

Thermodynamic Determination of Fugacity

Fugacity is an effective pressure introduced to describe the thermodynamic behavior of real gases. Since fugacity cannot be measured directly, it is determined from the fundamental laws of thermodynamics. The derivation begins with the differential form of Gibbs free energy and finally establishes a relationship between chemical potential and pressure. In this part, the derivation is carried out under isothermal conditions (constant temperature).

Fundamental Equation of Gibbs Free Energy

For a closed system containing a fixed amount of substance, the differential form of Gibbs free energy is

$$dG = VdP - SdT \quad (1)$$

where,

- **G** = Gibbs free energy
- **V** = Volume of the system
- **P** = Pressure
- **S** = Entropy
- **T** = Absolute temperature

Equation (1) shows that the change in Gibbs free energy depends upon changes in both pressure and temperature.

Condition of Constant Temperature

The thermodynamic determination of fugacity is carried out under isothermal conditions. Therefore, the temperature of the system remains constant throughout the process.

Hence,

$$dT = 0 \quad (2)$$

Substituting Eq. (2) into Eq. (1),

$$dG = VdP - S(0)$$

Since

$$S(0) = 0$$

therefore,

$$dG = VdP \quad (3)$$

Equation (3) indicates that under isothermal conditions, the change in Gibbs free energy depends only upon the change in pressure.

Chemical Potential of a Pure Substance

The chemical potential is defined as the partial molar Gibbs free energy of a component. Mathematically,

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T, P} \quad (4)$$

where,

- μ = Chemical potential
- G = Gibbs free energy
- n = Number of moles

Equation (4) states that the chemical potential is the increase in Gibbs free energy when one mole of a substance is added to the system while keeping temperature and pressure constant.

For one mole of a pure substance,

$$n = 1$$

Therefore, the total Gibbs free energy becomes equal to the chemical potential.

$$G = \mu \quad (5)$$

Differentiating Eq. (5),

$$dG = d\mu \quad (6)$$

Now substitute Eq. (6) into Eq. (3).

From Eq. (3),

$$dG = VdP$$

Replacing dG by $d\mu$ using Eq. (6),

$$d\mu = VdP \quad (7)$$

Equation (7) is a very important thermodynamic relation. It states that, at constant temperature, the infinitesimal change in chemical potential is equal to the product of the molar volume and the infinitesimal change in pressure.

It should be noted that Eq. (7) is completely general. It is applicable to both ideal gases and real gases because no assumption regarding the equation of state has yet been introduced. The only assumption made so far is that the temperature remains constant.

Application to an Ideal Gas

To proceed further, an expression for the molar volume is required. For an ideal gas, the ideal gas equation is

$$PV = nRT \quad (8)$$

For one mole of gas,

$$n = 1$$

Therefore, Eq. (8) becomes

$$PV = RT \quad (9)$$

Rearranging Eq. (9) to obtain the molar volume,

$$V = \frac{RT}{P} \quad (10)$$

Equation (10) is valid only for an ideal gas because it has been obtained directly from the ideal gas equation.

Substituting Eq. (10) into Eq. (7),

$$d\mu = \left(\frac{RT}{P} \right) dP$$

or,

$$d\mu = \frac{RT}{P} dP \quad (11)$$

Since the derivation is carried out at constant temperature, both **R** and **T** remain constant and may be taken outside the differential term.

Hence,

$$d\mu = RT \left(\frac{dP}{P} \right) \quad (12)$$

From elementary calculus,

$$d(\ln P) = \frac{dP}{P} \quad (13)$$

Substituting Eq. (13) into Eq. (12),

$$d\mu = RT d(\ln P) \quad (14)$$

Equation (14) gives the variation of chemical potential with pressure for an ideal gas. In the next part, Eq. (14) will be integrated to obtain the expression for the chemical potential of an ideal gas. It will then be shown why this equation cannot be applied to real gases, leading to the introduction of fugacity.

In the previous section, the following equation was obtained for an ideal gas:

$$d\mu = RT d(\ln P) \quad (15)$$

This equation gives the differential relationship between the chemical potential and the pressure of an ideal gas. The next step is to integrate this equation to obtain the expression for the chemical potential.

Integration of the Chemical Potential Equation

Equation (15) is

$$d\mu = RT d(\ln P)$$

Since the derivation is carried out under isothermal conditions, the temperature remains constant. Therefore, both **R** and **T** are constants and may be taken outside the integration.

Integrating both sides,

$$\int d\mu = \int RT d(\ln P)$$

or,

$$\int d\mu = RT \int d(\ln P) \quad (16)$$

The integration is carried out between a standard state and any arbitrary state of the gas.

For the chemical potential,

$$\mu^\circ \longrightarrow \mu$$

and for the pressure,

$$P^\circ \longrightarrow P$$

Therefore, Eq. (16) becomes

$$\int_{\mu^\circ}^{\mu} d\mu = RT \int_{P^\circ}^P d(\ln P) \quad (17)$$

On integrating the left-hand side,

$$\mu - \mu^\circ$$

and on integrating the right-hand side,

$$RT[\ln P - \ln P^\circ]$$

Hence,

$$\mu - \mu^\circ = RT(\ln P - \ln P^\circ) \quad (18)$$

Using the logarithmic identity,

$$\ln a - \ln b = \ln \left(\frac{a}{b} \right) \quad (19)$$

Eq. (18) becomes

$$\mu - \mu^\circ = RT \ln \left(\frac{P}{P^\circ} \right) \quad (20)$$

Rearranging Eq. (20),

$$\boxed{\mu = \mu^\circ + RT \ln \left(\frac{P}{P^\circ} \right)} \quad (21)$$

Equation (21) represents the chemical potential of an ideal gas at pressure **P**.

