

Fugacity

Lewis (1901) by utilising the free energy function G , introduced the concept of fugacity for representing the actual behaviour of real gases which is quite different from the behaviour of ideal gases.

Variation of free energy with pressure at constant temperature is given by

$$\left(\frac{\partial G}{\partial P}\right)_T = -V \quad \dots (1)$$

For 1 mole of an ideal gas,

$$V = \frac{RT}{P}$$

Substituting the value of V in equation (1) we get

$$(dG)_T = RT \frac{dP}{P} \quad \dots (2)$$

And for n moles

$$(dG)_T = nRT \frac{dP}{P} \quad \dots (3)$$

$$(dG)_T = nRT d(\ln P) \quad \dots (4)$$

Integrating equation (4) we get

$$G = G^0 + nRT \ln P \quad \dots (5)$$

where G^0 is the integration constant
When pressure $P=1$, the equation (5)
becomes

$$G = G^0$$

Thus, integration constant is the free
energy of n moles of an ideal gas
at temperature T when the pressure
 P is unity. Equation (5) gives the
free energy of an ideal gas at
temperature T and pressure P .

Integrating equation (3) between pressures P_1 and P_2 at constant T . We get:

$$\Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P}$$

$$\Delta G = nRT \ln \left(\frac{P_2}{P_1} \right) \quad \dots (6)$$

For 1 mole of gas, the equation (6) becomes

$$\Delta G = RT \ln \left(\frac{P_2}{P_1} \right) \quad \dots (7)$$

Equation (5) and (6) are not valid for real gases because V is not exactly equal to RT/P . In order to make the equations applicable to real gases, Lewis introduced a new function ' f ' which is called fugacity function.

It takes the place of ' P ' in equation (4)

$$(dG)_T = nRT d(\ln f) \quad \dots (8)$$

and equation (5) may be written as below:

$$G = G^0 + nRT \ln f \quad \dots (9)$$

where G^0 is the free energy of ' n ' moles of a real gas when its fugacity is unity.

Equation (9) gives the free energy of a real gas at temperature T and pressure P at which its fugacity is ' f '.

Integrating equation (8) between fugacities ' f_1 ' and ' f_2 ' at constant temperature T . We get

$$\Delta G = nRT \ln \left(\frac{f_2}{f_1} \right) \quad \dots \quad (10)$$

for one mole of gas (i.e. $n=1$), the above equation becomes

$$\Delta G = RT \ln \left(\frac{f_2}{f_1} \right) \quad \dots \quad (11)$$

Equation (10) and (11) are applicable to all gases irrespective of whether the gas is ideal or real.

Since both equation (7) and (11) are applicable to a system consisting of one mole of an ideal gas, therefore

$$f \propto P$$

$$\text{i.e. } f/P = \text{Constant} \quad \dots \quad (12)$$

For real gas however, the quantity f/P is not a constant. But as the pressure is decreased, a real gas approaches an ideal gas in its behaviour, i.e. ' f ' approaches ' P ' at sufficiently low pressure. Therefore the statement is

mathematically represented as

$$\lim_{P \rightarrow 0} \left(\frac{f}{P} \right) = 1 \quad \dots \quad (5)$$

Thus, at low pressure, fugacity is equal to pressure. The two forms differ only at high pressure.

Fugacity coefficient :- In general, fugacity of a real gas is related to its pressure by the equation

$$\frac{f}{P} = \gamma$$

where ' γ ' is called fugacity coefficient. It measures the deviations of a real gas from the ideal behaviour. At zero pressure, a real gas behaves like an ideal gas. Thus we can write

$$\lim_{P \rightarrow 0} \frac{f}{P} = \frac{f}{P} = \lim_{P \rightarrow 0} \gamma = 1$$

Fugacity of solids and liquids:

Every solid or liquid has a definite vapour pressure. At a definite pressure, a solid or liquid is in equilibrium with the constant temperature. Since the system is in equilibrium, the chemical potential of the solid or liquid must be the same as that of the vapour. Thus, the fugacity of solid or liquid will be approximately equal to its vapour pressure.

