Chapters 2 & 3 Energy Balances

Work done by the system, \( W = -\) Force applied to the system, \( F \Delta x \)

or \( W = -\int F(x) \, dx \)

Expansion/Contraction of a Closed System

\( W_{EC} = -\int PA \, dx = -\int P \, dV \)  \( \text{Force leads to a change in volume at constant pressure} \)

Shaft Work for an Open System

\( W_s = -\int_{in}^{out} V \, dP \)  \( \text{Pump leads to a change in pressure at constant volume} \)
**Work Associated with Flow**

\[
\dot{W}_{Flow} = (PV)_{in} \dot{m}_{in} - (PV)_{out} \dot{m}_{out}
\]

**Lost Work**

- Viscosity Gradient (Pressure Gradients)
- Temperature Gradient
- Concentration Gradient
- Friction (of a piston for instance)

**Reversible Process**

- Viscosity Gradient (Pressure Gradients)
- Temperature Gradient
- Concentration Gradient
- Friction (of a piston for instance)
Example 2.1 Isothermal reversible compression of an ideal gas

Calculate the work necessary to isothermally perform steady compression of two moles of an ideal gas from 1 to 10 bar and 311 K in a piston. An isothermal process is one at constant temperature. The steady compression of the gas should be performed such that the pressure of the system is always practically equal to the external pressure on the system. We refer to this type of compression as "reversible" compression.

Solution: System: closed; Basis: one mole

\[ W_{EC} = -\int PdV \]

\[ P = \frac{RT}{V} \implies W_{EC} = -\int \frac{V^2RT}{V}dV = -RT\int \frac{V^2}{V}dV = -RT\ln\left(\frac{V_2}{V_1}\right) \] (ig) 2.8

\[ \frac{V_2}{V_1} = \frac{(RT)/P_2}{(RT)/P_1} = \frac{P_1}{P_2} = \frac{1}{10} \] (ig) 2.9

\[ W_{EC} = -8.314 \text{ J/mol-K} \cdot 311 \text{ K} \ln(1/10) = 5954 \text{ J/mol} \]

\[ W_{EC} = 2(5954) = 11,908 \text{ J} \]

Note: Work is done on the gas since the sign is positive. This is the sign convention set forth in Eqn. 2.3. If the integral for Eqn. 2.3 is always written as shown with the initial state as the lower limit of integration and the \( P \) and \( V \) properties of the system, the work on the gas will always result with the correct sign.
Example 2.2 Work as a path function

Solution: First sketch the process on a diagram to visualize the process as shown in Fig. 2.2. Determine the initial volume:

![Diagram showing a path function with points labeled 1, 2, and 3.]

Figure 2.2 Schematic for Example 2.2.

\[ V = nR(T/P) = \frac{1.2 \text{ moles} \times 8.314 \text{ cm}^3 \text{ MPa}}{3 \text{ mole K} \times 0.2 \text{ MPa}} = 14,865 \text{ cm}^3 \]  

(ig)

1. Isothermally expand that gas:

\[ \Rightarrow W_{EC} = -\int PdV = -nRT_1 \ln(V_2/V_1) \]  

(ig) 2.11

\[ = \frac{1.2 \text{ moles} \times (8.314) \text{ cm}^3 \text{ MPa}}{3 \text{ mole K}} \times 298 \text{ K} \ln(2) = -2060 \text{ J} \]

2. Isothermally cool down to \( V_1 \):

\[ W_{EC} = -\int \frac{P_2 dV}{V_2} = -P_2(V_1 - V_2) = -0.1 \text{ MPa}(-14,865 \text{ cm}^3) = 1487 \text{ J} \]  

2.12

3. Heat at constant volume back to \( T_1 \):

\[ \Rightarrow W_{EC} = 0 \text{ (because } dV = 0 \text{ over entire step)} \]

We have returned the system to its original state and all state properties have returned to their initial values. What is the total work done on the system?

\[ W = W_{1 \rightarrow 2} + W_{2 \rightarrow 3} + W_{3 \rightarrow 1} = -nRT_1 \ln(V_2/V_1) + nP_2(V_2 - V_1) = -573 \text{ J} \]  

(ig) 2.13

Therefore, we conclude that work is a path function, not a state function.
Exercise: If we reverse the path, the work will be different; in fact, it will be positive instead of negative (+573.6 J). If we change the path to isobarically expand the gas to double the volume ($W = -2973$ J), cool to $T_1$ at constant volume ($W = 0$ J), then isothermally compress to the original volume ($W = -2060$ J), the work will be $-913$ J.

Note: Heat was added and removed during the process of Example 2.2 which has not been accounted for above. The above process transforms work into heat, and all we have done is computed the amount of work. The amount of heat is obviously equal in magnitude and opposite in sign, in accordance with the first law. The important thing to remember is that work is a path function, not a state function.
\[
\begin{bmatrix}
\text{energy accumulation within} \\
\text{system boundaries}
\end{bmatrix} = 
\begin{bmatrix}
\text{heat flow} \\
\text{into system}
\end{bmatrix} + 
\begin{bmatrix}
\text{work done} \\
\text{on system}
\end{bmatrix}
\]

Energy within the system is composed of the internal energy (e.g., \(U\)), and the kinetic (\(mu^2/2g_c\)) and potential energy (\(mgz/g_c\)) of the center of mass. For closed systems, the "check list" equation is:

\[
m \frac{d}{dt} \left[ U + \frac{v^2}{2g_c} + \frac{g_z}{g_c} \right] = dQ + dW_S + dW_{EC}
\]

The left-hand side summarizes changes occurring within the system boundaries and the right-hand side summarizes changes due to interactions at the boundaries. It is a recommended prac-
\[ m \frac{d}{dt} \left[ U + \frac{v^2}{2g_e} + \frac{g_e}{g_c} \right] = dQ + d\overline{W}_S + d\overline{W}_{EC} \]  \hspace{1cm} 2.15

\[ d \left[ U + \frac{v^2}{2g_e} + \frac{g_e}{g_c} \right] = dQ + d\overline{W}_S + d\overline{W}_{EC} \]  \hspace{1cm} 2.16

\[ \frac{dU}{dt} = \dot{Q} + \dot{W}_{EC} \]  \hspace{1cm} \text{or} \hspace{1cm} \Delta U = Q + W_{EC}  \hspace{1cm} 2.19
Example 2.3 Internal energy and heat

In Section 2.5 on page 46 we discussed that heat flow is related to the energy of system, and now we have a relation to quantify changes in energy. If 2000 J of heat are passed from the hot block to the cold block, how much has the internal energy of each block changed?

Solution: First choose a system boundary. Let us initially place system boundaries around each of the blocks. Let the warm block be block 1 and the cold block be block 2. Next, eliminate terms which are zero or are not important. The problem statement says nothing about changes in position or velocity of the blocks, so these terms can be eliminated from the balance. There is no shaft involved, so shaft work can be eliminated. The problem statement doesn't specify the pressure, so it is common to assume that the process is at a constant atmospheric pressure of 0.101 MPa. The cold block does expand slightly when it is warmed, and the warm block will contract; however, since we are dealing with solids, the work interaction is so small that it can be neglected. For example, the blocks together would have to change 10 cm³ at 0.101 MPa to equal 1 J out of the 2000 J that are transferred.

Therefore, the energy balance for each block becomes:

\[
d\left[ U + \frac{V}{2g_c} + \frac{\mathbf{Q}}{g_c} \right] = dQ + dW_s + dW_{EC}
\]

We can integrate the energy balance for each block:

\[
\Delta U_{\text{block} 1} = Q_{\text{block} 1} \quad \Delta U_{\text{block} 2} = Q_{\text{block} 2}
\]

The magnitude of the heat transfer between the blocks is the same since no heat is transferred to the surroundings, but how about the signs? Let's explore that further. Now, placing the system boundary around both blocks, the energy balance becomes:

\[
d\left[ U + \frac{V}{2g_c} + \frac{\mathbf{Q}}{g_c} \right] = dQ + dW_s + dW_{EC}
\]

Note that the composite system is an isolated system since all heat and work interactions across the boundary are negligible. Therefore, \( \Delta U = 0 \) or by dividing in subsystems, \( \Delta U_{\text{block} 1} + \Delta U_{\text{block} 2} = 0 \) which becomes \( \Delta U_{\text{block} 1} = -\Delta U_{\text{block} 2} \). Notice that the signs are important in keeping track of which system is giving up heat and which system is gaining heat. In this example, it would be easy to keep track, but other problems will be more complicated, and it is best to develop a good bookkeeping practice of watching the signs. In this example the heat transfer for the initially hot system will be negative, and the heat transfer for the other system will be positive. Therefore, the internal energy changes are \( \Delta U_{\text{block} 1} = -2000 \) J and \( \Delta U_{\text{block} 2} = 2000 \) J.
Steady-State Open System

Figure 2.4 Schematic of a steady-state flow system.
\[
\begin{align*}
\text{rate of energy accumulation within system boundaries} &= \begin{bmatrix}
\text{energy per unit mass of fluid at inlet} \\
\text{mass flow rate in}
\end{bmatrix} \begin{bmatrix}
\text{mass flow rate in}
\end{bmatrix} + \begin{bmatrix}
\text{energy per unit mass of fluid at outlet} \\
\text{mass flow rate out}
\end{bmatrix} \begin{bmatrix}
\text{mass flow rate out}
\end{bmatrix} + \begin{bmatrix}
\text{rate of heat flow into system}
\end{bmatrix} \\
+ \begin{bmatrix}
\text{rate that work is done on system}
\end{bmatrix}
\end{align*}
\]

\[
0 = \sum_{\text{inlets}} \left( U + \frac{v^2}{2g_e} + \frac{g_{zz}}{g_e} \right) \dot{m}_{in} \left( U + \frac{v^2}{2g_e} + \frac{g_{zz}}{g_e} \right) \dot{m}_{out} + \dot{Q} + \dot{W}_S + \dot{W}_{\text{flow}}
\]

\[
0 = \sum_{\text{inlets}} \left( U + \frac{v^2}{2g_e} + \frac{g_{zz}}{g_e} \right) \dot{m}_{in} \left( U + \frac{v^2}{2g_e} + \frac{g_{zz}}{g_e} \right) \dot{m}_{out} + \dot{Q} + \dot{W}_S
\]

\[
0 = \sum_{\text{inlets}} (PV) \dot{m}_{in} \left( U + PV + \frac{v^2}{2g_e} + \frac{g_{zz}}{g_e} \right) \dot{m}_{out} + \dot{Q} + \dot{W}_S
\]
\[ 0 = \sum_{\text{inlets}} \left[ U + PV + \frac{v^2}{2g_c} + \frac{\Delta h}{g_c} \right] \dot{m}^{\text{in}} - \sum_{\text{outlets}} \left[ U + PV + \frac{v^2}{2g_c} + \frac{\Delta h}{g_c} \right] \dot{m}^{\text{out}} + \dot{Q} + \dot{W_S} \]  

