

## Introduction

Application of the energy balance to a system of interest requires knowledge of the properties of the system and how these properties are related. The objective of this chapter is to introduce property relations relevant to engineering thermodynamics.

## State Principle

The *state* of a closed system at equilibrium is its condition as described by the values of its thermodynamic properties. It must be noted that values of all thermodynamic properties are determined from the independent subset of properties. The *state principle* is a general rule that has been developed to guide in determining the number of independent properties needed to specify the state of a system.

Based on experimental evidence, it is concluded that there is one independent property for each way a system's energy can be varied independently. We have noted that the energy of a closed system can be altered independently by *heat* or by *work*. Accordingly, an independent property can be associated with heat transfer as one way of varying the energy, and another independent property can be counted for each relevant way the energy can be changed through work. From experiments, it can be stated that the number of independent properties for systems is one plus the number of relevant work interactions. *This is the state principle*. Experimental evidence also indicates that, when counting the number of relevant work interactions, it suffices to consider only those that can occur as the system undergoes quasi-equilibrium processes.

The term *simple system* is applied when there is only *one* way the system energy can be significantly altered by work as the system undergoes quasi-equilibrium process. Therefore, counting one independent property for heat transfer and another for the single work mode gives a total of two independent properties needed to fix the state of a simple system. *This is the state principle for simple systems*. Example of simple systems is simple compressible systems, simple elastic and magnetic systems.

The only mode of energy transfer by work that can occur as a simple compressible system undergoes quasi-equilibrium processes is associated with volume change and is given by  $\int p dV$ . Since the influence of the earth's gravitational field is assumed negligible, pressure is uniform throughout the system.

Although any two independent properties are sufficient to fix the state of a simple compressible system in equilibrium, it is convenient to think in terms of a unit mass of substance. Hence, the state principle can be interpreted in terms of *intensive properties*. For example, the temperature,  $T$ , and another intensive property such as specific volume,  $v$ , might be selected to as the two independent properties. The state

principle asserts that the pressure, specific internal energy, and all other pertinent *intensive* properties could be determined as functions of  $T$  and  $v$ :  $p = p(T, v)$ ,  $u = u(T, v)$ , and so on.

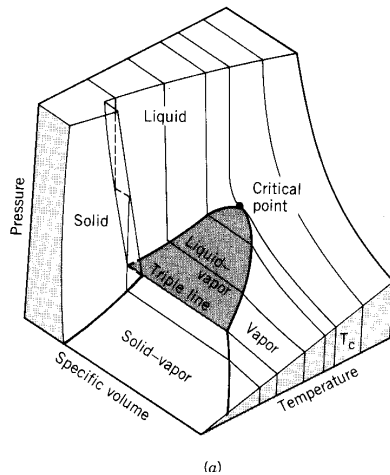
## Pure Substance

A pure substance is one of uniform and invariable chemical composition. Water, nitrogen, helium, carbon dioxide, for example, are all pure substances. Air a mixture of several gases is regarded as a pure substance because it has a uniform chemical composition. However, a mixture of oil and water is not a chemical substance since oil is not soluble in water.

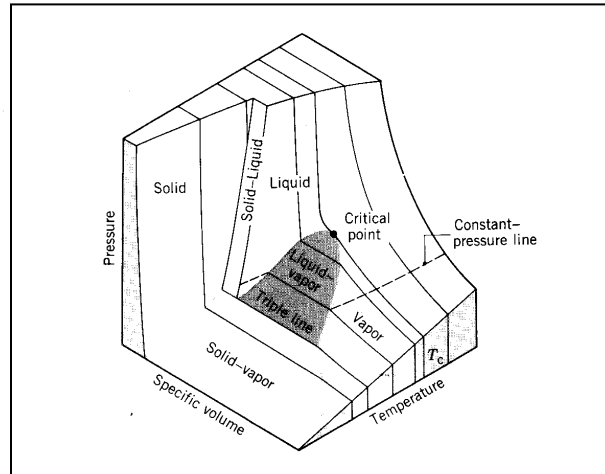
## $p$ - $v$ - $T$ Relation

In this section, we begin with consideration of the properties of pure, simple compressible substances and the relations among these properties, starting with pressure, specific volume, and temperature. From experiment, it is known that temperature and specific volume can be regarded as independent and pressure determined as a function of these two:  $p = p(T, v)$ . The graph of such a function is a surface, the  $p$ - $v$ - $T$  surface.

