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Lecture 3: Equation of State of an Ideal Gas

As mentioned earlier, the state of a system is the condition of the system (or part of the system) at an instant of time measured by its properties. Those properties are called *state variables*, such as T, p, and V. All the other properties will depend on the state defined by two independent variables by *state functions*.

PVT system: The simplest thermodynamic system consists of a fixed mass of a fluid uninfluenced by chemical reactions or external fields.

Such a system can be described by the pressure, volume and temperature, which are related by an equation of state

$$f(p, V, T) = 0, \tag{2.1}$$

where only two of them are independent.

From physical experiments, the equation of state that defines the ideal behavior for gases may be written as

$$p\alpha = RT, \tag{2.2}$$

or

$$p = \rho RT, \tag{2.3}$$

where

ρ: density ($=m/V$) in kg m^{-3},
α: specific volume ($=V/m=1/\rho$) in m^3 kg^{-1}.
R: <u>specific gas constant</u> ($R=R^*/M$),
[R=287 J kg^{-1} K^{-1} for dry air (R_d), 461 J kg^{-1} $K^{-1}$for water vapor for water vapor (R_v)].

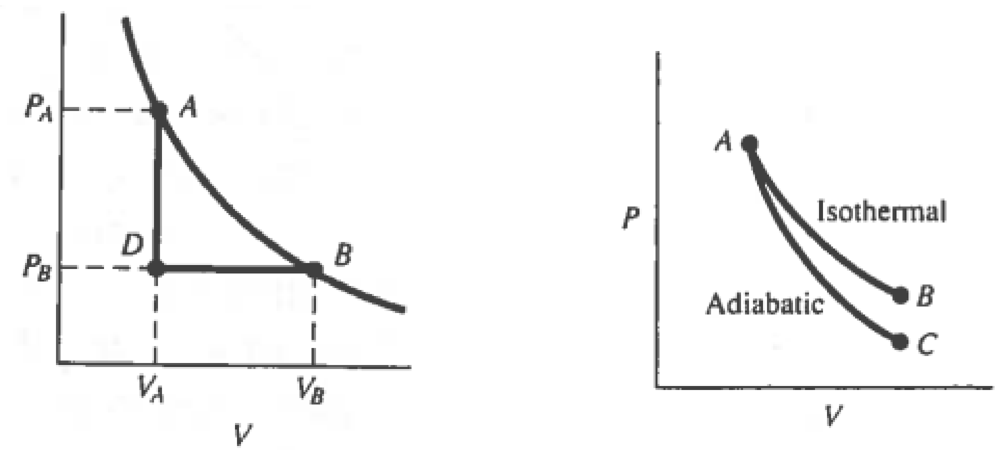

Fig. 4.1: Graphic representation of the equation of state (Eq. 2.2) for one unit mass (i.e., $pV = RT$) from state A to state B.

The equation of state may also be written in alternative forms,

$$pV = mRT = (m/M)R^*T = nR^*T, \qquad (2.4)$$

where

- p: pressure in Pa (Pascal)
- V: volume in m^3
- m: mass in kg
- R: specific gas constant
- T: temperature in K
- M: molecular weight (kg $kmol^{-1}$)
- R^*: universal gas constant (8314 J $kmol^{-1}$ K^{-1} or 1986 cal)
- n: number of molecules (measured in kmoles) contained in the system
- *kmole*: 1 kmole (N_A) = 10^3 moles = 6.022×10^{26} molecules

Notice that R^* in the above equation is constant, which can be inferred by the Avogadro's law.

Avogadro's Law: Gases containing the same number of molecules occupy the same volumes at the same temperature and pressure.

Therefore, for one kilomole of any gas the value of the gas constant is the same and is referred to as the universal gas constant R^* (8314 J $kmol^{-1}$ K^{-1}) because $R^* = pV/nT$ = constant.

The gas constant for one molecule of any gas is also a universal constant, known as Boltzmann's constant k,

$$k = R^*/N_A, \tag{2.5}$$

where N_A=1 kmole = 10^3 moles = 6.022×10^{26} molecules.
That is, $k = 1.381 \times 10^{-23}$ J molecule^{-1} K^{-1}.

Notice that the number of molecules measured in kilomoles (n) in a material with mass (m) in kg is given by

$$n = m/M \text{ or } m = nM$$

where M is the molecular weight (kg/kmole)

For example,

M = 18 kg kmol^{-1} for water (H_2O),
M = 32 kg kmol^{-1} for oxygen (O_2),
M = 28 kg kmol^{-1} for nitrogen (N_2),
1 mole = 6.022×10^{23} molecules,
1 kmole = 10^3 moles = 6.022×10^{26} molecules
(=N_A= Avogadro's number).

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Special cases for Equation of State:

(a) If the temperature of an ideal gas is held constant (isothermal), then the equation of state (Eq. (2.2)) reduces to Boyle's law (1660),

$$p\alpha = \text{constant}. \tag{2.6}$$

That is, the pressure and specific volume are inversely proportional to each other when the temperature is held constant.

(b) If the pressure of an ideal gas is held constant (isobaric), then the equation of state (Eq. (2.2)) reduces to Charles' first law (1802),

$$\alpha = (R/p)\, T \text{ or } \alpha \propto T, \tag{2.7a}$$

or

$$\alpha/T = \alpha_o/T_o, \tag{2.7b}$$

where T_o = 273.15 K and α_o = specific volume at T_o.

In words, the Charles' first law states that specific volume of an ideal gas is proportional to temperature if the pressure is held constant.

(c) If the volume and the mass of an ideal gas are held constant (isovolumic), then the equation of state reduces to Charles' second law,

$$p/T = \text{constant}. \tag{2.8}$$

That is, the pressure is proportional to the temperature of the system.

Notice that Eq . (2.2) only describes the behavior of ideal gases. The behavior of real gases can be described by a number of empirical or semi-empirical equations of state. For example, the Equation of van der Waals:

$$(p + A/V^2)\,(V\text{-}B) = nR^*T, \qquad (2.9)$$

where A and B are specific constants for each gas and the Equation of Kammerlingh-Onnes:

$$\begin{aligned} pV &= A + Bp + C\,p^2 + Dp^3 + \ldots.. \\ &= A\,(1 + B'p + C'p^2 + D'\,p^3 + \ldots.), \end{aligned} \qquad (2.10)$$

where $A, B, C, \ldots.$ are the virial coefficients and are functions of the temperature. In the above equation, $A=nR^*T$ for all gases, but ($B, C, D, \ldots$) and ($B', C', D', \ldots$) are different for different gases.