**Enthalpy**

Note that the quantity \((U + PV)\) arises quite naturally in the analysis of flow systems. Flow systems are very common, so it makes sense to define a single symbol that denotes this quantity:

\[ H = U + PV \]

Thus, we can tabulate precalculated values of \(H\) and save steps in calculations for flow systems. We call \(H\) the **enthalpy**.

\[ 0 = \sum_{\text{inlets}} \left[ H + \frac{v^2}{2g_c} + \frac{\Delta h}{g_c} \right] \dot{m}^{\text{in}} - \sum_{\text{outlets}} \left[ H + \frac{v^2}{2g_c} + \frac{\Delta h}{g_c} \right] \dot{m}^{\text{out}} + \dot{Q} + \dot{W_S} \]

When kinetic and potential energy changes are negligible, we may write

\[ 0 = -\Delta H \dot{m} + \dot{Q} + \dot{W_S} \]  
(once inlet/outlet)

where \(\Delta H = H^{\text{out}} - H^{\text{in}}\). We could use molar flow rates for Eqns. 2.24 through 2.26 with the usual care for unit conversions of kinetic and potential energy. For an open steady-state system meeting the restrictions of Eqn. 2.26, we may divide through by the mass flow rate to find

\[ 0 = -\Delta H + \dot{Q} + \dot{W_S} \]  
(once inlet/outlet)

In common usage, it is traditional to relax the convention of keeping only system properties on the left side of the equation. More simply we often write:

\[ \Delta H = \dot{Q} + \dot{W_S} \]  
(once inlet/outlet)
Consider steady-state, adiabatic, horizontal operation of a pump, turbine, or compressor. It is possible to conceive of a closed packet of fluid as the system while it flows through the equipment. After analyzing the system from this perspective, we can switch to the open-system perspective to gain insight about the relation between open systems and closed systems, energy and enthalpy, and EC work and shaft work. As a bonus, we obtain a handy relation for estimating pump work and the enthalpy of compressed liquids.

System: closed, adiabatic; Basis: packet of mass \( m \). The kinetic and potential energy changes are negligible:

\[
d\left[ U + \frac{V^2}{2g_c} + \frac{V^2}{2g_e} \right] = dQ + dW + dW_{EC}
\]

Integrating from the inlet (initial) state to the outlet (final) state:

\[
U_{out} - U_{in} = W_{EC}
\]

We may change the form of the integral representing work via integration by parts:

\[
W_{EC} = - \int_{in}^{out} PdV = - \left[ PV \right]_{in}^{out} + \int_{in}^{out} VdP
\]

We recognize the term \( PV \) as representing the work done by the flowing fluid entering and leaving the system; it does not contribute to the work of the device. Therefore, the work interaction with the turbine is the remaining integral, \( W_S = \int_{in}^{out} VdP \). Substitution gives,

\[
\Rightarrow \left[ U + PV \right]_{out} - \left[ U + PV \right]_{in} = \int_{in}^{out} VdP
\]

**Open System**

\[
\Delta H = Q + W_S \quad \text{(one inlet/outlet)}
\]

2.28

\[
H_{out} - H_{in} = Q + W_S
\]

2.30

\[
W_S = \int_{in}^{out} VdP \quad \text{reversible shaft work}
\]

2.31

*Note: The shaft work given by \( dW_S = VdP \) is distinct from expansion/contraction work, \( dW_{EC} = PdV \). Moreover, both are distinct from flow work, \( dW_{flow} = PVdm \).*
\[ W_S = \int_{in}^{out} VdP \quad \text{reversible shaft work} \]

**Note:** The shaft work given by \( dW_S = VdP \) is distinct from expansion/contraction work, \( dW_{EC} = PdV \). Moreover, both are distinct from flow work, \( dW_{flow} = PVdm \).

Several practical issues may be considered in light of Eqn. 2.31. First, the work done on the system is negative when the pressure change is negative, as in proceeding through a turbine or expander. This is consistent with our sign convention. Second, when considering gas flow, the integration may seem daunting if an ideal gas is not involved because of the complicated manner that \( V \) changes with \( T \) and \( P \). Rather, for gases, we can frequently work with the enthalpy for a given state change. The enthalpy values for a state change read from a table or chart lead to \( W_s \) directly using Eqn. 2.30. For liquids, however, the integral can be evaluated quickly. Volume can often be approximated as constant, especially when \( T_r < 0.75 \). In that case, we obtain by integration an equation for estimating pump work:

\[ W_S \approx V^L (P^{out} - P^{in}) = \frac{\Delta P}{\rho} \quad \text{liquid} \]
Example 2.4 Pump work for compressing H$_2$O

Use Eqn. 2.31 to estimate the work of compressing 20°C H$_2$O from a saturated liquid to 5 and 50 MPa. Compare to the values obtained using the compressed liquid steam tables.

**Solution:** For H$_2$O, $T_r = 0.75$ corresponds to 212°C, so we are safe on that count. We can calculate the pump work from Eqn. 2.31, reading $P_{stat} = 0.00234$ MPa and $V^L = 1.002$ cm$^3$/g from the saturation tables at 20°C:

\[
\Delta H \approx V^L \Delta P = 1.002 \text{ cm}^3/\text{g}(50 \text{ MPa} - 0.00234 \text{ MPa}) = 50.1 \text{ MPa-cm}^3/\text{g for 50 MPa}
\]

\[
\Delta H \approx V^L \Delta P = 1.002 \text{ cm}^3/\text{g}(100 \text{ MPa} - 0.00234 \text{ MPa}) = 100.2 \text{ MPa-cm}^3/\text{g for 100 MPa}
\]

A convenient way of converting units for these calculations is to multiply and divide by the gas constant, noting its different units. This shortcut is especially convenient in this case, e.g.,

\[
\Delta H = 50.1 \text{ MPa-cm}^3/\text{g} \cdot (8.314 \text{ J/mole-K})/(8.314 \text{ MPa-cm}^3/\text{mole-K}) = 50.1 \text{ kJ/kg}
\]

\[
\Delta H = 100.2 \text{ MPa-cm}^3/\text{g} \cdot (8.314 \text{ J/mole-K})/(8.314 \text{ MPa-cm}^3/\text{mole-K}) = 100.2 \text{ kJ/kg}
\]

Note that, for water, the change in enthalpy in kJ/kg is roughly equal to the pressure rise in MPa because the specific volume is so close to one and $P_{stat} \ll P$. That is really handy.

The saturation enthalpy is read from the saturation tables as 83.95 kJ/kg. The values given in the compressed liquid table (at the end of the steam tables) are 88.6 kJ/kg at 5 MPa and 130 kJ/kg at 50 MPa, corresponding to estimated work values of 4.65 and 46.1 kJ/kg. The estimation error in the computed work is about 7 to 9%, and smaller for lower pressures. This degree of precision is generally satisfactory because the pump work itself is usually small relative to other work and terms (like the work produced by a turbine in a power cycle).
General Equation for Open System

\[
\frac{d}{dt}\left[ m\left( U + \frac{v^2}{2g_c} + \frac{g_\text{z}}{g_c} \right) \right] = \sum_{\text{inlets}} \left[ H + \frac{v^2}{2g_c} + \frac{g_\text{z}}{g_c} \right] \dot{m}^\text{in} - \sum_{\text{outlets}} \left[ H + \frac{v^2}{2g_c} + \frac{g_\text{z}}{g_c} \right] \dot{m}^\text{out} + \dot{Q} + \dot{W}_E + \dot{W}_S
\]

**Figure 2.5** Schematic of a general system.
\[ \frac{d}{dt} \left[ m \left( U + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right) \right] = \sum_{\text{inlets}} \left[ H + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right] \dot{m}^{\text{in}} - \sum_{\text{outlets}} \left[ H + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right] \dot{m}^{\text{out}} + \dot{Q} + \dot{W}_{EC} + \dot{W}_S \]

\[ d \left[ m \left( U + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right) \right] = \sum_{\text{inlets}} \left[ H + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right] dm^{\text{in}} - \sum_{\text{outlets}} \left[ H + \frac{v^2}{2g_c} + \frac{gz}{g_c} \right] dm^{\text{out}} + d\dot{Q} + d\dot{W}_{EC} + d\dot{W}_S \]
\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad C_P = \left( \frac{\partial H}{\partial T} \right)_P \]

\[ \Delta H \equiv \Delta U + \Delta(PV) = \Delta U + R(\Delta T) \] \quad \text{Exact for an ideal gas.}

\[ C_P = C_V + R \] \quad \text{Exact for an ideal gas.}

\[ \Delta H_T \approx V\Delta P_T \] \quad \text{Liquids below } T_r = 0.75 \text{ and solids.}

\[ T_r = \frac{T}{T_c} \] \quad \text{is the reduced temperature calculated by dividing the absolute temperature by the critical}

\[ \Delta U = \int_{T_1}^{T_2} C_V(T) dT \] \quad \text{Ideal gas: exact.}

\[ \text{Real gas: valid only if } V = \text{constant.} \] \quad 2.40

\[ \Delta H = \int_{T_1}^{T_2} C_P(T) dT \] \quad \text{Ideal gas: exact.}

\[ \text{Real gas: valid only if } P = \text{constant.} \] \quad 2.41

\[ \Delta H \approx \int_{T_1}^{T_2} C_P(T) dT + V\Delta P \] \quad \text{Liquid below } T_r = 0.75 \text{ or solid: reasonable approximation.}

\[ \Delta U = \Delta H - \Delta(PV) \approx \Delta H - V\Delta P \approx \int_{T_1}^{T_2} C_P(T) dT \] \quad \text{Liquid below } T_r = 0.75 \text{ or solid: reasonable approximation when pressure change is below several MPa.}

