthalpy transport rate is given by

$$\Delta\dot{H} = \Delta\dot{U} + \Delta(P\dot{V}) \quad \dots\dots\dots (1.16)$$

Rearranging the earlier equations leads to the first law of thermodynamics for an open system under steady state:

$$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta K\dot{E} + \Delta P\dot{E} \quad \dots\dots\dots (1.17)$$

Steam turbine is an example of an open system. Electrical generating plants operate by generating steam at elevated temperatures and

pressures, then reducing the pressure in a turbine. As the pressure is reduced, the high pressure, high temperature steam expands (and cools down), driving the turbine. The shaft work produced by the turbine is transferred to a generator to produce electricity. One limitation on steam turbines is that they cannot tolerate small amounts of water in its liquid state in the gases passing through the turbine. If the liquid content of the steam is above the threshold limit (a few percentage points), the liquid droplets damage the turbine blades and lead to failure of the turbine. The steam tables in Appendix A.3 are used to determine the temperature, specific internal energy, and specific enthalpy of saturated steam and superheated steam.

**Example 1.5 Energy Balance for an Open System:
The Steam Turbine**

Steam flowing at a rate of 10 kg/h enters a steam turbine at a velocity of 50 m/s and leaves at a point 5 m below the inlet at a velocity of 300 m/s. The heat loss from the turbine is estimated to be 10 kW, and the turbine delivers shaft work at a rate of 70 kW. Calculate the change in enthalpy transport rate of the process.

Solution

Known quantities: Steam flow rate, inlet and exit velocity, heat loss, and work delivered.

Find: Change in enthalpy transport rate.

Analysis: Use the general energy balance equation for an open system.

System: Steam turbine as open system

The energy balance for an open system has been derived as

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

In this example, heat is lost (negative value) from the system:

$$Q = -10 \text{ kW} = -10 \text{ kJ/s}$$

The shaft work is delivered (positive value) by the system:

$$W_s = 70 \text{ kW} = 70 \text{ kJ/s}$$

The change in kinetic energy

$$\Delta KE = \frac{1}{2} \dot{m} (v_2^2 - v_1^2)$$

Substitute the values of mass flow rate (\dot{m}), inlet (v_1), and exit (v_2) velocities,

and use conversion factors (make sure units are consistent):

$$\begin{aligned} \Delta KE &= \frac{1}{2} \left(10 \frac{\text{kg}}{\text{h}} \frac{\text{h}}{3600 \text{ s}} \right) (300^2 - 50^2) \\ &\times \left(\frac{\text{m}}{\text{s}} \right)^2 \left| \frac{\text{N}}{\text{kg m/s}^2} \right| \left| \frac{\text{J}}{\text{N} \cdot \text{m}} \right| \left| \frac{\text{kJ}}{1000 \text{ J}} \right| = 0.12 \text{ kJ} \end{aligned}$$

Change in potential energy $\Delta PE = \dot{m} g (z_2 - z_1)$

Substitute the values of mass flow rate (\dot{m}), and inlet and exit heights from the surface of the earth (z_1, z_2):

$$\begin{aligned} \Delta PE &= 10 \frac{\text{kg}}{\text{h}} \frac{\text{h}}{3600 \text{ s}} \times 9.81 \frac{\text{m}}{\text{s}^2} \\ &\times (-5-0) \text{ m} \left| \frac{\text{N}}{\text{kg m/s}^2} \right| \left| \frac{\text{J}}{\text{N} \cdot \text{m}} \right| \left| \frac{\text{kJ}}{1000 \text{ J}} \right| = -0.00014 \text{ kJ} \end{aligned}$$

The change in potential energy is almost negligible compared to the magnitudes of heat and work. Substitute the values of Q , W_s , and changes in kinetic and potential energies in the energy balance equation for an open system:

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

$$\Delta\dot{H} + 0.12 \frac{\text{kJ}}{\text{s}} - 0.00014 \frac{\text{kJ}}{\text{s}} = -10 \frac{\text{kJ}}{\text{s}} - \left(70 \frac{\text{kJ}}{\text{s}} \right)$$

The change in enthalpy transport $\Delta\dot{H} = -80.12 \text{ kJ/s}$ rate is

Example 1.6 Use of a Steam Table

Use steam tables in the appendix to determine the temperature, specific Internal energy and specific enthalpy of saturated steam at 3.0 bar. What is the state of the steam at 10 bar and 400°C? (i.e., is it saturated or superheated steam?)

Solution

Known quantities: *Case 1:* 3 bar, saturated steam, *Case 2:* 10 bar, 400°C.

Find: Specific enthalpy (h) and specific internal energy (u), specific volume (v). The state of steam at 10 bar and 400°C.

Analysis: Two properties are needed to be able to use saturated steam table and superheated steam table in the appendix.

Case 1: At 3 bar, steam is saturated: use saturated steam table (Appendix A.3). The temperature is 133.5°C, specific enthalpy is 2724.7 kJ/kg, and specific internal energy is 2543 kJ/kg.

Case 2: At 10 bar and 400°C: At 10 bar the saturated temperature is 179.9°C, and since the steam is at 400°C, this temperature is higher than the saturated temperature at 10 bar. Therefore, the state of water is superheated steam, and hence, the superheated steam table (Table A.5) is

used. Specific enthalpy is 3264 kJ/kg, specific internal energy is 2958 kJ/kg, and specific volume is 0.307 m³/kg.

1.1.4 Steam Turbine

Steam turbines are open systems used to generate electricity; in most cases, the turbine operates adiabatically. The exit pressure of turbine is lower than the inlet pressure. Turbines produce work; by contrast, work should be provided to a compressor or a pump. The following examples explain the possible operations for a steam turbine.

Example 1.7 Steam Table and Turbine Work

Steam at a rate of 1500 kg/s enters a turbine at 40 bar and 400°C. It comes out of the turbine as wet steam at 4 bar. The turbine operates adiabatically and produces 1000 MW of work. What is the temperature of the steam leaving the turbine? What is the mass fraction of vapor in the stream leaving the turbine?

Solution

Known quantities: Steam mass flow rate (1500 kg/s), inlet conditions (40 bar and 400°C), exit steam conditions (4 bar, wet steam).

Find: Mass fraction of vapor in the stream leaving the turbine.

Assumptions: No change in kinetic and potential energy.

Analysis: Use steam tables to find inlet and exit enthalpy and the first law for an open system. Inlet and exit steam enthalpies: Saturated steam (Table A.4), superheated steam (Table A.5).

Inlet steam conditions: at 40 bar and 400°C: the enthalpy of the incoming steam is 3216 kJ/kg (Table A.5). Exit steam conditions: at 4 bar: steam is either wet or saturated (Table A.4). Since the steam leaving the turbine is a vapor–liquid mixture, it must be saturated. From Table A.4, for saturated steam at 4 bar the enthalpies of the liquid and vapor are 604.7 and 2737.6 kJ/kg,

$$\Delta \dot{H} = -\dot{W}_s$$

respectively, and the temperature is 143.6°C. The general energy balance applied to this process, after neglecting the potential and kinetic energy terms and bearing in mind that the turbine is adiabatic, can be expressed as

Rearranging the earlier equation,

$$-\dot{W}_s = \Delta \dot{H} = \dot{H}_{\text{out}} - \dot{H}_{\text{in}} = \dot{m}(h_{\text{out}} - h_{\text{in}})$$

Substituting known values of shaft work, mass flow rate, and inlet specific enthalpy, since the turbine is producing work, the sign of W_s is +:

$$-W_s = -1000 \text{ MW} = -1 \times 10^6 \frac{\text{kJ}}{\text{s}} = 1500 \frac{\text{kg}}{\text{s}}(h_{\text{out}} - 3216) \frac{\text{kJ}}{\text{kg}}$$

The specific enthalpy of the exit steam is $h_{\text{out}} = 2549.3 \text{ kJ/kg}$

Let x be the mass fraction of the steam that is in the vapor phase, then

$$h_{\text{out}} = 2549.3 \frac{\text{kJ}}{\text{kg}} = h_f + xh_{fg} = 604.7 \frac{\text{kJ}}{\text{kg}} + x(2133.0 \text{ kJ/kg})$$

The steam quality is $x = 0.912 \rightarrow$ The wet steam is 91.2 wt% vapor. The wet contains 91.2% water vapor and 8.80 wt% liquid water.

Example 1.8 Steam Turbine

Steam enters a turbine at a pressure of 10.0 bar (absolute) and a temperature of 600°C. The steam leaving the turbine is at 1 atm (absolute) pressure and is of 90% quality (90 wt% steam, 10 wt% liquid). How much steam has to go into the turbine to yield $1.5 \times 10^6 \text{ kW}$ of shaft work?

Solution

Known quantities: Steam inlet conditions (10 bar, 600°C), exit steam conditions (1 atm, 90% quality), shaft work is 1.5×10^6 kW.

Find: Amount of steam that has to go into the turbine.

Assumptions: No change in kinetic and potential energy, turbine is adiabatic.

Analysis: Use steam tables to find inlet and exit enthalpy and the first

law for an open system. From the first law,
$$\Delta H + \Delta KE + \Delta PE = Q - W_s$$

After applying the earlier assumptions, the equation is reduced to

$$\Delta \dot{H} = \dot{m}(h_{\text{out}} - h_{\text{in}}) = -W_s$$

To find the enthalpy of the steam leaving the turbine, use Table A.4. At 1 atm the enthalpies of saturated water and steam are 419.1 and 2676.0 kJ/kg, respectively.

Thus, the enthalpy of the steam leaving the turbine is

$$h_{\text{out}} = h_f + xh_{fg} = 419.1 + 0.9(2676.0 - 419.1) = 2450.3 \text{ kJ/kg}$$

The enthalpy of the input steam can be found from Table A.5 to be 3697 kJ/kg.

Substitute the values of inlet and outlet specific enthalpy and shaft work in the first law:

The required steam mass flow rate is $\dot{m} = 1.20 \times 10^3$ kg/s

1.1.5 Heaters and Coolers

Heaters and coolers such as shell and tube heat exchangers are open systems employed to cool down or heat up certain fluid streams. In most cases, the external surface of heaters and coolers is insulated and heat is just transferred between the cold and hot streams across the walls of the exchanger tubes. The following example illustrates the use of heat exchangers for cooling and heating purposes.

Example 1.9 Heat Exchanger

Steam at a rate of 60 kg/h, at 200°C, and 1 bar enters the tube side of a shell and tube heat exchanger. The steam is used to heat cold water flowing on the shell side; the steam leaves as saturated liquid. Neglect pressure drop of the steam on the tube side and the water on the shell side of the heat exchanger. How much heat must be transferred from the steam to the water side?

Solution

Known quantities: Mass flow rate (60 kg/h), inlet temperature and pressure (200°C, 1 bar), exit conditions (saturated water, 1 bar).

Find: Heat transfer rate from steam to water.

Assumptions: Pressure drop across the boiler is neglected, so exit pressure is at 1 bar.

Analysis: Use steam tables to find inlet and exit enthalpy.

Basis: 60 kg/h of feed steam. The schematic diagram of the problem is shown in Example Figure 8.9.1. From the superheated steam table (Table A.5),

Inlet: (1 bar, 200°C): $h_1 = 2875$ kJ/kg Using saturated steam table (Table A.4), **Outlet:** (1 bar, saturated water): $h_2 = h_f$ at 1 bar = 417.5 kJ/kg

No change in steam mass flow rate: $m = m_{in} = m_{out} = 60 \text{ kg/h}$

The general energy balance equation for an open system is

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

The following simplifying assumptions for the condenser are used:

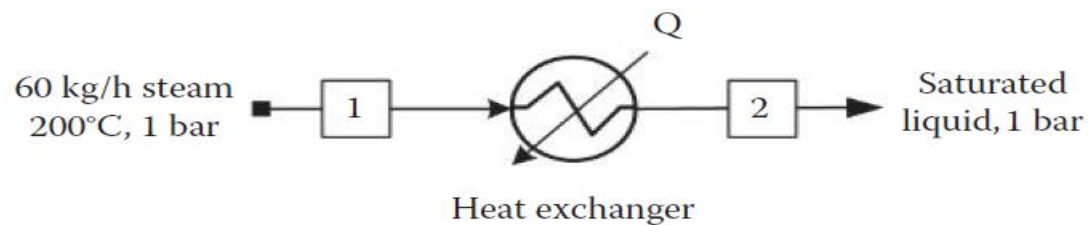
No shaft work: $\dot{W}_s = 0$.

No change in elevation. The inlet and outlet lines are at the same level:

$\Delta\dot{PE} = 0$.

Since we do not know anything about the diameters of the inlet and exit pipes, same pipe diameters are used for inlet and exit streams;

accordingly, there is no change in velocity, and change in kinetic energy is negligible: $\Delta\dot{KE} = 0$.



EXAMPLE FIGURE 1.9.1 Schematic of a heat exchanger system.

The simplified form of the energy balance is therefore

$$\dot{Q} = \Delta\dot{H} = \dot{H}_{out} - \dot{H}_{in}$$

The rate of enthalpy transport (\dot{H}) as a function of specific enthalpy (h),

$$\Delta\dot{H} = \dot{m}\Delta h$$

Replacing enthalpy change rate ($\Delta\dot{H}$) with specific enthalpy (Δh) at constant mass flow rate,

$$\dot{Q} = \dot{m}\Delta h = \dot{m}(h_{out} - h_{in})$$

Substituting the values of mass flow rate and exit and inlet specific enthalpy in the earlier equation,

$$\dot{Q} = \left(60 \frac{\text{kg}}{\text{h}} \right) (417.5 - 2875) \frac{\text{kJ}}{\text{kg}} = -147,450 \text{ kJ/h}$$

The value of heat transfer is negative; that is, heat is transferred from the system (steam) to the surrounding (cold water).

1.1.6 Compressors

Compressors are open systems utilized to raise the pressure of gas steams. The exit pressure is higher than the inlet pressure. Work is required for the compressor to operate. The following example illustrates the use of a compressor to pressurize a vapor steam.

Example 1.10 Compressor

The feed to a compressor is superheated steam at 300°C and 20 bar absolute pressure. It enters the compressor at a velocity of 20 m/s. The pipe inlet inside diameter is 0.10 m. The discharging pipe, after the compressor, has a smaller inside diameter and the discharge velocity is 170 m/s. The exit of the compressor is superheated steam at 350°C and 60 bar absolute. Heat loss from the compressor to the surroundings is 5 kW. Determine the compressor horsepower.

Solution

Known quantities: Inlet and exit steam temperature and pressure, inlet and exit velocities, heat loss from the compressor, inlet pipe diameter.

Find: Compressor horsepower.

Assumption: The system is located on a horizontal plane and no change in elevation between inlet and exit of the compressor; hence change in potential energy is negligible.

Analysis: The compressor is an open system. The steady-state energy balance can be used to describe the compressor system:

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

The general energy balance reduces to

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

Determination of the specific enthalpy and specific volume from the superheated steam table (Appendix A.3):

Inlet stream at $P_1 = 20$ bar, $T_1 = 300^\circ\text{C}$, $h_1 = 3025$ kJ/kg, $v_1 = 0.125\text{m}^3/\text{kg}$

Exit stream at $P_2 = 60$ bar, $T_2 = 350^\circ\text{C}$, $h_2 = 3046$ kJ/kg, $v_2 = 0.0422\text{m}^3/\text{kg}$

Mass flow rate of the inlet steam is equal to density multiplied by volumetric flow rate; the steam density is the inverse of steam specific

$$\dot{m} = \rho \times \dot{V} = \rho \times (v \times A) = \rho \times \left(v \times \frac{\pi D^2}{4} \right) = \frac{1}{v} \times \left(v \times \frac{\pi D^2}{4} \right)$$

volume:

Substitute the values of density, velocity, and diameter:

$$\dot{m} = \frac{1}{0.125 \text{ m}^3/\text{kg}} \times \left(\frac{20 \text{ m}}{\text{s}} \times \frac{\pi (0.1 \text{ m})^2}{4} \right) = 1.25 \text{ kg/s}$$

The change in enthalpy transport rate H is given by

$$\Delta \dot{H} = \dot{m}(h_2 - h_1) = 1.25 \frac{\text{kg}}{\text{s}} (3046 - 3025) \frac{\text{kJ}}{\text{kg}} = 26.5 \frac{\text{kJ}}{\text{s}} = 26.25 \text{ kW}$$

The change in kinetic energy $\Delta KE = \frac{1}{2} \dot{m} (v_2^2 - v_1^2)$ is

Substitute the values of mass and inlet and exit velocity:

$$\Delta KE = \frac{1}{2} \times 1.25 \frac{\text{kg}}{\text{s}} \left\{ \left(\frac{170 \text{ m}}{\text{s}} \right)^2 - \left(\frac{20 \text{ m}}{\text{s}} \right)^2 \right\} \\ \times \frac{\text{N}}{\text{kg m/s}^2} \left| \frac{\text{J}}{\text{N} \cdot \text{m}} \right| \frac{\text{kJ}}{1000 \text{ J}} = 18 \text{ kJ/s}$$

$$\Delta KE = 18 \text{ kW}$$

The change in the kinetic energy is

The heat loss from the system to the surroundings is 5 kW. Since heat is transferred from the system to the surroundings, $Q = -5$ kW.

The general energy balance equation $\Delta H + \Delta E_k = Q - W_s$ reduces to

Substituting the values of change in enthalpy, kinetic energy, and heat loss,

$$26.25 \text{ kW} + 18 \text{ kW} = -5 \text{ kW} - W_s$$

Rearranging and solving for the shaft work,

$$W_s = -49.25 \text{ kW}$$

$$\text{Power} = 49.25 \text{ kW} \left(\frac{1.341 \text{ hp}}{1 \text{ kW}} \right) = 66.04 \text{ hp}$$

The sign of the shaft work is negative since work is done on the system by compressor blades. To convert the shaft work to horsepower, use the proper conversion factor.

1.2 Mechanical Energy Balance

The mechanical energy balance is most useful for processes in which changes in the potential and kinetic energies are of primary interest, rather than changes in internal energy or heat associated with the process. Thus, the mechanical energy balance is mainly used for purely mechanical flow problems—that is, problems in which heat transfer, chemical reactions, or phase changes are not present. First, we assume the steady-state condition so that all terms on the left hand side become zero. Second, we assume that the system has only a single inlet and a single outlet. Moreover, steady state implies that the inlet mass flow rate must

equal the outlet mass flow rate, in order to avoid accumulation of material in the system. Let us start with the general energy balance equation:

Energy transferred = Energy out – Energy in

$$\dot{Q} - \dot{W}_s = \left(\dot{U}_{\text{out}} + K\dot{E}_{\text{out}} + P\dot{E}_{\text{out}} + P_{\text{out}}\dot{V}_{\text{out}} \right) - \left(\dot{U}_{\text{in}} + K\dot{E}_{\text{in}} + P\dot{E}_{\text{in}} + P_{\text{in}}\dot{V}_{\text{in}} \right) \quad \text{..(1.17)}$$

Rearrange the earlier equation by taking the mass flow rate (m) as a common factor. In this case, the internal energy and volumetric flow rate will become specific internal energy and specific volumetric flow rate, respectively:

$$\dot{Q} - W_s = \dot{m} \left(u_{\text{out}} + \frac{v_{\text{out}}^2}{2} + gz_{\text{out}} + P_{\text{out}}v_{\text{out}} - u_{\text{in}} - \frac{v_{\text{in}}^2}{2} - gz_{\text{in}} - P_{\text{in}}v_{\text{in}} \right) \quad \dots (1.18)$$

In this equation, subscript “in” refers to the inlet section, and subscript “out” to the outlet port. Now, we divide the entire equation by m , and express the specific volume (volume/mass) as $v = 1/\rho$, where ρ is the density (mass/volume) of the flowing material. Assuming incompressible flow rate, so that the density is constant, $v_{\text{in}} = v_{\text{out}} = 1/\rho$. Also, we define $\Delta u = u_{\text{out}} - u_{\text{in}}$ and $\Delta P = P_{\text{out}} - P_{\text{in}}$. With these changes, the general energy balance equation becomes

$$\frac{-W_s}{\dot{m}} = \frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + \Delta u - \frac{\dot{Q}}{\dot{m}} \quad \dots\dots\dots (1.19)$$

The term $(-u - Q /m)$ in the absence of chemical reactions, phase changes, or other sources of large amounts of heat transfer will generally represent heat generated due to the viscous friction in the fluid. In such situations, this term is called the friction loss and we will write it as F . With this last

change, the general energy balance represents the usual form of the mechanical energy balance

$$\frac{-\dot{W}_s}{\dot{m}} = \frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + F \quad \dots\dots\dots (1.20)$$

where W /m is the shaft work performed by the system on the surroundings, per unit mass of material passing through the system. The following example illustrates the use of the mechanical energy balance equation.

Example 1.11 Mechanical Energy Balance Equation

A water supply tank is capable of delivering 0.3 m³/s of water for firefighting purposes in a chemical plant. The water supply is to come from a lake, the elevation of the surface of the lake is 800 m and the elevation of the factory is 852 m from sea level. The water discharge pipe is located at a depth of 100 m from the surface of the lake. The frictional losses in the water line to the plant are given by the relation (0.01 m/s²) L , where L is the length of the pipe line. The water line to the supply tank has an inner diameter of 0.15 m and a length of 8000 m. How much energy must a pump deliver to the water?

Solution

Known quantities: Discharge line volumetric flow rate, initial and final elevation, friction losses, length and diameter of the pipe.

Find: Pump horsepower.

Assumption: Pressure drop is neglected because the pressure at both ends of line is atmospheric.

Analysis: Use the mechanical energy balance equation:

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + F = \frac{-\dot{W}_s}{\dot{m}}$$

The pressure at both ends of the line is atmospheric, so $\Delta P = 0$. The velocity at the inlet of the lake is zero but the velocity out of the discharge end of the pipe is

$$v_2 = \dot{V} \times \frac{1}{\frac{\pi D^2}{4}} = \left(0.3 \frac{\text{m}^3}{\text{s}} \right) \times \frac{1}{\frac{\pi (0.15 \text{ m})^2}{4}} = 17 \text{ m/s}$$

The mass flow rate .The $\dot{m} = \dot{V} \times \rho = \frac{0.3 \text{ m}^3}{\text{s}} \times \frac{1000 \text{ kg}}{\text{m}^3} = 300 \text{ kg/s}$

$$\frac{0}{\rho} + \frac{\left(17 \frac{\text{m}}{\text{s}} \right)^2}{2} + 9.81 \frac{\text{m}}{\text{s}^2} (152 \text{ m}) + 0.01 \frac{\text{m}}{\text{s}^2} (8000 \text{ m}) = \frac{-\dot{W}_s}{300 \text{ kg/s}}$$

elevation change is from 800 m (800–100 to the lake) to 852 to the factory, or the difference is equivalent to 152 m. So the mechanical energy balance becomes

Solving for shaft $-\dot{W}_s = 514,686 \text{ W} \times \frac{\text{hp}}{746} = 690 \text{ hp}$ work,

The minus sign indicates that the energy is going into the system.

Example 1.12 Fire Extinguishment Process

A large tank filled with water and open to atmosphere is used for fire extinguishment in an ethylene production plant. The water is taken from the tank, passed through a pump, and then delivered to hoses. It is desired to deliver 1890 L of water per minute at a pressure of 15 bar (gauge). If there is a negligible elevation change between the water level in the tank

and the discharge of the pump, no changes in the diameter of the pipes and hoses, and if the pump has an efficiency of 70.0%, how much work must be supplied to the pump in order to meet the pressure and discharge rate specifications?

Solution

Known quantities: Discharge line volumetric flow rate, initial and final elevation, friction losses, length and diameter of the pipe.

Find: Pump horsepower.

Assumption: Pressure drop is neglected because the pressure at both ends of the line is atmospheric.

Analysis: Use the mechanical energy balance to solve this problem:

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + F = \frac{-\dot{W}_s}{\dot{m}}$$

Because there is no change in elevation or velocity (no change in pipe/hose diameter) and no frictional losses are given, the earlier equation reduces to

$$\frac{\Delta P}{\rho} = \frac{-\dot{W}_s}{\dot{m}}$$

The water mass flow rate is

$$\dot{m} = \dot{V} \times \rho = 1890 \frac{\text{L}}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ kg}}{\text{L}} = 31.5 \text{ kg/s}$$

The discharge pressure is given as 15 bar (gauge). This means that the absolute pressure is this pressure plus the ambient pressure. Substitute the known values to get

$$\frac{\left[(15 \text{ bar} + P_{\text{ambient}}) - P_{\text{ambient}} \right] \frac{10^5 \text{ Pa}}{\text{bar}} \left| \frac{1 \text{ N/m}^2}{\text{Pa}} \right|}{1000 \frac{\text{kg}}{\text{m}^3}} = \frac{-\dot{W}_s}{31.5 \frac{\text{kg}}{\text{s}}}$$

Simplifying,

$$-\dot{W}_s = 47,250 \frac{\text{N} \cdot \text{m}}{\text{s}} \left| \frac{\text{J}}{\text{N} \cdot \text{m}} \right| \frac{\text{kJ}}{1000 \text{ J}} = 47.25 \frac{\text{kJ}}{\text{s}} = 47.25 \text{ kW}$$

The pump has an efficiency of 70.0%; accordingly, the actual work ($W_{s,a}$) that must be supplied to the pump in order to meet the pressure and discharge rate specifications is

$$-\dot{W}_{s,a} = \frac{62.7 \text{ hp}}{0.7} = 89.5 \text{ hp}$$

The sign of the work is negative, which means that the work is done on the system. The actual work that must be supplied to the pump in order to meet the pressure and discharge rate specifications is higher than the theoretical work.

1.3 Bernoulli's Equation

In many instances, the amount of energy lost to viscous dissipation in the fluid is small compared to magnitudes of the other terms in the general energy balance equation. In such a case, $F = 0$. Moreover, many common flows such as fluid flow through a pipe do not have any appreciable shaft work associated with them; accordingly, $W = 0$. For such frictionless flows with no shaft work, the mechanical energy balance simplifies to

Bernoulli's equation:

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z = 0 \quad \dots\dots\dots (1.21)$$

Bernoulli's equation has a wide range of applications, despite its simplified assumptions. The following example illustrates the use of Bernoulli's equation.

Example 1.13 Bernoulli's Equation

The pressure difference between the underside of the wing and the top of the wing that is necessary to lift the weight of an aircraft is 0.08 atm. At an elevation of approximately 10,000 m, the aircraft velocity is 275 m/s and the density of air is 0.45 kg/m^3 . Assume that the velocity of the air on the underside of the wing is the plane velocity of 275 m/s. What is the velocity of the air on the topside of the wing, which is necessary to generate the pressure difference needed to lift the plane?

Solution

Known values: Pressure drop around the wing, velocity of air on the underside of the wing

Find: Velocity of air on the topside of the wing

Analysis: Use Bernoulli's equation around the wing (1: topside of the wing, 2: underside of the wing). Use Bernoulli's Equation to relate the pressure difference to a velocity difference so that

$$\frac{P_2 - P_1}{\rho} + \frac{v_2^2 - v_1^2}{2} + g(z_2 - z_1) = 0$$

Neglect the effect of wing thickness on change in potential energy. The equation is reduced to

$$\frac{P_2 - P_1}{\rho} + \frac{v_2^2 - v_1^2}{2} + 0 = 0$$

Substituting the values of pressure drop, air density, and velocity under the wing,

$$\frac{0.08 \text{ atm} \left| \frac{101,325 \text{ Pa}}{1 \text{ atm}} \right|}{0.45 \text{ kg/m}^3} + \frac{275^2 - v_1^2}{2} = 0$$

Solving for velocity on the topside of the wing,

$$v_1 = 334 \frac{\text{m}}{\text{s}}$$

The velocity on the topside of the wing is higher than that on the underside of the wing.

1.4 Enthalpy Calculations

Change in enthalpy can occur because of change in temperature, change in phase, or mixing of solutions and reactions.

1.4.1 Enthalpy Change as a Result of Temperature

Sensible heat is the heat transferred to raise or lower the temperature of a material in the absence of phase change. In the energy balance calculations, sensible heat change is determined by using a property of matter called the heat capacity at constant pressure, or just heat capacity (CP). Units for CP are (J/mol/K) or (cal/g/°C). Appendix A.2 lists CP values for several organic and inorganic compounds. There are several methods for calculating enthalpy change using CP values. When CP is constant, the change in the enthalpy of a substance due to change in temperature at constant pressure is given by

$$\Delta H = mC_P(T - T_{\text{ref}}) \quad \dots\dots\dots (1.22)$$

Heat capacities for most substances vary with temperature where the values of C_P vary for the range of the change in temperature. Heat capacities are tabulated as polynomial functions of temperature such as

$$C_P = a + bT + cT^2 + dT^3 \dots\dots\dots (1.23)$$

Coefficients a , b , c , and d for a number of substances are given in Appendix A.2 In this case, the enthalpy change is

$$\Delta \dot{H} = \dot{m} \int_{T_{\text{ref}}}^T C_P dT = \dot{m} \int_{T_{\text{ref}}}^T (a + bT + cT^2 + dT^3) dT \dots\dots (1.24)$$

Sometimes, you need an estimate of specific enthalpy, specific internal energy, or specific volume at a temperature and a pressure that is between tabulated values. In this case, one can use a linear interpolation. The following example demonstrates the determination of internal energy from heat capacity.

Example 1.14 Internal Energy and Heat Capacity

A closed rigid vessel that contains 200 kg of a fluid is heated from 20°C to 150°C. Calculate the heat required for this purpose. The constant volume heat capacity of the fluid is given by the following relation:

$$C_v \left(\frac{\text{kJ}}{\text{kg} \cdot ^\circ\text{C}} \right) = a + bT = 0.855 + 9.42 \times 10^{-4} T$$

Solution

Known quantities: Mass of fluid, initial (20°C) and final temperature (150°C), heat capacity at constant volume as a function of temperature.

Find: Heat required to heat the content of the closed vessel.

Analysis: Use the general energy balance for a closed system, no change in kinetic and potential energies as the system is a rigid vessel:

$$Q - W = \Delta U$$

$W = 0.0$ (rigid vessel; no moving part), the change in internal energy is

$$Q = \Delta U$$

The change in internal energy is a function of heat capacity at constant volume; since the heat capacity is a function of temperature and mass, we

$$\Delta U = m \int_{T_1}^{T_2} C_v dT$$

multiply mass by heat capacity as follows:

Substitute the heat capacity at constant volume:

$$\Delta U = m \int_{T_1}^{T_2} (0.855 + 9.42 \times 10^{-4} T) dT$$

Integrating the earlier equation as a function of initial and final temperature, we obtain

$$\Delta U = m \left[0.855(T_2 - T_1) + 9.42 \times 10^{-4} \left(\frac{T_2^2 - T_1^2}{2} \right) \right]$$

Substituting the values of initial (20°C) and final temperature (150°C),

$$Q = \Delta U = 200 \text{ kg} \left[0.855(150 - 20) + 9.42 \times 10^{-4} \frac{(150^2 - 20^2)}{2} \right] \\ \times \left[\frac{\text{kJ}}{\text{kg} \cdot ^\circ\text{C}} \right] = 24,312 \text{ kJ}$$

Example 1.15 Use of Data from Tables and Reference State

The data shown in Table E1.15 are for a saturated fluid. Calculate Δh and Δu for the transition of saturated vapor from 10°C to -20°C.

Solution

Known quantities: Enthalpy, pressure, and temperature.

Find: Change of specific enthalpy and specific internal energy.

Analysis: The reference is liquid at -40°C, because the enthalpy at this temperature is zero. Change in specific enthalpy (Δh) and change in specific internal energy (Δu) for the transition of saturated CH₃Cl vapor from 10°C to -20°C can be calculated as

$$\Delta h = h_{-20^\circ\text{C}} - h_{10^\circ\text{C}} = 456 - 470 = -14 \text{ kJ/kg}$$

The change in specific internal energy starts using $h = u + Pv$ and $\Delta h = \Delta u + \Delta(Pv)$.

Rearranging for Δu ,

$$\Delta u = \Delta h - \Delta(Pv) = \Delta h - \left\{ (Pv)_{-20} - (Pv)_{10} \right\}$$

TABLE E1.15

Properties of Saturated Methyl Chloride

State	T (°C)	P (atm)	v (m ³ /kg)	h (kJ/kg)
Liquid	-40	0.47	0.001	0.00
Vapor	-20	1.30	0.310	456
Vapor	10	3.54	0.120	470

To calculate the change in internal energy,

$$\Delta u = -14 \frac{\text{kJ}}{\text{kg}} - \{1.30 \times 0.312 - 3.54 \times 0.12\} \left(\text{atm} \times \frac{\text{m}^3}{\text{kg}} \right) \\ \times \left(\frac{101.325 \text{ kN/m}^2}{1 \text{ atm}} \right) \left(\frac{\text{kJ}}{\text{kN} \cdot \text{m}} \right)$$

The rounded result of change in internal energy is $\Delta u = -12 \text{ kJ/kg}$

1.4.2 Constant Heat Capacity

Keeping P constant and letting T change, we can get the expression for the constant P part as $\Delta h = \int CP \, dT \approx CP\Delta T$ (at constant P). It is not necessary to know the reference state to calculate ΔH for the transition from one state to another. Δh from state 1 to state 2 equals $h_2 - h_1$ regardless of the reference state upon which h_1 and h_2 were based. If different tables are used, one must make sure they have the same reference state. h and u are state properties; their values depend only on the state of the species, temperature, and pressure and not on how the species reached its state. When a species passes from one state to another, both Δu and Δh for the process are independent of the path taken from the first state to the second one.

Example 1.16 Constant Heat Capacity

What is the change in the enthalpy of 100 g/s acid heated in a double pipe heat exchanger from 20°C to 80°C, if the average heat capacity at constant pressure is 0.50 cal/g°C?

Solution

Known quantities: Mass of acid, constant heat capacity, initial and final temperatures.

Find: Change in enthalpy.

Analysis: Use change in enthalpy with constant heat capacity. The change in enthalpy as a function of specific heat is given by

$$\Delta \dot{H} = \int_{T_1}^{T_2} \dot{m} C_P dT$$

Since the heat capacity (C_P) is constant, the earlier equation is simplified to

$$\Delta \dot{H} = \dot{m} C_P (T_2 - T_1)$$

Substitute the values of mass flow rate, heat capacity at constant pressure, and difference in temperature (the reference temperature is 20°C):

$$\Delta \dot{H} = \left(100 \frac{\text{g}}{\text{s}} \right) \left(0.5 \frac{\text{cal}}{\text{g}^\circ\text{C}} \right) (80 - 20)^\circ\text{C} = 3000 \text{ cal/s}$$

The change in enthalpy transport rate is $\dot{H} = 3.0 \text{ kcal/s}$

Example 1.17 Heat Added to a Boiler

Liquid water is fed to a boiler at 23°C under a pressure of 10 bar, and is converted at constant pressure to saturated steam. Calculate Δh for this process and the heat input required for producing 15,000 m³/h of steam at the exit conditions. Assume that the inlet velocity of liquid entering the boiler is negligible and that the steam is discharged through a 0.15 m ID (inner diameter) pipe (Example Figure 1.17.1). Inlet and exit pipes are at the same level.

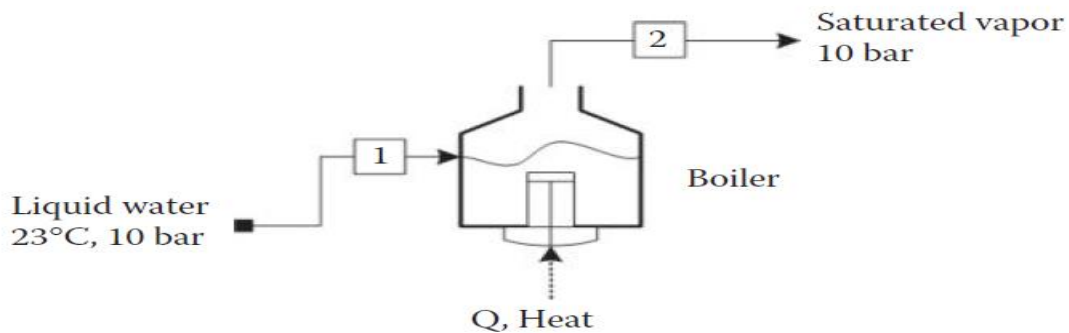
Solution

Known quantities: Water inlet conditions (23°C under a pressure of 10 bar), exit steam conditions (10 bar, saturated steam), exit steam volumetric flow rate (15,000 m³/h), exit pipe diameter (0.15 m).

Find: Change in specific enthalpy (Δh).

Analysis: The reboiler is an open system, and the general energy balance equation is

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



EXAMPLE FIGURE 1.17.1 Production of saturated steam.

Since the reboiler does not deliver shaft work, no change is seen in elevation between inlet and exit steams (change in potential energy is zero); the energy balance equation reduces to $Q_s = \dot{m}\Delta h + \Delta KE$

The change in specific enthalpy: Since no value of specific enthalpy is available at 23°C and 10 bar, the value is taken at 23°C (saturated water):

$$h_1|_{\text{at } 23^\circ\text{C}, 10 \text{ bar}} = 96.2 \text{ kJ/kg}$$

The specific enthalpy value for the exit conditions at 10 bar, saturated steam is

$$h_2|_{\text{at } 10 \text{ bar, sat'd steam}} = 2776.2 \text{ kJ/kg} \quad \text{The change in specific enthalpy}$$

is $\Delta h = h_2 - h_1$ Substitute the values of inlet and exit specific enthalpy:

$$\Delta h = 2776.2 \frac{\text{kJ}}{\text{kg}} - 96.2 \frac{\text{kJ}}{\text{kg}} = 2680 \text{ kJ/kg}$$

The discharge mass flow rate (m_2) is calculated at the exit steam because exit steam volumetric flow rate and diameter of discharge pipe are given. The density is calculated from the inverse of specific volume ($\rho = 1/v$).

The specific volume (v) at 10 bar, saturated steam is 0.1943 m³/kg (used saturated steam table, Appendix A.3):

$$\dot{m}_2 = \rho \times \dot{V} = \frac{1}{0.1943 \text{ m}^3/\text{kg}} \times 15,000 \frac{\text{m}^3}{\text{h}} \times \frac{\text{h}}{3600 \text{ s}} = 21.45 \text{ kg/s}$$

The inlet velocity is negligible as given in the problem statement. The exit velocity is calculated from the discharge volumetric flow rate divided by pipe cross sectional area:

$$v_2 = \frac{\dot{V}_2}{\frac{\pi D^2}{4}} = \frac{15,000 \text{ m}^3/\text{h}}{\frac{\pi(0.15)^2}{4} \text{ m}^2} \times \frac{\text{h}}{3600 \text{ s}} = 235.79 \text{ m/s}$$

The simplified general energy balance equation becomes

$$Q = \dot{m}\Delta h + \Delta KE = \dot{m}\Delta h + \frac{1}{2} \dot{m}(v_2^2 - v_1^2)$$

Substitute the values of mass flow rate, specific enthalpy, and velocity:

$$Q = 21.45 \frac{\text{kg}}{\text{s}} \times \left(2680 \frac{\text{kJ}}{\text{kg}} \right) + \frac{1}{2} \times 21.45 \frac{\text{kg}}{\text{s}} \left\{ \left(235.79 \frac{\text{m}}{\text{s}} \right)^2 - 0 \right\} \\ \times \frac{\text{kJ}}{1000 \text{ J}} = 58,082 \text{ kJ/s}$$

The sign of the heat transfer across system boundaries is positive; that is, heat is transferred from the surroundings to the system.

1.5 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, CP , for most incompressible liquids and solids is equal; $CP \approx C_v$ and for ideal gases, $CP = C_v + R$.

Example 1.18 Enthalpy of Phase Change

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 (H) in terms of specific enthalpy h ,

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

The change in specific enthalpy of $\Delta h_s = h_{s,2} - h_{s,1}$ steam is

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

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

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

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

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

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

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

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

1.5.1 Energy Balance for Open Systems with Multiple Inputs and Multiple Outputs

The general energy balance for an open system is

$$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta KE + \Delta PE \quad \dots\dots\dots (1.25)$$

The change in the rate of enthalpy for multiple streams is

$$\Delta\dot{H} = \sum \dot{H}_{\text{out}} - \sum \dot{H}_{\text{in}} \quad \dots\dots\dots (1.26)$$

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

$$\Delta\dot{H} = \sum \dot{m}_{\text{out}} h_{\text{out}} - \sum \dot{m}_{\text{in}} h_{\text{in}} \quad \dots\dots\dots (1.27)$$

Example 1.19 Enthalpy Change of Mixtures and Phase Change

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

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 (H) in terms of specific enthalpy h ,

$$\Delta\dot{H} = 0 = \sum \dot{m}_{\text{out}} h_{\text{out}} - \sum \dot{m}_{\text{in}} h_{\text{in}} \quad \text{In more detail,}$$

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

where

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

$\dot{m}_{a,\text{in}}, \dot{m}_{a,\text{out}}$ are the inlet and exit mass flow rates of acetone

$\dot{m}_{b,\text{in}}, \dot{m}_{b,\text{out}}$ are the inlet and exit mass flow rates of benzene

Rearranging the earlier equation,

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

where

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

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

Rearranging,

$$\Delta\dot{H} = 0 = \dot{m}_s \Delta h_s + \dot{m}_a \Delta h_a + \dot{m}_b \Delta h_b$$

where

Δh_s is the change in the specific enthalpy of steam

Δh_a is the change in the specific enthalpy of acetone

Δh_b is the change in the specific enthalpy 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

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

The change in mixture specific enthalpy is given by

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

The change in the specific enthalpy of steam, Δh_s , is $\Delta h_s = h_{s,2} - h_{s,1}$ given by

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

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

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

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

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

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

The specific heat capacity of the mixture is given by

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

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

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

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

Substitute the heat capacities of acetone and benzene:

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

Rearranging,

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

Substituting the mixture heat capacity,

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

Integrating,

$$\Delta h_{\text{mix}} = \int_{10^{\circ}\text{C}}^{50^{\circ}\text{C}} (124 + 0.20T) dT = (124T + 0.20T^2) \Big|_{10}^{50}$$

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

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

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

$$\begin{aligned} 0 &= \dot{m}_s \Delta h_s + \dot{m}_{\text{mix}} \Delta h_{\text{mix}} \\ &= \dot{m}_s \left(-1740 \frac{\text{kJ}}{\text{kg}} \right) + 1000 \frac{\text{kmol}}{\text{h}} \left(\frac{1000 \text{ mol}}{\text{kmol}} \right) \left(5200 \frac{\text{J}}{\text{mol}} \left| \frac{\text{kJ}}{1000 \text{ J}} \right. \right) \end{aligned}$$

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

The rounded value of the steam mass flow rate is $\dot{m}_s = 2990 \text{ kg/h}$. The amount of steam required for heating the acetone–benzene mixture is 2990 kg/h .

1.5.2 Enthalpy Change because of Mixing

The thermodynamic property of an ideal mixture is the sum of the contributions from the individual compounds. The following example illustrates the thermodynamic property of an ideal mixing.

Example 1.20 Mixing

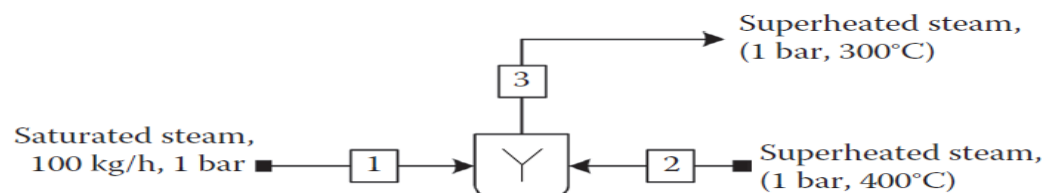
Hundred kilograms per hour of a saturated steam at 1 bar is mixed with superheated steam available at 400°C and 1 bar to produce superheated steam at 300°C and 1 bar. Calculate the amount of superheated steam produced at 300°C , and the required mass flow rate of the 400°C steam.

Solution

Known quantities: Stream 1: mass flow rate, saturated steam, 1 bar.
Stream 2: 400°C and 1 atm. Stream 3: superheated steam produced at 300°C, 1 bar.

Find: Volumetric flow rate of stream 2.

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



EXAMPLE FIGURE 1.20.1 Mixing of saturated and superheated steam.

Analysis: Use open system energy balance with multiple inputs, single output. The process flow sheet is shown in Example Figure 1.20.1. The general energy balance for an open system after applying the assumptions is reduced to

$$\Delta H = 0$$

For two inputs, single output,

$$\Delta \dot{H} = \dot{H}_3 - \dot{H}_1 - \dot{H}_2 = 0$$

Putting the equation in terms of mass flow rate and specific enthalpy,

$$\Delta \dot{H} = \dot{m}_3 h_3 - \dot{m}_1 h_1 - \dot{m}_2 h_2 = 0$$

Overall mass balance for the mixing system is

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 \Rightarrow 100 \frac{\text{kg}}{\text{h}} + \dot{m}_2 = \dot{m}_3$$

The specific enthalpy of stream 1 is

$$h_1|_{1 \text{ bar, sat'd steam}} = 2675.4 \text{ kJ/kg}$$

The specific enthalpy of stream 2 is

$$h_2|_{1 \text{ bar, } 400^\circ\text{C}} = 3278 \text{ kJ/kg}$$

The specific enthalpy of stream 3 is

$$h_3|_{1 \text{ bar, } 300^\circ\text{C}} = 3074 \text{ kJ/kg}$$

The general energy balance for the mixing process is

$$\dot{m}_1 \hat{H}_1 + \dot{m}_2 \hat{H}_2 = \dot{m}_3 \hat{H}_3$$

Substituting the values,

$$100 \frac{\text{kg}}{\text{h}} \left(2675.4 \frac{\text{kJ}}{\text{kg}} \right) + \dot{m}_2 \left(3278 \frac{\text{kJ}}{\text{kg}} \right) = \dot{m}_3 (3074 \text{ kJ/kg})$$

From the material balance equation,

$$\dot{m}_2 = \dot{m}_3 - 100$$

Substitute the value of \dot{m}_2 in the earlier equation:

$$100 \text{ kg/h} (2675.4 \text{ kJ/kg}) + (\dot{m}_3 - 100)(3278 \text{ kJ/kg}) = \dot{m}_3 (3074 \text{ kJ/kg})$$

Solving for \dot{m}_3 ,

$$100 \text{ kg/h} (2675.4 - 3278) \text{ kJ/kg} = \dot{m}_3 (3074 \text{ kJ/kg}) - \dot{m}_3 (3278 \text{ kJ/kg})$$

Rearranging,

$$\frac{100 \times (2675.4 - 3278) \frac{\text{kJ}}{\text{h}}}{(3074 - 3278) \frac{\text{kJ}}{\text{kg}}} = \dot{m}_3$$

The rounded values of the mass flow rates of streams 3 and 2 are

$$\dot{m}_3 = 295 \text{ kg/h and } \dot{m}_2 = 195 \text{ kg/h}$$

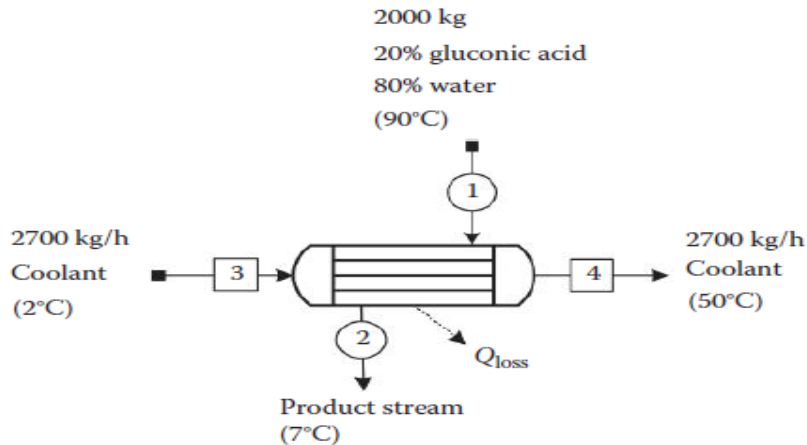
1.5.3 Energy Balance for Bioprocesses

Bioprocesses are unlike many chemical processes. Bioprocesses are not particularly energy intensive. Fermentation and enzyme reactors are operated at temperatures and pressures close to ambient conditions, and energy input for downstream processing is minimized to avoid damaging heat-labile products. Nevertheless, energy effects are important because biological catalysts are very sensitive to heat and changes in temperature. In large-scale processes, heat released during biochemical reactions can cause cell death of enzymes, if heat is not properly removed. The law of conservation of energy means that an energy accounting system can be set up to determine the amount of steam or cooling water required to maintain optimum process temperature [4].

Examples 1.21 Cooling of Fatty Acids

Problem

A liquid at the rate of 2000 kg/h fat (20 wt% acid, 80 wt% water) at 90°C is to be cooled to 7°C. Cooling is achieved by heat exchange with



EXAMPLE FIGURE 1.21.1

Shell and tube heat exchanger.

