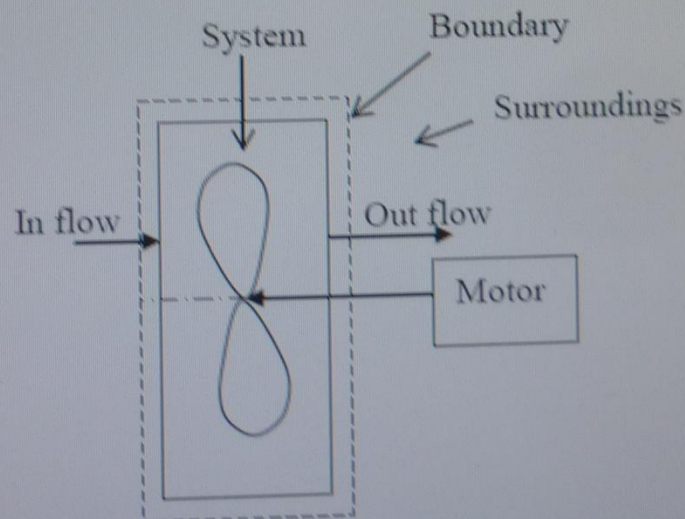# 1.1 Thermodynamic System

Thermodynamics is the science relating heat and work transfers and the related changes in the properties of the working substance. The working substance is isolated from its surroundings in order to determine its properties.

System – Collection of matter within prescribed and identifiable boundaries. A system may be either an open one, or a closed one, referring to whether mass transfer or does not take place across the boundary.

Surroundings – Is usually restricted to those particles of matter external to the system which may be affected by changes within the system, and the surroundings themselves may form another system.

Boundary – A physical or imaginary surface, enveloping the system and separating it from the surroundings.

1.2 Thermodynamic properties

Property - is any quantity whose changes are defined only by the end states and by the process. Examples of thermodynamic properties are the Pressure, Volume and Temperature of the working fluid in the system above.

Pressure (P) - The normal force exerted per unit area of the surface within the system. For engineering work, pressures are often measured with respect to atmospheric pressure rather than with respect to absolute vacuum.

$$P_{abs} = P_{atm} + P_{gauge}$$

In SI units the derived unit for pressure is the Pascal (Pa), where $1\ Pa = 1 N/m^2$. This is very small for engineering purposes, so usually pressures are given in terms of kiloPascals ($1\ kPa = 10^3\ Pa$), megaPascals ($1\ MPa = 10^6\ Pa$), or bars ($1\ bar = 10^5\ Pa$). The imperial unit for pressure are the pounds per square inch (Psi)) $1\ Psi = 6894.8\ Pa$.

Specific Volume (V) and Density (ρ)
For a system, the specific volume is that of a unit mass, i.e.

$$V = \frac{volume}{mass} \qquad\qquad \text{Units are } m^3/kg.$$

It represents the inverse of the density, $V = \dfrac{1}{\rho}$.

Temperature (T) - Temperature is the degree of hotness or coldness of the system. The absolute temperature of a body is defined relative to the temperature of ice; for SI units, the Kelvin scale. Another scale is the Celsius scale. Where

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the ice temperature under standard ambient pressure at sea level is: $0°C \equiv 273.15 \text{ K}$

and the boiling point for water (steam) is: $100°C \equiv 373.15 \text{ K}$

The imperial units of temperature is the Fahrenheit where

$$T°F = 1.8 \times T°C + 32$$

Internal Energy(u) - The property of a system covering all forms of energy arising from the internal structure of the substance.

conveniently defined as $h = u + PV$ where u is the internal

This will be discussed further later on.

1.3 Quality of the working Substance

A pure substance is one, which is homogeneous and chemically stable. Thus it can be a single substance which is present in more than one phase, for example liquid water and water vapour contained in a boiler in the absence of any air or dissolved gases.

Phase – is the State of the substance such as solid, liquid or gas.

Mixed Phase – It is possible that phases may be mixed, eg ice + water, water + vapour etc.

