APPENDIX#3:

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<u>Non-línear Curve fíttíng with</u> <u>Mícrosoft Excel Solver and Non-</u> <u>Línear Regression Statistícs</u>¹

A. CALCULATION OF KOBS, KREAL AND DEBYE-HÜCK	EL PLOT.
A1. Kinetics calculation: k_{obs} , k_{real} .	page 1
A1.1 "The crude" step	page 7
A1.2 Optimization step	page 9
A2. Debye-Hückel plot	page 18
B. NON-LINEAR STATISTICS	page 23

A. Calculation of kobs, kreat and Debye-Hückel plot.

A1. Kinetics: calculation of k_{obs} and k_{real} .

1. From File click on New.., then on General Workbook:



¹ E. J. Billo "*Excel*[®] for Chemists", 2nd ed., Wiley: New York, 2001, Chapiter 12. For questions you can contact Prof. Billo (Dept. Chem., Boston College, Chestnut Hill, MA): joseph.billo@bc.edu; see also: http://chemserv.bc.edu/faculty/billo.html



2. From File, Save as... the workbook. My preference for file name is Kinetics_MG (MG are my initials) and it is saved in the Personal folder.





3. Five sheets are necessary in your workbook. Four are for Kinetics data. The fifth is for Debye_Huckel calculation. <u>You have to append these five sheets to your written or Oral report.</u>

If there are not enough Sheets, click Insert and then Worksheet.



Name four sheets, each for a kinetic run. For example, I have chosen: **KineticsA** (for the 0.02M NaNO₃), **KineticsB** (for the 0.05M NaNO₃), **KineticsC**, (for the 0.1M NaNO₃) and **KineticsD** (for the 0.2M NaNO₃).

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4. Now is time to add your experimental data to the four sheets. Take for example, **KineticsB sheet**. Type in column A, the **time** (in seconds), and in column B the **experimental absorbances** (@420nm) corresponding to the respective time. Add on the Table two more columns. One for **calculated absorbances** (from equation 3) and a second column for the **square** of the difference **experimental absorbances** (column B)-calculated absorbances (column C).

1	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]
2	0	0.50723		
3	60	0.48962		
4	120	0.4733		
5	180	0.45877		
6	240	0.44608		
7	300	0.43346		
8	360	0.42337		
9	420	0.4129		
10	480	0.40375		
11	540	0.39626		
12	600	0.38828		
13	660	0.38049		
14	720	0.37381		
15	780	0.36777		
16	840	0.36227		
17	900	0.3568		
18	960	0.35213		
19	1020	0.34729		
20	1080	0.34312		
21	1140	0.33925		
22	1200	0,33557		
	Kini	eticsA) KineticsB	/ KineticsC / Ki	neticsD / Sheet5 /

5. Just as a reminder, the second order integrated kinetic equation, as it was presented to you in my hand-out, is printed next. The meaning of variables are the same as in the hand-out and the Lab Manual:

$$A = A_{f} \frac{1}{1 - \frac{A_{0} - A_{f}}{A_{0}}} exp(-c_{f}k_{obs}t)$$
(3)
Integrated second order kinetic equation in terms of
absorbance that is curve-fitted to the experimental data.
 A_{0} = initial absorbance
 $A = absorbance$ at time t
 A_{f} = absorbance when all H₂Asc has reacted.

- 6. We are now just a step before using Microsoft Excel Solver. On each kinetic sheet one must add cells containing two sets of information. In cells H2 and H3 are typed the values of the "fixed" variables A0 and epsilon, respectively. The content of the cells H5 (Af value) and H6 (kobs) is changing. Initially, "guess" values are typed in for the variables of Af and kobs. After the minimization process, Solver returns the regression coefficients in the changing cells H5 and H6, respectively. Solver is not providing the standard deviations of the coefficients; see B section.
- 7. In order to be automatically plugged into the kinetic equation, the cells containing the values of A0, epsilon, Af, kobs must be given a name (this is an Excel requirement).
- For **A0**, type =B2 in cell H2
- For **epsilon** type in cell H3, the value obtained by you for **epsilon** (calculated from Lambert-Beer equation, recorded during day #1). The slope of the least square straight line, calculated from my results, gave $\varepsilon = 1020$.
- Type in cell H5 the best guess value for **Af**, that is 0.25 (Why?).
- Type the your guess value for **kobs** in cell H6. My guess is 5.

