

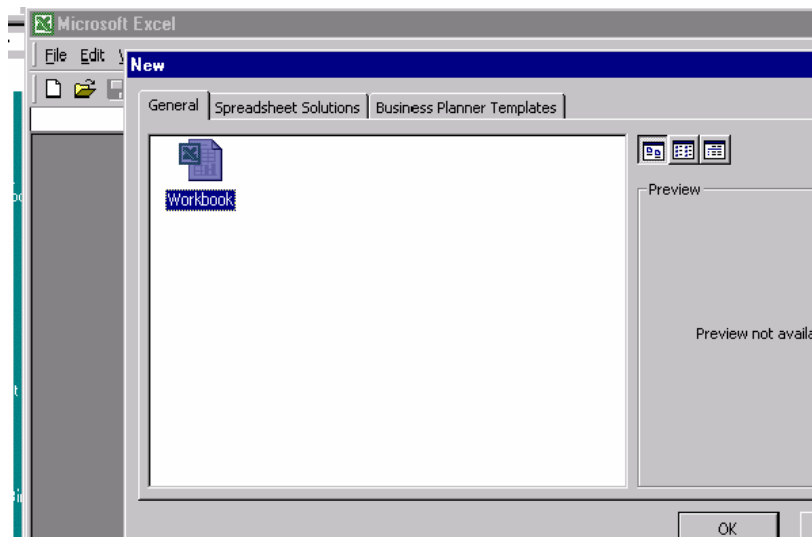
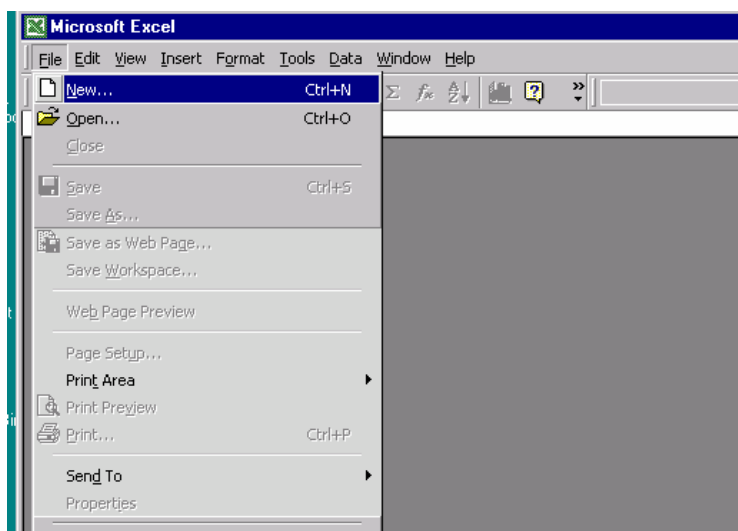
## Appendix#3:

### Non-linear Curve fitting with Microsoft Excel Solver.<sup>1</sup>

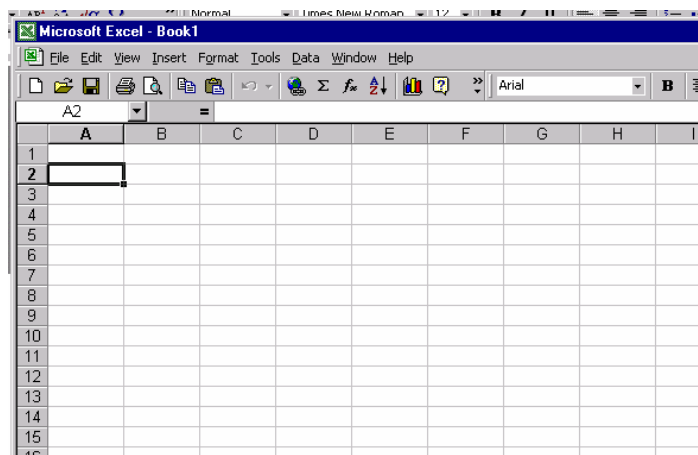
## Calculation of $k_{obs}$ , $k_{real}$ and Debye-Hückel plot.

### I. Kinetics: calculation of $k_{obs}$ and $k_{real}$ .

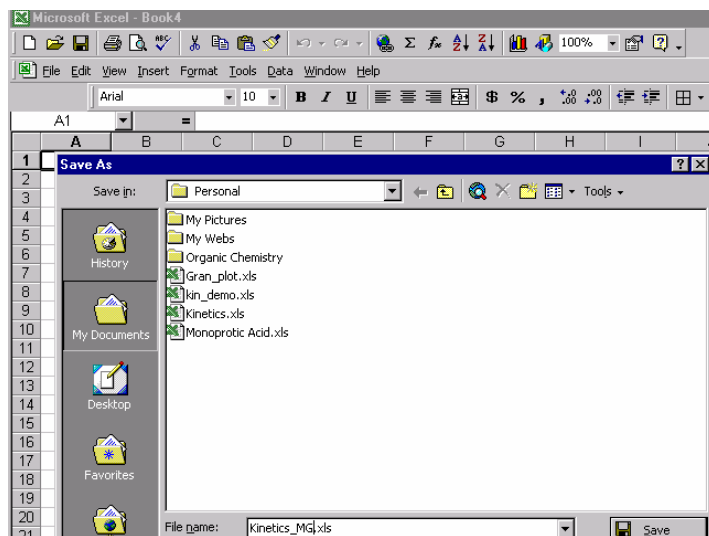
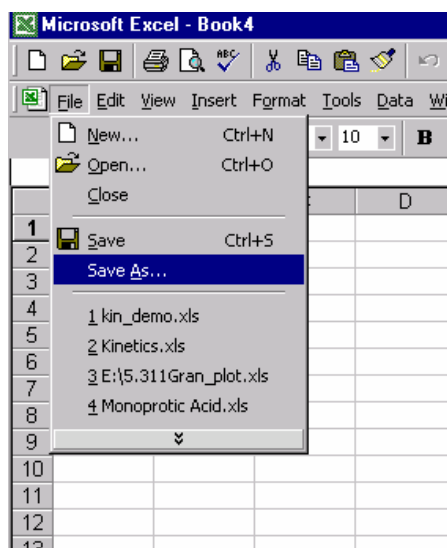
1. From **File** click on **New...**, then on **General Workbook**:



<sup>1</sup> Written by Dr. Mircea Gheorghiu.

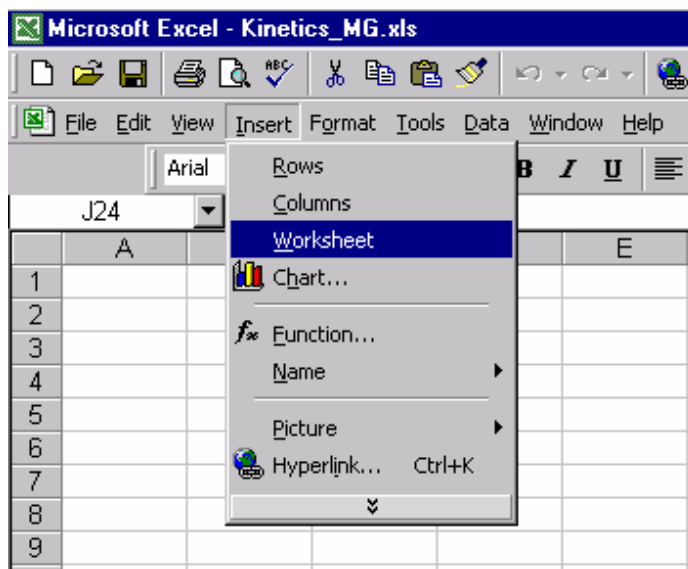


2. From **File**, **Save as...** the workbook. My preference for file name is **Kinetics\_MG** (MG are my initials) and it is saved in the **Personal** folder.

