Supplementary Information for: IPLOT-VKA: an Integral-method Powell-pLOT-enhanced Visual Kinetic Analysis for the determination of orders of reaction

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For a reaction

$$|\nu_{\mathrm{A}}|\mathrm{A} + |\nu_{\mathrm{B}}|\mathrm{B} \longrightarrow |\nu_{\mathrm{P}}|\mathrm{P} + |\nu_{\mathrm{Q}}|\mathrm{Q}$$

the stoichiometric coefficient $|\nu_{\mathrm{X}}|$ is the absolute values of the stoichiometric number ν_{X}, which is positive for products and negative for reagents. For the above reaction to be called *simple*, within all the data domain, the rate law must follow the equation

$$R = \frac{1}{\nu_{\mathrm{X}}}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{b} \tag{1}$$

for X any of A, B, P, Q, or, with $k_A = |\nu_A|k$,

$$R_A = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{A}}[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{b} \tag{2}$$

It can be useful to consider Eq. 2 first in the basic case $b = 0$ and from two perspectives. First, as a differential equation, it can be solved numerically, as it is mandatory for most chemical systems. According to one of the simplest numerical methods, known as middle-point or second-order Runge-Kutta,[25] for $n+1$ time values t_0, $t_1 \dots t_n$, and corresponding time intervals $\Delta t_i = t_i - t_{i-1}$, in order to get the concentration of P at time t, estimates are needed of the time derivatives of the rate R at the midpoint of the intervals. If the concentrations of A are already known at the chosen times, the needed estimates can be approximated as

$$[\mathrm{P}] - [\mathrm{P}]_0 = [\mathrm{A}]_0 - [\mathrm{A}] \simeq \Sigma_{i=1}^{n} R_A(t_i + \frac{\Delta t_i}{2})\Delta t_i = \Sigma_{i=1}^{n} k_A [A]^{\mathrm{a}} \Delta t_i, \tag{3}$$

which is the operative equation of the Variable Time Normalization Kinetics (VTNK), in case of a single reactant.[4] Essentially, one computes different estimates of [P] for different values of the order a, and then chooses the order of reaction, which best matches the experimental values. The very same strategy is shared from a second perspective, whereby the basic expression 2 is integrated analytically. To this end, after separating the variables, it is useful to render adimensional the two hand sides multiplying by a power of the initial concentration:

$$-[A]_0^{\mathrm{a}-1} \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^{\mathrm{a}}} = -\int_1^{\alpha} \frac{d\alpha}{\alpha^{\mathrm{a}}} = \Delta f \tag{4}$$

$$= kt[A]_0^{\mathrm{a}-1} = k\tau = \theta, \tag{5}$$

where we introduced $\alpha = \frac{[A]}{[A]_0}$, i.e. the fraction of unreacted substrate, and an initial-concentration-scaled time τ, and the dimensionless θ, called reduced time by Margerison.[10] The definite integral

$$\Delta f = f(1, \mathrm{a}) - f(\alpha, \mathrm{a}) = \frac{1 - \alpha^{1-\mathrm{a}}}{1 - \mathrm{a}} \tag{6}$$

can be straightforwardly computed and it is independent of initial concentrations (beware that for $\mathrm{a} = 1$, its limit form

$$\lim_{\mathrm{a}\to 1} \Delta f = -\ln \alpha \tag{7}$$

must be used).

Rather than plotting Δf vs t, as is typical in the integration method, Powell suggested to plot α against the decimal logarithm of time. The relationship between α and time can be worked out from Eq. 5 and 6 upon setting $k[A]_0^{1-\mathrm{a}} t^* = 1$, where t^* is the unit of time:

$$\alpha = [1 - (1 - \mathrm{a})t]^{\frac{1}{1-\mathrm{a}}}; \tag{8}$$

once more a limit form for $\mathrm{a} = 1$ is needed:

$$\lim_{\mathrm{a}\to 1} \ln \alpha = -\frac{t}{t^*} \tag{9}$$

Analysis of Eq. 2 as a simple reaction benefits from a check of whether the kinetic problem is one-dimensional, i.e. the stoichiometric coefficients are constant. In this case the disappearance of A and B are proportional to each other, $(\Delta[\mathrm{B}])/\Delta[\mathrm{A}] = \frac{\nu_B}{\nu_A} = r$, and it is possible to write

$$[\mathrm{B}] = [\mathrm{B}]_0[1 - r(1-\alpha)] = [\mathrm{A}]_0[I - r(1-\alpha)], \tag{10}$$

where $I = [\mathrm{B}]_0/[\mathrm{A}]_0$, so that the kinetic equation 2 can still be addressed by separation of variables α and t. In the special case of stoichiometric proportions of reactants, $I = \frac{\nu_B}{\nu_A} = r$, the integrated rate law coincides with that of a single reactant with order $m = \mathrm{a} + b$ (the kinetic constant gets multiplied by r^b). In the general case $I = r(1+c)$ and then, normalizing Eq. 2 for the initial concentration of A, we get

$$-[\mathrm{A}]_0^{\mathrm{a}+b-1} \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^b} = -\int_1^{\alpha} \frac{d\alpha}{\alpha^{\mathrm{a}}(\alpha + c)^b} = \Delta f(\alpha; \mathrm{a}, b, c) = k r^b \theta \tag{11}$$