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	H6	▼ = 5						
	A	В	С	D	E	F	G	H
1	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]				
2	0	0.50723					A0=	0.50723
3	60	0.48962					epsilon=	1020
4	120	0.4733						
5	180	0.45877					Af=	0.25
6	240	0.44608					kobs=	5
7	300	0.43346						

In order to be automatically inserted in equation 3, A0, epsilon, Af and kobs must be assigned a name. For example to name A0, first click on cell H2. Than click on Insert, Name, Define:

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4	120		∋uvbeninv∵	, CUITK		<u>A</u> pply								
5	180		*	\$		Label						Af=	0.25	
6	240	0.	.44608		_							kobs=	5	
7	200	0	10010											

The following window pops-up:



Please notice and check the correct location of the value of A0, in this case is (according to Excel grammar): KineticsB!\$H\$2, that is on **KineticsB** sheet and location H2. Click on **add** button. Click on **OK**. The **naming** continues for cells H3:H5. Next, let us name as **t** the vector A2:A22. First highlight the column A2:A22, then click on **Insert, Name, Define** and change the names in workbook as **t** (check **Refers to** address in order be correct). The **Define Name** window will look like:

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	time	experimental	Calculated	Diff^2				
	(seconds)	absorbances	absorbances	l(exp.calc)^2]				
1	(30001113)	(420 nm)	(equation 3)	[(cyb-carc) 5]				
2		0.50723					A0=	0.50723
3	60	0.48962					epsilon=	1020
4	120	0.4 Define	Name				? ×	
5	180	0.4						0.25
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13	720	0.3						
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17	900						=	
18	960	0.3	CSB1\$A\$2:\$A\$22					
19	1020	0.34729						

8. **Solver** optimizes the curve fitting in two steps:

- In the first step, "crude" values of absorbances are calculated.
- In the second step, the optimization step, the crude values of calculated absorbances are refined to best fit to experimental values.
- A. The "Crude" Step:

Type in cell C2 =Af/((1-((A0-Af)/A0)*EXP(-kobs*t*Af/epsilon))). Cell H2 is filled with the calculated absorbance for t=0 seconds. According to equation 3 it is equal with A0.

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	C2 = = Af/((1-((AD-Af)/AD)*EXP(-kobs*t*Af/epsilon)))								
	A	В	С	D	E	F	G	Н	
1	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]					
2	0	0.50723	0.50723				A0=	0.50723	
3	60	0.48962		ĺ			epsilon=	1020	
4	120	0.4733							
5	180	0.45877					Af=	0.25	
6	240	0.44608					kobs=	5	
7	300	0.43346							
8	360	0.42337							

In order to fill in cells C3 through C22, click on cell C2. Bring the cursor to the right low corner and press left mouse. Drag all the way down to cell C22. Depress the left mouse. All cells (C2:C22) are now filled in with the calculated ("crude") Absorbances:

	A	В	C	D
1	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]
2	0	0.50723	0.50723	
3	60	0.48962	0.47275	
4	120	0.4733	0.44466	
5	180	0.45877	0.42140	
6	240	0.44608	0.40187	
7	300	0.43346	0.38528	
8	360	0.42337	0.37104	
9	420	0.4129	0.35873	
10	480	0.40375	0.34800	
11	540	0.39626	0.33859	
12	600	0.38828	0.33029	
13	660	0.38049	0.32294	
14	720	0.37381	0.31640	
15	780	0.36777	0.31055	
16	840	0.36227	0.30531	
17	900	0.3568	0.30059	
18	960	0.35213	0.29634	
_10 € _€	1020 ▶ ▶ \ Kin	0 34729 eticsA KineticsB	KineticsC / Kir	neticsD / Sheet5 /

A2. Optimization step: Non-linear curve fitting step.

- 9. Type in cell D2=(B2-C2)^2. Press Enter key.
- 10. Click on cell D2. Drag all the way down to cell D22, as it was described for calculated absorbances.
- 11. In cell D23 sum (click on icon Σ) D2 through D22.

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21 1140 0.33925 0.28585 2.8512E-03 22 1200 0.33557 0.28298 2.7661E-03 23 =SUM(02:022)	20	1080	0.34312	0.28902	2.9273E-03	
22 1200 0.33557 0.28298 2.7661E-03 23 =SUM(02:022)	21	1140	0.33925	0.28585	2.8512E-03	
23 =SUM(D2:D22)	22	1200	0.33557	0.28298	2.7661E-03	
	23				=SUM(D2:D22)	

Than press Enter key.

12. Click on cell D23. Click Tools and than Solver...

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8	360	0.42337	Sol <u>v</u> er		E-03	
9	420	0.4129	Add- <u>I</u> ns		E-03	
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11	540	0.39626	Options		E-03	
12	600	0.38828	×		E-03	
13	660	0.38049	0.32294	3.3119	9E-03	
14	720	0.37381	0.31640	3.2963	3E-03	
15	780	0.36777	0.31055	3.2741	IE-03	
16	840	0.36227	0.30531	3 2447	7E-03	

The Solver Parameters window pops-up. The target cell is D23.

	Ar	rial	▼ 10 ▼ B	IŪĖĒ		\$%,	+.0 +.00	三年
	D23	▼ = =	SUM(D2:D22)					
	A	В	С	D	E	F	G	Н
7	300	0.43346	0.38528	2.3217E-03				_
8	360	C Solver Par	ameters				?	×
9	420	S <u>e</u> t Target	Cell: \$D\$23	3			<u>S</u> olve	1
10	480	C Equal To:	<u>М</u> ах О	Mi <u>n</u> O <u>V</u> alue o	f: 0		Close	1
11	540	Ey Changi	ng Cells:					- 1
12	600	[🔝 Gu	iess		
13	660	C Subject to	the Constraints:				Options	1
14	720					aa 1		- 1
15	780	C						
16	840	C			<u>C</u> ha	ange	Decet All	1
17	900				De De	lete	Keset All	1
18	960						<u>H</u> elp	
19	1020	6	0.272.00	3.0021E 03				
20	1080	0.34312	0.28902	2.9273E-03				

Type into **By Changing** the cells: H5 and H6 (that is \$H\$5 and \$H\$6).

