Joule-Thomson Coefficient:

When a fluid passes through a restriction such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases. The enthalpy of the fluid remains approximately constant during such a throttling process. The fluid may experience a large drop in its temperature as a result of throttling, which forms the basis of operation for refrigerators and air conditioners. This is not always the case, however. The temperature of the fluid may remain unchanged, or it may even increase during a throttling process.

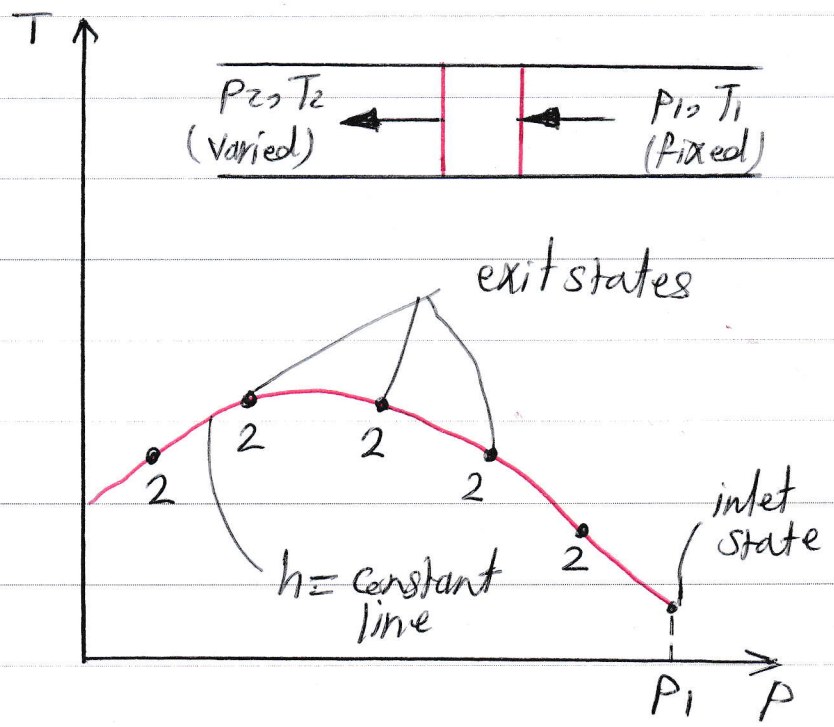
The temperature behavior of a fluid during a throttling (h = constant) process is described by the Joule-Thomson coefficient, defined as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h \qquad (80)$$

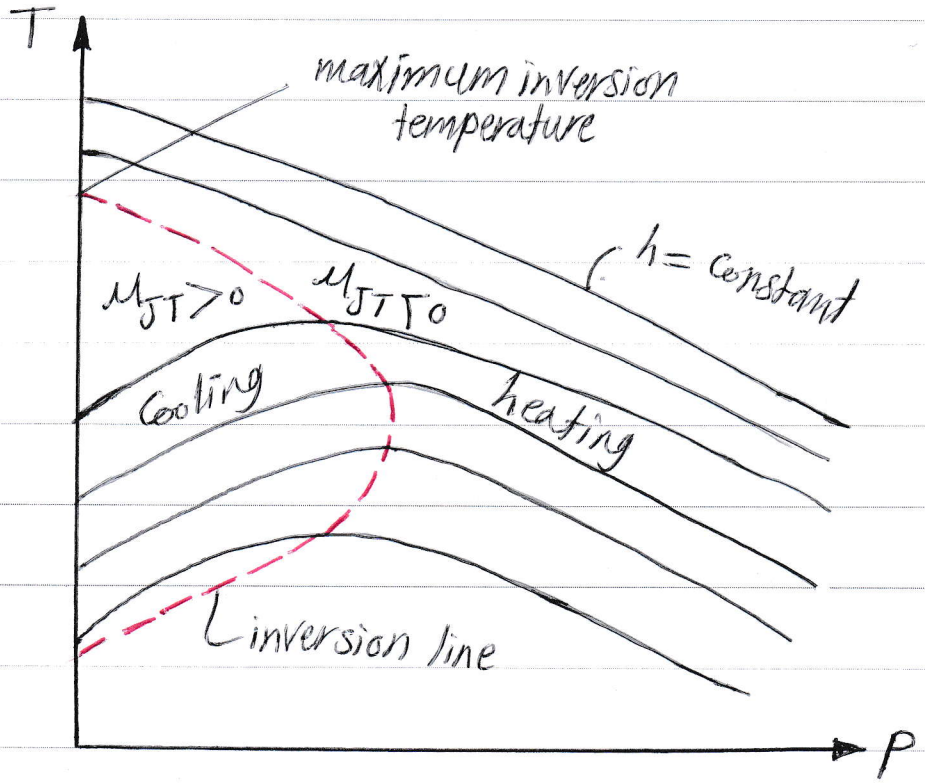
Where

$$\mu_{JT} \begin{cases} > 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ < 0 & \text{temperature decreases} \end{cases}$$

