Part 4. Formal Kinetics of Complex Reactions
What means ‘complex’?

Reactions of ‘Simple Types’ – rate can be described by the Law of Mass Action in its basic form

In the framework of the Formal Kinetics

Complex reaction – combination of several reactions of ‘simple types’:

1. parallel

\[ A \rightarrow B \]

2. consecutive

\[ A \rightarrow B \rightarrow P \]

3. reversible (two-side)

\[ A \rightleftharpoons B \]

Further Complication – combination of more than two ‘simple’ reactions in general –

\[ x(1) + y(2) + z(3) \]
What means ‘complex’?

\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>№</th>
<th>Стадия</th>
<th>(k_i)</th>
<th>(n)</th>
<th>(E)</th>
<th>(k_{-i})</th>
<th>(n)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>(\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH})</td>
<td>(1.92 \times 10^{14})</td>
<td>0.00</td>
<td>1.64 \times 10^4</td>
<td>(5.48 \times 10^{13})</td>
<td>0.39</td>
<td>(-2.93 \times 10^3)</td>
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<tr>
<td>3, 4</td>
<td>(\text{O} + \text{H}_2 \leftrightarrow \text{H} + \text{OH})</td>
<td>(5.08 \times 10^{14})</td>
<td>2.67</td>
<td>6.29 \times 10^3</td>
<td>(2.67 \times 10^4)</td>
<td>2.65</td>
<td>(4.88 \times 10^3)</td>
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<td>5, 6</td>
<td>(\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O})</td>
<td>(2.16 \times 10^8)</td>
<td>1.51</td>
<td>3.43 \times 10^3</td>
<td>(2.30 \times 10^8)</td>
<td>1.40</td>
<td>(1.83 \times 10^6)</td>
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<tr>
<td>7, 8</td>
<td>(\text{O} + \text{H}_2\text{O} \leftrightarrow 2\text{OH})</td>
<td>(2.97 \times 10^6)</td>
<td>2.02</td>
<td>1.34 \times 10^4</td>
<td>(1.47 \times 10^5)</td>
<td>2.11</td>
<td>(-2.93 \times 10^3)</td>
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<tr>
<td>9, 10</td>
<td>(\text{H}_2 + \text{M} \leftrightarrow 2\text{H} + \text{M})</td>
<td>(4.58 \times 10^{19})</td>
<td>-1.40</td>
<td>1.04 \times 10^5</td>
<td>(1.15 \times 10^{20})</td>
<td>-1.68</td>
<td>8.20 \times 10^2</td>
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<td>11, 12</td>
<td>(\text{O}_2 + \text{M} \leftrightarrow 2\text{O} + \text{M})</td>
<td>(4.52 \times 10^{17})</td>
<td>-0.64</td>
<td>1.19 \times 10^5</td>
<td>(6.17 \times 10^{15})</td>
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<tr>
<td>13, 14</td>
<td>(\text{OH} + \text{M} \leftrightarrow \text{O} + \text{H} + \text{M})</td>
<td>(9.88 \times 10^{17})</td>
<td>-0.74</td>
<td>1.02 \times 10^5</td>
<td>(4.71 \times 10^{18})</td>
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<td>15, 16</td>
<td>(\text{H}_2\text{O} + \text{M} \leftrightarrow \text{H} + \text{OH} + \text{M})</td>
<td>(1.91 \times 10^{21})</td>
<td>-1.83</td>
<td>1.19 \times 10^6</td>
<td>(4.50 \times 10^{22})</td>
<td>-2.00</td>
<td>0.00</td>
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<tr>
<td>17, 18</td>
<td>(\text{H} + \text{O}_2 + \text{M} \leftrightarrow \text{HO}_2 + \text{M})</td>
<td>(1.48 \times 10^{12})</td>
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<td>0.00</td>
<td>(3.09 \times 10^{12})</td>
<td>0.53</td>
<td>(4.89 \times 10^4)</td>
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<tr>
<td>19, 20</td>
<td>(\text{HO}_2 + \text{H} \leftrightarrow \text{H}_2 + \text{O}_2)</td>
<td>(1.66 \times 10^{13})</td>
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<td>8.23 \times 10^4</td>
<td>(3.16 \times 10^{13})</td>
<td>0.35</td>
<td>(5.55 \times 10^4)</td>
</tr>
<tr>
<td>21, 22</td>
<td>(\text{HO}_2 + \text{H} \leftrightarrow 2\text{OH})</td>
<td>(7.08 \times 10^{13})</td>
<td>0.00</td>
<td>2.95 \times 10^2</td>
<td>(2.63 \times 10^{16})</td>
<td>0.72</td>
<td>(3.68 \times 10^4)</td>
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<tr>
<td>23, 24</td>
<td>(\text{HO}_2 + \text{H} \leftrightarrow \text{OH} + \text{O}_2)</td>
<td>(3.25 \times 10^{13})</td>
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<td>0.00</td>
<td>(3.25 \times 10^{13})</td>
<td>0.33</td>
<td>(5.33 \times 10^4)</td>
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<tr>
<td>25, 26</td>
<td>(\text{HO}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{O}_2)</td>
<td>(2.89 \times 10^{13})</td>
<td>0.00</td>
<td>-4.97 \times 10^4</td>
<td>(5.86 \times 10^{13})</td>
<td>0.24</td>
<td>(6.91 \times 10^5)</td>
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<td>27, 28</td>
<td>(\text{H}_2\text{O}_2 + \text{O}_2 \leftrightarrow 2\text{HO}_2)</td>
<td>(4.63 \times 10^{16})</td>
<td>-0.35</td>
<td>5.07 \times 10^6</td>
<td>(4.2 \times 10^{14})</td>
<td>0.00</td>
<td>(1.2 \times 10^4)</td>
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<tr>
<td>29, 30</td>
<td>(\text{H}_2\text{O}_2 + \text{M} \leftrightarrow 2\text{OH} + \text{M})</td>
<td>(2.95 \times 10^{14})</td>
<td>0.00</td>
<td>4.84 \times 10^6</td>
<td>(3.66 \times 10^8)</td>
<td>1.14</td>
<td>(-2.58 \times 10^3)</td>
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<td>31, 32</td>
<td>(\text{H}_2\text{O}_2 + \text{H} \leftrightarrow \text{H}_2\text{O} + \text{OH})</td>
<td>(2.41 \times 10^{13})</td>
<td>0.00</td>
<td>3.97 \times 10^3</td>
<td>(1.27 \times 10^5)</td>
<td>1.31</td>
<td>(7.14 \times 10^6)</td>
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<td>33, 34</td>
<td>(\text{H}_2\text{O}_2 + \text{H} \leftrightarrow \text{H}_2 + \text{HO}_2)</td>
<td>(6.03 \times 10^{13})</td>
<td>0.00</td>
<td>7.95 \times 10^3</td>
<td>(1.04 \times 10^{12})</td>
<td>0.70</td>
<td>(2.40 \times 10^3)</td>
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<tr>
<td>35, 36</td>
<td>(\text{H}_2\text{O}_2 + \text{O} \leftrightarrow \text{OH} + \text{HO}_2)</td>
<td>(9.55 \times 10^6)</td>
<td>2.00</td>
<td>3.97 \times 10^3</td>
<td>(8.66 \times 10^7)</td>
<td>2.68</td>
<td>(1.86 \times 10^6)</td>
</tr>
<tr>
<td>37, 38</td>
<td>(\text{H}_2\text{O}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{HO}_2)</td>
<td>(1.00 \times 10^{12})</td>
<td>0.00</td>
<td>0.00</td>
<td>(1.84 \times 10^{10})</td>
<td>0.59</td>
<td>(3.09 \times 10^4)</td>
</tr>
</tbody>
</table>
What means ‘complex’?

