Chapter 3

3.3 Types of Thermodynamic Properties

The thermodynamic state of a system can be characterized by its properties that can be classified as measured, fundamental, or derived properties. We want to develop relationships to relate the changes in the fundamental and derived properties in terms of the measured properties that are directly accessible from laboratory measurements. Some of the measured properties are $P$, $v$, $T$, composition, $c_p$, and $c_v$. The small letters are used to denote specific quantities for example $v$ is specific volume. The heat capacities $c_p$, and $c_v$ are defined by

$$c_p = \left( \frac{\partial h}{\partial T} \right)_p \quad \text{and} \quad c_v = \left( \frac{\partial u}{\partial T} \right)_v$$  \hspace{1cm} (3.3-1a,b)

The fundamental properties are internal energy $u$ and entropy $s$. These properties arrive from the first and second law of thermodynamics. The first law states that energy is conserved, and the second law states that entropy of the universe always increases.

The derived properties are defined to facilitate the energy balance of systems in which the combination of internal energy and other properties often occurs. In open systems, the mass that crosses the boundary between the surroundings and the system always contributes to two terms in the energy balance: internal energy and flow work ($Pv$). For convenient we can define an enthalpy ($h$) as

$$h = u + Pv$$  \hspace{1cm} (3.3-2a)

In terms of the total enthalpy $H$, we have

$$H = U + PV$$  \hspace{1cm} (3.3-2b)

We can then make an enthalpy balance for an open system in which the flow work is included in the enthalpy term. Figure 3.3-1 shows a raindrop created from the surrounding super saturated vapor in the atmosphere. Not only the energy $U$ of the raindrop is needed but also some additional energy, equal to $PV$, is required to push the atmosphere out of the way to make room for the drop.

**Figure 3.3-1** An energy of $U + PV$ is required to create a raindrop.
Enthalpy is the total energy we would need, to create a system out of nothing and put it in an environment with constant pressure $P$. Or, if we could completely annihilate a system, $H$ is the energy we could recover: the system’s energy plus the work done by the collapsing atmosphere.

However, we usually are not interested in the total energy needed or the total energy that can be recovered from a system. We will be more interested in the work involved in a system. For isothermal surroundings, the system can extract heat from the surroundings for free, so the work required to create the system from nothing is equal to the internal energy minus the heat received. And if we annihilate the system, we generally cannot recover all its energy as work since we have to dispose of its entropy by dumping some heat into the surroundings. Therefore it is more convenient to define the *Helmholtz free energy*, $A$, for an environment at constant temperature $T$

$$A = U - TS \quad (3.3-3)$$

$A$ is the energy that must be provided as work if we create the system out of nothing. The heat extracted from the surroundings is $T\Delta S = T(S_f - S_i) = TS_f$ where $S_f$ is the system final entropy and $S_i$ the system zero initial entropy. If we annihilate a system with initial entropy $S_i$, $A$ is the amount of recovered work, since we have to dump some heat, equal to $TS_i$, into the environment to get rid of the system’s entropy.

Equation (3.3-3) includes all work, even the work done by the system’s surroundings. If the system is in an isothermal and isobaric environment, it is more convenient to use the *Gibbs free energy*

$$G = U - TS + PV \quad (3.3-4)$$

Gibbs free energy is the work required to create a system from nothing in an environment with constant $P$ and constant temperature $T$.

We usually are more interested in the change in states of a system rather than its creation or annihilation. We then want to look at the changes in $A$ and $G$. The change in $A$ at constant temperature is given by

$$\Delta A = \Delta U - T\Delta S = Q + W - T\Delta S \quad (3.3-5)$$

In this expression $Q$ is the heat added and $W$ is the work done on the system. If the process is reversible then $Q = T\Delta S$ and the change in $A$ is precisely equal to the work done on the system. If the process is irreversible then $Q < T\Delta S$ and $\Delta A < W$, the change in $A$ is less than the work done on the system.

For an environment with constant $P$ and constant temperature $T$, the change in $G$ is given by

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V \quad (3.3-6)$$
Example 3.3-1

A well-insulated rigid tank having a volume of 10 ft$^3$ contains saturated water vapor at 212$^\circ$F. The water is stirred until the pressure is 20 lbf/in$^2$. Determine the temperature at the final state, in $^\circ$F, and the work during the process, in Btu$^7$.

Solution

![Diagram](image)

Figure E3.3-1 $p-v$ and $T-v$ diagram for the initial and final states (1) and (2) respectively.

State (1) of the system is defined by saturated vapor at 212$^\circ$F which is then located in the $p-v$ and $T-v$ diagram in Figure E3.3-1 and also in Table E3.3-1 by specifying $T = 212^\circ$F and $x$ (quality) = 1. State (2) is defined by pressure at 20 lbf/in$^2$ and specific volume which is the same value obtained from state (1). The temperature at the final state (2) is then 445.1$^\circ$F.

