

Chapter 7: Energy and Energy Balances

Lecture 21

7.1 Forms of Energy: The First Law of Thermodynamics

The total energy of a system has three components:

- 1. Kinetic energy:** Energy due to the translational motion of the system as a whole relative to some frame of reference (usually the earth's surface) or to rotation of the system about some axis. In this text, we will deal only with translational kinetic energy.
- 2. Potential energy:** Energy due to the position of the system in a potential field (such as a gravitational or electromagnetic field). In this text, we will deal only with gravitational potential energy.
- 3. Internal energy:** All energy possessed by a system other than kinetic and potential energy, such as energy due to the motion of molecules relative to the center of mass of the system, to the rotational and vibrational motion and the electromagnetic interactions of the molecules, and to the motion and interactions of the atomic and subatomic constituents of the molecules.

Suppose a process system is **closed**, meaning that no mass is transferred across its boundaries while the process is taking place. Energy may be transferred between such a system and its surroundings in two ways:

1. As **heat**, or energy that flows as a result of temperature difference between a system and its surroundings. The direction of flow is always from a higher temperature to a lower one.
Heat is defined as positive when it is transferred to the system from the surroundings.
2. As **work**, or energy that flows in response to any driving force other than a temperature difference, such as a force, a torque, or a voltage. For example, if a gas in a cylinder expands and moves a piston against a restraining force, the gas does work on the piston (energy is transferred as work from the gas to its surroundings, which include the piston). *In this text, work is defined as positive when it is done by the system on the surroundings.* (Note: The opposite sign convention is sometimes used. The choice is arbitrary, as long as it is used consistently; however, to avoid confusion when reading thermodynamics references, you should be sure which convention has been adopted.)

The principle that underlies all energy balances is the law of conservation of energy, which states that energy can neither be created nor destroyed. This law is also called the **first law of thermodynamics**. In its most general form, the first law states that the rate at which energy (kinetic + potential + internal) is carried into a system by the input streams, plus the rate at which it enters as heat, minus the rate at which it is transported out of the system by the output streams, minus the rate at which it leaves as work, equals the rate of accumulation of energy in the system. (That is, accumulation = input – output, as would be expected.)

7.2 Kinetic and Potential Energy

The kinetic energy, E_k (J), of an object of mass m (kg) moving with velocity u (m/s) relative to the surface of the earth is

$$E_k = \frac{1}{2}mu^2 \quad (7.2-1a)$$

If a fluid enters a system with a mass flow rate \dot{m} (kg/s) and uniform velocity u (m/s), then

$$\dot{E}_k = \frac{1}{2}\dot{m}u^2 \quad (7.2-1b)$$

\dot{E}_k (J/s) may be thought of as the rate at which kinetic energy is transported into the system by the fluid.

EXAMPLE 7.2-1

Kinetic Energy Transported by a Flowing Stream

Water flows into a process unit through a 2-cm ID pipe at a rate of 2.00 m³/h. Calculate \dot{E}_k for this stream in joules/second.

SOLUTION

First calculate the linear velocity (which equals the volumetric flow rate divided by the cross-sectional area of the pipe) and the mass flow rate of the fluid:

$$u = \frac{2.00 \text{ m}^3}{\text{h}} \left| \begin{array}{c} 100^2 \text{ cm}^2 \\ 1^2 \text{ m}^2 \\ \pi(1)^2 \text{ cm}^2 \end{array} \right| \frac{1 \text{ h}}{3600 \text{ s}} = 1.77 \text{ m/s}$$

$$\dot{m} = \frac{2.00 \text{ m}^3}{\text{h}} \left| \begin{array}{c} 1000 \text{ kg} \\ \text{m}^3 \end{array} \right| \frac{1 \text{ h}}{3600 \text{ s}} = 0.556 \text{ kg/s}$$

Then, from Equation 7.2-1b

$$\dot{E}_k = \frac{0.556 \text{ kg/s}}{2} \left| \begin{array}{c} (1.77)^2 \text{ m}^2 \\ \text{s}^2 \end{array} \right| \frac{1 \text{ N}}{1 \text{ kg}\cdot\text{m/s}^2} = 0.870 \text{ N}\cdot\text{m/s} = \boxed{0.870 \text{ J/s}}$$

The gravitational potential energy of an object of mass m is

$$E_p = mgz \quad (7.2-2a)$$

where g is the acceleration of gravity and z is the height of the object above a reference plane at which E_p is arbitrarily defined to be zero. If a fluid enters a system with a mass flow rate \dot{m} and an elevation z relative to the potential energy reference plane, then

$$\dot{E}_p = \dot{m}gz \quad (7.2-2b)$$

\dot{E}_p (J/s) may be thought of as the rate at which gravitational potential energy is transported into the system by the fluid. Since we are normally interested in the *change* in potential energy when a body or fluid moves from one elevation to another [$\dot{E}_{p2} - \dot{E}_{p1} = \dot{m}g(z_2 - z_1)$], the elevation chosen as the reference plane does not matter.

EXAMPLE 7.2-2**Potential Energy Increase of a Flowing Fluid**

Crude oil is pumped at a rate of 15.0 kg/s from a point 220 meters below the earth's surface to a point 20 meters above ground level. Calculate the attendant rate of increase of potential energy.

SOLUTION

Let subscripts 1 and 2 denote the first and second points, respectively:

$$\begin{aligned}\Delta \dot{E}_p &= \dot{E}_{p2} - \dot{E}_{p1} = \dot{m}g(z_2 - z_1) \\ &= \frac{15.0 \text{ kg}}{\text{s}} \left| \frac{9.81 \text{ m}}{\text{s}^2} \right| \left| \frac{1 \text{ N}}{1 \text{ kg}\cdot\text{m/s}^2} \right| [20 - (-220)] \text{ m} \\ &= 35,300 \text{ N}\cdot\text{m/s} = \boxed{35,300 \text{ J/s}}\end{aligned}$$

The answer could also have been expressed as 35,300 W or 35.3 kW. A pump would have to deliver at least this much power to raise the oil at the given rate.

7.3 Energy Balances on Closed Systems

A system is termed **open** or **closed** according to whether or not mass crosses the system boundary during the period of time covered by the energy balance. A batch process system is, by definition, closed, and semibatch and continuous systems are open.

An integral energy balance may be derived for a closed system between two instants of time. Since energy can neither be created nor destroyed, the generation and consumption terms of the general balance (4.2-1) drop out, leaving

$$\text{accumulation} = \text{input} - \text{output} \quad (7.3-1)$$

$$\frac{\text{final system energy} - \text{initial system energy}}{\text{energy}} = \frac{\text{net energy transferred to the system (in - out)}}{\text{the system (in - out)}} \quad (7.3-2)$$

Now

$$\text{initial system energy} = U_i + E_{ki} + E_{pi}$$

$$\text{final system energy} = U_f + E_{kf} + E_{pf}$$

$$\text{energy transferred} = Q - W$$

where the subscripts i and f refer to the initial and final states of the system and U , E_k , E_p , Q , and W represent internal energy, kinetic energy, potential energy, heat transferred to the system from its surroundings, and work done by the system on its surroundings. Equation 7.3-2 then becomes

$$(U_f - U_i) + (E_{kf} - E_{ki}) + (E_{pf} - E_{pi}) = Q - W \quad (7.3-3)$$

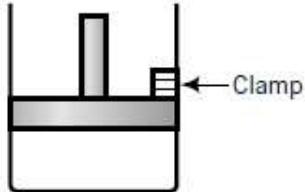
or, if the symbol Δ is used to signify (final - initial),

$$\Delta U + \Delta E_k + \Delta E_p = Q - W \quad (7.3-4)$$

EXAMPLE 7.3-1

Energy Balance on a Closed System

A gas is contained in a cylinder fitted with a movable piston.



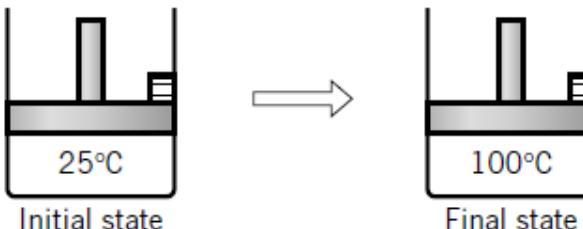
The initial gas temperature is 25°C.

The cylinder is placed in boiling water with the piston held in a fixed position. Heat in the amount of 2.00 kcal is transferred to the gas, which equilibrates at 100°C (and a higher pressure). The piston is then released, and the gas does 100 J of work in moving the piston to its new equilibrium position. The final gas temperature is 100°C.

Write the energy balance equation for each of the two stages of this process, and in each case solve for the unknown energy term in the equation. In solving this problem, consider the gas in the cylinder to be the system, neglect the change in potential energy of the gas as the piston moves vertically, and assume the gas behaves ideally. Express all energies in joules.

SOLUTION

1.



$$\Delta U + \Delta E_k + \Delta E_p = Q - W \quad (\text{Equation 7.3-4})$$

\downarrow
 $\Delta E_k = 0$ (the system is stationary)
 $\Delta E_p = 0$ (no vertical displacement)
 $W = 0$ (no moving boundaries)

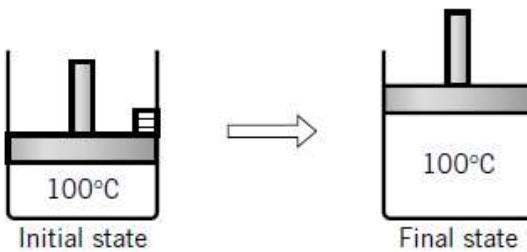
$$\Delta U = Q$$

\downarrow
 $Q = 2.00 \text{ kcal}$

$$\Delta U = \frac{2.00 \text{ kcal}}{\text{kcal}} \left| \begin{array}{c} 10^3 \text{ cal} \\ \hline \text{kcal} \end{array} \right| \frac{1 \text{ J}}{0.23901 \text{ cal}} = \boxed{8370 \text{ J} = \Delta U}$$

The gas thus gains 8370 J of internal energy in going from 25 to 100°C.

2.



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

\downarrow
 $\Delta E_k = 0$ (the system is stationary at the initial and final states)
 $\Delta E_p = 0$ (assumed negligible by hypothesis)
 $\Delta U = 0$ (U depends only on T for an ideal gas, and T does not change)

$$0 = Q - W$$

\downarrow
 $W = +100 \text{ J}$ (Why is it positive?)

$$\boxed{Q = 100 \text{ J}}$$

Thus an additional 100 J of heat is transferred to the gas as it expands and reequilibrates at 100°C.

Lecture 22

7.4 Energy Balances on Open Systems at Steady State

7.4a Flow Work and Shaft Work

The net rate of work done by an open system on its surroundings may be written as

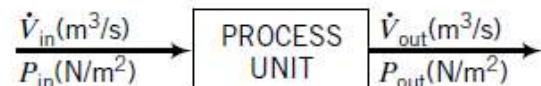
$$\dot{W} = \dot{W}_s + \dot{W}_{fl} \quad (7.4-1)$$

where

\dot{W}_s = **shaft work**, or rate of work done by the process fluid on a moving part within the system (e.g., a pump rotor)

\dot{W}_{fl} = **flow work**, or rate of work done by the fluid at the system outlet minus the rate of work done on the fluid at the system inlet

To derive an expression for \dot{W}_{fl} , we initially consider the single-inlet-single-outlet system shown here.



Fluid at a pressure $P_{in}(N/m^2)$ enters a pipe at a volumetric flow rate $\dot{V}_{in}(m^3/s)$ and exits at a pressure $P_{out}(N/m^2)$ and volumetric flow rate $\dot{V}_{out}(m^3/s)$. The fluid that enters the system has work done on it by the fluid just behind it at a rate

$$\dot{W}_{in}(N\cdot m/s) = P_{in}(N/m^2)\dot{V}_{in}(m^3/s) \quad (7.4-2)$$

while the fluid leaving the system performs work on the surroundings at a rate

$$\dot{W}_{out} = P_{out}\dot{V}_{out} \quad (7.4-3)$$

The net rate at which work is done by the system at the inlet and outlet is therefore

$$\dot{W}_{fl} = P_{out}\dot{V}_{out} - P_{in}\dot{V}_{in} \quad (7.4-4)$$

If several input and output streams enter and leave the system, the $P\dot{V}$ products for each stream must be summed to determine \dot{W}_{fl} .

7.4b Specific Properties and Enthalpy

A **specific property** is an intensive quantity obtained by dividing an extensive property (or its flow rate) by the total amount (or flow rate) of the process material. Thus, if the volume of a fluid is 200 cm³ and the mass of the fluid is 200 g, the **specific volume** of the fluid is 1 cm³/g. Similarly, if the mass flow rate of a stream is 100 kg/min and the volumetric flow rate is 150 L/min, the specific volume of the stream material is (150 L/min / 100 kg/min) = 1.5 L/kg; if the rate at which kinetic energy is transported by this stream is 300 J/min, then the **specific kinetic energy** of the stream material is (300 J/min) / (100 kg/min) = 3 J/kg. We will use the symbol $\hat{\cdot}$ to denote a specific property: \hat{V} will denote specific volume, \hat{U} specific internal energy, and so on.

If the temperature and pressure of a process material are such that the specific internal energy of the material is \hat{U} (J/kg), then a mass m (kg) of this material has a total internal energy

$$U(J) = m(\text{kg})\hat{U}(\text{J/kg}) \quad (7.4-5)$$

Similarly, a continuous stream of this material with a mass flow rate \dot{m} (kg/s) transports internal energy at a rate

$$\dot{U}(\text{J/s}) = \dot{m}(\text{kg/s})\hat{U}(\text{J/kg}) \quad (7.4-6)$$

A property that occurs in the energy balance equation for open systems (Section 7.4c) is the **specific enthalpy**, defined as

$$\hat{H} \equiv \hat{U} + P\hat{V} \quad (7.4-7)$$

where P is total pressure and \hat{U} and \hat{V} are specific internal energy and specific volume. The gas constants tabulated on the inside back cover provide a convenient source for the conversion factors needed to evaluate \hat{H} from Equation 7.4-7, as the following example shows.

EXAMPLE 7.4-1***Calculation of Enthalpy***

The specific internal energy of helium at 300 K and 1 atm is 3800 J/mol, and the specific molar volume at the same temperature and pressure is 24.63 L/mol. Calculate the specific enthalpy of helium at this temperature and pressure, and the rate at which enthalpy is transported by a stream of helium at 300 K and 1 atm with a molar flow rate of 250 kmol/h.

SOLUTION

$$\hat{H} = \hat{U} + P\hat{V} = 3800 \text{ J/mol} + (1 \text{ atm})(24.63 \text{ L/mol})$$

To convert the second term to joules we need the factor J/(L·atm). From the gas constant table on the inside back cover,

$$0.08206 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K}) = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$$

Dividing the right side by the left side yields the desired factor:

$$\frac{8.314 \text{ J}/\text{mol}\cdot\text{K}}{0.08206 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K})} = 101.3 \text{ J}/(\text{L}\cdot\text{atm})$$

Therefore,

$$\hat{H} = 3800 \text{ J/mol} + \frac{24.63 \text{ L}\cdot\text{atm}}{\text{mol}} \left| \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} \right| = \boxed{6295 \text{ J/mol}}$$

If $\dot{n} = 250 \text{ kmol/h}$

$$\dot{H} = \dot{n}\hat{H} = \frac{250 \text{ kmol}}{\text{h}} \left| \frac{10^3 \text{ mol}}{\text{kmol}} \right| \left| \frac{6295 \text{ J}}{\text{mol}} \right| = \boxed{1.57 \times 10^9 \text{ J/h}}$$

7.4c The Steady-State Open-System Energy Balance

The first law of thermodynamics for an open system at steady state has the form

$$\text{input} = \text{output} \quad (7.4-8)$$

If \dot{E}_j denotes the total rate of energy transport by the j th input or output stream of a process, and \dot{Q} and \dot{W} are again defined as the rates of flow of heat into and work out of the process, then Equation 7.4-8 may be written

$$\begin{aligned} \dot{Q} + \sum_{\text{input streams}} \dot{E}_j &= \sum_{\text{output streams}} \dot{E}_j + \dot{W} \\ \downarrow \\ \sum_{\text{output streams}} \dot{E}_j - \sum_{\text{input streams}} \dot{E}_j &= \dot{Q} - \dot{W} \end{aligned} \quad (7.4-9)$$

If \dot{m}_j , \dot{E}_{kj} , \dot{E}_{pj} , and \dot{U}_j are the flow rates of mass, kinetic energy, potential energy, and internal energy for the j th process stream, then the total rate at which energy is transported into or out of the system by this stream is

$$\begin{aligned} \dot{E}_j &= \dot{U}_j + \dot{E}_{kj} + \dot{E}_{pj} \\ \left| \begin{array}{l} \dot{U}_j = \dot{m}_j \hat{U}_j \\ \dot{E}_{kj} = \dot{m}_j u_j^2 / 2 \\ \dot{E}_{pj} = \dot{m}_j g z_j \end{array} \right. \\ \dot{E}_j &= \dot{m}_j \left(\hat{U}_j + \frac{u_j^2}{2} + g z_j \right) \end{aligned} \quad (7.4-10)$$

where u_j is the velocity of the j th stream and z_j is the height of this stream relative to a reference plane at which $E_p = 0$.

The total work \dot{W} done by the system on its surroundings equals the shaft work \dot{W}_s plus the flow work \dot{W}_{fl} (Equation 7.4-1). If \dot{V}_j is the volumetric flow rate of the j th stream and P_j is the pressure of this stream as it crosses the system boundary, then as was shown in Section 7.4a,

$$\begin{aligned}\dot{W}_{fl} &= \sum_{\text{output streams}} P_j \dot{V}_j - \sum_{\text{input streams}} P_j \dot{V}_j \\ \downarrow \dot{V}_j = \dot{m}_j \hat{V}_j \\ \dot{W} &= \dot{W}_s + \sum_{\text{output streams}} \dot{m}_j P_j \hat{V}_j - \sum_{\text{input streams}} \dot{m}_j P_j \hat{V}_j\end{aligned}\quad (7.4-11)$$

Substituting the expression for \dot{E}_j of Equation 7.4-10 and that for \dot{W} of Equation 7.4-11 into Equation 7.4-9 and bringing the $P\hat{V}$ terms to the left side yields

$$\sum_{\text{output streams}} \dot{m}_j \left[\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + gz_j \right] - \sum_{\text{input streams}} \dot{m}_j \left[\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + gz_j \right] = \dot{Q} - \dot{W}_s \quad (7.4-12)$$

Equation 7.4-12 could be used for all steady-state open system energy balance problems. As a rule, however, the term $\hat{U}_j + P_j \hat{V}_j$ is combined and written as \hat{H}_j , the variable previously defined as the specific enthalpy. In terms of this variable, Equation 7.4-12 becomes

$$\sum_{\text{output streams}} \dot{m}_j \left(\hat{H}_j + \frac{u_j^2}{2} + gz_j \right) - \sum_{\text{input streams}} \dot{m}_j \left(\hat{H}_j + \frac{u_j^2}{2} + gz_j \right) = \dot{Q} - \dot{W}_s \quad (7.4-13)$$

Finally, let us use the symbol Δ to denote total output minus total input, so that

$$\Delta \hat{H} = \sum_{\text{output streams}} \dot{m}_j \hat{H}_j - \sum_{\text{input streams}} \dot{m}_j \hat{H}_j \quad (7.4-14a)$$

Finally, let us use the symbol Δ to denote total output minus total input, so that

$$\Delta\dot{H} = \sum_{\text{output streams}} \dot{m}_j \hat{H}_j - \sum_{\text{input streams}} \dot{m}_j \hat{H}_j \quad (7.4-14a)$$

$$\Delta\dot{E}_k = \sum_{\text{output streams}} \dot{m}_j u_j^2/2 - \sum_{\text{input streams}} \dot{m}_j u_j^2/2 \quad (7.4-14b)$$

$$\Delta\dot{E}_p = \sum_{\text{output streams}} \dot{m}_j g z_j - \sum_{\text{input streams}} \dot{m}_j g z_j \quad (7.4-14c)$$

In terms of these quantities, Equation 7.4-13 becomes

$$\Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p = \dot{Q} - \dot{W}_s \quad (7.4-15)$$

Notice that if a process has a single input stream and a single output stream and there is no accumulation of mass in the system (so that $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$), the expression for $\Delta\dot{H}$ of Equation 7.4-14a simplifies to

$$\Delta\dot{H} = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = \dot{m}\Delta\hat{H} \quad (7.4-16)$$

Also notice that if a specific variable has the same value for all input and output streams, the corresponding term of Equation 7.4-15 drops out. For example, if \hat{H}_j is the same for all streams, then from Equation 7.4-14a

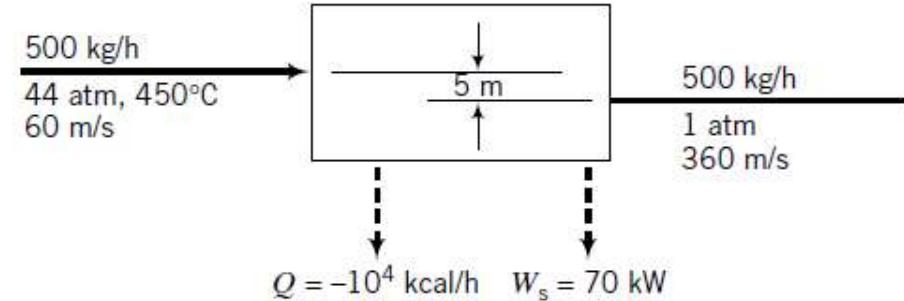
$$\Delta\dot{H} = \hat{H} \left[\sum_{\text{output streams}} \dot{m}_j - \sum_{\text{input streams}} \dot{m}_j \right] \quad (7.4-17)$$

EXAMPLE 7.4-2

Energy Balance on a Turbine

Five hundred kilograms per hour of steam drives a turbine. The steam enters the turbine at 44 atm and 450°C at a linear velocity of 60 m/s and leaves at a point 5 m below the turbine inlet at atmospheric pressure and a velocity of 360 m/s. The turbine delivers shaft work at a rate of 70 kW, and the heat loss from the turbine is estimated to be 10⁴ kcal/h. Calculate the specific enthalpy change associated with the process.

SOLUTION



From Equation 7.4-15

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

Normally, heat, work, and kinetic and potential energy terms are determined in different units. To evaluate $\Delta \dot{H}$, we will convert each term to kW (kJ/s) using conversion factors given on the inside front cover, first noting that $\dot{m} = (500 \text{ kg/h}) / (3600 \text{ s/h}) = 0.139 \text{ kg/s}$.

$$\begin{aligned}\Delta \dot{E}_k &= \frac{\dot{m}}{2} (u_2^2 - u_1^2) = \frac{0.139 \text{ kg/s}}{2} \left| \begin{array}{c} 1 \text{ N} \\ 1 \text{ kg} \cdot \text{m/s}^2 \end{array} \right| \left(\frac{(360^2 - 60^2) \text{ m}^2}{\text{s}^2} \right) \left| \begin{array}{c} 1 \text{ W} \\ 1 \text{ N} \cdot \text{m/s} \end{array} \right| \left| \begin{array}{c} 1 \text{ kW} \\ 10^3 \text{ W} \end{array} \right| \\ &= 8.75 \text{ kW}\end{aligned}$$

$$\Delta \dot{E}_p = \dot{m}g(z_2 - z_1) = \frac{0.139 \text{ kg/s}}{\text{kg}} \left| \begin{array}{c} 9.81 \text{ N} \\ \text{kg} \end{array} \right| \left| \begin{array}{c} (-5) \text{ m} \\ \text{m} \end{array} \right| \left| \begin{array}{c} 1 \text{ kW} \\ 10^3 \text{ N}\cdot\text{m/s} \end{array} \right| = -6.81 \times 10^{-3} \text{ kW}$$

$$\dot{Q} = \frac{-10^4 \text{ kcal}}{\text{h}} \left| \begin{array}{c} 1 \text{ J} \\ 0.239 \times 10^{-3} \text{ kcal} \end{array} \right| \left| \begin{array}{c} 1 \text{ h} \\ 3600 \text{ s} \end{array} \right| \left| \begin{array}{c} 1 \text{ kW} \\ 10^3 \text{ J/s} \end{array} \right| = -11.6 \text{ kW}$$

$$\dot{W}_s = 70 \text{ kW}$$



$$\Delta \dot{H} = \dot{Q} - \dot{W}_s - \Delta \dot{E}_k - \Delta \dot{E}_p = -90.3 \text{ kW}$$

But

$$\Delta \dot{H} = \dot{m}(\hat{H}_2 - \hat{H}_1) \quad (\text{from Equation 7.4-16})$$



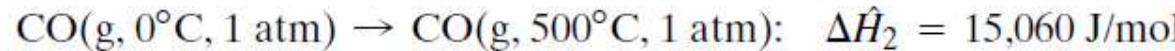
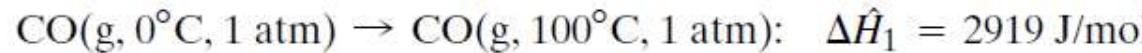
$$\hat{H}_2 - \hat{H}_1 = \Delta \dot{H} / \dot{m}$$

$$= \frac{-90.3 \text{ kJ/s}}{0.139 \text{ kg/s}} = \boxed{-650 \text{ kJ/kg}}$$

7.5 Tables of Thermodynamic Data

7.5a References States and State Properties

A convenient way to tabulate measured changes in \hat{U} or \hat{H} is to choose a temperature, pressure, and state of aggregation as a **reference state**, and to list $\Delta\hat{U}$ or $\Delta\hat{H}$ for changes from this state to a series of other states. Suppose, for example, that the enthalpy changes for carbon monoxide going from a reference state of 0°C and 1 atm to two other states are measured, with the following results:



Since \hat{H} cannot be known absolutely, for convenience we may assign a value $\hat{H}_0 = 0$ to the reference state; then $\Delta\hat{H}_1 = \hat{H}_1 - 0 = \hat{H}_1$, $\Delta\hat{H}_2 = \hat{H}_2$, and so on. A table may then be constructed for CO at 1 atm:

$T(\text{ }^\circ\text{C})$	$\hat{H}(\text{J/mol})$
0	0
100	2919
500	15,060

$\hat{H}_{\text{CO}}(\text{J/mol})$
Ref: CO(g) @ 0°C, 1 atm

$$\downarrow$$

15,060 500°C, 1 atm

2919 100°C, 1 atm

0 0°C, 1 atm

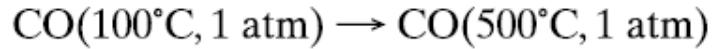
$\hat{H}_{\text{CO}}(\text{J/mol})$
Ref: CO(g) @ ?

$$\downarrow$$

12,560

419

-2500



$$\begin{aligned}\Delta\hat{H} &= (15,060 - 2919) \text{ J/mol} \\ &= (12,560 - 419) \text{ J/mol} \\ &= 12,141 \text{ J/mol}\end{aligned}$$

EXAMPLE 7.5-1 Use of Tabulated Enthalpy Data

The following entries are taken from a data table for saturated methyl chloride:

State	$T(\text{°F})$	$P(\text{psia})$	$\hat{V}(\text{ft}^3/\text{lb}_m)$	$\hat{H}(\text{Btu/lb}_m)$
Liquid	-40	6.878	0.01553	0.000
Vapor	0	18.90	4.969	196.23
Vapor	50	51.99	1.920	202.28

1. What reference state was used to generate the given enthalpies?
2. Calculate $\Delta\hat{H}$ and $\Delta\hat{U}$ for the transition of saturated methyl chloride vapor from 50°F to 0°F.
3. What assumption did you make in solving question 2 regarding the effect of pressure on specific enthalpy?

SOLUTION

1. Liquid at -40°F and 6.878 psia (the state at which $\hat{H} = 0$). You do not need this information to solve part 2.

2. $\Delta\hat{H} = \hat{H}(0^{\circ}\text{F}) - \hat{H}(50^{\circ}\text{F}) = (196.23 - 202.28) = -6.05 \text{ Btu/lb}_m$

$$\Delta\hat{U} = \Delta\hat{H} - \Delta P\hat{V} = \Delta\hat{H} - (P_{\text{final}}\hat{V}_{\text{final}} - P_{\text{initial}}\hat{V}_{\text{initial}})$$

$$= -6.05 \text{ Btu/lb}_m$$

$$= \frac{-[(18.90)(4.969) - (51.99)(1.920)] \text{ ft}^3 \cdot \text{psia/lb}_m}{10.73 \text{ ft}^3 \cdot \text{psia}}$$

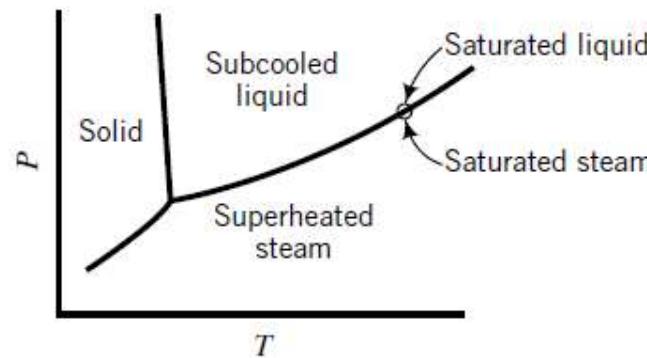
1.987 Btu

-4.96 Btu/lb_m

The value of the conversion factor $\text{Btu}/(\text{ft}^3 \cdot \text{psia})$ was obtained from the table of gas constants in back of the book. (Verify it!)

3. \hat{H} was assumed independent of P .

7.5b Steam Tables



Pure water may coexist as liquid and vapor only at temperature–pressure pairs that fall on the vapor–liquid equilibrium (VLE) curve. At points above the VLE curve (but to the right of the solid–liquid equilibrium curve), water is a **subcooled liquid**. At points on the VLE curve, water may be **saturated liquid** or **saturated steam** (vapor) or a mixture of both. At points below the VLE curve, water is **superheated steam**.

Table B.5 lists properties of saturated liquid water and saturated steam at temperatures from 0.01°C (the triple point temperature) to 102°C. The following properties can be determined for each tabulated temperature (and for intermediate temperatures by interpolation):

- **Column 2.** The pressure, P (bar), corresponding to the given temperature on the VLE curve—by definition, the vapor pressure of water at the given temperature. Instead of looking up a given temperature and finding the pressure, you could look up a given pressure in the second column and find the corresponding boiling point temperature in the first column.
- **Columns 3 and 4.** The specific volumes, \hat{V} (m^3/kg), of liquid water and saturated steam at the given temperature. The inverses of these quantities are the densities (kg/m^3) of liquid water and steam.
- **Columns 5 and 6.** The specific internal energies, \hat{U} (kJ/kg), of saturated liquid water and saturated steam at the given temperature *relative to a reference state of liquid water at the triple point*. (Remember, we can never know the absolute value of internal energy or enthalpy, but only how these quantities change when the substance goes from one state to another—in this case, from the reference state to the states listed in the table.)
- **Columns 7–9.** The specific enthalpies, \hat{H} (kJ/kg), of saturated liquid water (Column 7) and saturated steam (Column 9), and the difference between these quantities, known as the *heat of vaporization* (Column 8). The reference point for the tabulated values of \hat{H} is again liquid water at the triple point.

EXAMPLE 7.5-2

The Steam Tables

1. Determine the vapor pressure, specific internal energy, and specific enthalpy of saturated steam at 133.5°C.
2. Show that water at 400°C and 10 bar is superheated steam and determine its specific volume, specific internal energy, and specific enthalpy relative to liquid water at the triple point, and its dew point.
3. Show that \hat{U} and \hat{H} for superheated steam depend strongly on temperature and relatively slightly on pressure.

SOLUTION

Verify the results to be given.

1. Table B.5 does not go up to 133.5°C, so we turn to Table B.6. For saturated steam at the given temperature (Column 2),

$$p^* = 3.0 \text{ bar}, \hat{V} = 0.606 \text{ m}^3/\text{kg}, \hat{U} = 2543.0 \text{ kJ/kg}, \hat{H} = 2724.7 \text{ kJ/kg}$$

2. From Table B.7, $[T = 400^\circ\text{C}, P = 10 \text{ bar}]$ falls outside the closed region, showing that water is superheated steam at this temperature and pressure. The table also shows that at this condition,

$$\hat{H} = 3264 \text{ kJ/kg}, \hat{U} = 2958 \text{ kJ/kg}, \hat{V} = 0.307 \text{ m}^3/\text{kg}, T_{dp} = 179.9^\circ\text{C}$$

3. Look at the properties of water at 400°C and 450°C, both at a pressure of 10 bar. You will see that both \hat{U} and \hat{H} change by about 3% when water goes from the first temperature to the second one (3264 kJ/kg \rightarrow 3371 kJ/kg for \hat{H} , 2958 kJ/kg \rightarrow 3041 kJ/kg for \hat{U}).

Now consider the properties at 10 bar and 20 bar, both at a temperature of 400°C. Even though the pressure has doubled, the values of \hat{U} and \hat{H} change by much less than 1%. Similar results would be obtained for liquid water. The conclusion is that when you need a value of \hat{U} or \hat{H} for water (or for any other species) at a given T and P , you must look it up at the correct temperature—interpolating if necessary—but you don't have to find it at the exact pressure.

EXAMPLE 7.5-3

Energy Balance on a Steam Turbine

Steam at 10 bar absolute with 190°C of superheat is fed to a turbine at a rate $\dot{m} = 2000$ kg/h. The turbine operation is adiabatic, and the effluent is saturated steam at 1 bar. Calculate the work output of the turbine in kilowatts, neglecting kinetic and potential energy changes.

The energy balance for this steady-state open system is

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

(Why was the heat term dropped?)

