

4.6: Pressure Dependence of Gibbs Energy

The pressure and temperature dependence of G is also easy to describe. The best starting place is the definition of G .

$$G = U + pV - TS \quad (4.6.1)$$

Taking the total differential of G yields

$$dG = dU + pdV - p dV + V dp - T dS - S dT$$

The differential can be simplified by substituting the combined first and second law statement for dU (consider a reversible process and pV work only).

$$dG = \cancel{T dS} - \cancel{p dV} + \cancel{p dV} + V dp - \cancel{T dS} - S dT$$

Canceling the $T dS$ and $p dV$ terms leaves

$$dG = V dp - S dT \quad (4.6.2)$$

This suggests that the natural variables of G are p and T . So the total differential dG can also be expressed

$$dG = \left(\frac{\partial G}{\partial p} \right)_T dp + \left(\frac{\partial G}{\partial T} \right)_p dT \quad (4.6.3)$$

And by inspection of Equations 4.6.2 and 4.6.3, it is clear that

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

and

$$\left(\frac{\partial G}{\partial T} \right)_p = -S$$

It is also clear that the Maxwell relation on G is given by

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

which is an extraordinarily useful relationship, since one of the terms is expressible entirely in terms of measurable quantities!

$$\left(\frac{\partial V}{\partial T} \right)_p = V \alpha$$

The pressure dependence of G is given by the pressure derivative at constant temperature

$$\left(\frac{\partial G}{\partial p} \right)_T = V \quad (4.6.4)$$

which is simply the molar volume. For a fairly incompressible substance (such as a liquid or a solid) the molar volume will be essentially constant over a modest pressure range.

✓ Example 4.6.1: Gold under Pressure

The density of gold is 19.32 g/cm^3 . Calculate ΔG for a 1.00 g sample of gold when the pressure on it is increased from 1.00 atm to 2.00 atm .

Solution

The change in the Gibbs function due to an isothermal change in pressure can be expressed as

$$\Delta G = \int_{p_1}^{p_2} \left(\frac{\partial G}{\partial p} \right)_T dp$$

And since substituting Equation 4.6.4, results in

$$\Delta G = \int_{p_1}^{p_2} V dp$$

Assuming that the molar volume is independent of pressure over the stated pressure range, ΔG becomes

$$\Delta G = V(p_2 - p_1)$$

So, the molar change in the Gibbs function can be calculated by substituting the relevant values.

$$\Delta G = \left(\frac{197.0 \text{ g}}{\text{mol}} \times \frac{1}{19.32 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \right) (2.00 \text{ atm} - 1.00 \text{ atm}) \underbrace{\left(\frac{8.315 \text{ J}}{0.08206 \text{ atm L}} \right)}_{\text{conversion unit}} \quad (4.6.5)$$

$$= 1.033 \text{ J} \quad (4.6.6)$$

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