APPENDIX#3:

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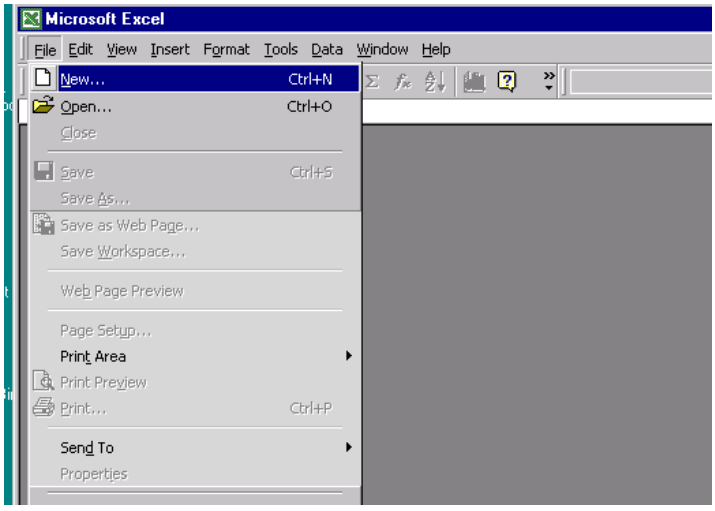
Non-linear Curve fitting with Microsoft Excel Solver and Non-Linear Regression Statistics[1]

A. CALCULATION OF K_{OBS}, K_{REAL} AND DEBYE-HÜCKEL 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

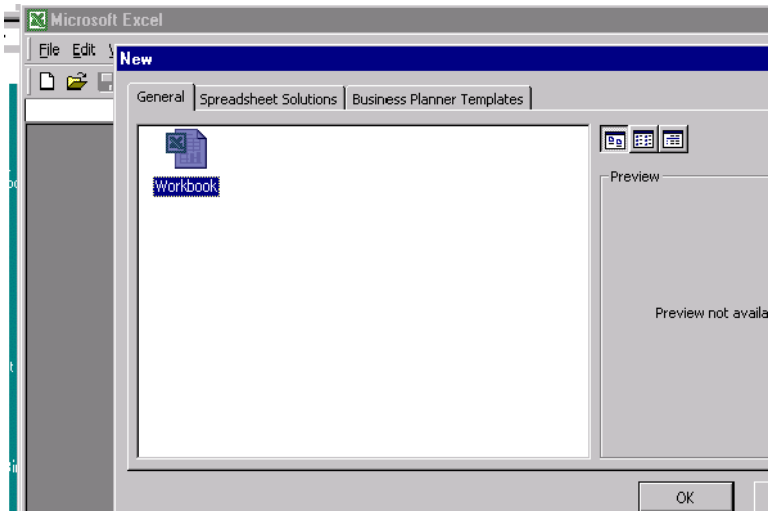
A. Calculation of k_{obs}, k_{real} and Debye-Hückel plot.

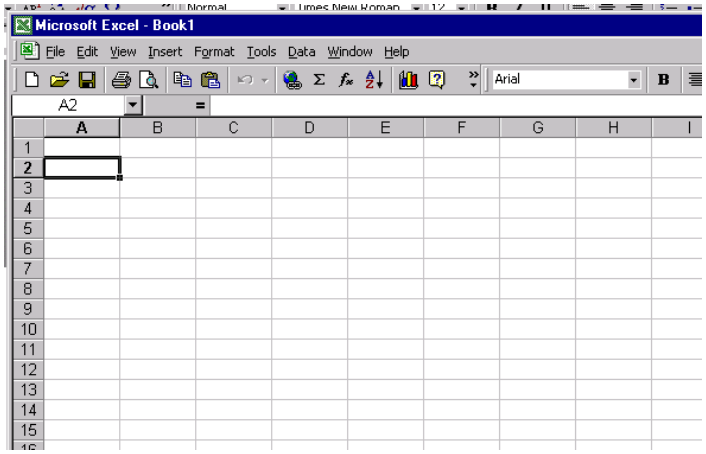
A1. Kinetics: calculation of k_{obs} and k_{real}.

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

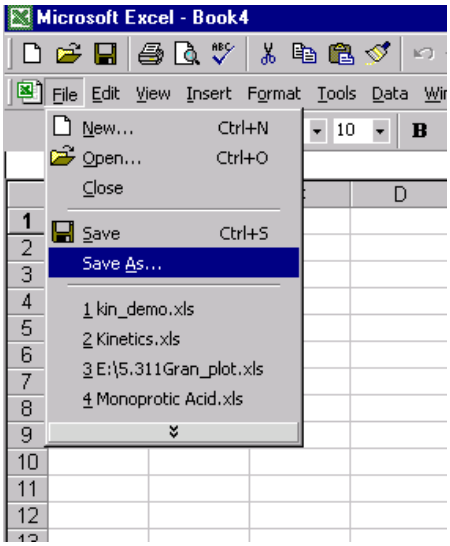


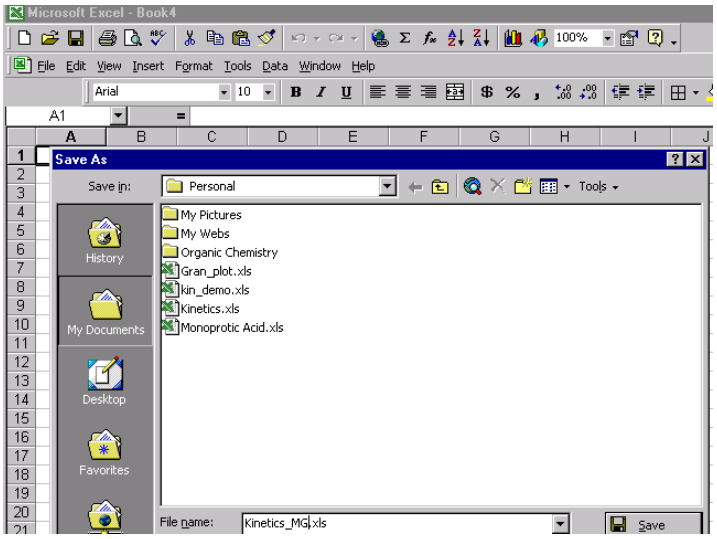
[1] E. J. Billo "*Excel® for Chemists*", 2nd ed., Wiley: New York, 2001, Chapiter 12. For questions you can contact Prof. Billo (Dept. Chem., Boston College, Chestnut Hill, MA): joseph.billo@bc.edu; see also: http://chemserv.bc.edu/faculty/billo.html





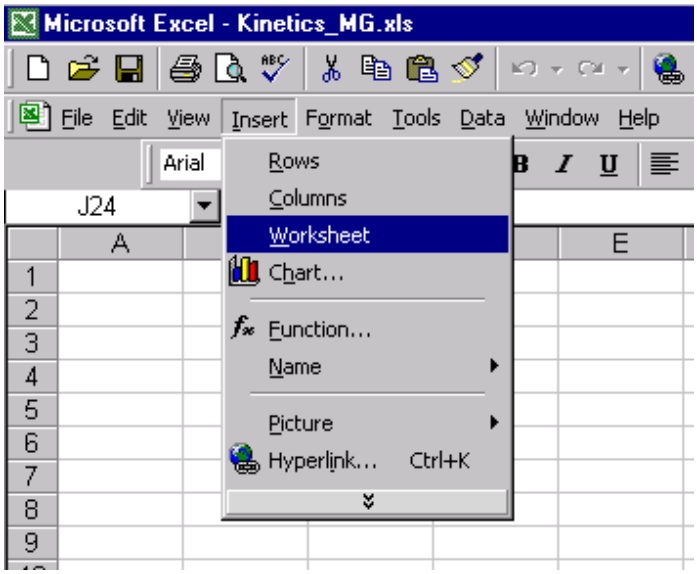
2. From **File**, **Save as…** the workbook. My preference for file name is **Kinetics_MG** (MG are my initials) and it is saved in the **Personal** folder.



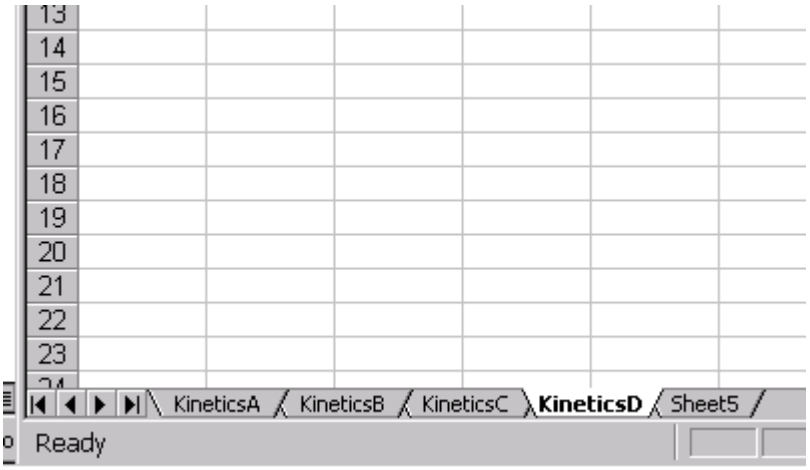


3. **Five sheets are necessary in your workbook**. Four are for Kinetics data. The fifth is for Debye_Huckel calculation. **You have to append these five sheets to your written or Oral report.**

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 $NaNO_3$), **KineticsB** (for the 0.05M $NaNO_3$), **KineticsC**, (for the 0.1M $NaNO_3$) and **KineticsD** (for the 0.2M $NaNO_3$).



