

12.12: Fugacity

Problem: The pressure of a mole of an ideal gas is increased isothermally from P_0 to P . What is the increase $G - G_0$ in its Gibbs free energy?

Solution: By integration of equation 12.6.12b, $\left(\frac{\partial G}{\partial P}\right)_T = V$, or by use of $dG = -SdT + VdP$, we have

$$G - G_0 = \int_{P_0}^P V dP. \quad (12.12.1)$$

For a mole of an ideal gas, $V = RT/P$, and hence

$$G - G_0 = RT \ln(P/P_0), \quad (12.12.2)$$

which agrees with equation 12.9.11.

Equation 12.13.1 enables us to calculate the change in the Gibbs free energy of a substance while its pressure is increased at constant temperature. Equation 12.13.2 gives the result for a mole of an ideal gas. If the substance is not an ideal gas, then we need to know the equation of state, $V = V(P, T)$ in order to integrate equation 12.13.1. For example, the equation of state for a van der Waals gas is $(P + a/V^2)(V - b) = RT$, where V is the molar volume, or $PV^3 - (bP + RT)V^2 + aV - ab = 0$.

Integrating equation 12.13.1 with this van der Waals equation of state may appear formidable. I am grateful to Dr J. Visvanathan of Chennai, India, for pointing out that it is not necessary. Instead one can calculate the change in the Helmholtz function, which, at constant temperature, is given by $A - A_0 = -\int_{V_0}^V PdV$, which is easy, and then use $G - G_0 = A - A_0 + PV - P_0V_0$. I am also indebted to Dr Justin Albert for pointing out that this amounts to integrating $\int_{P_0}^P V dP$ by parts, even if you had never heard of the Helmholtz function!

The *fugacity* f of a substance is defined in such a manner that, if the molar Gibbs free energy increases from G_0 to G , the ratio of the new fugacity to the initial fugacity, f/f_0 , is given by

$$G - G_0 = RT \ln(f/f_0) \quad (12.12.3)$$

In other words, for a real substance, we can use all (or at least most!) of the equations that we know for an ideal gas as long as we substitute fugacity for pressure.

That is,

$$f/f_0 = \exp\left(\frac{G - G_0}{RT}\right). \quad (12.12.4)$$

As for internal energy, only the *difference* between the Gibbs free energies of two states can be defined; likewise, only the *ratio* of the fugacities of two states is defined.

Combining equations 12.13.4 and 12.13.1 we obtain

$$\ln(f/f_0) = \frac{1}{RT} \int_{P_0}^P V dP, \quad (12.12.5)$$

which should enable us to find the relation between pressure and fugacity if we know the equation of state.

We note also that at very low pressures, a real gas behaves more and more like an ideal gas, and we can define the fugacity in units of pressure (pascal) in such a manner that, in the limit, as the pressure approaches zero, the fugacity equals the pressure. Indeed, we can then define the ratio of the fugacity to the pressure as the *activity coefficient*, which has the value unity at zero pressure.

Problem: Show that for a substance having the equation of state $P(V - b) = RT$ (V = molar volume), as the pressure increases from P_0 to P , the ratio of the final to initial fugacities is

$$\ln(f/f_0) = \ln(P/P_0) + \frac{b(P - P_0)}{RT}. \quad (12.12.6)$$

That is,

$$\ln f - \ln f_0 = \ln P - \ln P_0 + \frac{b(P - P_0)}{RT}. \quad (12.12.7)$$

Now suppose that P_0 is very small, and in the limit, as $P_0 \rightarrow 0$, $f_0 \rightarrow P_0$. We now find that the fugacity at temperature T and pressure P is given by

$$\ln f = \ln P + \frac{bP}{RT}. \quad (12.12.8)$$

This can be written

$$\frac{f}{P} = \exp\left(\frac{bP}{RT}\right). \quad (12.12.9)$$

The ratio f/P is called the activity coefficient. You can see that $f \approx P$ if P is small, or if b is small, as expected.

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