

Problems of Physical Chemistry 2

Reactional Dynamics

1 - Laidler and Chen studied the hydrolysis kinetics of ethyl acetate in aqueous solution at various temperatures and obtained the following values for the rate constant.

t(°C)	4	10	18	25
k(M ⁻¹ s ⁻¹)	0.028	0.0410	0.0680	0.1080

Determine E_a, ΔH[#], ΔS[#] e ΔG[#] (a 25°C).

R: E_a= 46.34 kJ mol⁻¹, ΔH[#]= 43.86 kJ mol⁻¹, ΔS[#]= -116.2 J K⁻¹ mol⁻¹, ΔG[#]= 78.5 kJmol⁻¹

2 - Laidler e Chen (Trans. Faraday Soc., 54, 1026, 1958) obtained the following data for the hydrolysis of ethyl acetate at 25°C.

p(MN m ⁻²)	0.1	27.6	55.2	82.7
k(M ⁻¹ s ⁻¹)	0.146	0.163	0.181	0.203

Knowing that the rate constant, k, varies with pressure p, according to equation

$$\left(\frac{\partial \ln k}{\partial p} \right)_T = - \frac{\Delta V^\#}{RT}$$

where V[#] is the activation volume and is equal to the volume change when going from the initial state (reagents) to the activated complex,

a) Calculate ΔV[#].

b) Determine approximately the value of k at the pressure of 1 atmosphere and at 25°C.

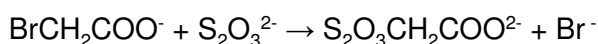


c) Determine the molecularity of the reaction.

d) From the value obtained for ΔV^\ddagger , make some comments about the structure of the activated complex.

R: a) $\Delta V^\ddagger = -9,8 \text{ cm}^3 \text{ mol}^{-1}$, c) it is not a unimolecular reaction, $\Delta V^\ddagger < 0$

3— The second order reaction between the bromoacetate ion and thiosulphate ion, both sodium salts, was studied.



and the rate data obtained were:

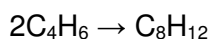
I/M	$[\text{S}_2\text{O}_3^{2-}]/\text{mM}$	$[\text{BrAc}^-]/\text{mM}$	$v/\text{M}^{-1}\text{min}^{-1}$
1.25×10^{-3}	0.250	0.500	0.298
1.665×10^{-3}	0.333	0.666	0.304
2.5×10^{-3}	0.500	1.000	0.317

a) Calculate the rate constant for the unit activity coefficient as well as the charge of the ions present in the activated complex.

b) Is the reaction favored by the ionic force?

R: a) $k^0 = 0,256 \text{ M}^{-1} \text{ min}^{-1}$, $Z_A Z_B = +2$; b) Yes

4 – Dimerization of butadiene into 3-vinyl-cyclohexene



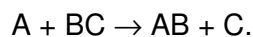
shows a rate constant, from 440 K to 660 K, given by

$$k_2 = 9.2 \times 10^9 \exp[-11965/T] \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Calculate ΔS^\ddagger e ΔG^\ddagger at a given temperature and comment the obtained data.

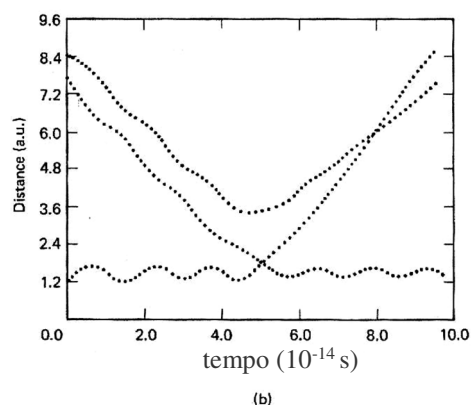
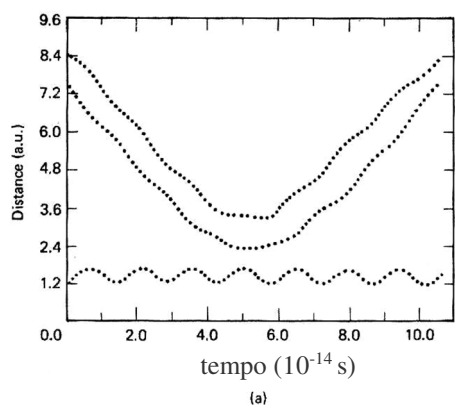
R: $\Delta S^\ddagger = -163 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta G^\ddagger = 172,8 \text{ kJ mol}^{-1}$,

5) Let us assume the atomic exchange reaction $H + H_2 \rightarrow H + H_2$, an example of a general case



Transcribe cases a) and b) and explain each of them in terms of collision efficiency, curve shape and identification of each species present

R:



6) In the following table we compare the values of the pre-exponential factor given by the Arrhenius equation, A_{exp} , with the data by the Collision Theory (without considering the stereochemical parameter p), A_{TC} , and with the data obtained by the Transition State Theory, A_{TCA} for 3 bimolecular reactions involving NO.