Now, the definite integral depends on three parameters, a, b and c, in addition to the unreacted fraction of substrate α. It can be expressed in terms of the hypergeometric function:

$$\Delta f(\alpha;\mathrm{a},b,c) = -\frac{{}_2\mathrm{F}_1\left(b, 1-\mathrm{a};\ 2-\mathrm{a};\ -\frac{1}{c}\right)}{c^b\left(\mathrm{a}-1\right)} + \frac{\alpha^{1-\mathrm{a}}\,{}_2\mathrm{F}_1\left(b, 1-\mathrm{a};\ 2-\mathrm{a};\ -\frac{\alpha}{c}\right)}{c^b\left(\mathrm{a}-1\right)} \tag{12}$$

. The hypergeometric function is readily calculated by a power series and coincides with common functions for special values of its parameters, although it suffers from singularities for special values of its parameters.[23] At semi-integer steps in the [-1,3] domain, 79 times out of 81, the hypergeometric function can be expressed in terms of common functions, 15 of which are common to Margerison's chapter, while the remaining solutions reported below are new. Some of Margerison's integrals had different analytic form for positive, negative or null values of c, but they all match exactly with those reported below. Some of the analytic integrals are not defined close to $c = 0$, where either a Taylor expansion or the hypergeometric function itself should be used. It can be useful to use the approximations

$$\begin{aligned}
-\frac{d\alpha}{dt} &= k_\mathrm{A}[\mathrm{A}]_0^{(\mathrm{a}+b-1)}\alpha^{\mathrm{a}+b}r^b\left(1+b\frac{c}{\alpha}\right) \qquad |c| << \alpha \\
-\frac{d\alpha}{dt} &= k_\mathrm{A}[\mathrm{A}]_0^{(\mathrm{a}+b-1)}\alpha^{\mathrm{a}}r^b c^b\left(1+b\frac{\alpha}{c}\right) \qquad \alpha << |c|
\end{aligned} \tag{13}$$

and then, considering that

$$\begin{aligned}
\frac{1}{1+b\frac{c}{\alpha}} &\simeq 1-b\frac{c}{\alpha} \qquad b|c| << \alpha \\
\frac{1}{1+b\frac{\alpha}{c}} &\simeq 1-b\frac{\alpha}{c} \qquad b\alpha << |c|
\end{aligned} \tag{14}$$

$$
\begin{aligned}
\frac{\alpha^{1-(a+b)}-1}{1-(a+b)} - bc\frac{\alpha^{-(a+b)}-1}{-(a+b)} &= -k_{\mathrm{A}}[\mathrm{A}]_0^{a+b-1} r^b t \qquad |c| << \alpha \\
\frac{\alpha^{1-a}-1}{1-a} - \frac{b}{c}\frac{\alpha^{2-a}-1}{2-a} &= -k_{\mathrm{A}}[\mathrm{A}]_0^{a+b-1} r^b c^b t \qquad \alpha << |c|
\end{aligned}
$$

In the following tables the analaytic results of the integral $\int_1^{\alpha} \frac{d\alpha}{\alpha^{\mathrm{a}}(\alpha+c)^b}$ are reported for different values of a and b. Please consider $x \equiv \alpha$.

Case $b = -1$

a	Analytic form
-1	$\frac{x^2\,(3\,c+2\,x)}{6} - \frac{c}{2} - \frac{1}{3}$
-0.5	$\frac{2\,x^{3/2}\,(5\,c+3\,x)}{15} - \frac{2\,c}{3} - \frac{2}{5}$
0	$\frac{(x-1)\,(2\,c+x+1)}{2}$
0.5	$\frac{2\,\sqrt{x}\,(3\,c+x)}{3} - 2\,c - \frac{2}{3}$
1	$x + c\,\ln(x) - 1$
1.5	$2\,c - \frac{2\,(c-x)}{\sqrt{x}} - 2$
2	$c + \ln(x) - \frac{c}{x}$
2.5	$\frac{2\,c}{3} - \frac{2\,c+6\,x}{3\,x^{3/2}} + 2$
3	$\frac{c}{2} - \frac{c+2\,x}{2\,x^2} + 1$

