9.3: Pressure Dependence of ΔG

$$\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}=V$$

We can now turn the attention to the second coefficient that gives how the Gibbs free energy changes when the pressure change. To do this, we put the system at constant T and $\{n_i\}$, and then we consider infinitesimal variations of G. From Equation 8.2.6:

$$dG=VdP-SdT+\sum_i \mu_i dn_i \quad \xrightarrow{\text{constant } T,\{n_i\}} \quad dG=VdP, \tag{9.3.1}$$

which is the differential equation that we were looking for. To study changes of G for macroscopic changes in P, we can integrate Equation 9.3.1 between initial and final pressures, and considering an ideal gas, we obtain:

$$\begin{aligned} \int_i^f dG &= \int_i^f VdP \\ \Delta G &= nRT\int_i^f \frac{dP}{P}=nRT\ln\frac{P_f}{P_i}. \end{aligned} \tag{9.3.2}$$

If we take $P_i=P^{\ominus}=1\text{ bar}$, we can rewrite Equation 9.3.2 as:

$$G=G^{\ominus}+nRT\ln\frac{P_f}{P^{\ominus}}, \tag{9.3.3}$$

which is useful to convert standard Gibbs free energies of formation at pressures different than standard pressure, using:

$$\Delta_f G=\Delta_f G^{\ominus}+nRT\ln\frac{P_f}{\underbrace{P^{\ominus}}_{=1\text{ bar}}}=\Delta_f G^{\ominus}+nRT\ln P_f \tag{9.3.4}$$

For liquids and solids, V is essentially independent of P (liquids and solids are incompressible), and Equation 9.3.1 can be integrated as:

$$\Delta G=\int_i^f VdP=V\int_i^f dP=V\Delta P. \tag{9.3.5}$$

The plots in Figure $9.3.1$ show the remarkable difference in the behaviors of $\Delta_f G$ for a gas and for a liquid, as obtained from eqs. 9.3.2 and 9.3.5.

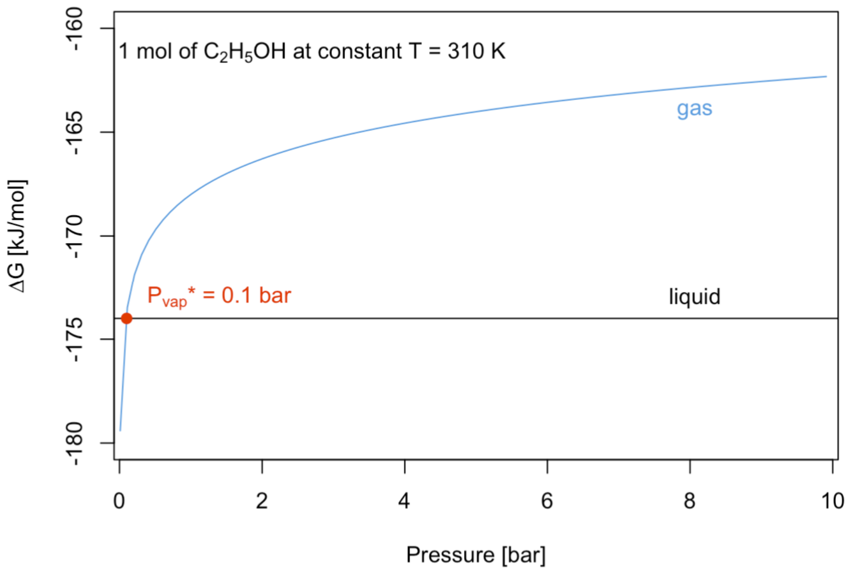

Figure 9.3.1: Dependence of the Gibbs Free Energy of Formation of Liquid and Gaseous Ethanol at T = 310 K. The Curves Cross at the Vapor Pressure of Liquid Ethanol at this Temperature, which is 0.1 bar.