The Joule-Thomson coefficient represents the slope of h = constant lines on a T-p diagram. Such diagrams can be easily constructed from temperature and pressure measurements alone during throttling processes. A fluid at a fixed temperature and pressure T_1 and p_1 (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream (T_2 and p_2) are measured. The experiment is repeated for different sizes of porous plugs, each giving a different set of T_2 and p_2. Plotting the temperatures against the pressures gives us an h = constant line on a T-p diagram, as shown in figure.



Repeating the experiment for different sets of inlet pressure and temperature and plotting the results, we can construct a T-P diagram for a substance with several h= constant lines, as shown in figure.



Some constant-enthalpy lines on the T-P diagram pass through a point of zero slope or zero Joule-Thomson coefficient. The line that passes through these points is called the inversion line, and the temperature at a point where a constant-enthalpy line intersects the inversion line is called the inversion temperature.

The temperature at the intersection of the $p=0$ line and the upper part of the inversion line is called the maximum inversion temperature. Notice that the slopes of the $h=$ constant line are negative ($\mu_{JT} < 0$) at states to the right of the inversion line and postive ($\mu_{JT} > 0$) to the left of the inversion line.

A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure, that is, from right to left. Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line. However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line. It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature. This presents a problem for substances whose maximum inversion temperature is well below room temperature. For hydrogen, for example, the maximum inversion temperature is $-68\,^{\circ}C$. Thus hydrogen must be cooled below this

temperature if any further cooling is to be achieved by throttling.

Now, we would like to develop a general relation for the Joule-Thomson Coefficient in terms of the specific heats, pressure, specific volume, and temperature. This is easily accomplished by modifying the generalized relation for enthalpy change (Eq 48),

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp \qquad (81)$$

For a constant enthalpy process $dh = 0$. Therefore,

$$0 = (c_p dT)_h + \left[\left\{ v - T\left(\frac{\partial v}{\partial T}\right)_p \right\} dp \right]_h$$

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v \right]} \qquad (82)$$

Ex: Show that the Joule-Thomson coefficient of an ideal gas is zero.

Solution:

For an ideal gas $v = \frac{RT}{p}$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

substituting in Eq(82) gives,

$$\mu_{JT} = \frac{1}{c_p}\left[T\frac{R}{P} - v\right] = \frac{1}{c_p}\left[v - v\right] = 0$$

Therefore, if an ideal gas is throttled, there will not be any change in temperature.

Ex: Show that the internal energy of an ideal gas is a function of temperature only, $u = u(T)$.

Solution:

The differential change in the internal energy of a general simple compressible system is given by Eq(44) as

$$du = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

Since $Pv = RT$ for ideal gas

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

$$\therefore T\left(\frac{\partial P}{\partial T}\right)_v - P = T\left(\frac{R}{v}\right) - P = P - P = 0$$

Thus,

$$du = c_v dT$$

To complet the proof, we need to show that C_v is not a function of v either.

Let $u = f(T, v)$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$= C_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \qquad (1)$$

Let $s = f(T, v)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \qquad (2)$$

Substituting above equation into $du = Tds - pdv$, gives

$$du = T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - p\right] dv \qquad (3)$$

From Eqs (1) and (3), we have

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T} \qquad (4)$$

substituting Eq(4) into 2 gives

$$ds = \left(\frac{C_v}{T}\right) dT + \left(\frac{\partial s}{\partial v}\right)_T dv \qquad (5)$$

From the third Maxwell relation, we have

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

Eq(5) becomes

$$ds = \left(\frac{C_v}{T}\right) dT + \left(\frac{\partial P}{\partial T}\right)_v dv \qquad (6)$$

Applying the test of exactness on Eq(6),

$$M = \frac{C_v}{T} \quad \text{and} \quad N = \left(\frac{\partial P}{\partial T}\right)_v$$

Since $\left(\frac{\partial M}{\partial v}\right)_T = \left(\frac{\partial N}{\partial T}\right)_v$

$$\therefore \left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$$

For an ideal gas $p = \frac{RT}{v}$, then

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)\right]_v = \left[\frac{\partial}{\partial T}\left(\frac{R}{v}\right)\right]_v = 0$$

Thus,

$$\left(\frac{\partial c_v}{\partial v}\right)_T = 0$$

which states that c_v does not change with specific volume. That is, c_v is not a function of specific volume. Therefore, we conclude that the internal energy of an ideal gas is a function of temperature only.

