Internal Assessment **IB DP Chemistry Higher Level**

RESEARCH QUESTION

How does varying *individual orders in a third order reaction* impact *half lives of reactants*, as measured using *partial pressure changes*?

BACKGROUND INFORMATION

Topic inspiration

Following my learning of reaction kinetics, in particular, a lesson on syllabus unit 16.1, *"Rate Expression"*, I was taught the method of determining and calculating rate orders of chemical reactions, in accordance with changes in experimental conditions (commonly temperature or solvent concentration). Yet a critical, personal inquiry remained; if rate order can only be experimentally determined and overall rate order of a reaction is the sum of individual orders, what insights can be revealed through comparing alternate compositions of overall rate order in terms of different individual order combinations? The inability to manipulate the rate order of a reaction experimentally without the modification of solvent or addition of a catalyst was the primary obstacle in the investigation of this inquiry, however the development of complex online simulations and generalised computational chemistry, such as simulation software *ChemReaX*, allows for theoretical testing of such scientific inquiries.

Thus, this investigation focuses on exemplifying the potency of chemical simulation in allowing newfound theoretical testing, whilst simultaneously aiming to uncover new insight into the nature of rate order composition in chemical reactions.

Rate equation and rate order

For each chemical reaction there exists a unique expression of it through a formula; the rate equation. As defined by the IUPAC Compendium of Chemical Terminology, the rate equation of a chemical reaction links the initial reaction rate of reactant concentration/pressures to constant parameters such as rate constants. The initial rate for any given chemical reaction is often presented by a form of power law such as;

$$v = k[\mathrm{R1}]^x[\mathrm{R2}]^y\ldots$$

Wherein;
v = reaction rate
k = rate constant (variance depending on certain conditions, predominantly temperature.)
R1 = reactant
^{x} = individual order of reaction (rate order) with respect to reactant R1
R2 = reactant
^{y} = individual order of reaction (rate order) with respect to reactant R2
R3 = reactant
^{y} = individual order of reaction (rate order) with respect to reactant R3
… = and so forth until all reactants are accounted for

In this form, the overall reaction order is the sum of the exponents, which are often whole numbers but can present as fractional in specific conditions or reactions. For an independent chemical reaction, reaction order can only be determined from experimental data using either the differential rate law or integrated rate law. Alternatively, with enough data, simply calculating observed effects of independently shifting compositions from a table is also applicable **[Image 1.1]**, and most investigations regarding rate order concern the effect of changing external conditions such as temperatures, presence of catalysts or different solvents on resultant rate order of a reaction. However, in this investigation, *ChemReaX*'s capability for full control over rate order specification allows for an alternate investigation; one in which combinations of individual rate order all reflecting the same overall reaction order becomes the independent variable rather than a dependent.

Example

$$2A + B \longrightarrow R + S$$

Experiment	Initial [A]	Initial [B]	Initial Rate
1	0.5	0.5	0.002
2	1.0	0.5	0.008
3	1.0	1.0	0.008
4	1.5	1.5	0.018

***Image 1.1** | Sample table used in determining rate order sourced from ScienceAid*

Fractional rate order

Expanding upon regular rate order, certain chemical reactions involve non-integer orders for individual reactants, and often indicate a complex reaction mechanism, i.e. a chemical chain reaction. For example, the decomposition of reactant phosgene ($COCl_2$) into products carbon monoxide and chlorine has order 1 with respect to phosgene and order 0.5 with respect to chlorine (Laidler, 1987), as indicated by the power law of;

$$v = k[COCl_2]\,[Cl_2]^{1/2}$$

For this investigation, one instance of equal fractional rate orders for both reactants is included within calculated data to provide indication as to how a reaction can involve a variation of different step processes; ranging from elementary reactions with single steps to complex reactions with multiple steps in the formation of products.

Exothermic synthesis of methanol from carbon monoxide and hydrogen

Methanol, commonly known in industry as 'wood alcohol' due to its original synthesis from pyrolysis of wood, is a valuable intermediate for a myriad of different chemical reactions. Reliance of production of further chemically useful products such as ethanoic acid and methanal on methanol as a reactant, as well as methanol's capabilities as a fuel source encourage greater research into the refinement of its synthesis. Although historically produced catalytically using slightly varying methodologies by chemicals companies BASF, ICI and Haldor Topsoe, the essential exothermic reaction is displayed as such;

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

(Thermodynamic data: $\Delta H_r^0 = -91 kJ\ mol^{-1}$, $\Delta S_r^0 = -220 JK\ mol^{-1}$)

Regarding production of methanol and its impact on the greenhouse effect, 5.7 million metric tons of methanol was produced in the United States in 2019 alone, and current methanol production stems almost entirely from sources of fossil fuel consumption; largely natural gas. Thus, this results in a "double whammy for the atmosphere" (Professor of Chemistry Michael Bowker in *Methanol synthesis from CO_2 Hydrogenation*), since the reforming methanol steam in traditional methanol synthesis is highly endothermic and requires vast amounts of energy, while combustion of natural gas radiatively heats reactor tubes (Bowker, 2019).

