Chapter 3

Evaluating Properties
Chapter Objective

introduce property relations relevant to engineering thermodynamics
Fixing the State

- the state can be uniquely determined by giving the values of the *independent* properties.
- Values for all other thermodynamic properties are determined once this independent subset is specified.
\( p-v-T \) Relation

**\( p-v-T \) Surface**

Coordinates of a point on the \( p-v-T \) surfaces represent the values that pressure, specific volume, and temperature would assume when the substance is at equilibrium.
$p$–$v$–$T$ Relation

$\textit{p–v–T Surface}$
$p$–$v$–$T$ Relation

$p$–$v$–$T$ Surface

**Single-phase regions**
- State is fixed by any two of the independent properties: pressure, specific volume, and temperature.

**Two-phase regions**
- Two phases exist in equilibrium: L–V, S–L, and S–V.
- Pressure & temperature are dependent.
- State cannot be fixed by temperature & pressure alone
- State can be fixed by specific volume and either pressure or temperature.

**Three phases:** can exist in equilibrium along the triple line
$p$–$v$–$T$ Relation

$p$–$v$–$T$ Surface

- **Saturation state**: state at which a phase change begins or ends.
- **Vapor dome**: dome shaped region composed of the two-phase liquid–vapor states.
  - Lines bordering the vapor dome are called saturated liquid and saturated vapor lines.
  - **Critical point**: At top of dome, where saturated liquid and saturated vapor lines meet.
- **Critical temperature $T_c$ of a pure substance**: max temperature at which liquid and vapor phases can coexist in equilibrium.
- **Critical pressure, $p_c$**: pressure at critical point.
- **Critical specific volume**: specific volume at critical point.
- **Tables A-1**: Values of critical point properties for a number of substances.
$p$–$v$–$T$ Relation

Projections of the $p$–$v$–$T$ Surface

The Phase Diagram

- A point on any of these lines represents all two-phase mixtures at that particular temperature and pressure.
- **Saturation temperature**: temperature at which a phase change takes place at a given pressure (**Saturation pressure**).
- For each saturation pressure there is a unique saturation temperature, and conversely.
Projections of the $p$–$v$–$T$ Surface

The Phase Diagram

- The triple line of the 3-D $p$–$v$–$T$ surface projects onto a point on the phase diagram called the **triple point**.
- The triple point of water is used as a reference in defining temperature scales (Sec. 1.6).
- By agreement, the temperature assigned to the triple point of water is $273.16^\circ$K.
- The measured pressure at the triple point of water is 0.6113 kPa.
$p-v-T$ Relation

Projections of the $p-v-T$ Surface

The Phase Diagram

- The line representing the two-phase $S-L$ slopes to the left for substances that expand on freezing and to the right for those that contract.
$p$–$v$–$T$ Relation

Projections of the $p$–$v$–$T$ Surface

$p$–$v$ Diagram

- Constant-temperature lines (isotherms)
- For $T < T_c$, pressure remains constant as the two-phase $L$–$V$ region is traversed
- In the single-phase liquid and vapor regions the pressure decreases at fixed temperature as specific volume increases.
- For $T \geq T_c$, pressure decreases continuously at fixed temperature as specific volume increases.
- The critical isotherm passes through a point of inflection at the critical point and the slope is zero there.
$p$–$v$–$T$ Relation

Projections of the $p$–$v$–$T$ Surface

$T$–$v$ Diagram

Projecting the liquid, two-phase L-V, and vapor regions of the $p$–$v$–$T$ surface onto the $T$–$v$ plane results in a $T$–$v$ diagram.

Figure 3.3 Sketch of a temperature–specific volume diagram for water showing the liquid, two-phase liquid–vapor, and vapor regions (not to scale).

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$p-v-T$ Relation

Studying Phase Change

- Consider a closed system consisting of a unit mass (1 kg) of liquid water at 20°C contained within a piston–cylinder assembly.

- Point I on Fig. 3.3

- Suppose the water is slowly heated while its pressure is kept constant and uniform throughout at 1.014 bar.
As the system is heated at constant pressure, temperature increases considerably while specific volume increases slightly.

Eventually, the system is brought to the state represented by the saturated liquid state corresponding to the specified pressure.

