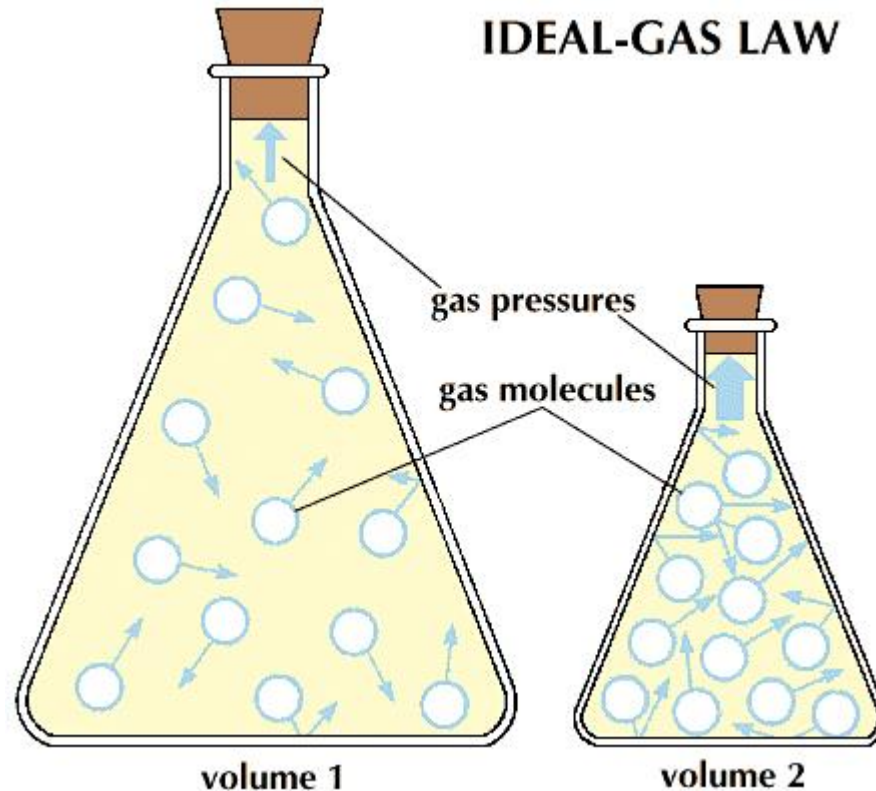


P-V-T properties of gases



<http://eps.mcgill.ca/~courses/c220/>



Robert Boyle, 1627-1691



Edme Mariotte, 1620-1684

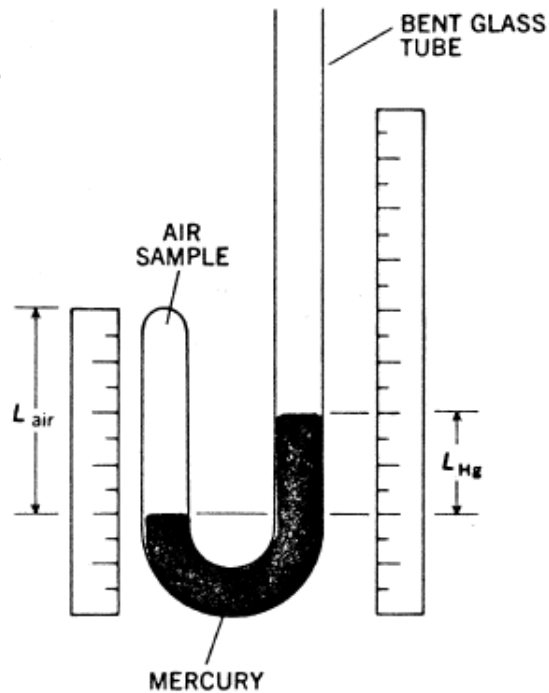


FIGURE 1-1
Apparatus for the measurement of the relation between the pressure and the volume of a sample of air.

At constant T (for an ideal gas), $V \propto 1/P$
or $PV = \text{constant}$
or $P_1V_1 = P_2V_2$

Boyle's or Mariotte's law (~ 1660) does not apply to liquids or solids where no simple relation exists between V and P .



Jacques Charles, 1746-1823



Joseph Gay-Lussac, 1778-1850

About a century later (1787 & 1808), they demonstrated that, if pressure is kept constant, the volume of a sample of gas varies linearly with the temperature.