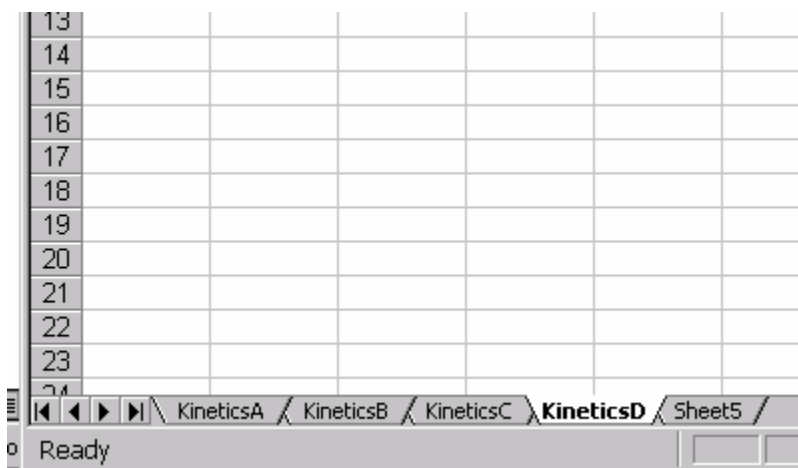


3. **Five sheets are necessary in your workbook.** Four are for Kinetics data. The fifth is for Debye\_Huckel calculation. **You must to append these five sheets to your written or Oral report.**

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<sub>3</sub>), **KineticsB** (for the 0.05M NaNO<sub>3</sub>), **KineticsC**, (for the 0.1M NaNO<sub>3</sub>) and **KineticsD** (for the 0.2M NaNO<sub>3</sub>).



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)**.

|    | time<br>(seconds) | experimental<br>absorbances<br>(420 nm) | Calculated<br>absorbances<br>(equation 3) | Diff^2<br>[(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                                 |   |                          |

5. The second order integrated kinetic equation is given below (see the lecture hand-out):

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

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  $t$

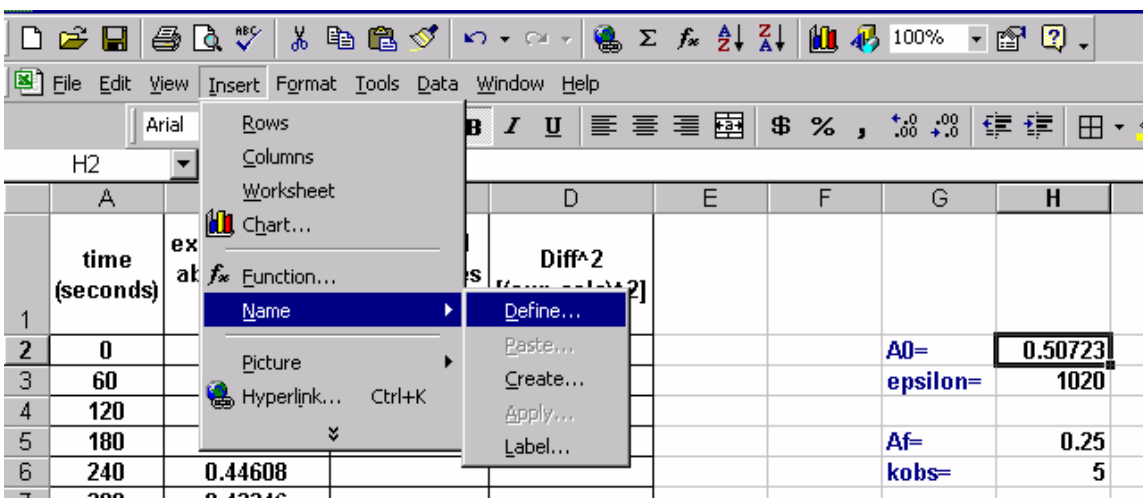
$A_f$  = absorbance when all  $H_2Asc$  has reacted.

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.**

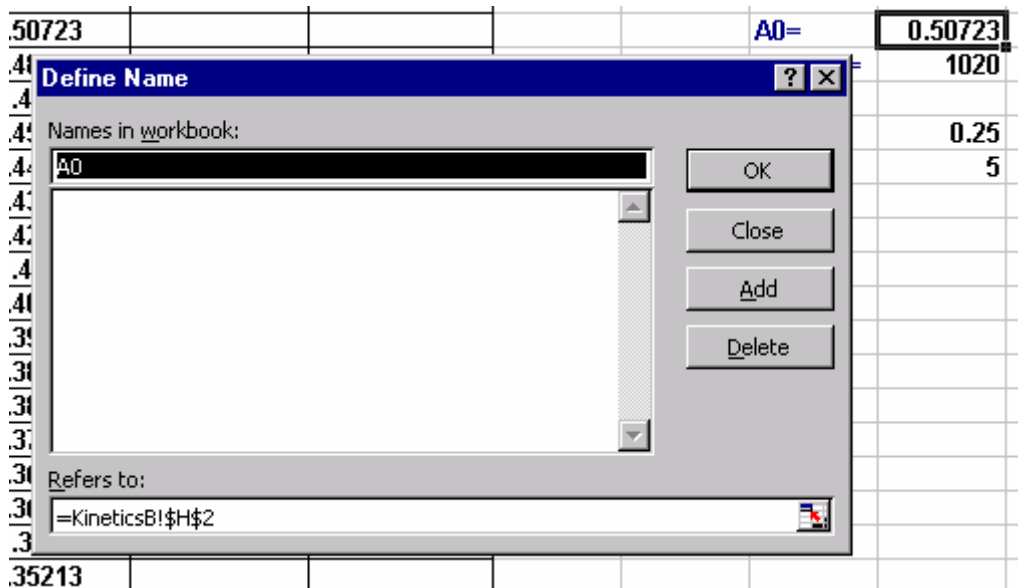
7. In order to be automatically plug into the kinetic equation (equation 3), the cells containing the values of **A0**, **epsilon**, **Af**, **kobs** must be given a name (this is an Excel requirement). First, input the required values.
  - For **A0**, type “=B2” in cell H2
  - For **epsilon** type in 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  $\epsilon = 1020$ .
  - 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.

|   | A              | B                                 | C                                   | D                     | E | F | G        | H       |
|---|----------------|-----------------------------------|-------------------------------------|-----------------------|---|---|----------|---------|
|   | time (seconds) | experimental absorbances (420 nm) | Calculated absorbances (equation 3) | Diff^2 [(exp-calc)^2] |   |   |          |         |
| 1 |                |                                   |                                     |                       |   |   |          |         |
| 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                           |                                     |                       |   |   |          |         |

