

Determination of Fugacity Using an Equation of State

Another method of determining the fugacity of a real gas is to use an equation of state. An equation of state gives the relationship between pressure, volume and temperature of a real gas. Once the molar volume of the gas is obtained from an appropriate equation of state, it can be used to calculate the fugacity.

For one mole of a real gas at constant temperature,

$$d\mu = VdP$$

and, in terms of fugacity,

$$d\mu = RTd(\ln f).$$

Equating these two expressions gives

$$RTd(\ln f) = VdP.$$

For an ideal gas, $V = RT/P$. For a real gas, however, the actual molar volume is obtained from the appropriate equation of state. The difference between the actual volume and the ideal-gas volume is therefore responsible for the difference between fugacity and pressure.

General Expression

Dividing the thermodynamic equation by RT ,

$$d(\ln f) = \frac{V}{RT} dP.$$

For an ideal gas,

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

Subtracting the ideal-gas contribution from the real-gas expression,

$$d(\ln f) - d(\ln P) = \left(\frac{V}{RT} - \frac{1}{P} \right) dP.$$

Using

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

we obtain

$$d \left[\ln \left(\frac{f}{P} \right) \right] = \left(\frac{V}{RT} - \frac{1}{P} \right) dP$$

Integration from the ideal-gas limiting state to the required pressure gives

$$\ln \left(\frac{f}{P} \right) = \int_0^P \left(\frac{V}{RT} - \frac{1}{P} \right) dP$$

Thus, if V is expressed as a function of P and T using an equation of state, the integral can be evaluated and the fugacity can be calculated.

Fugacity from the van der Waals Equation

As an illustration, consider one mole of a gas obeying the van der Waals equation,

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

Rearranging,

$$P = \frac{RT}{V - b} - \frac{a}{V^2}.$$

The constants a and b account for the attractive forces between molecules and the finite volume occupied by the molecules, respectively.

The fugacity can therefore be determined by substituting the molar volume obtained from this equation into the general thermodynamic expression. In practice, the calculation may be performed by integrating with respect to pressure or by changing the variable from pressure to volume.

Using

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV,$$

the fugacity expression becomes

$$\ln\left(\frac{f}{P}\right) = \int \left[\frac{V}{RT} - \frac{1}{P}\right] \left(\frac{\partial P}{\partial V}\right)_T dV.$$

The limits are chosen such that the lower limit corresponds to the low-pressure limit, where $V \rightarrow \infty$, and the upper limit corresponds to the molar volume of the gas at the required pressure.

The important point is that an equation of state supplies the P - V - T relationship required for evaluating the fugacity integral. More complicated equations of state can be treated in exactly the same thermodynamic manner.

Comparison of Methods

Method	Basis	Main Requirement
Compressibility-factor method	$Z = \frac{PV}{RT}$	Experimental or calculated Z -data
Virial equation method	Virial expansion of Z	Virial coefficients
Equation-of-state method	Real-gas equation of state	P - V - T relationship

All these methods are based on the same thermodynamic definition of fugacity. They differ only in the way the volume or compressibility behaviour of the real gas is represented.