Supporting Information

for

Catalysis Revisited – An Overview of Classical School Experiments and New Approaches for a Better Conceptual Understanding

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Evaluation of the kinetic data by the spreadsheet program Excel

The evaluation of the kinetic data was done by using MS Excel. For the approximations for all kind of curves in the text the “Solver” function was used. A detailed description of how to build the BYOD photometer can be looked up in the supporting information of the article “Glucose in the photobox – a new method for photometric glucose determination in chemistry classes by using digital media”. An example for using of the “Solver” in German language is given by Table 1* shown below. In this example, previously measured values were approximated by a general exponential function \( E(t) = A + E_0 \cdot e^{-k't} \).

### Table 1*: How to use the "Solver" function in MS Excel

- **First**, the "Solver" function in Excel must be activated:
  
  "Datei" > "Optionen" > "Add – Ins" > "Solver" > "Los" > "Solver" > "OK"

- **Now** the "Solver" function appears in the menu bar under "Data" on the right side.

- **The extinctions at** the respective measurement times are calculated and tabulated in a new column.

\[
E_{\text{Mess.}}(t) = \log(255/(\text{SUMME}(\text{RGB})))/3)
\]

- **In another column** the function for approximating the measured values is defined.

\[
E(t) = A + E_0 \cdot e^{-k't}
\]

\( A = \) residual extinction (Asymptote), \( E_0 = \) extinction in \( t = 0 \), \( k' = \) rate of the reaction, \( t = \) time
• The parameters $A$, $E_0$ and $k'$ are first assigned the value 1 in separate cells.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
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<td>20</td>
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</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• In a new column the function values are calculated with the values of the parameters at any time $t$. It is important to note that the values of the parameters are fixed with "$" for each row (for example: A$30 is the reference to the value in cell A30, which is taken over for every further calculation in the column).

\[= A$30 + B$30 \times \exp(-C$30 \times A4)\]

(exemplary for the first entry of column G of the calculated function values of the approximation)

• In another column the difference between measured value $E_{Mess.}(t)$ and calculated value $E(t)$ is calculated (distances)

\[= E4 - G4\]

• These distances are squared in a new column.

\[= H4^2\]
• The squares of the distances are added up and displayed in a new box.

\[ = \text{SUMME}(I4: I27) \]

• The "Solver" is opened via the menu-band and the calculated sum of the distance squares for the variation of the parameters \( A, E_0 \) and \( k' \) is minimized.

• For this purpose, the cell with the sum of the distance squares is selected,
• Minimization selected as the work step
• and select the cells with the values of the variables.

• Finally click on "Solve".

Values of the water electrolysis

Data:

<table>
<thead>
<tr>
<th>t [min]</th>
<th>Distilled water, 20 V DC anode(O_2)</th>
<th>cathode(H_2)</th>
<th>0.3 M (H_2SO_4), 10 V DC anode(O_2)</th>
<th>cathode(H_2)</th>
<th>0.3 M (H_2SO_4), 20 V DC anode(O_2)</th>
<th>cathode(H_2)</th>
</tr>
</thead>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0.6</td>
<td>1.2</td>
<td>1.2</td>
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</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>1.2</td>
<td>2.4</td>
<td>2.4</td>
<td>4.8</td>
</tr>
<tr>
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<td>0</td>
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<td>3.4</td>
<td>3.6</td>
<td>7.2</td>
</tr>
<tr>
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<td>0</td>
<td>2.2</td>
<td>4.4</td>
<td>4.8</td>
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</tr>
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<td>0</td>
<td>2.8</td>
<td>5.4</td>
<td>6.2</td>
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</tr>
<tr>
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<td>3.2</td>
<td>6.6</td>
<td>7.4</td>
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<td>0</td>
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<td>8.6</td>
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</tr>
<tr>
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<td>0</td>
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<tr>
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<td>10.8</td>
<td>12.6</td>
<td>24.4</td>
</tr>
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</table>
Reaction of sodium thiosulfate with hydrochloric acid

Derivation:

A simplified reaction equation for the acid catalysed decomposition of sodium thiosulfate is given by:

\[ Na_2S_2O_3 + 2 HCl \rightarrow \frac{1}{8} \cdot S_8 + SO_2 + 2 NaCl \]  

(1*)

Measuring the time until the reaction mixture becomes opaque, we measure the amount of sulphur being produced.

\[ \frac{d[S]}{dt} = k \cdot [Na_2S_2O_3] \cdot [HCl]^2 \]  

(2*)

The simplified equation illustrates the rate of the reaction to be first order in \([Na_2S_2O_3]\). This is just the case for assuming equation (1*) is taken as the basis for the following kinetic considerations. In reality the rate of the reaction is considered to be approximately of 3/2 order in sodium thiosulfate and 1/2 order in hydrochloric acid.