(equation 3)	[(exp-calc)^2]				
0.50723	0.0000E+00			A0=	0.50723
0.47275	2.8469E-04			epsilon=	1020
0.44466	8.2020E-04				
0.42140	1.3965E-03			Af=	0.25
0.40187	1.9547E-03			kobs=	5
Solver Para	meters				? ×
S <u>e</u> t Target C	iell: \$D\$23	<u>.</u>	_		<u>S</u> olve
Equal To: By Changing	● <u>M</u> ax ● Mi g Cells:	n O <u>V</u> al	ue of: 🛛)	Close
\$H\$5:\$H\$6 -Subject to t	- bl he Constraints:			<u>G</u> uess <u>A</u> dd	Options
			¥	<u>C</u> hange <u>D</u> elete	<u>R</u> eset All <u>H</u> elp
0 20250	ໄວ∩∩າ⊏∩ວໄ		1	1	

On Solver Parameters click on Options. Change Max Time to 1200 seconds (kinetics run time). Click OK.

2 2							
At	ial	▼ 10 ▼ B	IUE		\$%,	◆.0 .00 ●.0 ◆.0	■韓田・
23	▼ = =:	SUM(D2:D22)					
А	В	С	D	E	F	G	Н
time	experimental a <u>bsorbances</u>	Calculated	Diff^2				
conasj	Solver Optic	ons			? ×		
0	Mary Times	1200	T			A0=	0.50723
60	Max <u>n</u> me:		onas	OK		epsilon=	1020
120	Iterations:	100		Cancel			
180	Precision:	0.000001		Load Model		Af=	0.25
240	Televence	E		Cours Model		kobs=	5
300	roi <u>e</u> rance;			<u>5</u> ave Model			
360	Con <u>v</u> ergence	e: 0.0001		<u>H</u> elp			
420	Assume I	Linear Model	🔲 Use Aut	omatic Scaling			
480	Assume I		Show It	eration Results			
540	Estimates	Derivat	ives S	iearch	_		
600	• T <u>a</u> nger	nt 🔍 <u>F</u> o	rward	• <u>N</u> ewton			
660	O Quadra	atic <u>C</u> e	ntral	C C <u>o</u> njugate			
720							
700	~ ~ ~ ~ ~ ~ ~						

The Solver Parameters window comes back. Click first on Min and than on Solve button:

At [ial	▼ 10 ▼ B	IŪĒĒ		\$%	• 00 + 00 =		
D23	▼ = =:	SUM(D2:D22)						
A	В	С	D	E	F	G		
120	0.4733	0.44466	8.2020E-04					
180	0.45877	0.42140	1.3965E-03		Af=			
24 Solv	er Parameters			? × s=				
30	. I							
36 Set	Target Cell:	<u></u>			<u>S</u> olve			
42 Equ	alTo: 💽 <u>M</u> ax	⊙ Mi <u>n</u> C	Value of: 0		Close			
1 48 By	Changing Cells: ——							
54 \$	1\$5:\$H\$6		<u> </u>	Guess				
) 61 -Sub	ject to the Constra	ints:			Option	is		
			A	Add		···		
) UL				<u> </u>				
12			<u> </u>	hange	Death			
				elete	<u>k</u> eset /	411		
3 8 4					<u>H</u> elp			
90								
) 960	0.35213	0.29634	3.1123E-03					
			I		1	1		

The **Solver Results** window pops-up. Note that the values in cells H4 and H5 are updated. You know by now the value of **kobs** as **2.60**. Note that the initial value the "guess"} has been taken as 5.

][~	- =	$= \mathbf{m}_{\parallel}$	ч / о ј	.00 +.0 =	÷- ÷- Ш
3	▼ = =:	SUM(D2:D22)					
A	В	С	D	E	F	G	H
20	0.4733	0.47325	2.0632E-09				
80	0.45877	0.45879	5.1845E-10			Af=	0.263131
40	0.44608	0.44571	1.3668E-07			kobs=	2.601935
00	0.43346	0.43383	1.3543E-07				
60 📻					0		
20 80 40	Solver has converge constraints are satis	d to the current so fied.	olution, All	<u>R</u> eports Answer	Ā		
00	• Keep Solver So	lution		Sensitivity			
60	C Restore <u>O</u> rigina	al Values			~		
20 80	ОК	Cancel	<u>S</u> ave Scenario.		Help		
40 -	0.36227	0.36236	7.8227E-09				
~~	0.0500						

You can print some reports: **answer**, **sensitivity and limits**. For Example the **Answer Report** looks like:

	A	В		С	D	E	F
1	Micro	osofi	t Excel 9).0 Answer Rep	ort		
2	Work	she	et: [Kine	etics_MG.xls]Ki	neticsB		
3	Repo	rt C	reated:	12/28/01 5:39:24	I PM		
4							
5							
6	Targe	t Ce	ll (Min)				
7	C	ell		Name	Original Value	Final Value	
8	\$D	\$23	Diff^2	[(exp-calc)^2]	5.3191E-02	1.7040E-06	
9							
10							
11	Adjus	tabl	e Cells				
12	C	ell		Name	Original Value	Final Value	
13	\$H	\$5	Af		0.25	0.263131158	
14	\$H	\$6	kobs		5	2.601934917	
15							
16]						
17	Const	train	ts				
18	NC)NE					

Repeat steps 4 through 12 for sheets **KineticsA**, **KineticsC** and **KineticsD**. Whenever is necessary, please update the **Reference** in the **Define Name** window.