Choice of Standard State

Generally, the standard pressure is chosen as

$$P^\circ = 1 \text{ bar} \quad (22)$$

Since one bar is the standard pressure, the ratio

$$\frac{P}{P^\circ} = \frac{P}{1} = P$$

becomes numerically equal to the pressure expressed relative to the standard state. Therefore, Eq.

(21) is usually written in the simpler form

$$\mu = \mu^{\circ} + RT \ln P \quad (23)$$

Equation (23) is the fundamental expression for the chemical potential of an **ideal gas**. It shows that the chemical potential increases logarithmically with pressure.

Limitation of Equation (23)

Equation (23) has been derived using the ideal gas equation,

$$PV = RT \quad (24)$$

This equation assumes that

- gas molecules have negligible volume,
- no intermolecular attractive or repulsive forces exist, and
- the gas behaves ideally under all conditions.

These assumptions are valid only at low pressure and high temperature. Under ordinary conditions, particularly at high pressure, real gases deviate from ideal behavior because molecules possess finite volume and experience intermolecular forces.

Consequently, Eq. (23) cannot accurately describe the chemical potential of a real gas.

In other words, for a real gas,

$$\mu \neq \mu^{\circ} + RT \ln P \quad (25)$$

Therefore, pressure alone is no longer a correct measure of the thermodynamic state of a real gas.

Need for Fugacity

Since pressure fails to represent the thermodynamic behavior of a real gas, Lewis introduced a new thermodynamic quantity called **fugacity**. Fugacity has the same dimensions as pressure and represents the effective pressure of a real gas. By replacing pressure with fugacity, the chemical potential equation becomes applicable to real gases.

The derivation of this new equation will be carried out in the next section.

In the previous section, it was shown that the equation

$$\mu = \mu^{\circ} + RT \ln P \quad (26)$$

is valid only for an ideal gas. For a real gas, this equation cannot be used because pressure is not the true measure of the thermodynamic state of the gas. Therefore, a new quantity called **fugacity** is introduced.

Introduction of Fugacity

Lewis proposed that the pressure term in Eq. (26) should be replaced by a corrected pressure called **fugacity**, denoted by **f**. Fugacity represents the effective pressure of a real gas and accounts for the deviation of the gas from ideal behavior.

Therefore, the chemical potential equation for a real gas is written as

$$\mu = \mu^{\circ} + RT \ln f \quad (27)$$

Equation (27) has exactly the same mathematical form as the ideal gas equation, except that pressure has been replaced by fugacity.

Differential Form of the Fugacity Equation

To obtain the differential relationship between chemical potential and fugacity, differentiate Eq. (27).

Differentiating the left-hand side,

$$\frac{d\mu}{d\mu} = 1$$

Therefore,

$$d\mu = d(\mu)$$

Since the standard chemical potential μ° is constant at constant temperature,

$$d\mu^\circ = 0 \quad (28)$$

Differentiating Eq. (27),

$$d\mu = d(\mu^\circ) + d(RT \ln f) \quad (29)$$

Substituting Eq. (28) into Eq. (29),

$$d\mu = d(RT \ln f) \quad (30)$$

Since the derivation is carried out under isothermal conditions,

$$dT = 0 \quad (31)$$

Hence, both **R** and **T** are constants and may be taken outside the differentiation.

Therefore,

$$d\mu = RT d(\ln f) \quad (32)$$

Equation (32) is the **fundamental thermodynamic equation of fugacity**. It states that, at constant temperature, the infinitesimal change in chemical potential is proportional to the infinitesimal change in the natural logarithm of fugacity.

Comparison with the Ideal Gas Equation

For an ideal gas,

$$d\mu = RT d(\ln P) \quad (33)$$

For a real gas,

$$d\mu = RT d(\ln f) \quad (34)$$

Comparing Eqs. (33) and (34), it is evident that fugacity plays exactly the same role for a real gas as pressure does for an ideal gas. Thus, fugacity may be regarded as the effective pressure of a real gas.

Limiting Condition

At very low pressure, intermolecular forces become negligible and every real gas approaches ideal behavior.

Hence,

$$\lim_{P \rightarrow 0} f = P \quad (35)$$

or,

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1 \quad (36)$$

Equation (36) is known as the **limiting condition of fugacity**. It shows that fugacity becomes equal to pressure in the limit of zero pressure.

Significance of the Thermodynamic Determination of Fugacity

- The derivation establishes a direct relationship between chemical potential and fugacity.
- It proves that fugacity replaces pressure in thermodynamic equations for real gases.
- The equation is valid for all real gases irrespective of the equation of state.
- It forms the basis for the determination of fugacity using compressibility factor, virial equation, and other equations of state.
- It is widely used in phase equilibrium, chemical equilibrium, and high-pressure thermodynamics.

Important Equations

For an ideal gas,

$$\mu = \mu^\circ + RT \ln P$$

For a real gas,

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

Differential form,

$$d\mu = RT d(\ln f)$$

Limiting condition,

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

Conclusion

The thermodynamic determination of fugacity is based on the concept of chemical potential. Beginning with the Gibbs free energy equation, the chemical potential of an ideal gas was first derived. Since this expression failed for real gases, pressure was replaced by fugacity, resulting in the fundamental equation

$$d\mu = RT d(\ln f)$$

and its integrated form

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

These equations provide the thermodynamic foundation for all subsequent methods of calculating fugacity, such as the compressibility factor method and the virial equation method.