20. Generation of Stability Diagrams

Construction of real-solution stability diagrams

For each redox subsystem:

1. Construction of equilibrium equations.
2. Simulated titration to cover the whole range of independent variables.
3. Calculation of equilibrium lines for chemical reactions.
4. Calculation of equilibrium lines for electrochemical reactions.CA
5. Determination of predominance areas.

Construction of equilibrium equations

For each pair of species X and Y in a particular redox subsystem:

$$\nu_X X + \sum_{i=1}^{k} \nu_i A_i = Y + \nu_e e^-$$

where: A_i – basis species

General Formula:

$$X \equiv M_{X_1} H_{X_2} O_{X_3} C_{X_4} D_{X_5} E_{X_6} \ldots.$$

$$Y \equiv M_{Y_1} H_{Y_2} O_{Y_3} C_{Y_4} D_{Y_5} E_{Y_6} \ldots.$$

M-element associated with the redox system.

Basis species: Species that contain H, O, C, D, E, etc., but do not contain M:

(a) H^+ is the basis species that contains H,

(b) H_2O is the basis species that contains O,

(c) The basis species containing C, D, E, etc. are the ones with the minimum possible number of hydrogen and oxygen atoms in addition to C, D, E...

Examples

For a system composed of Cu, NH_3 and H_2O:

$$X \equiv Cu_{X_1} H_{X_2} O_{X_3} N^{-3}_{X_4}$$

Basis species: H^+, H_2O, $NH_{3(aq)}$

For a system composed of Fe, H_2O and sulfur-bearing species:

$$X \equiv Fe_{X_1} H_{X_2} O_{X_3} S^{-2}_{X_4} S^{0}_{X_5} S^{+6}_{X_6}$$

Basis species: H^+, H_2O, S^{2-}, $S^0_{(s)}$, SO_4^{2-}

Cases when both the metal and ligands are subject to redox equilibria

1. Determine which basis species are stable in which area of the stability diagram.
2. Retain only the stable species in the basis and delete the remaining ones. The deleted species are not used for constructing the equilibrium equations.

Simulated titrations

1. Titrate with a selected reactant (an acid, base, complexing agent) to vary the independent variable of interest.
2. Equilibrium calculations at each titration point involve the simultaneous solution of chemical (acid-base and redox) equilibria as well as phase equilibria.
3. Calculate the equilibrium compositions and activity coefficients for each titration point.
4. Use the compositions and and activity coefficients to calculate equilibrium lines.

Equilibrium lines for chemical reactions

Affinity of a reaction between X and Y:

$$\frac{A}{RT} = -\frac{1}{RT}\left(\overline{G}_Y - \nu_X \overline{G}_X - \sum_{i=1}^{k} \nu_i \overline{G}_{A_i}\right) =$$

$$= \ln K - \left(\ln a_Y - \nu_X \ln a_X - \sum_{i=1}^{k} \nu_i \ln a_{A_i}\right)$$

- Construct a discrete function of the independent variable:

$A_p = f(\text{var}_p)$,   p = 1…N

- Find the root:

$f(\text{var}_0) = 0$

Check which species are stable at var < var_0 and which at var > var_0.

Calculate equilibrium potentials for each pair of species X and Y:

$$E = E^0 + \frac{RT}{F\nu_e}\left(\ln a_Y - \nu_X \ln a_X - \sum_{i=1}^{k} \nu_i \ln a_{A_i} \right)$$

$$E^0 = \frac{\overline{G}_Y^0 - \nu_X \overline{G}_X^0 - \sum_{i=1}^{k} \nu_i \overline{G}_{A_i}^0}{F\nu_e}$$

Construct a discrete function of the independent variable:

$E_p = g(var_p)$ p=1,…N

Approximate the function using splines.

Determination of predominance areas

For each species:

1) Determine the boundaries:
    a) Upper boundaries: Equilibria with species in higher oxidation states
    b) Lower boundaries: Equilibria with species in lower oxidation states
    c) Right-hand side boundaries: Other species are more stable at higher independent variables
    d) Left-hand side boundaries: Other species are more stable at lower independent variables
2) Find intersections between boundaries
3) Determine which boundaries are active