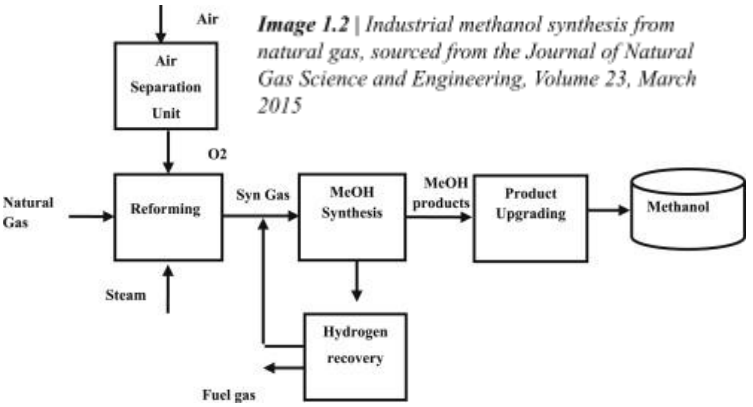


***Image 1.2** | Industrial methanol synthesis from natural gas, sourced from the Journal of Natural Gas Science and Engineering, Volume 23, March 2015*

Thus research into varying individual order compositions on half lives of reactants is advantageous in clarifying both relative efficiency of a reaction as well as understanding which specific combinations may minimise detrimental impacts.

Partial pressure as a measure of half life of a reactant

In accordance with Dalton's law of partial pressures, the total pressure of the composition of gases within this experiment is considered to be equal to the sum of the partial pressures of individual gases in the mixture;

$$P_{total} = P_x + P_y + P_z$$

This consideration involves several ideal gas assumptions such as ;
a) The molecules within a gas mixture do not interact with each other
b) A gas will diffuse to fill up a container entirely
c) Pressure of an ideal gas only involves the force exerted by collision with the container, not other molecules or substances

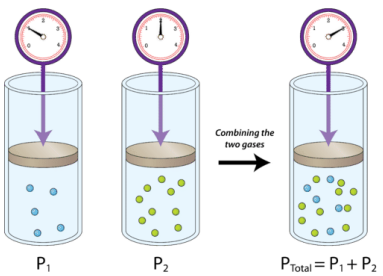


***Image 1.3** | Diagrammatic explanation of partial pressure sourced from Chemistry LibreTexts*

The half life of a reactant within this experiment is the time taken for either reactant to reach half its original quantity by conversion to methanol. Thus, the use of partial

pressures to model half life relies on the direct proportionality between the volume and resultant pressure of an individual gas; a combination of Charles' law and Gay-Lussac's law describes this relationship.

HYPOTHESIS

As individual orders for a reactant increase, so do partial pressures, thus the half-life of the reactant also increases.

Null hypothesis; there is no significant relationship between between half-lives and individual rate order

VARIABLES

Independent	**Likely impact**	**Methodology for changing variable**
Individual orders in a third order reaction	As stated in the hypothesis, it is predicted that as the individual order of a reactant increases, so too will the half-life of the reactant, although likely not resulting in strictly linear relationship.	Input into *ChemReaX* computational algorithm.
Dependent	**Contribution to answering the research question**	**Method of measurement**
Partial pressure changes (later used in calculations for half-lives of reactants)	Half-life describes the time required for any specified property to decrease by half. Partial pressures are a property of molecules describing the pressure that an individual gas exerts in a mixture of gases. Thus by calculating partial pressures, half-life is indirectly measured.	Computational algorithms with foundational concepts from a varied scope of contrasting scientific literature.
Controlled	**Likely Impact**	**Control of impact**
Temperature	As temperature increases, so does the kinetic energy (speed) of particles, increasing the chance of successful collisions, therefore increasing the rate of reaction and the rate constant, which then impacts individual rate order.	Temperature set to a value of 298.15K for every simulation.
Initial pressure	As temperature increases, so does the kinetic energy of particles, increasing the chance of successful collisions, therefore increasing the rate of reaction and altering half-life measurement.	Initial pressure is set to a value of 1 bar for every simulation.
Rate constant	The rate constant of a rate law is a constant of proportionality between the reaction rate and the reactant concentration (Chemistry LibreTexts, 2022), thus as it increases, so too must the reaction rate, thus altering half-life measurement.	Rate constant set to a value of 1 (a.u.) for every simulation .
Initial compositions of reactants/products	Greater initial composition directly affects the time for respective half-lives as there is a greater quantity of molecules to reduce. Products are additionally not formed before the reaction.	Initial compositions are set to 1, 1, 0 (bars) for CO, H_2 and CH_3OH respectively for every simulation.
Uncontrolled	**Likely Impact**	**Minimisation of Impact**
ChemReaX computational methodology	The foundational calculations for *ChemReaX* are the root source for all data within this investigation, thus any unconsidered variables or slight error within the algorithm will inadvertently have a great impact on calculated results.	No minimisation applicable as the experimenter is both lacking access to the script of *ChemReaX*, as well as having too little understanding of the formation of algorithms in *ChemReaX* to modify them.
Solvent	As stated in *Solvent Effects in Organic Chemistry* (1990, Reichardt, Marburg, Germany), the nature of the solvent can influence reaction rates and order of a chemical reaction; whether through equilibrium or frictional solvent effects.	Since no specification for solvent is available in the *ChemReaX* simulation, no potential impact can be minimised.
Processing potential of application	For *ChemReaX* to produce results, it relies on a server strength capable of supporting the program.	Jobs within *ChemReaX* are restricted to a maximum time and memory usage determined by the CGI scripts.

METHODOLOGY

ChemReaX validity

A free-for-use website based simulation, *ChemReaX* allows an incredibly vast range of sophisticated chemical reactions to be tested including, but not limited to; chemical thermodynamics, acid base titration and reaction kinetics. Using computer-generated algorithms with foundations in predetermined published chemical formulas, assimilated data of the simulation is sourced from various official research journals, higher level educational resources and computational modelling reviews detailing required software parameters of the simulation.

