

Fugacity

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Fugacity is a measure of [chemical potential](#) in the form of 'adjusted pressure.' It directly relates to the tendency of a substance to prefer one phase (liquid, solid, gas) over another. At a fixed [temperature](#) and [pressure](#), water will have a different fugacity for each phase. The phase with the lowest fugacity will be the most favorable; the substance minimizes [Gibbs free energy](#). The concept of fugacity was introduced by American chemist [Gilbert N. Lewis](#) in his paper "The osmotic pressure of concentrated solutions, and the laws of the perfect solution." ^[1]

Applications

As well as predicting the preferred phase of a single substance, fugacity is also useful for multi-component equilibrium involving any combination of solid, liquid and gas equilibria. It is useful as an engineering tool for predicting the final phase and reaction state of multi-component mixtures at various temperatures and pressures without doing the actual lab test.

Fugacity is not a physical property of a substance; rather it is a calculated property which is intrinsically related to [chemical potential](#). When a system approaches the ideal gaseous state (very low pressure), chemical potential approaches negative infinity, which for the purposes of mathematical modeling is undesirable. Under the same conditions, fugacity approaches zero and the fugacity coefficient (defined below) approaches 1. Thus, fugacity is much easier to manipulate mathematically.

Definition from Statistical Mechanics

In statistical mechanics, the fugacity is one of the parameters that define the [grand canonical ensemble](#) (a system that may exchange particles with the environment). It represents the effort of adding an additional particle to the system. Its logarithm, multiplied by $k_B T$, is the [chemical potential](#), μ

$$\mu = k_B T \log f$$

where, k_B is the [Boltzmann constant](#), and T is the temperature. (More commonly, the fugacity is denoted by symbol z instead of f used here.) In other words, fugacity

$$f = \exp(\mu/k_B T).$$

The grand canonical ensemble is a weighted sum over systems with different numbers of particles. Its [partition function](#), $Z(f, V, T)$ is defined as

$$Z(f, V, T) = \sum_{N=0}^{\infty} f^N Z(N, V, T)$$

where N is the number of particles of the system, and the canonical partition function is defined for a system with a fixed number of particles N , at temperature T , of volume V as,

$$Z(N, V, T) = \sum \exp\left(-\frac{E}{k_B T}\right).$$

Here the summation is performed over all microscopic states, and E is the energy of each microscopic state. The position of fugacity in grand canonical ensemble is similar to that of temperature in the [canonical ensemble](#) as a weighting factor.

Many physically important quantities can be obtained by differentiating the partition function. A most important relation is about the average number of particles of the grand canonical ensemble,

$$\langle N \rangle = f \frac{\partial}{\partial f} \ln Z(f, V, T)$$

while the partition function is related to the pressure P of the system as $PV = k_B T \ln[Z(f, V, T)]$.

Technical detail

Fugacity is a [state function](#) of [matter](#) at fixed [temperature](#). It only becomes useful when dealing with substances other than an [ideal gas](#). For an [ideal gas](#), fugacity is equal to [pressure](#). In the real world, though under low pressures and high temperatures some substances approach ideal behavior, no substance is truly ideal, so we use fugacity not only to describe non-ideal gases, but [liquids](#) and [solids](#) as well.

The **fugacity coefficient** is defined as the ratio fugacity/pressure. For [gases](#) at low pressures (where the [ideal gas law](#) is a good approximation), fugacity is roughly equal to pressure. Thus, for an ideal gas, the ratio $\phi = f/P$ between fugacity f and pressure P (the **fugacity coefficient**) is equal to 1. This ratio can be thought of as 'how closely the substance behaves like an ideal gas,' based on how far it is from 1.

For a given temperature T , the fugacity f satisfies the following differential relation:

$$d \ln \frac{f}{f_0} = \frac{dG}{RT} = \frac{\bar{V} dP}{RT}$$

where G is the [Gibbs free energy](#), R is the [gas constant](#), $\bar{V}$ is the fluid's [molar volume](#), and f_0 is a reference fugacity which is generally taken as that of an ideal gas at 1 bar. For an ideal gas, when $f = P$, this equation reduces to the [ideal gas law](#).

Thus, for any two mutually-[isothermal](#) physical states, represented by subscripts 1 and 2, the ratio of the two fugacities is as follows:

$$\frac{f_2}{f_1} = \exp\left(\frac{1}{RT} \int_{G_1}^{G_2} dG\right) = \exp\left(\frac{1}{RT} \int_{P_1}^{P_2} \bar{V} dP\right)$$

Fugacity and chemical potential

For every pure substance, we have the relation $dG = -SdT + VdP$ for [Gibbs free energy](#) and we can integrate this expression remembering the chemical potential is a function of T and P . We must also set a [reference state](#). In this case, for an ideal gas the only reference state will be the pressure, and we set $P = 1$ bar.

$$\int_{\mu^\circ}^{\mu} d\mu = \int_{P^\circ}^P \bar{V} dP$$

Now, for the ideal gas $\bar{V} = \frac{RT}{P}$

$$\mu - \mu^\circ = \int_{P^\circ}^P \frac{RT}{P} dP = RT \ln \frac{P}{P^\circ}$$

Reordering, we get

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

Which gives the chemical potential for an ideal gas in an isothermal process, where the reference state is $P=1$ bar.