Case $b = -0.5$

a	Analytic form
-1	$\frac{2\,(2\,c-3)\,(c+1)^{3/2}}{15} - \frac{2\,(c+x)^{3/2}\,(2\,c-3\,x)}{15}$
-0.5	$\frac{c^2\,\ln\left(c+2\,\sqrt{c+1}+2\right)}{8} - \left(\frac{c}{4}+\frac{1}{2}\right)\,\sqrt{c+1} - \frac{c^2\,\ln\left(c+2\,x+2\,\sqrt{x}\,\sqrt{c+x}\right)}{8} + \sqrt{x}\,\sqrt{c+x}\,\left(\frac{c}{4}+\frac{x}{2}\right)$
0	$\frac{2\,(c+x)^{3/2}}{3} - \frac{2\,(c+1)^{3/2}}{3}$
0.5	$\sqrt{x}\,\sqrt{c+x} - 2\,c\,\mathrm{atanh}\left(\frac{1}{\sqrt{c+1}-\sqrt{c}}\right) - \sqrt{c+1} + 2\,c\,\mathrm{atanh}\left(\frac{\sqrt{x}}{\sqrt{c+x}-\sqrt{c}}\right)$
1	$2\,\sqrt{c+x} - 2\,\sqrt{c}\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right) - 2\,\sqrt{c+1} + 2\,\sqrt{c}\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)$
1.5	$2x^{-0.5}c^{0.5}\ {}_2F_1(-0.5,-0.5;0.5;-x/c) + \mathrm{const}$
2	$\sqrt{c+1} - \frac{\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{\sqrt{c}} + \frac{\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{\sqrt{c}} - \frac{\sqrt{c+x}}{x}$
2.5	$\frac{2\,(c+1)^{3/2}}{3\,c} - \frac{2\,(c+x)^{3/2}}{3\,c\,x^{3/2}}$
3	$\frac{\sqrt{c+1}}{4} + \frac{\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{4\,c^{3/2}} + \frac{(c+1)^{3/2}}{4\,c} - \frac{\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{4\,c^{3/2}} - \frac{\sqrt{c+x}}{4\,x^2} - \frac{(c+x)^{3/2}}{4\,c\,x^2}$

Case $b = 0$

a	Analytic form
-1	$\frac{x^2}{2} - \frac{1}{2}$
-0.5	$\frac{2\,x^{3/2}}{3} - \frac{2}{3}$
0	$x - 1$
0.5	$2\,\sqrt{x} - 2$
1	$\ln{(x)}$
1.5	$2 - \frac{2}{\sqrt{x}}$
2	$1 - \frac{1}{x}$
2.5	$\frac{2}{3} - \frac{2}{3\,x^{3/2}}$
3	$\frac{1}{2} - \frac{1}{2\,x^2}$

Case $b = 0.5$

a	Analytic form
-1	$\frac{2\,(2\,c-1)\,\sqrt{c+1}}{3} - \frac{2\,\sqrt{c+x}\,(2\,c-x)}{3}$
-0.5	$2\,c\,\mathrm{atanh}\left(\frac{1}{\sqrt{c+1}-\sqrt{c}}\right) - \sqrt{c+1} + \sqrt{x}\,\sqrt{c+x} - 2\,c\,\mathrm{atanh}\left(\frac{\sqrt{x}}{\sqrt{c+x}-\sqrt{c}}\right)$
0	$2\,\sqrt{c+x} - 2\,\sqrt{c+1}$
0.5	$4\,\mathrm{atanh}\left(\frac{\sqrt{c+x}-\sqrt{c}}{\sqrt{x}}\right) - 4\,\mathrm{atanh}\left(\sqrt{c+1}-\sqrt{c}\right)$
1	$\frac{2\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{\sqrt{c}} - \frac{2\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{\sqrt{c}}$
1.5	$\frac{2\,\sqrt{c+1}}{c} - \frac{2\,\sqrt{c+x}}{c\,\sqrt{x}}$
2	$\frac{\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{c^{3/2}} + \frac{\sqrt{c+1}}{c} - \frac{\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{c^{3/2}} - \frac{\sqrt{c+x}}{c\,x}$
2.5	$\frac{2\,\sqrt{c+1}\,(c-2)}{3\,c^2} - \frac{2\,\sqrt{c+x}\,(c-2\,x)}{3\,c^2\,x^{3/2}}$
3	$\frac{5\,\sqrt{c+1}}{4\,c} - \frac{3\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{4\,c^{5/2}} - \frac{3\,(c+1)^{3/2}}{4\,c^2} + \frac{3\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{4\,c^{5/2}} - \frac{5\,\sqrt{c+x}}{4\,c\,x^2} + \frac{3\,(c+x)^{3/2}}{4\,c^2\,x^2}$