Inlet Steam

Table B.7 indicates that steam at 10 bar is saturated at 180°C (*verify*), so that the inlet steam temperature is 180°C + 190°C = 370°C. Interpolating in the same table,

$$\hat{H}_{\text{in}}(10 \text{ bar}, 370^\circ\text{C}) = 3201 \text{ kJ/kg}$$

Outlet Steam

From either Table B.6 or B.7, you can find that the enthalpy of saturated steam at 1 bar is

$$\hat{H}_{\text{out}}(1 \text{ bar, saturated}) = 2675 \text{ kJ/kg}$$

Energy Balance

$$\begin{aligned}\dot{W}_s &= -\Delta\dot{H} = -\frac{2000 \text{ kg}}{\text{h}} \left| \frac{(2675 - 3201) \text{ kJ}}{\text{kg}} \right| \frac{1 \text{ h}}{3600 \text{ s}} \\ &= 292 \text{ kJ/s} = \boxed{292 \text{ kW}}\end{aligned}$$

The turbine thus delivers 292 kW of work to its surroundings.

Table B.5 Properties of Saturated Steam: Temperature Table^a

T(°C)	P(bar)	\hat{V} (m ³ /kg)		\hat{U} (kJ/kg)		\hat{H} (kJ/kg)		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
0.01	0.00611	0.001000	206.2	zero	2375.6	+0.0	2501.6	2501.6
2	0.00705	0.001000	179.9	8.4	2378.3	8.4	2496.8	2505.2
4	0.00813	0.001000	157.3	16.8	2381.1	16.8	2492.1	2508.9
6	0.00935	0.001000	137.8	25.2	2383.8	25.2	2487.4	2512.6
8	0.01072	0.001000	121.0	33.6	2386.6	33.6	2482.6	2516.2
10	0.01227	0.001000	106.4	42.0	2389.3	42.0	2477.9	2519.9
12	0.01401	0.001000	93.8	50.4	2392.1	50.4	2473.2	2523.6
14	0.01597	0.001001	82.9	58.8	2394.8	58.8	2468.5	2527.2
16	0.01817	0.001001	73.4	67.1	2397.6	67.1	2463.8	2530.9
18	0.02062	0.001001	65.1	75.5	2400.3	75.5	2459.0	2534.5
20	0.0234	0.001002	57.8	83.9	2403.0	83.9	2454.3	2538.2
22	0.0264	0.001002	51.5	92.2	2405.8	92.2	2449.6	2541.8
24	0.0298	0.001003	45.9	100.6	2408.5	100.6	2444.9	2545.5
25	0.0317	0.001003	43.4	104.8	2409.9	104.8	2442.5	2547.3
26	0.0336	0.001003	41.0	108.9	2411.2	108.9	2440.2	2549.1
28	0.0378	0.001004	36.7	117.3	2414.0	117.3	2435.4	2552.7
30	0.0424	0.001004	32.9	125.7	2416.7	125.7	2430.7	2556.4
32	0.0475	0.001005	29.6	134.0	2419.4	134.0	2425.9	2560.0
34	0.0532	0.001006	26.6	142.4	2422.1	142.4	2421.2	2563.6
36	0.0594	0.001006	24.0	150.7	2424.8	150.7	2416.4	2567.2
38	0.0662	0.001007	21.6	159.1	2427.5	159.1	2411.7	2570.8
40	0.0738	0.001008	19.55	167.4	2430.2	167.5	2406.9	2574.4
42	0.0820	0.001009	17.69	175.8	2432.9	175.8	2402.1	2577.9
44	0.0910	0.001009	16.04	184.2	2435.6	184.2	2397.3	2581.5
46	0.1009	0.001010	14.56	192.5	2438.3	192.5	2392.5	2585.1
48	0.1116	0.001011	13.23	200.9	2440.9	200.9	2387.7	2588.6
50	0.1234	0.001012	12.05	209.2	2443.6	209.3	2382.9	2592.2
52	0.1361	0.001013	10.98	217.7	2446	217.7	2377	2595
54	0.1500	0.001014	10.02	226.0	2449	226.0	2373	2599
56	0.1651	0.001015	9.158	234.4	2451	234.4	2368	2602
58	0.1815	0.001016	8.380	242.8	2454	242.8	2363	2606
60	0.1992	0.001017	7.678	251.1	2456	251.1	2358	2609
62	0.2184	0.001018	7.043	259.5	2459	259.5	2353	2613
64	0.2391	0.001019	6.468	267.9	2461	267.9	2348	2616
66	0.2615	0.001020	5.947	276.2	2464	276.2	2343	2619
68	0.2856	0.001022	5.475	284.6	2467	284.6	2338	2623

Table B.5 (Continued)

T(°C)	P(bar)	\hat{V} (m ³ /kg)		\hat{U} (kJ/kg)		\hat{H} (kJ/kg)		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
70	0.3117	0.001023	5.045	293.0	2469	293.0	2333	2626
72	0.3396	0.001024	4.655	301.4	2472	301.4	2329	2630
74	0.3696	0.001025	4.299	309.8	2474	309.8	2323	2633
76	0.4019	0.001026	3.975	318.2	2476	318.2	2318	2636
78	0.4365	0.001028	3.679	326.4	2479	326.4	2313	2639
80	0.4736	0.001029	3.408	334.8	2482	334.9	2308	2643
82	0.5133	0.001030	3.161	343.2	2484	343.3	2303	2646
84	0.5558	0.001032	2.934	351.6	2487	351.7	2298	2650
86	0.6011	0.001033	2.727	360.0	2489	360.1	2293	2653
88	0.6495	0.001034	2.536	368.4	2491	368.5	2288	2656
90	0.7011	0.001036	2.361	376.9	2493	377.0	2282	2659
92	0.7560	0.001037	2.200	385.3	2496	385.4	2277	2662
94	0.8145	0.001039	2.052	393.7	2499	393.8	2272	2666
96	0.8767	0.001040	1.915	402.1	2501	402.2	2267	2669
98	0.9429	0.001042	1.789	410.6	2504	410.7	2262	2673
100	1.0131	0.001044	1.673	419.0	2507	419.1	2257	2676
102	1.0876	0.001045	1.566	427.1	2509	427.5	2251	2679

Table B.6 Properties of Saturated Steam: Pressure Table^a

P (bar)	T (°C)	\hat{V} (m ³ /kg)		\hat{U} (kJ/kg)		\hat{H} (kJ/kg)		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
0.00611	0.01	0.001000	206.2	zero	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	2660.1
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
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 atm)

Table B.6 (Continued)

P (bar)	T (°C)	\hat{V} (m ³ /kg)		\hat{U} (kJ/kg)		\hat{H} (kJ/kg)		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
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
10.0	179.9	0.001127	0.1943	761.5	2581.9	762.6	2013.6	2776.2
10.5	182.0	0.001130	0.1855	770.8	2583.3	772.0	2005.9	2778.0
11.0	184.1	0.001133	0.1774	779.9	2584.5	781.1	1998.5	2779.7
11.5	186.0	0.001136	0.1700	788.6	2585.8	789.9	1991.3	2781.3
12.0	188.0	0.001139	0.1632	797.1	2586.9	798.4	1984.3	2782.7
12.5	189.8	0.001141	0.1569	805.3	2588.0	806.7	1977.4	2784.1
13.0	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
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

Table B.6 (Continued)

P(bar)	T(°C)	$\hat{V}(\text{m}^3/\text{kg})$		$\hat{U}(\text{kJ/kg})$		$\hat{H}(\text{kJ/kg})$		
		Water	Steam	Water	Steam	Water	Evaporation	Steam
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
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 B.7 Properties of Superheated Steam^a

$P(\text{bar})$ ($T_{\text{sat.}} (\text{°C})$)	Sat'd Water	Sat'd Steam	Temperature (°C) →							
			50	75	100	150	200	250	300	350
0.0	\hat{H}	—	2595	2642	2689	2784	2880	2978	3077	3177
(—)	\hat{U}	—	2446	2481	2517	2589	2662	2736	2812	2890
	\hat{V}	—	—	—	—	—	—	—	—	—
0.1	\hat{H}	191.8	2584.8	2593	2640	2688	2783	2880	2977	3077
(45.8)	\hat{U}	191.8	2438.0	2444	2480	2516	2588	2661	2736	2812
	\hat{V}	0.00101	14.7	14.8	16.0	17.2	19.5	21.8	24.2	26.5
0.5	\hat{H}	340.6	2646.0	209.3	313.9	2683	2780	2878	2979	3076
(81.3)	\hat{U}	340.6	2484.0	209.2	313.9	2512	2586	2660	2735	2811
	\hat{V}	0.00103	3.24	0.00101	0.00103	3.41	3.89	4.35	4.83	5.29
1.0	\hat{H}	417.5	2675.4	209.3	314.0	2676	2776	2875	2975	3074
(99.6)	\hat{U}	417.5	2506.1	209.2	313.9	2507	2583	2658	2734	2811
	\hat{V}	0.00104	1.69	0.00101	0.00103	1.69	1.94	2.17	2.40	2.64
5.0	\hat{H}	640.1	2747.5	209.7	314.3	419.4	632.2	2855	2961	3065
(151.8)	\hat{U}	639.6	2560.2	209.2	313.8	418.8	631.6	2643	2724	2803
	\hat{V}	0.00109	0.375	0.00101	0.00103	0.00104	0.00109	0.425	0.474	0.522
10	\hat{H}	762.6	2776.2	210.1	314.7	419.7	632.5	2827	2943	3052
(179.9)	\hat{U}	761.5	2582	209.1	313.7	418.7	631.4	2621	2710	2794
	\hat{V}	0.00113	0.194	0.00101	0.00103	0.00104	0.00109	0.206	0.233	0.258
20	\hat{H}	908.6	2797.2	211.0	315.5	420.5	633.1	852.6	2902	3025
(212.4)	\hat{U}	906.2	2598.2	209.0	313.5	418.4	603.9	850.2	2679	2774
	\hat{V}	0.00118	0.09950	0.00101	0.00102	0.00104	0.00109	0.00116	0.111	0.125
40	\hat{H}	1087.4	2800.3	212.7	317.1	422.0	634.3	853.4	1085.8	2962
(250.3)	\hat{U}	1082.4	2601.3	208.6	313.0	417.8	630.0	848.8	1080.8	2727
	\hat{V}	0.00125	0.04975	0.00101	0.00102	0.00104	0.00109	0.00115	0.00125	0.0588
60	\hat{H}	1213.7	2785.0	214.4	318.7	423.5	635.6	854.2	1085.8	2885
(275.6)	\hat{U}	1205.8	2590.4	208.3	312.6	417.3	629.1	847.3	1078.3	2668
	\hat{V}	0.00132	0.0325	0.00101	0.00103	0.00104	0.00109	0.00115	0.00125	0.0361

80 (295.0)	\hat{H}	1317.1	2759.9	216.1	320.3	425.0	636.8	855.1	1085.8	2787	2990
	\hat{U}	1306.0	2571.7	208.1	312.3	416.7	628.2	845.9	1075.8	2593	2750
	\hat{V}	0.00139	0.0235	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.0243	0.0299
100 (311.0)	\hat{H}	1408.0	2727.7	217.8	322.9	426.5	638.1	855.9	1085.8	1343.4	2926
	\hat{U}	1393.5	2547.3	207.8	311.7	416.1	627.3	844.4	1073.4	1329.4	2702
	\hat{V}	0.00145	0.0181	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.00140	0.0224
150 (342.1)	\hat{H}	1611.0	2615.0	222.1	326.0	430.3	641.3	858.1	1086.2	1338.2	2695
	\hat{U}	1586.1	2459.9	207.0	310.7	414.7	625.0	841.0	1067.7	1317.6	2523
	\hat{V}	0.00166	0.0103	0.00101	0.00102	0.00104	0.00108	0.00114	0.00123	0.00138	0.0115
200 (365.7)	\hat{H}	1826.5	2418.4	226.4	330.0	434.0	644.5	860.4	1086.7	1334.3	1647.1
	\hat{U}	1785.7	2300.8	206.3	309.7	413.2	622.9	837.7	1062.2	1307.1	1613.7
	\hat{V}	0.00204	0.005875	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00136	0.00167
221.2(P_c) (374.15)(T_c)	\hat{H}	2108	2108	228.2	331.7	435.7	645.8	861.4	1087.0	1332.8	1635.5
	\hat{U}	2037.8	2037.8	206.0	309.2	412.8	622.0	836.3	1060.0	1302.9	1600.3
	\hat{V}	0.00317	0.00317	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00135	0.00163
250 (—)	\hat{H}	—	—	230.7	334.0	437.8	647.7	862.8	1087.5	1331.1	1625.0
	\hat{U}	—	—	205.7	308.7	412.1	620.8	834.4	1057.0	1297.5	1585.0
	\hat{V}	—	—	0.00100	0.00101	0.00103	0.00108	0.00113	0.00122	0.00135	0.00160
300 (—)	\hat{H}	—	—	235.0	338.1	441.6	650.9	865.2	1088.4	1328.7	1609.9
	\hat{U}	—	—	205.0	307.7	410.8	618.7	831.3	1052.1	1288.7	1563.3
	\hat{V}	—	—	0.0009990	0.00101	0.00103	0.00107	0.00113	0.00121	0.00133	0.00155
500 (—)	\hat{H}	—	—	251.9	354.2	456.8	664.1	875.4	1093.6	1323.7	1576.3
	\hat{U}	—	—	202.4	304.0	405.8	611.0	819.7	1034.3	1259.3	1504.1
	\hat{V}	—	—	0.0009911	0.00100	0.00102	0.00106	0.00111	0.00119	0.00129	0.00144
1000 (—)	\hat{H}	—	—	293.9	394.3	495.1	698.0	903.5	1113.0	1328.7	1550.5
	\hat{U}	—	—	196.5	295.7	395.1	594.4	795.3	999.0	1207.1	1419.0
	\hat{V}	—	—	0.0009737	0.0009852	0.001000	0.00104	0.00108	0.00114	0.00122	0.00131

Table B.7 (Continued)

P (bar) (T_{sat} , °C)	Temperature (°C) →								
	400	450	500	550	600	650	700	750	
0.0 (—)	\hat{H}	3280	3384	3497	3597	3706	3816	3929	4043
	\hat{U}	2969	3050	3132	3217	3303	3390	3480	3591
	\hat{V}	—	—	—	—	—	—	—	—
0.1 (45.8)	\hat{H}	3280	3384	3489	3596	3706	3816	3929	4043
	\hat{U}	2969	3050	3132	3217	3303	3390	3480	3571
	\hat{V}	21.1	33.3	35.7	38.0	40.3	42.6	44.8	47.2
0.5 (81.3)	\hat{H}	3279	3383	3489	3596	3705	3816	3929	4043
	\hat{U}	2969	3049	3132	3216	3302	3390	3480	3571
	\hat{V}	6.21	6.67	7.14	7.58	8.06	8.55	9.01	9.43
1.0 (99.6)	\hat{H}	3278	3382	3488	3596	3705	3816	3928	4042
	\hat{U}	2968	3049	3132	3216	3302	3390	3479	3570
	\hat{V}	3.11	3.33	3.57	3.80	4.03	4.26	4.48	4.72
5.0 (151.8)	\hat{H}	3272	3379	3484	3592	3702	3813	3926	4040
	\hat{U}	2964	3045	3128	3213	3300	3388	3477	3569
	\hat{V}	0.617	0.664	0.711	0.758	0.804	0.850	0.897	0.943
10 (179.9)	\hat{H}	3264	3371	3478	3587	3697	3809	3923	4038
	\hat{U}	2958	3041	3124	3210	3296	3385	3475	3567
	\hat{V}	0.307	0.330	0.353	0.377	0.402	0.424	0.448	0.472
20 (212.4)	\hat{H}	3249	3358	3467	3578	3689	3802	3916	4032
	\hat{U}	2946	3031	3115	3202	3290	3379	3470	3562
	\hat{V}	0.151	0.163	0.175	0.188	0.200	0.211	0.223	0.235
40 (250.3)	\hat{H}	3216	3331	3445	3559	3673	3788	3904	4021
	\hat{U}	2922	3011	3100	3188	3278	3368	3460	3554
	\hat{V}	0.0734	0.0799	0.0864	0.0926	0.0987	0.105	0.111	0.117
60 (275.6)	\hat{H}	3180	3303	3422	3539	3657	3774	3892	4011
	\hat{U}	2896	2991	3083	3174	3265	3357	3451	3545
	\hat{V}	0.0474	0.0521	0.0566	0.0609	0.0652	0.0693	0.0735	0.0776

80	\hat{H}	3142	3274	3399	3520	3640	3759	3879	4000
(295.0)	\hat{U}	2867	2969	3065	3159	3252	3346	3441	3537
	\hat{V}	0.0344	0.0382	0.0417	0.0450	0.0483	0.0515	0.0547	0.0578
100	\hat{H}	3100	3244	3375	3500	3623	3745	3867	3989
(311.0)	\hat{U}	2836	2946	3047	3144	3240	3335	3431	3528
	\hat{V}	0.0264	0.0298	0.0328	0.0356	0.0383	0.0410	0.0435	0.0461
150	\hat{H}	2975	3160	3311	3448	3580	3708	3835	3962
(342.1)	\hat{U}	2744	2883	2999	3105	3207	3307	3407	3507
	\hat{V}	0.0157	0.0185	0.0208	0.0229	0.0249	0.0267	0.0286	0.0304
200	\hat{H}	2820	3064	3241	3394	3536	3671	3804	3935
(365.7)	\hat{U}	2622	2810	2946	3063	3172	3278	3382	3485
	\hat{V}	0.009950	0.0127	0.0148	0.0166	0.0182	0.197	0.211	0.0225
221.2(P_c)	\hat{H}	2733	3020	3210	3370	3516	3655	3790	3923
(374.15)(T_c)	\hat{U}	2553	2776	2922	3045	3157	3265	3371	3476
	\hat{V}	0.008157	0.0110	0.0130	0.0147	0.0162	0.0176	0.0190	0.0202
250	\hat{H}	2582	2954	3166	3337	3490	3633	3772	3908
(—)	\hat{U}	2432	2725	2888	3019	3137	3248	3356	3463
	\hat{V}	0.006013	0.009174	0.0111	0.0127	0.0141	0.0143	0.0166	0.0178
300	\hat{H}	2162	2826	3085	3277	3443	3595	3740	3880
(—)	\hat{U}	2077	2623	2825	2972	3100	3218	3330	3441
	\hat{V}	0.002830	0.006734	0.008680	0.0102	0.0114	0.0126	0.0136	0.0147
500	\hat{H}	1878	2293	2723	3021	3248	3439	3610	3771
(—)	\hat{U}	1791	2169	2529	2765	2946	3091	3224	3350
	\hat{V}	0.001726	0.002491	0.003882	0.005112	0.006112	0.007000	0.007722	0.008418
1000	\hat{H}	1798	2051	2316	2594	2857	3105	3324	3526
(—)	\hat{U}	1653	1888	2127	2369	2591	2795	2971	3131
	\hat{V}	0.001446	0.001628	0.001893	0.002246	0.002668	0.003106	0.003536	0.003953

Lecture 23

7.6 Energy Balance Procedures

EXAMPLE 7.6-1

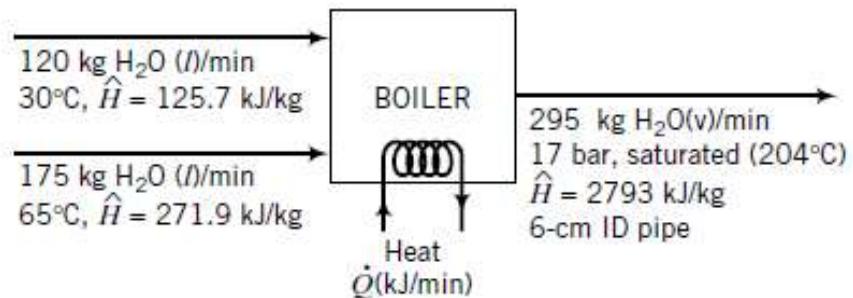
Energy Balance on a One-Component Process

Two streams of water are mixed to form the feed to a boiler. Process data are as follows:

Feed stream 1	120 kg/min @ 30°C
Feed stream 2	175 kg/min @ 65°C
Boiler pressure	17 bar (absolute)

The exiting steam emerges from the boiler through a 6-cm ID pipe. Calculate the required heat input to the boiler in kilojoules per minute if the emerging steam is saturated at the boiler pressure. Neglect the kinetic energies of the liquid inlet streams.

SOLUTION



- A first step in solving problems of this sort is to determine (if possible) the flow rates of all stream components using material balances.* In this case, it is a trivial matter to write and solve a mass balance on water to determine that the flow rate of the emerging steam is 295 kg/min.
- Next, determine the specific enthalpies of each stream component.* Tables B.5 and B.6 were used to determine \hat{H} for liquid water at 30°C and 65°C and for saturated steam at 17 bar. The latter entry in the table also furnished the temperature of the saturated steam corresponding to this pressure (204°C). Note that the entries for liquid water correspond to pressures that may or may not equal the actual pressures of the inlet streams (which we do not know); we assume, however, that the enthalpy of liquid water is approximately independent of pressure and use the tabulated values.
- The final step is to write the appropriate form of the energy balance and solve it for the desired quantity.* For this open process system,

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

↓ $\dot{W}_s = 0$ (no moving parts)
 ↓ $\Delta\dot{E}_p = 0$ (generally assumed unless displacements through
large heights are involved)

$$\dot{Q} = \Delta\dot{H} + \Delta\dot{E}_k$$

Evaluate $\Delta\dot{H}$

From Equation 7.4-14a,

$$\begin{aligned}\Delta\dot{H} &= \sum_{\text{outlet}} \dot{m}_i \hat{H}_f - \sum_{\text{inlet}} \dot{m}_i \hat{H}_i \\ &= \frac{295 \text{ kg}}{\text{min}} \left| \frac{2793 \text{ kJ}}{\text{kg}} \right. - \frac{120 \text{ kg}}{\text{min}} \left| \frac{125.7 \text{ kJ}}{\text{kg}} \right. - \frac{175 \text{ kg}}{\text{min}} \left| \frac{271.9 \text{ kJ}}{\text{kg}} \right. \\ &= 7.61 \times 10^5 \text{ kJ/min}\end{aligned}$$

Evaluate \dot{E}_k

From Table B.6, the specific volume of saturated steam at 17 bar is $0.1166 \text{ m}^3/\text{kg}$, and the cross-sectional area of the 6-cm ID pipe is

$$A = \pi R^2 = \frac{3.1416}{\left| \begin{array}{c} (3.00)^2 \text{ cm}^2 \\ 10^4 \text{ cm}^2 \end{array} \right|} \left| \begin{array}{c} 1 \text{ m}^2 \\ \end{array} \right| = 2.83 \times 10^{-3} \text{ m}^2$$

The steam velocity is

$$\begin{aligned} u(\text{m/s}) &= \dot{V}(\text{m}^3/\text{s}) / A(\text{m}^2) \\ &= \frac{295 \text{ kg}}{\text{min}} \left| \begin{array}{c} 1 \text{ min} \\ 60 \text{ s} \end{array} \right| \frac{0.1166 \text{ m}^3}{\text{kg}} \left| \begin{array}{c} \\ 2.83 \times 10^{-3} \text{ m}^2 \end{array} \right| \\ &= 202 \text{ m/s} \end{aligned}$$

Then, since the kinetic energies of the inlet streams are assumed negligible,

$$\begin{aligned} \Delta \dot{E}_k &\approx (\dot{E}_k)_{\text{outlet stream}} = \dot{m} u^2 / 2 \\ &= \frac{295 \text{ kg/min}}{2} \left| \begin{array}{c} (202)^2 \text{ m}^2 \\ \text{s}^2 \end{array} \right| \frac{1 \text{ N}}{1 \text{ kg} \cdot \text{m/s}^2} \left| \begin{array}{c} 1 \text{ kJ} \\ 10^3 \text{ N} \cdot \text{m} \end{array} \right| = 6.02 \times 10^3 \text{ kJ/min} \end{aligned}$$

Finally,

$$\begin{aligned} \dot{Q} &= \Delta \dot{H} + \Delta \dot{E}_k \\ &= [7.61 \times 10^5 + 6.02 \times 10^3] \text{ kJ/min} \\ &= \boxed{7.67 \times 10^5 \text{ kJ/min}} \end{aligned}$$

EXAMPLE 7.6-2

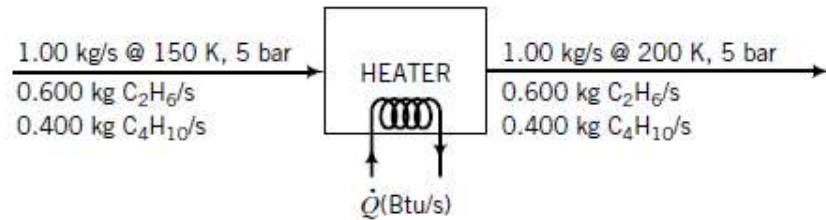
Energy Balance on a Two-Component Process

A liquid stream containing 60.0 wt% ethane and 40.0% *n*-butane is to be heated from 150 K to 200 K at a pressure of 5 bar. Calculate the required heat input per kilogram of the mixture, neglecting potential and kinetic energy changes, using tabulated enthalpy data for C₂H₆ and C₄H₁₀ and assuming that mixture component enthalpies are those of the pure species at the same temperature.

SOLUTION

Basis: 1 kg/s Mixture

The enthalpies of *n*-butane at 150 K and 5 bar and at 200 K and 5 bar are given on p. 2-223 of *Perry's Chemical Engineers' Handbook* (see footnote 2), and those of ethane at the same conditions are given on p. 2-234 of the *Handbook*. The tabulated enthalpy values are shown in the energy balance.



No material balances are necessary since there is only one input stream and one output stream and no chemical reactions, so we may proceed directly to the energy balance:

$$\begin{aligned}\dot{Q} - \dot{W}_s &= \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p \\ \downarrow \dot{W}_s = 0 \text{ (no moving parts)} \\ \downarrow \Delta\dot{E}_k = 0, \Delta\dot{E}_p = 0 \text{ (by hypothesis)} \\ \dot{Q} &= \Delta\dot{H}\end{aligned}$$

Since the process materials are all gases and we are assuming ideal gas behavior, we may set the enthalpies of each stream equal to the sums of the individual component enthalpies and write

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} = \sum_{\text{outlet components}} \dot{m}_i \hat{H}_i - \sum_{\text{inlet components}} \dot{m}_i \hat{H}_i \\ &= \frac{0.600 \text{ kg C}_2\text{H}_6}{\text{s}} \left| \frac{434.5 \text{ kJ}}{\text{kg}} \right. + \frac{0.400 \text{ kg C}_4\text{H}_{10}}{\text{s}} \left| \frac{130.2 \text{ kJ}}{\text{kg}} \right. \\ &\quad - [(0.600)(314.3) + (0.400)(30.0)] \text{ kJ/s} = 112 \text{ kJ/s} \implies \boxed{\frac{112 \text{ kJ}}{1.00 \text{ kg/s}}} = \boxed{\frac{112 \text{ kJ}}{\text{kg}}}\end{aligned}$$

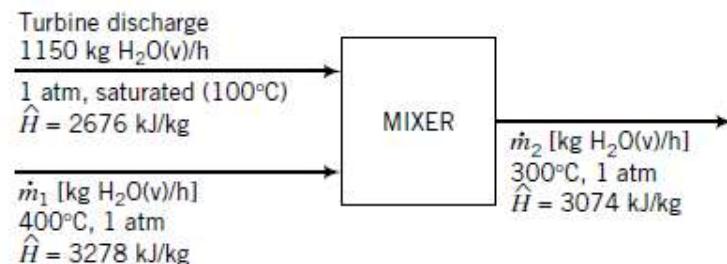
EXAMPLE 7.6-3

Simultaneous Material and Energy Balances

Saturated steam at 1 atm is discharged from a turbine at a rate of 1150 kg/h. Superheated steam at 300°C and 1 atm is needed as a feed to a heat exchanger; to produce it, the turbine discharge stream is mixed with superheated steam available from a second source at 400°C and 1 atm. The mixing unit operates adiabatically. Calculate the amount of superheated steam at 300°C produced and the required volumetric flow rate of the 400°C steam.

SOLUTION

Specific enthalpies of the two feed streams and the product stream are obtained from the steam tables and are shown below on the flowchart.



There are two unknown quantities in this process— \dot{m}_1 and \dot{m}_2 —and only one permissible material balance. (Why?) The material and energy balances must therefore be solved simultaneously to determine the two flow rates.

Mass Balance on Water $1150 \text{ kg/h} + \dot{m}_1 = \dot{m}_2$ (1)

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

$\left| \begin{array}{l} \dot{Q} = 0 \quad (\text{process is adiabatic}) \\ \dot{W}_s = 0 \quad (\text{no moving parts}) \\ \downarrow \Delta\dot{E}_k \approx 0, \Delta\dot{E}_p \approx 0 \quad (\text{assumption}) \end{array} \right.$

$$\Delta\dot{H} = \sum_{\text{outlet}} \dot{m}_i \hat{H}_i - \sum_{\text{inlet}} \dot{m}_i \hat{H}_i = 0$$

$$\frac{1150 \text{ kg}}{\text{h}} \left| \begin{array}{c} 2676 \text{ kJ} \\ \text{kg} \end{array} \right. + \dot{m}_1 (3278 \text{ kJ/kg}) = \dot{m}_2 (3074 \text{ kJ/kg}) \quad (2)$$

Solving Equations 1 and 2 simultaneously yields

$$\dot{m}_1 = 2240 \text{ kg/h}$$

$$\boxed{\dot{m}_2 = 3390 \text{ kg/h}} \quad (\text{product flow rate})$$

From Table B.7, the specific volume of steam at 400°C and 1 atm (≈ 1 bar) is $3.11 \text{ m}^3/\text{kg}$. The volumetric flow rate of this stream is therefore

$$\frac{2240 \text{ kg}}{\text{h}} \left| \begin{array}{c} 3.11 \text{ m}^3 \\ \text{kg} \end{array} \right. = \boxed{6980 \text{ m}^3/\text{h}}$$

If specific-volume data were not available, the ideal gas equation of state could be used as an approximation for the last calculation.

7.7 Mechanical Energy Balances

Another important class of operations is one for which the opposite is true—heat flows and internal energy changes are secondary in importance to kinetic and potential energy changes and shaft work. Most of these operations involve the flow of fluids to, from, and between tanks, reservoirs, wells, and process units. Accounting for energy flows in such processes is most conveniently done with **mechanical energy balances**.

Consider such a system, letting \dot{m} be the mass flow rate and \hat{V} the specific volume of the liquid. If \hat{V} is replaced by $1/\rho$, where ρ is the liquid density, then the open-system energy balance (Equation 7.4-12) may be written

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z + \left(\Delta \hat{U} - \frac{\dot{Q}}{\dot{m}} \right) = -\frac{\dot{W}_s}{\dot{m}} \quad (7.7-1)$$

In many cases only slight amounts of heat are transferred to or from the surroundings, there is little change in temperature from inlet to outlet, and no phase changes or reactions occur. Even under these circumstances, some kinetic or potential energy is always converted to thermal energy as a result of friction due to the movement of the fluid through the system. In consequence, the quantity $(\Delta \hat{U} - \dot{Q}/\dot{m})$ always has a positive component, termed the **friction loss** and is given the symbol \hat{F} . Equation 7.7-1 may therefore be written

$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z + \hat{F} = -\frac{\dot{W}_s}{\dot{m}}} \quad (7.7-2)$$

Equation 7.7-2 is referred to as the **mechanical energy balance**. Once again, it is valid for steady-state flow of an incompressible fluid.

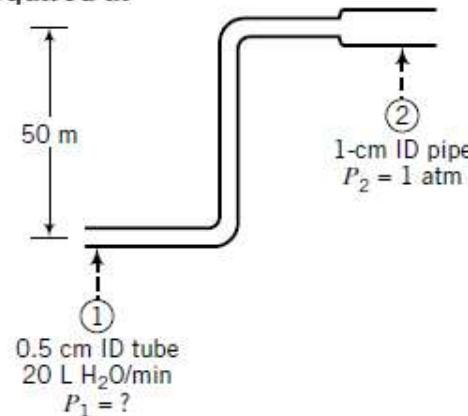
A simplified form of the mechanical energy balance is obtained for frictionless processes ($\hat{F} \approx 0$) in which no shaft work is performed ($\dot{W}_s = 0$):

$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z = 0} \quad (7.7-3)$$

Equation 7.7-3 is called the **Bernoulli equation**.

EXAMPLE 7.7-1**The Bernoulli Equation**

Water flows through the system shown here at a rate of 20 L/min. Estimate the pressure required at point ① if friction losses are negligible.

SOLUTION

All of the terms of the Bernoulli equation, Equation 7.7-3, are known except ΔP , the variable to be determined, and Δu^2 , which must be calculated from the known liquid flow rate and the diameters of the inlet and outlet pipes.