As explained by numerical analyst and Professor of Numerical Analysis Desmond J. Higham, the mathematical models of complex chemical reactions generated rely on modelling assumptions assimilated from various sources. Examples of source material of *ChemReaX* includes; *General Chemistry* by Pauling, L. (1988. New York: Dover Publications) and *College Chemistry, Schaum's Outline Series* by Rosenberg, J.L., Epstein, L.M., and Krieger, P.J. (2013. New York: McGraw Hill Education), thus the appropriateness of the model is directly conditional on the validity of theory and assumptions asserted in these sources (SIAM REVIEW c 2008 Society for Industrial and Applied Mathematics Vol. 50, No. 2, pp. 347). Therefore any computational errors within the program inextricably arise from errors in external scientific literature, and, upon review of aforementioned sources, the foundational theories incorporated in *ChemReaX* are valid and supported through further comparison with contrasting literature.

Rationale for utilising ChemReaX

Alternatively Reviewed Investigation Sources	Description	Applicability Comparison with *ChemReaX*
PUBChem	The world's largest collection of online chemical information as found in journals, reviews, investigations etc. Searching is not limited to specific titles, but allows generalised search terms including scientific denotation of chemical compounds.	A reliable and commended source of scientific literature, original simulation is not integrated within this alternative source. Thus, performing the experiment theoretically is impossible. Investigations involving largely PUBChem would consist primarily of source consolidation as the focal point of data assimilation and analysis, unlike individually calculated and simulated results supported by literature, as offered with the *ChemReaX* interface.
WEBMO	A website largely recognised for a free molecular editor/viewer with a click-and-drag interface, WEBMO additionally provides chemical information of simulated molecules as well as a central interface from which to run other popular chemistry programs.	Although WEBMO does support computational chemistry engines such as Gaussian, these interfaces are inappropriate for this experiment, as they do not provide the required kinetics data nor level of customisation for investigated reactions. *ChemReaX* allows both superior control over variables within the reaction, and provides calculated partial pressure changes over time; essential data required to calculate half-lives, the dependent variable of the investigation.
SDBS	Similar to PUBChem, SBDS is an online database with Japanese origins, allowing users to access a vast range of research.	Further similar to PUBChem, SDBS' nature as an online resource for investigations revolves primarily around the consolidation of multiple sources of data to achieve a conclusion, rather than performing a computationally simulated experiment.
Jmol	An online tool solely providing high definition rendering of molecules and relevant data on relative molecular information i.e. orbitals and symmetry	Due to Jmol being a program concerning only the creation and rendering of molecules, the resource is inherently inappropriate to the investigation, as it does not allow for reaction simulation nor the measurement of partial pressures

Process of utilising ChemReaX

While rate constants for products and reactants are often predetermined experimentally for given reactions and then inputted into *ChemReaX*, *ChemReaX's* software allows for the modification of these constants, thus the simulation methodology varies.

Modelling of kinetics on *ChemReaX*;

- Open panel for parameter specification **[Image 1.4]**
- Set temperature and pressure to desired values*
- Enter known, balanced reactants and products of intended reaction by selecting appropriate reactants/products from drop down lists and specifying the stoichiometric coefficients
- Indicate initial composition of reactants/products; as no product is formed before the commencing of a reaction, it is designated 0, whilst reactants are designated 1
- Set rate constant *k* of reaction*
- Set constants X, Y and Z into respectively labelled text boxes, in accordance to the designated unit (moles/L for concentration)
- Partial pressure changes are simulated and recorded in tabular form in a lower panel **[Image 1.5]**

*temperature, pressure and rate constant *k* were set consistently at 298.15K, 1 bar and 1L² mol⁻² s⁻¹ (due to the reaction being third order) respectively as controlled variables

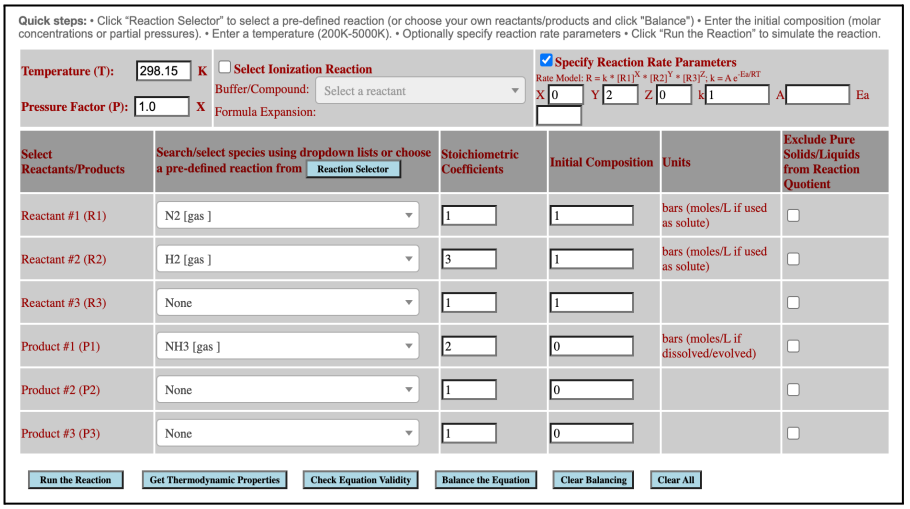
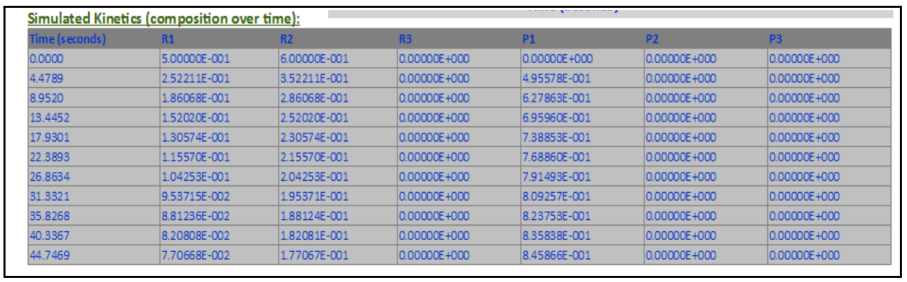


