

Thermodynamic Equation of State

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An equation of state is a thermodynamic equation relating state variables which describe the state of matter under a given set of physical conditions such as Pressure, volume, temperature or internal energy. At present there is no single equation of state that accurately predicts the properties of all substances under all conditions. An example of an equation of state correlates densities of gases and liquids to temp. and pressure known as ideal gas law which is roughly accurate for weakly polar gases at low pressure and moderate temperatures. This equation becomes increasingly inaccurate at higher pressure and lower temperatures and fails to predict condensation from a gas to a liquid.

Boyle's Law :- Boyle's Law was perhaps the first expression of equation of state. In many experiments Boyle noted that the gas volume varied inversely with the pressure. In mathematical form this can be stated as:

$$PV = \text{constant}$$

Charles's Law :- Jacques Charles found that oxygen, nitrogen, hydrogen, carbon dioxide and air expand to roughly the same extent. Later indicating a linear relationship between volume and temperature.

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

Dalton's Law of partial pressures

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

This can be represented for n species as :-

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n = P_{\text{total}}$$

The ideal gas Law - In 1834 Emile Clapeyron combined Boyle's Law and Charles law into the first Statement of the ideal gas law. Initially the law was formulated as

$$PV_m = R(T_c + 267)^\circ$$

Temp. expressed in degree 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 $0^\circ = 273.15K$

$$PV_m = R(T_c + 273.15^\circ C)$$

General form of an equation of state

For a given amount of substance contained in a system, the temp., volume and pressure, are not independent quantities. They are connected by a relationship to the general form.

$$f(P, V, T) = 0$$

In the following sections major equations of state will be described. Any consistent set of units may be used. Absolute temperature

To use of The Kelvin (K) or Rankine (R) temperature scales with zero being absolute zero.

P - Pressure (absolute,

V - Volume, n - no. of moles of a substance

$V_m = \frac{V}{n}$, molar volume, the volume of 1 mole of gas or liquid.

T - absolute temperature.

R - Ideal gas constant $\approx 8.314 \text{ J/mol}\cdot\text{K}$

P_c - Pressure at the critical point.

V_c - molar volume at the critical point.

T_c - absolute temp. at critical point.



Continued

In next class we will discuss about classical ideal gas and Van der Waals equation of state

Prof. Akhilesh