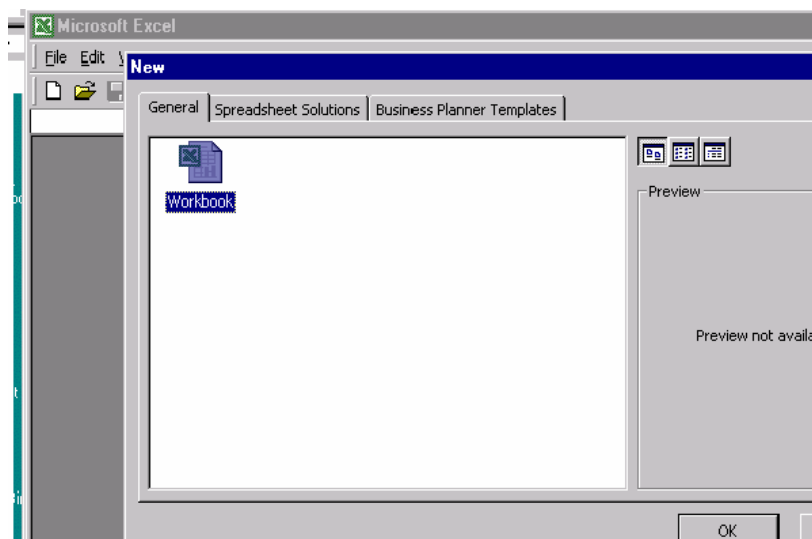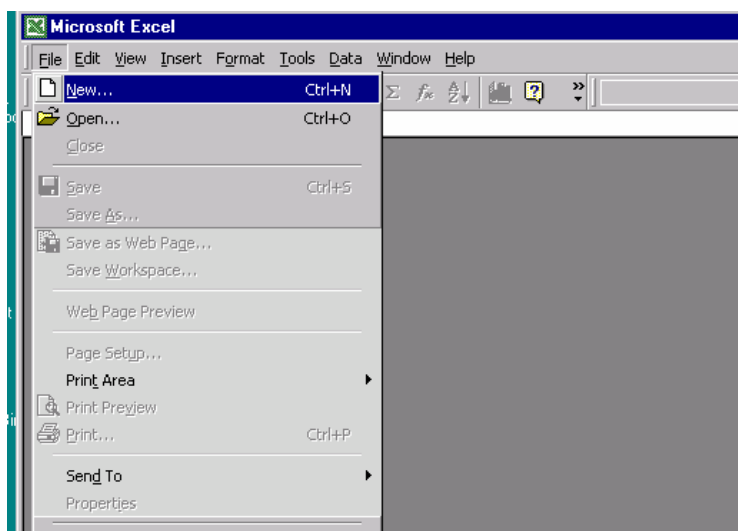# Appendix#3:

Non-linear Curve fitting with Microsoft Excel Solver.[1]
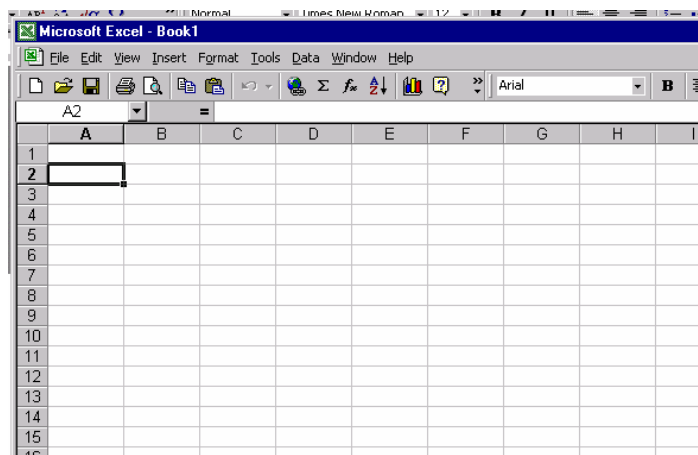
Calculation of kobs, kreal and Debye-Hückel plot.

I. Kinetics: calculation of k_{obs} and k_{real}.
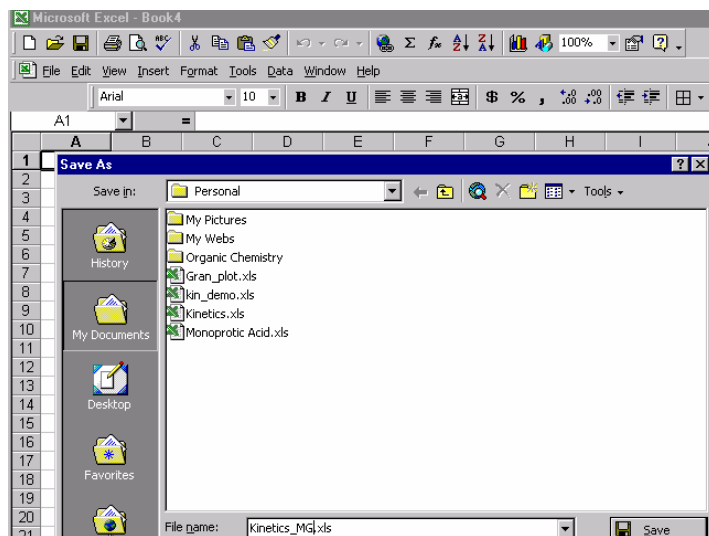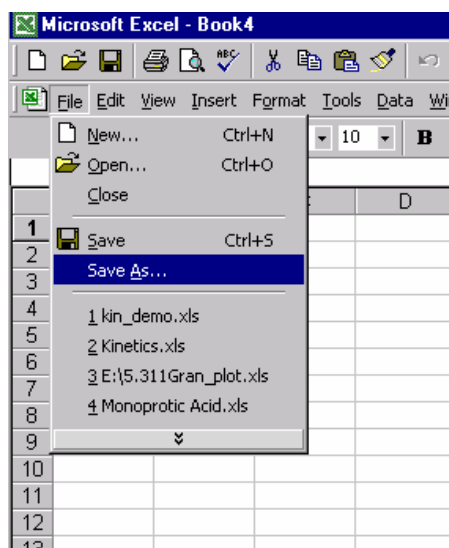
1. From **File** click on **New..,** then on **General Workbook:**


---

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 must to append these five sheets to your written or Oral report.**