Case $b = 1$

a	Analytic form
-1	$x - c\,\ln(c+x) + c\,\ln(c+1) - 1$
-0.5	$2\sqrt{c}\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right) - \mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right) + 2\sqrt{x} - 2$
0	$\ln(c+x) - \ln(c+1)$
0.5	$-\frac{2\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right) - \mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{\sqrt{c}}$
1	$\frac{\ln(c+1) - \ln\left(\frac{c}{x}+1\right)}{c}$
1.5	$\frac{2\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right) - \mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{c^{3/2}} + \frac{2}{c} - \frac{2}{c\sqrt{x}}$
2	$-\frac{c - c\,x - x\,\ln\left(\frac{1}{c+1}\right) + x\,\ln\left(\frac{x}{c+x}\right)}{c^2\,x}$
2.5	$\frac{2}{3\,c} - \frac{2\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right) - \mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{c^{5/2}} - \frac{2}{c^2} - \frac{2\,c - 6\,x}{3\,c^2\,x^{3/2}}$
3	$\frac{2\,\mathrm{atanh}\left(\frac{2}{c}+1\right)}{c^3} - \frac{c - \frac{c^2}{2}}{c^3} - \frac{2\,\mathrm{atanh}\left(\frac{2\,x}{c}+1\right)}{c^3} + \frac{c\,x - \frac{c^2}{2}}{c^3\,x^2}$

Case $b = 1.5$

a	Analytic form
-1	$\frac{4\,c+2\,x}{\sqrt{c+x}} - \frac{4\,c+2}{\sqrt{c+1}}$
-0.5	$\frac{2}{3}x^{\frac{3}{2}}c^{-\frac{3}{2}}{}_2F_1(1.5, 1.5; 2.5; -\frac{x}{c}) + \text{const}$
0	$\frac{2}{\sqrt{c+1}} - \frac{2}{\sqrt{c+x}}$
0.5	$\frac{2\,\sqrt{x}}{c\,\sqrt{c+x}} - \frac{2}{c\,\sqrt{c+1}}$
1	$\frac{2}{c\,\sqrt{c+x}} - \frac{2}{c\,\sqrt{c+1}} - \frac{2\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{c^{3/2}} + \frac{2\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{c^{3/2}}$
1.5	$\frac{2\,(c+2)}{c^2\,\sqrt{c+1}} - \frac{2\,(c+2\,x)}{c^2\,\sqrt{x}\,\sqrt{c+x}}$
2	$\frac{3\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{c^{5/2}} - \frac{3\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{c^{5/2}} + \frac{c+3}{c^2\,\sqrt{c+1}} - \frac{c+3\,x}{c^2\,x\,\sqrt{c+x}}$
2.5	$\frac{2\left(-c^2+4\,c\,x+8\,x^2\right)}{3\,c^3\,x^{3/2}\,\sqrt{c+x}} - \frac{-2\,c^2+8\,c+16}{3\,c^3\,\sqrt{c+1}}$
3	$\frac{15\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{4\,c^{7/2}} - \frac{15\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{4\,c^{7/2}} - \frac{-2\,c^2+5\,c+15}{4\,c^3\,\sqrt{c+1}} + \frac{-2\,c^2+5\,c\,x+15\,x^2}{4\,c^3\,x^2\,\sqrt{c+x}}$

Case $b = 2$

a	Analytic form
-1	$\ln(c+x) - \ln(c+1) + \frac{c}{c+x} - \frac{c}{c+1}$
-0.5	$\frac{1}{c+1} - \frac{\operatorname{atan}\left(\frac{1}{\sqrt{c}}\right) - \operatorname{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)}{\sqrt{c}} - \frac{\sqrt{x}}{c+x}$
0	$\frac{1}{c+1} - \frac{1}{c+x}$
0.5	$\frac{\sqrt{x}}{c\,(c+x)} - \frac{\operatorname{atan}\left(\frac{1}{\sqrt{c}}\right) - \operatorname{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)}{c^{3/2}} - \frac{1}{c\,(c+1)}$
1	$\frac{\ln(c+1)}{c^2} - \frac{1}{c\,(c+1)} + \frac{1}{c\,(c+x)} - \frac{\ln\left(\frac{c+x}{x}\right)}{c^2}$
1.5	$\frac{3\left(\operatorname{atan}\left(\frac{1}{\sqrt{c}}\right) - \operatorname{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{c^{5/2}} + \frac{2\,c+3}{c^2\,(c+1)} - \frac{2\,c+3\,x}{c^2\,\sqrt{x}\,(c+x)}$
2	$\frac{1}{c\,(c+1)} + \frac{2}{c^2\,(c+1)} - \frac{2\,\ln(c+1)}{c^3} - \frac{2}{c^2\,(c+x)} + \frac{2\,\ln\left(\frac{c+x}{x}\right)}{c^3} - \frac{1}{c\,x\,(c+x)}$
2.5	$\frac{-2\,c^2+10\,c\,x+15\,x^2}{3\,c^3\,x^{3/2}\,(c+x)} - \frac{-2\,c^2+10\,c+15}{3\,c^3\,(c+1)} - \frac{5\left(\operatorname{atan}\left(\frac{1}{\sqrt{c}}\right) - \operatorname{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{c^{7/2}}$
3	$\frac{6\,\operatorname{atanh}\left(\frac{c+2}{c}\right)}{c^4} - \frac{6\,\operatorname{atanh}\left(\frac{c+2\,x}{c}\right)}{c^4} - \frac{-c^2+3\,c+6}{2\,c^3\,(c+1)} + \frac{-c^2+3\,c\,x+6\,x^2}{2\,c^3\,x^2\,(c+x)}$

