

## 7.5: Non-ideality in Gases - Fugacity

The relationship for chemical potential

$$\mu = \mu^{\circ} + RT \ln\left(\frac{p}{p^{\circ}}\right)$$

was derived assuming **ideal gas** behavior. But for real gases that deviate widely from ideal behavior, the expression has only limited applicability. In order to use the simple expression on real gases, a “fudge” factor is introduced called **fugacity**. Using fugacity instead of pressure, the chemical potential expression becomes

$$\mu = \mu^{\circ} + RT \ln\left(\frac{f}{f^{\circ}}\right)$$

where  $f$  is the fugacity. Fugacity is related to pressure, but contains all of the deviations from ideality within it. To see how it is related to pressure, consider that a change in chemical potential for a single component system can be expressed as

$$d\mu = V dp - S dT$$

and so

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V \tag{7.5.1}$$

Differentiating the expression for chemical potential above with respect to pressure at constant volume results in

$$\left(\frac{\partial\mu}{\partial p}\right)_T = \left\{ \frac{\partial}{\partial p} \left[ \mu^{\circ} + RT \ln\left(\frac{f}{f^{\circ}}\right) \right] \right\}$$

which simplifies to

$$\left(\frac{\partial\mu}{\partial p}\right)_T = RT \left[ \frac{\partial \ln(f)}{\partial p} \right]_T = V$$

Multiplying both sides by  $p/RT$  gives

$$\left[ \frac{\partial \ln(f)}{\partial p} \right]_T = \frac{pV}{RT} = Z$$

where  $Z$  is the compression factor as discussed previously. Now, we can use the expression above to obtain the **fugacity coefficient**  $\gamma$ , as defined by

$$f = \gamma p$$

Taking the natural logarithm of both sides yields

$$\ln f = \ln \gamma + \ln p$$

or

$$\ln \gamma = \ln f - \ln p$$

Using some calculus and substitutions from above,

$$\begin{aligned} \int \left( \frac{\partial \ln \gamma}{\partial p} \right)_T dp &= \int \left( \frac{\partial \ln f}{\partial p} - \frac{\partial \ln p}{\partial p} \right)_T dp \\ &= \int \left( \frac{Z}{p} - \frac{1}{p} \right)_T dp \end{aligned}$$

Finally, integrating from 0 to  $p$  yields

$$\ln \gamma = \int_0^p \left( \frac{Z-1}{p} \right)_T dp$$

If the gas behaves ideally,  $\gamma = 1$ . In general, this will be the limiting value as  $p \rightarrow 0$  since all gases behave ideal as the pressure approaches 0. The advantage to using the fugacity in this manner is that it allows one to use the expression

$$\mu = \mu^o + RT \ln\left(\frac{f}{f^o}\right)$$

to calculate the chemical potential, insuring that Equation 7.5.1 holds even for gases that deviate from ideal behavior!

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