If there are not enough Sheets, click **Insert** and then **Worksheet**.
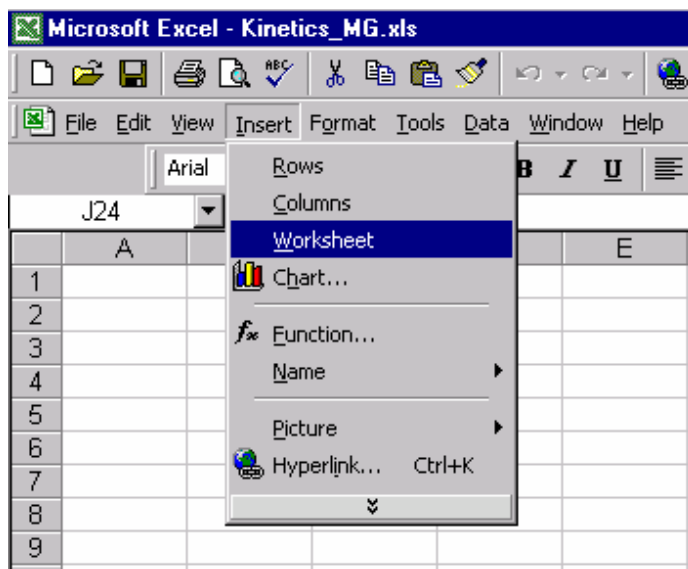
Name four sheets, each for a kinetic run. For example, I have chosen: **KineticsA** (for the 0.02M $NaNO_3$), **KineticsB** (for the 0.05M $NaNO_3$), **KineticsC**, (for the 0.1M $NaNO_3$) and **KineticsD** (for the 0.2M $NaNO_3$).
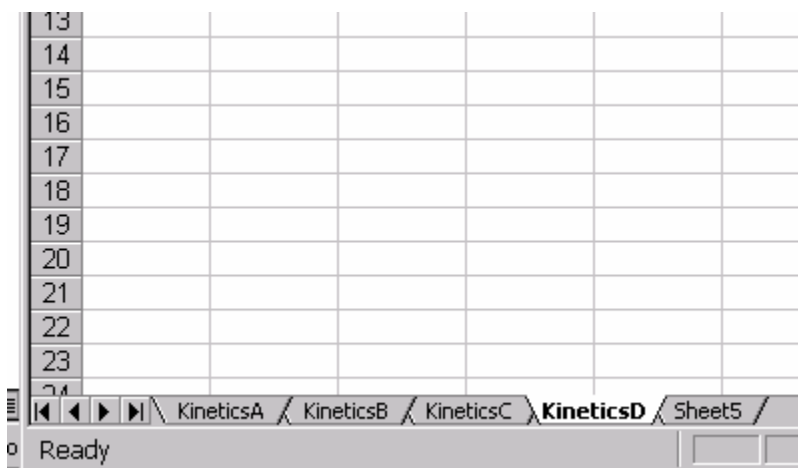
4. Add your experimental data to the four sheets. For example **Kinetics_B sheet is shown below**. Type in column A, the **time** (in seconds), and in column B the **experimental absorbances** (@420nm) corresponding to the respective time. Add two more columns. One for **calculated absorbances** (from equation 3) and one for the **square** of the difference, i.e., **experimental absorbances (column B)-calculated absorbances (column C)**.

3

	time (seconds)	experimental absorbances (420 nm)	Calculated absorbances (equation 3)	Diff^2 [(exp-calc)^2]
1				
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. The second order integrated kinetic equation is given below (see the lecture hand-out):

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

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. Before using **Microsoft Excel Solver cells containing two sets of information must be added to** each kinetic sheet. Cells H2 and H3 contain the values of the "fixed" variables **A0** and **epsilon,** respectively. The content of the cells H5 (**Af** value) and H6 (**kobs**) changes. Initially, "guess" values are typed in for the variables of **Af** and **kobs**. After the minimization process, **Solver** returns the regression coefficients to cells H5 and H6, respectively. **Solver does not provide the standard deviations of the coefficients.**

7. In order to be automatically plug into the kinetic equation (equation 3), the cells containing the values of **A0, epsilon, Af, kobs must be given a name** (this is an Excel requirement). First, input the required values.

- For **A0**, type "=B2" in cell H2
- For **epsilon** type in cell H3, your value 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 (Explain why in your report).
- Type your guess value for **kobs** in cell H6. My guess is 5.