2700 kg/h coolant fluid initially at 2°C. The final temperature of the coolant liquid is 50°C. The fat is flowing on the shell side and coolant liquid is on the tube side. The heat exchanger is not adiabatic, so part of the heat is lost through the exchanger walls and the rest to coolant fluid. What is the rate of heat loss from the acid solution to the surroundings? Assume the heat capacity of acid is 1.463 (kJ/kg°C). The process flow sheet is shown in Example Figure 1.21.1.

Solution

Known quantities: Inlet and exit conditions of cooling water, inlet and exit temperature liquid stream.

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

Find: Heat loss through surroundings.

Analysis: Use the first law for an open system:

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

The simplified equation is

$$Q - 0 = \Delta \dot{H} + 0 + 0$$

For multiple input and multiple outputs, this equation is written as follows:

$$Q = \Delta \dot{H} = \sum_{\text{out}} \dot{m}_i h_i - \sum_{\text{in}} \dot{m}_i h_i$$

Let the subscript “c” be for coolant, “a” be for acid, and “w” be for water associated with the fat:

$$Q_{\text{loss}} = \{m_c h_{c,4} + m_a h_{a,2} + m_w h_{w,2}\}_{\text{out}} - \{m_c h_{c,3} + m_a h_{a,1} + m_w h_{w,1}\}_{\text{in}}$$

The mass flow rates of coolant, acid, and water are constant. Rearranging,

$$Q_{\text{loss}} = m_c (h_{c,4} - h_{c,3}) + m_a (h_{a,2} - h_{a,1}) + m_w (h_{w,2} - h_{w,1})$$

The enthalpy of water is found from the steam table as saturated liquid water. The specific enthalpy of coolant medium at 2°C is 8.124 kJ/kg and at 50°C is 209.5 kJ/kg. Use the saturated steam table (Table A.4) to find the specific enthalpy of the water associated with the fat:

$$h_{w,1}|_{@90^\circ\text{C}} = 376.8 \frac{\text{kJ}}{\text{kg}}, \quad h_{w,1}|_{@7^\circ\text{C}} = 29.3 \frac{\text{kJ}}{\text{kg}}$$

Substituting the values of mass flow rates and specific enthalpies of coolant, and water associated with steam and acid,

$$\begin{aligned} Q &= 2700 \frac{\text{kg}}{\text{h}} \times \frac{\text{h}}{3600 \text{ s}} \left(209.5 \frac{\text{kJ}}{\text{kg}} - 8.124 \frac{\text{kJ}}{\text{kg}} \right) + \left(2000 \frac{\text{kg}}{\text{h}} \frac{\text{h}}{3600 \text{ s}} \right) \\ &\times \left(29.3 - 376.8 \frac{\text{kJ}}{\text{kg}} \right) + \left(400 \frac{\text{kg}}{\text{h}} \frac{\text{h}}{3600 \text{ s}} \right) \left(1.463 \frac{\text{kJ}}{\text{kg}^\circ\text{C}} \right) (7^\circ\text{C} - 90^\circ\text{C}) \end{aligned}$$

Solving for the heat loss Q ,

$$Q = 151 \text{ kJ/s} - 193 \text{ kJ/s} - 13.49 \text{ kJ/s} = -55.49 \text{ kJ/s}$$

The sign for the heat transfer through the exchanger’s wall is negative; that is, heat is lost from the fatty acid to the surroundings.

1.6 Psychrometric Chart

The psychrometric chart (Figure 1.3) displays the relationship between dry-bulb, wet-bulb, and dew point temperatures and specific and relative humidity. Given any two properties, the others can be calculated. To use the chart, take the point of intersection of the lines of any two known factors (interpolate if necessary), and, from that intersection point, follow the lines

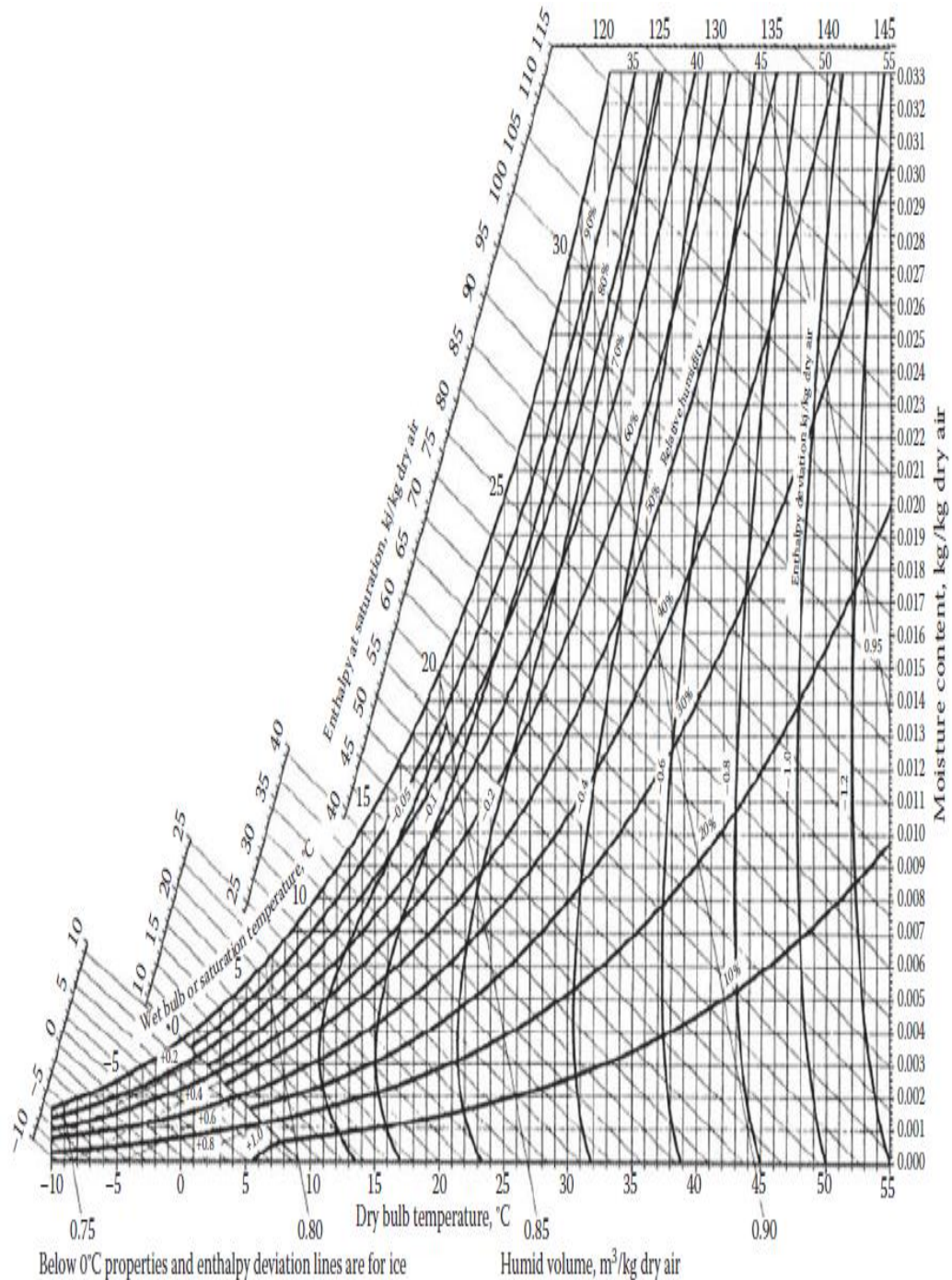


FIGURE 1.3

Psychrometric chart.

of the unknown factors to their numbered scales to obtain the corresponding values. The thermo-physical properties found on most psychrometric charts are as follows.

Dry-Bulb Temperature

Dry-bulb temperature is the temperature of an air sample, as determined by an ordinary thermometer, the thermometer bulb being dry. It is typically the abscissa or horizontal axis of the graph. The SI unit for temperature is Celsius, the other unit is Fahrenheit.

Wet-Bulb Temperature

Wet-bulb temperature is the temperature of an air sample after it has passed through a constant-pressure, ideal, adiabatic saturation process, that is, after the air has passed over a large surface of liquid water in an insulated channel. In practice, this is the reading of a thermometer whose sensing bulb is covered with a wet sock evaporating into a rapid stream of the air sample. The wet-bulb temperature is the same as the dry-bulb temperature when the air sample is saturated with water.

Dew Point Temperature

Dew point temperature is that temperature at which a moist air sample at the same pressure would reach water vapor saturation. At this saturation point, water vapor would begin to condense into liquid water fog.

Relative Humidity

Relative humidity is the ratio of the mole fraction of water vapor to the mole fraction of saturated moist air at the same temperature and pressure. Relative humidity is dimensionless, and is usually expressed as a percentage.

Humidity Ratio

Humidity ratio, also known as moisture content, mixing ratio, or specific humidity, is the proportion of mass of water vapor per unit mass of dry air at the given conditions. For a given dry-bulb temperature, there will be a particular humidity ratio for which the air sample is at 100% relative humidity. Humidity ratio is dimensionless, but is sometimes expressed as grams of water per kilogram of dry air.

Specific Enthalpy

Specific enthalpy, also called heat content per unit mass, is the sum of the internal (heat) energy of the moist air in question, including the heat of the air and water vapor within. In the approximation of ideal gases, lines of constant enthalpy are parallel to lines of constant wet-bulb temperature.

Specific Volume

Specific volume, also called inverse density, is the volume per unit mass of the air sample. The SI unit is cubic meters per kilogram of air; the other unit is cubic feet per pound of dry air.

Example 1.22 Psychrometric Chart

Humid air at 28°C has a dew point of 8°C. Using the psychrometric chart provided, determine the following: relative humidity, absolute humidity, wet-bulb temperature, dry-bulb temperature, humid volume, specific enthalpy, and mass of air that contains 2 kg of water, and volume occupied by air that contains 2 kg of water.

Solution

Known quantities: Humid air at 28°C has a dew point of 8°C. Air contains 2 kg of water, and volume occupied by air that contains 2 kg of water.

Find: Relative humidity, absolute humidity, wet-bulb temperature, dry bulb temperature, humid volume, specific enthalpy.

Analysis: Use psychrometric chart. Humid air at 28°C has a dew point of 8°C. Using the psychrometric chart provided, determine the following:

1. Relative humidity = 30% (Example Figure 1.22a.1).
2. Absolute humidity = 0.007 kg water/kg dry air (Example Figure 1.22b.1).

3. Wet-bulb temperature = 16.5°C (Example Figure 1.22c.1). Follow the constant enthalpy line from the intersection of the dry-bulb and dew point temperatures.

4. Dry-bulb temperature = 28°C.

5. Humid volume = 0.86 m³/kg (Example Figure 1.22d.1).

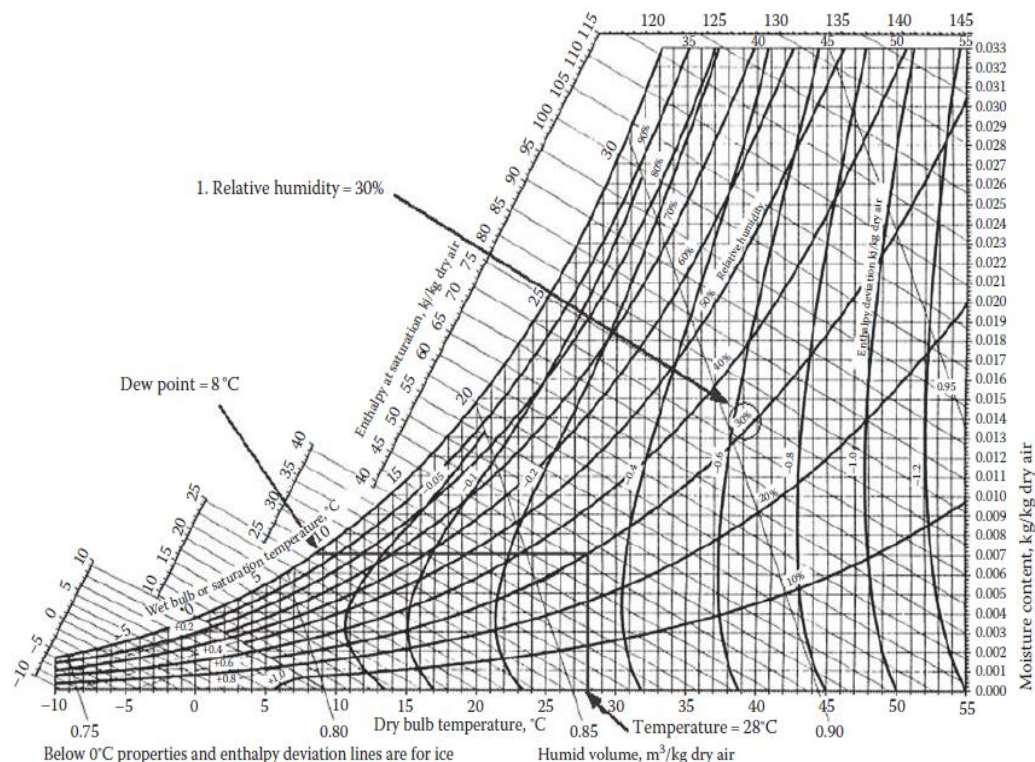
6. Specific enthalpy = 46 kJ/kg – 0.3 kJ/kg = 45.7 kJ/kg (Example Figure 1.22e.1).

7. Mass of air that contains 2 kg of water:

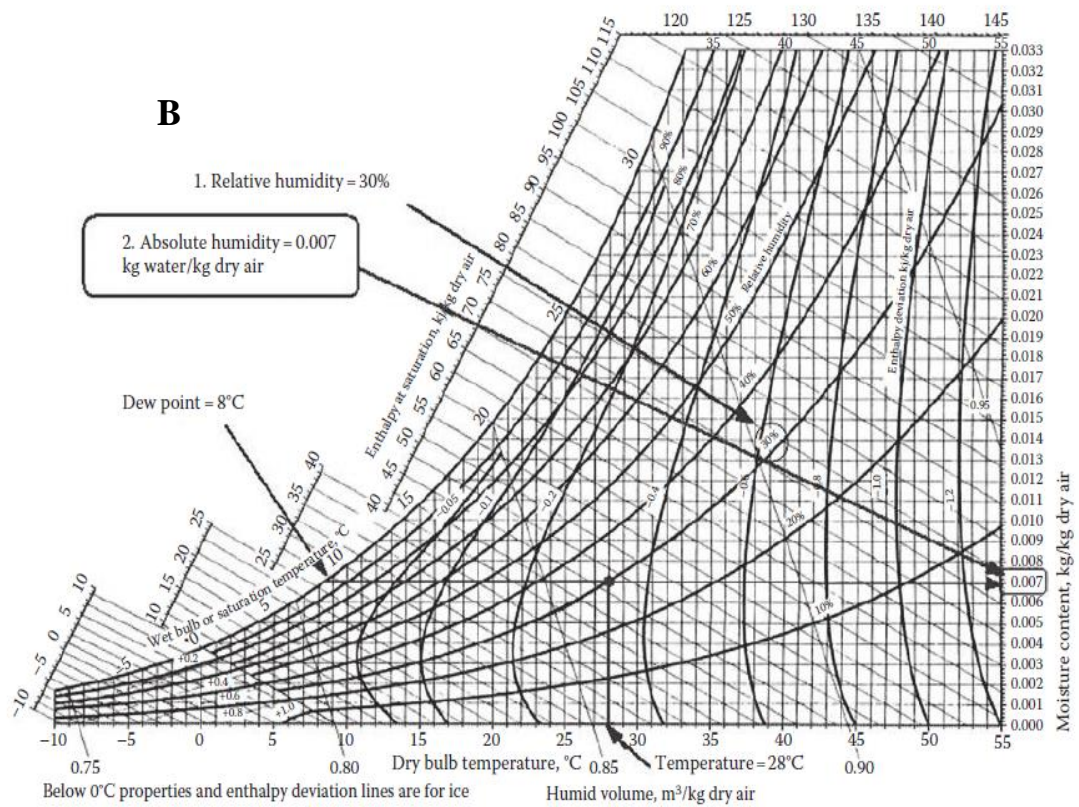
$$2 \text{ kg H}_2\text{O} \frac{\text{kg dry air}}{0.007 \text{ kg H}_2\text{O}} = 285.7 \text{ kg dry air}$$

8. Volume occupied by air that contains 2 kg of water:

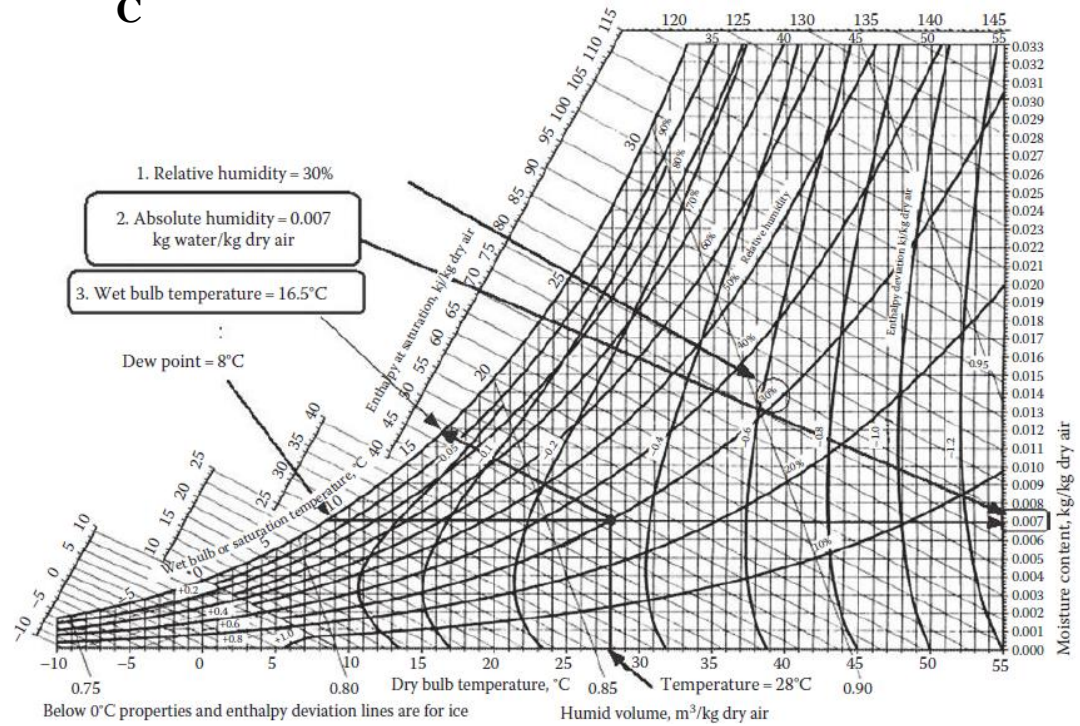
$$\frac{0.86 \text{ m}^3}{\text{kg dry air}} \frac{\text{kg dry air}}{0.007 \text{ kg H}_2\text{O}} 2 \text{ kg H}_2\text{O} = 245.7 \text{ m}^3$$



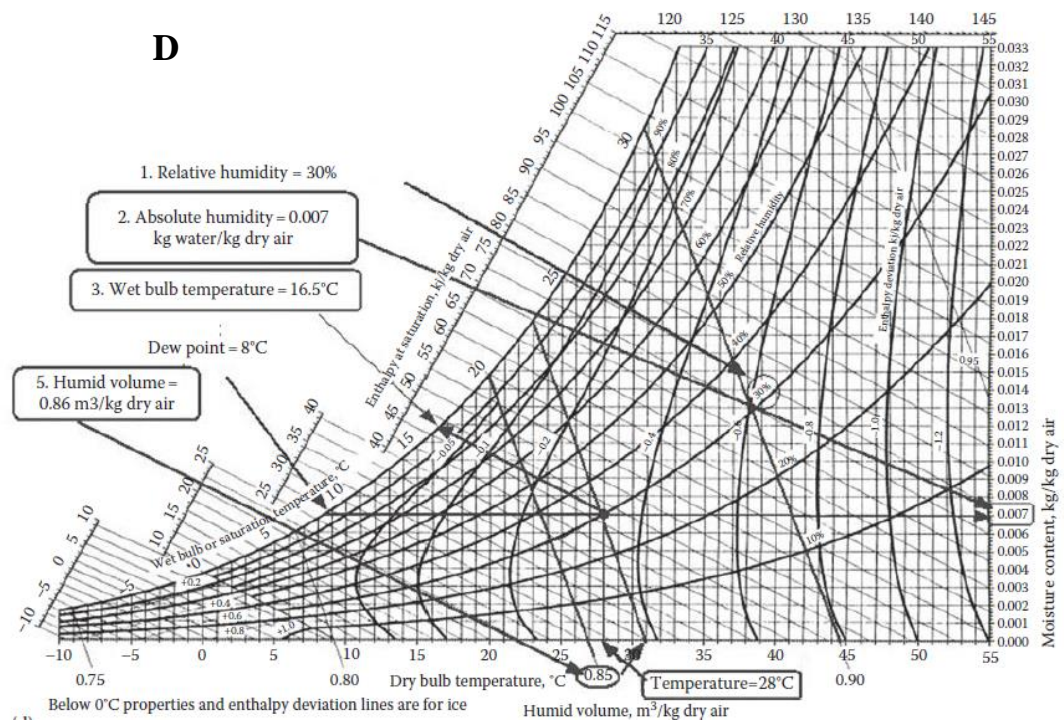
(a)

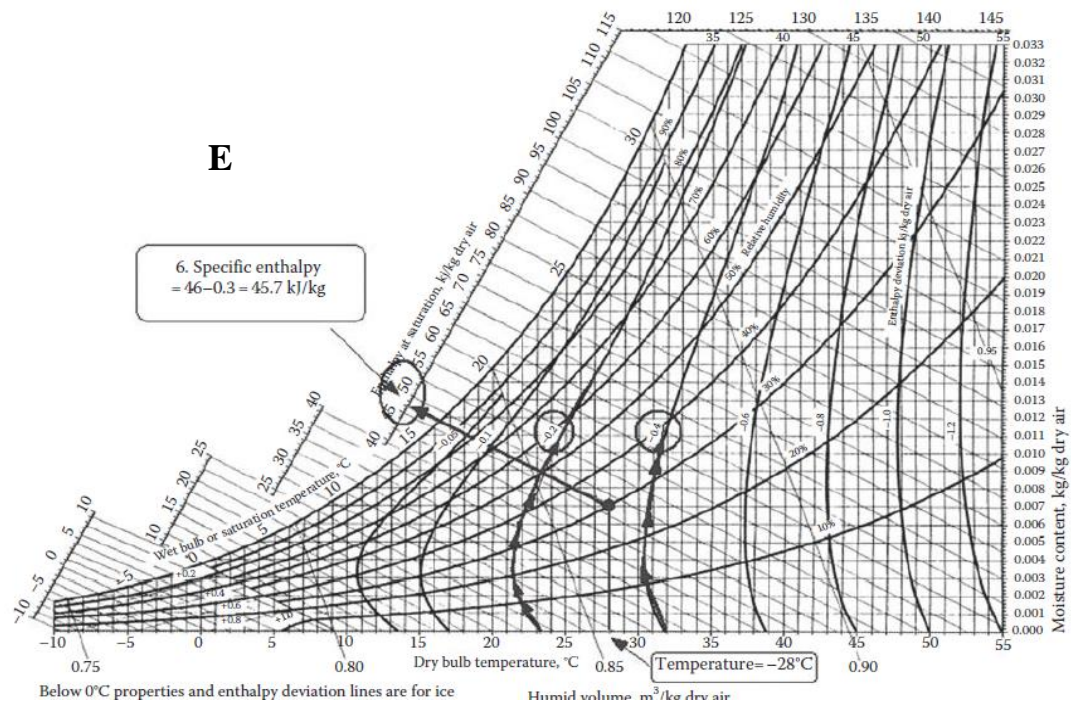


C



D





Solution

Known quantities: Inlet air flow rate temperature and pressure.

Find: The molar flow rates of water, dry air, and oxygen entering the process.

Analysis: First, we calculate the partial pressure of water by using the definition of relative humidity:

$$0.8 = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^*}$$

The vapor pressure at 25°C is 0.03 bar:

$$0.8 = \frac{p_{\text{H}_2\text{O}}}{0.03}$$

The partial pressure of water ($p_{\text{H}_2\text{O}}$) is 0.025 bar:

$$p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}}P$$

Substitute values of partial pressure and total pressure:

$$0.025 = y_{\text{H}_2\text{O}}(3.0)$$

The mole fraction of water is 0.008 mol water/mole humid air, and the mole fraction of dry air is 0.992. The molar flow rate of air can be obtained using ideal gas equation of state using the volumetric flow rate given in the problem statement. After substituting the known information into this equation, we have

$$n = \frac{PV}{RT} = \frac{(3 \text{ bar})(0.8 \text{ m}^3/\text{h})}{\left(8.314 \times 10^{-5} \frac{\text{m}^3 \cdot \text{bar}}{\text{mol K}}\right)(298 \text{ K})} = 96.87 \text{ mol/h}$$

The number of moles of dry air is

$$n_{\text{dry-air}} = y_{\text{dry-air}} \times \dot{n} = 0.992 \times 96.87 \frac{\text{mol}}{\text{h}} = 96.1 \text{ mol/h}$$

Example 1.25 Relative and Absolute Humidity

The dry-bulb temperature is measured as 20°C and the wet-bulb temperature as 15°C. If the total pressure is 1 atm, what are the relative humidity and the absolute humidity? Use the humidity chart.

Solution

Known quantities: Dry-bulb and wet-bulb temperatures of air.

Find: Relative and absolute humidity

Analysis: Use the psychrometric chart.

Relative humidity = 59%

Absolute humidity = 0.0087 kg water/kg dry air

1.7 Summary

The first law of thermodynamics for a closed system is

$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

The first law of thermodynamics for an open system at steady state (i.e., continuous) is

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}_s$$

Procedure for energy balance calculations:

1. Draw and completely label a process flowchart.
2. Perform all material balance calculations.
3. Write the appropriate form of the energy balance equation and remove any negligible terms.
4. Choose a reference state (phase-gas/liquid, T , P) for each species involved. If using enthalpy tables, use reference state to generate table. If no tables are available, choose one inlet or outlet condition as the reference state for the species.
5. Construct an inlet–outlet enthalpy table.
6. Calculate all required values of u_i or h_i and insert the values into the table.
7. Calculate ΔU or ΔH (e.g., $\Delta H = \sum m_i h_i - \sum m_i h_i$).
8. Calculate any other terms in the energy balance equation (i.e., W , ΔE_k , ΔE_p).
9. Solve for the unknown quantity in the energy balance equation.

Homework Problems

1.1 Liquid methanol at 25°C is heated and vaporized for use in a chemical reaction. How much heat is required to heat and vaporize 10 mol/s of methanol to 600°C. (744 kJ/s)

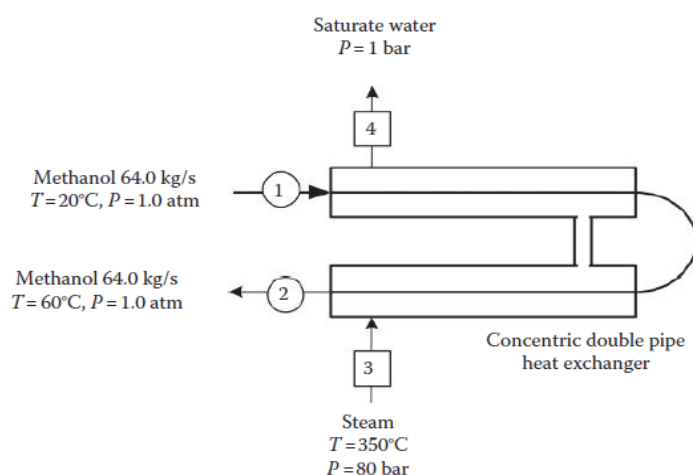
1.2 Propane gas at 40°C and 250 kPa enters an adiabatic heat exchanger and exits the heat exchanger at 240°C. The flow rate of propane is 100

mol/min. The saturated steam with a flow rate of 6 kg/min at 5 bar (absolute) enters the heat exchanger. The discharge wet steam (contains vapor and liquid) is at 3 bar. Calculate the exit steam quality and temperature. (0.86, 133.5°C)

1.3 Wet steam at 20 bar with 97% quality is passed through a throttling valve and expands to 1 bar pressure. Calculate the temperature of the steam that departs from the adiabatic expansion valve. (132.25°C)

1.4 Hundred kilograms per hour of wet steam at 20 bar with 97% quality is passed through a throttling valve and expands to 10 bar pressure. Calculate the temperature of the steam that departs from the adiabatic expansion valve and the quality of steam. (179.9°C, 0.982)

1.5 Methanol is heated by condensing steam in a concentric double pipe heat exchanger as depicted in Problem Figure 1.5.1. Methanol flowing through the inner pipe at 64.0 kg/s enters at 20°C and exits at 60°C. Steam enters the outer pipe at 350°C and 80 bar (absolute) and leaves the heat exchanger as saturated water at 1.0 bar. Assume that the outer pipe is well insulated and no heat is lost to the surroundings. Determine the mass flow rate of the steam. (2.57 kg/s)



PROBLEM FIGURE 1.5.1

Schematic of double pipe heat exchanger.

1.6 Calculate the heat rate required to heat 32.04 kg/s of liquid methyl alcohol (CH_3OH) at 5°C and 1 atm to vapor at 500°C and 1 atm. The heat of vaporization of methanol at 64.7°C and 1 atm is 35.27 kJ/mol. (69.0 MW)

1.7 Determine the total amount of heat required to convert 2.00 mol of liquid *n*-hexane (C_6H_{14}) at 10°C to vapor at 55°C in a closed container. Assume that hexane vapor behaves as an ideal gas at the system pressure. Neglect any effect of a change in pressure on the liquid enthalpy. The heat of vaporization of hexane at 68.74°C and 1 atm is 28.85 kJ/mol. (63.26 kJ)

1.8 A volume of 734 cm^3 of liquid acetone is contained in a closed cylinder fitted with a movable frictionless piston at 10°C . The acetone is heated via heating coil inserted inside the cylinder to vapor at 500°C . The piston area is 50.0 cm^2 , and the piston weighs 200 kg. The heat of vaporization of acetone at its normal boiling point (56.0°C) is 30.2 kJ/mol. Assume the cylinder is perfectly insulated and no heat is lost to the surroundings. Calculate the heat transferred from the heating process. (929 kJ)

1.9 A volume of 734 cm^3 of liquid acetone is contained in a closed (vertical) cylinder fitted with a movable frictionless piston at 10°C . The acetone is heated via heating coil inserted inside the cylinder to vapor at 500°C . The piston area is 50.0 cm^2 , and the piston weighs 200 kg. The heat of vaporization of acetone at its normal boiling point (56.0°C) is 30.2 kJ/mol. Assume the cylinder is perfectly insulated and no heat is lost to the surroundings. If the heat is provided by superheated steam at 550°C and 1.0 bar, the final condition of the steam is saturated at 100°C . How much steam is needed? (1.0 kg)

1.10 A hydroelectric project has a volumetric flow rate of 1.2 m^3/s . The water flowing in the river at atmospheric pressure and 20.4°C falls

vertically for 300 m and then passes through a turbine. The water exits the turbine at atmospheric pressure and 19°C. What is the power output of the turbine? (10.1 kW)

1.11 Air at 100 kPa and 10°C enters a compressor and is brought to 1000 kPa and 50°C. The constant pressure heat capacity of air is 1.01 kJ/kg K. If 15 kg/min of air are to be compressed, determine the power requirement of the compressor. State your assumptions. (12.625 kW)

1.12 A gasoline engine has an efficiency of 25%. If the engine consumes 0.75 L/h of gasoline with a heating value of 3.0×10^4 kJ/L, how much power does it provide? Express the answer in kilowatts. (1.56 kW) **1.13** A liquid stream (10 kg/min) flows through a heat exchanger in which it is heated from 25°C to 80°C. The liquid specific heat is 4.18 kJ/kg K. The inlet and outlet pipes have the same diameter, and there is no change in elevation between these points. Calculate the heat required. (38.3 kW)

1.14 Water (100 kg/s) passes through the gate of a dam and falls on a turbine 10 m below, which turns a shaft connected to a generator. The fluid velocity on both sides of the dam is negligible, and the water undergoes insignificant pressure and temperature changes between the inlet and outlet. Calculate the work generated by the turbine. (9.81 kW)

1.15 Crude oil is to be pumped at 1000 kg/min through a pipeline 2 km in length. The pipe inlet is 200 m below the outlet, the pipe diameter is constant. Neglect the pipe frictional losses. Calculate the work required by the pump. (32.7 kW)

1.16 A cylinder is fitted with a frictionless floating piston and contains 24.8 L of air at 25°C and 1 bar. The system is then heated to 250°C. ($C_v = 5R/2$). How much work was done by the system on the surroundings? (1.871 kJ)

1.17 A power plant (800 MW) burns natural gas to boil water producing saturated steam (100% quality) at 70 bar. This steam is expanded in a turbine to steam at 100°C and 1 bar. The steam enters the turbine at 10 m/s and exits 5 m below the entrance point level at 100 m/s. The turbine is connected to an electrical generator by a shaft. The efficiency of the turbine is 60%. What is the mass flow rate of steam to the turbine (kg/h)? (5.05×10^7 kg/h)

1.18 A large tank that is filled with water is open to the atmosphere. Water is taken from the tank, passed through a pump, and then delivered to the hoses of a firefighting extinguisher in a chemical factory. It is desired to deliver 69.5 lbm of water per second at a pressure of 200 psi (gauge). If there is a negligible elevation change between the water level in the tank and the discharge of the pump, no changes in the diameter of the pipes and hoses, and if the pump has an efficiency of 65.0%, how much work must be supplied to the pump in order to meet the pressure and discharge rate specifications? (89.7 hp)

1.19 Suppose you are operating a steam turbine where the steam leaving the turbine is at 5 bar (absolute). This steam contains 95 wt% vapors. If the shaft work produced by the turbine is 1100 kJ/kg and the high pressure, high temperature steam enters the turbine at 100 bar (abs), what is the temperature of the steam entering the turbine? If water at 10°C is supplied to the steam boiler to generate steam, how much heat is required per kilogram of steam produced? You may assume that heat losses from the turbine are negligible. (3700 kJ/kg)

1.20 Steam at 60 bar and 500°C enters an adiabatic turbine at a steady flow rate of 1 kg/s; the turbine outlet stream is at 1 bar and 400°C. The inlet and exit streams of the turbine are at the same height and the pipes have the same diameter of 0.15 m. How much work can be obtained from an adiabatic, continuous-flow turbine? (−144 kJ/s)

1.21 Consider taking 1000.0 kg of outside air, which is then heated to make your apartment comfortable in the winter. The outside air has a dry bulb temperature of 10.0°C and a wet-bulb temperature of 5°C. You want the air in your apartment to be at a dry-bulb temperature of 25°C and a relative humidity of 60.0%. (a) How much water must be added to the 1000.0 kg of outside air to reach the desired humidity level? (8.57 kg) (b) If the water you are using to alter the humidity of the air is coming from a tap (assume its temperature is 10°C), how much heat must be added to just the water to attain the desired temperature and humidity level in your apartment? (2.15×10^4 kJ)

1.22 For healthy air quality, it is recommended that a 200 m² house have an air exchange rate of 60.0 ft³ bone-dry air/min with the outside. It is also suggested that the relative humidity in the house be 65%. Suppose the outside air is at 30°F and a relative humidity of 40%. If this air is brought into the house and heated to 75°F without addition of water, what is the relative humidity? If you desire to maintain a relative humidity of 65%, how much water must be added to the air inside the house (g/min)? (24.3 g/min)

References

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2. Felder, R.M. and R.W. Rousseau (1999) *Elementary Principles of Chemical Processes*, 3rd edn., John Wiley, New York.
3. Himmelblau, D.M. (1974) *Basic Principles and Calculations in Chemical Engineering*, 3rd edn., Prentice-Hall, Englewood Cliffs, NJ.
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2

Energy Balance with Reaction

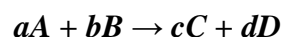
The large changes in enthalpy and internal energy throughout a chemical reaction require significant heat transfer (heating or cooling) from the reactor in order to eventually maintain the reactor under optimum operating conditions. This chapter demonstrates how to calculate the heat of reaction at a specific temperature and illustrates how to estimate the heat of reaction from the heat of formation. The energy balances for a reacting system using two methods are defined. Problems that involve the application of combined material and energy balances are addressed. Finally, a few applications, specifically, combustion, bioprocesses, and membrane reactors, are discussed at length to practice the concepts further. The following items outline the principal learning objectives of this chapter.

Learning Objectives

1. Calculate the heat of reaction (Section 2.1).
2. Estimate the heat of reaction from heats of formation (Section 2.2).
3. Establish the energy balance for a reacting system (Section 2.3).
4. Write simultaneous material and energy balances for a reacting system (Section 2.4).
5. Write the appropriate balances for combustion processes (Section 2.5).
6. Apply the energy balance to bioprocesses (Section 2.6).
7. Perform material and energy balances for a membrane reactor system (Section 2.7).

2.1 Heat of Reaction

The heat of reaction, $\Delta H_{\text{Rx}}(T, P)$, is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely to form products at the same temperature and pressure. Consider the following reaction:



The standard heat of reaction ($\Delta H_{R_x}^\circ$) is calculated as the difference between the product and reactant enthalpies when both reactants and products are at standard conditions, that is, at 25°C and 1 atm [1]. The symbol “o” denotes standard conditions. Therefore,

$$\begin{aligned}\Delta H_{R_x}^\circ [\text{kJ/mol}] &= H_{\text{products}} - H_{\text{reactants}} \\ &= c\Delta H_{f,C}^\circ + d\Delta H_{f,D}^\circ - a\Delta H_{f,A}^\circ - b\Delta H_{f,B}^\circ \\ &= \sum v_i \Delta H_i^\circ\end{aligned}$$

where ΔH_f° is the standard heat of formation. The reported ΔH_{R_x} applies to stoichiometric quantities of each species. Consider the following example:



The enthalpy change for the given reaction is

$$\frac{-150 \text{ kJ}}{1 \text{ mol A consumed}} = \frac{-150 \text{ kJ}}{2 \text{ mol B consumed}} = \frac{-150 \text{ kJ}}{3 \text{ mol C generated}}$$

If 150 mol/s of C was generated at 100°C and 1 atm, then

$$\Delta \dot{H} = \left(\frac{-150 \text{ kJ}}{3 \text{ mol C generated}} \right) \left(\frac{150 \text{ mol C generated}}{\text{s}} \right) = -7500 \text{ kJ/s}$$

If $\Delta H_{R_x}(T)$ is negative, the reaction is exothermic; that is, energy must be removed from the reactor to prevent the temperature from increasing. If $\Delta H_{R_x}(T)$ is positive, the reaction is endothermic; that is, energy must be added to the reactor to prevent the temperature from decreasing. The heat of reaction ($\Delta H_{R_x}(T, P)$) is nearly independent of pressure. The value of the heat of reaction depends on how the stoichiometric equation is written and on the phase of the reactants and products.

2.2 Heats of Formation and Heat of Combustion

The standard heat of reaction ($\Delta H_{R_x}^\circ$) can be calculated from the standard heat of formation (ΔH_f°). The standard heat of formation is the enthalpy change associated with the formation of 1 mol of the compound at 25°C and 1 atm. The values of ΔH_f°

for many compounds can be obtained from tabulated data (Table A.2). The standard heat of reaction ($\Delta H_{R_x}^\circ$) from the heat of formation ($\Delta H_f^\circ, i$) of any reaction can be calculated as

$$\Delta H_{R_x}^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ$$

where

ν_i is the stoichiometric coefficient of reactant or product species i

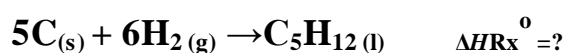
$\Delta H_f^\circ, i$ is the standard heat of formation of species i

The standard heats of formation of all elemental species are zero (H_2, O_2, N_2).

The standard heat of reaction ($\Delta H_{R_x}^\circ$) of any reaction involving only oxygen and a combustible species can be calculated as

$$\Delta H_{R_x}^\circ = - \sum_i \nu_i (\Delta H_c^\circ)_i$$

This is the reverse of determining the heat of reaction from heats of formation, where ν_i is the stoichiometric coefficient of reactant or product species i . ($\Delta H_c^\circ, i$) is the standard heat of combustion of species i . If any reactants or products are combustion products (i.e., CO_2, H_2O, SO_2), their heats of combustion are equal to zero. For many substances, it is much easier to measure the standard heat of combustion (ΔH_c°) than measuring the standard heat of formation (ΔH_f°). Consider the formation of pentane:



Carbon, hydrogen, and pentane can all be burned, and their standard heats of combustion can be determined experimentally. Therefore,

$$\Delta H_{R_x}^\circ = 5\Delta H_{c,C(s)}^\circ + 6\Delta H_{c,H_2(g)}^\circ - \Delta H_{c,C_5H_{12(l)}}^\circ$$

The standard enthalpy of combustion is the enthalpy change when 1 mol of a reactant completely burns in excess oxygen under standard thermodynamic conditions. The standard heat of combustion of a species i , $\Delta H_c^\circ, i$, is the enthalpy change associated with the complete combustion of 1 mol of species i with oxygen at $25^\circ C$ and 1 atm such that all the carbon forms $CO_2(g)$, all the hydrogen forms $H_2O(l)$, all the sulfur

forms SO_2 (g), and all the nitrogen forms NO_2 (g). The same value of standard heat of reaction can be used to measure the standard heat of formation of pentane:

$$\Delta H_{\text{Rx}}^{\circ} = \Delta H_{\text{f}, \text{C}_5\text{H}_{12}}^{\circ} (\text{l}) - 5\Delta H_{\text{f}, \text{C}}^{\circ} (\text{s}) - 6\Delta H_{\text{f}, \text{H}_2}^{\circ} (\text{g})$$

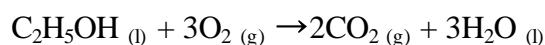
Since carbon and hydrogen are atoms, the magnitude of their standard heats of formation is zero. Accordingly,

$$\Delta H_{\text{Rx}}^{\circ} = \Delta H_{\text{f}, \text{C}_5\text{H}_{12}}^{\circ} (\text{l}) - 0 - 0$$

Example 2.1 Heat of Reaction from Heats of Formation

Problem

Consider the combustion of liquid ethanol as shown in the following reaction scheme:



Use heat of formation and heat of combustion to determine the standard heat of reaction.

Solution

Known quantities: Reaction stoichiometry.

Find: Standard heat of reaction.

Analysis: Values for standard heat of combustion and standard heat of formation are available in the appendix.

$$\Delta H_{\text{Rx}}^{\circ} = 3\Delta H_{\text{f}, \text{H}_2\text{O}}^{\circ} (\text{l}) + 2\Delta H_{\text{f}, \text{CO}_2}^{\circ} - 0 - \Delta H_{\text{f}, \text{C}_2\text{H}_5\text{OH}}^{\circ} (\text{l})$$

Substitute the values of the standard heat of formation:

$$\Delta H_{\text{Rx}}^{\circ} (\text{kJ/mol}) = 3(-285.84) + 2(-393.51) - 0 - (-277.63) = -1366.9 \text{ kJ/mol}$$

The standard heat of reaction is calculated from the standard heat of combustion as

$$\Delta H_{\text{Rx}}^{\circ} = \Delta H_{\text{c}, \text{C}_2\text{H}_5\text{OH}}^{\circ} (\text{l}) + 3\Delta H_{\text{c}, \text{O}_2}^{\circ} - 3\Delta H_{\text{c}, \text{H}_2\text{O}}^{\circ} (\text{l}) - 2\Delta H_{\text{c}, \text{CO}_2}^{\circ} (\text{g})$$

Substitute the values of the standard heat of combustion, knowing that the magnitudes of the standard heat of combustion of oxygen, water, and carbon dioxide are zero:

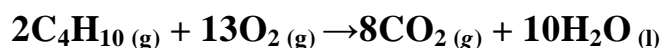
$$\Delta H_{\text{Rx}}^{\circ} (\text{kJ/mol}) = -1366.91 + 0 - 0 - 0 = -1366.9 \text{ kJ/mol}$$

Results reveal that both values of standard heat of reactions are identical.

Example 2.2

Problem

If 240 mol/s of CO_2 is produced in the following reaction where reactants and products are all at 25C, and no CO_2 is present in the feed stream,



what is the standard rate of change in enthalpy?

Solution

Known quantities: Molar flow rate of effluent CO_2 and reaction temperature.

Find: Standard rate of change in enthalpy.

Analysis: The standard heat of reaction from the heat of formation is as follows:

$$\Delta H_{\text{Rx}}^\circ (25^\circ\text{C}, 1 \text{ atm}) = \sum v_i \Delta H_{f,i}^\circ$$

The heat of reaction is given by

$$\Delta H_{\text{Rx}}^\circ (25^\circ\text{C}, 1 \text{ atm}) = 10\Delta H_{f,\text{H}_2\text{O}(\text{l})}^\circ + 8\Delta H_{f,\text{CO}_2}^\circ - 2\Delta H_{f,\text{C}_4\text{H}_{10}}^\circ - 13\Delta H_{f,\text{O}_2}^\circ$$

$$\Delta H_{\text{Rx}}^\circ (25^\circ\text{C}, 1 \text{ atm}) = 10(-285.84) + 8(-393.5) - 2(-124.7) - 13(0)$$

$$\Delta H_{\text{Rx}}^\circ (25^\circ\text{C}, 1 \text{ atm}) = -5757 \text{ kJ/mol}$$

The extent of reaction is calculated using the mole balance of CO_2 ; note that no carbon dioxide is present in the feed stream before the reaction takes place:

$$n_{\text{CO}_2} = 0 + 8\xi = 240 = 0 + 8\xi$$

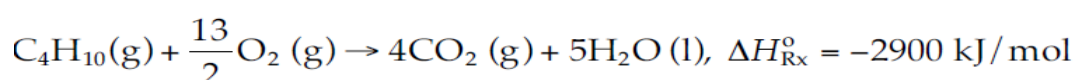
$$\xi = \frac{240}{8} = 30 \text{ mol/s}$$

The change in enthalpy transfer rate is

$$\dot{\Delta H} = \xi \times \Delta H_{\text{Rx}}^\circ = 30 \times -5757 \text{ kJ/mol} = -1.727 \times 10^5 \text{ kJ/s}$$

Example 9.3 Butane Combustion

The reaction stoichiometry and standard heat of the reaction on *n*-butane vapor is shown here:



Assume that 40 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C . The fresh feed to the reactor contains 20 mol/s of CO_2 . Calculate the rate of change in enthalpy $\dot{\Delta H}_{\text{Rx}}^\circ$ (kJ/s).

Solution

Known quantities: Inlet and exit CO₂ molar flow rate and reaction temperature.

Find: The rate of change in enthalpy.

Analysis: Since inlet and exit streams' temperature is equal, the change in the sensible heat is irrelevant. Accordingly, the rate of change in enthalpy is only due to heat of reaction and is calculated as

$$\Delta \dot{H} = \dot{\xi} \Delta H_{R_x}^{\circ}(T, P) \text{ at } 25^{\circ}\text{C}, \Delta \dot{H} = \dot{\xi} \Delta H_{R_x}^{\circ},$$

where $\Delta H_{R_x}^{\circ}$ is the standard heat of reaction.

The extent of reaction is calculated using the mole balance of CO₂:

$$\dot{n}_{\text{CO}_2} = \dot{n}_{\text{CO}_2, \text{feed}} + 4\dot{\xi}$$

Substitute the values of inlet and exit molar flow rates of carbon dioxide:

$$40 = 20 + 4\dot{\xi}$$

$$\text{The extent of reaction is } \dot{\xi} = \frac{40 - 20}{4} = \frac{20}{4} = 5 \text{ mol/s}$$

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

$$\Delta \dot{H} = \dot{\xi} \Delta H_{R_x}^{\circ} = \left(5 \frac{\text{mol}}{\text{s}} \right) \left(\frac{-2900 \text{ kJ}}{\text{mol}} \right) = -1.45 \times 10^4 \text{ kJ/s}$$

2.2.1 Extent of Reaction

If n_{A_r} is the moles of A generated or consumed by a reaction at a temperature T and pressure P , and ν_A is the stoichiometric coefficient of the reactant or product, the associated enthalpy change is

$$\Delta \dot{H} = \dot{\xi} \Delta H_{R_x}(T, P)$$

The extent of reaction, ξ , is a measure of how far a reaction has proceeded:

$$(\dot{n}_i)_{\text{out}} = (\dot{n}_i)_{\text{in}} + \nu_i \dot{\xi}$$

Rearranging, the extent of reaction is expressed as

$$\dot{\xi} = \frac{(\dot{n}_i)_{\text{out}} - (\dot{n}_i)_{\text{in}}}{\nu_i}$$

1.2.2 Reactions in Closed Processes

If the reaction is taking place in a closed system of constant volume, the change in the internal energy of reaction, ΔU_{Rx} , is given as

$$\Delta U_{\text{Rx}} = \Delta H_{\text{Rx}} - (\Delta n)RT$$

The change in the number of moles is equivalent to the change in the number of stoichiometric coefficients between the product and the reactant.