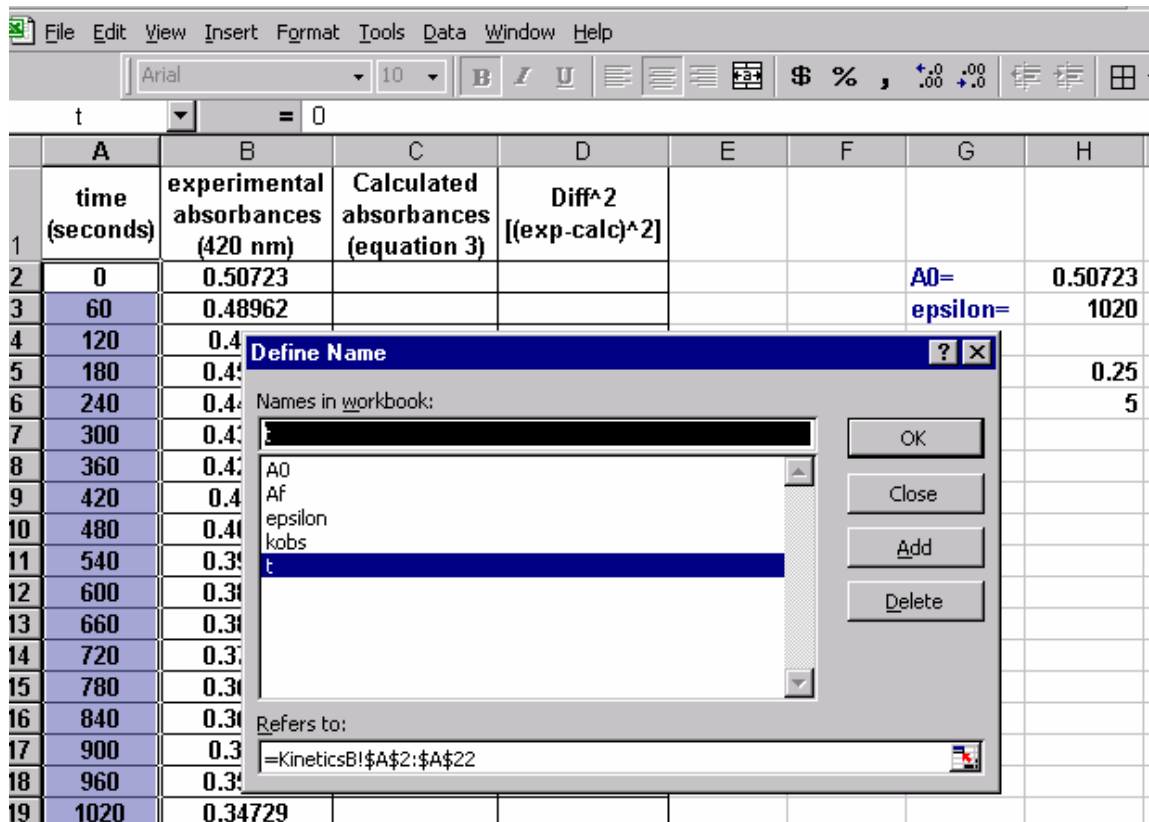
Next assign “Excel names” to **A0**, **epsilon**, **Af** and **kobs**. For example to name **A0**, first click on cell H2. Then click on **Insert, Name, Define**:



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  $=A_f/((1-((A_0-A_f)/A_0)*EXP(-k_{obs}*t*A_f/epsilon)))$ . Cell H2 is filled with the calculated absorbance for t=0 seconds. According to equation 3 it should equal A0.

The screenshot shows an Excel spreadsheet titled "Kinetics\_MG.xls". The formula bar for cell C2 contains the equation:  $=A_f/((1-((A_0-A_f)/A_0)*EXP(-k_{obs}*t*A_f/epsilon)))$ . The spreadsheet has columns A through H. Column A is "time (seconds)", B is "experimental absorbances (420 nm)", C is "Calculated absorbances (equation 3)", and D is "Diff^2 [(exp-calc)^2]". Rows 2 through 8 contain data points. Column G contains parameter values: A0=0.50723, epsilon=1020, Af=0.25, and kobs=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                           | 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                           |                                     |                       |   |   |          |         |

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 <sup>2</sup> [(exp-calc) <sup>2</sup> ] |
| 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                             |  |

**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  $\Sigma$ ) D2 through D22.

Microsoft Excel - Kinetics\_MG.xls

File Edit View Insert Format Tools Data Window Help

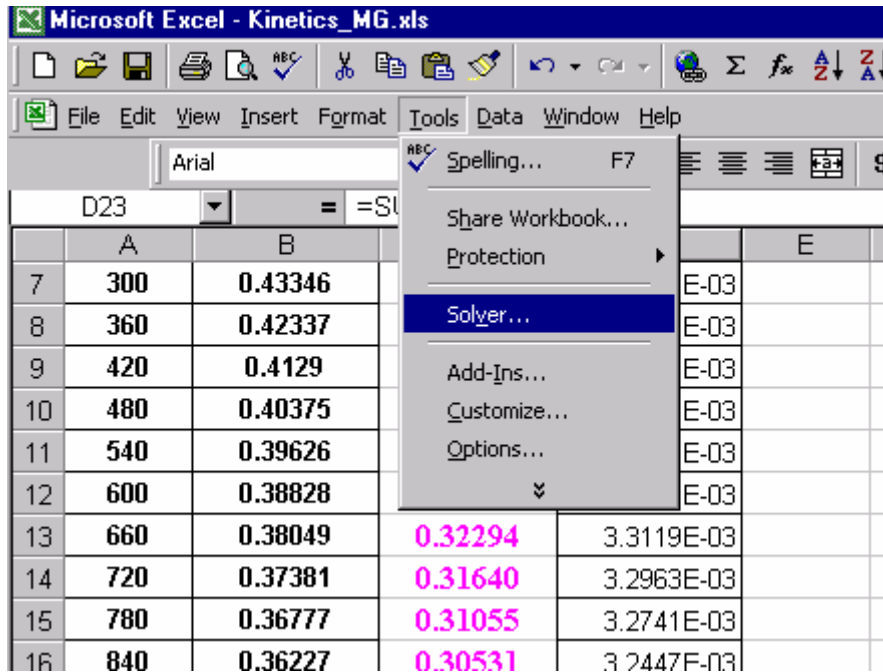
Arial 10 B I U

SUM X ✓ = =SUM(D2:D22)

