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An Alternative Method of Introducing Fugacity

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Abstract: In current textbooks fugacity is introduced according to its differential or integral mathematical formulation. In this article an alternative method of explanation is offered. It is suggested that the real state of a pure gas can be described by comparing it to a hypothetical idealized state. The differences between these two states can then be expressed in terms of a function, Φ, defined as $\Phi(T,P) = \mu_{real}(T,P) - \mu_{ideal}(T,P)$ where μ_{real} and μ_{ideal} are the chemical potentials of the gas in its real and ideal states, respectively**.** The function Φ is a molar excess quantity and is expressed as $\Phi(T,P) = RT\ln\phi$ where ϕ is the fugacity coefficient. This approach introduces fugacity deductively through the Φ function, which leads to ϕ, the fugacity coefficient. This method is also appropriate for introducing the activity of solution components and the fugacity of a real gas in gaseous mixtures.

Most basic textbooks introduce the fugacity, *f*, of a pure real gas mathematically, either according to the Lewis differential formulation [1–4],

$$d\mu_f = RTd\ln f \tag{1}$$

its integrated form [5–8],

$$\mu_f = \mu^0 + RT\ln f \tag{2}$$

or through the absolute activity [9]. In equations 1 and 2, μ_f is the chemical potential, *R* is the gas constant, and *T* is the absolute temperature. IUPAC suggests a definition derived from the absolute activity [10]. The basic definition is associated with one of the following relationships: $f \rightarrow P$ or $f/P \rightarrow 1$ when $P \rightarrow 0$.

There is, however, a certain difficulty in presenting this concept in the classroom. Even though students grasp the necessity of modifying the chemical potential expression when moving from an ideal gas to a real one, they don't readily understand why *f* is introduced into these relations. Consequently, the teacher frequently has to justify its introduction by pointing out the simplicity of the resulting μ_{real} expression and its validity for every gas, regardless of the equation of state used. This justification is not always convincing; however, and introduction of *f* still appears to be somewhat arbitrary. Because of this difficulty, I suggest a deductive way of introducing fugacity.

Having established the relationship for the chemical potential for an ideal gas:

$$\mu_{ideal}(T,P) = \mu^0_{ideal}(T) + RT\ln P$$

where the units of *P* depend on the defined standard pressure, one can explain that the energy of a gas in its real state is different from that in a hypothetical idealized state at the same temperature and pressure. The discrepancy between these energies can be expressed in terms of a function, Φ, the value of which depends on the values of *T* and *P*. The function,Φ, is an excess quantity, defined as the difference between the chemical potentials of the gas in the ideal and real states:

$$\Phi(T,P) = \mu_{real}(T,P) - \mu_{ideal}(T,P) \tag{3}$$

What are the properties of $\Phi(T,P)$?

- It is a molar energy, because μ is a molar quantity.
- It can be negative or positive depending on the real behavior of the gas with respect to the idealized state at the same temperature and pressure.
- It approaches zero as *P* approaches zero.

Φ can be expressed as $RT\ln\phi$, where *RT* is a molar energy and $\ln\phi$ is a dimensionless function that can be negative or positive and that tends to zero as *P* approaches zero. ϕ is called the fugacity coefficient, and it approaches 1 as *P* approaches zero. Equation 3 becomes:

$$\mu_{real}(T,P) = \mu_{ideal}(T,P) + RT\ln\phi \tag{4}$$

which leads by differentiation to the well-known relation:

$$\ln\phi = \int_0^P \left(\frac{V_{real}}{RT} - \frac{1}{P}\right) dP$$

Substituting for μ_{ideal} in equation 4 leads to:

$$\mu_{real}(T,P) = \mu^0_{ideal}(T) + RT\ln(P\phi)$$

or

$$\mu_{real}(T,P) = \mu^0_{ideal}(T) + RT\ln f$$

where *f* equals $P\phi$ by definition.

The fugacity of a pure real gas is introduced through the Φ function, with subsequent identification of the fugacity coefficient. This scientific approach, which is intended to help students better understand the concept of fugacity, consists of describing the behavior of real gases (which is generally complex and diversified) by reference to a fictitious ideal gas (which is easier to manipulate). This approach can also be used to introduce the activity of a component in a solution or the fugacity of a real gas in a gaseous mixture by referring to a hypothetical idealized state having the same temperature, pressure, and composition as the real one. It also corroborates the idea, developed elsewhere [11], that fugacity has no physical meaning.

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