Velocities

$$\dot{u}(\text{m/s}) = \dot{V}(\text{m}^3/\text{s}) / A(\text{m}^2)$$

The volumetric flow rate must be the same at points ① and ②. (Why?)

$$u_1 = \frac{20 \text{ L}}{\text{min}} \left| \begin{array}{c} 1 \text{ m}^3 \\ 10^3 \text{ L} \end{array} \right| \frac{\pi(0.25)^2 \text{ cm}^2}{\text{m}^2} \left| \begin{array}{c} 10^4 \text{ cm}^2 \\ \text{m}^2 \end{array} \right| \frac{1 \text{ min}}{60 \text{ s}} = 17.0 \text{ m/s}$$

$$u_2 = \frac{20 \text{ L}}{\text{min}} \left| \begin{array}{c} 1 \text{ m}^3 \\ 10^3 \text{ L} \end{array} \right| \frac{\pi(0.5)^2 \text{ cm}^2}{\text{m}^2} \left| \begin{array}{c} 10^4 \text{ cm}^2 \\ 1 \text{ m}^2 \end{array} \right| \frac{1 \text{ min}}{60 \text{ s}} = 4.24 \text{ m/s}$$



$$\begin{aligned}\Delta u^2 &= (u_2^2 - u_1^2) = (4.24^2 - 17.0^2) \text{ m}^2/\text{s}^2 \\ &= -271.0 \text{ m}^2/\text{s}^2\end{aligned}$$

Bernoulli Equation (Equation 7.7-3)

$$\frac{\Delta P(\text{N/m}^2)}{\rho(\text{kg/m}^3)} + \frac{\Delta u^2(\text{m}^2/\text{s}^2)}{2 \cdot 1[(\text{kg} \cdot \text{m/s}^2)/\text{N}]} + \frac{g(\text{m/s}^2)\Delta z(\text{m})}{1[(\text{kg} \cdot \text{m/s}^2)/\text{N}]}$$

$$\begin{array}{l} \Delta P = P_2 - P_1 \\ \rho = 1000 \text{ kg/m}^3 \\ \Delta u^2 = -271.0 \text{ m}^2/\text{s}^2 \\ g = 9.81 \text{ m/s}^2 \\ \Delta z = z_2 - z_1 \\ \quad = 50 \text{ m} \end{array}$$

$$\frac{P_2 - P_1}{1000 \text{ kg/m}^3} - 135.5 \text{ N} \cdot \text{m/kg} + 490 \text{ N} \cdot \text{m/kg} = 0$$

$$\begin{array}{l} P_2 = 1 \text{ atm} \\ \quad = 1.01325 \times 10^5 \text{ N/m}^2 \end{array}$$

$$P_1 = 4.56 \times 10^5 \text{ N/m}^2$$

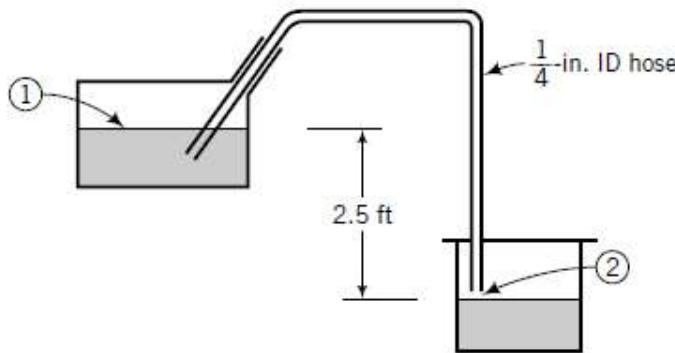
$$= 4.56 \times 10^5 \text{ Pa}$$

$$= \boxed{4.56 \text{ bar}}$$

EXAMPLE 7.7-2

Siphoning

Gasoline ($\rho = 50.0 \text{ lb}_m/\text{ft}^3$) is to be siphoned from a tank. The friction loss in the line is $F = 0.80 \text{ ft}\cdot\text{lb}_f/\text{lb}_m$. Estimate how long it will take to siphon 5.00 gal, neglecting the change in liquid level in the gasoline tank during this process and assuming that both point ① (at the liquid surface in the gas tank) and point ② (in the tube just prior to the exit) are at 1 atm.



SOLUTION

Point ①: $P_1 = 1 \text{ atm}$, $u_1 \approx 0 \text{ ft/s}$, $z_1 = 2.5 \text{ ft}$

Point ②: $P_2 = 1 \text{ atm}$, $u_2 = ?$, $z_2 = 0 \text{ ft}$

Mechanical Energy Balance (Equation 7.7-2)

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

$$\left| \begin{array}{l} \Delta P = 0 \\ \Delta u^2 \approx u_2^2 \\ g = 32.174 \text{ ft/s}^2 \\ \Delta z = -2.5 \text{ ft} \\ \hat{F} = 0.80 \text{ ft}\cdot\text{lb}_f/\text{lb}_m \\ \downarrow \dot{W}_s = 0 \end{array} \right.$$

$$\frac{u_2^2(\text{ft}^2/\text{s}^2)}{2} \left| \begin{array}{c} 1 \text{ lb}_f \\ 32.174 \text{ lb}_m \cdot \text{ft/s}^2 \end{array} \right| + \frac{32.174 \text{ ft/s}^2}{32.174 \text{ lb}_m \cdot \text{ft/s}^2} \left| \begin{array}{c} -2.5 \text{ ft} \\ 1 \text{ lb}_f \\ 32.174 \text{ lb}_m \cdot \text{ft/s}^2 \end{array} \right| + 0.80 \text{ ft}\cdot\text{lb}_f/\text{lb}_m$$

↓

$$u_2 = 10.5 \text{ ft/s}$$

(Verify that each additive term in the preceding equation has the units $\text{ft}\cdot\text{lb}_f/\text{lb}_m$.)

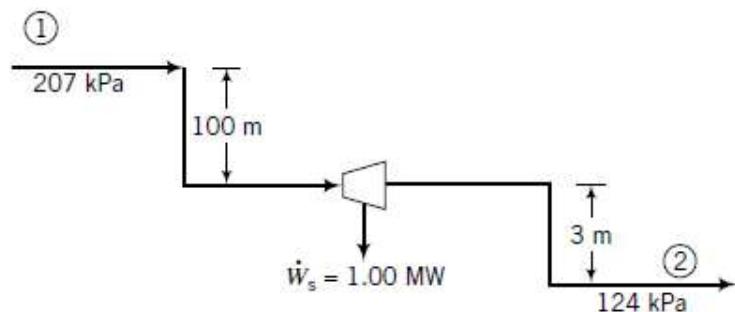
The volumetric flow rate of the fluid in the tube is

$$\begin{aligned} \dot{V}(\text{ft}^3/\text{s}) &= u_2(\text{ft/s}) \cdot A(\text{ft}^2) \\ &= \frac{10.5 \text{ ft}}{\text{s}} \left| \begin{array}{c} \pi(0.125)^2 \text{ in.}^2 \\ 144 \text{ in.}^2 \end{array} \right| = 3.58 \times 10^{-3} \text{ ft}^3/\text{s} \end{aligned}$$

$$\begin{aligned} t(\text{s}) &= \frac{\text{volume to be drained } (\text{ft}^3)}{\text{volumetric flow rate } (\text{ft}^3/\text{s})} \\ &= \frac{(5.00 \text{ gal})(0.1337 \text{ ft}^3/\text{gal})}{3.58 \times 10^{-3} \text{ ft}^3/\text{s}} = \frac{187 \text{ s}}{60 \text{ s/min}} = \boxed{3.1 \text{ min}} \end{aligned}$$

EXAMPLE 7.7-3**Hydraulic Power Generation**

Water flows from an elevated reservoir through a conduit to a turbine at a lower level and out of the turbine through a similar conduit. At a point 100 m above the turbine the pressure is 207 kPa, and at a point 3 m below the turbine the pressure is 124 kPa. What must the water flow rate be if the turbine output is 1.00 MW?

**SOLUTION**

No data are given for the friction loss so we will set $\hat{F} = 0$, recognizing that doing so introduces an error into the calculation. Since the diameters of the conduits at points ① and ② are the same and water may be considered incompressible, $\Delta u^2 = 0$. Equation 7.7-2 then becomes

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



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

$$\dot{W}_s = 1.00 \text{ MW} = 1.00 \times 10^6 \text{ N}\cdot\text{m/s} \quad (\text{convince yourself})$$

$$\Delta P = (124 - 207) \text{ kPa} = -83 \text{ kPa} = -83 \times 10^3 \text{ N/m}^2$$

$$\frac{\Delta P}{\rho} = \frac{-83 \times 10^3 \text{ N/m}^2}{1.00 \times 10^3 \text{ kg/m}^3} = -83 \text{ N}\cdot\text{m/kg}$$

$$g = 9.81 \text{ m/s}^2$$

$$\Delta z = -103 \text{ m}$$

$$g \Delta z = \frac{9.81 \text{ m}}{\text{s}^2} \left| \begin{array}{c|c|c} -103 \text{ m} & 1 \text{ N} \\ \hline & 1 \text{ kg}\cdot\text{m/s}^2 \end{array} \right| = -1010 \text{ N}\cdot\text{m/kg}$$

$$\dot{m} = \frac{-1.00 \times 10^6 \text{ N}\cdot\text{m/s}}{(-83 - 1010) \text{ N}\cdot\text{m/kg}} = \boxed{915 \text{ kg/s}}$$

Chapter 8 - Balances on Nonreactive Processes

Lecture 24

We have seen that for an open system in which shaft work and kinetic and potential energy changes can be neglected, the energy balance reduces to

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} \\ &= \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i\end{aligned}$$

where the \hat{H}_i 's are the specific enthalpies of the inlet and outlet stream components at their respective process conditions (temperatures, pressures, and states of aggregation) relative to those components at some reference conditions. For an integral balance on a closed constant-volume system ($W = 0$), n (amount) would replace \dot{n} (flow rate) in this equation, U (internal energy) would replace \dot{H} (rate of enthalpy transport) and \hat{U} (specific internal energy) would replace \hat{H} (specific enthalpy).

In Chapter 7, we dealt only with processes involving species for which specific enthalpies and internal energies at specified conditions could be found in tables. Unfortunately, you cannot count on finding such data for every species with which you work. This chapter presents procedures for evaluating $\Delta\dot{H}$ or ΔU when tables of \hat{H} and \hat{U} are not available for all process species. Once these calculations have been performed, the energy balance may be written and solved as before.

8.1 Elements of Energy Balance Calculations

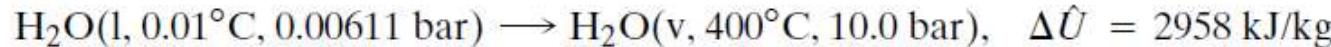
In this section, we outline a procedure for solving energy balance problems that will be applied to both nonreactive processes (this chapter) and reactive processes (Chapter 9). Section 8.1a reviews the concept of a *reference state* for specific internal energy and enthalpy calculations, and Section 8.1b reviews the fact that \hat{U} and \hat{H} are state properties, so that the values of ΔU or ΔH (closed system) and $\Delta \dot{H}$ (open system) calculated for a process are independent of the reference states chosen for calculations of \hat{U}_i and \hat{H}_i . Section 8.1c outlines a procedure for organizing energy balance calculations and presents an extended illustrative example. The remainder of the chapter presents formulas and methods for calculating ΔU , ΔH , and $\Delta \dot{H}$ for processes that involve heating and cooling, compression and decompression, phase changes, mixing of liquids, and dissolving of gases and solids in liquids.

8.1a Reference States – A Review

Recall that we can never know the absolute values of \hat{U} and \hat{H} for a species at a given state. \hat{U} (kJ/mol) is the sum of the energies of motion of all 6.02×10^{23} molecules in one gram-mole of the species plus the intramolecular kinetic and potential energies of all the atoms and subatomic particles, which are quantities we cannot determine. Since $\hat{H} = \hat{U} + P\hat{V}$ and we cannot know the value of \hat{U} , we also cannot know the value of \hat{H} at a specified state.

Fortunately, we never need to know the absolute values of \hat{U} or \hat{H} at specified states: we only need to know $\Delta\hat{U}$ and $\Delta\hat{H}$ for specified *changes* of state, and we can determine these quantities experimentally.¹ We may therefore arbitrarily choose a **reference state** for a species and determine $\Delta\hat{U} = \hat{U} - \hat{U}_{\text{ref}}$ for the transition from the reference state to a series of other states. If we set \hat{U}_{ref} equal to zero, then $\hat{U}(= \Delta\hat{U})$ for a specified state is the *specific internal energy at that state relative to the reference state*. The specific enthalpies at each state can then be calculated from the definition, $\hat{H} = \hat{U} + P\hat{V}$, provided that the specific volume (\hat{V}) of the species at the given temperature and pressure is known.

The values of \hat{U} and \hat{H} in the steam tables were generated using this procedure. The reference state was chosen to be liquid water at the triple point [$\text{H}_2\text{O(l, }0.01^\circ\text{C, 0.00611 bar)}$], at which point \hat{U} was defined to be zero. According to Table B.7, for water vapor at 400°C and 10.0 bar, $\hat{U} = 2958 \text{ kJ/kg}$. This does *not* mean that the absolute value of \hat{U} for water in the specified state is 2958 kJ/kg; remember, we cannot know the absolute value of \hat{U} . It means that \hat{U} of water vapor at 400°C and 10.0 bar is 2958 kJ/kg *relative to water at the reference state*, or



Relative to water at the same reference state, the specific enthalpy of water vapor at 400°C and 10.0 bar is

$$\begin{aligned}\hat{H} &= \hat{U} + P\hat{V} \\ &= 2958 \text{ kJ/kg} + \frac{10 \text{ bar}}{\text{kg}} \left| \begin{array}{c} 0.307 \text{ m}^3 \\ \text{kg} \end{array} \right| \left| \begin{array}{c} 10^3 \text{ L} \\ 1 \text{ m}^3 \end{array} \right| \left| \begin{array}{c} 8.314 \times 10^{-3} \text{ kJ/(mol}\cdot\text{K)} \\ 0.08314 \text{ L}\cdot\text{bar/(mol}\cdot\text{K)} \end{array} \right| \\ &= 3264 \text{ kJ/kg}\end{aligned}$$

8.1b Hypothetical Process Paths

In Chapter 7, we observed that \hat{U} and \hat{H} are **state properties** of a species: that is, their values depend only on the state of the species—primarily on its temperature and state of aggregation (solid, liquid, or gas) and, to a lesser extent, on its pressure (and for mixtures of some species, on its mole fraction in the mixture). A state property does not depend on how the species reached its state. Consequently, *when a species passes from one state to another, both $\Delta\hat{U}$ and $\Delta\hat{H}$ for the process are independent of the path taken from the first state to the second one.*

In most of this chapter and in Chapter 9, you will learn how to calculate internal energy and enthalpy changes associated with certain processes: specifically,

1. ***Changes in P at constant T and state of aggregation*** (Section 8.2).
2. ***Changes in T at constant P and state of aggregation*** (Section 8.3).
3. ***Phase changes at constant T and P***—melting, solidifying, vaporizing, condensing, sublimating (Section 8.4).
4. ***Mixing of two liquids or dissolving of a gas or a solid in a liquid at constant T and P*** (Section 8.5).
5. ***Chemical reaction at constant T and P*** (Chapter 9).

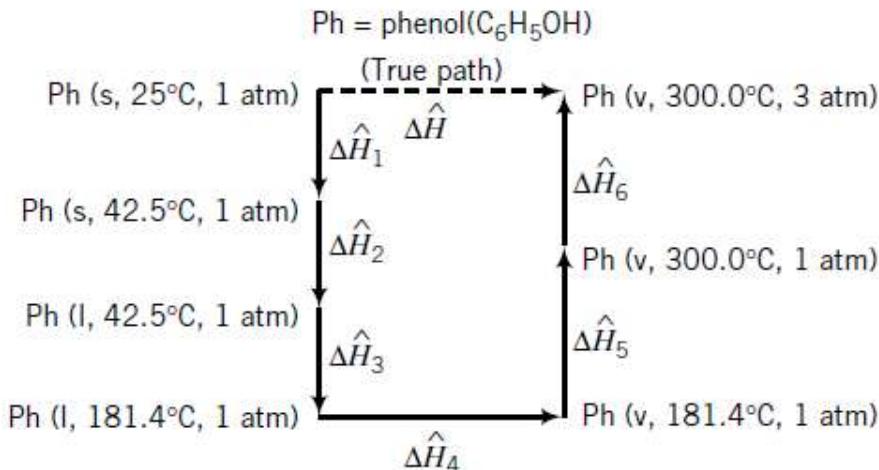
For example, compressing hydrogen gas from 1 atm to 300 atm at 25°C is a Type 1 process; melting ice at 0°C and then heating the liquid water to 30°C, all at 1 atm, is a Type 3 process followed by a Type 2 process; mixing sulfuric acid and water at a constant temperature of 20°C and a constant pressure of 1 atm is a Type 4 process.

Once we know how to calculate $\Delta\hat{U}$ and $\Delta\hat{H}$ for these five types of processes, we can calculate these quantities for *any* process by taking advantage of the fact that \hat{U} and \hat{H} are state properties. The procedure is to construct a hypothetical **process path** from the initial state to the final state consisting of a series of steps of the given five types. Having done this, we calculate $\Delta\hat{H}$ for each of the steps, and then add the $\Delta\hat{H}$'s for the steps to calculate $\Delta\hat{H}$ for the total process. *Since \hat{H} is a state property, $\Delta\hat{H}$ calculated for the hypothetical process path—which we constructed for convenience—is the same as $\Delta\hat{H}$ for the path actually followed by the process.* The same procedure can be followed to calculate $\Delta\hat{U}$ for any process.

Suppose, for example, that we wish to calculate $\Delta\hat{H}$ for a process in which solid phenol at 25°C and 1 atm is converted to phenol vapor at 300°C and 3 atm. If we had a table of enthalpies for phenol, we could simply subtract \hat{H} at the initial state from \hat{H} at the final state, or

$$\Delta\hat{H} = \hat{H}(\text{vapor, } 300^\circ\text{C, } 3 \text{ atm}) - \hat{H}(\text{solid, } 25^\circ\text{C, } 1 \text{ atm})$$

However, we do not have such a table. Our task is then to construct a hypothetical process path from the solid at 25°C and 1 atm to the vapor at 300°C and 3 atm. To do so, we will look ahead a bit and note that Table B.1 gives enthalpy changes for the melting of phenol at 1 atm and 42.5°C (the normal melting point of phenol) and for the vaporization of phenol at 1 atm and 181.4°C (the normal boiling point of phenol). We therefore choose the following hypothetical process path:



Notice that in this path, the first, third, and fifth steps are Type 2 (change in T at constant P), the second and fourth steps are Type 3 (change in phase at constant T and P), and the sixth step is Type 1 (change in P at constant T). Also notice that the phase changes were made to occur at the conditions for which tabulated enthalpy changes are available.

The next step in the calculation would be to determine the values of $\Delta\hat{H}$ for Steps 1, 3, 5, and 6 using methods to be given in Section 8.2; read the values of $\Delta\hat{H}_2$ and $\Delta\hat{H}_4$ from Table B.1; and then use the fact that enthalpy is a state property to calculate the desired $\Delta\hat{H}$ ($\Delta\hat{H}$ for the upper dashed line in the figure) as

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6$$

Lecture 25

Most of the problems at the end of this chapter and Chapter 9 look very much like the problems in Chapters 4 to 6: given values of some process variables (feed and product stream temperatures, pressures, phases, amounts or flow rates, and component mole fractions), calculate values of other process variables. Starting in this chapter, you will also be asked to calculate the heat transferred to or from the process system (one additional variable), which will require writing and solving an energy balance (one additional equation).

Here is the procedure to follow for the energy balance calculation.

- 1. Perform all required material balance calculations.**
- 2. Write the appropriate form of the energy balance (closed or open system) and delete any of the terms that are either zero or negligible for the given process system.** For a stationary closed system, drop ΔE_k and ΔE_p , and neglect W if the system volume is constant, there are no moving parts (such as a mixing impeller in a stirred tank), and no energy is transferred to or from the system by electricity or radiation. For an open system at steady state, drop $\Delta \dot{E}_p$ if there is no appreciable vertical separation between the inlet and outlet ports and drop \dot{W}_s if there are no moving parts (such as a pump or turbine impeller) and no energy is transferred by electricity or radiation. In addition, if temperature changes of more than a few degrees, phase changes, or chemical reactions occur in the process, $\Delta \dot{E}_k$ may usually be neglected.
- 3. Choose a reference state—phase, temperature, and pressure—for each species involved in the process.** If \hat{H} or \hat{U} for a species will be looked up in a table (such as the steam tables for water), choose the reference state used to generate the table; otherwise, choose one of the inlet or outlet states as the reference state for the species (so that at least one \hat{H} or \hat{U} may be set equal to zero).

4. For a closed constant-volume system, construct a table with columns for initial and final amounts of each species (n_i or \hat{n}_i) and specific internal energies relative to the chosen reference states (\hat{U}_i)². For an open system, construct a table with columns for inlet and outlet stream component flow rates (\dot{m}_i or $\dot{\hat{n}}_i$) and specific enthalpies relative to the chosen reference states (\hat{H}_i). Insert known values of the amounts or flow rates and the specific internal energies and enthalpies, and insert labels for the entries that must be calculated (e.g., $\hat{H}_1, \hat{H}_2, \dots$). The next example illustrates the construction of such a table.

5. Calculate all required values of \hat{U}_i (or \hat{H}_i) and insert the values in the appropriate places in the table. To perform the calculation for a species in a particular state (inlet or outlet), choose any convenient path from the reference state to the process state and determine \hat{U}_i (\hat{H}_i) as $\Delta\hat{U}$ ($\Delta\hat{H}$) for that path. Sections 8.2–8.5 outline these calculations for different types of processes.

6. Calculate

$$\text{Closed System: } \Delta U = \sum_{\text{final}} n_i \hat{U}_i - \sum_{\text{initial}} n_i \hat{U}_i \quad \text{or} \quad \sum_{\text{out}} \dot{m}_i \hat{U}_i - \sum_{\text{in}} \dot{m}_i \hat{U}_i$$

$$\text{Open System: } \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i \quad \text{or} \quad \sum_{\text{out}} \dot{m}_i \hat{H}_i - \sum_{\text{in}} \dot{m}_i \hat{H}_i$$

7. Calculate any work, kinetic energy, or potential energy terms that you have not dropped from the energy balance.

8. Solve the energy balance for whichever variable is unknown (often Q or \dot{Q}).

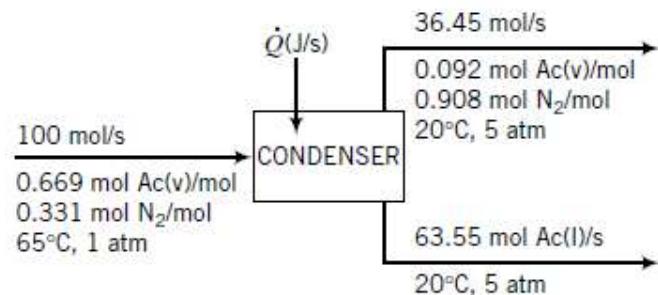
$$\text{Closed System: } Q - W = \Delta U + \Delta E_k + \Delta E_p$$

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

EXAMPLE 8.1-1

Energy Balance on a Condenser

Acetone (denoted as Ac) is partially condensed out of a gas stream containing 66.9 mole % acetone vapor and the balance nitrogen. Process specifications and material balance calculations lead to the flowchart shown below.



The process operates at steady state. Calculate the required cooling rate.

SOLUTION

We will follow the procedure given preceding this example.

1. *Perform required material balance calculations.* None are required in this example.
2. *Write and simplify the energy balance.*

For this open steady-state system, $\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$. There are no moving parts in the system and no energy is transferred by electricity or radiation, so $\dot{W}_s = 0$. No significant vertical distance separates the inlet and outlet ports, so $\Delta\dot{E}_p \approx 0$. Phase changes and nonnegligible temperature changes occur, so $\Delta\dot{E}_k \approx 0$ (relative to $\Delta\dot{H}$). The energy balance reduces to

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

3. Choose reference states for acetone and nitrogen.

The reference states may be chosen for computational convenience, since the choice has no effect on the calculated value of $\Delta\hat{H}$. You will later learn that Table B.8 lists specific enthalpies of nitrogen relative to $N_2(g, 25^\circ C, 1 \text{ atm})$, which makes this state a convenient choice for nitrogen. There are no tabulated enthalpy data for acetone in the text, so we will choose one of the process stream conditions, $Ac(l, 20^\circ C, 5 \text{ atm})$, as the reference state for this species, which will enable us to set the corresponding \hat{H} value equal to zero rather than having to calculate it.

4. Construct an inlet–outlet enthalpy table.

We first write the chosen reference states, then construct the table shown below:

References: $Ac(l, 20^\circ C, 5 \text{ atm})$, $N_2(g, 25^\circ C, 1 \text{ atm})$

Substance	\dot{n}_{in} (mol/s)	\hat{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/s)	\hat{H}_{out} (kJ/mol)
$Ac(v)$	66.9	\hat{H}_1	3.35	\hat{H}_3
$Ac(l)$	—	—	63.55	0
N_2	33.1	\hat{H}_2	33.1	\hat{H}_4

Note the following points about the table:

- Nitrogen has only one inlet state (gas, $65^\circ C, 1 \text{ atm}$) and one outlet state (gas, $20^\circ C, 5 \text{ atm}$), so we need only one row in the table for N_2 . Acetone has one inlet state (vapor, $65^\circ C, 1 \text{ atm}$) but two outlet states (vapor and liquid, each at $20^\circ C$ and 5 atm), so we need two rows for this species.
- We mark out (using dashes) the two cells corresponding to \dot{n}_{in} and \hat{H}_{in} for liquid acetone, since no liquid acetone enters the system.
- The \dot{n} values are obtained from the flowchart. The flow rate of acetone vapor at the inlet, for example, is determined as $(100 \text{ mol/s})[0.669 \text{ mol } Ac(v)/\text{mol}] = 66.9 \text{ mol } Ac(v)/\text{s}$.
- Since the liquid acetone leaving the system is at the reference state, we set its specific enthalpy equal to zero.
- Four unknown specific enthalpies have been labeled and must be determined in Step 5.

5. Calculate all unknown specific enthalpies.

To calculate the four unknown specific enthalpies in the table, we construct hypothetical process paths from the reference states to the states of the species in the process and evaluate $\Delta\hat{H}$ for each path. This is the part of the calculation you have not yet learned to do. We will show you the calculation of \hat{H}_1 to illustrate the method, give the results of the other calculations, and go into detail about the required procedures in Sections 8.2–8.5.

$$\begin{aligned}\hat{H}_1 &= \text{specific enthalpy of Ac(v, } 65^\circ\text{C, 1 atm) relative to Ac(l, } 20^\circ\text{C, 5 atm)} \\ &= \Delta\hat{H} \text{ for Ac(l, } 20^\circ\text{C, 5 atm) } \longrightarrow \text{Ac(v, } 65^\circ\text{C, 1 atm)}\end{aligned}$$

When choosing a process path for the determination of $\Delta\hat{H}$, it helps to know that formulas and data are given in this chapter for enthalpy changes corresponding to certain types of processes:

- Section 8.2 gives the formula $\Delta\hat{H} = \hat{V}\Delta P$ for a change in pressure (ΔP) undergone by a liquid or solid with constant specific volume \hat{V} . The value of \hat{V} for liquid acetone may be determined as 0.0734 L/mol from the specific gravity (0.791) given in Table B.1.
- Section 8.3 shows that $\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T) dT$ for a change from T_1 to T_2 at constant P . Formulas for $C_p(T)$, the *heat capacity at constant pressure*, are given in Table B.2. The formulas for acetone liquid and vapor are as follows:

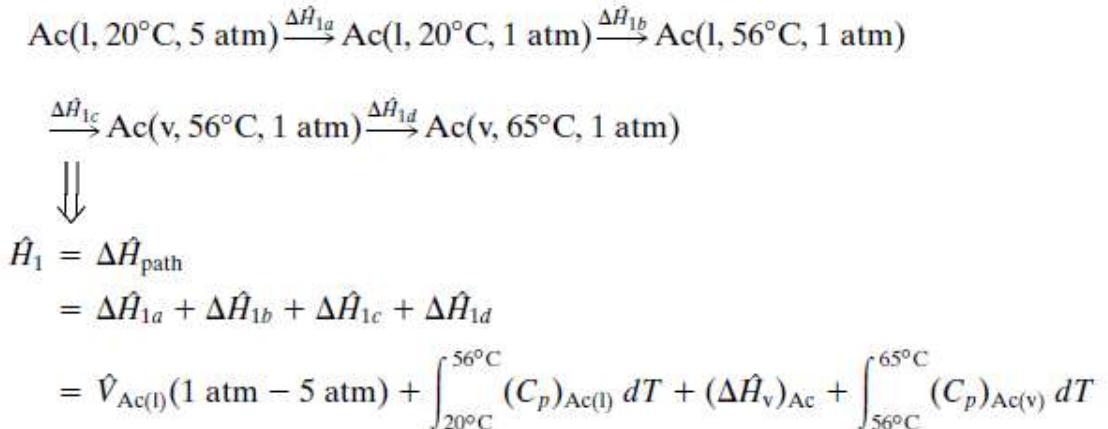
$$\text{Ac(l): } C_p \left(\frac{\text{kJ}}{\text{mol}\cdot^\circ\text{C}} \right) = 0.123 + 18.6 \times 10^{-5}T$$

$$\text{Ac(v): } C_p \left(\frac{\text{kJ}}{\text{mol}\cdot^\circ\text{C}} \right) = 0.07196 + 20.10 \times 10^{-5}T - 12.78 \times 10^{-8}T^2 + 34.76 \times 10^{-12}T^3$$

where T is in $^\circ\text{C}$.

- Section 8.4 defines the *heat of vaporization*, $\Delta\hat{H}_v(T_{bp})$, as $\Delta\hat{H}$ for a change from liquid to vapor at the normal boiling point, T_{bp} . Table B.1 lists T_{bp} for acetone as 56.0°C and $\Delta\hat{H}_v(T_{bp})$ as 30.2 kJ/mol.

The following process path from the reference state [Ac(l), 20°C, 5 atm] to the process state [Ac(v, 56°C, 1 atm)] enables us to use all this information in the determination of \hat{H}_1 :³



When we substitute the values of $\hat{V}_{\text{Ac(l)}}$ and $\Delta\hat{H}_v$ and the formulas for $C_p(T)$ into the expression for \hat{H}_1 and carry out the necessary unit conversions and integrations, we obtain $\hat{H}_1 = (0.0297 + 4.68 + 30.2 + 0.753) \text{ kJ/mol} = 35.7 \text{ kJ/mol}$.

Proceeding in a similar manner, we obtain the values for \hat{H}_2 , \hat{H}_3 , and \hat{H}_4 shown in the following revised enthalpy table:

References: Ac(l, 20°C, 5 atm), N₂(g, 25°C, 1 atm)

Substance	\dot{n}_{in} (mol/s)	\hat{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/s)	\hat{H}_{out} (kJ/mol)
Ac(v)	66.9	35.7	3.35	32.0
Ac(l)	—	—	63.55	0
N ₂	33.1	1.16	33.1	-0.10

6. Calculate \dot{H} .

$$\begin{aligned}\dot{H} &= \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i \\ &= (3.35 \text{ mol/s})(32.0 \text{ kJ/mol}) + [(63.55)(0) + (33.1)(-0.10) - (66.9)(35.7) - (33.1)(1.16)] \text{ kJ/s} \\ &= -2320 \text{ kJ/s}\end{aligned}$$

The factors in the last equation come directly from the inlet-outlet enthalpy table.

7. Calculate nonzero work, kinetic energy, and potential energy terms.

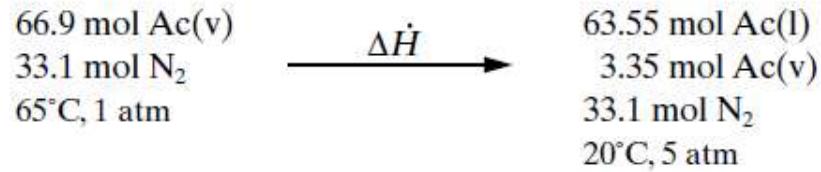
Since there is no shaft work and we are neglecting kinetic and potential energy changes, there is nothing to do in this step.

8. Solve the energy balance for \dot{Q} .

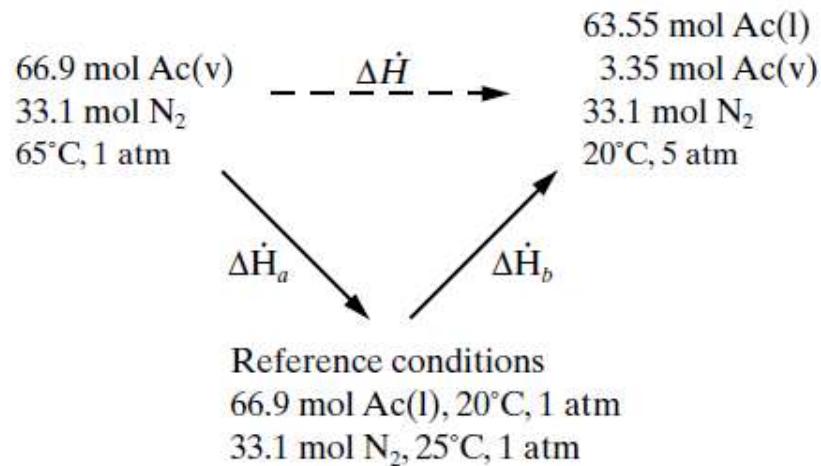
$$\dot{Q} = \dot{H} = -2320 \text{ kJ/s} = \boxed{-2320 \text{ kW}}$$

Heat must be transferred from the condenser at a rate of 2320 kW to achieve the required cooling and condensation.

Before we leave this section, let us consider what we just did from a different perspective. The process for which we need to calculate \dot{H} ($= \dot{Q}$) may be depicted as shown below:



To calculate \dot{H} , in effect we constructed the following process path:



The total enthalpy change for the first step, \dot{H}_a , is the negative of \dot{H} for the process in which acetone and nitrogen go from the reference conditions to the inlet conditions, or

$$\dot{H}_a = - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$

Similarly, \dot{H}_b is the enthalpy change for the process in which acetone and nitrogen go from the reference conditions to the outlet conditions, or

$$\dot{H}_b = \sum_{\text{out}} \dot{n}_i \hat{H}_i$$

Since enthalpy is a state function, the overall enthalpy change for the process must be

$$\Delta\dot{H} = \Delta\dot{H}_a + \Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$

It remains for us to outline methods for calculating $\Delta\hat{U}$ and $\Delta\hat{H}$ for the different types of processes we have discussed. The methods for the first four (change in P at constant T , change in T at constant P , change in phase at constant T and P , and mixing or dissolving at constant T and P) are outlined in Sections 8.2–8.5 of this chapter, and methods for chemical reactions at constant T and P are given in Chapter 9.