Case $b = 2.5$

a	Analytic form
-1	$\frac{4\,c+6}{3\,(c+1)^{3/2}} - \frac{4\,c+6\,x}{3\,(c+x)^{3/2}}$
-0.5	$\frac{2\,x^{3/2}}{3\,c\,(c+x)^{3/2}} - \frac{2}{3\,c\,(c+1)^{3/2}}$
0	$\frac{2}{3\,(c+1)^{3/2}} - \frac{2}{3\,(c+x)^{3/2}}$
0.5	$\frac{2\,\sqrt{x}\,(3\,c+2\,x)}{3\,c^2\,(c+x)^{3/2}} - \frac{2\,(3\,c+2)}{3\,c^2\,(c+1)^{3/2}}$
1	$\frac{2\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{c^{5/2}} - \frac{2\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{c^{5/2}} - \frac{8\,c+6}{3\,c^2\,(c+1)^{3/2}} + \frac{8\,c+6\,x}{3\,c^2\,(c+x)^{3/2}}$
1.5	$\frac{2\left(3\,c^2+12\,c+8\right)}{3\,c^3\,(c+1)^{3/2}} - \frac{2\left(3\,c^2+12\,c\,x+8\,x^2\right)}{3\,c^3\,\sqrt{x}\,(c+x)^{3/2}}$
2	$\frac{5\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{c^{7/2}} - \frac{5\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{c^{7/2}} + \frac{3\,c^2+20\,c+15}{3\,c^3\,(c+1)^{3/2}} - \frac{3\,c^2+20\,c\,x+15\,x^2}{3\,c^3\,x\,(c+x)^{3/2}}$
2.5	$\frac{2\left(-c^3+6\,c^2\,x+24\,c\,x^2+16\,x^3\right)}{3\,c^4\,x^{3/2}\,(c+x)^{3/2}} - \frac{2\left(-c^3+6\,c^2+24\,c+16\right)}{3\,c^4\,(c+1)^{3/2}}$
3	$\frac{35\,\mathrm{atanh}\left(\frac{\sqrt{c+1}}{\sqrt{c}}\right)}{4\,c^{9/2}} - \frac{35\,\mathrm{atanh}\left(\frac{\sqrt{c+x}}{\sqrt{c}}\right)}{4\,c^{9/2}} - \frac{-6\,c^3+21\,c^2+140\,c+105}{12\,c^4\,(c+1)^{3/2}} + \frac{-6\,c^3+21\,c^2\,x+140\,c\,x^2+105\,x^3}{12\,c^4\,x^2\,(c+x)^{3/2}}$

