LECTURE 6

Ideal and Real Gases

Pure Substance: A pure substance is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase but chemical composition is the same in all phases.

Some times the mixture of gases, such as air is considered a pure substance as long as there is no change of phase. Further our emphasis will be on simple compressible substances

Early experiments on the **variables of state** (such as T, P, V, and n) showed that only two of these variables of state need to be known to know the state of a sample of matter.

- **Extensive variables**: depend on the amount of substance present. Examples include the volume, energy, enthalpy, and heat capacity.

- **Intensive variables**: do not depend on the amount of substance present. Examples include the temperature and pressure.

Equations of State

An equation of state is an equation which relates the variables of state (T, P, V, and n). It's particularly useful when you want to know the effect of a change in one of the variables of state

- **Solids and Liquids:** If the pressure on a solid or liquid is increased, the volume does not change much. If the temperature is increased, the volume doesn't change much either. Therefore, an appropriate equation of state describing such systems would be: V(T,P) = constant.
- **Gases:** In contrast, changing the pressure or temperature of a gas will have an easily observable effect on the volume of that gas. For an **ideal gas** (no intermolecular interactions and no molecular volume) n appropriate equation of state would be: V(T,P,n) = (nRT)/P.

- There are many equations of state describing **real gases**. These equations take in consideration molecular volume and interactions. The most well-known such equations is probably the Van der Waals equation.

Ideal and real gases

An ideal gas is one which follows the ideal gas equation of state, namely

$$PV = (m/M)\ (MR)\ T = n\ R_u\ T$$

The universal gas constant has a value of 8.314 J/mol K or kJ/kmol K and is related to the specific gas constant by the relation $R_u = (R/M)$

The ideal gas equation of state can be derived from the kinetic theory of gases where the following assumptions are made:

1. The molecules are independent of each other. In other words, there are no attractive forces between the molecules.
2. The molecules do not occupy any volume. That is the volume occupied by the molecules is quite negligible compared to the volume available for motion of the molecules.

The internal energy of an ideal gas is a function of temperature only and is independent of pressure and volume. That is,
$$u = u(T)$$
$$(\partial u/\partial P)_T = 0, \ (\partial u/\partial v)_T = 0$$

Enthalpy and specific heat

$$h = u + Pv$$
For an ideal gas $u = u(T)$ only and $PV = mRT$ and hence $h = h(T)$ only.

The specific heat at constant volume is defined as the amount of energy transferred as heat at constant volume, per unit mass of a system to raise its temperature by one degree. That is,

$$C_v = (dq/dT)_v$$

The specific heat at constant pressure is defined as the energy transferred as heat at constant pressure, per unit mass of a substance to raise its temperature by one degree. That is $C_p = (dq/dT)_P$

For a constant pressure process dq = du + dw = du + Pdv = du+ Pdv +vdP(since dP=0 for a constant pressure process)

Or dq= du+d(Pv) = d(U+ Pv) = dh

or dq=dh

$$C_P = (\partial h/\partial T)_P$$

The ratio of specific heat (γ) is given by

$$\gamma = C_P/C_v$$

For mono-atomic ideal gases $\gamma = 1.67$ and for diatomic gases $\gamma = 1.4$.

Relation between two specific heats:

The two specific heats are related to each other.
$$h = u + Pv \text{ or } dh = du + d(Pv)$$
For an ideal gas, the above equation reduces to
$$dh = du + d(RT) = du + RdT \text{ or}$$
$$dh/dT = du/dT + R \text{ or } C_P = C_v + R$$
$$\text{or } C_P - C_v = R \text{ for an ideal gas.}$$

$$\gamma = C_P / C_v \text{ or } C_P = R/(\gamma-1) \text{ and } C_v = R\gamma/(\gamma-1)$$

Real gases:

The ideal gas law is only an approximation to the actual behavior of gases.

At high densities, that is at high pressures and low temperatures, the behavior of actual or real gases deviate from that predicted by the ideal gas law. In general, at sufficiently low pressures or at low densities all gases behave like ideal gases.

Van der Waals Equation of State

An equation of state taking account the volume occupied by the molecules and the attractive forces between them.

$$(P+a/v^2)(v-b) = RT$$

where a and b are van der Waals constants.

The equation is cubic in volume and in general there will be three values of v for given values of T and P.

However in some range of values of P and T there is only one real value v.

For $T > T_c$ (critical temperature) there will be only one real value of v and for $T < T_c$ there will be three real values.

In Figure, the solid curve represents the value predicted by the van der Waals equation of state and the points represent the experimentally determined values.

It can be observed that at temperatures greater than critical, there is only one real value of volume for a given P and T.

However at temperatures less than the critical, there are three real values of volume for a given value of P and T.

The experimental values differ from those predicted by van der Waals equation of state in region 2345 if $T<T_c$.

One can use the criterion that the critical isotherm (isotherm passing through the critical point) shows a point of inflexion. Stated mathematically

$$(\partial P/\partial v)_{T=Tc}= 0 \text{ and } (\partial^2 P/\partial v^2)_{T=Tc} = 0$$

$$(\partial P/\partial v)_{T=Tc} = -RT_c/(v_c - b)^2 + 2a/v_c^3 = 0$$
or
$$RT_c/(v_c - b)^2 = 2a/v_c^3$$

$$(\partial^2 P/\partial v^2)_{T=Tc} = 2RT_c/(v_c\text{-}b)^3 \text{ -}6a/v_c^4 = 0$$

or

$$2RT_c/(v_c\text{-}b)^3 = 6a/v_c^4$$

Therefore

$$2/(v_c - b) = 3/v_c \text{ or } v_c = 3b$$

At the critical point, the van der Waal's equation is given by

$$P_c = RT_c/(v_c - b) - a/v_c^2$$

From these equations,

$$a = 27R^2Tc^2/64 \; P_c \text{ and } b = RT_c/8P_c$$

Compressibility Factor:

The deviation from ideal behavior of a gas is expressed in terms of the compressibility factor Z, which is defined as the ratio of the actual volume to the volume predicted by the ideal gas law.

Z = Actual volume/volume predicted by ideal gas law = v/RT/P = Pv/RT

For an ideal gas Pv = RT and hence Z = 1 at all temperatures and pressures.

The experimental P-v-T data is used to prepare the compressibility chart.

Reduced pressure, P_R = P/P_c,
Reduced temperature, T_R = T/T_c
Reduced volume, v_R = v/v_c

Where P_c, T_c and v_c denote the critical pressure, temperature and volume respectively.

These equations state that the reduced property for a given state is the value of this property in this state divided by the value of this same property by at the critical point.

The striking fact is that when such Z versus P_r diagrams are prepared for a number of different substances, all of them very nearly coincide, especially when the substances have simple, essentially spherical molecules.

We need to know only critical temperature and critical pressure to use this basic generalized chart.

In general it can be noted that idealized gas behavior for very low pressures as compared to critical) regardless of temperature. Furthermore, at high temperatures (greater than twice T_c), the ideal-gas model can be assumed to good accuracy to pressures as high as 4-5 times P_c.