A3. Debye-Hückel equation.

In the "Kinetics" hand-out (see there the meanings of variables), the **Debye-Hückel** equation is defined as:

$$\log \mathbf{k}_{\text{real}} = \log \mathbf{k}_0 + 1.02 * \mathbf{Z}_1 * \mathbf{Z}_2 \frac{\mathbf{I}^{1/2}}{1 + \mathbf{I}^{1/2}} = \log \mathbf{k}_0 + 1.02 * 3 * \frac{\mathbf{I}^{1/2}}{1 + \mathbf{I}^{1/2}}$$
(6)

where k_{real} is given by equation (4):

$$\mathbf{k}_{\text{real}} = \mathbf{k}_{\text{obs}} \frac{\left[\mathbf{H}^{+}\right]}{\mathbf{K}_{\text{al}}} \quad (4)$$

Use the sheet#5 (renamed as **Debye-Hückel**) to compute and draw the linear plot **logkreal** (y axis) versus $I^{0.5}/(I^{0.5}+1)$ (x axis). When fished the contend of the **Debye-Hückel** worksheet will look like:

	Α	В	C	[)	E	F	G	
1	l^1/2/(l^1/2+1)	logkreal	kobs	kre (kobs*([H	eal +]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2	
2	0.1091	2.17	2.070	147	.01	0.0204	0.0150	0.1225	
3	0.1472	2.27	2.602	184	.75	0.0500	0.0298	0.1726	
4	0.1898	2.43	3.793	269	.30	0.1002	0.0549	0.2343	
5	0.2447	2.53	4.808	341	.40	0.2003	0.1050	0.3240	
6									
7	HNO3 (molarity)=	0.0096			2.60 T				
8	Ascorbic acid, Ka1=	6.76E-05			2.55	Debye	-Huckel		
9					2.45 +				
10	Slope=	2.78		6	240		/		
11	Intercept=	1.87		물	2.70				
12	k0=	73.90		<u> </u>	2.50 T				
13	R^2=	0.9809			2.30 +		/		
14					2.25 +	$- \frown$		1 0000	
15					2.20 +	_/	y = 2.7835	<u>(+1.8686</u>	
16					2 15	<u> </u>	$R^2 = 0$	9809	
17					2.10 2.40				
18					2.10 +		<u>т</u> т	i	
19					0.1	00	15 0.2	0 0.2	5
	KineticsB	/ KineticsC / Kin	neticsD λ D_H	1_demo 🏑	Debye_Huck	el / 🚺			

- Build a Table of 7 columns and 5 rows. The order and the content of the headings are suggested in Fig. X. Remember that in Excel x-axis values have to stay left to y-axis values (for example, column A values are on x-axis, column B values are displayed on y-axis).
- Fill in kobs values by reading the address from the respective worksheet. Click, for example on cell C2 and type: KineticsA!\$H\$6. Cell two is filled with the value 2.07 for kobs. Cell C3 has to be filled with KineticsB!\$H\$6, cell C4 with KineticsC!\$H\$6 and cell C5 with KineticsD!\$H\$6.

M	licrosoft Excel - I	Kinetics_MG.xls					
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	C5 🔽	= =Kinet	icsD!\$H\$6				
	A	В	С	D	E	F	G
1	1		kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2			2.070				
3			2.602				
4			3.793				
5			4.808	<u> </u>			
6							

3. Add on the worksheet information regarding the HNO₃ molarity (cell B7). Type the acidity constant for ascorbic acid (Ka1= $6.76*10^{-5}$) into cell B8.

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	B15 🔹	=		l.			
	A	В	С	D	E	F	G
1	l^1/2/(l^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2			2.070				
3			2.602				
4			3.793				
5			4.808				
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, Ka1=	6.76E-05					
9							

4. Fill in the column D2 through D5 with calculate kreal (see equation 4). For example in cell D2: =(C2/\$B\$8)*0.5*\$B\$7 (0.5 appears because the HNO₃ in the UV cuvette is the half diluted HNO₃ stock solution). Because cells B7 and B8 are referred to absolute address, for example \$B\$7, you can generate automatically the content of the subsequent D2:D5 cells. Click on D2, move the cursor to right lower corner and pressing left mouse, drag all the way down to D5. Cells are filled automatically.