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		

KineticsA KineticsB KineticsC KineticsD 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:

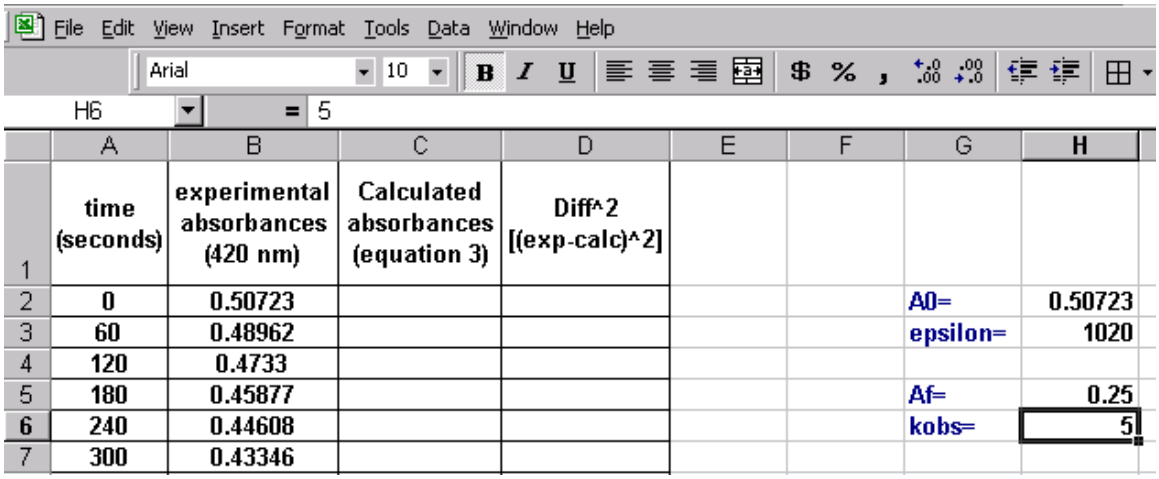
$$A = A_f \frac{1}{1 - \frac{A_0 - A_f}{A_0} \exp(-c_f k_{obs} t)} \quad (3)$$

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 H_2Asc 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.**

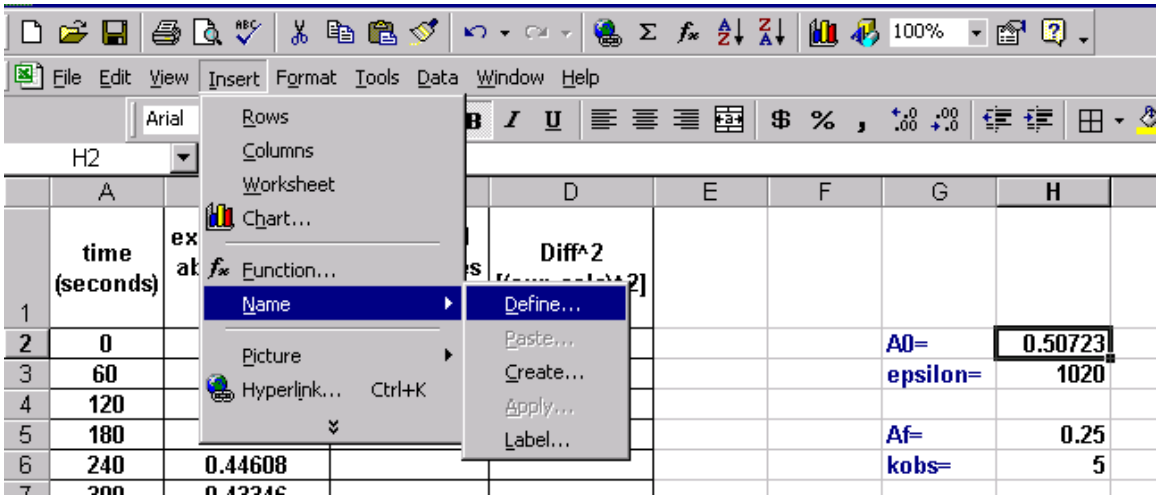
7. In order to be automatically plugged into the kinetic equation, the cells containing the values of **A0, epsilon, Af, kobs must be given a name** (this is an Excel requirement).

- 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 ε = 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.

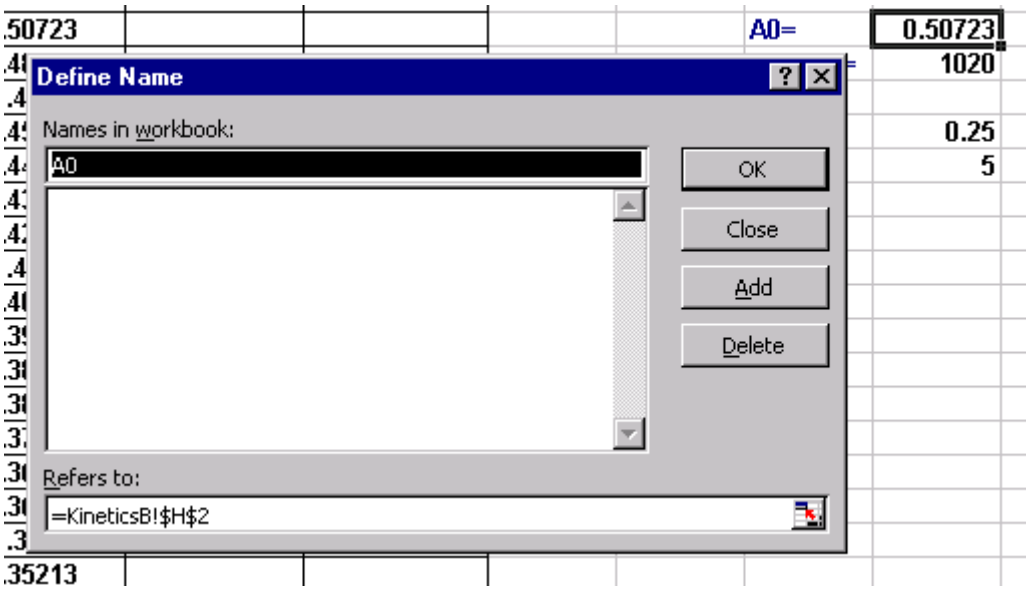


	A	B	C	D	E	F	G	H
1	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]				
2	0	0.50723					A0=	0.50723
3	60	0.48962					epsilon=	1020
4	120	0.4733						
5	180	0.45877					Af=	0.25
6	240	0.44608					kobs=	5
7	300	0.43346						

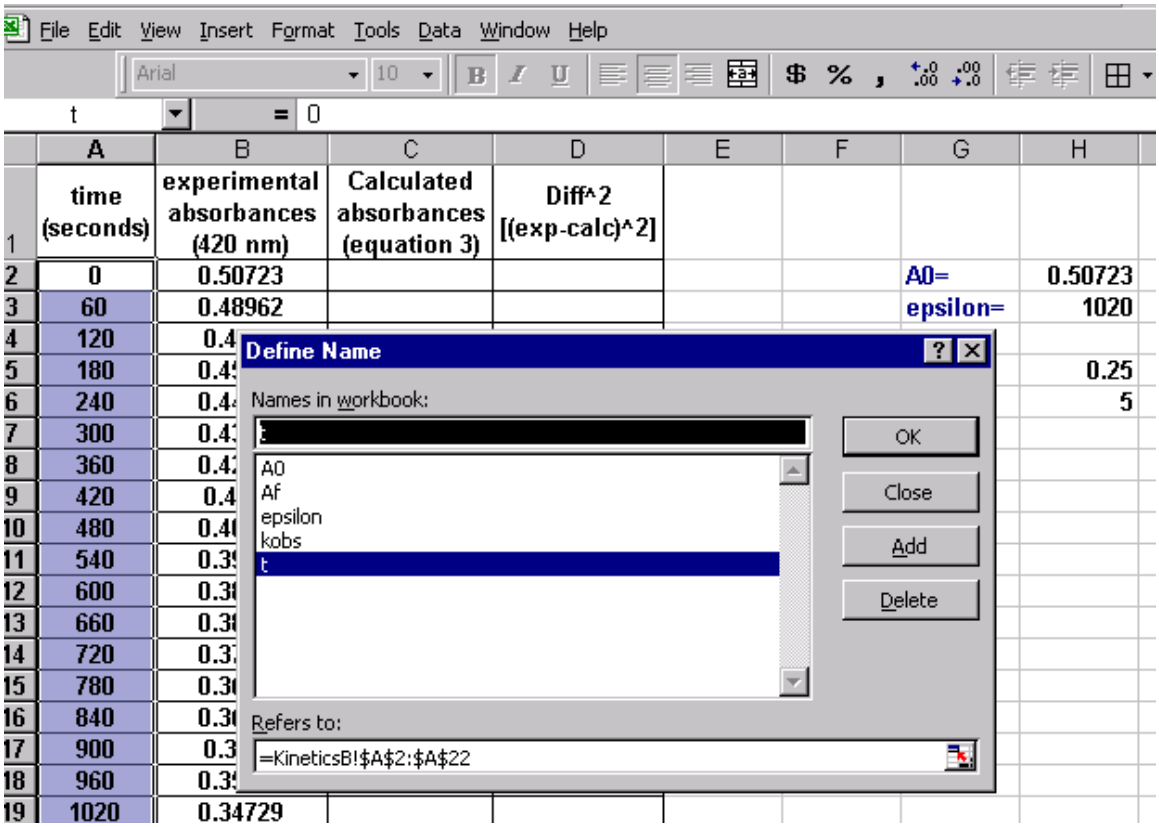
In order to be automatically inserted in equation **3**, **A0, epsilon, Af and kobs** must be assigned a name. For example to name **A0**, first click on cell H2. Than click on **Insert**, **Name**, **Define**:



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:

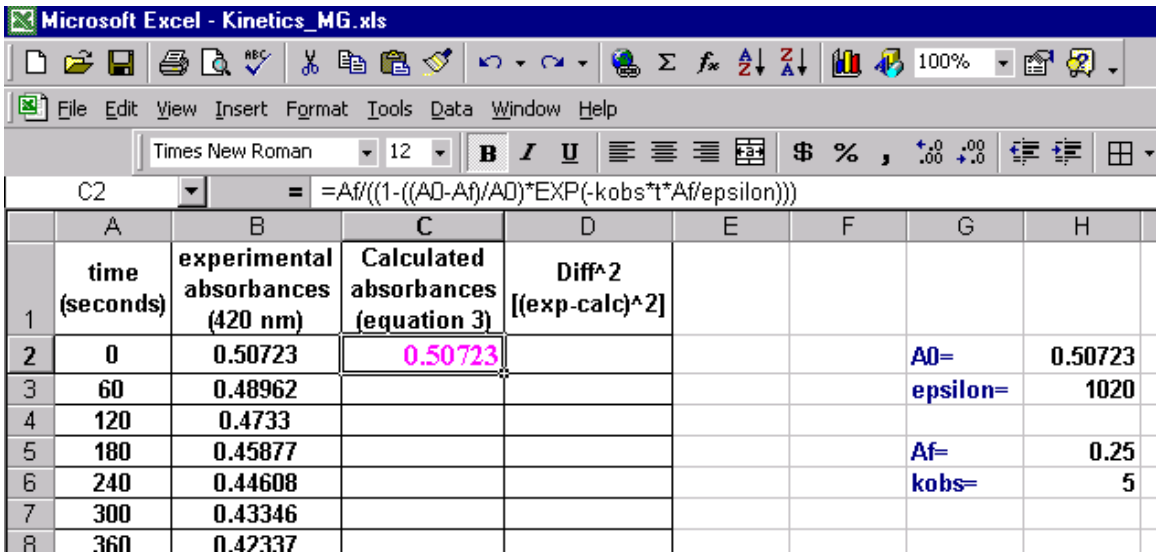


8. **Solver** optimizes the curve fitting in two steps:

- 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**.