For water at 1.014 bar the saturation temperature is 100°C.

The liquid states along the path from l to f are called sub-cooled liquid states because the temperature at these states is less than the saturation temperature at the given pressure.

These states are also called compressed liquid states because the pressure at each state is higher than the saturation pressure corresponding to the temperature at the state.
**p–v–T Relation**

**Studying Phase Change**

**Two-phase, liquid–vapor Mixture**

- When the system is at the saturated liquid state (state f), additional heat transfer at fixed pressure results in formation of vapor without any change in temperature but with a considerable increase in specific volume.
- The system would now consist of a two-phase L-V mixture.
- When a mixture of liquid and vapor exists in equilibrium, the liquid phase is a saturated liquid and the vapor phase is a saturated vapor.

- If the system is heated further until the last bit of liquid has vaporized, it is brought to point g, saturated vapor state.
- For a two-phase L-V mixture, the ratio of mass of vapor present to total mass of mixture is its *quality*, \( x \).

\[
x = \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}}
\]
**p–v–T Relation**

**Studying Phase Change**

**Vapor States**

- When the system is at the saturated vapor state (state g), further heating at fixed pressure results in increases in both temperature and specific volume.

- The state labeled s is representative of the states that would be attained by further heating while keeping the pressure constant.

- A state such as s is called **superheated vapor** state because the system would be at a temperature greater than the saturation temperature corresponding to the given pressure.

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Let the system initially contain a liquid at 20°C.

Let us study the system if it were heated slowly at 10 MPa.

At this pressure, vapor would form at a higher temperature than in the previous example, because the saturation pressure is higher.

In addition, there would be somewhat less of an increase in specific volume from saturated liquid to vapor.
\( p-v-T \) Relation

Studying Phase Change

Vapor States

- Consider the behavior of the system where it heated at the critical pressure, or higher.
  - There would be no change in phase from liquid to vapor.
  - At all states there would be only one phase.
  - Vaporization can occur only when the pressure is less than the critical pressure.
  - Thus, at states where pressure is greater than the critical pressure, the terms liquid and vapor tend to lose their significance.

- Still, for ease of reference to such states, we use the term liquid when the temperature is less than the critical temperature and vapor when the temperature is greater than the critical temperature.
Consider a system consisting of a unit mass of ice at a temperature below the triple point temperature.

Let us begin with the case where the system is at state $a$, where pressure is greater than the triple point pressure.
**$p$–$v$–$T$ Relation**

**Studying Phase Change**

**Melting and Sublimation**

- Suppose the system is slowly heated while maintaining the pressure constant and uniform throughout.
- The temperature increases with heating until point $b$ is attained. At this state the ice is a saturated solid.
- Additional heat transfer at fixed pressure results in the formation of liquid without any change in temperature.
- As the system is heated further, the ice continues to melt until eventually the last bit melts, and the system contains only saturated liquid.
During the melting process the temperature and pressure remain constant.

For most substances, the specific volume increases during melting, but for water the specific volume of the liquid is less than the specific volume of the solid.

Further heating at fixed pressure results in an increase in temperature as the system is brought to point C.
$p-v-T$ Relation

**Studying Phase Change**

**Melting and Sublimation**

- Consider the case where the system is initially at state $a'$, where the pressure is less than the triple point pressure.
- If the system is heated at constant pressure it passes through the two-phase S-V region into the vapor region along the line $a'b'c'$.
- The case of vaporization is shown by line $a''b''c''$. 

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Retrieving Thermodynamic Properties

- Tables A-2 through A-6: saturated water tables.
- Tables A-7 through A-9: Refrigerant 22,
- Tables A-10 through A-12: Refrigerant 134a,
- Tables A-13 through A-15: ammonia,
- Tables A-16 through A-18: propane
Retrieving Thermodynamic Properties

Vapor and Liquid Tables

- **Tables A-4**: superheated vapor tables
- **Tables A-5**: compressed liquid tables
- Since pressure and temperature are independent properties in the single-phase liquid and vapor regions, they can be used to fix the state in these regions.
Retrieving Thermodynamic Properties