Figs 4.1 and 4.2 illustrate the  $p$ - $v$ - $T$  surfaces of substances that expand and contract on freezing, respectively. The 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.



**Fig. 4.1**  $p$ - $v$ - $T$  surface of a substance that expands on freezing



**Fig. 4.1**  $p$ - $v$ - $T$  surface of a substance that contracts on freezing

There are regions on the  $p$ - $v$ - $T$  surfaces of Figs. 4.1 and 4.2 labelled *solid*, *liquid* and *vapour*. In these *single-phase* regions, the state is fixed by *any* two of the properties pressure, specific volume, and temperature, since all of these are independent when there is a single phase present. Located between the single-phase regions are two-

phase regions where two phases exist in equilibrium: Liquid-vapour, solid-liquid, and solid-vapour. Two phases can coexist during changes in phase such as vaporization, melting, and sublimation. Within the two regions pressure and temperature are not independent; one cannot be changed without changing the other. In these regions, the state cannot be fixed by temperature and pressure alone; however, the state can be fixed by specific volume and either pressure or temperature. Three phases can exist in equilibrium along the line labelled triple line.

A state at which the phase change begins or ends is called a *saturation* state. The dome-shaped region composed of the two-phase liquid-vapour states is called the vapour dome. The lines bordering the vapour dome are called *saturated liquid* and *saturated vapour lines*. At the top of the dome, where the saturated liquid and saturated vapour lines meet, is called the *critical point*. The critical temperature  $T_c$  of a pure substance is the maximum temperature at which liquid and vapour phases can coexist in equilibrium. The pressure at the critical point is called the critical pressure,  $p_c$ . The specific volume at this state is the *critical specific volume*.

#### 4.3.1 Projections of the $p$ - $v$ - $T$ Surface

**The phase diagram** If the  $p$ - $v$ - $T$  surface is projected onto the pressure-temperature plane, a property diagram known as a *phase diagram* results. When projected in this way, the two-phase regions reduce to lines as shown in Figs. 4.3. A point on any of these lines represents all two-phase mixtures at that particular temperature and pressure. Substances that expand and contract on freezing differ only in the melting line on the  $p$ - $T$  diagram.

The term *saturation temperature* designates the temperature at which a phase change takes place at a given pressure, and this pressure is called the *saturation pressure* for the given temperature. It must be noted that for each saturation pressure, there is one saturation temperature, and conversely.

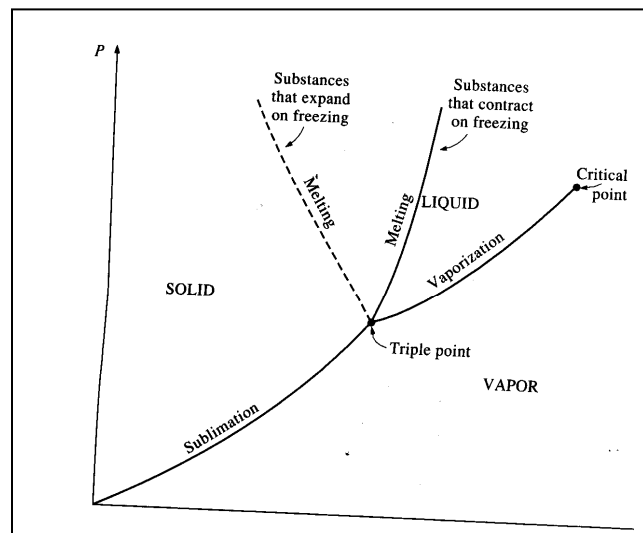
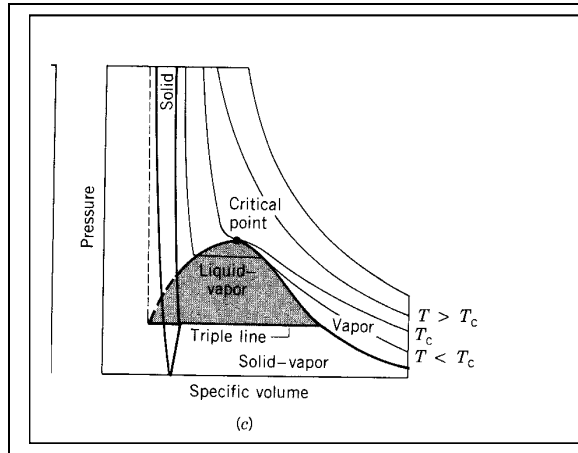


