

Chapter 1-

Thermodynamic : Deal with the properties of system at equilibrium time is not included. It is concerned with initial and final state.

System : A thermodynamic system is a part of the universe that under consideration. It is separated from the rest of the universe by a boundary.

Surrounding : It is a part of the universe outside of the boundary.

Isolated system : The system in which there is no interaction between the system and the surrounding.

Closed system : The system in which the material cannot be transferred from the surrounding to the system or vice versa, but the system may exchange work or heat with its surrounding.

open system : The system in which the matter can be transferred from the surrounding to the system or vice versa.

Homogeneous system : System with uniform properties single phase.

Heterogeneous system : The system with more than one phase.

Adiabatic System : The system in which there is no exchangers of heat through the boundary between the system and its surrounding -

State Variable: Pressure, temperature and volume.

Extensive properties: depend on mass (volume)

Intensive properties: independent on mass (pressure and

Equation of State: $PV = nRT$

Zero Law of thermodynamic: " If system A is in equilibrium with system C and system C is in equilibrium with system B, then system A is in equilibrium with system B."

R = gas constant.

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

$$R = 0.08314 \text{ L} \cdot \text{bar} / \text{mol} \cdot \text{K}$$

$$R = 0.082 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$$

Ideal gas Law : $PV = nRT$

Non ideal gas Law :

(A) Compressibility factor : (Z) ضمان، ضا

$$Z = \frac{PV}{RT}$$

The virial equation : The equation which expresses the compressibility factor (Z) as a power series in $\frac{1}{V}$

$$Z = \frac{P \cdot V}{R \cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (1)$$

Where B is the second virial coefficient $\{ \text{ثاني، اثنى، اثنى، اثنى} \}$
C is the third virial coefficient $\{ \text{ثالث، اثنى، اثنى، اثنى} \}$

$$Z = \frac{P \cdot V}{R \cdot T} = 1 + B'P + C'P^2 \quad (2)$$

Solve eqn. (1) for P

$$P = \frac{RT}{V} + \frac{BRT}{V^2} + \frac{CRT}{V^3} \quad (3)$$

$$P^2 = \left(\frac{RT}{V}\right)^2 + \frac{2B(RT)^2}{V^3} \quad (4)$$

Subst. P and P^2 in Eq. (2)

$$Z = 1 + B' \left[\frac{RT}{V} + \frac{BRT}{V^2} \right] + C' \left[\left(\frac{RT}{V}\right)^2 + \frac{2B(RT)^2}{V^3} \right]$$

$$B = B'RT$$

$$C = B'BR + C'(RT)^2$$

$$\text{OR } \boxed{B' = \frac{B}{RT}} \quad \text{and} \quad \boxed{C' = \frac{C \cdot B^2}{R}}$$

Ex. 1 What is the molar volume of $N_2(g)$ at 500 K and 600 bar according to
 (a) a perfect gas Law
 (b) The virial equation
 given the virial coefficient (B) of $N_2(g)$ at 500 K is $0.0169 \text{ L mol}^{-1}$.

a.

Solu.

$$PV = nRT \quad n = 1 \text{ mole}$$

$$(a) \quad V = \frac{RT}{P} = \frac{8.3144 \times 10^2 (500)}{600} = 6.93 \times 10^2 \text{ L/mol}$$

$$(b) \quad z = 1 + B'P \quad B' = \frac{B}{RT}$$

$$\text{OR } z = 1 + \frac{BP}{RT}$$

$$z = 1 + \frac{(0.0169)(600)}{8.314 \times 10^2 \times 500} = 1.244$$

$$PV = znRT \quad n = 1$$

$$V = \frac{zRT}{P} = (1.244)(6.93 \times 10^2) = 8.62 \times 10^2 \text{ L/mol}$$



(B) The Vander Waals Equation :

$$(P + \frac{a}{V^2})(V - b) = RT$$

where a, b are constants from tables 1.3 Page 16
 a, b can be calculated from the critical properties
 $P_c, V_c, T_c.$

$$a = \frac{27 R^2 T_c^2}{64 P_c}$$

(13)

$$b = \frac{R \cdot T_c}{8 P_c}$$

(12)

where T_c is critical temp.
 P_c is critical pressure

The critical constant :

At a sufficiently low temp. gases can be liquified by pressures, since volume is reduced and the molecules become so close together that the attractive force between them become largers enough to cause condensation. Two criteria exist for pure substance concerning the critical state.

1. critical temp. for pure liquid; it is the highest temp. at which gas and liquid can exist as separated phases

Critical pressure (P_c):

is the pressure at critical point (T_c) the critical temp. and V_c the critical molar volume.