\textit{Note: These formulas do not account for phase changes which may occur.}
Note that the heat capacity of a monatomic ideal gas can be obtained by differentiating the internal energy as given in Chapter 1, resulting in $C_V = 3/2 \ R$ and $C_P = 5/2 \ R$. Heat capacities for diatomics are larger, $C_P = 7/2 \ R$, and $C_V = 5/2 \ R$ near room temperature, and polyatomics are larger still. According to classical theory, each degree of freedom\(^5\) contributes $1/2R$ to $C_V$. Kinetic and potential energy each contribute a degree of freedom in each dimension. A monatomic ideal gas has only three kinetic energy degrees of freedom, thus $C_V = 3/2 \ R$. Diatomic molecules are linear so they have two additional degrees of freedom for the linear (one-dimensional) bond that has kinetic and potential energy both. In complicated molecules, the vibrations are characterized by modes. See the endflap to make a quick comparison. Monatomic solids have three degrees of freedom each for kinetic and vibrational energy, one for each principle direction, thus the law of Dulong and Petit, $C_V^S = 3R$ is a first approximation. Low-temperature heat capacities of monatomic solids are
Example 2.5 Enthalpy change of an ideal gas: Integrating $C_P^{ig}(T)$

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy using the ideal gas law.

**Solution:** The ideal gas change is calculated via Eqn. 2.41 and is independent of pressure. The heat capacity constants are obtained from Appendix E.

\[
H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^3) dT = \\
= A(T_2 - T_1) + B \left( \frac{T_2^2 - T_1^2}{2} \right) + \frac{C}{3} (T_2^3 - T_1^3) + \frac{D}{4} (T_2^4 - T_1^4) \\
= -4.224(463.15 - 378.15) + \frac{0.3063}{2} (463.15^2 - 378.15^2) + \\
\frac{-1.586 \times 10^{-4}}{3} (463.15^3 - 378.15^3) + \frac{3.215 \times 10^{-8}}{4} (463.15^4 - 378.15^4) = 8405 \text{ J/mol}
\]
Example 2.6 Enthalpy of compressed liquid

The compressed liquid tables are awkward to use for compressed liquid enthalpies because the pressure intervals are large. Using saturated liquid enthalpy values for water and hand calculations, estimate the enthalpy of liquid water at 20°C H₂O and 5 and 50 MPa. Compare to the values obtained using the compressed liquid steam tables.

Solution: This is a common calculation needed for working with power plant condensate streams at high pressure. The relevant equation is Eqn. 2.42, but we can eliminate the temperature integral by selecting saturated water at the same temperature and then applying the pressure correction, i.e., applying Eqn. 2.39, \( \Delta H \approx V\Delta P \) relative to the saturation condition, giving \( H = H^{sat} + V\Delta P \). The numerical calculations have already been done in Example 2.4 on page 55. Both calculations use the same approximation, even though the paths are slightly different. A more rigorous analysis is shown later in Example 6.1.

Example 2.7 Adiabatic compression of an ideal gas in a piston/cylinder

Nitrogen is contained in a cylinder and is compressed adiabatically. The temperature rises from 25°C to 225°C. How much work is performed? Assume that the heat capacity is constant \((C_p/R = 7/2)\), and that nitrogen follows the ideal gas law.

Solution: System is the gas. Closed system, system size changes, adiabatic.

\[
d\left[U + \frac{V^2}{2g_c} + \frac{g}{g_c} \right] = dQ + dW_S + dW_{EC}
\]

\[
\int dU = \int dW_{EC} = W_{EC}
\]

\[
dU = C_v dT \Rightarrow W_{EC} = \int C_v dT = C_v \Delta T = (C_p - R) \Delta T \tag{*ig}
\]

\[
= \left(\frac{5}{2}\right) 8.314(200) = 4157 \text{ J/mol}
\]

Note that because the temperature rise is specified, we do not need to know if the process was reversible.
Phase Transitions (Liquid-Vapor)

\[
\Delta U^{vap} = \Delta H^{vap} - P^{sat} V^V = \Delta H^{vap} - RT^{sat}
\]

Estimation of Enthalpies of Vaporization

If the enthalpy of vaporization cannot be located in the appendices or a standard reference book, it may be estimated by several techniques offered and reviewed in the Chemical Engineer’s Handbook and The Properties of Gases and Liquids. One particularly convenient correlation is\(^{10}\)

\[
\frac{\Delta H^{vap}}{RT_c} = 7(1 - T_r)^{0.354} + 11 \omega (1 - T_r)^{0.456}
\]

where \(T_r\) is reduced temperature, \(\omega\) is theacentric factor (to be described in Chapter 7), also available on the back flap. If accurate vapor pressures are available, the enthalpy of vaporization can be estimated far from the critical point (i.e., \(T_r < 0.75\)) by the Clausius–Clapeyron equation:

\[
\Delta H^{vap} = -R \frac{d \ln P^{sat}}{d(1/T)} \quad (T_r < 0.75)
\]

The background for this equation is developed in Section 9.2. Vapor pressure is often represented by the Antoine equation, \(\log P^{sat} = A - B/(T + C)\). If Antoine parameters are available, they may be used to estimate the derivative of Eqn. 2.46,

\[
\frac{d \ln P^{sat}}{d(1/T)} = \frac{2.3026 d \ln P^{sat}}{d(1/T)} = \frac{-2.3026 B(T + 273.15)^2}{(T + C)^2}
\]

where \(T\) is in °C, and \(B\) and \(C\) are Antoine parameters for the common logarithm of pressure. For Antoine parameters intended for other temperature or pressure units, the equation must be carefully converted. The temperature limits for the Antoine parameters must be carefully followed because the Antoine equation does not extrapolate well outside the temperature range where the constants have been fit. If Antoine parameters are unavailable, they can be estimated to roughly 10% accuracy by the shortcut vapor pressure (SCVP) model, discussed in Section 9.3,

\[
A = \log_{10} P_c + 7(1 + \omega)/3; \quad B = -7(1 + \omega)T_c/3; \quad C = 273.15
\]

where the units of \(P_c\) match the units of \(P^{sat}\), \(T_c\) is in K, and \(T\) is in °C.
Phase Transitions (Liquid-Vapor)

\[ \Delta U^{vap} = \Delta H^{vap} - P^{sat} V^V = \Delta H^{vap} - RT^{sat} \]

\[ \Delta U^{fus} = \Delta H^{fus} - \Delta(PV)^{fus} = \Delta H^{fus} - P(V^L - V^S) = \Delta H^{fus} \]

**Ideal Gas Properties**

For an ideal gas, we must specify only the reference \( T \) and \( P \). An ideal gas cannot exist as a liquid or solid, and this fact completely specifies the state of our system. In addition, we need to set \( H^R \) or \( U^R \) (but not both!) equal to zero.

\[ U^{ig} = \int_{T^R}^{T} C_v dT + U^R \] \hspace{1cm} (ig) 2.49

\[ H^{ig} = \int_{T^R}^{T} C_p dT + H^R \] \hspace{1cm} (ig) 2.50

Also at all states, including the reference state, \( U^{ig} = H^{ig} - PV = H^{ig} - RT \) so \( U^{ig}_R = H^{ig}_R - RT_R \). The ideal gas approximation is reliable when contributions from intermolecular potential energy are relatively small. A convenient guideline is, in term of reduced temperature \( T_r = T/T_c \), and reduced pressure \( P_r = P/P_c \) where \( P_c \) is the critical pressure.

Assume ideal gas behavior if \( P < P^{sat} \) and \( T_r > 0.5 + 2P_r \) \hspace{1cm} (ig) 2.51
Figure 2.6 Illustrations of state pathways to calculate properties involving liquid/vapor phase changes.

The examples are representative, and modified paths would apply for states above the normal boiling point, $T_b$. Similar pathways apply for solid/liquid or solid/vapor transformations. Note that a generalized correlation is used for $\Delta H_{vap}$ which differs from the normal boiling point value. The method is intended to be used at subcritical conditions. Pressure corrections are not illustrated for any paths here.
Example 2.8 Acetone enthalpy using various reference states

Calculate the enthalpy values for acetone as liquid at 20°C and vapor at 90°C and the difference in enthalpy using the following reference states: (a) liquid at 20°C; (b) ideal gas at 25°C and \( \Delta H^{\text{vap}} \) at the normal boiling point; (c) ideal gas at 25°C and the generalized correlation for \( \Delta H^{\text{vap}} \) at 20°C. Ignore pressure corrections and treat vapors as ideal gases.

Solution: Heat capacity constants are available in Appendix E. For all cases, 20°C is 293.15K, 90°C is 363.15K, and the normal boiling point is \( T_b = 329.15K \).

(a) \( H^L = 0 \) because the liquid is at the reference state. The vapor enthalpy is calculated analogous to Fig. 2.6, pathway (a). The three terms of pathway (a) are \( H^V = 4639 + 30200 + 2799 = 37,638 \) J/mol. The difference in enthalpy is \( \Delta H = 37,638 \) J/mol.

(b) \( H^L \) will use a path analogous to Fig. 2.6, pathway (b). The three terms of pathway (b) are \( H^L = 2366 – 30200 – 4638 = -32472 \) J/mol. \( H^V \) is calculated using Eqn. 2.50, \( H^V = 5166 \) J/mol. The difference is \( \Delta H = 5166 + 32472 = 37,638 \) J/mol, same as part (a).