![Table](image)

Table E3.3-1 Steam properties at state (1) and (2)

- $T$ (F): 212, 445.1
- $p$ (psia): 14.7, 20
- $v$ (ft$^3$/lbf): 26.8, 26.8
- $u$ (Btu/lbm): 1078, 1161

State (1) is Saturated Vapor at 212$^\circ$F and 14.7 lbf/in$^2$, while state (2) is Superheated Vapor at 20 lbf/in$^2$.

The energy balance on the system is written as

$$\Delta E = E_2 - E_1 = \Delta KE + \Delta PE + \Delta U = Q + W$$

Since $\Delta KE = 0$, $\Delta PE = 0$, and $Q = 0$, we have

$$W = \Delta U = m(u_2 - u_1)$$

$$W = \frac{10 \text{ ft}^3}{26.8 \text{ ft}^3/\text{lb}} (1161 - 1078) \text{ Btu/lb} = 31.0 \text{ Btu (transfer to the system)}$$

Example 3.3-2

Water contained in a piston-cylinder assembly undergoes two processes in series from an initial state where the pressure is 10 bar (1 MPa) and the temperature is 400°C.

Process 1-2: The water is cooled as it is compressed at a constant pressure of 10 bar to the saturated vapor state.
Process 2-3: The water is cooled at constant volume to 150°C.

For the overall process determine the work and the heat transfer in kJ/kg.

Solution

State (1) of the system is defined by the temperature at 400°C and the pressure at 10 bar (1 MPa), which is then located in the p-v and T-v diagram in Figure E3.2-2 and also in Table E3.2-2 by specifying $T = 400°C$ and $p = 1$ MPa. State (2) is defined by $p = 10$ bar (1 MPa) and $x = 1$ and state (3) is defined by $T = 150°C$ and specific volume $v = 0.1944 \text{ m}^3/\text{kg}$.

### Table E3.3-2 Steam properties at state (1), (2), and (3)

<table>
<thead>
<tr>
<th></th>
<th>$T$</th>
<th>$p$</th>
<th>$v$</th>
<th>$u$</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>1</td>
<td>0.3066</td>
<td>2957</td>
<td>Dense Fluid (T&gt;TC)</td>
</tr>
<tr>
<td>2</td>
<td>179.9</td>
<td>1</td>
<td>0.1944</td>
<td>2584</td>
<td>Saturated Vapor</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>0.4759</td>
<td>0.1944</td>
<td>1583</td>
<td>Liquid Vapor Mixture</td>
</tr>
</tbody>
</table>

\[
W = - \int_1^3 pdV = - \int_1^2 pdV + 0 \text{ (since } dV = 0 \text{ for process 2-3)}
\]

\[
W = - p(V_2 - V_1) = - mp(v_2 - v_1)
\]

\[
W/m = -(10^6 \text{ Pa})(0.1944 - 0.3066) \text{ m}^3/\text{kg} = 112.2 \text{ kJ/kg} \text{ (work done on the system)}
\]

Energy balance: $m(u_3 - u_1) = Q + W \implies Q/m = u_3 - u_1 - W/m$

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Using Table A2 given in the text, we must first determine the quality of steam from the following relation

\[ v_3 = 0.1944 = (1 - x)v_{f3} + xv_{g3} \Rightarrow x = \frac{v_3 - v_{f3}}{v_{g3} - v_{f3}} \]

\[ x = \frac{0.1944 - 1.0905 \times 10^{-3}}{0.3928 - 1.0905 \times 10^{-3}} = 0.494 \]

The specific internal energy of liquid vapor mixture at state 3 is then calculated:

\[ u_3 = (1 - x)u_{f3} + xu_{g3} = (1 - 0.494)(631.68) + 0.494(2559.5) = 1583.9 \text{ kJ/kg} \]

**Example 3.3-3**

A closed rigid vessel having a volume of 1 m³ is filled with steam at 10 bar (1 MPa) and 300°C. Heat is removed until the temperature reach 200°C. Determine the quantity of heat removed.

**Solution**

<table>
<thead>
<tr>
<th>C</th>
<th>MPa</th>
<th>m³/kg</th>
<th>u, kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>1</td>
<td>0.2579</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>0.8084</td>
<td><strong>0.2579</strong></td>
</tr>
</tbody>
</table>

State (1) is defined by temperature \( T_1 = 300°C \) and pressure \( p_1 = 1 \text{ MPa} \) and state (2) is defined by temperature \( T_2 = 200°C \) and specific volume \( v_2 = v_1 = 0.2579 \text{ m}^3/\text{kg} \).