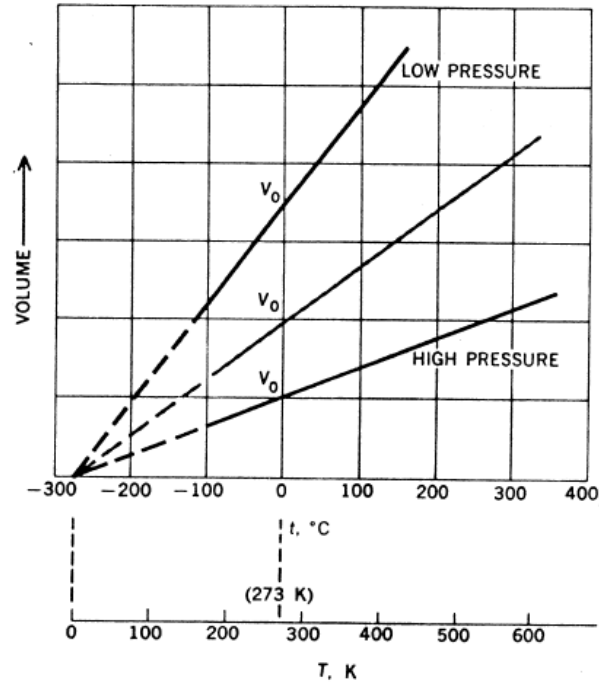


FIGURE 1-3
Variation of the volume of a sample of gas at different constant pressures as a function of the temperature according to Gay-Lussac's law. All slopes are equal to $V_0/273$.

$$T \text{ (K)} = t \text{ (}^\circ\text{C)} + 273.15$$

At constant P (for an ideal gas), $V \propto T$
or $V/T = \text{constant}$
or $V_1/T_1 = V_2/T_2$

Combining laws (Boyle/Mariotte and Charles/Gay-Lussac) leads to:

$$V \propto T/P$$

$$\text{or } PV/T = \text{constant}$$

$$\text{or } (P_1 V_1)/T_1 = (P_2 V_2)/T_2$$

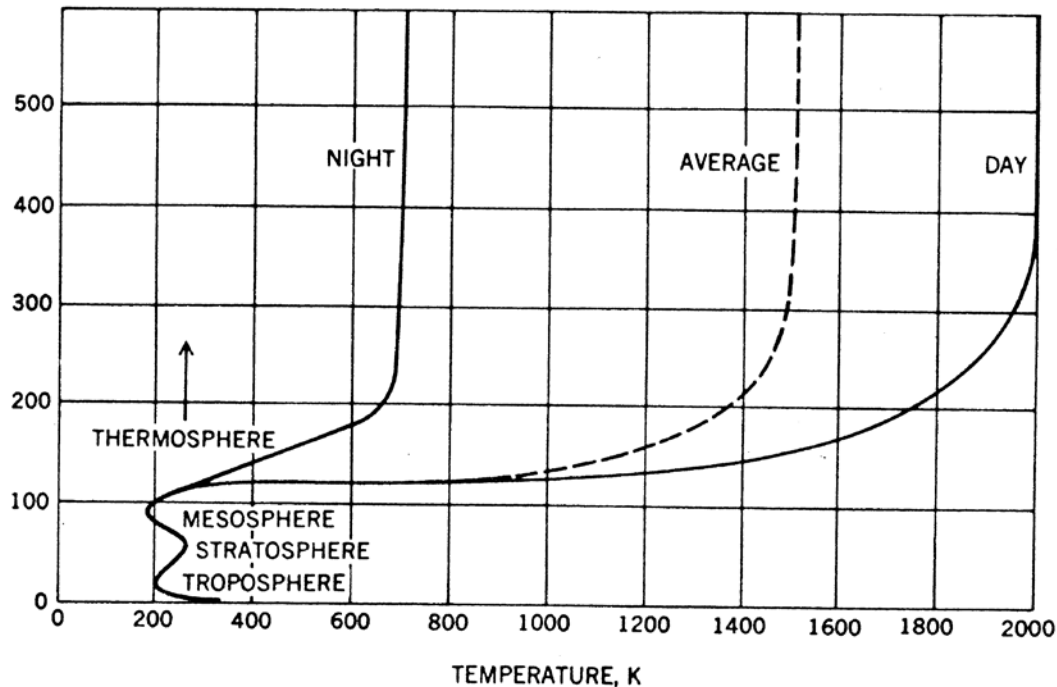


TABLE 1-2 Data for a "model atmosphere"

