

6.4: Volume Dependence of Helmholtz Energy

If one needs to know how the Helmholtz function changes with changing volume at constant temperature, the following expression can be used:

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V} \right)_T dV \quad (6.4.1)$$

But how does one derive an expression for the partial derivative in Equation 6.4.1? This is a fairly straight forward process that begins with the definition of A :

$$A = U - TS$$

Differentiating (and using the chain rule to evaluate $d(TS)$) yields

$$dA = dU - TdS - SdT \quad (6.4.2)$$

Now, it is convenient to use the combined first and second laws

$$dU = TdS - pdV \quad (6.4.3)$$

which assumes:

1. a reversible change and
2. only pV work is being done.

Substituting Equation 6.4.3 into Equation 6.4.2 yields

$$dA = \cancel{TdS} - pdV - \cancel{TdS} - SdT \quad (6.4.4)$$

Canceling the TdS terms gives the important result

$$dA = -pdV - SdT \quad (6.4.5)$$

The natural variables of A are therefore V and T ! So the total differential of A is conveniently expressed as

$$dA = \left(\frac{\partial A}{\partial V} \right)_T dV + \left(\frac{\partial A}{\partial T} \right)_V dT \quad (6.4.6)$$

and by simple comparison of Equations 6.4.5 and 6.4.6, it is clear that

$$\begin{aligned} \left(\frac{\partial A}{\partial V} \right)_T &= -p \\ \left(\frac{\partial A}{\partial T} \right)_V &= -S \end{aligned}$$

And so, one can evaluate Equation 6.4.1 as

$$\Delta A = - \int_{V_1}^{V_2} p dV$$

If the pressure is independent of the temperature, it can be pulled out of the integral.

$$\Delta A = -p \int_{V_1}^{V_2} dV = -p(V_2 - V_1)$$

Otherwise, the temperature dependence of the pressure must be included.

$$\Delta A = - \int_{V_1}^{V_2} p(V) dV$$

Fortunately, this is easy if the substance is an ideal gas (or if some other equation of state can be used, such as the van der Waals equation.)

✓ Example 6.4.1: Ideal Gas Expansion

Calculate ΔA for the isothermal expansion of 1.00 mol of an ideal gas from 10.0 L to 25.0 L at 298 K.

Solution

For an ideal gas,

$$p = \frac{nRT}{V}$$

So

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

becomes

$$\left(\frac{\partial A}{\partial V}\right)_T = -\frac{nRT}{V}$$

And so (Equation 6.4.1)

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV$$

becomes

$$\Delta A = -nRT \int_{V_1}^{V_2} \frac{dV}{V} dT$$

or

$$\Delta A = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Substituting the values from the problem

$$\Delta A = -(1.00 \text{ mol})(8.314 \text{ J/(mol K)})(298 \text{ K}) \ln\left(\frac{25.0 \text{ L}}{10.0 \text{ L}}\right)$$

But further, it is easy to show that the Maxwell relation that arises from the simplified expression for the total differential of A is

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

This particular Maxwell relation is exceedingly useful since one of the terms depends only on p , V , and T . As such it can be expressed in terms of our old friends, α and κ_T !

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

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