To verify the reaction order of the reaction between sodium thiosulfate and hydrochloric acid, we need the kinetic data from the experiment. The data show, that the relation between the inverse time until complete turbidity and the concentration of sodium thiosulfate is linear.

We measure the time to complete turbidity of the reaction mixture. The amount of colloidal sulfur formed is the same at the point of maximum turbidity for all initial concentrations of sodium thiosulfate. \(d[S] = const.\) is the same for all initial concentrations. Since we are looking at the average rate, \(dt = t - t_0 = t\) and corresponds to the time elapsed until complete turbidity. From the graphical plot of the inverse reaction time \(t^{-1}\) against the initial concentration of sodium thiosulfate, it is obvious that they are proportional to each other.

\[ v_{avg.} = \frac{d[S]_{const.}}{t} \sim [Na_2S_2O_3]_0 \]  

(3*)

For a short period of time, the average speed approximately corresponds to the momentary speed. Using (1*), it follows:

\[ v = \frac{d[S]}{dt} \sim [Na_2S_2O_3] \Rightarrow \frac{d[S]}{dt} = k' \cdot [Na_2S_2O_3] \]  

(4*)

\[ \frac{d[S]}{dt} = - \frac{d[Na_2S_2O_3]}{dt} = k' \cdot [Na_2S_2O_3] \]  

(5*)

\[ \Rightarrow \frac{d[Na_2S_2O_3]}{dt} = -k' \cdot [Na_2S_2O_3] \]  

(6*)

According to our measurements, the reaction is first order in the concentration of sodium thiosulfate. We can write:

\[ [Na_2S_2O_3](t) = [Na_2S_2O_3]_0 \cdot e^{-k't} \]  

(7*)
Due to the linearity of the curve of the logarithmized equation (7*), we assume that at the points of complete turbidity $\ln((Na_2S_2O_3)(t_{turb.})) = 0$. By transformation equation (7*) simplifies to:

$$\Leftrightarrow k' = \frac{\ln (c_0(Na_2S_2O_3))}{t}$$  

(8*)

The calculated values for $k$ are shown in table 2 of the manuscript. The activation energy can be calculated as described in the text.

Iodation of acetone

Derivation:

The reaction mechanism is shown in the following equation 1) and 2).

1) 

\[ \text{H}^+ + \text{Ac} \xleftrightarrow[K]{ \text{H}^+} \text{AcH}^+ \]

2) 

\[ \text{Ac} + \text{I}_2 \xrightarrow[k_2]{ \text{H}^+} \text{Ac} \text{H}^+ + \text{I}^- \]

Using the equation 1), the equilibrium constant $K$ for formation of the protonated transition state of acetone $[AcH^+]$ is given by following equation.

$$K = \frac{[AcH^+]}{[Ac] \cdot [H^+]}$$  

(9*)

The rate equation for the enol can be set up using the second part of equation 1) and equation 2).

$$\frac{d[Enol]}{dt} = k_1[AcH^+] - k_{-1}[Enol][H^+] - k_2[Enol][I_2]$$  

(10*)

In the equilibrium, the concentration of the enol is assumed to remain unchanged. Equal amounts of the enol are produced by the reaction of acetone with hydrochloric acid as they are consumed reacting with the iodine in solution. The concentration of the enol is supposed to be quasi-stationary. To simplify the calculation, we can use the steady state approximation and equation (12).

$$\frac{d[Enol]}{dt} = k_1[AcH^+] - k_{-1}[Enol][H^+] - k_2[Enol][I_2] = 0$$  

$$\Leftrightarrow [Enol] = \frac{k_1 \cdot K \cdot [Ac] \cdot [H^+]}{k_{-1}[H^+] - k_2[I_2]}$$  

(11*)
In the last reaction step, the same amount of iodoacetone [AcI] produced as the amount of iodine is consumed. The rate equation for the iodine consumption is therefore minus the rate equation for the formation of iodine.

\[
\frac{d[I_2]}{dt} = -\frac{d[AcI]}{dt} = -k_3[Enol][I_2] \quad (12^*)
\]

\[
\frac{d[I_2]}{dt} = -k_3 \cdot \frac{k_1 \cdot K \cdot [Ac] \cdot [H^+]}{k_{-1}[H^+] - k_2[I_2]} \quad [I_2] \quad (13^*)
\]