Image 1.4 | *Reaction rate parameter specification panel for the synthesis of Ammonia with second rate order, sourced from ChemReaX, 2021*



Simulated Kinetics (composition over time):

Time (seconds)	R1	R2	R3	P1	P2	P3
0.0000	5.00000E-001	6.00000E-001	0.00000E+000	0.00000E+000	0.00000E+000	0.00000E+000
4.4789	2.52211E-001	3.52211E-001	0.00000E+000	4.95578E-001	0.00000E+000	0.00000E+000
8.9520	1.86068E-001	2.86068E-001	0.00000E+000	6.27863E-001	0.00000E+000	0.00000E+000
13.4452	1.52020E-001	2.52020E-001	0.00000E+000	6.95960E-001	0.00000E+000	0.00000E+000
17.9301	1.30574E-001	2.30574E-001	0.00000E+000	7.38853E-001	0.00000E+000	0.00000E+000
22.3893	1.15570E-001	2.15570E-001	0.00000E+000	7.68860E-001	0.00000E+000	0.00000E+000
26.8634	1.04253E-001	2.04253E-001	0.00000E+000	7.91493E-001	0.00000E+000	0.00000E+000
31.3321	9.53715E-002	1.95371E-001	0.00000E+000	8.09257E-001	0.00000E+000	0.00000E+000
35.8268	8.81236E-002	1.88124E-001	0.00000E+000	8.23753E-001	0.00000E+000	0.00000E+000
40.3367	8.20808E-002	1.82081E-001	0.00000E+000	8.35838E-001	0.00000E+000	0.00000E+000
44.7469	7.70668E-002	1.77067E-001	0.00000E+000	8.45866E-001	0.00000E+000	0.00000E+000

Image 1.5 | *Results and generated graph panel for the synthesis of Ammonia with second rate order, sourced from ChemReaX, 2021*

N.B. due to the nature of methodology of this experiment, no apparatus but a laptop to run the simulation on is required

QUANTITATIVE DATA

(all tables reflect the third order reaction of exothermic synthesis of methanol from CO and H_2 (3 d.p.))

Table 1.1 | *partial pressure changes of CO [3] and H_2 [0]*

Time (s) ± 0.001	CO [gas] ± 0.001 (a.u.)	H_2 [gas] ± 0.001 (a.u.)	CH_3OH [gas] ± 0.001 (a.u.)
0.000	1.000	1.000	0.000
0.148	0.879	0.757	0.121
0.295	0.793	0.586	0.207
0.443	0.728	0.456	0.272
0.589	0.677	0.355	0.323
0.737	0.636	0.271	0.364
0.884	0.601	0.202	0.399
1.032	0.571	0.142	0.429
1.179	0.546	0.091	0.454
1.326	0.523	0.046	0.477
1.473	0.503	0.006	0.497

Table 1.2 | *partial pressure changes of CO [2] and H_2 [1]*

Time (s) ± 0.001	CO [gas] ± 0.001 (a.u.)	H_2 [gas] ± 0.001 (a.u.)	CH_3OH [gas] ± 0.001 (a.u.)
0.000	1.000	1.000	0.000
0.771	0.685	0.370	0.315
1.545	0.599	0.198	0.401
2.314	0.559	0.118	0.441
3.085	0.537	0.075	0.463
3.857	0.524	0.048	0.476
4.631	0.516	0.032	0.484
5.402	0.511	0.021	0.489
6.171	0.507	0.014	0.493
6.945	0.505	0.010	0.495
7.712	0.503	0.006	0.497

Table 1.3 | *partial pressure changes of CO [3/2] and H_2 [3/2]*

Time (s) ± 0.001	CO [gas] ± 0.001 (a.u.)	H_2 [gas] ± 0.001 (a.u.)	CH_3OH [gas] ± 0.001 (a.u.)
0.000	1.000	1.000	0.000
2.952	0.572	0.145	0.428
5.895	0.534	0.068	0.466
8.845	0.520	0.041	0.480
11.798	0.514	0.027	0.486
14.746	0.510	0.020	0.490
17.701	0.507	0.015	0.493
20.628	0.506	0.012	0.494
23.597	0.505	0.009	0.495
26.535	0.504	0.008	0.496
29.466	0.503	0.006	0.497

Table 1.4 | *partial pressure changes of CO [1] and H_2 [2]*

Time (s) ± 0.001	CO [gas] ± 0.001 (a.u.)	H_2 [gas] ± 0.001 (a.u.)	CH_3OH [gas] ± 0.001 (a.u.)
0.000	1.000	1.000	0.000
14.898	0.527	0.055	0.473
29.851	0.515	0.030	0.485
44.788	0.510	0.020	0.490
59.603	0.508	0.016	0.492
74.544	0.506	0.013	0.494
89.447	0.505	0.011	0.495
104.360	0.505	0.009	0.495
119.183	0.504	0.008	0.496
134.097	0.504	0.007	0.496
148.974	0.503	0.006	0.497

Table 1.5 | *partial pressure changes of CO [0] and H_2 [3]*

Time (s) ± 0.001	CO [gas] ± 0.001 (a.u.)	H_2 [gas] ± 0.001 (a.u.)	CH_3OH [gas] ± 0.001 (a.u.)
0.000	1.000	1.000	0.000
100.105	0.525	0.050	0.475
200.367	0.518	0.035	0.482
300.357	0.514	0.029	0.486
400.802	0.512	0.025	0.488
501.606	0.511	0.022	0.489
600.689	0.510	0.020	0.490
702.253	0.509	0.019	0.491
801.488	0.509	0.018	0.491
900.203	0.508	0.017	0.492
1000.000	0.503	0.006	0.497

QUALITATIVE DATA

Due to the nature of methodology of this experiment, no qualitative data can be recorded.

