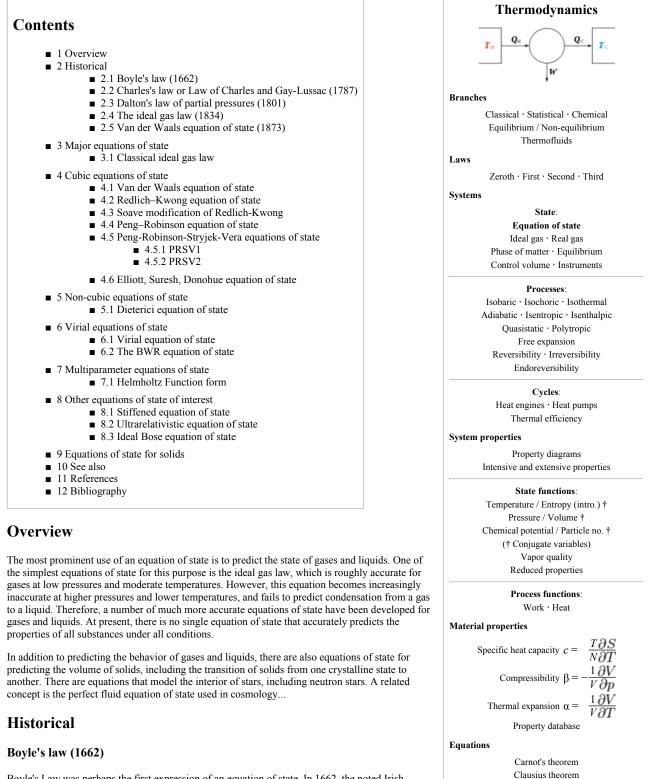
Equation of state

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In physics and thermodynamics, an **equation of state** is a relation between state variables.^[1] More specifically, an equation of state is a thermodynamic equation describing the state of matter under a given set of physical conditions. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or internal energy. Equations of state are useful in describing the properties of fluids, mixtures of fluids, solids, and even the interior of stars.



Boyle's Law was perhaps the first expression of an equation of state. In 1662, the noted Irish physicist and chemist Robert Boyle performed a series of experiments employing a J-shaped glass tube, which was sealed on one end. Mercury was added to the tube, trapping a fixed quantity of air in the short, sealed end of the tube. Then the volume of gas was carefully measured as additional mercury was added to the tube. The pressure of the gas could be determined by the difference

Table of thermodynamic equations

Fundamental relation

Ideal gas law

Maxwell relations

between the mercury level in the short end of the tube and that in the long, open end. Through these experiments, Boyle noted that the gas volume varied inversely with the pressure. In mathematical form, this can be stated as:

pV = constant.

The above relationship has also been attributed to Edme Mariotte and is sometimes referred to as **Mariotte's law**. However, Mariotte's work was not published until 1676.

Charles's law or Law of Charles and Gay-Lussac (1787)

In 1787 the French physicist Jacques Charles found that oxygen, nitrogen, hydrogen, carbon dioxide, and air expand to the same extent over the same 80 kelvin interval. Later, in 1802, Joseph Louis Gay-Lussac published results of similar experiments, indicating a linear relationship between volume and temperature:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}.$$

Dalton's law of partial pressures (1801)

Dalton's Law of partial pressure states that the pressure of a mixture of gases is equal to the sum of the pressures of all of the constituent gases alone.

Mathematically, this can be represented for *n* species as:

$$p_{\text{total}} = p_1 + p_2 + \dots + p_n = p_{\text{total}} = \sum_{i=1}^n p_i.$$

The ideal gas law (1834)

In 1834 Émile Clapeyron combined Boyle's Law and Charles' law into the first statement of the *ideal gas law*. Initially the law was formulated as $pV_m = R(T_C + 267)$ (with temperature expressed in degrees Celsius), where *R* is the gas constant. However, later work revealed that the number should actually be closer to 273.2, and then the Celsius scale was defined with 0 °C = 273.15 K, giving:

$$pV_m = R(T_C + 273.15).$$

Van der Waals equation of state (1873)

In 1873, J. D. van der Waals introduced the first equation of state derived by the assumption of a finite volume occupied by the constituent molecules.^[2] His new formula revolutionized the study of equations of state, and was most famously continued via the Redlich–Kwong equation of state and the Soave modification of Redlich-Kwong.