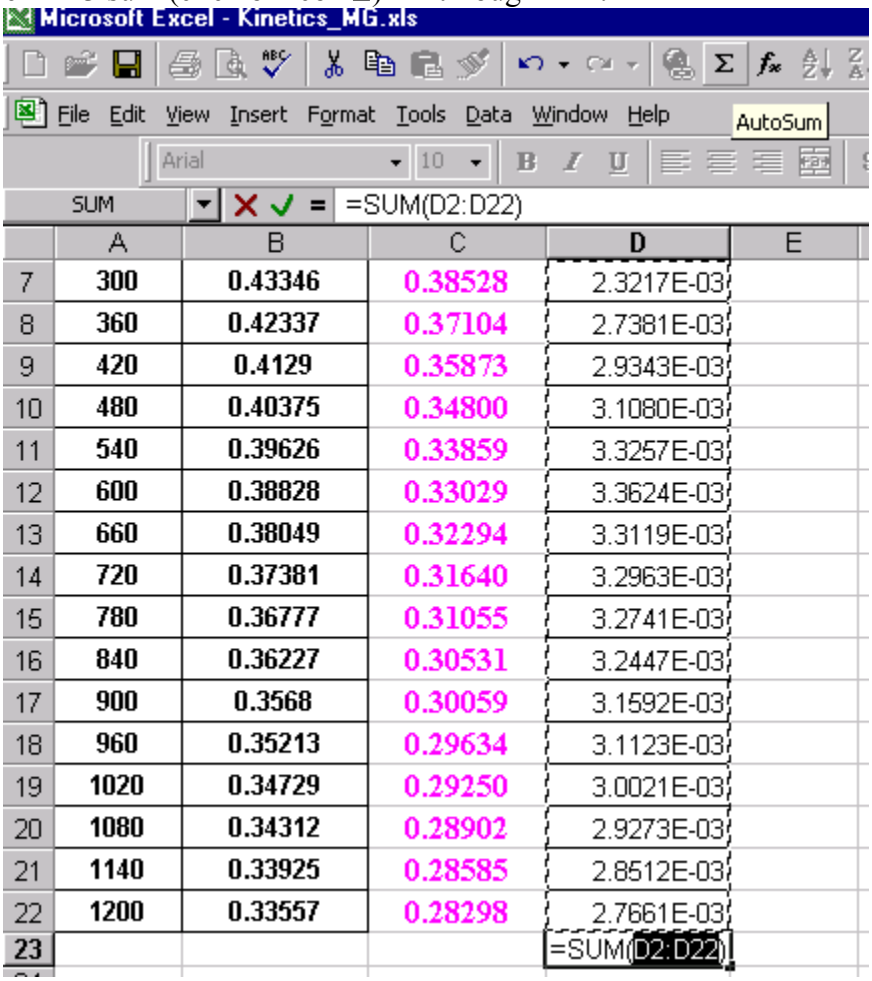
	A	B	C	D	E	F	G	H
1	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]				
2	0	0.50723	0.50723				A0=	0.50723
3	60	0.48962					epsilon=	1020
4	120	0.4733						
5	180	0.45877					Af=	0.25
6	240	0.44608					kobs=	5
7	300	0.43346						
8	360	0.42337						

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	B	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	
19	1020	0.34729	0.29250	

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

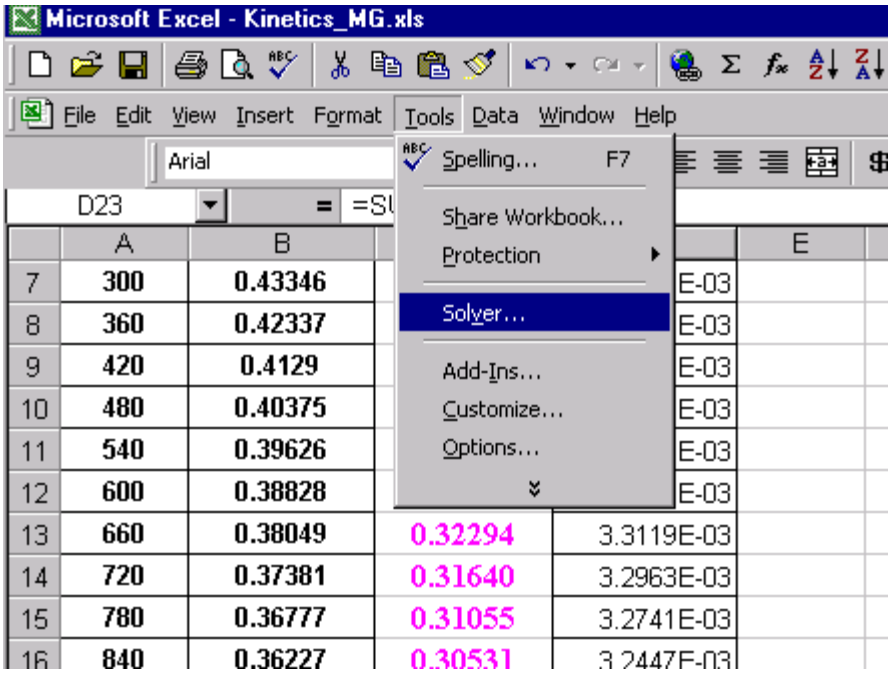
9. Type in cell D2=(B2-C2)^2. Press **Enter** key.
10. Click on cell D2. Drag all the way down to cell D22, as it was described for calculated absorbances.
11. In cell D23 sum (click on icon **Σ**) D2 through D22.



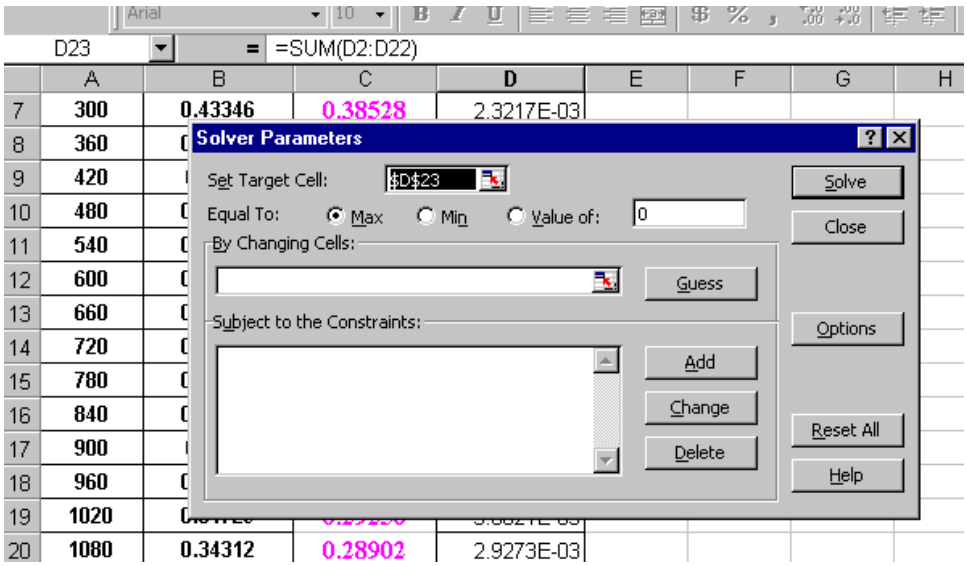
	A	B	C	D	E
7	300	0.43346	0.38528	2.3217E-03	
8	360	0.42337	0.37104	2.7381E-03	
9	420	0.4129	0.35873	2.9343E-03	
10	480	0.40375	0.34800	3.1080E-03	
11	540	0.39626	0.33859	3.3257E-03	
12	600	0.38828	0.33029	3.3624E-03	
13	660	0.38049	0.32294	3.3119E-03	
14	720	0.37381	0.31640	3.2963E-03	
15	780	0.36777	0.31055	3.2741E-03	
16	840	0.36227	0.30531	3.2447E-03	
17	900	0.3568	0.30059	3.1592E-03	
18	960	0.35213	0.29634	3.1123E-03	
19	1020	0.34729	0.29250	3.0021E-03	
20	1080	0.34312	0.28902	2.9273E-03	
21	1140	0.33925	0.28585	2.8512E-03	
22	1200	0.33557	0.28298	2.7661E-03	
23				=SUM(D2:D22)	

Than press **Enter** key.

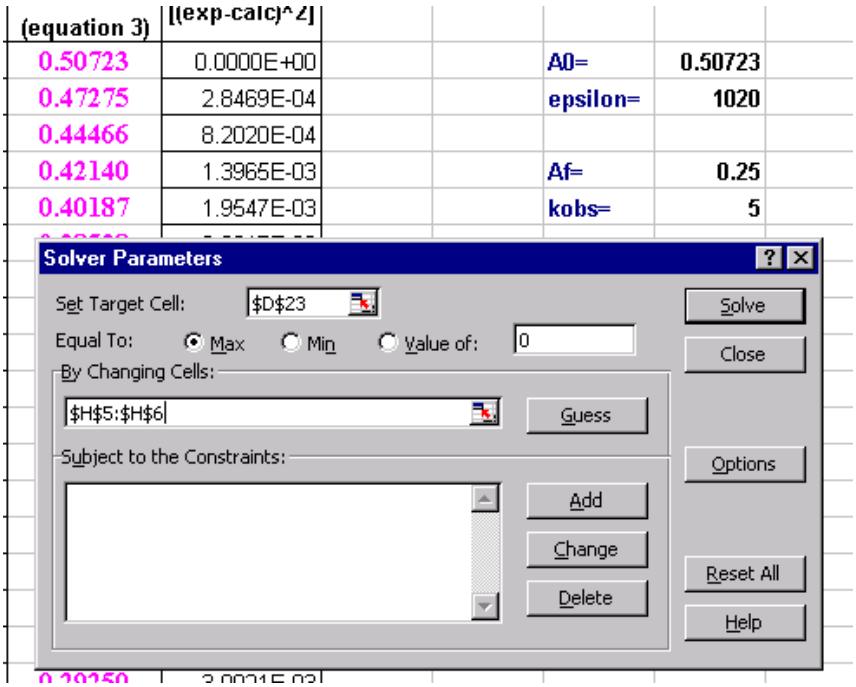
12. Click on cell D23. Click **Tools** and than **Solver…**