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	Arial	•	10 - B	<i>I</i> <u>U</u> ≣ ≣ ≡	■ \$ %	•.0 .00 •	🗏 🗐 🖬 • 🦄
	D5 🔽	= =(C5/\$	B\$8)*0.5*\$	B\$7			
	A	В	C	D	E	F	G
1	l^1/2/(l^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2			2.070	147.01			
3			2.602	184.75			
4			3.793	269.30			
5			4.808	341.40	[
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, Ka1=	6.76E-05					
9							

5. Calculate logkreal in cell D2 as LOG10(D2). Drag the cell content as described above all the way down to B5:

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	Arial		10 - B		· 🔤 💲 🤅	%, ^{+.0} , .00	∰ ∰ ⊞ • <
<u> </u>	B5 💌	= =LO0	G10(D5)				
	A	В	С	D	Е	F	G
1	l^1/2/(l^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2		2.17	2.070	147.01			
3		2.27	2.602	184.75			
4		2.43	3.793	269.30			
5		2.53	4.808	341.40			
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, Ka1=	6.76E-05					
9							

- 6. The remaining calculation refers to $I^{0.5}/(I^{0.5}+1)$ the x-axis variable calculation in column A.
 - First fill in NaNO₃ stock solution molarities. In my experiments I used the values printed in columns E2:E5.
 - Second, in column F2:F5 calculated the real NaNO3 + HNO3 molarities. For example in cell F2, calculate =(E2+\$B\$7)*0.5. Multiplication with 0.5 is because in the UV cuvette the stock solution become half diluted as result of the 3 mL+ 3mL mixing (see the experiment and handouts). Remember that for monovalent anions and cations, molarities are numerically equal to **Ionic Strength**.

8	<u>File E</u> dit <u>V</u> iew <u>I</u> r	nsert F <u>o</u> rmal	t <u>T</u> ools <u>D</u> at	a <u>W</u> indow <u>H</u> elp			
	Arial		• 10 •	B <i>I</i> <u>U</u> ≡ ≡	≣ ⊡ \$	°%, *.00∔	% 🛊 🛊 🖽
	G2 🔽	=					
	A	В	С	D	E	F	G
1	l^1/2/(l^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2		2.17	2.070	147.01	0.0204	0.0150	
3		2.27	2.602	184.75	0.0500	0.0298	l l l l l l l l l l l l l l l l l l l
4		2.43	3.793	269.30	0.1002	0.0549	
5		2.53	4.808	341.40	0.2003	0.1050	
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, Ka1=	6.76E-05					
9							

- Third, in cells G2:G5 calculate the square root of value from cell F2:F5.
- For example, in cell G2 type =SQRT(F2), and press Enter. Fourth, in cells A2:A5 calculate $I^{0.5}/(I^{0.5}+1)$. For example, type =G2/(G2+1) in cell A2. Click on the cell. Drag the lower right corner all • the way down to A5.

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\vdash	nart Area 💽	=	-	-		_	-
	A	В	С	D	E	F	G
1	l^1/2/(l^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2	0.1091	2.17	2.070	147.01	0.0204	0.0150	0.1225
3	0.1472	2.27	2.602	184.75	0.0500	0.0298	0.1726
4	0.1898	2.43	3.793	269.30	0.1002	0.0549	0.2343
5	0.2447	2.53	4.808	341.40	0.2003	0.1050	0.3240
6							
	HNO3	0.0006					
7	(molarity)=	0.0030					
8	Ascorbic acid, Ka1=	6.76E-05					
9							
10	Slope=	2.78					
11	Intercept=	1.87					
12	k0=	73.90					
13	R^2=	0.9809					
4.4							

A2. The Debye-Hückel plot.

• Highlight columns A2:B5. Click on **Insert** than **Chart...**:

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	A2 🔻	⊆olumns									
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2	0.1091	· Picture ·			147	. .01					
3	0.1472	Hypenijnk Ctri+k		+κ	184	.75					
4	0.1898		×			269	.30				
5	0.2447	2	.53	4.80	8	341	.40				
6			Ĩ								
7	HNO3 (molarity)=	0.0	1096								
8	Ascorbic aci Ka1=	d, 6.76	6E-05								
9											
10											

• In the Chart Wizard window Step 1, choose Chart type: XY(Scatter); and the highlighted Chart sub-type.



• Click next to steps 2 and 3. Fill in the chart title, value (X) axis and value (Y) axis respectively.