Next assign "Excel names" to **A0, epsilon, Af and kobs.** For example to name **A0**, first click on cell H2. Then click on **Insert**, **Name**, **Define**:
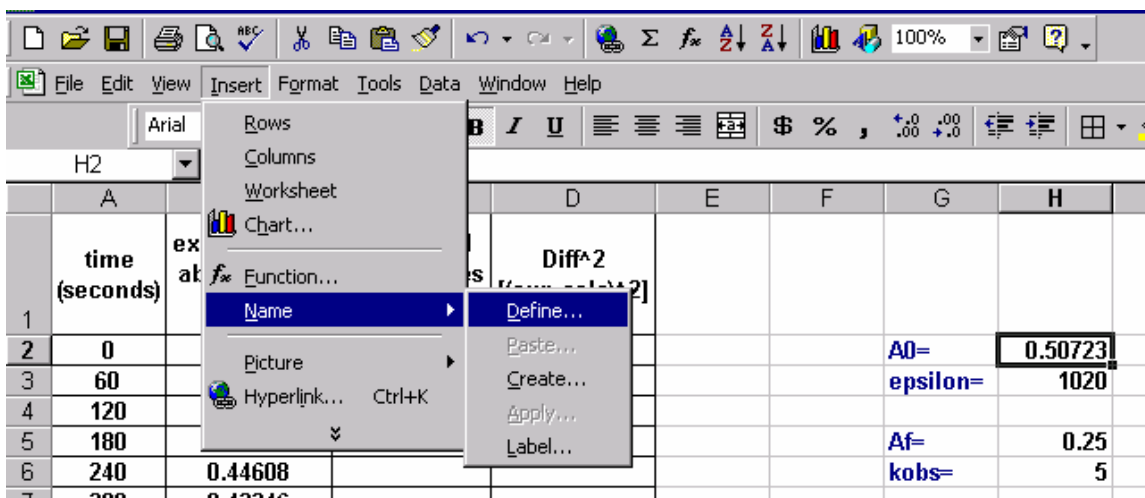
The following window pops-up:
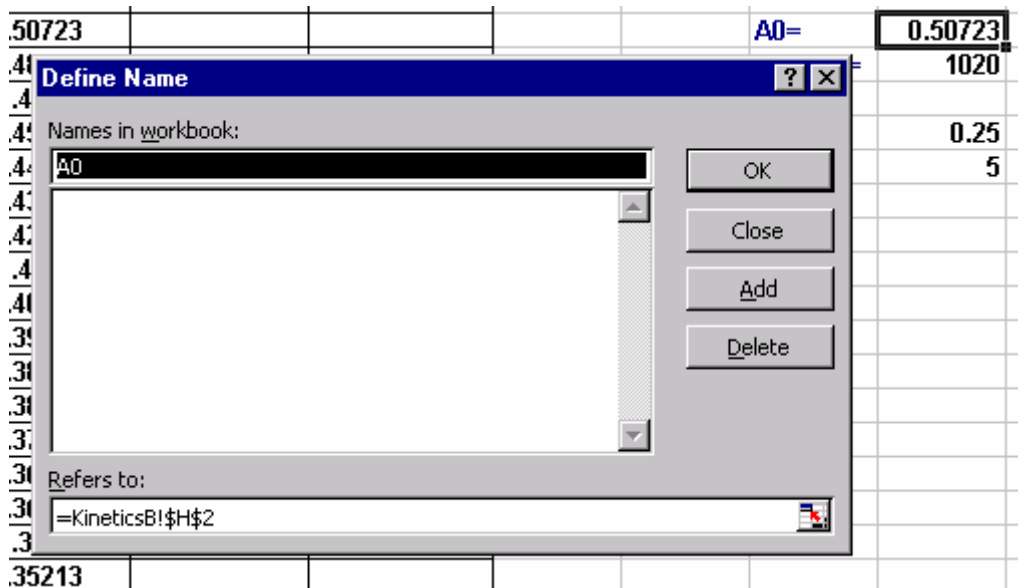
Please check the location of the value of **A0**. In this example A0 is in (according to Excel grammar): KineticsB!$H$2, that is on **KineticsB** sheet in location H2. Click on **add** button. Click on **OK**. Continue **naming** cells H3:H5. Next, name as **t** the vector A2:A22. First highlight the column A2:A22, then click on **Insert, Name, Define** and change the name in the workbook as **t** (check the **Refers to** address in order be sure the correct set of cells are defined). The **Define Name** window will look like:
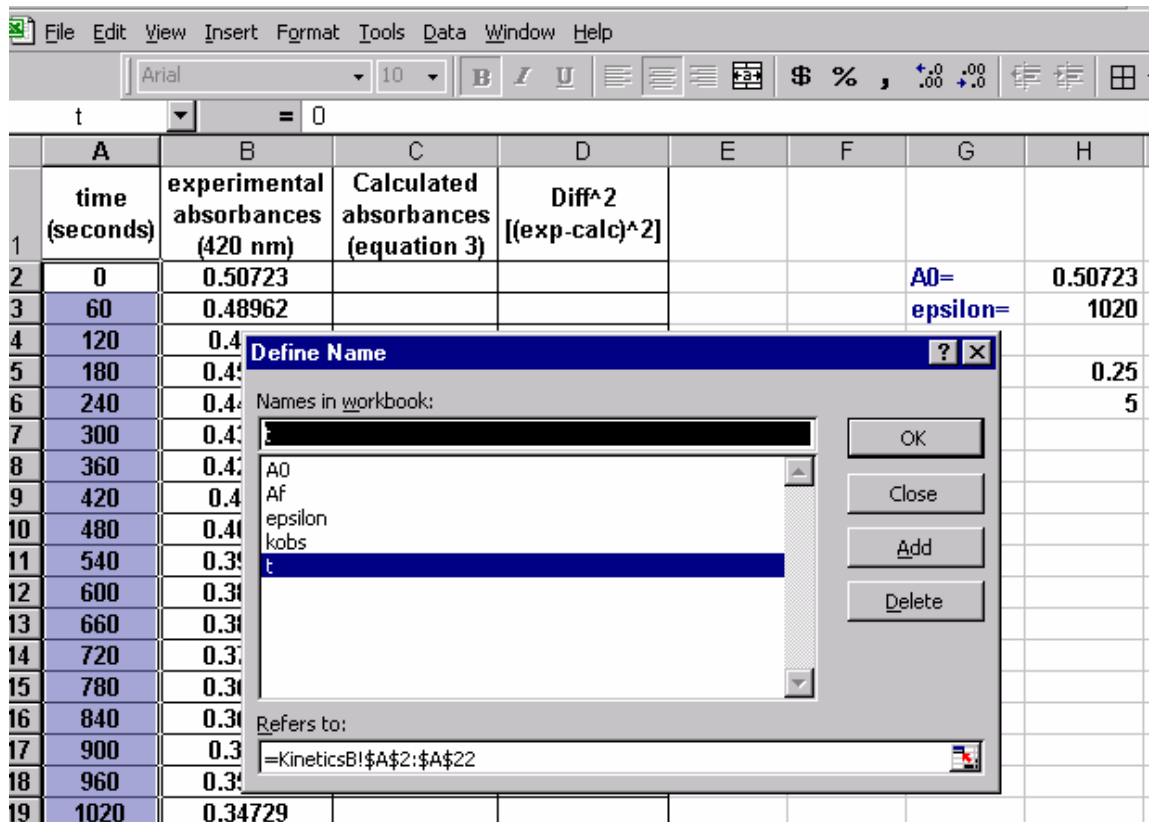
8.   **Solver** optimizes the curve fitting in two steps:

- 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 the experimental values.

A. The **"Crude Calculation"** 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 should equal **A0**.

To fill cells C3 through C22, click on cell C2. Bring the cursor to the right low corner and press left mouse and drag all the way down to cell C22. Depress the left mouse. All cells (C2:C22) should now be 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	

KineticsA **KineticsB** KineticsC KineticsD Sheet5

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

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

File Edit View Insert Format Tools Data Window Help   AutoSum

Arial   10   B I U

SUM   X ✓ = =SUM(D2:D22)