(c) \( H^L \) will use a path analogous to Fig. 2.6, pathway (c). The generalized correlation of Eqn. 2.45 predicts a heat of vaporization at \( T_b \) of 29,280 J/mol, about 3% low. At 20°C, the heat of vaporization is predicted to be 31,420 J/mol. The two steps in Fig. 2.6 (c) are \( H^L = -365 – 31420 = -31785 \) J/mol. The enthalpy of vapor is the same calculated in part (b), \( H^V = 5166 \) J/mol. The enthalpy difference is \( \Delta H = 5166 + 31785 = 36,950 \) J/mol, about 2% low relative to part (b).
Example 2.9 Comparing changes in kinetic energy, potential energy, internal energy, and enthalpy

For a system of 1 kg water, what are the internal energy and enthalpy changes for raising the temperature 1°C as a liquid and as a vapor from 24°C to 25°C? What are the internal energy enthalpy changes for evaporating from the liquid to the vapor state? How much would the kinetic and potential energy need to change to match the magnitudes of these changes?

**Solution:** The properties of water and steam can be found from the saturated steam tables, interpolating between 20°C and 25°C. For saturated water or steam being heated from 24°C to 25°C, and for vaporization at 25°C:

<table>
<thead>
<tr>
<th></th>
<th>ΔU(J)</th>
<th>ΔH(J)</th>
<th>ΔU_vap(KJ)</th>
<th>ΔH_vap(KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>4184</td>
<td>4184</td>
<td></td>
<td></td>
</tr>
<tr>
<td>steam</td>
<td>1362</td>
<td>1816</td>
<td>2304.3</td>
<td>2441.7</td>
</tr>
</tbody>
</table>

Of these values, the values for ΔU of steam are lowest and can serve as the benchmark. How much would kinetic and potential energy of a system have to change to be comparable to 1000 J?

**Kinetic energy:** If ΔKE = 1000 J, and if the kg is initially at rest, then the velocity change must be,

\[ \Delta(v^2) = \frac{2 \times 1000 \text{J}}{1 \text{kg}} \text{ or } \Delta v = 44.7 \text{ m/s} \]

This corresponds to a velocity change of 161 kph (100 mph). A velocity change of this order of magnitude is unlikely in most applications except nozzles (discussed below). Therefore, kinetic energy changes can be neglected in most calculations when temperature changes occur.

**Potential energy:** If ΔPE = 1000 J, then the height change must be,

\[ \Delta z = \frac{1000 \text{ J}}{1 \left( 9.8066 \text{ N/kg} \right) \frac{1}{1}} = 102 \text{ m} \]

This is equivalent to about one football field in position change. Once again this is very unlikely in most process equipment, so it can usually be ignored relative to heat and work interactions. Further, when a phase change occurs, these changes are even less important relative to heat and work interactions.
Example 2.10 Transformation of kinetic energy into enthalpy

Water is flowing in a straight horizontal pipe of 2.5 cm ID with a velocity of 6.0 m/s. The water flows steadily into a section where the diameter is suddenly increased. There is no device present for adding or removing energy as work. What is the change in enthalpy of the water if the downstream diameter is 5 cm? If it is 10 cm? What is the maximum enthalpy change for a sudden enlargement in the pipe? How will these changes affect the temperature of the water?

Solution: A boundary will be placed around the expansion section of the piping. The system is fixed volume, \( \dot{W}_{EC} = 0 \), adiabatic without shaft work. The open steady-state system is under steady-state flow, so the left side of the energy balance is zero.

\[
0 = \sum_{\text{inlets}} \left[ H + \frac{v^2}{2g_e} + \frac{\rho g}{g_c} \right] m^{in} - \sum_{\text{outlets}} \left[ H + \frac{v^2}{2g_e} + \frac{\rho g}{g_c} \right] m^{out} + \dot{Q} + \dot{W}_{EC} + \dot{W}_R
\]

Simplifying: \( \Delta H = \frac{-\Delta(v^2)}{2g_e} \)

Liquid water is incompressible, so the volume (density) does not change from the inlet to the outlet. Letting \( A \) represent the cross-sectional area, and letting \( D \) represent the pipe diameter, \( v = v_1 A_1 = v_2 A_2 \Rightarrow v_2 = v_1 (A_1/A_2) \),

\[
\Delta(v^2) = v_1^2 \left( \frac{D_1}{D_2} \right)^4 - 1
\]

\[
\Delta H = \frac{-v_1^2}{2g_e} \left( \frac{D_1}{D_2} \right)^4 - 1
\]

\( D_2/D_1 = 2 \Rightarrow \Delta H = -6.0^2 \text{ m}^2/\text{s}^2 \left( \text{J/kg-m}^2/\text{s}^2 \right) \left( \frac{2^4}{1} \right) = 17 \text{ J/kg} \)

\( D_2/D_1 = 4 \Rightarrow \Delta H = 18 \text{ J/kg} \)

\( D_2/D_1 = \infty \Rightarrow \Delta H = 18 \text{ J/kg} \)

To calculate the temperature rise, we can relate the enthalpy change to temperature since they are both state properties. From Eqn. 2.42, neglecting the effect of pressure,

\[
\Delta H = C_p \Delta T
\]

\[
C_p = 4184 \frac{J}{\text{kgK}} \Rightarrow \Delta T = \frac{18.00 (\text{J/kg})}{4184 (\text{J/(kgK)})} = 0.004 \text{ K}
\]
Nozzles

Nozzles are specially designed devices utilized to convert pressure drop into kinetic energy. Common engineering applications involve gas flows. An example of a nozzle is a booster rocket. Nozzles are also used on the inlets of impulse turbines to convert the enthalpy of the incoming stream to a high velocity before it encounters the turbine blades. $\Delta u$ is significant for nozzles. A nozzle is designed with a specially tapered neck on the inlet and sometimes the outlet as shown schematically in Fig. 2.7. Nozzles are optimally designed at particular velocities/pressures of operation to minimize viscous dissipation.

\[
0 = \left[ H + \frac{v^2}{2g_c} + \frac{g_z}{g_c} \right] \dot{m}^{\text{in}} - \left[ H + \frac{v^2}{2g_c} + \frac{g_z}{g_c} \right] \dot{m}^{\text{out}} + \dot{Q} + \dot{W}_{EC} + \dot{W}_S
\]

\[
\Delta H = \left( -\Delta (v^2)/(2g_c) \right) \text{ for nozzles}
\]

Figure 2.7 Illustration of a converging-diverging nozzle showing the manner in which inlets and outlets are tapered.
Cocurrent
Countercurrent
Superheater

0 = \Delta H_A m_A - \Delta H_B m_B \quad \text{overall heat exchanger}
Adiabatic Turbines or Adiabatic Expanders

Figure 2.9 Illustration of a turbine. The rotor (shaft) turns due to the flow of gas. The blades connected to the shell are stationary (stators), and are sometimes curved shapes to perform as nozzles. The stator blades are not shown to make the rotors more clear.
Calculation of Shaft Work

\[ W_S = \int_{in}^{out} V dP \]

reversible pump, compressor, turbine

\[ W_S \approx V^L (P_{out}^{out} - P_{in}^{in}) = \frac{\Delta P}{\rho} \]

liquid pump

Figure 2.9 Illustration of a turbine. The rotor (shaft) turns due to the flow of gas. The blades connected to the shell are stationary (stators), and are sometimes curved shapes to perform as nozzles. The stator blades are not shown to make the rotors more clear.
2.14 STRATEGIES FOR SOLVING PROCESS THERMODYNAMICS PROBLEMS

1. Choose system boundaries; decide whether this boundary location will make the system open or closed.

2. Identify all given state properties of fluids in system and crossing boundaries. Identify which are invariant with time. Identify your system as steady or unsteady state. (For unsteady-state pumps, turbines, or compressors, the accumulation of energy within the device is usually neglected.) For open, steady-state systems, write the mass balance and solve if possible.

3. Identify how many state variables are unknown for the system. Recall that only two state variables are required to specify the state of a pure, single-phase fluid. The number of unknowns will equal the number of independent equations necessary for a solution. (Remember in a system of known total volume \( V \); that if \( n \) is known, the state variable \( V \) is known.)

4. Write the mass balance and the energy balance. These are the first equations to be used in the solution. Specify reference states for all fluids if necessary. Simplify energy balance to eliminate terms which are zero for the system specified in step 1. Combine the mass balance and the energy balance for open systems.

   For unsteady-state problems:

   (a) Identify whether the individual terms in the energy balance may be integrated directly without combining with other energy balance terms. Often the answer is obtained most easily this way. This is almost always possible for closed-system problems.

   (b) If term-by-term integration of the energy balance is not possible, rearrange the equation to simplify as much as possible before integration.

5. Look for any other information in the problem statement that will provide additional equations if unknowns remain. Look for key words such as adiabatic, isolated, throttling, nozzle, reversible, and irreversible. Using any applicable constraints of throttling devices, nozzles, and so on, relate stream properties for various streams to one another and to the system state properties. Constraints on flow rates, heat flow, and so on, provide additional equations. With practice, many of these constraints may be recognized immediately before writing the energy balance in steps 3 and 4.

6. Introduce the thermodynamic properties of the fluid (the equation of state). This provides all equations relating \( P, V, T, U, H, C_p \), and \( C_v \). The information will consist of either 1) the ideal gas approximation; 2) a thermodynamic chart or table; or 3) a volumetric equation of state (which will be introduced in Chapter 7). Using more than one of these sources of information in the same problem may introduce inconsistencies in the properties used in the solution, depending on the accuracy of the methods used.

   Combine the thermodynamic information with the energy balance. Work to minimize the number of state variables which remain unknown. Many problems are solved at this point.

7. Do not hesitate to move your system boundary and try again if you are stuck. Do not forget to try an overall balance (frequently, two open systems can be combined to give an overall closed system, and strategy 4a can be applied). Make reasonable assumptions.

8. After an answer is obtained, verify assumptions that were made to obtain the solution.
Example 2.11 Adiabatic, reversible expansion of an ideal gas

Suppose an ideal gas in a piston + cylinder is adiabatically and reversibly expanded to twice its original volume. What will be the final temperature?

