e- ISSN: 2394-5532
p- ISSN: 2394-823X

Scientific Journal Impact Factor: 3.762

International Journal of Applied And Pure Science and Agriculture

www.ijapsa.com

Kinetic Estimation of D-Sorbitol using Redox indicator reactions with Cerium (IV) in Sulphuric Acid Medium.

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Abstract

Kinetic estimations of D-sorbitol and with cerium (IV) in sulphuric Acid Medium has been carried out after elaborating the kinetic and mechanistic features of this redox indicator reactions which can be expressed as

$$C_6H_{14}O_6 + 2\ Ce(IV) + H_2O \rightarrow C_6H_{12}O_6 + 2Ce(III) + 2H^+ + HCOOH$$

These reaction showed firstorder kinetics with respect to initialcon centarations of eacting speciescerium(IV),sorbitol and sulphuricacidunder the experimental pseudo first order conditions and a free radical mechanism producing D-glucoseas intial reaction product.

The observed decreasing absorbance with time at different initial concentrations of respective hexitols has been used for the .kinetic estimations adopting (a) Rate constant, (b) variation of absorbance at fixed time (c) variation of time at fixed absorbance of (d) One point and (e) Two point methods using respective calibration plots .The consistency and reproducibility of these results have clearly showed these kinetic estimations of sorbitol can be used as an alternative/additional analytical method to the existing traditional estimation methods in the present day laboratory conditions and also as advance laboratory experiments/student's projects.

Key Words: Kinetic estimation, Hexitols, Cerium(IV) oxidation, Electron transfer reaction,

I. Introduction

Alditols areacyclic, polyhydric alcohols with wide spread occurrence in nature, particularly in the lower form of life, points to their biological and hence pharmaceutical importance.D-Sorbitol, also known as glucitol metabolizes slowly in human body. It is a sugar substitute sweetener and can be used as non stimulant laxative. It has many healthcare, food and cosmetics industrial applications.

The kinetic and mechanistic studies of red-ox reactions of alditols with metal ion oxidant in acid medium include Vanadium(V) /1/, Cerium(IV) /2/, Manganese (III) /3/, Thallium (III) /4/ and Iron (III) /5/ have been earlier reported.

Kinetic Cerimetric estimation of D-Sorbitol

The kinetics of red-ox reaction of D-sorbitol with cerium(IV) in sulphuric acid medium has been studied by monitoring the decrease in absorbance at 360nm due to changing concentrations cerium(IV) in presence of excess concentrations of D-sorbitol and sulphuric acid. The decreasing concentration of cerium (IV) with time followed first order kinetics uniformly upto two half lives of reaction.The pseudo first order rate constant k_{obs} (s^{-1}) calculated using integrated form of first order rate equation The The results of variations of k_{obs} (s^{-1}) with cerium(IV) , D-sorbitol , H_2SO_4, H^+ and HSO_4^- concentration can now be summarized as :

- K_{obs} (s^{-1}) shows a slight increase with increasing concentration of initial concentration of cerium(IV) as indicated by a positive value 0.290 of log-log plot.

- First order dependence on D-sorbitol with 1.040 slope value of log-log plot suggest the suitability of this red-ox indicator reaction of kinetic estimation of D-sorbitol under present experimental conditions.
- The observed decrease in rate constant with $H_2SO_4$and HSO_4^- whereas increase in concentration with $[H^+]$ show the involvement of sulphato complex of cerium(IV) as active species in this reaction.

The specific rate constant of this red-ox reaction has been calculated by using equ.1 and from the slopes of the log-log plots in respective variations

$k_s = k_{obs}[\text{D-sorbitol}]^{1.040} [H_2SO_4]^{2.379}$ -----(1)

$= 2.86 \times 10^{-4} [2.5\times 10^{-3}]^{-1.040} [0.7]^{2.379} = 6.22 \times 10^{-2}$

Thermodynamic parameters have been calculated from corresponding Arrhenius plot obtained from the temperature variation data as

E_aK.J.mol^{-1}	$\Delta H^{\neq}$ K.J.mol^{-1}	$-\Delta S^{\neq}$ J.K^{-1}.mol^{-1}	$\Delta G^{\neq}$ K.J.mol^{-1}
106.5±0.4	**104.00±0.3**	**193.80±0.5**	**58.43±0.6**

Stoichiometry and Reaction steps

Stoichiometry of the red-ox reactions has been studied in the left over reaction mixtures used in kinetic studies to confirm D-Glucose as initial reaction product by paper chromatography. Thus the stoichiometric reaction may therefore be represented as in equation (2)

$C_6H_{14}O_6 + 2Ce(IV) \longrightarrow C_6H_{12}O_6 + 2Ce(III) + 2H^+$ -----(2)

In presence of excess of concentration of cerium(IV) (~ 20 fold) over D-sorbitol.
HCOOH has been confirmed as final reaction product by paper chromatography showing stoichiometric reaction as in equation (3)

$C_6H_{14}O_6 + 14Ce(IV) + 6H_2O \longrightarrow 6HCOOH + 14\,Ce(III) + 14H^+$-------(3)

The following reaction steps now can be considered for present red-ox reaction.

$CH_2OH(CHOH)_4CH_2OH + Ce(IV) \underset{}{\overset{K}{\rightleftharpoons}} (Complex)^{\neq}$

$(Complex)^{\neq} \xrightarrow[+H_2O]{\text{slow}} CH_2OH(CHOH)_4\dot{C}HOH + Ce(III) + H_3O^+$ -----(4)

Free radical

$CH_2OH(CHOH)_4\dot{C}HOH + Ce(IV) \xrightarrow{\text{fast}} CH_2OH(CHOH)_4CHO + Ce(III) + H+$

D-Glucose-----(5)

The formation of intermediate free radical was confirmed by induced polymerization reaction with acryl nitrile and also by earlier ESR spin trapping studies/6/.It can be considered that cerium (IV) is present as in its initial form $Ce(SO_4)_2$ and its possibly modified sulphato form such as $H_4Ce(SO_4)_4$.