Quality of a Mixed Phase or Dryness Fraction (x)

The dryness fraction is defined as the ratio of the mass of pure vapour present to the total mass of the mixture (liquid and vapour; say 0.9 dry for example). The quality of the mixture may be defined as the percentage dryness of the mixture (ie, 90% dry).

Saturated State - A saturated liquid is a vapour whose dryness fraction is equal to zero. A saturated vapour has a quality of 100% or a dryness fraction of one.

Superheated Vapour - A gas is described as superheated when its temperature at a given pressure is greater than the saturated temperature at that pressure, ie the gas has been heated beyond its saturation temperature.

Degree of Superheat - The difference between the actual temperature of a given vapour and the saturation temperature of the vapour at a given pressure.

- $P_{CR} = 22.09$ MPa
- $T_{CR} = 374.14\,°C$ (or $647.3\,°K$)
- $V_{CR} = 0.003155$ m³/kg
- $u_f = u_g = 2014$ kJ/kg
- $h_f = h_g = 2084$ kJ/kg
- $s_f = s_g = 4.406$ kJ/kgK

1.4 Thermodynamic Processes

A process is a path in which the state of the system change and some properties vary from their original values. There are six types of Processes associated with Thermodynamics:

Adiabatic : no heat transfer from or to the fluid

Isothermal : no change in temperature of the fluid

Isobaric : no change in pressure of the fluid

Isochoric : no change in volume of the fluid

Isentropic : no change of entropy of the fluid

Isenthalpic : no change of enthalpy of the fluid

2.1 The Ideal Gas

Ideally, the behaviour of air is characterised by its mass, the volume it occupies, its temperature and the pressure condition in which it is kept. An ideal gas is governed by the perfect gas equation of state which relates the state pressure, volume and temperature of a fixed mass (m is constant) of a given gas (R is constant) as:

$$\frac{PV}{T} = mR \tag{1}$$

Where
P – Pressure (Pa)
V – Volume (m³)
T – Absolute Temperature (K)
$T(K) = 273 + t \, (C)$
m – mass (kg)
R – gas constant (J/kgK)

The equation of state can be written in the following forms, depending on what is needed to be calculated

1. In terms of the pressure $\qquad P = \dfrac{mRT}{V}$ (2)

2. In terms of the volume $\qquad V = \dfrac{mRT}{P}$ (3)

3. In terms of the mass $\qquad m = \dfrac{PV}{RT}$ (4)

4. In terms of the temperature $\qquad T = \dfrac{PV}{mR}$ (5)

5. In terms of the gas constant $\qquad R = \dfrac{PV}{mT}$ (6)

6. In terms of the density $\qquad \rho = \dfrac{m}{V} = \dfrac{P}{RT}$ (7)

The specific gas constant R, is a property related to the molar mass (M) in kg/kmol, of the gas and the Universal gas constant R_o as

$$R = R_o / M \qquad (8)$$

where $R_o = 8314.3$ J/kgK

The ideal gas equation can also be written on time basis, relating the mass flow rate (kg/s) and the volumetric flow rate (m³/s) as follows:

$$P V_t = m_t R T \qquad (9)$$

2.2 Alternative Gas Equation During A Change Of State:

The equation of state can be used to determine the behaviour of the gas during a process, i.e. what happens to its temperature, volume and pressure if any one property is changed. This is defined by a simple expression relating the initial and final states such as :

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
(10)

this can be rewritten in terms of the final condition, hence the following equations are geerated :

Final Pressure $$P_2 = P_1 \times \frac{T_2}{T_1} \times \frac{V_1}{V_2}$$ (11)

Final Temperature $$T_2 = T_1 \times \frac{P_2}{P_1} \times \frac{V_2}{V_1}$$ (12)

Final Volume $$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$ (13)

2.3 Thermodynamic Processes for gases

There are four distinct processes which may be undertaken by a gas (see Figure 2.1):-

Final Volume
$$V_2 = V_1 x \frac{P_1}{P_2} x \frac{T_2}{T_1}$$
(13)