Case $b = 3$

a	Analytic form
-1	$\frac{(x-1)\,(c+2\,x+c\,x)}{2\,(c+x)^2\,(c+1)^2}$
-0.5	$\frac{c-1}{4\,c\,(c+1)^2} - \frac{\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right)-\mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)}{4\,c^{3/2}} - \frac{\sqrt{x}\,(c-x)}{4\,c\,(c+x)^2}$
0	$\frac{1}{2\,(c+1)^2} - \frac{1}{2\,(c+x)^2}$
0.5	$\frac{\sqrt{x}\,(5\,c+3\,x)}{4\,c^2\,(c+x)^2} - \frac{5\,c+3}{4\,c^2\,(c+1)^2} - \frac{3\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right)-\mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{4\,c^{5/2}}$
1	$\frac{\ln(c+1)+\frac{2}{c+1}-\frac{1}{2\,(c+1)^2}}{c^3} - \frac{\ln\left(\frac{c+x}{x}\right)+\frac{2\,x}{c+x}-\frac{x^2}{2\,(c+x)^2}}{c^3}$
1.5	$\frac{15\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right)-\mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{4\,c^{7/2}} + \frac{8\,c^2+25\,c+15}{4\,c^3\,(c+1)^2} - \frac{8\,c^2+25\,c\,x+15\,x^2}{4\,c^3\,\sqrt{x}\,(c+x)^2}$
2	$\frac{6\,\mathrm{atanh}\left(\frac{c+2\,x}{c}\right)}{c^4} - \frac{6\,\mathrm{atanh}\left(\frac{c+2}{c}\right)}{c^4} + \frac{2\,c^2+9\,c+6}{2\,c^3\,(c+1)^2} - \frac{2\,c^2+9\,c\,x+6\,x^2}{2\,c^3\,x\,(c+x)^2}$
2.5	$\frac{-8\,c^3+56\,c^2\,x+175\,c\,x^2+105\,x^3}{12\,c^4\,x^{3/2}\,(c+x)^2} - \frac{-8\,c^3+56\,c^2+175\,c+105}{12\,c^4\,(c+1)^2} - \frac{35\left(\mathrm{atan}\left(\frac{1}{\sqrt{c}}\right)-\mathrm{atan}\left(\frac{\sqrt{x}}{\sqrt{c}}\right)\right)}{4\,c^{9/2}}$
3	$\frac{12\,\mathrm{atanh}\left(\frac{c+2}{c}\right)}{c^5} - \frac{12\,\mathrm{atanh}\left(\frac{c+2\,x}{c}\right)}{c^5} - \frac{-c^3+4\,c^2+18\,c+12}{2\,c^4\,(c+1)^2} + \frac{-c^3+4\,c^2\,x+18\,c\,x^2+12\,x^3}{2\,c^4\,x^2\,(c+x)^2}$

