Exercises Topic 6: Chemical kinetics

1. The activation energy of an elementary chemical reaction is 30 kcal mol^{-1}. Determine:
a) The increase in the reaction rate when the temperature increases from 300ºC· to 360ºC
b) The increase in temperature necessary to double the rate of the reaction at 300ºC
Solution: a) Rate constant will increase a factor 12; b) Temperature must be increased 15.5ºC ºC.

2. A reaction A+B+C → Products yielded the following data:

	Initial concentration (mmol L^{-1})			Initial rate (-d[A]/dt)
Experiment	$[A]_0$	$[B]_0$	$[C]_0$	(mmol L^{-1} s^{-1})
1	1.25	1.25	1.25	8.7
2	2.50	1.25	1.25	17.4
3	1.25	3.02	1.25	50.8
4	1.25	3.02	3.75	457

a) Write the rate law for this reaction
b) If the initial reactant concentrations were $[A]_0$ = 2 mmol L^{-1}, $[B]_0$ = 1.5 mmol L^{-1} and $[C]_0$ =1.15 mmol L^{-1}, indicate what would be the initial rate of disappearance of A.
Solution:

a) $$-\frac{d[A]}{dt} = k[A]\cdot[B]^2\cdot[C]^2$$

b) $$-\frac{d[A]}{dt} = 16.97 mmol\cdot L^{-1}\cdot s^{-1}$$

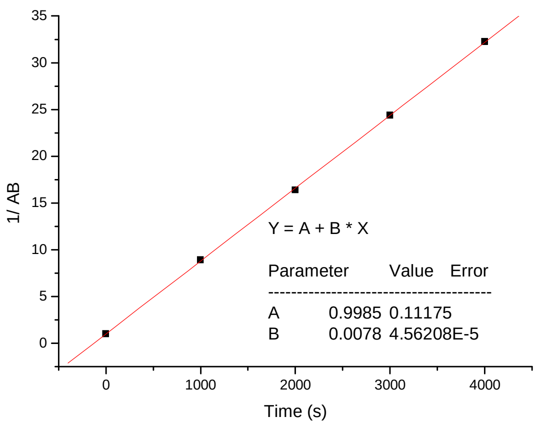
3. The following table shows how the concentration of AB varies in the reaction:

$$2\ AB(g) \rightarrow A_2(g) + B_2(g).$$

Time (s)	0	1000	2000	3000	4000
[AB] (mol/L)	1.00	0.112	0.061	0.041	0.031

Determine:
a) The global reaction order.
b) The kinetic constant for the rate of disappearance of AB.
c) The kinetic constant for the rate law (independent of the reactant).

Solution:
a) Assuming this is an elementary reaction we can propose 2 as reaction order.The kinetic equation is $-\frac{d[AB]}{dt} = k\cdot[AB]^2$. To check, 1/[AB] is plotted against time and the result is



b) The slope of the straight line is the reaction constant: k = 7.8· 10^{-3} s^{-1}.
c) Reaction rate can be defined in another way independent of reactant: $-\frac{1}{2}\frac{d[AB]}{dt} = k'\cdot[AB]^2$. So the new constant k' isk/2 = 3.9· 10^{-3}.

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4. The following reaction A → B + C has a rate constant of 0.02 L mol^{-1} min^{-1}. A daily production of 9000 mol/day is aimed for, using a batch reactor. To avoid secondary reactions the maximum conversion of 75% is the limit. Knowing that the initial concentration of A is 1 mol·L^{-1} and the conditioning time for the reactor is 1.5 h, calculate the minimum volume of the reactor.
Solution: Volume = 2000 L

5. In a batch reactor of 18 L volume an isothermal irreversible reaction takes place R→P, in liquid phase. The kinetic constant is expressed as k = 4.48×10^6 exp(-7000/T), in s^{-1}, where T is the process temperature expressed in Kelvin.

a) Calculate the time required to reach a conversion of 80% at 40 ºC if $[R]_o$ = 3 mol/L.
b) Indicate the daily molar production of P under the conditions in section (a), knowing that the load, unload and conditioning time is 22 minutes (assume 24 working h/day).
c) If the conversion desired is 95%, without changing the operating conditions in section (a), calculate the time necessary to achieve it.
d) What should be the temperature of the process for a conversion rate of 95% without changing the time of the reaction determined in (a)?

Solution:

a) t = 0.509 h
b) Daily production of P = 1166.4 moles P/day
c) t = 0.948 h; daily production = 936 mol P/day
d) T = 48.9 ºC

6. Half-life time for substance A in a second order reaction A→ Products at 20 ºC is 25 seconds when $[A]_0$=0.8 mol/L.

a) Calculate the time required so that the concentration of A is reduced to one fifth of its initial value.
b) If the rate of the reaction is doubled when temperature increases from 20ºC to 30ºC, calculate the activation energy of the process.