2.3 Thermodynamic Processes for gases

There are four distinct processes which may be undertaken by a gas (see Figure 2.1):-

a) Constant volume process, known as isochoric process; given by:-

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
(14)

b) Constant pressure process; known as isobaric process, given by:-

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
(15)

c) Constant temperature process, known as isothermal process, given by:-

$$P_1V_1 = P_2V_2$$
(16)

d) Polytropic process given by:-

$$P_1 V_1^n = P_2 V_2^n$$

(17)

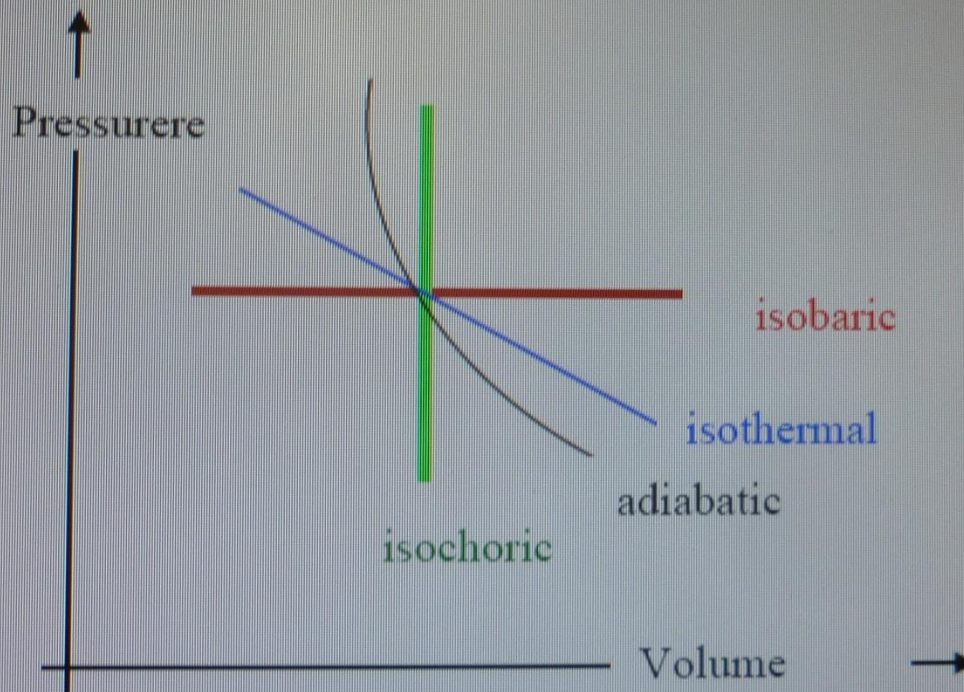Note when n = Cp/Cv, the process is known as adiabatic process.

