

## 11.4: Fugacity

The chemical potential of a pure ideal gas can be calculated using Equation 9.4.5. Since we are not interested in mixture, we can drop the asterisk in  $\mu^*$ , and rewrite Equation 9.4.5 as:

$$\mu_{\text{ideal}} = \mu^{\ominus} + RT \ln \frac{P}{P^{\ominus}}. \quad (11.4.1)$$

For a non-ideal gas, the pressure cannot be used in Equation 11.4.1 because each gas response to changes in pressure is not universal. We can, however, define a new variable to replace the pressure in Equation 11.4.1 and call it fugacity ( $f$ ).

### Definition: Fugacity

The effective pressure of a non-ideal gas that corresponds to the pressure of an ideal gas with the same temperature and chemical potential of the non-ideal one.

Equation 11.4.1 then becomes:

$$\mu_{\text{non-ideal}} = \mu^{\ominus} + RT \ln \frac{f}{P^{\ominus}}. \quad (11.4.2)$$

Since the chemical potential of a gas  $\mu$  is equal to the standard chemical potential  $\mu^{\ominus}$  when  $P = P^{\ominus}$ , it is easy to use Equation 11.4.2 to demonstrate that:

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1, \quad (11.4.3)$$

in other words, any non-ideal gas will approach the ideal gas behavior as  $P \rightarrow 0$ . This condition, in conjunction with the  $T \rightarrow \infty$  behavior obtained in the previous section, results in the following statement:

The highest chances for any gas to behave ideally happen at high temperature and low pressure.

We can now return our attention to the definition of fugacity. Remembering that the chemical potential is the molar Gibbs free energy of a substance, we can write:

$$d\mu_{\text{ideal}} = \bar{V}_{\text{ideal}} dP, \quad (11.4.4)$$

and:

$$d\mu_{\text{non-ideal}} = \bar{V}_{\text{non-ideal}} dP, \quad (11.4.5)$$

Subtracting Equation 11.4.4 from Equation 11.4.5, we obtain:

$$d\mu_{\text{non-ideal}} - d\mu_{\text{ideal}} = (\bar{V}_{\text{non-ideal}} - \bar{V}_{\text{ideal}}) dP, \quad (11.4.6)$$

which we can then integrate between 0 and  $P$ :

$$\mu_{\text{non-ideal}} - \mu_{\text{ideal}} = \int_0^P (\bar{V}_{\text{non-ideal}} - \bar{V}_{\text{ideal}}) dP. \quad (11.4.7)$$

Using eqs. 11.4.1 and 11.4.2 we can then replace the definition of chemical potentials, resulting into:

$$\ln f - \ln P = \frac{1}{RT} \int_0^P (\bar{V}_{\text{non-ideal}} - \bar{V}_{\text{ideal}}) dP, \quad (11.4.8)$$

which gives us a mathematical definition of the fugacity, as:

$$f = P \cdot \underbrace{\exp \left[ \frac{1}{RT} \int_0^P (\bar{V}_{\text{non-ideal}} - \bar{V}_{\text{ideal}}) dP \right]}_{\text{fugacity coefficient, } \phi(T,P)}. \quad (11.4.9)$$

The exponential term in Equation 11.4.9 is complicated to write, but it can be interpreted as a coefficient—unique to each non-ideal gas—that can be measured experimentally. Such coefficients are dependent on pressure and temperature and are called the *fugacity coefficients*. Using letter  $\phi$  to represent the fugacity coefficient, we can rewrite Equation 11.4.9 as:

$$f = \phi P, \quad (11.4.10)$$

which gives us a straightforward interpretation of the fugacity as an effective pressure. As such, the fugacity will have the same unit as the pressure, while the fugacity coefficients will be adimensional.

As we already saw in chapter 10, the fugacity can be used to replace the pressure in the definition of the equilibrium constant for reactions that involve non-ideal gases. The new constant is usually called  $K_f$ , and is obtained from:

$$K_f = \prod_i f_{i,\text{eq}}^{\nu_i} = K_P \prod_i \phi_i^{\nu_i}. \quad (11.4.11)$$

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