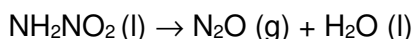




Problems of Physical Chemistry 2

Chemical Kinetics

1) Nitramide (NH_2NO_2) decomposes in basic media to give nitrous oxide (N_2O) and water (H_2O). It is a 1st order reaction.



50 mg of NH_2NO_2 at 15 °C was added to a given volume of phosphate buffer containing 0.15 M HPO_4^{2-} and 0.10 M H_2PO_4^- sodium acetate, pH=7.4. After 70 minutes 6.19 mL of gas had already been released (volume of dry gas at 15 °C and $P = 1$ atm). Calculate the half-reaction time at this temperature.

$$\text{R: } t_{1/2} = 123 \text{ min}$$

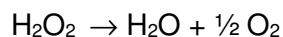
2) The cis-trans isomerization of 1,2-dimethylcyclopropane at 450 °C is a reversible 1st order reaction. The composition of the mixture in percent molar is given in the following table:

t (s)	0	45	90	225	270	360	495	∞
% trans	0	10.8	18.9	37.7	41.8	49.3	56.5	70.0

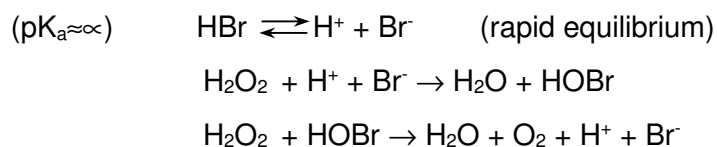
Calculate the equilibrium constant and the kinetic constants of the forward and reverse reaction.

$$\text{R: } k_1 = 2,33 \times 10^{-3} \text{ s}^{-1}, k_{-1} = 1 \times 10^{-3} \text{ s}^{-1}, K = 2,33$$

3) Hydrogen peroxide (H_2O_2) slowly decomposes in the absence of catalyst to give water and oxygen.



The process is catalyzed, for example, in the presence of hydrobromic acid and the following mechanism has been suggested:



a) "The reaction rate is directly proportional to the amount of hydrobromic acid added".
Prove this statement.

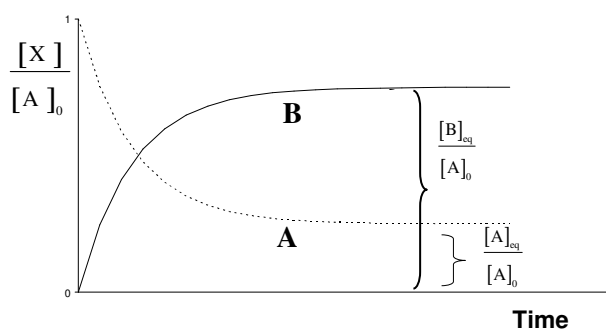
b) Say all the information you can draw according to the Activated Complex Theory, by performing this reaction in the presence of an electrolyte (NaCl), in addition to 0.05 M hydrobromic acid, knowing that for $[NaCl] = 0.5\text{ M}$ the observed rate constant for 25°C is 0.10 s^{-1} and for $[NaCl] = 1.5\text{ M}$ is 0.03 s^{-1} at the same temperature.

R: a) $v=2K_a k_2[H_2O_2][HBr]$; b) $Z_A Z_B = -1$

4) The following reversible reaction is given in a single step $A \xrightleftharpoons[k_{-1}]{k_1} B$ and the variation of the concentration of A and B in time is typically given by the figure below.

$$\frac{[A]}{[A]_0} = \frac{k_{-1} + k_1 e^{-(k_1 + k_{-1})t}}{k_1 + k_{-1}}$$

$$\frac{[B]}{[A]_0} = \frac{k_1 - k_{-1} e^{-(k_1 + k_{-1})t}}{k_1 + k_{-1}}$$



Knowing that at $t=0.17\text{ s}$ and 25°C the concentration of B is half the equilibrium concentration of B ($[B]_{eq}$) and the equilibrium constant at this temperature é 3, calculate k_1 and k_{-1} .