Fig. 4.3  $p$ - $T$  diagram of a pure substance

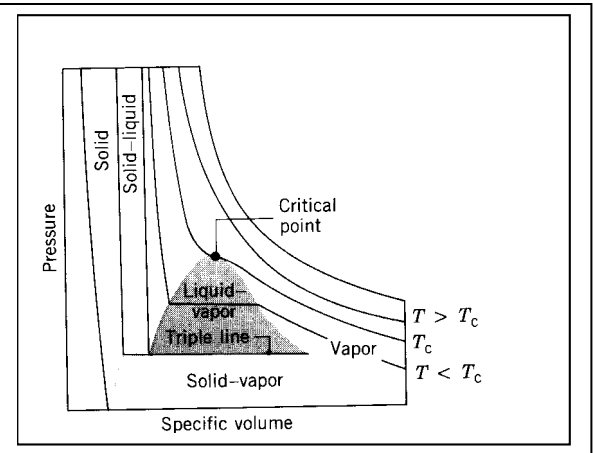
#### 4.3.1.1 $p$ - $v$ Diagram

Projecting the  $p$ - $v$ - $T$  surface onto the pressure-specific volume plane results in a  $p$ - $v$  diagram, as shown in Figs. 4.4 and 4.5.

Notes: It can be noted from Figs. 4.4 and 4.5 ( $p$ - $v$  diagrams) that:



**Fig. 4.5**  $p$ - $v$  diagram for a substance that expands on freezing

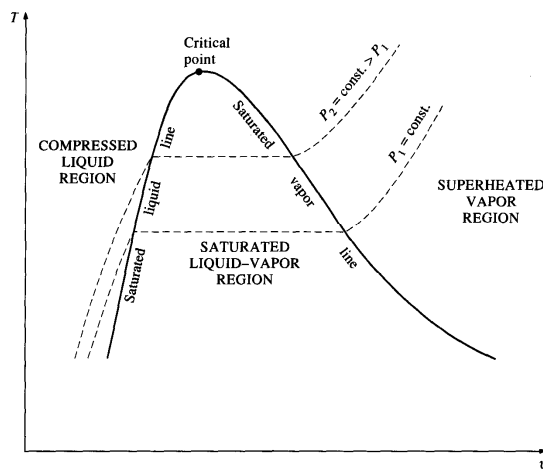


**Fig. 4.6**  $p$ - $v$  diagram for a substance that contracts on freezing

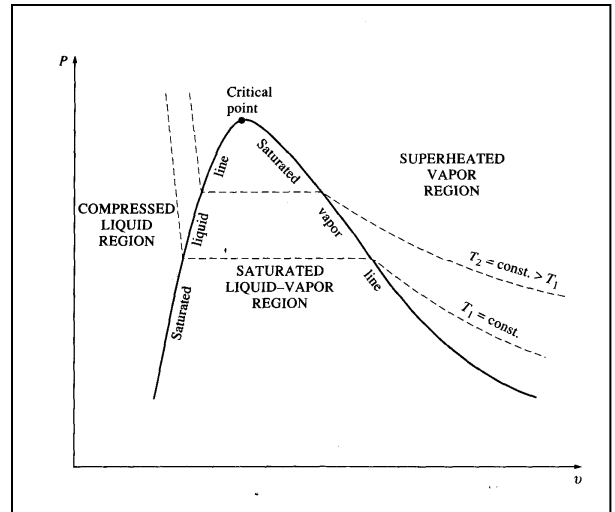
- For temperatures less than the critical temperature, pressure remains constant as the two-phase liquid-vapour region is traversed, but in the single-phase liquid and vapour regions the pressure decreases at fixed temperature as specific volume decreases.
- For temperatures greater than the critical temperature, pressure decreases continuously at fixed temperature as specific volumes increases. There is no passage across the two-phase liquid-vapour region.
- The critical isotherm passes through a point of inflection at the critical point and the slope is zero there.

