26.10: Real Gases Are Expressed in Terms of Partial Fugacities

The relationship for chemical potential

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

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

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

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

$$d\mu - Vdp - SdT$$

and so

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V \tag{26.10.1}$$

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

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

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** γ, 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,

$$\int \left(\frac{\partial\ln\gamma}{\partial p}\right)_T dp = \int \left(\frac{\partial\ln f}{\partial p} - \frac{\partial\ln p}{\partial p}\right)_T dp$$

$$= \int \left(\frac{Z}{\partial p} - \frac{1}{\partial p}\right)_T dp$$

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 $p \to 0$ 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 26.10.1 holds even for gases that deviate from ideal behavior!

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