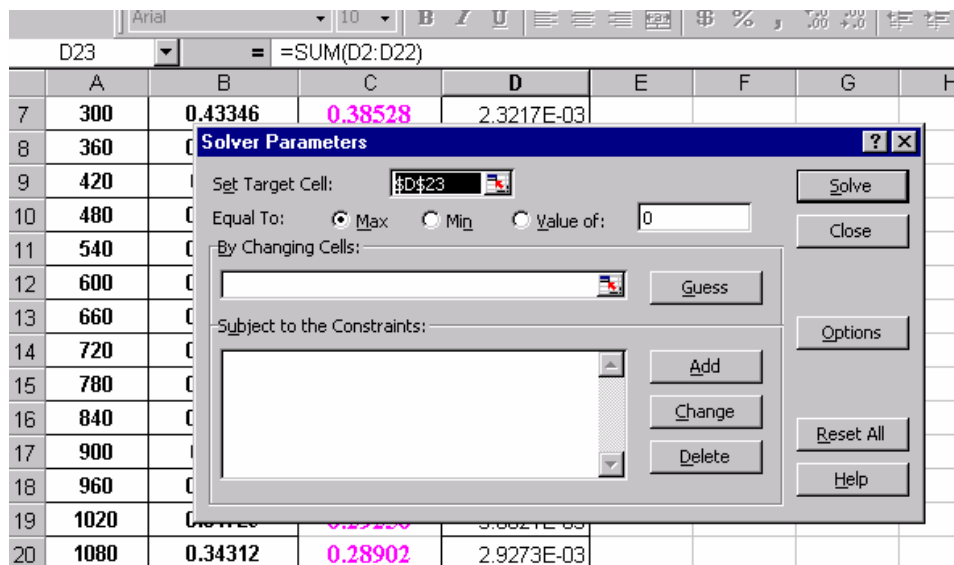
|    | A    | B       | C       | D            | E |
|----|------|---------|---------|--------------|---|
| 7  | 300  | 0.43346 | 0.38528 | 2.3217E-03   |   |
| 8  | 360  | 0.42337 | 0.37104 | 2.7381E-03   |   |
| 9  | 420  | 0.4129  | 0.35873 | 2.9343E-03   |   |
| 10 | 480  | 0.40375 | 0.34800 | 3.1080E-03   |   |
| 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.

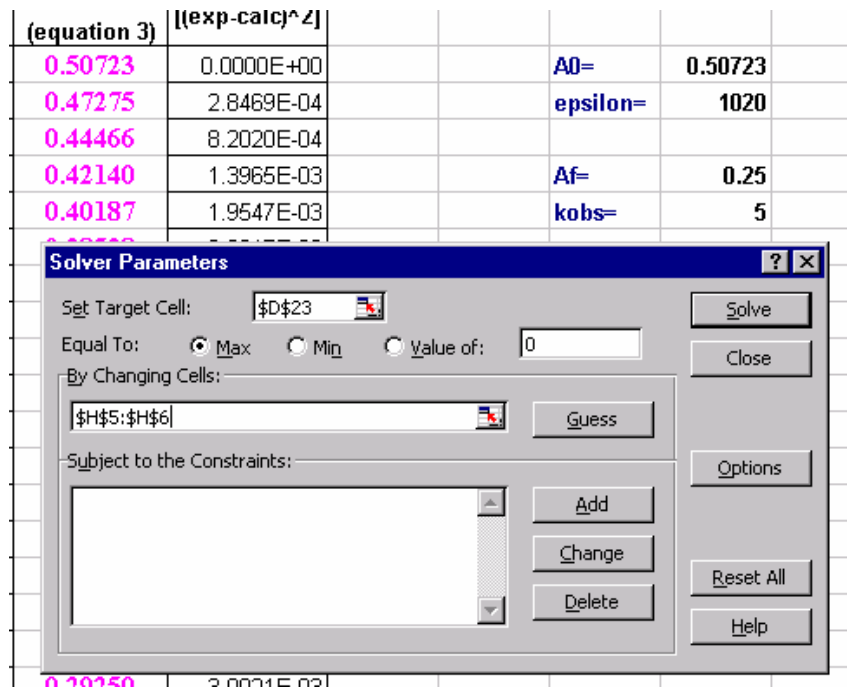
12. Click on cell D23, then click on **Tools** followed by **Solver...**



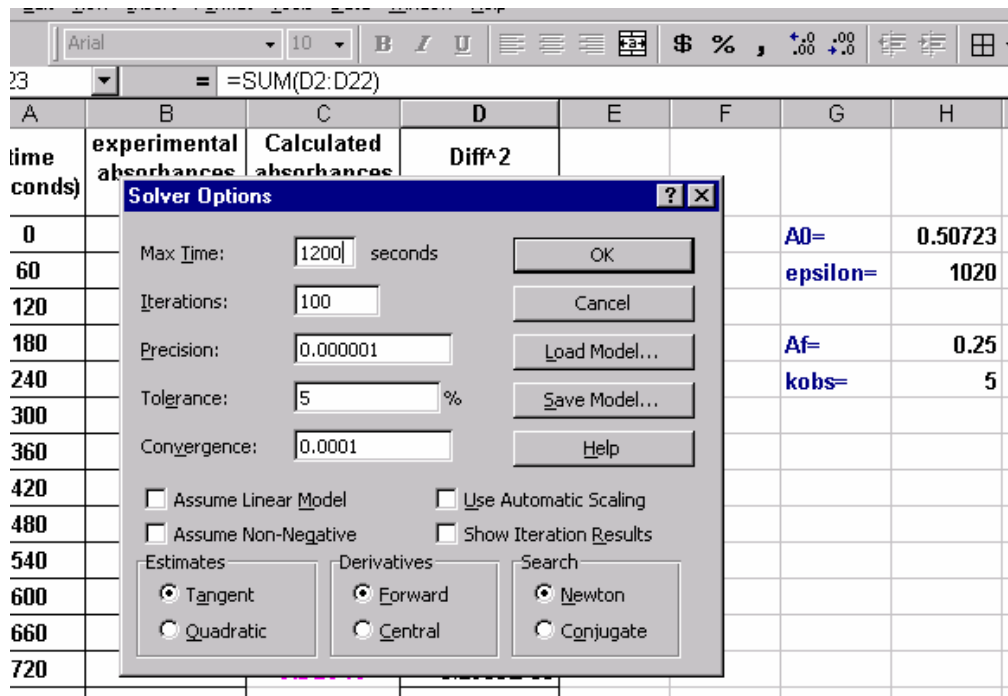
The Solver Parameters window pops-up. Set target cell: \$D\$23.



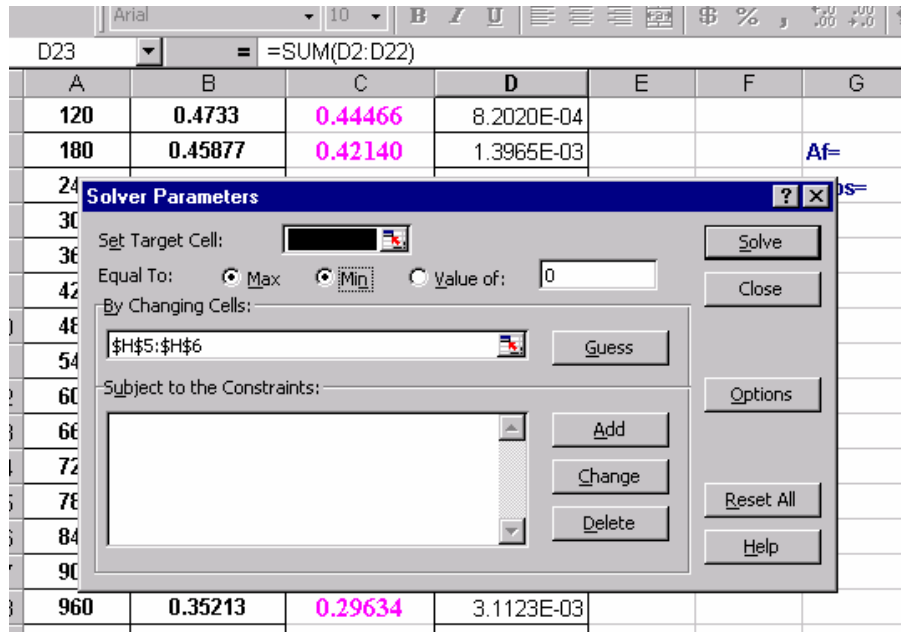
Type into "By Changing Cells: \$H\$5 and \$H\$6.