#### 4.3.1.2 $T$ - $v$ Diagram

Projecting the liquid, two-phase liquid-vapour, and vapour regions of the  $p$ - $v$ - $T$  surface onto the temperature-specific volume plane results in a  $T$ - $v$  diagram as in Figs. 4.6. Since consistent patterns are revealed in the  $p$ - $v$ - $T$  behaviour of all substances, Fig. 4.6 showing a  $T$ - $v$  diagram for water can be regarded as representative.



**Fig. 4.6** T-v diagram for a pure substance



*Notes:* It can be noted from Fig. 4.6 that:

- For pressures less than the critical pressure, the pressure remains constant with temperature as the two-phase region is traversed; but in the single-phase liquid and vapour regions the temperature increases at fixed pressure as the specific volume increases.
- For pressures greater than or equal to the critical pressure, temperature increases continuously at fixed pressure as the specific volume increases. There is no passage across the two-phase liquid-vapour region.

### 4.3.2 Phase Change

It is instructive to study some of the events that occur as a pure substance undergoes a phase change. Consider a closed system consisting of 1 kg of water contained within a piston-cylinder assembly. Suppose the water is slowly heated while its pressure is kept constant and uniform pressure.

As the system is heated at constant pressure, the temperature increases considerably while the specific volume increases slightly. Eventually, the system is brought to the saturated line state corresponding to the specified pressure.

When the system is at the saturated liquid state, additional heat transfer at fixed pressure results in the formation of vapour without any change in the temperature but with considerable increase in specific volume. If the system is heated further until the last bit of liquid has vaporized, it is brought to the saturation vapour state. The intervening two-phase liquid-vapour mixtures can be distinguished from one another by the *quality*, an intensive property. The amount energy absorbed or released during a phase is called **latent heat**. The amount of energy released during vaporization is called the enthalpy of vaporization, which is equivalent to energy released during

condensation. The amount of energy absorbed during melting is called enthalpy of fusion, which is equivalent to energy released during freezing.

For a liquid-vapour mixture, the ratio of the mass of water vapour to the total mass of the mixture is defined as the quality,  $x$ , and is given by:

$$x = \frac{m_{\text{vapour}}}{m_{\text{total}}} \text{ where } m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapour}} = m_f + m_g \quad (4.1)$$

Quality has significance for *saturated mixtures* only. It has no meaning in the compressed liquid or superheated vapour regions. Its values ranges between 0 and 1. But the total of the mixture is the sum of the volume of the saturated liquid and the saturated vapour. That is:

$$V = V_f + V_g$$

But  $V = m v \quad \rightarrow \quad m_{\text{total}} v_{\text{av}} = m_f v_f + m_g v_g \quad (4.2)$

Substituting for  $m_f$  in terms of  $m_{\text{total}}$  and  $m_g$  in Eq. 4.2 and dividing the resulting expression by  $m_{\text{total}}$  and replacing  $m_g / m_{\text{total}}$  by  $x$  we obtain

$$v_{\text{av}} = (1 - x)v_f + x v_g = v_f + x v_{fg} \quad (4.3)$$

where  $v_{fg} = v_g - v_f$

The expression provided in Eq. 4.3 can be repeated for internal energy and enthalpy.

#### 4.4 Thermodynamic Property Data

Thermodynamic property data for engineering use appears in various forms, including tables, graphs, and equations. The emphasis of the current section is on the use of tables of thermodynamic properties, since tables are commonly available for pure, simple compressible substances on engineering interest. The present discussion will centre on the tables giving the properties of water, refrigerants and other simple compressible substances; these are commonly referred to as the *steam tables* (Thermodynamic and Transport properties of Fluids, 4<sup>th</sup> Edition).

