UNIT 5

EQUATIONS OF STATE

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معادلات الحالة

- Aggregate state of matter may be found, in one of the following forms:

gaseous, liquid or solid states.

- The gaseous state is simpler than either solid or liquid states and gives a convenient introduction to the study of the matter.

Gases is differing from liquids and solids in several aspects:

☐ A gas expands to fill its container. Volumes of solid and liquid are not determined by the container.

☐ When pressure is applied to a gas, its volume readily contracts. Liquids and solids are not very compressible.

☐ Two or more gases form homogeneous mixtures in all proportions. Liquids often do not form homogeneous mixtures.

☐ The characteristic properties of gases arise because the individual molecules of a gas are relatively far apart.

In a liquid, the individual molecules are close together and are constantly in contact with neighbors and perform attractive forces for one another keeping them together.

When a pair of molecules come close together, repulsive forces prevent any closer approach.

- ☐ Gas molecules are in constant motion, and they frequently collide and they remain fairly far apart.

Each molecule tends to behave as though the others weren't there.

- ☐ Therefore, the gaseous state is simpler than either solid or liquid states and gives a convenient introduction to the study of the matter. Gases, differing from liquid and solids, occupy volumes that affected to a very great extent by changes in temperature and pressure.

- The quantitative functional relations between the properties of a system (phase) can be described by various kinds of equations.
- Among such equations the equation of state of a phase. This equation relates, in general form, the pressure, temperature, density (or volume), composition and other properties of each phase of a system in equilibrium, which may be written as:

$$V = f(T,P,n) \qquad (1.1)$$

1.1 The State Equation of Ideal Gas

The concept of an ideal gas has been explained through the assumptions of the kinetic theory of gases to include:

1. A gas consists of a very large number of molecules which are in a state of continual random motion.
2. A molecule has a negligible size.
3. The pressure of a gas is a consequence of the force on a measuring object, such as the container, of molecular collisions.

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4. Collisions between molecules or between a molecule and an inert surface are perfectly elastic, with no change in the total kinetic energy of the gas molecules.
5. No forces are exerted between molecules except through collisions. Therefore between collisions, a molecule travels in a straight line at a constant speed.
6. The average kinetic energy per gas molecule independent of the nature of the gas and is directly proportional to the absolute temperature.

Based on the above assumptions, the simplest equation of state for an ideal gas have been predicted, taking the following form:

$$PV = nRT \qquad (1.2)$$

in which:

P: is the pressure of the gas.
V: its volume.
T: its absolute temperature.
n: number of moles.

where:

n=m/M (mass of gas/its molecular mass)

R: is called the universal gas constant.

The universal gas constant has different values according to the units of the other parameters. Its different values may be found as follows:

Referring to Avogadro's Law, which states that:-

The volume occupied by one mole of any gas at standard temperature and pressure ,(S.T.P), equals to 22.41 L

$$R = PV / nT$$

R= 0.08208 (atm. lit)/(K. mole)

R= 8.314 joule / K mole

R= 1.98 calorie/ K mole

Example (1.1)

A 0.02 m^3 vessel contains 35 gm of nitrogen gas at a pressure of 1140 mm. Hg. What is the temperature of the gas?.

Solution:

Applying the ideal gas equation (1.2)

$$PV = nRT$$

Where:

$P = (1140) / (760) = 1.5$ atm

$V = (0.02)(1000) = 20$ liters

$n = m/M_w = 35/28 = 1.25$ moles

$R = 0.08208$ atm. lit / K mole

$\therefore T = (1.5)(20) / (1.25)(0.08208) =$ 292.4 K = 19.4 °C

Example (1.2)

Calculate the density of CO_2 gas at a pressure of 760 mm.Hg and at a temperature of 27 °C.

Solution:

$PV = nRT$, putting $n = m / M_w$

$$\rho = PM_w/RT \quad .... \quad (1.3)$$

$P = 760 / 760 = 1$ atm.

$M_{CO_2} = 44$ gm/mole

$T = 27 + 273 = 300$ K

$R = 0.08208$ atm.lit / K mole

$\rho = (1)(44) / (300)(0.08208)$

$= 1.7869$ gm/ lit.