Solution: First consider the energy balance. The system will be the gas in the cylinder. The system will be closed. Since a basis is not specified, we can choose 1 mole. Since there is no mass flow, heat transfer, or shaft work, the energy balance becomes:

$$dU = \sum \left( \frac{\mu}{\beta_{\kappa}} + \frac{E}{\kappa} \right) = \sum dQ + \sum dW_E + \sum dW_{EC}$$

$$dU = -PdV$$

In this case, as we work down to step 4 in the strategy, we see that we cannot integrate the sides independently since $P$ depends on $T$. Therefore, we need to combine terms before integrating.

$$C_v dT = -RT \frac{dV}{V} \text{ which becomes } C_v \frac{dV}{V} = -RT dV \quad \text{(ig) 2.62}$$

The technique that we have performed is called separation of variables. All of the temperature dependence is on the left-hand side of the equation and all of the volume dependence is on the right-hand side. Now, if we assume a constant heat capacity for simplicity, we can see that this integrates to

$$C_v \ln \frac{T}{T_i} = \ln \frac{V}{V_i} \quad \text{(ig)}$$

$$\left( \frac{T}{T_i} \right)^{C_v/R} = \frac{V}{V_i} \quad \text{(ig) 2.63}$$

Example 2.11 Adiabatic, reversible expansion of an ideal gas (Continued)

Although not required, several rearrangements of this equation are useful for other problems. Note that we may insert the ideal gas law to convert to a formula relating $T$ and $P$. Using $T = \frac{PV}{R}$,

$$\left( \frac{T}{T_i} \right)^{C_v/R} = \left( \frac{T}{T_i} \right)^{(C_v/R)+1} = \frac{P}{P_i} \quad \text{(ig)}$$

Rearranging,

$$\left( \frac{T}{T_i} \right)^{(C_v/R)} = \left( \frac{T}{T_i} \right)^{(C_v/R)+1} = \frac{P}{P_i} \quad \text{(ig)}$$

which becomes

$$\left( \frac{T}{T_i} \right)^{(C_v/R)} = \frac{P}{P_i} \quad \text{(ig) 2.64}$$

We may also insert the ideal gas law into Eqn. 2.63 to convert to a formula relating $P$ and $V$.

Using $T = \frac{PV}{R}$,

$$\left( \frac{PV}{R} \right)^{(C_v/R)} = \frac{V}{V_i} \quad \text{(ig)}$$

$$\frac{P}{P_i} = \left( \frac{V}{V_i} \right)^{(R/C_v)} \frac{V_i}{V} = \left( \frac{V}{V_i} \right)^{(R/C_v)+1} = \left( \frac{V}{V_i} \right)^{(C_v/C_p)} \quad \text{(ig)}$$

which may be written

$$\frac{P}{P_i} = \text{const} \quad \text{(ig) 2.65}$$
Example 2.12 Continuous adiabatic, reversible compression of an ideal gas

Suppose 1 kmol/h of air at 5 bars and 298 K is adiabatically and reversibly compressed in a continuous process to 25 bars. What will be the outlet temperature and power requirement for the compressor in hp?

Solution: Note that air is composed primarily of oxygen and nitrogen and these both satisfy the stipulations for diatomic gases with their reduced temperatures high and their reduced pressures low. In other words, the ideal gas approximation with $C_p/R = 7/2$ is clearly applicable. Next consider the energy balance. The system is the compressor. The system is open. Since it is a steady-state process with no heat transfer, the simplification of the energy balance has been discussed on page 73 and shown on page 72, and the energy balance becomes:

$$\Delta H = \dot{Q} + W_S$$  \hspace{1cm} 2.66$$

We can adapt Eqn. 2.31 for an ideal gas as follows:

$$dW_S = dH = V dP$$

In this case, as we work down to step 4 in the strategy, we see that we cannot integrate the sides independently since $P$ depends on $T$. Therefore, we need to combine terms before integrating.

$$C_p dT = RT \frac{dP}{P} \text{ which becomes } \frac{C_p}{T} dT = \frac{R}{P} dP$$  \hspace{1cm} (ig) 2.67

Once again, we have performed separation of variables. The rest of the derivation is entirely analogous to Example 2.11, and, in fact, the resultant formula is identical.

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{C_p}{R}}$$  \hspace{1cm} (ig) 2.68

Note that this formula comes up quite often as an approximation for both open and closed systems. Making the appropriate substitutions,

$$T_2 = 298 \left( \frac{25}{5} \right)^\frac{7}{2} = 472 \text{ K.}$$

Adapting the adiabatic energy balance and assuming $C_p$ is constant,

$$W_S^{ig} = \Delta H^{ig} = C_p^{ig} \Delta T = C_p^{ig} \left[ \frac{P_2}{P_1} \right]^{\frac{R/C_p}{\gamma}} - 1$$  \hspace{1cm} (ig) 2.69

Substituting, $W_S^{ig} = 3.5 \cdot 8.314 \cdot (472 - 298) = 5063 \text{ J/mole}$

At the given flow rate, and reiterating that this problem statement specifies a reversible process:

$$W_S^{rev} = 5063 \text{ J/mole [1000mole/hr]/[1hr/3600sec] [1hp/(745.73/s)]} = 1.9 \text{ hp}$$
**Example 2.13 Continuous, isothermal, reversible compression of an ideal gas**

Repeat the compression from the previous example, but consider steady-state isothermal compression. What will be the heat removal rate and power requirement for the compressor in hp?

**Solution:** Let’s return to the perspective of the section ‘Understanding Enthalpy and Shaft Work’ on page 54 and analyze the EC work and flow work for an ideal gas packet of unit mass. The $W_{EC}$ is,

$$W_{EC} = -[PdV - \frac{(RT/V)dV}{V_2/V_1}] = -RT\ln(V_2/V_1) \quad (*)_{ig}$$

For an isothermal, ideal gas, $V_2/V_1 = P_1/P_2$. Noting the reciprocal and negative logarithm,

$$W_{EC} = -RT\ln(V_2/V_1) = RT\ln(P_2/P_1) \quad (**_{ig})$$

This is the work to isothermally squeeze an ideal gas packet of unit mass to a given pressure. The flow work performed on an ideal gas packet of unit mass is,

$$W_{flow} = PV_{out} - PV_{in} = RT_{out} - RT_{in} = 0 \quad (**_{ig})$$

Therefore, the total requirement for isothermally compressing an ideal gas packet of unit mass is,

$$W_S = RT\ln(P_2/P_1) \quad (**_{ig})$$

$$W_S = RT\ln\left(\frac{P_2}{P_1}\right) = 8.314(298)\ln5 = 3987 \frac{J}{mol} \quad (ig) 2.70$$

At the given flow rate, and reiterating that this problem statement specifies a reversible process,

$$W_S^{rev} = 3987 \frac{J}{mole \cdot [1000mole/hr] \cdot [1hr/3600sec] \cdot [1hp/745.7J/s]} = 1.5 \text{ hp}$$
Example 2.14 Heat loss from a turbine

High-pressure steam at a rate of 1100 kg/h initially at 3.5 MPa and 350°C is expanded in a turbine to obtain work. Two exit streams leave the turbine. Exiting stream (2) is at 1.5 MPa and 225°C and flows at 110 kg/h. Exiting stream (3) is at 0.79 MPa and is known to be a mixture of saturated vapor and liquid. A fraction of stream (3) is bled through a throttle valve to 0.10 MPa and is found to be 120°C. If the measured output of the turbine is 100 kW, estimate the heat loss of the turbine. Also, determine the quality of the steam in stream (3).

Solution: First draw a schematic. Designate boundaries. Both System A and System B are open steady-state systems.

Stream (1) 3.5 MPa 350°C 1100 kg/h

System A

Stream (2) 1.5 MPa 225°C 110 kg/h

Stream (3)

System B

Stream (4) 0.1 MPa 120°C 0.79 MPa sat’d mix

The mass balance gives $m_3 = 990$ kg/h. Next, determine which streams are completely specified: Streams (1), (2), and (4) are fully specified. Since Stream (3) is saturated, the temperature and pressure and specific enthalpies of the saturated vapor and liquid can be found, but the quality needs to be calculated to determine the overall molar enthalpy of the stream. From the steam tables we find $H_1$ directly. For $H_2$ we use linear interpolation. The value $H(1.5$ MPa, 225°C) is not available directly, so we need to first interpolate at 1.4 MPa between 200°C and 250°C to find $H(1.4$ MPa, 225°C) and then interpolate between this value and the value at 1.6 MPa:

$$H(1.4$ MPa, 225°C) = \frac{1}{2}(2803.0 + 2927.9) = 2865.5$ kJ/kg

$$H(1.6$ MPa, 225°C) = 2792.8 + \frac{23.6}{48.6}(2919.9 - 2792.8) = 2854.5$ kJ/kg

Then to find $H_2$: $H_2 = 0.5(2865.5 + 2854.5) = 2860.0$ kJ/kg. For $H_4$ we can interpolate in the superheated steam tables:

$$H_4 = 2675.8 + \frac{20}{50}(2776.6 - 2675.8) = 2716.1$ kJ/kg

Example 2.14 Heat loss from a turbine (Continued)

Recognize System B as a throttle valve; therefore, $H_3 = H_4 = 2716.1$ kJ/kg. We make a table to summarize the results so that we can easily find values:

<table>
<thead>
<tr>
<th>Stream</th>
<th>1</th>
<th>2</th>
<th>3, 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$(kJ/kg)</td>
<td>3104.8</td>
<td>2860.0</td>
<td>2716.1</td>
</tr>
</tbody>
</table>

The energy balance for System A gives, using $\dot{W}_S = -100$ kW given in the problem statement,

$$0 = H_1 \dot{m}_1 - H_2 \dot{m}_2 - H_3 \dot{m}_3 + \dot{Q} + \dot{W}_S - 3104.8(1100) - 2860.0(110) - 2716.1(990) + \dot{Q} + \dot{W}_S$$

$$\dot{Q} = \frac{-411,741}{3600} \text{kJ} \text{s}^{-1} + \frac{100 \text{kJ}}{s} = -4.4 \text{kJ/s}$$

To find the quality of stream (3), $H_3 \dot{m}_3 = H^L \dot{m}_3^L - H^V \dot{m}_3^V$.

$$H_3 = H^L \frac{\dot{m}_3^L}{\dot{m}_3} - H^V \frac{\dot{m}_3^V}{\dot{m}_3} = H^L + q(H^\text{qph})$$

At 0.79 MPa from the sat’d P table, $H^L = 718.5$ kJ/kg and $\Delta H^V = 2049$ kJ/kg.

$$q = \frac{2716.1 - 718.5}{2049} = 0.975$$
Example 2.15 Adiabatic expansion of an ideal gas from a leaky tank

An ideal gas is leaking from an insulated tank. Relate the change in temperature to the change in pressure for gas leaking from a tank. Derive an equation for ΔU for the tank.