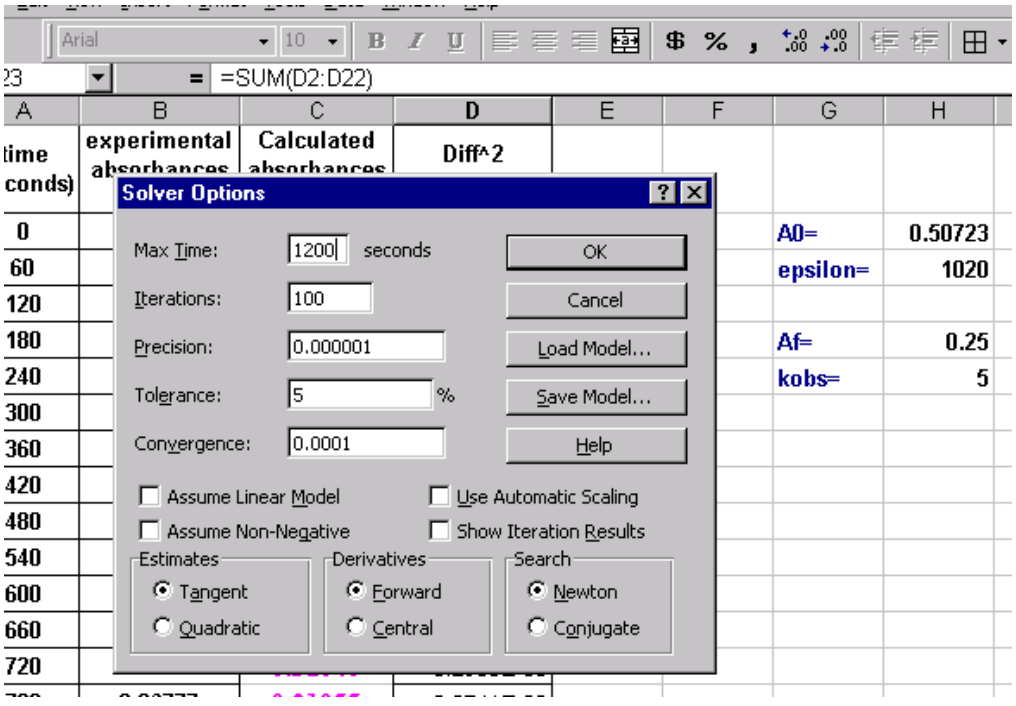
The **Solver Parameters** window pops-up. The target cell is **D23**.



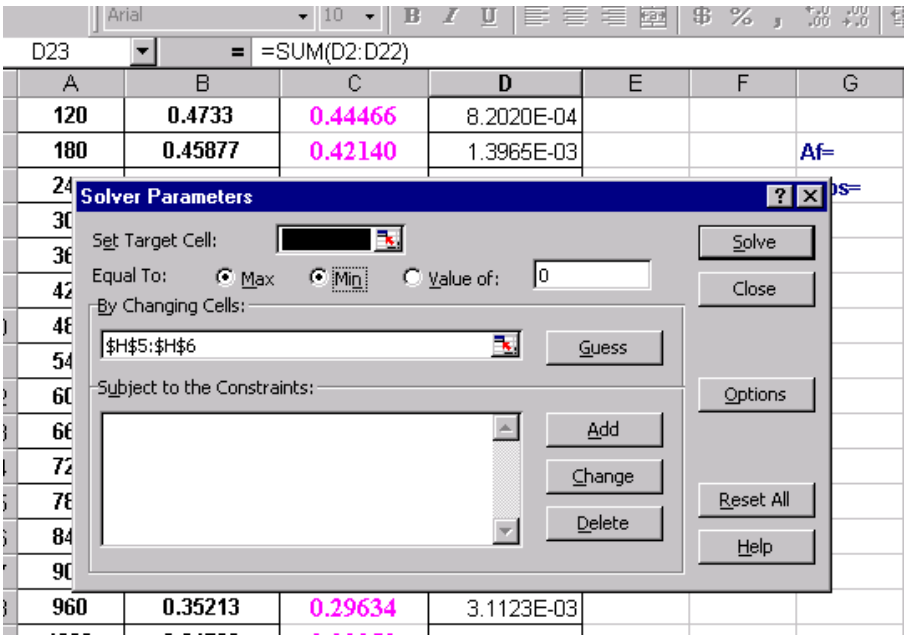
Type into **By Changing** the cells: H5 and H6 (that is $H$5 and $H$6).



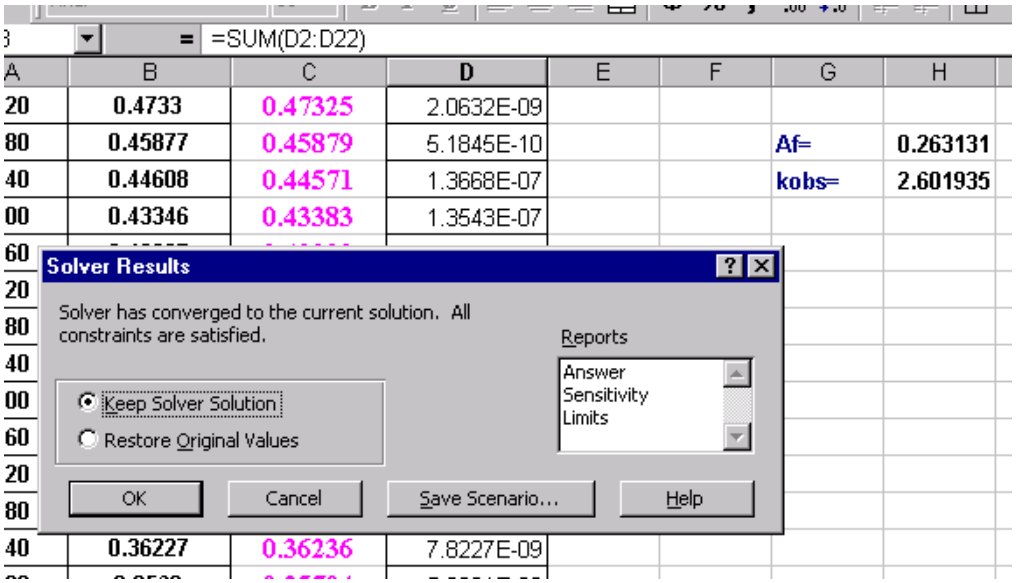
On **Solver Parameters** click on **Options.** Change **Max Time** to **1200 seconds** (kinetics run time). Click **OK**.



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



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.



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

	A	B	C	D	E	F
1	**Microsoft Excel 9.0 Answer Report**					
2	**Worksheet: [Kinetics_MG.xls]KineticsB**					
3	**Report Created: 12/28/01 5:39:24 PM**					
4						
5						
6	Target Cell (Min)					
7		**Cell**	**Name**	**Original Value**	**Final Value**	
8		$D$23	Diff^2	[(exp-calc)^2]	5.3191E-02	1.7040E-06
9						
10						
11	Adjustable Cells					
12		**Cell**	**Name**	**Original Value**	**Final Value**	
13		$H$5	Af		0.25	0.263131158
14		$H$6	kobs		5	2.601934917
15						
16						
17	Constraints					
18		NONE				

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:

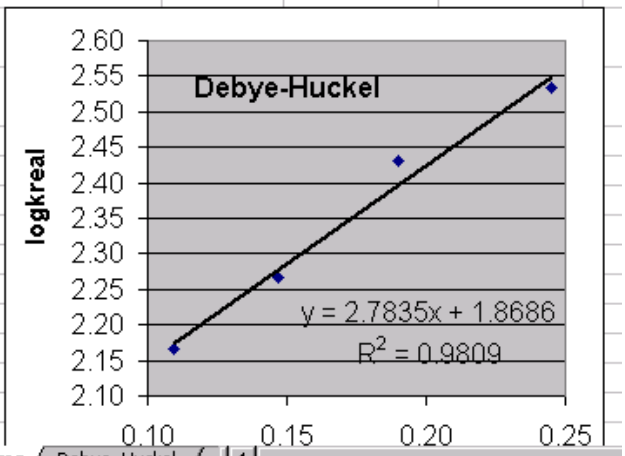
$$\log k_{real} = \log k_0 + 1.02 * Z_1 * Z_2 \frac{I^{1/2}}{1 + I^{1/2}} = \log k_0 + 1.02 * 3 * \frac{I^{1/2}}{1 + I^{1/2}} \quad (6)$$

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

$$k_{real} = k_{obs} \frac{[H^+]}{K_{a1}} \quad (4)$$

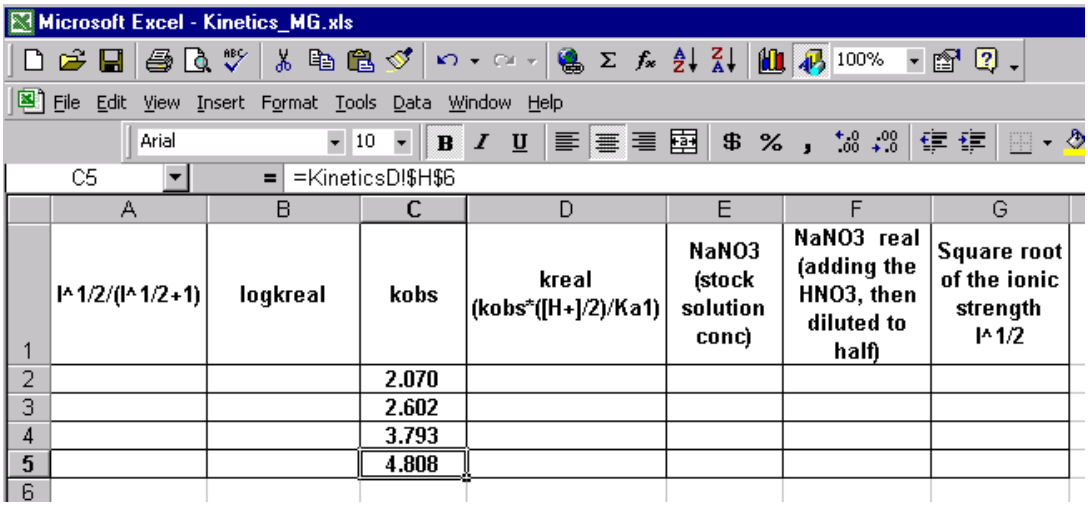
Use the sheet#5 (renamed as **Debye-Hückel**) to compute and draw the linear plot **logkreal** (y axis) versus $I^{0.5}/(I^{0.5}+1)$ (x axis). When fished the contend of the **Debye-Hückel** worksheet will look like:

	A	B	C	D	E	F	G
1	I^1/2/(I^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							
7	HNO3 (molarity)=	0.0096					
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					
14							
15							
16							
17							
18							
19							



