Nonideal gas:

We know that the PVT behavior of gases has been presumed to correspond to Boyle's Law, to provide a common basis for an absolute temperature scale, and to conform to Avogadro's hypothesis.

All this is summarized into the Ideal-gas equation

$PV = nRT$

Or

$PV = RT$

But, if the measurements are performed at medium or high pressure, this equation is not obeyed. The ideal laws are not followed.

Deviations are observed from ideal-gas laws. Thus, the gas is said to behave as a real, nonideal or imperfect gas.

As seen in the following figure, the product PV is nearly but not exactly constant.

Refer to Figure 1.8

The molar volume, V is calculated as 24.8 L for an ideal gas at pressure, P = 1 bar and temperature, T = 298 K.

But this not true for nonideal gas. The molar volume is different for a real gas.

Thus, we can use the molar volume for calculating the extent of deviation of nonideal gas from ideal gas a particular T and P.

The Compressibility Factor Z:

Compressibility factor is nothing but a factor, which measures the extent of deviation of nonideal gas from real gas at a particular T and P.

Let us say that V is a actual volume of 1 mol of gas and not a measured quantity from equation PV =RT.
Then,

For
Ideal gas: $PV/(RT) = 1$

Nonideal gas: $PV/(RT) \neq 1$

We call $Z = PV / (RT)$ as compressibility factor, which measures the extent to which the value of $PV / (RT)$ deviates from 1.

Thus, for

Ideal gas: $Z = 1$

While for

Nonideal gas: $Z \neq 1$

Virial Equations:

Now let us take a look at relation between Z and P
At Low or medium Pressure
A linear relation is observed between Z and P.
At high pressure,
A Z versus P deviates from linearity.

Refer to Figure 1.9

In order to accommodate this PVT behavior for nonideal gas, we write a equation based on experimental data.

$$Z = PV / (RT) = 1 + B_P P + C_P P^2 + \ldots\ldots\ldots\ldots\ldots \quad (14)$$

Where B_P is called second virial coefficient, C_P is called third virial coefficient, and so on.

This equation gives us mathematical expression, which expresses Z as a series of pressure terms and evaluating its coefficients of these terms so that equation fits the experimental results.

This is called as Virial Equation. The word viral comes from a Latin word force.

Thus the coefficients in the virial equation depend on the forces of interaction between the molecules of the gas.

The Boyle temperature:

At low temperature, initial slope of curve is negative.

While at high temperature, slope is positive.

These initial-slope values correspond to the B_P coefficients of virial equation.

Thus, at particular temperature, when an initial-slope (i.e. B_p) is equal to zero, the PV/(RT) is constant and is independent of pressure is known as Boyle Temperature.

Thus, at Boyle temperature

Z = PV (RT) = 1

Critical point:
A gas condenses to a liquid, if the pressure is high enough and the temperature I slow enough.

Refer to Figure 1.10

Critical point is the point at which gas-liquid equilibrium occurs.

Thus, the temperature above which the gas-liquid conversion cannot be made to occur is know as critical temperature.

The pressure at which the gas-liquid conversion occurs at critical temperature is known as critical pressure.

The molar volume at critical temperature and critical pressure is known as critical volume.

Critical Point Data for Methane:

Pc = 46.3 bar, Tc = 190.6 K, Vc =0.099 L mol^{-1}, Zc = 0.29.

PV isotherms:

PV isotherms display the conditions for which a gas, a liquid, or a mixture of the two exists for various temperatures.

At higher-temperature, a slight deviation is observed from hyperbolic curves expected for an ideal gas.

The low-temperature isotherms conform to the ideal-gas behavior only in the lower-pressure or higher-volume region.

At low temperature, if a pressure is applied on a sample of gas, volume decreases. If we further increase pressure, at some point there is a sudden decrease in the volume with no further increase in the pressure. This region is called as liquid-vapor region. After this region, even if we apply large pressure there is no further decrease in the volume.

Refer to Figure 1.11

The Critical Point and Reduced variable:

The extent to which the PVT behavior of gas is nonideal depends upon its P, T. We can use critical point (compressibility factor) data of gas as a reference. Since, the compressibility factor value is nearly same i.e. 0.3 for all gases at critical point.

Thus at critical point all gases are equally nonideal.

Thus, we introduce new variables, P_R, V_R, and T_R, called reduced variables that relate P, V and T in terms of critical constant P_C, V_C, and T_C.

Therefore,

$P_R = P / P_C$

$V_R = V / V_C$

$T_R = T / T_C$

Refer to Table 1.3