(Implying an atmosphere in which the variations with day and night, location, and so forth, are avoided and the data form a self-consistent set)

Altitude (km)	Temperature (K)	Pressure (atm)	Density ($\text{kg m}^{-3} = \text{g liter}^{-1}$)
0	288	1.00	1.22
20	217	5.4×10^{-2}	8.9×10^{-2}
40	261	3.0×10^{-3}	4.0×10^{-3}
60	254	2.5×10^{-4}	3.5×10^{-4}
80	166	9.9×10^{-6}	2.1×10^{-5}
100	199	2.1×10^{-7}	3.7×10^{-7}
200	1404	1.6×10^{-9}	3.7×10^{-10}
300	1423	2.5×10^{-10}	4.7×10^{-11}
400	1480	5.6×10^{-11}	9.0×10^{-12}
500	1576	1.6×10^{-11}	2.2×10^{-12}
600	1691	5.2×10^{-12}	6.6×10^{-13}
700	1812	2.0×10^{-12}	2.3×10^{-13}

FIGURE 1-5

Temperature trends in the earth's atmosphere.

IDEAL GAS LAW

We know that the volume of a gas is proportional to the amount of gas present or the number of moles of gas (n), so that:

$$V \propto n T/P$$

Under standard conditions ($T = 273.15\text{K}$ or $t = 0^\circ\text{C}$ and $P = 1\text{ atm}$), the volume occupied by one mole of an ideal gas is equal to 22.414 liters, hence,

$$PV/(nT) = \mathbf{R} = (1\text{ atm}) (22.414\text{ liters})/((1\text{ mol}) (273.15\text{K})) = 0.082056\text{ liter atm K}^{-1}\text{ mol}^{-1}$$

$$\text{Pressure x volume} = (\text{force/area}) \times (\text{area} \times \text{length}) = \text{force} \times \text{length}$$

Given that $1\text{ liter} = 10^{-3}\text{ m}^3$ and $1\text{ atm} = 101,325\text{ N m}^{-2} = 101,325\text{ Pa}$

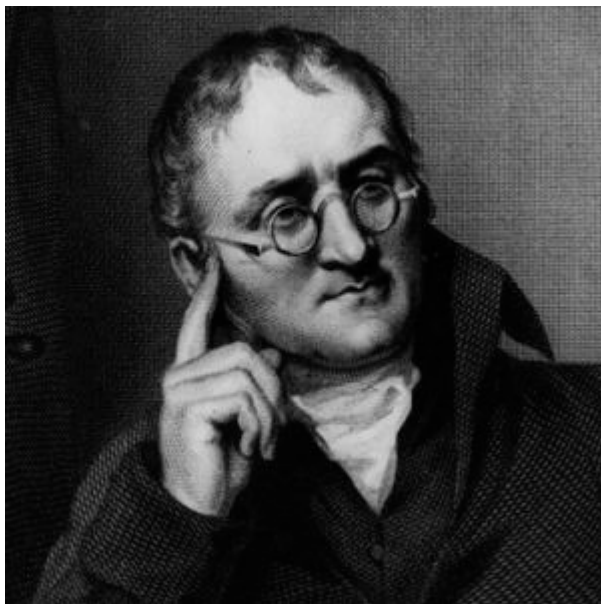
$$R = 0.082056\text{ liter atm K}^{-1}\text{ mol}^{-1} \times 1\text{ m}^3/10^{-3}\text{ L} \times 101,325\text{ N m}^{-2}/\text{atm} = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$$

($R = 1.987\text{ cal K}^{-1}\text{ mol}^{-1}$)

$$PV = n RT$$

GAS MIXTURES

According to Dalton's law for ideal gases, the total pressure exerted by a mixture of gases is equal to the sum of the pressures which each component would exert if placed separately into a container.



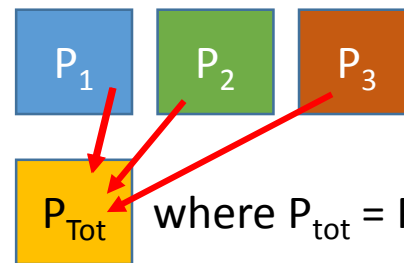
John Dalton, 1766-1844

For gas #1 - $P_1 V = n_1 RT$

For gas #2 - $P_2 V = n_2 RT$

For gas #3 - $P_3 V = n_3 RT$

For gas #i - $P_i V = n_i RT$



where $P_{tot} = P_1 + P_2 + P_3$

$$(P_1 + P_2 + P_3 + \dots + P_i) V = (n_1 + n_2 + n_3 + \dots + n_i) P$$

$$V \sum P_i = RT \sum n_i$$

where $\sum n_i = n_{tot}$ and $\sum P_i = P_{tot}$

and P_i is the partial pressure of gas i (pressure exerted by one component of the gas mixture).