EX: Find the value of coefficient of volume expansion β and isothermal compressibility K for a Vander Waals' gas obeying

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Solution: Van der Waals equation is

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where a and b are constant.
Rearranging this equation, we can write

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

Since $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$

To determine $(\partial v/\partial T)_p$, we can use the cyclic relation

$$\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T = -1$$

Hence

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{-\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}$$

From the Van der Waals equation,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

$$\therefore \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v}\left[-\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}\right]$$

$$\therefore \beta = \frac{1}{v}\left[-\frac{\frac{R}{v-b}}{\frac{-RT}{(v-b)^2}+\frac{2a}{v^3}}\right]$$

$$= \frac{Rv^2(v-b)}{RTv^3-2a(v-b)^2}$$

Also,

$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{v}\left[\frac{1}{\frac{-RT}{(v-b)^2}+\frac{2a}{v^3}}\right]$$

$$= \frac{v^2(v-b)^2}{RTv^3-2a(v-b)^2}$$

Sheet No. 3

Q1: Using the Maxwell relations, determine a relation for $(\partial s/\partial v)_T$ for a gas whose equation of state is

$$\left(P - \frac{a}{v^2}\right)(v - b) = RT.$$

Where a and b are emperical constants.

Q2: show that

$$c_v = -T\left(\frac{\partial v}{\partial T}\right)_s \left(\frac{\partial P}{\partial T}\right)_v, \text{ and}$$

$$c_p = T\left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial v}{\partial T}\right)_P$$

Q3: Temperature and pressure may be defined as

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad \text{and} \quad P = -\left(\frac{\partial u}{\partial v}\right)_s$$

Using these definitions, prove that for a simple compressible substance

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{P}{T}$$

Q4: Steam is throttled from 2.5 Mpa and 400 c° to 1.2 Mpa. Estimate the temperature change of the steam during this process and the average Joule-Thomson Coefficient.

Q5: show that

$$h-u=T^2\left[\left(\frac{\partial}{\partial T}\left(\frac{a}{T}\right)\right)_v-\left(\frac{\partial}{\partial T}\left(\frac{g}{T}\right)\right)_p\right]$$

Where
a is the Helmholtz function, and
g is the Gibbs function.

Ideal and Real Gases :-

An ideal gas is defined as a gas having no forces of intermolecular attraction. The gases which follow the gas laws at all ranges of pressures and temperatures are considered as ideal gases. However, real gases follow these laws at low pressures or high temperatures or both. This is because the forces of attraction between molecules tend to be very small at reduced pressures and elevated temperatures.

In reality there is no ideal or perfect gas. At a very low pressure and at a very high temperature, real gases like hydrogen, oxygen, nitrogen, helium etc. behave nearly the same way as perfect gases. These gases are called semi-perfect or permanent gases. The term semi-perfect has the implication that the behaviour of the gases are nearly the same as that of a perfect gas. The term 'permanent' was used for these gases by earlier chemists who thought that these gases did not change their phase (i.e., did not condense to liquid state). Hence, they are called permanent gases. There is no

gas which does not change phase, and there is no permanent gas in the real sense. However, these gases can be changed into a liquid phase only if they are subjected to a great decrease in temperature and increase in pressure.

All gases behave in nearly in a similar way, especially at pressures considerably lower than the critical pressure, and at temperatures above the critical temperature. The relation between the independent properties, such as pressure, specific volume and temperature for a pure substance is known as the 'equation of state'. For engineering calculations, the equation of state for perfect gases can be used for real gases so long as the temperature are well below their critical pressure and the temperatures are above the critical temperature.

The Ideal- Gas Equation of State:-

Boyle's Law:

It states that volume of a given mass of the ideal gas varies inversely as the absolute pressure when temperature is Constant.

If p is the absolute pressure of the gas and v is the volume occupied by the gas, then

$$V \propto \frac{1}{P} \quad , \text{or} \quad pV = \text{constant}, \text{ so long as}$$

the temperature is constant.

