Determination of Fugacity

Fugacity is a thermodynamic property and cannot be measured directly like pressure or temperature. Instead, it is calculated from measurable properties such as pressure, volume, temperature, and the compressibility factor of a real gas. The determination of fugacity is based on the relationship between **chemical potential** and **Gibbs free energy**.

The derivation begins with the fundamental equation of thermodynamics for a closed system at constant temperature.

Step 1: Gibbs Free Energy and Chemical Potential

The chemical potential of a substance is defined as the partial molar Gibbs free energy.

$$\boxed{\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P}}$$

For one mole of a pure substance,

$$\boxed{G = \mu}$$

At constant temperature,

$$dG = V\,dP - S\,dT$$

Since temperature is constant,

$$dT = 0$$

Therefore,

$$\boxed{dG = V\,dP}$$

As $G = \mu$ for one mole,

$$\boxed{d\mu = V\,dP}$$

This equation gives the variation of chemical potential with pressure.

Step 2: For an Ideal Gas

For one mole of an ideal gas,

$$PV = RT$$

Hence,

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

Substituting into the previous equation,

$$d\mu = \frac{RT}{P}\, dP$$

Rearranging,

$$d\mu = RT\frac{dP}{P}$$

Since

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

Therefore,

$$\boxed{d\mu = RT\, d(\ln P)}$$

Integrating between two states,

$$\boxed{\mu = \mu^\circ + RT \ln P}$$

This equation is valid only for an ideal gas.

Step 3: For a Real Gas

Real gases do not obey the ideal gas equation because intermolecular attractive and repulsive forces become significant. Therefore,

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

Hence, pressure can no longer represent the true thermodynamic behavior of the gas.

Lewis introduced a new quantity called **fugacity**, denoted by

f, which replaces pressure in the chemical potential equation.

Thus,

$$\boxed{d\mu = RT\, d(\ln f)}$$

Integrating,

$$\boxed{\mu = \mu^\circ + RT \ln f}$$

This is the fundamental equation used for real gases.

Comparison of Ideal and Real Gases

Ideal Gas	Real Gas
$\mu = \mu^\circ + RT \ln P$	$\mu = \mu^\circ + RT \ln f$
Pressure is sufficient.	Fugacity replaces pressure.
Obeys ideal gas equation.	Shows deviation from ideal behavior.

Fugacity Coefficient

To compare fugacity with pressure, Lewis defined the **fugacity coefficient**, represented by ϕ.

$$\boxed{\phi = \frac{f}{P}}$$

or

$$\boxed{f = \phi P}$$

The value of the fugacity coefficient indicates the deviation of a gas from ideal behavior.

- $\phi = 1$

  : Ideal gas.

- $\phi < 1$

  : Attractive forces dominate; fugacity is less than pressure.

- $\phi > 1$

  : Repulsive forces dominate; fugacity is greater than pressure.

Limiting Condition

At very low pressure, all gases behave ideally.

Hence,

$$\boxed{\lim_{P \to 0} f = P}$$

or

$$\boxed{\lim_{P \to 0} \phi = 1}$$

This limiting condition is the basis for determining fugacity experimentally.

Key Formulae

Chemical potential of an ideal gas:

$$\boxed{\mu = \mu^\circ + RT \ln P}$$

Chemical potential of a real gas:

$$\boxed{\mu = \mu^\circ + RT \ln f}$$

Fugacity coefficient:

$$\boxed{\phi = \frac{f}{P}}$$

Relation between fugacity and pressure:

$$\boxed{f = \phi P}$$

Conclusion

The thermodynamic determination of fugacity is based on the relationship between chemical potential and Gibbs free energy. For an ideal gas, pressure directly determines the chemical potential. However, for a real gas, pressure is replaced by fugacity, which accurately accounts for intermolecular interactions. Thus, fugacity provides the correct thermodynamic description of real gases and forms the basis for equilibrium calculations in physical chemistry.

Determination of Fugacity Using the Compressibility Factor (Z)

In the previous section, it was shown that the chemical potential of a real gas is expressed as

$$d\mu = RT\, d\ln f$$

whereas from the fundamental equation of thermodynamics, for one mole of any gas at constant temperature,

$$d\mu = V\, dP$$

Since both equations represent the change in chemical potential under the same conditions, they can be equated.

$$V\, dP = RT\, d\ln f$$

Therefore,

$$\boxed{d\ln f = \frac{V}{RT}\, dP}$$

Compressibility Factor

For a real gas, the molar volume is expressed in terms of the compressibility factor, **Z**.