Major equations of state

For a given amount of substance contained in a system, the temperature, volume, and pressure are not independent quantities; they are connected by a relationship of the general form:

$$f(p, V, T) = 0.$$

In the following equations the variables are defined as follows. Any consistent set of units may be used, although SI units are preferred. Absolute temperature refers to use of the Kelvin (K) or Rankine ($^{\circ}$ R) temperature scales, with zero being absolute zero.

p = pressure (absolute) V = volume n = number of moles of a substance $V_m = \frac{V}{n} = \text{molar volume, the volume of 1 mole of gas or liquid}$ T = absolute temperature $R = \text{ideal gas constant (8.314472 J/(mol \cdot K))}$ $p_c = \text{pressure at the critical point}$ $V_c = \text{molar volume at the critical point}$ $T_c = \text{absolute temperature at the critical point}$

Classical ideal gas law

The classical ideal gas law may be written:

$$pV = nRT$$
.

The ideal gas law may also be expressed as follows

Potentials Free energy · Free entropy

Internal energy U(S,V)Enthalpy H(S,p) = U + pVHelmholtz free energy A(T,V) = U - TSGibbs free energy G(T,p) = H - TS

History and culture

Philosophy:

Entropy and time · Entropy and life Brownian ratchet Maxwell's demon Heat death paradox Loschmidt's paradox Synergetics

History:

General · Heat · Entropy · Gas laws Perpetual motion **Theories**: Caloric theory · Vis viva Theory of heat Mechanical equivalent of heat Motive power

Publications:

"An Experimental Enquiry Concerning ... Heat" "On the Equilibrium of Heterogeneous Substances" "Reflections on the Motive Power of Fire"

Timelines of:

Thermodynamics · Heat engines

Art:

Maxwell's thermodynamic surface

Education:

Entropy as energy dispersal

Scientists

Daniel Bernoulli Sadi Carnot Benoît Paul Émile Clapeyron Rudolf Clausius Hermann von Helmholtz Constantin Carathéodory Pierre Duhem Josiah Willard Gibbs James Prescott Joule James Clerk Maxwell Julius Robert von Mayer William Rankine John Smeaton Georg Ernst Stahl Benjamin Thompson William Thomson, 1st Baron Kelvin John James Waterston

$$p = \rho(\gamma - 1)e$$

where ρ is the density, $\gamma = C_p / C_v$ is the adiabatic index (ratio of specific heats), $e = C_v T$ is the internal energy per unit mass (the "specific internal energy"), C_v is the specific heat at constant volume, and C_p is the specific heat at constant pressure.

Cubic equations of state

Van der Waals equation of state

The Van der Waals equation of state may be written:

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

where V_m is molar volume, and a and b are substance-specific constants. They can be calculated from the critical properties p_c , T_c and V_c (noting that V_c is the *molar* volume at the critical point) as:

$$a = 3p_c V_c^2$$
$$b = \frac{V_c}{3}.$$

Also written as

$$a = \frac{27(RT_c)^2}{64p_c}$$
$$b = \frac{RT_c}{8p_c}.$$

Proposed in 1873, the van der Waals equation of state was one of the first to perform markedly better than the ideal gas law. In this landmark equation a is called the attraction parameter and b the repulsion parameter or the effective molecular volume. While the equation is definitely superior to the ideal gas law and does predict the formation of a liquid phase, the agreement with experimental data is limited for conditions where the liquid forms. While the van der Waals equation is commonly referenced in text-books and papers for historical reasons, it is now obsolete. Other modern equations of only slightly greater complexity are much more accurate.

The van der Waals equation may be considered as the ideal gas law, "improved" due to two independent reasons:

- 1. Molecules are thought as particles with volume, not material points. Thus V cannot be too little, less than some constant. So we get (V b) instead of V.
- 2. While ideal gas molecules do not interact, we consider molecules attracting others within a distance of several molecules' radii. It makes no effect inside the material, but surface molecules are attracted into the material from the surface. We see this as diminishing of pressure on the outer shell (which is used in the ideal gas law), so we write (p + something) instead of p. To evaluate this 'something', let's examine an additional force acting on an element of gas surface. While the force acting on each surface molecule is $\sim \rho$, the force acting on the whole element is $\sim \rho^2 \sim \frac{1}{2}$.

element is
$$\sim \rho \sim \overline{V_n}$$

With the reduced state variables, i.e. $V_r = V_m/V_c$, $P_r = P/P_c$ and $T_r = T/T_c$, the reduced form of the Van der Waals equation can be formulated:

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

The benefit of this form is that for given T_r and P_r, the reduced volume of the liquid and gas can be calculated directly using Cardono's method for the reduced cubic form:

$$V_r^3 - \left(\frac{1}{3} + \frac{8T_r}{3P_r}\right)V_r^2 + \frac{3V_r}{P_r} - \frac{1}{P_r} = 0$$

For $P_r < 1$ and $T_r < 1$, the system is in a state of vapor-liquid equilibrium. The reduced cubic equation of state yields in that case 3 solutions. The largest and the lowest solution are the gas and liquid reduced volume.