Kinetic cerimetric estimation of D-Sorbitol

Kinetic cerimetric estimations of simulated samples of D-sorbitol have been done using present red-ox indicator reaction (equ.2) and calibration plots obtained following relationships (equs.6-9) rate data given in the tables 1-5

conditions given in the tables 1-5 and summarized in table -6

(a) Rate Constant Method

$$k_{obs} = k_0 [\text{D-Sorbitol}]_0 \quad \text{----------(6)}$$

(b) Fixed Time Method

$$(\text{Absorbance})_0 = k_0 [\text{D-Sorbitol}] \quad \text{----------(7)}$$

(c) Fixed Absorbance Method

$$\text{Time} = k [\text{D-Sorbitol}]^{-1} = k [\text{Absorbance}]^{-1} \quad \text{----(8)}$$

(d) One Point (fixed absorbance) Method

$$\frac{(\text{time})_{known}}{(\text{time})_{simulted}} = \frac{(\text{Absorbance})_{simulated}}{(\text{Absorbance})_{known}} \quad \text{------(9)}$$

TABLE- 1
VARIATION OF ABSORBANCE WITH SORBITOL CONCENTRATION

$10^4[Ce(IV)]=2.5 moldm^{-3}$ $[H_2SO_4]=0.7 moldm^{-3}$
Temperature=296±0.5K λ =360nm

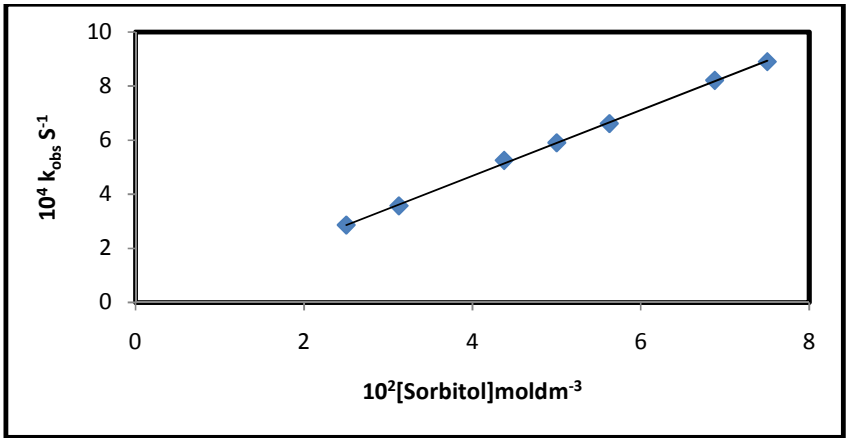
	10^2[Sorbitol]mol dm^{-3}				
10^{-2}Time (sec.)	2.50	3.125	4.375	5.00	5.625
0	1.036	1.036	1.036	1.036	1.036
3	0.955	0.928	0.883	0.867	0.849
6	0.879	0.833	0.758	0.732	0.694
9	0.806	0.755	0.644	0.612	0.577
12	0.738	0.676	0.539	0.509	0.464

15	0.678	0.613	0.479	0.429	0.382
18	0.611	0.542	0.405	0.358	0.321
21	0.554	0.491	0.335	0.297	0.264
24	0.499	0.445	0.302	0.245	0.204
27	0.468	0.394	0.258	0.212	0.175
$10^4k_{obs.}$	2.86±0.03	3.57±0.04	5.25±0.02	5.9±0.01	6.61±0.03

	10^2[Sorbitol]mol dm^{-3}			
10^{-2}Time (sec.)	**6.875**	**7.50**	**Simulated-1**	**Simulated-2**
0	1.036	1.036	1.036	1.036
3	0.811	0.791	0.904	0.831
6	0.628	0.611	0.799	0.664
9	0.504	0.465	0.712	0.535
12	0.386	0.353	0.619	0.429
15	0.311	0.274	0.516	0.348
18	0.232	0.214	0.481	0.283
21	0.182	0.154	0.411	0.214
24	0.141	0.127	0.347	0.166
27	0.112	0.093	0.321	0.132
$10^4k_{obs.}$	8.21±0.02	8.9±0.01	4.41±0.04	7.41±0.02

(A) RATE CONSTANT METHOD

S.No.	**10^2[Sorbitol]moldm^{-3}**	**10^4k_{obs} (s^{-1})**
1	2.5	2.86±0.03
2	3.12	3.57 ±0.04
3	4.37	5.25±0.02
4	5	5.9±0.04
5	5.62	6.61±0.01
6	6.87	8.21±0.02
7	7.5	8.9±0.03
8	Simulated-1	4.41±0.04
9	Simulated-2	7.41±0.03



Regression Equation:

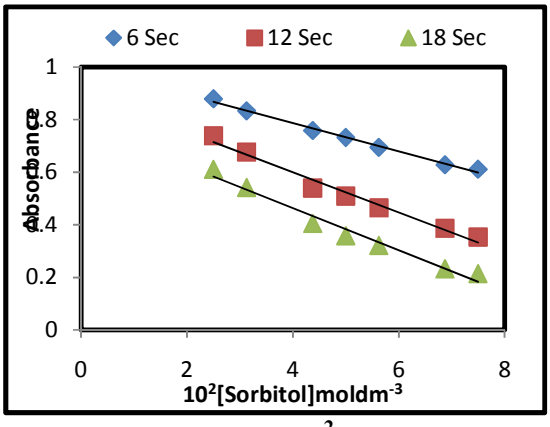
$10^4 k_{obs}$ =1.213[Sorbitol] – 0.167 Corr.Coeff.= 0.999

Results:-

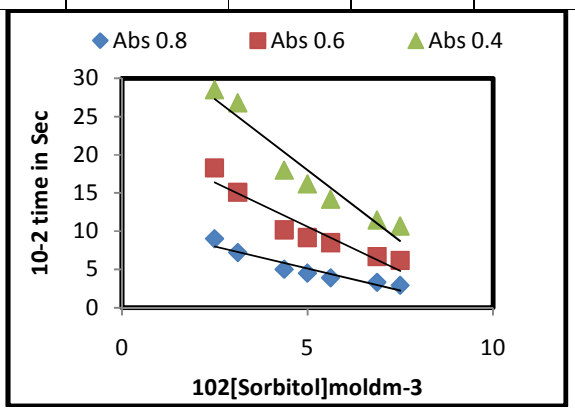
10^2[simulated-1]mol dm^{-3}	**3.77±0.02(Calculated):3.75(Actual)**
10^2[simulated-2]mol dm^{-3}	**6.24±0.01(Calculated):6.25(Actual)**