**Saturation Tables:** The saturation tables, list property values for the saturated liquid and vapour states. The property values at these states are denoted by the subscripts  $f$  and  $g$ , respectively. Tables in the steam tables as listed on pages 2, is called the temperature table, because temperatures are listed in the first column in convenient increments. The second column gives the corresponding saturation pressures. The next columns list the specific volume of saturated vapour,  $v_g$ , specific enthalpy of saturated

liquid  $h_f$ , specific enthalpy of vaporization  $h_{fg}$ , and specific enthalpy of saturated vapour  $h_g$ , specific entropy of saturated liquid  $s_f$ , specific entropy of vaporization  $s_{fg}$ , and specific entropy of saturated vapour  $s_g$ , respectively. Tables as listed on pages 3-5 is called the pressure tables, because pressures are listed in the first column in convenient increments. The corresponding saturation temperatures are given in the second column. The next columns list the specific volume of saturated vapour,  $v_g$ , specific internal energy of saturated liquid  $u_f$ , specific internal energy of saturated vapour  $u_g$ , specific enthalpy of saturated liquid  $h_f$ , specific enthalpy of vaporization  $h_{fg}$ , and specific enthalpy of saturated vapour  $h_g$ , specific entropy of saturated liquid  $s_f$ , specific entropy of vaporization  $s_{fg}$ , and specific entropy of saturated vapour  $s_g$ , respectively.

Tables of superheated steam and supercritical steam are presented from pages 6 through to 9. On page 10 further properties of water and steam are provided.

#### (a) Saturated liquid and saturated vapour states

The subscript  $f$  is used to denote properties of a saturated liquid, and subscript  $g$  to denote the properties of saturated vapour. The subscript  $fg$  denotes the difference between the saturated vapour and the saturated liquid values of the same property. For example,  $h_{fg} = h_g - h_f$

The quantity  $h_{fg}$  is called the enthalpy of vaporization and it represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increases, and becomes zero at the critical point.

#### (b) Saturated liquid-vapour mixture

The analysis provided under section 4.3.2 for specific volume is repeated for internal energy and enthalpy.

#### (c) Superheated vapour

In the region to the right of the saturated vapour line, a substance exists as superheated vapour. The superheated region is a single-phase region and pressure and temperature are no longer dependent properties and they can be conveniently used as independent properties. Superheated vapour is characterised by:

- Lower pressures ( $p < p_{\text{sat}}$  at a given  $T$ )
- Higher temperature ( $T > T_{\text{sat}}$  at a given  $p$ )
- Higher specific volumes ( $v > v_g$  at a given  $p$  or  $T$ )
- Higher internal energies ( $u > u_g$  at a given  $p$  or  $T$ )
- Higher enthalpies ( $h > h_g$  at a given  $p$  or  $T$ )

**(d) Compressed liquid (See also section 4.5)**

In the absence of compressed liquid, a general approximation is *to treat compressed liquid as saturated liquid at the given temperature*. This is because the compressed liquid data depend on temperature more strongly than they do on pressure. Thus,

$$y \cong y_f @ T$$

for compressed liquids, where  $y$  is  $v$ ,  $u$ , or  $h$ . However, the error in  $h$  at very high pressure can be reduced by evaluating it using Eq. 4.7.

**4.5 Approximations for liquids using saturated liquid data.**

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

$$v(T, p) \approx v_f(T) \quad ; \quad u(T, p) \approx u_f(T) \quad (4.5)$$

An approximate value of  $h$  at liquid states can be obtained using the Eq. (4.5) and the definition  $h = u + pv$ ; thus

$$h(T, p) \approx u_f(T) + pv_f(T) \quad (4.6)$$

Equation 4.6 can be expressed alternatively as

$$h(T, p) = h_f(T) + v_f(T)[p - p_{sat}(T)] \quad (4.7)$$

where,  $p_{sat}$  denotes the saturation pressure at the given temperature. When the contribution of the last term of Eq. 4.7 is small, the specific enthalpy can be expressed by the saturation liquid value i.e.  $h(T, p) \approx h_f(T)$ . Equation 4.7 is used *when only liquid data available are for saturated liquid states*.

