Answer to Question #50797, Chemistry, Physical Chemistry

Derive the equation of corresponding states

Solution:

$$P_r = \frac{P}{P_c}$$
$$V_r = \frac{V}{V_c}$$
$$T_r = \frac{T}{T_c}$$

Van der Waals proposed in 1873 a correction for the ideal gas model based on two simple ideas. First, van der Waals realized that attractive forces among particles, known as van der Waals forces, would reduce the gas pressure compared to the ideal gas model:

$$P_{actual} = P_{ideal} - \frac{a}{v^2}$$

On the other hand, if particle size is finite, the volume available for particle motion reduces, thus for clustered particles we have:

$$P = \frac{R \times T}{v - b} - \frac{a}{v^2}$$

that is the van der Waals equation of state. The constants can be evaluated from suitable PVT data, and are constants for each substance.

If no data is available but the most rudimentary, as the pressure, temperature and volume at the critical point, then we can use the criteria described earlier to find the constants:

$$\frac{dp}{dv} = -\frac{R \times T_c}{(v_c - b)^2} - \frac{2a}{v_c^3} = 0$$
$$\frac{d^2p}{dv^2} = \frac{2R \times T_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0$$

which gives two equations to calculate the two parameters a and b:

$$a = \frac{9RT_c v_c}{8}$$
$$b = \frac{v_c}{3}$$

Using a and b at the critical state, we can calculate the critical pressure:

$$P_c = \frac{3RT_c}{8v_c}$$

Notice that any two of P_c, T_c and v_c can be used to calculate the parameters a and b, and the third variable of the critical state is predicted.

The two-parameter EOS's previously described can be written in the form:

$$Z = Z(T_r, P_r)$$

The prediction of this unique relationship between Z and the reduced pressure and temperature is known as the van der Waals corresponding states principle. It states that any gas at the same reduced temperature and pressure should have the same compressibility factor.

$$Z = \frac{P_r \times v_r}{T_r} \times \frac{P_c \times v_c}{R \times T_c} = \frac{P_r \times v_r}{T_r} \times Z_c$$

which implies that the reduced specific volume will not correlate well since the above described EOS's cannot predict accurately Z_c. The quantity $v_r Z_c$ will however correlate well.