The reaction (discoloration) takes place rather quickly, therefore the reaction rate of the formation of iodoacetone and thereby of the consumption iodine is much higher, than the reaction rate of the reverse reaction of the formation of the enol:

\[
k_2[I_2] \gg k_{-1}[H^+] \quad (14^*)
\]

Therewith, equations (16) and (17) can be combined and simplified.

\[
\frac{d[I_2]}{dt} = -k_2 \cdot \frac{k_1 \cdot K \cdot [Ac] \cdot [H^+]}{k_2[I_2]} \cdot [I_2] = -k_1 \cdot K \cdot [Ac] \cdot [H^+] = K^* \cdot [Ac] \cdot [H^+] \quad (15^*)
\]

The mathematical investigations show, that the rate of the consumption of iodine during the reaction is zero order with respect to iodine. The degression of its concentration is linear, verifying the order of the reaction. The mathematical investigations also prove, that in the degression of the iodine concentration is first order with respect to both acetone [Ac] and hydrochloric acid [H+], in total second order. The experimental data verify this interdependence by varying the concentrations of the reactants and measuring the reaction rate.

**Enzyme catalysis**

**Verification of equation (15) of the manuscript**

In the measurement, we consider the average velocity. It is directly proportional to the concentration of the product.

\[
v_0 = \frac{dc(S)}{dt} = \frac{c_0(S) - c_t(S)}{dt} \quad \text{at constant}\quad \tau \cdot (c_0(S) - c_t(S)) = \tau \cdot c(P) \quad (16^*)
\]

- With Labert-Beer’s law it follows:

\[
E = \varepsilon_\lambda \cdot c \cdot d = \varepsilon_\lambda \cdot c(P) \cdot d = \varepsilon_\lambda \cdot \frac{v_0}{\tau} \cdot d
\]

\[
\Leftrightarrow \; v_0 = \frac{\tau \cdot E}{\varepsilon_\lambda \cdot d} \quad ; \quad \theta = \frac{\tau}{\varepsilon_\lambda \cdot d} \quad (17^*)
\]
\[
v_0 = \frac{v_{\text{max}} \cdot c(S)}{K_M + c(S)} = \theta \cdot E \iff E = \frac{1}{\theta} \cdot \frac{v_{\text{max}} \cdot c(S)}{K_M + c(S)} = \frac{v_{\text{max}} \cdot c(S)}{K_M + c(S)} ; \quad v_{\text{max}} = \frac{v_{\text{max}}}{\theta} \tag{19*}
\]

- So we rewrote the equation for Michaelis–Menten kinetics according to the absorbance E:

\[
E = \frac{v_{\text{max}} \cdot c(S)}{K_M + c(S)} \tag{20*}
\]

- \(c(S)\) is unknown to us, we only know \(c(P)\) and the initial concentration of the enzyme, because we have created a calibration curve.

- We now rewrite \(c(S)\) (see Michaelis–Menten derivation\(^2\)):

\[
c(S) = K_M \cdot \frac{c(ES)}{c(E)} = K_M \cdot \frac{c_0(E) - c(E)}{c(E)} = K_M \cdot \left(\frac{c_0(E)}{c(E)} - 1\right) \tag{21*}
\]

\[
\frac{dc(ES)}{dt} = 0 \text{ (steady state). It follows: } 0 = \frac{d(c_0(E) - c(E))}{dt} \iff c(E) = \text{const.} \tag{22*}
\]

\[
\Rightarrow c(S) \sim c_0(E), \text{ thus } c(S) = \phi \cdot c_0(E) \tag{23*}
\]

- If we put this into the equation for the extinction, we get:

\[
E = \frac{v_{\text{max}}^* \cdot c(S)}{K_M + c(S)} = \frac{v_{\text{max}}^* \cdot \phi \cdot c_0(E)}{K_M + \phi \cdot c_0(E)} = \frac{1}{\phi} \cdot \frac{v_{\text{max}}^* \cdot c_0(E)}{K_M + c_0(E)} = \frac{v_{\text{max}}^* \cdot c_0(E)}{K_M + c_0(E)} \tag{24*}
\]

Equation (24*) in the supporting information is equation (19) of the manuscript text.

References

1 Fleischer, H.; Reinmold, M.; Salzner, J.; Lühken, A. Glucose in the Photobox – A New Method for Photometric Glucose Determination in Chemistry Classes by Using Digital Media. CHEMKON, 2023, https://doi.org/10.1002/ckon.202200056

2 Atkins, P. & De Paula, J. Physical Chemistry; Macmillan, 2006; 840-841