Stoichiometry

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Chemical equations

- a chemical reaction involves p reactants, q products (molecules)
- expressed as

$$a_1 R_1 + \cdots + a_p R_p \longrightarrow b_1 P_1 + \cdots + b_q P_q.$$

  - reactants $R_1, \ldots, R_p$, products $P_1, \ldots, P_q$
  - coefficients $a_1, \ldots, a_p, b_1, \ldots, b_q > 0$
- coefficients usually integers, but can be scaled
  - *e.g.*, multiplying all coefficients by $1/2$ doesn't change the reaction

Example

electrolysis of water:

$$2H_2O \longrightarrow 2H_2 + O_2$$

- one reactant: water (H_2O)
- two products: hydrogen (H_2) and oxygen (O_2)
- reaction consumes 2 water molecules and produces 2 hydrogen molecules and 1 oxygen molecule

Balancing equations

- each molecule (reactant/product) contains specific numbers of (types of) atoms, given in its formula
  - *e.g.*, H_2O contains two H and one O
- *conservation of mass*: total number of each type of atom in a chemical equation must *balance*
- for each atom, total number on LHS must equal total on RHS
- *e.g.*, electrolysis reaction is balanced:
  - 4 units of H on LHS and RHS
  - 2 units of O on LHS and RHS
- finding (nonzero) coefficients to achieve balance is called *balancing* equations

Reactant and product matrices

- consider reaction with m types of atoms, p reactants, q products
- $m \times p$ *reactant matrix* R is defined by

$$R_{ij} = \text{number of atoms of type } i \text{ in reactant } R_j,$$

  $i = 1, \ldots, m, \quad j = 1, \ldots, p$
- with $a = (a_1, \ldots, a_p)$ (vector of reactant coefficients)

$$Ra = \text{(vector of) total numbers of atoms of each type in reactants}$$

- define product $m \times q$ matrix P in similar way
- m-vector Pb is total numbers of atoms of each type in products
- conservation of mass is $Ra = Pb$

Balancing equations via linear equations

- conservation of mass is $\begin{bmatrix} R & -P \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0$
- simple solution is $a = b = 0$
- to find a nonzero solution, set any coefficient (say, a_1) to be 1
- balancing chemical equations can be expressed as solving a set of $m+1$ linear equations in $p+q$ variables

$$\begin{bmatrix} R & -P \\ e_1^T & 0 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = e_{m+1}$$

(we ignore here that a_i and b_i should be nonnegative integers)

Conservation of charge

- can extend to include charge, *e.g.*, $\mathrm{Cr}_2O_7^{2-}$ has charge -2
- *conservation of charge*: total charge on each side of reaction must balance
- we can simply treat charge as another type of atom to balance

Example

- reaction to balance

$$a_1\mathrm{Cr_2O_7^{2-}} + a_2\mathrm{Fe^{2+}} + a_3\mathrm{H^+} \longrightarrow b_1\mathrm{Cr^{3+}} + b_2\mathrm{Fe^{3+}} + b_3\mathrm{H_2O}$$

- 5 atoms/charge: as Cr, O, Fe, H, charge
- reactant and product matrix:

$$R = \begin{bmatrix} 2 & 0 & 0 \\ 7 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ -2 & 2 & 1 \end{bmatrix}, \qquad P = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \\ 3 & 3 & 0 \end{bmatrix}$$

Balancing equations example

- balancing: system of equations (including $a_1 = 1$ constraint)

$$\begin{bmatrix} 2 & 0 & 0 & -1 & 0 & 0 \\ 7 & 0 & 0 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -2 \\ -2 & 2 & 1 & -3 & -3 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Balancing equations example

- solving the system yields

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 6 \\ 14 \\ 2 \\ 6 \\ 7 \end{bmatrix}$$

- the balanced equation is

$$\mathrm{Cr_2O_7^{2-}} + 6\mathrm{Fe}^{2+} + 14\mathrm{H}^{+} \longrightarrow 2\mathrm{Cr}^{3+} + 6\mathrm{Fe}^{3+} + 7\mathrm{H_2O}$$