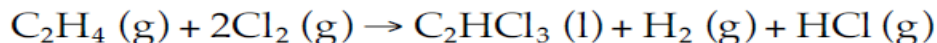
Substituting $\Delta n = \sum \nu_i,$

$$\Delta U_{\text{Rx}} = \Delta H_{\text{Rx}} - RT \sum \nu_i$$

where ν_i is the stoichiometric coefficient of the gaseous reactant or product component (+for product, -for reactant).

Example 2.4 Heat of Reaction from Internal Energy

Calculate the standard heat of the reaction of the following reaction:



The internal energy of reaction at standard conditions (25°C, 1 atm) is

$$\Delta U_{\text{Rx}} = -418 \text{ kJ/mol.}$$

Solution

Known quantities: Internal energy of reaction.

Find: The standard heat of reaction.

Analysis: Use the following equation for closed system:

$$\Delta U_{\text{Rx}}(T) = \Delta H_{\text{Rx}}(T) - RT \sum \nu_i$$

Substitute known quantities:

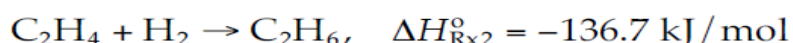
$$-418 \text{ kJ/mol} = \Delta H_{\text{Rx}}^\circ - \frac{8.314 \text{ J}}{\text{mol K}} \frac{1 \text{ kJ}}{1000 \text{ J}} \times 298.15 \text{ K} \times (1 + 1 + 0 - 2 - 1)$$

$$\Delta H_{\text{Rx}}^\circ = -420.5 \text{ kJ/mol}$$

Note that ν_i is the stoichiometric coefficient (+for product, -for reactant) of the gaseous reactant or product component only (not liquids or solids components). If a set of reactions can be manipulated through a series of algebraic operations to yield the desired reaction, then the desired heat of reaction can be obtained by performing the same algebraic operations on the heats of reaction of the manipulated set of reactions (Hess law).

Example 2.5 Standard Heat of Reaction

Calculate the heat of combustion for C_2H_6 from the following reactions:



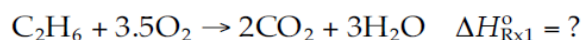
Solution

Known quantities: Standard heat of reaction.

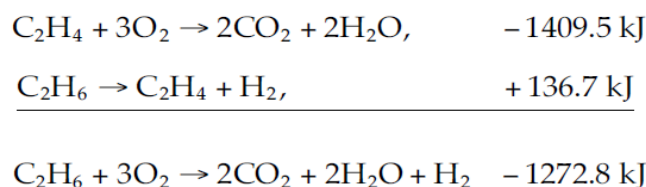
Find: Standard heat of reaction for the combustion of ethane.

Analysis: Use Hess' law.

The reaction for combustion of ethane is as follows:



The first reaction minus the second reaction based on one mole reacted



Accordingly, the heat of combustion of C_2H_6 is -1558.3 kJ .

Example 2.6 Dehydrogenation of Ethane

Calculate the standard heat of reaction from the dehydrogenation of ethane using the standard heats of combustion:



Solution

$$\Delta H_{\text{Rx}}^{\circ} = \Delta H_{\text{c}, \text{C}_2\text{H}_6}^{\circ} - \Delta H_{\text{c}, \text{C}_2\text{H}_4}^{\circ} - \Delta H_{\text{c}, \text{H}_2}^{\circ}$$

Substituting the values of standard heat of combustion (from the appendix) yields

$$\Delta H_{\text{Rx}}^{\circ} \text{ (kJ/mol)} = -1559.9 - (-1410.99) - (-285.84) = 136.93 \text{ kJ/mol}$$

2.3 Energy Balance for Reactive Processes

For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method (extent of reaction) and the heat of formation method (element balance). These two methods differ in the choice of the reference state [2, 3].

2.3.1 Heat of Reaction Method

The heat of reaction method is ideal when there is a single reaction for which $\Delta H_{\text{Rx}}^{\circ}$ is known. This method requires calculation of the extent of reaction, ξ . The extent of reaction can be obtained by performing material balance for any reactant or product for which the feed and product flow rates are known. The reference state is such that all reactant and product species are at 25° C and 1 atm in the states for which the heat of reaction is known (Figure 2.1).

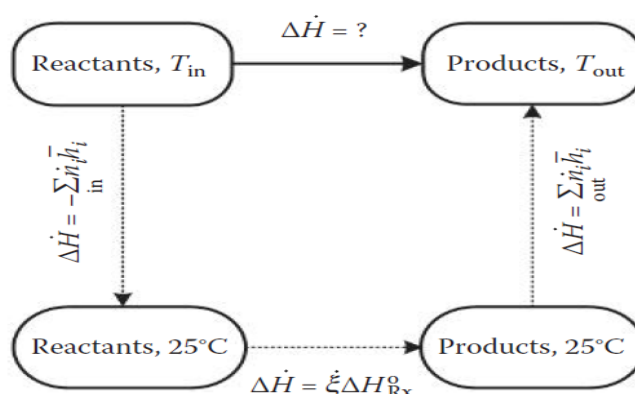


FIGURE 2.1 Rate of change in enthalpy for a reactive process.

For a single reaction at a reference state of 25°C and 1 atm while reactant and product are at different inlet and exit temperatures [4],

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

where h_i (J/mol) is the specific molar enthalpy of a definite component. For multiple reactions, where the reference state is 25° C and 1 atm and the inlet and exit streams are at temperatures other than the reference states,

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

A reference temperature other than 25° C can be considered in this case, and the heat of reaction should be calculated at the new reference state:

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

The heat of reaction at any temperature

$$\Delta H_{R_x} = \Delta H_{R_x}^o (25^\circ\text{C}) + \int_{25^\circ\text{C}} \Delta C_p dT$$

$$\text{where } \Delta C_p = \sum v_i C_{p,i}$$

2.3.2 Heat of Formation or Element Balance Method

In the heat of formation method, the heats of reaction terms (ΔH_{rxn}^o) are not required as they are implicitly included when heats of formation of the reactants are subtracted from the products [5]. For single and multiple reactions,

$$\Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

where h_i accounts for the change in molar enthalpy with T and phase + ΔH_f^o (Figure 2.2). In this case we find the enthalpy of all of the compounds relative to the elements at 25° C. No heat of reaction needs to be calculated at all. We then plug these enthalpies directly into the energy balance expression. In the absence of kinetic and potential energy, the energy balance equation is

$$Q - W = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

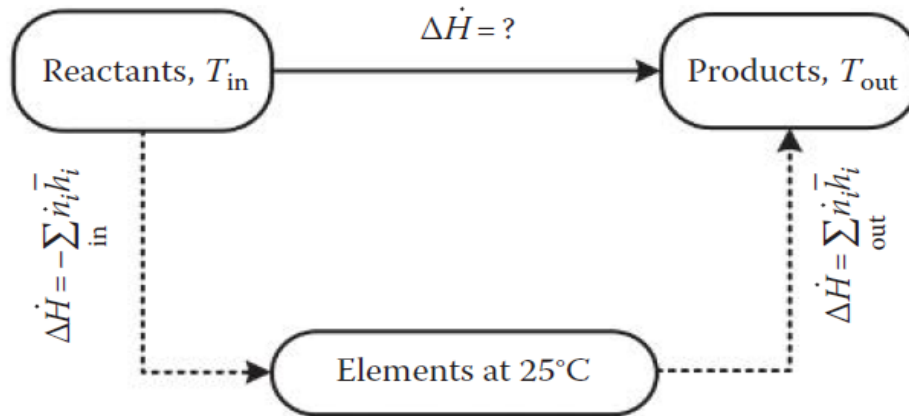


FIGURE 2.2

Heat of formation or element balance method.

where the specific molar enthalpy of component i in the inlet streams is

$$\bar{h}_{i,\text{in}} = \int_{25}^{T_{\text{in}}} C_{p,i} dT + \Delta H_{f,i}^\circ$$

Specific molar enthalpy of component i in the exit streams is

$$\bar{h}_{i,\text{out}} = \int_{25}^{T_{\text{out}}} C_{p,i} dT + \Delta H_{f,i}^\circ$$

2.4 Simultaneous Material and Energy Balances

Material balances could be written on either compound that requires the extent of reaction or their elements, which requires only balances without generation terms for each element. Similarly, we can also write down energy balances using either compounds or elements. From material balances with reaction that we had discussed, there are three methods of analyzing these types of reactive processes: atomic species balances, extents of reaction, and component balances. For energy balances with reaction, we have two methods for solving these types of problems: the heat of reaction method and the heat of formation method or element balance method.

Example 2.7 Gas Phase Reaction

Gas phase reaction is taking place in a continuous reactor. Stoichiometric proportions of CO₂ and H₂ are fed to the reactor at 400° C. The reaction proceeds to 80% completion. Given 1 mol of carbon dioxide, estimate the heat that must be provided or removed, if the gas exit streams are to be kept at 500° C. Perform the energy balance using the heat of reaction method at two reference temperatures (500° C and 25° C) and the heat of formation method.

Solution

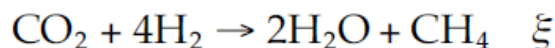
Known quantities: Inlet and exit temperatures, percent conversion, inlet flow rate of carbon dioxide and hydrogen.

Find: The amount of heat added or removed.

Analysis: The schematic diagram is shown in Example Figure 2.7.1.

Basis: 1 mol of CO₂ and 4 mol of H₂. The process flow diagram is shown in Example Figure 2.7.1.

Material balance (Extent of reaction method)



Component balance is calculated using the extent of reaction method as follows:

$$\text{CO}_2: n_{\text{CO}_2} = 1 - \xi$$

$$\text{H}_2: n_{\text{H}_2} = 4 - 4\xi$$

$$\text{CH}_4: n_{\text{CH}_4} = 0 + \xi$$

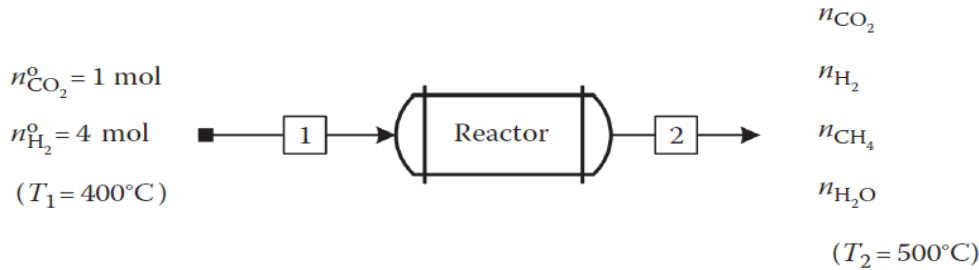
$$\text{H}_2\text{O}: n_{\text{H}_2\text{O}} = 0 + 2\xi$$

From the fractional conversion of CO₂,

$$f = \frac{n_{\text{CO}_2}^o - n_{\text{CO}_2}}{n_{\text{CO}_2}^o}$$

$$0.8 = \frac{1.0 - n_{\text{CO}_2}}{1.0}$$

$$n_{\text{CO}_2} = 1.0 - 0.8 = 0.2 \text{ mol}$$



EXAMPLE FIGURE 2.7.1 Process flow diagram of gas phase reaction.

Accordingly, the number of moles of carbon dioxide leaving the reactor is $n_{\text{CO}_2} = 0.2 \text{ mol}$.

The extent of reaction, ζ , is calculated by substituting $n_{\text{CO}_2} = 0.2 \text{ mol}$ in the CO_2 mole balance equation: $0.2 = 1 - \zeta$.

Solving for the extent of reaction, $\zeta = 0.8$.

To calculate moles of exit components, substitute values of the extent of reaction in the mole component balance equations given earlier. The following results are obtained:

$$n_{\text{H}_2} = 0.8, n_{\text{CH}_4} = 0.8, n_{\text{H}_2\text{O}} = 1.6$$

Energy balance (Heat of reaction method)

The energy balance is performed at two reference temperatures; exit stream temperature (500°C) and at the standard heat of reaction temperature (25°C). First, prepare the following data table using the polynomial form of the specific heat capacity:

$$C_p(\text{J/mol}^\circ\text{C}) = a + bT + cT^2$$

The standard heats of formation at 25°C can be obtained from Table A.2 (Appendix A.1). Components of heat capacity (Appendix A.2) and heats of formation (Table A.2):

Components	v_i	a	b	c	ΔH_f°
CO ₂	-1	36.11	0.04233	-2.887×10^{-5}	-393.5
H ₂	-4	28.84	0.0000765	0.3288×10^{-5}	00.00
H ₂ O	2	33.46	0.006880	0.7604×10^{-5}	-241.83
CH ₄	1	34.31	0.054690	0.3661×10^{-5}	-74.85
Δ		-50.24	0.025810	3.4600×10^{-5}	-165.00

Note: $\Delta = \text{CH}_4 + 2\text{H}_2\text{O} - 4\text{H}_2 - \text{CO}_2$

The ΔH_f° in the last column is for the heats of formation. The Δ in the last row is the difference between the product and reactants based on the stoichiometric coefficient; for example, the Δa is calculated as

$$\Delta a = \sum v_i a = -1 \times 36.11 - 4 \times 28.84 + 2 \times 33.46 + 34.31 = -50.24$$

The same method is used for calculating the values of Δb , Δc , and ΔH_f° .

Reference temperature = 500° C

In this approach, we perform the energy balance using the heat of reaction method at the reference temperature of 500° C: $T_{\text{ref}} = 500^\circ \text{C}$. This requires knowledge of the heat of reaction at 500° C. The energy balance for this process includes the sensible heat to change the temperature of everything in the inlet stream from 500° C to 400° C and the heat of reaction at 500° C times the extent of reaction. Recall that the heat of reaction was expressed in kilojoules per mole, where the mole basis was per molar extent of reaction:

$$Q = \xi \Delta H_{\text{Rx}}(T_{\text{ref}}) + H_{\text{out}} - H_{\text{in}}$$

For multiple input and exit components,

$$Q = \int_{500^\circ \text{C}}^{500^\circ \text{C}} \sum_{\text{out}} n_i C_{p_i} dT - \int_{500^\circ \text{C}}^{400^\circ \text{C}} \sum_{\text{in}} n_i^\circ C_{p_i} dT + \xi \Delta H_{\text{Rx}} \Big|_{500^\circ \text{C}}$$

Substituting the proper values,

$$Q = 0 + \int_{400^\circ \text{C}}^{500^\circ \text{C}} \sum_i n_i^\circ C_{p_i} dT + \xi \Delta H_{\text{Rx}} \Big|_{500^\circ \text{C}}$$

The heat of reaction at 500° C is then

$$\Delta H_{\text{Rx}}|_{500^{\circ}\text{C}} = \Delta H_{\text{Rx}}^{\circ} + \int_{25^{\circ}\text{C}}^{500^{\circ}\text{C}} \Delta C_p \, dT = \Delta H_{\text{Rx}}^{\circ} + \int_{25}^{500} (\Delta a + \Delta bT + \Delta cT^2) dT$$

The ΔC_p for the reaction is immediately obtained from the Δ row for use in integration from one temperature to another:

$$\begin{aligned} \Delta H_{\text{Rx}}|_{500^{\circ}\text{C}} &= -165 \text{ kJ/mol} + [(-50.24)(500 - 25) + \frac{1}{2}(0.02581)(500^2 - 25^2) \\ &\quad + \frac{1}{3}(3.46 \times 10^{-5})(500^3 - 25^3)] \frac{\text{J}}{\text{mol}} \frac{\text{kJ}}{1000 \text{ J}} = -184.6 \text{ kJ/mol} \end{aligned}$$

The heat of reaction at 500°C is

$$\Delta H_{\text{Rx}}|_{500^{\circ}\text{C}} = -184.6 \text{ kJ/mol}$$

Now the sensible heat term (first terms shown in the earlier equation) includes only the moles of those compounds in the inlet stream. This gives

$$\begin{aligned} H_{\text{in}} &= \int_{500^{\circ}\text{C}}^{400^{\circ}\text{C}} \sum_i n_i^{\circ} C_{p_i} dT = (1) \int_{500}^{400} C_{p_{\text{CO}_2}} dT \\ &\quad + (4) \int_{500}^{400} C_{p_{\text{H}_2}} dT = 1(-5) + 4(-2.95) \text{ kJ} = -16.80 \text{ kJ} \end{aligned}$$

$$H_{\text{out}} = \int_{500^{\circ}\text{C}}^{500^{\circ}\text{C}} \sum_i \dot{n}_i C_{p_i} dT = 0$$

So finally, substitute estimated inlet, exit enthalpies and heat of reaction in the general energy balance equation shown here:

$$Q = \xi \Delta H_{\text{Rx}} (T_{\text{ref}}) + H_{\text{out}} - H_{\text{in}}$$

$$Q = (0.8 \text{ mol}) (-184.6 \text{ kJ/mol}) + 0 - (-16.80 \text{ kJ}) = -131 \text{ kJ}$$

Reference temperature = 25° C

The energy balance for this process at this reference temperature includes the sensible heat to change the temperature of everything in the inlet stream from 25° C to 400° C and also to change everything in the product stream from 25° C to 500° C. Again, the

heat of reaction at 25° C must be multiplied by the extent of reaction. The heat of the process at 25° C is

$$Q = H_{\text{out}} - H_{\text{in}} + \xi \Delta H_{\text{Rx}}^{\circ} = \int_{25^{\circ}\text{C}}^{500^{\circ}\text{C}} \sum_{\text{out}} n_i C_{P_i} dT - \int_{25^{\circ}\text{C}}^{400^{\circ}\text{C}} \sum_{\text{in}} n_i^{\circ} C_{P_i} dT + \xi \Delta H_{\text{Rx}}^{\circ}$$

The enthalpy of inlet stream relative to reference temperature (25° C) is

$$\begin{aligned} H_{\text{in}} &= \int_{25^{\circ}\text{C}}^{400^{\circ}\text{C}} \sum_i n_i^{\circ} C_{P_i} dT = (1 \text{ mol}) \int_{25^{\circ}\text{C}}^{400^{\circ}\text{C}} C_{P_{\text{CO}_2}} dT \\ &\quad + (4 \text{ mol}) \int_{25^{\circ}\text{C}}^{400^{\circ}\text{C}} C_{P_{\text{H}_2}} dT = 16.35 + 43.54 = 59.89 \text{ kJ} \end{aligned}$$

The heat of reaction term at 25° C is found from the Δ term in the table for the heats of formation. Likewise, we have already found in method 1 that $\xi = 0.8 \text{ mol}$. Thus, the reaction term is

$$\xi \Delta H_{\text{Rx}}^{\circ} = (0.8 \text{ mol})(-165 \text{ kJ/mol}) = -132 \text{ kJ}$$

We can now calculate the sensible heat term for heating everything in the outlet stream from 25° C to 500° C. The enthalpy change of the outlet stream with respect to reference temperature (25° C) is

$$\begin{aligned} H_{\text{out}} &= \int_{25^{\circ}\text{C}}^{500^{\circ}\text{C}} \sum_i n_i C_{P_i} dT = (0.2 \text{ mol}) \int_{25}^{500} C_{P_{\text{CO}_2}} dT + (0.8 \text{ mol}) \int_{25}^{500} C_{P_{\text{H}_2}} dT \\ &\quad + (0.8 \text{ mol}) \int_{25}^{500} C_{P_{\text{CH}_4}} dT + (1.6 \text{ mol}) \int_{25}^{500} C_{P_{\text{H}_2\text{O}}} dT \end{aligned}$$

Integration of the earlier equation after substitution of components heat capacity yields

$$H_{\text{out}} = \int_{25^{\circ}\text{C}}^{500^{\circ}\text{C}} \sum_i n_i C_{P_i} dT = (4.27 + 11.06 + 18.48 + 27.22) \text{ kJ} = 61.03 \text{ kJ}$$

Finally, we obtain

$$\begin{aligned} Q &= H_{\text{out}} - H_{\text{in}} + \xi \Delta H_{\text{Rx}}^{\circ} = \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i^{\circ} \bar{h}_i + \xi \Delta H_{\text{Rx}}^{\circ} \\ &= 61.03 - 59.89 - 132 = -131 \text{ kJ} \end{aligned}$$

The heat transferred from the system is 131 kJ.

Heat of formation method (Element balance)

In this case, no heat of reaction needs to be calculated at all. We write the energy balance as follows:

$$Q = \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

Next, we compute the enthalpy of each component in each stream relative to their elements. The compound is formed from its elements at 25°C (this is the heat of formation), and then we raise the temperature of the compound up to the temperature of the stream.

The specific enthalpy of outlet compounds

$$\text{CH}_4 : \bar{h}_{\text{CH}_4} = \Delta H_f^\circ(25) + \int_{25^\circ\text{C}}^{500^\circ\text{C}} C_{P,\text{CH}_4} dT = -74.85 + 23.10 = -51.75 \text{ kJ/mol}$$

$$\text{H}_2\text{O} : \bar{h}_{\text{H}_2\text{O}} = \Delta H_f^\circ(25) + \int_{25^\circ\text{C}}^{500^\circ\text{C}} C_{P,\text{H}_2\text{O}} dT = -241.83 + 17.01 = -224.8 \text{ kJ/mol}$$

$$\text{CO}_2 : \bar{h}_{\text{CO}_2} = \Delta H_f^\circ(25) + \int_{25^\circ\text{C}}^{500^\circ\text{C}} C_{P,\text{CO}_2} dT = -393.5 + 21.34 = -372.2 \text{ kJ/mol}$$

$$\text{H}_2 : \bar{h}_{\text{H}_2} = 0 + \int_{25^\circ\text{C}}^{500^\circ\text{C}} C_{P,\text{H}_2} dT = 13.83 \text{ kJ/mol}$$

Thus, the sum of all of the outlet specific enthalpies is

$$H_{\text{out}} = \sum_{\text{out}} n_i \bar{h}_i = (0.2)(-372.2) + (0.8)(13.83) + (0.8)(-51.75) + (1.6)(-224.8) = -464.5 \text{ kJ}$$

The specific enthalpies of inlet compounds

$$\text{CO}_2 : h_{\text{CO}_2}^\circ = \Delta H_f^\circ + \int_{25^\circ\text{C}}^{400^\circ\text{C}} C_{P,\text{CO}_2} dT = -393.5 + 16.35 = -377.2 \text{ kJ/mol}$$

$$\text{H}_2 : h_{\text{H}_2}^\circ = 0 + \int_{25^\circ\text{C}}^{400^\circ\text{C}} C_{P,\text{H}_2} dT = 10.89 \text{ kJ/mol}$$

Thus, the sum of all of the inlet enthalpies is

$$H_{\text{in}} = \sum_{\text{in}} n_i h_i = (1)(-377.2) + (4)(10.89) = -333.6 \text{ kJ}$$

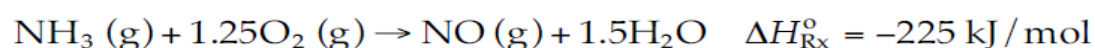
Finally, from the energy balance we obtain

$$Q = H_{\text{out}} - H_{\text{in}} = -464.5 \text{ kJ} + 333.6 \text{ kJ} = -131 \text{ kJ}$$

The heat calculated using the three methods are equal.

Example 2.8 Oxidation of Ammonia

Hundred moles per minute of ammonia (NH_3) and 200 mol/min of oxygen (O_2) 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 NH_3

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,

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

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; $n \cdot \text{NH}_3 = 0$

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

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_{pi} (J/mol.C) are

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

$$C_{p\text{NO}} = 29.5 + 0.008188T - 0.2925 \times 10^{-5}T^2$$

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

Substitute known values:

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

$$\times \left[75 \int_{25^\circ\text{C}}^{300^\circ\text{C}} C_{P\text{O}_2} dT + 100 \int_{25}^{300} C_{P\text{NO}} dT + 150 \int_{25}^{300} C_{P\text{H}_2\text{O}} dT \right]_{\text{out}}$$

$$- \frac{\text{kJ}}{1000 \text{ J}} \left[100 \int_{25}^{25} C_{P\text{NH}_3} dT + 200 \int_{25}^{25} C_{P\text{O}_2} dT \right]_{\text{in}}$$

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

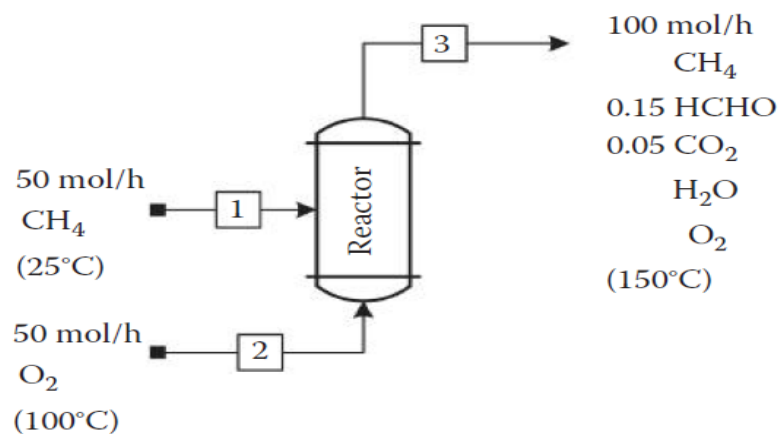
$$Q = \Delta \dot{H} = 100 \text{ mol} \left[\frac{-225 \text{ kJ}}{\text{mol}} \right] + [75(8.47) + 100(8.45) + 150(9.57)] - 0$$

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

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

Example 2.9 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.

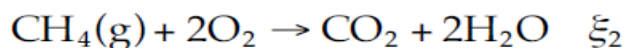
Find: Heat transfer rate from or to the system.

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, ΔH_{R1}° , is given by

$$\Delta H_{R1}^\circ = \Delta H_{f, H_2O(v)}^\circ + \Delta H_{f, HCHO(g)}^\circ - \Delta H_{f, CH_4(g)}^\circ$$

$$\Delta H_{R1}^\circ = (-241.83) + (-115.9) - (-74.85) = -282.88 \text{ kJ/mol}$$

The standard heat of the second reaction, ΔH_{R2}° , is given by

$$\Delta H_{R2}^\circ = 2\Delta H_{f, H_2O(v)}^\circ + \Delta H_{f, CO_2(g)}^\circ - \Delta H_{f, CH_4(g)}^\circ$$

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

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

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

$$C_{pCH_4} = 34.31 + 0.05469T + 0.3661 \times 10^{-5}T^2$$

$$C_{pHCHO} = 34.28 + 0.04268T$$

$$C_{pCO_2} = 36.11 + 0.04233T - 2.887 \times 10^{-5}T^2$$

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

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

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

$$Q = \dot{\xi}_1 \Delta H_{R1}^\circ + \dot{\xi}_2 \Delta H_{R2}^\circ + \left\{ \dot{n}_{CH_4} \bar{h}_{CH_4} + \dot{n}_{HCHO} \bar{h}_{HCHO} + \dot{n}_{CO_2} \bar{h}_{CO_2} + \dot{n}_{H_2O} \bar{h}_{H_2O} + \dot{n}_{O_2} \bar{h}_{O_2} \right\}_{\text{out}} - \left\{ \dot{n}_{CH_4} \bar{h}_{CH_4} + \dot{n}_{O_2} \bar{h}_{O_2} \right\}_{\text{in}}$$

Substitute known quantities:

$$\begin{aligned}
 Q = \Delta \dot{H} = \dot{\xi}_1 \Delta H_{R \times 1}^o + \dot{\xi}_2 \Delta H_{R \times 2}^o + & \left\{ 30 \int_{25^\circ \text{C}}^{150^\circ \text{C}} C_{P \text{CH}_4} dT \right. \\
 & + 15 \int_{25}^{150} C_{P \text{HCHO(g)}} dT + 5 \int_{25}^{150} C_{P \text{CO}_2} dT + 25 \int_{25}^{150} C_{P \text{H}_2\text{O}} dT \\
 & \left. + 25 \int_{25}^{150} C_{P \text{O}_2} dT \right\} - \left\{ 50 \int_{25}^{25} C_{P \text{CH}_4} dT + 50 \int_{25}^{100} C_{P \text{O}_2} dT \right\}
 \end{aligned}$$

Substituting the expressions of the heat capacities and integrating,

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

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

Example 2.10 Methane Combustion

Problem

Methane and oxygen are fed in stoichiometric proportions to a continuous reactor at 25°C and 1 atm. The reaction proceeds to completion and the effluent stream is found to be at 200°C . Calculate the heat transfer rate from the reactor. On the basis of 1 mol of methane set up an energy balance using the elements balance approach. The combustion reaction of methane is as follows:

Solution

Known quantities: Inlet temperature and pressure, stoichiometric proportions of feed.

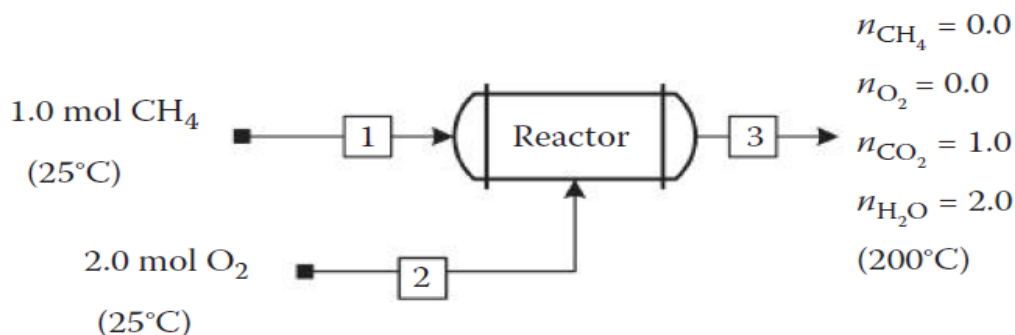
Find: Heat transfer rate from the reactor, Q .

Analysis: Start by calculating the enthalpy at the stream condition for each individual compound in each stream relatively to the elements at 25°C . We then plug these enthalpies into the normal energy balance expression.

Material balance:

Basis: 1 mol/s of methane and 2 mol/s of oxygen

Since the reaction goes to completion and the feed enters the reactor in stoichiometric proportions, the exit molar flow rate of methane and oxygen are zero. Based on the balance reaction stoichiometry for 1 mol of carbon dioxide reacted, 1 mol of carbon dioxide and 2 mol of water are produced.



EXAMPLE FIGURE 2.10.1: Schematic of a methane combustion reactor.

The schematic diagram of the combustion process is shown in Example Figure 2.10.1.

Energy balance:

The specific molar flow rate and molar enthalpies of inlet and exit components are arranged in the following table:

Species	n_{in}	h_{in}	n_{out}	h_{out}
CH ₄	1	$\bar{h}_{CH_4}(T_1)$	0	—
O ₂	2	$\bar{h}_{O_2}(T_2)$	0	—
CO ₂	0	—	1	$\bar{h}_{CO_2}(T_3)$
H ₂ O	0	—	2	$\bar{h}_{H_2O}(T_3)$

From the following data

$$\Delta H_{f,CH_4}^\circ = -74.85 \text{ kJ/mol}$$

$$\Delta H_{f,CO_2}^\circ = -393.5 \text{ kJ/mol}$$

$$\Delta H_{f,H_2O}^\circ = -241.83 \text{ kJ/mol}$$

$$C_{p,CO_2} \text{ (J/mol}^\circ\text{C)} = 36.11 + 0.04233T - 2.887 \times 10^{-5}T^2$$

$$C_{p,H_2O} \text{ (J/mol}^\circ\text{C)} = 33.46 + 0.00688T + 0.7604 \times 10^{-5}T^2$$

The general energy balance equation is

$$Q = \sum_{\text{out}, 200^{\circ}\text{C}} \dot{n}_i \bar{h}_i - \sum_{\text{in}, 25^{\circ}\text{C}} \dot{n}_i^{\circ} \bar{h}_i = \left[\dot{n}_{\text{CO}_2} \bar{h}_{\text{CO}_2} + \dot{n}_{\text{H}_2\text{O}} \bar{h}_{\text{H}_2\text{O}} \right]_{\text{out}} - \left[\dot{n}_{\text{CH}_4} \bar{h}_{\text{CH}_4} + \dot{n}_{\text{O}_2} \bar{h}_{\text{O}_2} \right]_{\text{in}}$$

Specific molar enthalpy of inlet streams at $T_1 = 25^{\circ}\text{C}$ is

$$\text{CH}_4: \bar{h}_{\text{CH}_4}(T_1) = \Delta H_{f,\text{CH}_4}^{\circ} + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} C_{p,\text{CH}_4} dT = -74.85 \text{ kJ/mol} + 0 = -74.85 \text{ kJ/mol}$$

Specific molar enthalpy of inlet oxygen at $T_2 = 25^{\circ}\text{C}$ is

$$\text{O}_2: \bar{h}_{\text{O}_2}(T_2) = 0 + \int_{25^{\circ}\text{C}}^{25^{\circ}\text{C}} C_{p,\text{O}_2} dT = 0 + 0 = 0$$

Specific molar enthalpies of the exit streams at $T_3 = 200^{\circ}\text{C}$ are

$$\begin{aligned} \text{CO}_2: \bar{h}_{\text{CO}_2}(T_3) &= \Delta H_{f,\text{CO}_2}^{\circ} + \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^{\circ}\text{C}}^{200^{\circ}\text{C}} C_{p,\text{CO}_2} dT = -393.5 + 7.08 \\ &= -386.42 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \text{H}_2\text{O}: \bar{h}_{\text{H}_2\text{O}}(T_3) &= \Delta H_{f,\text{H}_2\text{O}}^{\circ} + \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^{\circ}\text{C}}^{200^{\circ}\text{C}} C_{p,\text{H}_2\text{O}} dT = -241.83 + 6.01 \\ &= -235.82 \text{ kJ/mol} \end{aligned}$$

Using the values calculated by the procedures shown earlier, we simply plug the values of specific enthalpies into the general energy balance equation using the element balance approach:

$$Q = \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i$$

Substitute the calculated values of specific enthalpies:

$$Q = \left[\dot{n}_{\text{CO}_2} \bar{h}_{\text{CO}_2} + \dot{n}_{\text{H}_2\text{O}} \bar{h}_{\text{H}_2\text{O}} \right]_{\text{out}} - \left[\dot{n}_{\text{CH}_4} \bar{h}_{\text{CH}_4} + \dot{n}_{\text{O}_2} \bar{h}_{\text{O}_2} \right]_{\text{in}}$$

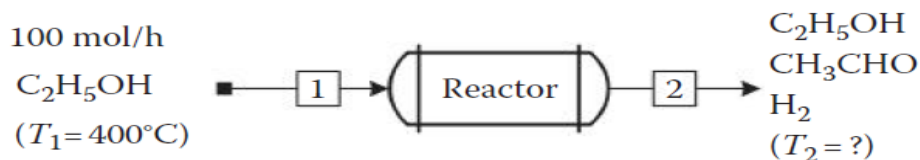
$$Q = \left[1(-386.42) + 2(-235.82) \right] - \left[1(0) + 1(-74.85) \right] = -783.21 \text{ kJ/s}$$

2.4.1 Unknown Process Exit Temperature

Another set of problems involves the calculation of outlet temperature when the inlet conditions and heat input or output are specified. These types of problems require that the enthalpies be evaluated in terms of the unknown outlet temperature. The resulting enthalpy expressions are then substituted into the general energy balance equation and solved for the outlet temperature. The following example explains this case.

Example 2.11 Dehydrogenation of Ethanol Problem

Dehydrogenation of ethanol to form acetaldehyde is carried out in an adiabatic reactor. Hundred moles per hour of ethanol at 400°C is fed to a continuous reactor. The reactor conversion is 30%. The gas average heat capacities of $\text{C}_2\text{H}_5\text{OH}$, CH_3CHO , and H_2 are 78, 96, and 29 (J/mol K), respectively. Calculate the reactor exit stream temperature. The following reaction takes place in gas phase:



EXAMPLE FIGURE 2.11.1: Ethanol dehydration process, reactor system.

Solution

Known quantities: Inlet ethanol molar flow rate, temperature, and percent conversion.

Find: The product stream temperature.

Analysis: The exit temperature is unknown, so a simultaneous material and energy balance is required. The schematic diagram of the dehydrogenation process is shown in Example Figure 2.11.1.

Basis: One hour of operation, accordingly all calculated flow rates are on per one hour basis.

Material balance

Using the extent of reaction method,

$$n_{\text{C}_2\text{H}_5\text{OH}} = 100 - \xi$$

$$n_{\text{CH}_3\text{CHO}} = 0 + \xi$$

$$n_{\text{H}_2} = 0 + \xi$$

A 30% conversion of methanol is achieved:

$$0.3 = \frac{100 - n_{\text{C}_2\text{H}_5\text{OH}}}{100} \Rightarrow n_{\text{C}_2\text{H}_5\text{OH}} = 70 \text{ mol}$$

Substitute known values ($n_{\text{C}_2\text{H}_5\text{OH}}$) in the ethanol mole balance equation:

$$70 = 100 - \xi \Rightarrow \xi = 30 \text{ mol}$$

Substitute the extent of reaction in the material balance equations to get the following results:

$$n_{\text{C}_2\text{H}_5\text{OH}} = 70 \text{ mol}, n_{\text{CH}_3\text{CHO}} = 30 \text{ mol}, n_{\text{H}_2} = 30 \text{ mol}$$

Energy balance:

Reference temperature: 25° C

Using the heat of reaction approach, the general energy balance equation is

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

The standard heat of reaction is calculated from the heats of formation as follows:

$$\Delta H_{\text{Rx}}^{\circ} = \Delta H_{\text{f}, \text{H}_2}^{\circ} + \Delta H_{\text{f}, \text{CH}_3\text{CHO}}^{\circ} - \Delta H_{\text{f}, \text{C}_2\text{H}_5\text{OH}}^{\circ}$$

Substituting tabulated standard heat of formation values (from the appendix) yields

$$\Delta H_{\text{Rx}}^{\circ} = 0 + (-166.2) - (-235.31) = 69.11 \text{ kJ/mol}$$

Open system, adiabatic process, no change in potential and kinetic energy, accordingly the general energy balance is simplified to the following form:

$$Q = \Delta H \cdot = 0.$$

The change in enthalpy is a function of heat of reaction and sensible heat as follows:

$$0 = \xi \Delta H_{\text{Rx}}^{\circ} + \left\{ n_{\text{C}_2\text{H}_5\text{OH}} \bar{h}_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{CH}_3\text{CHO}} \bar{h}_{\text{CH}_3\text{CHO}} + n_{\text{H}_2} \bar{h}_{\text{H}_2} \right\}_{\text{out}, T_2=?} - \left\{ n_{\text{C}_2\text{H}_5\text{OH}} \bar{h}_{\text{C}_2\text{H}_5\text{OH}} \right\}_{\text{in}, 400^{\circ}\text{C}}$$

Substituting specific molar enthalpies in terms of heat capacities,

$$0 = \xi \Delta H_{\text{Rx}}^{\circ} + \left\{ n_{\text{C}_2\text{H}_5\text{OH}} \int_{25}^{T_2} C_{\text{P}_{\text{C}_2\text{H}_5\text{OH}}} dT + n_{\text{CH}_3\text{CHO}} \int_{25}^{T_2} C_{\text{P}_{\text{CH}_3\text{CHO}}} dT + n_{\text{H}_2} \int_{25}^{T_2} C_{\text{P}_{\text{H}_2}} dT \right\} \\ - \left\{ n_{\text{C}_2\text{H}_5\text{OH}} \int_{25^{\circ}\text{C}}^{400^{\circ}\text{C}} C_{\text{P}_{\text{C}_2\text{H}_5\text{OH}}} dT \right\}$$

Substitute the values of the molar flow rates of inlet and exit components and heat capacities of each component:

$$0 = 30 \times 69.11 \text{ kJ/mol} + \{70 \times 78(T_2 - 25) + 30 \times 96(T_2 - 25) \\ + 30 \times 29(T_2 - 25)\} - \{100 \times 78(400 - 25)\}$$

Rearranging by taking $(T_2 - 25)$ as common factor,

$$0 = 30 \times 69.11 \frac{\text{kJ}}{\text{mol}} \frac{1000 \text{ J}}{\text{kJ}} + (T_2 - 25) \{70 \times 78 + 30 \times 96 + 30 \times 29\} \\ - \{100 \times 78(400 - 25)\}$$

Simplifying and rearranging leads to the following value of reactor exit temperature:

$$T_2 = \frac{851,700}{9210} + 25 = 117.5^{\circ}\text{C}$$

Example 9.12 Methanol Dehydrogenation

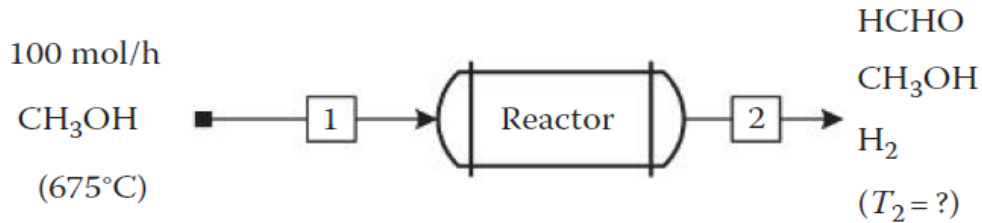
Problem

Hundred moles per hour of methanol at 675°C and 1 bar is fed to an adiabatic reactor, where 25% of it is dehydrogenated to formaldehyde. Calculate the temperature of the gases leaving the reactor, assuming constant average heat capacities of 17, 12, and $7 \text{ cal/mol } ^{\circ}\text{C}$ for methanol, formaldehyde, and hydrogen, respectively. The dehydrogenation of methanol proceeds according to the following reaction:



The heats of formation in kcal/mol are as follows:

$$\Delta H_{\text{f,HCHO}}^{\circ} = -27.7 \text{ kcal/mol}, \quad \Delta H_{\text{f,CH}_3\text{OH}}^{\circ} = -48.08 \text{ kcal/mol}$$



EXAMPLE FIGURE 2.12.1: Formaldehyde production in an adiabatic reactor.

Solution

Known quantities: Inlet temperature, pressure, and molar flow rate are known.

Find: Exit stream temperature.

Analysis: The process flow sheet is shown in Example Figure 2.12.1. In the solution of this example, use the extent of reaction method.

Material balance

Basis: 100 mol/h of methanol

The extent of reaction method is used to calculate exit number of moles:

$$\text{HCHO: } \dot{n}_{\text{HCHO}} = 0 + \xi$$

$$\text{CH}_3\text{OH: } \dot{n}_{\text{CH}_3\text{OH}} = 100 - \xi$$

$$\text{H}_2: \dot{n}_{\text{H}_2} = 0 + \xi$$

The single-pass conversion of methanol

$$f = 0.25 = \frac{100 - \dot{n}_{\text{CH}_3\text{OH}}}{100}, \quad \dot{n}_{\text{CH}_3\text{OH}} = 75 \text{ mol/h}$$

Substitute $n \cdot \text{CH}_3\text{OH} = 75 \text{ mol/h}$ in the methanol balance equation and calculate the extent of reaction: $\xi = 25 \text{ mol/h}$. Substitute the extent of reaction in the formaldehyde and hydrogen mole balance equation to get the following results:

$$\dot{n}_{\text{HCHO}} = 25 \text{ mol/h}, \quad \dot{n}_{\text{CH}_3\text{OH}} = 75 \text{ mol/h}, \quad \dot{n}_{\text{H}_2} = 25 \text{ mol/h}$$

Energy balance

The system is open so the first law of thermodynamics for open systems is used as follows:

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

Neglecting kinetic and potential energies, no shaft work is done, and the reactor is adiabatic. The energy balance equation is simplified to the following form:

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

The enthalpy consists of enthalpy of reaction and the sensible heat:

$$0 = \Delta H = \xi \Delta H_{\text{Rx}}(T_{\text{ref}}) + \sum_{\text{product}} n_i \int_{T_{\text{ref}}}^{T_{\text{out}}} C_{\text{pi}} dT - \sum_{\text{reactant}} n_i \int_{T_{\text{ref}}}^{T_{\text{in}}} C_{\text{pi}} dT$$

Reference temperature = 675°C

$$\Delta \dot{H} = \xi \Delta H_{\text{Rx}}|_{675^\circ\text{C}} + \sum_{\text{product}} n_i \int_{675^\circ\text{C}}^T C_{\text{pi}} dT - \sum_{\text{reactant}} n_i \int_{675^\circ\text{C}}^{675^\circ\text{C}} C_{\text{pi}} dT$$

The heat capacity of this problem is constant and the effect of temperature on the heat capacity is negligible:

$$\Delta H_{\text{Rx}}|_{675^\circ\text{C}} = \Delta H_{\text{Rx}}^\circ + \Delta C_p (675 - 25)$$

The standard heat of reaction at 25°C is

$$\begin{aligned} \Delta H_{\text{Rx}}^\circ &= \Delta H_{\text{f}, \text{HCHO}}^\circ + \Delta H_{\text{f}, \text{H}_2}^\circ - \Delta H_{\text{f}, \text{CH}_3\text{OH}}^\circ = -27.7 + 0 - (-48.08) \\ &= 20.38 \text{ kcal/mol} \end{aligned}$$

The change in the heat capacity, ΔC_p , is given by

$$\Delta C_p = C_{\text{pH}_2} + C_{\text{pHCHO}} - C_{\text{pCH}_3\text{OH}}$$

Substituting known values to calculate the heat of reaction at 675°C,

$$\begin{aligned} \Delta H_{\text{Rx}}|_{675^\circ\text{C}} &= 20.38 \text{ kcal/mol} + (7 + 12 - 17) \left[\frac{1 \text{ kcal}}{1000 \text{ cal}} \right] (675 - 25) \\ &= 21.68 \text{ kcal/mol} \end{aligned}$$

The rate of change in enthalpy is

$$\Delta \dot{H} = \xi \Delta H_{\text{Rx}}|_{675^\circ\text{C}} + (n_{\text{HCHO}} C_{\text{pHCHO}} + n_{\text{CH}_3\text{OH}} C_{\text{pCH}_3\text{OH}} + n_{\text{H}_2} C_{\text{pH}_2}) (T_2 - 675) - 0$$

Substitute the extent of reaction, heat of reaction, and heat capacities to calculate the exit temperature:

$$0 = 25 \times 21.68 \text{ kcal/mol} + (25 \times 12 + 75 \times 17 + 25 \times 7) \left(\frac{1 \text{ kcal}}{1000 \text{ cal}} \right) (T_2 - 675)$$

Rearranging and simplifying,

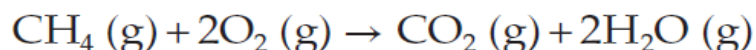
$$0 = 542 + 1.75(T_2 - 675)$$

Solving for T ,

$$T = 365.3^\circ\text{C}$$

2.5 Combustion Processes

Combustion or burning is an exothermic chemical reaction between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species [4]. For example, the complete combustion of methane is given by the following reaction:



The result is carbon dioxide and water vapor, with a standard enthalpy of reaction at 25° C and 1 atm being -242 kJ/mol; complete combustion is almost impossible to achieve. As actual combustion reactions come to equilibrium, a wide variety of major and minor species will be present, such as carbon monoxide. Total inlet oxygen is the sum of the theoretical oxygen and excess oxygen. The equation for percent excess air is as follows:

$$\% \text{ excess air} = \frac{(\text{moles of air})_{\text{fed}} - (\text{moles of air})_{\text{theoretical}}}{(\text{moles of air})_{\text{theoretical}}}$$

Theoretical oxygen is the calculated amount of oxygen required to oxidize a compound to its final oxidation products. In the methane oxidation reaction, 2 mol of oxygen is required to oxidize 1 mol of methane. For 100 mol of CH₄ the theoretical oxygen is calculated as follows:

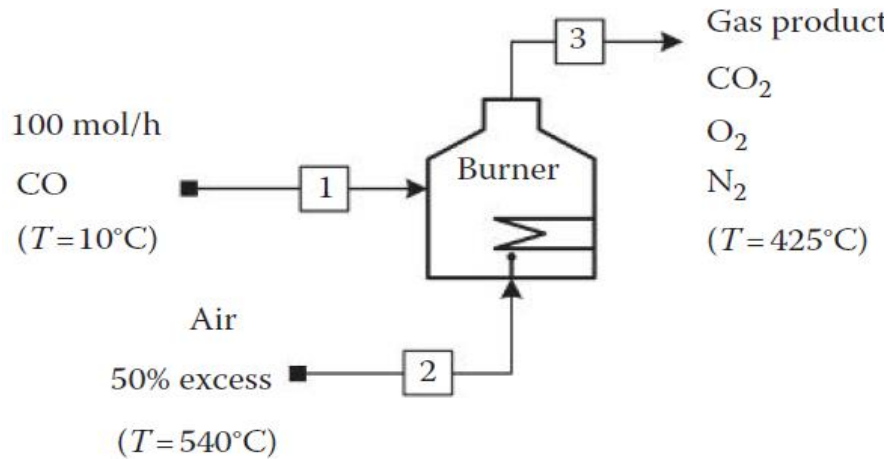
$$\text{Theoretical oxygen demand} = 100 \text{ mol CH}_4 \times \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} = 200 \text{ mol of O}_2$$

If the oxygen fed to the reactor is in excess amount than the theoretical oxygen, then the percent excess oxygen is

$$\% \text{ excess O}_2 = \frac{(\text{moles of O}_2)_{\text{fed}} - (\text{moles of O}_2)_{\text{theoretical}}}{(\text{moles of O}_2)_{\text{theoretical}}}$$

Example 2.13 Combustion of Carbon Monoxide Problem

Carbon monoxide (CO) at 10° C is completely burned at 1 atm pressure with 50% excess air that is fed to a burner at a temperature of 540° C. The combustion products leave the burner chamber at a temperature of 425° C. Given 100 mol/h of carbon monoxide, calculate the heat evolved from the burner.