Lecture 26

8.2 Changes in Pressure at Constant Temperature

It has been observed experimentally that internal energy is nearly independent of pressure for solids and liquids at a fixed temperature, as is specific volume. Therefore, *if the pressure of a solid or liquid changes at constant temperature, you may write $\Delta\hat{U} \approx 0$ and $\Delta\hat{H} [= \Delta\hat{U} + \Delta(P\hat{V})] \approx \hat{V}\Delta P$.*

Both \hat{U} and \hat{H} are independent of pressure for ideal gases. Consequently, *you may generally assume $\Delta\hat{U} \approx 0$ and $\Delta\hat{H} \approx 0$ for a gas undergoing an isothermal pressure change unless gases at temperatures well below 0°C or well above 1 atm are involved.* [If tables of $\hat{U}(T, P)$ or $\hat{H}(T, P)$ are available for the gas, there is of course no need to make this assumption.] If gases are far from ideal or if they undergo large pressure changes, you must either use tables of thermodynamic properties (such as the steam tables for water) or thermodynamic correlations beyond the scope of this text to determine $\Delta\hat{U}$ or $\Delta\hat{H}$. A good source for such correlations is Chapter 5 of Reid, Prausnitz, and Poling.⁴

8.3 Changes in Temperature

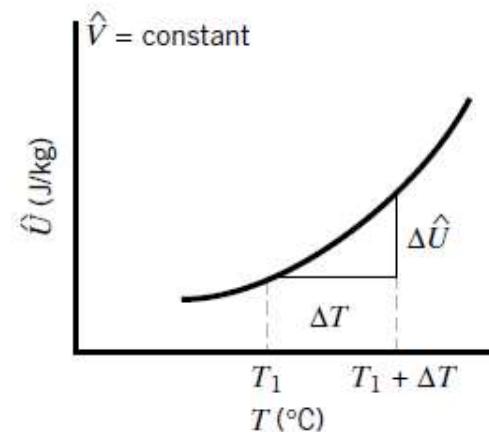
8.3a Sensible heat and Heat Capacities

The term **sensible heat** signifies heat that must be transferred to raise or lower the temperature of a substance or mixture of substances. The quantity of heat required to produce a temperature change in a system can be determined from the appropriate form of the first law of thermodynamics:

$$Q = \Delta U \quad (\text{closed system}) \quad (8.3-1)$$

$$\dot{Q} = \Delta \dot{H} \quad (\text{open system}) \quad (8.3-2)$$

The specific internal energy of a substance depends strongly on temperature. If the temperature is raised or lowered in such a way that the system volume remains constant, the specific internal energy might vary as shown in the following plot:



A temperature change ΔT from T_1 leads to a change $\Delta \hat{U}$ in specific internal energy. As $\Delta T \rightarrow 0$, the ratio $\Delta \hat{U}/\Delta T$ approaches a limiting value (i.e., the slope of the curve at T_1), which is by definition the **heat capacity at constant volume** of the substance, denoted by C_v .

$$C_v(T) = \left\{ \lim_{\Delta T \rightarrow 0} \frac{\Delta \hat{U}}{\Delta T} \right\} = \left(\frac{\partial \hat{U}}{\partial T} \right)_V \quad (8.3-3)$$

Since the plot of \hat{U} versus T is not generally a straight line, C_v (the slope of the curve) is a function of temperature.

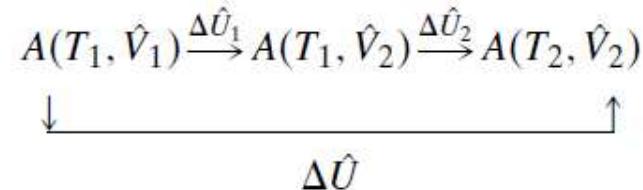
The change in \hat{U} for a temperature rise from T to $T + dT$ at constant volume is from Equation 8.3-3

$$d\hat{U} = C_v(T) dT \quad (8.3-4)$$

and the change $\Delta \hat{U} = \hat{U}_2 - \hat{U}_1$ associated with a temperature change from T_1 to T_2 at constant volume is, accordingly,

$$\Delta \hat{U} = \int_{T_1}^{T_2} C_v(T) dT \quad (8.3-5)$$

Now, suppose both the temperature and the volume of a substance change. To calculate $\Delta \hat{U}$, you may break the process into two steps—a change in \hat{V} at constant T followed by a change in T at constant \hat{V} .



$$\Delta \hat{U} \approx \int_{T_1}^{T_2} C_v(T) dT$$

Ideal gas: exact

Solid or liquid: good approximation

Nonideal gas: valid only if V is constant

$$(8.3-6)$$

EXAMPLE 8.3-1**Evaluation of an Internal Energy Change from Tabulated Heat Capacity**

Calculate the heat required to raise 200 kg of nitrous oxide from 20°C to 150°C in a constant-volume vessel. The constant-volume heat capacity of N₂O in this temperature range is given by the equation

$$C_v \text{ (kJ/kg} \cdot ^\circ\text{C)} = 0.855 + 9.42 \times 10^{-4}T$$

where T is in °C.

SOLUTION

From Equation 8.3-6,

$$\begin{aligned}\Delta\hat{U}(\text{kJ/kg}) &= \int_{20^\circ\text{C}}^{150^\circ\text{C}} (0.855 + 9.42 \times 10^{-4}T) \left(\frac{\text{kJ}}{\text{kg} \cdot ^\circ\text{C}} \right) dT \\ &= 0.855T]_{20^\circ\text{C}}^{150^\circ\text{C}} + \frac{9.42 \times 10^{-4}T^2}{2} \Big|_{20^\circ\text{C}}^{150^\circ\text{C}} \\ &= (111 + 10.4) \text{ kJ/kg} = 121 \text{ kJ/kg}\end{aligned}$$

The energy balance for this closed system is

$$Q = \Delta U = m(\text{kg}) \Delta\hat{U}(\text{kJ/kg}) = (200 \text{ kg})(121 \text{ kJ/kg}) = \boxed{24,200 \text{ kJ}}$$

Next, let us suppose that we heat a substance at constant pressure and consider the resulting change in enthalpy. Like internal energy, enthalpy depends strongly on temperature. If $\Delta\hat{H}$ is the change in specific enthalpy resulting from a temperature increase at constant pressure from T to $T + \Delta T$, then as ΔT approaches zero the ratio $\Delta\hat{H}/\Delta T$ approaches a limiting value, defined as the **heat capacity at constant pressure** and denoted by C_p .

$$C_p(T) = \left\{ \lim_{\Delta T \rightarrow 0} \frac{\Delta\hat{H}}{\Delta T} \right\} = \left(\frac{\partial\hat{H}}{\partial T} \right)_P \quad (8.3-7)$$

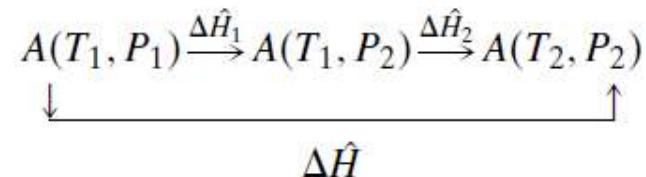
Proceeding as before, we observe that the change in \hat{H} for a temperature change at constant pressure from T to $T + dT$ is

$$d\hat{H} = C_p(T) dT$$

and so for a change from T_1 to T_2 at constant pressure

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T) dT \quad (8.3-8)$$

For a process $A(T_1, P_1) \rightarrow A(T_2, P_2)$, we may construct a two-step process path



The first step is a change in pressure at constant temperature, the type of process described in Section 8.2. We saw in that section that

$$\begin{aligned}\Delta\hat{H}_1 &= 0 \quad (\text{ideal gas}) \\ &\approx \hat{V} \Delta P \quad (\text{solid or liquid})\end{aligned}\tag{8.3-9}$$

The second step is a change in temperature at constant pressure, so that $\Delta\hat{H}_2$ is given by Equation 8.3-8. Finally, since $\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2$ (why?), we obtain

$$\boxed{\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T) dT} \quad \begin{array}{l} \text{Ideal gas: exact} \\ \text{Nonideal gas: exact only if } P \text{ is constant} \end{array} \tag{8.3-10a}$$

$$\boxed{\Delta\hat{H} = \hat{V} \Delta P + \int_{T_1}^{T_2} C_p(T) dT} \quad \text{Solid or liquid} \tag{8.3-10b}$$

8.3b Heat Capacity Formulas

Heat capacities are functions of temperature and are frequently expressed in polynomial form ($C_p = a + bT + cT^2 + dT^3$). Values of the coefficients a , b , c , and d are given in Table B.2 of Appendix B for a number of species at 1 atm, and listings for additional substances are given on pp. 2-161 to 2-186 of *Perry's Chemical Engineers' Handbook*.

When reading the coefficients of a heat capacity formula from Table B.2, do not mistake their orders of magnitude: if a value of 72.4 is read from the column labeled $b \cdot 10^5$, then the value of b must be five orders of magnitude *less* than 72.4, or $b = 72.4 \times 10^{-5}$.

Simple relationships exist between C_p and C_v in two cases:

$$\boxed{\textbf{\i} \textit{Liquids and Solids: } C_p \approx C_v} \quad (8.3-11)$$

$$\boxed{\textbf{\i} \textit{Ideal Gases: } C_p = C_v + R} \quad (8.3-12)$$

where R is the gas constant. (Try to prove the second relation.) The relationship between C_p and C_v for nonideal gases is complex and will not be discussed in this text.

EXAMPLE 8.3-2

Cooling of an Ideal Gas

Assuming ideal gas behavior, calculate the heat that must be transferred in each of the following cases.

1. A stream of nitrogen flowing at a rate of 100 mol/min is heated from 20°C to 100°C.
2. Nitrogen contained in a 5-liter flask at an initial pressure of 3 bar is cooled from 90°C to 30°C.

SOLUTION

Neglecting kinetic energy changes, the energy balance equation for the open system of part 1 is $Q = \Delta H$, and that for the closed system of part 2 is $Q = \Delta U$. (Prove it.) The problem is therefore to evaluate ΔH and ΔU for the two specified processes.

1. From Table B.2, Appendix B, the heat capacity of N₂ at a constant pressure of 1 atm is

$$C_p[\text{kJ}/(\text{mol}\cdot\text{°C})] = 0.02900 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3$$

where T is in $^{\circ}\text{C}$. Since we are assuming ideal gas behavior, the enthalpy change for the gas is independent of any pressure change that may occur, and hence, from Equation 8.3-10a,

$$\Delta\hat{H} = \int_{20^{\circ}\text{C}}^{100^{\circ}\text{C}} C_p(T) dT$$



$$\begin{aligned}\Delta\hat{H}(\text{kJ/mol}) &= 0.02900T \left[\frac{T^4}{2} \right]_{20^{\circ}\text{C}}^{100^{\circ}\text{C}} + 0.2199 \times 10^{-5} \left[\frac{T^2}{2} \right]_{20^{\circ}\text{C}}^{100^{\circ}\text{C}} + 0.5723 \times 10^{-8} \left[\frac{T^3}{3} \right]_{20^{\circ}\text{C}}^{100^{\circ}\text{C}} \\ &\quad - 2.871 \times 10^{-12} \left[\frac{T^4}{4} \right]_{20^{\circ}\text{C}}^{100^{\circ}\text{C}} \\ &= (2.320 + 0.0106 + 1.9 \times 10^{-3} - 7 \times 10^{-5}) \text{ kJ/mol} = 2.332 \text{ kJ/mol}\end{aligned}$$

Finally,

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} = \dot{n} \Delta\hat{H} \\ &= 100 \frac{\text{mol}}{\text{min}} \left| \frac{2.332 \text{ kJ}}{\text{mol}} \right. = \boxed{233 \text{ kJ/min}}\end{aligned}$$

2. To evaluate ΔU , we need the number of moles n , which may be calculated using the ideal gas equation of state, and $\Delta \hat{U}$. To determine the latter quantity we need the constant-volume heat capacity, which from Equation 8.3-12 is

$$C_v = C_p - R$$

$$\downarrow \begin{array}{l} C_p \text{ given above} \\ \downarrow R = [8.314 \text{ J } (\text{mol}\cdot\text{K})](1 \text{ K}/1^\circ\text{C})(1 \text{ kJ}/10^3 \text{ J}) \end{array}$$

$$C_v[\text{kJ}/(\text{mol}\cdot{}^\circ\text{C})] = 0.02069 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3$$

Calculate $\Delta \hat{U}$

$$\Delta \hat{U} = \int_{90^\circ\text{C}}^{30^\circ\text{C}} C_v(T) dT$$

$$\downarrow$$

$$\begin{aligned} \Delta \hat{U} &= 0.02069T \left[\frac{T^2}{2} \right]_{90^\circ\text{C}}^{30^\circ\text{C}} + 0.2199 \times 10^{-5} \left[\frac{T^3}{3} \right]_{90^\circ\text{C}}^{30^\circ\text{C}} + 0.5723 \times 10^{-8} \left[\frac{T^4}{4} \right]_{90^\circ\text{C}}^{30^\circ\text{C}} - 2.871 \times 10^{-12} \\ &= (-1.241 - 7.92 \times 10^{-3} - 1.34 \times 10^{-3} + 5 \times 10^{-5}) \text{ kJ/mol} = -1.250 \text{ kJ/mol} \end{aligned}$$

Calculate n

At the initial condition (the only point at which we know P , V , and T)

$$\begin{aligned} n &= PV/RT \\ &= \frac{(3.00 \text{ bar})(5.00 \text{ L})}{[0.08314 \text{ L}\cdot\text{bar}/(\text{mol}\cdot\text{K})](363 \text{ K})} = 0.497 \text{ mol} \end{aligned}$$

Calculate Q

$$\begin{aligned} Q &= \Delta U = n \Delta \hat{U} \\ &= (0.497 \text{ mol})(-1.250 \text{ kJ/mol}) = \boxed{-0.621 \text{ kJ}} \end{aligned}$$

EXAMPLE 8.3-3**Evaluation of $\Delta\dot{H}$ Using Heat Capacities and Tabulated Enthalpies**

Fifteen kmol/min of air is cooled from 430°C to 100°C. Calculate the required heat removal rate using (1) heat capacity formulas from Table B.2 and (2) specific enthalpies from Table B.8.

SOLUTION

With $\Delta\dot{E}_k$, $\Delta\dot{E}_p$, and \dot{W}_s deleted, the energy balance is

$$\dot{Q} = \Delta\dot{H} = \dot{n}_{\text{air}}\hat{H}_{\text{air,out}} - \dot{n}_{\text{air}}\hat{H}_{\text{air,in}} = \dot{n}_{\text{air}} \Delta\hat{H}$$

Assume ideal gas behavior, so that pressure changes (if there are any) do not affect $\Delta\hat{H}$.

1. The hard way. Integrate the heat capacity formula in Table B.2.

$$\begin{aligned}\Delta\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right) &= \int_{430^\circ\text{C}}^{100^\circ\text{C}} C_p(T) dT \\ &= \int_{430^\circ\text{C}}^{100^\circ\text{C}} \left[0.02894 + 0.4147 \times 10^{-5}T + 0.3191 \times 10^{-8}T^2 - 1.965 \times 10^{-12}T^3 \right] dT \\ &= \left[0.02894(100 - 430) + \frac{0.4147 \times 10^{-5}}{2}(100^2 - 430^2) \right. \\ &\quad \left. + \frac{0.3191 \times 10^{-8}}{3}(100^3 - 430^3) - \frac{1.965 \times 10^{-12}}{4}(100^4 - 430^4) \right] \text{kJ/mol} \\ &= (-9.5502 - 0.3627 - 0.0835 + 0.0167) \text{ kJ/mol} = -9.98 \text{ kJ/mol}\end{aligned}$$

2. The easy way. Use tabulated enthalpies from Table B.8.

\hat{H} for air at 100°C can be read directly from Table B.9 and \hat{H} at 430°C can be estimated by linear interpolation from the values at 400°C (11.24 kJ/mol) and 500°C (14.37 kJ/mol).

$$\hat{H}(100^\circ\text{C}) = 2.19 \text{ kJ/mol}$$

$$\hat{H}(430^\circ\text{C}) = [11.24 + 0.30(14.37 - 11.24)] \text{ kJ/mol} = 12.17 \text{ kJ/mol}$$



$$\Delta\hat{H} = (2.19 - 12.17) \text{ kJ/mol} = -9.98 \text{ kJ/mol}$$

Either way $\Delta\hat{H}$ is determined,

$$\dot{Q} = \Delta\dot{H} = \dot{n} \Delta\hat{H} = \frac{15.0 \text{ kmol}}{\text{min}} \left| \begin{array}{c|c|c|c|c} 10^3 \text{ mol} & -9.98 \text{ kJ} & 1 \text{ min} & 1 \text{ kW} \\ \hline 1 \text{ kmol} & \text{mol} & 60 \text{ s} & 1 \text{ kJ/s} \end{array} \right| = \boxed{-2500 \text{ kW}}$$

Lecture 27

8.3c Estimation of Heat Capacities

(for mixtures)

The polynomial expressions for C_p in Table B.2 are based on experimental data for the listed compounds and provide a basis for accurate calculations of enthalpy changes. Several approximate methods follow for estimating heat capacities in the absence of tabulated formulas.

Kopp's rule is a simple empirical method for estimating the heat capacity of a solid or liquid at or near 20°C. According to this rule, C_p for a molecular compound is the sum of contributions (given in Table B.10) for each element in the compound. For example, the heat capacity of solid calcium hydroxide, $\text{Ca}(\text{OH})_2$, would be estimated from Kopp's rule as

$$\begin{aligned}(C_p)_{\text{Ca}(\text{OH})_2} &= (C_{pa})_{\text{Ca}} + 2(C_{pa})_{\text{O}} + 2(C_{pa})_{\text{H}} \\ &= [26 + (2 \times 17) + (2 \times 9.6)] \text{ J}/(\text{mol}\cdot^\circ\text{C}) = 79 \text{ J}/(\text{mol}\cdot^\circ\text{C})\end{aligned}$$

[The true value is 89.5 J/(mol·°C).]

More accurate heat capacity estimation formulas for various types of gases and liquids are given in Chapter 5 of Reid, Prausnitz, and Poling (see footnote 4), and several correlations are presented by Gold and Ogle.⁶

Suppose you wish to calculate the enthalpy change associated with a change in temperature undergone by a mixture of substances. Enthalpies and heat capacities of certain mixtures are tabulated in standard references. Lacking such data, you may use the following approximation:

Rule 1. *For a mixture of gases or liquids, calculate the total enthalpy change as the sum of the enthalpy changes for the pure mixture components.* You are in effect neglecting enthalpy changes associated with the mixing of the components, which is an excellent approximation for mixtures of gases and for mixtures of similar liquids such as pentane and hexane but a poor one for dissimilar liquids such as nitric acid and water. Enthalpies of mixing for systems of the latter type are discussed in detail in Section 8.5.

Rule 2. For highly dilute solutions of solids or gases in liquids, neglect the enthalpy change of the solute. The more dilute the solution, the better this approximation.

The calculation of enthalpy changes for the heating or cooling of a mixture of known composition may often be simplified by calculating a heat capacity for the mixture in the following manner:

$$(C_p)_{\text{mix}}(T) = \sum_{\substack{\text{all} \\ \text{mixture} \\ \text{components}}} y_i C_{pi}(T) \quad (8.3-13)$$

where

$(C_p)_{\text{mix}}$ = heat capacity of the mixture

y_i = mass or mole fraction of the i th component

C_{pi} = heat capacity of the i th component

If C_{pi} and $(C_p)_{\text{mix}}$ are expressed in molar units, then y_i must be the mole fraction of the i th component, and if the heat capacities are expressed in mass units, then y_i must be the mass fraction of the i th component. Once $(C_p)_{\text{mix}}$ is known, $\Delta\hat{H}$ for a change in temperature from T_1 to T_2 may be calculated as

$$\Delta\hat{H} = \int_{T_1}^{T_2} (C_p)_{\text{mix}}(T) dT \quad (8.3-14)$$

Equation 8.3-14 is valid to the extent that enthalpies of mixing may be neglected.

EXAMPLE 8.3-4**Heat Capacity of a Mixture**

Calculate the heat required to bring 150 mol/h of a stream containing 60% C₂H₆ and 40% C₃H₈ by volume from 0°C to 400°C. Determine a heat capacity for the mixture as part of the problem solution.

SOLUTION

The polynomial heat capacity formulas for ethane and propane given in Table B.2 are substituted into Equation 8.3-13 to yield

$$\begin{aligned}(C_p)_{\text{mix}}[\text{kJ}/(\text{mol}\cdot^\circ\text{C})] &= 0.600(0.04937 + 13.92 \times 10^{-5}T - 5.816 \times 10^{-8}T^2 + 7.280 \times 10^{-12}T^3) \\ &\quad + 0.400(0.06803 + 22.59 \times 10^{-5}T - 13.11 \times 10^{-8}T^2 + 31.71 \times 10^{-12}T^3) \\ &= 0.05683 + 17.39 \times 10^{-5}T - 8.734 \times 10^{-8}T^2 + 17.05 \times 10^{-12}T^3 \\ \Delta\hat{H} &= \int_{0^\circ\text{C}}^{400^\circ\text{C}} (C_p)_{\text{mix}} dT = 34.89 \text{ kJ/mol}\end{aligned}$$

where T is in °C. If potential and kinetic energy changes and shaft work are neglected, the energy balance becomes

$$\dot{Q} = \Delta\hat{H} = \dot{n}\Delta\hat{H} = \frac{150 \text{ mol}}{\text{h}} \left| \frac{34.89 \text{ kJ}}{\text{mol}} \right. = \boxed{5230 \frac{\text{kJ}}{\text{h}}}$$

As usual, we have assumed that the gases are sufficiently close to ideal for the formulas for C_p at 1 atm to be valid.

8.3d Energy Balances on Single-Phase Systems

We are now in a position to perform energy balances on any processes that do not involve phase changes, mixing steps for which enthalpy changes cannot be neglected, or chemical reactions.

If a process only involves heating or cooling a single species from T_1 to T_2 , the procedure is straightforward:

1. Evaluate $\Delta\hat{U} = \int_{T_1}^{T_2} C_v dT$ or $\Delta\hat{H} = \int_{T_1}^{T_2} C_p dT$, correcting for pressure changes if necessary.
2. For a closed system at constant volume, calculate $\Delta U = n \Delta\hat{U}$ (where n is the amount of the species being heated or cooled). For a closed system at constant pressure, calculate $\Delta H = n \Delta\hat{H}$. For an open system, calculate $\Delta\dot{H} = \dot{n} \Delta\hat{H}$, where \dot{n} is the species flow rate.
3. Substitute for ΔU , ΔH , or $\Delta\dot{H}$ in the appropriate energy balance equation to determine the required heat transfer, Q , or heat transfer rate, \dot{Q} . (See Example 8.3-2.)

If more than one species is involved or if there are several input or output streams instead of just one of each, the procedure given in Section 8.1 should be followed: choose reference states for each species, prepare and fill in a table of amounts and specific internal energies (closed system) or species flow rates and specific enthalpies (open system), and substitute the calculated values into the energy balance equation. The next example illustrates the procedure for a continuous heating process.

EXAMPLE 8.3-5

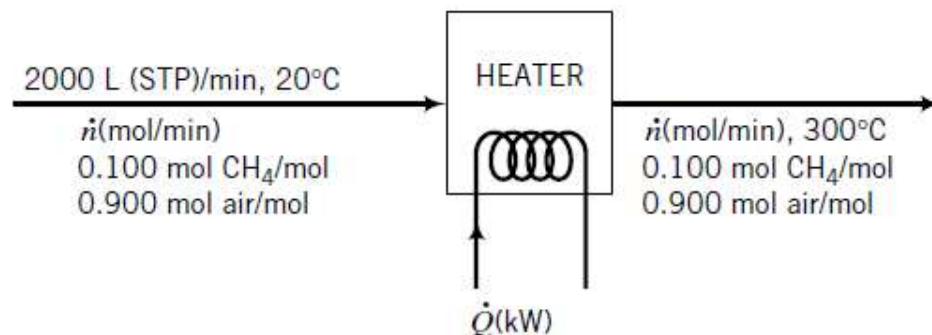
Energy Balance on a Gas Preheater

A stream containing 10% CH₄ and 90% air by volume is to be heated from 20°C to 300°C. Calculate the required rate of heat input in kilowatts if the flow rate of the gas is 2.00 × 10³ liters (STP)/min.

SOLUTION

Basis: Given Flow Rate

Assume ideal gas behavior.



Recall that specifying the flow rate in liters (STP)/min does not imply that the feed gas is at standard temperature and pressure; it is simply an alternative way of giving the molar flow rate.

$$\dot{n} = \frac{2000 \text{ L (STP)}}{\text{min}} \left| \frac{1 \text{ mol}}{22.4 \text{ L (STP)}} \right. = 89.3 \text{ mol/min}$$

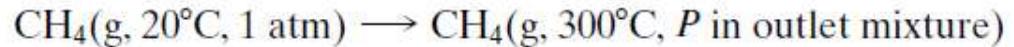
The energy balance with kinetic and potential energy changes and shaft work omitted is $\dot{Q} = \Delta\dot{H}$. The task is to evaluate $\Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$. Since each species has only one inlet condition and one outlet condition in the process, two rows are sufficient for the enthalpy table.

References: CH₄(g, 20°C, 1 atm), air(g, 25°C, 1 atm)

Substance	\dot{n}_{in} (mol/min)	\hat{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/min)	\hat{H}_{out} (kJ/mol)
CH ₄	8.93	0	8.93	\hat{H}_1
Air	80.4	\hat{H}_2	80.4	\hat{H}_3

The reference condition for methane was chosen so that \hat{H}_{in} could be set equal to zero, and that for air was chosen so that \hat{H}_{in} and \hat{H}_{out} could be determined directly from Table B.8.

The next step is to evaluate all of the unknown specific enthalpies in the table. \hat{H}_1 , for example, is the specific enthalpy of methane in the outlet gas mixture at 300°C relative to pure methane at its reference temperature of 20°C. In other words, it is the specific enthalpy change for the process



We neglect the effect of pressure on enthalpy (i.e., we assume ideal gas behavior) and we always neglect heats of mixing of gases, so that the enthalpy change is calculated for the heating of pure methane at 1 atm:

$$\hat{H}_1 = \int_{20^\circ\text{C}}^{300^\circ\text{C}} (C_p)_{\text{CH}_4} dT$$

↓ Substitute for C_p from Table B.2

$$= \int_{20^\circ\text{C}}^{300^\circ\text{C}} (0.03431 + 5.469 \times 10^{-5}T + 0.3661 \times 10^{-8}T^2 - 11.0 \times 10^{-12}T^3) dT$$

$$= 12.09 \text{ kJ/mol}$$

The enthalpies of air at the inlet and outlet conditions relative to air at the reference state (\hat{H}_2 and \hat{H}_3 , respectively) are determined from Table B.8 as

$$\hat{H}_2 = -0.15 \text{ kJ/mol}, \quad \hat{H}_3 = 8.17 \text{ kJ/mol}$$

The energy balance now yields

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i \\ &= (8.93 \text{ mol/min})(12.09 \text{ kJ/mol}) + [(80.4)(8.17) - (8.93)(0) - (80.4)(-0.15)] \text{ kJ/min}\end{aligned}$$

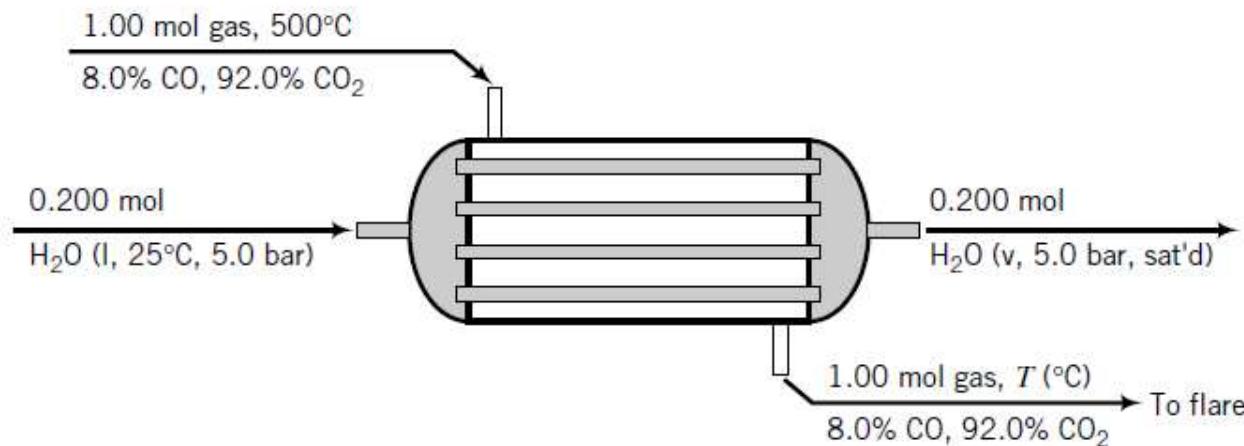


$$\dot{Q} = \frac{776 \text{ kJ}}{\text{min}} \left| \begin{array}{c|c|c} 1 \text{ min} & & 1 \text{ kW} \\ \hline 60 \text{ s} & & 1 \text{ kJ/s} \end{array} \right| = \boxed{12.9 \text{ kW}}$$

EXAMPLE 8.3-6

Energy Balance on a Waste Heat Boiler

A gas stream containing 8.0 mole% CO and 92.0 mole% CO₂ at 500°C is fed to a **waste heat boiler**, a large metal shell containing a bundle of small-diameter tubes. The hot gas flows over the outside of the tubes. Liquid water at 25°C is fed to the boiler in a ratio 0.200 mol feedwater/mol hot gas and flows inside the tubes. Heat is transferred from the hot gas through the tube walls to the water, causing the gas to cool and the water to heat to its boiling point and evaporate to form saturated steam at 5.0 bar. The steam may be used for heating or power generation in the plant or as the feed to another process unit. The gas leaving the boiler is flared (burned) and discharged to the atmosphere. The boiler operates adiabatically—all the heat transferred from the gas goes into the water, as opposed to some of it leaking through the outside boiler wall. The flowchart for an assumed basis of 1.00 mol feed gas is shown below.



What is the temperature of the exiting gas?

SOLUTION

Since no material balances are required in this problem, we may proceed directly to the energy balance, which for this adiabatic unit reduces to

$$\Delta H = \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i = 0$$

We do not write $\Delta \dot{H}$ and \dot{n}_i since a quantity (1 mol feed gas) and not a flow rate has been assumed as a basis of calculation.

(Exercise: What assumptions have been made in writing the energy balance?)

References: CO(g, 500°C, 1 atm), CO₂(g, 500°C, 1 atm), H₂O(l, triple point)

Substance	n_{in}	\hat{H}_{in}	n_{out}	\hat{H}_{out}
CO	0.080 mol	0 kJ/mol	0.080 mol	\hat{H}_1 (kJ/mol)
CO ₂	0.920 mol	0 kJ/mol	0.920 mol	\hat{H}_2 (kJ/mol)
H ₂ O	0.00360 kg	\hat{H}_3 (kJ/kg)	0.00360 kg	\hat{H}_4 (kJ/kg)

The solution strategy will be to calculate $\hat{H}_1(T)$ and $\hat{H}_2(T)$ by integrating the heat capacity formulas of Table B.2 from the reference temperature (500°C) to the unknown T at the gas outlet, look up \hat{H}_3 and \hat{H}_4 in the steam tables, substitute for \hat{H}_1 through \hat{H}_4 in the energy balance, and solve the resulting equation for T using a spreadsheet.

Note the following points about the enthalpy table.

- We chose the reference states for CO and CO₂ as the gas inlet temperature and 1 atm. We assume ideal gas behavior so that deviations of the pressure from 1 atm have no effect on enthalpies, and accordingly set the inlet enthalpies of the gas species equal to zero.
- We will find the enthalpies of the feedwater and product steam in the steam tables. Knowing this, we chose the reference state for the steam tables (liquid water at the triple point) as our reference for water, and knowing that the enthalpies in the steam tables are in kJ/kg, we list the quantity of water in kg ($m = 0.200 \text{ mol H}_2\text{O} \times 0.0180 \text{ kg/mol} = 0.00360 \text{ kg}$).
- We will integrate the heat capacity formulas of Table B.2 for CO and CO₂ even though enthalpies for those species are listed in Table B.8, since we do not know the temperature at which to look them up.