Figure 2.1: Process paths

2.4 Van der Waals gas Equation of state for gases

The perfect gas equation derived above assumed that the gas particles do not interact or collide with each other. In fact, this is not true. The simpliest of the equations to try to treat real gases was developed by Johannes van der Waals. Based on experiments on pure gases in his laboratory, van der Waals recognized that the variation of each gas from ideal behavior could be treated by introducing two additional terms into the ideal gas equation. These terms account for the fact that real gas particles have some finite volume, and that they also have some measurable intermolecular force. The two equations are presented below:
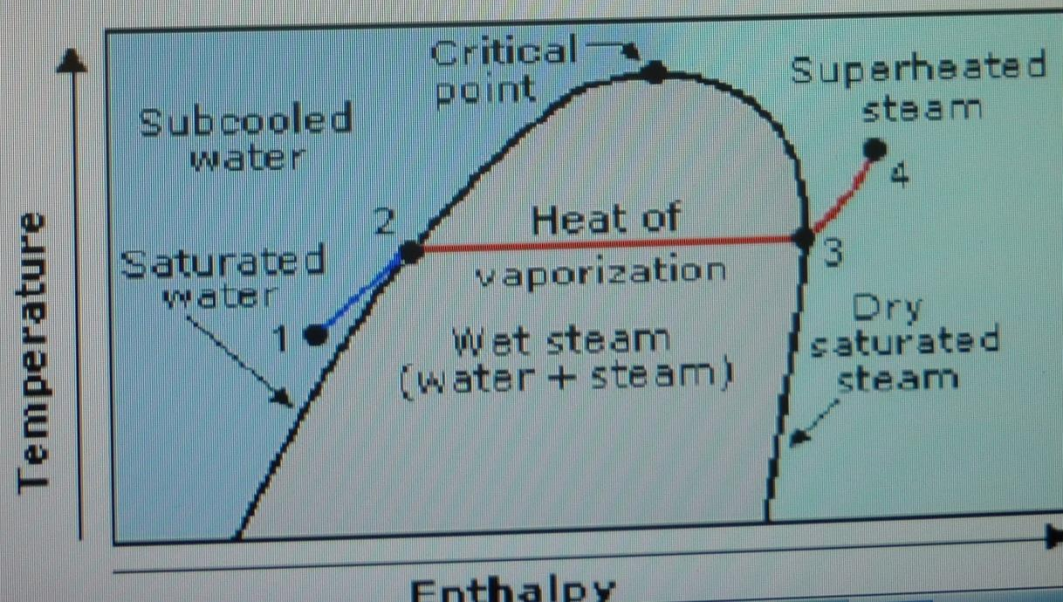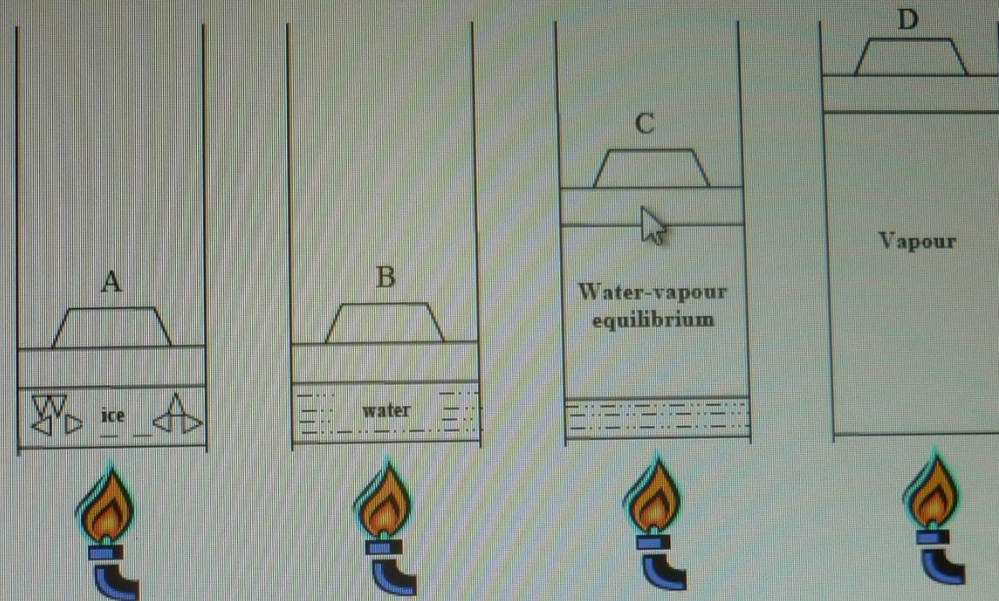
$$PV = mRT$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{18}$$

where v is the specific volume (V/m), and the Numerical values of a & b can be calculated as follows:

$$a = \frac{27 \cdot R^2 \cdot T_{critical}^2}{64 \cdot P_{critical}} \quad \text{and} \quad b = \frac{R \cdot T_{critical}}{8 \cdot P_{critical}} \tag{19}$$

Table 2.1, presents the various thermal properties of some gases and the values of the constants (a, and b) in Van der Waals equation.