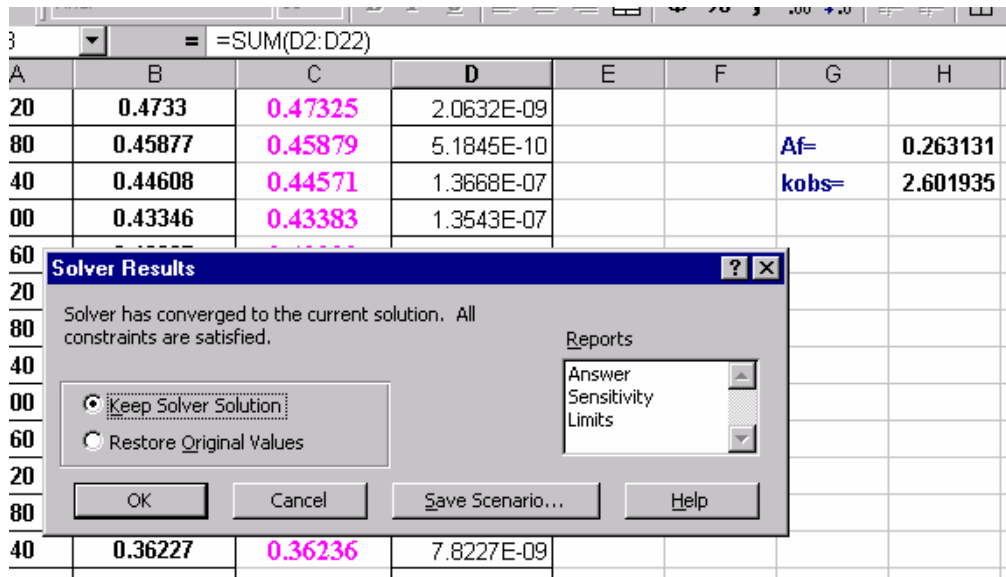
On **Solver Parameters** click on **Options**. Change **Max Time** to **1200 seconds** (kinetics run time). Click **OK**.



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:

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

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.

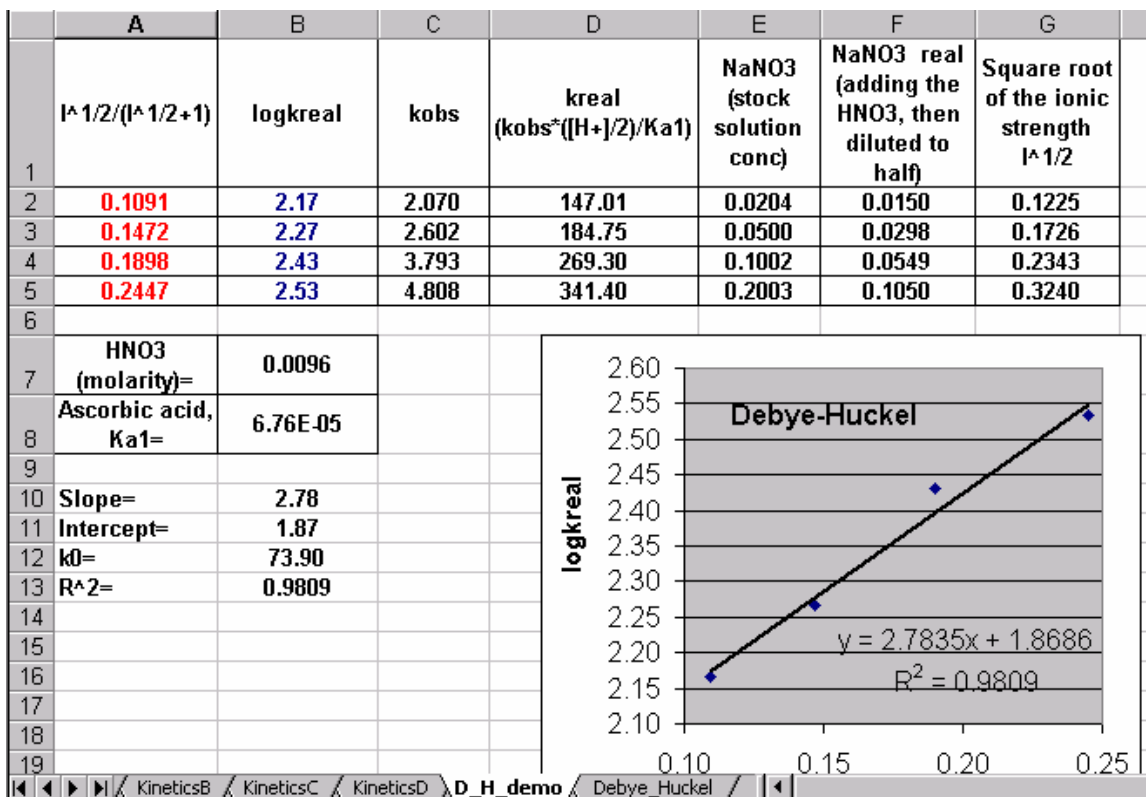
In the “Kinetics” hand-out, the **Debye-Hückel** equation is defined as:

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

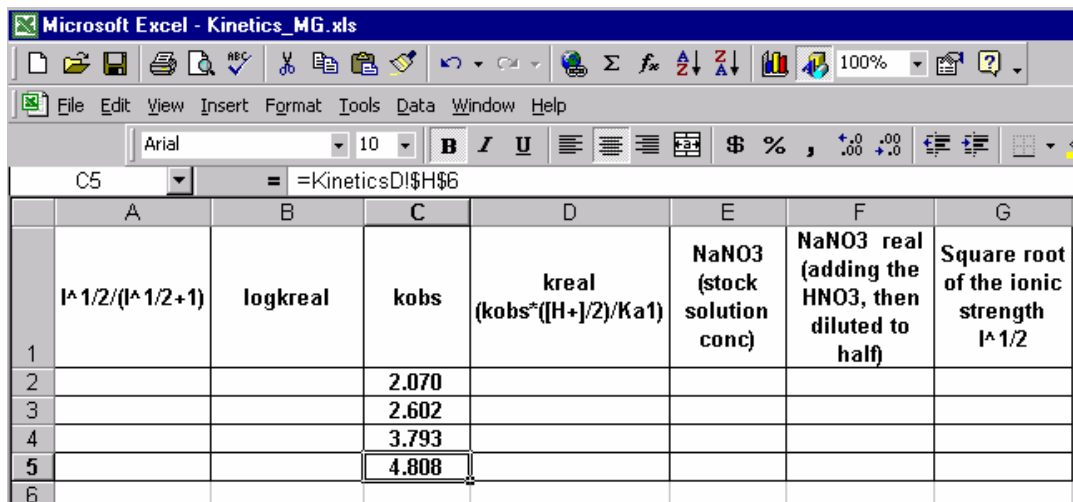
where  $k_{\text{real}}$  is given by equation (4):

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

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:



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”.