The energy balance on the system, which is steam inside the vessel, is written as

\[ Q/m = 1583 - 2957 - 112.2 = -1,485.2 \text{ kJ/kg} \]
\[ \Delta E = E_2 - E_1 = \Delta KE + \Delta PE + \Delta U = Q + W \]

Since \( \Delta KE = 0 \), \( \Delta PE = 0 \), and \( W = 0 \), we have

\[ Q = U_2 - U_1 = m(u_2 - u_1) = \frac{V}{v} (u_2 - u_1) \]

\[ Q = \frac{1 \text{ m}^3}{0.2579 \text{ m}^3/\text{kg}} (2630 - 2793) \text{ kJ/kg} = -632 \text{ kJ} \]

### 3.4 Equations of State

Pressure \( p \), temperature \( T \), and molar volume \( \bar{v} \) are the three intensive variables that can be measured experimentally. For any pure substance, only two intensive properties are independent therefore we seek to come up with an equation that relates \( p, T, \bar{v} \) by fitting experimental data. We want an equation of the form

\[ f(p, T, \bar{v}) = 0 \]

Such an equation is known as an equation of state since it allows us to calculate the unknown property from the two that constrain the state. Equations of state can be explicit in pressure, that is,

\[ p = f(T, \bar{v}) \]

in molar volume,

\[ \bar{v} = f(p, T) \]

or in terms of the dimensionless compressibility factor, \( Z \),

\[ Z = \frac{p\bar{v}}{RT} \quad (3.4-1) \]

In this equation, \( \bar{R} \) is the *universal gas constant*. Its value as determined experimentally is

\[ \bar{R} = \begin{cases} 
8.314 \text{ kJ/kmol} \cdot \text{K} \\
1.986 \text{ Btu/lbmol} \cdot \text{oR} \\
1545 \text{ ft} \cdot \text{lbf} /\text{lbmol} \cdot \text{oR} 
\end{cases} \quad (3.4-2) \]

Even though there are many equations of state, we will limit our discussion to the *ideal gas law*, the *compressibility factor equation of state*, the *virial equation of state*, and the *Soave-Redlich-Kwong equation of state*. 

\[ \]
3.4-1 Ideal Gas Law

When the pressure $p$ is small relative to the critical pressure $p_c$ and/or the temperature $T$ is large relative to the critical temperature $T_c$, the compressibility factor $Z$ is approximately 1. We then have the ideal gas law

$$\frac{p\bar{v}}{RT} = 1 \quad (3.4-3)$$

With $\bar{v} = V/n$, Eq. (3.4-3) can be expressed as

$$pV = n\bar{R}T \quad (3.4-4)$$

The gas constant $R$ for a specific gas whose molecular weight is $M$ is given by

$$R = \bar{R}/M \quad (3.4-5)$$

Equation (3.4-3) can also be written as

$$\frac{p\bar{v}}{MRT} = \frac{pv}{RT} = 1 \quad (3.4-6)$$

For an ideal gas the internal energy is a function of temperature only. The enthalpy for ideal also depends on temperature only since

$$H = U + pV = U + n\bar{R}T \quad (3.4-7)$$

Example 3.4-1 ———————————————————————————————————————————

One pound of air in a piston-cylinder assembly undergoes a thermodynamic cycle consisting of three processes. 9

Process 1-2: Constant specific volume
Process 2-3: Constant-temperature expansion
Process 3-1: Constant-pressure compression

At state (1), the temperature is 540°F, and the pressure is 1 atm. At state (2), the pressure is 2 atm. Air is an ideal gas with molecular weight $M = 28.97$ lb/lbmol. Universal gas constant $\bar{R}$ = 1454 ft-lbf/lbmol·°R.

(a) Sketch the cycle on $p-v$ coordinates.
(b) Determine the temperature at state (2), in °R
(c) Determine the specific volume at state (3), in ft³/lb.

Solution ———————————————————————————————————————————

(a) Sketch the cycle on $p-v$ coordinates:

The cycle is shown in Figure E3.4-1. Since $\frac{pv}{RT} = 1$ and temperature is constant, the process 2-3 on the $p$-$v$ diagram is not a straight line.

![Figure E3.4-1 Cycle on $p$-$v$ diagram](image)

(b) Determine the temperature at state (2), in °R

Applying the ideal gas law at states (1) and (2) we have

\[
p_2v_2 = RT_2
\]

\[
p_1v_1 = RT_1
\]

Since $v_1 = v_2$, taking the ratio of the two equations we have

\[
\frac{p_2}{p_1} = \frac{T_2}{T_1} \Rightarrow T_2 = \frac{p_2}{p_1} T_1 = \left(\frac{2 \text{ atm}}{1 \text{ atm}}\right) (540°\text{R}) = 1080°\text{R}
\]

(c) Determine the specific volume at state (3), in $\text{ft}^3/\text{lb}$.

The specific volume at state (3) is $v_3 = RT_3/p_3$

Since $T_3 = T_2$ and $p_3 = p_1$ we have

\[
v_3 = RT_3/p_1 = \frac{RT_2}{Mp_1}
\]

\[
v_3 = \left(\frac{1545 \text{ ft} \cdot \text{lbf/lbmol} \cdot °\text{R}}{28.97 \text{ lb/lbmol}}\right) \frac{1080°\text{R}}{14.7 \text{ lbf/in}^2} = 27.2 \text{ ft}^3/\text{lb}
\]