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ME 209
Basic Thermodynamics
(van-der-Waals Equation)

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Properties-1

- We saw previously that simple substances are those which have one reversible work mode.
- According to the state principle such substances can have only two properties that can be defined independently.
- Equation of state is the relationship that connects a third property to the other two independent properties.
- The simplest is the one we saw and extensively used is the ideal gas law.
- Now we shall build on this and see how real substances can be modelled

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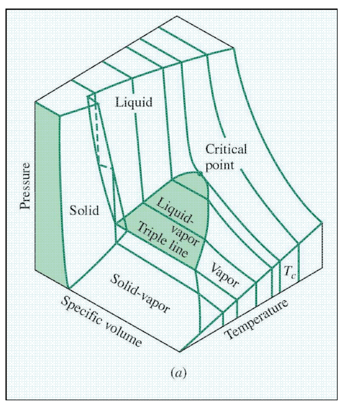
Properties-2

- The most commonly talked of intensive properties are p,v,T.
- Thus, f (p,v,T) = 0 is an equation of state
- Geometrically, this can be viewed as a three dimensional surface, which can be fairly complex, if all the solid liquid and gas transformations are represented
- A typical surface is as shown



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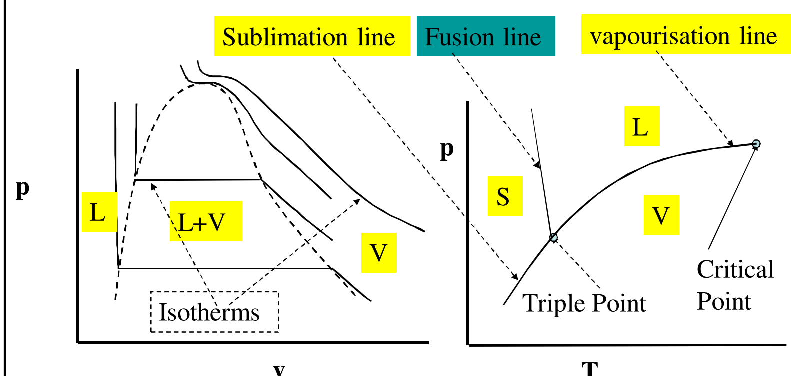
Properties-3

- The projection of this surface on two dimensional planes such as the ones shown below are familiar



Equation of State

- Remember p,v,T surface is just one such surface.
- We can generate many such surfaces like, s,v,T; h,s,T, etc.
- First we will address p,v,T surface now and then we shall look at more property relations later in the course.
- The foundation for ideal gas was laid by Robert Boyle in 1660, who showed that at lower pressures pV = constant for a gas at same temperature.
- The general interpretation is that as the volume is halved then the number density of molecules double and twice as many molecules bang the wall resulting in double pressure.

Ideal Gas Law

- Combining Boyle's law, Charles Law and Avogadro's hypothesis, the ideal gas equation was constructed

$p \;\alpha\; 1/V \qquad p \;\alpha\; T \qquad p \;\alpha\; n$

$$\Rightarrow p \;\alpha\; \frac{nT}{V} \qquad \Rightarrow pV = nR_uT$$

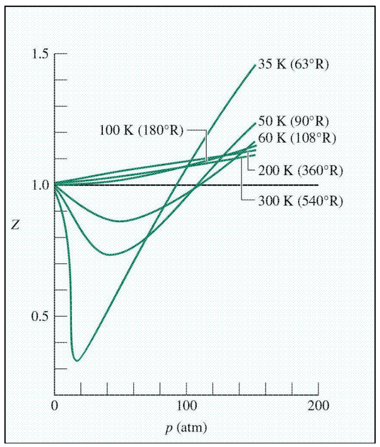
- This is a simpler form of what is called a generalised compressible gas law given by

$$pv = Z\left(\frac{R_u}{M}\right)T$$

Z is the generalised compressibility factor
Z = 1 for ideal gas

Compressibility Factor-I

- Standard texts give variation of Z for typical gases as a function of pressure at constant Ts as shown in the adjacent figure.
- It may be observed that as p tends to 0, Z tends to 1
- A curve such as the one shown motivates one to write



$$Z = 1 + c1(T)p + c2(T)p^2 + c3(T)p^3 + ...$$

Called Virial Expansion

Compressibility Factor-II

- Another type of expansion used is

$$Z = 1 + \frac{c1(T)}{v} + \frac{c2(T)}{v^2} + \frac{c3(T)}{v^3} + ...$$

Also called Virial Expansion

- In the above expansions, as p is small or when v is large, Z reduces to 1 leading to ideal gas.
- One of the first modification to ideal gas was proposed by van der Waals to explain the real gas behaviour. The equation is given by