<u> </u>	<u>E</u> dit <u>V</u> iew <u>I</u> nser	t F <u>o</u> rmat <u>1</u>	<u>T</u> ools <u>D</u> ata	<u>W</u> indow	<u>H</u> elp									
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							NaN()3	NaN (add	03 real ling the	Square	e root		
	l^1/2/(l^1/2+1)	logkreal	Chart V	Vizard - S	Step 3 o	f 4 -	Chart O	ption	\$? ×
1			Title	s Axe	es 🛛 Gri	dlines	Leger	nd	Data L	abels				
2	0.1091	2.17	🦾 Charl	: <u>ti</u> tle:										-11
3	0.1472	2.27		ebye-Huck	vel					Deb	ge-Huckel			- 11
4	0.1898	2.43		(Y) avis:				2.6						- 11
5	0.2447	2.53		0.5/(TAD	5+1)	_	_	2.5	55		•	•		- 11
6				0.0/(1 0.				_ 2.4	15					- 11
7	HNO3 (molarity)=	0.0096		(Y) axis: igkreal				e 2.4 2.3 2.3	0 5 0				 Serie 	::1
	Ascorbic acid,	6 76E 05	Seco	nd categor	v (X) axis:			2.2	5		+			- 11
8	Ka1=	0.702-03	Г		7 (1)		_	2.2	15	•				- 11
9				al calca A				2.1		0 1000	0 2000	0.300	•	- 11
10			Secol	na value (n) axis:		_		0.0000	1^0.57	(I^0.5+1)	0.000		
11														
12														
13			2				Cance			Back	Next >		Finish	
14							Cance			Face	- HOAC >			

- Click Next and than Finish.
- After a few editing, the graph looks:

	A	В	С		D	E	F	G	H
2	0.1091	2.17	2.070	14	47.01	0.0204	0.0150	0.1225	
3	0.1472	2.27	2.602	11	84.75	0.0500	0.0298	0.1726	
4	0.1898	2.43	3.793	20	69.30	0.1002	0.0549	0.2343	
5	0.2447	2.53	4.808	34	41.40	0.2003	0.1050	0.3240	
6									
	HNO3	0 0006			1.60				
7	(molarity)=	0.0030			2.60 T				
	Ascorbic acid,	6 76E 05			2.50 +	Debye	-Huckel	•	
8	Ka1=	0.702-03					•		
9				, and a second sec	2.40 +				
10				20	\$° 2 30 ⊥				
11					- 2.00	•	•		
12					2.20 +	•			
13					2.10	•			
14					2.10 ♥		1 1		
15					0.10	0 0.	15 0.2	0 0.2	5
16							I^0.5/(I^0.5+	·1)	
17									

• The least square straight line is added on the graph, by clicking on **Chart**, than **Add trendline**..

3)	<u>File E</u> dit <u>V</u> iew <u>I</u> i	nsert F <u>o</u> rma	t <u>T</u> ools	<u>⊂</u> hart ⊻	<u>/</u> indow	Help						
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3	0.1472	2.27	2.602					0.0500	().0298	0.1726	
4	0.1898	2.43	3.793	<u>A</u> dd I	Data		L	0.1002	().0549	0.2343	
5	0.2447	2.53	4.808	Add	T <u>r</u> endlin	e	L	0.2003	().1050	0.3240	
5				3-D <u>y</u>	/jew		L					
7	HNO3 (molarity)=	0.0096				2.60	T					
	Ascorbic acid,	C 7CE 05				2.50	+	<u> </u>	<u>/e-Hu</u>	ckel	•	
З	Ka1=	0.702-03			eal					•		
Э.					<u>کے</u>	2.40	t					
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2					-	2.20	+	•				
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5						U	. I	U	0.10 ^	 .5/(I^0.5	20 0.2 +1)	20
7											1	

Choose Type the Trend/Regression type, Linear.



• Click on **Options**. Check display equation on the chart and Display R-squared value on the chart:

				•	N X N E		Ψ /0	y .00 +	.0 ₩ ₩ 🖽
P	lot Area	-	=						
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4	0.							549	0.2343
5	0.	Туре	Options					D50	0.3240
6		⊢Trendlin	ne name – – – – –				1		
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12								<u> </u>	
13		🗌 <u>S</u> et in	ntercept =	0					
14		🔽 Displa	ay <u>e</u> quation o	n chart				[~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~
15		🔽 Displa	ay <u>R</u> -squared	value on cha	rt)			0.2	0 0.25
16								Y(I^U.5+	1)
17									
18									
19									
-20								1	

• The least square straight line has the equation: y = 2.7835x + 1.8686 and $R^2=0.9809$ (satisfactory, however I am confident that 5.311 students will get a better R^2).



- In order to compute the slope (1.02*Z₁*Z₂) and intercept, ko (rate constant at I=0), and R2, let first add these cells (H10:H12) to the Debye-Hückel worksheet.
- Type =SLOPE(B2:B5,A2:A5) into cell next (B10) to Slope=.
- Type = INTERCEPT(B2:B5,A2:A5) into cell next (B11) to Intercept=
- Type = 10^{B11} into cell next (B12) to **k0**=
- Type =RSQ(B2:B5,A2:A5) next (B13) to R^2=

	<u>File E</u> dit <u>V</u> iew Ir	nsert F <u>o</u> rmat <u>T</u> oo	ols <u>D</u> ata <u>W</u>	indow <u>H</u> elp					
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3	0.1472	2.27	2.602	184.75	0.0)500	0.0298	0.1726	
4	0.1898	2.43	3.793	269.30	0.1	1002	0.0549	0.2343	
5	0.2447	2.53	4.808	341.40	0.2	2003	0.1050	0.3240	
6									
	HNO3	aenn n		260					
7	(molarity)=	0.0050		2.00					
	Ascorbic acid,	6 76E J		2.55	D	ebye-	Huckel	/•	
8	Ka1=	0.102-03		2.50	-	-			
9				2.45	-				
10	Slope=	2.78		2 240			/		
11	Intercept=	1.87		5 235					
12	k0=	73.90		<u>e</u> 2.00					
13	R^2=	0.9809		2.30		-			
14				2.25		/		/ 1 0606	
15				2.20		·	<u>y = 2.(835)</u>	(+1.0000)	
16				2.15	•		$R^2 = 0$.9809	
17				2 10					
18				2.10		~	· · ·	· ·	_
19				C	.10	0.1		.0 0.2	৽∟
20							ro.a(ro.a+	-1)	