EXAMPLE FIGURE 2.13.1: Schematic of the combustion of carbon monoxide.

Solution

Known quantities: CO and air inlet temperature and pressure, complete combustion, 50% excess air.

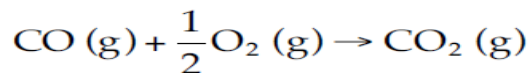
Find: Heat evolved from the burner.

Analysis: Perform material balance and then energy balance.

Material balance

Basis: 100 mol/h of inlet CO

The following reaction takes place in the burner:



The schematic diagram of the burning process is shown in Example Figure 2.13.1.

$$\text{Theoretical O}_2: 100 \text{ mol/h CO} \left(\frac{0.5 \text{ mol O}_2}{1 \text{ mol CO}} \right) = 50 \text{ mol/h O}_2$$

Total inlet oxygen is the sum of the theoretical oxygen and excess oxygen. For 50% excess air, the total inlet oxygen is the theoretical plus excess oxygen:

$$\dot{n}_{\text{O}_2}^{\text{o}} = 1.0(50 \text{ mol O}_2) + 0.5(50 \text{ mol O}_2) = 75 \text{ mol/h O}_2$$

Nitrogen is inert and the total inlet nitrogen is the number of moles of nitrogen in the air associated with the 75 mol of oxygen. That is,

$$\dot{n}_{\text{N}_2}^{\text{o}} = \frac{79}{21} \times \text{Total inlet oxygen} = \frac{79}{21} \times 75 \text{ mol} = 282 \text{ mol/h N}_2$$

Since the reaction goes to completion (i.e., complete composition), no carbon monoxide leaves the reactor, all is burned. Mole balance of carbon monoxide (CO) is calculated using the extent of reaction method:

$$n_{\text{CO}} = n_{\text{CO}}^{\circ} - \xi$$

$$0 = 100 - \xi \Rightarrow \xi = 100 \text{ mol}$$

Component mole balance

$$\text{CO}_2: n_{\text{CO}_2} = 0 + \xi$$

$$\text{O}_2: n_{\text{O}_2} = n_{\text{O}_2}^{\circ} - 0.5\xi$$

$$\dot{n}_{\text{O}_2} = 75 - 0.5 \times 100 = 25 \text{ mol/h}$$

The exit number of moles of carbon dioxide is 100 mol; $n_{\text{CO}_2} = 100 \text{ mol}$. Nitrogen is an inert gas and is not involved in the reaction. Accordingly, the inlet number of moles equals the exit number of moles:

$$\dot{n}_{\text{N}_2} = 282 \text{ mol/h}$$

Energy balance

Reference temperature, $T_{\text{ref}} = 25^{\circ} \text{ C}$

The standard heat of reaction is calculated as

$$\Delta H_{\text{Rx}}^{\circ} = \Delta H_{\text{f}, \text{CO}_2}^{\circ} - \Delta H_{\text{f}, \text{CO}}^{\circ} - \frac{1}{2} \Delta H_{\text{f}, \text{O}_2}^{\circ}$$

$$\Delta H_{\text{Rx}}^{\circ} = -393.5 \text{ kJ/mol} - (-110.52 \text{ kJ/mol}) - 0 = -282.98 \text{ kJ/mol}$$

Heat capacities C_p (J/mol.C) as a function of temperature of components involved in the process are

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

$$C_{p\text{N}_2} = 29 + 0.002199T + 0.5723 \times 10^{-5} T^2$$

$$C_{p\text{CO}} = 28.95 + 0.00411T + 0.3548 \times 10^{-5} T^2$$

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

Enthalpies of inlet components:

The enthalpies of inlet components are defined from the following expressions. The integration is from the reference temperature to the inlet temperature.

Specific molar enthalpy of oxygen is obtained as follows

$$\bar{h}_{\text{in}}(\text{O}_2) = \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^\circ\text{C}}^{540^\circ\text{C}} C_{\text{P O}_2} dT = 16.38 \text{ kJ/mol}$$

Specific inlet enthalpy of nitrogen is calculated as follows:

$$\bar{h}_{\text{in}}(\text{N}_2) = \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^\circ\text{C}}^{540^\circ\text{C}} C_{\text{P N}_2} dT = 15.49 \text{ kJ/mol}$$

Specific inlet enthalpy of carbon monoxide is obtained as follows:

$$\bar{h}_{\text{in}}(\text{CO}) = \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^\circ\text{C}}^{10^\circ\text{C}} C_{\text{P CO}} dT = -0.4353 \text{ kJ/mol}$$

Enthalpies of exit components:

The enthalpies of exit components are defined from the following expressions. The integration is from the reference temperature to the exit temperature:

$$\text{Oxygen: } \bar{h}_{\text{out}}(\text{O}_2) = \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^\circ\text{C}}^{425^\circ\text{C}} C_{\text{P O}_2} dT = 12.54 \text{ kJ/mol}$$

$$\text{Nitrogen: } \bar{h}_{\text{out}}(\text{N}_2) = \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^\circ\text{C}}^{425^\circ\text{C}} C_{\text{P N}_2} dT = 11.92 \text{ kJ/mol}$$

$$\text{Carbon dioxide: } \bar{h}_{\text{out}}(\text{CO}_2) = \frac{1 \text{ kJ}}{1000 \text{ J}} \int_{25^\circ\text{C}}^{425^\circ\text{C}} C_{\text{P CO}_2} dT = 17.58 \text{ kJ/mol}$$

Summary of the calculated enthalpies is shown in the following table:

Compound i	$\dot{n}_{i, \text{in}}$ (mol/h)	$\bar{h}_{i, \text{in}}$ (kJ/mol)	$\dot{n}_{i, \text{out}}$ (mol/h)	$\bar{h}_{i, \text{out}}$ (kJ/mol)
O ₂	75	16.38	25	12.54
N ₂	282	15.49	282	11.92
CO	100	-0.44	0	—
CO ₂	0	—	100	17.58

The heat removed from the burner, Q , is given by

$$Q = \Delta H = \xi \Delta H_r^\circ + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

Substituting inlet and exit moles multiplied by specific enthalpies of inlet and exit streams, respectively, from the table in the earlier equation yields the heat released from the burner, Q :

$$Q = \xi \times \Delta H_{R_x}^{\circ} + \left\{ \dot{n}_{O_2} \bar{h}_{O_2} + \dot{n}_{N_2} \bar{h}_{N_2} + \dot{n}_{CO_2} \bar{h}_{CO_2} \right\}_{out} - \left\{ \dot{n}_{O_2} \bar{h}_{O_2} + \dot{n}_{N_2} \bar{h}_{N_2} + \dot{n}_{CO} \bar{h}_{CO} \right\}_{in}$$

Substitute component specific enthalpies:

$$Q = 100 \times (-282.98 \text{ kJ/mol}) + \left\{ 25(12.54) + 282(11.92) + 100(17.58) \right\} - \left\{ 75(16.38) + 282(15.49) + 100(-0.44) \right\}$$

The heat lost from the reactor is

$$Q = -284,177 \text{ kJ/h} (-78.94 \text{ kW})$$

The negative sign indicates that heat is released from the process.

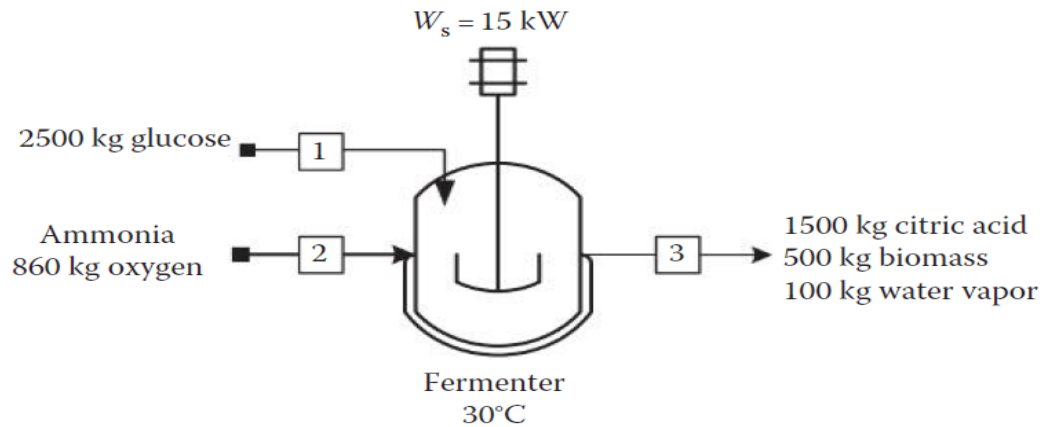
2.6 Energy Balance in Bioprocesses

Energy contributions of bioprocesses contributions to sensible heat are insignificant compared with the total magnitude of $\Delta H_{R_x}^{\circ}$ and can, therefore, be ignored without much loss of accuracy. This situation is typical of most reactions in bioprocessing where the actual temperature of reaction is not significantly different from 25° C [5-7].

Example 2.14 Fermentation and Citric Acid Production Problem

An amount of 2500 kg of glucose and 860 kg of oxygen are consumed to produce 1500 kg citric acid, 500 kg biomass, and other products. Ammonia is used as a nitrogen source. Power input to the system by mechanical agitation of the broth is about 15 kW; approximately 100 kg water is evaporated during the culture period. Estimate the cooling requirements during 2 days of operation. The latent heat of evaporation of water at 30° C is 2430.7 kJ/kg. The heat of reaction at 30° C is -460 kJ/mol O₂ consumed. The batch reactor operates at 30° C. The reaction taking place in the fermenter is given by





EXAMPLE FIGURE 2.14.1: Production of a citric acid fermenter.

Solution

Known quantities: Inlet flow and exit mass flow rate, shaft work, fermenter initial temperature.

Find: Heat transfer from the reactor.

Analysis: The reaction that takes place in the current fermentation process (Example Figure 2.14.1) follows the reaction shown above

The general energy balance equation is

$$Q - W_s = \xi \Delta H_{\text{reaction}} + m_v \Delta H_v$$

Heat released due to the reaction is

$$\xi \Delta H_{\text{reaction}} = 860 \text{ kg O}_2 \text{ consumed} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| \left| \frac{1 \text{ mol}}{32 \text{ g}} \right| \left(\frac{-460 \text{ kJ}}{\text{mol}} \right) = -1.24 \times 10^7 \text{ kJ}$$

Heat needed for evaporation is

$$m_v \Delta H_v = (100 \text{ kg})(2430.7 \text{ kJ/kg}) = 2.43 \times 10^5 \text{ kJ}$$

The system shaft work is expressed as

$$W_s = \left(-15 \frac{\text{kJ}}{\text{s}} \right) (2 \text{ days}) \frac{3600 \text{ s}}{1 \text{ h}} \left| \frac{24 \text{ h}}{1 \text{ day}} \right| = -2.59 \times 10^6 \text{ kJ}$$

The general energy balance equation is

$$Q - W_s = \xi \Delta H_{\text{rxn}} + m_v \Delta H_v$$

Substitute known quantities to yield

$$Q - (-2.59 \times 10^6 \text{ kJ}) = -1.24 \times 10^7 \text{ kJ} + 2.43 \times 10^5 \text{ kJ}$$

$$Q = -1.475 \times 10^7 \text{ kJ}$$

The negative sign indicates that heat is removed from the system.

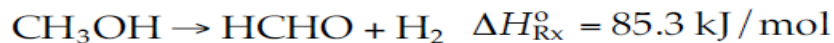
2.7 Energy Balance in Membrane Reactors

A membrane reactor is actually just a plug-flow reactor that contains an additional cylinder of some porous material within it. Its configuration is similar to that of a shell-and-tube heat exchanger, with a tube within the shell of the exchanger. This porous inner cylinder is the membrane that gives the membrane reactor its name.

Example 2.15 Membrane Reactor

Problem

A membrane reactor is used to produce formaldehyde by dehydrogenation of methanol. The conversion of methanol to formaldehyde takes place on the tube side of the membrane, which is an endothermic reaction:



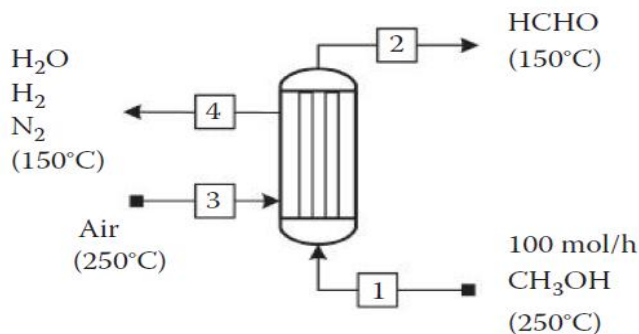
The following side reaction takes place as well on the shell side of the membrane. The reaction is exothermic and its heat is utilized to preserve the temperature of the gas stream at 150° C:



Methanol vapor stream at a flow rate of 100 mol/min and 250° C enters the tube side of the membrane. Assume that the entire methanol reacts to form formaldehyde and the whole produced hydrogen penetrates through the membrane tube walls to the shell side where sufficient amount of it is burned on the shell side. Sufficient amount of oxygen from air is supplied and reacts completely with the hydrogen. How much hydrogen must be burned to keep the reactor effluent temperature at 150° C? What is the molar flow rate of the stream leaving the reactor?

Data:

The average molar heat capacities of the various materials in this temperature range are: CH₃OH = 0.0568 kJ/(mol ° C), HCHO = 0.0380 kJ/(mol ° C), H₂ = 0.0289 kJ/(mol ° C), O₂ = 0.0309 kJ/(mol ° C), N₂ = 0.0296 kJ/(mol ° C), and H₂O = 0.0341 kJ/(mol ° C).



of 150° C. The schematic diagram of the membrane reactor is shown in Example Figure 9.15.1. The hydrogen reaction takes place on the shell side with sufficient amount of oxygen associated with inlet air. All inlet oxygen is consumed.

Solution

Known quantities: Inlet flow of methanol, complete conversion of methanol, and inlet oxygen.

Find: Amount of hydrogen burned to keep the membrane effluent streams at 150° C.

Analysis: First we need to determine how much heat is required for the methanol to formaldehyde reaction to be kept at the temperature of 150° C. The schematic diagram of the membrane reactor is shown in Example Figure 2.15.1. The hydrogen reaction takes place on the shell side with sufficient amount of oxygen associated with inlet air. All inlet oxygen is consumed.

Material balance (tube side):

The exit stream from the tube side contains formaldehyde, and hydrogen penetrates membrane walls to the shell side; since complete reaction is achieved, 100 mol/min of formaldehyde leave the tube side, and 100 mol/min of hydrogen penetrate the membrane walls to the shell side. of 150° C. The schematic diagram of the membrane reactor is shown in Example Figure 2.15.1. The hydrogen reaction takes place on the shell side with sufficient amount of oxygen associated with inlet air. All inlet oxygen is consumed.

Material balance (tube side):

The exit stream from the tube side contains formaldehyde, and hydrogen penetrates membrane walls to the shell side; since complete reaction is achieved, 100 mol/min of formaldehyde leave the tube side, and 100 mol/min of hydrogen penetrate the membrane walls to the shell side.

Energy balance (tube side):

Tube side energy balance

$$Q_{\text{tub}} = \xi_1 \Delta H_{\text{Rx},1}^{\circ} + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

The inlet stream to the tube side contains only methanol, where it reacts completely:

$$\sum_{\text{in}} n_i \bar{h}_i = n_{\text{CH}_3\text{OH}}^{\circ} C_{\text{PCH}_3\text{OH}} (T_1 - T_{\text{ref}})$$

$$\sum_{\text{in}} n_i \bar{h}_i = 100 \frac{\text{mol}}{\text{min}} 0.0568 \frac{\text{kJ}}{\text{mol}^{\circ}\text{C}} (250 - 25)^{\circ}\text{C} = 12.78 \text{ kJ/min}$$

The heat of reaction term for methanol dehydrogenation can be computed from heats of formation of the two compounds. Thus,

$$\Delta H_{\text{Rx}}^{\circ} = -115.90 - (-201.2) = 85.3 \text{ kJ/mol}$$

$$\sum_{\text{out}} n_i \bar{h}_i = (\dot{n}_{\text{HCHO}} C_{\text{P,HCHO}} + \dot{n}_{\text{H}_2} C_{\text{P,H}_2}) (T_2 - T_{\text{ref}})$$

Moles of formaldehyde and hydrogen produced are equal (100 mol/min):

$$\sum_{\text{out}} n_i \bar{h}_i = 100 \frac{\text{mol}}{\text{min}} (0.038 + 0.0289) \frac{\text{kJ}}{\text{mol}^{\circ}\text{C}} (150^{\circ}\text{C} - 25^{\circ}\text{C}) = 836.25 \text{ kJ/min}$$

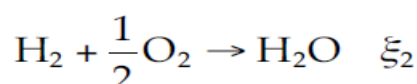
Thus, the heat required to maintain the desired reactor temperature is

$$\begin{aligned} Q_{\text{tub}} &= \xi_1 \Delta H_{\text{Rx}}^{\circ} + \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i = (100 \times 85.3) \frac{\text{kJ}}{\text{min}} \\ &\quad + 836.25 \text{ kJ/min} - 12.78 \text{ kJ/min} = 8088.25 \text{ kJ/min} \end{aligned}$$

That is, 8088 kJ/min of heat must be supplied by the hydrogen combustion reaction taking place on the shell side in order for the temperature at the completion of the reaction to be 150° C. Since the hydrogen combustion is also occurring at 150° C we need its heat of reaction at 150° C. This would correspond to the following enthalpy calculation pathway.

Material balance (shell side)

The following reaction takes place:



The specific molar flow rates of components leaving the shell side are

Unreacted hydrogen: $n_{\text{H}_2} = 100 - \xi_2$

Water vapor generated: $n_{\text{H}_2\text{O}} = \xi_2$

Nitrogen (inert): $n_{\text{N}_2} = n_{\text{N}_2}^{\circ} = \frac{0.79}{0.21} 0.5 \xi_2$

Oxygen (complete conversion): $n_{\text{O}_2} = 0$

Energy balance (shell side)

On the shell side, hydrogen is burned with sufficient amount of oxygen from the air fed to the shell side. The exit stream of the shell side is water vapor, unreacted hydrogen, and nitrogen; accordingly, the following overall energy balance for the shell side can be written:

$$Q_{\text{shell}} = \xi_2 \Delta H_{\text{Rx},2}^{\circ} + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

Inlet stream to the shell

$$\sum_{\text{in}} n_i \bar{h}_i = \left\{ n_{\text{H}_2}^{\circ} C_{P,\text{H}_2} + n_{\text{O}_2}^{\circ} C_{P,\text{O}_2} + n_{\text{N}_2}^{\circ} C_{P,\text{N}_2} \right\} (T_3 - T_{\text{ref}})$$

$$n_{\text{H}_2}^{\circ} = 100 \text{ mol/min}$$

$$n_{\text{N}_2}^{\circ} = \frac{0.79}{0.21} n_{\text{O}_2}^{\circ}$$

$$\begin{aligned} \sum_{\text{in}} n_i \bar{h}_i &= \left\{ 100(0.0289) + 0.5 n_{\text{H}_2}^{\circ} (0.0309) + \frac{0.79}{0.21} 0.5 n_{\text{H}_2}^{\circ} (0.0296) \right\} \\ &\times (250^{\circ}\text{C} - 25^{\circ}\text{C}) \end{aligned}$$

Simplifying yields

$$\sum_{\text{in}} n_i \bar{h}_i = 650.25 + 15.98 n_{\text{H}_2}^{\circ}$$

The shell side outlet stream enthalpy:

$$\sum_{\text{out}} n_i \bar{h}_i = \left\{ n_{\text{H}_2} C_{P,\text{H}_2} + n_{\text{H}_2\text{O}} C_{P,\text{H}_2\text{O}} + n_{\text{N}_2} C_{P,\text{N}_2} \right\} (T_4 - T_{\text{ref}})$$

Substituting heat capacity values and molar flow rates of the shell side exit stream gives

$$\sum_{\text{out}} n_i \bar{h}_i = \left\{ (100 - \xi_2)(0.0289) + \xi_2(0.0341) + \frac{0.79}{0.21} 0.5 \xi_2 (0.0296) \right\} (150 - 25)^\circ\text{C}$$

Thus we would get

$$\sum_{\text{out}} n_i \bar{h}_i = \{2.89 - 0.06\xi_2\} (150 - 25)^\circ\text{C}$$

Simplifying further,

$$\sum_{\text{out}} n_i \bar{h}_i = 361.25 - 7.5\xi_2$$

The heat of reaction term is just the heat of formation of water as a vapor; this is - 241.83 kJ/mol. So for the hydrogen combustion reaction we get

$$Q_{\text{shell}} = \xi_2 \Delta H_{\text{Rx},2}^\circ + \sum_{\text{out}} n_i \bar{h}_i - \sum_{\text{in}} n_i \bar{h}_i$$

$$Q_{\text{shell}} = \xi_2(-241.83) + 361.25 - 7.5\xi_2 - 650.25 + 15.98\xi_2$$

Simplifying,

$$Q_{\text{shell}} = -233.35\xi_2 - 289$$

Since heat lost from the shell side is gained by components on the tube side to maintain 150°C in the reactor,

$$Q_{\text{shell}} = -Q_{\text{tube}}$$

Substituting heat lost from the shell side and heat gained by the tube side yields

$$-233.35\xi_2 - 289 = -8088.25 \text{ kJ/min}$$

Solving for ξ_2 ,

$$\xi_2 = 33.42 \text{ mol/min}$$

Thus the combustion rate of hydrogen must be 33.4 mol/min.

2.8 Summary

The main difference between using a component balance and an element balance is that we must calculate the heat of reaction when using a component balance, but we simply use the heats of formation when writing down a balance based on the elements as the reference.

General procedure for energy balance with reaction

1. Draw the process flow diagram.
2. Complete the material balance calculations for the reactor (using either extent of reaction or atomic species balances).
3. Prepare the inlet and outlet enthalpy table, inserting known molar amounts (or flow rates) for each stream component (and phase).
4. Choose your reference state for specific enthalpy calculations.
5. Calculate each unknown stream component enthalpy, h_i .
6. Calculate $\Delta H \cdot$ for the reactor.
7. Using the general energy balance equation, solve for the unknown quantity.

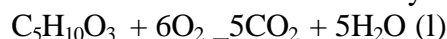
Steps 4-6 depend on the energy balance method used (i.e., heat of reaction or heat of formation).

Homework Problems

2-1 Determine the heat of reaction for the liquid phase of lactic acid ($C_3H_6O_3$) with ethanol (C_2H_5OH) to form ethyl lactate ($C_5H_{10}O_3$) and liquid water at $25^\circ C$. The heat of combustion of ethyl acetate is -2685 (kJ/mol). (-32.7 kJ/mol) The liquid-phase reaction of lactic acid with ethanol is



The combustion reaction of ethyl lactate is



The following table shows the standard heats of formation data:

Compound	Δ_f° (kJ/mol)
$C_3H_6O_3$	-687.0
C_2H_5OH	-277.6
$C_5H_{10}O_3$	—
H_2O (liquid)	-285.8
CO_2 (gas)	-393.5
O_2 (gas)	0

2-2 Superheated steam at 40 bar and $350^\circ C$ is produced from liquid water at 40 bar and $50^\circ C$ in a methane-fired boiler. To ensure complete combustion of the methane, 10% excess air is provided. Both methane and combustion air enter the boiler at $25^\circ C$. Determine the outlet temperature of the flue gas from the boiler, if 19.85 kg/min of superheated steam is produced from the combustion of 1.4 kg/min of methane. Assume the boiler is perfectly insulated. ($458^\circ C$)

2-3 Ammonia is synthesized through the reaction of nitrogen with hydrogen. The reactor feed temperature is $400^\circ C$. The fresh feed consists of 1 mol% argon and stoichiometric amount of nitrogen and hydrogen. The fractional conversion of N_2 to NH_3 in the reactor is 0.15. The converter is operated adiabatically and the heat of reaction at $400^\circ C$ is -53 kJ/mol. Given 100 mol of feed stream, estimate the temperature of the effluent gases from the converter. The average heat capacities at the pressure of the reactor for ammonia, hydrogen, nitrogen, and argon are 49.4, 29.5, 31.0, and 20.8 (J/mol $^\circ C$), respectively. ($467.8^\circ C$)

2-4 Toluene reacts to form benzene and *o*-xylene according to the following reaction:



Toluene may also react with hydrogen in the reactor to form benzene and methane:



In this process, toluene reacts with a fractional conversion of 0.80, resulting in benzene and xylene yields of 0.505 and 0.495, respectively.

Here yields are defined as moles of component produced/moles of toluene reacted. If the fresh toluene stream, fresh hydrogen stream, and product stream are all at 400° C and 15 bar absolute, determine the heat requirements for the reactor to maintain reaction temperature at 400° C and a pressure of 15 bar absolute in the vapor phase. The fresh feed stream contains 225 mol/h of toluene. Average heat capacities: benzene = 82.44 J/(mol K), toluene = 103.7 J/(mol K), *o*-xylene = 353.6 J/(mol K), methane = 35.69 J/(mol K), and hydrogen = 28.82 J/(mol K). (7725.4 kJ/h)

2.5 Methane at 25° C is burned in a boiler furnace with 10.0% excess air. The air enters the burner at a temperature of 100° C. Ninety percent of the methane fed is consumed; the product gas is analyzed and found to contain 10.0 mol CO₂ per 1 mol of CO. The exhaust gases exit the furnace at 400° C. Calculate the rate of heat transferred from the furnace, given that a molar flow rate of 100 mol/s CH₄ is fed to the furnace. (−58,626 kJ/s)

2.6 A certain bacterium is grown in a continuous culture at 30° C. Glucose is used as carbon source and ammonia is the nitrogen source. A mixture of glycerol and ethanol is produced. The reactant contains 36 kg/h glucose and 0.4 kg/h ammonia. The product stream contains 2.81 kg/h cells, 7.94 kg/h glycerol, 11.9 kg/h ethanol, and 0.15 kg/h water. Estimate the cooling requirement. (1.392 × 10⁴ kJ) Heat of combustion:

Glucose = −1.558 × 10⁴ kJ/kg

NH₃ = −2.251 × 10⁴ kJ/kg

Glycerol = −1.799 × 10⁴ kJ/kg

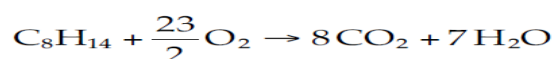
Ethanol = −2.971 × 10⁴ kJ/kg

Cell = −2.120 × 10⁴ kJ/kg

The reaction:

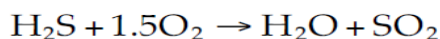
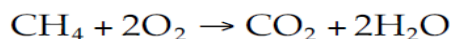
Glucose + NH₃ → Biomass + glycerol + ethanol + CO₂ + H₂

2.7 One mole of C₈H₁₄ and 14.0 mol of oxygen are placed into a lab scale batch reactor. The reactor then is placed into a water bath at 25° C; the water bath contains 20.0 kg of water. The contents of the reactor are burned. The C₈H₁₄ combusts completely to give H₂O and CO₂. At the end of the combustion, the water bath and the reactor and its contents are at 90° C. Under these conditions, the water produced during the combustion can be assumed to be completely in its liquid form. The top surface of the batch reactor is insulated such that all heat lost from the reactor goes to the water bath. What is the standard state heat of combustion of the C₈H₁₄? (−5500 kJ/mol) The following reaction took place:



2.8 Natural gas stream contains 90 mol% methane and the balance H₂S. The stream flowing at a molar flow rate of 100 mol/min and 25° C enters a combustor chamber. Water in the shell side of the combustor is supplied to maintain the combustor exit stream temperature at 25° C. If 50% excess air is used for the combustion, what is the molar flow rate of the gases leaving the combustion process and what is the

heat released from the combustor? (–77,395 kJ/min) The stream is burned completely where the following two reactions take place:



9.9 Propane (C_3H_8) enters a combustion chamber at 200°C at a rate of 100 mol/h. The gas is mixed and burned with 50% excess air that enters the combustion chamber at 200°C . An analysis of the combustion gases reveals that 90% of the propane carbon burns to CO_2 , with the remaining 10% forming CO , if the exit temperature of the combustion gases is 200°C . The average specific heats of propane, oxygen, carbon dioxide, carbon monoxide, and water vapor are 73.5, 29.4, 37.4, 28.6, and 34.7 J/mol K, respectively. The standard heats of formation of propane, carbon dioxide, carbon monoxide, and water vapor are –103.85, –393.51, –110.52, and –241.86 kJ/mol, respectively. Determine the rate of heat transfer from the combustion chamber. (–54 kW)

2.10 Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25°C , and it is burned with air that enters the combustion chamber at the same state. Determine the adiabatic flame temperature for a complete combustion at 400% theoretical air given 1 kmol octane. Assume constant heat capacities 45, 35, 30, and 30 kJ/kmol K, for CO_2 , H_2O , O_2 , and N_2 , respectively. (977 K)

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3

Simultaneous Material and Energy Balances

Material and energy balances are very important in the chemical industries. Material quantities can be described by material balances. Similarly, energy quantities can be described by energy balances. If there is no accumulation, what goes into a process must come out. Material and energy balances are fundamental to the control of processing, particularly in the control of yields of the products. After completing this chapter, the following learning objectives should be accomplished

Learning Objectives

1. Understand the basic definitions needed in solving material balance problems, for example, conversion, yield, extent of reaction, and standard heat of reaction (Section 3.1).
2. Write an energy balance for a reacting system (Section 3.2).

3.1 Material Balances

There are frequently used definitions that should be known when solving material and energy balance problems involving chemical reactions. As the definitions include conversion, yield, selectivity, and extent of reaction, these are briefly explained in subsequent sections. The general material balance equation takes the form [1, 2]

$$\text{Accumulation} = (\text{in} - \text{out}) + (\text{generation} - \text{consumption})$$

3.1.1 Conversion

Generally, syntheses of chemical products do not involve a single reaction but rather multiple reactions. The purpose, in this case, is to maximize the production of the desirable product and minimize the production of unwanted by-products. Conversion is the ratio of the moles that react to the moles that are fed to a reactor. Relative to species (i), the fractional conversion can be calculated using the following equation: Fractional conversion of component i

$$f_i = \frac{\{\text{moles of component } i\}_{\text{in}} - \{\text{moles of component } i\}_{\text{out}}}{\{\text{moles of component } i\}_{\text{in}}} \quad \dots\dots\dots (3-1)$$

$$f_i = \frac{n_{i0} - n_i}{n_{i0}}$$

3.1.2 Yield

The yield of a reaction is the ratio of the desired product formed (in moles) to the total amount that could have been produced if conversion of the limiting reactant was complete (i.e., 100%) and no side reactions occurred [3].

$$\text{Yield} = \frac{\text{moles of desired product formed}}{\text{moles formed if there were no side reactions and limiting reactant reacted completely}} \quad \dots\dots\dots (3-2)$$

3.1.3 Selectivity

The selectivity of a reaction is the ratio of the desired product formed (in moles) to the undesired product formed (in moles):

$$\text{Selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}} \quad \dots\dots\dots (3-3)$$

3.1.4 Extent of Reaction (ξ)

The concept of extent of reaction can also be applied to multiple reactions, with each reaction having its own extent. The extent of reaction is the amount in moles (or molar flow rate) that is converted in a given reaction. If a set of reactions take place in a batch or continuous steady state reactor, we can write

$$n_i = n_{i0} + \sum_j \nu_{ij} \xi_j \quad \dots\dots\dots (3-4)$$

where

ν_{ij} is the stoichiometric coefficient of substance i in reaction j

ξ_j is the extent of reaction for reaction j

\dot{n}_{i0} is the inlet molar flow rate of component i

For a single reaction, the earlier equation reduces to the following equation:

$$\dot{n}_i = \dot{n}_{i0} + \nu_i \dot{\xi} \quad \text{..... (3-5)}$$

3.2 Energy Balances

The general energy balance equation for an open system at steady state is as follows [4]:

$$\dot{Q} - \dot{W}_s = \Delta \dot{H} + \Delta KE + \Delta PE \quad \text{..... (3-6)}$$

$$\Delta KE = \frac{1}{2} \dot{m} (v_2^2 - v_1^2) \quad \text{..... (3-7)}$$

$$\Delta PE = \dot{m} g (z_2 - z_1) \quad \text{..... (3-8)}$$

Methods differ in reference state (and thus in the calculation of $\Delta \dot{H}$).

3.2.1 Heat of Reaction Method

In this method, the reference state is such that the reactants and products are at 25°C and 1 atm:

$$\Delta \dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta H_{R,j}^0 + \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i \quad \text{..... (3-9)}$$

$$\bar{h}_i = \int_{T_{\text{ref}}}^T C_{p,i} dT \quad \text{..... (3-10)}$$

$$\Delta H_{R,j}^0 = \sum_i^n \nu_i \Delta H_{f,i}^0 \quad \text{..... (3-11)}$$

3.2.2 Heat of Formation Method

In this method, the reference state is the elemental species that constitutes the reactants and products in the states they occur in nature at 25°C and 1 atm:

$$\Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \bar{h}_i - \sum_{\text{in}} \dot{n}_i \bar{h}_i \quad \text{..... (3-12)}$$

The enthalpy in this case includes the sensible heat and the enthalpy of formation:

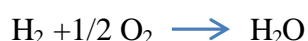
$$\Delta \dot{H}_i \big|_{at T} = \Delta H_f^0 + \int_{T_{ref}}^T C_{p_i} dT \quad \dots\dots (3-13)$$

3.2.3 Concept of Atomic Balances

Consider the reaction of hydrogen with oxygen to form water:



We may attempt to do our calculations with this reaction, but there is something seriously wrong with this equation. It is not balanced; as written, it implies that an atom of oxygen is somehow “lost” in the reaction, but this is in general impossible. Therefore, we must compensate by writing



The number of atoms of any given element does not change in any reaction (assuming that it is not a nuclear reaction).

3.2.4 Mathematical Formulation of the Atomic Balance

Now recall the general balance equation:

$$(\text{In} - \text{out}) + (\text{generation} - \text{consumption}) = \text{accumulation}$$

Moles of atoms of any element are conserved; therefore, generation = 0. So we have the following balance on a given element A:

$$\sum \dot{n}_{A,in} - \sum \dot{n}_{A,out} = 0 \quad \dots\dots (3-14)$$

When analyzing a reacting system you must choose either an atomic balance or a molecular species balance but not both. An atomic balance often yields simpler algebra, but also will not directly tell you the extent of reaction, and will not tell you whether the system specifications are actually impossible to achieve for a given set of equilibrium reactions.

3.2.5 Degrees of Freedom Analysis for the Atomic Balance

As before, to do a degrees of freedom analysis, it is necessary to count the number of unknowns and the number of equations one can write, and then subtract them. However, there are a couple of important things to be aware of with these balances: when doing atomic balances, the extent of reaction does not count as an unknown, while with a molecular species balance it does. This is the primary advantage of this method. The extent of reaction does not matter since atoms of elements are conserved

regardless of how far the reaction has proceeded. When doing an atomic balance, only reactive species are included, and not inert.

Example 3.1 Natural Gas Burner

Problems

Suppose you have a gas mixture that contains nitrous oxide, oxygen, and methane. The natural gas is burned. The following chemical reaction occurs in it. How many atomic balance equations can you write?



Solution

Known quantities: Balanced reaction.

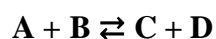
Find: The number of atomic balance equations that could be written.

Analysis: There would be four equations that you can write: three atomic balances (C, H, and O) and a molecular balance on nitrous oxide (inert and not involved in reaction). You would not include the moles of nitrous oxide in the atomic balance on oxygen.

Example 3.2 Equilibrium Reactions

Problem

An amount of 10 kg of compound A is added to 100 kg of 16 wt% aqueous solution of B, which has a density of 0.90 kg/L. A has a molecular weight of 25 kg/kmol and B has a molecular weight of 47 g/mol. If the equilibrium constant, K, for this reaction is 200 at 300 K, how much of compound C could you obtain from this reaction? Adding 10 kg of A to the solution causes the volume to increase by 9 L. The following reaction occurs:



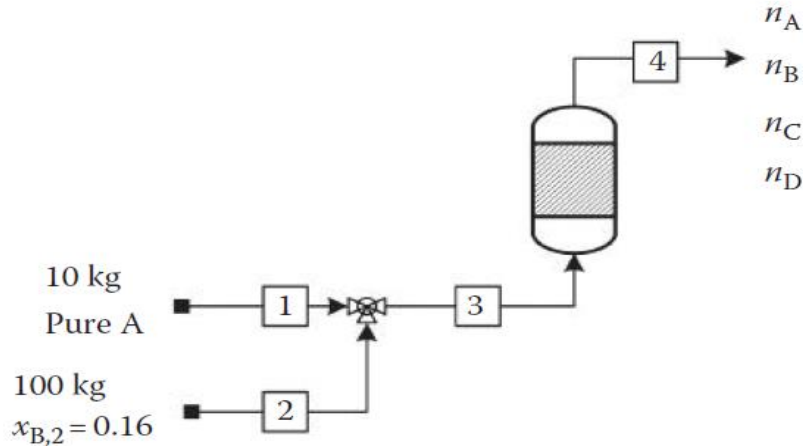
Solution

Known quantities: Mass of components A and B.

Find: Amount of compound C that could be obtained from this reaction.

Analysis: The process flowchart is shown in Example Figure 3.2.1. Since all of the species are dissolved in water, we should write the equilibrium constant in terms of molarities (mol/L):

$$K = 200 = C_{\text{C}}C_{\text{D}}/C_{\text{A}}C_{\text{B}}$$



EXAMPLE FIGURE 3.2.1: Schematic diagram of the equilibrium reaction process.

The number of moles of A we have initially is

$$n_{A0} = 10 \text{ kg A} \times \frac{1 \text{ kmol}}{25 \text{ kg}} = 0.4 \text{ kmol}$$

The number of moles of B we have initially is

$$n_{B0} = 100 \text{ kg solution} \times \frac{0.16 \text{ kg B}}{\text{kg solution}} \frac{1 \text{ kmol}}{47 \text{ kg}} = 0.34 \text{ kmol}$$

Now, the volume contributed by 100 kg of 16% B solution is

$$V_B = \frac{m}{\rho} = \frac{100 \text{ kg}}{0.90 \frac{\text{kg}}{\text{L}}} = 111 \text{ L}$$

After adding 9 L of A to the volume, the new volume is

$$V_{\text{final}} = 111 + 9 \text{ L} = 120 \text{ L}$$

There is no C or D in the solution initially:

$$C_{C0} = C_{D0} = 0$$

Plugging all the known values into the equilibrium equation for liquids, the following equation is obtained:

$$200 = \frac{\left(\frac{\xi}{120}\right)\left(\frac{\xi}{120}\right)}{\left(\frac{0.40 - \xi}{120}\right)\left(\frac{0.34 - \xi}{120}\right)}$$

Simplifying,

$$200 = \frac{\xi^2}{(0.40 - \xi)(0.34 - \xi)}$$

Rearranging,

$$200(0.40 - \xi)(0.34 - \xi) = \xi^2$$

$$27.2 - 148\xi + 200\xi^2 = \xi^2$$

$$27.2 - 148\xi + 199\xi^2 = 0$$

This equation can be solved using trial and error or any available software package:

$$\xi = 0.411 \text{ kmol}$$

$$n_{C_} = 0.411 \text{ kmol}$$

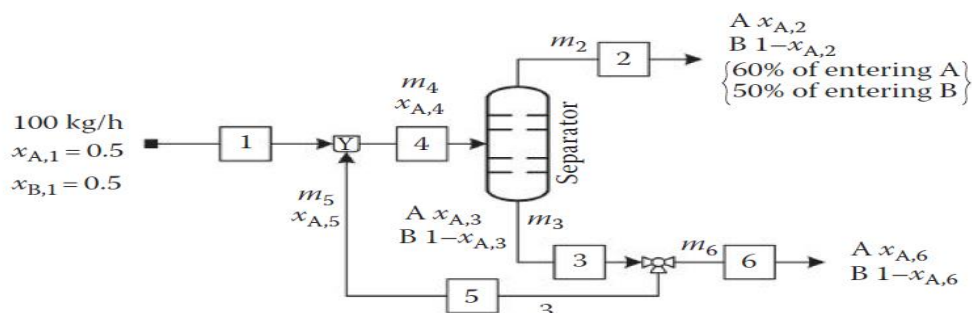
A total of 411 mol of component C can be produced by this reaction.

3.2.6 Implementing Recycle on the Separation Process

Recycle may improve reaction conversion enough to eliminate the need for a second reactor to achieve an economical conversion. Recycle reduces the amount of waste that a company generates. Not only it is the most environmentally sound way to go about but it also saves the company money in disposal costs. Using recycle, it is possible to recover expensive catalysts and reagents. Catalysts are not cheap, and if we do not try to recycle them into the reactor, they may be lost in the product stream. This not only gives us a contaminated product but also wastes a lot of catalyst

Example 3.3 Separation of Binary Liquid Mixture Problem

Fresh feed stream (100 kg/h) contains equal mass fractions of A and B joining a recycle stream and fed to a separator. The top product stream of the separator contains 60% of A and 50% of the B that is fed to the separator and not that of the fresh feed stream. The recycle system is set up in which half of the separator bottom product stream is recycled and recombined with the fresh feed. Calculate the compositions of A in all streams.



Solution

Known quantities: Fresh feed stream flow rate and composition.

Find: Exit stream molar flow rates.

Analysis: The process flow sheet is shown in Example Figure 3.3.1. The number of degrees of freedom (NDF) of each process:

	Mixing	Separator	Splitter	Overall
Number of unknowns	4	6	6	4
Number of independent equations	2	2	1	2
Number of auxiliary relations	0	2	1	0
NDF	2	2	4	2

Since none of the units got zero degree of freedom, by contrast, the whole process is solvable because the number of independent equations plus auxiliary relations (7 + 3) equals the total number of unknowns (10 unknowns) in the process:

System: Overall

$$\text{Overall mass balance: } 100 \frac{\text{kg}}{\text{h}} = \dot{m}_2 + \dot{m}_6$$

$$\text{Overall mass balance on A: } 50 \frac{\text{kg}}{\text{h}} = \dot{m}_2 \times x_{A,2} + \dot{m}_6 \times x_{A,6}$$

We have four unknowns and two equations at this point. First, combine this information with the splitting ratio and constant composition at the splitter.

$$\text{Splitting ratio: } \dot{m}_6 = \frac{\dot{m}_3}{2}$$

$$\text{Constant composition: } x_{A,6} = x_{A,3}$$

$$\text{Plugging these into the overall balances, we have } 100 = \dot{m}_2 + \frac{\dot{m}_3}{2}$$

$$\text{Component balance (A): } 50 = x_{A,2}\dot{m}_2 + x_{A,3}\frac{\dot{m}_3}{2}$$

Relations: Translating words in the relations into algebraic equations.

If 60% of A entering the separator goes into stream 2, then 40% of A entering the separator goes into stream 3, and then

$$x_{A,2}\dot{m}_2 = 0.6x_{A,4}\dot{m}_4$$

$$x_{A,3}\dot{m}_3 = 0.4x_{A,4}\dot{m}_4$$

If 50% of B entering the separator goes into stream 2, then 50% of B entering the separator goes into stream 3, and then

$$(1 - x_{A,2})\dot{m}_2 = 0.5(1 - x_{A,4})\dot{m}_4$$

$$(1 - x_{A,3})\dot{m}_3 = 0.5(1 - x_{A,4})\dot{m}_4$$

Plugging in all of these into the existing balances, we finally obtain two equations in two unknowns:

System: Overall

Component balances:

$$A: 50 = 0.6x_{A,4}\dot{m}_4 + \frac{0.4}{2}x_{A,4}\dot{m}_4 \Rightarrow x_{A,4}\dot{m}_4 = 62.5$$

$$B: 50 = 0.5(1 - x_{A,4})\dot{m}_4 + \frac{0.5}{2}(1 - x_{A,4})\dot{m}_4 \Rightarrow 50 = 0.75\dot{m}_4 - 0.75x_{A,4}\dot{m}_4$$

Substitute $x_{A,4}\dot{m}_4 = 62.5$ in B component balance equation:

$$50 = 0.75\dot{m}_4 - 0.75(62.5)$$

Solving these equations gives

$$\dot{m}_4 = 129.17 \frac{\text{kg}}{\text{h}}, \quad x_{A,4} = 0.484$$

System: Mixer

Total balance

$$100 + \dot{m}_5 = \dot{m}_4 = 129.17 \Rightarrow \dot{m}_5 = 29.17 \text{ kg/h}$$

System: Splitter

The recycle stream (\dot{m}_5) is half of the separator bottom product stream (\dot{m}_3): $\dot{m}_3 = 2\dot{m}_5 = 2 \times 29.17 = 58.34 \text{ kg/h}$

System: Overall

$$100 = \dot{m}_2 + 29.165 \Rightarrow \dot{m}_2 = 70.835 \text{ kg/h}$$

Relations:

$$x_{A,2}\dot{m}_2 = 0.6x_{A,4}\dot{m}_4$$

$$x_{A,2} \times 70.835 = 0.6 \times 0.484 \times 129.17 \Rightarrow x_{A,2} = 0.530$$

$$x_{A,3}\dot{m}_3 = 0.4x_{A,4}\dot{m}_4$$

$$x_{A,3} \times 58.34 = 0.4 \times 0.484 \times 129.17 \Rightarrow x_{A,3} = 0.429$$

Example 3.4 Methane Oxidization

Problem

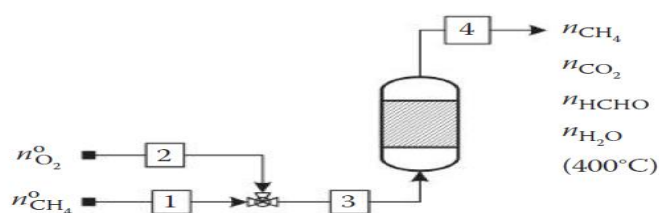
Methane and oxygen at 25°C are fed to a continuous reactor in stoichiometric amounts according to the following reaction to produce formaldehyde:



In a side reaction, methane is oxidized to carbon dioxide and water:



The product gases emerge at 400°C, and the number of moles of CO₂ in the effluent gases is 0.15, and there is no remaining O₂ found in the effluent gases stream. Determine the composition of effluent gas per mole of CH₄ fed to the reactor. Determine the amount of heat removed from the reactor per mole of CH₄ fed to the reactor.



EXAMPLE FIGURE 3.4.1: Schematic diagram of the methane oxidation process.

Solution

Known quantities: Inlet component molar flow rate and compositions.

Find: The amount of heat removed from the reactor per mole of CH₄ fed to the reactor.

Analysis: The process flow sheet is shown in Example Figure 3.4.1.

Material balance

Material balance using the extent of reaction method is given by

$$n_{\text{CH}_4} = 1 - \xi_1 - \xi_2$$

There is no remaining O₂:

$$n_{\text{O}_2} = 0 = 1 - \xi_1 - 2\xi_2$$

$$n_{\text{HCHO}} = \xi_1$$

The number of moles of CO₂ in the effluent stream is 0.15 mol:

$$n_{\text{CO}_2} = \xi_2 = 0.15$$

$$n_{\text{H}_2\text{O}} = \xi_1 + 2\xi_2$$

Hence, $1 - \xi_1 - 2\xi_2 = 0$ and $n_{\text{CO}_2} = \xi_2 = 0.15$

Substituting $\xi_2 = 0.15$ in the earlier equation and solving for ξ_1 , we get $\xi_1 = 0.7$

Substitute values of $\xi_2 = 0.15$ and $\xi_1 = 0.7$ in the mole balance equations:

$$\dot{n}_{\text{CH}_4} = 0.15 \text{ mol/s}, \quad \dot{n}_{\text{HCHO}} = 0.7 \text{ mol/s}, \quad \dot{n}_{\text{CO}_2} = 0.15 \text{ mol/s},$$

$$\dot{n}_{\text{H}_2\text{O}} = 1 \text{ mol/s}$$

The amount of heat removed from the reactor per mole of CH_4 fed to the reactor. The heat capacities are taken from tabulated values as a function of temperature.

Energy balance

Reference temperature = 25°C

The standard heats of reaction for both reactions at 25°C are calculated from the standard heats of formation.