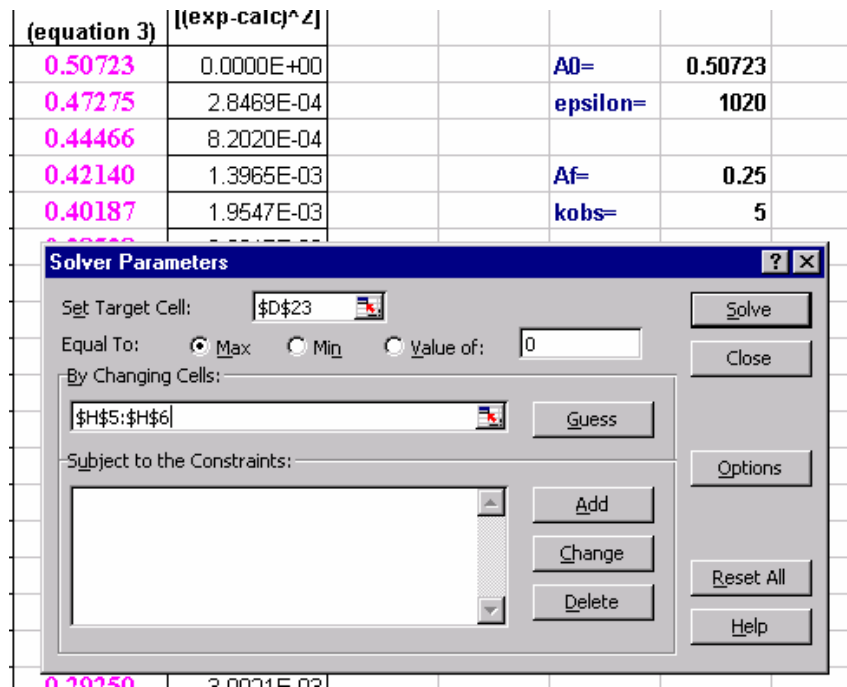|	A	B	C	D	E
7	300	0.43346	0.38528	2.3217E-03	
8	360	0.42337	0.37104	2.7381E-03	
9	420	0.4129	0.35873	2.9343E-03	
10	480	0.40375	0.34800	3.1080E-03	
11	540	0.39626	0.33859	3.3257E-03	
12	600	0.38828	0.33029	3.3624E-03	
13	660	0.38049	0.32294	3.3119E-03	
14	720	0.37381	0.31640	3.2963E-03	
15	780	0.36777	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)	

Then press the **Enter** key.

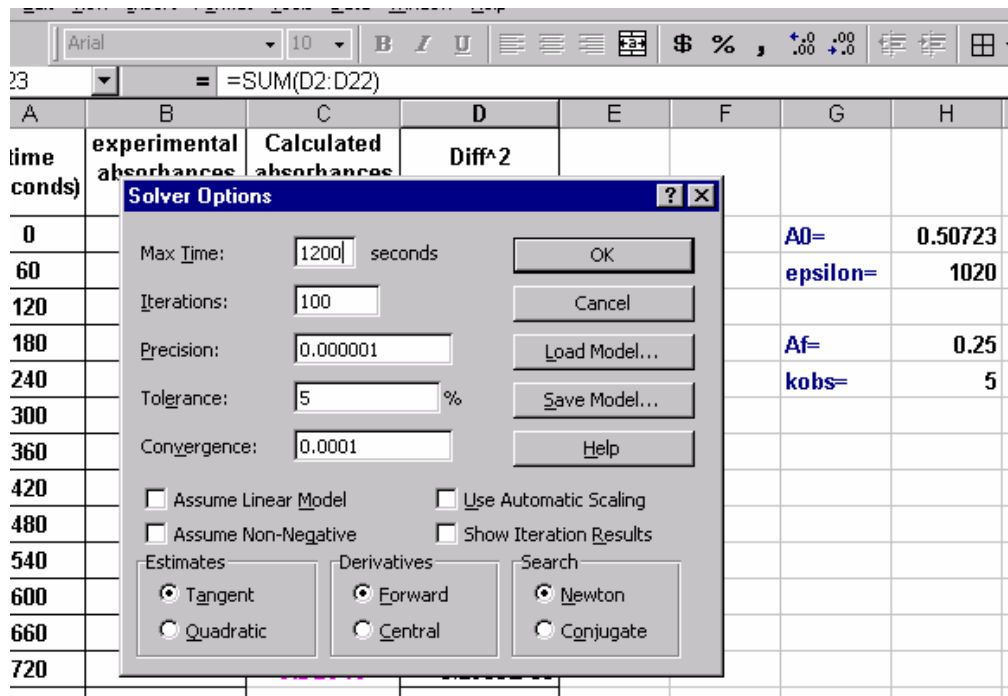12. Click on cell D23, then click on **Tools** followed by **Solver…**
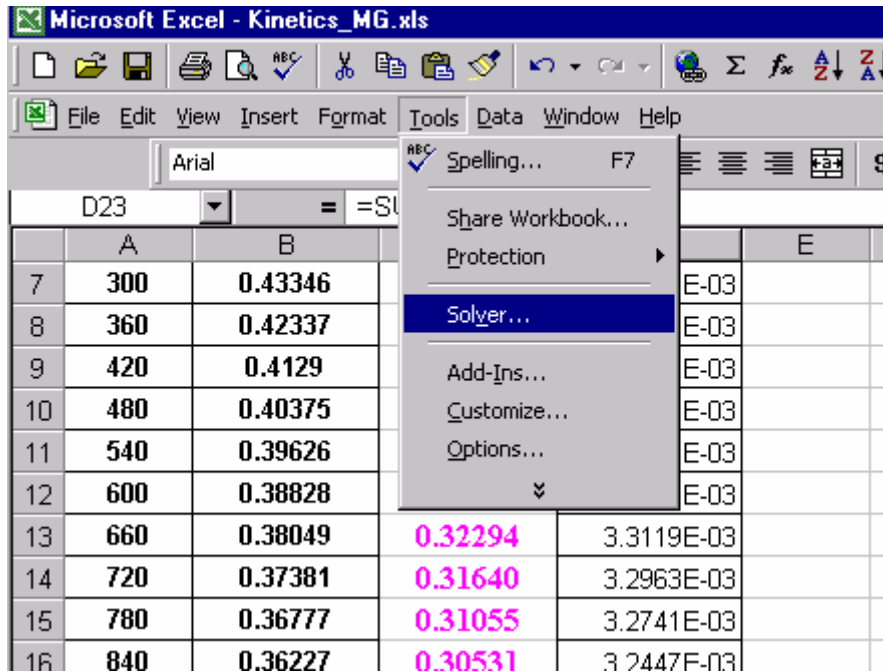
The **Solver Parameters** window pops-up. **Set target cell: $D$23**.
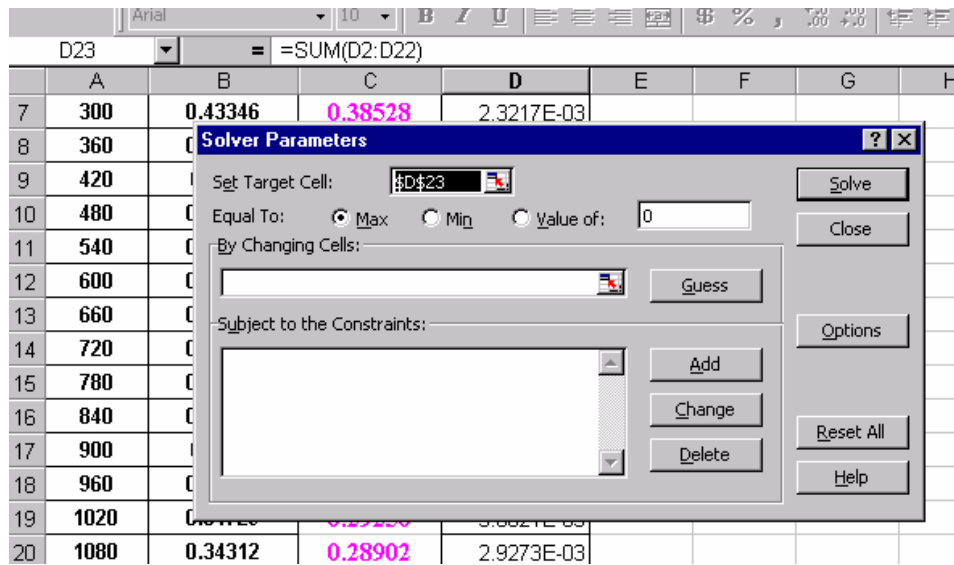