For a real gas, we cannot calculate $\int_{P^\circ}^P \bar{V} dP$ because we do not have a simple expression for a real gas' molar volume. On the other hand, even if we did have one expression for it (we could use the [Van der Waals equation](#), Redlich-Kwong or any other [equation of state](#)), it would depend on the substance being studied and would be therefore of a very limited usability.

We would like the expression for a real gas' chemical potential to be similar to the one for an ideal gas.

We can define a magnitude, called fugacity, so that the chemical potential for a real gas becomes

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

with a given reference state (discussed later).

We can see that for an ideal gas, it must be $f = P$.

But for $P \rightarrow 0$, every gas is an ideal gas. Therefore, fugacity must obey the [limit](#) equation

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

We determine f by defining a function

$$\Phi = \frac{P\bar{V} - RT}{P}$$

We can obtain values for Φ experimentally easily by measuring V , T and P . (note that for an ideal gas, $\Phi = 1$).

From the expression above we have

$$\bar{V} = \frac{RT}{P} + \Phi$$

We can then write

$$\int_{\mu^\circ}^{\mu} d\mu = \int_{P^\circ}^P \bar{V} dP = \int_{P^\circ}^P \frac{RT}{P} dP + \int_{P^\circ}^P \Phi dP$$

where

$$\mu = \mu^\circ + RT \ln \frac{P}{P^\circ} + \int_{P^\circ}^P \Phi dP$$

Since the expression for an ideal gas was chosen to be $\mu = \mu^\circ + RT \ln \frac{f}{f^\circ}$, we must have

$$\mu^\circ + RT \ln \frac{f}{f^\circ} = \mu^\circ + RT \ln \frac{P}{P^\circ} + \int_{P^\circ}^P \Phi dP$$

$$\Rightarrow RT \ln \frac{f}{f^\circ} - RT \ln \frac{P}{P^\circ} = \int_{P^\circ}^P \Phi dP$$

$$RT \ln \frac{f P^\circ}{P f^\circ} = \int_{P^\circ}^P \Phi dP$$

Suppose we choose $P \rightarrow 0$. Since $\lim_{P \rightarrow 0} f = P$, we obtain

$$RT \ln \frac{f}{P} = \int_0^P \Phi dP$$

The fugacity coefficient will then verify

$$\ln \phi = \frac{1}{RT} \int_0^P \Phi dP$$

The integral can be evaluated via graphical integration if we measure experimentally values for ϕ while varying P . We can then find the fugacity coefficient of a gas at a given pressure P and calculate

$$f = \phi P$$

The reference state for the expression of a real gas' chemical potential is taken to be "ideal gas, at $P = 1$ bar and work T ". Since in the reference state the gas is considered to be ideal (it is an hypothetical reference state), we can write that for the real gas

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

Alternative methods for calculating fugacity

If we suppose that Φ is constant between 0 and P (assuming it is possible to do this approximation), we have

$$\frac{f}{P} = e^{\frac{\Phi P}{RT}}$$

Expanding in [Taylor series](#) about 0,

$$\frac{f}{P} \approx 1 + \frac{\Phi P}{RT} = 1 + \frac{1}{RT} \left(\frac{P\bar{V} - RT}{P} \right) P = 1 + \frac{P\bar{V}}{RT} - 1 = \frac{P\bar{V}}{RT}$$

Finally, we get

$$f \approx \frac{P^2\bar{V}}{RT}$$

This formula allows us to calculate quickly the fugacity of a real gas at ***P***, ***T***, given a value for *V* (which could be determined using any [equation of state](#)), if we suppose is constant between 0 and ***P***.

We can also use [generalized charts](#) for gases in order to find the fugacity coefficient for a given [reduced temperature](#).

Fugacity could be considered a “corrected pressure” for the real gas, but should *never* be used to replace pressure in equations of state (or any other equations for that matter). That is, it is *false* to write expressions such as ***fV*** = ***nRT***. Fugacity is strictly a tool, conveniently defined so that the chemical potential equation for a real gas turns out to be similar to the equation for an ideal gas.

References

1. [^](#) *J. Am. Chem. Soc.* **30**, 668-683 (1908)