Saturation Tables

- The specific volume of a two-phase L-V mixture can be determined by using the saturation tables and the definition of quality given by Eq. 3.1

- Total volume of mixture is the sum of the volumes of the liquid and vapor phases

\[
V = V_{\text{liq}} + V_{\text{vap}} \\
\nu = \frac{V}{m} = \frac{V_{\text{liq}}}{m} + \frac{V_{\text{vap}}}{m} \\
\nu = \left(\frac{m_{\text{liq}}}{m}\right)\nu_f + \left(\frac{m_{\text{vap}}}{m}\right)\nu_g \\
\nu = (1 - x)\nu_f + x\nu_g = \nu_f + x(\nu_g - \nu_f)
\]

(3.2)
EXAMPLE 3.1

Heating Water at Constant Volume

A closed, rigid container of volume 0.5 m\(^3\) is placed on a hot plate. Initially, the container holds a two-phase mixture of saturated liquid water and saturated water vapor at \(p_1 = 1\) bar with a quality of 0.5. After heating, the pressure in the container is \(p_2 = 1.5\) bar. Indicate the initial and final states on a \(T-v\) diagram, and determine

a. the temperature, in °C, at each state.

b. the mass of vapor present at each state, in kg.

c. If heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

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EXAMPLE 3.2

Heating Ammonia at Constant Pressure

A vertical piston–cylinder assembly containing 0.05 kg of ammonia, initially a saturated vapor, is placed on a hot plate. Due to the weight of the piston and the surrounding atmospheric pressure, the pressure of the ammonia is 1.5 bars. Heating occurs slowly, and the ammonia expands at constant pressure until the final temperature is 25°C. Show the initial and final states on $T$–$v$ and $p$–$v$ diagrams, and determine

a. the volume occupied by the ammonia at each state, in m$^3$.

b. the work for the process, in kJ.
Retrieving Thermodynamic Properties
Evaluating Specific Internal Energy and Enthalpy

\[ u = (1 - x)u_f + xu_g = u_f + x(u_g - u_f) \]
Retrieving Thermodynamic Properties

Reference States and Reference Values

- Values of $u$, $h$, and $s$ given in the property tables are not obtained by direct measurement but are calculated from other data that can be more readily determined experimentally.
- When applying the energy balance, it is differences in internal, kinetic, and potential energy between two states that are important, and *not* the values of these energy quantities at each of the two states.
- **Example:** consider the case of potential energy.
  - The numerical value of potential energy determined relative to surface of earth is different from the value relative to the top of a tall building at the same location.
  - Difference in potential energy between any two elevations is precisely the same regardless of the datum selected.

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Retrieving Thermodynamic Properties
Reference States and Reference Values

- Similarly, values can be assigned to specific internal energy and enthalpy relative to arbitrary reference values at arbitrary reference states.
- Use of values of a particular property determined relative to an arbitrary reference is unambiguous as long as the calculations being performed involve only differences in that property, for then the reference value cancels.

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Retrieving Thermodynamic Properties

Reference States and Reference Values

- Tabular values of $u$ & $h$ for water, ammonia, propane, and Refrigerants 22 and 134a provided in Appendix are relative to the following reference states and values:
  - For water, reference state is saturated liquid at 0.01°C.
    - At this state, specific internal energy is set to zero.
    - Values of specific enthalpy are calculated from $h = u + pv$
  - For ammonia, propane, and the refrigerants, the reference state is saturated liquid at 40°C.
    - At this reference state specific enthalpy is set to zero.
    - Values of specific internal energy are calculated from $u = h - pv$
- The values assigned to particular states change if the reference state or reference values change, but the differences remain the same.
Retrieving Thermodynamic Properties
Evaluating Properties Using Computer Software

- The software available with this text, *Interactive Thermodynamics: IT*
- A tool that can be used not only for routine problem solving by providing data at individual state points, but also for simulation and analysis.

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EXAMPLE 3.3

Stirring Water at Constant Volume

A well-insulated rigid tank having a volume of 0.25 m$^3$ contains saturated water vapor at 100°C. The water is rapidly stirred until the pressure is 1.5 bars. Determine the temperature at the final state, in °C, and the work during the process, in kJ.
EXAMPLE 3.4

Analyzing Two Processes in Series

Water contained in a piston–cylinder assembly undergoes two processes in series from an initial state where the pressure is 10 bar and the temperature is 400°C.