ETHICAL AND RISK CONSIDERATIONS

N.B. due to the computational nature of this experiment, no ethical or risk considerations are applicable when retrieving data

DATA PROCESSING AND CALCULATIONS

Calculating half-lives

To maximise reliability of results, two methodologies of calculating reactant half-lives will be performed and then averaged.

Methodology 1 | Use of exponential decay equation

Using the first of three equivalent formulas described on the right **[Image 1.6]**, the relationship between $\mathbf{t_{1/2}}$, **t**, $\mathbf{N_0}$ and $\mathbf{N_t}$ can be rearranged **[Image 1.7].** Thus, if three of the aforementioned values are known, it enables calculated determination of remaining unknown values. For this experiment, all final simulated times are used in calculation.

(1) $N(t) = N_0 \left(\frac{1}{2}\right)^{\frac{t}{t_{\frac{1}{2}}}}$

(2) $N(t) = N_0 e^{-\frac{t}{\tau}}$

(3) $N(t) = N_0 e^{-\lambda t}$

[Image 1.6]
Sourced from calculator.net

$$t_{\frac{1}{2}} = \frac{t \cdot \ln(2)}{\ln\left(\frac{N_0}{N_t}\right)}$$

[Image 1.7]
Sourced from 1278.org

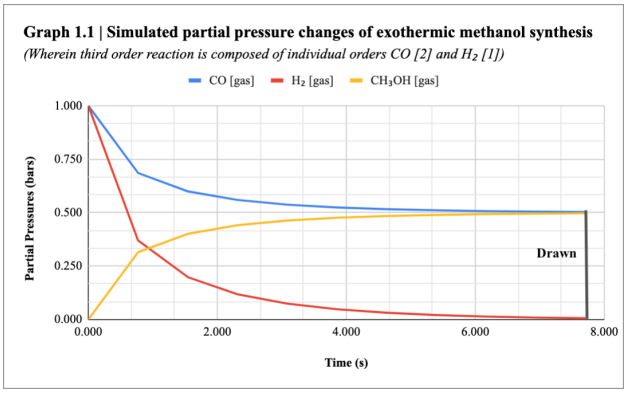
Wherein;
$\mathbf{N_0}$ is initial quantity
$\mathbf{N_t}$ is remaining quantity after a time **t**
$\mathbf{t_{1/2}}$ is the half-life
$\boldsymbol{\tau}$ is the mean lifetime
$\boldsymbol{\lambda}$ is the decay constant, although in this instance decay is considered the rate of diminishing reactant concentration

Example:
For CO in the third order combination *CO [3] and H_2 [0]* ;
at $\mathbf{t} = 1.473$, $\mathbf{N_0} = 1$ and $\mathbf{N_t} = 0.503$: $\mathbf{t_{1/2}} = 1.485$

Methodology 2 | Graphically observed predictions

Plotting a graph for each individual rate order combination, and drawing a vertical line at the point where a reactant reaches approximately half its original pressure value also provides an alternative measurement option, albeit simpler. **[Image 1.8]**

The approximate time observed where the vertical line intersects the x axis is the half-life.



(left) [Image 1.8] *Graph representing recorded data of **Table 1.2** with additional drawn line for methodology 2*

Example:
For CO in the third order combination *CO [2] and H_2 [1]* ;
at **Partial Pressures** = 0.5, the drawn vertical line approximately intersects the x-axis at 7.45, thus $\mathbf{t_{1/2}} \approx 1.45$

Mean Value

A mean or average value is required and can be calculated using the formula;

$$\bar{x} = \frac{\Sigma x}{n}$$ wherein; n = sample size and $\bar{x}$ = mean

For example with the methodology results of third order combination *CO [3] and H_2 [0]* ;

$$\bar{x} = \frac{(1.485 + 1.500)}{2} = 1.493 \text{ (3 d.pd)}$$

Table 2.1 | *Independently measured half-lives and calculated half-life means for both CO and H_2* (3 d.p.)

Specific individual order combinations of CO and H_2	Determined half-lives (Methodology 1) ± 0.001 (s)		Determined half-lives (Methodology 2) ± 0.100 (s)		Mean half-life ± 0.200 (s)	
	CO	*H_2*	*CO*	*H_2*	*CO*	*H_2*
CO [3] and H_2 [0]	1.485	0.200	1.500	0.300	1.493	0.250
CO [2] and H_2 [1]	7.779	1.045	7.700	1.000	7.740	1.023
CO [3/2] and H_2 [3/2]	29.723	3.992	30.000	3.000	29.862	3.496
CO [1] and H_2 [2]	150.271	20.184*	130.000	12.500*	140.136	20.142
CO [0] and H_2 [3]	1008.705	135.486*	1000.000	75.000*	1004.353	105.243

N.B. the coloured boxes indicate most notable variance among two methodologies, and under great scrutiny could be considered minor anomalies, as discussed further in this investigation

Assigning and Calculating Uncertainties

In almost all instances within this experiment, values are calculated or measured computationally using algorithms, thus all sources of error are unequivocally systematic. As such, very little human error is introduced within the experiment and all possible error stems from foundationally incorrect aspects of aforementioned algorithms, and most uncertainties are assigned a value of the lowest decimal point (i.e. 0.001).