Solution: Let us choose our system as the gas in the tank at any time. This will be an open, unsteady-state system. There is no inlet stream and one outlet stream. The mass balance gives \( \dot{m} = - \dot{m}_{\text{out}} \).

We can neglect kinetic and potential energy changes. Although the gas is expanding, the system size remains unchanged, and there is no expansion/contraction work. The energy balance becomes (on a molar basis):

\[
d(nU) = H^{	ext{in}} - H^{	ext{out}} + dU + dU_{\text{EC}} + dU_{\text{g}}
\]

Since the enthalpy of the exit stream matches the enthalpy of the tank, \( H^\text{out} = H \).

\[
d(nU) = -dH + dU_{\text{EC}} + dU_{\text{g}}
\]

Collecting terms in the energy balance,

\[
n \dot{m} dT = (\dot{H} - \dot{U}) d\dot{n}
\]

Performing some substitutions, the energy balance can be written in terms of \( T \) and \( n \),

\[
\left( \frac{H - U}{T} \right) = PV - kT; \quad \dot{n} = \frac{C_v}{R} \frac{dT}{T} - \frac{n}{R} \Rightarrow \frac{C_v}{R} \ln \frac{T}{T_i} = \ln \frac{n}{n_i}
\]

The volume of the tank is constant, \( V = \text{constant} \); therefore,

\[
\ln \frac{n}{n_i} = \ln \frac{P}{P_i} = - \ln \frac{T}{T_i} = - \ln \frac{P}{P_i} = \frac{C_v}{R} \ln \frac{T}{T_i}
\]

Substituting,

\[
\left( \frac{C_v}{R} + 1 \right) \ln \frac{T}{T_i} = \frac{C_v}{R} \ln \frac{T}{T_i} = \ln \frac{P}{P_i}
\]

Recognizing the relation between \( C_v \) and \( C_p \), defining \( \gamma = C_p / C_v (= 1.4 \) for an ideal diatomic gas), note \( R/C_p = (C_p - C_v) / C_p = 1 - (1/\gamma) = (\gamma - 1)/\gamma \):

\[
\frac{T}{T_i} = \left( \frac{P}{P_i} \right)^{\gamma - 1} \quad \text{(*ig 2.71)}
\]

Through the ideal gas law \( PV = RT \), we can obtain other arrangements of the same formula:

\[
\frac{V}{V_i} = \left( \frac{P}{P_i} \right)^{1/\gamma}; \quad \frac{P_i}{P} = \left( \frac{V}{V_i} \right)^{\gamma - 1} = \left( \frac{T}{T_i} \right)^{1/\gamma} - 1; \quad \frac{T}{T_i} = \left( \frac{V}{V_i} \right)^{\gamma - 1} \quad \text{(*ig 2.72)}
\]

The numerical value for the change in internal energy of the system depends on the reference state because the reference state temperature will appear in the result:

\[
\Delta U = n \left[ C_v (T - T_i) + U_R \right] - n_i \left[ C_v (T_i - T_i) + U_R \right] \quad \text{(*ig)}
\]
Example 2.16 Adiabatically filling a tank with an ideal gas

Helium at 300 K and 3000 bar is fed into an evacuated cylinder until the pressure in the tank is equal to 3000 bar. Calculate the final temperature of the helium in the cylinder \((C_p/R = 5/2)\).

**Solution**: The system will be the gas inside the tank at any time. The system will be an open, unsteady-state system. The mass balance is \(dn = dn^{in}\). The energy balance becomes:

\[
d(nU) = H^i dn^{in} - H^{out} dn^{out} + dQ + dW_{EC} + dW_S
\]

We recognize that \(H^i\) will be constant throughout the tank filling. Therefore, by hint 4a from the problem-solving strategy, we can integrate terms individually. We need to be careful to keep the superscript since the incoming enthalpy is at a different state than the system. The right-hand side of the energy balance can be integrated to give

\[
\int_i^f H^i dn = H^i \int_i^f dn = H^i (n^f - n^i) = H^i n^f
\]

The left-hand side of the energy balance becomes

\[
\Delta(U)n = U_f n^f - U_i n^i = U_{n^f}
\]

Combining the result with the definition of enthalpy,

\[
U_f = H^i = U^{in} + PV^{in} = U^{in} + RT^{in}
\]

And with our definition of heat capacity, we can find temperatures:

\[
\Delta U = C_v (T^f - T^{in}) = RT^{in} \Rightarrow T^f = T^{in}(R + C_v)/C_v = T^{in}C_p/C_v
\]

\(^*\)ig

Note that the final temperature is independent of pressure for the case considered here.
Example 2.17 Adiabatic expansion of steam from a leaky tank

An insulated tank contains 500 kg of steam and water at 215°C. Half of the tank volume is occupied by vapor and half by liquid: 25 kg of dry vapor is vented slowly enough that temperature remains uniform throughout the tank. What is the final temperature and pressure?

Solution: There are some similarities with the solution to Example 2.15 on page 81; however, we can no longer apply the ideal gas law. The energy balance reduces in a similar way, but we note that the exiting stream consists of only vapor; therefore, it is not the overall average enthalpy of the tank:

\[ d(mU) = -H^{\text{out}} dm^{\text{out}} = H^{V} dm \]

The sides of the equation can be integrated independently if the vapor enthalpy is constant. Looking at the steam table, the enthalpy changes only about 10 kJ/kg out of 2800 kJ/kg (0.3%) along the saturation curve down to 195°C. Let us assume it is constant at 2795 kJ/kg making the integral of the right-hand side simply \( H^{V} \Delta m \). Note that this procedure is equivalent to a numerical integration by trapezoidal rule as given in Appendix B on page 822. Many students forget that analytical solutions are merely desirable, not absolutely necessary. The energy balance then can be integrated using hint 4a on page 74.

\[ \Delta U = m^{f}U^{f} - m^{l}U^{l} = 2795(m^{f} - m^{l}) = 2795(-25) = -69,875 \text{ kJ} \]

The quantity \( m^{f} = 475 \), and \( m^{U^{l}} \) will be easy to find, which will permit calculation of \( U^{f} \). For each m\(^{3}\) of the original saturated mixture at 215°C,

\[
\begin{array}{c|c|c}
\text{0.5 m}^{3} \text{ vapor} & \text{kg vapor} & = 5.28 \text{ kg vapor} \\
& 0.0947 \text{ m}^{3} \text{ vapor} & \\
\text{0.5 m}^{3} \text{ liquid} & \text{kg liquid} & = 423.4 \text{ kg liquid} \\
& 0.001181 \text{ m}^{3} \text{ liquid} & \\
\end{array}
\]
Therefore,

\[ V^f = \frac{m^3}{423.4 + 5.28 \text{ kg}} = 0.00233 \text{ m}^3/\text{kg} \]

So the tank volume, quality, and internal energy are:

\[ V^f = \frac{500 \text{ kg \ m}^3}{428.63} = 1.166 \text{ m}^3 \]

\[ q^f = 5.28 \text{ kg vapor / 428.63 kg} = 0.0123 U^f - 918.04 + 0.0123(1681.9) = 938.7 \text{ kJ/kg} \]

\[ U^f = 938.7 \text{ kJ/kg} \times 500 \text{ kg} = 469,400 \text{ kJ} \]

Then, from the energy balance and mass balance,

\[ U^f = (-69.875 + 469,400) \text{ kJ / 475 kg} = 841.0 \text{ kJ/kg} \]

\[ V^f = 1.166 \text{ m}^3 / 475 \text{ kg} = 0.00245 \text{ m}^3/\text{kg} \]

We need to find \( P^f \) and \( T^f \) which correspond to these state variables. The answer will be along the saturation curve because the overall specific volume is intermediate between saturated vapor and liquid values at lower pressures. We will guess \( P^f \) (and the corresponding saturation \( T^f \)), find \( q \) from \( V^f \), then calculate \( U^f_{\text{calc}} \), and compare to \( U^f = 841.0 \text{ kJ/kg} \). If \( U^f_{\text{calc}} \) is too high, the \( P^f \) (and \( T^f \)) guess will be lowered.

Since \( V = V^L + q(V^V - V^L) \),

\[ q = \frac{0.00245 - V^L}{V^V - V^L} \text{ and from this value of } q, \ U^f_{\text{calc}} = U^L + q(U^V - U^L) \]

To guide our first guess, we need \( U^f_{\text{calc}} < U^f = 841.0 \text{ kJ/kg} \). Our first guess is \( T^f = 195\degree \text{C} \). Values for the properties from the steam tables are shown in the table below. This initial guess gives \( U^f_{\text{calc}} = 845 \text{ kJ/kg} \); no further iteration is necessary. The \( H^f \) at this state is 2789; therefore, our assumption of \( H^f \approx \text{constant} \) is valid.