(B & C) Fixed Time and Fixed Absorbance Method

10^2[Sorbitol] moldm^{-3}	**Absorbance at fixed 10^{-2} time(sec)**			**^{2} time(sec) at fixed absorban**		
	6	**12**	**18**	**0.8**	**0.6**	**0.4**
2.5	0.879	0.738	0.611	9	18.3	28.5
3.125	0.833	0.676	0.542	7.2	15.1	26.8
4.375	0.758	0.539	0.405	5	10.2	18
5	0.732	0.509	0.358	4.5	9.5	16.2
5.625	0.694	0.464	0.321	3.9	8.5	14.2
6.875	0.628	0.386	0.232	3.3	6.7	11.5
7.5	0.611	0.353	0.214	2.9	6.2	10.7
Simulated-1	**0.799**	**0.619**	**0.481**	**6.2**	**12.9**	**21.8**
10^2[simulated-1]mol dm^{-3}	**3.77**	**3.76**	**3.77**	**3.8**	**3.8**	**3.8**
Simulated-2	**0.664**	**0.429**	**0.283**	**3.5**	**7.5**	**13.1**
10^2[simulated-2]mol dm^{-3}	**6.27**	**6.26**	**6.25**	**6.23**	**6.2**	**6.23**



Absorbance at fixed 10^{-2} time



Time at fixed Absorbance

Regression Equation

A_{600} = -0.054[Sorbitol] + 1.003	Corr.Coeff.=0.993
A_{1200}= -0.076[Sorbitol] + 0.905	Corr.Coeff.=0.979
A_{1800}= -0.080[Sorbitol] + 0.783	Corr.Coeff.=0.974
$t_{0.8}$ = -1.144[Sorbitol]+ 10.63	Corr.Coeff.=0.901
$t_{0.6}$ = -02.316[Sorbitlol]+ 21.88	Corr.Coeff.=0.903
$t_{0.4}$= -3.72 [Sorbitol]+ 36.28	Corr.Coeff.=0.934

RESULTS:-

10^3[simulated-1](mol dm^{-3}) [Fixed Time Method]	**3.76±0.01**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.26±0.01**	**(Calculated):6.25 (Actual)**
10^3[simulated -1](mol dm^{-3}) [Fixed Abs. Method]	**3.8±0.05**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.23±0.02**	**(Calculated):6.25 (Actual)**

TABLE-2
VARIATION OF ABSORBANCE WITH SORBITOL CONCENTRATION

10^4[Ce(IV)]=2.5moldm^{-3} $[H_2SO_4]$=0.45moldm^{-3}
Temperature=296±0.5K λ =360nm

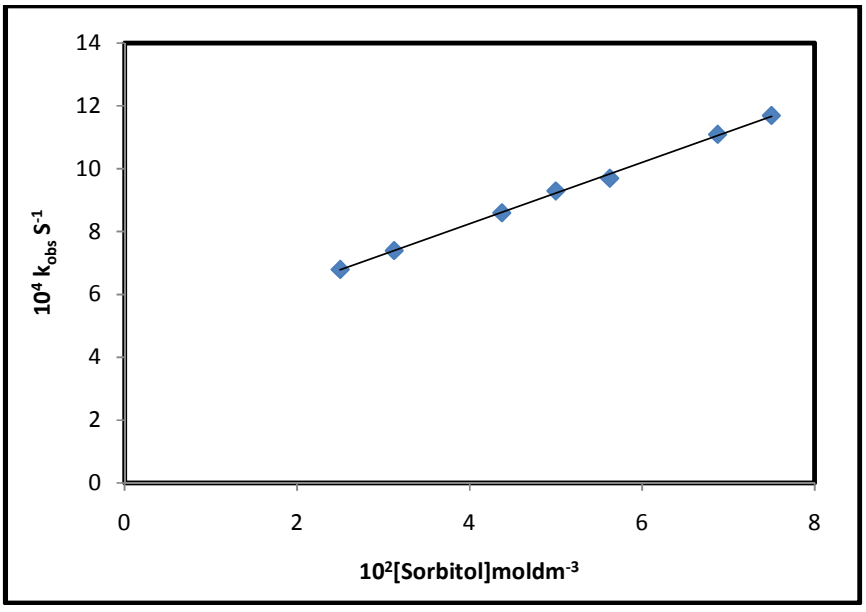
	10^2[Sorbitol]moldm^{-3}				
10^{-2}Time (sec.)	**2.50**	**3.125**	**4.375**	**5.00**	**5.625**
0	1.036	1.036	1.036	1.036	1.036
3	0.843	0.829	0.798	0.782	0.773
6	0.692	0.662	0.617	0.591	0.576
9	0.565	0.535	0.479	0.447	0.428
12	0.458	0.425	0.368	0.335	0.322
15	0.371	0.341	0.279	0.255	0.242
18	0.302	0.277	0.221	0.191	0.179
21	0.247	0.216	0.169	0.144	0.135
24	0.201	0.178	0.131	0.109	0.101
27	0.169	0.141	0.101	0.082	0.074
$10^4k_{obs.}$	6.8±0.02	7.4±0.01	8.6±0.02	9.3±0.05	9.7±0.04

	10^2[Sorbitol]moldm^{-3}			
10^{-2}Time (sec.)	**6.875**	**7.50**	**Simulated-1**	**Simulated-2**
0	1.036	1.036	1.036	1.036
3	0.741	0.728	0.812	0.752

6	0.531	0.511	0.644	0.556
9	0.375	0.361	0.492	0.398
12	0.276	0.257	0.392	0.294
15	0.195	0.177	0.308	0.214
18	0.139	0.128	0.241	0.154
21	0.099	0.088	0.191	0.111
24	0.072	0.062	0.146	0.084
27	0.051	0.042	0.109	0.058
10^4k_{obs}.	11.1±0.03	11.7±0.04	8.1±0.02	10.6±0.01

(A) RATE CONSTANT METHOD

S.No.	10^2[Sorbitol]moldm^{-3}	10^4k_{obs} (s^{-1})
1	2.5	6.8±0.02
2	3.12	7.4 ±0.01
3	4.37	8.6±0.02
4	5	9.3±0.05
5	5.62	9.7±0.04
6	6.87	11.1±0.03
7	7.5	11.7±0.04
8	Simulated-1	8.1±0.02
9	Simulated-2	10.6±0.01



Regression Equation:

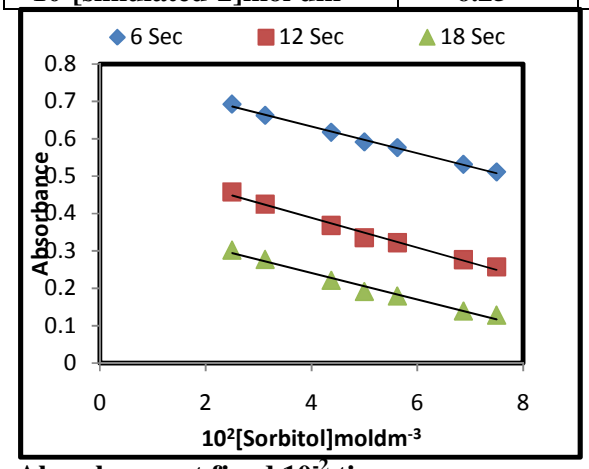
$10^4 k_{obs}$=0.978 [Sorbitol] +4.446 Corr.Coeff.= 0.998

Results:

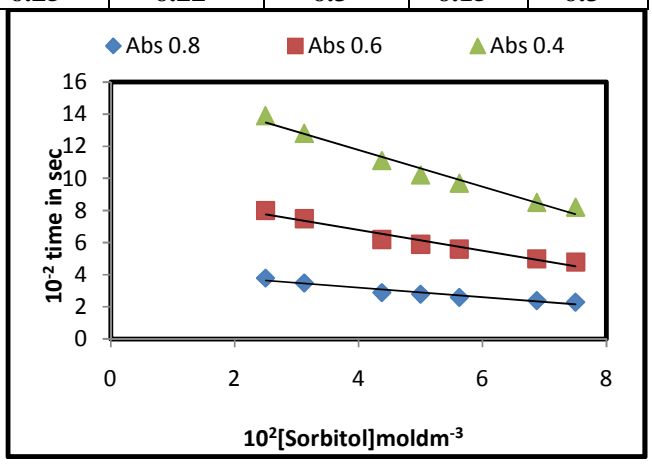
10^2[simulated-1]mol dm^{-3}	**±0.02(Calculated):3.75(Actual)**
10^2[simulated-2]mol dm^{-3}	**±0.03(Calculated):6.25(Actual)**

(B & C) Fixed Time and Fixed Absorbance Method

10^2[Sorbitol]mol dm^{-3}	**Absorbance at fixed 10^{-2} time(sec)**			**$^{-2}$ time(sec) at fixed absorbanc**		
	6	**12**	**18**	**0.8**	**0.6**	**0.4**
2.5	0.692	0.458	0.302	3.8	8	13.9
3.125	0.662	0.425	0.277	3.5	7.5	12.8
4.375	0.617	0.368	0.221	2.9	6.2	11.1
5	0.591	0.335	0.191	2.8	5.9	10.2
5.625	0.576	0.322	0.179	2.6	5.6	9.7
6.875	0.531	0.276	0.139	2.4	5	8.5
7.5	0.511	0.257	0.128	2.3	4.8	8.2
Simulated-1	**0.644**	**0.392**	**0.241**	**3.1**	**6.9**	**12**
10^2[simulated-1]mol dm^{-3}	**3.74**	**3.74**	**3.74**	**3.64**	**3.82**	**3.79**
Simulated-2	**0.556**	**0.294**	**0.154**	**2.5**	**5.4**	**9**
10^2[simulated-2]mol dm^{-3}	**6.25**	**6.25**	**6.22**	**6.3**	**6.15**	**6.3**



Absorbance at fixed 10^{-2} time



Time at fixed Absorbance

Regression Equation

A_{600} = -0.035[Sorbitol] + 0.775 Corr.Coeff.=0.996
A_{1200}= -0.039[Sorbitol] + 0.538 Corr.Coeff.=0.988
A_{1800}= -0.035[Sorbitol] + 0.372 Corr.Coeff.=0.981

$t_{0.8}$ = -0.295[Sorbitol]+ 4.376 Corr.Coeff.=0.942
$t_{0.6}$ = -0.643[Sorbitlol]+ 9.358 Corr.Coeff.=0.959
$t_{0.4}$= -1.141 [Sorbitol]+ 16.33 Corr.Coeff.=0.976

RESULTS:-

10^3[simulated-1](mol dm^{-3})	**3.74±0.01**	**(Calculated):3.75(Actual)**
[Fixed Time Method]		
10^3[simulated-2] (mol dm^{-3})	**6.24±0.01**	**(Calculated):6.25 (Actual)**
10^3[simulated -1](mol dm^{-3})	**3.75**	**(Calculated):3.75(Actual)**
[Fixed Abs. Method]		
10^3[simulated-2] (mol dm^{-3})	**6.25**	**(Calculated):6.25 (Actual)**

TABLE-3
VARIATION OF ABSORBANCE WITH SORBITOL CONCENTRATION

10^4[Ce(IV)]=2.5moldm^{-3} $[H_2SO_4]$=0.95moldm^{-3}
Temperature=296±0.5K λ =360nm

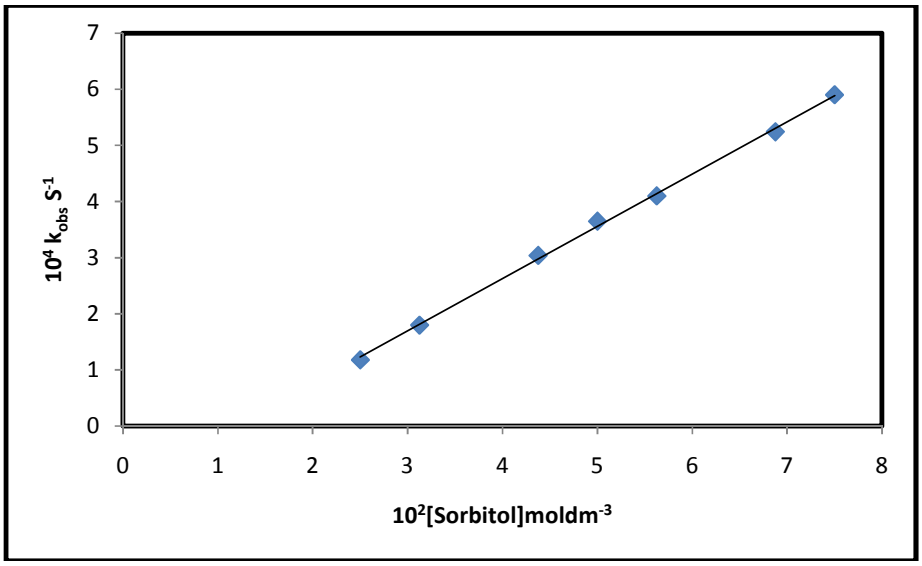
	10^2[Sorbitol]mol dm^{-3}				
10^{-2}Time (sec.)	**2.50**	**3.125**	**4.375**	**5.00**	**5.625**
0	1.032	1.032	1.032	1.032	1.032
3	0.994	0.978	0.938	0.926	0.914
6	0.966	0.925	0.861	0.829	0.804
9	0.929	0.872	0.781	0.745	0.716
12	0.897	0.835	0.721	0.662	0.631
15	0.865	0.785	0.651	0.598	0.562
18	0.853	0.758	0.606	0.532	0.492
21	0.798	0.713	0.544	0.475	0.441
24	0.764	0.684	0.512	0.432	0.382
27	0.742	0.633	0.448	0.387	0.341
$10^4k_{obs.}$	1.18±0.02	1.8±0.04	3.04±0.03	3.65±0.04	4.1±0.01