1.2 State Equation of Ideal Gas for Gas Mixture:

The partial pressure of any component in a gas mixture, is the pressure that the component would exert if it was alone occupying the entire volume of the gas mixture at the same temperature.

Dalton's law of partial pressures relates the total pressure exerted by a gas mixture with the partial pressures of the individual components.

$$P_T = \sum_{i=1}^{N} P_i \text{..........} (1 - 4)$$

The pure component volume of a component gas in a mixture of gases is defined as the volume which would be occupied by that component gas if it was present, alone, at the same temperature and pressure as the original mixture.

Amagates Law relates the total volume of the mixture or gases to the partial volume of each component.

$$V_T = \sum_{i=1}^{N} V_i \text{..........} (1 - 5)$$

The ideal gas equation can be applied to each component individually as follows:

For the first component $P_1V=n_1RT$

For the second component $P_2V=n_2RT$

For the third component $P_3V=n_3RT$

and so on ....

For N component $P_NV=n_NRT$

$$(P_1+P_2+P_3+..+P_N)V=(n_1+n_2+n_3+..+n_N)RT$$

or $P_T\,V = n_T\,R\,T$

We divide its specific ideal gas equation by the ideal gas equation of the whole mixture:

$$p_i/P_T=n_i/n_T=y_i$$

Example (1.3)

Calculate the partial pressure of oxygen, O_2, in a sample of air whose composition as weight percentage is given as: CO_2=0.04% , O_2=22.83, N_2=75.33% and H_2O=1.8%. If the pressure of air is given as 760 mm Hg.

Solution

Consider that we have 100 gm of air, then:

$n_{CO_2}=m_{CO_2}/M_{CO_2}$=0.04/44=0.00091 mole

Similarly; n_{O_2}= 0.71344 mole

n_{N_2}=2.69036 mole

n_{H_2O}= 0.1 mole

n_T = 3.50571 mole

$y_{O_2}=n_{O_2}/n_T$=0.71344/3.50471= 0.203

$P_{O_2}=P_Ty_{O_2}$= 154.71 mm.Hg

Example (1.4)

The flow rate of air from a commercial blower is to be determined.

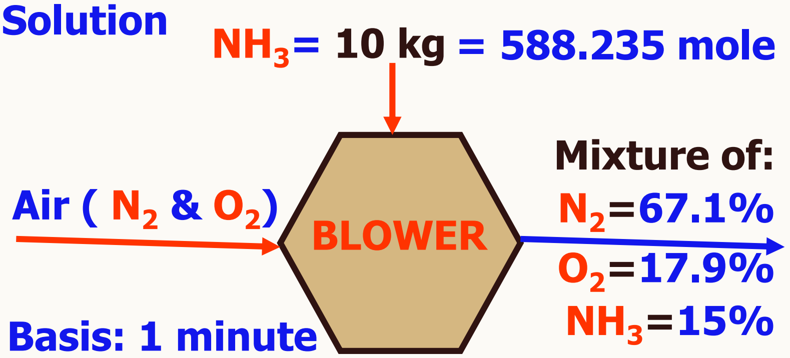
The blower delivers dry air at 50 °C and 750 mm Hg.

10 kg of ammonia per minute is added to the air, and a sample of the gaseous mixture indicates 67.1% N_2 , 17.9% O_2 , and 15% NH_3 by volume.

Calculate the rate of air delivery by the blower in cubic meters per minute.

(Dry air can be considered as 21% O_2 and 79% N_2 by volume).

Solution



NH_3= 10 kg = 588.235 mole

Air (N_2 & O_2)

BLOWER

Mixture of:
N_2=67.1%
O_2=17.9%
NH_3=15%

Basis: 1 minute

Number of gm moles of ammonia entering the mixture=10000/17=588.235 mole.

Let x to be the total mole of O_2 , N_2 and NH_3 in the mixture; then by material balance on NH_3:

$0.15\,x = 588.235 \Rightarrow x = 3921.5$ mole

n_{air}=3921.5-588.5=3333.332 mole.