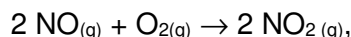
R: $k_1=3\text{ s}^{-1}$, $k_{-1}=1\text{ s}^{-1}$,

5) A gas phase reaction of type $2\text{ A (g)} \rightarrow \text{B (g)}$, of second order with respect to A, occurs in full length in a reactor of constant volume and temperature, and has a half-reaction time of 1 hour for an initial pressure of A of 1.00 bar. Assuming that there is no B at the initial time, what are the partial pressures of A and B and the total pressure at the end of

- 1 h
- 2 h
- when the reaction ends

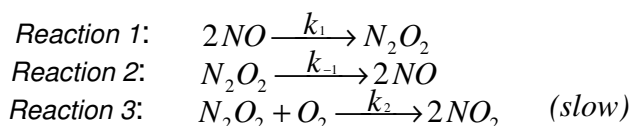
- R: a) $p_A=0,50$ bar, $p_B=0,25$ bar, $P_t=0,75$ bar
 b) $p_A=0,33$ bar, $p_B=0,33$ bar, $P_t=0,66$ bar
 c) $p_A=0$ bar, $p_B=0,50$ bar, $P_t=0,50$ bar

6) An example of the so-called *anti-Arrhenius dependence of temperature* is what is observed in the reaction between nitric oxide and molecular oxygen,



being the 3rd order global kinetics.

One of the mechanisms proposed for this reaction was the following:



Knowing that the activation energies for each reaction are $E_1=79.5 \text{ kJ mol}^{-1}$, $E_{-1}=205 \text{ kJ mol}^{-1}$ and $E_2=84 \text{ kJ mol}^{-1}$, calculate the overall activation energy according to this mechanism. Justify the answer.

R: $E_a = -41,5 \text{ kJ mol}^{-1}$

7) The $2\text{A} \rightarrow 3\text{B}$ gas phase reaction composition was followed by measuring the total pressure as a function of time, giving the following results:

t/min	0	4	8	12	16	20
p/bar	1.250	1.298	1.342	1.381	1.416	1.448

Calculate the order and rate constant of the reaction, assuming that at the initial time the partial pressure of B was 0.25 bar and justify all the options that you will take.

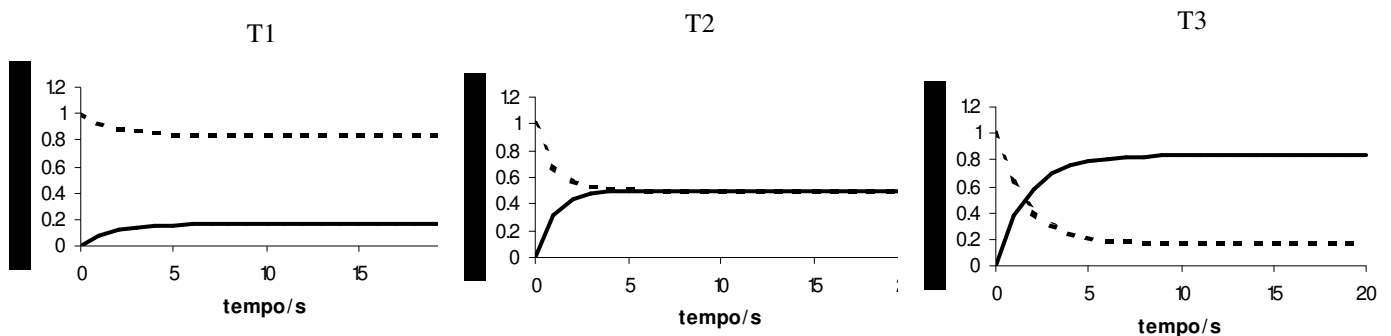
R: 1st order, $k=0,0126 \text{ min}^{-1}$

8) The following graphs represent the variation of the normalized concentration of species A and B over time (that means, divided by $[A]_0$) for a $\text{A} \rightleftharpoons \text{B}$ type of reaction close to equilibrium, at 3 different temperatures, so that $T_1 < T_2 < T_3$

a) Knowing that the concentrations of the species are given by

$$\frac{[A]}{[A]_0} = \frac{k_{-1} + k_1 e^{-(k_1+k_{-1})t}}{k_1 + k_{-1}} \qquad \frac{[B]}{[A]_0} = \frac{k_1 - k_1 e^{-(k_1+k_{-1})t}}{k_1 + k_{-1}}$$

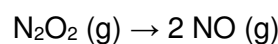
and that the curves cross for T_3 at $t=2.0$ seconds, calculate the kinetic constants of the direct reaction (k_1) and inverse reaction (k_{-1}) at this temperature.



b) Calculate the equilibrium constant for each temperature and say whether the reaction is endothermic or exothermic, justifying the answer.