The compressibility factor is defined as

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

Hence,

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

Substitution in the Fugacity Equation

Substituting the value of molar volume,

$$d\ln f = \frac{ZRT}{PRT}\,dP$$

The terms RT cancel,

$$d\ln f = \frac{Z}{P}\,dP$$

Now write

$$Z = (Z-1) + 1$$

Therefore,

$$d\ln f = \frac{Z-1}{P}\,dP + \frac{1}{P}\,dP$$

Since

$$\frac{1}{P}\,dP = d(\ln P)$$

Hence,

$$d\ln f = d\ln P + \frac{Z-1}{P}\,dP$$

Rearranging,

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

Using the logarithmic identity,

$$\ln f - \ln P = \ln\left(\frac{f}{P}\right)$$

Therefore,

$$\boxed{d\ln\left(\frac{f}{P}\right) = \frac{Z-1}{P}\,dP}$$

Integration

Integrating both sides from zero pressure to pressure P,

$$\int_0^P d\ln\left(\frac{f}{P}\right) = \int_0^P \frac{Z-1}{P}\,dP$$

Thus,

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

Since

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

the above equation may also be written as

$$\boxed{\ln\phi = \int_0^P \frac{Z-1}{P}\,dP}$$

Finally,

$$\boxed{\phi = \exp\left[\int_0^P \frac{Z-1}{P}\,dP\right]}$$

and therefore,

$$\boxed{f = P\exp\left[\int_0^P \frac{Z-1}{P}\,dP\right]}$$

Physical Significance

- If $Z = 1$, the integral becomes zero.
- Hence, $\phi = 1$ and $f = P$.
- This represents ideal gas behaviour.

- If $Z < 1$, attractive forces dominate and $f < P$.
- If $Z > 1$, repulsive forces dominate and $f > P$.

Advantages of this Method

- Requires only experimentally measured compressibility-factor data.
- Applicable to almost all real gases.
- Provides accurate fugacity values over a wide pressure range.
- Frequently used in phase-equilibrium and chemical-equilibrium calculations.

Important Formulae

Compressibility factor:

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

Fugacity coefficient:

$$\boxed{\phi = \frac{f}{P}}$$

Fundamental fugacity equation:

$$\boxed{\ln \phi = \int_0^P \frac{Z-1}{P}\, dP}$$

Fugacity:

$$\boxed{f = P \exp\left[\int_0^P \frac{Z-1}{P}\, dP\right]}$$

Determination of Fugacity Using the Virial Equation of State

In the previous section, the fugacity coefficient was expressed in terms of the compressibility factor as

$$\boxed{\ln \phi = \int_0^P \frac{Z-1}{P}\, dP}$$

To evaluate this integral, an expression for the compressibility factor is required. One of the most useful equations describing the behaviour of real gases at low and moderate pressures is the **Virial Equation of State**.

Virial Equation of State

The virial equation expresses the compressibility factor as a power series of pressure.

$$\boxed{Z = 1 + BP + CP^2 + DP^3 + \cdots}$$

where

- B = Second virial coefficient
- C = Third virial coefficient
- D = Fourth virial coefficient

The virial coefficients depend only on temperature and provide information about intermolecular interactions.

- The second virial coefficient mainly represents pairwise molecular interactions.
- The third virial coefficient represents interactions among three molecules.
- Higher virial coefficients account for more complex molecular interactions.

Substitution into the Fugacity Equation

The fundamental equation is

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

Substitute the virial equation,

$$Z - 1 = BP + CP^2 + DP^3 + \cdots$$

Therefore,

$$\ln \phi = \int_0^P \frac{BP + CP^2 + DP^3 + \cdots}{P}\, dP$$

Dividing each term by P,

$$\ln \phi = \int_0^P (B + CP + DP^2 + \cdots)\, dP$$

Integration

Integrating term by term,

$$\ln \phi = BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots$$

Hence,

$$\boxed{\ln \phi = BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots}$$

Expression for Fugacity Coefficient

Taking the exponential of both sides,

$$\boxed{\phi = e^{\left(BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots\right)}}$$

Expression for Fugacity

Since

$$f = \phi P$$

therefore,

$$\boxed{f = Pe^{\left(BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots\right)}}$$

Low-Pressure Approximation

At sufficiently low pressure, the higher-order virial terms become extremely small and may be neglected.

Therefore,

$$Z = 1 + BP$$

Hence,

$$\boxed{\ln \phi = BP}$$

or

$$\boxed{\phi = e^{BP}}$$

Thus,

$$\boxed{f = Pe^{BP}}$$

This simplified equation is widely used for gases at low pressures.

Physical Interpretation of Virial Coefficients

- If **B = 0**, the gas behaves ideally.
- If **B < 0**, attractive intermolecular forces dominate, causing the gas to be more compressible than an ideal gas.
- If **B > 0**, repulsive intermolecular forces dominate, making the gas less compressible.
- As pressure increases, higher virial coefficients become increasingly important.

Advantages of the Virial Equation Method

- Provides an accurate description of gases at low and moderate pressures.
- Relates fugacity directly to experimentally determined virial coefficients.
- Explains the effect of intermolecular forces quantitatively.
- Frequently used in thermodynamic and phase-equilibrium calculations.

Limitations

- Not suitable for very high pressures.
- Requires experimental values of virial coefficients.
- Many virial coefficients are needed for highly accurate calculations at high pressure.

Important Formulae

Virial equation:

$$\boxed{Z = 1 + BP + CP^2 + DP^3 + \cdots}$$

Fugacity coefficient:

$$\boxed{\ln \phi = BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots}$$

Fugacity:

$$\boxed{f = Pe^{\left(BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots\right)}}$$

Conclusion

The virial equation provides a convenient method for determining the fugacity of real gases. By substituting the virial expression for the compressibility factor into the fundamental fugacity equation, the fugacity coefficient and fugacity can be calculated directly. The method is particularly useful for gases at low and moderate pressures and forms the basis of many practical thermodynamic calculations.