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. The equation which relates to T, p, and V is called equation of state. Since they are related by the equation of state, only two of them are independent. Thus, all the other thermodynamic 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

$$f(p,\ V,\ T) = 0, \qquad\qquad (2.1)$$

where only two of them are independent.

From physical experiments, the equation of state for an ideal gas, which is defined as a hypothetical gas whose molecules occupy negligible space and have no interactions, may be written as

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

or

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

where

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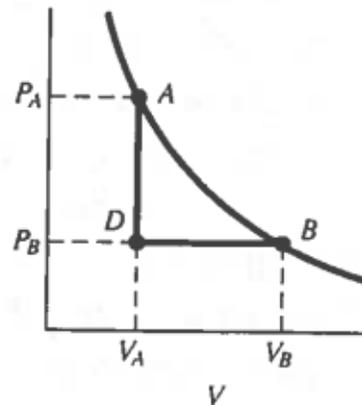

Fig. 4.1: Graphic representation of the equation of state (Eq. 2.2) for one unit mass (i.e., $pV = RT$) from state A to state B.

The isotherm in Fig. 4.1 is represented as a *hyperbola* since $p\alpha =$ constant, assuming a constant mass.

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

$$pV = mRT, \qquad (2.4)$$

where

p: pressure in Pa (Pascal)
V: volume in m^3
m: mass in kg
R: specific gas constant ($=R^*/M$; *287.058 J/kg-K for air*)
T: temperature in K

Since $m = nM$, where M is the molecular weight (in *kg/kmole*) and n is the # of molecules (counted) in kmoles, we have

$$pV = nMRT = n(MR)T, \qquad (2.4)'$$

Avogadro's Law: At the same temperature and pressure, gases containing the same number of molecules occupy the same volume.

Therefore, for one kilomole of any gas the value of the gas constant is the same, i.e. $MR = pV/nT$=constant. We may define this constant as

$$R^* = MR,$$

which is referred to as the universal gas constant (8314 J kmol^{-1} K^{-1}). Thus, the equation of state may also be written as

$$pV = nR^*T, \qquad (2.4)''$$

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In the above equations,

    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
    mole: 6.022×10^{23} molecules
    kmole: 10^3 moles $= 1$ kmole (N_A) $= 6.022 \times 10^{26}$ molecules

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

$$k = R^*/N_A, \qquad\qquad\qquad (2.5)$$

where $N_A = 1$ kmole $= 10^3$ moles $= 6.022 \times 10^{26}$ 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 $= 6.022 \times 10^{23}$ molecules,
    1 kmole $= 10^3$ moles $= 6.022 \times 10^{26}$ molecules

$$= N_A \text{ (Avogadro's number)}.$$

Special cases for Equation of State:

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

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

The above equation gives a hyperbola. That is, the pressure is inversely proportional to specific volume when the temperature is held constant.

(b) If the pressure of an ideal gas is held constant (isobaric process), 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 the 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 the Charles' second law,

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

That is, the pressure is proportional to the temperature of the system when the volume of a gas system is held constant.

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:

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

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

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

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