Type into "**By Changing Cells**: **$H$5 and $H$6**.

(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 Parameters

Set Target Cell: `$D$23`

Equal To: ● Max ○ Min ○ Value of: `0`

By Changing Cells:

`$H$5:$H$6`

Subject to the Constraints:

[Solve] [Close] [Guess] [Options] [Add] [Change] [Delete] [Reset All] [Help]

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

`23` `=SUM(D2:D22)`

A	B	C	D	E	F	G	H
time (conds)	experimental absorbances	Calculated absorbances	Diff^2				
0						A0=	0.50723
60						epsilon=	1020
120							
180						Af=	0.25
240						kobs=	5
300							
360							
420							
480							
540							
600							
660							
720							

Solver Options

Max Time: `1200` seconds

Iterations: `100`

Precision: `0.000001`

Tolerance: `5` %

Convergence: `0.0001`

[OK] [Cancel] [Load Model...] [Save Model...] [Help]

☐ Assume Linear Model ☐ Use Automatic Scaling
☐ Assume Non-Negative ☐ Show Iteration Results

Estimates: ● Tangent ○ Quadratic
Derivatives: ● Forward ○ Central
Search: ● Newton ○ Conjugate

The **Solver Parameters** window returns back. Click first on the **Min** and then on the **Solve** buttons:
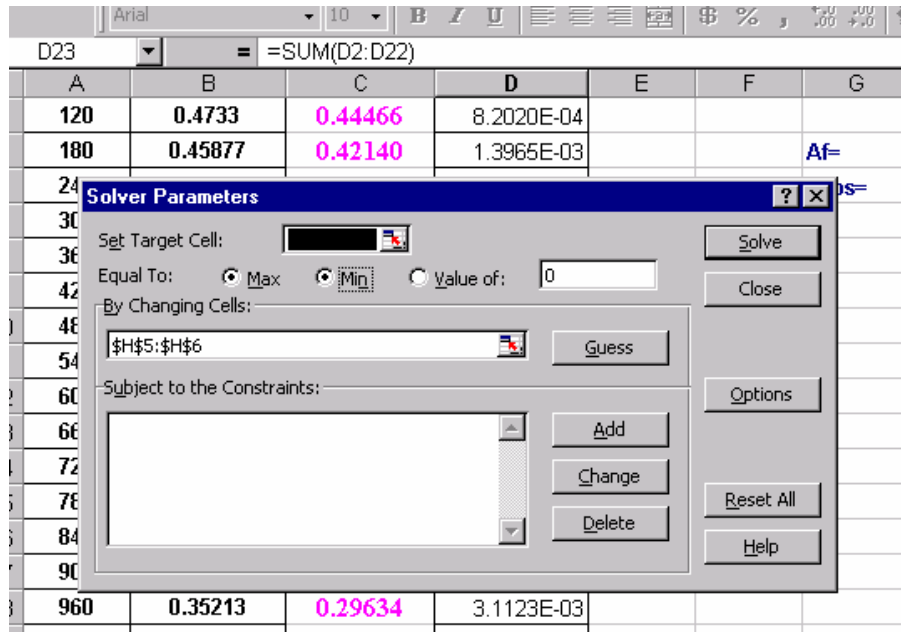
The **Solver Results** window pops-up. Note that the values in cells H4 and H5 are updated. You know by now the value of **kobs** is now **2.60**. (Note the initial value of **kobs**, the "guess," was 5.)
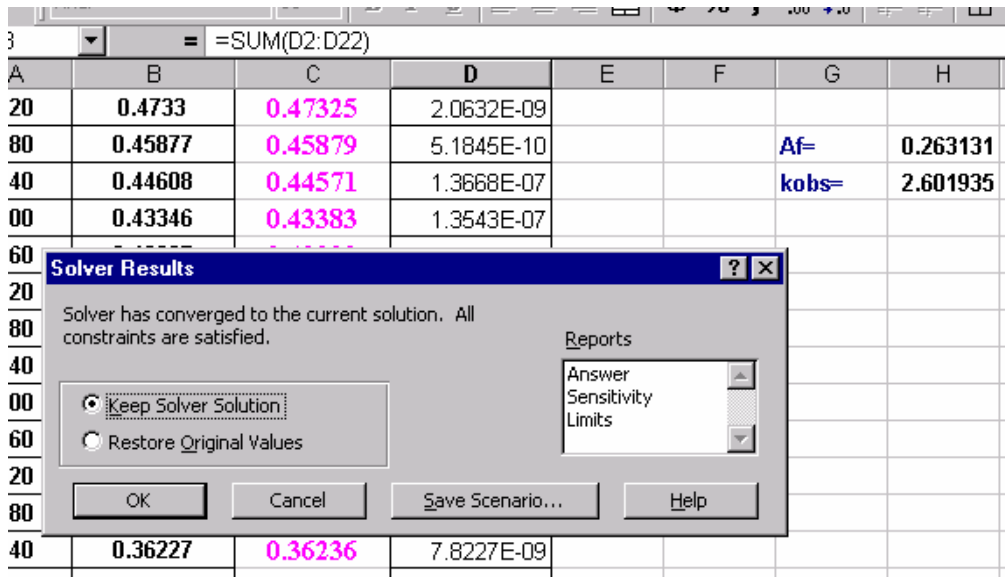
You can next print reports: **answer, sensitivity and limits**. For example, the **Answer Report** looks like:

Repeat steps 4 through 12 for sheets **KineticsA, KineticsC and KineticsD**. It will be necessary to change the **Reference** in the **Define Name** window to match each sheet.