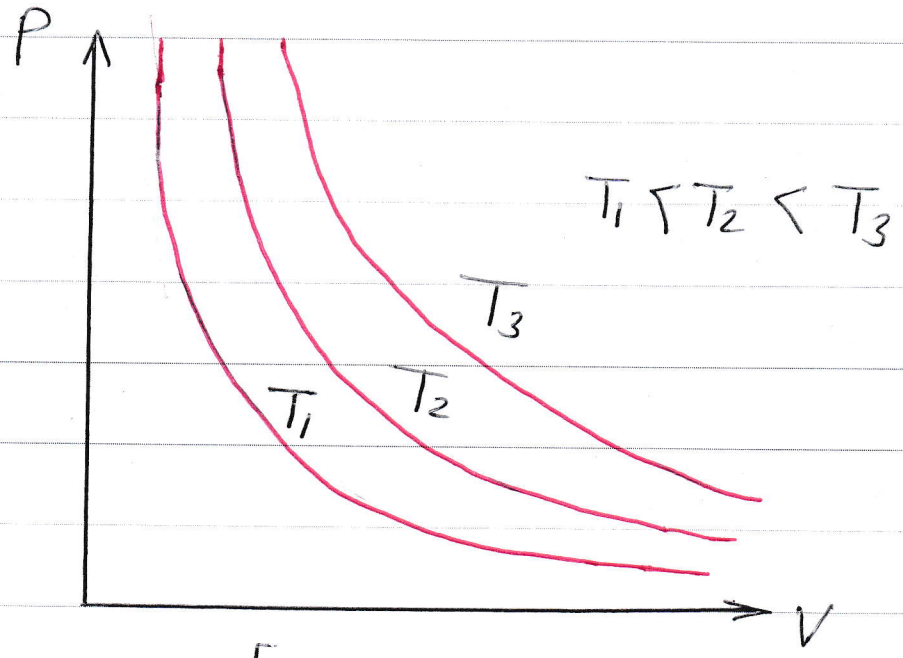


Figure 1-

For any two points on the curve,

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \qquad (1)$$

Charle's Law: It states that if any gas is heated at constant pressure, its volume changes directly as

its absolute temperature.
In other words, $V \propto T$

or, $\frac{V}{T}$ = Constant, so long as pressure is Constant.

If a gas changes its volume from V_1 to V_2 and absolute temperature from T_1 to T_2 without any change of pressure, then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

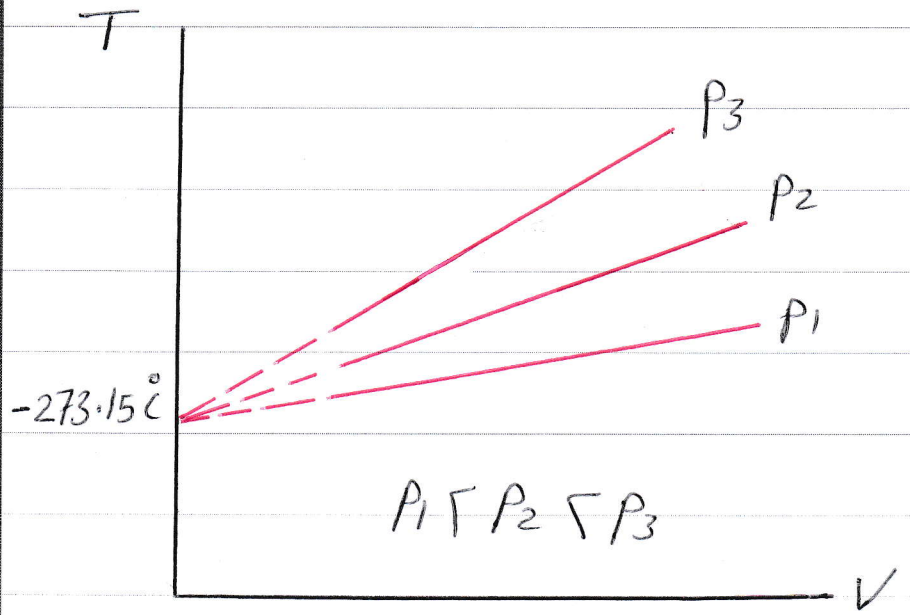


Figure 2.

To derive the equation of state for the ideal gas let us consider a unit mass of the ideal gas to change its state in the following two successive pro-

cesses:

(a) process $1-2'$: $p =$ constant

(b) process $2'-2$: $T =$ Constant

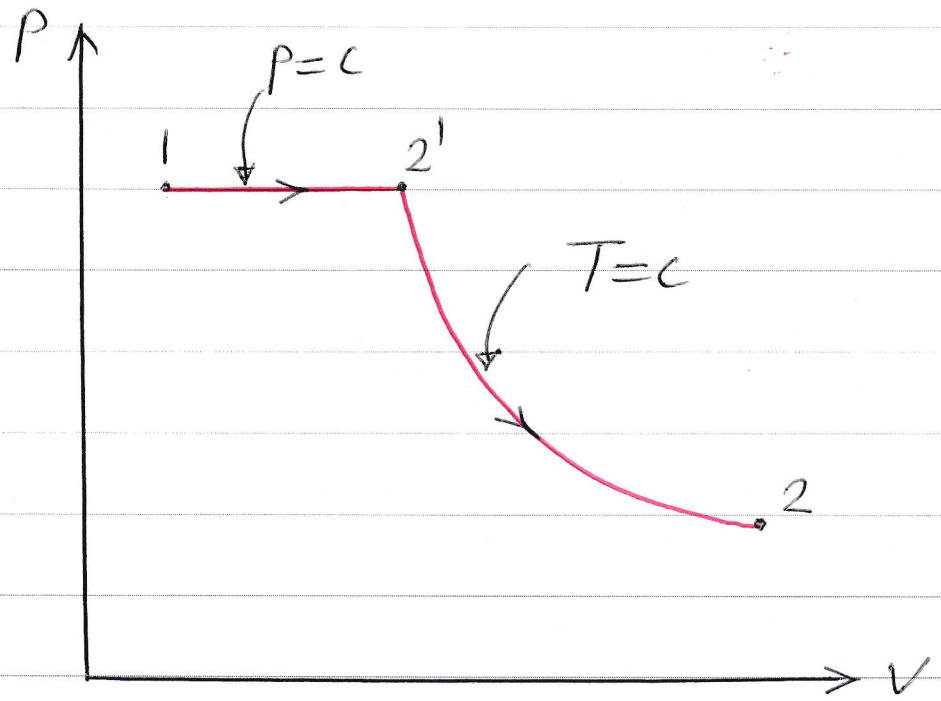


Figure 3.

For the process $1-2'$, applying Charle's law

$$\frac{v_1}{T_1} = \frac{v_{2'}}{T_{2'}}$$, since $T_{2'} = T_2$, we may

write

$$\frac{v_1}{T_1} = \frac{v_{2'}}{T_2} \qquad (2)$$

For the process $2'-2$, using Boyle's law

$P_2' v_2' = P_2 v_2$, and since $P_2' = P_1$

$\therefore P_1 v_2' = P_2 v_2$

i.e., $v_2' = \dfrac{P_2 v_2}{P_1}$ (3)

substituting the value of v_2' from Eq (3) in Eq (2), we get

$$\frac{v_1}{T_1} = \frac{P_2 v_2}{P_1 T_2}$$

or,

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

i.e, $\dfrac{Pv}{T} = \text{constant}$ (4)

The magnitude of the constant in Eq (4) depends upon the particular gas and it is denoted by R, where R is called the specific gas constant. Then

$$\frac{Pv}{T} = R$$

The equation of the state for the ideal gas is thus

given by the equation

$$pv = RT \quad (5)$$

or,

$$pV = mRT \quad (6)$$

The equation may be written as

$$pV_o = MRT \quad (7)$$

where

V_o = molar volume.

M = Molecular weight of the gas

Avogadro discovered that V_o is the same for all gases at the same pressure and temperature and therefore it may be seen that

MR = Constant = R_o and thus

$$pV_o = R_o T \quad (8)$$

R_o is called the molar or universal gas constant and its value is 8.3143 kJ/kmol.K. If there are n moles present then the ideal gas equation may be written as:

$$pV = nR_o T \qquad (9)$$

where V is the volume occupied by n moles at pressure p and temperature T.

Is Water Vapour an Ideal Gas?

This question cannot be answered with a simple yes or no. The error involved in treating water vapour