<table>
<thead>
<tr>
<th>State</th>
<th>( P \text{(MPa)} )</th>
<th>( T \text{(\degree C)} )</th>
<th>( P^L )</th>
<th>( V^L )</th>
<th>( T^L )</th>
<th>( \Delta U^\text{vap} )</th>
<th>( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.106</td>
<td>215</td>
<td>0.001181</td>
<td>0.0947</td>
<td>918.04</td>
<td>1681.9</td>
<td>0.0123</td>
</tr>
<tr>
<td>Guess</td>
<td>1.3988</td>
<td>195</td>
<td>0.001149</td>
<td>0.1409</td>
<td>828.18</td>
<td>1763.6</td>
<td>0.0093</td>
</tr>
</tbody>
</table>

\[ P^f = 1.4 \text{ MPa}, \ T^f = 195\degree \text{C}, \ \Delta P = 0.7 \text{ MPa}, \ \Delta T = 26\degree \text{C} \]
Important Equations

\[ \Delta U = Q + W_{EC} \]  \text{closed systems}

\[ \Delta H = Q + W_S \]  \text{open, steady systems}

\[ d(nU) = H^n dn^{in} - H^o^{out} dn^{out} + dQ + dW_{EC} + dW_S \]  \text{open, unsteady-state systems}

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Work Formula (ig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>[ W_{EC} = -\int PdV = -RT\int \frac{dV}{V} = -RT\ln \frac{V_2}{V_1} ] (ig)</td>
</tr>
<tr>
<td>Isobaric</td>
<td>[ W_{EC} = -\int PdV = -P(V_2 - V_1) ] (ig)</td>
</tr>
<tr>
<td>Adiabatic and reversible</td>
<td>[ W_{EC} = -\int PdV = -\int \text{const} \frac{dV}{V(c_p/c_v)} ] (*ig) or [ \Delta U = C_V(T_2 - T_1) = W_{EC} ] (*ig) [ \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(R/C_v)} = \left(\frac{V_1}{V_2}\right)^{(R/C_v)} ] (*ig)</td>
</tr>
</tbody>
</table>
Test Yourself

1. Write the energy balance without looking at the book. To help remember the terms, think about the properties the terms represent rather than memorizing the symbols.

2. In the presentation of the text, which side of the balance represents the system and which terms represent interactions at the boundaries?

3. Explain the terms “closed-system,” “open-system,” and “steady state” to a friend of the family member who is not an engineer.

4. Explain how a reference state helps to solve problems. Select a reference state for water that is different from the steam table reference state. Create a path starting from saturated liquid below the normal boiling point, through the normal boiling point, and cooling down to saturated vapor at the initial temperature. Use heat capacities and the latent heat at the normal boiling point to estimate the heat of vaporization and compare it with the steam table value.

5. Write a MATLAB, Excel, or calculator routine that will enable you to calculate heat capacity integrals easily.

6. Think of as many types of paths as you can from memory (isothermal, adiabatic, etc.) and try to derive the heat and work flow for a piston/cylinder system along each path.
2.19 PRACTICE PROBLEMS

A. General Reductions of the Energy Balance

The energy balance can be developed for just about any process. Since our goal is to learn how to develop model equations as well as to simply apply them, it is valuable practice to obtain the appropriate energy balance for a broad range of odd applications. If you can deduce these energy balances, you should be well prepared for the more common energy balances encountered in typical chemical engineering processes.

P2.1 A pot of water is boiling in a pressure cooker when suddenly the pressure relief valve becomes stuck, preventing any steam from escaping. System: the pot and its contents after the valve is stuck. (ANS. \(d[mU]/dt = \dot{Q}\))

P2.2 The same pot of boiling water as above. System: the pot and its contents before the valve is stuck. (ANS. \(d[mU] = inHV + \dot{Q}\))

P2.3 An gas home furnace has been heating the house steadily for hours. System: the furnace. (ANS. \(\Delta H = \dot{Q}\) (gas furnace))

P2.4 An gas home furnace has been heating the house steadily for hours. System: the house and all contents. (ANS. \(d[mU]/dt = \dot{Q}_{Heat} + \dot{Q}_{Loss}\) (gas furnace))

P2.5 A child is walking to school when he is hit by a snowball. He stops in his tracks. System: the child. (ANS. \(\Delta[mU + mv^2/2g_c] = m_{snow}[H + v^2/(2g_c)]_{snow}\))

P2.6 A sealed glass bulb contains a small paddle-wheel (Crookes radiometer). The paddles are painted white on one side and black on the other. When placed in the sun, the paddle wheel begins to turn steadily. System: the bulb and its contents. (ANS. \(\Delta U = 0\))

P2.7 A sunbather lays on a blanket. At 11:30 A.M., the sunbather begins to sweat. System: the sunbather at noon. (ANS. \((d[mU]/dt) = \dot{m}HV + \dot{Q}\))

P2.8 An inflated balloon slips from your fingers and flies across the room. System: balloon and its contents. (ANS. \(d[mU + mv^2_{balloon}/2g_c]/dt = [H + v^2/(2g_c)]^{old} dm/dt + W_{EC}\))
B. Numerical Problems

P2.9 Consider a block of concrete weighing 1 kg.

(a) How far must it fall to change its potential energy by 1 kJ? (ANS. 100 m)
(b) What would be the value of its velocity at that stage? (ANS. 44.7 m/s)

P2.10 A block of copper weighing 0.2 kg with an initial temperature of 400 K is dropped into 4 kg of water initially at 300 K contained in a perfectly insulated tank. The tank is also made of copper and weighs 0.5 kg. Solve for the change in internal energy of both the water and the block given \( C_p = 4.184 \text{ J/g-K} \) for water and 0.380 J/g-K for copper. (ANS. 7480 J, –7570 J)

P2.11 In the preceding problem, suppose that the copper block is dropped into the water from a height of 50 m. Assuming no loss of water from the tank, what is the change in internal energy of the block? (ANS. –7570 J)

P2.12 In the following take \( C_p = 5 \) and \( C_p = 7 \text{ cal/mol-K} \) for nitrogen gas:

(a) Five moles of nitrogen at 100°C is contained in a rigid vessel. How much heat must be added to the system to raise its temperature to 300°C if the vessel has a negligible heat capacity? (ANS. 5000 cal) If the vessel weighs 80 g and has a heat capacity of 0.125 cal/g-K, how much heat is required? (ANS. 7000 cal)

(b) Five moles of nitrogen at 300°C is contained in a piston/cylinder arrangement. How much heat must be extracted from this system, which is kept at constant pressure, to cool it to 100°C if the heat capacity of the piston and cylinder is neglected? (ANS. 7000 cal)

P2.13 A rigid cylinder of gaseous hydrogen is heated from 300 K and 1 bar to 400 K. How much heat is added to the gas? (ANS. 2080 J/mole)

P2.14 Saturated steam at 660°F is adiabatically throttled through a valve to atmospheric pressure in a steady-state flow process. Estimate the outlet quality of the steam. (ANS. \( q = 0.96 \))

P2.15 Refer to Example 2.10 about transformation of kinetic energy to enthalpy. Instead of water, suppose \( N_2 \) at 1 bar and 298 K was flowing in the pipe. How would that change the answers? In particular, how would the temperature rise change? (ANS. max ~0.001K)

P2.16 Steam at 150 bars and 600°C passes through process equipment and emerges at 100 bars and 700°C. There is no flow of work into or out of the equipment, but heat is transferred.

(a) Using the steam tables, compute the flow of heat into the process equipment per kg of steam. (ANS. 288 kJ/kg)

(b) Compute the value of enthalpy at the inlet conditions, \( H_{in} \), relative to an ideal gas at the same temperature, \( H^\text{ig} \). Consider steam at 1 bar and 600°C as an ideal gas. Express your answer as \( (H_{in} - H^\text{ig})/RT_{in} \). (ANS. –0.305)
P2.17 A 700 kg piston is initially held in place by a removable latch above a vertical cylinder. The cylinder has an area of 0.1 m², the volume of the gas within the cylinder initially is 0.1 m³ at a pressure of 10 bar. The working fluid may be assumed to obey the ideal gas equation of state. The cylinder has a total volume of 0.25 m³, and the top end is open to the surrounding atmosphere at 1 bar.

(a) Assume that the frictionless piston rises in the cylinder when the latches are removed and the gas within the cylinder is always kept at the same temperature. This may seem like an odd assumption, but it provides an approximate result that is relatively easy to obtain. What will be the velocity of the piston as it leaves the cylinder? (ANS. 13.8 m/s)
(b) What will be the maximum height to which the piston will rise? (ANS. 9.6 m)
(c) What is the pressure behind the piston just before it leaves the cylinder? (ANS. 4 bar)
(d) Now suppose the cylinder was increased in length such that its new total volume is 0.588 m³. What is the new height reached by the piston? (ANS. ~13 m)
(e) What is the maximum height we could make the piston reach by making the cylinder longer? (ANS. ~13 m)

P2.18 A tennis ball machine fires tennis balls at 40 mph. The cylinder of the machine is 1 m long; the installed compressor can reach about 50 psig in a reasonable amount of time. The tennis ball is about 3 inches in diameter and weighs about 0.125 lb. Estimate the initial volume required in the pressurized firing chamber. [Hint: Note the tennis ball machine fires horizontally and the tennis ball can be treated as a frictionless piston. Don’t be surprised if an iterative solution is necessary and \( \ln \left( \frac{V_2}{V_1} \right) = \ln(1 + \frac{\Delta V}{V_1}) \)]. (ANS. 390 cm³)

P2.19 A 700 kg piston is initially held in place by a removable latch inside a horizontal cylinder. The totally frictionless cylinder (assume no viscous dissipation from the gas also) has an area of 0.1 m²; the volume of the gas on the left of the piston is initially 0.1 m³ at a pressure of 8 bars. The pressure on the right of the piston is initially 1 bar, and the total volume is 0.25 m³. The working fluid may be assumed to follow the ideal gas equation of state. What would be the highest pressure reached on the right side of the piston and what would be the position of the piston at that pressure? (a) Assume isothermal; (b) What is the kinetic energy of the piston when the pressures are equal? (partial ANS. 1.6 bars)
2.20 HOMEWORK PROBLEMS

2.1 Three moles of an ideal gas (with temperature-independent \( C_P = (7/2)R \), \( C_V = (5/2)R \)) is contained in a horizontal piston/cylinder arrangement. The piston has an area of 0.1 m\(^2\) and mass of 500 g. The initial pressure in the piston is 101 kPa. Determine the heat that must be extracted to cool the gas from 375°C to 275°C at: (a) constant pressure; (b) constant volume.