II. Debye-Hückel equation.

In the "Kinetics" hand-out, 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 sheet#5 (named as **Debye-Hückel**) to compute and draw the linear plot **logkreal** (y axis) versus $I^{0.5}/(I^{0.5}+1)$ (x axis). When finished the **Debye-Hückel** worksheet will look like:

|	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					

Debye-Huckel

$y = 2.7835x + 1.8686$
$R^2 = 0.9809$

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 above. Remember in Excel x-axis values are left of y-axis values (for example, column A values are on the x-axis, column B values are displayed on the y-axis).

2. Fill in kobs values by using the address from the respective worksheet. Click, for example on cell C2 and type: "**=KineticsA!$H$6**". Cell two is filled with the value 2.07. Cell C3: "**=KineticsB!$H$6**", cell C4: "**=KineticsC!$H$6**" and cell C5: "**=KineticsD!$H$6**".
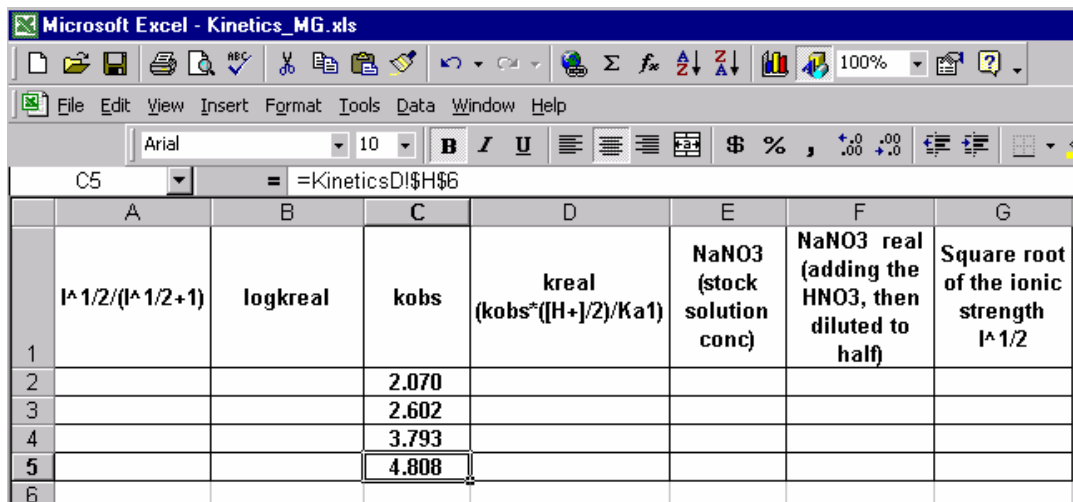
3. Place the HNO$_3$ molarity in cell B7 and the acidity constant for ascorbic acid (Ka1=6.76*10^{-5}) in cell B8.

4. Type in the column D2 through D5 the calculated kreal (see equation **4**). For example in cell D2 type: "**=(C2/$B$8)*0.5*$B$7**" (the 0.5 appears because the HNO$_3$ in the UV cuvette is half the concentration of the HNO$_3$ stock solution). Because cells B7 and B8 are referred to by 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.

5. Calculate logkreal in cell B2 as LOG10(D2). Drag the cell content as described above down to B5:

	A	B	C	D	E	F	G
	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							

Microsoft Excel - Kinetics_MG.xls

File Edit View Insert Format Tools Data Window Help

Arial   10   B I U $ % ,

B5   =   =LOG10(D5)

6. To calculate in column A $I^{0.5}/(I^{0.5}+1)$, the x-axis variable:
   - 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 calculate the real NaNO3 + HNO3 molarities. For example in cell F2, type "**=(E2+$B$7)*0.5**". Multiplication with 0.5 is because in the UV cuvette the stock solution is diluted by half as result of the 3 mL+ 3mL mixing (see the experiment and handouts). For monovalent anions and cations, molarities are numerically equal to **Ionic Strength**.

	A	B	C	D	E	F	G
	File Edit View Insert Format Tools Data Window Help						
	Arial		10				
	G2	=					
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 $I^{0.5}/(I^{0.5}+1)$. For example, in cell A2 type "**=G2/(G2+1)**" and press **Enter**. Click on the cell. Drag the lower right corner all the way down to A5.

Microsoft Excel - Kinetics_MG.xls

	A	B	C	D	E	F	G
	File Edit View Insert Format Tools Chart Window Help						
	Arial		10				
	Chart Area	=					
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					

7. The last step consists of the **Debye-Hückel** plot.
- Highlight columns A2:B5. Click on **Insert,** then **Chart…**:

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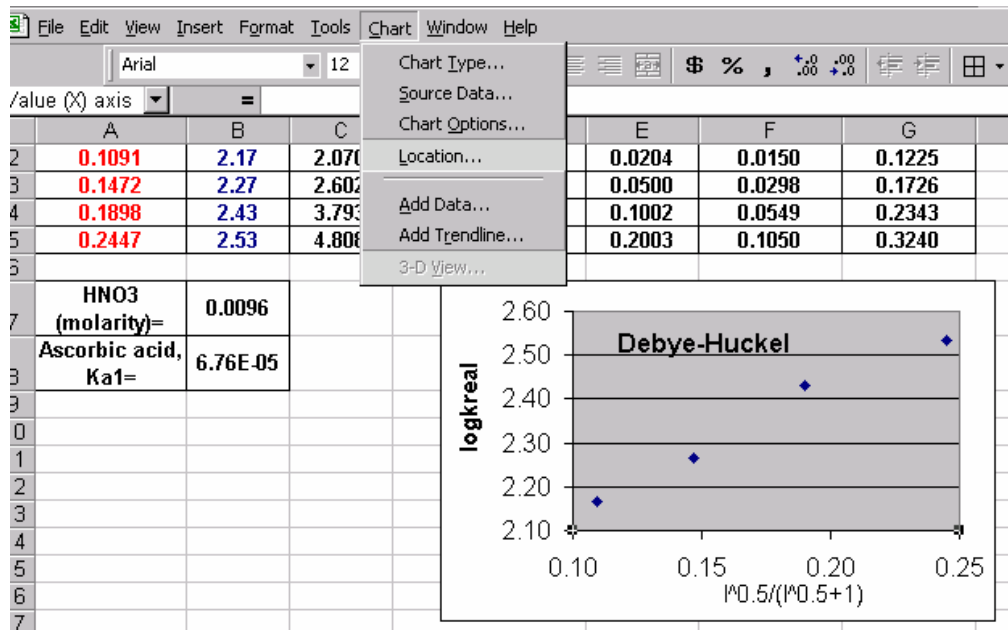