- Place the  $\text{HNO}_3$  molarity in cell B7 and the acidity constant for ascorbic acid ( $K_{a1}=6.76 \times 10^{-5}$ ) in cell B8.

|   | A                               | B        | C     | D   | E  | F   | G  |
|---|---------------------------------|----------|-------|---|--|---|--|
| 1 | $I^{1/2}/(I^{1/2}+1)$           | logkreal | kobs  | kreal<br>( $k_{obs} * ([H^+]/2) / K_{a1}$ ) | NaNO <sub>3</sub><br>(stock<br>solution<br>conc) | NaNO <sub>3</sub> real<br>(adding the<br>HNO <sub>3</sub> , then<br>diluted to<br>half) | Square root<br>of the ionic<br>strength<br>$I^{1/2}$ |
| 2 |                                 |          | 2.070 |   |  |   |  |
| 3 |                                 |          | 2.602 |   |  |   |  |
| 4 |                                 |          | 3.793 |   |  |   |  |
| 5 |                                 |          | 4.808 |   |  |   |  |
| 6 |                                 |          |       |   |  |   |  |
| 7 | HNO <sub>3</sub><br>(molarity)= | 0.0096   |       |   |  |   |  |
| 8 | Ascorbic acid,<br>Ka1=          | 6.76E-05 |       |   |  |   |  |
| 9 |                                 |          |       |   |  |   |  |

- 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  $\text{HNO}_3$  in the UV cuvette is half the concentration of the  $\text{HNO}_3$  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.

|   | A                               | B        | C     | D   | E  | F   | G  |
|---|---------------------------------|----------|-------|---|--|---|--|
| 1 | $I^{1/2}/(I^{1/2}+1)$           | logkreal | kobs  | kreal<br>( $k_{obs} * ([H^+]/2) / K_{a1}$ ) | NaNO <sub>3</sub><br>(stock<br>solution<br>conc) | NaNO <sub>3</sub> real<br>(adding the<br>HNO <sub>3</sub> , then<br>diluted to<br>half) | Square root<br>of the ionic<br>strength<br>$I^{1/2}$ |
| 2 |                                 |          | 2.070 | 147.01                                      |  |   |  |
| 3 |                                 |          | 2.602 | 184.75                                      |  |   |  |
| 4 |                                 |          | 3.793 | 269.30                                      |  |   |  |
| 5 |                                 |          | 4.808 | 341.40                                      |  |   |  |
| 6 |                                 |          |       |   |  |   |  |
| 7 | HNO <sub>3</sub><br>(molarity)= | 0.0096   |       |   |  |   |  |
| 8 | Ascorbic acid,<br>Ka1=          | 6.76E-05 |       |   |  |   |  |
| 9 |                                 |          |       |   |  |   |  |

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<br>( $k_{obs} \cdot ([H^+]/2)/K_{a1}$ ) | NaNO3<br>(stock<br>solution<br>conc) | NaNO3 real<br>(adding the<br>HNO3, then<br>diluted to<br>half) | Square root<br>of the ionic<br>strength<br>$I^{1/2}$ |
| 1 |                        |          |       |   |                                      |  |  |
| 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<br>(molarity)=    | 0.0096   |       |   |                                      |  |  |
| 8 | Ascorbic acid,<br>Ka1= | 6.76E-05 |       |   |                                      |  |  |
| 9 |                        |          |       |   |                                      |  |  |

6. To calculate in column A  $I^{0.5}/(I^{0.5}+1)$ , the x-axis variable:
- First fill in NaNO<sub>3</sub> **stock solution** molarities. In my experiments I used the values printed in columns E2:E5.
  - Second, in column F2:F5 calculate the real NaNO<sub>3</sub> + HNO<sub>3</sub> 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  |
|---|------------------------|----------|-------|---|--------------------------------------|--|--|
| 1 | $I^{1/2}/(I^{1/2}+1)$  | logkreal | kobs  | kreal<br>( $k_{obs} * ([H^+]/2)/K_{a1}$ ) | NaNO3<br>(stock<br>solution<br>conc) | NaNO3 real<br>(adding the<br>HNO3, then<br>diluted to<br>half) | Square root<br>of the ionic<br>strength<br>$I^{1/2}$ |
| 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<br>(molarity)=    | 0.0096   |       |   |                                      |  |  |
| 8 | Ascorbic acid,<br>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.

|    | A                      | B        | C     | D   | E                                    | F  | G  |
|----|------------------------|----------|-------|---|--------------------------------------|--|--|
| 1  | $I^{1/2}/(I^{1/2}+1)$  | logkreal | kobs  | kreal<br>( $k_{obs} * ([H^+]/2)/K_{a1}$ ) | NaNO3<br>(stock<br>solution<br>conc) | NaNO3 real<br>(adding the<br>HNO3, then<br>diluted to<br>half) | Square root<br>of the ionic<br>strength<br>$I^{1/2}$ |
| 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<br>(molarity)=    | 0.0096   |       |   |                                      |  |  |
| 8  | Ascorbic acid,<br>Ka1= | 6.76E-05 |       |   |                                      |  |  |
| 9  |                        |          |       |   |                                      |  |  |
| 10 | Slope=                 | 2.78     |       |   |                                      |  |  |
| 11 | Intercept=             | 1.87     |       |   |                                      |  |  |
| 12 | k0=                    | 73.90    |       |   |                                      |  |  |
| 13 | R^2=                   | 0.9809   |       |   |                                      |  |  |

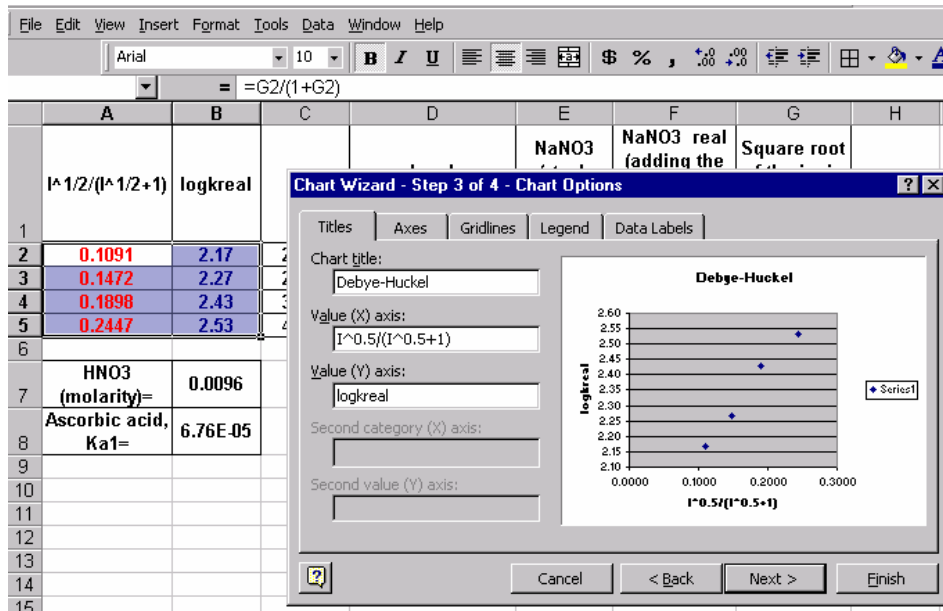
7. The last step consists of the **Debye-Hückel** plot.
  - Highlight columns A2:B5. Click on **Insert**, then **Chart...**

