

Systems with more than one component: chemical potential

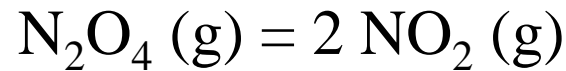
Up to this point we have derived state functions for pure systems. (The one exception is the entropy of mixing). However, in order for a chemical change to occur we must have more than one component present. We need generalize the methods to account for the presence of more than one type of molecule. In the introduction we stated that we would do this using a quantity called the chemical potential. The chemical potential is nothing more than the molar Gibbs free energy of a particular component. Formally we write it this way:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,j \neq i}$$

Rate of change of G as number of moles of i changes with all other variables held constant.

Example: a gas phase reaction

Let's consider a gas phase reaction as an example. We will use a textbook example:



We know how to write the equilibrium constant for this reaction.

$$K = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

At constant T and P we will write the total Gibbs energy as:

$$dG = \mu_{\text{NO}_2} dn_{\text{NO}_2} + \mu_{\text{N}_2\text{O}_4} dn_{\text{N}_2\text{O}_4}$$

$$dG = 2\mu_{\text{NO}_2} dn - \mu_{\text{N}_2\text{O}_4} dn$$

We use the reaction stoichiometry to obtain the factor 2 for NO_2 .

Definition of the Gibbs free energy change for chemical reaction

We now define $\Delta_{\text{rxn}}G$:

$$\Delta_{\text{rxn}}G = \left(\frac{\partial G_m}{\partial n} \right)_{T,P}$$

This is $\Delta_{\text{rxn}}G$ but it is not $\Delta_{\text{rxn}}G^\circ$! Note that we will use $\Delta_{\text{rxn}}G$ and ΔG interchangeably. If we now apply the pressure dependence for one component,

$$G_m(T) = G_m^\circ(T) + RT \ln \left(\frac{P}{1 \text{ bar}} \right)$$

to a multicomponent system:

$$\mu(T) = \mu^\circ(T) + RT \ln \left(\frac{P}{1 \text{ bar}} \right)$$

These two expressions are essentially identical. The chemical potential, μ_i , is nothing more than a molar free energy.

Application of definitions to the chemical reaction

We can write the Gibbs energy as:

$$\Delta G = 2\mu_{NO_2} - \mu_{N_2O_4}$$

and use the chemical potentials:

$$\begin{aligned}\mu_{NO_2} &= \mu_{NO_2}^0 + RT \ln P_{NO_2} \\ \mu_{N_2O_4} &= \mu_{N_2O_4}^0 + RT \ln P_{N_2O_4}\end{aligned}$$

to obtain the following:

$$\begin{aligned}\Delta G &= 2\mu_{NO_2}^0 - \mu_{N_2O_4}^0 + RT \ln P_{NO_2}^2 - RT \ln P_{N_2O_4} \\ \Delta G &= \Delta G^0 + RT \ln Q\end{aligned}$$

$$\Delta G^0 = 2\mu_{NO_2}^0 - \mu_{N_2O_4}^0 \quad \text{and} \quad Q = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

Note the significance of ΔG and ΔG°

The change ΔG is the change in the Gibbs energy function.

It has three possible ranges of value:

$\Delta G < 0$ (process is spontaneous)

$\Delta G = 0$ (system is at equilibrium)

$\Delta G > 0$ (reverse process is spontaneous)

On the other hand ΔG° is the standard molar Gibbs energy change for the reaction. It is a constant for a given chemical reaction. We will develop these ideas for a general reaction later in the course. For now, let's consider the system at equilibrium. Equilibrium means $\Delta G = 0$ so:

$$\Delta G = \Delta G^\circ + RT \ln K = 0$$

$$\Delta G^\circ = -RT \ln K$$