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{<products>} \]
What means ‘complex’?

Chemical Kinetics – the doctrine of the Chemical Processes, their mechanisms and development in time and space

Mechanism of reaction:

for complex (multi-step) reaction –
the sequence of chemical steps and intermediate products (intermediates) that leads from the initial reactant(s) to the final product(s);

for elementary reactions –
trajectories of motions of atomic nuclei, variations of electron density and energetic state of the system during its transition from reactant(s) to product(s)
Direct Kinetic Problem (Task) –

to predict (simulate) the system behaviour based on the existing kinetic model (reaction scheme, kinetic equations) and its parameters

Reverse Kinetic Problem (Task) –

to determine the type of kinetic model (to chose among possible types of description, kinetic equations, etc.) and/or its parameters based on the existing data on the system behaviour (experimental data)

– as a rule, incorrectly determined task; has no rigorous and unambiguous solution exclusively based on the kinetic data;

– requires repeated solution of Direct Kinetic Problem and selection of ‘optimal’ description of experimental data
What means ‘complex’?
Reactions of ‘Simple Types’ – rate can be described by the Law of Mass Action in its basic form.
Scientific Laws – models of Objects and Phenomena that reflect:

(i) the current level of their comprehension;
(ii) stable (repeatable, reproducible) relation(ship)s between them ⇒

based on practice (observations, experiment, etc.)