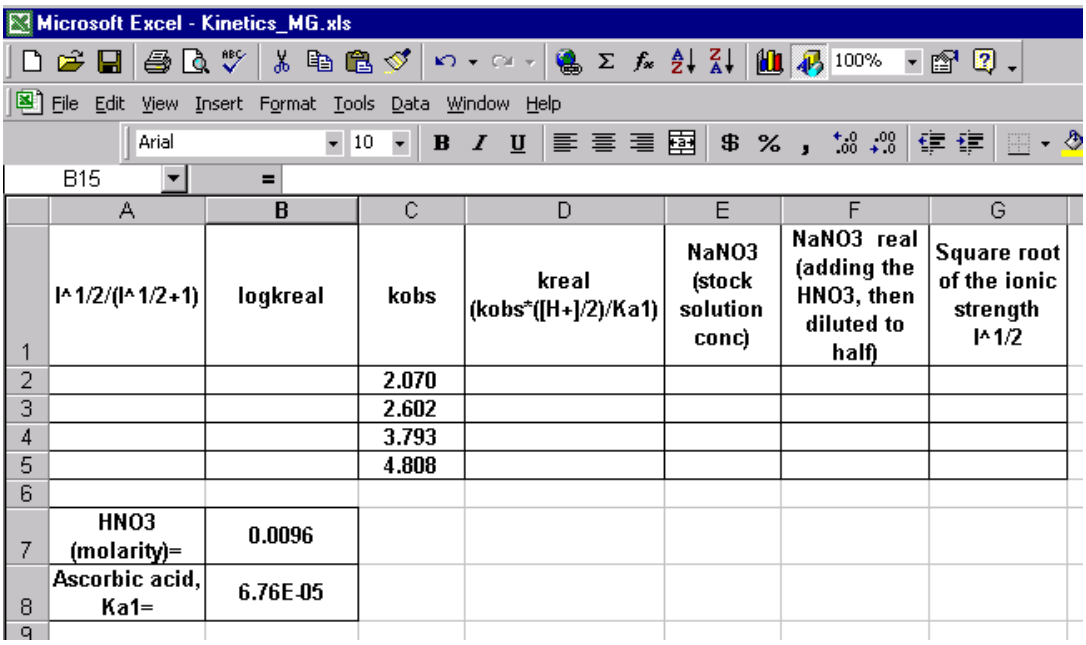
KineticsB | KineticsC | KineticsD | D_H_demo | Debye_Huckel

1. 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).
2. 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**.



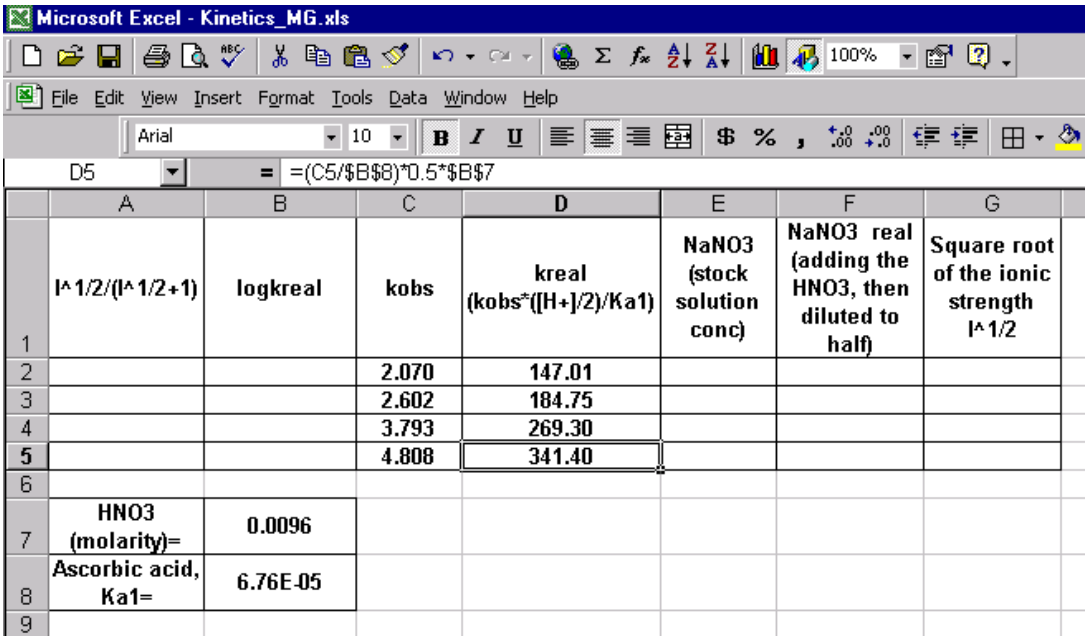
	A	B	C	D	E	F	G
1	I^1/2/(I^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2			2.070				
3			2.602				
4			3.793				
5			4.808				
6							

3. Add on the worksheet information regarding the HNO_3 molarity (cell B7). Type the acidity constant for ascorbic acid ($Ka1=6.76*10^{-5}$) into cell B8.



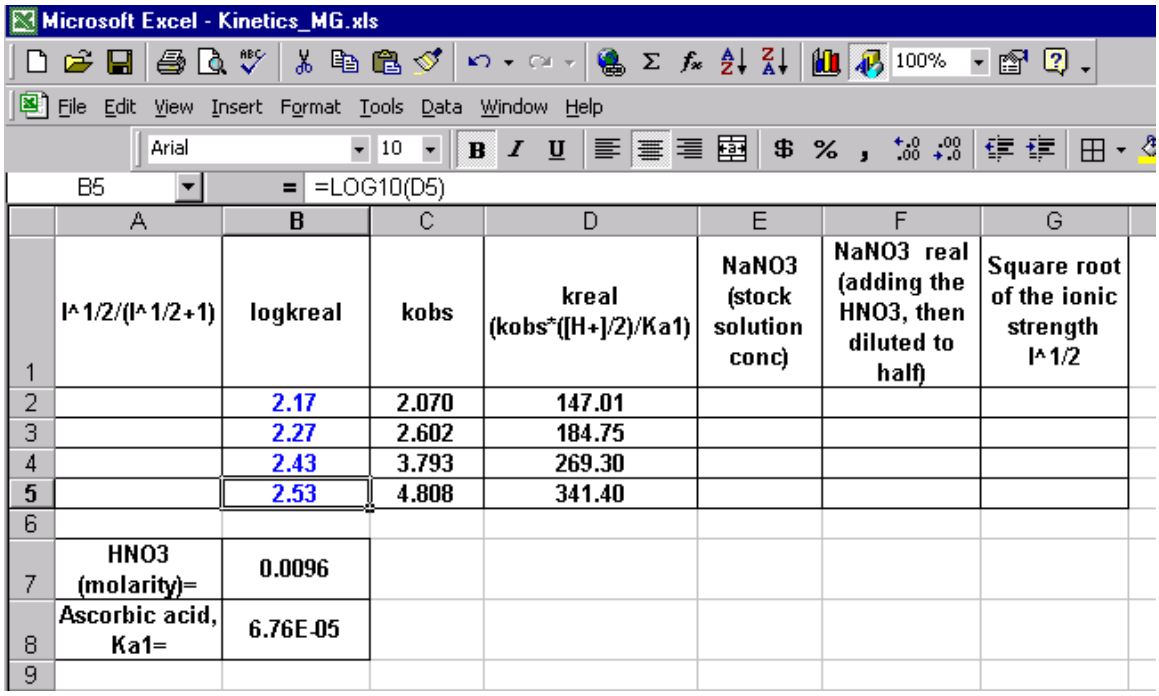
	A	B	C	D	E	F	G
1	I^1/2/(I^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2			2.070				
3			2.602				
4			3.793				
5			4.808				
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, 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 HNO_3 in the UV cuvette is the half diluted HNO_3 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.



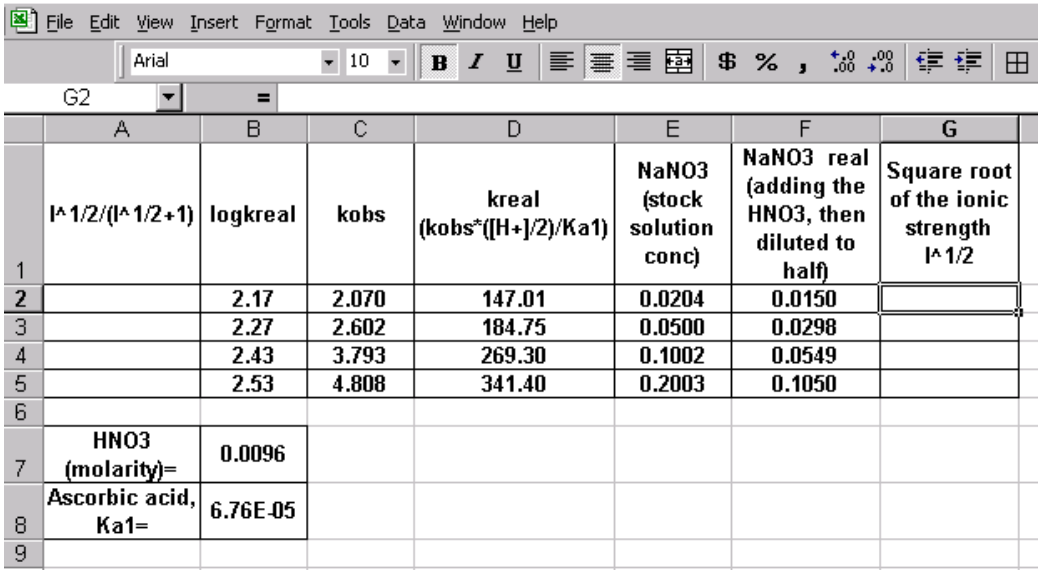
	A	B	C	D	E	F	G
1	I^1/2/(I^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2			2.070	147.01			
3			2.602	184.75			
4			3.793	269.30			
5			4.808	341.40			
6							
7	HNO3 (molarity)=	0.0096					
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:



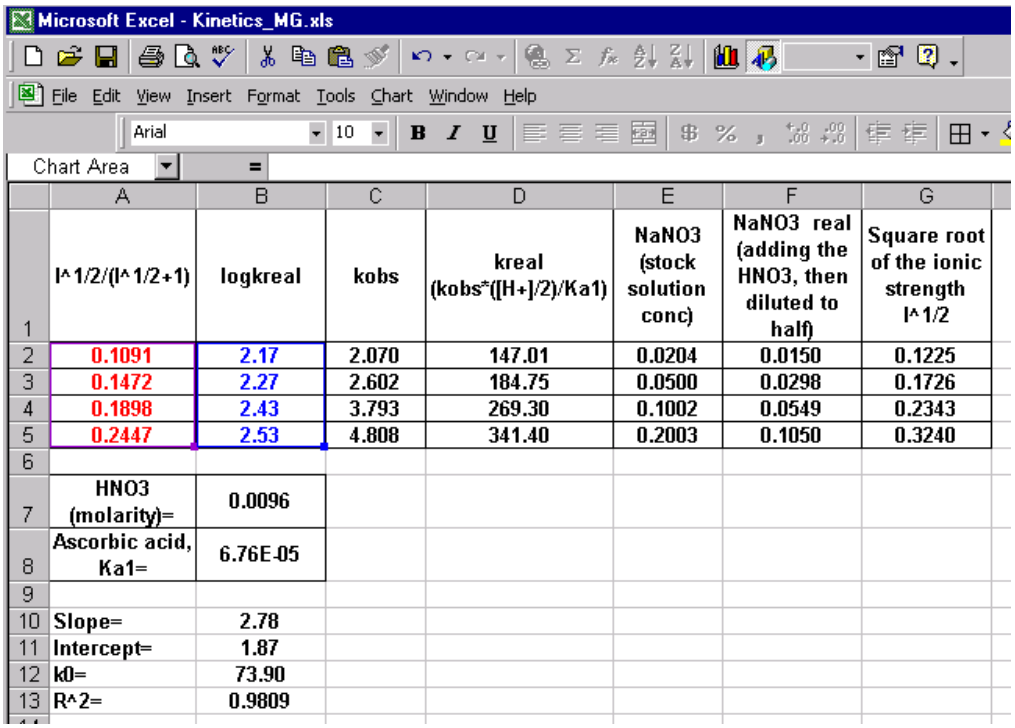
	A	B	C	D	E	F	G
1	I^1/2/(I^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2		2.17	2.070	147.01			
3		2.27	2.602	184.75			
4		2.43	3.793	269.30			
5		2.53	4.808	341.40			
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, Ka1=	6.76E-05					
9							

6. The remaining calculation refers to $\mathbf{I^{0.5}/(I^{0.5}+1)}$ the x-axis variable calculation in column A.
    - First fill in $NaNO_3$ **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**.



	A	B	C	D	E	F	G
1	I^1/2/(I^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	
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							

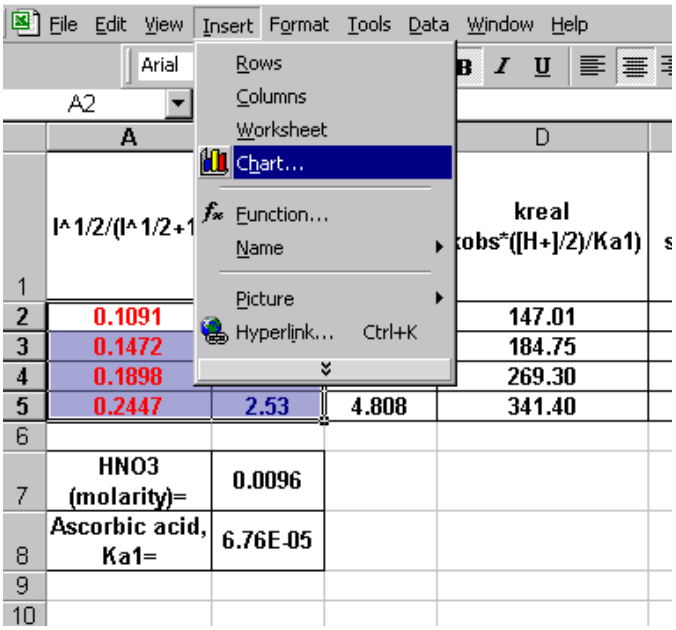
- Third, in cells G2:G5 calculate the square root of value from cell F2:F5. For example, in cell G2 type =SQRT(F2), and press **Enter**.
- Fourth, in cells A2:A5 calculate $\mathbf{I^{0.5}/(I^{0.5}+1)}$. For example, type =G2/(G2+1) in cell A2. Click on the cell. Drag the lower right corner all the way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



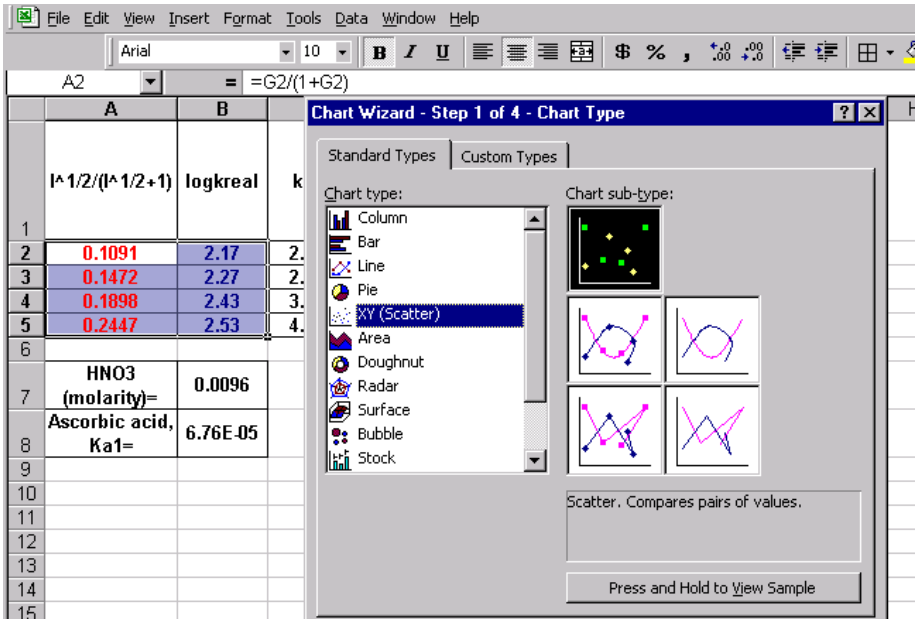
	A	B	C	D	E	F	G
1	I^1/2/(I^1/2+1)	logkreal	kobs	kreal (kobs*([H+]/2)/Ka1)	NaNO3 (stock solution conc)	NaNO3 real (adding the HNO3, then diluted to half)	Square root of the ionic strength I^1/2
2	0.1091	2.17	2.070	147.01	0.0204	0.0150	0.1225
3	0.1472	2.27	2.602	184.75	0.0500	0.0298	0.1726
4	0.1898	2.43	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							
7	HNO3 (molarity)=	0.0096					
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					

A2. The Debye-Hückel plot.

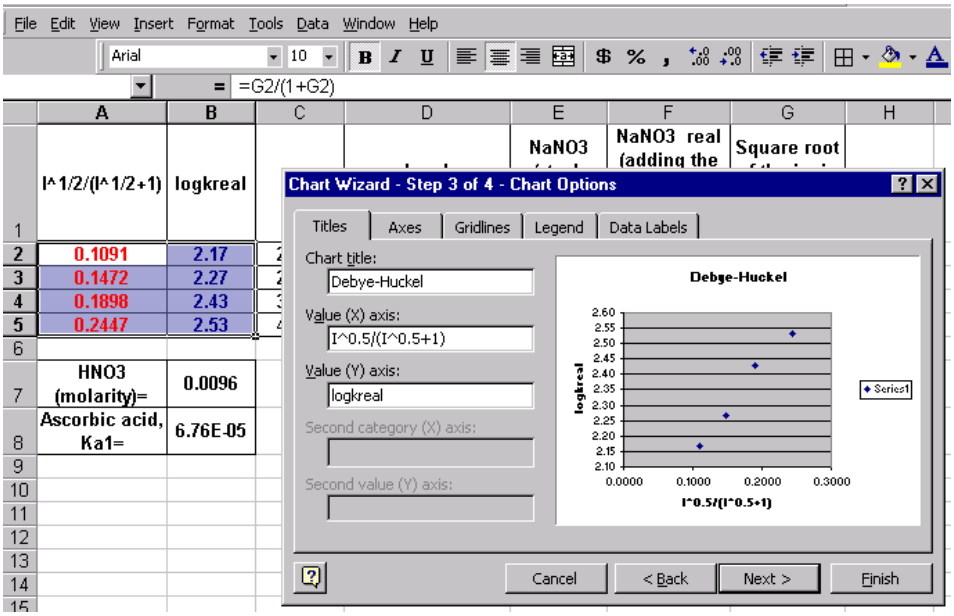
- Highlight columns A2:B5. Click on **Insert** than **Chart…**:



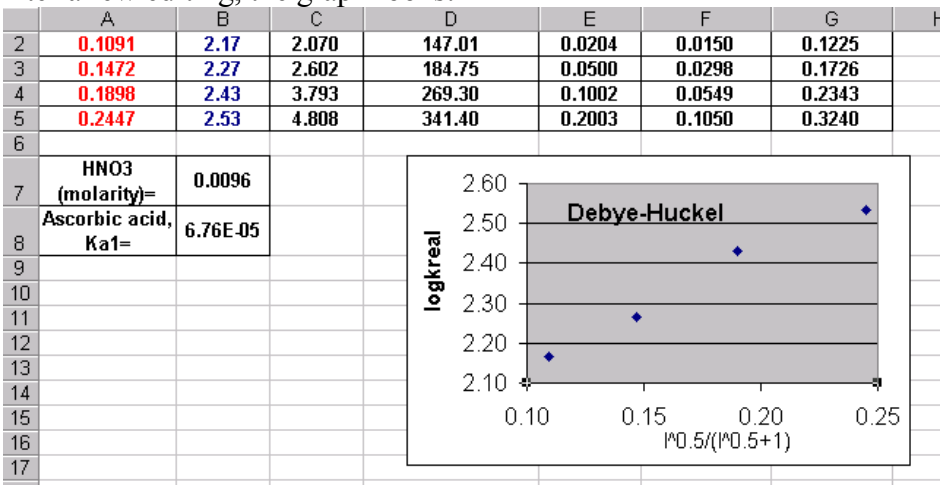
- In the **Chart Wizard** window **Step 1**, choose **Chart type**: **XY(Scatter)**; and the highlighted **Chart sub-type**.