**4.6 Linear interpolation**

The states encountered when solving problems often do not fall exactly on the grid of values provided by property tables. Interpolation between adjacent table entries then becomes necessary. Linear interpolation can be used with acceptable accuracy when using the abridged tables in the steam tables.



### Tutorial Set IV

1. Is iced water a pure substance? Why?
2. What is the difference between saturated vapour and superheated vapour?
3. Is there any difference between the properties of saturated vapour at a given temperature and the vapour of a saturated mixture at the same temperature?
4. Is there any difference between the properties of saturated liquid at a given temperature and the liquid of a saturated mixture at the same temperature?
5. Is it true that water boils at higher temperatures at higher pressure?
6. If the pressure of a substance is increased during a boiling process, will the temperature also increase or will it remain constant? Why?
7. A househusband is cooking beef stew for his family in a pan that is (a) uncovered, (b) covered with a tight lid, and (c) covered with a heavy lid. For which case will the cooking time be the shortest? Why?
8. How does the boiling process at supercritical pressures differ from the boiling process at sub-critical pressures?
9. In which kind of pot will a given volume of water boil at a higher temperature: a tall narrow one or a short and wide one? Explain
10. A perfectly fitting pot and its lid often stick after cooking, and it becomes difficult to open the lid when the pot cools down. Explain why this happens and what you would do to open<sup>the</sup> lid.
11. It is well that warm air in a cooler environment rises. Now consider a warm mixture of air and gasoline on top of an open gasoline can. Do you think this gas mixture will rise in a cooler environment?
12. Is it true that it takes more energy to vaporise 1 kg of saturated liquid water at 100 °C than it would to vaporise 1 kg of saturated liquid at 120 °C?
13. Which requires more energy: completely vaporising 1 kg of saturated liquid water at 1 atm pressure or completely vaporising 1 kg saturated liquid water at 8 atm pressure?
14. Does  $h_{fg}$  change with pressure? How?
15. Complete the following table for water.

$T/^{\circ}\text{C}$	$p/\text{kPa}$	$v/(\text{m}^3/\text{kg})$	Phase description
50		4.16	
	200		Saturated vapour
250	400		
110	600		

16. Complete the following table for water.

$T/^{\circ}\text{C}$	$p/\text{kPa}$	$h/(\text{kJ/kg})$	$x$	Phase description
	325		0.4	
160		1682		
	950		0.0	
80	500			
	800	3162		

17. Complete the following table for water.

$T/^{\circ}\text{C}$	$p/\text{kPa}$	$v/(\text{m}^3/\text{kg})$	Phase description
125		0.53	
	1000		Saturated liquid
25	750		
500		0.130	

18. Complete the following table for water.

$T/^{\circ}\text{C}$	$p/\text{kPa}$	$u/(\text{kJ/kg})$	Phase description
	325	2452	
170			Saturated vapour
190	2000		
	4000	3040	

19. A cooking pan whose inner diameter is 20 cm is filled with water and covered with a 4-kg lid. If the local atmospheric pressure is 101 kPa, determine the temperature at the water will start boiling when it is heated. [100.2  $^{\circ}\text{C}$ ]

20. Water is being heated in a vertical piston-cylinder device. The piston has a mass of 20 kg and a cross-sectional area of 100 cm<sup>2</sup>. If the local atmospheric pressure is 100 kPa, determine the temperature at which the water will start boiling.

21. A rigid tank with a volume of 2.5 m<sup>3</sup> contains 5 kg of saturated liquid vapour mixture of water at 75  $^{\circ}\text{C}$ . Now the water is slowly heated. Determine the temperature at which the liquid in the tank is completely vaporised. Also show the process on a T-v diagram with respect saturation lines. [140.7  $^{\circ}\text{C}$ ]

22. A piston-cylinder device initially contains 50 litres of liquid at 25  $^{\circ}\text{C}$  and 300 kPa. Heat is added to the water at constant pressure until the entire liquid is vaporised.

- What is the mass of the water?
  - What is the final temperature?
  - Determine the total enthalpy change
  - Show the process on a T-v diagram with respect to saturation lines.
- [**(a) 49.85 kg**      **(b) 133.6  $^{\circ}\text{C}$**       **(c) 130,727 kJ**]