$P\,V=n\,R\,T \Rightarrow V_{air}$ =89551.259 L/min

Example (1.5)

N_2O_4 partially dissociated according to the following equation: $N_2O_4 \Leftrightarrow 2\,NO_2$

If it is found that 24 gm of a gaseous mixture containing N_2O_4 and NO_2 occupies a volume of 15000 cm^3 at 363 K and 97.3 KPa pressure. Calculate the percentage dissociation of N_2O_4 to NO_2.

Solution

Basis: 1 mole of N_2O_4 in the original mixture before dissociation.

Let x be the fraction dissociated of N_2O_4

$\therefore$ Moles of N_2O_4 remaining $= 1 - x$

$\therefore$ Moles of NO_2 formed $= 2x$

$\therefore$ Total moles $= (1-x) + 2x = 1 + x$

$y_{N2O4} = (1-x) / (1+x)$

Now we have 24 gm of the mixture at a pressure of 97.3 KPa = 97300/101325 = 0.9603 atm. and occupies a volume of 15 liters at a temperature of 363 K.

From $PV = nRT \Rightarrow n = 0.48345$ moles.

$\therefore$ Average molecular weight of the gas mixture $M_{av} = m/n = 49.6432$ gm/mole

But $M_{av} = y_1 M_1 + y_2 M_2$

$\therefore 92\,y_1 + 46\,y_2 = 49.6432$ and

$y_1 + y_2 = 1$

Solving the last two equations

$y_1 = y_{N2O4} = 0.0792 = (1-x)/1+x)$

$x = 0.8532 \Rightarrow$ % dissociation of $N_2O_4 = 85.32\%$

1.3 The State Equation of Real Gas

The fact that all gases can be liquefied if they are compressed and cooled sufficiently is an indication that all gases become non ideal at high pressures and low temperatures.

For one mole of gas, n=1; the quantity (PV/RT) should therefore equal 1 if the gas is ideal.

Figure (1.1) shows the quantity (PV/RT) plotted as a function of pressure for a few gaseous substances compared with the expected behavior of an ideal gas.

Equations of State for Gases

- **Ideal gas** $$\frac{PV_M}{RT} = 1$$
- **Real gas** $$\frac{PV_M}{RT} = Z$$

Z is the ratio of the "real molar volume" over the "ideal molar volume" of a substance measured at the same pressure and temperature.

$$\left(\frac{PV_M}{RT}\right)\left(\frac{RT}{PV_M{}^{id}}\right) = \frac{Z}{1} = Z$$

However, the pressures shown are very high; at more ordinary pressures, below 10 atm, the deviations from ideal behavior are not so large, and the ideal-gas equation can be used without serious error.

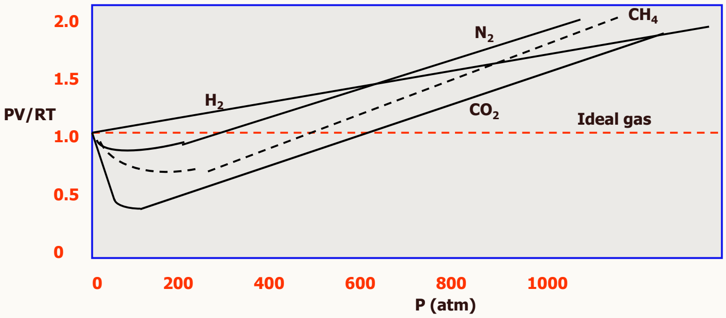


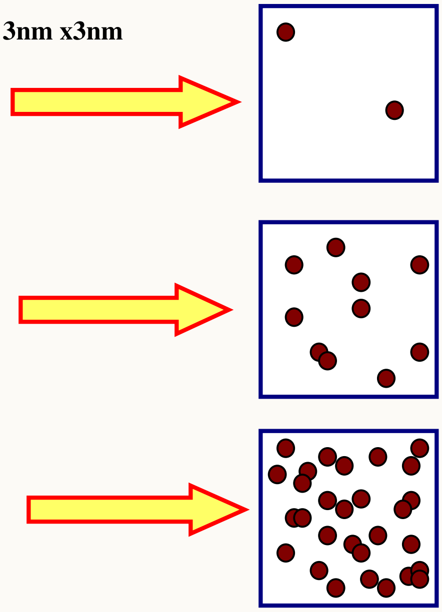
Fig. (1.1): PV/RT behavior as function of pressure for N_2, CH_4, H_2 and CO_2 compared with that for ideal gas behavior.