Determination of fugacity

The following methods are used to determine the fugacity of gases, liquid mixtures etc.

In Conceptual method: We know that the fugacity of a real gas is equal to its pressure at ~~very~~ low pressures.

For a very small reversible stage of an isothermal change, we get from $dg = VdP - SdT$,

$$dg = VdP \quad \dots \quad (12)$$

Combining equations (8) and (12), we get

$$RT d \ln f = VdP \quad \left\{ \text{for 1 mole} \right\} \quad \dots \quad (13)$$

$$\left\{ \frac{\partial \ln f}{\partial P} \right\}_T = \frac{V}{RT} \quad \dots \quad (14)$$

Now a function ' α ' is introduced in equation (8) which is defined as,

$$\alpha = \frac{RT}{P} - V$$

$$V = \left(\frac{RT}{P} - \alpha \right) \quad \dots \quad (15)$$

Substituting the value of ' V ' in equation (13) we get

$$RT d \ln f = \left(\frac{RT}{P} - \alpha \right) \cdot dP \quad \dots \quad (16)$$

Integrating equation (16) between a very low pressure (zero) and a given pressure P at constant temperature, we get

$$RT \ln f = RT \int_0^P \frac{dP}{P} - \int_0^P \alpha dP$$

$$\ln f = \ln P - \frac{1}{RT} \int_0^P \alpha dP \quad (17)$$

In order to find out the value of fugacity (f), we should know that the value of $\int_0^P \alpha dP$ which can be obtained by plotting a graph between α/RT and P as shown in figure 1. The area under the curve between $P=0$ and $P=P$ gives the value of integral. The value of f can be easily calculated.

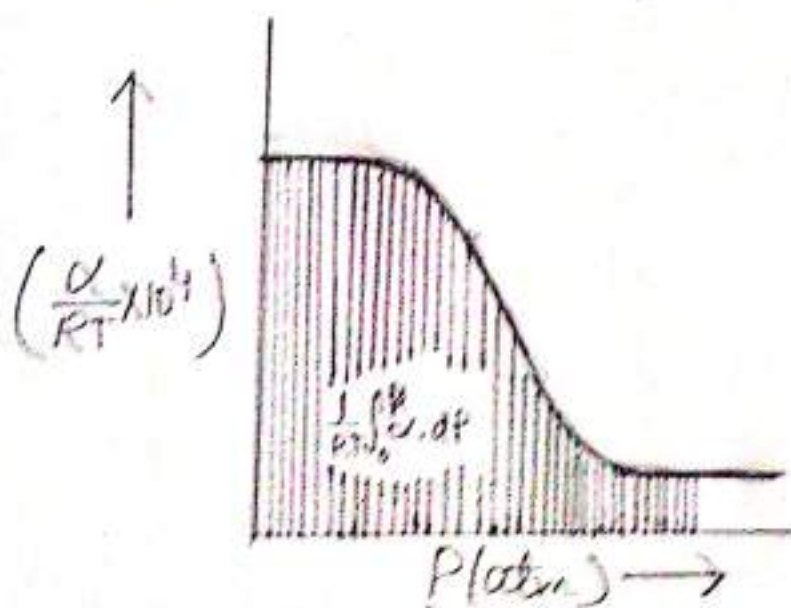


Fig. Value of Integral

(2) Approximate calculation method: Van der Waals (1873)

$$\alpha^2 = \frac{RT}{P} - V$$

The value of α^2 is nearly constant over a large range of moderate pressures. Thus equation (1) becomes,

$$RT - \frac{a}{V} = \frac{RT}{P} - V$$

$$RT - \frac{a}{V} = \frac{RT}{P} - V$$

$$RT - \frac{a}{V} = \frac{RT}{P} - V \quad (12)$$

At moderate pressures, $\frac{1}{P} = 1$, therefore

$$RT - \frac{a}{V} = \frac{RT}{P} - V \quad \frac{1}{P} \log d = d - 1 \text{ when } d \rightarrow 1$$

Thus equation (12) becomes

$$\frac{1}{P} - 1 = - \frac{a}{RTV}$$

Substituting the value of α^2 in equation (9) we get

$$f = \frac{3}{RT} V$$

This gives accurate result at low pressures and high temperatures.