	10^2[Sorbitol]mol dm^{-3}			
10^{-2}Time (sec.)	**6.875**	**7.50**	**Simulated-1**	**Simulated-2**
0	1.032	1.032	1.032	1.032
3	0.882	0.866	0.955	0.896
6	0.749	0.722	0.894	0.776
9	0.645	0.611	0.822	0.681
12	0.553	0.511	0.782	0.592
15	0.467	0.424	0.716	0.504
18	0.404	0.351	0.669	0.432

21	0.341	0.288	0.613	0.377
24	0.292	0.251	0.576	0.332
27	0.253	0.213	0.523	0.287
10^4k_{obs}.	5.24±0.03	5.9±0.04	2.5±0.02	4.75±0.01

(A) RATE CONSTANT METHOD

S.No.	10^2[Sorbitol]moldm^{-3}	10^4k_{obs} (s^{-1})
1	2.5	1.1±0.02
2	3.12	1.8 ±0.04
3	4.37	3.0±0.03
4	5	3.6±0.04
5	5.62	4.1±0.01
6	6.87	5.2±0.03
7	7.5	5.9±0.04
8	Simulated-1	2.5±0.02
9	Simulated-2	4.7±0.01



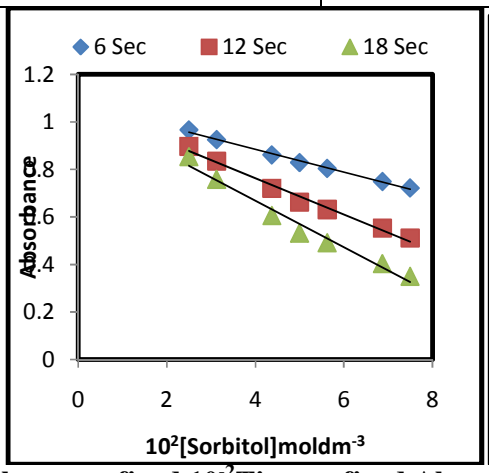
Regression Equation:
10^4k_{obs} =0.931 [Sorbitol] – 1.096 Corr.Coeff.= 0.998

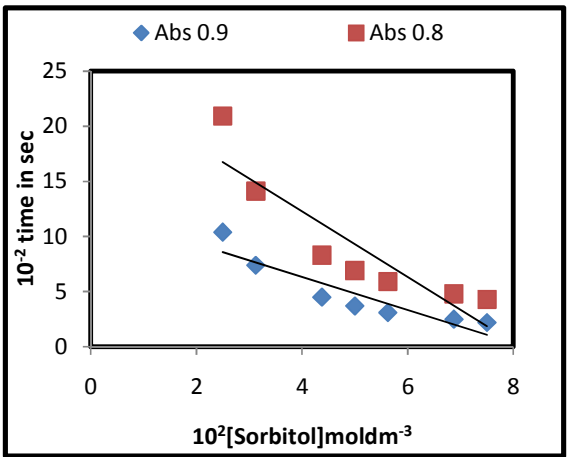
Results

10^2[simulated-1]mol dm^{-3}	**3.78±0.03(Calculated):3.75(Actual)**
10^2[simulated-2]mol dm^{-3}	**6.27±0.02(Calculated):6.25(Actual)**

(B & C) Fixed Time and Fixed Absorbance Method

10^2[Sorbitol]mol dm^{-3}	Absorbance at fixed 10^{-2} time(sec)			^{2} time(sec) at fixed absorban	
	6	**12**	**18**	**0.9**	**0.8**
2.5	0.966	0.897	0.853	10.4	20.9
3.125	0.925	0.835	0.758	7.4	14.1
4.375	0.861	0.721	0.606	4.5	8.3
5	0.829	0.662	0.532	3.7	6.9
5.625	0.804	0.631	0.492	3.1	5.9
6.875	0.749	0.553	0.404	2.5	4.8
7.5	0.722	0.511	0.351	2.3	4.3
Simulated-1	**0.894**	**0.782**	**0.669**	**6.2**	**11.6**
10^2[simulated-1]mol dm^{-3}	**3.78**	**3.76**	**3.78**	**3.88**	**3.8**
Simulated-2	**0.776**	**0.592**	**0.432**	**2.8**	**5**
10^2[simulated-2]mol dm^{-3}	**6.25**	**6.26**	**6.2**	**6.15**	**6.19**





Absorbance at fixed 10^{-2}Time at fixed Absorbance

Regression Equation

A_{600} = -0.048[Sorbitol] + 1.076 Corr.Coeff.=0.996

A_{1200}= -0.076[Sorbitol] + 1.068 Corr.Coeff.=0.986

A_{1800}= -0.098[Sorbitol] + 1.040 Corr.Coeff.=0.975

$t_{0.9}$ = - 1.504[Sorbitol]+ 12.05 Corr.Coeff.=0.846

$t_{0.8}$ = - 2.975[Sorbitlol]+ 23.19 Corr.Coeff.=0.813

RESULTS:-

10^3[simulated-1](mol dm^{-3}) [Fixed Time Method]	**3.77±0.02**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.23±0.02**	**(Calculated):6.25 (Actual)**
10^3[simulated -1](mol dm^{-3}) [Fixed Abs. Method]	**3.8 ±0.05**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.2±0.05**	**(Calculated):6.25 (Actual)**

