Balancing Chemical Equations

\[ a\text{AlCl}_3(s) + b\text{H}_3\text{PO}_4(l) \rightarrow x\text{PCl}_5(g) + y\text{Al}_2\text{O}_3(s) + z\text{H}_2\text{O}(l) \]
Balancing Chemical Equations

\[ \text{AlCl}_3(\text{s}) + \text{H}_3\text{PO}_4(\text{l}) \rightarrow \text{PCl}_5(\text{g}) + \text{Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \]
Balancing Chemical Equations

\[ \text{aAlCl}_3(s) + \text{bH}_3\text{PO}_4(l) \rightarrow \text{xPCl}_5(g) + \text{yAl}_2\text{O}_3(s) + \text{zH}_2\text{O(l)} \]
Balancing Chemical Equations

\[ a = 2y \]
\[ 3a = 5x \]
\[ 3b = 2z \]
\[ b = x \]
\[ 4b = 3y + z \]
Balancing Chemical Equations

\[ a = 2y \]
\[ 3a = 5x \]
\[ 3b = 2z \]
\[ b = x \]
\[ 4b = 3y + z \]

\[
\begin{bmatrix}
1 & 0 & 2 & 0 \\
3 & 0 & 5 & 0 \\
0 & 3 & 0 & 0 \\
0 & 1 & 1 & 0 \\
0 & 4 & 0 & 3 \\
\end{bmatrix}
\rightarrow
\begin{bmatrix}
1 & 0 & 0 & 2 & 0 \\
0 & 1 & 0 & \frac{3}{4} & \frac{1}{4} \\
0 & 0 & 1 & -\frac{3}{4} & -\frac{1}{4} \\
0 & 0 & 0 & -\frac{3}{4} & \frac{5}{12} \\
0 & 0 & 5 & -6 & 0 \\
\end{bmatrix}
\]
Balancing Chemical Equations

$$\begin{bmatrix} 1 & 0 & 0 & -2 & 0 \\ 3 & 0 & -5 & 0 & 0 \\ 0 & 3 & 0 & 0 & 2 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 4 & 0 & -3 & 1 \end{bmatrix} \rightarrow \begin{bmatrix} 1 & 0 & 0 & 0 & 10 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 5 \end{bmatrix}$$

$\text{AlCl}_3(s) + 6\text{H}_3\text{PO}_4(l) \rightarrow 6\text{PCl}_5(g) + 5\text{Al}_2\text{O}_3(s) + 9\text{H}_2\text{O}(l)$
Balancing Chemical Equations

\[
\begin{bmatrix}
1 & 0 & 0 & -2 & 0 \\
3 & 0 & -5 & 0 & 0 \\
0 & 3 & 0 & 0 & 2 \\
0 & 1 & -1 & 0 & 0 \\
0 & 4 & 0 & -3 & 1 \\
\end{bmatrix} \rightarrow 
\begin{bmatrix}
1 & 0 & 0 & 0 & \frac{10}{3} \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & \frac{9}{3} \\
\end{bmatrix}
\]

\[10\text{AlCl}_3(\text{s}) + 6\text{H}_3\text{PO}_4(\text{l}) \rightarrow 6\text{PCl}_5(\text{g}) + 5\text{Al}_2\text{O}_3(\text{s}) + 9\text{H}_2\text{O}(\text{l})\]
Group Theory and Molecular Symmetry

Check all four rules of groups.
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1. Must include the identity operation
2. The combination of any pair of elements must also be an element of the group.
3. Every operation must have an inverse
4. Any combination of operations must be associative
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1. Must include the identity operation
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4. Any combination of operations must be associative

**Figure:** Ammonia molecule point group
Select a basis \((s_N, s_1, s_2, s_3)\) that consists of the valence s orbitals on the nitrogen atom and the three hydrogen atoms. Define the symmetry operations on the basis.

\[
E (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3)
\]
\[
C_3^+ (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1)
\]
\[
C_3^- (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2)
\]
\[
\sigma_V (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2)
\]
\[
\sigma'_V (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3)
\]
\[
\sigma''_V (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1)
\]
\[ \Gamma(E) = (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \]

\[ \Gamma(C_3^+) = (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \]
Symmetry Matrix Operations

\[
\Gamma(C^-) = (s_N, s_1, s_2, s_3) \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
0 & 1 & 0 & 0
\end{pmatrix} = (s_N, s_3, s_1, s_2)
\]

\[
\Gamma(\sigma_v) = (s_N, s_1, s_2, s_3) \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0
\end{pmatrix} = (s_N, s_1, s_3, s_2)
\]
Symmetry Matrix Operations

\[
\Gamma(\sigma'') = (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1)
\]

\[
\Gamma(\sigma''') = (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_2, s_1, s_3)
\]
We can construct a first order rate matrix from the rate constants of different chemical reactions. Consider three chemical species $A$, $B$, and $C$, and the corresponding rate matrix.

\[
K = \begin{bmatrix}
-k_{AA} & k_{BA} & k_{CA} \\
k_{AB} & -k_{BB} & k_{CB} \\
k_{AC} & k_{BC} & -k_{CC}
\end{bmatrix}
\]
We can construct a first order rate matrix from the rate constants of different chemical reactions. Consider three chemical species $A$, $B$, and $C$, and the corresponding rate matrix.

$$K = \begin{bmatrix} -k_{AA} & k_{BA} & k_{CA} \\ k_{AB} & -k_{BB} & k_{CB} \\ k_{AC} & k_{BC} & -k_{CC} \end{bmatrix}$$

1. The sum of elements in each column is always zero.
2. For reversible reactions, the elements on either side of the main diagonal proceed in the opposite direction.
First Order Kinetics

We can construct a first order rate matrix from the rate constants of different chemical reactions. Consider three chemical species $A$, $B$, and $C$, and the corresponding rate matrix.

$$K = \begin{bmatrix} -k_{AA} & k_{BA} & k_{CA} \\ k_{AB} & -k_{BB} & k_{CB} \\ k_{AC} & k_{BC} & -k_{CC} \end{bmatrix}$$

1. The sum of elements in each column is always zero
2. For reversible reactions, the elements on either side of the main diagonal proceed in the opposite direction

**Irreversible consecutive reactions** $A \rightarrow B \rightarrow C$

$$K = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & 0 & k_2 \end{bmatrix}$$
Consecutive Equilibria $A \Leftrightarrow B \Leftrightarrow C \Leftrightarrow D$

$$K = \begin{bmatrix} -k_1 & k_{-1} & 0 & 0 \\ k_1 & -(k_{-1} + k_2) & k_{-2} & 0 \\ 0 & k_2 & -(k_{-2} + k_3) & k_{-3} \\ 0 & 0 & k_3 & -k_{-3} \end{bmatrix}$$
Further Exploration

- Solving First-Order reaction schemes
- Use of eigenvalues and eigenvectors to solve homogeneous linear systems of differential equations
- Quantum Mechanics
- Absorption Towers and miscellaneous chemical engineering applications
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- Claire Vallance, Molecular Symmetry
- Lionello Pogliani, Matrix and Convolution Methods in Chemical Kinetics