2.2 One mole of an ideal gas \( (C_P = 7R/2) \) in a closed piston/cylinder is compressed from \( T^i = 100 \) K, \( P^i = 0.1 \) MPa to \( P^f = 0.7 \) MPa by the following pathways. For each pathway, calculate \( \Delta U \), \( \Delta H \), \( Q \), and \( W_{EC} \): (a) isothermal; (b) constant volume; (c) adiabatic.

2.3 One mole of an ideal gas \( (C_P = 5R/2) \) in a closed piston/cylinder is compressed from \( T^i = 100 \) K, \( P^i = 0.1 \) MPa to \( P^f = 0.25 \) MPa by the following pathways. For each pathway, calculate \( \Delta U \), \( \Delta H \), \( Q \), and \( W_{EC} \): (a) isothermal; (b) constant volume; (c) adiabatic.

2.4 One mole of an ideal gas \( (C_P = 7R/2) \) in a closed piston/cylinder is expanded from \( T^i = 700 \) K, \( P^i = 0.75 \) MPa to \( P^f = 0.1 \) MPa by the following pathways. For each pathway, calculate \( \Delta U \), \( \Delta H \), \( Q \), and \( W_{EC} \): (a) isothermal; (b) constant volume; (c) adiabatic.

2.5 One mole of an ideal gas \( (C_P = 5R/2) \) in a closed piston/cylinder is expanded from \( T^i = 500 \) K, \( P^i = 0.6 \) MPa to \( P^f = 0.1 \) MPa by the following pathways. For each pathway, calculate \( \Delta U \), \( \Delta H \), \( Q \), and \( W_{EC} \): (a) isothermal; (b) constant volume; (c) adiabatic.
2.6 (a) What is the enthalpy change needed to change 3 kg of liquid water at 0°C to steam at 0.1 MPa and 150°C?
(b) What is the enthalpy change needed to heat 3 kg of water from 0.4 MPa and 0°C to steam at 0.1 MPa and 150°C?
(c) What is the enthalpy change needed to heat 1 kg of water at 0.4 MPa and 4°C to steam at 150°C and 0.4 MPa?
(d) What is the enthalpy change needed to change 1 kg of water of a water-steam mixture of 60% quality to one of 80% quality if the mixture is at 150°C?
(e) Calculate the $\Delta H$ value for an isobaric change of steam from 0.8 MPa and 250°C to saturated liquid.
(f) Repeat part (e) for an isothermal change to saturated liquid.
(g) Does a state change from saturated vapor at 230°C to the state 100°C and 0.05 MPa represent an enthalpy increase or decrease? A volume increase or decrease?
(h) In what state is water at 0.2 MPa and 120.21°C? At 0.5 MPa and 151.83°C? At 0.5 MPa and 153°C?
(i) A 0.15 m³ tank containing 1 kg of water at 1 MPa and 179.88°C has how many m³ of liquid water in it? Could it contain 5 kg of water under these conditions?
(j) What is the volume change when 2 kg of H₂O at 6.8 MPa and 93°C expands to 1.6 bar and 250°C?
(k) Ten kg of wet steam at 0.75 MPa has an enthalpy of 22,000 kJ. Find the quality of the wet steam.
2.7 Steam undergoes a state change from 450°C and 3.5 MPa to 150°C and 0.3 MPa. Determine $\Delta H$ and $\Delta U$ using the following:

(a) Steam table data.
(b) Ideal gas assumptions. (Be sure to use the ideal gas heat capacity for water.)

2.8 Five grams of the specified pure solvent is placed in a variable volume piston. What are the molar enthalpy and total enthalpy of the pure system when 50% and 75% have been evaporated at: (i) 30°C; (ii) 50°C? Use liquid at 25°C as a reference state.

(a) Benzene ($\rho^L = 0.88$ g/cm$^3$)
(b) Ethanol ($\rho^L = 0.79$ g/cm$^3$)
(c) Water without using the steam tables ($\rho^L = 1$ g/cm$^3$)
(d) Water using the steam tables

2.9 Create a table of $T$, $U$, $H$ for the specified solvent using a reference state of $H=0$ for liquid at 25°C and 1 bar. Calculate the table for: (i) liquid at 25°C and 1 bar; (ii) saturated liquid at 1 bar; (iii) vapor at 1 bar; (iv) vapor at 110°C and 1 bar. Use the Antoine equation (Appendix E) to relate the saturation temperature and saturation pressure. Use the ideal gas law to model the vapor phase.

(a) Benzene
(b) Ethanol
(c) Water without using the steam tables
(d) Water using the steam tables

2.10 One kg of methane is contained in a piston/cylinder device at 0.8 MPa and 250°C. It undergoes a reversible isothermal expansion to 0.3 MPa. Methane can be considered an ideal gas under these conditions. How much heat is transferred?

2.11 One kg of steam in a piston/cylinder device undergoes the following changes of state. Calculate $Q$ and $W$ for each step.

(a) Initially at 350 kPa and 250°C, it is cooled at constant pressure to 150°C.
(b) Initially at 350 kPa and 250°C, it is cooled at constant volume to 150°C.

2.12 In one stroke of a reciprocating compressor, helium is isothermally and reversibly compressed in a piston + cylinder from 298 K and 20 bars to 200 bars. Compute the heat removal and work required.

2.13 Air at 30°C and 2 MPa flows at steady state in a horizontal pipeline with a velocity of 25 m/s. It passes through a throttling valve where the pressure is reduced to 0.3 MPa. The pipe is the same diameter upstream and downstream of the valve. What is the outlet temperature and velocity of the gas? Assume air is an ideal gas with a temperature-independent $C_p = 7R/2$, and the average molecular weight of air is 28.8.

2.14 Argon at 400 K and 50 bar is adiabatically and reversibly expanded to 1 bar through a turbine in a steady process. Compute the outlet temperature and work derived per mole.

2.15 Steam at 500 bar and 500°C undergoes a throttling expansion to 1 bar. What will be the temperature of the steam after the expansion? What would be the downstream temperature if the steam were replaced by an ideal gas, $C_p/R = 7/2$?

7, 8, 12, 13, 15
2.16 An adiabatic turbine expands steam from 500°C and 3.5 MPa to 200°C and 0.3 MPa. If the turbine generates 750 kW, what is the flow rate of steam through the turbine?

2.17 A steam turbine operates between 500°C and 3.5 MPa to 200°C and 0.3 MPa. If the turbine generates 750 kW and the heat loss is 100 kW, what is the flow rate of steam through the turbine?

2.18 Valves on steam lines are commonly encountered and you should know how they work. For most valves, the change in velocity of the fluid flow is negligible. Apply this principle to solve the following problems.

(a) A pressure gauge on a high-pressure steam line reads 80 bar absolute, but temperature measurement is unavailable inside the pipe. A small quantity of steam is bled out through a valve to atmospheric pressure at 1 bar. A thermocouple placed in the bleedstream reads 400°C. What is the temperature inside the high-pressure duct?

(b) Steam traps are common process devices used on the lowest points of steam lines to remove condensate. By using a steam trap, a chemical process can be supplied with so-called dry steam, i.e., steam free of condensate. As condensate forms due to heat losses in the supply piping, the liquid runs downward to the trap. As liquid accumulates in the steam trap, it causes a float mechanism to move. The float mechanism is attached to a valve, and when the float reaches a control level, the valve opens to release accumulated liquid, then closes automatically as the float returns to the control level. Most steam traps are constructed in such a way that the inlet of the steam trap valve is always covered with saturated liquid when opened or closed. Consider such a steam trap on a 7 bar (absolute) line that vents to 1 bar (absolute). What is the quality of the steam that exits the steam trap at 1 bar?

2.19 An overall balance around part of a plant involves three inlets and two outlets which only contain water. All streams are flowing at steady state. The inlets are: 1) liquid at 1 MPa, 25°C, \( \dot{m} = 54 \) kg/min; 2) steam at 1 MPa, 250°C, \( \dot{m} = 35 \) kg/min; 3) wet steam at 0.15 MPa, 90% quality, \( \dot{m} = 30 \) kg/min. The outlets are: 1) saturated steam at 0.8 MPa, \( \dot{m} = 65 \) kg/min; 2) superheated steam at 0.2 MPa and 300°C, \( \dot{m} = 54 \) kg/min. Two kW of work are being added to the portion of the plant to run miscellaneous pumps and other process equipment, and no work is being obtained. What is the heat interaction for this portion of the plant in kW? Is heat being added or removed?

2.20 Steam at 550 kPa and 200°C is throttled through a valve at a flow rate of 15 kg/min to a pressure of 200 kPa. What is the temperature of the steam in the outlet state, and what is the change in specific internal energy across the valve, \( U^{\text{out}} - U^{\text{in}} \)?

2.21 A 0.1 m³ cylinder containing an ideal gas \( (C_p/R = 3.5) \) is initially at a pressure of 10 bar and a temperature of 300 K. The cylinder is emptied by opening a valve and letting pressure drop to 1 bar. What will be the temperature and moles of gas in the cylinder if this is accomplished in the following ways:

(a) Isothermally.
(b) Adiabatically. (Neglect heat transfer between the cylinder walls and the gas.)

2.22 As part of a supercritical extraction of coal, an initially evacuated cylinder is fed with steam from a line available at 20 MPa and 400°C. What is the temperature in the cylinder immediately after filling?
2.23 A large air supply line at 350 K and 0.5 MPa is connected to the inlet of a well-insulated 0.002 m³ tank. The tank has mass flow controllers on the inlet and outlet. The tank is at 300 K and 0.1 MPa. Both valves are rapidly and simultaneously switched open to a flow of 0.1 mol/min. Model air as an ideal gas with \( C_p = 29.3 \text{ J/mol-K} \), and calculate the pressure and temperature as a function of time. How long does it take until the tank is within 5 K of the steady-state value?

2.24 An adiabatic tank of negligible heat capacity and 1 m³ volume is connected to a pipeline containing steam at 10 bar and 200°C, filled with steam until the pressure equilibrates, and disconnected from the pipeline. How much steam is in the tank at the end of the filling process, and what is its temperature if the following occurs:

(a) The tank is initially evacuated.
(b) The tank initially contains steam at 1 bar and 150°C.