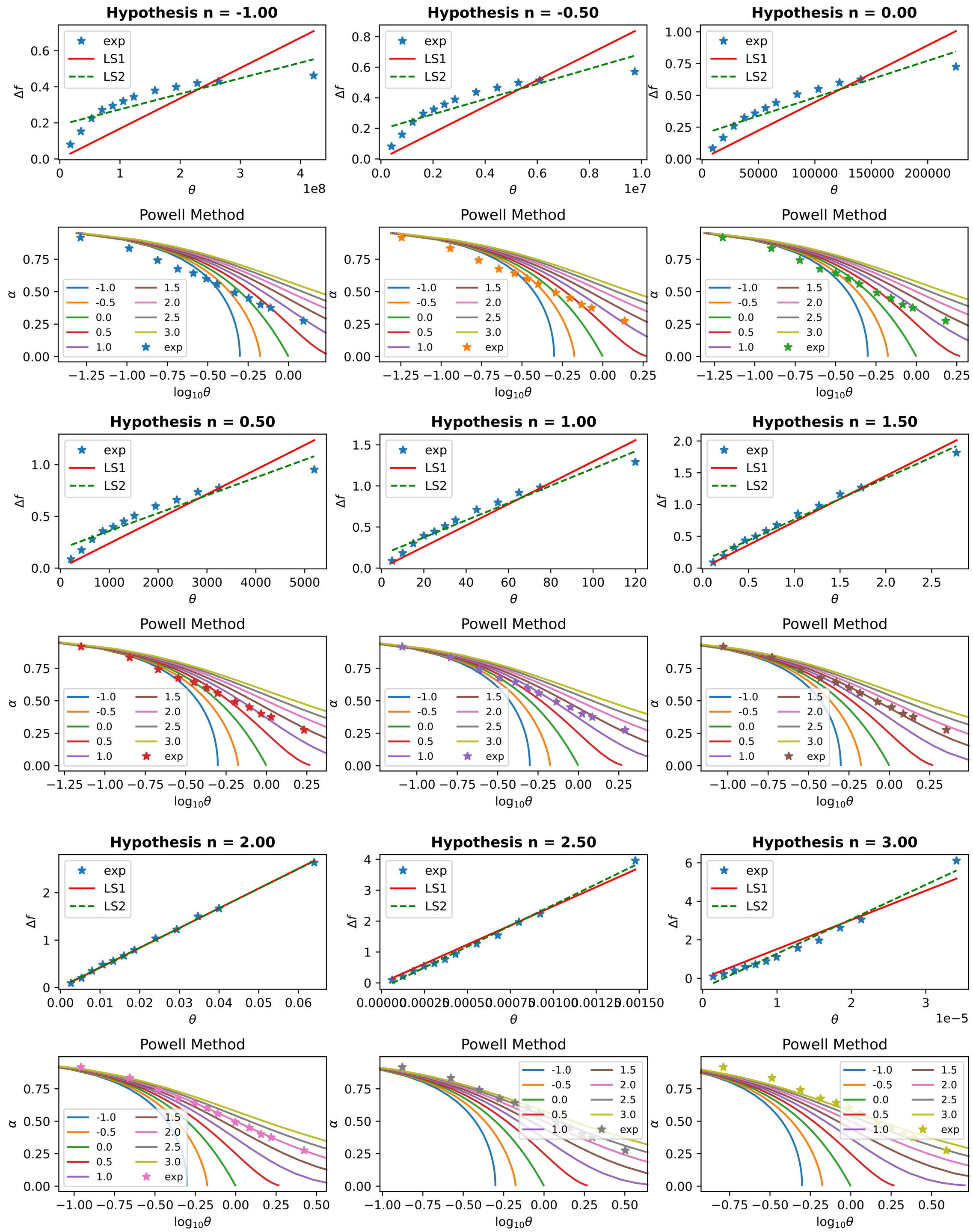

Figure 1: The Powell method applied to the kinetic data reported in ref.,[20] showing the unfit for orders different fromn 2.

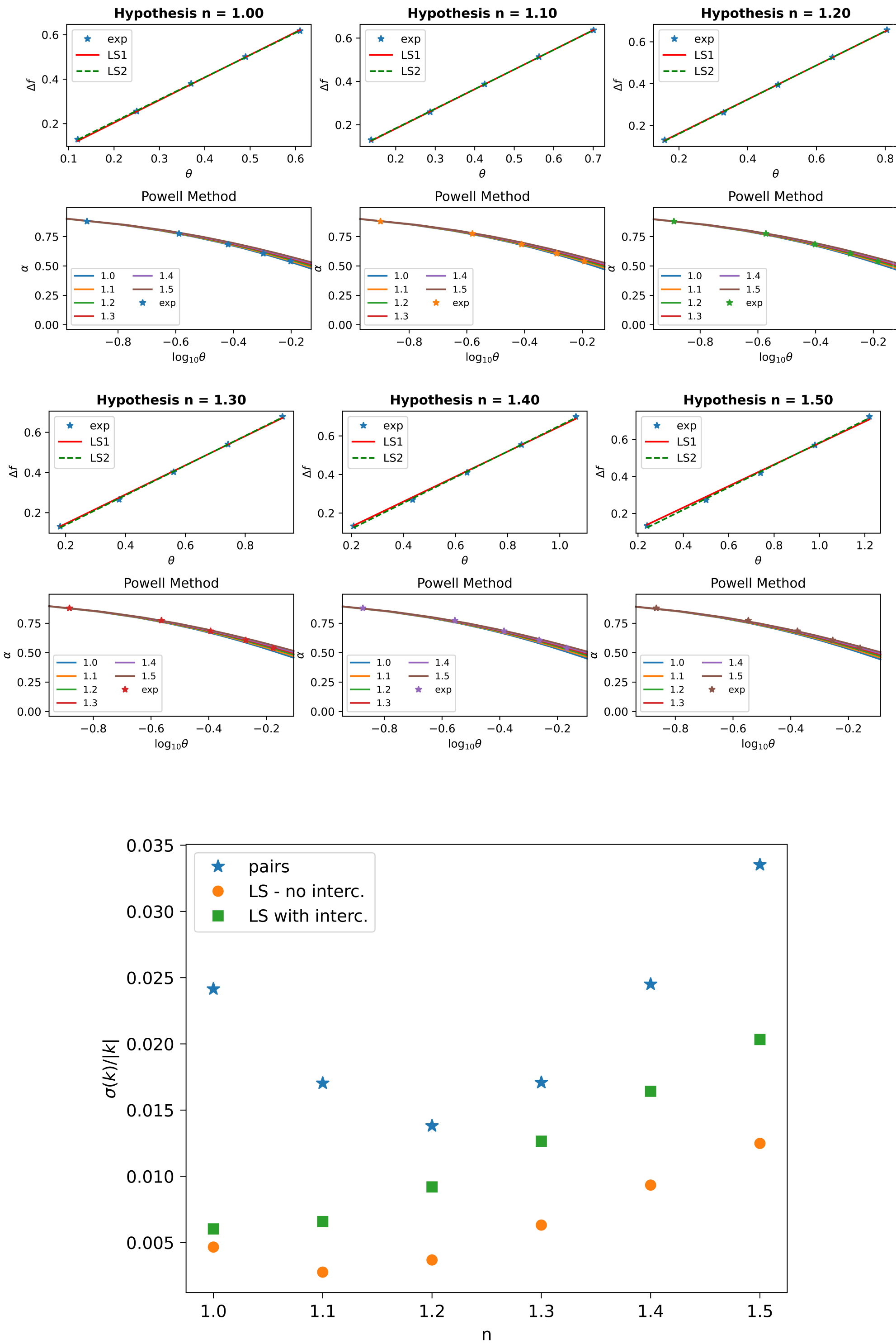

Figure 2: The Powell-Margerison plot method applied to the kinetic data reported in ref.[4] The single dataset with c closer to 0 has been considered for the integration method and Powell-Margerison plot. Bottom: the relative errors on the kinetic constant for the trials considered.