However, the visually-determined half lives in Methodology 2 do provide a source of human error, since the dependent variable in graphs used to determine half-lives is presented with little enough specificity that fallacies arise in measurement using the human eye and provide greater uncertainty, which is then carried through to calculating the mean. This average uncertainty can be approximated through the following formula;

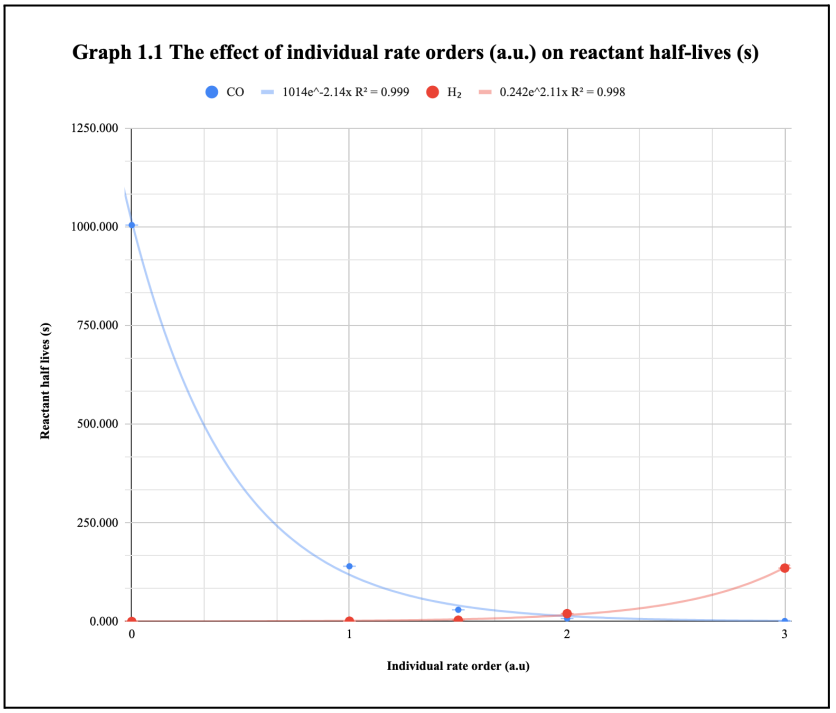
$$\bar{u} = \frac{\Sigma x}{n}$$ | wherein; x = sum of uncertainties, n = number of values measured and $\bar{u}$ = mean uncertainty

$$\text{Thus, } \bar{u} = \frac{(0.001+0.100)}{5} = 0.200 \text{ (3 d.p.)}$$

ANALYSIS

Since the exothermic synthesis of methanol from CO and H_2 involves two reactants, two separate trend lines are expressed when final half-lives are plotted against changing individual orders in **[Graph 1.1]**, each of which presenting varying relationships.

Trends for individual reactants



As can be seen in **[Graph 1.1]**, the relationship between individual rate order and CO half-life displays a negative exponential curve as a trend. As individual rate order incrementally increases, by 1 arbitrary unit, the rate of reaction decreases exponentially, thus resulting in consistently decreasing instantaneous half-lives (indicated by independent tangents drawn at any point aligning with the trendline) as expressed by a trendline equation of 1014e^-2.14x. Thus expressing a relationship wherein a rate order of 0 results in a maximum half-life, and each incremental increase in individual rate order decreases half-life by approximately 1 order of magnitude; 1004.353s → 140.136s → 29.862s → 7.740s → 1.493s. As can also be interpreted by the data progression, half-lives converge as indicated by decreasing absolute differences between consecutive calculated half-lives; i.e. a decrease of 864.217 between 1004.353s → 140.136s, compared to a decrease of 6.247 between 7.740s → 1.493s. However, unlike absolute differences, relative differences (indicated by comparing percentage differences or two separate sets of consecutively calculated half-lives) reveal a distinct similarity as exemplified by a decrease of 14% in 1004.353s → 140.136s (CO [0] → CO [1]) and a decrease of 19% between 7.740s → 1.493s (CO [2] → CO [3]).

Contrastingly, all trends for H_2 seem to present inversely when compared to the trends associated with CO. For example, the relationship between individual rate order and H_2 half-life displays a positive exponential curve as a trend rather than negative. A trendline equation of 0.242e^2.11x for individual reactant H_2 further indicates decreased strength of correlation when compared to that of the CO trendline, as evidenced by both the visual interpretation of trendlines supported by the comparison of variation factors -2.14x and 2.11x within equations for CO and H_2 respectively. The absolute differences in 0.250s →1.023s (H_2 [0] → H_2 [1]) and 20.142s → 1.493s (H_2 [2] → H_2 [3]) are 0.773 and 85.101, and relative differences are increases of 24% and 19% respectively. Thus, although absolute difference between consecutive half-lives is significantly greater for the trendline of CO than that of H_2, the changes in relative differences between consecutive half lives both present approximate variation of 5% for different individual rate order combinations (14%-19% and 24%-19%), thus indicating that relative rate of change is comparable for both reactants.