**Process 1–2:** water is cooled as it is compressed at a constant pressure of 10 bar to the saturated vapor state.

**Process 2–3:** water is cooled at constant volume to 150°C.

a. Sketch both processes on T–v and p–v diagrams
b. For the overall process determine the work, in kJ/kg
c. For the overall process determine the heat transfer in kJ/kg
EXAMPLE 3.5
Plotting Thermodynamic Data Using Software

For the system of Example 3.1, plot the heat transfer, in kJ, and the mass of saturated vapor present, in kg, each versus pressure at state 2 ranging from 1 to 2 bar. Discuss the results.
Retrieving Thermodynamic Properties

Evaluating Specific Heats $c_v$ and $c_p$

- The intensive properties $c_v$ and $c_p$ are defined for pure, simple compressible substances as partial derivatives of the functions $u(T, v)$ and $h(T, p)$, respectively:

\[
    c_v = \left( \frac{\partial u}{\partial T} \right)_v \\
    c_p = \left( \frac{\partial h}{\partial T} \right)_p
\]

- The specific heat ratio, $k$,

\[
k = \frac{c_p}{c_v}
\]
Retrieving Thermodynamic Properties

Evaluating Specific Heats $c_v$ and $c_p$

$c_v$ is a function of $v$ and $T$ (or $p$ and $T$), and $c_p$ depends on both $p$ and $T$ (or $v$ and $T$).
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids
Approximations for Liquids Using Saturated Liquid Data

- Approximate values for $v$, $u$, and $h$ at liquid states can be obtained using saturated liquid data.
- Refer to the compressed liquid Tables A-5.
- Because values of $v$ and $u$ vary only gradually as pressure changes at fixed temperature, the following approximations are reasonable for many engineering calculations:

\[
\begin{align*}
    v(T, p) & \approx v_f(T) \\
    u(T, p) & \approx u_f(T)
\end{align*}
\]
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids
Approximations for Liquids Using Saturated Liquid Data

- For liquids $v$ and $u$ may be evaluated at saturated liquid state corresponding to the temperature at the given state.
- An approximate value of $h$ at liquid states can be obtained using Eqs. 3.11 & 3.12 in the definition $h = u + pv$
  \[
  h(T, p) \approx u_f(T) + pv_f(T)
  \]
  \[
  h(T, p) \approx h_f(T) + v_f(T)[p - p_{sat}(T)]
  \]
- $p_{sat}$ denotes saturation pressure at the given temperature.
- When the contribution of the underlined term of Eq. 3.13 is small, specific enthalpy can be approximated by the saturated liquid value, as for $v$ and $u$
  \[
  h(T, p) \approx h_f(T)
  \]
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids
Approximations for Liquids Using Saturated Liquid Data

- Although approximations given here have been presented with reference to liquid water, they also provide plausible approximations for other substances when the only liquid data available are for saturated liquid states.
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids

Incompressible Substance Model

- There are regions where specific volume of liquid water varies little and specific internal energy varies mainly with temperature.
- The same general behavior is exhibited by the liquid phases of other substances and by solids.
- To simplify evaluations involving liquids or solids, specific volume (density) is often assumed to be constant and specific internal energy assumed to vary only with temperature.
- A substance idealized in this way is called *incompressible*.
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids
Incompressible Substance Model

➢ Since specific internal energy of a substance modeled as incompressible depends only on temperature, specific heat $c_v$ is also a function of temperature alone

$$c_v(T) = \frac{du}{dT} \quad \text{(incompressible)} \quad (3.15)$$

➢ Although specific volume is constant and internal energy depends on temperature only, enthalpy varies

$$h(T, p) = u(T) + pv \quad \text{(incompressible)} \quad (3.16)$$
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids

Incompressible Substance Model

- For a substance modeled as incompressible, specific heats $c_v$ and $c_p$ are equal. This is seen by differentiating Eq. 3.16 with respect to temperature while holding pressure fixed to obtain

$$\frac{\partial h}{\partial T}_p = \frac{du}{dT}$$

- The left side of this expression is $c_p$ by definition (Eq. 3.9), so using Eq. 3.15 on the right side gives

$$c_p = c_v \quad \text{(incompressible)} \quad (3.17)$$
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids

Incompressible Substance Model

- It is unnecessary to distinguish between $c_p$ and $c_v$, and both can be represented by the same symbol, $c$.
- **Tables A-19**: Specific heats of some common liquids and solids versus temperature
- Over limited temperature intervals the variation of $c$ with temperature can be small. In such instances, the specific heat $c$ can be treated as constant without a serious loss of accuracy.
- Using Eqs. 3.15 and 3.16, changes in specific internal energy and specific enthalpy between two states are given, respectively, by

\[
\begin{align*}
    u_2 - u_1 &= \int_{T_1}^{T_2} c(T) \, dT \quad \text{(incompressible)} \\
    h_2 - h_1 &= u_2 - u_1 + v(p_2 - p_1) \\
    &= \int_{T_1}^{T_2} c(T) \, dT + v(p_2 - p_1) \quad \text{(incompressible)}
\end{align*}
\]
Retrieving Thermodynamic Properties
Evaluating Properties of Liquids and Solids
Incompressible Substance Model

- If specific heat $c$ is taken as constant, Eqs. 3.18 and 3.19 become, respectively,

\[
\begin{align*}
\frac{u_2 - u_1}{\rho} &= c(T_2 - T_1) \\
\frac{h_2 - h_1}{\rho} &= c(T_2 - T_1) + \frac{v}{\rho}(p_2 - p_1)
\end{align*}
\]

(incompressible, constant $c$)  \hspace{1cm} (3.20a)

(incompressible, constant $c$)  \hspace{1cm} (3.20b)

- In Eq. 3.20b, the underlined term is often small relative to the first term on the right side and then may be dropped.
Let a gas be confined in a cylinder by a piston and the entire assembly held at a constant temperature.

The piston can be moved to various positions so that a series of equilibrium states at constant temperature can be visited.

Suppose the pressure and specific volume are measured at each state and the value of the ratio \( \frac{p\bar{v}}{T} \) is determined. These ratios can then be plotted versus pressure at constant temperature.
Generalized Compressibility Chart

Universal Gas Constant, $R$

- $\bar{R}$ denotes the common limit for all temperatures.
- If this procedure were repeated for other gases, it would be found in every instance that the limit of the ratio as $p$ tends to zero at fixed temperature is the same.
- Since the same limiting value is exhibited by all gases, it is called the *universal gas constant*.

$$\bar{R} = 8.314 \text{ kJ/kmol} \cdot \text{K}$$
Generalized Compressibility Chart

Compressibility Factor, Z

The *compressibility factor* $Z$

$$Z = \frac{\overline{pv}}{RT}$$  \hspace{1cm} (3.23)

$$Z = \frac{p_v}{RT}$$  \hspace{1cm} (3.24)

$$R = \frac{\overline{R}}{M}$$  \hspace{1cm} (3.25)

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Generalized Compressibility Chart

Compressibility Factor, $Z$

- Equation 3.21 can be expressed in terms of the compressibility factor as

$$\lim_{p \to 0} Z = 1$$

Figure 3.11  Variation of the compressibility factor of hydrogen with pressure at constant temperature.
Generalized Compressibility Chart

Generalized Compressibility Data, Z Chart

- Compressibility factor $Z$ is plotted versus a dimensionless *reduced pressure* $p_R$ and *reduced temperature* $T_R$, defined as

\[ p_R = \frac{p}{p_c} \quad \text{and} \quad T_R = \frac{T}{T_c} \quad (3.27) \]
Generalized Compressibility Chart

Generalized Compressibility Data, Z Chart

\[ Z = \frac{p}{RT} \]

\[ T_R = 2.00, 1.50, 1.30, 1.20, 1.10, 1.00 \]

Legend:
- Methane
- Isopentane
- Ethylene
- n-Heptane
- Ethane
- Nitrogen
- Propane
- Carbon dioxide
- n-Butane
- Water