Redlich-Kwong equation of state

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$
$$a = \frac{0.42748 R^2 T_c^{2.5}}{p_c}$$
$$b = \frac{0.08662 RT_c}{p_c}$$

Introduced in 1949 the Redlich–Kwong equation of state was a considerable improvement over other equations of the time. It is still of interest primarily due to its relatively simple form. While superior to the van der Waals equation of state, it performs poorly with respect to the liquid phase and thus cannot be used for accurately calculating vapor-liquid equilibria. However, it can be used in conjunction with separate liquid-phase correlations for this purpose.

The Redlich–Kwong equation is adequate for calculation of gas phase properties when the ratio of the pressure to the critical pressure (reduced pressure) is less than about one-half of the ratio of the temperature to the critical temperature (reduced temperature):

$$\frac{p}{p_c} < \frac{T}{2T_c}.$$

Soave modification of Redlich-Kwong

$$\begin{split} p &= \frac{RT}{V_m - b} - \frac{a \, \alpha}{V_m \left(V_m + b\right)} \\ a &= \frac{0.42748 \, R^2 \, T_c^2}{P} \\ b &= \frac{0.08664 \, R \, T_c}{P_c} \\ \alpha &= \left(1 + \left(0.48508 + 1.55171 \, \omega - 0.15613 \, \omega^2\right) \left(1 - T_r^{0.5}\right)\right)^2 \\ T_r &= \frac{T}{T_c} \end{split}$$

Where ω is the acentric factor for the species.

This formulation for $\boldsymbol{\alpha}$ is due to Graboski and Daubert. The original formulation from Soave is:

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

for hydrogen:

$$\alpha = 1.202 \exp\left(-0.30288 T_r\right)$$

In 1972 G. Soave^[3] replaced the $1/\sqrt{T}$ term of the Redlich-Kwong equation with a function $\alpha(T,\omega)$ involving the temperature and the acentric factor (the resulting equation is also known as the Soave–Redlich–Kwong equation). The α function was devised to fit the vapor pressure data of hydrocarbons and the equation does fairly well for these materials.

Note especially that this replacement changes the definition of a slightly, as the T_c is now to the second power.

Peng-Robinson equation of state

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

$$a = \frac{0.457235 R^2 T_c^2}{p_c}$$

$$b = \frac{0.077796 RT_c}{p_c}$$

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

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

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

In polynomial form:

$$A = \frac{a\alpha p}{R^2 T^2}$$

$$B = \frac{bp}{RT}$$

$$Z^3 - (1 - B) Z^2 + (A - 2B - 3B^2) Z - (AB - B^2 - B^3) = 0$$

where, ω is the acentric factor of the species, R is the universal gas constant and Z=PV/(RT) is compressibility factor.

The Peng–Robinson equation was developed in 1976 in order to satisfy the following goals:^[4]

^{1.} The parameters should be expressible in terms of the critical properties and the acentric factor.

^{2.} The model should provide reasonable accuracy near the critical point, particularly for calculations of the compressibility factor and liquid density.

- 3. The mixing rules should not employ more than a single binary interaction parameter, which should be independent of temperature pressure and composition.
- 4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

For the most part the Peng-Robinson equation exhibits performance similar to the Soave equation, although it is generally superior in predicting the liquid densities of many materials, especially nonpolar ones. The departure functions of the Peng-Robinson equation are given on a separate article.

Peng-Robinson-Stryjek-Vera equations of state

PRSV1

A modification to the attraction term in the Peng-Robinson equation of state published by Stryjek and Vera in 1986 (PRSV) significantly improved the model's accuracy by introducing an adjustable pure component parameter and by modifying the polynomial fit of the acentric factor^[5].

The modification is:

$$\begin{split} \kappa &= \kappa_0 + \kappa_1 \left(1 + T_r^{0.5} \right) (0.7 - T_r) \\ \kappa_0 &= 0.378893 + 1.4897153 \,\omega - 0.17131848 \,\omega^2 + 0.0196554 \,\omega^3 \end{split}$$

where κ_1 is an adjustable pure component parameter. Stryjek and Vera published pure component parameters for many compounds of industrial interest in their original journal article^[5].

PRSV2

A subsequent modification published in 1986 (PRSV2) further improved the model's accuracy by introducing two additional pure component parameters to the previous attraction term modification^[6].