|    | A                      | B        | C     | D                                       |
|----|------------------------|----------|-------|---|
| 1  | $I^{1/2}/(I^{1/2}+1)$  |          |       | kreal<br>$\text{obs}^*([H^+]/2)/K_{a1}$ |
| 2  | 0.1091                 |          |       | 147.01                                  |
| 3  | 0.1472                 |          |       | 184.75                                  |
| 4  | 0.1898                 |          |       | 269.30                                  |
| 5  | 0.2447                 | 2.53     | 4.808 | 341.40                                  |
| 6  |                        |          |       |   |
| 7  | HNO3<br>(molarity)=    | 0.0096   |       |   |
| 8  | Ascorbic acid,<br>Ka1= | 6.76E-05 |       |   |
| 9  |                        |          |       |   |
| 10 |                        |          |       |   |

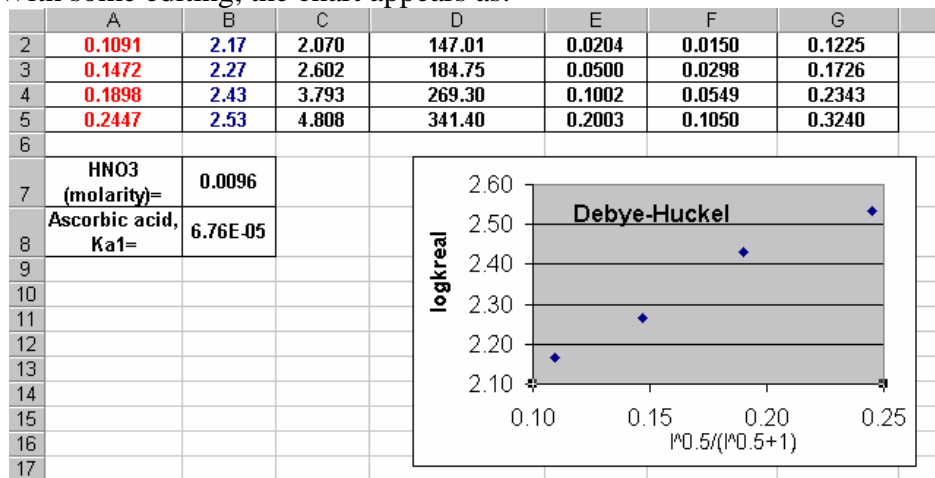
- In the **Chart Wizard** window **Step 1**, choose **Chart type: XY(Scatter)**; and the highlighted **Chart sub-type**.

|    | A                      | B        | C  |
|----|------------------------|----------|----|
| 1  | $I^{1/2}/(I^{1/2}+1)$  | logkreal | k  |
| 2  | 0.1091                 | 2.17     | 2. |
| 3  | 0.1472                 | 2.27     | 2. |
| 4  | 0.1898                 | 2.43     | 3. |
| 5  | 0.2447                 | 2.53     | 4. |
| 6  |                        |          |    |
| 7  | HNO3<br>(molarity)=    | 0.0096   |    |
| 8  | Ascorbic acid,<br>Ka1= | 6.76E-05 |    |
| 9  |                        |          |    |
| 10 |                        |          |    |
| 11 |                        |          |    |
| 12 |                        |          |    |
| 13 |                        |          |    |
| 14 |                        |          |    |
| 15 |                        |          |    |

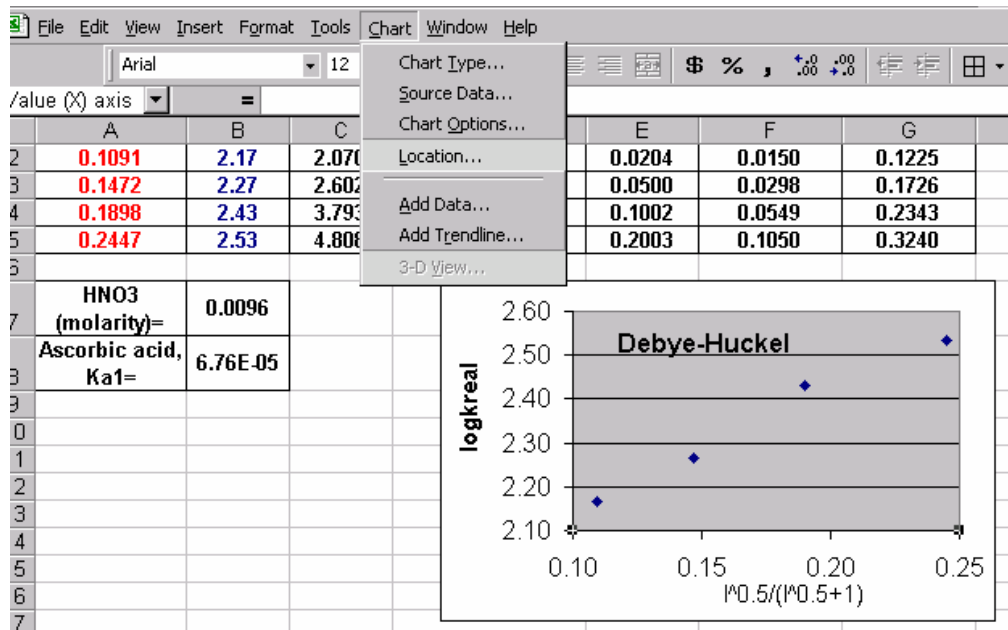
- Click next to steps 2 and 3. In step 3 fill in the **chart title**, **value (X) axis** and **value (Y) axis** respectively.