TABLE-4
VARIATION OF ABSORBANCE WITH SORBITOL CONCENTRATION

10^4[Ce(IV)]=2.5moldm^{-3} [$HClO_4$]=0.95moldm^{-3}
Temperature=296±0.5K λ =360nm

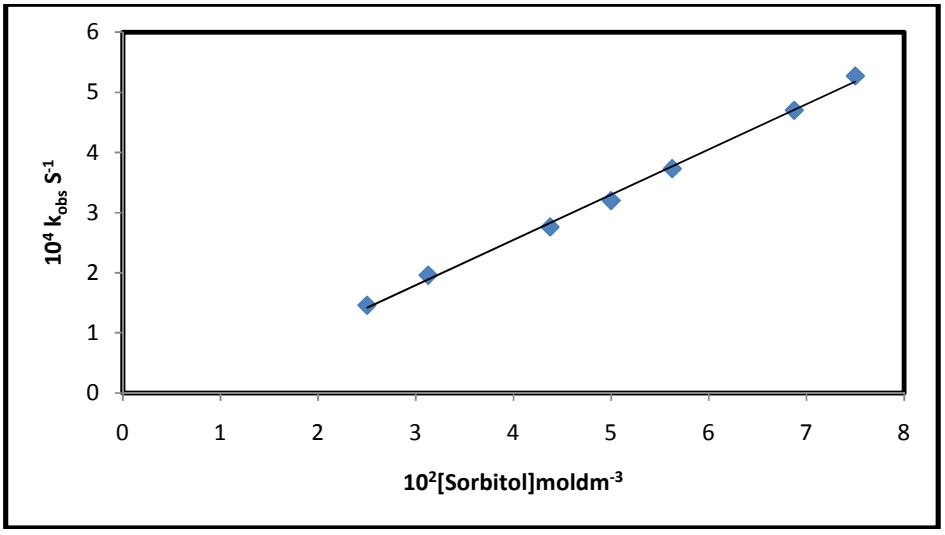
	10^2[Sorbitol]mol dm^{-3}				
10^{-2}Time(sec.)	**2.50**	**3.125**	**4.375**	**5.00**	**5.625**
0	1.014	1.014	1.014	1.014	1.014
3	0.972	0.958	0.934	0.919	0.905
6	0.931	0.904	0.862	0.832	0.812
9	0.892	0.848	0.789	0.758	0.725
12	0.854	0.811	0.724	0.686	0.646
15	0.818	0.763	0.672	0.623	0.582
18	0.781	0.714	0.609	0.552	0.521
21	0.742	0.658	0.568	0.517	0.461
24	0.693	0.617	0.522	0.462	0.409
27	0.664	0.588	0.485	0.417	0.373
10^4k_{obs}.	1.46±0.02	1.96±0.01	2.76±0.04	3.2±0.03	3.73±0.05

	10^2[Sorbitol]mol dm^{-3}			
10^{-2}Time(sec.)	**6.875**	**7.50**	**Simulated-1**	**Simulated-2**
0	1.014	1.014	1.014	1.014
3	0.881	0.866	0.942	0.895
6	0.762	0.741	0.882	0.787
9	0.662	0.633	0.821	0.696
12	0.573	0.542	0.769	0.616
15	0.506	0.457	0.702	0.541
18	0.442	0.397	0.668	0.479
21	0.374	0.339	0.617	0.425
24	0.323	0.279	0.574	0.381
27	0.287	0.247	0.532	0.329
10^4k_{obs}.	4.7±0.03	5.27±0.02	2.4±0.01	4.2±0.02

(A) RATE CONSTANT METHOD

S.No.	**10^2[Sorbitol]moldm^{-3}**	**10^4k_{obs} (s^{-1})**
1	2.5	1.4±0.02

2	3.12	1.9±0.01
3	4.37	2.7±0.04
4	5	3.2±0.03
5	5.62	3.7±0.05
6	6.87	4.7±0.03
7	7.5	5.2±0.02
8	Simulated-1	2.4±0.01
9	Simulated-2	4.2±0.02



Regression Equation $10^4 k_{obs}$ = 0.751 [Sorbitol] - 0.441 Corr.Coeff.=0.997

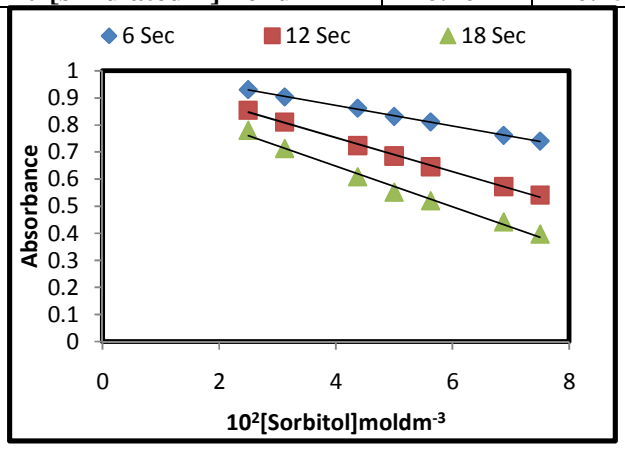
Results:-

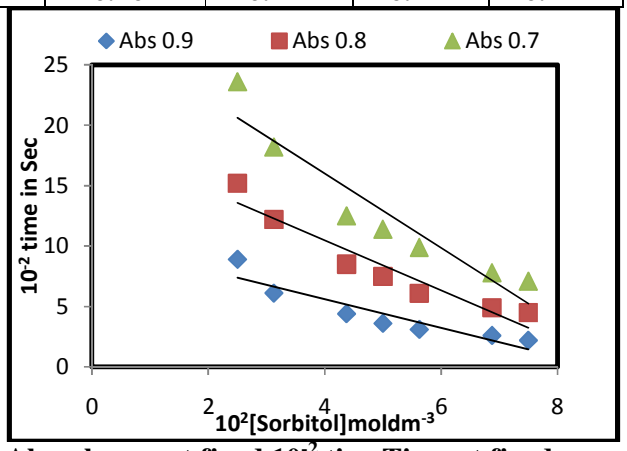
10^2[simulated-1]mol dm^{-3}	**3.78±0.03(Calculated):3.75(Actual)**
10^2[simulated-2]mol dm^{-3}	**6.2±0.05(Calculated):6.25(Actual)**