The modification is:

$$\kappa = \kappa_0 + \left[\kappa_1 + \kappa_2 \left(\kappa_3 - T_r\right) \left(1 - T_r^0.5\right)\right] \left(1 + T_r^{0.5}\right) (0.7 - T_r)$$

$$\kappa_0 = 0.378893 + 1.4897153 \omega - 0.17131848 \omega^2 + 0.0196554 \omega^3$$

where κ_1, κ_2 , and κ_3 are adjustable pure component parameters.

PRSV2 is particularly advantageous for VLE calculations. While PRSV1 does offer an advantage over the Peng-Robinson model for describing thermodynamic behavior, it is still not accurate enough, in general, for phase equilibrium calculations^[5]. The highly non-linear behavior of phase-equilibrium calculation methods tends to amplify what would otherwise be acceptably small errors. It is therefore recommended that PRSV2 be used for equilibrium calculations when applying these models to a design. However, once the equilibrium state has been determined, the phase specific thermodynamic values at equilibrium may be determined by one of several simpler models with a reasonable degree of accuracy^[6].

Elliott, Suresh, Donohue equation of state

The Elliott, Suresh, and Donohue (ESD) equation of state was proposed in 1990.^[7] The equation seeks to correct a shortcoming in the Peng– Robinson EOS in that there was an inaccuracy in the van der Waals repulsive term. The EOS accounts for the effect of the shape of a non-polar molecule and can be extended to polymers with the addition of an extra term (not shown). The EOS itself was developed through modeling computer simulations and should capture the essential physics of the size, shape, and hydrogen bonding.

$$\frac{pV_m}{RT} = Z = 1 + Z^{\text{rep}} + Z^{\text{att}}$$

where:

$$Z^{\text{rep}} = \frac{4c\eta}{1 - 1.9\eta}$$
$$Z^{\text{att}} = -\frac{z_m q\eta Y}{1 + k_1 \eta Y}$$

and

c is a "shape factor", with c = 1 for spherical molecules For non-spherical molecules, the following relation is suggested:

$$c = 1 + 3.535\omega + 0.533\omega^2$$
 where ω is the acentric factor

The reduced number density η is defined as $\eta = \frac{v^*n}{V}$

where

 v^* is the characteristic size parameter

n is the number of molecules

V is the volume of the container

The characteristic size parameter is related to the shape parameter c through

http://en.wikipedia.org/wiki/Equation of state

$$v^* = \frac{kT_c}{P_c}\Phi$$

where

$$\Phi = \frac{0.0312 + 0.087(c-1) + 0.008(c-1)^2}{1.000 + 2.455(c-1) + 0.732(c-1)^2} \text{ and } k \text{ is Boltzmann's constant.}$$

Noting the relationships between Boltzmann's constant and the Universal gas constant, and observing that the number of molecules can be expressed in terms of Avogadro's number and the molar mass, the reduced number density η can be expressed in terms of the molar volume as

$$\eta = \frac{RT_c}{P_c} \Phi \frac{1}{V_m}.$$

The shape parameter q appearing in the Attraction term and the term Y are given by

 $q = 1 + k_3(c - 1)$ (and is hence also equal to 1 for spherical molecules).

$$Y = \exp\left(\frac{\epsilon}{kT}\right) - k_2$$

where ϵ is the depth of the square-well potential and is given by

 $\frac{\epsilon}{k} = \frac{1.000 + 0.945(c - 1) + 0.134(c - 1)^2}{1.023 + 2.225(c - 1) + 0.478(c - 1)^2}$ $z_m, k_1, k_2 \text{ and } k_3 \text{ are constants in the equation of state:}$ $z_m = 9.49 \text{ for spherical molecules (c=1)}$ $k_1 = 1.7745 \text{ for spherical molecules (c=1)}$ $k_2 = 1.0617 \text{ for spherical molecules (c=1)}$ $k_3 = 1.90476.$

The model can be extended to associating components and mixtures of nonassociating components. Details are in the paper by J.R. Elliott Jr *et al.* (1990).^[7]

Non-cubic equations of state

Dieterici equation of state

$$p(V-b) = RTe^{-a/RTV}$$

where *a* is associated with the interaction between molecules and *b* takes into account the finite size of the molecules, similarly to the Van der Waals equation.

The reduced coordinates are:

$$T_c = \frac{a}{4Rb}, \ p_c = \frac{a}{4b^2e^2}, \ V_c = 2b.$$

Virial equations of state

Virial equation of state

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots$$
$$B = -V_c$$
$$C = \frac{V_c^2}{3}$$

Although usually not the most convenient equation of state, the virial equation is important because it can be derived directly from statistical mechanics. This equation is also called the Kamerlingh Onnes equation. If appropriate assumptions are made about the mathematical form of intermolecular forces, theoretical expressions can be developed for each of the coefficients. In this case *B* corresponds to interactions between pairs of molecules, *C* to triplets, and so on. Accuracy can be increased indefinitely by considering higher order terms. The coefficients *B*, *C*, *D*, etc. are functions of temperature only.