The heats of formation are

$$\Delta H_{f,\text{CH}_4}^0 = -74.85 \text{ kJ/mol}$$

$$\Delta H_{f,\text{O}_2}^0 = 0$$

$$\Delta H_{f,\text{HCHO}} = -115.9 \text{ kJ/mol}$$

$$\Delta H_{f,\text{H}_2\text{O}}^0 = -241.83 \text{ kJ/mol}$$

$$\Delta H_{f,\text{CO}_2}^0 = -393.5 \text{ kJ/mol}$$

The standard heats of reaction are

$$\Delta H_{\text{Rx},1}^0 = \Delta H_{f,\text{H}_2\text{O}}^0(\text{g}) + \Delta H_{f,\text{HCHO}}^0(\text{g}) - \Delta H_{f,\text{CH}_4}^0(\text{g}) - \Delta H_{f,\text{O}_2}^0(\text{g})$$

$$\Delta H_{\text{Rx},1}^0 = -115.9 - 241.83 - (-74.85) - (0) = -282.88 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_{\text{Rx},2}^0 = 2\Delta H_{f,\text{H}_2\text{O}}^0(\text{g}) + \Delta H_{f,\text{CO}_2}^0(\text{g}) - \Delta H_{f,\text{CH}_4}^0(\text{g}) - 2\Delta H_{f,\text{O}_2}^0(\text{g})$$

$$\Delta H_{\text{Rx},2}^0 = 2(-241.83) + (-393.5) - (-74.85) - 2(0) = -802.31 \frac{\text{kJ}}{\text{mol}}$$

The sensible heat is calculated using specific heat:

$$C_p \left(\frac{\text{J}}{\text{mol } ^\circ\text{C}} \right) = a + bT + cT^2 + dT^3$$

The specific heat can be found from Table A.3:

$$\text{HCHO: } a = 34.28, \quad b = 4.268 \times 10^{-2}, \quad c = 0.0, \quad d = -8694 \times 10^{-9}$$

$$\text{CH}_4: \quad a = 34.31, \quad b = 5.469 \times 10^{-2}, \quad c = 0.3661 \times 10^{-5}, \quad d = -11 \times 10^{-9}$$

$$\text{CO}_2: \quad a = 36.11, \quad b = 4.233 \times 10^{-2}, \quad c = -2.887 \times 10^{-5}, \quad d = 7.464 \times 10^{-9}$$

$$\text{H}_2\text{O: } a = 33.46, \quad b = 0.688 \times 10^{-2}, \quad c = 0.7604 \times 10^{-5}, \quad d = -3.593 \times 10^{-9}$$

Calculation of enthalpies of outlet and inlet streams relative to the reference temperature (i.e., 25°C) is shown in the following.

Enthalpy of outlet stream components:

$$\bar{h}_{\text{HCHO}} = \int_{25}^{400} C_p \, dT = \int_{25}^{400} (34.28 + 4.268 \times 10^{-2} T + 0T^2 - 8694 \times 10^{-9} T^3) \, dT$$

$$\bar{h}_{\text{HCHO}} = \int_{25}^{400} C_p \, dT = \left[34.28T + 4.268 \times 10^{-2} \frac{T^2}{2} - 3(8694 \times 10^{-9}) \frac{T^4}{4} \right]_{25}^{400}$$

$$\bar{h}_{\text{HCHO}} = \frac{\text{kJ}}{1000 \text{ J}} \left[34.28(400 - 25) + 4.268 \times 10^{-2} \frac{(400^2 - 25^2)}{2} - 8694 \times 10^{-9} \times \frac{(400^4 - 25^4)}{4} \right]$$

Note that $(400^2 - 25^2) \neq (400 - 25)^2$

The results are

$$\bar{h}_{\text{HCHO}} = 16.2 \frac{\text{kJ}}{\text{mol}}, \quad \bar{h}_{\text{CH}_4} = 17.23 \frac{\text{kJ}}{\text{mol}}, \quad \bar{h}_{\text{CO}_2} = 16.35 \frac{\text{kJ}}{\text{mol}},$$

$$\bar{h}_{\text{H}_2\text{O}} = 13.23 \frac{\text{kJ}}{\text{mol}}$$

The general energy balance equation is

$$Q = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i + \xi_1 \Delta H_{\text{rxn}1}^0 + \xi_2 \Delta H_{\text{rxn}2}^0$$

Substituting known quantities,

$$\dot{Q} = \left\{ \dot{n}_{\text{CH}_4} (\bar{h}_{\text{CH}_4}) + \dot{n}_{\text{CO}_2} (\bar{h}_{\text{CO}_2}) + \dot{n}_{\text{HCHO}} (\bar{h}_{\text{HCHO}}) + \dot{n}_{\text{H}_2\text{O}} (\bar{h}_{\text{H}_2\text{O}}) \right\}_{400^\circ\text{C}}$$

$$- \left\{ \dot{n}_{\text{CH}_4} (\bar{h}_{\text{CH}_4}) + \dot{n}_{\text{O}_2} (\bar{h}_{\text{O}_2}) \right\}_{25^\circ\text{C}} + \dot{\xi}_1 \Delta H_{\text{Rx},1}^0 + \dot{\xi}_2 \Delta H_{\text{Rx},2}^0$$

The enthalpy of inlet stream components is zero because inlet temperature is at reference temperature; therefore, the enthalpy of inlet components relative to reference temperature of 25°C is zero:

$$\dot{Q} = \{0.15(17.23) + 0.15(16.35) + 0.7(16.2) + 1(13.23)\}_{\text{out}} - \{0 + 0\}_{\text{in}}$$

$$+ 0.7(-282.88) + 0.15(-802.31)$$

$$= -288.76 \text{ kJ/s}$$

Example 3.5 Adiabatic Saturation Temperature

Problem

Air at a temperature of 50°C and 10% relative humidity is to be humidified adiabatically (constant wet-bulb temperature line) to 40% relative humidity. Use the psychrometric chart to estimate the adiabatic saturation temperature of the air, the rate at which water must be added to humidify 15 kg/min of the entering air and the final temperature of air.

Solution

Known quantities: Inlet air temperature and relative humidity.

Find: The adiabatic saturation temperature of the air.

Analysis: Refer to a psychrometric chart:

$$\text{at } T_{db} = 50^{\circ}\text{C and } h_r = 10\% \Rightarrow T_{as} = T_{wb} = 23.5^{\circ}\text{C}$$

$$h_a = 0.0077 \frac{\text{kg H}_2\text{O}}{\text{kg DA}}$$

The state of the exit air lies on the line $T_{wb} = 23.5^{\circ}\text{C}$. From the intersection of this line and the 40% relative humidity curve, the absolute humidity of exit air is determined to be

$$h_a = 0.014 \text{ kg H}_2\text{O/kg dry air}$$

The rate at which water must be added to humidify 15 kg/min of the entering air is

$$\frac{15 \text{ kg air}}{\text{min}} \left| \frac{1 \text{ kg DA}}{1.0077 \text{ kg air}} \right| \left| \frac{0.014 - 0.0077}{\text{kg DA}} \right| = 0.0938 \frac{\text{kg H}_2\text{O}}{\text{min}}$$

From the intersection of the 40% relative humidity curve and the $T_{wb} = 23.6^{\circ}\text{C}$ line, the dry-bulb temperature of exit gas is found to be around 35°C .

Example 3.6 Partial Condensation of Cyclopentane Problem

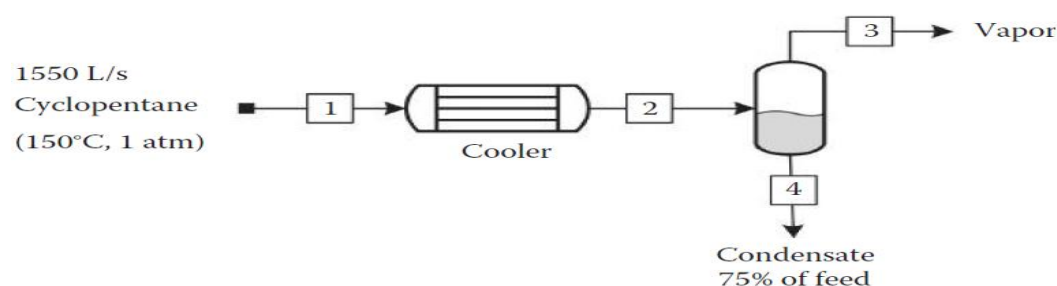
A stream of pure cyclopentane vapor is flowing at a rate of 1550 L/s, at a temperature of 150°C , and at a pressure of 1 atm it enters a cooler. Seventy-five percent of the feed is condensed and exits the cooler at 1 atm. What is the temperature of the exiting streams from the cooler?

Solution

Known quantities: Inlet stream volumetric flow, inlet temperature, and pressure.

Find: Temperature of the exiting streams from the cooler.

Analysis: The process flow diagram is shown in Example Figure 3.6.1. The exit stream temperature must be 49.3°C for cyclopentane, because the boiling point of cyclopentane at 1 atm pressure is 49.3°C . Taking the reference temperature at 49.3°C and cyclopentane in liquid state



EXAMPLE FIGURE 3.6.1: Partial condensation of cyclopentane.

(i.e., $T_{ref} = 49.3^{\circ}\text{C}$, liquid state), the number of moles of inlet cyclopentane in vapor phase, using the ideal gas law, is

$$n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 1550 \text{ L/s}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (150 + 273.15)\text{K}} = 44.64 \frac{\text{mol}}{\text{s}}$$

The inlet specific molar enthalpy of vapor cyclopentane at 150°C relative to reference temperature (49.3°C , liquid) is shown in the following equation:

$$\bar{h}_{in} = \Delta\bar{h}_{vap} + \int_{49.3^{\circ}\text{C}}^{150^{\circ}\text{C}} C_{p,v} dT$$

Heat capacity of cyclopentane vapor (C_{pv}) as a function of temperature is shown here:

$$C_{pv} \left(\frac{\text{J}}{\text{mol K}} \right) = 73.39 + 0.3928T - 2.554 \times 10^{-4}T^2$$

The change in specific molar enthalpy of cyclopentane vapor is

$$\Delta\bar{h}_v = \int_{49.3^{\circ}\text{C}}^{150^{\circ}\text{C}} C_p dT = \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 \right]_{49.3^{\circ}\text{C}}^{150} = 11,060 \frac{\text{J}}{\text{mol}}$$

The heat of vaporization of cyclopentane at 1 atm and its boiling point 49.3°C is

$$\Delta\bar{h}_{vap} = 27.30 \frac{\text{kJ}}{\text{mol}}$$

Substituting heat of vaporization and sensible heat,

$$\bar{h}_{in} = \Delta\bar{h}_v + \int_{49.3}^{150} C_{pv} dT = 27.3 + 11.06 = 38.36 \text{ kJ/mol}$$

The resultant enthalpies can be summarized in the following table. Enthalpies Relative to Reference Conditions ($T_{ref} = 49.3^{\circ}\text{C}$, liquid state, 1 atm)

Substance	$\dot{n}_{in} (\text{mol/s})$	$\bar{h}_{in} (\text{kJ/mol})$	$\dot{n}_{out} (\text{mol/s})$	$\bar{h}_{out} (\text{kJ/mol})$
Cyclopentane (<i>v</i>)	44.64	38.36	11.14	27.3
Cyclopentane (<i>l</i>)	—	—	33.5	0

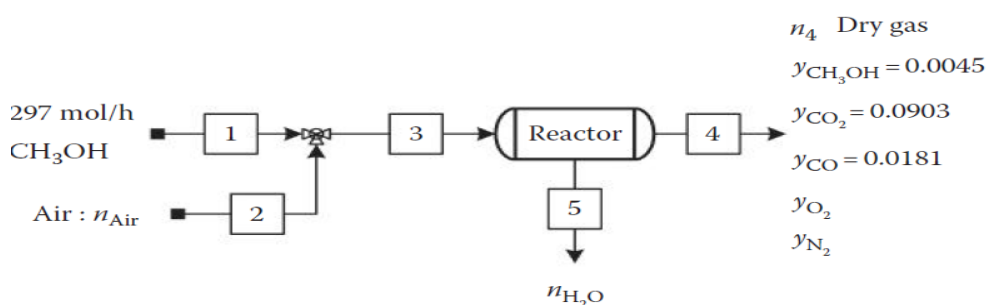
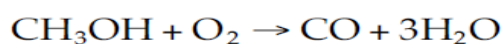
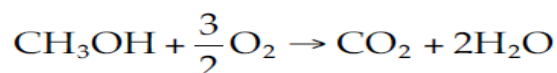
$$\text{Total energy balance: } Q = \sum_{out} n_i \bar{h}_i - \sum_{in} n_i \bar{h}_i$$

$$Q = \left(11.14 \frac{\text{mol}}{\text{s}} \right) \left(27.30 \frac{\text{kJ}}{\text{mol}} \right) - 44.64 \frac{\text{mol}}{\text{s}} (38.36) \frac{\text{kJ}}{\text{mol}} = -1408 \frac{\text{kJ}}{\text{s}}$$

Example 3.7 Methanol Combustion Process

Problem

Methanol (CH_3OH) is fed at a rate of 297 mol/h and burned with excess air. The product gas is analyzed, and the following dry-basis mole percentages are determined: $\text{CH}_3\text{OH} = 0.45\%$, $\text{CO}_2 = 9.03\%$ and $\text{CO} = 1.81\%$. Calculate the fractional conversion of methanol, the percentage excess air fed, and the mole fraction of water in the product gas. The equations of the chemical reactions taking place in the heater are



EXAMPLE FIGURE 3.7.1: Schematic of the methanol combustion process.

Solution

Known quantities: Methanol volumetric flow rate, dry gas composition.

Find: The fractional conversion of methanol, the percentage excess air fed, and the mole fraction of water in the product gas.

Analysis: The labeled flowchart is shown in Example Figure 3.7.1. Degrees of Freedom Analysis (Atomic Balance)

Number of unknowns	4
Atomic balance equations (C, H, O)	3
Number of relations	1
NDF	0

Atomic balance

Basis: 297 mol/h of inlet methanol

C balance:

$$n_{\text{dry gas}} = \frac{297 \text{ mol/h}}{0.1129} = 2631 \text{ mol/h}$$

$$297 \frac{\text{mol}}{\text{h}} = (0.0045 + 0.0903 + 0.0181)n_{\text{dry gas}}$$

H balance:

$$297 \text{ mol} \frac{\text{CH}_3\text{OH}}{\text{h}} \times \frac{4 \text{ mol H}}{\text{mol CH}_3\text{OH}} \\ = 2n_{\text{H}_2\text{O}} + 0.0045 \text{ mol CH}_3\text{OH} \frac{4 \text{ mol H}}{\text{mol CH}_3\text{OH}} n_{\text{dry gas}}$$

$$n_{\text{H}_2\text{O}} = 570.3 \text{ mol/s}$$

$$\text{Total moles out} = 570.3 + 2631 = 3201 \text{ mol}$$

$$\text{Fraction of water in the product stream} = \frac{570.3}{3201} = 0.178$$

$$\text{Fractional conversion of methanol} = x = \frac{297 - 0.0045 \times 2631}{297} = 0.96$$

Calculation of the amount of excess air:

O balance:

$$2(0.21 \times n_{\text{Air}}) + 297 = (0.0045 + 2 \times 0.0903 + 0.0181 + 2 \times y_{\text{O}_2}) \times 2631 + 569.2$$

N balance:

$$2(0.79 \times n_{\text{Air}}) = 2 \times (1 - 0.0045 - 0.0903 - 0.0181 - y_{\text{O}_2}) \times 2631$$

Solving for air, oxygen, and nitrogen,

$$n_{\text{Air}} = 2733.41 \text{ mol/s}, \quad y_{\text{N}_2} = 0.822, \quad y_{\text{O}_2} = 0.065$$

To calculate the percent excess air, first calculate the theoretical oxygen using the complete combustion reaction:

$$\text{Theoretical oxygen} = \frac{297 \text{ mol CH}_3\text{OH}}{\text{h}} \left| \frac{\frac{3}{2} \text{ mol O}_2 \text{ consumed}}{1 \text{ mol CH}_3\text{OH}} \right| = 445.5 \frac{\text{mol}}{\text{h}}$$

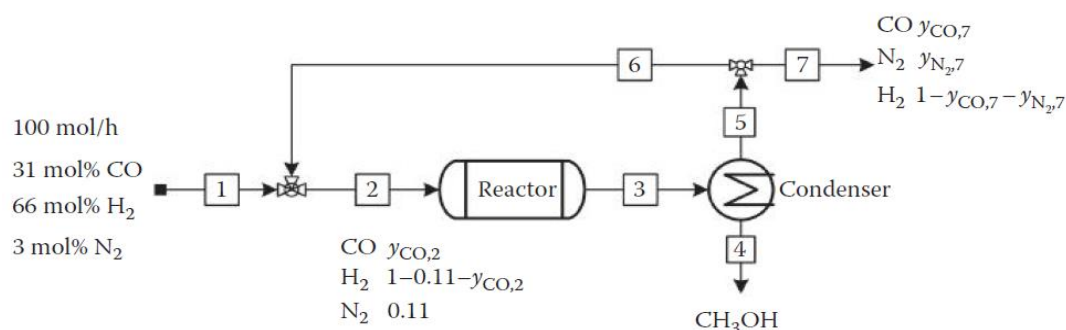
$$\text{Theoretical air} = \frac{\dot{n}_{\text{O}_2}}{0.21} = \frac{445.5 \text{ mol O}_2/\text{h}}{0.21} = 2121.43 \text{ mol/h}$$

$$\% \text{ Excess air} = \frac{\text{Total inlet air} - \text{Theoretical air}}{\text{Theoretical air}} = \frac{2733.41 - 2121.43}{2121.43} \\ \times 100\% = 28.85$$

Example 3.8 Methanol Synthesis

Problem

A fresh feed stream is flowing at 100 mol/h, containing 31% carbon monoxide (CO), 66 mol% hydrogen (H₂), and 3 mol% nitrogen. The fresh feed stream joins a recycle stream, and the combined stream is fed to a catalytic reactor for methanol synthesis. This stream is mixed with a recycle stream in a ratio of 4 mol recycle to 1 mol of fresh feed to enter the reactor, and the stream entering the reactor contains 11 mol% N₂. The reactor effluent goes to a condenser, from which two streams emerge: a liquid stream containing pure liquid CH₃OH and a gas stream containing all the CO, H₂, and N₂. The gas stream from the condenser is split into a purge stream, and the remainder is recycled to mix with the fresh feed to enter the reactor. Calculate the production rate of methanol (mol/h), the molar flow rate and composition of the purge gas, and the overall conversion of CO.



EXAMPLE FIGURE 3.8.1: Schematic diagram of the methanol production process.

Solution

Known quantities: Fresh feed stream flow rate and composition.

Find: The production rate of methanol (mol/h), the molar flow rate and composition of the purge gas, and the overall conversion of CO.

Analysis: The process flowchart is shown in Example Figure 3.8.1.

Basis: 100 mol/h of fresh feed

Degrees of Freedom Analysis

Degrees of Freedom Analysis	Overall Process	Mixing Point
Number of unknowns	5 ($\dot{n}_4, \dot{n}_7, y_{\text{CO},7}, y_{\text{N}_2,7}, \xi$)	5 ($\dot{n}_2, y_{\text{CO},2}, \dot{n}_6, y_{\text{N}_2,6}, y_{\text{CO},6}$)
Number of equations	4	4
Number of relations	—	1
NDF	1	0

System: Mixing point balances

From the relation recycle stream = 4 times of the fresh feed stream,

$$n_6 = 400 \text{ mol/h}$$

$$n_2 = 500 \text{ mol/h}$$

N₂ balance:

$$3 + y_{N_2,6} \times 400 = 0.11 \times 500$$

$$y_{N_2,6} = 0.13$$

System: Overall balance

N₂ balance:

$$3 = y_{N_2,7} \times n_7$$

Since the composition of recycle stream and purge stream are the same,

$$y_{N_2,7} = y_{N_2,6} = 0.13$$

The flow rate of purge is

$$n_7 = 23 \text{ mol/h}$$

Atomic C balance:

$$31 \text{ mol CO} \times 1 = n_4 \text{ mol CH}_3\text{OH} + y_{CO,7} \times 23$$

Simplify

$$n_4 = 31 - 23 \times y_{CO,7}$$

Substituting $n_4 = 31 - 23 \times y_{CO,7}$ in the earlier equation yields

$$132 = (31 - 23y_{CO,7}) \times 4 + 40.02 - 46y_{CO,7}$$

$$-32.02 = -138 \times y_{CO,7}$$

$$y_{CO,7} = 0.23$$

$$y_{H_2,7} = 0.87 - 0.23 = 0.64 \frac{\text{mol H}_2}{\text{mol}}$$

$$n_4 = 25.71 \text{ mol CH}_3\text{OH}$$

$$\text{Overall conversion} = \frac{31 \text{ mol} - 0.23 \times 23}{31} = 0.83$$

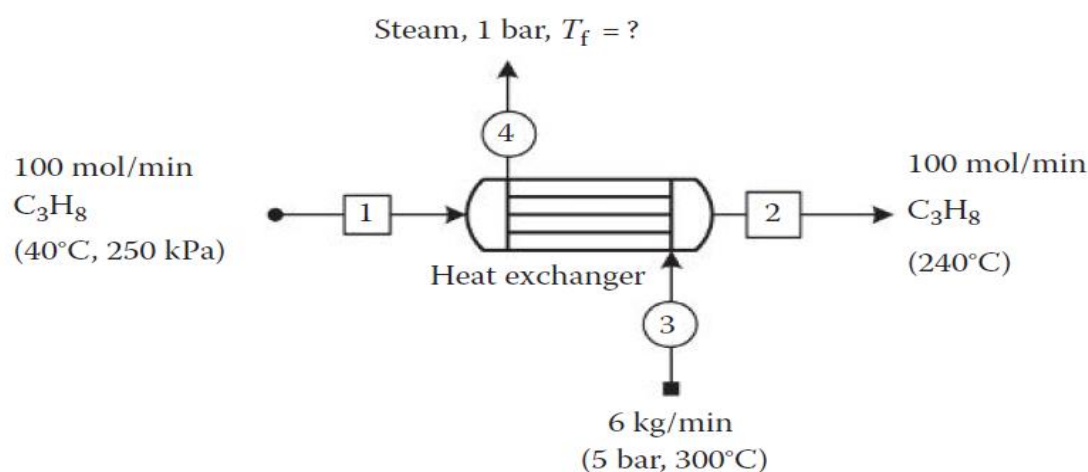
Overall, 83% conversion of CO is achieved.

Atomic H balance:

$$\begin{aligned} 2 \times 66 \text{ mol H}_2 &= \left(n_4 \text{ mol CH}_3\text{OH} \frac{4 \text{ mol H}}{\text{mol CH}_3\text{OH}} \right) \\ &+ \left((1 - 0.13 - y_{CO,7}) \frac{2 \text{ mol H}}{\text{mol H}_2\text{O}} \times 23 \right) \end{aligned}$$

Example 3.9 Heating of Propane Gas Problem

Propane gas at 40° C and 250 kPa enters a continuous adiabatic heat exchanger where no heat is lost from the outside of the unit while heat is transferred between streams. The stream exits at 240° C. The flow rate of propane is 100 mol/min, and superheated steam at 5 bar absolute pressure and 300° C enters the heat exchanger with a flow rate of 6 kg/min. The steam exits the heat exchanger at 1 bar absolute pressure. Calculate the temperature of the exit steam.



EXAMPLE FIGURE 3.9.1: Heating of propane.

Solution

Known quantities: Propane gas temperature, pressure flow rate.

Find: Temperature of the exit steam.

Analysis: The process flow sheet is shown in Example Figure 3.9.1. For a heat capacity of propane,

$$a = 68.032, \quad b = 0.2259, \quad c = -1.311 \times 10^{-4}, \quad d = 3.171 \times 10^{-8}$$

Substituting values of a , b , c , and d and integrating,

$$\begin{aligned} \Delta \bar{h}_{\text{C}_3\text{H}_8} &= \int_{40^\circ\text{C}}^{240^\circ\text{C}} C_p \left(\frac{\text{J}}{\text{mol } ^\circ\text{C}} \right) dT = \int_{40^\circ\text{C}}^{240^\circ\text{C}} (a + bT + cT^2 + dT^3) dT \\ \Delta \bar{h}_{\text{C}_3\text{H}_8} &= 0.68[T_2 - T_1] + \frac{0.2259}{2}[T_2^2 - T_1^2] + \frac{-1.311 \times 10^{-4}}{3}[T_2^3 - T_1^3] \\ &\quad + \frac{3.171 \times 10^{-8}}{4}[T_2^4 - T_1^4] \end{aligned}$$

Substituting the given values of inlet and exit temperatures,

$$= 0.68[240 - 40] + \frac{0.2259}{2}[240^2 - 40^2] + \frac{-1.311 \times 10^{-4}}{3}[240^3 - 40^3] + \frac{3.171 \times 10^{-8}}{4}[240^4 - 40^4]$$

The change in specific molar enthalpy \bar{h} (J/mol) is

$$\Delta \bar{h}_{\text{C}_3\text{H}_8} = 13,606.4 + 6325.2 - 13 + 26.3 = 19,360 \frac{\text{J}}{\text{mol}}$$

The amount of heat transferred from the steam to heat propane is

$$\dot{n} \Delta \bar{h} = 100 \frac{\text{mol}}{\text{min}} \times 19.36 \frac{\text{kJ}}{\text{mol}} = 1936 \frac{\text{kJ}}{\text{min}}$$

The change in mass specific enthalpy of steam, h (J/g), is

$$\dot{m} \Delta h = 6 \frac{\text{kg}}{\text{min}} [h_{\text{out}} - 3065] \frac{\text{kJ}}{\text{kg}}$$

$$\dot{Q} = 0 = 1936 \frac{\text{kJ}}{\text{min}} + 6 \frac{\text{kg}}{\text{min}} [h_{\text{out}} - 3065] \frac{\text{kJ}}{\text{kg}}$$

$$\frac{1936}{6} \frac{\text{kJ}}{\text{kg}} + 3065 \frac{\text{kJ}}{\text{kg}} = h_4$$

Using the superheated steam table calculate the temperature at 1 bar absolute pressure and enthalpy, $h_4 = 2742.3$ kJ/kg. Since the value of the calculated enthalpy at 1 bar does not exist in the steam table, interpolation is required to get the value of the exit temperature:

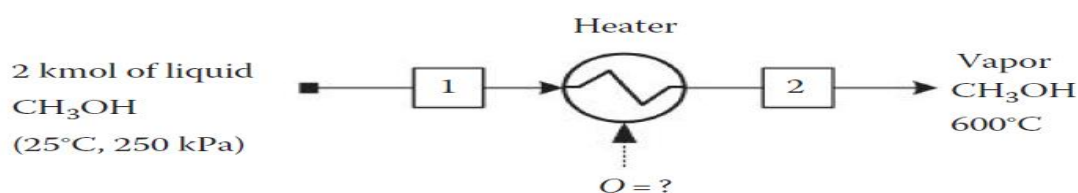
$$\frac{2776 - 2676}{150 - 100} = \frac{2776 - 2742.3}{150 - T_f} \Rightarrow T_f = 133^\circ\text{C}$$

Example 3.10 Heating of Liquid Methanol

Problem

Liquid methanol at 25° C is heated and vaporized for use in a chemical reaction.

How much heat is required to heat and vaporize 2 kmol/h of methanol to 600° C.



EXAMPLE FIGURE 3.10.1: Schematic of heating liquid methanol.

Solution

Known quantities: Inlet liquid methanol temperature and flow rate.

Find: Heat required to heat and vaporize 2 kmol of methanol to 600° C.

Analysis: The inlet and exit conditions of the heater are shown in Example Figure 3.10.1. Consider $T_{ref} = 25^\circ \text{C}$ and methanol in liquid phase as reference conditions.

The normal boiling point of methanol is 64.7° C. Accordingly, the change of methanol enthalpy is the sum of change in the enthalpy of the liquid methanol, heat of vaporization, and the change in enthalpy of vapor methanol from its boiling point to its final temperature. The enthalpy change for methanol liquid is

$$\begin{aligned}\Delta \bar{h}_{\text{CH}_3\text{OH}} &= \int_{25^\circ \text{C}}^{64.7^\circ \text{C}} C_{p\text{CH}_3\text{OH},l} dT = 0.07586 [64.7 - 25] \\ &+ \frac{16.83 \times 10^{-5}}{2} [64.7^2 - 25^2] = 3.312 \text{ kJ/mol}\end{aligned}$$

The enthalpy change for methanol vapor is

$$\begin{aligned}\Delta \bar{h}_{\text{CH}_3\text{OH}} &= \int_{64.7^\circ \text{C}}^{600^\circ \text{C}} C_{p,v} dT = 0.68 [600 - 64.7] + \frac{0.2259}{2} [600^2 - 64.7^2] \\ &+ \frac{-1.31 \times 10^{-4}}{3} [600^3 - 64.7^3] - \frac{3.71 \times 10^{-8}}{4} [600^4 - 64.7^4] \\ &= 68.21 \text{ kJ/mol}\end{aligned}$$

The methanol latent heat of vaporization is

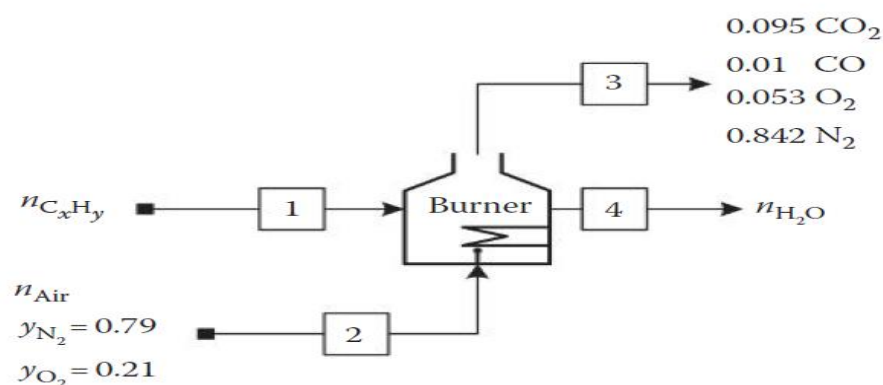
$$\Delta \bar{h}_{\text{vapor}} = 36.14 \frac{\text{kJ}}{\text{mol}}$$

The change in enthalpy of the methanol heated from 25°C to 600°C is

$$Q = 2000 \frac{\text{mol}}{\text{h}} \times [3.312 + 68.21 + 36.14] \frac{\text{kJ}}{\text{mol}} = 2,15,324 \frac{\text{kJ}}{\text{h}}$$

Example 3.11 Turbine Power Plant Problem

A hydrocarbon fuel whose composition is unknown but may be represented by the expression C_xH_y is burned with excess air. An analysis of the product gas gives the following results in mol% on a moisture-free basis: 9.51% CO_2 , 1.0% CO , 5.3% O_2 , and 84.2% N_2 . Given 100 mol/h of flue gas dry gas, determine the molar ratio of hydrogen to carbon in the fuel, r , where $r = y/x$, and the percentage of excess air used in the combustion.



EXAMPLE FIGURE 3.11.1: Schematic diagram of burning hydrocarbon.

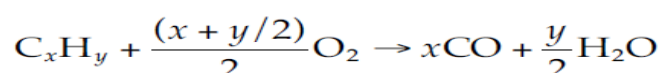
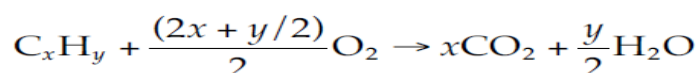
Solution

Known quantities: Dry gas mole fraction.

Find: The ratio of hydrogen to carbon in the used fluid.

Analysis: The number of independent chemical reactions in the process is two since the flue gases contain CO , which means that there is a side reaction and the combustion is not complete.

Basis: 100 mol of flue gases (dry basis).



The flowchart of this process is shown in Example Figure 3.11.1.

Degrees of Freedom Analysis

Degrees of Freedom Analysis	Overall Process (Atomic Balance)
Number of unknowns	5 ($n_{C_xH_y}$, n_{H_2O} , x , y , n_2)
Number of independent equations	4
Number of relations	—
NDF	1

Atomic balance:

$$\text{C atomic balance: } x n_{\text{CxHy}} = 9.5 + 1.0$$

$$\text{H atomic balance: } y n_{\text{CxHy}} = 2 \times n_{\text{H}_2\text{O}}$$

$$\text{N atomic balance: } 2(0.79 n_{\text{Air}}) = 2(84.2 \text{ mol})$$

$$n_{\text{air}} = 106.6 \text{ mol}$$

$$\text{O atomic balance: } 2 \times (106.6 \times 0.21) = (2 \times 9.5) + 1.0 + (2 \times 5.3) + n_{\text{H}_2\text{O}}$$

$$n_{\text{H}_2\text{O}} = 14.17$$

The molar ratio of hydrogen to carbon in the fuel $r = y/x$, and the percentage of excess air used in the combustion can thus be calculated from the following equations:

$$\text{C atomic balance: } x n_{\text{CxHy}} = 9.5 + 1.0$$

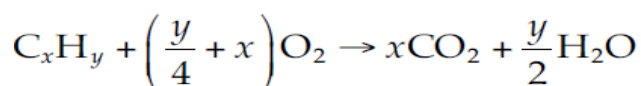
$$\text{H atomic balance: } y n_{\text{CxHy}} = 2 \times 14.17$$

Divide H atomic balance equation by C atomic balance

$$\frac{y \times \cancel{n_{\text{CxHy}}}}{x \times \cancel{n_{\text{CxHy}}}} = \frac{2 \times 14.17}{9.5 + 1.0}$$

$$r = \frac{y}{x} = \frac{28.34}{10.5}$$

For complete combustion, the following reaction is taking place:



For 106.6 mol air fed, 10.5 mol of CO₂ produced, $x = 10.5$, $y = 28.34$. The percentage of excess air used in the combustion:

Moles of C_xH_y can be found from the equation of C atomic balance:

$$10.5 \times n_{\text{CxHy}} = 9.5 + 1.0$$

$$n_{\text{CxHy}} = \frac{10.5}{10.5} = 1 \text{ mol}$$

Per one mole of C_xH_y fed to the burner,

$$\text{Theoretical O}_2 = 1 \text{ mol C}_x\text{H}_y \times \frac{\left(\frac{y}{4} + x \right) \text{O}_2}{\text{mol C}_x\text{H}_y} = \frac{28.34}{4} + 10.5 = 17.59 \text{ mol O}_2$$

$$\text{Theoretical N}_2 = 17.59 \text{ mol O}_2 \times \frac{0.79 \text{ mol N}_2}{0.21 \text{ mol O}_2} = 66.15 \text{ mol N}_2$$

The associated theoretical nitrogen is thus calculated.

$$\begin{aligned}\text{Theoretical air} &= \text{moles of theoretical oxygen} + \text{nitrogen} \\ &= 17.59 + 66.15 = 83.74 \text{ mol}\end{aligned}$$

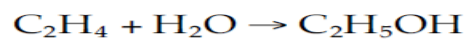
$$\text{Excess air: } 106.6 - 83.74 = 22.86 \text{ mol}$$

$$\% \text{ excess air} = \frac{22.8}{83.7} \times 100\% = 27\% \text{ excess air}$$

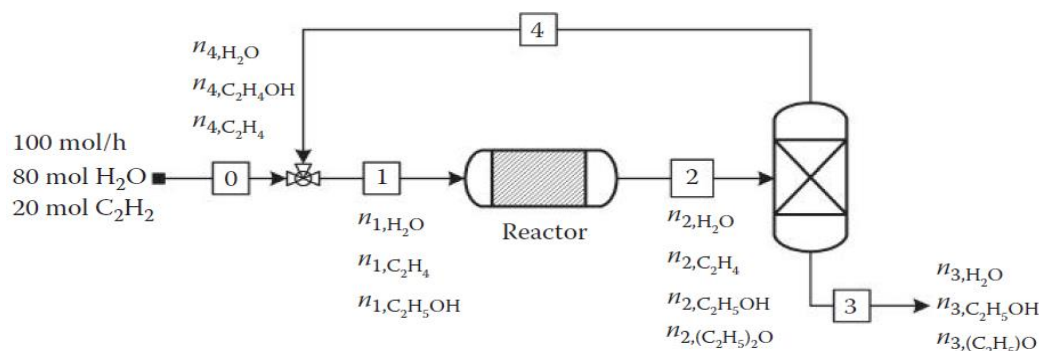
Example 3.12 Ethanol Production

Problem

Fresh feed containing 20.0% C_2H_4 and 80.0% H_2O is fed to a continuous reactor. The reaction products are fed to a condenser that has two product streams: a vapor stream that contains C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$, and water vapor; and a liquid stream that contains the remaining ethanol, ethylene oxide, and water. The vapor stream from the condenser is recycled and mixed with the fresh feed to be fed to the reactor. The overall process yield is 80% of ethanol produced. In the reactor, ethanol ($\text{C}_2\text{H}_5\text{OH}$) is produced by steam (H_2O) reformation with ethylene (C_2H_4). An undesirable side reaction, ethylene oxide is formed:



If the ratio of water in the recycle stream to water in the product stream is 1:10, and the ratio of the ethylene in the recycle to ethylene in the fresh feed is 4:1. The mole fraction of ethanol in the reactor exit stream is 0.157. Determine the recycle flow rate and the single-pass conversion of ethylene in the reactor.



EXAMPLE FIGURE 3.12.1: Schematic of the ethanol production process.

Solution

Known quantities: Fresh feed containing 20.0% C_2H_4 and 80.0% H_2O is fed to a continuous reactor.

Find: The recycle flow rate and the single-pass conversion of ethylene in the reactor.

Analysis: The flowchart of the process is shown in Example Figure 3.12.1. Degrees of Freedom Analysis

Degrees of Freedom Analysis	Overall Process
Number of unknowns	3 ($n_{3,\text{H}_2\text{O}}$, $n_{3,\text{C}_2\text{H}_4\text{OH}}$, $n_{3,(\text{C}_2\text{H}_5)_2\text{O}}$)
Number of reactions	1
Number of atomic balances	3
Number of relations	1 (overall conversion)
NDF	0

System: Overall process

$$\text{Overall yield : } 0.8 = \frac{n_{\text{C}_2\text{H}_4\text{OH}}}{20}$$

$$n_{3,\text{C}_2\text{H}_4\text{OH}} = 16 \text{ mol}$$

$$\text{C atomic balance: } 20 \times 2 = 4n_{3,(\text{C}_2\text{H}_4)_2\text{O}} + 16 \times 2$$

$$n_{3,(\text{C}_2\text{H}_4)_2\text{O}} = 2 \text{ mol}$$

$$\text{O atomic balance: } 80 = 2 + 16 + n_{3,\text{H}_2\text{O}}$$

$$n_{3,\text{H}_2\text{O}} = 62 \text{ mol}$$

Relation: The ratio of water vapor in the recycle stream (4) to liquid water in the product stream (3) is 1/10:

$$\frac{n_{4,\text{H}_2\text{O}}}{n_{3,\text{H}_2\text{O}}} = \frac{1}{10}$$

$$n_{4,\text{H}_2\text{O}} = \frac{1}{10} n_{3,\text{H}_2\text{O}} = \frac{1}{10} \times 62$$

$$n_{4,\text{H}_2\text{O}} = 6.2 \text{ mol}$$

Mixing point balance: water in the recycle stream + water in the fresh stream

$$n_{1,\text{H}_2\text{O}} = 80 + 6.2 = 86.2 \text{ mol}$$

Water balance around the condenser:

$$n_{2,\text{H}_2\text{O}} = 62 + 6.2 = 68.2 \text{ mol}$$

$$\frac{\text{Ethylene in recycle}}{\text{Ethylene in fresh feed}} = \frac{n_{4,\text{C}_2\text{H}_4}}{20} = \frac{4}{1}$$

$$n_{4,\text{C}_2\text{H}_4} = 80 \text{ mol}$$

Also 80 mol C_2H_4 enters the condenser. The exit of the reactor contains the following:

$$80 \text{ mol } \text{C}_2\text{H}_4$$

$$2 \text{ mol } (\text{C}_2\text{H}_5)_2\text{O}$$

$$68.2 \text{ mol H}_2\text{O}$$

$$y_{\text{C}_2\text{H}_5\text{OH}} = 0.157$$

$$f_{\text{C}_2\text{H}_4} = \frac{n_{1,\text{C}_2\text{H}_4} - n_{2,\text{C}_2\text{H}_4}}{n_{1,\text{C}_2\text{H}_4}}$$

$$\% \text{ Conversion} = \frac{100 - 80}{100} = 20\%$$

Total moles of reactor effluent stream

$$80 + 2 + 68.2 = (1 - 0.157)n_2$$

Solving for n_2 ,

$$n_2 = \frac{150.2}{0.843} = 178.10 \text{ mol}$$

Total moles of ethanol present in the reactor effluent

$$n_{2,\text{CH}_3\text{OH}} = 0.157 \times 178.10 = 27.96 \text{ mol}$$

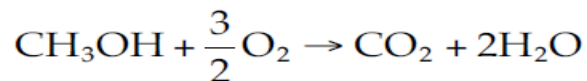
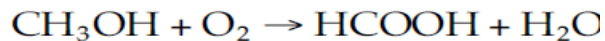
The flow rate of recycle stream is $27.96 - 16 = 11.96$ mol of ethanol:

$$\text{Recycle} = 80 \text{ mol C}_2\text{H}_4 + 6.2 \text{ mol H}_2\text{O} + 11.9 \text{ mol ethanol} = 98.1 \text{ mol}$$

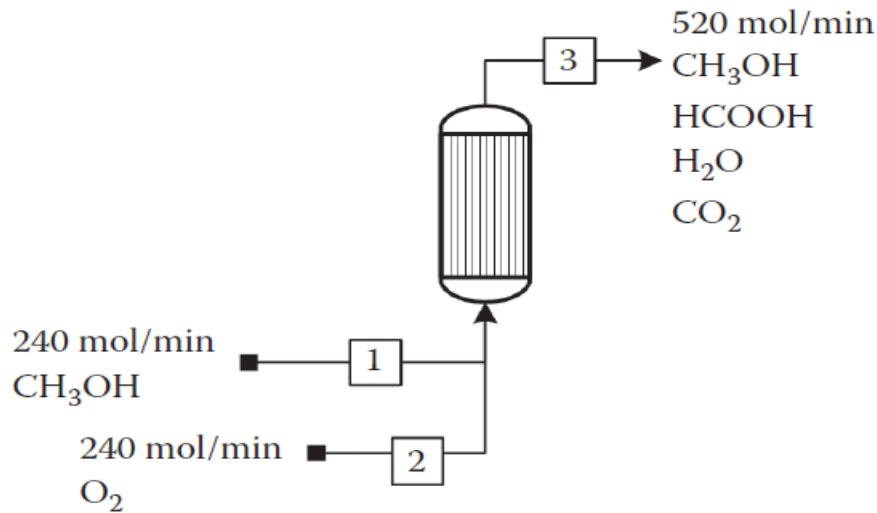
Example 3.13 Methanol Combustion

Problem

Methanol (CH_3OH) at 240 mol/min and oxygen (O_2) at a rate of 240 mol/min are fed to an isothermal reactor operating at 25°C . The reactor operates at steady state. Two reactions take place:



The flow rate out of the reactor is 520 mol/min. No oxygen was found in the reactor product stream. Determine the heat that must be withdrawn to keep the reactor at constant temperature. Determine the fractional conversion of methanol. Determine the selectivity for the conversion of methanol to formic acid.



EXAMPLE FIGURE 10.13.1: Process flow sheet of the methanol combustion process.

Solution

Known quantities: Inlet and product stream flow rates.

Find: The fractional conversion of methanol, selectivity for the methanol.

Analysis: The process flowchart is shown in Example Figure 3.13.1.

Material balance

Using the extent of reaction method,

$$\text{CH}_3\text{OH}: \quad n_{\text{CH}_3\text{OH}} = 240 - \xi_1 - \xi_2$$

$$\text{HCOOH}: \quad n_{\text{HCOOH}} = 0 + \xi_1$$

$$\text{H}_2\text{O}: \quad n_{\text{H}_2\text{O}} = 0 + \xi_1 + 2\xi_2$$

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

$$\text{O}_2: \quad n_{\text{O}_2} = 240 - \xi_1 - \frac{3}{2}\xi_2$$

$$n_3 = 480 + \frac{1}{2}\xi_2$$

The total molar flow rate out of the reactor

$$\dot{n}_3 = 480 + \frac{1}{2}\dot{\xi}_2 = 520$$

$$\text{Solving: } \dot{\xi}_2 = 80 \text{ gmol/min}$$

O₂ mole balance: (note that no oxygen is found in the reactor effluent stream)

$$\dot{n}_{3,\text{O}_2} = 240 - \dot{\xi}_1 - \frac{3}{2}\dot{\xi}_2 = 240 - \dot{\xi}_1 - 120 = 0$$

Solving for the extent of reaction 1,

$$\dot{\xi}_1 = 120 \text{ gmol/min}$$

Energy balance

Since the reactor is isothermal (25°C), the heat released is the heat of reaction:

$$Q = \Delta H_{\text{Rx}}^0$$

The standard heat of reaction

$$Q = \Delta H_{\text{Rx}}^0 = \xi_1 \Delta H_{\text{Rx},1}^0 + \xi_2 \Delta H_{\text{Rx},2}^0$$

The standard heat of reaction from the heat of formations

$$\Delta H_{\text{Rx},1}^0 = \Delta H_{\text{f},\text{H}_2\text{O}}^0 + \Delta H_{\text{f},\text{HCOOH}}^0 - \Delta H_{\text{f},\text{O}_2}^0 - \Delta H_{\text{f},\text{CH}_3\text{OH}}^0$$

Substitute standard heat of formation found in Table A.2:

$$\Delta H_{\text{Rx},1}^0 = -241.83 + (-115.9) - 0 - (-238.6) = -119.13 \text{ kJ/mol}$$

The standard heat of reaction for the second reaction

$$\Delta H_{\text{Rx},2}^0 = 2\Delta H_{\text{f},\text{H}_2\text{O}}^0 + \Delta H_{\text{f},\text{CO}_2}^0 - \frac{3}{2}\Delta H_{\text{f},\text{O}_2}^0 - \Delta H_{\text{f},\text{CH}_3\text{OH}}^0$$

Substitute the values of standard heat of formation for the second reaction:

$$\Delta H_{\text{Rx},2}^0 = 2(-241.83) + (-393.5) - \frac{3}{2}(0) - (-238.6) = -638.56 \text{ kJ/mol}$$

The heat evolved from the reactor, Q , is given by

$$Q = \xi_1 \Delta H_{\text{Rx},1}^0 + \xi_2 \Delta H_{\text{Rx},2}^0$$

Substitute the values of heat of reaction and extent of reaction:

$$Q = 120(-119.13) + 80(-638.56) = -65,380.4 \text{ kJ/min}$$

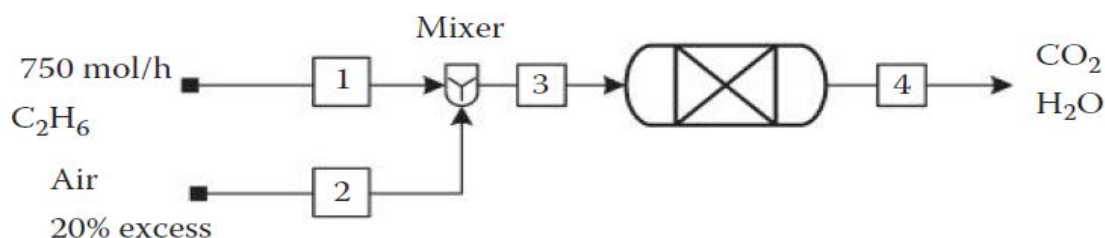
Fractional conversion of methanol: $\frac{\dot{\xi}_1 + \dot{\xi}_2}{\dot{n}_{1,\text{CH}_3\text{OH}}} = \frac{120 + 80}{240} = 0.833$

Fractional selectivity to formic acid: $\frac{\dot{\xi}_1}{\dot{\xi}_1 + \dot{\xi}_2} = \frac{120}{120 + 80} = 0.60$

Example 3.14 Ethane Combustion

Problem

Ethane (C_2H_6) at a molar flow rate of 750 mol/h is mixed with 20% excess air and fed to a burner where the mixture is completely combusted isothermally at $25^\circ C$, using cold water. What is the air flow rate to the burner (mol/h) and what is the amount of heat released to the cold water?



EXAMPLE FIGURE 3.14.1: Ethane combustion process flow sheet.

Solution

Known quantities: Ethane molar flow rate and percent excess air.

Find: The air flow rate to the burner (mol/h) and the amount of heat released to the cooling water.

Analysis: The process flowchart is shown in Example Figure 3.14.1.