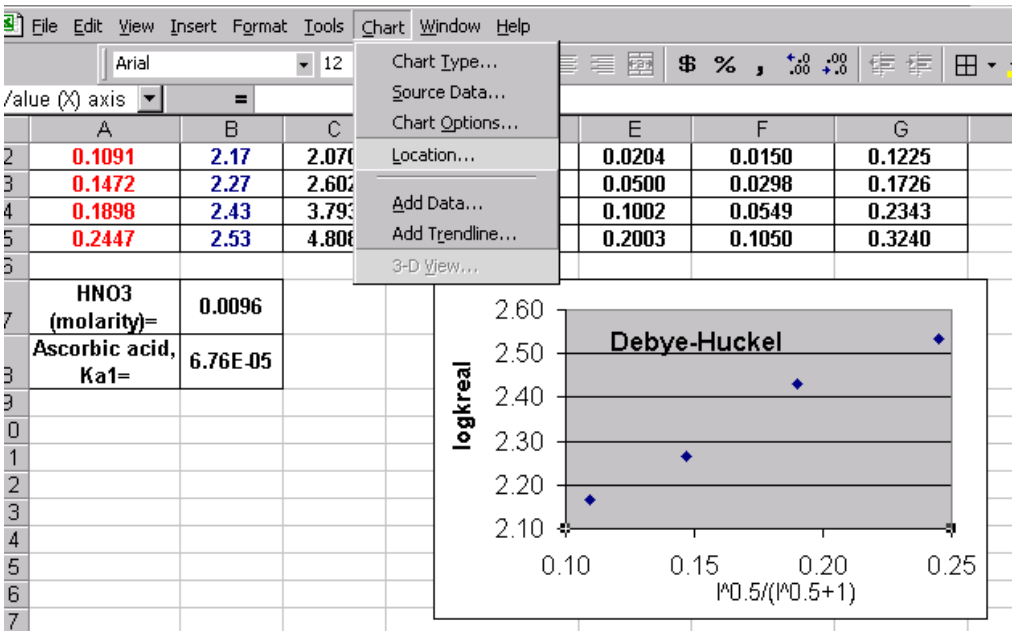
- Click next to steps 2 and 3. Fill in the **chart title, value (X) axis and value (Y) axis** respectively.



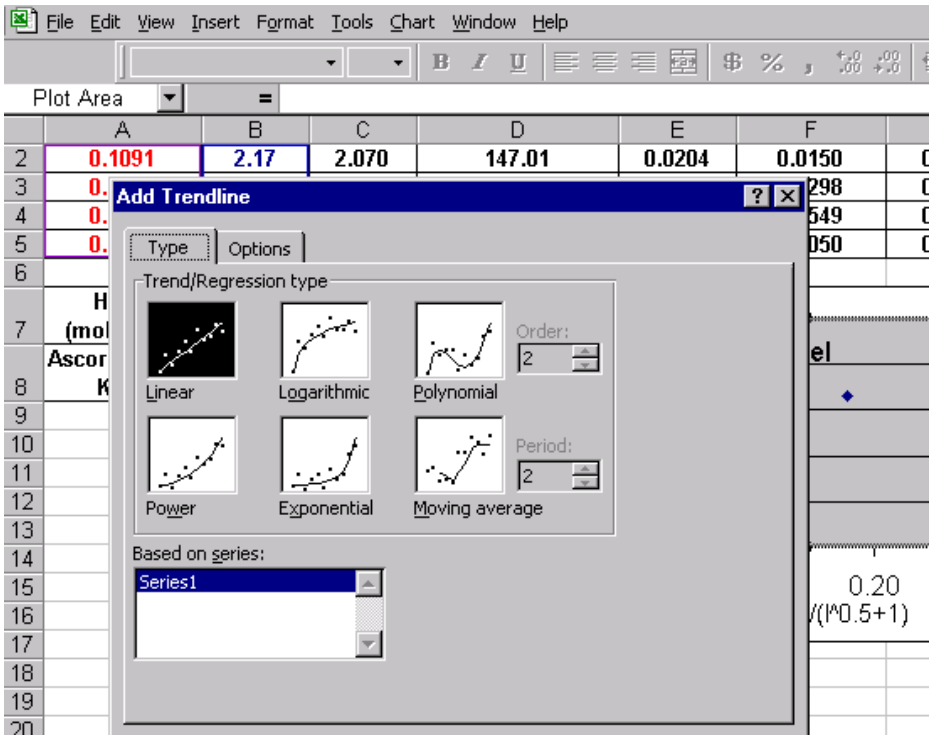
- Click **Next** and than **Finish**.
- After a few editing, the graph looks:



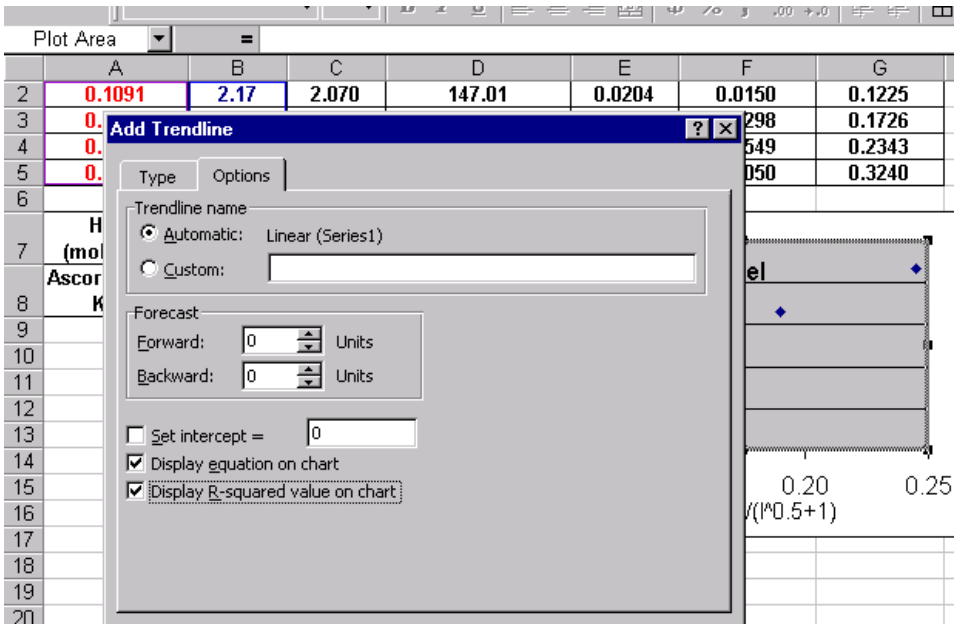
- The least square straight line is added on the graph, by clicking on **Chart**, than **Add trendline..**



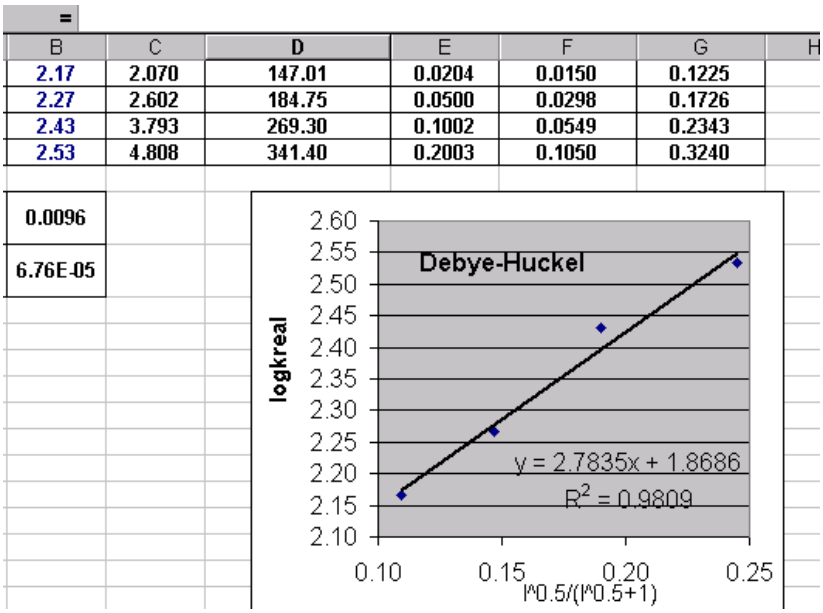
Choose **Type the Trend/Regression type, Linear**.



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

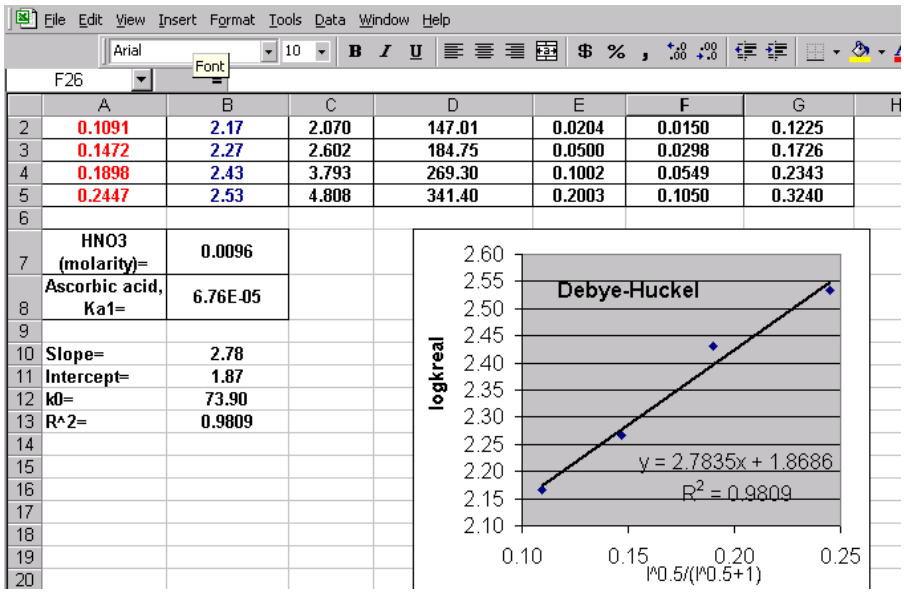


- The least square straight line has the equation: y = 2.7835x + 1.8686 and R^2=0.9809 (satisfactory, however I am confident that 5.311 students will get a better R^2).



