

Determination of Fugacity by Compressibility Factor

The compressibility factor provides one of the most convenient methods for determining the fugacity of a real gas. Since the compressibility factor expresses the deviation of a real gas from ideal behaviour, the fugacity can be related directly to experimentally measured values of Z . This method is particularly useful because compressibility factor data are available for most gases over a wide range of temperatures and pressures.

The derivation starts from the fundamental thermodynamic relation between chemical potential and pressure. For one mole of a real gas at constant temperature,

$$d\mu = VdP \quad (1)$$

The chemical potential of a real gas may also be written in terms of fugacity as

$$d\mu = RTd(\ln f) \quad (2)$$

Since Eqs. (1) and (2) represent the same differential change in chemical potential,

$$VdP = RTd(\ln f) \quad (3)$$

To eliminate the molar volume from this equation, the compressibility factor is introduced. It is defined as

$$Z = \frac{PV}{RT} \quad (4)$$

Rearranging Eq. (4),

$$V = \frac{ZRT}{P} \quad (5)$$

Substituting Eq. (5) into Eq. (3),

$$\frac{ZRT}{P} dP = RT d(\ln f) \quad (6)$$

Since the temperature is constant, **R** and **T** are constants and appear on both sides of the equation. Dividing both sides by **RT**,

$$\frac{Z}{P} dP = d(\ln f) \quad (7)$$

Equation (7) gives the differential change in the logarithm of fugacity. However, the required expression is not in terms of fugacity alone but in terms of the ratio of fugacity to pressure, that is, **f/P**. To obtain this form, the differential of **ln P** is introduced.

From elementary calculus,

$$d(\ln P) = \frac{dP}{P} \quad (8)$$

Subtracting Eq. (8) from Eq. (7),

$$d(\ln f) - d(\ln P) = \frac{Z}{P} dP - \frac{dP}{P} \quad (9)$$

Taking **dP/P** common on the right-hand side,

$$d(\ln f) - d(\ln P) = \frac{(Z - 1)}{P} dP \quad (10)$$

Using the logarithmic identity,

$$\ln a - \ln b = \ln \left(\frac{a}{b} \right) \quad (11)$$

its differential form is

$$d(\ln f) - d(\ln P) = d \left[\ln \left(\frac{f}{P} \right) \right] \quad (12)$$

Substituting Eq. (12) into Eq. (10),

$$d \left[\ln \left(\frac{f}{P} \right) \right] = \frac{Z - 1}{P} dP \quad (13)$$

Equation (13) is the required differential equation. The next step is to integrate this equation between suitable limits to obtain the final expression for fugacity in terms of the compressibility factor.

Integrating Eq. (13) between the limiting state of zero pressure and the actual pressure P gives

$$d \left[\ln \left(\frac{f}{P} \right) \right] = \frac{Z - 1}{P} dP \quad (14)$$

To obtain the relation between fugacity and pressure, both sides are integrated. The integration is performed from a very low pressure, approaching zero, to the pressure P at which the fugacity is required.

Thus,

$$\int_{P \rightarrow 0}^P d \left[\ln \left(\frac{f}{P} \right) \right] = \int_0^P \frac{Z - 1}{P} dP \quad (15)$$

Consider first the left-hand side. The integral of a differential quantity is simply the difference between its value at the upper and lower limits. Therefore,

$$\int_{P \rightarrow 0}^P d \left[\ln \left(\frac{f}{P} \right) \right] = \left[\ln \left(\frac{f}{P} \right) \right]_{P \rightarrow 0}^P \quad (16)$$

Applying the upper and lower limits,

$$= \ln \left(\frac{f}{P} \right) - \lim_{P \rightarrow 0} \ln \left(\frac{f}{P} \right) \quad (17)$$

Now consider the lower limit. At very low pressure, a real gas approaches ideal-gas behaviour. For an ideal gas, fugacity is equal to pressure. Therefore,

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1 \quad (18)$$

Taking the natural logarithm of both sides,

$$\lim_{P \rightarrow 0} \ln \left(\frac{f}{P} \right) = \ln 1 = 0 \quad (19)$$

Substituting Eq. (19) into Eq. (17),

$$\int_{P \rightarrow 0}^P d \left[\ln \left(\frac{f}{P} \right) \right] = \ln \left(\frac{f}{P} \right) - 0 \quad (20)$$

Hence,

$$\int_{P \rightarrow 0}^P d \left[\ln \left(\frac{f}{P} \right) \right] = \ln \left(\frac{f}{P} \right) \quad (21)$$

Substituting Eq. (21) into Eq. (15), we obtain

$$\boxed{\ln \left(\frac{f}{P} \right) = \int_0^P \frac{Z - 1}{P} dP} \quad (22)$$

This is the required expression for determining the fugacity of a real gas from its compressibility factor.

Expression in Terms of Fugacity Coefficient

The fugacity coefficient φ is defined as the ratio of fugacity to pressure:

$$\varphi = \frac{f}{P} \quad (23)$$

Therefore,

$$\ln \varphi = \ln \left(\frac{f}{P} \right) \quad (24)$$

Using Eq. (22),

$$\ln \varphi = \int_0^P \frac{Z - 1}{P} dP \quad (25)$$

Taking the exponential of both sides,

$$\varphi = \exp \left[\int_0^P \frac{Z - 1}{P} dP \right] \quad (26)$$

Since

$$f = \varphi P, \quad (27)$$

substitution of Eq. (26) gives

$$f = P \exp \left[\int_0^P \frac{Z - 1}{P} dP \right] \quad (28)$$