R: a) $k_1=0,39 \text{ s}^{-1}$, $k_{-1}=0,098 \text{ s}^{-1}$, b) endothermic reaction

9) The reaction



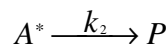
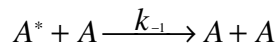
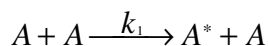
is 1st order with respect to N_2O_2 . Derive an expression for the variation of the NO partial pressure as a function of time.

R: $[\text{NO}]=2[\text{N}_2\text{O}_2]_0(1-e^{-kt})$

10) Calculate the forward and reverse rate constants for the liquid state reaction, $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, knowing that the study of this kinetics was performed by a 298K temperature drop relaxation method. The system response was followed by conductivity measurements and showed a relaxation time of 37 μs . Data: $K_w(298\text{K})=0.98 \times 10^{-14}$ and $\tau=1/(k_1([\text{OH}^-]_{298\text{K}} + [\text{H}^+]_{298\text{K}})+k_2)$

R: $k_1=1,4 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$, $k_2=1,4 \times 10^{-3} \text{ s}^{-1}$,

11) The $\text{A} \rightarrow \text{P}$ reaction does not always occur in a single step. A proposed mechanism comprises 3 elemental steps where two molecules of reagent collide forming an excess of energy in one of them, becoming that energetically excited molecule that finally decays for products.



a) Using the approximation of the steady state to the excited molecule, A^* , get the rate of formation of product P equation

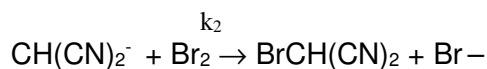
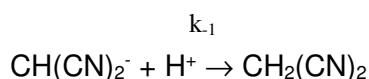
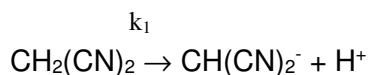
b) Show that if the step with the rate constant k_2 is very slow, it is possible to simplify the global rate constant and, if we express the constants k_1 e k_{-1} as a function of the equilibrium constant (thermodynamic variable), the rate equation will depend only on a kinetic constant - that of the determining step. Comment.

$$R: v = k_1 k_2 [A]^2 / (k_2 + k_{-1} [A]); \text{ b) } v = K k_2 [A]$$

12) Steady-state approximation is widely used in the elucidation of kinetic schemes, namely in the numerous organic reactions that occur through the initial ionization of a C-H bond. An important example is the bromination of dicyanomethane:



whose mechanism can be represented by:



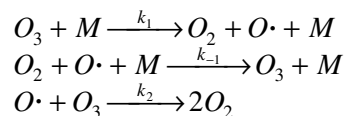
a) Derive the equation for the rate of formation of dicyanobromomethane, $d[\text{BrCH}(\text{CN})_2]/dt$, applying the approximation of the steady state to the anion $\text{CH}(\text{CN})_2^-$.

b) Show that when the concentration of bromine is much higher than the concentration of the H^+ ion, it is possible to simplify the deduced velocity equation in a), becoming a first-order kinetics where the determining step is the ionization of $\text{CH}_2(\text{CN})_2$.

$$R: dP/dt = k_1 k_2 [\text{CH}_2(\text{CN})_2] [\text{Br}_2] / (k_{-1} [\text{H}^+] + k_2 [\text{Br}_2]); \text{ b) } dP/dt = k_1 [\text{CH}_2(\text{CN})_2]$$



13) The decomposition of ozone in the presence of excess O_2 occurs according to the mechanism

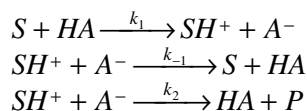


where M is an inert substance whose function is to absorb the energy released in the production of $O\cdot$.