The specific enthalpies are

$$\begin{aligned}\hat{H}_1 &= \int_{500^\circ\text{C}}^T (C_p)_{\text{CO}} dT \\ &= \int_{500^\circ\text{C}}^T (0.02895 + 0.4110 \times 10^{-5}T + 0.3548 \times 10^{-8}T^2 - 2.220 \times 10^{-12}T^3) dT\end{aligned}$$

$$\begin{aligned}\hat{H}_2 &= \int_{500^\circ\text{C}}^T (C_p)_{\text{CO}_2} dT \\ &= \int_{500^\circ\text{C}}^T (0.03611 + 4.223 \times 10^{-5}T - 2.887 \times 10^{-8}T^2 + 7.464 \times 10^{-12}T^3) dT\end{aligned}$$

$$\hat{H}_3 = \hat{H}[\text{H}_2\text{O(l, }25^\circ\text{C, 5 bar)}] \approx 105 \text{ kJ/kg} \quad (\text{Table B.5: neglect effect of pressure on } \hat{H})$$

$$\hat{H}_4 = \hat{H}[\text{H}_2\text{O(v, 5 bar, sat'd)}] = 2747.5 \text{ kJ/kg} \quad (\text{Table B.6})$$

Integrating the expressions for \hat{H}_1 and \hat{H}_2 and substituting the resulting expressions and the values of \hat{H}_3 and \hat{H}_4 into the energy balance ($\Delta H = 0$) yields the following equation:

$$1.672 \times 10^{-12}T^4 - 0.8759 \times 10^{-8}T^3 + 1.959 \times 10^{-5}T^2 + 0.03554T - 12.16 = 0$$

The problem is to find the value of T ($^{\circ}\text{C}$) that satisfies this equation. The calculations can be done conveniently using a spreadsheet. Let us first estimate the solution by neglecting all terms

of second-order and higher in T :

$$0.03554T - 12.16 = 0 \implies T \approx 342^{\circ}\text{C}$$

We will use this estimate as the first guess in the spreadsheet solution. In one cell (Cell A1 in this illustration) we insert the initial guess for T (342°C), and in the next cell (B1) we insert the formula for the fourth-order polynomial on the left-hand side of the equation to be solved:

Cell A1: 342

Cell B1: = 1.672e-12 * A1^4 - 0.8759e-8 * A1^3 + 1.959e-5 * A1^2 + 0.3554 * A1 - 12.16

(In some spreadsheet programs, the exponentiation function would be ** instead of $^{\wedge}$.) The two cells of the spreadsheet would then display the following values:

	A	B
1	342	1.9585

Our goal is to find the value in Cell A1 that drives the value in Cell B1 to zero. We could perform the trial-and-error search manually, but if the spreadsheet program has a goalseek tool (most programs do), we would select it and use it to perform the search automatically (Set Cell B1 to 0 by varying Cell A1). Either way, at the end of the search the two cells would display values close to those shown below:

	A	B
1	299.0654	3.791E - 06

The solution is therefore $T = 299^{\circ}\text{C}$. The heat transferred from the specified quantity of gas as it cools from 500°C to 299°C goes to convert the specified amount of feedwater into steam.

Lecture 28

8.4 Phase Change Operations

8.4a Latent heats

Latent heats for the two most commonly encountered phase changes are defined as follows:

1. **Heat of fusion** (or heat of melting). $\Delta\hat{H}_m(T, P)$ is the specific enthalpy difference between the solid and liquid forms of a species at T and P .⁷
2. **Heat of vaporization.** $\Delta\hat{H}_v(T, P)$ is the specific enthalpy difference between the liquid and vapor forms of a species at T and P .

EXAMPLE 8.4-1

Heat of Vaporization

At what rate in kilowatts must heat be transferred to a liquid stream of methanol at its normal boiling point to generate 1500 g/min of saturated methanol vapor?

SOLUTION

From Table B.1, $\Delta\hat{H}_v = 35.3 \text{ kJ/mol}$ at $T_{bp} = 64.7^\circ\text{C}$. The energy balance with potential and kinetic energy changes neglected is

$$\dot{Q} = \dot{\Delta H} = \dot{n} \Delta\hat{H}_v$$



$$\dot{Q} = \frac{1500 \text{ g CH}_3\text{OH}}{\text{min}} \left| \begin{array}{c} 1 \text{ mol} \\ 32.0 \text{ g CH}_3\text{OH} \end{array} \right| \frac{35.3 \text{ kJ}}{\text{mol}} \left| \begin{array}{c} 1 \text{ min} \\ 60 \text{ s} \end{array} \right| \frac{1 \text{ kW}}{1 \text{ kJ/s}} = \boxed{27.6 \text{ kW}}$$

EXAMPLE 8.4-2

Vaporization and Heating

One hundred g-moles per hour of liquid *n*-hexane at 25°C and 7 bar is vaporized and heated to 300°C at constant pressure. Neglecting the effect of pressure on enthalpy, estimate the rate at which heat must be supplied.

SOLUTION

An energy balance yields

$$\dot{Q} = \Delta\dot{H} \quad (\dot{W}_s = \Delta\dot{E}_p = 0, \Delta\dot{E}_k \approx 0)$$

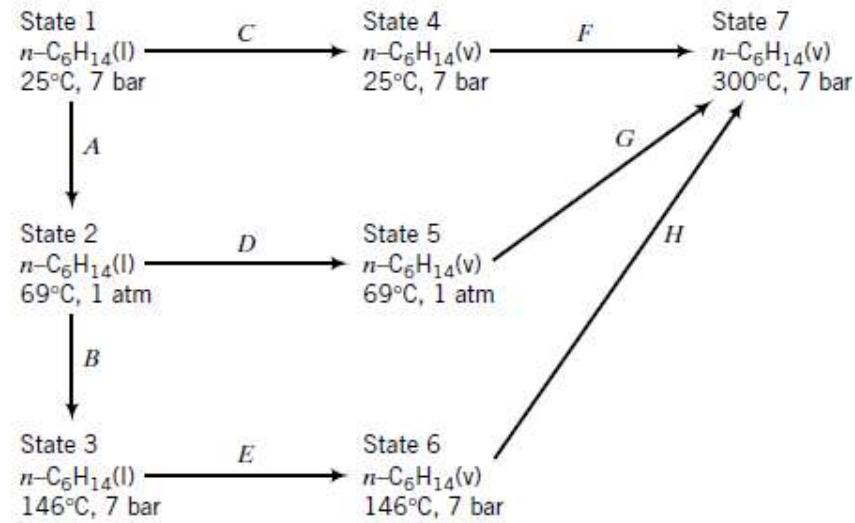
Therefore an evaluation of $\Delta\dot{H}$ will yield the desired value of \dot{Q} .

From Figure 6.1-4, the temperature at which the vapor pressure of *n*-hexane is 7 bar (104 psia) is approximately 295°F (146°C), and this is therefore the temperature at which the vaporization actually occurs. However, Table B.1 lists a value of $\Delta\hat{H}_v$ at the normal boiling point of *n*-hexane,

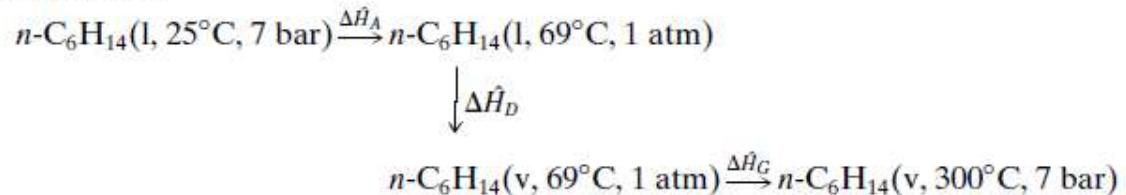
$$\Delta\hat{H}_v = 28.85 \text{ kJ/mol at } 69^\circ\text{C}$$

We must therefore find a path that takes hexane from a liquid to a vapor at 69°C, rather than at the true vaporization temperature of 146°C.

As noted previously, the change in enthalpy associated with a process may be determined from any convenient path as long as the initial and final points of the chosen path correspond to those of the process. The diagram shown on the following page illustrates several possible paths from liquid hexane at 25°C to hexane vapor at 300°C.



If we knew $\Delta\hat{H}_v$ at 146°C , we would follow path $ABEH$ (the true process path) to evaluate the overall $\Delta\hat{H}$ for the process, or if we knew $\Delta\hat{H}_v$ at 25°C , we would follow path CF , which would require only two calculations. Since we have $\Delta\hat{H}_v$ at 69°C , we must follow path ADG , which includes vaporization at that temperature.



$$\Delta\hat{H}_A = \dot{V} \Delta P + \int_{25^\circ\text{C}}^{69^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_{14}(\text{l})} dT \quad (\text{from Equation 8.3-10b})$$

Table B.1 \implies SG = 0.659 \implies $\rho = 0.659 \text{ kg/L}$
 Table B.2 \implies $C_p = 0.2163 \text{ kJ}/(\text{mol}\cdot^\circ\text{C})$
 $\downarrow 1 \text{ atm} = 1.013 \text{ bar}$

$$\Delta\hat{H}_A = \frac{1 \text{ L}}{0.659 \text{ kg}} \left| \begin{array}{l} (1.013 - 7.0) \text{ bar} \\ 1000 \text{ mol} \end{array} \right| \frac{86.17 \text{ kg}}{0.08314 \text{ L}\cdot\text{bar}/(\text{mol}\cdot\text{K})}$$

$$+ \frac{0.2163 \text{ kJ}}{\text{mol}\cdot^\circ\text{C}} \left| \begin{array}{l} (69 - 25)^\circ\text{C} \end{array} \right| = (-0.0782 + 9.517) \text{ kJ/mol} = 9.44 \text{ kJ/mol}$$

$$\Delta\hat{H}_D = (\Delta\hat{H}_v)_{\text{C}_6\text{H}_{14}}(69^\circ\text{C}, 1 \text{ atm}) = 28.85 \text{ kJ/kg}$$

$$\Delta\hat{H}_G = \int_{69^\circ\text{C}}^{300^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_{14}(v)} dT \quad (\text{from Equation 8.3-10a})$$

$$\downarrow C_p[\text{kJ}/(\text{mol}\cdot^\circ\text{C})] = 0.13744 + 40.85 \times 10^{-5}T - 23.92 \times 10^{-8}T^2 + 57.66 \times 10^{-12}T^3$$

$$\Delta\hat{H}_G = 47.1 \text{ kJ/mol}$$

For the overall process

$$\dot{Q} = \Delta\dot{H} = \dot{n}(\text{mol/h})\Delta\hat{H}(\text{kJ/mol})$$

$$\downarrow \Delta\dot{H} = \Delta\hat{H}_A + \Delta\hat{H}_D + \Delta\hat{H}_G = 85.5 \text{ kJ/mol}$$

$$\dot{Q} = \frac{100 \text{ mol}}{\text{h}} \left| \begin{array}{l} 85.5 \text{ kJ} \\ \text{mol} \end{array} \right| \frac{1 \text{ h}}{3600 \text{ s}} \left| \begin{array}{l} 1 \text{ kW} \\ 1 \text{ kJ/s} \end{array} \right| = \boxed{2.38 \text{ kW}}$$

Notice that the pressure change term in the first step ($\hat{V} \Delta P = -0.0782 \text{ kJ/mol}$) accounts for less than 0.1% of the overall process enthalpy change. We will generally neglect the effects of pressure changes on $\Delta\hat{H}$ unless ΔP is on the order of 50 atm or more.

8.4b Estimation and Correlation of Latent Heats

A simple formula for estimating a standard heat of vaporization ($\hat{\Delta H}_v$ at the normal boiling point) is **Trouton's rule**:

$$\begin{aligned}\hat{\Delta H}_v(\text{kJ/mol}) &\approx 0.088T_b(\text{K}) \quad (\text{nonpolar liquids}) \\ &\approx 0.109T_b(\text{K}) \quad (\text{water, low molecular weight alcohols})\end{aligned}\quad (8.4-3)$$

where T_b is the normal boiling point of the liquid. Trouton's rule provides an estimate of $\hat{\Delta H}_v$ accurate to within 30%. Another formula that provides roughly 2% accuracy is **Chen's equation**:

$$\hat{\Delta H}_v(\text{kJ/mol}) = \frac{T_b[0.0331(T_b/T_c) - 0.0327 + 0.0297 \log_{10} P_c]}{1.07 - (T_b/T_c)} \quad (8.4-4)$$

where T_b and T_c are the normal boiling point and critical temperature in kelvin and P_c is the critical pressure in atmospheres.

A formula for approximating a standard heat of fusion is

$$\begin{aligned}\hat{\Delta H}_m(\text{kJ/mol}) &\approx 0.0092T_m(\text{K}) \quad (\text{metallic elements}) \\ &\approx 0.0025T_m(\text{K}) \quad (\text{inorganic compounds}) \\ &\approx 0.050T_m(\text{K}) \quad (\text{organic compounds})\end{aligned}\quad (8.4-5)$$

Latent heats of vaporization may be estimated from vapor pressure data by using the Clausius–Clapeyron equation, which was discussed in Section 6.1b.

$$\ln p^* = -\frac{\hat{\Delta H}_v}{RT} + B \quad (8.4-6)$$

Provided that $\hat{\Delta H}_v$ is constant over the range of temperatures encompassed by the vapor pressure data, the latent heat of vaporization may be determined from a plot of $\ln p^*$ versus $1/T$. (See Example 6.1-1.)

In many cases the latent heat of vaporization varies considerably with temperature, invalidating Equation 8.4-6. It is then necessary to use the **Clapeyron equation**, from which Equation

8.4-6 was derived. From Equation 6.1-2,

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta \hat{H}_v}{R} \quad (8.4-7)$$

The heat of vaporization at a temperature T may be estimated from vapor pressure data by plotting $\ln p^*$ versus $1/T$, determining $[d(\ln p^*)/d(1/T)]$ at the temperature of interest as the slope of the tangent to the curve, and solving Equation 8.4-7 for $\Delta \hat{H}_v$. The slope may be determined graphically or by any of several numerical differentiation techniques outlined in texts on numerical analysis.

A procedure for calculating the latent heat of vaporization at one temperature from a known value at any other temperature was presented in Section 8.4a. The technique outlined is rigorous but time-consuming, and it requires heat capacity data that might not be available for the substance of interest. A useful approximation for estimating $\Delta \hat{H}_v$ at T_2 from a known value at T_1 is **Watson's correlation**:

$$\Delta \hat{H}_v(T_2) = \Delta \hat{H}_v(T_1) \left(\frac{T_c - T_2}{T_c - T_1} \right)^{0.38} \quad (8.4-8)$$

where T_c is the critical temperature of the substance.

EXAMPLE 8.4-3***Estimation of a Heat of Vaporization***

The normal boiling point of methanol is 337.9 K, and the critical temperature of this substance is 513.2 K. Estimate the heat of vaporization of methanol at 200°C.

SOLUTION

We first use Trouton's rule to estimate $\hat{\Delta H}_v$ at the normal boiling point, and then Watson's correlation to estimate $\hat{\Delta H}_v(473\text{ K})$ from $\hat{\Delta H}_v(337.9\text{ K})$.

Trouton's Rule $\hat{\Delta H}_v(337.9\text{ K}) = (0.109)(337.9) = 36.8\text{ kJ/mol}$

(The measured value is 35.3 kJ/mol. Chen's equation yields 37.2 kJ/mol, so in this unusual case Trouton's rule provides the better estimate.)

Watson's Correlation

Using the value of $\hat{\Delta H}_v$ estimated by Trouton's rule

$$\hat{\Delta H}_v(473\text{ K}) = 36.8 \left(\frac{513.2 - 473}{513.2 - 337.9} \right)^{0.38} = \boxed{21.0\text{ kJ/mol}}$$

The measured value is 19.8 kJ/mol.

Lecture 29

8.4c Energy Balances on Processes Involving Phase Changes

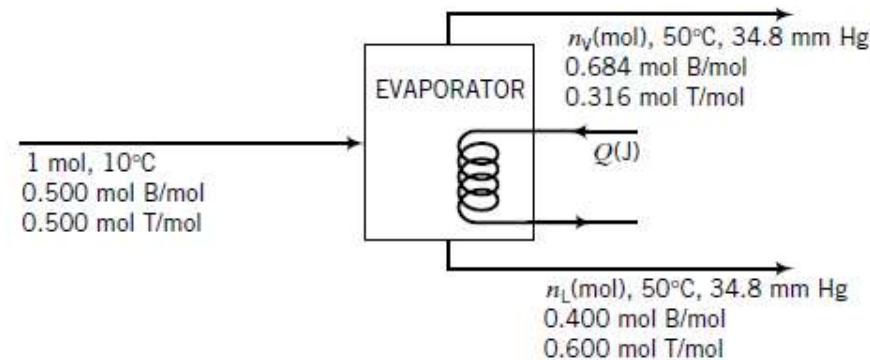
EXAMPLE 8.4-4

Partial Vaporization of a Mixture

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole% B, and the vapor product is 68.4 mole% B. How much heat must be transferred to the mixture per g-mole of feed?

SOLUTION

Basis: 1 mol Feed



We start with a degree-of-freedom analysis:

3 unknown variables (n_V, n_L, Q)
–2 material balances
–1 energy balance
= 0 degrees of freedom

We could count each specific enthalpy to be determined as an unknown variable, but then we would also count the equations for each of them in terms of heat capacities and latent heats, leaving the number of degrees of freedom unchanged.

We next determine n_V and n_L from material balances, and then Q from an energy balance.

$$\begin{array}{ll} \text{Total Mass Balance:} & 1.00 \text{ mol} = n_V + n_L \\ \text{Benzene Balance:} & 0.500 \text{ mol} = 0.684n_V + 0.400 n_L \end{array} \left. \begin{array}{l} 1.00 \text{ mol} = n_V + n_L \\ 0.500 \text{ mol} = 0.684n_V + 0.400 n_L \end{array} \right\} \Rightarrow \begin{array}{l} n_V = 0.352 \text{ mol} \\ n_L = 0.648 \text{ mol} \end{array}$$

The energy balance for this process has the form $Q = \Delta H$. An enthalpy table for the process appears as follows:

References: B(l, 10°C, 1 atm), T(l, 10°C, 1 atm)

Substance	n_{in} mol	\hat{H}_{in} (kJ/mol)	n_{out} (mol)	\hat{H}_{out} (kJ/mol)
B(l)	0.500	0	0.259	\hat{H}_1
T(l)	0.500	0	0.389	\hat{H}_2
B(v)	—	—	0.241	\hat{H}_3
T(v)	—	—	0.111	\hat{H}_4

The values of n_{out} were determined from the known mole fractions of benzene and toluene in the outlet streams and the calculated values of n_V and n_L . We do not know the feed-stream pressure and so we assume that ΔH for the change from 1 atm to P_{feed} is negligible, and since the process is not running at an unusually low temperature or high pressure, we neglect the effects of pressure

on enthalpy in the calculations of \hat{H}_1 through \hat{H}_4 . The heat capacity and latent heat data needed to calculate the outlet enthalpies are obtained from Tables B.1 and B.2.

The formulas and values of the unknown specific enthalpies are given below. Convince yourself that the formulas represent $\Delta\hat{H}$ for the transitions from the reference states to the process states.

$$\hat{H}_1 = \int_{10^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_6(\text{l})} dT = 5.332 \text{ kJ/mol}$$

$$\hat{H}_2 = \int_{10^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_7\text{H}_8(\text{l})} dT = 6.340 \text{ kJ/mol}$$

$$\begin{aligned}\hat{H}_3 &= \int_{10^\circ\text{C}}^{80.1^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_6(\text{l})} dT + (\Delta\hat{H}_v)_{\text{C}_6\text{H}_6}(80.1^\circ\text{C}) + \int_{80.1^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_6(\text{v})} dT \\ &= 37.52 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\hat{H}_4 &= \int_{10^\circ\text{C}}^{110.62^\circ\text{C}} (C_p)_{\text{C}_7\text{H}_8(\text{l})} dT + (\Delta\hat{H}_v)_{\text{C}_7\text{H}_8}(110.62^\circ\text{C}) + \int_{110.62^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_7\text{H}_8(\text{v})} dT \\ &= 42.93 \text{ kJ/mol}\end{aligned}$$

The energy balance is

$$Q = \Delta H = \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i \implies Q = 17.7 \text{ kJ}$$

8.4d Psychrometric Charts

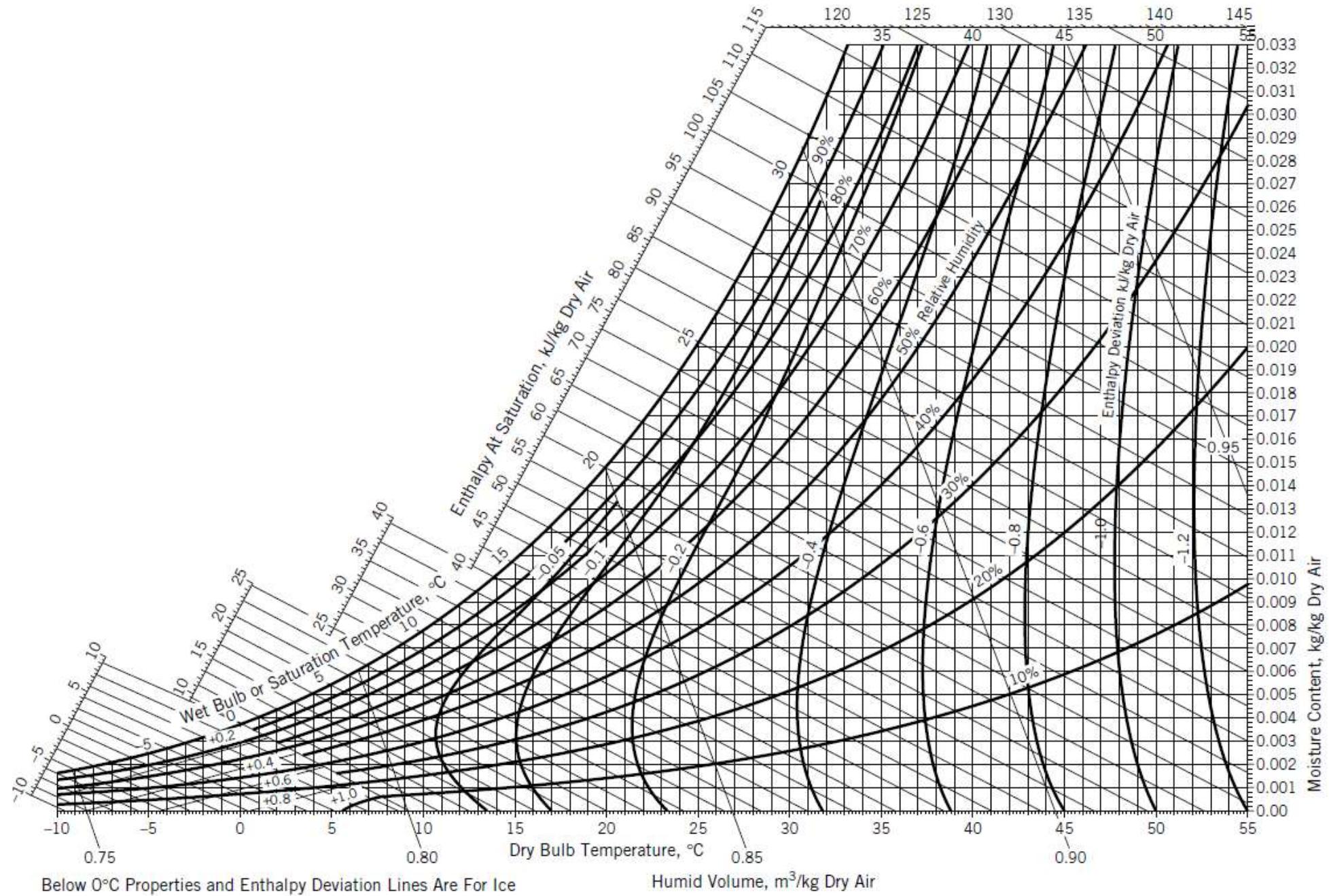
On a **psychrometric chart** (or **humidity chart**) several properties of a gas–vapor mixture are cross-plotted, providing a concise compilation of a large quantity of physical property data. The most common of these charts—that for the air–water system at 1 atm—is used extensively in the analysis of humidification, drying, and air-conditioning processes.

A psychrometric chart in SI units for the air–water system at 1 atm is shown in Figure 8.4-1, and a second chart in American engineering units is shown in Figure 8.4-2. Charts that cover wider temperature ranges are given on pp. 12-4 through 12-7 of *Perry's Chemical Engineers' Handbook* (see footnote 5).

The following paragraphs define and describe the different properties of humid air at 1 atm that appear on the psychrometric chart. Once you know the values of any two of these properties, you can use the chart to determine the values of the others. We will use the abbreviation DA for dry air.

- **Dry-bulb temperature, T** —the abscissa of the chart. This is the air temperature as measured by a thermometer, thermocouple, or other conventional temperature-measuring instrument.
- **Absolute humidity, h_a [kg H₂O(v)/kg DA]** (called **moisture content** on Figure 8.4-1)—the ordinate of the chart.

This ratio can easily be calculated from or converted to the mass fraction of water. If, for example, the absolute humidity is 0.0150 kg H₂O/kg DA, then for every kilogram of dry air there is 0.015 kg of water vapor, for a total of 1.015 kg. The mass fraction of water is $(0.0150 \text{ kg H}_2\text{O}) / (1.015 \text{ kg humid air}) = 0.0148 \text{ kg H}_2\text{O/kg}$.



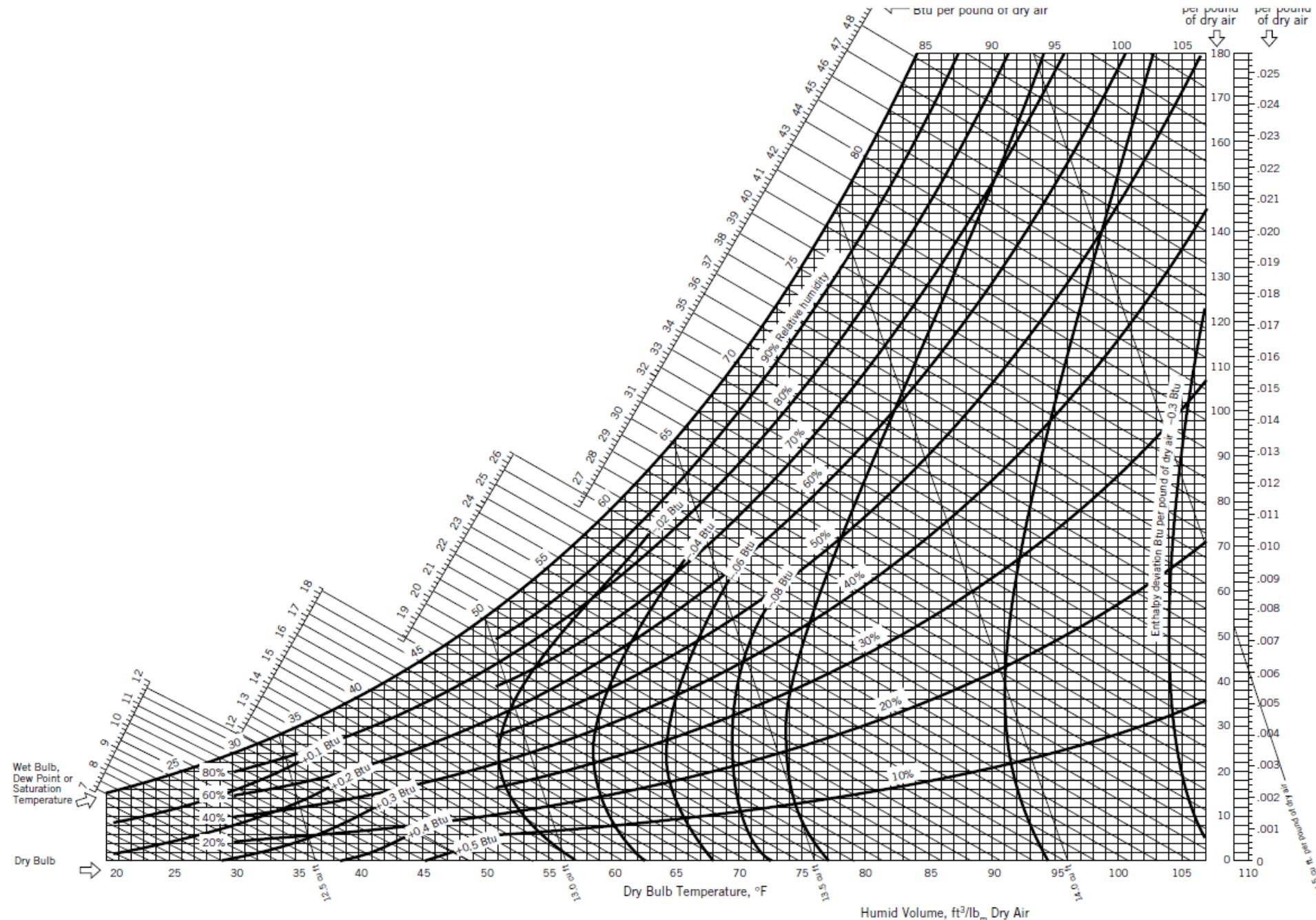


Figure 8.4-2 Psychrometric chart—American Engineering units. Reference states: H_2O (L, 32°F, 1 atm), dry air (0°F, 1 atm). (Reprinted with permission of Carrier Corporation.)

- **Relative humidity**, $h_r = [100 \times p_{\text{H}_2\text{O}} / p_{\text{H}_2\text{O}}^*(T)]$.

Curves on the psychrometric chart correspond to specified values of h_r (100%, 90%, 80%, etc.). The curve that forms the left boundary of the chart is the **100% relative humidity curve**, also known as the **saturation curve**.

- **Dew point**, T_{dp} —the temperature at which humid air becomes saturated if it is cooled at constant pressure.

The dew point of humid air at a given point on the psychrometric chart can easily be determined. For example, locate the point on Figure 8.4-1 corresponding to air at 29°C and 20% relative humidity. Cooling this air at constant pressure ($= 1 \text{ atm}$) corresponds to moving horizontally (at constant absolute humidity) to the saturation curve. T_{dp} is the temperature at the intersection, or 4°C. (Verify this statement.)

- **Humid volume**, \hat{V}_H ($\text{m}^3/\text{kg DA}$).

The humid volume is the volume occupied by 1 kg of dry air plus the water vapor that accompanies it. Lines of constant humid volume on the psychrometric chart are steep and have negative slopes. On Figure 8.4-1, humid volume lines are shown corresponding to 0.75, 0.80, 0.85, and 0.90 m^3/kg dry air.

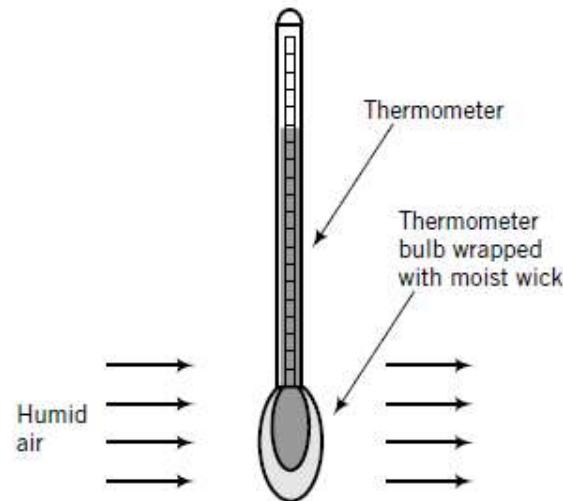
To determine the volume of a given mass of wet air using the psychrometric chart, you must first determine the corresponding mass of dry air from the absolute humidity, then multiply this mass by \hat{V}_H . Suppose, for example, you wish to know the volume occupied by 150 kg of humid air at $T = 30^\circ\text{C}$ and $h_r = 30\%$. From Figure 8.4-1, $h_a = 0.0080 \text{ kg H}_2\text{O(v)/kg DA}$ and $\hat{V}_H \approx 0.87 \text{ m}^3/\text{kg DA}$. The volume may then be calculated as

$$V = \frac{150 \text{ kg humid air}}{1.008 \text{ kg humid air}} \left| \frac{1.00 \text{ kg DA}}{\text{kg DA}} \right| \left| \frac{0.87 \text{ m}^3}{\text{kg DA}} \right| = 129 \text{ m}^3$$

(In this calculation, we used the fact that if the absolute humidity is 0.008 kg H₂O/kg DA, then 1 kg DA is accompanied by 0.008 kg water for a total of 1.008 kg humid air.)

- **Wet-bulb temperature, T_{wb} .**

This quantity is best defined in terms of how it is measured. A porous material like cloth or cotton is soaked in water and wrapped around the bulb of a thermometer to form a *wick*, and the thermometer is placed in a stream of flowing air, as in the figure shown below.⁹ Evaporation of water from the wick into the flowing air is accompanied by a transfer of heat from the bulb, which in turn causes a drop in the bulb temperature and hence in the thermometer reading.¹⁰ Provided that the wick remains moist, the bulb temperature falls to a certain value and remains there. The final temperature reading is the wet-bulb temperature of the air flowing past the wick.



The wet-bulb temperature of humid air depends on both the dry-bulb temperature and the moisture content of the air. If the air is saturated (100% relative humidity), no water evaporates from the wick, and the wet-bulb and dry-bulb temperatures are the same. The lower the humidity, the greater the difference between the two temperatures.

The humid air conditions that correspond to a given wet-bulb temperature fall on a straight line on the psychrometric chart, called a **constant wet-bulb temperature line**. The constant wet-bulb temperature lines for air–water at 1 atm appear on Figures 8.4-1 and 8.4-2 as lines with negative slopes extending beyond the saturation curve that are less steep than the lines of constant humid volume. The value of T_{wb} corresponding to a given line can be read at the intersection of the line with the saturation curve.

For example, suppose you wish to determine the wet-bulb temperature of air at 30°C (dry bulb) with a relative humidity of 30%. Locate the point on Figure 8.4-1 at the intersection of the vertical line corresponding to $T = 30^\circ\text{C}$ and the curve corresponding to $h_r = 30\%$. The diagonal line through the point is the constant wet-bulb temperature line for air at the given condition. Follow that line upward to the left until you reach the saturation curve. The temperature value you read on the curve (or vertically down from it on the abscissa) is the wet-bulb temperature of the air. You should get a value of 18°C. This means that if you wrap a wet wick around a thermometer bulb and blow air with $T = 30^\circ\text{C}$ and $h_r = 30\%$ past the bulb, the thermometer reading will drop and eventually stabilize at 18°C.

- *Specific enthalpy of saturated air*

The diagonal scale above the saturation curve on the psychrometric chart shows the enthalpy of a unit mass (1 kg or 1 lb_m) of dry air plus the water vapor it contains at saturation. The reference states are liquid water at 1 atm and 0°C (32°F) and dry air at 1 atm and 0°C (Figure 8.4-1) or 0°F (Figure 8.4-2). To determine the enthalpy from the chart, follow the constant wet-bulb temperature line from the saturation curve at the desired temperature to the enthalpy scale.