Reaction	$A_{\text{exp}} \text{ (M}^{-1}\text{s}^{-1}\text{)}$	$A_{\text{TC}} \text{ (M}^{-1}\text{s}^{-1}\text{)}$	$A_{\text{TCA}} \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$2 \text{ NOCl} \rightarrow 2 \text{ NO} + \text{Cl}_2$	9.4×10^9	5.9×10^{10}	4.0×10^8
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	7.9×10^8	5.0×10^{10}	4.0×10^8
$2 \text{ NO}_2 \rightarrow 2 \text{ NO} + \text{O}_2$	2.0×10^9	4.0×10^{10}	5.0×10^9

Comment out the values in the table and relate them to the two theories.

$$A_{\text{TC}} = p \sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A \quad A = e^n \frac{k_B T}{h} \left(\frac{RT}{p^0} \right)^{(n-1)} \exp\left(\frac{\Delta S^\ddagger}{R} \right)$$

R:



7) Here are some unimolecular reactions:

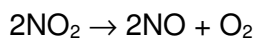
Reaction	ln (A/s ⁻¹)	E _a (kJ mol ⁻¹)
<u>Isomerizations</u>		
ciclopropene ⇒ propinyl	29.9	147
CH ₃ NC ⇒ CH ₃ CN	31.3	131
<u>Decompositions</u>		
Ethyl chloride ⇒ HCl + ethene	32.2	244
Ethyl iodide ⇒ HI + ethene	32.5	221

Explain using Transition State Theory why a unimolecular reaction normally has a pre-exponential factor of the order of 10¹³ s⁻¹.

$$A_{TC} = p \sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A \quad A = e^n \frac{k_B T}{h} \left(\frac{RT}{p^0} \right)^{(n-1)} \exp\left(\frac{\Delta S^\ddagger}{R} \right)$$

R: ΔS^\ddagger near zero

8) Calculate ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger for the decomposition reaction of NO₂ (2nd order reaction) at 500 K.



T/K	k/M ⁻¹ s ⁻¹
300	9,4x10 ⁻¹¹
400	6,4x10 ⁻⁶
500	5,06x10 ⁻³
600	0,434
700	10,42

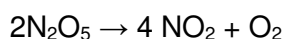
R: $\Delta H^\ddagger = 102,7 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -118,8 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta G^\ddagger = 162,1 \text{ kJ mol}^{-1}$,



9) A reaction occurs through non-catalyzed (n.c.) and catalyzed (v.c.) routes. The entropy of activation by the uncatalyzed pathway exceeds that of the pathway catalyzed in $10 \text{ J K}^{-1} \text{ mol}^{-1}$. The activation energy of the uncatalyzed pathway exceeds that of the catalyzed pathway in 10 kJ mol^{-1} . Indicate the assumptions and/or approximations you need, calculate for 25°C how many times is the rate constant of the catalyzed route higher than that of the non-catalyzed route.

$$R: k_{vc} = 17 k_{nc}$$

10 – The following gas phase reaction is considered as biomolecular reaction



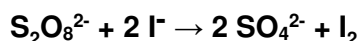
The rate constant is given by

$$k = 2.05 \times 10^{13} \exp[-24650/RT] \quad (\text{s}^{-1})$$

Calculate ΔS^\ddagger and ΔH^\ddagger and comment the data obtained.

$$R: \Delta S^\ddagger = 1.3 \text{ J K}^{-1} \text{ mol}^{-1}; \Delta H^\ddagger = 22.1 \text{ kJ mol}^{-1}$$

11- The most common method of determining the amount of persulfate ($\text{S}_2\text{O}_8^{2-}$) in a reactional solution is an iodometric method based on the oxidation reaction of iodide.



In order to study the effect of ionic strength in this reaction the following stock solutions were prepared: 250 cm^3 of 0.01 M sodium persulfate, 250 cm^3 of 0.01 M sodium iodide and 500 cm^3 of $\text{NaNO}_3 \text{ } 1 \text{ M}$. For each erlenmeyer the following volumes of these solutions were added:

Erlenmeyer	1	2	3	4	5
Vol $\text{Na}_2\text{S}_2\text{O}_8 / \text{cm}^3$	25	25	25	25	25
Vol NaI / cm^3	25	25	25	25	25
Vol $\text{NaNO}_3 / \text{cm}^3$	0	25	50	75	100
Vol $\text{H}_2\text{O} / \text{cm}^3$	100	75	50	25	0



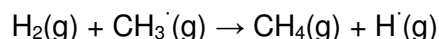
For each erlenmeyer the following rate constants were observed:

Erlenmeyer	1	2	3	4	5
$k / 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	2,9	13,5	28,9	52,1	85,8

Deduce which charges are presente in the Activated Complex for the reaction limiting step.

R: -2 and -1 or +2 and +1

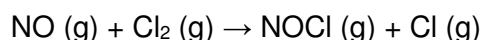
12 - Calculate the pre-exponential factor for the bimolecular reaction



according to the Theory of Collisions at 298 K, knowing that the diameters of the reactive species are $d(\text{CH}_3^{\cdot})=350 \text{ pm}$ and $d(\text{H}_2)=251 \text{ pm}$. Comment and compare with the value obtained experimentally of $1,5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

R: $A_{\text{TC}}=3.22 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$

13 – For the reaction



predict the rate constant at 550 K according to the Collision Theory considering 90% of the collisions as effective and knowing that $d(\text{NO})=370 \text{ pm}$; $d(\text{Cl}_2)=540 \text{ pm}$.

Compare and comment on the experimental value obtained at the same temperature, knowing that $A_{\text{exp}}=1,5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $E_a=84,9 \text{ kJ mol}^{-1}$.

R: $k_{\text{TC}}=2.6 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$

14 - The following table shows the variation of the rate constant of the demethylation reaction of N-methylpyridinium bromide by an aqueous solution of sodium hydroxide as a function of temperature.

$k / 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	8,39	21,0	77,2	238
T / K	298	313	333	353

Calculate ΔS^\ddagger and ΔH^\ddagger according to the Transition State Theory, at 298 K. Comment the values obtained.

R: $\Delta S^\ddagger = -151.8 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta H^\ddagger = 51.1 \text{ kJ mol}^{-1}$