Balanced reaction is $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$

Air flow at 20% above the stoichiometric requirement is calculated as

$$\begin{aligned} \text{Theoretical air} &= \left(\frac{750 \text{ mol ethane}}{\text{h}} \right) \left(\frac{3.5 \text{ mol } O_2}{\text{mol ethane}} \right) \\ &\times \left(\frac{1 \text{ mol air}}{0.21 \text{ mol } O_2} \right) = 12,500 \text{ mol/h} \end{aligned}$$

Excess air:

$$\text{Excess air} = 0.2(\text{Theoretical air}) = 0.2(12,500 \text{ mol/h}) = 2500 \text{ mol/h}$$

$$\text{Total air} = \text{Theoretical} + \text{excess} = 12,500 + 2500 = 15,000 \text{ mol/h}$$

The heat released to the coolant is given by

$$Q = \dot{\xi} \times \Delta \hat{H}_{\text{rxn}}^0$$

$$\Delta H_{\text{Rx}}^0 = 3\Delta H_{f,\text{H}_2\text{O}}^0 + 2\Delta H_{f,\text{CO}_2}^0 - \Delta H_{f,\text{C}_2\text{H}_6}^0 - \frac{7}{2}\Delta H_{f,\text{O}_2}^0$$

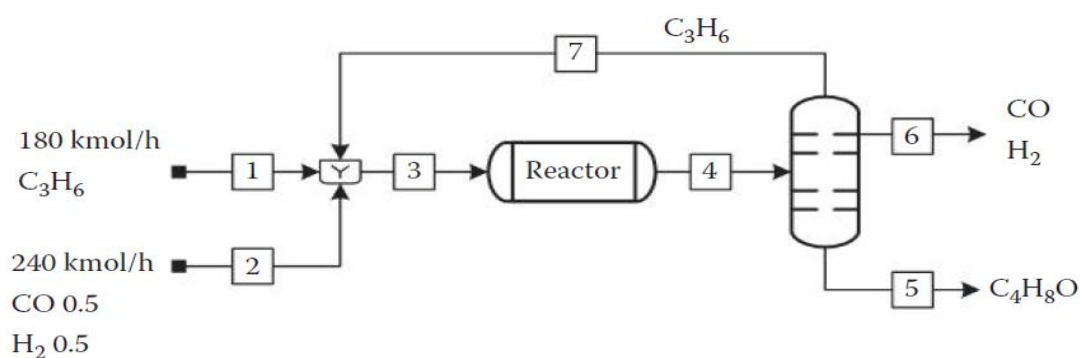
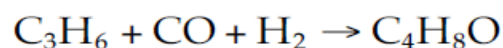
$$\Delta H_{\text{Rx}}^0 = 3(-241.83) + 2(-393.5) - (-84.67) - 0 = -1427.8 \text{ kJ/mol}$$

$$Q = 750 \text{ mol/h} (-1427.8 \text{ kJ/mol}) = -1.24 \times 10^6 \text{ kJ/h}$$

Example 3.15 Chemical Reactors with Recycle

Problem

180 kmol/h of propylene (C_3H_6) is mixed with 240 kmol/h of a mixture containing 50% CO and 50% H_2 and with a recycle stream containing only unreacted propylene and then fed to a reactor. A single-pass conversion of propylene of 30% is achieved. Butanol (C_4H_8O), used to make laundry detergents, is made by the reaction of propylene (C_3H_6) with CO and H_2 :



EXAMPLE FIGURE 3.15.1: Process flow sheet for butanol production.

The desired product butanol (B) is removed in one stream, unreacted CO and H_2 are removed in a second stream, and unreacted C_3H_6 is recovered and recycled. Calculate production rate of butanol (kmol/h) and the flow rate of the recycle stream (kmol/h).

Solution

Known quantities: Inlet stream molar flow rate and compositions.

Find: Production rate of butanol (kmol/h) and the flow rate of the recycle stream (kmol/h).

Analysis: The process flow sheet is shown in Example Figure 3.15.1. First choose the entire process as the system. Since no propylene leaves the process, the overall conversion is 100% (fractional conversion = 1.0).

Basis: 180 kmol/h of propylene feed.

Therefore

$$1 = \frac{\dot{\xi}}{180} \quad \text{or} \quad \dot{\xi} = 180 \text{ kmol/h}$$

The balance on butanol is simply $\dot{n}_{5, C_4H_8O} = \dot{\xi} = 180 \text{ kmol/h}$.
Butanol (C_4H_8O) production rate is 180 kmol/h.

Now choose the reactor as the system. The fractional single-pass conversion = 0.3. The extent of reaction is the same as that for overall process because the reactor is the only unit where reaction takes place in the process. Therefore,

$$0.3 = \frac{\dot{\xi}}{\dot{n}_{3,\text{C}_3\text{H}_6}} = \frac{180}{\dot{n}_{3,\text{C}_3\text{H}_6}}$$

Solving for the molar flow rate of propylene fed to the reactor,

$$\dot{n}_{3,\text{C}_3\text{H}_6} = 600 \text{ kmol/h}$$

From a balance around the mixer, we can find that the recycle rate must be

$$600 - 180 = 420 \text{ kmol/h}$$

Homework Problems

3.1 An adiabatic pot is used to cool and condense 10 kg of hot ethanol (150°C , 1.2 atm) by mixing it with cold ethanol (5°C , 1.2 atm). If the final ethanol product is to be at 25°C and 1.2 atm, the heat capacity of liquid and vapor ethanol is 112 and 65.6 J/mol $^\circ \text{C}$. Boiling point of ethanol is 78.3°C . The latent heat of vaporization of ethanol is 36,600 J/mol. How much cold ethanol (kg) must be added? (220 kg)

3.2 A quantity of 100 mol/h acetylene (C_2H_2) is mixed with 2000 mol/h air (79 mol% N_2 , 21 mol% O_2) and the mixture (at 298 K and 1 atm) fed to a reactor, where complete combustion takes place. The reactor is equipped with cooling tubes. The combustion mixture leaving the reactor is at 1000 K and 1 atm. Draw and label the process flowchart. How much heat (kJ/h) was removed in the reactor? ($-82,370 \text{ kJ/h}$) Suppose the coolant supply was suddenly shut off. What reactor outlet temperature would be reached?

$$C_{\text{pCO}_2} = 37 \text{ J/mol } ^\circ\text{C}, \quad C_{\text{pH}_2\text{O}} = 33.6 \text{ J/mol } ^\circ\text{C}, \\ C_{\text{pO}_2} = 29.3 \text{ J/mol } ^\circ\text{C}, \quad C_{\text{pN}_2} = 29.3 \text{ J/mol } ^\circ\text{C}$$

Assume these values to be constant and independent of temperature.

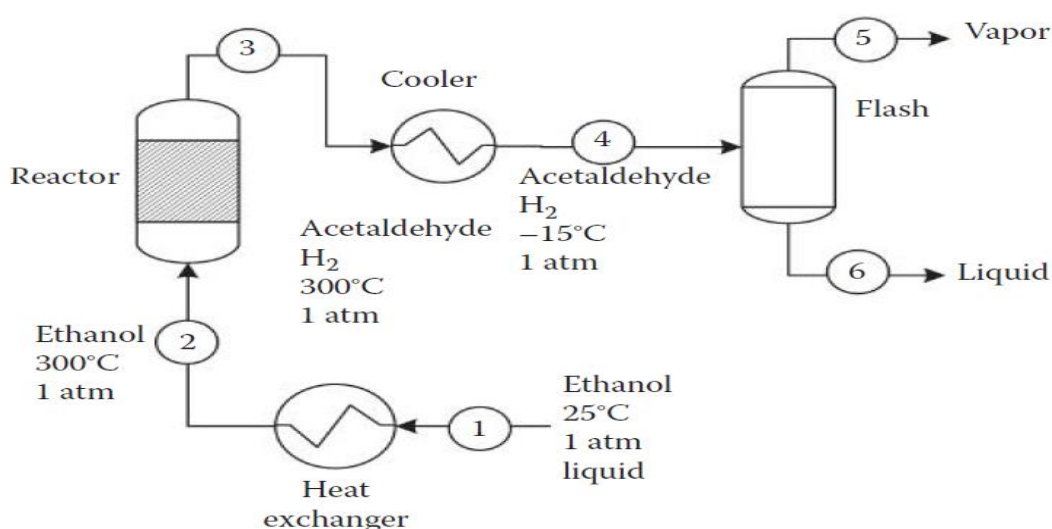
3.3 Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is dehydrogenated in a catalytic reactor to acetaldehyde (CH_3CHO), with hydrogen (H_2) as a by-product. In an existing process, 100 mol/min liquid ethanol at 25°C and 1 atm pressure is first heated to 300°C in a heat exchanger, and then fed to the reactor. One hundred percent of the ethanol is converted to products, and the product stream leaves the reactor at 300°C and 1 atm (760 mmHg). The product stream leaving the reactor is cooled to -15°C , and sent to a flash drum, where vapor and liquid streams are separated (Problem Figure 3.3.1).

How much heat must be supplied to the first heat exchanger? (6400 kJ/min)

How much heat must be supplied to or removed from (state which one) the reactor in order to maintain a constant temperature of 300°C ? (7100 kJ/min)

What are the flow rates of the vapor and liquid streams leaving the flash drum? (126 mol/min, 74 mol/min)

Species	T_b $^\circ\text{C}$	$\Delta H_{\text{vap}}(T_b)$ kJ/gmol	$C_p(\text{liquid})$ kJ/gmol $^\circ\text{C}$	$C_p(\text{gas})$ kJ/gmol $^\circ\text{C}$	$\Delta H_f^0(25^\circ\text{C})$ kJ/gmol
H_2	-252.76	0.904	—	0.029	0 (g)
CH_3CHO	20.2	25.1	0.089	0.055	-166.2 (g)
$\text{C}_2\text{H}_5\text{OH}$	78.5	38.58	0.158	0.077	-277.63 (L) -235.31 (g)



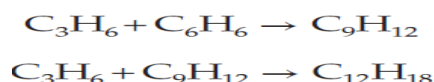
PROBLEM FIGURE 3.3.1: Ethanol ($\text{C}_2\text{H}_5\text{OH}$) dehydrogenation process.
Antoine equation:

$$\text{Ethanol: } \log_{10} P_{\text{sat}} (\text{mmHg}) = 8.04494 - \frac{1554.3}{222.65 + T(^{\circ}\text{C})}$$

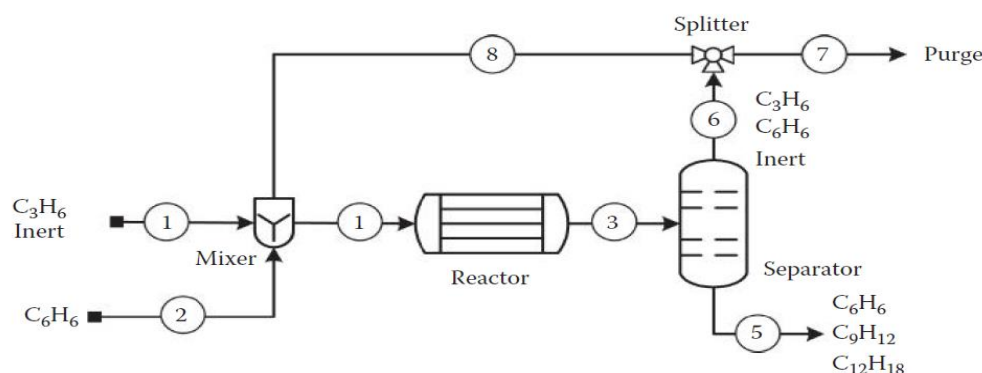
$$\text{Acetaldehyde: } \log_{10} P_{\text{sat}} (\text{mmHg}) = 6.81089 - \frac{992}{230 + T(^{\circ}\text{C})}$$

3.4 A gas contains the following compounds: CH_4 , C_2H_6 , O_2 , CO_2 , CO , H_2O , and H_2 . What is the maximum number of independent chemical reactions that can be written involving these compounds? (Four independent equations)

3.5 Cumene (C_9H_{12}) is synthesized from propylene (C_3H_6) and benzene (C_6H_6). Unfortunately, a side reaction also occurs, in which diisopropylbenzene ($\text{C}_{12}\text{H}_{18}$) is generated by reaction of propylene with cumene. The two balanced reactions are



A block flow diagram for the cumene manufacturing process is shown in Problem Figure 3.5.1. A quantity of 100 kmol/h of a gas containing 95 mol% Propylene and 5 mol% Inert is mixed with 80 kmol/h benzene plus a recycle stream. The mixer outlet is fed to a reactor. The fractional conversions achieved in the reactor based on the reactor feed stream are: the fractional conversion of benzene is 0.9 and the



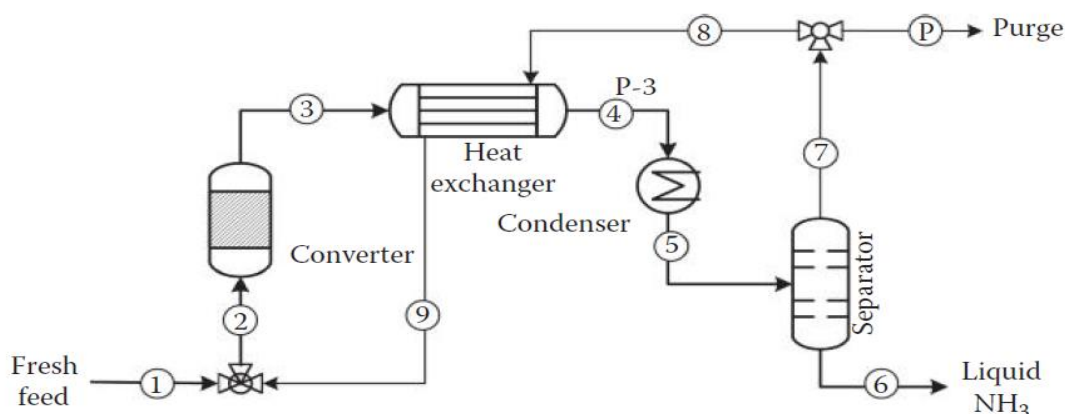
PROBLEM FIGURE 3.5.1: Cumene (C_9H_{12}) synthesis process.

fractional conversion of propylene is 0.7. The reactor outlet is sent to a separator, where all of the propylene, all of the Inert, and 10% of the benzene are recovered in stream 6, and the remaining benzene and all of the cumene and di-isopropyl benzene are recovered as bottom product. Stream 6 is sent to a splitter. Eighty-five percent of the splitter feed is recycled to the mixer and the remainder is purged. Calculate the following:

- Flow rates of propylene and benzene (kmol/h) in stream 3. (80.7 kmol/h)
- Mol% Inert in purge stream. (46%)
- Selectivity for converting benzene to cumene achieved by the overall process. (0.77)

3.6 Ammonia is synthesized through the reaction of nitrogen with hydrogen as follows: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

Problem Figure 10.6.1 shows a process flow sheet for the ammonia synthesis process. In this process, the fresh feed consists of argon (1 mol%) and stoichiometric amounts of N_2 and H_2 . The reactor feed has a molar flow rate of 100 mol/min and a composition of 15 mol% argon, 21.25 mol% N_2 , and 63.75 mol% H_2 . The reactor feed temperature is 400°C . The fractional conversion of N_2 to NH_3 in the reactor is 0.15 mol N_2 reacted/mol N_2 feed to the reactor. The hot reactor effluent gas is used to heat the recycle gas from the separator in a combined reactor effluent/recycle heat exchanger. After passing through this heat exchanger, the reactor effluent gas passes through a condenser where the NH_3 product is condensed. The liquid NH_3 is separated from the non-condensable recycle gases. A purge stream is taken



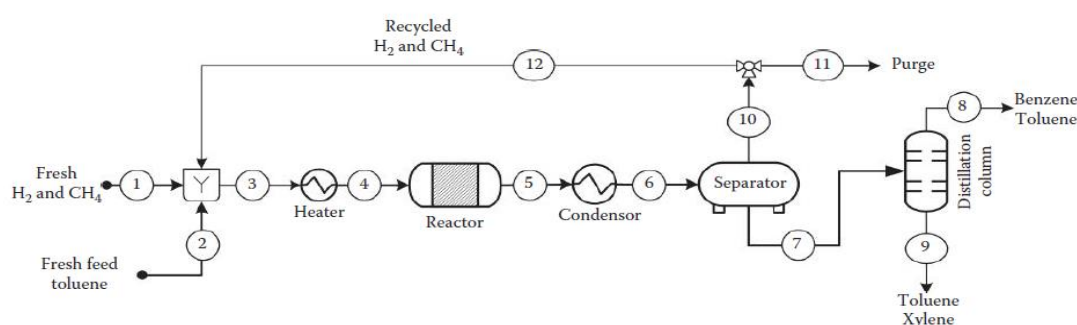
PROBLEM FIGURE 3.6.1: Ammonia synthesis process.

off the separator off-gas to maintain the level of argon at 15 mol% feed to the reactor. In this particular process, the converter is operated adiabatically and the heat of reaction at 400°C was found to be -53.109 kJ/mol at the pressure of the reactor. The following table gives the heat capacities at the pressure of the reactor. Note that the given heat capacities are assumed to be constant over the temperature range found in the reactor:

Compound	C_p (J/mol $^\circ\text{C}$)
NH_3	49.4
H_2	29.5
N_2	31.0
Argon	20.8

- Determine the flow rates in moles per minute and compositions in mole percent of
- Fresh feed stream. (12.5 mol/min)
 - Separator purge gas stream. (0.74 mol/min)
 - Recycle gas stream. (87.5 mol/min)
 - Estimate the temperature of the effluent gases from the converter. (460.776°C)
 - If the recycle gas stream enters the heat exchanger at 50°C and leaves the exchanger at 400°C , determine the outlet temperature of the reactor effluent stream from the heat exchanger. Assume no condensation of ammonia in the heat exchanger. (147.271°C)

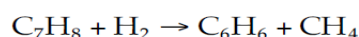
3.7 Toluene (225 kmol/h) is fed to a reactor to produce benzene. In this process (Problem Figure 3.7.1), toluene reacts with a fractional conversion of 0.80, resulting in benzene and xylene yields of 0.505 and 0.495, respectively:



PROBLEM FIGURE 3.7.1: Process flow sheet of benzene production process.



Toluene also may dealkylate in the reactor to form benzene and methane:



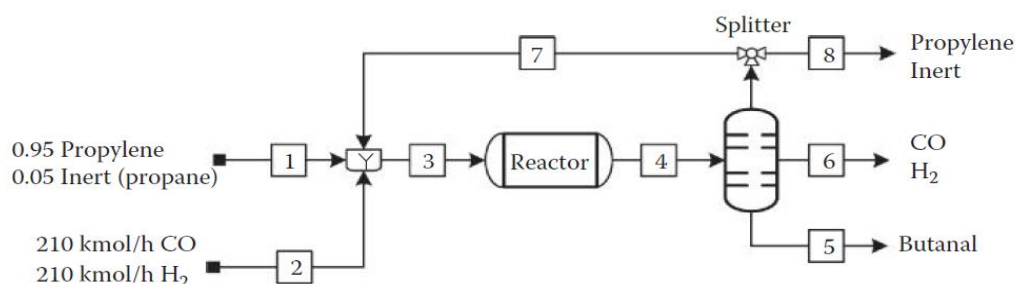
Yields are defined as moles of product/moles of toluene reacted. In this process, the reactor effluent is condensed and separated. The separator liquid is sent to a benzene distillation column where benzene with a purity of 99.5 mol% (balance toluene) is removed as the overhead product. The bottom products contain benzene, unreacted toluene, and xylene. A purge stream containing 90% hydrogen and 10% methane is taken off the separator gas stream. The rest of this separator gas stream is combined with a fresh hydrogen stream containing hydrogen and methane with concentrations of 95.0 and 5.0 mol%, respectively. These combined hydrogen streams are added

to the fresh toluene feed and sent to the reactor heater. If the liquid toluene fresh feed stream, fresh hydrogen stream, and recycled streams are all at 25°C and 15 bar absolute, determine the heat requirements for the reactor heater to provide the reactor with a combined feed at 400°C and 15 bar absolute in the vapor phase.

3.8 The dehydrogenation of propane is carried out in a continuous reactor. Pure propane is fed to the reactor at 1300°C and at a rate of 100 mol/s. Heat is supplied at a rate of 1.34 kW. If the product temperature is 1000°C , calculate the extent of reaction. ($\zeta = 26$)

3.9 A fresh feed stream contains 5% inert (propane) and 95% propylene. The fresh feed of propylene and inert (propane) is mixed with 210 mol/h carbon dioxide and same amount of hydrogen. At your reactor conditions, propane (I) is an inert, and it is too expensive to separate propane from propylene, so you decide to install a purge stream. The single-pass conversion of propylene in the reactor is 0.3. The production rate of butanol is 180 kmol/h. An overall conversion of 0.90 can be achieved. The purge stream is necessary to avoid inert accumulation in the process. Calculate the flow rate of the contaminated propylene stream to the process (Problem Figure 3.9.1). (210.5 kmol/h)

3.10 Steam flowing at a mass flow rate of 1500 kg/h, a pressure of 20 bar, and 350°C is fed to a turbine that operates adiabatically and at steady state. The steam leaves the turbine at 1.0 bar and 150°C and is cooled in a heat exchanger to a saturated liquid. Draw and label the process flow diagram. How much work (kJ/h) is extracted in the turbine? (541,650 kW) How much heat (kJ/h) is removed in the heat exchanger? (-3.54×10^6 kJ/h)



PROBLEM FIGURE 3.9.1: Butanal production process.

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4 CHAPTER FOUR

Unsteady-State Material and Energy Balances

This chapter focuses briefly on unsteady-state processes in which the value of the state, dependent variable, as a function of time is of interest. The term “unsteady state” refers to processes in which quantities or operating conditions within the system change with time. The word transient state applies to such processes. A wide variety of important industrial problems fall into this category, such as start-up/shut-down of process equipment, batch processing, the change from one set of operating conditions to another, and the perturbations that develop as process conditions fluctuate. The following items outline the principal learning objectives of this chapter.

Learning Objectives

1. Develop unsteady-state material balance equations and solve simultaneous

First-order ordinary differential material balance equations

2. Develop unsteady-state energy balance equations and explain the rational changes in concentration or temperature versus time (Section 4.2).

4.1 Unsteady-State Material Balance

Unsteady or transient state refers to processes in which quantities or operating conditions within the system change with time [1–3]. For such processes, the accumulation term in the mass balance equation cannot be neglected and must be accounted for (Figure 4.1).

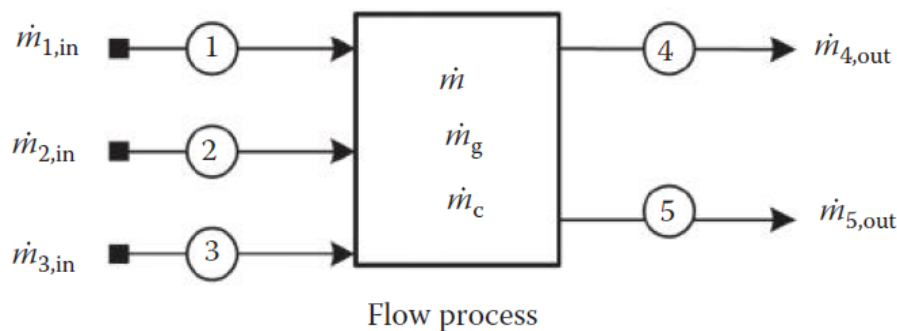


FIGURE 4.1: Open system with multiple input and output streams.

The general material balance equation takes the following form:

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_g - \dot{m}_c \quad \dots\dots\dots(4-1)$$

where

m is the mass accumulated in the system [mass]

\dot{m}_{in} is the inlet mass flow rate [mass/time]

\dot{m}_{out} is the outlet mass flow rate [mass/time]

\dot{m}_g is the generated mass flow rate [mass/time]

\dot{m}_c is the consumed mass flow rate [mass/time]

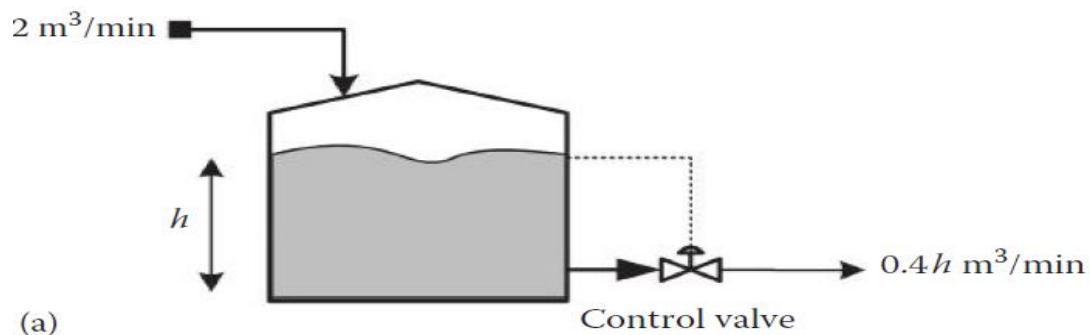
$$\dot{m}_{\text{in}} = \sum_{\text{in}} \dot{m}_{i,\text{in}}$$

$$\dot{m}_{\text{out}} = \sum_{\text{out}} \dot{m}_{i,\text{out}}$$

Example 4.1 Filling Controlled Level Storage Tank

Problem

A storage tank that is 2.0 m in diameter is filled at a rate of 2.0 m³/min. When the height of the liquid is 2 m in the tank, a control valve installed on the exit stream at the bottom of the tank opens up, and the fluid flows at a rate proportional to the head of the fluid, that is, 0.4 h m³/min, where h is the height of fluid in meters. Plot the height of the liquid as a function of time. What is the steady-state height of the fluid in the tank?



EXAMPLE FIGURE 4.1.1: (a) Schematic of a storage tank.

Solution

Known quantities: Inlet and exit tank volumetric flow rate.

Find: Plot the height of the tank as a function of time.

Analysis: The tank flowchart is shown in Example Figure 4.1a.1. Unsteady-state mass balance:

Neither generation nor consumption occurs in the process:

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

$$m = \rho V = \rho(Ah), \quad A = \pi D^2/4$$

where

A is the cross-sectional area of the tank

V is the volume of the system

\dot{V} is the volumetric flow rate

$$\dot{m} = \rho \times \dot{V}$$

\dot{V}_{in} and \dot{V}_{out} are the volumetric flow rates of inlet and exit streams, respectively. Simplifying the material balance equations in terms of one variable (h) with time gives

$$\frac{d(\rho Ah)}{dt} = \rho \dot{V}_{in} - \rho \dot{V}_{out}$$

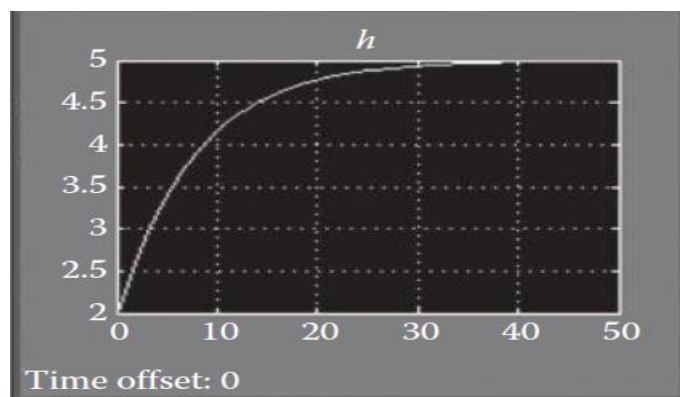
Assume density is constant; the equation is then simplified to

$$A \frac{dh}{dt} = \dot{V}_{in} - \dot{V}_{out}$$

where

$\dot{V}_{in} = \text{constant} = 2 \text{ m}^3/\text{min}$

\dot{V}_{out} is a function of the height of fluid in the tank, which is $0.4h$

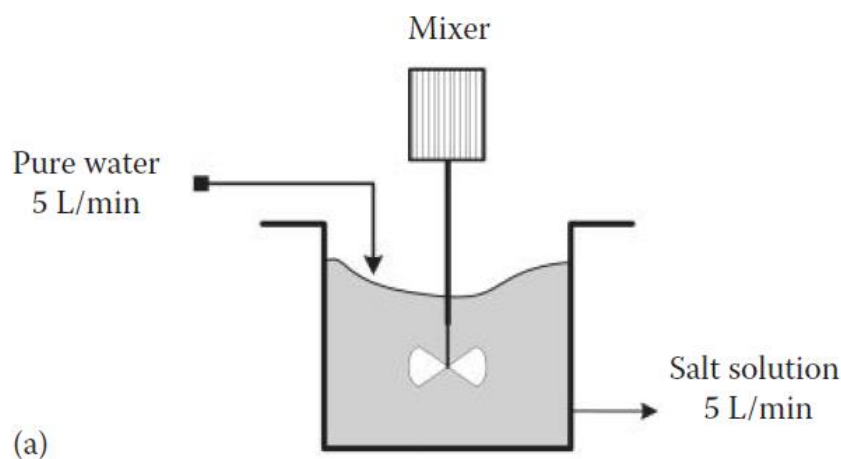


It can be seen that the height of the tank increases sharply with time at the very beginning of the process and slowly with time later on until it reaches the steady state, which is at approximately 5 m. The steady-state height is calculated by setting the differential term to zero. The height is found to be approximately 5 m.

Example 4.2 Dilution of a Salt Solution

Problem

A tank holds 100 L of a salt–water solution in which 5.0 kg of salt is dissolved. Water runs into the tank at a rate of 5 L/min, and salt solution overflows at the same rate. Plot the concentration of the salt versus time. How much salt is in the tank at the end of 10 min?



EXAMPLE FIGURE 4.2.1: (a) Dilution of salt–water solution.

Solution

Known quantities: Volume, mass, and inlet flow rate are known.

Find: The amount of salt in the tank at the end of 10 min.

Analysis: Assume that the solution in the tank is well mixed and the density of the salt solution is essentially the same as that of pure water. The process flow sheet is shown in Example Figure 11.2a.1. The general unsteady-state mass balance is

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_g - \dot{m}_c$$

Since there are no reactions, generation and consumption terms are dropped and the general material balance equation is reduced to

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}}$$

The inlet mass flow rate as a function of salt concentration is

$$\dot{m}_{in} = \dot{V}_{in} C_{in} [=] \frac{\cancel{\text{L}}}{\text{min}} \left| \frac{\text{kg}}{\cancel{\text{L}}} \right| = \frac{\text{kg}}{\text{min}}$$

The outlet mass flow rate is

$$\dot{m}_{out} = \dot{V}_{out} C_{out} [=] \frac{\cancel{\text{L}}}{\text{min}} \left| \frac{\text{kg}}{\cancel{\text{L}}} \right| = \frac{\text{kg}}{\text{min}}$$

Accumulated mass (note that, in the accumulated mass, V is the volume of the fluid in the tank) is

$$\frac{d(m)}{dt} = \frac{d(VC)}{dt} [=] \frac{\cancel{\text{L}} \frac{\text{kg}}{\cancel{\text{L}}}}{\text{min}} = \frac{\text{kg}}{\text{min}}$$

Substitution of these terms in the simplified material balance equation yields the following equation:

$$\frac{d(VC)}{dt} = (\dot{V}_{in} C_{in}) - (\dot{V}_{out} C_{out})$$

Assuming the tank is well mixed, the outlet salt concentration equals the concentration in the tank:

$$\frac{d(VC)}{dt} = (\dot{V}_{in} C_{in}) - (\dot{V}_{out} C)$$

The inlet is pure water, which means inlet salt concentration is zero $\Rightarrow C_{in} = 0$.

Inlet and outlet volumetric flow rates are equal $\Rightarrow \dot{V}_{in} = \dot{V}_{out}$.

Volume of fluid in the tank is constant $\Rightarrow V = \text{constant}$:

$$V \frac{d(C)}{dt} = 0 - \dot{V}_{out} C$$

Solving the resulting differential equation requires an initial condition, which is the concentration of salt in the tank at time zero:

$$C|_{at\ t=0} = \frac{5 \text{ kg}}{100 \text{ L}} = 0.05 \text{ kg/L}$$

Integrating the developed ordinary differential equation and solving for concentration at time equal to 10 min will give the analytical solution as follows:

$$\frac{dC}{C} = -\frac{\dot{V}_{\text{out}}}{V} dt$$

Integrating,

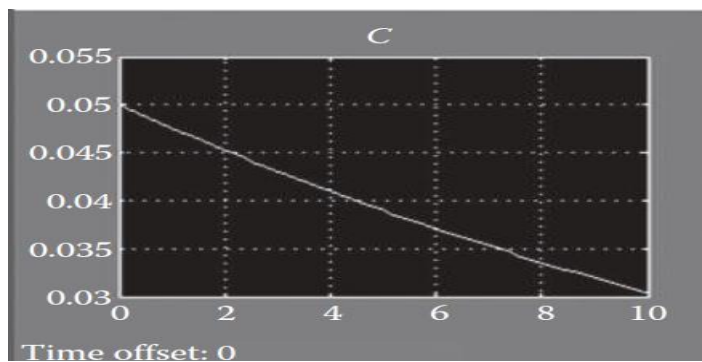
$$\ln \frac{C}{C_o} = -\frac{\dot{V}_{\text{out}}}{V} t$$

Substituting known quantities,

$$\ln \frac{C}{0.05} = -\frac{5 \text{ L/min}}{1 \text{ L}} \times 10 \text{ min}$$

Rearranging,

$$C = 0.05 \exp\left(-\frac{5 \text{ L/min}}{100 \text{ L}} \times 10 \text{ min}\right) = 0.03 \text{ kg/L}$$

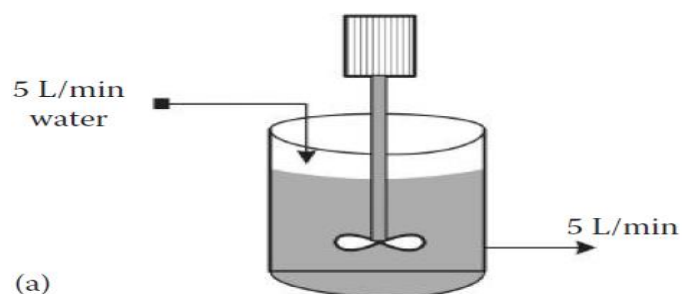


the salt concentration in the tank decreases with time. At the end of 10 min the salt concentration in the tank is 0.03 kg/L.

Example 4.3 Dilution of Salt Solution

Problem

The average ocean water of salinity 35 ppt flows into a 100 L tank containing 1.5 kg salt at a rate of 5 L/min. The salt solution overflows out of the tank at 5 L/min. How much salt remains in the tank at the end of 15 min?



EXAMPLE FIGURE4.3.1(a)
Schematic of a salt dilution

tank.

Solution

Known quantities: Water concentration, exit flow rate are known.

Find: The amount of salt in the tank at the end of 15 min.

Analysis: The dilution process flow sheet is shown in Example Figure 4.3a.1. Assume the fluid in the tank is well mixed and the density of salt solution is constant and equal to that of water. If we have 1 g of salt and 1000 g of water, the salinity is 1 ppt. The general unsteady-state material balance is

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_g - \dot{m}_c$$

Since there are no reactions, generation and consumption terms are dropped and the general material balance equation is reduced to the following form:

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

Replacing mass flow rates in terms of concentration, as done in Example 11.2, yields

$$\frac{d(VC)}{dt} = (\dot{V}_{in}C_{in}) - (\dot{V}_{out}C_{out})$$

Assuming the solution in the tank is well mixed, the outlet salt concentration equals the concentration in the tank; this assumption reduces the earlier equation to the following form:

$$\frac{d(VC)}{dt} = (\dot{V}_{in}C_{in}) - (\dot{V}_{out}C)$$

Inlet and outlet volumetric flow rates are equal $\Rightarrow \dot{V}_{in} = \dot{V}_{out}$.

Volume of fluid in the tank is constant $\Rightarrow V = \text{constant}$:

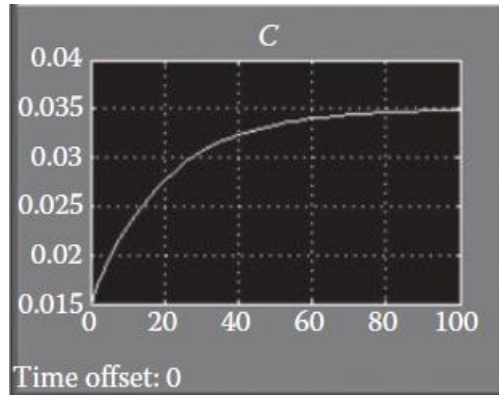
$$V \frac{dC}{dt} = \dot{V}_{in}C_{in} - \dot{V}_{out}C$$

Solving the resultant differential equation requires an initial condition, which is the concentration of salt in the tank at time zero:

$$C|_{at=0} = \frac{1.5 \text{ kg}}{100 \text{ L}} = 0.015 \text{ kg/L}$$

The ocean salt concentration in kilograms per liter is

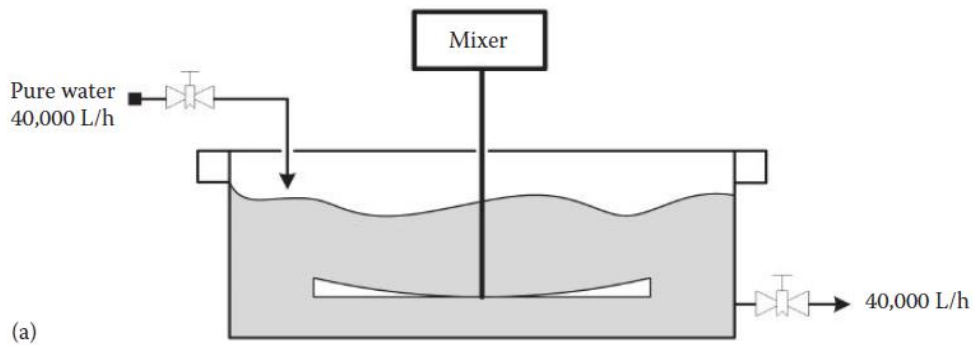
$$C_{in} = 35 \text{ ppt} \left| \frac{1 \text{ g salt}}{1000 \text{ g water}} \right| \left| \frac{1000 \text{ g water}}{1 \text{ L}} \right| \left| \frac{1 \text{ kg}}{1000 \text{ g}} \right| = 0.035 \text{ kg/L}$$



The concentration of salt in the tank after 15 min (90 s) is approximately 0.035 kg/L. Since the volume of the tank is 100 L, accordingly, the amount of salt is 3.5 kg.

Example 4.4 Sewage Treatment Problem

In a sewage treatment plant, a large concrete tank initially contains 440,000 L liquid and 10,000 kg fine suspended solids. To flush this material out of the tank, water is pumped into the vessel at a rate of 40,000 L/h, and liquid containing solids leave at the same rate. Estimate the concentration of suspended solids in the tank at the end of 4 h.



EXAMPLE FIGURE 4.4.1: (a) Sewage treatment tank.

Solution

Known quantities: Tank volume, initial fine solid concentration, flow rates.

Find: The concentration of suspended solids in the tank at the end of 4 h.

Analysis: The process flow diagram is shown in Example Figure 11.4a.1. The general unsteady-state material balance equation is

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + \dot{m}_g - \dot{m}_c$$

Since there are no reactions, generation and consumption terms are dropped, and the general material balance equation is reduced to the following form:

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

Replacing mass flow rates in terms of concentration, as done in Example 4.3, yields

$$\frac{d(VC)}{dt} = (\dot{V}_{in}C_{in}) - (\dot{V}_{out}C_{out})$$

Assuming the solution in the tank is well mixed, the outlet suspended solid concentration equals the concentration in the tank; this assumption reduces the preceding equation to the following form:

$$\frac{d(VC)}{dt} = (\dot{V}_{in}C_{in}) - (\dot{V}_{out}C)$$

Inlet and outlet volumetric flow rates are equal $\Rightarrow \dot{V}_{in} = \dot{V}_{out} = 40,000 \text{ L/h}$.
Volume of fluid in the tank is constant $\Rightarrow V = \text{constant} = 440,000 \text{ L}$.

Pure water is pumped into the vessel at a rate of 40,000 L/h; concentration of solids in the inlet pure water is zero, $C_{in} = 0$, accordingly, solid component balance is

$$V \frac{d(C)}{dt} = 0 - (\dot{V}_{out}C)$$

Solving the resultant differential equation requires an initial condition, which is the concentration of solids in the sewage tank at time zero:

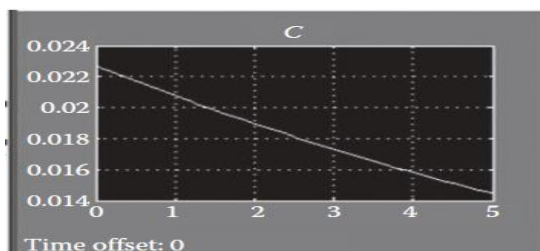
$$C|_{at\ t=0} = \frac{10,000 \text{ kg}}{440,000 \text{ L}} = 0.023 \text{ kg/L}$$

The analytical solution shows the following results:

$$\frac{d(C)}{C} = -\frac{\dot{V}_{out}}{V}, \quad \ln \frac{C_f}{C_o} = -\frac{\dot{V}_{out}}{V}t \Rightarrow C_f = C_o \exp\left(-\frac{\dot{V}_{out}}{V}t\right)$$

Substitute known quantities:

$$C_f = 0.023 \frac{\text{kg}}{\text{L}} \exp\left(-\frac{40,000 \text{ L/h}}{440,000 \text{ L}} 4h\right) = 0.016 \text{ kg/L}$$

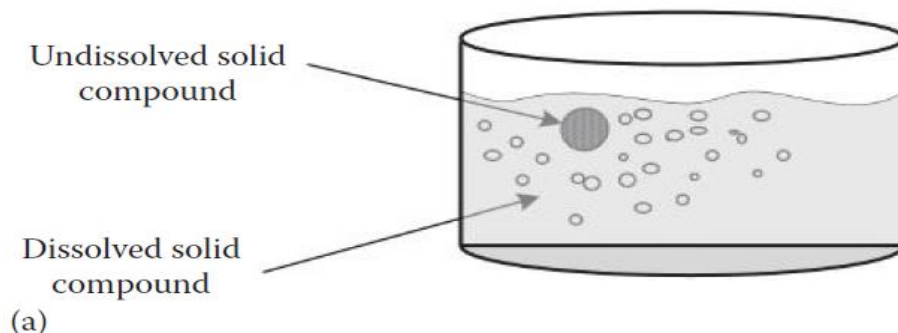


The concentration of suspended solids in the tank after 4 h of operation is approximately 0.016 kg/L, which is the same as the values of the concentration obtained analytically.

Example 4.5 Diffusion of a Solid into a Liquid

Problem

A compound dissolves in water at a rate proportional to the product of the amount of undissolved solid and the difference between the concentration in a saturated solution and the actual solution, that is, $C_{\text{sat}} - C(t)$. The dissolution rate is 0.257 h^{-1} . A saturated solution of this compound contains 0.4 g solid/g water. In a test run starting with 20 kg of undissolved compound in 100 kg of water, how many kilograms of compound will remain undissolved after 10 h? Assume that the system is isothermal.



EXAMPLE FIGURE 4.5.1: (a) Diffusion of solid into water.

Solution

Known quantities: The dissolution rate is 0.257 h^{-1} . A saturated solution of this compound contains 0.2 g solid/g water.

Find: The kilograms of solid compound that will remain undissolved after 10 h.

Analysis: Example Figure 11.5a.1 is a schematic of the process of diffusion of solids in water. Let us assign m for the mass of the undissolved compound at any time, m_0 is the initial mass of the undissolved compound at time zero, and C is the concentration of the dissolved compound in water.

General material balance on the undissolved compound is

$$\frac{dm}{dt} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} + \dot{m}_g - \dot{m}_c$$

There is no inlet or outlet mass flow rate to the tank: $\dot{m}_{\text{in}} = \dot{m}_{\text{out}} = 0$.

There is no generation of the undissolved solid: $\dot{m}_g = 0$.

The rate of consumption: $\dot{m}_c = km(C_{\text{sat}} - C)$

Rearranging the general material balance equation leads to the following equation:

$$\frac{dm}{dt} = -k_m (C_{\text{sat}} - C)$$

Mass of solids in the tank as a function of concentration is

$$C = \frac{m_0 - m}{W} \Rightarrow m = m_0 - C \times W$$

$$C = \frac{m_0}{W} - \frac{1}{W} m$$

Differentiation of this relation leads to

$$\frac{dC}{dt} = -\frac{1}{W} \frac{dm}{dt}$$

Rearranging so as to replace mass by solid concentration yields

$$\frac{dm}{dt} = -W \frac{dC}{dt}$$

$$\frac{dC}{dt} = \frac{k_m}{W} (C_{\text{sat}} - C)$$

Substituting concentration instead of mass of undissolved compound,

$$\frac{dC}{dt} = \frac{k_m (m_0 - C \cdot W)}{W} (C_{\text{sat}} - C)$$

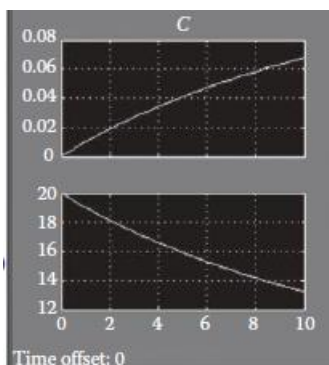
With the following data, solve the earlier equations using Simulink:

$$k = 0.257 \text{ h}^{-1}$$

$$W = 100 \text{ kg} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| = 100,000 \text{ g}$$

$$C_{\text{sat}} = 0.2 \frac{\text{g solid}}{\text{g water}}$$

$$\text{Initial undissolved solid: } m_0 = 20 \text{ kg} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| = 20,000 \text{ g}$$



The diagram reveals the solid concentration is increasing with time. The amount of undissolved solid after 10 h is around 13.21 kg (13,210 g).

4.2 Unsteady-State Energy Balance

Consider the mixing tank shown in Figure 4.2 where heat is added or removed from the tank through jacketed inlet and exit streams [4, 5]. The general form of the energy balance under unsteady-state condition takes the form

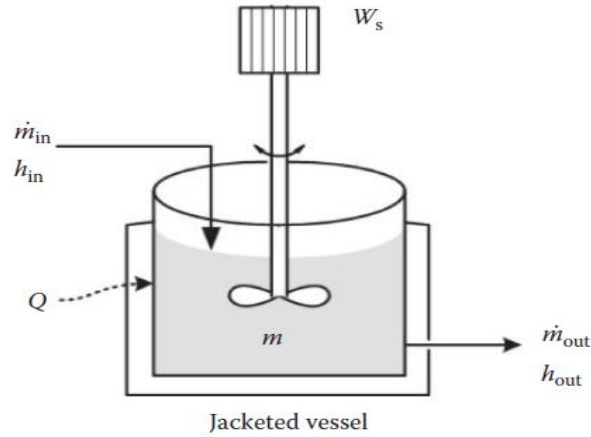


FIGURE 4.2: Energy balance on unsteady state process.

$$\frac{d(U)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

where

U is the internal energy; $U = mC_vT$

h_{in} is the specific enthalpy of the inlet stream

h_{out} is the specific enthalpy of the exit stream

\dot{Q} is the heat added to the system (+). If the heat is lost or transferred from the system to the surroundings, then the sign is negative.

\dot{W}_s is the work done by the system on the surroundings (+). If the work is done on the system, then the sign is negative (-).

For liquids and solids $C_v \approx C_p$ because $\frac{d(PV)}{dt} \oplus 0$:

$$H = U + PV$$

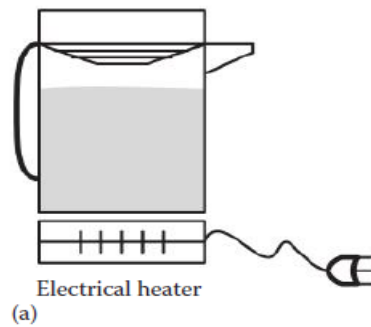
$$\frac{dH}{dt} = \frac{dU}{dt} + \cancel{\frac{d(PV)}{dt}}$$

$$\text{This leads to } \frac{dH}{dt} = \frac{dU}{dt}$$

Example 4.6 Heating of a Closed System

Problem

A kettle used to boil water containing 1.00 L of water at 20°C is placed on an electric heater ($\dot{Q} = 2200 \text{ J/s}$). Find out the time at which water begins to boil.



EXAMPLE FIGURE 4.6.1: (a) Schematic of an electrical heater kettle.

Solution

Known quantities: Kettle volume, initial water temperature, heat supplied.

Find: The time at which water begins to boil.

Analysis: The tank flowchart is shown in Example Figure 4.1a.1. The normal boiling water temperature is 100°C. The kettle heater diagram is shown in Example Figure 4.6a.1. The general energy balance equation is

$$\frac{d(U)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

The kettle is batch; inlet and outlet mass flow rates are zero; $\dot{m}_{in} = \dot{m}_{out} = 0$.

No shaft work: $\dot{W}_s = 0$, For liquids: $C_p \approx C_v$, Specific heat of water: $C_p = 4.18 \text{ J/g}^\circ\text{C}$

The general energy balance equation is simplified to the following equation:

$$\frac{d(mC_p T)}{dt} = \dot{Q}$$

The mass of liquid water inside the kettle is

$$m = \rho V$$

Substituting m in the simplified energy balance equation gives

$$\frac{d(mC_p T)}{dt} = \dot{Q}$$

Rearranging,

$$\frac{dT}{dt} = \frac{\dot{Q}}{\rho V C_p}$$

Solve this ordinary differential equation using the following data:

Heat added to the kettle: $\dot{Q} = 2200 \text{ J/s}$, Specific heat of water: $C_p = 4.18 \text{ J/g}^\circ\text{C}$

Volume of the kettle: $V = 1.0 \text{ L}$, Density of the water in the kettle: $\rho = 1000 \text{ g/L}$

The analytical solution is obtained by integrating the first-order energy balance equation:

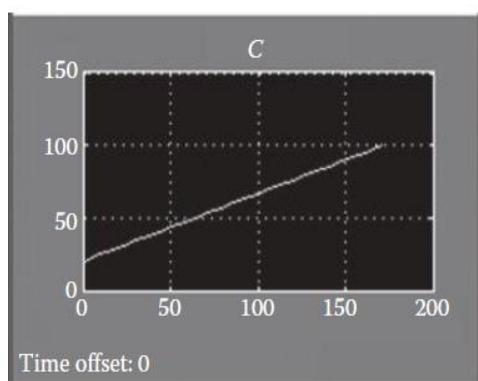
$$T_2 - 20 = \frac{\dot{Q}}{\rho V C_p} t$$

Since water boils at 100°C, accordingly $T_2 = 100$. Substitute known values and solve for time:

$$200 - 20 = \frac{2200 \text{ J/s}}{\frac{1000 \text{ g}}{\text{L}} \times 1 \text{ L} \times 4.18 \text{ J/g}^\circ\text{C}} t$$

$$\frac{80 \times 1000 \times 4.18}{2200} \text{ s} = t$$

$$t = \text{time} = 152 \text{ s (2.53 min)}$$



The time required to heat the water to its boiling temperature in the mentioned kettle is 171.5 s (2.86 min).