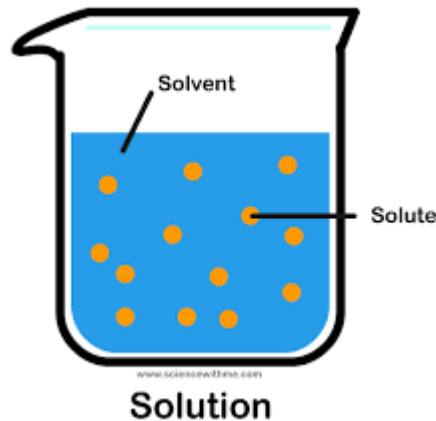
SOLUTIONS

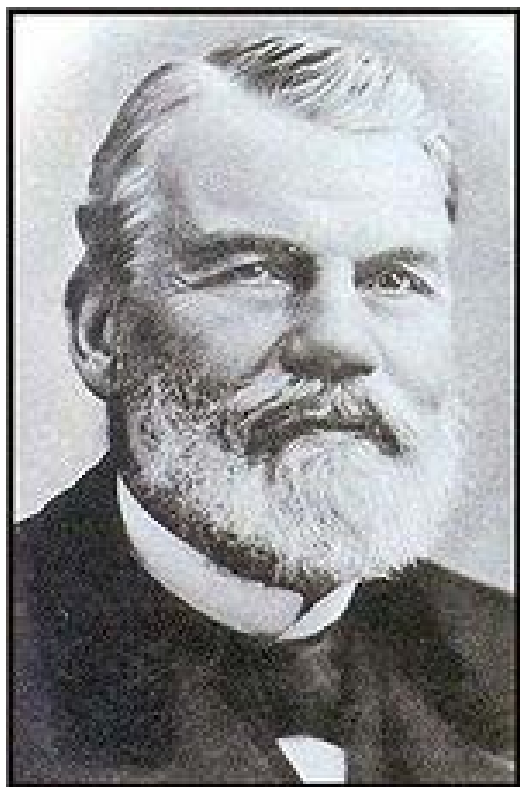
Solutions are defined as homogeneous phases formed by dissolving one or more substances (gas, liquid, solid) in another substance.

Whether you consider a gaseous, a liquid or a solid solution, compositional variations within a mixture can be expressed in terms of a number of moles of each species present (n_1, n_2, n_3, \dots) or as the mole fraction, X , defined for the i th species as:

$$X_i = \text{number of moles of } i / \text{total number of moles} \\ = n_i / \sum n$$