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

'a' accounts for inter molecular attraction and 'b' the size of atoms

Van der Waals Equation-I

- Van der Waals equation can be rewritten as

$$p = -\frac{a}{v^2} + \frac{RT}{(v-b)} \qquad \Rightarrow pv = RT\left(1-\frac{b}{v}\right)^{-1} - \frac{a}{v}$$

- Using binomial theorem, we can expand and write

$$pv = RT + \frac{RTb - a}{v} + RT\left(\frac{b}{v}\right)^2 + RT\left(\frac{b}{v}\right)^3 + ...$$

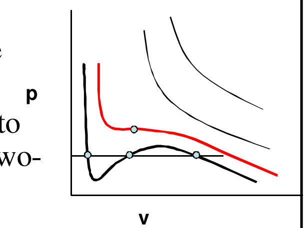
- The above can be assumed to be a kind of virial expansion expression
- Another way of looking at Van der Waals equation is

$$pv^3 - (pb + RT)v^2 + av - ab = 0$$

Cubic equation

Van der Waals Equation-II

- We had already noted that Van der Waals equation reduces to ideal gas equation at large v's
- Because of cubic nature, it has 3 roots for v for a given p below a critical pressure
- As v tends to b, the pressure goes very large, thereby mimicking the liquid behaviour
- However, this equation also fails to predict the real behaviour in the two-phase dome
- This may be easily visualized by plotting the behaviour



Van der Waals Equation-III

- It may be noted that there is a point of inflexion at the critical point. Thus

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

$$\left.\frac{\partial p}{\partial v}\right|_T = \left.\frac{\partial^2 p}{\partial v^2}\right|_T = 0$$

At critical point

$$\Rightarrow \left.\frac{\partial p}{\partial v}\right|_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \qquad \Rightarrow \left.\frac{\partial^2 p}{\partial v^2}\right|_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

- Using $T = T_c$, $p = p_c$ and $v = v_c$, we can solve for p_c, v_c and T_c in terms of a and b using the above three relations to give

$$p_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad T_c \frac{8a}{27Rb}$$

Van der Waals Equation-IV

- If we have measured values of p_c, v_c and T_c, we have three equations to determine 2 constants a and b
- The expression for b from second equation and from solving first and third equations are

$$b = \frac{v_c}{3} \text{ and } b = \frac{RT_c}{8p_c}$$

- The values of b from the above two equations do not agree
- Elimination of b from the above two equations give the value of $Z_c = 3/8$ or 0.375

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Van der Waals Equation-V

- However, the values of Z_c are reasonably fair and deviates further for heavier gases

Element	Z_c
He	0.327
H_2	0.306
O_2	0.292
CO_2	0.277
H_2O	0.233

- We can generalize the properties by introducing reduced coordinates defined by

$$p_r = \frac{p}{p_c}, \; v_r = \frac{v}{v_c} \; and \; T_r = \frac{T}{T_c}$$

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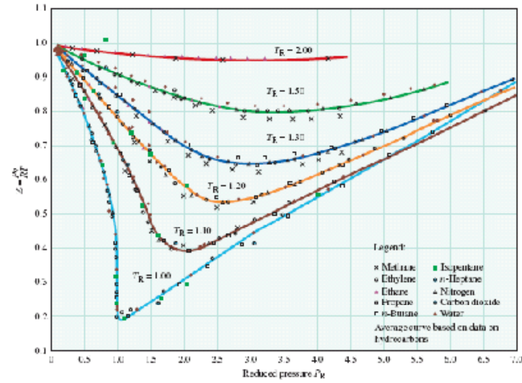
Principle of Corresponding States-I

- If we plot the compressibility factor in reduced coordinates with p_r as variable and T_r as a parameter, we get



There appears to be universal agreement

Refer any standard Text

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Principle of Corresponding States-II

- Such plots to compute enthalpy and entropy are also available in standard texts (Van Wylen and Sonntag)
- Vander der Waals equation can also be reduced to and will be done as home work

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

- There are more accurate empirical equations of state such as Redlich-Kwong, Peng-Robinson, Lee-Kessler equations that have more parameters and predict better. You can refer to standard texts