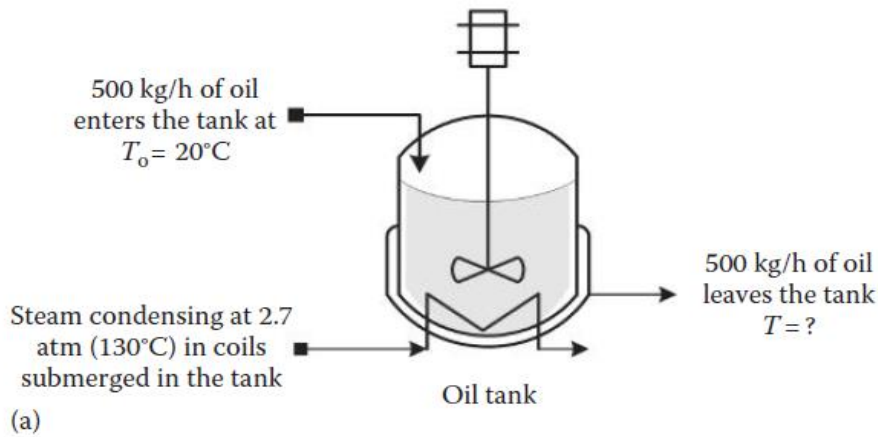
Example 4.7 Heating of a Stirred Tank

Problem

Oil at 20°C is being heated in a stirred tank. Oil enters the tank at a rate of 500 kg/h at 20°C and leaves at temperature T . The tank holds 2300 kg of oil, which is initially at 20°C. The heat is provided by steam condensing at 130°C in coils submerged in the tank. The rate of heat transfer is given by

$$Q = h (T_{\text{steam}} - T_{\text{oil}})$$

The heat capacity of the oil is given by $C_p = 2.1 \text{ J/(g } ^\circ\text{C)}$ and the heat transfer coefficient is $h = 115 \text{ J/s } ^\circ\text{C}$. The shaft work of the stirrer is 560 W. Once the process is started, how long does it take before the oil leaving the tank is at 30°C?



EXAMPLE FIGURE 4.7.1: (a) Schematic of an oil heating tank.

Solution

Known quantities: Inlet and exit tank volumetric flow rate.

Find: Plot the height of the tank as a function of time.

Analysis: The tank flowchart is shown in Example Figure 4.1a.1. The general energy balance equation is

$$\frac{d(u)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

Reference: Inlet oil temperature (i.e., $T_{ref} = T_0 = 20^\circ\text{C}$).

System: Oil in the tank (Example Figure 4.7a.1).

For liquids, C_p and C_v are approximately equal.

Specific heat of oil: $C_p = 2.1 \text{ J/g } ^\circ\text{C}$.

The shaft work of the stirrer is 560 W.

The work done on the system $W_s = -560 \text{ W} = -560 \text{ J/s}$.

The heat added to the oil from the steam is $Q = h (T_{\text{steam}} - T)$.

The heat transfer coefficient is $h = 115 \text{ J/(s}^\circ\text{C)}$.

$$\text{Mass of oil in the tank } m = 2300 \text{ kg} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| = 2.3 \times 10^6 \text{ g}$$

$$\text{Inlet and exit mass flow rates: } \dot{m} = \frac{500 \text{ kg}}{\text{h}} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| \left| \frac{\text{h}}{3600 \text{ s}} \right| = 139 \text{ g/s}$$

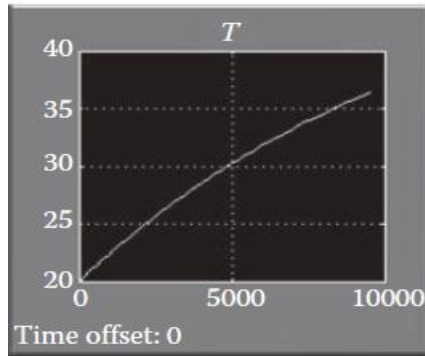
The general energy balance equation is simplified to the following equation:

$$\frac{d(mC_p T)}{dt} = \sum \dot{m}_{in} \hat{H}_{in} - \sum \dot{m}_{out} \hat{H}_{out} + \dot{Q} - \dot{W}_s$$

Rearranging the equation in order to collect and separate variables leads to

$$mC_p \frac{d(T)}{dt} = 0 - \dot{m}C_p(T - T_0) + h(T_{\text{steam}} - T) - \dot{W}_s$$

$$\frac{dT}{dt} = \frac{[0 - \dot{m}C_p(T - T_0) + h(T_{\text{steam}} - T) - \dot{W}_s]}{mC_p}$$



The result reveals that the temperature of oil reaches 35°C in approximately 123 min.

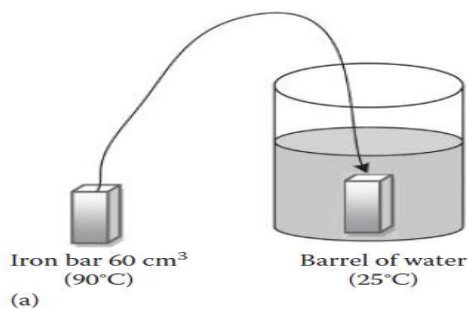
Example 4.8 Quenching of an Iron Bar

Problem

The volume of a cubic iron bar is 60 cm³ at a temperature of 95°C, the heat transfer area of the block is 112 cm². The iron bar is dropped into a barrel of water at 25°C. Density of the iron bar is 11.34 g/cm³. The barrel is large enough so that the water temperature rise is negligible as the bar cools down. The rate at which heat is transferred from the bar to the water is given by the expression

$$Q \text{ (J/min)} = UA (T - T_w)$$

where U is the heat transfer coefficient, which is 0.050 J/(min cm² °C). The heat capacity of the iron bar is 0.460 J/(g °C). Plot the temperature of the bar as a function of time, and calculate the time for the bar to cool to 30°C.



EXAMPLE FIGURE 4.8.1: (a) Schematic of cooling of iron bar block in a large tank of water.

Solution

Known quantities: Inlet and exit tank volumetric flow rate.

Find: Plot the height of the tank as a function of time.

Analysis: The tank flowchart is shown in Example Figure 4.8a.1. Assume the heat conduction in iron is rapid enough for the temperature of the bar to be uniform throughout. This latter concept is an important approximation called lumped capacitance, and it allows us to considerably simplify the problem because we do not have to worry about heat transfer within the solid bar itself. Assume also temperature of water to remain constant.

System: Iron block.

Reference temperature: 25°C

Schematic of the process is shown in Example Figure 4.8a.1.

The general energy balance equation is

$$\frac{d(mC_p T)}{dt} = \sum \dot{m}_{in} \hat{H}_{in} - \sum \dot{m}_{out} \hat{H}_{out} + \dot{Q} - \dot{W}_s$$

Note that for solids and liquids C_p and C_v are equal.

No inlet or exit flowing streams: $\sum \dot{m}_{in} h_{in} = \sum \dot{m}_{out} h_{out} = 0$.

The barrel is large enough so that the water temperature rise is negligible as the bar cools; this means the water temperature remains constant, $T_w = \text{constant}$.

No stirrer or shaft work: $W_s = 0$.

The heat transfer from the iron block: $Q(\text{J/s}) = -UA(T - T_w)$

Heat transfer coefficient, $U = \frac{0.050 \text{ J}}{\text{min} \cdot \text{cm}^2 \cdot ^\circ\text{C}} \left| \frac{1 \text{ min}}{60 \text{ s}} \right| = 8.33 \times 10^{-4} \frac{\text{J}}{\text{s} \cdot \text{cm}^2 \cdot ^\circ\text{C}}$.

The heat capacity of the bar: $C_{pb} = 0.460 \text{ J/(g}^\circ\text{C)}$.

Heat conduction in iron is rapid enough for the temperature of the bar to be uniform throughout.

Density of the iron bar: $\rho_b = 11.34 \text{ g/cm}^3$

Mass of the block: $m = \rho_b V_b$

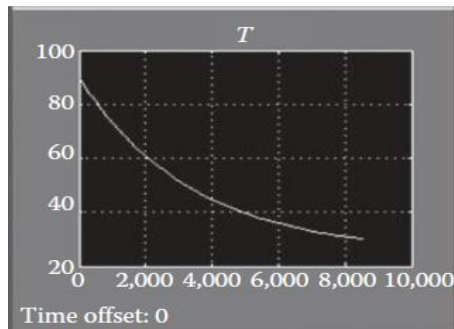
Heat transfer area of the block: $A = 112 \text{ cm}^2$

We now rearrange the equation to obtain it in terms of the two variables T and t (T dependent variable, t independent variable):

$$\frac{dT}{dt} = \frac{\dot{Q}}{mC_p}$$

Substituting the heat transferred from the block (i.e., $Q = -UA(T - T_w)$),

$$\frac{dT}{dt} = \frac{-UA(T - T_w)}{mC_p}$$



the time required to cool the block to 30°C, which is around 2.39 h

Example 4.9 Heating of a Solution

Problem

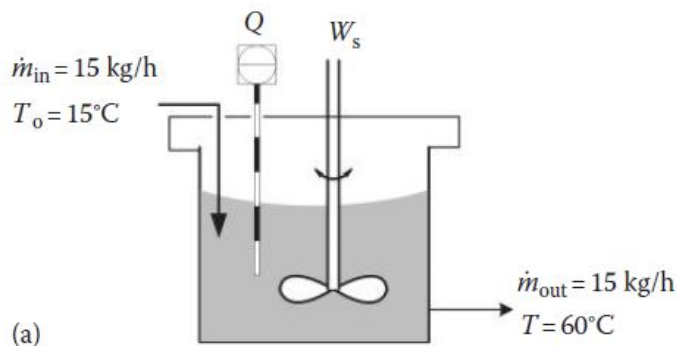
An electric heating coil is immersed in a stirred tank. The shaft work of the stirrer is 560 W. A solvent at 15°C with a heat capacity of 2.1 J/g °C is fed into the tank at a rate of 15 kg/h. Heated solvent is discharged at the same flow rate. The tank is filled initially with 125 kg cold solvent at 10°C. The rate of heating the electric coil is 2000 W. Calculate the time required for the temperature of the solvent to reach 60°C.

Solution

Known quantities: Inlet and exit flow rate, initial tank temperature.

Find: The time required for the temperature of the solvent to reach 60°C.

Analysis: The tank flowchart is shown in Example Figure 4.9a.1. Assume the tank reference temperature is 15°C. The general energy balance equation is simplified to the following equation:



EXAMPLE FIGURE 4.9.1: (a) Schematic of a heating tank.

Solution

Known quantities: Inlet and exit flow rate, initial tank temperature.

Find: The time required for the temperature of the solvent to reach 60°C.

Analysis: The tank flowchart is shown in Example Figure 4.9a.1.

Assume the tank reference temperature is 15°C. The general energy balance equation is simplified to the following equation:

$$\frac{d(mC_p T)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

Rearranging the equation in order to collect and separate variables gives

$$mC_p \frac{d(T)}{dt} = 0 - \dot{m}C_p(T - T_0) + \dot{Q} - \dot{W}_s$$

$$\frac{dT}{dt} = \frac{[0 - \dot{m}C_p(T - T_0) + \dot{Q} - \dot{W}_s]}{mC_p}$$

The schematic diagram is shown in Example Figure 11.9a.1.

Solving the earlier equation necessitates the units to be consistent.

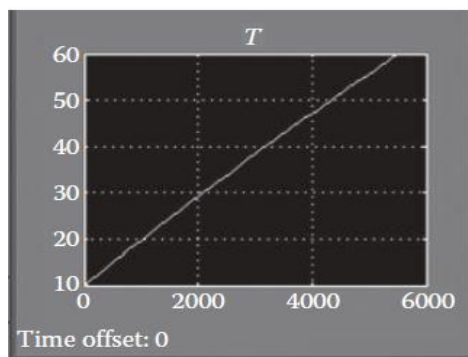
$$\text{Mass of oil: } m = 125 \text{ kg} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| = 1.25 \times 10^5 \text{ g.}$$

$$\text{Inlet and exit oil flow rates: } \dot{m} = \frac{15 \text{ kg}}{\text{h}} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| \left| \frac{\text{h}}{3600 \text{ s}} \right| = 4.17 \text{ g/s.}$$

Heat capacity: $C_p = 2.1 \text{ J/g } ^\circ\text{C}$.

Heat added to the oil from the cooling coil: $\dot{Q} = 2000 \text{ J/s}$.

Work applied on the system from the stirrer: $\dot{W}_s = -560 \text{ J/s}$.



The time required for temperature to reach 60°C is around 5521 s (1.53 h).

Example 4.10 Heating a Glycol Solution

Problem

An adiabatic stirred tank is used to heat 100 kg of a 45 wt% glycol solution in water (mass heat capacity 3.54 J/g °C). An electrical coil delivers 2.5 kJ/s of power to the tank; 88% of the energy delivered by the coil goes into heating the vessel contents. The shaft work of the stirrer is 500 W. The glycerol solution is initially at 15°C. How long will the solution take to reach 90°C?

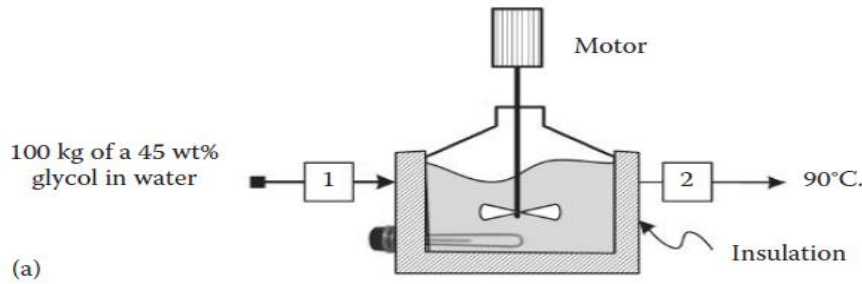


FIGURE 4.10: (a) Schematic of a glycol heating tank.

Solution

Known quantities: Mass of glycol in the tank, heat capacity, heat supplied from coil.

Find: The time taken for the glycol solution to reach 90°C.

Analysis: Assume a reference temperature of 15°C. The schematic diagram of the adiabatic stirred tank heater is shown in Figure 4.10a.

The general energy balance equation is simplified to the following equation:

$$\frac{d(u)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

$$\frac{d(mC_v T)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

Note that for solids and liquids C_p and C are equal:

$$\frac{d(mC_p T)}{dt} = \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} + \dot{Q} - \dot{W}_s$$

The system is adiabatic, that is, no heat is transferred to or from the surroundings, but still there is heat added by the electrical coil:

$$\dot{Q}_{net} = \dot{Q}_e + \dot{Q}_{sur}$$

Since the system is adiabatic, $\dot{Q}_{sur} = 0$. Heat added to the glycol solution is 88% of that of the heating coil:

$$\dot{Q}_e = 0.88 \times 2.5 \text{ kJ/s} = 2.2 \text{ kJ/s}$$

The mass of the glycol solution in the heated tank: $m = 100 \text{ kg}$.

The heat capacity of the glycol solution: $C_p = 3.54 \text{ J/g °C}$.

Rearranging the equation in order to collect and separate variables gives

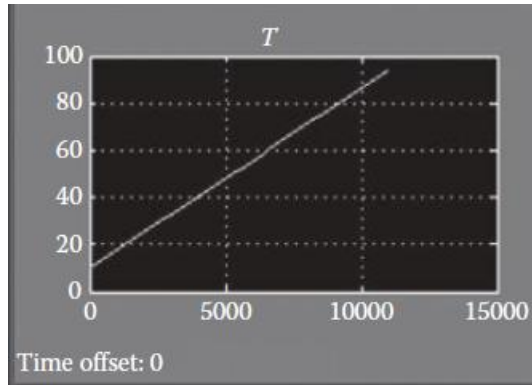
$$\frac{dT}{dt} = \frac{[\dot{Q} - \dot{W}_s]}{mC_p}$$

Use the following data:

$$\dot{Q} = \frac{2.2 \text{ kJ}}{\text{s}} \left| \frac{1000 \text{ J}}{\text{kJ}} \right| = 2200 \text{ J/s}$$

$$W_s = -500 \text{ J/s}, \quad m = 100 \text{ kg}$$

$$C_p = 3.54 \text{ J/g } ^\circ\text{C}$$



the solution shows that it will take around 10,000 s (2.78 h) for the glycol solution to reach the temperature of 90°C .

Homework Problems

4.1 A storage tank that is 2.0 m in diameter is filled at a rate of $2.0 \text{ m}^3/\text{min}$. The exit fluid flow rate is proportional to the head of the fluid ($0.5h \text{ m}^3/\text{min}$), where h is the height of fluid in meters. Plot the height of the liquid as a function of time. What is the steady-state height of the fluid in the tank? (4 m)

4.2 A boiler used to boil water, containing 100 L of water at a temperature of 25°C , is placed on an electric heater ($Q = 3000 \text{ J/s}$). Find the time at which water begins to boil. (100 min)

4.3 A tank containing 1000 kg water at 25°C is heated using saturated steam at 130°C . The rate of heat transfer from the steam is given by the following equation:

$$\dot{Q} = UA (T - T_c)$$

\dot{Q} is the rate of heat transfer to the system. U is the overall heat transfer coefficient, A is the surface area for heat transfer, and T is the temperature. The heat transfer area provided by the coil is 0.3 m^2 , and the heat transfer coefficient is $220 \text{ (kcal)/m}^2 \text{ h}^\circ\text{C}$. The condensate leaves the coil as saturated steam.

a. The tank has a surface area of 0.9 m^2 exposed to the ambient air. The tank exchanges heat through this exposed surface at a rate given by an equation similar to

that given earlier. For heat transfer to or from the surrounding air, the heat transfer coefficient is $25 \text{ (kcal)/m}^2 \text{ h}^\circ\text{C}$. If the air temperature is 20°C , calculate the time required to heat the water to 80°C . (5.9 h)

b. How much time can be saved if the tank is insulated? (4.2 h)

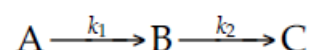
4.4 A stirred tank is used to heat 100 kg of a solvent (mass heat capacity $2.5 \text{ J/g}^\circ\text{C}$). An electrical coil delivers 2.0 kJ/s of power to the tank; the shaft work of the stirrer is 560 W . The solvent is initially at 25°C . The heat lost from the walls of the tank is 200 J/s .

a. Write a differential equation for the energy balance.

b. Solve the equation using the available software package.

c. How long will the solution take to reach 70°C ? (1.33 h)

4.5 The following series reaction takes place in a constant volume batch reactor:



Each reaction is of first order and is irreversible. If the initial concentration of A is 1 mol/L and if only A is present initially, find an expression for the concentrations of A, B, and C as a function of time ($k_1 = 0.1/\text{s}$, $k_2 = 0.2/\text{s}$).

References

1. Himmelblau, D.M. (1996) *Basic Principles and Calculations in Chemical Engineering*, 6th edn., Prentice-Hall, Upper Saddle River, NJ.
2. Doran, P. (1995) *Bioprocess Engineering Principles*, Academic Press, San Diego, CA.
3. Reklaitis, G.V. (1983) *Introduction to Material and Energy Balances*, John Wiley & Sons, New York.
4. Felder, R.M. and R.W. Rousseau (1999) *Elementary Principles of Chemical Processes*, 3rd edn., John Wiley, New York.
5. Atkinson, B. and F. Mavituna (1991) *Biochemical Engineering and Biotechnology Handbook*, 2nd edn., Macmillan, Basingstoke, UK.

Appendix

Physical properties (Appendix A.1), heat capacities (Appendix A.2), and saturated and superheated steam table (Appendix A.3) are adapted with permission from the following references:

1. Himmelblau, D.M. (1996) *Basic Principles and Calculations in Chemical Engineering*, 6th edn., Prentice-Hall, Upper Saddle River, NJ (Appendices A.1 and A.2)
2. Haywood, R.W. (1968) *Thermodynamic Tables in SI (Metric) Units*, Cambridge University Press, London, U.K. (Appendix A.3).

Appendix A.1

Table A.1 contains physical properties of various organic and inorganic substances such as molecular weight, critical temperature, critical pressure, specific gravity, melting temperature, heat of fusion, boiling temperature, and heat of vaporization. Table A.2 contains standard heats of formation and standard heats of combustion.

TABLE A.1

Physical Properties of Various Organic and Inorganic Substances

No.	Compound	Formula	Molecular Weight	T_c K	P_c atm	Sp. Gr.	T_m K	$\Delta \bar{h}_u$ KJ/mol	T_b K	$\Delta \bar{h}_u$ KJ/mol
1	Acetaldehyde	CH ₃ CHO	44.05	461.0		0.78	149.5		293.2	
2	Acetic acid	CH ₃ COOH	60.05	594.8	57.1	1.05	289.9	12.09	390.4	24.4
3	Acetone	C ₃ H ₆ O	58.08	508.0	47.0	0.79	178.2	5.69	329.2	30.2
4	Acetylene	C ₂ H ₂	26.04	309.5	61.6		191.7	3.7	191.7	17.5
5	Air					1.00				
6	Ammonia	NH ₃	17.03	405.5	111.3	0.81	195.40	5.653	239.73	23.35
7	Ammonium carbonate	(NH ₄) ₂ CO ₃ ·H ₂ O	114.11							
8	Ammonium chloride	NH ₄ Cl	53.50			2.53				
9	Ammonium nitrate	NH ₄ NO ₃	80.05			1.73	442.8	5.4		
10	Ammonium sulfate	(NH ₄) ₂ SO ₄	132.14			1.77	786			
11	Aniline	C ₆ H ₇ N	93.12	699	52.4	1.02	266.9		457.4	
12	Benzaldehyde	C ₆ H ₅ CHO	106.12			1.05	247.16		452.16	38.40
13	Benzene	C ₆ H ₆	78.11	562.6	48.6	0.88	278.693	9.837	353.26	30.76
14	Benzoic acid	C ₇ H ₆ O ₂	122.12			1.32	395.4		523.0	
15	Benzyl alcohol	C ₇ H ₈ O	108.13			1.05	257.8		478.4	
16	Boron oxide	B ₂ O ₃	69.64			1.85	723	22.0		
17	Bromine	Br ₂	159.83	584	102	3.12	265.8	10.8	331.78	31.0
18	1,2-Butadiene	C ₄ H ₆	54.09	446		0.65	136.7		283.3	
19	1,3-Butadiene	C ₄ H ₆	54.09	425	42.7	0.62	164.1		268.6	
20	Butane	<i>n</i> -C ₄ H ₁₀	58.12			0.58	134.83	4.661	272.66	22.31
21	<i>iso</i> -Butane	<i>iso</i> -C ₄ H ₁₀	58.12			0.56	113.56	4.540	261.43	21.29
22	1-Butene	C ₄ H ₈	56.10	419.6	39.7	0.60	87.81	3.848	266.91	21.92
23	Butyl phthalate	C ₈ H ₂₂ O ₄	278.34			1.05			613	

24	<i>n</i> -Butyric acid	<i>n</i> -C ₄ H ₈ O ₂	88.10			0.96	267		437.1
25	<i>iso</i> -Butyric acid	<i>iso</i> -C ₄ H ₈ O ₂	88.10			0.95	226		427.7
26	Calcium arsenate	Ca ₃ (AsO ₄) ₂	398.06				1723		
27	Calcium carbide	Ca ₂ C ₂	64.10			2.22	2573		
28	Calcium carbonate	CaCO ₃	100.09			2.93			
29	Calcium chloride	CaCl ₂	110.99			2.15	1055	28.4	
		CaCl ₂ ·H ₂ O	129.01						
		CaCl ₂ ·2H ₂ O	147.03						
		CaCl ₂ ·6H ₂ O	219.09			1.78	303.4	37.3	
30	Calcium cyanamide	CaCN ₂	80.11			2.29			
31	Calcium cyanide	Ca(CN) ₂	92.12						
32	Calcium hydroxide	Ca(OH) ₂	74.10			2.24			
33	Calcium oxide	CaO	56.08			2.62	2873	50	3123
34	Calcium phosphate	Ca ₃ (PO ₄) ₂	310.19			3.14	1943		
35	Calcium silicate	CaSiO ₃	117.17			2.92	1803	48.62	
36	Calcium sulfate	CaSO ₄ ·2H ₂ O	172.18			2.32			
37	Carbon	C	12.010			2.26	3873	46.0	4473
38	Carbon dioxide	CO ₂	44.01	304.2	72.9		217.0	8.32	
39	Carbon disulfide	CS ₂	76.14			1.26	161.1	4.39	319.41
40	Carbon monoxide	CO	28.01	133.0	34.5		68.10	0.837	81.66
41	Carbon tetrachloride	CCl ₄	153.84	556.4	45.0	1.60	250.3	2.5	349.9
42	Chlorine	Cl ₂	70.91	417.0	76.1		172.16	6.406	239.10
43	Chlorobenzene	C ₆ H ₅ Cl	112.56	632.4	44.6	1.11	228		405.26
44	Chloroform	CHCl ₃	119.39	536.0	54.0	1.49	209.5		334.2
45	Chromium	Cr	52.01			7.1			
46	Copper	Cu	63.54			8.92	1356.2	13.0	2855
47	Cumene	C ₉ H ₁₂	120.19			0.86	177.125	7.1	425.56

(Continued)

TABLE A.1 (Continued)
Physical Properties of Various Organic and Inorganic Substances

No.	Compound	Formula	Molecular Weight	T _c K	P _c atm	Sp. Gr.	T _m K	Δ \bar{h}_m KJ/mol	T _b K	Δ \bar{h}_m KJ/mol
48	Cupric sulfate	CuSO ₄	159.61			3.61				
49	Cyclohexane	C ₆ H ₁₂	84.16	553.7	40.4	0.78	279.83	2.677	353.90	30.1
50	Cyclopentane	C ₅ H ₁₀	70.13	511.8	44.55	0.75	179.71	0.6088	322.42	27.30
51	Decane	C ₁₀ H ₂₂	142.28	619.0	20.8	0.73	243.3		447.0	
52	Dibutyl phthalate	C ₁₈ H ₂₂ O ₄	278.34			1.05			613	
53	Diethyl ether	(C ₂ H ₅) ₂ O	74.12	467	35.6	0.71	156.86	7.301	307.76	26.05
54	Ethane	C ₂ H ₆	30.07	305.4	48.2		89.89	2.860	184.53	14.72
55	Ethanol	C ₂ H ₅ OH	46.07	516.3	63.0	0.79	158.6	5.021	351.7	38.6
56	Ethyl acetate	C ₄ H ₈ O ₂	88.10	523.1	37.8	0.90	189.4		350.2	
57	Ethyl benzene	C ₈ H ₁₀	106.16	619.7	37.0	0.87	178.185	9.163	409.35	36.0
58	Ethyl bromide	C ₂ H ₅ Br	108.98	504	61.5	1.46	154.1		311.4	
59	Ethyl chloride	C ₂ H ₅ Cl	64.52	460.4	52.0	0.90	134.83	4.452	285.43	25
60	3-Ethyl hexane	C ₈ H ₁₈	114.22	567.0	26.4	0.72			391.69	34.3
61	Ethylene	C ₂ H ₄	28.05	283.1	50.5		103.97	3.351	169.45	13.54
62	Ethylene glycol	C ₂ H ₆ O ₂	62.07			1.11	260	11.23	470.4	56.9
63	Ferric oxide	Fe ₂ O ₃	159.70			5.12	1833			
64	Ferric sulfide	Fe ₂ S ₃	207.90			4.30				
65	Ferrous sulfide	FeS	87.92			4.84	1466			
66	Formaldehyde	H ₂ CO	30.03			0.81	154.9		253.9	24.5
67	Formic acid	CH ₂ O ₂	46.03			1.22	281.46	12.7	373.7	22.3
68	Glycerol	C ₃ H ₈ O ₃	92.09			1.26	291.36	18.30	563.2	
69	Helium	He	4.00	5.26	2.26		3.5	0.02	4.216	0.084
70	Heptane	C ₇ H ₁₆	100.20	540.2	27.0	0.68	182.57	14.03	371.59	31.69
71	Hexane	C ₆ H ₁₄	86.17	507.9	29.9	0.66	177.84	13.03	341.90	28.85

72	Hydrogen	H ₂	2.016	33.3	12.8		13.96	0.12	20.39	0.904
73	Hydrogen chloride	HCl	36.47	324.6	81.5		158.94	1.99	188.11	16.15
74	Hydrogen fluoride	HF	20.01	503.2	—	1.15	238		293	
75	Hydrogen sulfide	H ₂ S	34.08	373.6	88.9		187.63	2.38	212.82	18.67
76	Iodine	I ₂	253.8	826.0	—	4.93	386.5		457.4	
77	Iron	Fe	55.85	—	—	7.70	1808	15	3073	353
78	Iron oxide	Fe ₃ O ₄	231.55			5.20	1867	138		
79	Lead	Pb	207.21			11.34	600.6	5.10	2023	180
80	Lead oxide	PbO	223.21			9.50	1159	11.7	1745	213
81	Magnesium	Mg	24.32			1.74	923	9.2	1393	132
82	Magnesium chloride	MgCl ₂	95.23			2.33	987	43.1	1691	137
83	Magnesium hydroxide	Mg(OH) ₂	58.34			2.40				
84	Magnesium oxide	MgO	40.32			3.65	3173	77.4	3873	
85	Mercury	Hg	200.61			13.54				
86	Methane	CH ₄	16.04	190.70	45.8		90.68	0.941	111.67	8.180
87	Methanol	CH ₃ OH	32.04			0.79	175.26	3.17	337.9	35.3
88	Methyl acetate	C ₃ H ₆ O ₂	74.08	506.7	46.30	0.93	174.3		330.3	
89	Methyl amine	CH ₃ N	31.06	429.9	73.60	0.70	180.5		266.3	
90	Methyl chloride	CH ₃ Cl	50.49	416.1	65.80		175.3		249	
91	Methyl ethyl ketone	C ₄ H ₈ O	72.10			0.81	186.1		352.6	
92	Methyl cyclohexane	C ₇ H ₁₄	98.18			0.77	146.58	6.751	374.10	31.7
93	Molybdenum	Mo	95.95			10.2				
94	Napthalene	C ₁₀ H ₈	128.16			1.15	353.2		491.0	
95	Nickel	Ni	58.69			8.90	1725		3173	
96	Nitric acid	HNO ₃	63.02			1.50	231.56	10.47	359	30.30
97	Nitrobenzene	C ₆ H ₅ O ₂ N	123.11			1.20	278.7		483.9	
98	Nitrogen	N ₂	28.02	126.20	33.5		63.15	0.720	77.34	5.577
99	Nitrogen dioxide	NO ₂	46.01	431.0	100.0		263.86	7.334	294.46	14.73

(Continued)

TABLE A.1 (Continued)

Physical Properties of Various Organic and Inorganic Substances

No.	Compound	Formula	Molecular Weight	T _c K	P _c atm	Sp. Gr.	T _m K	Δ \bar{h}_m KJ/mol	T _b K	Δ \bar{h}_m KJ/mol
100	Nitrogen (nitric) oxide	NO	30.01	179.20	65.0		109.51	2.301	121.39	13.78
101	Nitrogen pentoxide	N ₂ O ₅	108.02			1.63	303		320	
102	Nitrogen tetraoxide	N ₂ O ₄	92	431.0	99.0	1.45	263.7		294.3	
103	Nitrogen trioxide	N ₂ O ₃	76.02			1.45	171		276.5	
104	Nitrous oxide	N ₂ O	44.02	309.5	71.70	1.23	182.1		184.4	
105	n-Nonane	C ₉ H ₂₀	128.25	595	23.0	0.72	219.4		423.8	
106	n-Octane	C ₈ H ₁₈	114.22	595.0	22.5	0.70	216.2		398.7	
107	Oxalic acid	C ₂ H ₂ O ₄	90.04			1.90				
108	Oxygen	O ₂	32.00	154.4	49.7		54.40	0.443	90.19	6.820
109	n-Pentane	C ₅ H ₁₂	72.15	469.80	33.3	0.63	143.49	8.393	309.23	25.77
110	iso-Pentane	iso-C ₅ H ₁₂	72.15	461.0	32.9	0.62	113.1		300.9	
111	1-Pentane	C ₅ H ₁₀	70.13	474	39.9	0.64	107.96	4.937	303.13	
112	Phenol	C ₆ H ₅ OH	94.11	692.1	60.5	1.07	315.66	11.43	454.56	
113	Phenyl hydrazine	C ₆ H ₅ N ₂	108.14			1.10	292.76	16.43	51.66	
114	Phosphoric acid	H ₃ PO ₄	98.00			1.83	315.51	10.5		
115	Phosphorus (red)	P ₄	123.90			2.20	863	81.17	863	41.84
116	Phosphorus (white)	P ₄	123.90			1.82	317.4	2.5	553	49.71
117	Phosphorus pentoxide	P ₂ O ₅	141.95			2.39				
118	Propane	C ₃ H ₈	44.09	369.9	42.0		85.47	3.524	231.09	18.77
119	Propene	C ₃ H ₆	42.08	365.1	45.4		87.91	3.002	255.46	18.42
120	Propionic acid	C ₃ H ₆ O ₂	74.08			0.99	252.2		414.4	

121	<i>n</i> -Propyl alcohol	C ₃ H ₇ OH	60.09	536.7	49.95	0.80	146		370.2	
122	<i>iso</i> -Propyl alcohol	C ₃ H ₇ O	60.09	508.8	53.0	0.79	183.5		355.4	
123	<i>n</i> -Propyl benzene	C ₉ H ₁₂	120.19	638.7	31.3	0.86	173.660	8.54	432.38	38.2
124	Silicon dioxide	SiO ₂	60.09			2.25	1883	8.54	2503	
125	Sodium bisulfate	NaHSO ₄	120.07			2.74	455			
126	Sodium carbonate	Na ₂ CO ₃ ·10H ₂ O	286.15			1.46	306.5			
127	Sodium carbonate	Na ₂ CO ₃	105.99			2.53	1127	33.4		
128	Sodium chloride	NaCl	58.45			2.16	1081	28.5	1738	171
129	Sodium cyanide	NaCN	49.01				835	16.7	1770	155
130	Sodium hydroxide	NaOH	40.00			2.13	592	8.4	1663	
131	Sodium nitrate	NaNO ₃	85.00			2.26	583	15.9		
132	Sodium nitrite	NaNO ₂	69.00			2.17	544			
133	Sodium sulfate	Na ₂ SO ₄	142.05			2.70	1163	24.3		
134	Sodium sulfide	Na ₂ S	78.05			1.86	1223	6.7		
135	Sodium sulfite	Na ₂ SO ₃	126.05			2.63				
136	Sodium thiosulfate	Na ₂ S ₂ O ₃	158.11			1.67				
137	Sulfur (rhombic)	S ₈	256.53			2.07	386	10.0	717.76	84
138	Sulfur (monoclinic)	S ₈	256.53			1.96	392	14.17	717.76	84
139	Sulfur chloride (mono)	S ₂ Cl ₂	135.05			1.69	193.0		411.2	36.0
140	Sulfur dioxide	SO ₂	64.07	430.7	77.8		197.68	7.402	263.14	24.92
141	Sulfur trioxide	SO ₃	80.07	491.4	83.8		290.0	24.5	316.5	41.8
142	Sulfuric acid	H ₂ SO ₄	98.08			1.83	283.51	9.87		
143	Toluene	C ₆ H ₅ CH ₃	92.13	593.9	40.3	0.87	178.169	6.619	383.78	33.5
144	Water	H ₂ O	18.016	647.4	218.3	1.00	273.16	6.009	373.16	40.65
145	<i>m</i> -Xylene	C ₈ H ₁₀	106.16	619	34.6	0.86	225.288	11.57	412.26	34.4
146	<i>o</i> -Xylene	C ₈ H ₁₀	106.16	631.5	35.7	0.88	247.978	13.60	417.58	36.8
147	<i>p</i> -Xylene	C ₈ H ₁₀	106.16	619	33.9	0.86	286.423	17.11	411.51	36.1
148	Zinc	Zn	65.38			7.14	692.7	6.673	1180	114.8
149	Zinc sulfate	ZnSO ₄	161.44			3.74				

TABLE A.2
Heats of Formation and Combustion

No.	Compound	Formula	Molecular Weight	State	ΔH_f° KJ/mol	ΔH_c° KJ/mol
1	Acetic acid	CH ₃ COOH	60.05	l	-486.2	-871.69
2	Acetaldehyde	CH ₃ CHO	40.052	g	-166.4	-919.73
3	Acetone	C ₃ H ₆ O	58.08	aq	-410.03	-1192.36
4	Acetylene	C ₂ H ₂	26.04	g	-216.69	-1821.38
5	Ammonia	NH ₃	17.032	l	226.75	-1299.61
6	Ammonium carbonate	(NH ₄) ₂ CO ₃	96.09	g	-67.20	-382.58
7	Ammonium chloride	NH ₄ Cl	53.50	aq	-46.191	-941.86
8	Ammonium hydroxide	NH ₄ OH	35.05	c	-315.4	-366.5
9	Ammonium nitrate	NH ₄ NO ₃	80.05	aq	-366.1	-339.4
10	Ammonium sulfate	(NH ₄) ₂ SO ₄	132.15	l	-1179.3	-1173.1
11	Benzaldehyde	C ₆ H ₅ CHO	106.12	g	-88.83	-3267.6
12	Benzene	C ₆ H ₆	78.11	l	-40.0	-3301.5
13	Boron oxide	B ₂ O ₃	69.64	g	82.927	-1263
14	Bromine	Br ₂	159.832	c	-1245.2	0
15	<i>n</i> -Butane	C ₄ H ₁₀	58.12	l	30.7	-2855.6
16	Isobutane	C ₄ H ₁₀	58.12	g	-147.6	-2878.52
17	1-Butene	C ₄ H ₈	56.104	l	-124.73	-2849.0
18	Calcium arsenate	Ca ₃ (AsO ₄) ₂	398.06	g	-158.5	-2868.8
19	Calcium carbide	CaC ₂	64.10	g	-134.5	-2718.58
20	Calcium carbonate	CaCO ₃	100.09	g	1.172	-3330.5
21	Calcium chloride	CaCl ₂	110.99	c	-62.7	-1206.9
22	Calcium cyanamide	CaCN ₂	80.11	c	-794.9	-352
23	Calcium hydroxide	Ca(OH) ₂	74.10	c	-986.56	-635.6
24	Calcium oxide	CaO	56.08	c	-4137.6	-1584
25	Calcium phosphate	Ca ₃ (PO ₄) ₂	310.19	c		
26	Calcium silicate	CaSiO ₃	116.17	c		

(Continued)

TABLE A.2 (Continued)

Heats of Formation and Combustion

No.	Compound	Formula	Molecular Weight	State	Δh_f° KJ/mol	Δh_c° KJ/mol
27	Calcium sulfate	CaSO_4	136.15	c	-1432.7	
				aq	-1450.5	
28	Calcium sulfate (gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	172.18	c	-2021.1	
29	Carbon	C	12.01	c	0	-393.51
30	Carbon dioxide	CO_2	44.01	g	-393.51	
				l	-412.92	
31	Carbon disulfide	CS_2	76.14	l	87.86	-1075.2
				g	115.3	-1102.6
32	Carbon monoxide	CO	28.01	g	-110.52	-282.99
33	Carbon tetrachloride	CCl_4	153.838	l	-139.5	-352.2
				g	-106.69	-384.9
34	Chloroethane	$\text{C}_2\text{H}_5\text{Cl}$	64.52	g	-105.0	-1421.1
				l	-41.20	-5215.44
35	Cumene (isopropylbenzene)	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$	120.19	g	3.93	-5260.59
				g	-769.86	
36	Cupric sulfate	CuSO_4	159.61	aq	-843.12	
				c	-751.4	
37	Cyclohexane	C_6H_{12}	84.16	g	-123.1	-3953.0
38	Cyclopentane	C_5H_{10}	70.130	l	-105.8	-3290.9
				g	-77.23	-3319.5
39	Ethane	C_2H_6	30.07	g	-84.667	-1559.9
40	Ethyl acetate	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	88.10	l	-442.92	-2274.48
41	Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	46.068	l	-277.63	-1366.91
				g	-235.31	-1409.25
42	Ethyl benzene	$\text{C}_6\text{H}_5\text{-C}_2\text{H}_5$	106.16	l	-12.46	-4564.87
				g	29.79	-4607.13
43	Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	64.52	g	-105	
44	Ethylene	C_2H_4	28.052	g	52.283	-1410.99
45	Ethylene chloride	$\text{C}_2\text{H}_2\text{Cl}_2$	62.50	g	31.38	-1271.5
46	3-Ethyl hexane	C_8H_{18}	114.22	l	-250.5	-5470.12
				g	-210.9	-5509.78
47	Ferric chloride	FeCl_3		g	-403.34	
48	Ferric oxide	Fe_2O_3	159.70	g	-822.156	
49	Ferric sulfide	FeS_2	119.98	g	-177.9	
50	Ferrosulfuric oxide	Fe_3O_4	231.55	c	-1116.7	
51	Ferrous chloride	FeCl_2		c	-342.67	-303.76

(Continued)

TABLE A.2 (Continued)

Heats of Formation and Combustion

No.	Compound	Formula	Molecular Weight	State	ΔH_f° KJ/mol	ΔH_c° KJ/mol
52	Ferrous oxide	FeO	71.85	c	-267	
53	Ferrous sulfide	FeS	87.92	c	-95.06	
54	Formaldehyde	H ₂ CO	30.026	g	-115.89	-563.46
55	<i>n</i> -Heptane	C ₇ H ₁₆	100.20	l	-224.4	-4816.91
				g	-187.8	-4853.48
56	<i>n</i> -Hexane	C ₆ H ₁₄	86.17	l	-198.8	-4163.1
				g	-167.2	-4194.753
57	Hydrogen	H ₂	2.016	g	0	-285.84
58	Hydrogen bromide	HBr	80.924	g	-36.23	
59	Hydrogen chloride	HCl	36.465	g	-92.311	
60	Hydrogen cyanide	HCN	27.026	g	130.54	
61	Hydrogen sulfide	H ₂ S	34.082	g	-20.15	-562.589
62	Iron sulfide	FeS ₂	119.98	c	-177.9	
63	Lead oxide	PbO	223.21	c	-219.2	
64	Magnesium chloride	MgCl ₂	95.23	c	-641.83	
65	Magnesium hydroxide	Mg(OH) ₂	58.34	c	-924.66	
66	Magnesium oxide	MgO	40.32	c	-601.83	
67	Methane	CH ₄	16.041	g	-74.84	-890.4
68	Methyl alcohol	CH ₃ OH	32.042	l	-238.64	-726.55
				g	-201.25	-763.96
69	Methyl chloride	CH ₃ Cl	50.49	g	-81.923	-766.63
70	Methyl cyclohexane	C ₇ H ₁₄	98.182	l	-190.2	-4565.29
				g	-154.8	-4600.68
71	Methyl cyclopentane	C ₆ H ₁₂	84.156	l	-138.4	-3937.7
				g	-106.7	-3969.4
72	Nitric acid	HNO ₃	63.02	l	-173.23	
				aq	-206.57	
73	Nitric oxide	NO	30.01	g	90.374	
74	Nitrogen dioxide	NO ₂	46.01	g	33.85	
75	Nitrous oxide	N ₂ O	44.02	g	81.55	
76	<i>n</i> -Pentane	C ₅ H ₁₂	72.15	l	-173.1	-3509.5
				g	-146.4	-3536.15
77	Phosphoric acid	H ₃ PO ₄	98.00	c	-1281	
				aq	-1278	
78	Phosphorus	P ₄	123.90	c	0	
79	Phosphorus pentoxide	P ₂ O ₅	141.95	c	-1506	

TABLE A.2 (Continued)
Heats of Formation and Combustion

No.	Compound	Formula	Molecular Weight	State	$\Delta \hat{h}_f^\circ$ KJ/mol	$\Delta \hat{h}_c^\circ$ KJ/mol
80	Propane	C_3H_8	44.09	l	-119.84	-2204.0
				g	-103.85	-2220.0
81	Propene	C_3H_6	42.078	g	20.41	-2058.47
82	<i>n</i> -Propyl alcohol	C_3H_8O	60.09	g	-255	-2068.6
83	<i>n</i> -Propylbenzene	$C_6H_5-CH_2-C_2H_5$	120.19	l	-38.40	-5218.2
				g	7.824	-5264.5
84	Silicon dioxide	SiO_2	60.09	c	-851.0	
85	Sodium bicarbonate	$NaHCO_3$	84.01	c	-945.6	
86	Sodium bisulfate	$NaHSO_4$	120.07	c	-1126	
87	Sodium carbonate	Na_2CO_3	105.99	c	-1130	
88	Sodium chloride	$NaCl$	58.45	c	-411.00	
89	Sodium cyanide	$NaCN$	49.01	c	-89.79	
90	Sodium nitrate	$NaNO_3$	85.00	c	-466.68	
91	Sodium nitrite	$NaNO_2$	69.00	c	-359	
92	Sodium sulfate	Na_2SO_4	142.05	c	-1384.5	
93	Sodium sulfide	Na_2S	78.05	c	-373	
94	Sodium sulfite	Na_2SO_3	126.05	c	-1090	
95	Sodium thiosulfate	$Na_2S_2O_3$	158.11	c	-1117	
96	Sulfur	S	32.07	c	0	
97	Sulfur chloride	S_2Cl_2	135.05	l	-60.3	
98	Sulfur dioxide	SO_2	64.066	g	-296.90	
99	Sulfur trioxide	SO_3	80.066	g	-395.18	
100	Sulfuric acid	H_2SO_4	98.08	l	-811.32	
				aq	-907.51	
101	Toluene	$C_6H_5CH_3$	92.13	l	11.99	-3909.9
				g	50.000	-3947.9
102	Water	H_2O	18.016	l	-285.840	
				g	-241.826	
103	<i>m</i> -Xylene	$C_6H_4(CH_3)_2$	106.16	l	-25.42	-4551.86
				g	17.24	-4594.53
104	<i>o</i> -Xylene	$C_6H_4(CH_3)_2$	106.16	l	-24.44	-4552.86
				g	19.00	-4596.29
105	<i>p</i> -Xylene	$C_6H_4(CH_3)_2$	106.16	l	-24.43	-4552.86
				g	17.95	-4595.25
106	Zinc sulfate	$ZnSO_4$	161.45	c	-978.55	
				aq	-1059.93	

Note: Heats of formation and combustion of compounds at 25°C. Standard states of products for \hat{h}_c° are CO_2 (g), H_2O (l), N_2 (g), SO_2 (g), and HCl (aq).

Appendix A.2

Table A.3 contains heat capacity equations for organic and inorganic compounds as a function of temperature.