(B & C) Fixed Time and Fixed Absorbance Method

10^2[Sorbitol]mol dm^{-3}	**Absorbance at fixed 10^{-2} time(sec)**			**0^{-2} time(sec) at fixed absorbance**		
	6	**12**	**18**	**0.9**	**0.8**	**0.7**
2.5	0.931	0.854	0.781	8.9	15.2	23.8
3.125	0.904	0.811	0.714	6.1	12.2	18.2
4.375	0.862	0.724	0.609	4.4	8.5	12.5
5	0.832	0.686	0.552	3.6	7.5	11.4
5.625	0.812	0.646	0.521	3.1	6.1	9.9
6.875	0.762	0.573	0.442	2.6	4.9	7.8
7.5	0.741	0.542	0.397	2.2	4.5	7.1

Simulated-1	**0.882**	**0.769**	**0.668**	**5.9**	**10**	**15.6**
10^2[simulated-1]mol dm^{-3}	**3.76**	**3.78**	**3.74**	**3.74**	**3.74**	**3.8**
Simulated-2	**0.787**	**0.616**	**0.479**	**2.9**	**4.9**	**8.9**
10^2[simulated-2]mol dm^{-3}	**6.26**	**6.25**	**6.26**	**6.27**	**6.21**	**6.24**





Absorbance at fixed 10^{-2} timeTime at fixed Absorbance

Regression Equation

A_{600} = -0.038[Sorbitol] + 1.025 Corr.Coeff.=0.999
A_{1200}= -0.062[Sorbitol] + 1.004 Corr.Coeff.=0.997
A_{1800}= -0.075[Sorbitol] + 0.949 Corr.Coeff.=0.989

$t_{0.9}$ = - 1.187[Sorbitol]+ 10.35 Corr.Coeff.=0.854
$t_{0.8}$ = - 2.065[Sorbitlol]+ 17.73 Corr.Coeff.=0.918
$t_{0.7}$ = - 3.070[Sorbitlol]+ 28.08 Corr.Coeff.=0.896

RESULTS:-

10^3[simulated-1](mol dm^{-3}) [Fixed Time Method]	**3.76±0.01**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.25**	**(Calculated):6.25 (Actual)**
10^3[simulated -1](mol dm^{-3}) [Fixed Abs. Method]	**3.76 ±0.01**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.24 ±0.01**	**(Calculated):6.25 (Actual)**

TABLE-5
VARIATION OF ABSORBANCE WITH SORBITOL CONCENTRATION

10^4[Ce(IV)]=2.5moldm^{-3} [$HClO_4$]=0.7moldm^{-3}
Temperature=296±0.5K λ =360nm

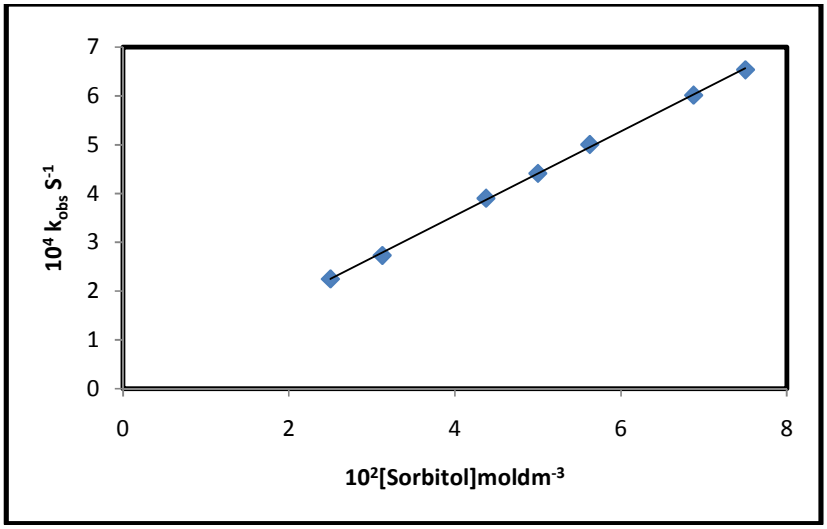
	10^2[Sorbitol]mol dm^{-3}				
10^{-2}Time (sec.)	**2.50**	**3.125**	**4.375**	**5.00**	**5.625**
0	1.011	1.011	1.011	1.011	1.011
3	0.944	0.932	0.902	0.886	0.869
6	0.885	0.857	0.798	0.772	0.751
9	0.824	0.791	0.714	0.678	0.642
12	0.772	0.728	0.627	0.602	0.554

15	0.725	0.661	0.561	0.522	0.481
18	0.674	0.616	0.498	0.456	0.418
21	0.627	0.572	0.437	0.408	0.352
24	0.588	0.524	0.394	0.349	0.302
27	0.549	0.491	0.352	0.298	0.267
$10^4k_{obs.}$	2.25±0.02	2.73±0.04	3.9±0.02	4.41±0.05	5.1±0.03

	10^2[Sorbitol]mol dm^{-3}			
10^{-2}Time(sec.)	**6.875**	**7.50**	**Simulated-1**	**Simulated-2**
0	1.011	1.011	1.011	1.011
3	0.846	0.834	0.914	0.856
6	0.703	0.681	0.833	0.734
9	0.587	0.563	0.744	0.618
12	0.491	0.458	0.678	0.521
15	0.423	0.376	0.609	0.449
18	0.341	0.312	0.556	0.376
21	0.285	0.262	0.511	0.321
24	0.236	0.209	0.456	0.266
27	0.194	0.171	0.408	0.227
$10^4k_{obs.}$	6.01±0.03	6.53±0.01	3.34±0.02	5.5±0.04

(A) RATE CONSTANT METHOD

S.No.	**10^2[Sorbitol]moldm^{-3}**	**10^4k_{obs} (s^{-1})**
1	2.5	2.2±0.02
2	3.12	2.7 ±0.04
3	4.37	3.9±0.02
4	5	4.4±0.05
5	5.62	5.1±0.03
6	6.87	6.0±0.03
7	7.5	6.5±0.01
8	Simulated-1	3.3±0.02
9	Simulated-2	5.5±0.04