(*) General method: From equation (1) we have

$$\alpha = \frac{RT}{P} - V = \frac{RT}{P} \left(1 - \frac{PV}{RT} \right) \quad (21)$$

The compressibility factor (k) of a gas is defined as

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

Substituting the value of (k) in equation (21), we get

$$\alpha = \frac{RT}{P} (1 - k) \quad (22)$$

Now substituting the value of (α) in equation (1), we have

$$\ln f = \ln P - \int_0^P \left(\frac{k}{P} \right) dP \quad (23)$$

Replacing the P term by the corresponding values of reduced pressure (π), we get

$$\ln f = \ln P_1 \int_0^\pi \frac{(k-1)}{\pi} d\pi \left(\pi = \frac{P}{P_1} \right) \quad (24)$$

$$\ln f/P = \int_0^\pi \frac{(k-1)}{\pi} d\pi \quad (25)$$

Since the compressibility factors of all gases are approximately equal at given reduced temperature and pressure, equation (25) is a general expression which may be plotted taking f/P as ordinate and reduced pressure π as abscissa and O is plotted as parameter as shown in figure (a). The value of (k) is

derived from the other curve of $\frac{P}{P_0}$ and T as shown in figure 3 (a). The value of integral of equation (25) can be evaluated graphically.

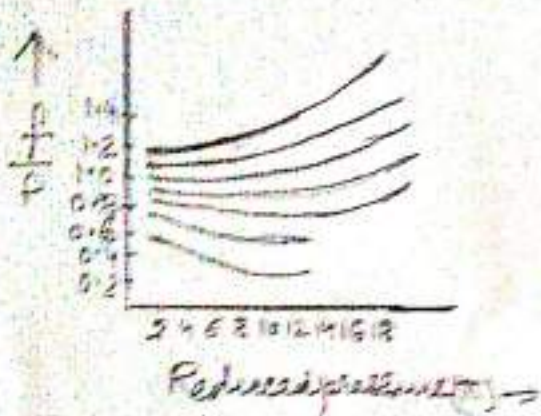


Fig 2. (a)

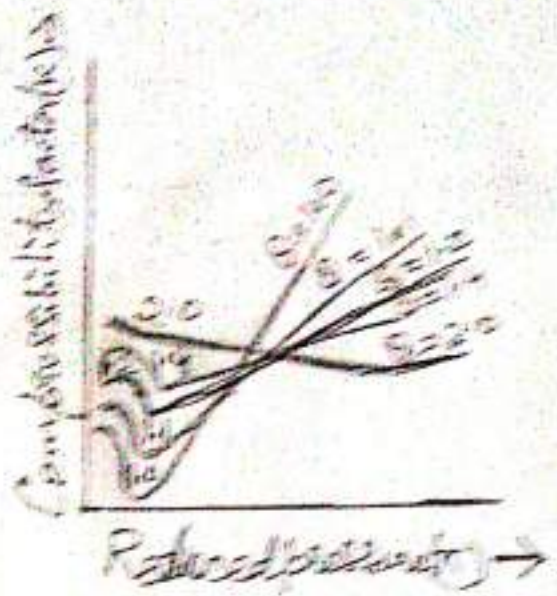


Fig 2. (b)

(4). From equation of state:

If f and f_0 represent the fugacities of a gas at pressure P and at low pressure P_0 on integrating equation (4), we get

$$RT \int_{f_0}^f \frac{df}{f} = \int_{P_0}^P V dP$$

$$\ln \frac{f}{f_0} = \frac{1}{RT} \int_{P_0}^P V dP \dots \dots (25)$$

Now integrating by parts

$$\int_{P_0}^P V dP = [PV]_{P_0}^P - \int_{P_0}^P P dV$$

$$= PV - P_0 V_0 - \int_{V_0}^V P \cdot dV$$

Now V_0 represents molar volume at low pressure P_0 .