Principles – also based on practice ‘tools of knowledge’, but sublimed to the level of ‘common sense’, i.e. higher degree of generalization than laws.

Any scientific discipline (including Chemical Kinetics) operates both laws and principles
What means ‘complex’?

Reactions of ‘Simple Types’ – rate can be described by the Law of Mass Action in its basic form

\[ W = k \prod_{i=1}^{m} [C_i]^{n_i} \]

Complex reactions –

Independence Principle (W.F. Ostwald):

the Law of Mass Action can be used for each ‘simple’ reaction occurring in the system as if it is the only reaction in given conditions
Complex Reaction

What means ‘complex’?
Reactions of ‘Simple Types’ – rate can be described by the Law of Mass Action in its basic form.

\[ W = k \prod_{i=1}^{m} [C_i^{n_i}] \]

- parallel
  \[ -d[A]/dt = k_1[A] + k_2[A] = k'[A] \]

- consecutive
  \[ -d[A]/dt = k_1[A]; \quad d[B]/dt = k_1[A] - k_2[B] \]

- reversible (two-side)
  \[ -d[A]/dt = k_1[A] - k_2[B] \]

+ mass-balance equations, i.e. \([A] + [B] + [D] + [P] = [A]_0\)
‘Simple Complexity’ – some features of parallel reactions:

\[ \begin{align*}
A & \xrightarrow[]{} P_1 & \text{if } n_1 = n_2 = 1: \\
& & X = 1 - e^{-(k_1 + k_2)t}; \quad Y_j = \frac{X k_j}{\Sigma k_i}; \quad S_j = \frac{k_j}{\Sigma k_i}
\end{align*} \]

\[ \begin{align*}
n_1 \ A & \rightarrow P_1 & \text{if } n_1 = n_2: & \quad S_1 = S_2 \quad @ \text{any } X \\
n_2 \ A & \rightarrow P_2 & \text{if } n_1 < n_2: & \quad S_1/S_2 \uparrow \quad @ \text{X} \uparrow
\end{align*} \]
‘Simple Complexity’ – some features of reversible (two-side) reactions:

\[ A \rightleftharpoons B \]

if \( n_1 = n_{-1} = 1 \):

\[-\frac{d(1-X)}{dt} = k_1(1-X) - k_{-1}X; \quad Y = 1 - X\]

and

\[ X = \left[ 1 - e^{-(k_1+k_{-1})t} \right] \frac{1}{1+k_{-1}/k_1} < 1 \]

\( t \to \infty \Rightarrow \)

\[ k_1C(A) = k_{-1}C(P) \Rightarrow X \to X_\infty = \frac{1}{1+k_{-1}/k_1} \]

EQUILIBRIUM: rates of all reciprocally reverse processes (i.e., chemical reactions) are equal
REVERSIBILITY and EQUILIBRIUM

(L. Botzman, J.C. Maxwell, R. Wegscheider, R.C. Tolman, A. Einstein, G.N. Lewis, L. Onzager, …)
REVERSIBILITY and EQUILIBRIUM

(L. Botzman, J.C. Maxwell, R. Wegscheider, R.C. Tolman, A. Einstein, G.N. Lewis, L. Onzager, …)

Microscopic Reversibility Principle (for Chemistry):
any ‘simple’ (elementary) chemical reaction can proceed in both reciprocally reverse directions

Detailed Equilibrium (or Balance) Principle:
if the state of global equilibrium is reached in some system, any partial equilibria are also achieved

or

at equilibrium each elementary process should be balanced by its reverse process
Microscopic Reversibility Principle (for Chemistry):

any ‘simple’ (elementary) chemical reaction can proceed in both reciprocally reverse directions

‘thermodynamic consistency’ in microkinetic analysis – ensures that complex system reaches global equilibrium at $t \rightarrow \infty$
Detailed Equilibrium (or Balance) Principle:
if the state of global equilibrium is reached in some system, any
partial equilibria are also achieved

Example: Selection of catalysts

‘basic’ reactions: \[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \]
\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

‘target’ reaction: \[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \]
Detailed Equilibrium (or Balance) Principle:

if the state of global equilibrium is reached in some system, any partial equilibria are also achieved

**Example: Selection of catalysts**

‘basic’ reactions: \[ \text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 5\text{H}_2 \]

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \]

‘target’ reaction: \[ \text{C}_2\text{H}_6 + \text{H}_2 \rightleftharpoons 2\text{CH}_4 \]
Thank You for Your Attention!

Lecture Course from Russian Catalytic Society and Haldor Topsoe

Catalysis and Chemical Engineering: Theoretical Bases and Selected Applications

2016-2017