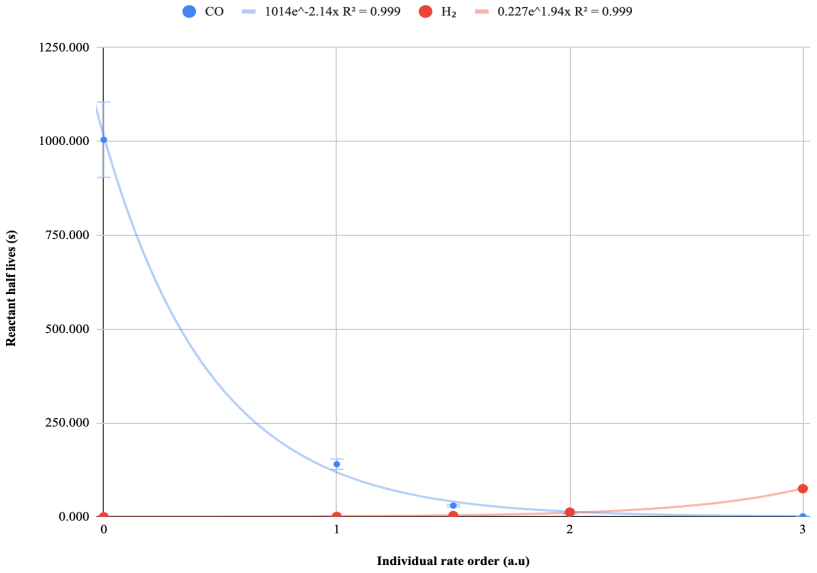
Reliability/appropriateness of investigation

The range of data recorded and presented revealed a significant level of precision and accuracy within the experiment. R-squared values indicate the 'goodness of fit', or accountability of variation of any set of data in correlation with the chosen model, and is scaled between 0 and 1 (e.g. an R-squared of 0.5 indicates that 50% of the variability in the outcome data cannot be explained by the model). Since R-squared values described in both trendlines are exceedingly high (0.999 for CO, and 0.998 for H_2) the graph and overall experiment are considered as very precise, and appropriate to either prove or disprove the hypothesis of the investigation. Furthermore, as discussed briefly earlier under "***Assigning and Calculating Uncertainties***", all data is computationally derived using complex algorithms, and therefore anomalous data does not arise in the base process of assimilating data from *ChemReaX;* zero human involvement inextricably results in zero human error. However, there is a possible source of anomaly within this investigation associated with Methodology 1. First, as detailed under "**DATA PROCESSING AND CALCULATIONS**", only final simulated times are used in calculation although the relationship between individual rate order and reactant half life is inherently exponential, thus the formula may negate the

true nature of the relationship and therefore be less accurate. When compared to alternative data methodologies, although Methodology 2 is inherently less precise, the experimenter is able to draw lines based upon where the value of partial pressure reached approximately half, and from this, estimate time and calculate half-life. This slight disparity is most notable in the data of H_2 [2] and H_2 [3]. To enhance reliability, both methodologies were averaged in an attempt to compensate for these sources of minor inaccuracy and imprecision. However, even after removing omitting 'anomalous' data points most likely affected by this flaw prior to calculating averaged data, the resulting trendline for H_2 remained the same shape and slope, albeit peaking slightly lower than the original **[Graph 1.2]**. It can therefore be concluded that the presence of aforementioned anomalous data is too little to have a significant impact, thus validity of the investigation remains high.

Graph 1.2 The effect of individual rate orders (a.u.) on reactant half-lives (s)

(Wherein errors in calculation for have been omitted for H_2 in rate combinations CO [1] H_2 [2] and CO [0] H_2 [3])



Relative scientific literature

Due to the highly theoretical nature of this investigation, reports and journals with foundations of physically performed experiments wherein individual rate order combinations is the independent variable are quite few in number, however scientific discussion and alternative methanol synthesis testing on the root concepts surrounding this experiment are numerous. The inherent rate equation for methanol synthesis from CO and H_2 proposed in *La Chimica e L'Industria* (Natta, Pino et al. 1953) contains four constants, three of which determined from initial rate, and performed in conditions not unlike this simulated investigation, although having a significant difference of varying initial pressures. As discussed alternatively in a *Rate of Methanol Synthesis* (Uchida. Hiroshi, Ogino. Yoshisada, Government Chemical Industrial Research Institute, Tokyo Shibuya-ku, Tokyo), the assigning of appropriate constant values for the aforementioned proposed Natta et al. rate equation should theoretically represent the experimental results to a high degree of accuracy. However, trial and error must be used to determine these values, and thus results in a very tedious calculation process. Contrastingly, *Rate of Methanol Synthesis* as a source clearly presents the effect of total pressure and/or the ratio of hydrogen to carbon monoxide on methanol concentration, as well as conversion efficiency. Within this methodology, the established rate equation for methanol synthesis is derived based on assumption of logarithmic adsorption isotherm and of the methanol desorption as the rate determining step, and does not require trial and error to assign constant values, thus proving to be more efficient and reliable methodology.

EVALUATION AND IMPROVEMENT

Limitation	Likely impact on investigation	Suggested improvement
Reliance on algorithm	The computational algorithm forms the backbone of data with which this investigation concerns and analyses, thus any computational error or unconsidered limit will directly impact the accuracy of the investigation. Since precision is a measure of result consistency, computational precision will be maintained as there exists no random error, although systematic error still remains a possible source of limitation.	The only inherent feasible improvement to the computational algorithm used in the *ChemReaX* simulation is to switch to alternative simulations that may incorporate alternative algorithms. *N.B. To modify the core script of the algorithm with which ChemReaX simulates reactions, an experimenter would be required to have an additional comprehension of not only general chemistry, but also complex computer science linkages, thus this improvement is unfeasible*