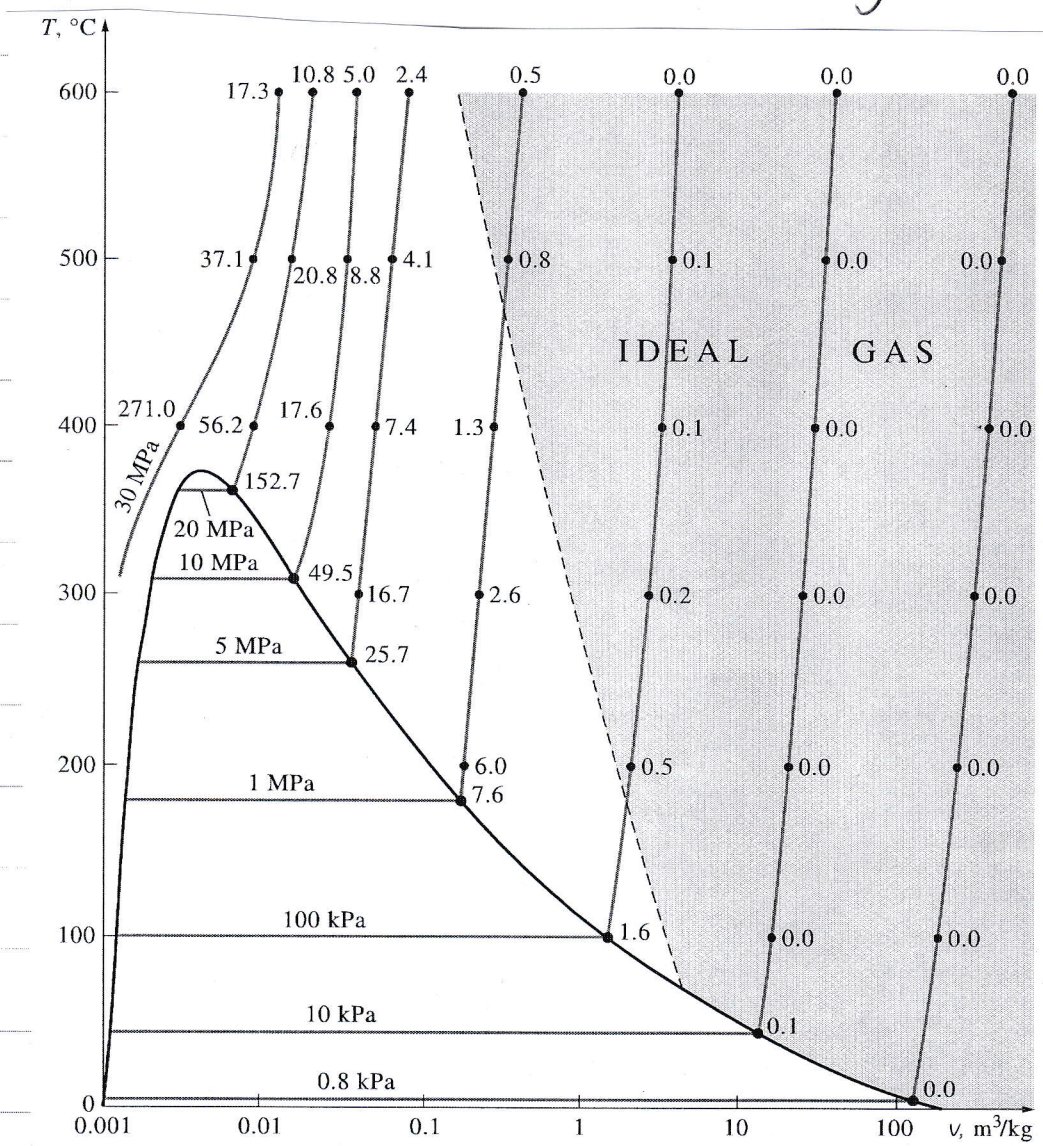


Figure 4.

as an ideal gas is calculated and plotted in figurer. It is clear from this figure that at pressures below 10 kPa, water vapour can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent). At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapour line (over 100 percent). Therefore, in air-conditioning applications, the water vapour in the air can be treated as an ideal gas with essentially no error since the pressure of the water vapour is very low. In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

The percentage of error in figure can be calculated as:

$$\left[\frac{v_{table} - v_{ideal}}{v_{table}}\right] \times 100$$

Compressibility Factor – A Measure of Deviation from Ideal-Gas Behavior:–

The ideal-gas equation is very simple and thus very convenient to use. However, as shown in figure 4, gases deviate from ideal-gas behavior significantly at states near the saturation region and the critical point. This deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted for by the introduction of a correction factor called the compressibility factor Z defined as

$$Z = \frac{Pv}{RT} \qquad (10)$$

It can also be expressed as

$$Z = \frac{v_{actual}}{v_{ideal}} \qquad (11)$$

Where

$$v_{ideal} = \frac{RT}{P}$$

$$Z \begin{cases} >1 & \text{Real gases} \\ =1 & \text{Ideal gas} \\ <1 & \text{Real gases} \end{cases}$$

Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures. The normalization is done as

$$P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}}$$

Here P_R is called the reduced pressure and T_R the reduced temperature. The Z factor for all gases is approximately the same at the same reduced pressure and temperature. This is called the principle of corresponding states.

Figure (5) shows that the compressibility factor for several gases.

The following observations can be made from the generalized compressibility

1. At very low pressures ($P_R \ll 1$), gases behave as an ideal gas regardless of temperature.
2- At high temperatures ($T_R > 2$), ideal-gas behavior can be assumed with good accuracy regardless of pressure (except when $P_R \gg 1$).
3- The deviation of a gas from ideal-gas behavior is greatest in the vicinty of the critical point, see figure (4).