Therefore, $\sum X_i = 1$





François-Marie Raoult,
1830-1901

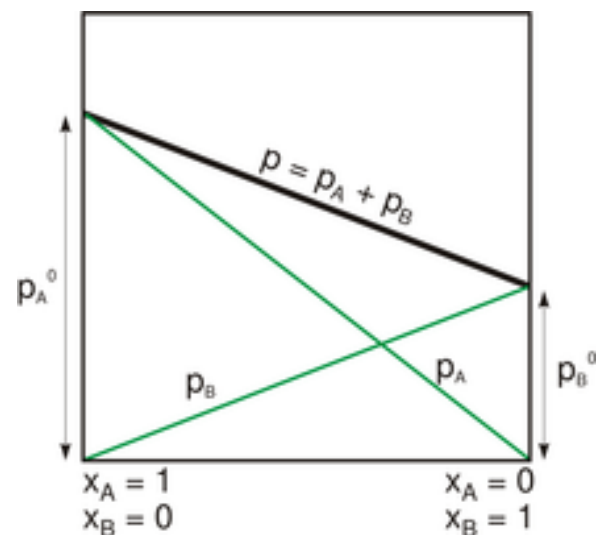
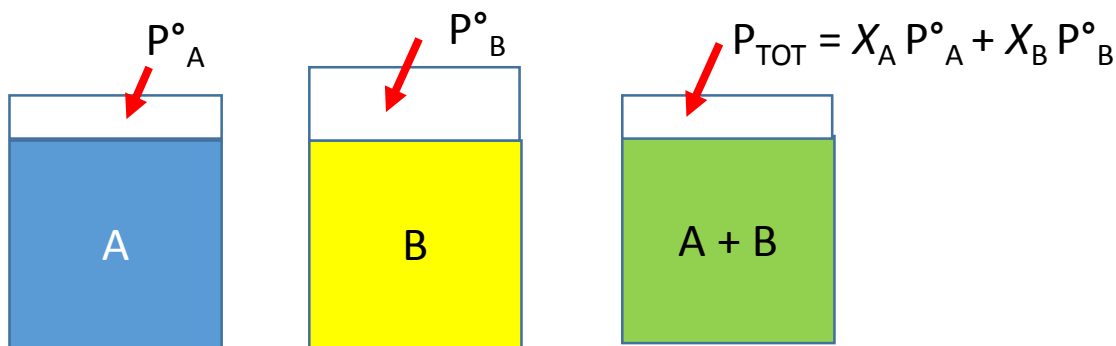
In 1886, Raoult first observed that the vapour pressure (a measure of the escaping velocity) of very similar components in solution (ethylene bromide and propylene bromide) depends only on the mole fraction of each component present in solution **at constant pressure and temperature**.

In other words, if $P_A = X_A P_A^\circ$

where P_A is the vapour pressure of A in the mixture and P_A° is the vapour pressure of pure A, then

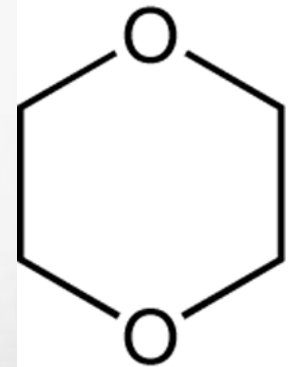
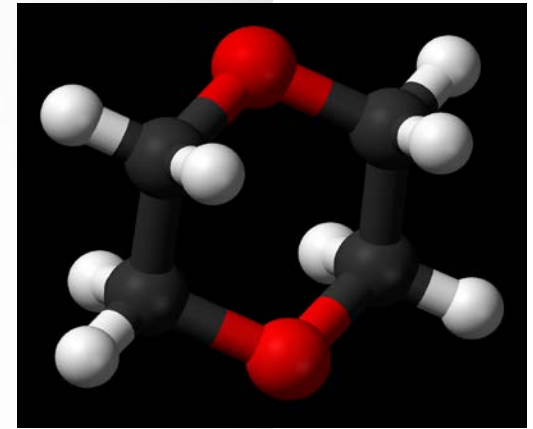
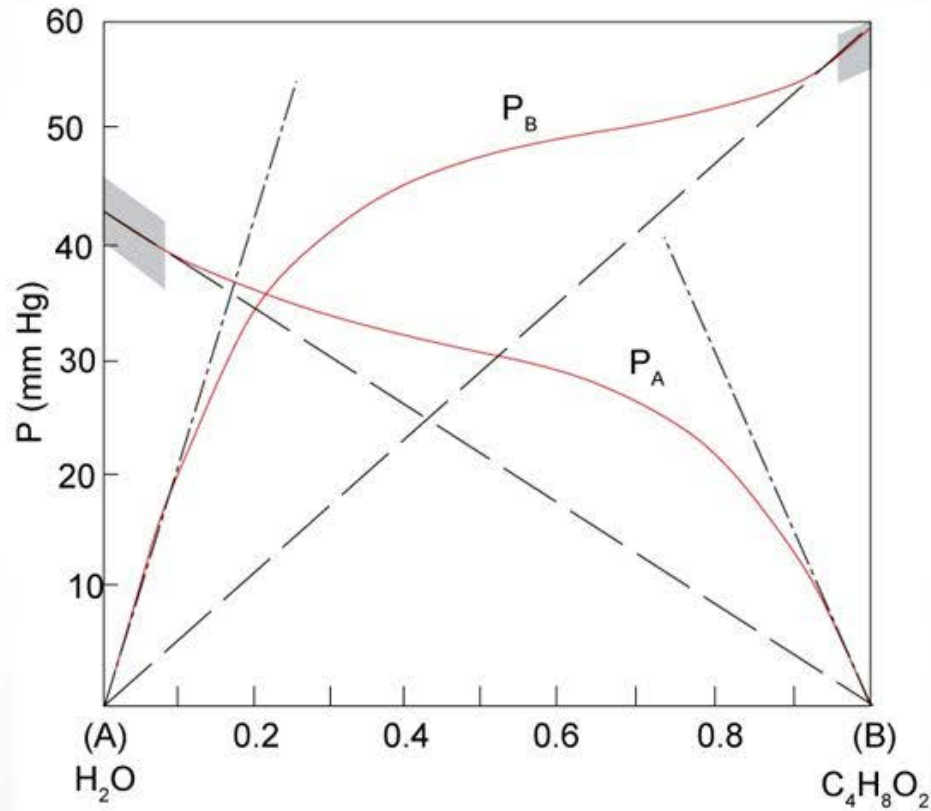
$$\begin{aligned}\sum P_i &= P_A + P_B + P_C + \dots = P_{\text{TOT}} \\ &= (X_A + X_B + X_C + \dots) P_{\text{TOT}}\end{aligned}$$