Real Gases

- **Real molecules** **do take up space** and **do interact** with each other (especially polar molecules).
- Need to **add correction factors** to the ideal gas law to account for these.

Ideally, the VOLUME of the molecules was neglected:

Ar gas, ~to scale, in a box 3nm x 3nm x3nm



at **1** Atmosphere Pressure

at **10** Atmospheres Pressure

at **30** Atmospheres Pressure

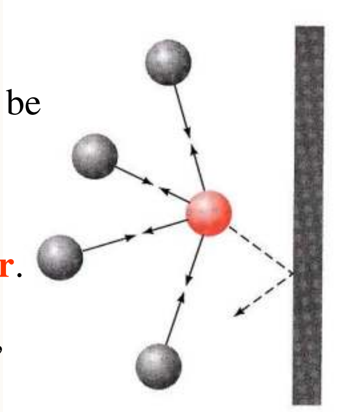
But since real gases <u>do have volume</u>, we need:

Volume Correction

- The **actual volume** free to move in is **less** because of particle size.
- **More molecules** will have **more effect**.
- Corrected volume **$V' = V - nb$**
- "**b**" is a constant that **differs for each gas**.

Pressure Correction

- Because the **molecules are attracted** to each other, the **pressure** on the container will be **less than ideal**.
- Pressure **depends on** the **number of molecules per liter**.
- Since **two molecules interact**, the **effect must be squared**.



$$\boxed{P_{\text{observed}} = P - a\left(\frac{n}{V}\right)^2}$$

Van der Waal's equation

$$[P_{\text{obs}} + a\left(\frac{n}{V}\right)^2]\,(V - nb) = nRT$$

Corrected Pressure **Corrected Volume**

- "**a**" and "**b**" are **determined by experiment**
- "**a**" and "**b**" are **different for each gas**
- **bigger molecules** have **larger "b"**
- "**a**" depends on both **size and polarity**

Johannes Diderik van der Waals
Mathematician & Physicist
Leyden, The Netherlands
November 23, 1837 – March 8, 1923

Van der Waal's equation

$$p_{obs} + a\,(\frac{n}{V})^2\,]\,(V - nb) = nRT$$

$$p = \frac{nRT}{V - nb} - a(\tfrac{n}{V})^2$$

$$p = \frac{RT}{V_m - nb} - \frac{a}{{V_m}^2}$$

$$V_m = V / n$$

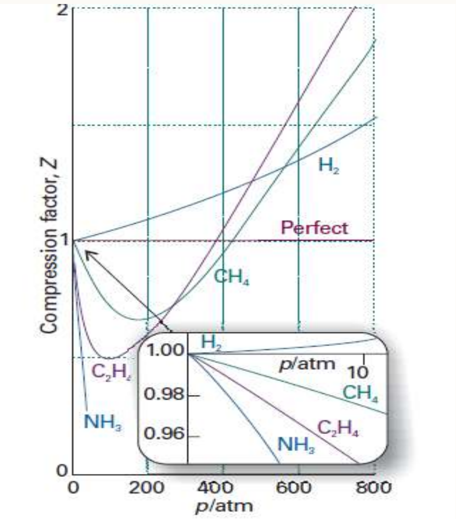


Fig. 1.14 The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \to 0$, they do so with different slopes.

Compressibility Factor

The most useful way of displaying this new law for real molecules is to plot the compressibility factor, **Z** :

For **n = 1**

$$Z = PV / RT$$

Ideal Gases have **Z = 1**

Figure (1.4) shows the (PV/RT) behavior for CH_4 as a function of temperature.