For example, saturated air at 25°C and 1 atm—which has an absolute humidity $h_a = 0.0202 \text{ kg H}_2\text{O/kg DA}$ —has a specific enthalpy of 76.5 kJ/kg DA. (Verify these values of both h_a and \hat{H} on Figure 8.4-1.) The enthalpy is the sum of the enthalpy changes for 1.00 kg dry air and 0.0202 kg water going from their reference conditions to 25°C. The computation shown below uses heat capacity data from Table B.2 for air and data from the steam tables (Table B.5) for water.

$$1.00 \text{ kg DA}(0^\circ\text{C}) \rightarrow 1 \text{ kg DA}(25^\circ\text{C})$$



$$\Delta H_{\text{air}} = (1.00 \text{ kg DA}) \left(\frac{1 \text{ kmol}}{29.0 \text{ kg}} \right) \left[\int_0^{25} C_{p,\text{air}}(T) dT \right] \left(\frac{\text{kJ}}{\text{kmol}} \right) = 25.1 \text{ kJ}$$

$$0.0202 \text{ kg H}_2\text{O(l, }0^\circ\text{C)} \rightarrow 0.0202 \text{ kg H}_2\text{O(v, }25^\circ\text{C)}$$



$$\Delta H_{\text{water}} = (0.0202 \text{ kg}) [\hat{H}_{\text{H}_2\text{O(v, }25^\circ\text{C)}} - \hat{H}_{\text{H}_2\text{O(l, }0^\circ\text{C)}}] \left(\frac{\text{kJ}}{\text{kg}} \right) = 51.4 \text{ kJ}$$

$$\hat{H} = \frac{(\Delta H_{\text{air}} + \Delta H_{\text{water}})(\text{kJ})}{1.00 \text{ kg DA}} = \frac{(25.1 + 51.4) \text{ kJ}}{1.00 \text{ kg DA}} = 76.5 \text{ kJ/kg DA}$$

- **Enthalpy deviation**

The remaining curves on the psychrometric chart are almost vertical and convex to the left, with labeled values (on Figure 8.4-1) of -0.05 , -0.1 , -0.2 , and so on. (The units of these numbers are kJ/kg DA). These curves are used to determine the enthalpy of humid air that is not saturated. The procedure is as follows: (a) locate the point on the chart corresponding to air at its specified condition; (b) interpolate to estimate the enthalpy deviation at this point;

(c) follow the constant wet-bulb temperature line to the enthalpy scale above the saturation curve, read the value on that scale, and add the enthalpy deviation to it.

For example, air at 35°C and 10% relative humidity has an enthalpy deviation of about -0.52 kJ/kg DA . The specific enthalpy of saturated air at the same wet-bulb temperature is 45.0 kJ/kg DA . (Verify both of these numbers.) The specific enthalpy of the humid air at the given condition is therefore $(45.0 - 0.52) \text{ kJ/kg DA} = 44.5 \text{ kJ/kg DA}$.

The basis for the construction of the psychrometric chart is the Gibbs phase rule (Section 6.3a), which states that specifying a certain number of the intensive variables (temperature, pressure, specific volume, specific enthalpy, component mass or mole fractions, etc.) of a system automatically fixes the value of the remaining intensive variables. Humid air contains one phase and two components,¹¹ so that from Equation 6.2-1 the number of degrees of freedom is

$$F = 2 + 2 - 1 = 3$$

Specifying three intensive variables therefore fixes all other system properties. If the system pressure is fixed at 1 atm, then all other properties may be plotted on a two-dimensional plot, such as those shown in Figures 8.4-1 and 8.4-2.

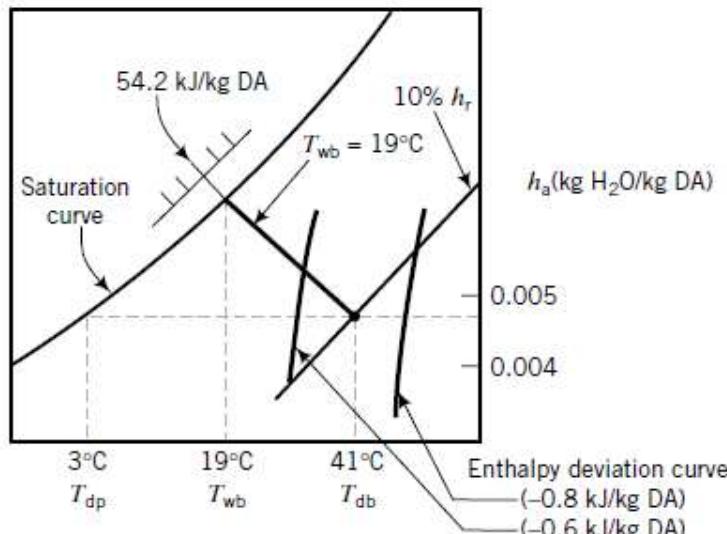
EXAMPLE 8.4-5

The Psychrometric Chart

Use the psychrometric chart to estimate (1) the absolute humidity, wet-bulb temperature, humid volume, dew point, and specific enthalpy of humid air at 41°C and 10% relative humidity, and (2) the amount of water in 150 m³ of air at these conditions.

SOLUTION

Following is a sketch of the psychrometric chart (Figure 8.4-1) showing the given state of the air:



1. Reading from the chart,

$$h_a \approx 0.0048 \text{ kg H}_2\text{O/kg DA}$$

$$T_{wb} = 19^\circ\text{C}$$

$$\hat{V}(\text{m}^3/\text{kg DA}) \approx 0.897 \text{ (curve not shown)}$$

The dew point is the temperature at which the air with the given water content would be saturated at the same total pressure (1 atm) and is therefore located at the intersection of the horizontal constant absolute humidity line ($h_a = 0.0048$) and the saturation curve, or

$$T_{dp} = 3^\circ\text{C}$$

The specific enthalpy of saturated air at $T_{wb} = 19^\circ\text{C}$ is 54.2 kJ/kg DA. Since the point corresponding to 41°C and 10% relative humidity falls roughly midway between the enthalpy deviation curves corresponding to -0.6 kJ/kg and -0.8 kJ/kg , we may calculate \hat{H} as

$$\hat{H} = (54.2 - 0.7) \text{ kJ/kg DA}$$



$$\boxed{\hat{H} = 53.5 \text{ kJ/kg DA}}$$

2. **Moles of humid air.** From Figure 8.4-1, the humid volume of the air is $0.897 \text{ m}^3/\text{kg DA}$. We therefore calculate

$$\begin{array}{c|c|c|c} 150 \text{ m}^3 & 1.00 \text{ kg DA} & 0.0048 \text{ kg H}_2\text{O} & \\ \hline & 0.897 \text{ m}^3 & 1.00 \text{ kg DA} & \boxed{0.803 \text{ kg H}_2\text{O}} \end{array}$$

The psychrometric chart can be used to simplify the solution of material and energy balance problems for constant-pressure air–water systems, at the expense of some precision. Note the following points:

1. Heating or cooling humid air at temperatures above the dew point corresponds to horizontal movement on the psychrometric chart. The ordinate on the chart is the ratio $\text{kg H}_2\text{O}/\text{kg dry air}$, which does not change as long as no condensation occurs.
2. If superheated humid air is cooled at 1 atm, the system follows a horizontal path to the left on the chart until the saturation curve (dew point) is reached; thereafter, the gas phase follows the saturation curve.
3. Since the psychrometric chart plots the mass ratio $\text{kg H}_2\text{O}/\text{kg dry air}$ rather than the mass fraction of water, it is usually convenient to assume a quantity of dry air in a feed or product stream as a basis of calculation if the chart is to be used in the solution.

EXAMPLE 8.4-6

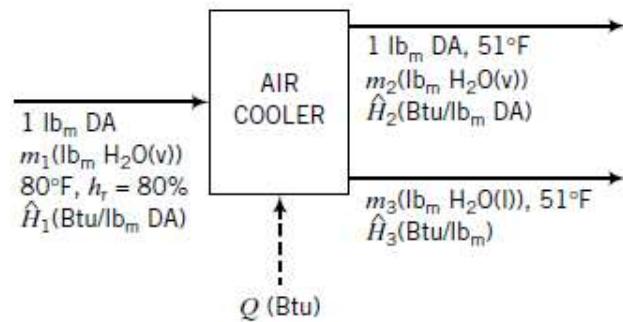
Material and Energy Balances on an Air Conditioner

Air at 80°F and 80% relative humidity is cooled to 51°F at a constant pressure of 1 atm. Use the psychrometric chart to calculate the fraction of the water that condenses and the rate at which heat must be removed to deliver 1000 ft³/min of humid air at the final condition.

SOLUTION

Basis: 1 lb_m Dry Air¹²

A flowchart for the process is shown below. By convention we show heat transfer (Q) into the process unit, but since the air is being cooled we know that Q will be negative.



Note: In labeling the outlet gas stream, we have implicitly written a balance on dry air.

Degree-of-Freedom Analysis

7 unknowns ($m_1, m_2, m_3, \hat{H}_1, \hat{H}_2, \hat{H}_3, Q$)

- 1 material balance (H_2O —dry air is already balanced on the chart)
 - 2 absolute humidities from psychrometric chart (for inlet and outlet air)
 - 2 enthalpies from psychrometric chart (for inlet and outlet air)
 - 1 enthalpy of condensate (from known heat capacity of liquid water)
 - 1 energy balance
-
- = 0 degrees of freedom

Point 1

$$\left. \begin{array}{l} 80^{\circ}\text{F} \\ 80\% \text{ RH} \end{array} \right\} \xrightarrow{\text{Figure 8.4-2}} \begin{array}{l} h_a = 0.018 \text{ lb}_m \text{ H}_2\text{O/lb}_m \text{ DA} \\ \hat{H}_1 = 38.8 \text{ Btu/lb}_m \text{ DA} \end{array}$$
$$m_1 = \frac{1.0 \text{ lb}_m \text{ DA}}{\left| \begin{array}{c} 0.018 \text{ lb}_m \text{ H}_2\text{O} \\ \text{lb}_m \text{ DA} \end{array} \right|} = 0.018 \text{ lb}_m \text{ H}_2\text{O}$$

Point 2

$$\left. \begin{array}{l} 51^{\circ}\text{F} \\ \text{Saturated} \end{array} \right\} \xrightarrow{\text{Figure 8.4-2}} \begin{array}{l} h_a = 0.0079 \text{ lb}_m \text{ H}_2\text{O/lb}_m \text{ DA} \\ \hat{H}_2 = 20.9 \text{ Btu/lb}_m \text{ DA} \end{array}$$
$$m_2 = \frac{1.0 \text{ lb}_m \text{ DA}}{\left| \begin{array}{c} 0.0079 \text{ lb}_m \text{ H}_2\text{O} \\ \text{lb}_m \text{ DA} \end{array} \right|} = 0.0079 \text{ lb}_m \text{ H}_2\text{O}$$

Balance on H_2O

$$m_1 = m_2 + m_3$$

$$\begin{array}{c} \uparrow \\ m_1 = 0.018 \text{ lb}_m \\ \downarrow \\ m_2 = 0.0079 \text{ lb}_m \end{array}$$

$$m_3 = 0.010 \text{ lb}_m \text{ H}_2\text{O condensed}$$

Fraction $\text{H}_2\text{O Condensed}$

$$\frac{0.010 \text{ lb}_m \text{ condensed}}{0.018 \text{ lb}_m \text{ fed}} = \boxed{0.555}$$

Enthalpy of Condensate

Since the reference condition for water on Figure 8.4-2 is liquid water at 32°F, we must use the same condition to calculate \hat{H}_3 .



$$\Delta\hat{H} = \hat{H}_3 = 1.0 \frac{\text{Btu}}{\text{lb}_m \cdot ^\circ\text{F}} (51^\circ\text{F} - 32^\circ\text{F}) = 19.0 \text{ Btu/lb}_m \text{ H}_2\text{O}$$

Energy Balance

The open-system energy balance with W_s , ΔE_k , and ΔE_p set equal to zero is

$$Q = \Delta H = \sum_{\text{out}} m_i \hat{H}_i - \sum_{\text{in}} m_i \hat{H}_i$$

(There are no dots over the extensive variables in this equation because the basis of calculation is an amount, not a flow rate.) The enthalpy table for the process is shown below. Since (1) the enthalpies (\hat{H}_i) of the humid air streams are obtained from the psychrometric chart in Btu/lb_m dry air, and (2) the mass units of m_i and \hat{H}_i must cancel when the two are multiplied in the energy balance, the tabulated values of m_i for these streams must be in lb_m dry air.

References: Dry air (DA) (g, 0°F, 1 atm), H₂O (l, 32°F, 1 atm)

Substance	m_{in}	\hat{H}_{in}	m_{out}	\hat{H}_{out}
Humid air	1.0 lb _m DA	38.8 Btu/lb _m DA	1.0 lb _m DA	20.9 Btu/lb _m DA
H ₂ O(l)	—	—	0.010 lb _m	19 Btu/lb _m

The references were of necessity chosen to be the ones used to generate the psychrometric chart.

Substituting the values in the table into the energy balance yields

$$Q = \Delta H = \frac{1.0 \text{ lb}_m \text{ DA}}{\text{lb}_m \text{ DA}} \left| \begin{array}{c} 20.9 \text{ Btu} \\ + 0.010 \text{ lb}_m \text{ H}_2\text{O(l)} \end{array} \right| \frac{19 \text{ Btu}}{\text{lb}_m \text{ H}_2\text{O}} - \frac{1.0 \text{ lb}_m \text{ DA}}{\text{lb}_m \text{ DA}} \left| \begin{array}{c} 38.8 \text{ Btu} \end{array} \right|$$
$$= -17.7 \text{ Btu}$$

To calculate the cooling requirement for 1000 ft³/min of delivered air, we must first determine the volume of delivered air corresponding to our assumed basis and scale the calculated value of Q by the ratio (1000 ft³/min)/(V_{basis}). From the psychrometric chart, for humid air saturated at 51°F

$$\hat{V}_H = 13.0 \text{ ft}^3/\text{lb}_m \text{ DA}$$



$$V_{\text{basis}} = \frac{1.0 \text{ lb}_m \text{ DA}}{\text{lb}_m \text{ DA}} \left| \begin{array}{c} 13.0 \text{ ft}^3 \end{array} \right| = 13.0 \text{ ft}^3$$



$$\dot{Q} = \frac{-17.7 \text{ Btu}}{13.0 \text{ ft}^3} \left| \begin{array}{c} 1000 \text{ ft}^3/\text{min} \\ \hline 13.0 \text{ ft}^3 \end{array} \right| = \boxed{-1360 \text{ Btu/min}}$$

Lecture 30

8.5 Mixing and Solution

Suppose you mix 1 mol of pure liquid sulfuric acid with water at a specified temperature and pressure and then cool the mixture at constant pressure to bring it back to the initial temperature. The energy balance for this constant-pressure process is

$$Q = \Delta H = H_{\text{H}_2\text{SO}_4(\text{aq})} - (H_{\text{H}_2\text{SO}_4(\text{l})} + H_{\text{H}_2\text{O}})$$

where ΔH —the difference between the enthalpy of the solution at the specified temperature and pressure and the total enthalpy of the pure solute and solvent at the same T and P —is the *heat of solution* at that temperature and pressure. For the sulfuric acid dilution, we know $Q < 0$ (the container must be cooled to keep the solution temperature from rising) and so it follows that ΔH —the heat of solution—is negative for this process.

An **ideal mixture** is one for which the heat of mixing or solution is negligible and so $H_{\text{mixture}} \approx \sum n_i \hat{H}_i$, where n_i is the amount of mixture component i and \hat{H}_i is the specific enthalpy of the pure component at the temperature and pressure of the mixture. Up to now in this text, we have assumed ideal mixture behavior for all mixtures and solutions. This assumption works well for nearly all gas mixtures and for liquid mixtures of similar compounds (such as mixtures of paraffins or of aromatics), but for other mixtures and solutions—such as aqueous solutions of strong acids or bases or certain gases (such as hydrogen chloride) or solids (such as sodium hydroxide)—heats of solution should be included in energy balance calculations. This section outlines the required procedures.

8.5a Heats of Solution and Mixing

The **heat of solution** $\Delta\hat{H}_s(T,r)$ is defined as the change in enthalpy for a process in which 1 mole of a solute (gas or solid) is dissolved in r moles of a liquid solvent at a constant temperature T . As r becomes large, $\Delta\hat{H}_s$ approaches a limiting value known as the **heat of solution at infinite dilution**. The **heat of mixing** has the same meaning as the heat of solution when the process involves mixing two fluids rather than dissolving a gas or solid in a liquid.

Perry's Chemical Engineers' Handbook (see footnote 5) on pp. 2-201 through 2-204 gives heats of solution of various substances in water at either 18°C or “room temperature,” which is roughly 25°C. *Caution:* The values given in the *Handbook* are *negatives* of the heats of solution ($-\Delta\hat{H}_s$), although they are not identified as such explicitly.

As an illustration of how to use these data, suppose you wish to calculate ΔH for a process in which 2 mol of potassium cyanide (KCN) is dissolved in 400 mol of water at 18°C. First, calculate the moles of solvent per mole of solute:

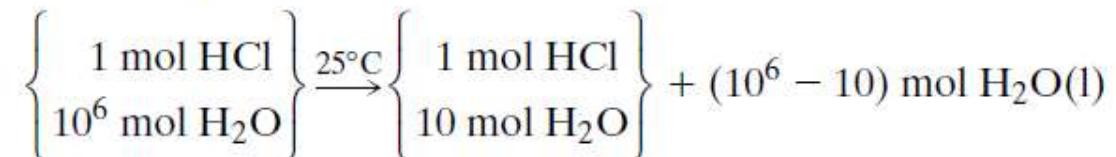
$$r = 400/2 = 200 \text{ mol H}_2\text{O/mol KCN}$$

The value of $-\Delta\hat{H}_s$ (18°C, $r = 200$) is listed as -3.0 kcal/mol (meaning per mol of KCN dissolved). The total enthalpy change is therefore

$$\Delta H = n \Delta\hat{H}_s = \frac{2.0 \text{ mol KCN}}{\text{mol KCN}} \left| \begin{array}{c} 3.0 \text{ kcal} \\ \hline \end{array} \right. = +6.0 \text{ kcal}$$

Table B.11 lists values of the heats of solution at 25°C of HCl(g) and NaOH(s) in water, and the heat of mixing at 25°C of H₂SO₄(l) and water. Heats of solution such as those given in Table B.11 may be used to determine directly the specific enthalpies of solutions at 25°C relative to the pure solute and solvent at this temperature. Another common choice of reference conditions, however, is the pure solvent and an infinitely dilute solution at 25°C.

Consider, for example, a hydrochloric acid solution for which $r = 10$ moles H₂O/mole HCl. From Table B.11, the specific enthalpy of this solution relative to pure HCl(g) and H₂O(l) at 25°C is $\Delta\hat{H}_s(r = 10) = -69.49$ kJ/mol HCl. Now, the enthalpy of the solution relative to H₂O(l) and a highly dilute solution of HCl (say, $r = 10^6$ moles H₂O/mole HCl) is the enthalpy change for the isothermal process



We may evaluate this enthalpy change using any convenient reference state—in particular, taking pure HCl(g) and H₂O(l) at 25°C as references. In view of the latter choice, \hat{H} for the $(10^6 - 10)$ moles of pure water equals zero, and the enthalpy change for the process is therefore

$$\begin{aligned}\Delta\hat{H} &= \Delta\hat{H}_s(r = 10) - \Delta\hat{H}_s(r = \infty) \\ &= (-69.49 + 75.14) \text{ kJ/mol HCl} = 5.65 \text{ kJ/mol HCl}\end{aligned}$$

In general, the enthalpy of a solution containing r moles H₂O/mole solute is for reference states of pure solute and solvent at 25°C and 1 atm

$$\boxed{\hat{H} = \Delta\hat{H}_s(r)} \quad (8.5-1)$$

and for reference states of pure solvent and an infinitely dilute solution at 25°C and 1 atm

$$\boxed{\hat{H} = \Delta\hat{H}_s(r) - \Delta\hat{H}_s(\infty)} \quad (8.5-2)$$

Note again that these enthalpies are expressed per mole of *solute*, not per mole of solution.

Table B.11 Integral Heats of Solution and Mixing at 25°C

r (mol H ₂ O/mol solute)	$(\Delta\hat{H}_s)_{\text{HCl(g)}}$ kJ/mol HCl	$(\Delta\hat{H}_s)_{\text{NaOH(s)}}$ kJ/mol NaOH	$(\Delta\hat{H}_m)_{\text{H}_2\text{SO}_4}$ kJ/mol H ₂ SO ₄
0.5	—	—	-15.73
1	-26.22	—	-28.07
1.5	—	—	-36.90
2	-48.82	—	-41.92
3	-56.85	-28.87	-48.99
4	-61.20	-34.43	-54.06
5	-64.05	-37.74	-58.03
10	-69.49	-42.51	-67.03
20	-71.78	-42.84	—
25	—	—	-72.30
30	-72.59	-42.72	—
40	-73.00	-42.59	—
50	-73.26	-42.51	-73.34
100	-73.85	-42.34	-73.97
200	-74.20	-42.26	—
500	-74.52	-42.38	-76.73
1 000	-74.68	-42.47	-78.57
2 000	-74.82	-42.55	—
5 000	-74.93	-42.68	-84.43
10 000	-74.99	-42.72	-87.07
50 000	-75.08	-42.80	—
100 000	-75.10	—	-93.64
500 000	—	—	-95.31
∞	-75.14	-42.89	-96.19

8.5b Balances on Dissolution and Mixing Processes

When setting up an energy balance on a process that involves forming, concentrating, or diluting a solution for which the heat of solution or mixing cannot be neglected, prepare an inlet-outlet enthalpy table considering the solution as a single substance and the pure components at 25°C as reference states. To calculate the enthalpy of the solution at a temperature $T \neq 25^\circ\text{C}$, first calculate its enthalpy at 25°C from tabulated heat of solution data, then add the enthalpy change for the heating or cooling of the solution from 25°C to T . The enthalpy change for the latter step should be calculated from tabulated solution heat capacities if they are available [e.g., if they are listed on pp. 2-184 and 2-185 of *Perry's Chemical Engineers' Handbook* (see footnote 5)]; otherwise, use the average heat capacity determined using Equation 8.3-13 for liquid mixtures or the heat capacity of the pure solvent for dilute solutions.

EXAMPLE 8.5-1

Production of Hydrochloric Acid

Hydrochloric acid is produced by absorbing gaseous HCl (hydrogen chloride) in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and H₂O(l) at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl(aq) at 40°C.

SOLUTION

Hydrochloric acid is produced by absorbing gaseous HCl (hydrogen chloride) in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and H₂O(l) at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl(aq) at 40°C.

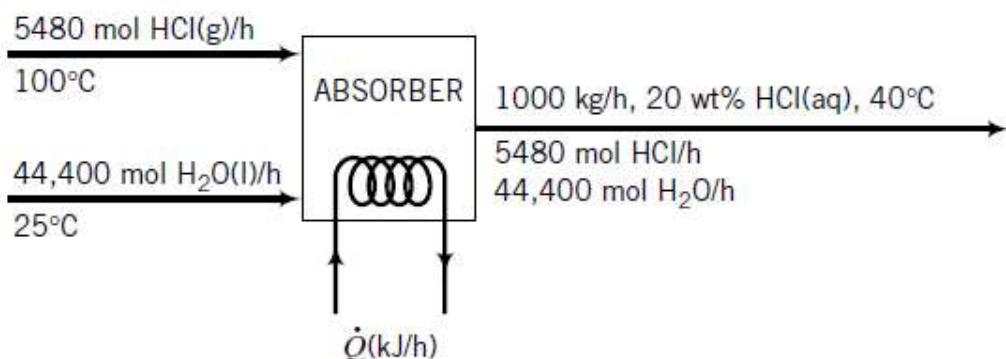
It is advisable to determine the molar amounts or flow rates of the components of all feed and product solutions before drawing and labeling the flowchart. In this case

1000 kg/h of 20.0 wt% HCl(aq)



$$\dot{n}_{\text{HCl}} = \frac{1000 \text{ kg}}{\text{h}} \left| \begin{array}{c} 0.200 \text{ kg HCl} \\ \text{kg} \end{array} \right| \frac{10^3 \text{ mol}}{36.5 \text{ kg HCl}} = 5480 \text{ mol HCl/h}$$

$$\dot{n}_{\text{H}_2\text{O}} = \frac{1000 \text{ kg}}{\text{h}} \left| \begin{array}{c} 0.800 \text{ kg H}_2\text{O} \\ \text{kg} \end{array} \right| \frac{10^3 \text{ mol}}{18.0 \text{ kg H}_2\text{O}} = 44,400 \text{ mol H}_2\text{O/h}$$

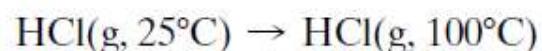


The enthalpy table for the process is shown below. As usual, physical property data valid at $P = 1$ atm are used and the effects on enthalpy of any pressure differences that may occur in the process are neglected. Note that the value of \dot{n} for the product solution is the molar flow rate of the *solute* (HCl) rather than the solution, since the enthalpy will be determined in kJ/mol solute.

References: HCl(g), H₂O(l) at 25°C and 1 atm

Substance	\dot{n}_{in}	\hat{H}_{in}	\dot{n}_{out}	\hat{H}_{out}
HCl(g)	5480 mol HCl	\hat{H}_1 (kJ/mol HCl)	—	—
H ₂ O(l)	44,400 mol H ₂ O	0	—	—
HCl(aq)	—	—	5480 mol HCl	\hat{H}_2 (kJ/mol HCl)

Calculate \hat{H}_1 and \hat{H}_2



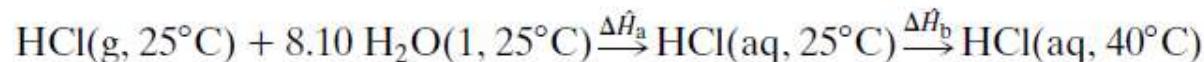
$$\hat{H}_1 = \Delta\hat{H} = \int_{25^\circ\text{C}}^{100^\circ\text{C}} C_p \, dT$$

\Downarrow
C_p for HCl(g) from Table B.2

$$\hat{H}_1 = 2.178 \text{ kJ/mol}$$

For the product solution,

$$r = (44,400 \text{ mol H}_2\text{O}) / (5480 \text{ mol HCl}) = 8.10$$



$$\Delta\hat{H}_a = \Delta\hat{H}_s(25^\circ\text{C}, r = 8.1) \xrightarrow{\text{Table B.11}} -67.4 \text{ kJ/mol HCl}$$

The heat capacities of aqueous hydrochloric acid solutions are listed on p. 2-184 of *Perry's Chemical Engineers' Handbook* (see footnote 5) as a function of the mole fraction of HCl in the solution, which in our problem is

$$\frac{5480 \text{ mol HCl/h}}{(5480 + 44,400) \text{ mol/h}} = 0.110 \text{ mol HCl/mol}$$



$$C_p = \frac{0.73 \text{ kcal}}{\text{kg}\cdot^\circ\text{C}} \left| \frac{1000 \text{ kg solution}}{5480 \text{ mol HCl}} \right| \frac{4.184 \text{ kJ}}{\text{kcal}} = 0.557 \frac{\text{kJ}}{\text{mol HCl}\cdot^\circ\text{C}}$$

$$\Delta\hat{H}_b = \int_{25^\circ\text{C}}^{40^\circ\text{C}} C_p dT = 8.36 \text{ kJ/mol HCl}$$



$$\hat{H}_2 = \Delta\hat{H}_a + \Delta\hat{H}_b = (-67.4 + 8.36) \text{ kJ/mol HCl} = -59.0 \text{ kJ/mol HCl}$$

Energy Balance

$$\begin{aligned} \dot{Q} &= \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i \\ &= (5480 \text{ mol HCl/h})(-59.0 \text{ kJ/mol HCl}) - (5480 \text{ mol HCl/h})(2.178 \text{ kJ/mol HCl}) \\ &= \boxed{-3.35 \times 10^5 \text{ kJ/h}} \end{aligned}$$

Heat must be transferred out of the absorber at a rate of 335,000 kJ/h to keep the product temperature from rising above 40°C.

Lecture 31

8.5c Enthalpy-Concentration Charts – Single Liquid Phase

Energy balance calculations on liquid-phase systems involving mixtures can be cumbersome when heats of mixing are significant. The calculations can be simplified for binary (two-component) systems by using an **enthalpy-concentration chart**, a plot of specific enthalpy versus mole fraction (or mole percent) or mass fraction (or weight percent) of one component. An \hat{H} - x chart for aqueous solutions of sulfuric acid at several temperatures is shown in Figure 8.5-1. The reference conditions for the plotted enthalpies are pure liquid H_2SO_4 at 77°F and liquid water at 32°F.

Example 8.5-1

The points on the isotherms of Figure 8.5-1 were determined using the procedure outlined in the last section. Suppose, for example, you wish to calculate the specific enthalpy (Btu/lb_m) of a 40 wt% sulfuric acid solution at 120°F. If you know the heat of mixing of sulfuric acid at 77°F, the process path you would follow would be to bring pure liquid water from its reference temperature of 32°F to 77°F (the sulfuric acid starts at 77°F and so does not require this step), mix the two liquids at 77°F, bring the product solution to 120°F, and calculate and add the enthalpy changes for each of these steps.

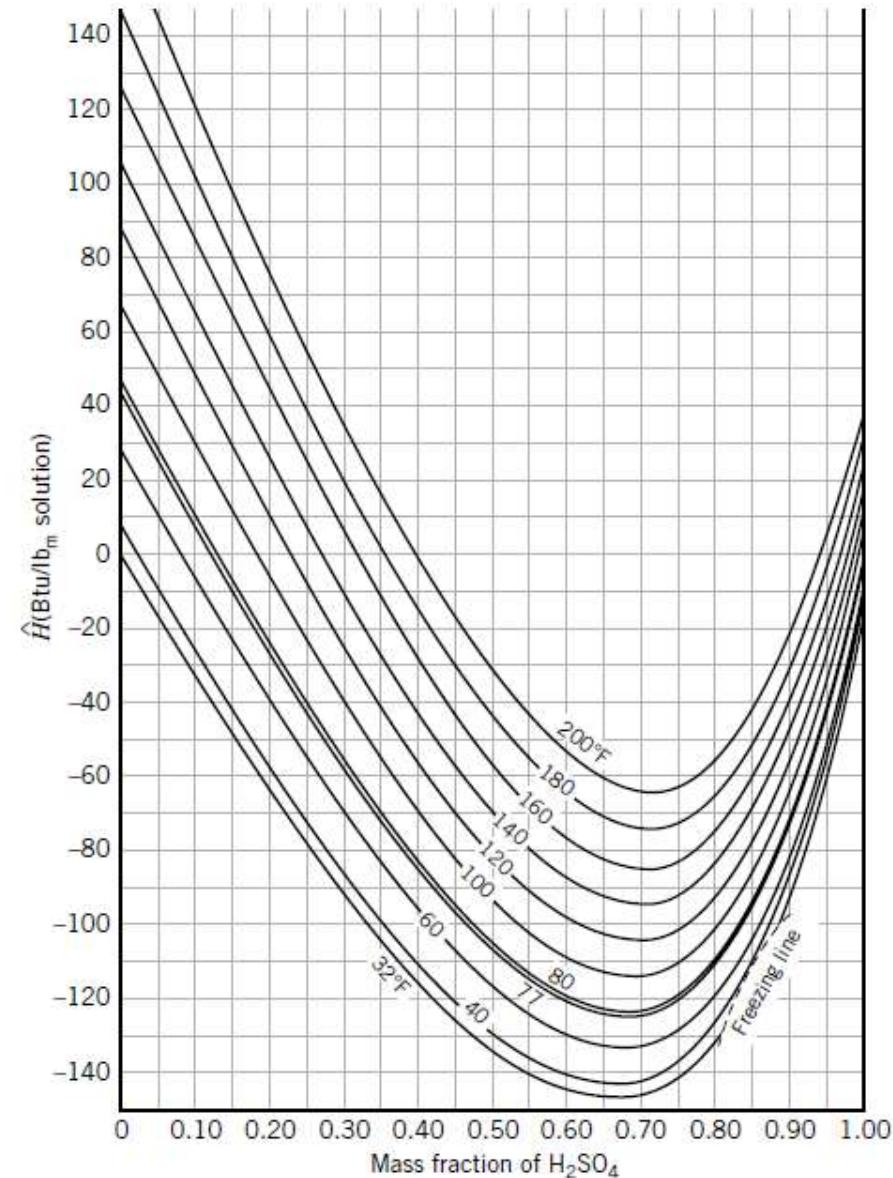


Figure 8.5-1 Enthalpy-concentration chart for $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$. (Redrawn from the data of W. D. Ross, *Chem. Eng. Progr.*, **43**:314, 1952.)

Solution

Basis: 1 lb_m solution (\Rightarrow 0.40 lb_m H₂SO₄ = 4.08×10^{-3} lb-mole, 0.60 lb_m H₂O = 3.33×10^{-2} lb-mole)

- 0.60 lb_m H₂O(l, 32°F) \rightarrow 0.60 lb_m H₂O (l, 77°F)

$$\Delta H_1(\text{Btu}) = (0.60 \text{ lb}_m \text{ H}_2\text{O}) \left[\int_{32^\circ\text{F}}^{77^\circ\text{F}} (C_p)_{\text{H}_2\text{O}} dT \right] \left(\frac{\text{Btu}}{\text{lb}_m} \right)$$

The heat capacity of liquid water is approximately 1 Btu/(lb_m·°F).

- 0.40 lb_m H₂SO₄(77°F) + 0.60 lb_m H₂O (77°F) \rightarrow 1.0 lb_m H₂SO₄ solution (aq, 77°F)

$$\Delta H_2(\text{Btu}) = (0.40 \text{ lb}_m \text{ H}_2\text{SO}_4) \left[\hat{H}_s \left(77^\circ\text{F}, r = 8.2 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole H}_2\text{SO}_4} \right) \left(\frac{\text{Btu}}{\text{lb}_m \text{ H}_2\text{SO}_4} \right) \right]$$

The heat of mixing can be determined from the data in Table B.11 to be -279 Btu/lb_m H₂SO₄.