B. Non-linear statistics²

The non-linear statistics is performed with the SolvStat macro written by Prof. Billo. You have to reload the macro each time whenever you want to perform the non-linear statistics.



This will launch the Excel loaded with the macro SolvStat under the Tools button:

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<u>s</u>) (Eile Edit ⊻iew Inse	rt F <u>o</u> rmat	<u>T</u> oo	ls [<u>)</u> ata <u>W</u> indow <u>H</u>	<u>l</u> elp	0		
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	H3 🗸	fx		Soly	<u>e</u> r				
	А	В		Solv	er Statistics		D	Е	
1	A0=	0.507		<u>M</u> ac	ro I		time	A(calc)	
2	Af=	0.263	31		0.50723		0	0.50723	
3	kobs=	2.806	0		0.48962		60	0.48931	
4	epsilon=	1100)		0.4733		120	0.47325	
5					0.45877		180	0.45879	
6					0.44608		240	0.44571	
7					0.10010		200	0.40000	

 $^{^{2}}$ This package is available from the CD accompanying Prof. Bilo's book (see footnote 1). It is installed on the Dell Optiplex.

For each **kobs** there are <u>four quick steps</u> to calculate the standard deviation.

2. In Step 1 select the range of the experimental absorbances. Is very expeditious to highlight with the mouse the column containing the experimental Absorbances. The window is filled in automatically.

0.50723 0 0.50723 0.00E+00 0.48962 60 0.48931 9.47E-08 0.4733 SOLVER STATISTICS - STEP 1 OF 4 ? > 0.45877 Select range of known y's. 0.44608 (Range must be a single row or column.) 0.42337	absorbance (420 nm)	time	A(calc)	Diff(A- Acalc)^2	
0.48962 60 0.48931 9.47E-08 0.4733 SOLVER STATISTICS - STEP 1 OF 4 ?>> 0.45877 Select range of known y's. Select range of known y's. 0.43346 (Range must be a single row or column.) 0.42337 (Range must be a single row or column.) 0.4129 (Range must be a single row or column.) 0.4129 (C\$2:\$C\$22 0.39626 (OK Cancel) 0.38828 OK Cancel 0.37381 720 0.37419 0.36277 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.50723	0	0.50723	0.00E+00	
0.4733 SOLVER STATISTICS - STEP 1 OF 4 ? 0.45877 Select range of known y's. 0.44608 (Range must be a single row or column.) 0.42337 (Range must be a single row or column.) 0.4129 (\$<\$2:\$C\$22 0.40375 OK 0.39626 OK 0.38828 OK 0.37381 720 0.36777 780 0.36227 840 0.36227 840 0.36227 0.2620	0.48962	60	0.48931	9.47E-08	
0.45877 Select range of known y's. 0.44608 (Range must be a single row or column.) 0.43346 (************************************	0.4733	SOLVER	STATISTICS -	STEP 1 OF 4	? ×
0.44608 (Range must be a single row or column.) 0.43346 (Range must be a single row or column.) 0.42337 (Range must be a single row or column.) 0.4129 (************************************	0.45877	Select rand	qe of known y's.		
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0.42337	0.43346	(Range mu	ust be a single ro	w or column.)	
0.4129 ↓ 0.40375 ↓ 0.39626 ○K 0.38828 ○K 0.38049 660 0.38080 9.62E-08 0.37381 720 0.37419 1.48E-07 0.36277 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.42337				
0.40375 IPC\$2:\$C\$22 0.39626 OK Cancel 0.38828 0K Cancel 0.38049 660 0.38080 9.62E-08 0.37381 720 0.37419 1.48E-07 0.36277 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.4129	toto.tot			
0.39626 OK Cancel 0.38828 0K Cancel 0.38049 660 0.38080 9.62E-08 0.37381 720 0.37419 1.48E-07 0.36777 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.40375	[\$C\$2:\$C\$	22		
0.38828 Cancel 0.38049 660 0.38080 9.62E-08 0.37381 720 0.37419 1.48E-07 0.36777 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.39626				
0.38049 660 0.38080 9.62E-08 0.37381 720 0.37419 1.48E-07 0.36777 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.38828				incei
0.37381 720 0.37419 1.48E-07 0.36777 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.38049	660	0.38080	9.62E-08	
0.36777 780 0.36806 8.56E-08 0.36227 840 0.36236 7.87E-09	0.37381	720	0.37419	1.48E-07	
0.36227 840 0.36236 7.87E-09	0.36777	780	0.36806	8.56E-08	
	0.36227	840	0.36236	7.87E-09	
0.3568 900 0.35704 5.95E-08	0.3568	900	0.35704	5.95E-08	
0.35213 960 0.35208 2.13E-09	0.35213	960	0.35208	2.13E-09	
0.34729 1020 0.34745 2.48E-08	0.34729	1020	0.34745	2.48E-08	
0.34312 1080 0.34311 1.51E-10	0.34312	1080	0.34311	1.51E-10	
0.33925 1140 0.33904 4.41E-08	0.33925	1140	0.33904	4.41E-08	
0.33557 1200 0.33522 1.21E-07	0.33557	1200	0.33522	1.21E-07	