Regression Equation

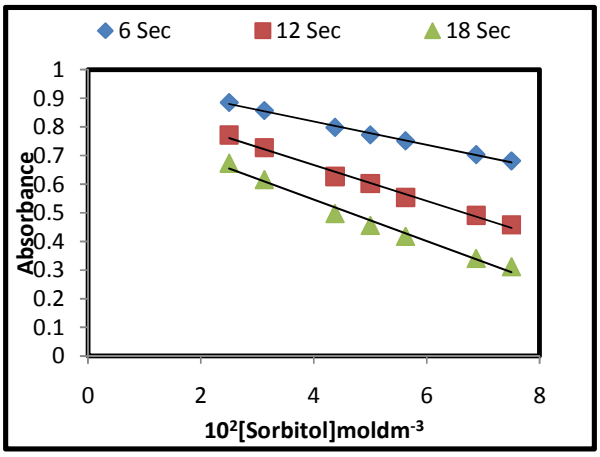
$10^4 k_{obs} = 0.863$ [Sorbitol] + 0.087 Corr.Coeff.=0.999

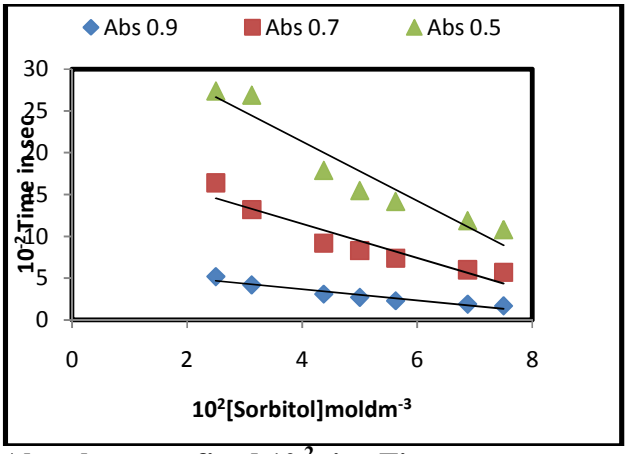
Results:-

10^2[simulated-1]mol dm^{-3} 3.76±0.01(Calculated):3.75(Actual)
10^2[simulated-2]mol dm^{-3} 6.27±0.02(Calculated):6.25(Actual)

(B & C) Fixed Time and Fixed Absorbance Method

10^2[Sorbitol]mol dm^{-3}	Absorbance at fixed 10^{-2} time(sec)			0^{-2} time(sec) at fixed absorbance		
	6	12	18	0.9	0.7	0.5
2.5	0.885	0.772	0.674	5.2	16.4	27.4
3.125	0.857	0.728	0.616	4.2	13.2	26.9
4.375	0.798	0.627	0.498	3.1	9.2	17.9
5	0.772	0.602	0.456	2.7	8.3	15.5
5.625	0.751	0.554	0.418	2.3	7.4	14.2
6.875	0.703	0.491	0.341	1.9	6	11.9
7.5	0.681	0.458	0.312	1.7	5.7	10.8
Simulated-1	**0.833**	**0.678**	**0.556**	**3.8**	**11.4**	**21.3**
10^2[simulated-1]mol dm^{-3}	**3.72**	**3.75**	**3.77**	**3.8**	**3.8**	**3.72**
Simulated-2	**0.734**	**0.521**	**0.376**	**2.2**	**6.6**	**12.3**
10^2[simulated-2]mol dm^{-3}	**6.22**	**6.2**	**6.2**	**6.22**	**6.2**	**6.26**





Absorbance at fixed 10^{-2} timeTime at fixed Absorbance

Regression Equation

A_{600} = -0.040[Sorbitol] + 0.982	Corr.Coeff.=0.996
A_{1200}= -0.064[Sorbitol] + 0.918	Corr.Coeff.=0.991
A_{1800}= -0.074[Sorbitol] + 0.835	Corr.Coeff.=0.984
$t_{0.9}$ = - 0.667[Sorbitol]+ 6.352	Corr.Coeff.=0.927
$t_{0.7}$ = - 2.036[Sorbitlol]+ 19.24	Corr.Coeff.=0.897
$t_{0.5}$ = - 3.541[Sorbitlol]+ 34.50	Corr.Coeff.=0.919

RESULTS:-

10^3[simulated-1](mol dm^{-3}) [Fixed Time Method]	**3.74±0.01**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.22 ±0.03**	**(Calculated):6.25 (Actual)**
10^3[simulated -1](mol dm^{-3}) [Fixed Abs. Method]	**3.77 ±0.02**	**(Calculated):3.75(Actual)**
10^3[simulated-2] (mol dm^{-3})	**6.22 ±0.03**	**(Calculated):6.25 (Actual)**

TABLE -6

Summary of the Kinetic Cerimetric estimation of D-Sorbitol

10^4[Ce(IV]= 2.50 $moldm^{-3}$, Temp.= 296K , λ= 360nm

Table No.	[Acid] $moldm^{-3}$		Concentration of simulated samples ($moldm^{-3}$)			
			A (Rate constant method)	B (Fixed time method)	C (Fixed Abs. method)	Average value
3.8	$[H_2SO_4]$ 0.7	10^3 [Simulated-1] 10^3 [Simulated-2]	3.77 6.24	3.76 6.26	3.8 6.23	3.77 6.24
3.9	0.45	10^3 [Simulated-1] 10^3 [Simulated-2]	3.73 6.28	3.74 6.24	3.75 6.25	3.74 6.25
3.10	0.95	10^3 [Simulated-1] 10^3 [Simulated-2]	3.78 6.27	3.77 6.23	3.8 6.20	3.78 6.23

3.11	$[HClO_4]$ 0.95	10^3 [Simulated-1] 10^3 [Simulated-2]	3.78 6.20	3.76 6.25	3.76 6.24	3.76 6.23
3.12	0.7	10^3 [Simulated-1] 10^3 [Simulated-2]	3.76 6.27	3.74 6.22	3.77 6.22	3.75 6.23

10^3[Simulated-1]moldm^{-3} = 3.75(actual value)
10^3[Simulated-2]moldm^{-3} = 6.25(actual value)

The results of these kinetic cerimetric estimations of D-sorbitol have been summarized in table 6 which indicate the usefulness of this estimation methodThe results of kinetic cerimetric estimations of D-sorbitol can easily be extended to other alditols and other pharmaceutical products belonging to this group as it was done earlier for aldohexoses , pentoses and tetroses./ 7/

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