- 1.0 lb_m H₂SO₄ solution (aq, 77°F) \rightarrow 1.0 lb_m H₂SO₄ solution (aq, 120°F)

$$\Delta H_3(\text{Btu}) = (1.0 \text{ lb}_m) \int_{77^\circ\text{F}}^{120^\circ\text{F}} (C_p)_{40\% \text{ H}_2\text{SO}_4(\text{aq})} dT$$

The heat capacity of the 40% sulfuric acid solution is roughly 0.67 Btu/(lb_m·°F).¹⁵

- $\hat{H}(40\% \text{ H}_2\text{SO}_4, 120^\circ\text{F}) = \frac{(\Delta H_1 + \Delta H_2 + \Delta H_3)(\text{Btu})}{1.0 \text{ lb}_m \text{ solution}} \approx \boxed{-56 \text{ Btu/lb}_m}$

(Verify that this is the value shown in Figure 8.5-1.)

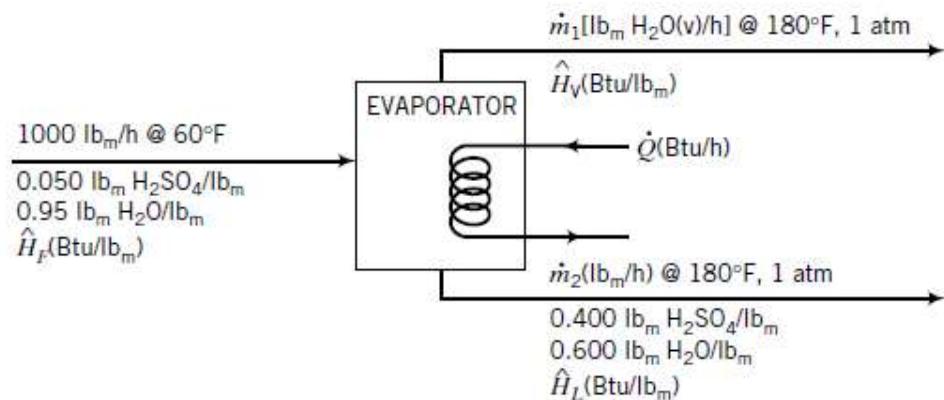
EXAMPLE 8.5-2

Concentration of an Aqueous H_2SO_4 Solution

A 5.0 wt% H_2SO_4 solution at 60°F is to be concentrated to 40.0 wt% by evaporation of water. The concentrated solution and water vapor emerge from the evaporator at 180°F and 1 atm. Calculate the rate at which heat must be transferred to the evaporator to process 1000 lb_m/h of the feed solution.

SOLUTION

Basis: Given Feed Rate of 5% Solution



$$H_2SO_4 \text{ Balance} \quad (0.050)(1000) \text{ lb}_m/\text{h} = 0.400\dot{m}_2 \implies \dot{m}_2 = 125 \text{ lb}_m/\text{h}$$

$$\text{Total Mass Balance} \quad 1000 \text{ lb}_m/\text{h} = \dot{m}_1 + \dot{m}_2 \implies \dot{m}_1 = 875 \text{ lb}_m/\text{h}$$

Reference States for Energy Balance $\text{H}_2\text{O(l, 32°F)}$, $\text{H}_2\text{SO}_4(\text{l, 77°F})$

From Figure 8.5-1:

$$\hat{H}_F = 10 \text{ Btu/lb}_m \quad (5\% \text{ H}_2\text{SO}_4 \text{ at } 60^\circ\text{F})$$

$$\hat{H}_L = -17 \text{ Btu/lb}_m \quad (40\% \text{ H}_2\text{SO}_4 \text{ at } 180^\circ\text{F})$$

The enthalpy of water vapor at 180°F and 1 atm relative to liquid water at 32°F may be obtained from the steam tables in *Perry's Chemical Engineers' Handbook* (see footnote 5) as

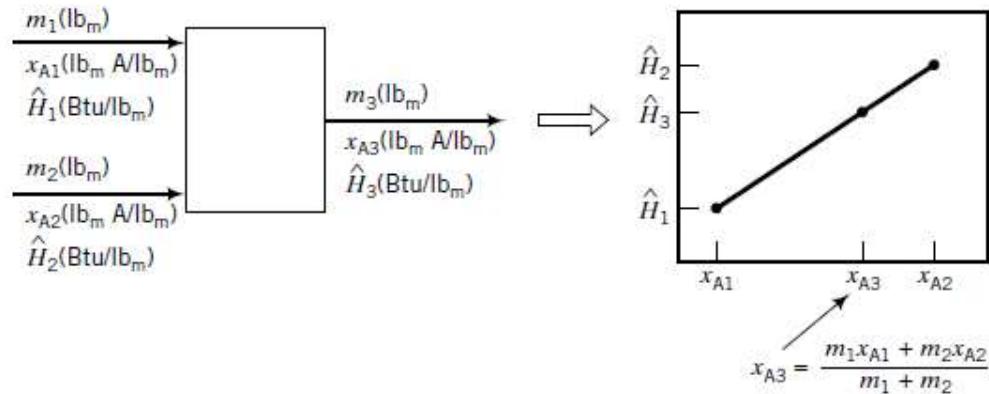
$$\hat{H}_V = 1138 \text{ Btu/lb}_m$$

Energy Balance

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} = \dot{m}_1\hat{H}_V + \dot{m}_2\hat{H}_L - (1000\text{lb}_m/\text{h})\hat{H}_F \\ &= [(875)(1138) + (125)(-17) - (1000)(10)] \text{ Btu/h} \\ &= \boxed{984,000 \text{ Btu/h}}\end{aligned}$$

Compare the ease of this computation with that of Example 8.5-1. Having the enthalpy-concentration chart eliminates the need for all of the hypothetical heating, cooling, and isothermal mixing steps that would normally be required to evaluate the total enthalpy change for the process.

Adiabatic mixing processes are particularly simple to analyze when an \hat{H} - x chart is available. Suppose x_A is the mass fraction of A in a mixture of two species, A and B, and that a mass m_1 of Solution 1 (x_{A1}, \hat{H}_1) is mixed adiabatically with a mass m_2 of Solution 2 (x_{A2}, \hat{H}_2). We will show that the condition of the product mixture, (x_{A3}, \hat{H}_3), is on a straight line on the \hat{H} - x chart between the points corresponding to the feed stream conditions.



To prove this result, we write a total mass balance, a material balance on species A, and an energy balance ($\Delta H = 0$ for this constant-pressure batch process):

Total Mass Balance:
$$m_1 + m_2 = m_3 \quad (\text{a})$$

A Balance:
$$m_1 x_{A1} + m_2 x_{A2} = m_3 x_{A3} \quad (\text{b})$$

\Downarrow Substitute for m_3 from (a), rearrange

$$m_1(x_{A3} - x_{A1}) = m_2(x_{A2} - x_{A3}) \quad (\text{c})$$

Energy Balance:
$$\Delta H = m_3 \hat{H}_3 - m_1 \hat{H}_1 - m_2 \hat{H}_2 = 0$$

\Downarrow Substitute for m_3 from (a), rearrange

$$m_1(\hat{H}_3 - \hat{H}_1) = m_2(\hat{H}_2 - \hat{H}_3) \quad (\text{d})$$

Dividing (d) by (c) yields

$$\frac{\hat{H}_3 - \hat{H}_1}{x_{A3} - x_{A1}} = \frac{\hat{H}_2 - \hat{H}_3}{x_{A2} - x_{A3}} \quad (\text{e})$$

Since the slope of the line segment from (x_{A1}, \hat{H}_1) to (x_{A3}, \hat{H}_3) (the left-hand side of this equation) equals the slope of the segment from (x_{A3}, \hat{H}_3) to (x_{A2}, \hat{H}_2) (the right-hand side) and the

segments have a point in common, the three points must lie on a straight line. The value of x_{A3} can be calculated from Equations a and b:

$$x_{A3} = \frac{m_1 x_{A1} + m_2 x_{A2}}{m_1 + m_2} \quad (8.5-3)$$

It follows that if two feed solutions of known masses and compositions ($m_i, x_i, i = 1, 2$) are mixed adiabatically and you have an \hat{H} - x chart, you may (i) calculate x_3 for the product mixture from Equation 8.5-3, (ii) draw a line connecting the points on the chart corresponding to the two feeds, and (iii) read the enthalpy and temperature of the product mixture from the point on the connecting line for which $x = x_3$.

EXAMPLE 8.5-3

Adiabatic Mixing

Pure water at 60°F is mixed with 100 g of an aqueous 80 wt% H₂SO₄ solution, also at 60°F. The mixing vessel is insulated well enough to be considered adiabatic.

1. If 250 g H₂O is mixed with the acid, what will the final solution temperature be?
2. What is the maximum attainable solution temperature and how much water must be added to achieve it?

SOLUTION

1. From Equation 8.5-3, the mass fraction of H₂SO₄ in the product solution is

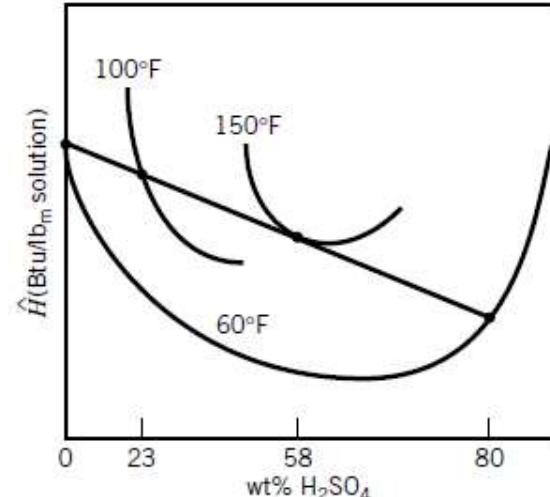
$$x_p = \frac{[(100)(0.80) + (250)(0)] \text{ g H}_2\text{SO}_4}{(100 + 250)\text{g}} = 0.23 \text{ g H}_2\text{SO}_4/\text{g}$$

A straight line on Figure 8.5-1 between points at ($x = 0, T = 60^\circ\text{F}$) and ($x = 0.80, T = 60^\circ\text{F}$) goes through the point ($x = 0.23, T \approx 100^\circ\text{F}$). (Verify this result.)

2. The line between ($x = 0, T = 60^\circ\text{F}$) and ($x = 0.80, T = 60^\circ\text{ F}$) passes through a temperature maximum at roughly ($x \approx 0.58, T \approx 150^\circ\text{F}$). (Verify.) From Equation 8.5-3,

$$0.58 = \frac{(100)(0.80) \text{ g} + (m_w)(0)}{100 \text{ g} + m_w} \implies m_w = 38 \text{ g H}_2\text{O}$$

The graphical construction of these solutions is illustrated below.



8.5d Use of the Enthalpy-Concentration System for a Two-Phase System

Enthalpy-concentration charts are particularly useful for two-component systems in which vapor and liquid phases are in equilibrium. The Gibbs phase rule (Equation 6.2-1) specifies that such a system has $(2 + 2 - 2) = 2$ degrees of freedom. If as before we fix the system pressure, then specifying only one more intensive variable—the system temperature, or the mass or mole fraction of either component in either phase—fixes the values of all other intensive variables in both phases. An \hat{H} - x diagram for the ammonia–water system at 1 atm is shown in Figure 8.5-2. The specific enthalpies of aqueous solutions and gaseous mixtures of ammonia and water are shown on the two curves on this figure.

Suppose the mass fraction of ammonia in a liquid solution of NH_3 and H_2O at 1 atm is specified to be 0.25. According to the phase rule, the system temperature and the mass fraction of NH_3 in the vapor phase are uniquely determined by these specifications. (*Verify.*) A **tie line** may therefore be drawn on the enthalpy-concentration chart from $x = 0.25$ on the liquid-phase curve to the corresponding point on the vapor-phase curve, which is at $y = 0.95$; and the tie line may be labeled with the corresponding temperature, 100°F. Several tie lines constructed in this manner are shown in Figure 8.5-2; once drawn, the lines may be used to determine the equilibrium composition and the specific enthalpy of each phase at a specified temperature.

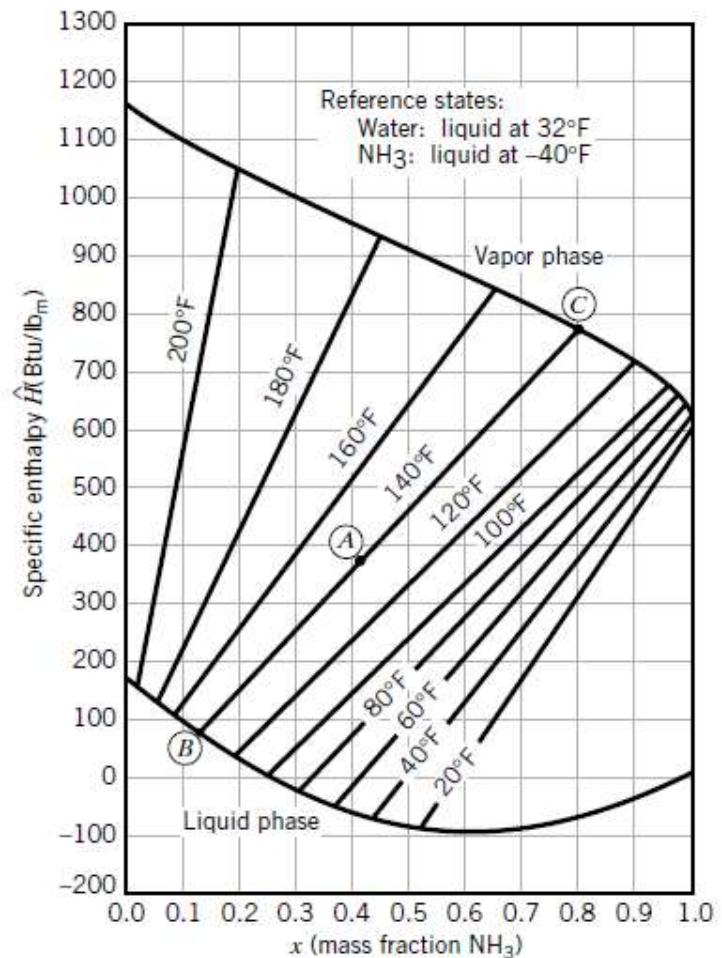


Figure 8.5-2 Enthalpy-concentration diagram for the ammonia–water system at 1 atm. (From G. G. Brown et al., *Unit Operations*, ©1950, Figure 551. Reprinted by permission of John Wiley & Sons.)

EXAMPLE 8.5-4

Use of the Enthalpy-Concentration Chart for a Two-Phase System

An aqueous ammonia solution is in equilibrium with a vapor phase in a closed system at 160°F and 1 atm. The liquid phase accounts for 95% of the total mass of the system contents. Use Figure 8.5-2 to determine the weight percent of NH₃ in each phase and the enthalpy of the system per unit mass of the system contents.

SOLUTION

The mass fractions of ammonia and specific enthalpies of each phase may be read from the intersections of the 160°F tie line with the vapor and liquid equilibrium curves on Figure 8.5-2.

Liquid Phase 8% NH₃, 92% H₂O; $\hat{H}_L = 110 \text{ Btu/lb}_m$

Vapor Phase 64% NH₃, 36% H₂O; $\hat{H}_V = 855 \text{ Btu/lb}_m$

Basis 1 lb_m total mass \implies 0.95 lb_m liquid, 0.05 lb_m vapor

$$\begin{aligned}\hat{H}(\text{Btu/lb}_m) &= \frac{0.95 \text{ lb}_m \text{ liquid}}{\text{lb}_m} \left| \frac{110 \text{ Btu}}{\text{lb}_m} \right. + \frac{0.05 \text{ lb}_m \text{ vapor}}{\text{lb}_m} \left| \frac{855 \text{ Btu}}{\text{lb}_m} \right. \\ &= \boxed{147 \text{ Btu/lb}_m}\end{aligned}$$

If the overall composition of a two-phase two-component system at a given temperature and pressure is known, the fraction of the system that is liquid or vapor may easily be determined from the enthalpy-concentration chart.

Suppose, for example, that a mixture of ammonia and water that is 40% NH₃ by mass is contained in a closed vessel at 140°F and 1 atm. Point A on Figure 8.5-2 corresponds to this condition. Since this point lies between the vapor and liquid equilibrium curves, the mixture separates into two phases whose compositions are found at the extremities of the 140°F tie line (points B and C).

In general, if F , L , and V are the total mass of the mixture, the mass of the liquid phase and the mass of the vapor phase, respectively, and x_F , x_L , and x_V are the corresponding mass fractions of NH₃, then

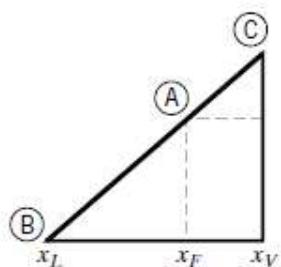
Total balance:
$$F = L + V \quad (8.5-4)$$

NH₃ balance:
$$x_F F = x_L L + x_V V \quad (8.5-5)$$

Substituting the expression of Equation 8.5-4 for F into Equation 8.5-5 and rearranging the result yields

$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L} \quad (8.5-6)$$

The tie line in question appears as shown below:



From the properties of similar triangles, the right side of Equation 8.5-6 equals the ratio of distances $\overline{AC}/\overline{AB}$. We have thus proved the following general rule: if A , B , and C are the points on a tie line corresponding to the total mixture, the liquid phase, and the vapor phase, respectively, and if F , L , and V are the corresponding masses, then the liquid-to-vapor mass ratio is

$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L} = \frac{\overline{AC}}{\overline{AB}} \quad (8.5-7)$$

This is the *lever rule*. It is also not difficult to prove that the mass fractions of the liquid and vapor phases are

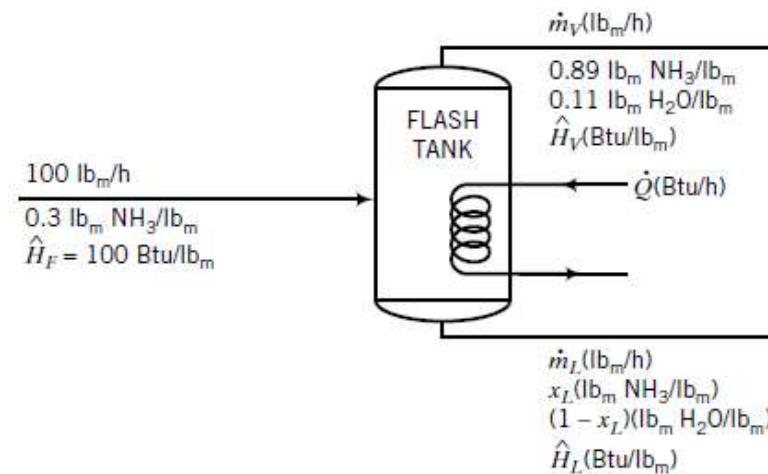
$$\frac{L}{F} = \frac{x_V - x_F}{x_V - x_L} = \frac{\overline{AC}}{\overline{BC}} \quad (8.5-8)$$

$$\frac{V}{F} = \frac{x_F - x_L}{x_V - x_L} = \frac{\overline{AB}}{\overline{BC}} \quad (8.5-9)$$

Once you have located the total mixture on the chart from a specified set of feed conditions, it becomes a simple matter to determine the compositions, enthalpies, and relative proportions of each phase, calculations that would take much more time in the absence of the chart.

EXAMPLE 8.5-5**Equilibrium Flash Vaporization**

A 30 wt% NH₃ solution at 100 psia is fed at a rate of 100 lb_m/h to a tank in which the pressure is 1 atm. The enthalpy of the feed solution relative to the reference conditions used to construct Figure 8.5-2 is 100 Btu/lb_m. The vapor composition is to be 89 wt% NH₃. Determine the temperature of the stream leaving the tank, the mass fraction of NH₃ in the liquid product, the flow rates of the liquid and vapor product streams, and the rate at which heat must be transferred to the vaporizer.

SOLUTION**Basis: 100 lb_m/h Feed**

From Figure 8.5-2,

$$x_V = 0.89 \text{ lb}_m \text{ NH}_3/\text{lb}_m$$

$$T = 120^\circ\text{F}$$

$$x_L = 0.185 \text{ lb}_m \text{ NH}_3/\text{lb}_m$$

$$\hat{H}_V = 728 \text{ Btu/lb}_m$$

$$\hat{H}_L = 45 \text{ Btu/lb}_m$$

From Equation 8.5-8

$$\frac{\dot{m}_L}{100 \text{ lb}_m/\text{h}} = \frac{x_V - x_F}{x_V - x_L}$$



$$\dot{m}_L = (100 \text{ lb}_m/\text{h}) \frac{0.89 - 0.30}{0.89 - 0.185} = \boxed{84 \text{ lb}_m/\text{h liquid product}}$$

$$\dot{m}_V = (100 - 84) \text{ lb}_m/\text{h} = \boxed{16 \text{ lb}_m/\text{h vapor product}}$$

Energy Balance $\dot{Q} = \Delta \dot{H} = \dot{m}_V \hat{H}_V + \dot{m}_L \hat{H}_L - 100 \hat{H}_F$

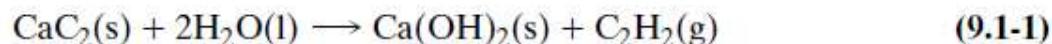
$$= [(16)(728) + (84)(45) - (100)(100)] \text{ Btu/h} = \boxed{5400 \text{ Btu/h}}$$

Chapter 9 - Balances on Reactive Processes

Lecture 32

9.1 Heats of Reaction

Consider the reaction between solid calcium carbide and liquid water to form solid calcium hydroxide and gaseous acetylene:



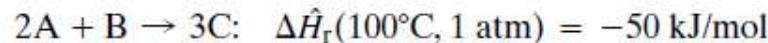
The expression *stoichiometric quantities of reactants* means molar amounts of the reactants numerically equal to their stoichiometric coefficients. For the calcium carbide reaction, stoichiometric quantities of the reactants in the SI system of units would be 1 mol of $\text{CaC}_2(\text{s})$ and 2 mol of $\text{H}_2\text{O}(\text{l})$. If stoichiometric quantities of the reactants are fed and the reaction proceeds to completion, both reactants would be completely consumed and stoichiometric quantities of the products would be formed. (Convince yourself.)

The heat of reaction (or enthalpy of reaction), $\hat{\Delta H_r}(T, P)$, is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely in a single reaction to form products at the same temperature and pressure. For example, the heat of the calcium carbide reaction at 25°C and 1 atm is

$$\hat{\Delta H_r}(25^\circ\text{C}, 1 \text{ atm}) = -125.4 \text{ kJ/mol} \quad (9.1-2)$$

Equations 9.1-1 and 9.1-2 together signify that if 1 mol of solid calcium carbide reacts completely with 2 mol of liquid water to form 1 mol of solid calcium hydroxide and 1 mol of gaseous acetylene, and the initial and final temperatures are both 25°C and the initial and final pressures are both 1 atm, then $H_{\text{products}} - H_{\text{reactants}} = -125.4 \text{ kJ}$. If the reaction is run under conditions such that the energy balance reduces to $Q = \Delta H$, then 125.4 kJ of heat must be transferred from the reactor in the course of the reaction. (Recall that a negative Q implies flow of heat out of the system.)

The units of $\Delta\hat{H}_r$ often cause confusion. For example, if the heat of a reaction is reported to be -50 kJ/mol , you might ask “per mol of what?” This difficulty is avoided if you recall that the given $\Delta\hat{H}_r$ applies to stoichiometric quantities of each species. For example,



means that the enthalpy change for the given reaction is

$$\frac{-50 \text{ kJ}}{2 \text{ mol A consumed}} = \frac{-50 \text{ kJ}}{1 \text{ mol B consumed}} = \frac{-50 \text{ kJ}}{3 \text{ mol C generated}}$$

If you knew, say, that 150 mol of C/s was generated in the given reaction at 100°C and 1 atm, you could calculate the associated enthalpy change as

$$\Delta\dot{H} = \frac{-50 \text{ kJ}}{3 \text{ mol C generated}} \left| \frac{150 \text{ mol C generated}}{\text{s}} \right. = -2500 \text{ kJ/s}$$

More generally, if ν_A is the stoichiometric coefficient of a reactant or reaction product A (positive if A is a product, negative if it is a reactant) and $n_{A,r}$ moles of A are consumed or generated at $T = T_0$ and $P = P_0$, then the associated enthalpy change is

$$\Delta H = \frac{\Delta\hat{H}_r(T_0, P_0)}{|\nu_A|} n_{A,r}$$

In Chapter 4, we defined the *extent of reaction*, ξ , as a measure of how far a reaction has proceeded. From Equation 4.6-3, this quantity is

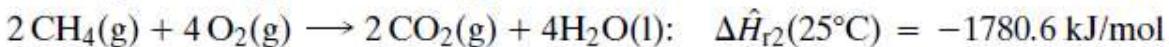
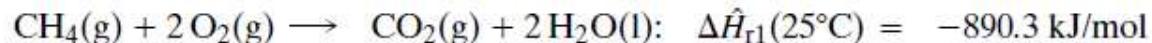
$$\xi = \frac{|n_{A,\text{out}} - n_{A,\text{in}}|}{|\nu_A|} = \frac{n_{A,r}}{|\nu_A|} \quad (9.1-3)$$

From the preceding two equations, it follows that if a reaction takes place at a temperature T_0 and pressure P_0 and the extent of reaction is ξ , the associated enthalpy change is

$$\Delta H = \xi \Delta\hat{H}_r(T_0, P_0) \quad (9.1-4)$$

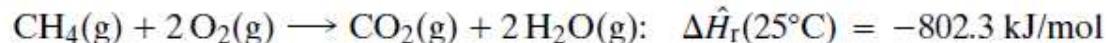
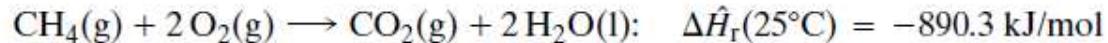
Following are several important terms and observations related to heats of reaction.

1. If $\Delta\hat{H}_r(T, P)$ is negative the reaction is **exothermic** at temperature T and pressure P , and if $\Delta\hat{H}_r(T, P)$ is positive the reaction is **endothermic** at T and P . These definitions of exothermic and endothermic are equivalent to the ones given earlier in terms of chemical bond strengths. (Convince yourself.)
2. *At low and moderate pressures, $\Delta\hat{H}_r(T, P)$ is nearly independent of pressure.* We will presume this independence in the balance of this chapter and write the heat of reaction as $\Delta\hat{H}_r(T)$.
3. *The value of the heat of a reaction depends on how the stoichiometric equation is written.* For example,



This result should seem reasonable to you if you look back at the definition of $\Delta\hat{H}_r$. The first line states that the combined enthalpy of 1 gram-mole of CO_2 plus 2 gram-moles of liquid water is 890.3 kJ lower than the combined enthalpy of 1 gram-mole of methane plus 2 gram-moles of oxygen at 25°C . Doubling the quantity of reactants at a given condition doubles the total enthalpy of the reactants at that condition, and similarly for the products. The difference between the product and reactant enthalpies in the second reaction (by definition, $\Delta\hat{H}_{r2}$) must therefore be double the enthalpy difference in the first reaction ($\Delta\hat{H}_{r1}$).

4. *The value of a heat of reaction depends on the states of aggregation (gas, liquid, or solid) of the reactants and products.* For example,



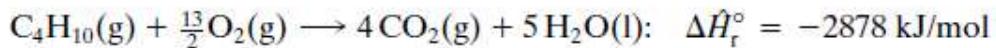
The only difference between the reactions is that the water formed is a liquid in the first one and a vapor in the second. Since enthalpy is a state function, the difference between the two heats of reaction must be the enthalpy change associated with the vaporization of 2 mol of water at 25°C —that is, $2\Delta\hat{H}_v(25^\circ\text{C})$.

5. The **standard heat of reaction**, $\Delta\hat{H}_r^\circ$, is the heat of reaction when both the reactants and products are at a specified reference temperature and pressure, usually (and always in this text) 25°C and 1 atm.

EXAMPLE 9.1-1

Calculation of Heats of Reaction

1. The standard heat of the combustion of *n*-butane vapor is



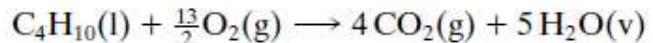
Calculate the rate of enthalpy change, $\Delta\dot{H}(\text{kJ/s})$, if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

2. What is the standard heat of the reaction



Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in *this* reaction and the reactants and products are all at 25°C.

3. The heats of vaporization of *n*-butane and water at 25°C are 19.2 kJ/mol and 44.0 kJ/mol, respectively. What is the standard heat of the reaction



Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

SOLUTION

1. From Equation 9.1-3,

$$\dot{\xi} = \frac{(\dot{n}_{\text{CO}_2})_r}{|\nu_{\text{CO}_2}|} = \frac{2400 \text{ mol/s}}{4} = 600 \text{ mol/s}$$

\downarrow
Equation 9.1-4

$$\Delta\dot{H} = \dot{\xi} \Delta\dot{H}_r^\circ = \left(600 \frac{\text{mol}}{\text{s}}\right) \left(-2878 \frac{\text{kJ}}{\text{mol}}\right) = -1.73 \times 10^6 \text{ kJ/s}$$

2. Since doubling the stoichiometric coefficients of a reaction must double the heat of reaction,

$$\Delta\hat{H}_{r2}^\circ = 2\Delta\hat{H}_{r1}^\circ = 2(-2878 \text{ kJ/mol}) = -5756 \text{ kJ/mol}$$

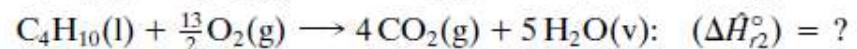
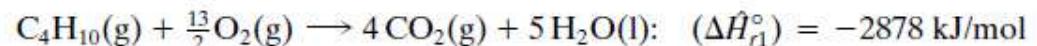
The enthalpy change associated with the production of 2400 mol/s of CO₂ at 25°C cannot depend on how the stoichiometric equation is written (the same quantities of reactants and products at the same temperatures must have the same enthalpies), and so Δ̄H must be the value calculated in part (a). Let us do the calculation and prove it, however. From Equation 9.1-3,

$$\dot{\xi} = \frac{(\dot{n}_{\text{CO}_2})_{\text{out}}}{|\nu_{\text{CO}_2}|} = \frac{2400 \text{ mol/s}}{8} = 300 \text{ mol/s}$$

↓ Equation 9.1-4

$$\Delta\dot{H} = \dot{\xi} \Delta\hat{H}_r^\circ = \left(300 \frac{\text{mol}}{\text{s}}\right) \left(-5756 \frac{\text{kJ}}{\text{mol}}\right) = -1.73 \times 10^6 \text{ kJ/s}$$

3. Compare the two reactions:



The total enthalpy of the products in the second reaction [4 mol CO₂(g) + 5 mol H₂O(g) at 25°C] is greater than that of the products in the first reaction [4 mol CO₂(g) + 5 mol H₂O(l) at 25°C] by five times the heat of vaporization of water. Similarly, the total enthalpy of the reactants in the second reaction is lower than that of the reactants in the first reaction by the heat of vaporization of butane. (Why?) Since Δ̄H_r = H_{products} − H_{reactants}, it follows that

$$\begin{aligned} (\Delta\hat{H}_{r2}^\circ) &= (\Delta\hat{H}_{r1}^\circ) + 5(\Delta\hat{H}_v)_{\text{H}_2\text{O}} + (\Delta\hat{H}_v)_{\text{C}_4\text{H}_{10}} \\ &= [-2878 + 5(44.0) + 19.2] \text{ kJ/mol} = \boxed{-2639 \text{ kJ/mol}} \end{aligned}$$

$$\Delta\dot{H} = \dot{\xi} \Delta\hat{H}_{r2}^\circ = \left(600 \frac{\text{mol}}{\text{s}}\right) \left(-2639 \frac{\text{kJ}}{\text{mol}}\right) = \boxed{-1.58 \times 10^6 \text{ kJ/s}}$$

If a reaction takes place in a closed reactor at constant volume, the heat released or absorbed is determined by the change in internal energy between reactants and products. The **internal energy of reaction**, $\Delta\hat{U}_r(T)$, is the difference $U_{\text{products}} - U_{\text{reactants}}$ if stoichiometric quantities of reactants react completely at temperature T .

Suppose a reaction occurs, and ν_i is the stoichiometric coefficient of the i th gaseous reactant or product. If ideal gas behavior can be assumed and specific volumes of liquid and solid reactants and products are negligible compared with those of the gases, the internal energy of reaction is related to the heat of reaction by

$$\Delta\hat{U}_r(T) = \Delta\hat{H}_r(T) - RT \left(\sum_{\text{gaseous products}} |\nu_i| - \sum_{\text{gaseous reactants}} |\nu_i| \right) \quad (9.1-5)$$

For example, for the reaction



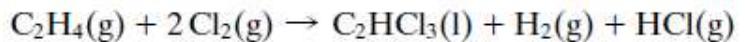
the internal energy of reaction is

$$\begin{aligned}\Delta\hat{U}_r(T) &= \Delta\hat{H}_r(T) - RT(6 + 7 - \frac{19}{2}) \\ &= \Delta\hat{H}_r(T) - \frac{7}{2}RT\end{aligned}$$

If there are no gaseous reactants or products, then to a good approximation $\Delta\hat{U}_r = \Delta\hat{H}_r$.

EXAMPLE 9.1-2**Evaluation of $\Delta\hat{U}_r$**

The standard heat of the reaction



is $\Delta\hat{H}_r^\circ = -420.8 \text{ kJ/mol}$. Calculate $\Delta\hat{U}_r^\circ$ for this reaction.

