

5.2: Chemical Potential and Fugacity

The **chemical potential**, μ , of a pure substance has as one of its definitions (Sec. 5.5)

$$\mu \stackrel{\text{def}}{=} G_{\text{m}} = \frac{G}{n} \quad (7.8.1)$$

(pure substance)

That is, μ is equal to the molar Gibbs energy of the substance at a given temperature and pressure. (Section 9.2.6 will introduce a more general definition of chemical potential that applies also to a constituent of a mixture.) The chemical potential is an intensive state function.

The total differential of the Gibbs energy of a fixed amount of a pure substance in a single phase, with T and p as independent variables, is $dG = -S dT + V dp$ (Eq. 5.4.4). Dividing both sides of this equation by n gives the total differential of the chemical potential with these same independent variables:

$$d\mu = -S_{\text{m}} dT + V_{\text{m}} dp \quad (7.8.2)$$

(pure substance, $P=1$)

(Since all quantities in this equation are intensive, it is not necessary to specify a closed system; the amount of the substance in the system is irrelevant.)

We identify the coefficients of the terms on the right side of Eq. 7.8.2 as the partial derivatives

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -S_{\text{m}} \quad (7.8.3)$$

(pure substance, $P=1$)

and

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V_{\text{m}} \quad (7.8.4)$$

(pure substance, $P=1$)

Since V_{m} is positive, Eq. 7.8.4 shows that the chemical potential increases with increasing pressure in an isothermal process.

The **standard chemical potential**, μ° , of a pure substance in a given phase and at a given temperature is the chemical potential of the substance when it is in the standard state of the phase at this temperature and the standard pressure p° .

There is no way we can evaluate the absolute value of μ at a given temperature and pressure, or of μ° at the same temperature—at least not to any useful degree of precision. The values of μ and μ° include the molar internal energy whose absolute value can only be calculated from the Einstein relation; see Sec. 2.6.2. We can however measure or calculate the *difference* $\mu - \mu^\circ$. The general procedure is to integrate $d\mu = V_{\text{m}} dp$ (Eq. 7.8.2 with dT set equal to zero) from the standard state at pressure p° to the experimental state at pressure p' :

$$\mu(p') - \mu^\circ = \int_{p^\circ}^{p'} V_{\text{m}} dp \quad (7.8.5)$$

(constant T)

7.8.1 Gases

For the standard chemical potential of a gas, this e-book will usually use the notation $\mu^\circ(\text{g})$ to emphasize the choice of a *gas* standard state.

An *ideal gas* is in its standard state at a given temperature when its pressure is the standard pressure. We find the relation of the chemical potential of an ideal gas to its pressure and its standard chemical potential at the same temperature by setting V_{m} equal to RT/p in Eq. 7.8.5: $\mu(p') - \mu^\circ = \int_{p^\circ}^{p'} (RT/p) dp = RT \ln(p'/p^\circ)$. The general relation for μ as a function of p , then, is

$$\mu = \mu^\circ(\text{g}) + RT \ln \frac{p}{p^\circ} \quad (7.8.6)$$

(pure ideal gas, constant T)

This function is shown as the dashed curve in Fig. 7.6.

If a gas is *not* an ideal gas, its standard state is a hypothetical state. The **fugacity**, f , of a real gas (a gas that is not necessarily an ideal gas) is defined by an equation with the same form as Eq. 7.8.6:

$$\mu = \mu^\circ(\text{g}) + RT \ln \frac{f}{p^\circ} \quad (7.8.7)$$

(pure gas)

or

$$f \stackrel{\text{def}}{=} p^\circ \exp \left[\frac{\mu - \mu^\circ(\text{g})}{RT} \right] \quad (7.8.8)$$

(pure gas)

Note that fugacity has the dimensions of pressure. Fugacity is a kind of effective pressure. Specifically, it is the pressure that the hypothetical ideal gas (the gas with intermolecular forces “turned off”) would need to have in order for its chemical potential at the given temperature to be the same as the chemical potential of the real gas (see point C in Fig. 7.6). If the gas is an ideal gas, its fugacity is equal to its pressure.