The critical point C indicates T_c, P_c, V_c from table 1.1 -

Reduced properties: الخواص المُختزلة

Reduced pressure = P_r $P_r = \frac{P}{P_c}$

Reduced Temp. $T_r = \frac{T}{T_c}$

Reduced volume $V_r = \frac{V}{V_c}$

$$Z_c = \frac{P_c V_c}{R T_c}$$

So that the vanden waals equation becomes

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

Ex. 2 What is the molar volume of ethane at 350 K and 70 bar according to

- a) The perfect gas Law.
- b) The Van der waals equation.

Soln. data: $n = 1 \text{ mol}$ $v = ?$
 $T = 350 \text{ K}$
 $P = 70 \text{ bar}$

(a) Perfect gas law.

$$V = \frac{nRT}{P} = \frac{(1) (0.083144) (350)}{70} = 0.416 \text{ L/mol.}$$

(b) Vander waals equation :

For ethane ~~at~~ 350 from table

$$a = 5.562 \text{ L}^2 \text{ bar/mol}^2$$

$$b = 0.0638 \text{ L/mol.}$$

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

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

$$V = b + \frac{RT}{\left(P + \frac{a}{V^2}\right)}$$

$$V = 0.063 + \frac{(0.083144)(350)}{\left(70 + \frac{5.562}{V^2}\right)}$$

using successive approximation to solve V.

let $V = 0.41 \text{ L}$

$$V = 0.063 + \frac{29.1}{\left(70 + \frac{5.562}{0.41^2}\right)} = 0.345$$

Let $V = 0.345$

$$V = 0.063 + \frac{29.1}{\left(70 + \frac{5.562}{0.345^2}\right)} = 0.312$$

Let $V = 0.312$

$$V = 0.063 + \frac{29.1}{\left(70 + \frac{5.562}{0.312^2}\right)} = 0.29$$

وهكذا نقر حتماً زفير الى تقارب مقبول.

$$\Rightarrow v \approx 0.23 \text{ L}$$



c. The Redlich Kwong eqn.

$$P = \frac{R \cdot T}{v - b} - \frac{a}{T^{1/2} \cdot v(v + b)}$$

where $a = 0.42748 R^2 T_c^{2.5} / P_c$

$$b = 0.08664 \frac{RT_c}{P_c}$$

OR $v = b + RT \left[P + \frac{a}{T^{1/2} v(v + b)} \right]^{-1}$

Barometric Formula

$$P = \rho g h$$

$$dp = -\rho g dh$$

[الدشام السالة بسبب العلاقة التامة بين الارتفاع والضغط]

For perfect (ideal) gas

$$\rho = \frac{PM}{RT}$$

$$\therefore dp = - \frac{PMg}{RT} dh$$

$$\int_{P_0}^P \frac{dp}{P} = - \int_0^h \frac{Mg}{RT} dh$$

$$\ln \frac{P}{P_0} = - \frac{gM}{RT} h$$

$$P = P_0 \exp(-gMh/RT) \quad \text{barometric formula}$$

معادلة عند استعمال هذه (المعادلة تكون لبيانات لكل من كالاتي)

$$P : \text{bar}$$

$$g : 9.81 \text{ m/s}^2$$

$$M : \text{g/mol} \quad \rightarrow \quad \text{يجب ان يكون بـ } 10^{-3} \text{ لغرض قياس الوحدات}$$

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$T = \text{°K}$$

Ex: Assuming air is 20% O_2 and 80% N_2 at sea level and the pressure is 1 bar, what is the composition and pressure at 10 km, if the atmosphere has a temperature of 0°C independent of altitude?

$$P = P_0 \exp\left(-\frac{gMh}{RT}\right)$$

For O_2 : $P_{O_2} = 0.2 \exp\left(-9.8 \times 32 \times 10^{-3} \times 10^4\right) / (8.314 \times 273)$
 $P_{O_2} = 0.0503 \text{ bar.}$

For N_2 $P_{N_2} = 0.8 \exp\left(-9.8 \times 28 \times 10^{-3} \times 10^4\right) / (8.314 \times 273)$
 $= 0.239 \text{ bar.}$

The total pressure = $P_{O_2} + P_{N_2} = 0.0503 + 0.239$
 $= 0.2893 \text{ bar}$

$$y_{O_2} = \frac{P_{O_2}}{P_T} = \frac{0.0503}{0.2893} = 0.1738$$

$$y_{N_2} = \frac{P_{N_2}}{P_T} = \frac{0.239}{0.2893} = 0.826$$