Average curve based on data on hydrocarbons

\[ \text{Reduced pressure } p_R \]

\[ \text{Figure 3.12} \quad \text{Generalized compressibility chart for various gases.} \]
Generalized Compressibility Chart

Generalized Compressibility Data, Z Chart

- **Fig. A-1**: $\rho_R$ ranges from 0 to 1.0
- **Fig. A-2**: $\rho_R$ ranges from 0 to 10.0
- **Fig. A-3**: $\rho_R$ ranges from 10.0 to 40.0

- At any one temperature, the deviation of observed values from those of the generalized chart increases with pressure.
- For the 30 gases used in developing the chart, deviation is at most on the order of 5% and for most ranges is much less.
- **Figs. A-1 and A-2**: the value of $Z$ tends to unity for all temperatures as pressure tends to zero, in accord with Eq. 3.26.
- **Fig. A-3**: $Z$ also approaches unity for all pressures at very high temperatures.
Generalized Compressibility Chart

Generalized Compressibility Data, Z Chart

- Values of specific volume are included on the generalized chart through the variable called the *pseudo-reduced specific volume*,

\[ v'_R = \frac{\bar{v}}{RT_c/p_c} \quad (3.28) \quad v_R = \frac{\bar{v}}{\bar{v}_c} \]

- For correlation purposes, the pseudo-reduced specific volume has been found to be preferable to the *reduced* specific volume.

- Using the critical pressure and critical temperature of a substance of interest, the generalized chart can be entered with various pairs of the variables \( T_R, p_R \).

- **Tables A-1:** critical constants for several substances
EXAMPLE 3.6

Using the Generalized Compressibility Chart

A closed, rigid tank filled with water vapor, initially at 20 MPa, 520°C, is cooled until its temperature reaches 400°C. Using the compressibility chart, determine

a. specific volume of the water vapor in \( m^3/kg \) at the initial state.

b. the pressure in MPa at the final state.

Compare the results of parts (a) and (b) with the values obtained from the superheated vapor table, Table A-4.

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Equations of State

- Considering the curves of Figs. 3.11 and 3.12, it is reasonable to think that the variation with pressure and temperature of the compressibility factor for gases might be expressible as an equation, at least for certain intervals of $p$ and $T$.

- One gives the compressibility factor as an infinite series expansion in pressure:

$$Z = 1 + \hat{B}(T)p + \hat{C}(T)p^2 + \hat{D}(T)p^3 + \cdots$$  \hspace{1cm} (3.29)
Equations of State

- \( \hat{B}, \hat{C}, \hat{D}, \ldots \) depend on temperature only.
- The other is a series form entirely analogous to Eq. 3.29 but expressed in terms of instead of \( \frac{1}{1/v} \)

\[
Z = 1 + \frac{B(T)}{\bar{u}} + \frac{C(T)}{\bar{u}^2} + \frac{D(T)}{\bar{u}^3} + \cdots
\]  

Equations 3.29 and 3.30 are known as **virial equations of state**, and the coefficients are called **virial coefficients**.
Evaluating Properties Using the Ideal Gas Model

- At states where the pressure $p$ is small relative to the critical pressure $p_c$ (low $p_R$) and/or the temperature $T$ is large relative to the critical temperature $T_c$ (high $T_R$), the compressibility factor, $Z = \frac{pv}{RT}$, is approximately 1.

- At such states, we can assume with reasonable accuracy that $Z = 1$, or

  \[
  \begin{align*}
  pv &= RT \\
  pV &= mRT \\
  p\bar{v} &= \bar{R}T \\
  \bar{p} = \bar{R}T \\
  pV &= n\bar{R}T
  \end{align*}
  \]

  (3.32) (3.33) (3.34) (3.35)
Ideal Gas Model

- For any gas whose equation of state is given exactly by \( pv = RT \), the specific internal energy depends on temperature only.
- Experimental observations by Joule (1843) showed that the internal energy of air at low density depends primarily on temperature.
- The specific enthalpy of a gas described by \( pv = RT \) also depends on temperature only.

\[
\begin{align*}
pv &= RT \\
u &= u(T) \\
h &= h(T) = u(T) + RT
\end{align*}
\]
Ideal Gas Model