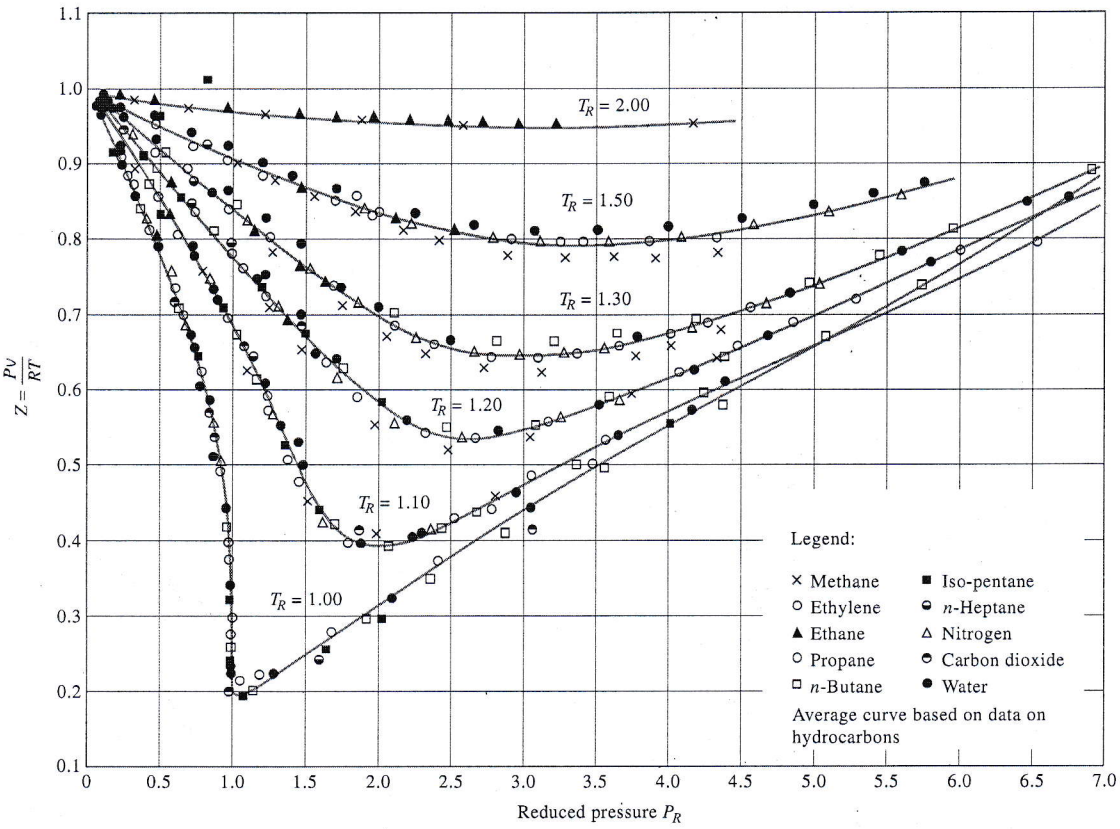


Figure (5)

Real gases:-

The ideal-gas equation of state is very simple, but its range of applicability is limited. It is desirable to have equations of state that represent the p-v-T behavior of substances accurately over a larger region with no limitions. such equations are naturally more complicated. Several equations have been proposed for this purpose.

Van der Waals Equation of State:-

The Van der Waals equation of state was proposed in 1873, and it has two constants that are determined from the behavior of a substance at the critical point. It is given by

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT \qquad (12)$$

Van der Waals intended to improve the ideal gas equation of state by including two of the effects not considered in the ideal-gas model:

the intermolecular attraction forces and the volume occupied by the molecules themselves. The term a/v^2 accounts for the intermolecular forces, and b accounts for the volume occupied by the gas molecules. In a room at atmospheric pressure and temperature, the volume actually occupied by molecules is only about one-thousandth of the volume of the room. As the pressure increases, the volume occupied by the molecules becomes an increasingly significant part of the total volume. Van der Waals proposed to correct this by replacing v in the ideal-gas relation with the quantity $v-b$, where b represents the volume occupied by the gas molecules per unit mass.

