Chemical Potentials

For a closed system containing $k$ chemical substances, the differential dependence of Gibbs energy on temperature, pressure and chemical composition, is given by the following equation.

$$dG = -S \cdot dT + V \cdot dp + \sum_{j=1}^{k} \left( \frac{\partial G}{\partial n_j} \right)_{T,p,n(i\neq j)} \cdot dn_j \quad (a)$$

The condition at constant $n(i\neq j)$ indicates that the amounts of each $i$ chemical substance except chemical substance $j$ is constant. The Gibbs energy of a closed system is a thermodynamic potential function; equation (b).

$$dG = -S \cdot dT + V \cdot dp - A \cdot d\xi \quad (b)$$

Here $A$ is the affinity for spontaneous chemical reaction producing a change in extent of reaction, $d\xi$, in this case a change in composition. Further the chemical potential of chemical substance $j$,

$$\mu_j = \left( \frac{\partial G}{\partial n_j} \right)_{T,p,n(i\neq j)} \quad (c)$$

Comparison of equations (a) and (b) yields equation (d).

$$-A \cdot d\xi = \sum_{j=1}^{k} \mu_j \cdot dn_j \quad (d)$$

The stoichiometry in a chemical reaction for chemical substance $j$, $\nu_j$ is defined such that $\nu_j$ is positive for products and negative for reactants; a mnemonic is ‘P for P’.

$$\nu_j = dn_j / d\xi \quad (e)$$

Hence the affinity for spontaneous change, $A = -\sum_{j=1}^{k} \nu_j \cdot \mu_j \quad (f)$

But at equilibrium, the affinity for spontaneous change $A$ is zero.

Then, $\sum_{j=1}^{k} \nu_j \cdot \mu_j^{eq} = 0 \quad (g)$
Equation (g) in terms of its simplicity is misleading. Chemists are experts at assaying a system at equilibrium in order to determine the chemical substances present and their amounts. For example, an assay of a given system yields (for defined temperature and pressure) the amounts of un-dissociated acid CH$_3$COOH(aq), and the conjugate base CH$_3$COO$^-$(aq) and hydrogen ions at equilibrium. We write equation (g) as follows.

\[\mu_{eq}^{CH_3COOH} (aq) + \mu_{eq}^{CH_3COO^-} (aq) + \mu_{eq}^{H^+} (aq) = 0 \quad (h)\]

Or, representing a balance of chemical potentials, (a useful approach)

\[\mu_{eq}^{CH_3COOH} (aq) = \mu_{eq}^{CH_3COO^-} (aq) + \mu_{eq}^{H^+} (aq) \quad (i)\]

The concept of a balance of equilibrium chemical potentials at thermodynamic equilibrium is often the starting point for a description of the properties of closed systems.