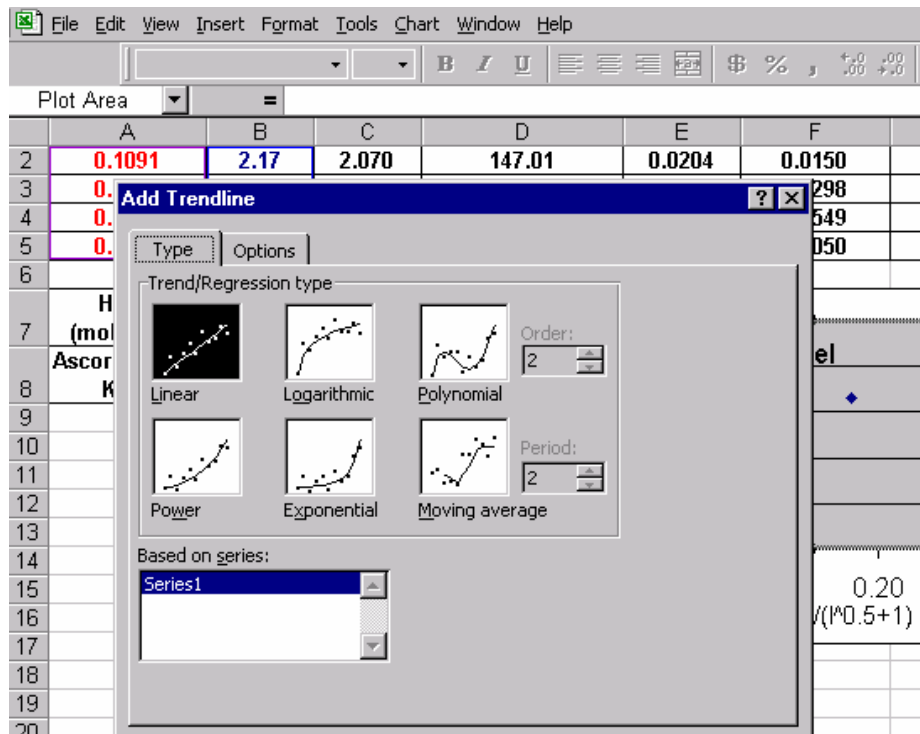
- Click **Next** and then **Finish**.
- With some editing, the chart appears as:



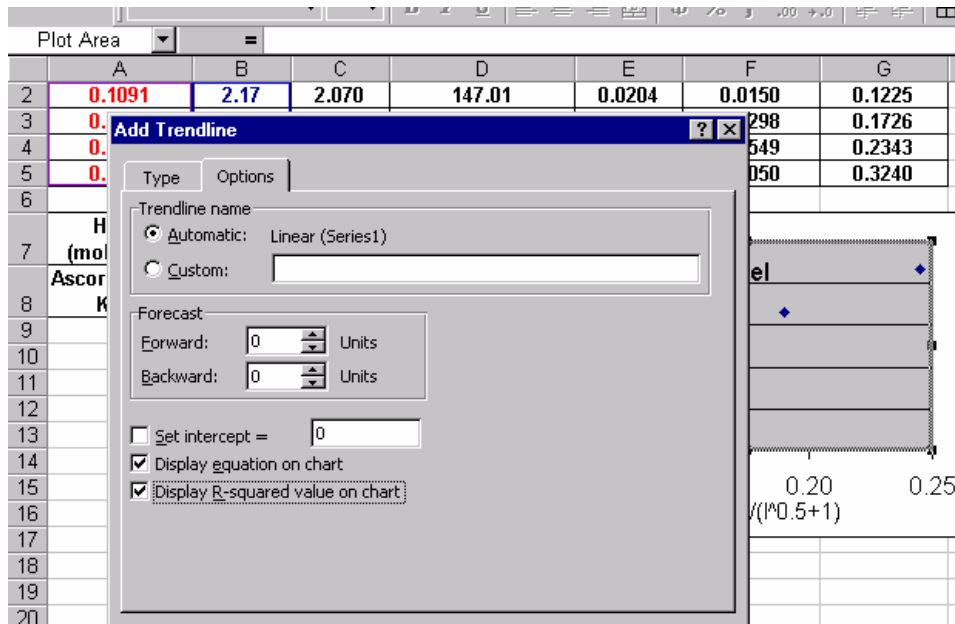
- The least square straight line is added on the graph, by clicking on **Chart**, then **Add trendline**.



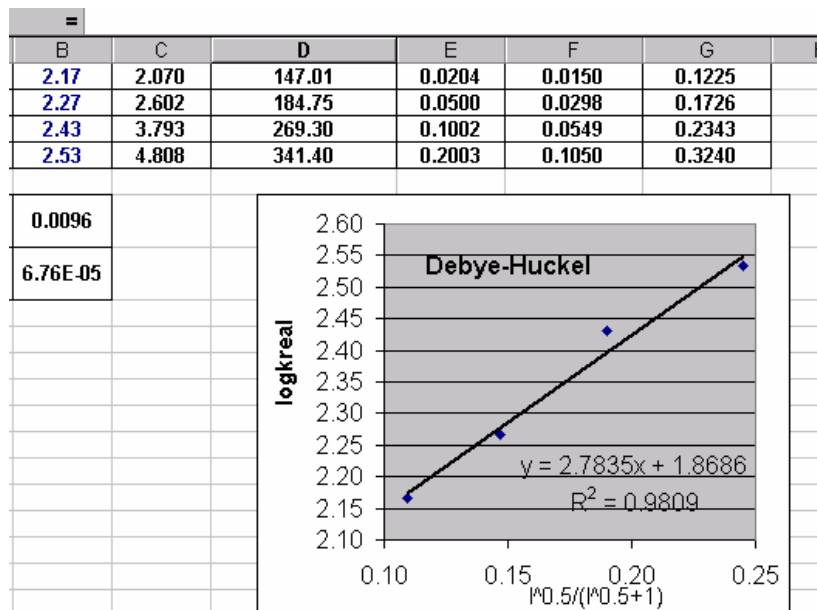
Under **Type: Trend/Regression type**, choose **Linear**.



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



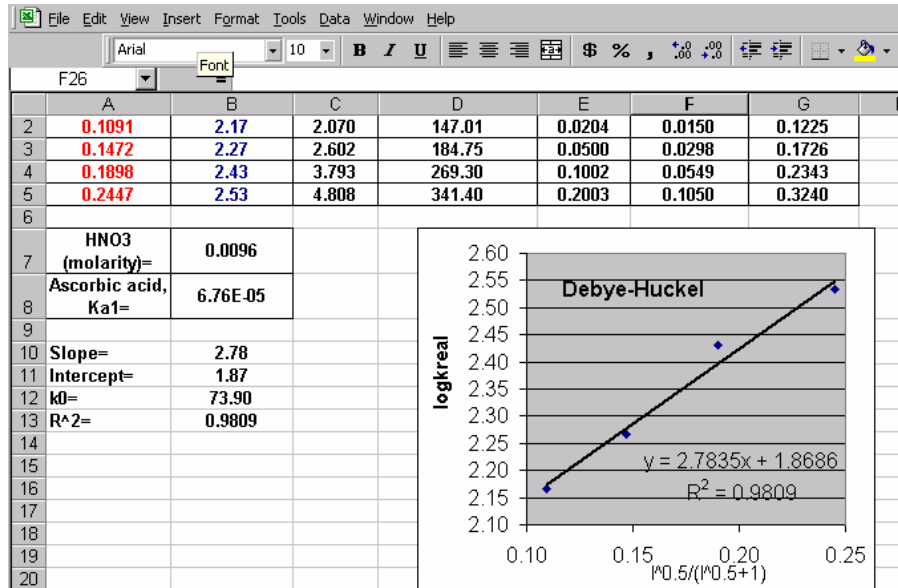
- The least square straight line below has the equation:  $y = 2.7835x + 1.8686$  and  $R^2=0.9809$  (satisfactory, however I am confident that 5.310 students will get a better  $R^2$ ).



- To compute the slope ( $1.02 \cdot Z_1 \cdot Z_2$ ) and intercept ( $k_0$  the rate constant at  $I=0$ ), and  $R^2$ , 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=



- Finally print copies of all 5 sheets for inclusion with your report.