SOLUTION

From the stoichiometric equation

$$\sum \nu_i (\text{product gases}) = 1 + 1 = 2$$

$$\sum \nu_i (\text{reactant gases}) = 1 + 2 = 3$$

From Equation 9.1-5

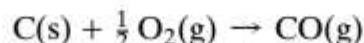
$$\begin{aligned}\Delta\hat{U}_r &= \Delta\hat{H}_r - RT(2 - 3) \\ &= -420.8 \text{ kJ/mol} - \frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}} \left| \frac{298 \text{ K}}{-1} \right| \frac{1 \text{ kJ}}{10^3 \text{ J}} \\ &= \boxed{-418.3 \text{ kJ/mol}}\end{aligned}$$

Lecture 33

9.2 Measurement and Calculation of Heats of Reaction: Hess's Law

A heat of reaction may be measured in a **calorimeter**—a closed reactor immersed in a fluid contained in a well-insulated vessel. The rise or fall of the fluid temperature can be measured and used to determine the energy released or absorbed by the reaction, and the value of $\Delta\hat{H}_r^\circ$ may then be calculated from that energy and known reactant and product heat capacities.

There are serious limitations to this technique, however. Suppose, for example, you wish to determine $\Delta\hat{H}_r^\circ$ for the reaction



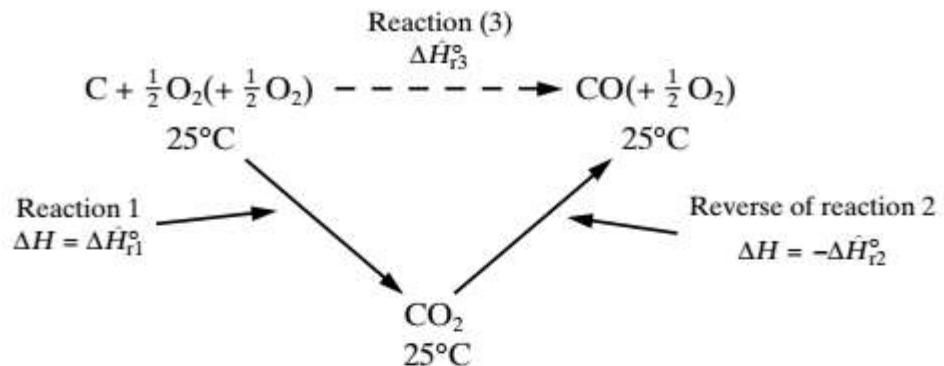
You could put 1 mole of carbon and 0.5 mole of oxygen together in a reactor, but you would never get 1 mole of carbon monoxide as the final product. If the reactants are at or near 25°C or lower, nothing apparent would occur since the rate at which carbon and oxygen react at this temperature is immeasurably low. If, on the other hand, the mixture were heated to a temperature at which C and O₂ react at a measurable rate, the product would be either pure CO₂ or at best a mixture of CO and CO₂, making it impossible to determine the heat of the CO formation reaction alone.

However, you *can* carry out the reactions

1. C + O₂ → CO₂: $\Delta\hat{H}_{r1}^\circ = -393.51 \text{ kJ/mol}$
2. CO + $\frac{1}{2}$ O₂ → CO₂: $\Delta\hat{H}_{r2}^\circ = -282.99 \text{ kJ/mol}$

and determine their heats of reaction experimentally. You may then construct a process path for the reaction

3. C + $\frac{1}{2}$ O₂ → CO: $\Delta\hat{H}_{r3}^\circ = ?$

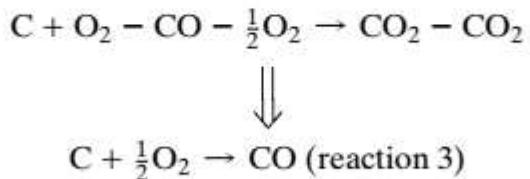


Since \hat{H} is a state function,

$$\Delta\hat{H}_{r3}^\circ = \Delta\hat{H}_{r1}^\circ + (-\Delta\hat{H}_{r2}^\circ) = (-393.51 + 282.99) \text{ kJ/mol} = -110.52 \text{ kJ/mol}$$

You have thus calculated the desired heat of reaction, which could not be measured directly, from two measurable heats of reaction.

This result could have been obtained more concisely by treating the stoichiometric equations for reactions 1 and 2 as algebraic equations. If the equation for reaction 2 is subtracted from that for reaction 1, the result is



The standard heat of reaction 3 may be calculated by applying the same operation to the heats of reactions 1 and 2—that is, $\Delta\hat{H}_{r3}^\circ = \Delta\hat{H}_{r1}^\circ - \Delta\hat{H}_{r2}^\circ$ —confirming the result previously obtained.

The general statement of the validity of this procedure is called **Hess's law**: *If the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, ..., then the heat of reaction $\Delta\hat{H}_{r1}^\circ$ can be obtained by performing the same operations on the heats of reactions $\Delta\hat{H}_{r2}^\circ, \Delta\hat{H}_{r3}^\circ, \dots$*

EXAMPLE 9.2-1**Hess's Law**

The standard heats of the following combustion reactions have been determined experimentally:

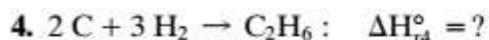
1. $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$: $\Delta\hat{H}_{r1}^\circ = -1559.8 \text{ kJ/mol}$
2. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$: $\Delta\hat{H}_{r2}^\circ = -393.5 \text{ kJ/mol}$
3. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$: $\Delta\hat{H}_{r3}^\circ = -285.8 \text{ kJ/mol}$

SOLUTION

The standard heats of the following combustion reactions have been determined experimentally:

1. $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$: $\Delta\hat{H}_{r1}^\circ = -1559.8 \text{ kJ/mol}$
2. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$: $\Delta\hat{H}_{r2}^\circ = -393.5 \text{ kJ/mol}$
3. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$: $\Delta\hat{H}_{r3}^\circ = -285.8 \text{ kJ/mol}$

Use Hess's law and the given heats of reaction to determine the standard heat of the reaction



Since

$$(4) = 2 \times (2) + 3 \times (3) - (1)$$

(verify), from Hess's law

$$\Delta\hat{H}_{r4}^\circ = 2\Delta\hat{H}_{r2}^\circ + 3\Delta\hat{H}_{r3}^\circ - \Delta\hat{H}_{r1}^\circ = -84.6 \text{ kJ/mol}$$

This heat of reaction could not have been measured directly, since you cannot react carbon and hydrogen in such a way that ethane is the only reaction product.

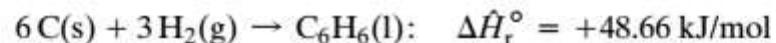
9.3 Formation Reactions and Heats of Formation

A **formation reaction** of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in nature (e.g., O₂ rather than O). The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually 25°C and 1 atm) is the **standard heat of formation** of the compound, $\Delta\hat{H}_f^\circ$.

Standard heats of formation for many compounds are listed in Table B.1 of this text and on pp. 2-187 through 2-198 of *Perry's Chemical Engineers' Handbook*.¹ For example, $\Delta\hat{H}_f^\circ$ for crystalline ammonium nitrate is given in Table B.1 as -365.14 kJ/mol, signifying



Similarly, for liquid benzene $\Delta\hat{H}_f^\circ = 48.66 \text{ kJ/mol}$, or



The standard heat of formation of an elemental species (e.g., O₂) is zero. (Why?)

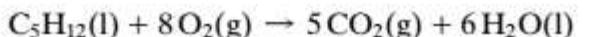
It may be shown using Hess's law that if v_i is the stoichiometric coefficient of the i^{th} species participating in a reaction (+ for products, - for reactants) and $\Delta\hat{H}_{fi}^\circ$ is the standard heat of formation of this species, then the standard heat of the reaction is

$$\boxed{\Delta\hat{H}_r^\circ = \sum_i v_i \Delta\hat{H}_{fi}^\circ = \sum_{\text{products}} |v_i| \Delta\hat{H}_{fi}^\circ - \sum_{\text{reactants}} |v_i| \Delta\hat{H}_{fi}^\circ} \quad (9.3-1)$$

The standard heats of formation of all elemental species should be set equal to zero in this formula. The validity of Equation 9.3-1 is illustrated in the next example.

EXAMPLE 9.3-1**Determination of a Heat of Reaction from Heats of Formation**

Determine the standard heat of reaction for the combustion of liquid *n*-pentane, assuming H₂O(l) is a combustion product.

**SOLUTION**

From Equation 9.3-1

$$\begin{aligned}\Delta\hat{H}_r^\circ &= 5(\Delta\hat{H}_f^\circ)_{\text{CO}_2(g)} + 6(\Delta\hat{H}_f^\circ)_{\text{H}_2\text{O}(l)} - (\Delta\hat{H}_f^\circ)_{\text{C}_5\text{H}_{12}(l)} \\ &\quad \downarrow \text{Heats of formation from Table B.1} \\ \Delta\hat{H}_r^\circ &= [5(-393.5) + 6(-285.84) - (-173.0)] \text{ kJ/mol} \\ &= \boxed{-3509 \text{ kJ/mol}}\end{aligned}$$

To verify the formula for $\Delta\hat{H}_r^\circ$, we may write the stoichiometric equations for the formation reactions of the reactants and products:

1. $5 \text{C(s)} + 6 \text{H}_2\text{(g)} \rightarrow \text{C}_5\text{H}_{12}(l)$: $\Delta\hat{H}_{r1}^\circ = (\Delta\hat{H}_f^\circ)_{\text{C}_5\text{H}_{12}(l)}$
2. $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$: $\Delta\hat{H}_{r2}^\circ = (\Delta\hat{H}_f^\circ)_{\text{CO}_2(g)}$
3. $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$: $\Delta\hat{H}_{r3}^\circ = (\Delta\hat{H}_f^\circ)_{\text{H}_2\text{O}(l)}$

The desired reaction,

4. $\text{C}_5\text{H}_{12}(l) + 8 \text{O}_2\text{(g)} \rightarrow 5 \text{CO}_2\text{(g)} + 6 \text{H}_2\text{O(l)}$: $\Delta\hat{H}_r^\circ = ?$

may be obtained as $5 \times (2) + 6 \times (3) - (1)$ (*verify*), and the given formula for $\Delta\hat{H}_r^\circ$ then follows from Hess's law.

Table B.1 Selected Physical Property Data^a

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m (°C) ^b	$\Delta\hat{H}_m(T_m)$ ^{c,j} kJ/mol	T_b (°C) ^d	$\Delta\hat{H}_v(T_b)$ ^{e,j} kJ/mol	T_c (K) ^f	P_c (atm) ^g	$(\Delta\hat{H}_f^\ominus)$ ^{h,j} kJ/mol	$(\Delta\hat{H}_c^\ominus)$ ^{i,j} kJ/mol
Acetaldehyde	CH ₃ CHO	44.05	0.783 ^{18*}	-123.7	—	20.2	25.1	461.0	—	-166.2(g)	-1192.4(g)
Acetic acid	CH ₃ COOH	60.05	1.049	16.6	12.09	118.2	24.39	594.8	57.1	-486.18(l)	-871.69(l)
Acetone	C ₃ H ₆ O	58.08	0.791	-95.0	5.69	56.0	30.2	508.0	47.0	-438.15(g)	-919.73(g)
Acetylene	C ₂ H ₂	26.04	—	—	—	-81.5	17.6	309.5	61.6	+226.75(g)	-1299.6(g)
Ammonia	NH ₃	17.03	—	-77.8	5.653	-33.43	23.351	405.5	111.3	-248.2(l)	-1785.7(l)
Ammonium hydroxide	NH ₄ OH	35.03	—	—	—	—	—	—	—	-46.19(g)	-1821.4(g)
Ammonium nitrate	NH ₄ NO ₃	80.05	1.725 ^{25*}	169.6	5.4	Decomposes at 210°C				-365.14(c)	—
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.14	1.769	513	—	Decomposes at 513°C after melting				-399.36(aq)	—
Aniline	C ₆ H ₇ N	93.12	1.022	-6.3	—	184.2	—	699	52.4	-1179.3(c)	—
Benzaldehyde	C ₆ H ₅ CHO	106.12	1.046	-26.0	—	179.0	38.40	—	—	-1173.1(aq)	—
Benzene	C ₆ H ₆	78.11	0.879	5.53	9.837	80.10	30.765	562.6	48.6	-88.83(l)	-3520.0(l)
Benzoic acid	C ₇ H ₆ O ₂	122.12	1.266 ^{15*}	122.2	—	249.8	—	—	—	-40.04(g)	—
Benzyl alcohol	C ₇ H ₈ O	108.13	1.045	-15.4	—	205.2	—	—	—	-3226.7(g)	—
Bromine	Br ₂	159.83	3.119	-7.4	10.8	58.6	31.0	584	102	0(l)	-3741.8(l)
1,2-Butadiene	C ₄ H ₆	54.09	—	-136.5	—	10.1	—	446	—	—	—
1,3-Butadiene	C ₄ H ₆	54.09	—	-109.1	—	-4.6	—	425	42.7	—	—
n-Butane	C ₄ H ₁₀	58.12	—	-138.3	4.661	-0.6	22.305	425.17	37.47	-147.0(l)	-2855.6(l)
Isobutane	C ₄ H ₁₀	58.12	—	-159.6	4.540	-11.73	21.292	408.1	36.0	-124.7(g)	-2878.5(g)
1-Butene	C ₄ H ₈	56.10	—	-185.3	3.8480	-6.25	21.916	419.6	39.7	-158.4(l)	-2849.0(l)
Calcium carbide	CaC ₂	64.10	2.22 ^{18*}	2300	—	—	—	—	—	-134.5(g)	-2868.8(g)
Calcium carbonate	CaCO ₃	100.09	2.93	Decomposes at 825°C				—	—	-62.76(c)	-2718.6(g)
Calcium chloride	CaCl ₂	110.99	2.152 ^{15*}	782	28.37	>1600	—	—	—	-794.96(c)	—

Lecture 34

9.4 Heats of Combustion

The **standard heat of combustion** of a substance, $\Delta\hat{H}_c^\circ$, is the heat of the combustion of that substance with oxygen to yield specified products [e.g., $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$], with both reactants and products at 25°C and 1 atm (the arbitrary but conventional reference state).

Table B.1 lists standard heats of combustion for a number of substances. The given values are based on the following assumptions: (a) all carbon in the fuel forms $\text{CO}_2(\text{g})$, (b) all hydrogen forms $\text{H}_2\text{O}(\text{l})$, (c) all sulfur forms $\text{SO}_2(\text{g})$, and (d) all nitrogen forms $\text{N}_2(\text{g})$. The standard heat of combustion of liquid ethanol, for example, is given in Table B.1 as $\Delta\hat{H}_c^\circ = -1366.9 \text{ kJ/mol}$, which signifies



Additional heats of combustion are given on pp. 2-195 through 2-199 of *Perry's Chemical Engineers' Handbook* (see footnote 1).

Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion, in another application of Hess's law. A hypothetical reaction path may be constructed in which (a) all combustible reactants are burned with O_2 at 25°C and (b) CO_2 and H_2O combine to form the reaction products plus O_2 . Step (b) involves the reverse of the combustion reactions of the reaction products. Since both steps involve only combustion reactions, the total enthalpy change—which equals the desired heat of reaction—can be determined entirely from heats of combustion as

$$\Delta\hat{H}_r^\circ = - \sum_i \nu_i (\Delta\hat{H}_c^\circ)_i = \sum_{\text{reactants}} |\nu_i| (\Delta\hat{H}_c^\circ)_i - \sum_{\text{products}} |\nu_i| (\Delta\hat{H}_c^\circ)_i \quad (9.4-1)$$

If any of the reactants or products are themselves combustion products [CO_2 , $\text{H}_2\text{O}(\text{l})$, SO_2 , ...], their $\Delta\hat{H}_c^\circ$ terms in Equation 9.4-1 should be set equal to 0.

Note that this formula is similar to that used to determine $\Delta\hat{H}_f^\circ$ from heats of formation, except that in this case the negative of the sum is taken. The validity of this formula is illustrated in the next example.

Table B.1 Selected Physical Property Data^a

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m (°C) ^b	$\Delta\hat{H}_m(T_m)$ ^{c,j} kJ/mol	T_b (°C) ^d	$\Delta\hat{H}_v(T_b)$ ^{e,j} kJ/mol	T_c (K) ^f	P_c (atm) ^g	$(\Delta\hat{H}_f^\circ)$ ^{h,j} kJ/mol	$(\Delta\hat{H}_c^\circ)$ ^{i,j} kJ/mol
Acetaldehyde	CH ₃ CHO	44.05	0.783 ^{18*}	-123.7	—	20.2	25.1	461.0	—	-166.2(g)	-1192.4(g)
Acetic acid	CH ₃ COOH	60.05	1.049	16.6	12.09	118.2	24.39	594.8	57.1	-486.18(l)	-871.69(l)
Acetone	C ₃ H ₆ O	58.08	0.791	-95.0	5.69	56.0	30.2	508.0	47.0	-438.15(g)	-919.73(g)
Acetylene	C ₂ H ₂	26.04	—	—	—	-81.5	17.6	309.5	61.6	+226.75(g)	-1299.6(g)
Ammonia	NH ₃	17.03	—	-77.8	5.653	-33.43	23.351	405.5	111.3	-67.20(l)	-46.19(g)
Ammonium hydroxide	NH ₄ OH	35.03	—	—	—	—	—	—	—	-366.48(aq)	—
Ammonium nitrate	NH ₄ NO ₃	80.05	1.725 ^{25*}	169.6	5.4	Decomposes at 210°C			—	-365.14(c)	—
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.14	1.769	513	—	Decomposes at 513°C after melting			—	-399.36(aq)	—
Aniline	C ₆ H ₇ N	93.12	1.022	-6.3	—	184.2	—	699	52.4	-1179.3(c)	—
Benzaldehyde	C ₆ H ₅ CHO	106.12	1.046	-26.0	—	179.0	38.40	—	—	-1173.1(aq)	—
Benzene	C ₆ H ₆	78.11	0.879	5.53	9.837	80.10	30.765	562.6	48.6	-88.83(l)	-3520.0(l)
Benzoic acid	C ₇ H ₆ O ₂	122.12	1.266 ^{15*}	122.2	—	249.8	—	—	—	-40.04(g)	—
Benzyl alcohol	C ₇ H ₈ O	108.13	1.045	-15.4	—	205.2	—	—	—	-3226.7(g)	—
Bromine	Br ₂	159.83	3.119	-7.4	10.8	58.6	31.0	584	102	-3741.8(l)	—
1,2-Butadiene	C ₄ H ₆	54.09	—	-136.5	—	10.1	—	446	—	—	—
1,3-Butadiene	C ₄ H ₆	54.09	—	-109.1	—	-4.6	—	425	42.7	—	—
<i>n</i> -Butane	C ₄ H ₁₀	58.12	—	-138.3	4.661	-0.6	22.305	425.17	37.47	-147.0(l)	-2855.6(l)
Isobutane	C ₄ H ₁₀	58.12	—	-159.6	4.540	-11.73	21.292	408.1	36.0	-124.7(g)	-2878.5(g)
1-Butene	C ₄ H ₈	56.10	—	-185.3	3.8480	-6.25	21.916	419.6	39.7	-134.5(g)	-2849.0(l)
Calcium carbide	CaC ₂	64.10	2.22 ^{18*}	2300	—	—	—	—	—	+1.17(g)	-2868.8(g)
Calcium carbonate	CaCO ₃	100.09	2.93	Decomposes at 825°C			—	—	—	-2718.6(g)	—
Calcium chloride	CaCl ₂	110.99	2.152 ^{15*}	782	28.37	>1600	—	—	—	-62.76(c)	—
										-794.96(c)	—

EXAMPLE 9.4-1***Calculation of a Heat of Reaction from Heats of Combustion***

Calculate the standard heat of reaction for the dehydrogenation of ethane:

**SOLUTION**

From Table B.1,

$$(\Delta\hat{H}_c^\circ)_{\text{C}_2\text{H}_6} = -1559.9 \text{ kJ/mol}$$

$$(\Delta\hat{H}_c^\circ)_{\text{C}_2\text{H}_4} = -1411.0 \text{ kJ/mol}$$

$$(\Delta\hat{H}_c^\circ)_{\text{H}_2} = -285.84 \text{ kJ/mol}$$

From Equation 9.4-1, therefore,

$$\Delta\hat{H}_r^\circ = (\Delta\hat{H}_c^\circ)_{\text{C}_2\text{H}_6} - (\Delta\hat{H}_c^\circ)_{\text{C}_2\text{H}_4} - (\Delta\hat{H}_c^\circ)_{\text{H}_2} = \boxed{136.9 \text{ kJ/mol}}$$

As an illustration, let us demonstrate the validity of this formula using Hess's law. The combustion reactions are

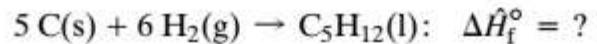
1. $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O}$
2. $\text{C}_2\text{H}_4 + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}$
3. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

It is easy to show that

4. $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$

is obtained as (1) – (2) – (3). (Show it.) The desired result follows from Hess's law.

One of the principal applications of Equation 9.4-1 is to determine heats of formation for combustible substances whose formation reactions do not occur naturally. For example, the formation reaction of pentane



cannot be carried out in a laboratory, but carbon, hydrogen, and pentane can all be burned and their standard heats of combustion determined experimentally. The heat of formation of pentane may then be calculated from Equation 9.4-1 as

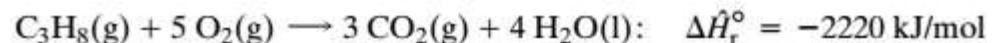
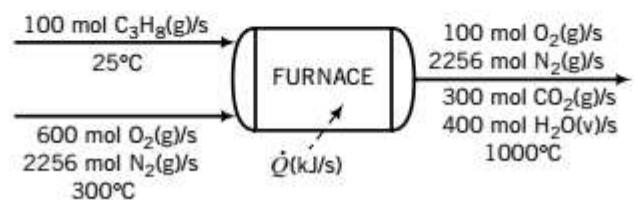
$$(\Delta\hat{H}_f^\circ)_{\text{C}_5\text{H}_{12}\text{(l)}} = 5(\Delta\hat{H}_c^\circ)_{\text{C(s)}} + 6(\Delta\hat{H}_c^\circ)_{\text{H}_2\text{(g)}} - (\Delta\hat{H}_c^\circ)_{\text{C}_5\text{H}_{12}\text{(l)}}$$

9.5 Energy Balances on Reactive Processes

9.5a General Procedures

To perform energy balance calculations on a reactive system, proceed much as you did for nonreactive systems: (a) draw and label a flowchart; (b) use material balances and phase equilibrium relationships such as Raoult's law to determine as many stream component amounts or flow rates as possible; (c) choose reference states for specific enthalpy (or internal energy) calculations and prepare and fill in an inlet-outlet enthalpy (or internal energy) table; and (d) calculate $\Delta\dot{H}$ (or $\Delta\dot{U}$ or $\Delta\dot{H}$), substitute the calculated value in the appropriate form of the energy balance equation, and complete the required calculation.

Two methods are commonly used to choose reference states for enthalpy calculations and to calculate specific enthalpies and $\Delta\dot{H}^3$. We outline the two approaches below, using a propane combustion process to illustrate them. For simplicity, the material balance calculations for the illustrative process have been performed and the results incorporated into the flowchart.



Heat of Reaction Method. This method is generally preferable when there is a single reaction for which $\Delta\hat{H}_r^\circ$ is known.

1. Complete the material balance calculations on the reactor to the greatest extent possible.
2. Choose reference states for specific enthalpy calculations. The best choices are generally reactant and product species at 25°C and 1 atm in the states for which the heat of reaction is known [C₃H₈(g), O₂(g), CO₂(g), and H₂O(l) in the example process], and nonreacting species at any convenient temperature, such as the reactor inlet or outlet temperature or the reference condition used for the species in an available enthalpy table [N₂(g) at 25°C and 1 atm, the reference state for Table B.8].
3. For a single reaction in a continuous process, calculate the extent of reaction, $\dot{\xi}$, from Equation 9.1-3.⁴ When writing the equation, choose as species A any reactant or product for which the feed and product flow rates are known. In the example, we may choose any reactant or product since we know all inlet and outlet species flow rates and calculate the rate of consumption or generation of A ($\dot{n}_{A,r}$ in Equation 9.1-3) as $|(\dot{n}_A)_{\text{out}} - (\dot{n}_A)_{\text{in}}|$. If A is propane,

$$\dot{\xi} = \frac{|(\dot{n}_{\text{C}_3\text{H}_8})_{\text{out}} - (\dot{n}_{\text{C}_3\text{H}_8})_{\text{in}}|}{\nu_{\text{C}_3\text{H}_8}} = \frac{|0 - 100| \text{ mol/s}}{1} = 100 \text{ mol/s}$$

As an exercise, let A be O₂, CO₂, or H₂O and verify that the value of $\dot{\xi}$ is independent of the species chosen.

4. Prepare the inlet-outlet enthalpy table, inserting known molar amounts (n_i) or flow rates (\dot{n}_i) for all inlet and outlet stream components. If any of the components is at its reference state, insert 0 for the corresponding \hat{H}_i . For the example process, the table would appear as follows:

References: C₃H₈(g), O₂(g), N₂(g), CO₂(g), H₂O(l) at 25°C and 1 atm

Substance	\dot{n}_{in} (mol/s)	\hat{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/s)	\hat{H}_{out} (kJ/mol)
C ₃ H ₈	100	0	—	—
O ₂	600	\hat{H}_2	100	\hat{H}_4
N ₂	2256	\hat{H}_3	2256	\hat{H}_5
CO ₂	—	—	300	\hat{H}_6
H ₂ O	—	—	400	\hat{H}_7

5. Calculate each unknown stream component enthalpy, \hat{H}_i , as $\Delta\hat{H}$ for the species going from its reference state to the process state, and insert the enthalpies in the table. In the example,

$$\hat{H}_2 = \Delta\hat{H} \text{ for } O_2(25^\circ C) \rightarrow O_2(300^\circ C) = 8.47 \text{ kJ/mol (from Table B.8)}$$

We proceed in the same manner to calculate $\hat{H}_3 = 8.12 \text{ kJ/mol}$, $\hat{H}_4 = 32.47 \text{ kJ/mol}$, $\hat{H}_5 = 30.56 \text{ kJ/mol}$, $\hat{H}_6 = 48.60 \text{ kJ/mol}$, and $\hat{H}_7 = 81.71 \text{ kJ/mol}$.

Consider the last result. By definition

$$\hat{H}_7 = \Delta\hat{H} \text{ for } H_2O(l, 25^\circ C) \rightarrow H_2O(g, 1000^\circ C)$$

We could either use steam tables to determine $\Delta\hat{H}$ in one step or heat the liquid water from 25°C to 100°C, vaporize it, heat the vapor from 100°C to 1000°C, and calculate $\hat{H}_7 = \int_{25^\circ C}^{100^\circ C} C_{pl} dT + \Delta\hat{H}_v(100^\circ C) + \int_{100^\circ C}^{1000^\circ C} C_{pv} dT$.

6. Calculate $\Delta\dot{H}$ for the reactor. Use one of the following formulas:

$$\Delta\dot{H} = \dot{\xi} \Delta\hat{H}_r^o + \sum \dot{n}_{out} \hat{H}_{out} - \sum \dot{n}_{in} \hat{H}_{in} \quad (\text{single reaction}) \quad (9.5-1a)$$

$$\Delta\dot{H} = \sum_{\text{reactions}} \dot{\xi}_j \Delta\hat{H}_{rj}^o + \sum \dot{n}_{out} \hat{H}_{out} - \sum \dot{n}_{in} \hat{H}_{in} \quad (\text{multiple reactions}) \quad (9.5-1b)$$

A derivation of these equations is outlined following the presentation of the heat of formation method. Substitution of the previously calculated values into Equation 9.5-1a yields $\Delta\dot{H} = -1.26 \times 10^5 \text{ kJ/s}$.

7. Substitute the calculated value of $\Delta\dot{H}$ in the energy balance ($\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$ for an open system) and complete the required calculations.

Heat of Formation Method: This method is generally preferable for multiple reactions and single reactions for which $\Delta\hat{H}_r$ is not readily available.

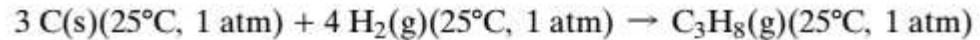
1. Complete the material balance calculations on the reactor to the greatest extent possible.
2. Choose reference states for enthalpy calculations. (This is the step that distinguishes the preceding method from this one.) The choices should be the elemental species that constitute the reactants and products in the states in which the elements are found at 25°C and 1 atm [C(s), H₂(g), etc.] and nonreacting species at any convenient temperature. In the example, the reference states would be C(s), H₂(g), and O₂(g) at 25°C (the elemental species constituting the reactants and products), and N₂ at 25°C (the reference temperature of Table B.8).
3. Prepare the inlet–outlet enthalpy table, inserting known molar amounts (n_i) or flow rates (\dot{n}_i) for all inlet and outlet stream components. For the example process, the table would appear as follows:

References: C(s), H₂(g), O₂(g), N₂(g) at 25°C and 1 atm

Substance	\dot{n}_{in} (mol/s)	\hat{H}_{in} (kJ/mol)	\dot{n}_{out} (mol/s)	\hat{H}_{out} (kJ/mol)
C ₃ H ₈	100	\hat{H}_1	—	—
O ₂	600	\hat{H}_2	100	\hat{H}_4
N ₂	2256	\hat{H}_3	2256	\hat{H}_5
CO ₂	—	—	300	\hat{H}_6
H ₂ O	—	—	400	\hat{H}_7

4. Calculate each unknown specific enthalpy. For a reactant or product, start with the elemental species at 25°C and 1 atm (the references) and form 1 mol of the process species at 25°C and 1 atm ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$ from Table B.1). Then bring the species from 25°C and 1 atm to its process state, calculating $\Delta\hat{H}$ using the appropriate heat capacities from Table B.2, specific enthalpies from Table B.8 or B.9, and latent heats from Table B.1. The specific enthalpy that goes in the inlet–outlet table is the sum of the enthalpy changes for each step in the process path.

In the example, we would first calculate the specific enthalpy of the entering propane (\hat{H}_1) as follows:



$$\hat{H}_1 = (\Delta\hat{H}_f^\circ)_{\text{C}_3\text{H}_8(\text{g})} = -103.8 \text{ kJ/mol} \text{ (from Table B.1)}$$

This is the enthalpy of propane at 25°C (the process state) relative to C(s) and H₂(g) at 25°C (the reference states). If the propane had entered at a temperature T_0 other than 25°C, a term of the form $\int_{25^\circ\text{C}}^{T_0} C_p dT$ would be added to the heat of formation of propane.

Next, we calculate the specific enthalpy of O₂ at 300°C (the process state) relative to O₂ at 25°C (the reference state) as $\hat{H}_2 = 8.47 \text{ kJ/mol}$ (from Table B.8). There is no heat of formation term, since O₂ is an elemental species. We proceed in the same manner to calculate $\hat{H}_3 = 8.12 \text{ kJ/mol}$, $\hat{H}_4 = 32.47 \text{ kJ/mol}$, $\hat{H}_5 = 30.56 \text{ kJ/mol}$, $\hat{H}_6 = -344.9 \text{ kJ/mol}$, and $\hat{H}_7 = -204.1 \text{ kJ/mol}$. To calculate \hat{H}_6 and \hat{H}_7 , we form the corresponding species [CO₂(g) and H₂O(v)] at 25°C from their elements ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$), then heat them from 25°C to 1000°C ($\Delta\hat{H} = \hat{H}_{1000^\circ\text{C}}$ from Table B.8), and add the formation and heating terms.

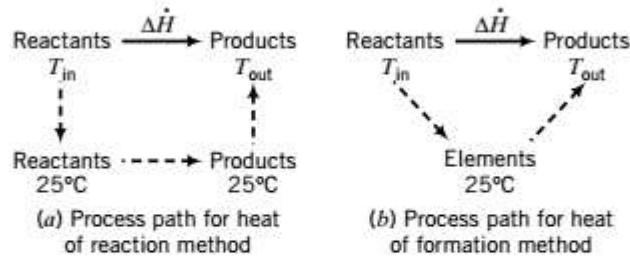
5. Calculate $\Delta\dot{H}$ for the reactor. For both single and multiple reactions, the formula is

$$\Delta\dot{H} = \sum \dot{n}_{\text{out}} \hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}} \hat{H}_{\text{in}} \quad (9.5-2)$$

Note that heat of reaction terms are not required if the elements are chosen as references. The heats of reaction are implicitly included when the heats of formation of the reactants (included in the \hat{H}_{in} terms) are subtracted from those of the products (in the \hat{H}_{out} terms) in the expression for $\Delta\dot{H}$. Substituting the calculated \dot{n} and \hat{H} values into Equation 9.5-2 yields $\Delta\dot{H} = -1.26 \times 10^5 \text{ kJ/s}$.

6. Substitute the calculated value of $\Delta\dot{H}$ in the energy balance equation and complete the required calculations.

The process paths that correspond to the heat of reaction and heat of formation methods are shown below.



The heat of reaction method amounts to bringing the reactants from their inlet conditions to their reference states at 25°C ($\Delta\dot{H} = - \sum \dot{n}_{in} \hat{H}_{in}$), carrying out the reaction at 25°C (from Equation 9.1-3, $\Delta\dot{H} = \xi \Delta\dot{H}_r^\circ$ or the summation of such terms for multiple reactions), bringing the products from their reference states at 25°C to their outlet states ($\Delta\dot{H} = \sum \dot{n}_{out} \hat{H}_{out}$), and summing the enthalpy changes for these three steps to calculate $\Delta\dot{H}$ for the overall process. The heat of formation method amounts to bringing the reactants from their inlet conditions to their constituent elements at 25°C ($\Delta\dot{H} = - \sum \dot{n}_{in} \hat{H}_{in}$), taking the elements to the products at their outlet states ($\Delta\dot{H} = \sum \dot{n}_{out} \hat{H}_{out}$), and summing the enthalpy changes for these two steps to calculate $\Delta\dot{H}$ for the overall process.