

Chemical Equilibrium

Given enough time, any closed system with chemical reaction(s) shall reach the state of chemical equilibrium where the temperature, pressure and chemical composition no longer change. Reactants as well as products are present in equilibrium.

Extent of Reaction

In reaction
$$0 = \sum_{i=1}^k \nu_i R_i$$

the extent of reaction is defined as

$$\zeta = \frac{n_i - n_i^\circ}{\nu_i} \quad \Rightarrow \quad n_i = n_i^\circ + \nu_i \zeta$$

where n_i° is the initial amount of compound i . This is at the same time also a **mass balance** for the compound – number of moles of any component in a reaction can be expressed with single variable, the extent of reaction ζ .

Gibbs (Reaction) Isotherm

Searching for the state of chemical equilibrium is equivalent to minimization of the Gibbs energy of reacting system with respect to the extent of reaction. Gibbs (reaction) isotherm is the relation between Gibbs energy change and actual activities of reaction species at given temperature and pressure

$$\Delta G_r = \Delta G_r^\circ + RT \ln \prod_{i=1}^n a_i^{\nu_i}$$

In equilibrium ($\Delta G_r = 0$ [T, p]) we find

$$\Delta G_r^\circ = -RT \ln \prod_{i=1}^n a_{i, \text{rovn}}^{\nu_i} = -RT \ln K$$

where $a_{i, \text{rovn}}$ stands for activities of reaction components in equilibrium and K the **equilibrium constant**. The value of equilibrium constant depends on standard states applied for the activities, and on the format of chemical reaction (stoichiometric coefficients). The choice of standard states for different reaction species may vary, depending usually on the phase of a given compound. ΔG_r° is standard reaction Gibbs energy that can be evaluated from (tabulated) formation Gibbs energies of individual reaction species

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_{f,i}^\circ$$

Temperature Dependence of Equilibrium Constant

$$\left(\frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta H_r^\circ}{RT^2}$$

where ΔH_r° is standard reaction enthalpy of the reaction. This equation is often called *van't Hoff isobar*.

Pressure Dependence of Equilibrium Constant

Standard states at temperature and pressure of the system lead to pressure-independent values of equilibrium constant. The extent of reaction, however, does change with pressure. For standard state at the temperature of the system and at standard pressure

$$\left(\frac{\partial \ln K}{\partial p} \right)_T = \frac{-\Delta V_r^\circ}{RT}$$

Calculation of Equilibrium Composition

1. Write mass balance for reaction species, using e.g. the extent of reaction as a variable.
2. Write equilibrium constant for a given reaction stoichiometry, choose appropriate standard states for reaction species and introduce mass balance equations.
3. Find the value of equilibrium constant – usually it is calculated from tabulated data on standard formation Gibbs energies of reaction species.
4. Evaluate activity coefficients of reaction species using published data or an appropriate estimation method.
5. Solve the equation for equilibrium constant with unknown variable – the extent of reaction. Introduce calculated value of ζ to mass balance equations and evaluate equilibrium composition.

Example: calculation of equilibrium composition in a reaction with gaseous reactants

 Reaction $\text{CO(g)} + \text{H}_2\text{O(g)} = \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$

 Initial composition – 1 mol CO, 1 mol H₂O, $T = 298 \text{ K}$, $p = 2 \text{ MPa}$

$$1. \quad n_{\text{CO}} = 1 - \zeta, \quad n_{\text{H}_2\text{O}} = 1 - \zeta, \quad n_{\text{CO}_2} = \zeta, \quad n_{\text{H}_2} = \zeta, \quad n = \sum n_i = 2$$

$$2. \quad K = \frac{a_{\text{CO}_2} a_{\text{H}_2}}{a_{\text{CO}} a_{\text{H}_2\text{O}}} = \frac{n_{\text{CO}_2} n_{\text{H}_2}}{n_{\text{CO}} n_{\text{H}_2\text{O}}} \frac{\gamma_{\text{CO}_2} \gamma_{\text{H}_2}}{\gamma_{\text{CO}} \gamma_{\text{H}_2\text{O}}} = \frac{\zeta^2}{(1 - \zeta)^2} \frac{\gamma_{\text{CO}_2} \gamma_{\text{H}_2}}{\gamma_{\text{CO}} \gamma_{\text{H}_2\text{O}}}$$

