

**Equation of state:**

In physics and thermodynamics, an equation of state is a relation between state variables. 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 (1662):**

Boyle's law was perhaps the first expression of an equation of state.

In mathematical form, this can be stated as,

$$pV = \text{constant}$$

It is also referred as Mariotte's law.

**Charles's Law:**

Indicates a linear relationship b/w volume and temperature.

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

**Dalton's law of partial pressures:**

It states that the pressure of a mixture of gases is equal to the sum of the pressures of all of the constituent gases alone.

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

**The ideal gas law:**

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

**Van der Waals equation of state:**

It may be written as

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

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  $V_C$ ,  $V_C$  is the molar volume critical point.

$$a = 3p_c V_c^2$$

$$b = \frac{V_c}{3}$$

Also

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

**Redlich - Kwong equation of state:**

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

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.08662 R T_c}{p_c}$$

**Peng-Robinson equation of state:**

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

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

$$b = \frac{0.077796 R T_c}{p_c}$$

$$A = (1 + k(1 - T_r^{0.5}))^2$$

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

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

The expansion of a gas is much more complicated than the expansion of a

solid or a liquid. This is because gases are able to expand to fill whatever container we put them in.

The volume of a gas depends on pressure. However it also depends on the temperature. As it that is not enough, we also need to consider its mass. Therefore in order to develop a proper mathematical model of a gas we need to consider its volume, pressure, temperature and mass. We need an equation of state.

A relation between the physical terms pressure  $P$  volume  $V$  and temperature  $T$  is called an equation of state. State simply means the physical condition of the system. The parameters  $p$ ,  $V$  and  $T$  are called state variables.

### **Applications of second law of thermodynamics:**

Second Law of T.D. says that heat flows from body at high temperature to the body at low temperature. If you want to transfer heat from low temperature to high temperature body, external work has to be done.

The second Law of thermodynamics is considered to be the most fundamental law of science. It explains not only the working of engines, refrigerators and other equipments used in our daily life, but also highly advanced theories like big bang, expansion of universe, heat death etc.

In his book "Reflections on the Motive Power of Fire" published in the year

1824, Carnot said that the efficiency of the heat engine was independent on the type of fluid used in the engine. As per him efficiency of the heat engine is dependent just on two temperatures. The temperature of the source (hot body) from where the engine absorbs heat and the temperature of the sink (atmosphere) where the engine gives up the exhaust heat.

Concept of the second law of thermodynamics plied to heat engine is equally applicable on the internal combustion engines used in our cars, motorcycles, ships, airplanes, etc.

In the Internal combustion engines the heat is generated by combustion of fuel inside the engine. The combustion of fuel takes place of fuel to generation of the spark (spark ignition or SI engines) and in case of the gasoline engines or due to compression of the fuel (compression ignition or CI engines) as in case of the diesel engines.

Some part of the heat generated inside the engine is used to perform the work moving piston inside the engine cylinder. The piston is connected to the crankshaft via connecting rod. The reciprocating motion of the piston is converted into the rotary motion of the crankshaft, which is converted to the rotary motion of the wheels via gear box. The remaining part of the heat generated inside the engine is released to the atmosphere as the exhaust gases or tailpipe emissions. In this case the

engine where heat is generated is called as source, where as the atmosphere where heat is released is called as sink. As per the second law of

thermodynamics, higher the temperature of the source and lower the temperature of the sink, higher is the efficiency of the engine.

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