Deduce the rate law by applying steady state approximation to $O\cdot$.

$$R: d[O_3]/dt = 2k_1k_2[O_3]^2[M]/(k_{-1}[O_2][M] + k_2[O_3])$$

14) The acid heterogeneous catalysis mechanism $S + HA \rightarrow HA + P$ occurs through the formation of the acid form of the substrate, SH^+ , by transfer of the proton of HA acid and subsequently the acid form of the substrate reacts, not with the solvent molecule, but with the conjugate base of the acid.



Deduce the expression of the rate for the formation of product P applying the steady-state approximation to the intermediate SH^+ .

$$R: dP/dt = k_1k_2[S][HA]/(k_{-1} + k_2)$$

15) The gaseous dimethyl ether undergoes decomposition at elevated temperatures which is a 1st order reaction

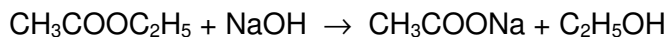


A quantity of ether was introduced into a flask at 504 °C and pressure was measured over time.

t(s)	390	777	1587	3155	∞
p (mm Hg)	408	480	624	779	931

Calculate the kinetic constant and half-reaction time for this temperature.

16 – Hydrolysis of ethyl acetate



was followed at 25 °C over time, and the following results were obtained:

t(s)	0	178	273	531	866	1510	1918	2401
$10^3 [\text{x}] \text{ (M)}$	0.00	0.88	1.16	1.88	2.56	3.35	3.77	4.06

where x represents the product concentration. Initial concentrations are NaOH $9.8 \times 10^{-3} \text{ M}$ and $\text{CH}_3\text{COOC}_2\text{H}_5$ $4.86 \times 10^{-3} \text{ M}$.

Determine the order of the reaction and the kinetic constant.

R: 2nd global order, $k = 0,106 \text{ M}^{-1} \text{ s}^{-1}$

17) The composition of the gas phase reaction $2\text{A} \rightarrow \text{B}$ was followed by total pressure measurement as a function of time, giving the following results:

t(s)	0	100	200	300	400
p (mm Hg)	400	322	288	268	256

Calculate the order of the reaction and the kinetic constant

R: 2nd order, $k = 10^{-5} \text{ mmHg}^{-1} \text{ s}^{-1}$

18) At 378 °C, the $t_{1/3}$ for the 1st order thermal decomposition of the ethylene oxide is 575 min and the activation energy of the reaction is 217 kJ mol⁻¹. From these data, calculate the time required to decompose 75% of the ethylene oxide at 450 °C.

R: 13,3 min



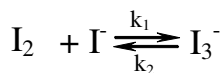
19) Knowing that the initial rates of the reaction between A and B for different initial concentrations of the reactants are:

$v_0/\text{M s}^{-1}$	$[\text{A}]_0/\text{M}$	$[\text{B}]_0/\text{M}$
5×10^{-4}	0,1	0,1
2×10^{-3}	0,2	0,1
1×10^{-3}	0,1	0,2

calculate the order of reaction with respect to A and B and the reaction rate when $[\text{A}] = 0.15 \text{ M}$ and $[\text{B}] = 0.25 \text{ M}$ at the same temperature.

$$\text{R: } v = 0,5[\text{A}]^2[\text{B}]; v = 2,81 \times 10^{-3} \text{ M s}^{-1}$$

20) This reaction



was studied using laser-induced temperature jumping techniques, analyzing the relaxation of the system. Relaxation times were measured at various equilibrium concentrations at 25 °C.