It can also be used to work out the Boyle Temperature (the temperature at which B = 0 and ideal gas laws apply) from a and b from the Van der Waals equation of state, if you use the value for B shown below:

$$B = b - \frac{a}{RT}.$$

The BWR equation of state

Main article: Benedict-Webb-Rubin equation

$$p = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right) \rho^2 + \left(bRT - a - \frac{d}{T}\right) \rho^3 + \alpha \left(a + \frac{d}{T}\right) \rho^6 + \frac{c\rho^3}{T^2} \left(1 + \gamma \rho^2\right) \exp\left(-\gamma \rho^2\right) + \frac{c\rho^3}{T^2} \left(1 + \gamma \rho^2\right) \exp\left($$

where

p = pressure $\rho = \text{the molar density}$

Values of the various parameters for 15 substances can be found in K.E. Starling (1973). Fluid Properties for Light Petroleum Systems. Gulf Publishing Company.

Multiparameter equations of state

Helmholtz Function form

Multiparameter equations of state (MEOS) can be used to represent pure fluids with high accuracy, in both the liquid and gaseous states. MEOS's represent the Helmholtz function of the fluid as the sum of ideal gas and residual terms. Both terms are explicit in reduced temperature and reduced density - thus:

$$\frac{a(T,\rho)}{RT} = \frac{a^o(T,\rho) + a^r(T,\rho)}{RT} = \alpha^o(\tau,\delta) + \alpha^r(\tau,\delta)$$

Where:

$$\tau = \frac{T_r}{T}, \delta = \frac{\rho}{\rho_r}$$

The reduced density and temperature are typically, though not always, the critical values for the pure fluid. Other thermodynamic functions can be derived from the MEOS by using appropriate derivatives of the Helmholtz function; hence, because integration of the MEOS is not required, there are few restrictions as to the functional form of the ideal or residual terms. Typical MEOS use upwards of 50 fluid specific parameters, but are able to represent the fluid's properties with high accuracy. MEOS are available currently for about 50 of the most common industrial fluids including refrigerants. Mixture models also exist.

Other equations of state of interest

Stiffened equation of state

When considering water under very high pressures (typical applications are underwater nuclear explosions, sonic shock lithotripsy, and sonoluminescence) the stiffened equation of state is often used:

$$p = \rho(\gamma - 1)e - \gamma p^0$$

where e is the internal energy per unit mass, γ is an empirically determined constant typically taken to be about 6.1, and p^0 is another constant, representing the molecular attraction between water molecules. The magnitude of the correction is about 2 gigapascals (20,000 atmospheres).

The equation is stated in this form because the speed of sound in water is given by $c^2 = \gamma (p + p^0) / \rho$.

Thus water behaves as though it is an ideal gas that is *already* under about 20,000 atmospheres (2 GPa) pressure, and explains why water is commonly assumed to be incompressible: when the external pressure changes from 1 atmosphere to 2 atmospheres (100 kPa to 200 kPa), the water behaves as an ideal gas would when changing from 20,001 to 20,002 atmospheres (2000.1 MPa to 2000.2 MPa).

This equation mispredicts the specific heat capacity of water but few simple alternatives are available for severely nonisentropic processes such as strong shocks.

Ultrarelativistic equation of state

An ultrarelativistic fluid has equation of state

$$\rho = \rho_m c_s^2$$

L

where p is the pressure, ρ_m is the mass density, and c_s is the speed of sound.

Ideal Bose equation of state

The equation of state for an ideal Bose gas is

$$pV_m = RT \frac{\text{Li}_{\alpha+1}(z)}{\zeta(\alpha)} \left(\frac{T}{T_c}\right)^{\alpha}$$

where α is an exponent specific to the system (e.g. in the absence of a potential field, $\alpha = 3/2$), z is $\exp(\mu/kT)$ where μ is the chemical potential, Li is the polylogarithm, ζ is the Riemann zeta function, and T_c is the critical temperature at which a Bose–Einstein condensate begins to form.

Equations of state for solids

- Rose–Vinet equation of state
- Birch-Murnaghan equation of state
- Johnson-Holmquist damage model
- Mie-Gruneisen equation of state

See also

- Gas laws
- Departure function
- Table of thermodynamic equations Real gas
- Cluster Expansion

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