

Determination of Fugacity by Virial Equation

The fugacity of a real gas can also be determined with the help of the virial equation of state. This method is particularly useful at low and moderate pressures, where the virial equation gives a satisfactory representation of the behaviour of real gases.

For one mole of a gas, the virial equation may be written in terms of pressure as

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots$$

where B' , C' , D' , etc. are the pressure-form virial coefficients and may depend upon temperature.

The fugacity coefficient of a real gas is related to the compressibility factor by

$$\ln \varphi = \int_0^P \frac{Z - 1}{P} dP$$

For the virial equation,

$$Z - 1 = B'P + C'P^2 + D'P^3 + \dots$$

Therefore,

$$\frac{Z - 1}{P} = B' + C'P + D'P^2 + \dots$$

Substitution in the fugacity expression gives

$$\ln \varphi = \int_0^P (B' + C'P + D'P^2 + \dots) dP$$

At constant temperature, the virial coefficients are constants with respect to pressure. Hence,

integration gives

$$\ln \varphi = B'P + \frac{C'P^2}{2} + \frac{D'P^3}{3} + \dots$$

Thus,

$$\ln \varphi = B'P + \frac{C'P^2}{2} + \frac{D'P^3}{3} + \dots$$

Since the fugacity coefficient is defined by

$$\varphi = \frac{f}{P},$$

we have

$$\ln \left(\frac{f}{P} \right) = B'P + \frac{C'P^2}{2} + \frac{D'P^3}{3} + \dots$$

Taking the exponential of both sides,

$$f = P \exp \left(B'P + \frac{C'P^2}{2} + \frac{D'P^3}{3} + \dots \right)$$

At Low Pressure

At sufficiently low pressure, the higher-order terms become very small and may be neglected. The virial equation can then be approximated by

$$Z = 1 + B'P$$

Thus,

$$Z - 1 = B'P$$

and therefore

$$\frac{Z - 1}{P} = B'.$$

The fugacity coefficient then becomes

$$\ln \varphi = \int_0^P B' dP$$

giving

$$\boxed{\ln \varphi = B'P}$$

or

$$\boxed{\varphi = e^{B'P}}$$

Since $f = \varphi P$,

$$f = Pe^{B'P}$$

For very low pressures, $B'P$ is small. Using the approximation $e^x \approx 1 + x$ for small x ,

$$f \approx P(1 + B'P)$$

Thus, at sufficiently low pressure, f approaches P , as expected for a gas approaching ideal behaviour.

Relation with the Virial Coefficient in Volume Form

The virial equation is also commonly expressed in terms of molar volume as

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

where B , C , etc. are the virial coefficients in the volume form.

At low pressure, the pressure-form and volume-form coefficients are related approximately by

$$B' = \frac{B}{RT}.$$

Therefore, when only the second virial coefficient is significant,

$$\ln \varphi = \frac{BP}{RT}$$

and hence

$$f = P \exp \left(\frac{BP}{RT} \right)$$

The sign of the second virial coefficient determines the direction of deviation from ideal behaviour. A negative B generally indicates predominance of attractive interactions and gives

$f < P$, whereas a positive B indicates predominance of repulsive effects and gives $f > P$.