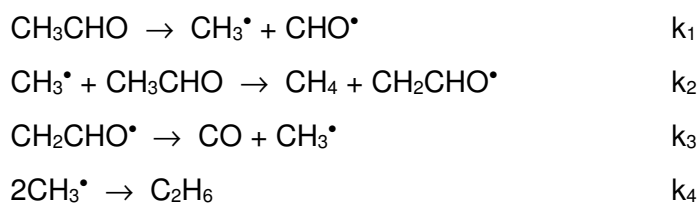
$[\text{I}^-] \times 10^3/\text{M}$	$[\text{I}_2] \times 10^3/\text{M}$	τ/ns
0,57	0,36	71
1,58	0,24	50
2,39	0,39	39
2,68	0,16	38
3,45	0,14	32

a) Calculate k_1 and k_{-1} .

b) Compare the results with $K = 720$.

$$\text{R: a) } k_1 = 6 \times 10^9 \text{ M}^{-1} \text{s}^{-1}, k_2 = 8 \times 10^6 \text{ s}^{-1}, \text{ b) } K = 750$$

21) Rice-Herzfeld mechanism for the decomposition of acetaldehyde is as follows:



- a) Determine the rate of methane formation.
b) The energies of activation of the different reaction steps are:
 $E_{a1} = 318 \text{ kJ mol}^{-1}$, $E_{a2} = 42 \text{ kJ mol}^{-1}$, $E_{a3} = 75 \text{ kJ mol}^{-1}$, $E_{a4} = 0 \text{ kJ mol}^{-1}$,
Calculate the activation energy of methane formation.

R: a) $v = (k_2^2 k_1 / k_4)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$, b) $E_a = 201 \text{ kJ mol}^{-1}$,

22) The reaction between the persulfate ion ($\text{S}_2\text{O}_8^{2-}$) and the ferricyanide ion ($\text{Fe}(\text{CN})_6^{4-}$) was studied at 35°C . The method used was spectrophotometry, measuring the absorbance of the solution at 420 nm. For this wavelength the ferricyanide is practically transparent and the molar extinction coefficient of the persulfate is $1060 \pm 10 \text{ M}^{-1}\text{cm}^{-1}$. Using a 1 cm cell of optical path, the initial reaction rate, expressed as change in absorbance per unit time, was measured for various initial concentrations of the reactants, yielding the following results :

$[\text{S}_2\text{O}_8^{2-}] / \text{M}$	3×10^{-3}	2×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}
$[\text{Fe}(\text{CN})_6^{4-}] / \text{M}$	1×10^{-3}	1×10^{-3}	1×10^{-3}	1.5×10^{-3}	2×10^{-3}	2.5×10^{-3}	3×10^{-3}
$-\frac{dA}{dt} \times 10^5 / \text{s}^{-1}$	2.05	1.30	0.62	1.45	2.40	3.52	5.00

- a) Determine the partial orders of the reaction with respect to persulfate and ferricyanide.
b) Calculate the reaction rate constants for the indicated conditions.

23) The following reaction is considered of 2nd order considering reagent A



The variation of the pressure of the system in time was followed for a given temperature, obtaining:

tempo	16,7 min	170 min	27,5 h	10 days
P (bar)	0,495	0,529	0,651	0,734

Considering the reaction as complete, calculate the kinetic constant and the half-time reaction at this temperature.



24) For a given reaction of type $A + 2B \Rightarrow C + 2D$ the following values were recorded at 17°C:

$v_0 / M s^{-1}$	$[A]_0 / M$	$[B]_0 / M$
0,0063	0,21	0,70
0,0041	0,15	0,90
0,0125	0,21	1,39
0,0208	0,38	0,70

Determine the reaction rate law.

25) The reaction $N_2O_2 (g) \rightarrow 2 NO (g)$ is of first order with respect to N_2O_2 . Prove it, knowing that at the initial time there is already 0.25 bar of NO and the total pressure of the system varies in the following way as a function of time.

t / min	1	2	3	5	20	100
p_t / bar	2,30	2,62	2,85	3,14	3,45	3,45

26) For a given reaction of type $A + 2B \Rightarrow C + 2D$ the following values were recorded at 17°C, being the volumes referred for the following stock solutions: stock solution A 0.5 M and stock solution B 2.1 M:

$v_0 / 10^{-5} M s^{-1}$	Vol A / mL	Vol B / mL	Vol H ₂ O / mL	Vol total / mL
7,64	42	33	25	100
5,08	30	43	27	100
12,0	42	52	6	100
18,2	76	24	0	100
2,26	20	43	37	100

Determine the reaction rate law.