and $P_A = X_A P_{\text{TOT}}$ or $P_i = X_i P_{\text{TOT}}$



Vapour pressures in a water-dioxane solution

(the positive deviations from ideality are a macroscopic manifestation of the repulsive forces between water and dioxane molecules)



$P_B = h X_B$, where h is Henry's constant (in honour of William Henry, 1774-1836).
The value of h is dependent on the solute and solvent.

Real gases and the equation of state

One measure of the deviations (f(nature of the gas, T and P)) of a gas from ideal behavior is given by the compressibility factor, Z:

$$Z = P\bar{V}/RT$$

where \bar{V} is the volume of one mole of a real gas (V/n).

Given that:

$\bar{V} = RT/P$, a gas at 0K would have a null volume!

$$\rightarrow \bar{V} = RT/P + b \text{ or } P = RT/(\bar{V} - b)$$

where b is the hypothetical volume of a gas at 0K.

When a gas is on the verge of condensation to a liquid, gas molecules are attracted to each other, resulting in a decrease in pressure. The attractive forces are proportional to the square of their concentration.

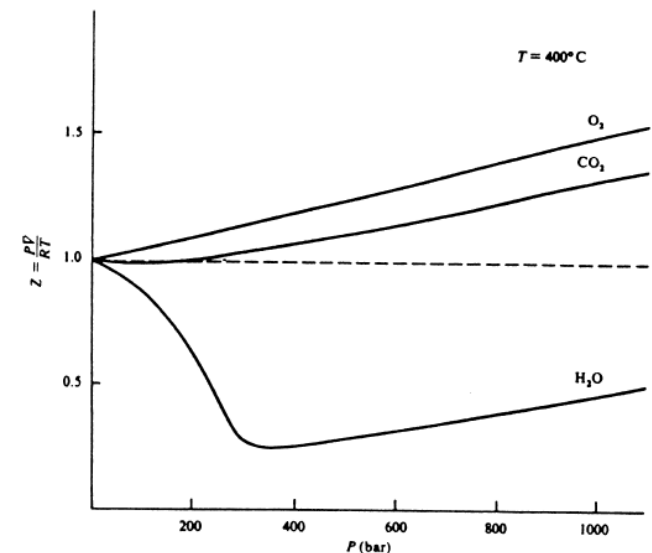


Figure 2-1. Compressibility factors for O₂, CO₂, and H₂O plotted as functions of pressure at 400°C. The dashed line (Z = 1.0) represents ideal gas behavior.

The van der Waals and Redlich-Kwong equations

Since $c = n/V = 1/\bar{V}$, the attractive forces are proportional to $1/\bar{V}^2$. These attractive forces reduce the total pressure of the gas and, thus (van de Waals equation):

$$P = RT/(\bar{V} - b) - a/\bar{V}^2 \quad (\text{van der Waals equation})$$

where a is a proportionality constant for attraction.

Subsequently, many alternative equations have been proposed that are also based on the sum of repulsive and attractive forces, including the one introduced by Redlich and Kwong in 1949:

$$P = RT/(\bar{V} - b) - a/(T^{0.5}\bar{V}(\bar{V}-b))$$

or

$$\bar{P}\bar{V}/RT = 1 + B/\bar{V} + C/\bar{V}^2 + D/\bar{V}^3$$

where B , C , and D are the second, third and fourth virial coefficients (experimentally determined).