- Click next to steps 2 and 3. In step 3 fill in the **chart title, value (X) axis and value (Y) axis** respectively.
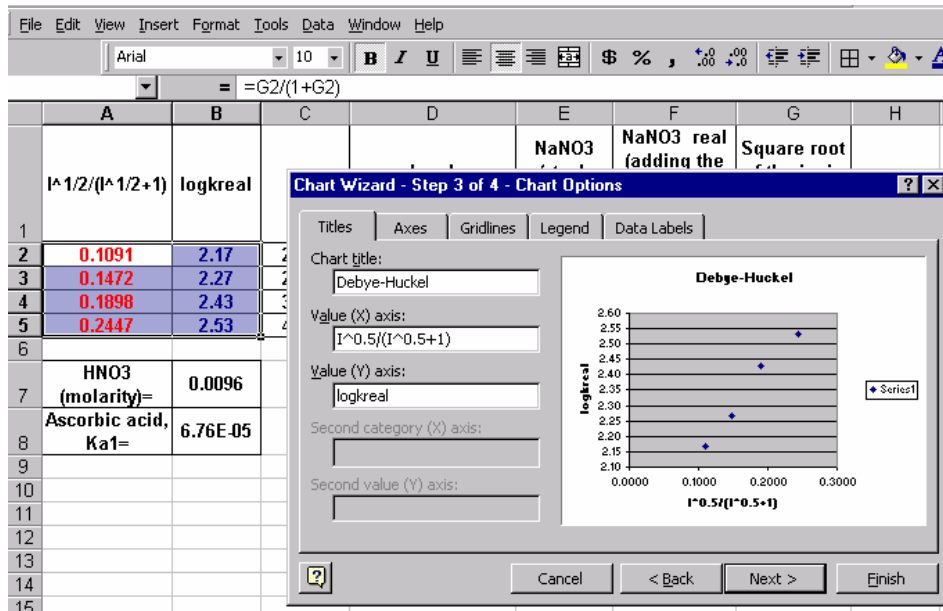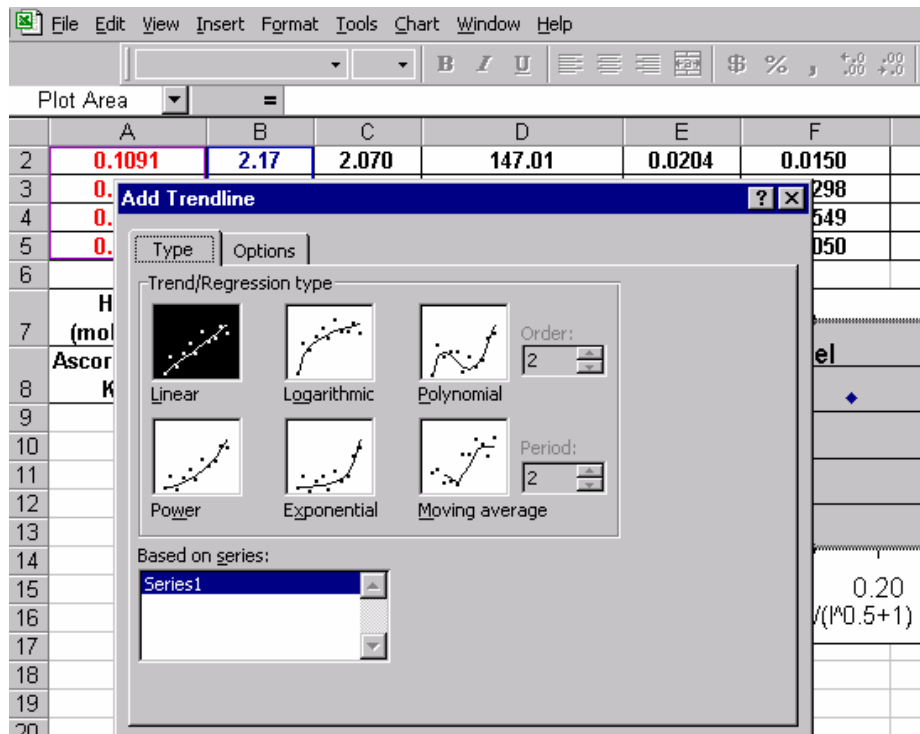
- Click **Next** and then **Finish**.
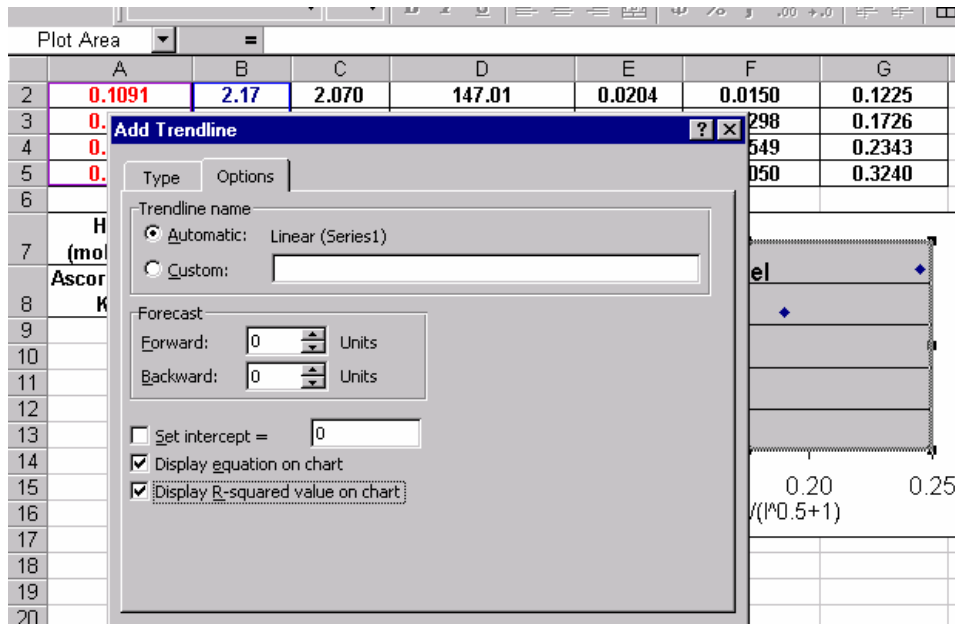- With some editing, the chart appears as:
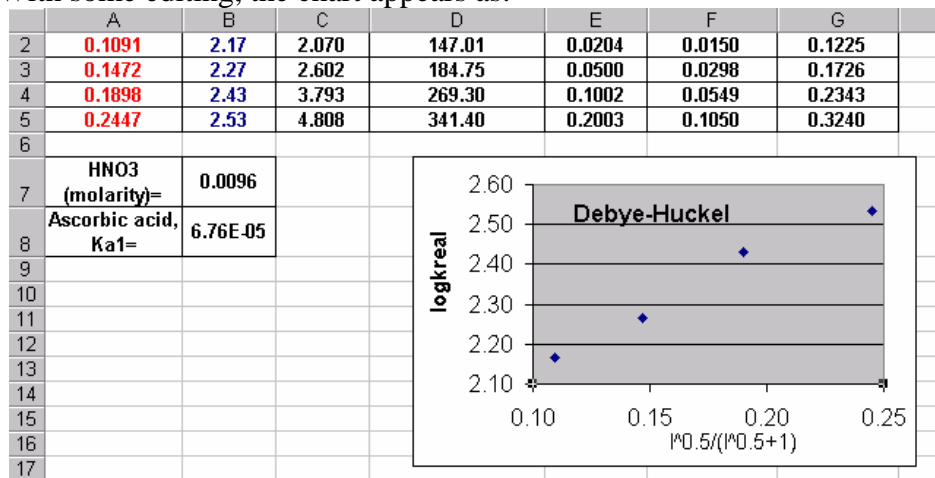
- The least square straight line is added on the graph, by clicking on **Chart**, then **Add trendline..**
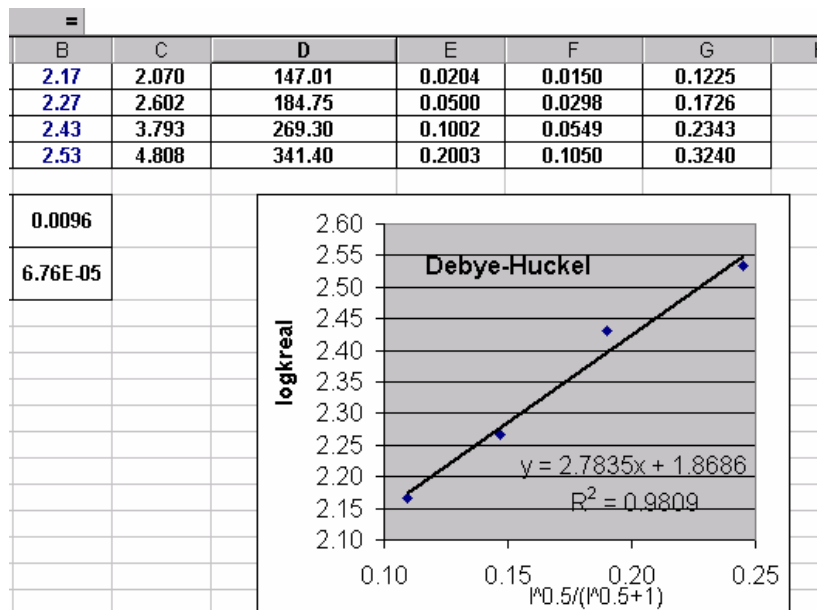
19