The determination of the two constants appearing in this equation is based on the observation that the critical isotherm on a $p-v$ diagram has a horizontal inflection point at the critical point (Figure 6.). Thus, the first and second derivatives of p with respect

to v at the critical point must be zero. That is

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}=\text{Constant}} = 0 \qquad (13)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}=\text{Constant}} = 0 \qquad (14)$$

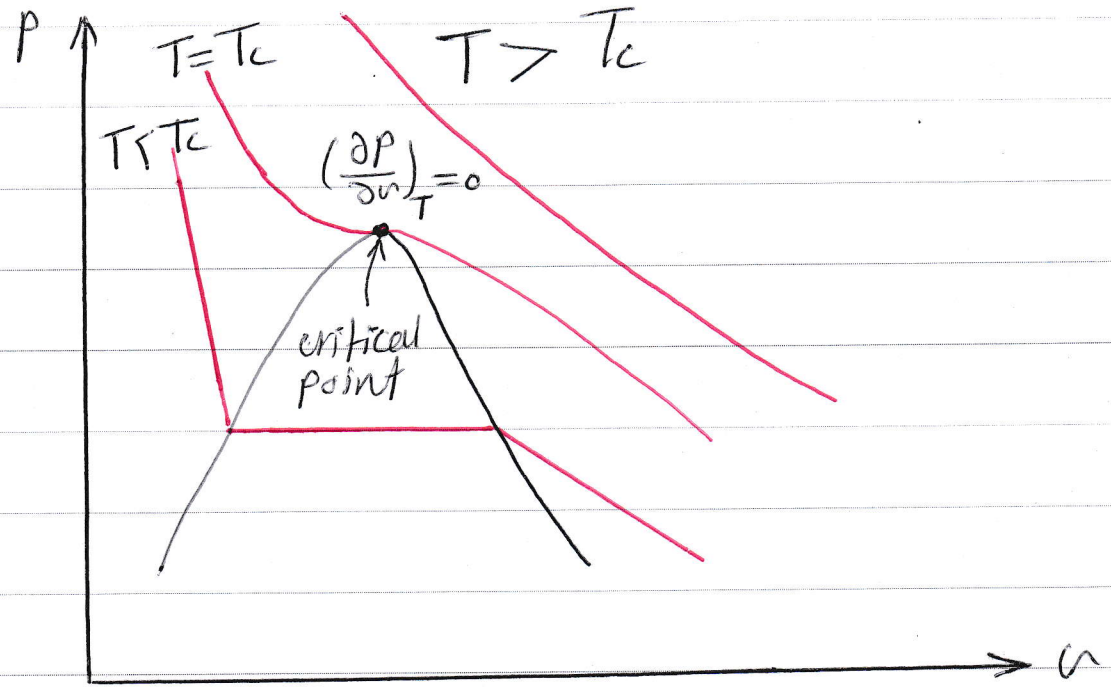


Figure (6)

Rearranging eq (12), gives

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad (15)$$

For the Van der Waals equation at the critical point

$$P_c = \frac{R T_c}{v_c - b} - \frac{a}{v_c^2} \qquad (16)$$

Applying Eqs (13) and (14) with the Van der Waals equation gives

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{R T_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0 \qquad (17)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2 R T_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0 \qquad (18)$$

Solving Eqs (16), (17) and (18) for a, b and v_c in terms of the critical pressure and critical temperature

$$a = \frac{27 R^2 T_c^2}{64 P_c} \qquad (19)$$

$$b = \frac{R T_c}{8 P_c} \qquad (20)$$

$$v_c = \frac{3RT_c}{8P_c} \qquad (21)$$

The constant a and b can be determined for any substance from the critical point data alone (Table A-1).

The accuracy of the Van der Waals equation of state is often inadequate, but it can be improved by using values of a and b that are based on the actual behavior of the gas over a wider range instead of a single point. Despite its limitations, the Van der Waals equation of state has a historical value in that it was one of the first attempts to model the behavior of real gases. The Van der Waals equation of state can be expressed on a unit-mole basis by replacing the v by $\bar{v}$ and the R by R_o.

Redlich-Kwong Equation of state:-

The Redlich-Kwong equation of state is given by

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{1/2}} \qquad (22)$$

This equation, proposed in 1949, is mainly emperical in nature. Although the Redlich-kwong equation is somewhat more difficult to manipulate mathematically than the Van der Waals equation, it is more accurate, particularly at higher pressures.

The constants a and b in Eq (22) can be evaluated using Eqs (13) and (14), as for Van der Waals equation. The result is

$$a = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} \qquad (23)$$

$$b = 0.08664 \frac{R T_c}{P_c} \qquad (24)$$

Note the constants a and b in the Redlich-kwong equation are different from those for the Van der Waals constants and cannot be interchanged.

Beattie-Bridgeman Equation of state:-

The Beattie-Bridgeman equation, proposed i 1928, is an equation of state based on five experimentally determined constants. It is expressed as