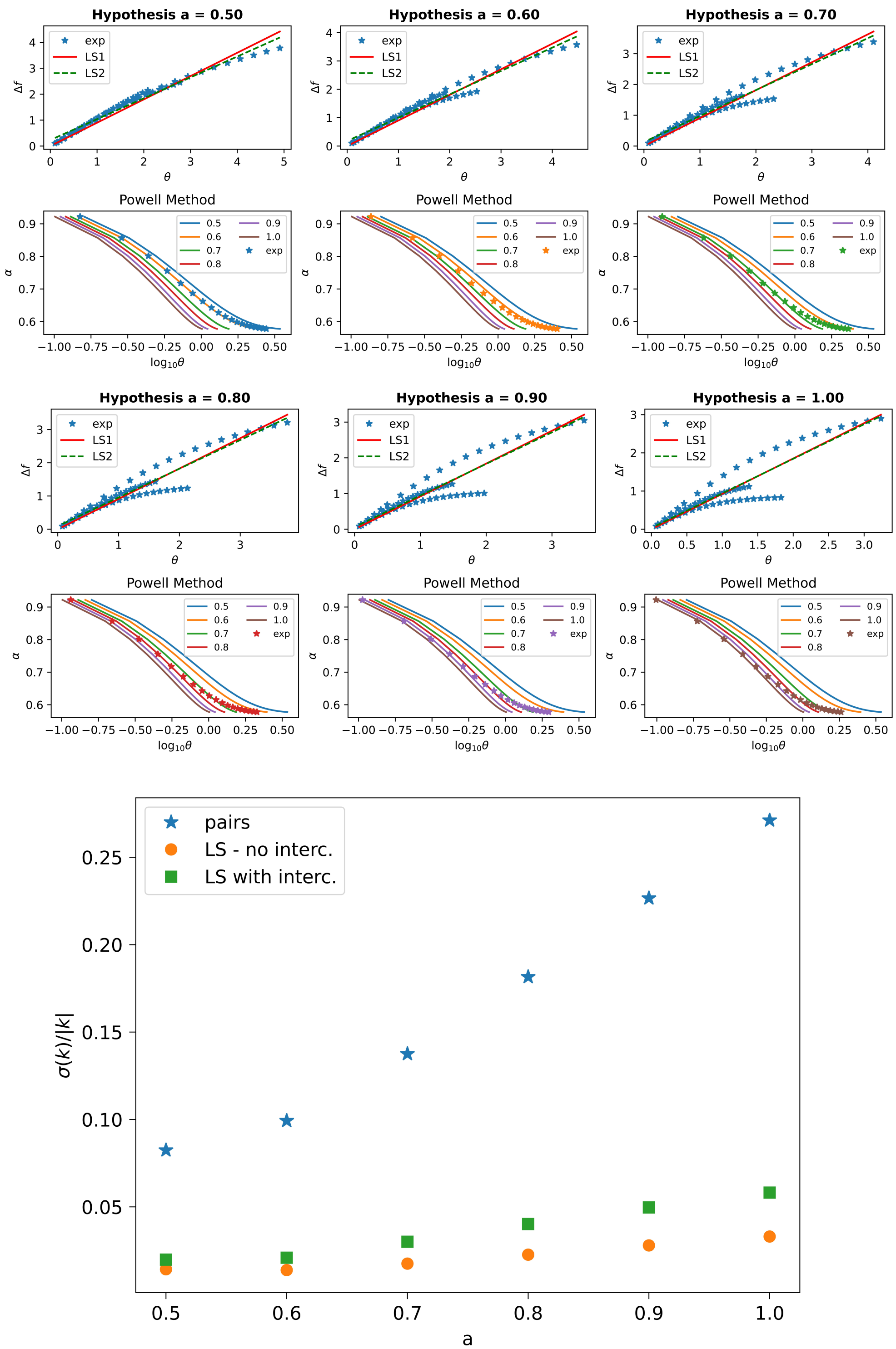

Figure 3: The Powell-Margerison plot method applied to the kinetic data reported in ref.[4] for the determination of partial orders of reaction. Bottom: the relative errors on the kinetic constant for the trials considered.

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