It is obviated that positive departure at high pressures is larger when the gas is at lower temperature.

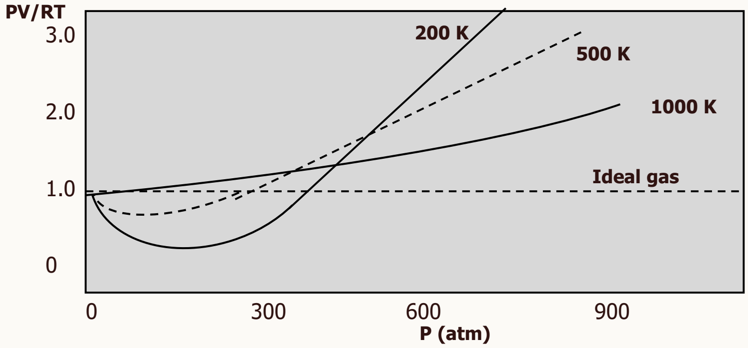


Fig. (1.4): PV/RT behavior for CH_4 as function of temperature. behavior.

1.4 The Reduced Form of Equations of State

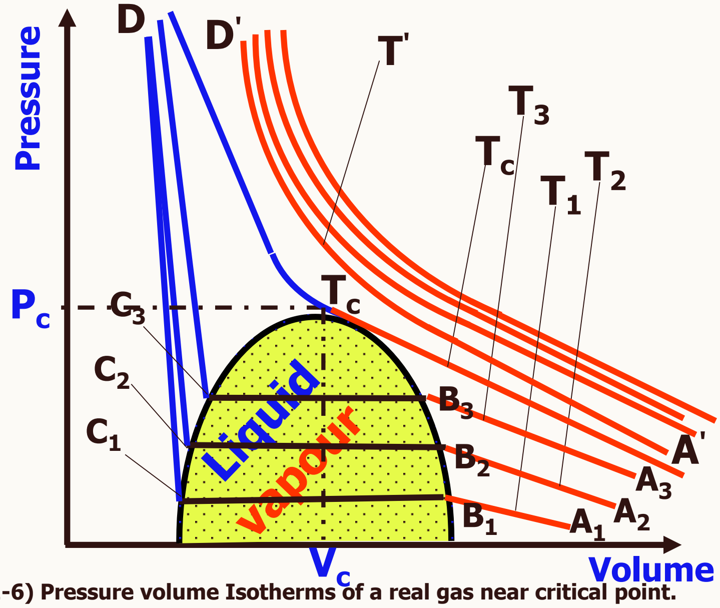


Fig. (1-6) Pressure volume Isotherms of a real gas near critical point.

Above critical temperature on the isotherm, such as curve 1', in Fig. (1.6), compression changes the system from a low density state (point A') to the high-density state (point D') without phase transition.

The critical data, (P_c, V_c and T_c), for a gas are used to obtain the reduced parameters which are included in the reduced equation of state as will be presented in the following discussion:

☐ The constants (a & b) of the van der Waals equation are related to the critical values of the volume, pressure and temperature.
In order to establish this relationship, let us rewrite Eqn. (1.7) in the form of a cubic equation :

$$V^3-(b+RT/P)V^2+(a/P)V-(ab/P)=0$$

or in the binomial form:

$$(V-V_1)(V-V_2)(V-V_3)=0$$

Where V_1, V_2 and V_3 are the three roots of the cubic Eqn. (1.9).

At the critical point $V_1 = V_2 = V_3 = V_c$

$$\therefore (V-V_c)^3=0 \Rightarrow V^3-3(V_c)V^2+3(V_c)^2V-(V_c)^3=0$$

Substituting the critical values P_c and T_c, into Eqn. (1.9) instead of P and T, it becomes:

$$V^3-(b+RT_c/P_c)V^2+(a/P_c)V-(ab/P_c)=0$$

$$V^3-(b+RT/P)V^2+(a/P)V-(ab/P)=0$$

Now, comparing the coefficients of the last two equations

$3V_c=b+RT_c/P_c$, $3(V_c)^2=a/P$, $(V_c)^3=ab/P_c$

$a=3P_c(V_c)^2$, $b=(1/3)V_c$, $R=(8/3)P_cV_c/T_c$

Substituting with the values of both a, b and R ⇒ $[P+(3P_cV_c^2/V^2)](V-V_c/3) =(8/3)(P_cV_c/T_c)]T$,

dividing both sides of this equation by (P_cV_c) and multiplying by3

$$[(P/P_c)+3(V_c/V)^2][3(V/Vc)-1]=8(T/Tc)$$

$$(P_r+3/V_r^2)(3V_r-1)=8T_r$$

which called reduced form

Example (1.7)

Calculate the molar volume of oxygen, O_2, at a temperature of 27°C and pressure of 15 atm.

Solution

(a) Assuming ideal behavior: $PV=nRT$

$V =$ (1) (0.08206) (300) / (15) = 1.6416 liter.

(b) Assuming real behavior and van der Waals equation applies: $(P+a/V^2)(V-b)=RT$

Put van der Waals equation in the following iterative form: $V=[RT/(P+a/V^2)]+b$

from Appendix (12), for oxygen gas, $a=1.36$ atm.lit²/mole² and $b = 0.0318$ lit./mole.

Using the volume found via the ideal gas equation V_o =1.6416 L

$V_1=[(0.08206)(300)]/[(15)+(1.36)/(1.6416)^2]+0.03183$ =1.6200 L

$V_2=[(0.08206)(300)]/[(15)+(1.36)/(1.62)^2]+0.03183$ =1.6186 L

V_3 = 1.61851L and V_4 = 1.61851L

(c) Using the generalized compressibility factor, (Z):

Using Appendix (3), P_c = 49.7 atm. , T_c= -118.8 C

$P_r=P/P_c$ =0 .3018 , $T_r=T/T_c$= 1.9455, and using appendix (5)

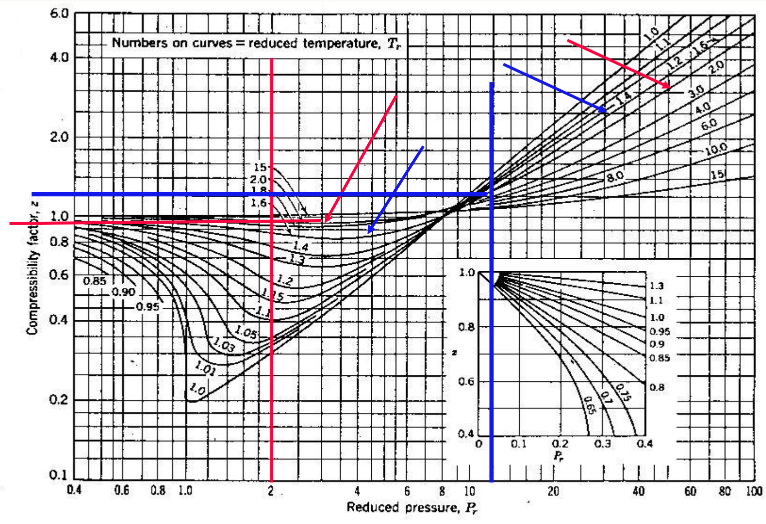
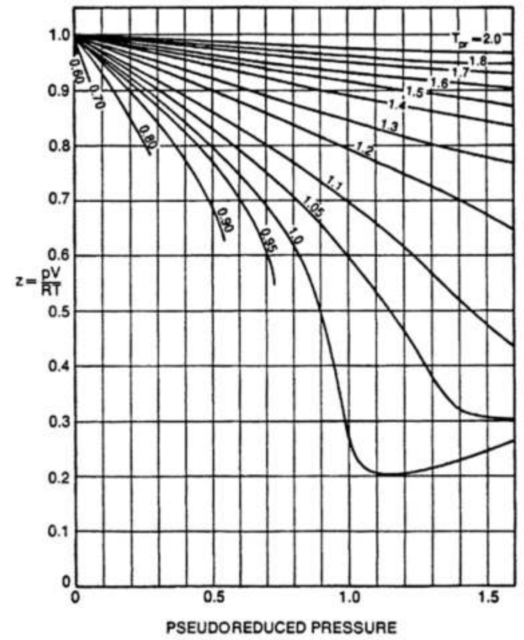
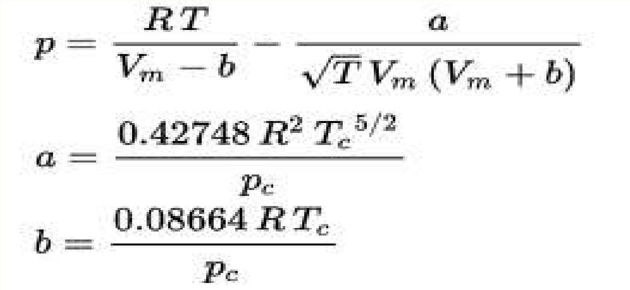