D

C

Vapour

A

B

Water-vapour
equilibrium

ice   water

Temperature

Critical
point

Subcooled
water

Superheated
steam

2

Heat of
vaporization

Saturated
water

4

1

Wet steam
(water + steam)

3

Dry
saturated
steam

Enthalpy

Temperature-Entropy-Diagram

Temperature in Grade Celsius

Entropy in kJ / (kg x K)

p=1000.0 bar
p=900.0 bar
p=500.0 bar
p=300.0 bar
p=200.0 bar
p=150.0 bar
p=100.0 bar
p=60.0 bar
p=30.0 bar
p=15.0 bar
p=10.0 bar
p=6.0 bar
p=2.0 bar
p=1.0 bar
p=0.6 bar
p=0.4 bar
p=0.2 bar

v=0.005m3/kg
v=0.01m3/kg
v=0.02m3/kg
v=0.05m3/kg
v=0.1m3/kg
v=0.2m3/kg
v=0.5m3/kg
v=1m3/kg
v=10m3/kg

v=25m3/kg
v=50m3/kg
v=100m3/kg

X=0.0   X=0.2   X=0.4   X=0.6   X=0.8   X=1.0

0

0,0   5,0   10,0

Entropy in kJ / (kg x K)
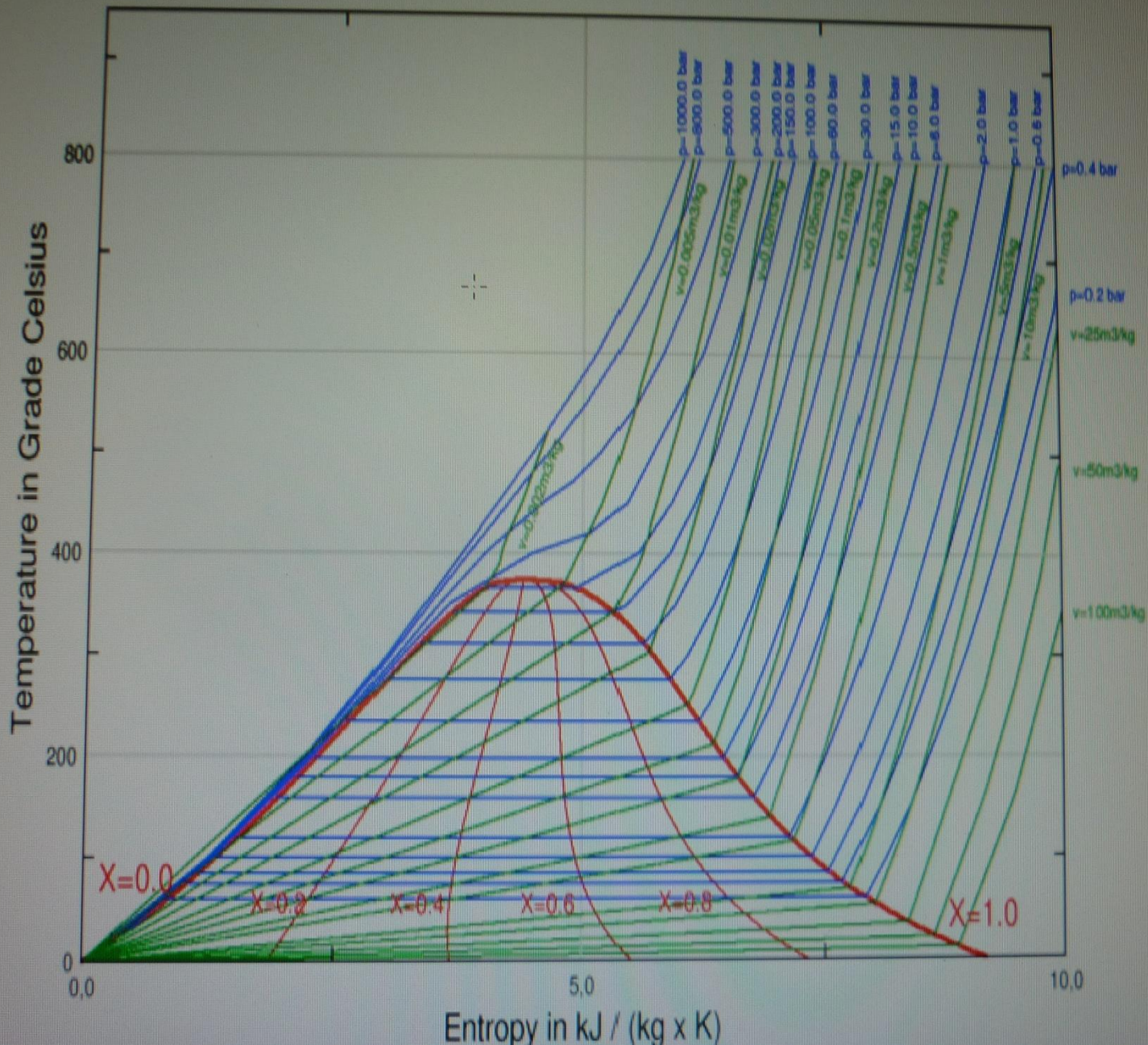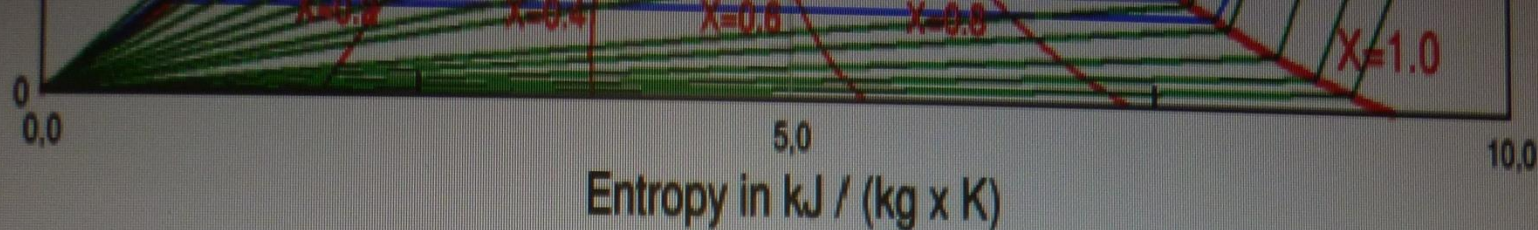
Figure 2.4: Temperature – Entropy chart for Water/Steam