- The specific internal energy and enthalpy of gases generally depend on two independent properties, not just temperature as presumed by the ideal gas model.
- Moreover, the ideal gas equation of state does not provide an acceptable approximation at all states.
- Accordingly, whether the ideal gas model is used depends on the error acceptable in a given calculation.
- Still, gases often do approach ideal gas behavior, and a particularly simplified description is obtained with the ideal gas model.
- To verify that a gas can be modeled as an ideal gas, the states of interest can be located on a compressibility chart to determine how well $Z = 1$ is satisfied.
Ideal Gas Model

Microscopic Interpretation

- As $p$ approaches 0 and $v$ approaches infinity, the force of interactions between molecules of a gas become weaker, and the virial expansions approach $Z = 1$ in the limit.
- The dependence of the internal energy of a gas on pressure, or specific volume, at a specified temperature arises primarily because of molecular interactions.
- Accordingly, as the density of a gas decreases at fixed temperature, there comes a point where the effects of intermolecular forces are minimal.
- The internal energy is then determined principally by the temperature.
- From the microscopic point of view, the ideal gas model adheres to several idealizations:
  1. The gas consists of molecules that are in random motion and obey the laws of mechanics;
  2. the total number of molecules is large, but the volume of the molecules is a negligibly small fraction of the volume occupied by the gas;
  3. no appreciable forces act on the molecules except during collisions.
EXAMPLE 3.7

Air as an Ideal Gas Undergoing a Cycle

One pound of air undergoes a thermodynamic cycle consisting of three processes.

**Process 1–2:** constant specific volume

**Process 2–3:** constant-temperature expansion

**Process 3–1:** constant-pressure compression

At state 1, the temperature is 300K, and the pressure is 1 bar. At state 2, the pressure is 2 bars. Employing the ideal gas equation of state,

a. sketch the cycle on $p-v$ coordinates.

b. determine the temperature at state 2, in K;

c. determine the specific volume at state 3, in $m^3/kg$.  

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Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

- specific internal energy depends only on temperature.
- Hence, the specific heat \( c_v \), defined by Eq. 3.8, is also a function of temperature alone. That is,

\[
    c_v(T) = \frac{du}{dT} \quad \text{(ideal gas)} \tag{3.38}
\]

\[
    u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T) \, dT \quad \text{(ideal gas)} \tag{3.40}
\]
Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

Similarly, for a gas obeying the ideal gas model, the specific enthalpy depends only on temperature, so the specific heat $c_p$, defined by Eq. 3.9, is also a function of temperature alone. That is

$$c_p(T) = \frac{dh}{dT} \quad \text{(ideal gas)}$$  \hspace{1cm} (3.41)

$$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T) \, dT \quad \text{(ideal gas)}$$  \hspace{1cm} (3.43)

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Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

- An important relationship between the ideal gas specific heats can be developed by differentiating Eq. 3.37 with respect to temperature.

\[
\frac{dh}{dT} = \frac{du}{dT} + R
\]

\[
c_p(T) = c_v(T) + R \quad \text{(ideal gas)} 
\]  

(3.44)
Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

- For an ideal gas, the specific heat ratio, $k$, is also a function of temperature only

\[
k = \frac{c_p(T)}{c_v(T)} \quad \text{(ideal gas)}
\]  

(3.46)

\[
c_p(T) = \frac{kR}{k - 1} \quad \text{(ideal gas)}
\]

(3.47a)

\[
c_v(T) = \frac{R}{k - 1}
\]

(3.47b)

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Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

Using Specific Heat Functions

Figure 3.13 Variation of $\frac{c_p}{R}$ with temperature for a number of gases modeled as ideal gases.
Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

Using Specific Heat Functions

- **Tables A-20**: specific heat data for selected gases.
- Specific heats are also available in equation form. An equation that is relatively easy to integrate is the polynomial form

\[
\frac{\bar{c}_p}{R} = \alpha + \beta T + \gamma T^2 + \delta T^3 + \varepsilon T^4
\]  

(3.48)

- Values of the constants \(\alpha, \beta, \gamma, \delta, \) and \(\varepsilon\) are listed in Tables A-21.
Evaluating $\Delta u$ and $\Delta h$