FIG. 2. The compressibility chart.

Z= 0.98 and substituting in PV=ZnRT⇒ V=1.61 L



Redlich-Kwong equation of state

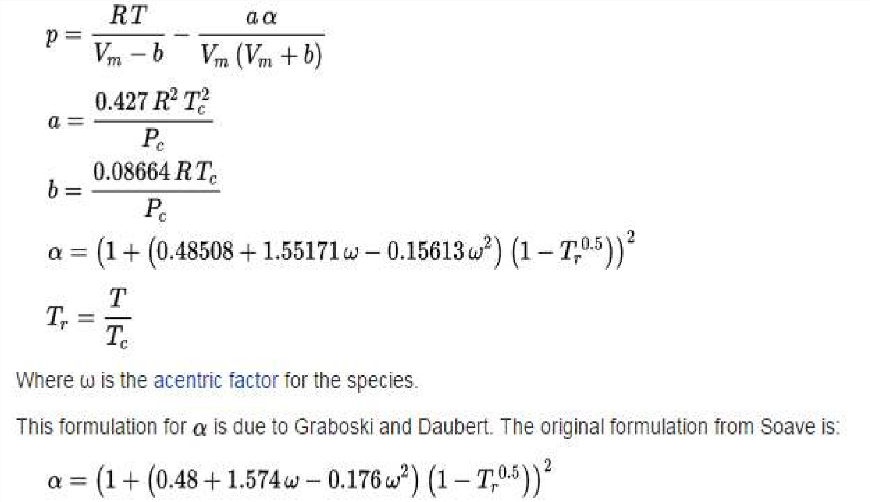


$$p = \frac{R\,T}{V_m - b} - \frac{a}{\sqrt{T}\,V_m\,(V_m + b)}$$

$$a = \frac{0.42748\,R^2\,{T_c}^{5/2}}{p_c}$$

$$b = \frac{0.08664\,R\,T_c}{p_c}$$

Soave modification of Redlich-Kwong



$$p = \frac{R\,T}{V_m - b} - \frac{a\,\alpha}{V_m\,(V_m + b)}$$

$$a = \frac{0.427\,R^2\,T_c^2}{P_c}$$

$$b = \frac{0.08664\,R\,T_c}{P_c}$$

$$\alpha = \left(1 + \left(0.48508 + 1.55171\,\omega - 0.15613\,\omega^2\right)\left(1 - T_r^{\,0.5}\right)\right)^2$$

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

Where ω is the acentric factor for the species.

This formulation for α is due to Graboski and Daubert. The original formulation from Soave is:

$$\alpha = \left(1 + \left(0.48 + 1.574\,\omega - 0.176\,\omega^2\right)\left(1 - T_r^{\,0.5}\right)\right)^2$$

Peng–Robinson equation of state

$$p = \frac{R\,T}{V_m - b} - \frac{a\,\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45724\,R^2\,T_c^2}{p_c}$$

$$b = \frac{0.07780\,R\,T_c}{p_c}$$

$$\alpha = \left(1 + \kappa\left(1 - T_r^{\,0.5}\right)\right)^2$$

$$\kappa = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$$

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