

## Thermodynamic equation of state

### Classical ideal gas law

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The classical ideal gas may be written as:-

$$PV = nRT$$

In the form shown above the equation of state is thus

$$f(P, V, T) = PV - nRT = 0$$

If the calorically perfect gas approximation is used, then the ideal gas law may be expressed as follows:-

$$P = \rho(\gamma - 1)e$$

where  $\rho$  is the density,  $\gamma = C_p - C_v$  is the ratio of specific heats.

$e = C_v T$  is the inter energy per unit mass,  $C_v$  is the specific heat at constant volume and  $C_p$  is the specific heat at constant pressure.

### Van der Waals equation of state

The Van der Waals equation of state may be written as:-

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

Where  $V_m$  is the molar volume. The substance specific constants  $a$  and  $b$  can be calculated from the critical properties  $P_c$ ,  $T_c$  and  $V_c$  as

$$a = 3P_c V_c^2$$

$$b = \frac{V_c}{3}$$

Also written as  $a = \frac{27(RT_c)^2}{64P_c}$

$$b = \frac{RT_c}{8P_c}$$

Vander Waals equation of state was first to perform better than ideal gas law. In this equation  $a$  is called the attractions parameter and  $b$  repulsion parameter.

~~state~~ The Vander Waals equation may be considered as the ideal gas law "improve" due to two independent reasons

1) Molecules are thought as particles with volume, not material points.

Thus  $V_m$  cannot be less than some constant. So we get  $(V_m - b)$  instead of  $V_m$ .

2) While ideal gas molecule do not interact we consider molecules attracting others within a distance of several molecules radii. It makes no effect inside the material but surface molecules



are attracted into the material from the surface. We see this as diminishing of pressure on the outer shell which is used in the ideal gas. So we can write  $(P + \text{something})$  instead of  $P$ . To evaluate this something let us examine an additional force acting on an element of gas surface.

While the force acting on ~~each~~ each surface molecule is  $\sim f$ , the force acting on the whole element is  $\sim f \frac{1}{V_m^2}$  with the reduced state variables i.e.

$V_r = V_m/V_c$ ,  $P_r = P/P_c$  and  $T_r = T/T_c$ , the reduced form of the Van der Waals can be formulated as

$$\left( P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8T_r$$

The benefit of this form is that for given  $T_r$  and  $P_r$ , the reduced volume of the liquid and gas can be calculated directly using Cardano's method for the reduced cubic form:-

$$V_r^3 - \left( \frac{1}{3} + \frac{8T_r}{3P_r} \right) V_r^2 + \frac{3V_r}{P_r} - \frac{1}{P_r} = 0$$

for  $P_r < 1$  and  $T_r < 1$ , the system is in the state of vapour-liquid equilibrium. The reduced cubic equation of state yields in that solution the largest and the lowest solution are the gas and liquid reduced volume.