3. In Step 2 select the range of the calculated absorbances.

	В	С	D	E
	0.50723	absorbance (420 nm)	time	A(calc)
	0.2631	0.50723	0	0.50723
	2.8060	0.48962	60	0.48931
= s	OLVER STATISTIC	S - STEP 2 OF 4	? ×	0.47325
	oloct range of calculate	ad ula		0.45879
	electralige of calculate	su y s.		0.44571
(Range must be a single	row or column.)		0.43383
				0.42300
				0.41309
	\$E\$2:\$E\$22			0.40400
_			1	0.39564
_		OK	Cancel	0.38793
		0.38049	000	0.38080
		0.37381	720	0.37419
		0.36777	780	0.36806
		0.36227	840	0.36236
		0.3568	900	0.35704
		0.35213	960	0.35208
		0.34729	1020	0.34745
		0.34312	1080	0.34311
		0.33925	1140	0.33904
		0.33557	1200	0.33522

4. In Step 3 select the range of the parameters **kobs** and **Af**, respectively.

	А	В	С	D	E	F
	۵0=	0 50723	absorbance	time	A(calc)	Diff(A-
1		0.00720	SOLVER STATIS	TICS - STE	P 3 OF 4	?≍alc)^
2	Af=	0.2631	Select cells containi	na least-sauar	es coefficients	0.00E
3	kobs=	2.8060	obtained by using th	ne Solver.	00 00011101100	9.471
4	epsilon=	1100	(Cells can be non-au	djacent, in wh	ich case hold dov	wn 2.071
5			between selections.	selecting, or e)	nter a comma	5.18
6				,		1.371
7			\$B\$2:\$B\$3			1.35
8					_	1.40
9				OK	Canc	^{el} 3.60I
10			0.40375	480	0.40400	6.32
11			0.39626	540	0.39564	3.84

5. In Step 4 is self explanatory.

A0=	0.50723	absorbance (420 nm)	time	A(calc)	Diff(A- Acalc)^2
Af=	0.2631	0.50723	0	0.50723	0.00E+00
kobs=	2.8060	0.48962	60	0.48931	9.47E-08
epsilon=	1100	0.4733	120	0.47325	2.07E-09
		0.45877	180	0.45879	5.18E-10
		SOLVER STAT	FISTICS - S	TEP 4 OF 4	?≍β7E-07
		Select a 3-row x	: 2 column are	a	35E-07
		for results.			40E-07
		1			50E-08
		1			32E-08
					B4E-07
		[\$A\$8:\$B\$10			23E-07
					52E-08
					48E-07
		0.36777	780	0.36806	8.56E-08
		0.36227	840	0.36236	7.87E-09

By clicking on **OK**, SolvStat prints in the selected area the numbers:

A0=	0.50723	absorbance (420 nm)	time	A(calc)	Ļ
Af=	0.2631	0.50723	0	0.50723	
kobs=	2.8060	0.48962	60	0.48931	
epsilon=	1100	0.4733	120	0.47325	
		0.45877	180	0.45879	
		0.44608	240	0.44571	
		0.43346	300	0.43383	
0.263133066	2.80603402	0.42337	360	0.42300	
0.000925759	0.017169362	0.4129	420	0.41309	
0.999968406	0.000299472	0.40375	480	0.40400	
		0.39626	540	0.39564	
		0.38828	600	0.38793	
		0.38049	660	0.38080	

First row contains the parameters **Af** and kobs.

Second row contains the standard deviation of the respective parameters. The third row contains R^2 and SE(y).

After some editing the table looks like this:

А	В	С
A0-	0 50723	absorbance
A0-	0.50725	(420 nm)
Af=	0.2631	0.50723
kobs=	2.8060	0.48962
epsilon=	1100	0.4733
		0.45877
		0.44608
Af=	kobs	0.43346
0.2631	2.8060	0.42337
Std. Dev=	Std. Dev.=	0.4129
0.0009	0.0172	0.40375
R^2=	SE(y)=	0.39626
0.99997	0.00030	0.38828
		0.38049
		0 37381

6. After running SolvStat for each kobs, the four calculated kobs and the associated standard deviation are collected on a separate worksheet, which you must append to your written Report:

Microsoft Excel - Kinetics.xls			
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	D6	▼ f _x	
	A	В	С
1	Kobs	Std.dev	
2	2.2329	0.0090	
3	2.8060	0.0172	
4	4.0901	0.0232	
5	5.1851	0.0492	
6			
7			