To evaluate the fugacity of a real gas at a given T and p , we must relate the chemical potential to the pressure–volume behavior. Let μ' be the chemical potential and f' be the fugacity at the pressure p' of interest; let μ'' be the chemical potential and f'' be the fugacity of the same gas at some low pressure p'' (all at the same temperature). Then we use Eq. 7.8.5 to write $\mu' - \mu^\circ(\text{g}) = RT \ln(f'/p^\circ)$ and $\mu'' - \mu^\circ(\text{g}) = RT \ln(f''/p^\circ)$, from which we obtain

$$\mu' - \mu'' = RT \ln \frac{f'}{f''} \quad (7.8.9)$$

By integrating $d\mu = V_m dp$ from pressure p'' to pressure p' , we obtain

$$\mu' - \mu'' = \int_{\mu''}^{\mu'} d\mu = \int_{p''}^{p'} V_m dp \quad (7.8.10)$$

Equating the two expressions for $\mu' - \mu''$ and dividing by RT gives

$$\ln \frac{f'}{f''} = \int_{p''}^{p'} \frac{V_m}{RT} dp \quad (7.8.11)$$

In principle, we could use the integral on the right side of Eq. 7.8.11 to evaluate f' by choosing the lower integration limit p'' to be such a low pressure that the gas behaves as an ideal gas and replacing f'' by p'' . However, because the integrand V_m/RT becomes very large at low pressure, the integral is difficult to evaluate. We avoid this difficulty by subtracting from the preceding equation the identity

$$\ln \frac{p'}{p''} = \int_{p''}^{p'} \frac{dp}{p} \quad (7.8.12)$$

which is simply the result of integrating the function $1/p$ from p'' to p' . The result is

$$\ln \frac{f'p''}{f''p'} = \int_{p''}^{p'} \left(\frac{V_m}{RT} - \frac{1}{p} \right) dp \quad (7.8.13)$$

Now we take the limit of both sides of Eq. 7.8.13 as p'' approaches zero. In this limit, the gas at pressure p'' approaches ideal-gas behavior, f'' approaches p'' , and the ratio $f'p''/f''p'$ approaches f'/p' :

$$\ln \frac{f'}{p'} = \int_0^{p'} \left(\frac{V_m}{RT} - \frac{1}{p} \right) dp \quad (7.8.14)$$

The integrand $(V_m/RT - 1/p)$ of this integral approaches zero at low pressure, making it feasible to evaluate the integral from experimental data.

The **fugacity coefficient** ϕ of a gas is defined by

$$\phi \stackrel{\text{def}}{=} \frac{f}{p} \quad \text{or} \quad f = \phi p \quad (7.8.15)$$

(pure gas)

The fugacity coefficient at pressure p' is then given by Eq. 7.8.14:

$$\ln \phi(p') = \int_0^{p'} \left(\frac{V_m}{RT} - \frac{1}{p} \right) dp \quad (7.8.16)$$

(pure gas, constant T)

The isothermal behavior of real gases at low to moderate pressures (up to at least 1 bar) is usually adequately described by a two-term equation of state of the form given in Eq. 2.2.8:

$$V_m \approx \frac{RT}{p} + B \quad (7.8.17)$$

Here B is the second virial coefficient, a function of T . With this equation of state, Eq. 7.8.16 becomes

$$\ln \phi \approx \frac{Bp}{RT} \quad (7.8.18)$$

For a real gas at temperature T and pressure p , Eq. 7.8.16 or 7.8.18 allows us to evaluate the fugacity coefficient from an experimental equation of state or a second virial coefficient. We can then find the fugacity from $f = \phi p$.

As we will see in Sec. 9.7, the dimensionless ratio $\phi = f/p$ is an example of an *activity coefficient* and the dimensionless ratio f/p° is an example of an *activity*.

7.8.2 Liquids and solids

The dependence of the chemical potential on pressure at constant temperature is given by Eq. 7.8.5. With an approximation of zero compressibility, this becomes

$$\mu \approx \mu^\circ + V_m(p - p^\circ) \quad (7.8.19)$$

(pure liquid or solid,
constant T)

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