7. In order to compute the slope ($1.02*Z_1*Z_2$) 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=**



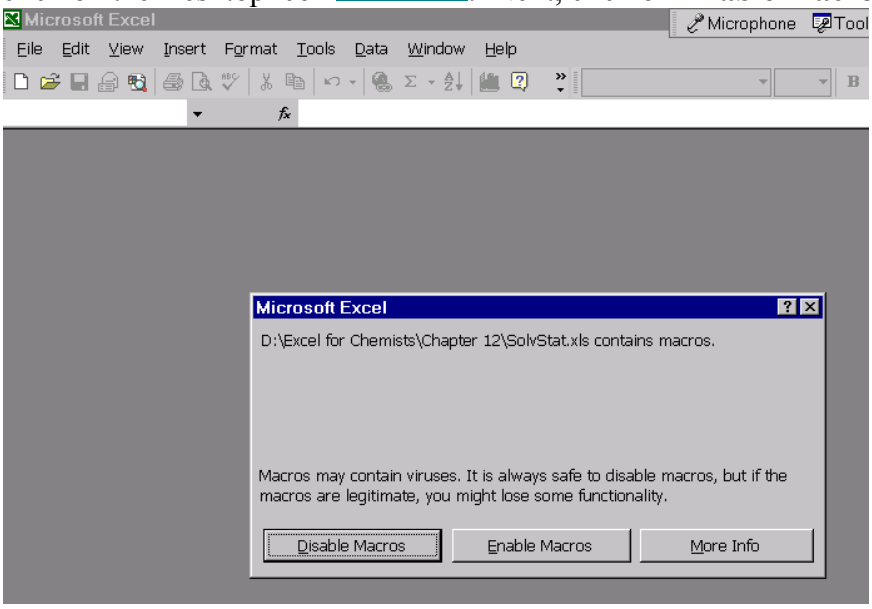
	A	B	C	D	E	F	G
2	0.1091	2.17	2.070	147.01	0.0204	0.0150	0.1225
3	0.1472	2.27	2.602	184.75	0.0500	0.0298	0.1726
4	0.1898	2.43	3.793	269.30	0.1002	0.0549	0.2343
5	0.2447	2.53	4.808	341.40	0.2003	0.1050	0.3240
6							
7	HNO3 (molarity)=	0.0096					
8	Ascorbic acid, Ka1=	6.76E-05					
9							
10	Slope=	2.78					
11	Intercept=	1.87					
12	k0=	73.90					
13	R^2=	0.9809					
14							
15							
16							
17							
18							
19							
20							

B. Non-linear statistics[2]

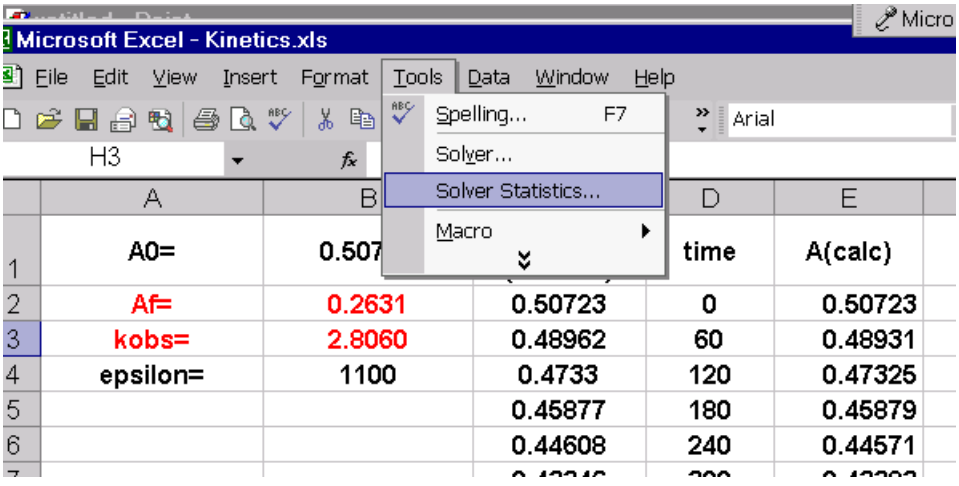
The non-linear statistics is performed with the SolvStat macro written by Prof. Billo. You have to reload the macro each time whenever you want to perform the non-linear statistics.

1. Double click on the Desktop icon 

. Next, click on **Enable Macros** button.



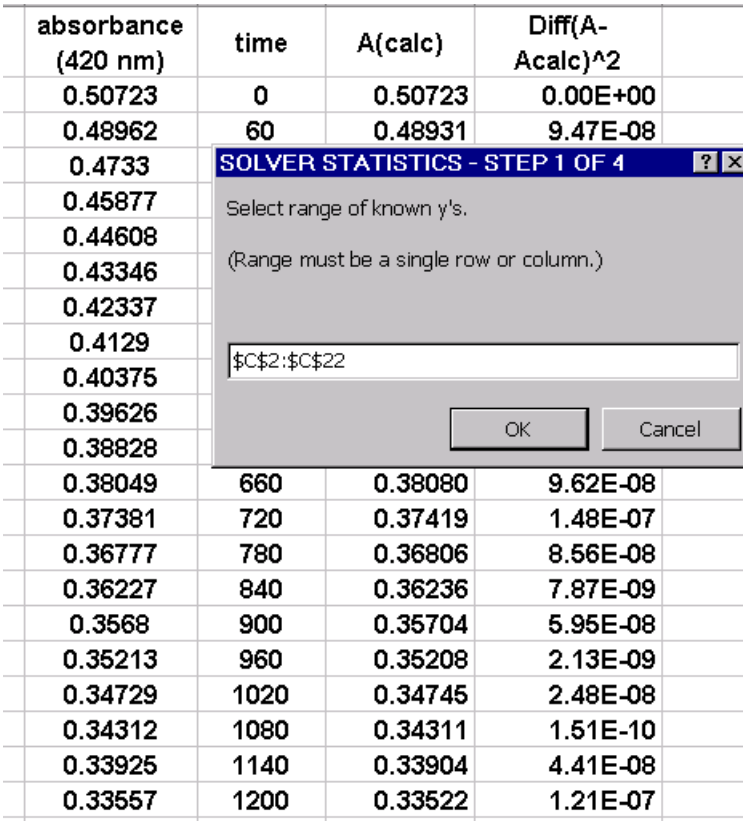
This will launch the Excel loaded with the macro **SolvStat** under the **Tools** button:



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

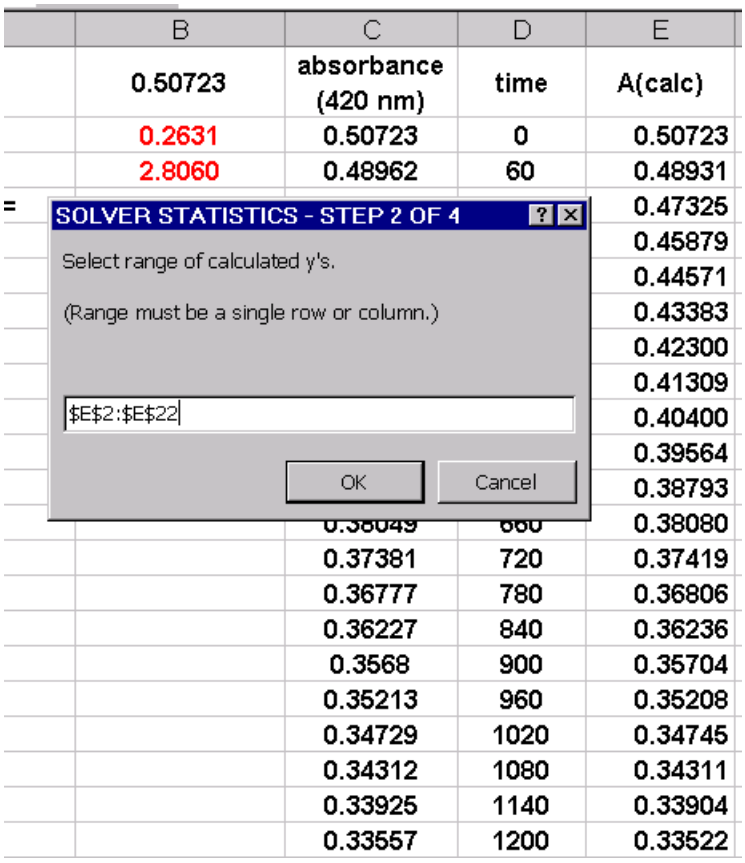
For each **kobs** there are four quick steps to calculate the standard deviation.

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.

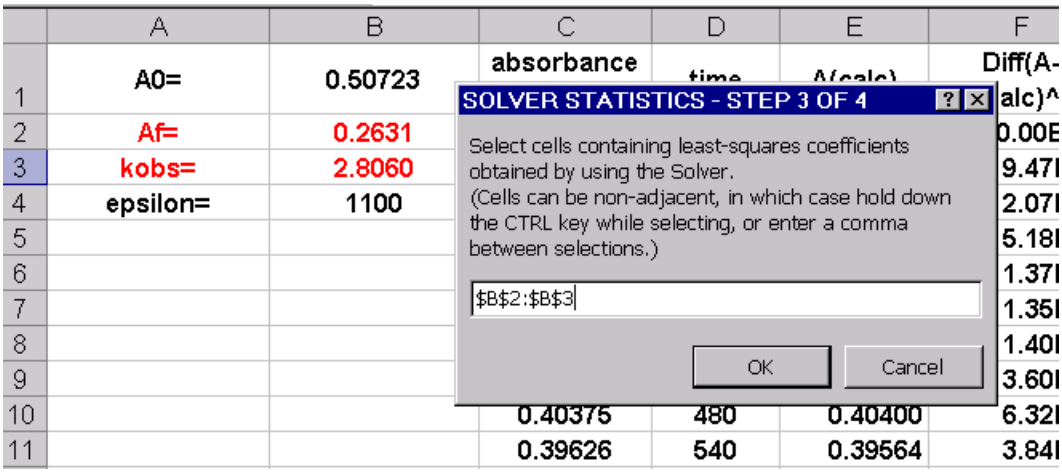


absorbance (420 nm)	time	A(calc)	Diff(A-Acalc)^2
0.50723	0	0.50723	0.00E+00
0.48962	60	0.48931	9.47E-08
0.4733			
0.45877			
0.44608			
0.43346			
0.42337			
0.4129			
0.40375			
0.39626			
0.38828			
0.38049	660	0.38080	9.62E-08
0.37381	720	0.37419	1.48E-07
0.36777	780	0.36806	8.56E-08
0.36227	840	0.36236	7.87E-09
0.3568	900	0.35704	5.95E-08
0.35213	960	0.35208	2.13E-09
0.34729	1020	0.34745	2.48E-08
0.34312	1080	0.34311	1.51E-10
0.33925	1140	0.33904	4.41E-08
0.33557	1200	0.33522	1.21E-07

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

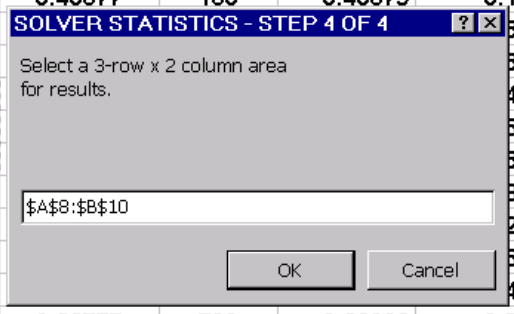


4. In Step 3 select the range of the parameters **kobs** and **Af**, respectively.



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
					37E-07
					35E-07
					40E-07
					60E-08
					32E-08
					34E-07
					23E-07
					62E-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)	
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:

A	B	C
A0=	0.50723	absorbance (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:**