3. Values from Webbook: CO - $\Delta H_f^\circ = -110,5 \text{ kJ/mol}$, $S^\circ = 197,7 \text{ J/K/mol}$; H₂O - $\Delta H_f^\circ = -241,8 \text{ kJ/mol}$, $S^\circ = 188,8 \text{ J/K/mol}$; CO₂ - $\Delta H_f^\circ = -393,5 \text{ kJ/mol}$, $S^\circ = 213,7 \text{ J/K/mol}$; H₂ - $S^\circ = 130,7 \text{ J/K/mol}$; C(s) - $S^\circ = 5,6 \text{ J/K/mol}$; O₂ - $S^\circ = 205,2 \text{ J/K/mol}$. ΔG_f° is evaluated from $\Delta G_f^\circ = \Delta H_f^\circ - TS^\circ + T \sum S_{\text{el}}^\circ$ where the summation includes all elements in a given compound: $\Delta G_f^\circ(\text{CO}) = -137,2 \text{ kJ/mol}$; $\Delta G_f^\circ(\text{H}_2\text{O}) = -228,5 \text{ kJ/mol}$; $\Delta G_f^\circ(\text{CO}_2) = -394,4 \text{ kJ/mol}$. $\Delta G_f^\circ(\text{H}_2) = 0$ (element in its standard state). $\Delta G_r^\circ = -28,7 \text{ kJ/mol}$, $K = 106734$.

4. Good approximation for gaseous species is activity coefficient equal to unity.

5. Solving the equation we get $\zeta = 0,9969$ (equilibrium includes predominantly products and only traces of reactants).

Example: calculation of equilibrium composition in a reaction in solution

 Reaction $\text{HCOOH(aq)} = \text{H}^+\text{(aq)} + \text{HCOO}^-\text{(aq)}$

 Index aq is for aqueous species. Initial composition – aqueous solution of HCOOH with molality $m = 0,05 \text{ mol/kg}$, $T = 298 \text{ K}$, $p = 0,1 \text{ MPa}$

$$1. \quad m_{\text{HCOOH}} = 0,05 - \zeta, \quad m_{\text{H}^+} = \zeta, \quad m_{\text{HCOO}^-} = \zeta$$

$$2. \quad K = \frac{a_{\text{H}^+} a_{\text{HCOO}^-}}{a_{\text{HCOOH}}} = \frac{m_{\text{H}^+} m_{\text{HCOO}^-}}{m_{\text{HCOOH}}} \frac{\gamma_{\text{H}^+}^{[\text{m}]} \gamma_{\text{HCOO}^-}^{[\text{m}]}}{\gamma_{\text{HCOOH}}^{[\text{m}]}} = \frac{\zeta^2}{0,05 - \zeta} \frac{\gamma_{\text{H}^+}^{[\text{m}]} \gamma_{\text{HCOO}^-}^{[\text{m}]}}{\gamma_{\text{HCOOH}}^{[\text{m}]}} = \frac{\zeta^2}{0,05 - \zeta} \frac{(\gamma_{\pm}^{[\text{m}]})^2}{\gamma_{\text{HCOOH}}^{[\text{m}]}}$$

3. Values from NBS Tables: HCOOH(aq) - $\Delta G_f^\circ = -372,3 \text{ kJ/mol}$, HCOO⁻(aq) - $\Delta G_f^\circ = -351,0 \text{ kJ/mol}$, formation properties of H⁺(aq) are zero by definition (hydrogen convention). $\Delta G_r^\circ = 21,3 \text{ kJ/mol}$, $K = 0,000185436$.

4. Activity coefficient of undissociated acid in dilute solution is close to unity, mean activity coefficient for the ions is obtained from Debye-Hückel (Pitzer) equation:

$$\ln \gamma_{\pm}^{[\text{m}]} = -A_{\phi} \left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) = -0,3915 \left(\frac{\zeta^{1/2}}{1 + 1,2\zeta^{1/2}} + \frac{2}{1,2} \ln(1 + 1,2\zeta^{1/2}) \right)$$

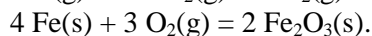
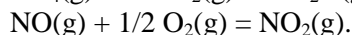
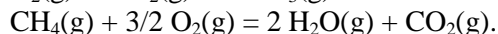
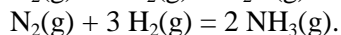
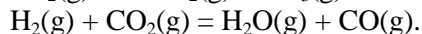
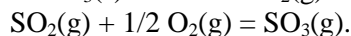
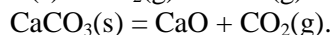
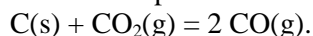
5. Solving the (algebraic) equation we get $\zeta = 0,00314$.

Simultaneous Reactions

The same procedure is followed as in the case of simple reaction, except that we must solve the system of equilibrium equations with several unknown variables (= extents of reaction). Problem may arise when we do not know *a priori* what reactions proceed – only the species that are (or may be) present in the system. In such situation the approaches minimizing Gibbs energy of the system possess substantial advantage, namely the non-stoichiometric algorithms that apply mass balance not for reaction species (compounds), but for present elements. More information can be found e.g. in:

White, W.B., Johnson, S.M., Dantzig, G.B.: J. Chem. Phys., 28, 751 (1958), in Czech e.g.

Holub R., Voňka P.: Chemická rovnováha heterogenních a kondenzovaných soustav, Academia, 1984.

Homework 6: Find equilibrium composition at 598,15 K and 30 MPa for the reaction


Initial composition is a stoichiometric mixture of reactants. Assume ideal behavior of gaseous species.