Solution: a) t = 100 s**;** b) E_a = 51.2 kJ/mol

7. Sucrose or common sugar ($C_{12}H_{22}O_{11}$) is hydrolyzed with water to form fructose ($C_6H_{12}O_6$) and glucose ($C_6H_{12}O_6$). The mix of fructose and glucose is known as inverted sugar and it is very important because it does not crystallize, so soft candies can be produced. From the following kinetic data, determine:

Reaction time (min)	0	60	96.4	157.5
$[C_{12}H_{22}O_{11}]$ (mol L^{-1})	0,57	0,45	0,39	0,3

a) The order of the reaction;
b) Time required for 50% of sucrose to hydrolyze;
c) For an ideal perfect mix batch reactor, what is the reactor volume required to obtain 2000 kg of inverted sugar in every batch (for a conversion rate of 93%)?

Solution:
a) Order 1; b) b) t = 170.3 min
c) Volume = 139.2 m^3

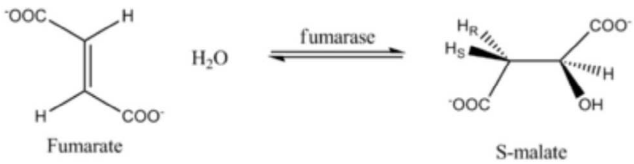
8. Human blood contains an enzyme (carbonic anhydrase) that catalyzes the formation HCO_3^- and the hydration of CO_2 (H_2CO_3) according to the following reaction.

$$CO_2 + H_2O \xrightarrow{\text{Carbonic Anh}} HCO_3^- + H^+$$

Its Michaelis-Menten constants are $k_2 = 6 \cdot 10^5\ s^{-1}$ and $K_M = 8 \cdot 10^{-3}\ mol \cdot L^{-1}$. If the concentration of dissolved CO_2 (non hydrated) is 0.5 M, the non-hydrated CO_2 reaction order will be 1 or 0? ¿How long would take to hydrate 50% of dissolved CO_2 if the enzyme concentration is $1 \cdot 10^{-6}$ M?

Solution: a) [S]/(Km+[S]) = 0.98≈ 1 so reaction order is zero; b) t = 0.42 s

9. Fumarase (or fumarate hydratase) is an enzyme that catalyzes the reversible hydration/dehydration of Fumarate to L-malate according to the following reaction.



The reverse reaction has been studied at pH = 6.7 with two different phosphate buffers 0.005 M and 0.05 M. For several concentrations of L-malate the initial reaction rates were measured and results are presented in the next table

0.005 M Buffer		0.05 M Buffer	
Initial rate v (relative units)	[L-malate] $mol \cdot L^{-1}$	Initial rate v (relative units)	[L-malate] $mol \cdot L^{-1}$
4.2	$0.333 \cdot 10^{-3}$	1.5	$0.333 \cdot 10^{-3}$
6.1	$1.00 \cdot 10^{-3}$	5.3	$3.33 \cdot 10^{-3}$
6.5	$3.33 \cdot 10^{-3}$	6.7	$10.0 \cdot 10^{-3}$
7.2	$10.0 \cdot 10^{-3}$	-	-

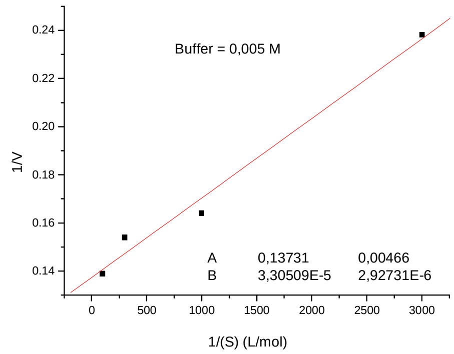
All the solutions contain the same concentration of enzyme.

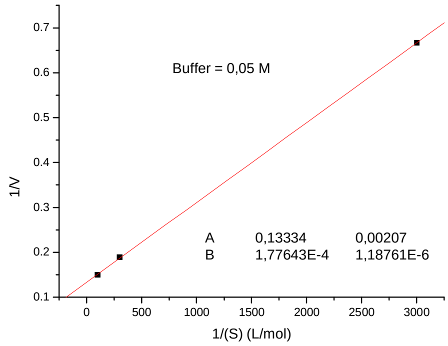
a) Plot 1/v against 1/[S] and determine a value for K_M in $mol \cdot L^{-1}$ for each experiment

b) Which seems to be the effect of the buffer on the kinetics?

Solution:

a)





b) High buffer concentration seems to decrease the activity of the enzyme