Courtesy of: http://en.wikipedia.org/

Calculations of steam properties in the mixed region:

The dryness fraction is an added property needed to define the mixture of water liquid and vapour during iits transformation (condensation or evaporation) and is defined as follows:-

$$x = \frac{mass\ of\ vapour}{total\ mass\ of\ the\ system} \tag{21}$$

The total mass = mass of vapour + mass of liquid; Hence the system volume along the two-phase, process 2-3 (Figure 2.3) is:

$$v = (1 - x) v_f + x v_g \qquad (22)$$

At point state point 2, $x = 0$

at state point 3, $x = 1$ (Figure 2.3)

Values of v_f and v_g and other properties for real substances are normally given in tables. Suffix 'f' refers to the liquid; Suffix 'g' refers to the dry vapour; and Suffix 'fg' refers to the mixed phase.

$$v_{fg} = v_g - v_f$$
$$h_{fg} = h_g - h_f$$
$$S_{fg} = S_g - S_f$$

For wet steam of dryness fraction x

$$v = (1 - x) \cdot v_f + x \cdot v_g$$
$$= v_f + x \cdot (v_g - v_f)$$
$$= v_f + x \cdot v_{fg}$$

Similar relations for u, h and s.

$$v = v_f + x \, v_{fg}$$
$$u = u_f + x \, u_{fg}$$
$$h = h_f + x \, h_{fg}$$
$$s = s_f + x \, s_{fg}$$

$$(23)$$

Table 2.3 Superheated Steam table at selected pressures

Worked Example 2.1

Self ignition would occur in the engine using certain brand of petrol if the temperature due to compression reached 350°C.

Calculate the highest ratio of compression that may be used to avoid pre-ignition if the law of compression is

$$PV^{1.3} = c$$

$$PV^{1.4} = c$$

Calculate the final pressure in each case. Assume inlet condition of 27°C and 1 bar.