Forms	Heat Capacity
1.	$C_p \text{ J/(mol)(K or } ^\circ\text{C)} = a + bT + cT^2 + dT^3$
2.	$C_p \text{ J/(mol)(K or } ^\circ\text{C)} = a + bT + cT^{-2}$

TABLE A.3

Heat Capacity Equations for Organic and Inorganic Compounds (at Low Pressures)

No.	Compound	Formula	Mol. Wt.	State	Form	T	a	b	c	d	Temp. Range
1	Acetone	CH ₃ COCH ₃	58.08	l	1	°C	123.0	0.186			-30 to 60
			58.08	g	1	°C	71.96	0.201	-1.278 × 10 ⁻⁴	3.476 × 10 ⁻⁴	0-1200
2	Acetylene	C ₂ H ₂	26.04	g	1	°C	42.43	0.06053	-5.033 × 10 ⁻⁵	1.820 × 10 ⁻⁴	0-1200
3	Air		29.0	g	1	°C	28.94	0.004147	0.3191 × 10 ⁻⁵	-1.965 × 10 ⁻⁹	0-1500
				g	1	K	28.09	0.001965	0.4799 × 10 ⁻⁵	-1.965 × 10 ⁻⁹	273-1800
4	Ammonia	NH ₃	17.03	g	1	°C	35.15	0.02954	0.4421 × 10 ⁻⁵	-6.686 × 10 ⁻⁹	0-1200
5	Ammonium sulfate	(NH ₄) ₂ SO ₄	132.15	c	1	K	215.9		0		275-328
6	Benzene	C ₆ H ₆	78.11	l	1	°C	126.5	0.234			6-67
				g	1	°C	74.06	0.3295	-2.520 × 10 ⁻⁴	7.757 × 10 ⁻⁴	0-1200
7	Isobutane	C ₄ H ₁₀	58.12	g	1	°C	89.46	0.3013	-1.891 × 10 ⁻⁴	4.987 × 10 ⁻⁴	0-1200
8	n-Butane	C ₄ H ₁₀	58.12	g	1	°C	92.30	0.2788	-1.547 × 10 ⁻⁴	3.498 × 10 ⁻⁴	0-1200
9	Isobutene	C ₄ H ₈	56.10	g	1	°C	82.88	0.2564	-1.727 × 10 ⁻⁴	5.050 × 10 ⁻⁴	0-1200
10	Calcium carbide	CaC ₂	64.10	c	2	K	68.62	0.0119	-8.66 × 10 ⁻⁵	—	298-720
11	Calcium carbonate	CaCO ₃	100.09	c	2	K	82.34	0.04975	-1.287 × 10 ⁻⁴	—	273-1033
12	Calcium hydroxide	Ca(OH) ₂	74.10	c	1	K	89.5				276-373
13	Calcium oxide	CaO	56.08	c	2	K	41.84	0.0203	-4.52 × 10 ⁻⁵		10273-1173
14	Carbon	C	12.01	c*	2	K	11.18	0.01095	-4.891 × 10 ⁻⁵		273-1373
15	Carbon dioxide	CO ₂	44.01	g	1	°C	36.11	0.04233	-2.887 × 10 ⁻⁵	7.464 × 10 ⁻⁹	0-1500
16	Carbon monoxide	CO	28.01	g	1	°C	28.95	0.00411	0.3548 × 10 ⁻⁵	-2.220 × 10 ⁻⁹	0-1500
17	Carbon tetrachloride	CCl ₄	153.84	l	1	K	12.285	0.0001095	-3.1826 × 10 ⁻³	3.4252 × 10 ⁻⁶	273-343
18	Chlorine	Cl ₂	70.91	g	1	°C	33.60	0.01367	-1.607 × 10 ⁻⁵	6.473 × 10 ⁻⁹	0-1200
19	Copper	Cu	63.54	c	1	K	22.76	0.0006117			273-1357
20	Cumene	C ₉ H ₁₂	120.19	g	1	°C	139.2	0.5376	-3.979 × 10 ⁻⁴	1.205 × 10 ⁻⁷	0-1200

(Continued)

TABLE A.3 (Continued)

Heat Capacity Equations for Organic and Inorganic Compounds (at Low Pressures)

No.	Compound	Formula	Mol. Wt.	State	Form	T	a	b	c	d	Temp. Range
21	Cyclohexane	C ₆ H ₁₂	84.16	g	1	°C	94.140	0.4962	-3.190 × 10 ⁻⁴	8.063 × 10 ⁻⁴	0-1200
22	Cyclopentane	C ₅ H ₁₀	70.13	g	1	°C	73.39	0.3928	-2.554 × 10 ⁻⁴	6.866 × 10 ⁻⁴	0-1200
23	Ethane	C ₂ H ₆	30.07	g	1	°C	49.37	0.1392	-5.816 × 10 ⁻⁵	7.280 × 10 ⁻⁹	0-1200
24	Ethyl alcohol	C ₂ H ₅ O	46.07	l	1	°C	158.8				100
				g	1	°C	61.34	0.1572	-8.749 × 10 ⁻⁵	1.983 × 10 ⁻⁴	0-1200
25	Ethylene	C ₂ H ₄	28.05	g	1	°C	40.75	0.1147	-6.891 × 10 ⁻⁵	1.766 × 10 ⁻⁴	0-1200
26	Ethylbenzene	C ₂ H ₅ Cl ₂	98.96	l	1	°C	182.0				
				g	1	°C	118	0.30			
27	Ethylene oxide	C ₂ H ₄ O	44.05	g	1	K	-4.69	0.206	-9.995 × 10 ⁻⁵		
28	Ferric oxide	Fe ₂ O ₃	159.70	g	2	K	103.4	0.06711	-17.72 × 10 ⁻⁵	—	273-1097
29	Formaldehyde	CH ₂ O	30.03	g	1	°C	34.28	0.04268	0.0000	-8.694 × 10 ⁻⁹	0-1200
30	Helium	He	4.00	g	1	°C	20.8				All
31	n-Hexane	C ₆ H ₁₄	86.17	l	1	K	31.421	0.0097606	-2.3537 × 10 ⁻³	3.0927 × 10 ⁻⁶	273-400
				g	1	°C	137.44	0.4085	-2.392 × 10 ⁻⁴	5.766 × 10 ⁻⁴	0-1200
32	Hydrogen	H ₂	2.016	g	1	°C	28.84	0.0000765	0.3288 × 10 ⁻⁵	-0.8698 × 10 ⁻⁹	0-1500
33	Hydrogen bromide	HBr	80.92	g	1	°C	29.10	-0.000227	0.9887 × 10 ⁻⁵	-4.858 × 10 ⁻⁹	0-1200
34	Hydrogen chloride	HCl	36.47	g	1	°C	29.13	-0.001341	0.9715 × 10 ⁻⁵	-4.335 × 10 ⁻⁹	0-1200
35	Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	0.02908	1.092 × 10 ⁻⁵		0-1200

36	Hydrogen sulfide	H ₂ S	34.08	g	1	°C	33.51	0.01547	0.3012 × 10 ⁻⁵	-3.292 × 10 ⁻⁹	0-1500
37	Magnesium chloride	MgCl ₂	95.23	c	1	K	72.4	0.0158			273-991
38	Magnesium oxide	MgO	40.32	c	2	K	45.44	0.005008	-8.732 × 10 ⁻⁵		273-2073
39	Methane	CH ₄	16.04	g	1	°C	34.31	0.05469	0.3661 × 10 ⁻⁵	-1.100 × 10 ⁻⁸	0-1200
				g	1	K	19.87	0.05021	1.268 × 10 ⁻⁵	-1.100 × 10 ⁻⁸	273-1500
40	Methyl alcohol	CH ₃ OH	32.04	l	1	°C	75.86	0.1683			0-65
				g		°C	42.93	0.08301	-1.87 × 10 ⁻⁵	-8.03 × 10 ⁻⁹	0-700
41	Methyl cyclohexane	C ₇ H ₁₄	98.18	g	1	°C	121.3	0.5653	-3.772 × 10 ⁻⁴	1.008 × 10 ⁻⁷	0-1200
42	Methyl cyclopentane	C ₆ H ₁₂	84.16	g	1	°C	98.83	0.45857	-3.044 × 10 ⁻⁴	8.381 × 10 ⁻⁸	0-1200
43	Nitric acid	HNO ₃	63.02	l	1	°C	110.0				25
44	Nitric oxide	NO	30.01	g	1	°C	29.50	0.008188	-0.2925 × 10 ⁻⁵	0.3652 × 10 ⁻⁹	0-3500
45	Nitrogen	N ₂	28.02	g	1	°C	29.00	0.002199	0.5723 × 10 ⁻⁵	-2.871 × 10 ⁻⁹	0-1500
46	Nitrogen dioxide	NO ₂	46.01	g	1	°C	36.07	0.0397	-2.88 × 10 ⁻⁵	7.87 × 10 ⁻⁹	0-1200
47	Nitrogen tetroxide	N ₂ O ₄	92.02	g	1	°C	75.7	0.125	-1.13 × 10 ⁻⁴		0-300
48	Nitrous oxide	N ₂ O	44.02	g	1	°C	37.66	0.04151	-2.694 × 10 ⁻⁵	1.057 × 10 ⁻⁸	0-1200
49	Oxygen	O ₂	32.00	g	1	°C	29.10	0.01158	-0.6076 × 10 ⁻⁵	1.311 × 10 ⁻⁹	0-1500
50	n-Pentane	C ₅ H ₁₂	72.15	l	1	K	33.24	1.9241	-2.3687 × 10 ⁻³	1.7944 × 10 ⁻⁵	270-350
				g	1	°C	114.8	0.3409	-1.899 × 10 ⁻⁴	4.226 × 10 ⁻⁸	0-1200
51	Propane	C ₃ H ₈	44.09	g	1	°C	68.032	0.2259	-1.311 × 10 ⁻⁴	3.171 × 10 ⁻⁸	0-1200
52	Propylene	C ₃ H ₆	42.08	g	1	°C	59.580	0.1771	-1.017 × 10 ⁻⁴	2.460 × 10 ⁻⁸	0-1200
53	Sodium carbonate	Na ₂ CO ₃	105.99	c	1	K	121				288-371

(Continued)

TABLE A.3 (Continued)

Heat Capacity Equations for Organic and Inorganic Compounds (at Low Pressures)

No.	Compound	Formula	Mol. Wt.	State	Form	T	a	b	c	d	Temp. Range
54	Sodium carbonate	Na ₂ CO ₃ ·10H ₂ O	286.15	c	1	K	535.6				298
55	Styrene	C ₈ H ₈	104.2	l	1	°C	209.0				
				g		°C	115.0	0.270			
56	Sulfur	S	32.07	c ^b	1	K	15.2	0.0268			273-368
				c ^c	1	K	18.5	0.0184			368-392
57	Sulfuric acid	H ₂ SO ₄	98.08	l	1	°C	139.1	0.1559			10-45
58	Sulfur dioxide	SO ₂	64.07	g	1	°C	38.91	0.03904	-3.104 × 10 ⁻⁵	8.606 × 10 ⁻⁹	0-1500
59	Sulfur trioxide	SO ₃	80.07	g	1	°C	48.50	0.09188	-8.540 × 10 ⁻⁵	3.240 × 10 ⁻⁸	0-1000
60	Toluene	C ₇ H ₈	92.13	l	1	K	1.8083	0.81222	-151.27 × 10 ⁻⁵	1.630 × 10 ⁻⁶	270-370
				g	1	°C	94.18	0.3800	-27.86 × 10 ⁻⁵	8.033 × 10 ⁻⁸	0-1200
61	Water	H ₂ O	18.016	l	1	K	18.2964	0.47212	-133.88 × 10 ⁻⁵	1.3142 × 10 ⁻⁶	273-373
				g	1	°C	33.46	0.00688	0.7604 × 10 ⁻⁵	-3.593 × 10 ⁻⁹	0-1500

^a Graphite.

^b Rhombic.

^c Monoclinic (at 1 atm).

Appendix A.3: Steam Table

Table A.4 contains properties of saturated steam, specific volume, specific internal energy, and specific enthalpy. Table A.5 contains properties of superheated steam.

TABLE A.4

Properties of Saturated Steam

P (bar)	T (°C)	v (m ³ /kg)		u (kJ/kg)		h (kJ/kg)		
		Water, v_f	Steam, v_g	Water, u_f	Steam, u_g	Water, h_f	Evap. h_{fg}	Steam, h_g
0.00611	0.01	0.001000	206.2	0.0	2375.6	0.0	2501.6	2501.6
0.008	3.8	0.001000	159.7	15.8	2380.7	15.8	2492.6	2508.5
0.010	7.0	0.001000	129.2	29.3	2385.2	29.3	2485.0	2514.4
0.012	9.7	0.001000	108.7	40.6	2388.9	40.6	2478.7	2519.3
0.014	12.0	0.001000	93.9	50.3	2392.0	50.3	2473.2	2523.5
0.016	14.0	0.001001	82.8	58.9	2394.8	58.9	2468.4	2527.3
0.018	15.9	0.001001	74.0	66.5	2397.4	66.5	2464.1	2530.6
0.020	17.5	0.001001	67.0	73.5	2399.6	73.5	2460.2	2533.6
0.022	19.0	0.001002	61.2	79.8	2401.7	79.8	2456.6	2536.4
0.024	20.4	0.001002	56.4	85.7	2403.6	85.7	2453.3	2539.0
0.026	21.7	0.001002	52.3	91.1	2405.4	91.1	2450.2	2541.3
0.028	23.0	0.001002	48.7	96.2	2407.1	96.2	2447.3	2543.6
0.030	24.1	0.001003	45.7	101.0	2408.6	101.0	2444.6	2545.6
0.035	26.7	0.001003	39.5	111.8	2412.2	111.8	2438.5	2550.4
0.040	29.0	0.001004	34.8	121.4	2415.3	121.4	2433.1	2554.5
0.045	31.0	0.001005	31.1	130.0	2418.1	130.0	2428.2	2558.2
0.050	32.9	0.001005	28.2	137.8	2420.6	137.8	2423.8	2561.6
0.060	36.2	0.001006	23.74	151.5	2425.1	151.5	2416.0	2567.5
0.070	39.0	0.001007	20.53	163.4	2428.9	163.4	2409.2	2572.6
0.080	41.5	0.001008	18.10	173.9	2432.3	173.9	2403.2	2577.1

0.090	43.8	0.001009	16.20	183.3	2435.3	183.3	2397.9	2581.1
0.10	45.8	0.001010	14.67	191.8	2438.0	191.8	2392.9	2584.8
0.11	47.7	0.001011	13.42	199.7	2440.5	199.7	2388.4	2588.1
0.12	49.4	0.001012	12.36	206.9	2442.8	206.9	2384.3	2591.2
0.13	51.1	0.001013	11.47	213.7	2445.0	213.7	2380.4	2594.0
0.14	52.6	0.001013	10.69	220.0	2447.0	220.0	2376.7	2596.7
0.15	54.0	0.001014	10.02	226.0	2448.9	226.0	2373.2	2599.2
0.16	55.3	0.001015	9.43	231.6	2450.6	231.6	2370.0	2601.6
0.17	56.6	0.001015	8.91	236.9	2452.3	236.9	2366.9	2603.8
0.18	57.8	0.001016	8.45	242.0	2453.9	242.0	2363.9	2605.9
0.19	59.0	0.001017	8.03	246.8	2455.4	246.8	2361.1	2607.9
0.20	60.1	0.001017	7.65	251.5	2456.9	251.5	2358.4	2609.9
0.22	62.2	0.001018	7.00	260.1	2459.6	260.1	2353.3	2613.5
0.24	64.1	0.001019	6.45	268.2	2462.1	268.2	2348.6	2616.8
0.26	65.9	0.001020	5.98	275.6	2464.4	275.7	2344.2	2619.9
0.28	67.5	0.001021	5.58	282.7	2466.5	282.7	2340.0	2622.7
0.30	69.1	0.001022	5.23	289.3	2468.6	289.3	2336.1	2625.4
0.35	72.7	0.001025	4.53	304.3	2473.1	304.3	2327.2	2631.5
0.40	75.9	0.001027	3.99	317.6	2477.1	317.7	2319.2	2636.9
0.45	78.7	0.001028	3.58	329.6	2480.7	329.6	2312.0	2641.7
0.50	81.3	0.001030	3.24	340.5	2484.0	340.6	2305.4	2646.0
0.55	83.7	0.001032	2.96	350.6	2486.9	350.6	2299.3	2649.9
0.60	86.0	0.001033	2.73	359.9	2489.7	359.9	2293.6	2653.6
0.65	88.0	0.001035	2.53	368.5	2492.2	368.6	2288.3	2656.9
0.70	90.0	0.001036	2.36	376.7	2494.5	376.8	2283.3	2660.0
0.75	91.8	0.001037	2.22	384.4	2496.7	384.5	2278.6	2663.0
0.80	93.5	0.001039	2.087	391.6	2498.8	391.7	2274.1	2665.8

(Continued)

TABLE A.4

Properties of Saturated Steam

P (bar)	T (°C)	v (m ³ /kg)		u (kJ/kg)		h (kJ/kg)		
		Water, v_f	Steam, v_g	Water, u_f	Steam, u_g	Water, h_f	Evap. h_{fg}	Steam, h_g
0.00611	0.01	0.001000	206.2	0.0	2375.6	0.0	2501.6	2501.6
0.008	3.8	0.001000	159.7	15.8	2380.7	15.8	2492.6	2508.5
0.010	7.0	0.001000	129.2	29.3	2385.2	29.3	2485.0	2514.4
0.012	9.7	0.001000	108.7	40.6	2388.9	40.6	2478.7	2519.3
0.014	12.0	0.001000	93.9	50.3	2392.0	50.3	2473.2	2523.5
0.016	14.0	0.001001	82.8	58.9	2394.8	58.9	2468.4	2527.3
0.018	15.9	0.001001	74.0	66.5	2397.4	66.5	2464.1	2530.6
0.020	17.5	0.001001	67.0	73.5	2399.6	73.5	2460.2	2533.6
0.022	19.0	0.001002	61.2	79.8	2401.7	79.8	2456.6	2536.4
0.024	20.4	0.001002	56.4	85.7	2403.6	85.7	2453.3	2539.0
0.026	21.7	0.001002	52.3	91.1	2405.4	91.1	2450.2	2541.3
0.028	23.0	0.001002	48.7	96.2	2407.1	96.2	2447.3	2543.6
0.030	24.1	0.001003	45.7	101.0	2408.6	101.0	2444.6	2545.6
0.035	26.7	0.001003	39.5	111.8	2412.2	111.8	2438.5	2550.4
0.040	29.0	0.001004	34.8	121.4	2415.3	121.4	2433.1	2554.5
0.045	31.0	0.001005	31.1	130.0	2418.1	130.0	2428.2	2558.2
0.050	32.9	0.001005	28.2	137.8	2420.6	137.8	2423.8	2561.6
0.060	36.2	0.001006	23.74	151.5	2425.1	151.5	2416.0	2567.5
0.070	39.0	0.001007	20.53	163.4	2428.9	163.4	2409.2	2572.6
0.080	41.5	0.001008	18.10	173.9	2432.3	173.9	2403.2	2577.1

TABLE A.4 (Continued)

Properties of Saturated Steam

P (bar)	T (°C)	v (m ³ /kg)		u (kJ/kg)		h (kJ/kg)		
		Water, v_f	Steam, v_g	Water, u_f	Steam, u_g	Water, h_f	Evap. h_{fg}	Steam, h_g
0.85	95.2	0.001040	1.972	398.5	2500.8	398.6	2269.8	2668.4
0.90	96.7	0.001041	1.869	405.1	2502.6	405.2	2265.6	2670.9
0.95	98.2	0.001042	1.777	411.4	2504.4	411.5	2261.7	2673.2
1.00	99.6	0.001043	1.694	417.4	2506.1	417.5	2257.9	2675.4
1.01325	100.0	0.001044	1.673	419.0	2506.5	419.1	2256.9	2676.0
1.1	102.3	0.001046	1.549	428.7	2509.2	428.8	2250.8	2679.6
1.2	104.8	0.001048	1.428	439.2	2512.1	439.4	2244.1	2683.4
1.3	107.1	0.001049	1.325	449.1	2514.7	449.2	2237.8	2687.0
1.4	109.3	0.001051	1.236	458.3	2517.2	458.4	2231.9	2690.3
1.5	111.4	0.001053	1.159	467.0	2519.5	467.1	2226.2	2693.4
1.6	113.3	0.001055	1.091	475.2	2521.7	475.4	2220.9	2696.2
1.7	115.2	0.001056	1.031	483.0	2523.7	483.2	2215.7	2699.0
1.8	116.9	0.001058	0.977	490.5	2525.6	490.7	2210.8	2701.5
1.9	118.6	0.001059	0.929	497.6	2527.5	497.8	2206.1	2704.0
2.0	120.2	0.001061	0.885	504.5	2529.2	504.7	2201.6	2706.3
2.2	123.3	0.001064	0.810	517.4	2532.4	517.6	2193.0	2710.6
2.4	126.1	0.001066	0.746	529.4	2535.4	529.6	2184.9	2714.5
2.6	128.7	0.001069	0.693	540.6	2538.1	540.9	2177.3	2718.2
2.8	131.2	0.001071	0.646	551.1	2540.6	551.4	2170.1	2721.5
3.0	133.5	0.001074	0.606	561.1	2543.0	561.4	2163.2	2724.7
3.2	135.8	0.001076	0.570	570.6	2545.2	570.9	2156.7	2727.6
3.4	137.9	0.001078	0.538	579.6	2547.2	579.9	2150.4	2730.3
3.6	139.9	0.001080	0.510	588.1	2549.2	588.5	2144.4	2732.9
3.8	141.8	0.001082	0.485	596.4	2551.0	596.8	2138.6	2735.3
4.0	143.6	0.001084	0.462	604.2	2552.7	604.7	2133.0	2737.6
4.2	145.4	0.001086	0.442	611.8	2554.4	612.3	2127.5	2739.8
4.4	147.1	0.001088	0.423	619.1	2555.9	619.6	2122.3	2741.9
4.6	148.7	0.001089	0.405	626.2	2557.4	626.7	2117.2	2743.9
4.8	150.3	0.001091	0.389	633.0	2558.8	633.5	2112.2	2745.7
5.0	151.8	0.001093	0.375	639.6	2560.2	640.1	2107.4	2747.5
5.5	155.5	0.001097	0.342	655.2	2563.3	655.8	2095.9	2751.7
6.0	158.8	0.001101	0.315	669.8	2566.2	670.4	2085.0	2755.5
6.5	162.0	0.001105	0.292	683.4	2568.7	684.1	2074.7	2758.9
7.0	165.0	0.001108	0.273	696.3	2571.1	697.1	2064.9	2762.0
7.5	167.8	0.001112	0.2554	708.5	2573.3	709.3	2055.5	2764.8
8.0	170.4	0.001115	0.2403	720.0	2575.5	720.9	2046.5	2767.5
8.5	172.9	0.001118	0.2268	731.1	2577.1	732.0	2037.9	2769.9
9.0	175.4	0.001121	0.2148	741.6	2578.8	742.6	2029.5	2772.1
9.5	177.7	0.001124	0.2040	751.8	2580.4	752.8	2021.4	2774.2
10	179.9	0.001127	0.1943	761.5	2581.9	762.6	2013.6	2776.2
11	184.1	0.001133	0.1774	779.9	2584.5	781.1	1998.5	2779.7
12	188.0	0.001139	0.1632	797.1	2586.9	798.4	1984.3	2782.7
13	191.6	0.001144	0.1511	813.2	2589.0	814.7	1970.7	2785.4
14	195.0	0.001149	0.1407	828.5	2590.8	830.1	1957.7	2787.8
15	198.3	0.001154	0.1317	842.9	2592.4	844.7	1945.2	2789.9
16	201.4	0.001159	0.1237	856.7	2593.8	858.6	1933.2	2791.7
17	204.3	0.001163	0.1166	869.9	2595.1	871.8	1921.5	2793.4
18	207.1	0.001168	0.1103	882.5	2596.3	884.6	1910.3	2794.8
19	209.8	0.001172	0.1047	894.6	2597.3	896.8	1899.3	2796.1
20	212.4	0.001177	0.0995	906.2	2598.2	908.6	1888.6	2797.2

(Continued)

TABLE A.4 (Continued)

Properties of Saturated Steam

P (bar)	T (°C)	v (m ³ /kg)		u (kJ/kg)		h (kJ/kg)		
		Water, v_f	Steam, v_g	Water, u_f	Steam, u_g	Water, h_f	Evap. h_{fg}	Steam, h_g
21	214.9	0.001181	0.0949	917.5	2598.9	920.0	1878.2	2798.2
22	217.2	0.001185	0.0907	928.3	2599.6	931.0	1868.1	2799.1
23	219.6	0.001189	0.0868	938.9	2600.2	941.6	1858.2	2799.8
24	221.8	0.001193	0.0832	949.1	2600.7	951.9	1848.5	2800.4
25	223.9	0.001197	0.0799	959.0	2601.2	962.0	1839.0	2800.9
26	226.0	0.001201	0.0769	968.6	2601.5	971.7	1829.6	2801.4
27	228.1	0.001205	0.0740	978.0	2601.8	981.2	1820.5	2801.7
28	230.0	0.001209	0.0714	987.1	2602.1	990.5	1811.5	2802.0
29	232.0	0.001213	0.0689	996.0	2602.3	999.5	1802.6	2802.2
30	233.8	0.001216	0.0666	1004.7	2602.4	1008.4	1793.9	2802.3
32	237.4	0.001224	0.0624	1021.5	2602.5	1025.4	1776.9	2802.3
34	240.9	0.001231	0.0587	1037.6	2602.5	1041.8	1760.3	2802.1
36	244.2	0.001238	0.0554	1053.1	2602.2	1057.6	1744.2	2801.7
38	247.3	0.001245	0.0524	1068.0	2601.9	1072.7	1728.4	2801.1
40	250.3	0.001252	0.0497	1082.4	2601.3	1087.4	1712.9	2800.3
42	253.2	0.001259	0.0473	1096.3	2600.7	1101.6	1697.8	2799.4
44	256.0	0.001266	0.0451	1109.8	2599.9	1115.4	1682.9	2798.3
46	258.8	0.001272	0.0430	1122.9	2599.1	1128.8	1668.3	2797.1
48	261.4	0.001279	0.0412	1135.6	2598.1	1141.8	1653.9	2795.7
50	263.9	0.001286	0.0394	1148.0	2597.0	1154.5	1639.7	2794.2
52	266.4	0.001292	0.0378	1160.1	2595.9	1166.8	1625.7	2792.6
54	268.8	0.001299	0.0363	1171.9	2594.6	1178.9	1611.9	2790.8
56	271.1	0.001306	0.0349	1183.5	2593.3	1190.8	1598.2	2789.0
58	273.3	0.001312	0.0337	1194.7	2591.9	1202.3	1584.7	2787.0
60	275.6	0.001319	0.0324	1205.8	2590.4	1213.7	1571.3	2785.0
62	277.7	0.001325	0.0313	1216.6	2588.8	1224.8	1558.0	2782.9
64	279.8	0.001332	0.0302	1227.2	2587.2	1235.7	1544.9	2780.6
66	281.8	0.001338	0.0292	1237.6	2585.5	1246.5	1531.9	2778.3
68	283.8	0.001345	0.0283	1247.9	2583.7	1257.0	1518.9	2775.9
70	285.8	0.001351	0.0274	1258.0	2581.8	1267.4	1506.0	2773.5
72	287.7	0.001358	0.0265	1267.9	2579.9	1277.6	1493.3	2770.9
74	289.6	0.001364	0.0257	1277.6	2578.0	1287.7	1480.5	2768.3
76	291.4	0.001371	0.0249	1287.2	2575.9	1297.6	1467.9	2765.5
78	293.2	0.001378	0.0242	1296.7	2573.8	1307.4	1455.3	2762.8
80	295.0	0.001384	0.0235	1306.0	2571.7	1317.1	1442.8	2759.9
82	296.7	0.001391	0.0229	1315.2	2569.5	1326.6	1430.3	2757.0
84	298.4	0.001398	0.0222	1324.3	2567.2	1336.1	1417.9	2754.0
86	300.1	0.001404	0.0216	1333.3	2564.9	1345.4	1405.5	2750.9
88	301.7	0.001411	0.0210	1342.2	2562.6	1354.6	1393.2	2747.8
90	303.3	0.001418	0.02050	1351.0	2560.1	1363.7	1380.9	2744.6
92	304.9	0.001425	0.01996	1359.7	2557.7	1372.8	1368.6	2741.4
94	306.4	0.001432	0.01945	1368.2	2555.2	1381.7	1356.3	2738.0
96	308.0	0.001439	0.01897	1376.7	2552.6	1390.6	1344.1	2734.7
98	309.5	0.001446	0.01849	1385.2	2550.0	1399.3	1331.9	2731.2
100	311.0	0.001453	0.01804	1393.5	2547.3	1408.0	1319.7	2727.7
105	314.6	0.001470	0.01698	1414.1	2540.4	1429.5	1289.2	2718.7
110	318.0	0.001489	0.01601	1434.2	2533.2	1450.6	1258.7	2709.3
115	321.4	0.001507	0.01511	1454.0	2525.7	1471.3	1228.2	2699.5
120	324.6	0.001527	0.01428	1473.4	2517.8	1491.8	1197.4	2689.2
125	327.8	0.001547	0.01351	1492.7	2509.4	1512.0	1166.4	2678.4

(Continued)

TABLE A.4 (Continued)

Properties of Saturated Steam

P (bar)	T (°C)	v (m ³ /kg)		u (kJ/kg)		h (kJ/kg)		
		Water, v_f	Steam, v_g	Water, u_f	Steam, u_g	Water, h_f	Evap. h_{fg}	Steam, h_g
130	330.8	0.001567	0.01280	1511.6	2500.6	1532.0	1135.0	2667.0
135	333.8	0.001588	0.01213	1530.4	2491.3	1551.9	1103.1	2655.0
140	336.6	0.001611	0.01150	1549.1	2481.4	1571.6	1070.7	2642.4
145	339.4	0.001634	0.01090	1567.5	2471.0	1591.3	1037.7	2629.1
150	342.1	0.001658	0.01034	1586.1	2459.9	1611.0	1004.0	2615.0
155	344.8	0.001683	0.00981	1604.6	2448.2	1630.7	969.6	2600.3
160	347.3	0.001710	0.00931	1623.2	2436.0	1650.5	934.3	2584.9
165	349.8	0.001739	0.00883	1641.8	2423.1	1670.5	898.3	2568.8
170	352.3	0.001770	0.00837	1661.6	2409.3	1691.7	859.9	2551.6
175	354.6	0.001803	0.00793	1681.8	2394.6	1713.3	820.0	2533.3
180	357.0	0.001840	0.00750	1701.7	2378.9	1734.8	779.1	2513.9
185	359.2	0.001881	0.00708	1721.7	2362.1	1756.5	736.6	2493.1
190	361.4	0.001926	0.00668	1742.1	2343.8	1778.7	692.0	2470.6
195	363.6	0.001977	0.00628	1763.2	2323.6	1801.8	644.2	2446.0
200	365.7	0.00204	0.00588	1785.7	2300.8	1826.5	591.9	2418.4
205	367.8	0.00211	0.00546	1810.7	2274.4	1853.9	532.5	2386.4
210	369.8	0.00220	0.00502	1840.0	2242.1	1886.3	461.3	2347.6
215	371.8	0.00234	0.00451	1878.6	2198.1	1928.9	366.2	2295.2
220	373.7	0.00267	0.00373	1952	2114	2011	185	2196
221.2	374.15	0.00317	0.00317	2038	2038	2108	0	2108

TABLE A.5

Properties of Superheated Steam

P (bar) (T_{sat} °C)		Saturated Water	Saturated Steam	Temperature (°C)							
				50	75	100	150	200	250	300	350
0.0	h	—	—	2595	2642	2689	2784	2880	2978	3077	3177
(—)	u	—	—	2446	2481	2517	2589	2662	2736	2812	2890
	v	—	—	—	—	—	—	—	—	—	—
0.1	h	191.8	2584.8	2593	2640	2688	2783	2880	2977	3077	3177
(45.8)	u	191.8	2438.0	2444	2480	2516	2588	2661	2736	2812	2890
	v	0.00101	14.7	14.8	16.0	17.2	9.5	21.8	24.2	26.5	28.7
0.5	h	340.6	2646.0	209.3	313.9	2683	2780	2878	2979	3076	3177
(81.3)	u	340.6	2484.0	209.2	313.9	2512	2586	2660	2735	2811	2889
	v	0.00103	3.24	0.00101	0.00103	3.41	3.89	4.35	4.83	5.29	5.75
1.0	h	417.5	2675.4	209.3	314.0	2676	2776	2875	2975	3074	3176
(99.6)	u	417.5	2506.1	209.2	313.9	2507	2583	2658	2734	2811	2889
	v	0.00104	1.69	0.00101	0.00103	1.69	1.94	2.17	2.40	2.64	2.87
5.0	h	640.1	2747.5	209.7	314.3	419.4	632.2	2855	2961	3065	3168
(151.8)	u	639.6	2560.2	209.2	313.8	418.8	631.6	2643	2724	2803	2883
	v	0.00109	0.375	0.00101	0.00103	0.00104	0.00109	0.425	0.474	0.522	0.571
10	h	762.6	2776.2	210.1	314.7	419.7	632.5	2827	2943	3052	3159
(179.9)	u	761.5	2582	209.1	313.7	418.7	631.4	2621	2710	2794	2876
	v	0.00113	0.194	0.00101	0.00103	0.00104	0.00109	0.206	0.233	0.258	0.282
20	h	908.6	2797.2	211.0	315.5	420.5	633.1	852.6	2902	3025	3139
(212.4)	u	906.2	2598.2	209.0	313.5	418.4	603.9	850.2	2679	2774	2862
	v	0.00118	0.09950	0.00101	0.00102	0.00104	0.00109	0.00116	0.111	0.125	0.139

(Continued)

TABLE A.5 (Continued)

Properties of Superheated Steam

P (bar) (T_{sat} °C)		Saturated Water	Saturated Steam	Temperature (°C)							
				50	75	100	150	200	250	300	350
40	h	1087.4	2800.3	212.7	317.1	422.0	634.3	853.4	1085.8	2962	3095
(250.3)	u	1082.4	2601.3	208.6	313.0	417.8	630.0	848.8	1080.8	2727	2829
	v	0.00125	0.04975	0.00101	0.00102	0.00104	0.00109	0.00115	0.00125	0.0588	0.0665
60	h	1213.7	2785.0	214.4	318.7	423.5	635.6	854.2	1085.8	2885	3046
(275.6)	u	1205.8	2590.4	208.3	312.6	417.3	629.1	847.3	1078.3	2668	2792
	v	0.00132	0.0325	0.00101	0.00103	0.00104	0.00109	0.00115	0.00125	0.0361	0.0422
80	h	1317.1	2759.9	216.1	320.3	425.0	636.8	855.1	1085.8	2787	2990
(295.0)	u	1306.0	2571.7	208.1	312.3	416.7	628.2	845.9	1075.8	2593	2750
	v	0.00139	0.0235	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.0243	0.0299
100	h	1408.0	2727.7	217.8	322.9	426.5	638.1	855.9	1085.8	1343.4	2926
(311.0)	u	1393.5	2547.3	207.8	311.7	416.1	627.3	844.4	1073.4	1329.4	2702
	v	0.00145	0.0181	0.00101	0.00102	0.001049	0.00109	0.00115	0.00124	0.00140	0.0224
150	h	1611.0	2615.0	222.1	326.0	430.3	641.3	858.1	1086.2	1338.2	2695
(342.1)	u	1586.1	2459.9	207.0	310.7	414.7	625.0	841.0	1067.7	1317.6	2523
	v	0.00166	0.0103	0.00101	0.00102	0.00104	0.00108	0.00114	0.00123	0.00138	0.0115
200	h	1826.5	2418.4	226.4	330.0	434.0	644.5	860.4	1086.7	1334.3	1647.1
(365.7)	u	1785.7	2300.8	206.3	309.7	413.2	622.9	837.7	1062.2	1307.1	1613.7
	v	0.00204	0.005875	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00136	0.00167
221.2(Pc)	h	2108	2108	228.2	331.7	435.7	645.8	861.4	1087.0	1332.8	1635.5
(374.15)(Tc)	u	2037.8	2037.8	206.0	309.2	412.8	622.0	836.3	1060.0	1302.9	1600.3
	v	0.00317	0.00317	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00135	0.00163

250	h	—	—	230.7	334.0	437.8	647.7	862.8	1087.5	1331.1	1625.0
(—)	u	—	—	205.7	308.7	412.1	620.8	834.4	1057.0	1297.5	1585.0
	v	—	—	0.00100	0.00101	0.00103	0.00108	0.00113	0.00122	0.00135	0.00160
300	h	—	—	235.0	338.1	441.6	650.9	865.2	1088.4	1328.7	1609.9
(—)	u	—	—	205.0	307.7	410.8	618.7	831.3	1052.1	1288.7	1563.3
	v	—	—	0.0009990	0.00101	0.00103	0.00107	0.00113	0.00121	0.00133	0.00155
500	h	—	—	251.9	354.2	456.8	664.1	875.4	1093.6	1323.7	1576.3
(—)	u	—	—	202.4	304.0	405.8	611.0	819.7	1034.3	1259.3	1504.1
	v	—	—	0.0009911	0.00100	0.00102	0.00106	0.00111	0.00119	0.00129	0.00144
1000	h	—	—	293.9	394.3	495.1	698.0	903.5	1113.0	1328.7	1550.5
(—)	u	—	—	196.5	295.7	395.1	594.4	795.3	999.0	1207.1	1419.0
	v	—	—	0.0009737	0.0009852	0.00100	0.00104	0.00108	0.00114	0.00122	0.00131

P (bar) (T_{sat} °C)		Saturated Water	Saturated Steam	Temperature (°C)							
				400	450	500	550	600	650	700	750
0.0	h	—	—	3280	3384	3497	3597	3706	3816	3929	4043
	u	—	—	2969	3050	3132	3217	3303	3390	3480	3591
	v	—	—	—	—	—	—	—	—	—	—
0.1	h	191.8	2584.8	3280	3384	3489	3596	3706	3816	3929	4043
(45.8)	u	191.8	2438.0	2969	3050	3132	3217	3303	3390	3480	3571
	v	0.00101	14.7	21.1	33.3	35.7	38.0	40.3	42.6	44.8	47.2
0.5	h	340.6	2646.0	3279	3383	3489	3596	3705	3816	3929	4043
(81.3)	u	340.6	2484.0	2969	3049	3132	3216	3302	3390	3480	3571
	v	0.00103	3.24	6.21	6.67	7.14	7.58	8.06	8.55	9.01	9.43
1.0	h	417.5	2675.4	3278	3382	3488	3596	3705	3816	3928	4042
(99.6)	u	417.5	2506.1	2968	3049	3132	3216	3302	3390	3479	3570
	v	0.00104	1.69	3.11	3.33	3.57	3.80	4.03	4.26	4.48	4.72

(Continued)

TABLE A.5 (Continued)

Properties of Superheated Steam

P (bar) (T_{sat} °C)		Saturated Steam	Saturated Steam	Temperature (°C)							
				400	450	500	550	600	650	700	750
5.0 (151.8)	h	640.1	2747.5	3272	3379	3484	3592	3702	3813	3926	4040
	u	639.6	2560.2	2964	3045	3128	3213	3300	3388	3477	3569
	v	0.00109	0.375	0.617	0.664	0.711	0.758	0.804	0.850	0.897	0.943
10 (179.9)	h	762.6	2776.2	3264	3371	3478	3587	3697	3809	3923	4038
	u	761.5	2582	2958	3041	3124	3210	3296	3385	3475	3567
	v	0.00113	0.194	0.307	0.330	0.353	0.377	0.402	0.424	0.448	0.472
20 (212.4)	h	908.6	2797.2	3249	3358	3467	3578	3689	3802	3916	4032
	u	906.2	2598.2	2946	3031	3115	3202	3290	3379	3470	3562
	v	0.00118	0.09950	0.151	0.163	0.175	0.188	0.200	0.211	0.223	0.235
40 (250.3)	h	1087.4	2800.3	3216	3331	3445	3559	3673	3788	3904	4021
	u	1082.4	2601.3	2922	3011	3100	3188	3278	3368	3460	3554
	v	0.00125	0.04975	0.0734	0.0799	0.0864	0.0926	0.0987	0.105	0.111	0.117
60 (275.6)	h	1213.7	2785.0	3180	3303	3422	3539	3657	3774	3892	4011
	u	1205.8	2590.4	2896	2991	3083	3174	3265	3357	3451	3545
	v	0.00132	0.0325	0.0474	0.0521	0.0566	0.0609	0.0652	0.0693	0.0735	0.0776
80 (295.0)	h	1317.1	2759.9	3142	3274	3399	3520	3640	3759	3879	4000
	u	1306.0	2571.7	2867	2969	3065	3159	3252	3346	3441	3537
	v	0.00139	0.0235	0.0344	0.0382	0.0417	0.0450	0.0483	0.0515	0.0547	0.0578
100 (311.0)	h	1408.0	2727.7	3100	3244	3375	3500	3623	3745	3867	3989
	u	1393.5	2547.3	2836	2946	3047	3144	3240	3335	3431	3528
	v	0.00145	0.0181	0.0264	0.0298	0.0328	0.0356	0.0383	0.0410	0.0435	0.0461
150 (342.1)	h	1611.0	2615.0	2975	3160	3311	3448	3580	3708	3835	4962
	u	1586.1	2459.9	2744	2883	2999	3105	3207	3307	3407	3507
	v	0.00166	0.0103	0.0157	0.0185	0.0208	0.0229	0.0249	0.0267	0.0286	0.0304
200 (365.7)	h	1826.5	2418.4	2820	3064	3241	3394	3536	3671	3804	3935
	u	1785.7	2300.8	2622	2810	2946	3063	3172	3278	3382	3485
	v	0.00204	0.005875	0.009950	0.0127	0.0148	0.0166	0.0182	0.0197	0.0211	0.0225
221.2(Pc) (374.15)(Tc)	h	2108	2108	2733	3020	3210	3370	3516	3655	3790	3923
	u	2037.8	2037.8	2553	2776	2922	3045	3157	3265	3371	3476
	v	0.00317	0.00317	0.008157	0.0110	0.0130	0.0147	0.0162	0.0176	0.0190	0.0202
250 (—)	h	—	—	2582	2954	3166	3337	3490	3633	3772	3908
	u	—	—	2432	2725	2888	3019	3137	3248	3356	3463
	v	—	—	0.006013	0.009174	0.0111	0.0127	0.0141	0.0143	0.0166	0.0178
300 (—)	h	—	—	2162	2826	3085	3277	3443	3595	3740	3880
	u	—	—	2077	2623	2825	2972	3100	3218	3330	3441
	v	—	—	0.002830	0.006734	0.008680	0.0102	0.0114	0.0126	0.0136	0.0147
500 (—)	h	—	—	1878	2293	2723	3021	3248	3439	3610	3771
	u	—	—	1791	2169	2529	2765	2946	3091	3224	3350
	v	—	—	0.001726	0.002491	0.003882	0.005112	0.006112	0.007000	0.007722	0.008418
1000 (—)	h	—	—	1798	2051	2316	2594	2857	3105	3324	3526
	u	—	—	1653	1888	2127	2369	2591	2795	2971	3131
	v	—	—	0.001446	0.00162	0.001893	0.00224	0.00266	0.00310	0.003536	0.00395

Systems of Units

Systems of units are defined with reference to Newton's second law for a system of constant mass: $F = ma$ (mass-length/time²)

where F is the force required to accelerate a body of mass, m , at a rate a (length/time²)

System	Length	Time	Mass	Force	g_c
SI	Meter m	Second s	Kilogram kg	Newton N	1.0 (kg.m)/(N · s ²)
CGS	Centimeter cm	Second s	Gram g	dyne	1.0 (g.cm)/(dyne.s ²)
AES	Foot ft	Second s	Pound mass lb _m	Pound force lb _f	32.17 (lb _m .ft)/(lb _f .s ²)

1.0 N = Force that will accelerate a mass of 1.0 kg by 1.0 m/s²

1.0 dyne = Force that will accelerate a mass of 1.0 g by 1.0 cm/s²

1.0 lb_f = Force that will accelerate a mass of 1.0 lb_m by 32.174 ft/s²

Metric prefixes

10 ¹²	T	Tera	Trillion	10 ⁻¹	d	Deci	Tenths
10 ⁹	G	Giga	Billion	10 ⁻²	c	Centi	Hundredths
10 ⁶	M	Mega	Million	10 ⁻³	m	Milli	Thousandths
10 ³	k	Kilo	Thousand	10 ⁻⁶	μ	Micro	Millionths
10 ²	h	Hecto	Hundred	10 ⁻⁹	n	Nano	Billionths
10 ¹	da	Deca	Ten	10 ⁻¹²	p	Pico	Trillionths

Acceleration of gravity $g = 9.8066 \text{ m/s}^2$ (sea level, 45° latitude)
 $g = 32.174 \text{ ft/s}^2$

Gas constant
 $R = 10.731 \text{ psia-ft}^3/\text{lbmol} = 0.7302 \text{ atm-ft}^3/\text{lbmol}$
 $R = 0.082056 \text{ atm-L/mol-K} = 8.3143 \text{ Pa-m}^3/\text{mol-K}$
 $R = 0.08314 \text{ L-bar/mol-K} = 1.987 \text{ Btu/lb mol} = 8314.3 \text{ J/kg mol-K}$
 $R = 8.3143 \text{ J/mol-K} = 62.36 \text{ L-mmHg/mol-K} = 1.987 \text{ cal/mol-K}$

Density of water at 4°C
 $\rho (\text{H}_2\text{O}, 4^\circ\text{C}) = 1.0 \text{ g/cm}^3 = 1.0 \text{ kg/L} = 10^3 \text{ kg/m}^3$
 $\rho (\text{H}_2\text{O}, 4^\circ\text{C}) = 8.34 \text{ lb}_m/\text{gal} = 62.43 \text{ lb}_m/\text{ft}^3$

Specific gravity of water
 $= 1.0$

Specific gravity of Hg
 $= 13.6$

Conversion Factors

Mass	$1 \text{ lb}_m = 5 \times 10^{-4} \text{ t} = 0.453593 \text{ kg} = 453.593 \text{ g} = 16 \text{ oz}$ $1 \text{ kg} = 1000 \text{ g} = 2.20462 \text{ lb}_m = 0.001 \text{ t}$ $1 \text{ t} = 2000 \text{ lb}_m; 1 \text{ t} = 1000 \text{ kg}$
Length	$1 \text{ ft} = 12 \text{ in.}; 1 \text{ ft} = 0.3048 \text{ m} = 30.48 \text{ cm}; 1 \text{ in.} = 2.54 \text{ cm}; 1 \text{ mile} = 5280 \text{ ft}$ $1 \text{ m} = 10^{10} \text{ Å} = 39.37 \text{ in.} = 3.2808 \text{ ft} = 1.0936 \text{ yd} = 0.0006214 \text{ mi}$
Volume	$1 \text{ ft}^3 = 7.481 \text{ gal} = 1728 \text{ in.}^3 = 28.317 \text{ L} = 28,317 \text{ cm}^3$ $1 \text{ gal} = 231 \text{ in.}^3; 1 \text{ in.}^3 = 16.387 \text{ cm}^3$ $1 \text{ cc} = 1 \text{ cm}^3 = 1 \text{ mL}; 1000 \text{ mL} = \text{L}$ $1000 \text{ L} = 1 \text{ m}^3 = 35.3145 \text{ ft}^3 = 220.83 \text{ imperial gallons} = 264.17 \text{ gal} = 1056.68 \text{ qt}$ $8 \text{ fl oz} = 1 \text{ cup}; 4 \text{ cup} = 1 \text{ quart}; 4 \text{ quart} = 1 \text{ gal} = 128 \text{ fl oz}$
Density	$1 \text{ g/cm}^3 = 1 \text{ kg/L} = 1000 \text{ kg/m}^3 = 62.428 \text{ lb/ft}^3 = 8.345 \text{ lb}_m/\text{gal}$
Force	$1 \text{ lb}_f = 32.174 \text{ lb}_m \cdot \text{ft/s}^2 = 4.448222 \text{ N} = 4.4482 \times 10^5 \text{ dynes}$ $1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2 = 10^5 \text{ dynes} = 10^6 \text{ g} \cdot \text{cm/s}^2 = 0.22481 \text{ lb}_f$
Pressure	$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa} = 10^5 \text{ N/m}^2$ Pascal (Pa) is defined as $1 \text{ N/m}^2 = 1 \text{ kg/m} \cdot \text{s}^2$ $1 \text{ atm} = 1.01325 \text{ bar} = 14.696 \text{ lb}_f/\text{in.}^2 = 760 \text{ mmHg at } 0^\circ\text{C (torr)} = 29.92 \text{ in Hg at } 0^\circ\text{C}$ $1 \text{ psi} = 1 \text{ lb}_f/\text{in.}^2; \text{psia (absolute)} = \text{psig (gauge)} + 14.696$
Temperature	$1 \text{ K} = 1.8^\circ\text{R (absolute temperature)}$ $T(^{\circ}\text{C}) = T(\text{K}) - 273.15$ $T(^{\circ}\text{F}) = T(^{\circ}\text{R}) - 459.67$ $T(^{\circ}\text{F}) = 1.8T(^{\circ}\text{C}) + 32$
Energy	$1 \text{ J} = 1 \text{ N} \cdot \text{m} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 10^7 \text{ ergs} = 10^7 \text{ dyne} \cdot \text{cm} = 2.778 \times 10^{-7} \text{ kW} \cdot \text{h}$ $= 0.23901 \text{ cal} = 0.7376 \text{ ft} \cdot \text{lb}_f = 9.486 \times 10^{-4} \text{ Btu}$ $1 \text{ cal} = 4.1868 \text{ J}; 1 \text{ Btu} = 778.17 \text{ ft} \cdot \text{lb}_f = 252.0 \text{ cal}$ $1 \text{ Btu/lb}_m \cdot ^\circ\text{F} = 1 \text{ cal/g} \cdot ^\circ\text{C}$
Power	$1 \text{ hp} = 550 \text{ ft} \cdot \text{lb}_f/\text{s} = 0.74570 \text{ kW}$ $1 \text{ W} = 1 \text{ J/s} = 0.23901 \text{ cal/s} = 0.7376 \text{ ft} \cdot \text{lb}_f/\text{s} = 9.486 \times 10^{-4} \text{ Btu/s}$ $1 \text{ kW} = 1000 \text{ J/s} = 3412.1 \text{ Btu/h} = 1.341 \text{ hp}$