Using Ideal Gas Tables

- **Tables A-22 and A-23**: give $u$ and $h$ versus temperature.
- To obtain enthalpy versus temperature, write Eq. 3.43 as
  \[
  h(T) = \int_{T_{\text{ref}}}^{T} c_p(T) \, dT + h(T_{\text{ref}})
  \]
  - $T_{\text{ref}}$ = arbitrary reference temperature
  - $h(T_{\text{ref}})$ = arbitrary value for enthalpy at reference temperature.
- Tables A-22 and A-23 are based on the selection $h = 0$ at $T_{\text{ref}} = 0$ K. Accordingly, a tabulation of enthalpy versus temperature is developed through the integral
  \[
  h(T) = \int_{0}^{T} c_p(T) \, dT
  \]
- Tabulations of internal energy versus temperature are obtained from the tabulated enthalpy values by using $u = h - RT$.  

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Evaluating $\Delta u$ and $\Delta h$

Assuming Constant Specific Heats

When the specific heats are taken as constants, Eqs. 3.40 and 3.43 reduce, respectively, to

\[
\begin{align*}
    u(T_2) - u(T_1) &= c_v(T_2 - T_1) \quad \text{(3.50)} \\
    h(T_2) - h(T_1) &= c_p(T_2 - T_1) \quad \text{(3.51)}
\end{align*}
\]

\[
\begin{align*}
    c_v &= \frac{\int_{T_1}^{T_2} c_v(T) \, dT}{T_2 - T_1}, \\
    c_p &= \frac{\int_{T_1}^{T_2} c_p(T) \, dT}{T_2 - T_1}
\end{align*}
\]
Example 3.8
Using the Energy Balance and Ideal Gas Tables

A piston-cylinder assembly contains 0.9 kg of air at a temperature of 300K and a pressure of 1 bar. The air is compressed to a state where the temperature is 470K and the pressure is 6 bars. During the compression, there is a heat transfer from the air to the surroundings equal to 20 kJ. Using the ideal gas model for air, determine the work during the process, in kJ.

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Example 3.9

Using the Energy Balance and Constant Specific Heats

Two tanks are connected by a valve. One tank contains 2 kg of carbon monoxide gas at 77°C and 0.7 bar. The other tank holds 8 kg of the same gas at 27°C and 1.2 bar. The valve is opened and the gases are allowed to mix while receiving energy by heat transfer from the surroundings. The final equilibrium temperature is 42°C. Using the ideal gas model, determine

a. The final equilibrium pressure, in bar
b. The heat transfer for the process, in kJ
Example 3.1 0

Using the Energy Balance and Software

One kmol of carbon dioxide gas (CO$_2$) in a piston–cylinder assembly undergoes a constant-pressure process at 1 bar from $T_1 = 300$ K to $T_2$. Plot the heat transfer to the gas, in kJ, versus $T_2$ ranging from 300 to 1500 K. Assume the ideal gas model, and determine the specific internal energy change of the gas using

a. data from $IT$

b. a constant evaluated at $T1$ from $IT$

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Polypotropic Process of an Ideal Gas

A *polypotropic* process of a closed system is described by a pressure–volume relationship of the form

$$pV^n = \text{constant}$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(n-1)/n} = \left(\frac{V_1}{V_2}\right)^{n-1} \quad \text{(ideal gas)}$$  (3.56)

$$\int_1^2 p \, dV = \frac{mR(T_2 - T_1)}{1 - n} \quad \text{(ideal gas, } n \neq 1)$$  (3.57)

$$\int_1^2 p \, dV = mRT \ln \frac{V_2}{V_1} \quad \text{(ideal gas, } n = 1)$$  (3.58)
Example 3.11
Polytropic Process of Air as an Ideal Gas

Air undergoes a polytropic compression in a piston–cylinder assembly from $p_1 = 1$ bar, $T_1 = 22^\circ C$ to $p_2 = 5$ bars. Employing the ideal gas model, determine the work and heat transfer per unit mass, in kJ/kg, if $n = 1.3$. 

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Home Work Assignment # 3
1, 7, 14, 22, 26, 32
Due Saturday 3/3/2012
Home Work Assignment # 4

40, 47, 48, 52, 60, 62, 69

Due Saturday 10/3/2012