At very low pressure $P_0 V_0 = RT$. Thus

$$\int_{P_0}^P V dP = PV - RT - \int_{V_0}^V P dV \quad \dots (27)$$

From equations (26) and (27), we get

$$\ln \frac{f}{f_0} = \frac{1}{RT} \left[PV - RT - \int_{V_0}^V P \cdot dV \right] \quad \dots (28)$$

But at very low pressures, $\ln \frac{f}{f_0} = \ln \frac{f}{P_0}$

From equation (28), we have

$$\ln \frac{f}{P_0} = \frac{1}{RT} \left[PV - RT - \int_{V_0}^V P \cdot dV \right]$$

$$\ln f - \ln P_0 = \frac{1}{RT} \left[PV - RT - \int_{V_0}^V P \cdot dV \right]$$

$$\ln f = \ln P_0 + \frac{1}{RT} \left[PV - RT - \int_{V_0}^V P \cdot dV \right] \quad \dots (29)$$

From equation (29), fugacity may be calculated if the value of $\int_{V_0}^V P \cdot dV$ is known. This value can be calculated from equation of state like Vander Waal's equation which is as follows:

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

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \dots (30)$$

Multiplying equation (30) by dV and then integrating, we get

$$\int_{V_0}^V P dV = \int_{V_0}^V \frac{RT}{V-b} dV - \int_{V_0}^V \frac{a}{V^2} dV$$

$$= RT \ln \left(\frac{V-b}{V_0-b} \right) + \frac{a}{V} - \frac{a}{V_0} \quad (31)$$

Since V_0 is very large as compared to b , thus $V_0 - b$ may be replaced by V_0 which is equal to RT/P_0 and a/V_0 may be neglected. Thus equation (31) becomes

$$\int_{V_0}^V P dV = RT \frac{V-b}{V_0} + \frac{a}{V} \quad (32)$$

Substituting equation (32) in equation (33) we get

$$\ln f = \ln P_0 + \frac{1}{RT} \left[PV - RT - RT \ln \frac{V-b}{V_0} - \frac{a}{V} \right] \quad (33)$$

On multiplying equation (33) by V and subtracting RT from both, we get

$$PV - RT = \left[\frac{RTV}{V-b} - \frac{a}{V} \right] - RT$$

$$PV - RT = \left[\frac{RTb}{V-b} - \frac{a}{V} \right] \quad (34)$$

Substituting equation (34) in equation (33) we get

$$\begin{aligned}
\ln f &= \ln p_0 + \frac{1}{RT} \left[\frac{RTb}{V-b} - \frac{a}{V} - RT \ln \frac{V-b}{V_0} - \frac{a}{V} \right] \\
&= \ln p_0 + \frac{b}{V-b} - \frac{2a}{RTV} - \ln \frac{V-b}{V_0} \\
&= \ln p_0 + \frac{b}{V-b} - \frac{2a}{RTV} - [\ln(V-b) - \ln V_0] \\
&= \ln p_0 + \frac{b}{V-b} - \frac{2a}{RTV} - [\ln(V-b) - \ln \frac{RT}{p_0}] \\
&\hspace{15em} (p_0 V_0 = RT) \\
&= \ln p_0 + \frac{b}{V-b} - \frac{2a}{RTV} [\ln(V-b) - \ln RT] - \ln p_0 \\
&= \frac{b}{V-b} - \frac{2a}{RTV} - \ln \left(\frac{V-b}{RT} \right)
\end{aligned}$$

$$\ln f = \frac{b}{V-b} - \frac{2a}{RTV} + \ln \left(\frac{RT}{V-b} \right) \quad \dots (35)$$

From equation (35), the fugacity at any pressure can be calculated if the Vander Waal's Constant 'a' and 'b' are known.