Densities of liquids and Solids

The following equations can be used to find densities of liquids mixtures and a solution of solids in a liquid.

$$\bar{\rho} = \frac{1}{\sum_{1}^{n} \frac{x_i}{\rho_i}}$$

Where $\bar{\rho}$ is density of mixture containing n species, x_i is mass fraction of species i and ρ_i is density of species i.

The other way of finding density is $\bar{\rho} = \sum_{i}^{n} x_i \rho_i$

Gases

Gases that obey the equation $PV = nRT$ are called ideal gases. The equation relating pressure, volume and temperature is called an equation of state. Note that for flow problems, the volume term in the equation is volumetric flow rate.

The ideal gas equation could also be written as $P\hat{V} = RT$ where $\hat{V} = V/n$ is specific molar volume of the gas.

For ideal gas mixtures, the mole fraction of a gas in the mixture equals its volume fraction (can you derive it? Try)

Ideal gas equation breaks down at low temperatures and high pressures when the volume occupied by the gas molecules becomes significant and there are attractive forces between the molecules. Gases that do not obey ideal gas equation are called non ideal gases

Several equations of state are available for non ideal gases. We are not concerned with the derivation of equations; we will learn only how to use them.

The non ideality of a gas depends on how close the gas is to its critical temperature, T_c and critical pressure, P_c. T_c is the highest temperature at which a species can exist in two phases (liquid and vapour). P_c is the pressure corresponding to T_c.

Virial equation of state

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \ldots$$

This equation has a basis in statistical mechanics, which is outside the scope of the course to discuss.

B, C, D are functions of temperature and are called second, third and fourth Virial coefficients.

The following procedure should be used to find $\hat{V}$ or P for a given T.

First calculate reduced temperature, $T_r = \frac{T}{T_c}$. Then, estimate the value of B from the following equations

$$B_o = 0.083 - \frac{0.422}{T_r^{1.6}}; \quad B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}; \quad B = \frac{RT_c}{P_c}\left(B_o + wB_1\right)$$

w is acentric factor, which can be found from the following Table.

Compound	**Acentric factor**
Ammonia	0.25
Argon	-0.004
Carbon dioxide	0.225
Carbon monoxide	0.049
Chlorine	0.073
Ethane	0.098
Hydrogen sulphide	0.100
Methane	0.008
Methanol	0.559
Hydrogen	0.040
Oxygen	0.021
Propane	0.152
Sulphur dioxide	0.251
Water	0.344

Substitute the value of B in Virial equation of state to determine the unknown quantity. Note that we have made $C = D = 0$.

Cubic equations of state

A popular is van der Waals equation: $P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2}$

Where $a = \frac{27R^2T_c^2}{64P_c^2}$ and $b = \frac{RT_c}{P_c}$

Other important equation of state is Soave-Redlich-Kwong (SRK) according to which

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}\left(\hat{V} + b\right)}$$

The following correlations are used to estimate the three parameters, a, b and α

$$a = 0.42747\frac{R^2T_c^2}{P_c}$$

$$b = 0.08664\frac{RT_c}{P_c}$$

$$m = 0.48508 + 1.55171w - 0.1561w^2$$

$$T_r = \frac{T}{T_c}$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$$

Equations of state need parameters to be estimated. These equations are valid only in the range where predictions match experimental values. Outside the range, the predictions are questionable. *Use them with caution.*

Compressibility factor

Another equation of state for non-ideal gases is obtained from a compressibility factor, z, defined as

$$z = \frac{P\hat{V}}{RT}$$

It could be written as $PV = znRT$

The value of z is obtained from generalized compressibility charts. To use the charts, first find the value of P_r and then draw a straight line from P_r to curve corresponding to T_r. Intersection of horizontal line drawn parallel to x-axis with y-axis provides the value for z.

If the gas in question is either hydrogen or helium, do the following corrections for critical values and then calculate T_r and P_r.

$$T_c^a = T_c + 8K$$

$$P_c^a = P_c + 8atm$$

A PHOTOCOPY OF COMPRESSIBILITY CHARTS IS KEPT IN HOSTEL 10 PHOTOCOPY SHOP.

Non-ideal gas mixtures

Kay's rule applies for non-ideal gas mixtures. If the mixture contains n species with a mole fractions, y_A, y_B, y_C and so on.

Calculate the following:

Pseudo critical temperature: $T_c^{'} = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + ...$

Pseudo critical pressure: $P_c^{'} = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + ...$

Now, calculate reduced temperature and reduced pressure and look up for compressibility factor, z.

Standard Temperature and Pressure

Sometimes, the volumetric flow rate of a gas is reported as so many SCMH (standard cubic meters per hour) or so many SCFH (standard cubic feet per hour). This means that if the temperature and pressure of the gas were changed to standard temperature, 0^oC, and standard pressure, 1 atm, the flow rate would be so many SCMH or SCFH. The actual flow rate would be different from SCMH or SCFH. To determine actual flow rate, use

$$\frac{P_s V_s}{T_s} = \frac{PV}{T}$$

s stands for standard conditions. You could use the fact that one g-mole of a gas occupies 22.4 liters or one lb-mole occupies 359 ft^3 at standard conditions of temperature and pressure to convert SCMH or SCFH to g-moles or lb-moles.

Test Your Understanding

1. One of your friends says that carbon dioxide at 273 K and 20 bar pressure behaves as an ideal gas and another disagrees. What do you think? Justify your position.
2. Explain in your own words the meaning of flow rate of CO is 150 SCMH at 200^oC and 2 atm. What is the molar flow rate of the gas in g-mol/h?
3. 50 moles of nitrogen are contained in a 10-liter vessel at -25^oC. What is the pressure in the vessel? Use compressibility charts.
4. For the above problem, report percentage error if ideal gas equation is used.
5. For the above problem, use SRK and Virial equations of states.