Under **Type: Trend/Regression type,** choose **Linear**.

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

- The least square straight line below has the equation: y = 2.7835x + 1.8686 and R^2=0.9809 (satisfactory, however I am confident that 5.310 students will get a better R^2).

8. To compute the slope ($1.02*Z_1*Z_2$) and intercept (ko the rate constant at I=0), and R2, first add these cells (A10:A13; B10:B13) to the **Debye-Hückel** worksheet.

- Type" **=SLOPE(B2:B5,A2:A5)**" in cell B10, next to **Slope=.**
- Type "**= INTERCEPT(B2:B5,A2:A5)**" in cell B11, next to **Intercept=**
- Type "**=10^B11**" in cell B12, next to **k0=**

- Type "**=RSQ(B2:B5,A2:A5**)" in cell B13, next to **R^2=**

	A	B	C	D	E	F	G	H
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								
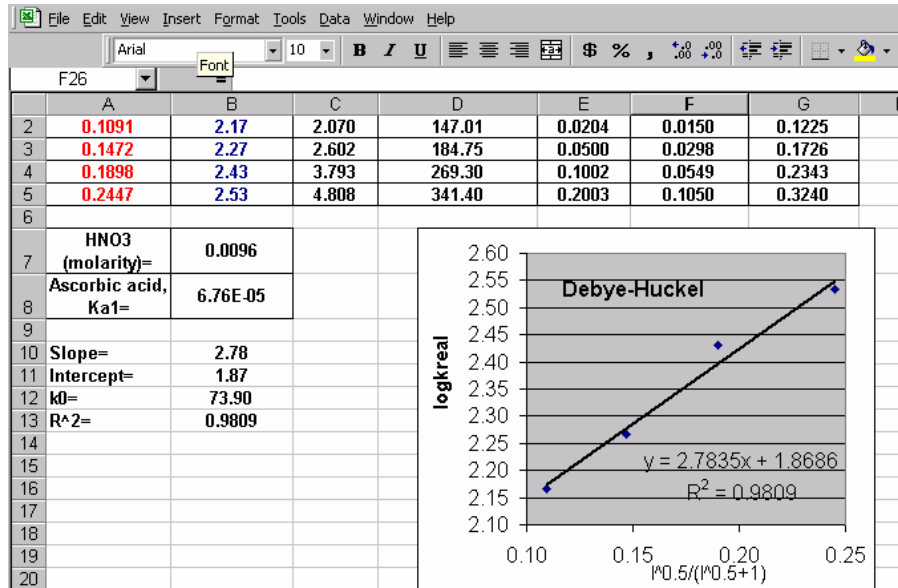
9. Finally print copies of all 5 sheets for inclusion with your report.