Lack of control of solvent	Similar to the limitation of algorithm reliance, controlled variables are essential to realistically simulating a chemical reaction, and as such, any such variable that hosts a potential impact on results. One such variable, unable to be controlled due to not being listed in the parameter specifications of the simulation, is the solvent of the reaction.	The only inherent feasible improvement is to switch to alternative simulations that may incorporate alternative algorithms.
Inability to compare with experimental results	Without an experimentally appropriate physical methodology through which to test the research question, the concept remains theoretical. Although having minimal impact on investigation results, an experimental method would allow a greater depth of understanding, involving a real world scenario to provide physical confirmation of theoretical predictions or simulated trends.	Since concepts such as manipulation of rate order as an independent variable are currently purely theoretical and can only be simulated using computational chemistry, there is no feasible improvement until experimentation under the same conditions can be realistically mirrored physically.
Scale of dependent variable	Since varying partial pressure changes calculated by *ChemReaX* are produced additionally varying in time, as can be seen in the shifting values in all data tables, visual representation of the data could provide confusion as to the true nature of trends.	Incorporate the usage of an exponential scale along the x-axis to better visually represent data. Perhaps relative scale involving percentage change would better represent the data.
Scope of independent variable; almost limitless possibilities, further research into fractional order	Although not an inherent weakness, a greater scope of independent variables may shed unique trends or results not revealed through the original scope of the investigation.	Increase scope; primarily including increasing the number of fractional orders combined such as those involving ½ etc.
Lack of consideration for exponential nature in calculations of Methodology 1	Although partially compensated by averaging calculated half-lives with those measured in Methodology 2, the weakness that is the inconsideration of exponential nature could lead to an incomplete or, in the extreme, false portrayal of the results of this investigation.	A more suitable formula for Methodology 1 should be crafted, perhaps inspired by the possible derivation of a relationship between $\mathbf{t_{1/2}}$, $\boldsymbol{\tau}$, and $\boldsymbol{\lambda}$ and a method of involving all simulated times as generated by *ChemReaX*.

Quantification of random error

A common weakness of experimental data assimilation is the presence of random error, often quantified by use of standard deviation. The standard deviation is a common measure of the random error of a large number of observations, wherein the data is placed within any set number of 'standard deviations'. i.e. 68% lies within one standard deviation. From this, random error and possible anomalies can be identified and either accounted for, or removed from the investigation. The calculation of standard deviation for results either methodology in this investigation is redundant for:

Absence of random error across trials
Since all trials are consistently calculated by the computational algorithm, no variation exists between trials in both. Thus since only one data point is retrieved for any number of trials, standard deviation cannot be performed due to a lack of large amounts of data.

Absence of variation throughout both data processing methodologies
Since a single line is drawn, the measurement will be the same across all observations thus again, standard deviation cannot be calculated due to a lack of large amounts of varied data.

CONCLUSION

The research question ***"What is the effect of varying individual orders in a third order reaction on half lives of reactants measured using partial pressure changes"*** was addressed by inputting constants for certain external factors such as initial pressure in an attempt to control their effect, then assimilating data from computationally calculated tabular values as generated by the algorithms of the *ChemReaX* simulation. As displayed in graphs, the trends gathered both simultaneously

support and refute the hypothesis of ***"As individual orders for a reactant increase, so do partial pressures, thus the half-life of the reactant also increases."*** when considered through independent scopes of individual reactant orders. For the trend of CO, a strong negative exponential curve was produced as individual rate order increased, however the trend for H_2 provided completely contrasting results, wherein a weak positive exponential curve was produced. Since the concept investigated is highly theoretical and a realistic methodology for shifting solely rate order has not been devised for experimentation, no published experimental data achieving similar results can be compared to and thus no percent error can be calculated, however the R-squared values (0.999 for CO, and 0.998 for H_2) indicate a very high appropriateness of graph as well as a high validity/reliability as indicated by the minimal change in general trend following the removal of possible minor anomalous data. In conclusion, since the error within the investigation is negligible, a directly inverse relationship between two reactants in a third order reaction can be observed by the opposing trends of CO and H_2, and although graphically dissimilar, the percentage change between consecutive half-lives was observed as similar (both sharing approximate variation of 5%), thus revealing an inextricable link between the simultaneous variation of individual rate orders or both reactants, and the interconnectedness of reactant behaviour in a third order reaction. Additionally, the results of this investigation prove computational chemical methodology to be a valid source of data that can allow both independent indications as well as provide a reliable source of comparison for experimentally performed reactions. Furthermore, the investigation concretely displays the increasing potency of computational chemistry in the exploration of inquiries previously impossible to explore; a new era of chemistry available to a rapidly increasing number of aspiring chemists.

FURTHER EXTENSION

Alternative method/extension on investigation	Reasoning
Greater usage of RPKA (reaction progress kinetic analysis)	The methodology of this investigation, in which concentrations of multiple reactants are changing constantly over the course of the reaction, is initially quite comparable to the root methodology of RPKA, wherein 'reactions are probed at synthetically relevant conditions' (i.e. with concentrations and reagent ratios resembling those used in the reaction when not exploring the rate law) rather than simply an overwhelming excess of a single target reactant, as identifiable in most common pseudo-first-order analyses. However, RPKA, unlike the methodology of this investigation where only final *ChemReaX* determined values of time are used in calculation for half-lives. By further aligning with RPKA methodology, a greater depth of kinetic insight can be observed; involving unexpected phenomena such as catalyst deactivation or induction periods to be better understood.
Investigating impact of varying rate constant *k*	Following rate law, the rate constant *k* directly impacts the rate of reaction, thus variation of it would provide interesting insight into the gravitas of its effect on the chosen chemical reaction.
Investigating bio-chemistry using computational kinetics	Extending upon the capabilities of computational chemistry to model bio-chemical processes, investigating what usually displays as qualitative fidelity amongst bio-chemical models could be incorporated into new algorithmic methodologies to produce lucid results. As Bhandari, Rangarajan and Mavrikakis discuss in their paper on understanding of the catalytic active site in situ. (, modelling outcomes through parameter estimation and parity between density functional theory and microkinetic modelling allows for refining of the mechanistic model, and therefore reveals insights previously unknown.

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