Solution

(a)
$$\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{n-1}}$$

$$\left(\frac{V_1}{V_2}\right)_i = \left(\frac{349 + 273}{300}\right)^{\frac{1}{0.3}} = 11.36$$

(a)

$$\left(\frac{V_1}{V_2}\right)_i = \left(\frac{349 + 273}{300}\right)^{\frac{1}{0.3}} = 11.36$$

$$\left(\frac{V_1}{V_2}\right)_{ii} = \left(\frac{349 + 273}{300}\right)^{\frac{1}{0.4}} = 6.19$$

(b)

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^n$$

$$P_{2i} = 1(11.36)^{1.3} = 23.5 \ bar$$

$$P_{2ii} = 1(6.19)^{1.4} = 12.8 \ bar$$

$$P_{2ii} = 1(6.19)^{1.4} = 12.8 \ bar$$

Worked Example 2.2

Calculate the density of Ethane at 171 bar and 458K; assume for Ethane:

T_c=305 K

P_c=48.80 bar

$R = 319.3 \ J/kgK$

a) assuming it behaves as a perfect gas
b) using the compressibility chart.

Solution:

a) for a perfect gas

$$\rho = \frac{P}{R.T} = \frac{171x10^5}{319.3x458} = 117 \ kg/m^3$$

b) using the com[pressibility chart:

$T_R = T / T_{CR} = 458 / 305.4 = 1.5$

$P_R = P / P_{CR} = 171 / 48.8 = 3.52.7$

READ Z from the chart (Z = 0.8)

ie 80% less dense compared with the perfect gas behaviour.

Or density = 146 kg/m³

Worked Example 2.3

Find the specific volume for H_2O at 10 MPa and 500°C using:

a) Compressibility chart;

b) Steam tables (below)

T	$p = 10.0$ MPa (311.06 deg-C)			
	v	u	H	s
Sat.	0.018026	2544.4	2724.7	5.6141
325	0.019861	2610.4	2809.1	5.7568
350	0.02242	2699.2	2923.4	5.9443
400	0.02641	2832.4	3096.5	6.2120
450	0.02975	2943.4	3240.9	6.4190
500	0.03279	3045.8	3373.7	6.5966
550	0.03564	3144.6	3500.9	6.7561
600	0.03837	3241.7	3625.3	6.9029

Source: http://www.sfsb.hr/

Solution:

a) Compressibility Chart

$$P_R = \frac{P}{P_c} = \frac{100}{221.2} = 0.47$$

$$T_R = \frac{T}{T_c} = \frac{500 + 273}{374.15 + 273} = 1.19$$

but $R = 8.3144/18.015 = 0.4615 \, kJ/kgK$

Using Figure 2.2, $Z = 0.9$ $\qquad \therefore \frac{PV}{RT} = 0.9$

$$V = \frac{R \times T \times Z}{P} = \frac{461.5 \times 773}{100 \times 10^5} \times 0.9 = 0.032 m^3 / kg$$

b) From Steam Tables:

The steam is superheated

The steam is superheated

At 100 bar and 500°C , v = 0.03279 m³ /kg

Both results are similar within to the 3rd decimalplace.

Worked Example 2.4

Determine the pressure of water vapour at 300°C, if its specific volume is 0.2579 m³/kg, using the following methods:

a) Ideal gas equation
b) Van-der-Waals equations

Solution:

a) $Pv = RT$

$$P = \frac{RT}{v} = \frac{461.5 \times 573}{0.2579} = 1.025 MPa$$

b) $a = \dfrac{27R^2Tc^2}{64Pc} = \dfrac{27 \times 461.5^2 \times 647.3^2}{64 \times 22.09 \times 10^6} = 1704$

$b = \dfrac{RTc}{8Pc} = \dfrac{461.5 \times 647.3}{8 \times 22.09 \times 10^6} = 1.69 \times 10^{-3}$

$P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$

$= \dfrac{461.5 \times 573}{0.2579 - 1.69 \times 10^{-3}} - \dfrac{1704}{0.2579^2}$

$= 1032120.1 - 25619$

$= 1.006 \text{ MPa}$