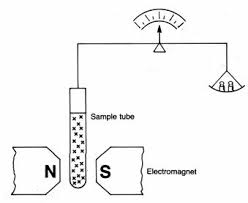
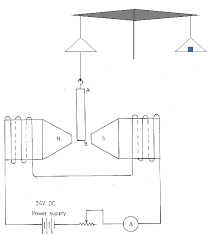
**Magnetic properties of transition metal complex**

The Gouy balance, invented by Louis Georges Gouy, is a device for measuring the magnetic susceptibility of a sample.

**Procedure**

The Gouy balance measures the apparent change in the mass of the sample as it is repelled or attracted by the region of a high magnetic field between the poles. Some commercially available balances have a port at their base for this application. In use, a long, cylindrical sample to be tested is suspended from a balance, partially entering between the poles of a magnet. The sample can be in solid or liquid form and is often placed in a cylindrical container such as a test tube. Solid compounds are generally ground into fine powder to allow for uniformity amongst the sample. The sample is suspended between the magnetic poles through an attached thread or string. The experimental procedure requires two separate readings to be performed. An initial balance reading is performed on the sample of interest without a magnetic field (m a). A subsequent balance reading is taken with an applied magnetic field (mb). The difference between these two readings relates to the magnetic force on the sample (mb – ma).

## Concept

The apparent change in mass from the two balance readings is a result of the magnetic force on the sample. The magnetic force is applied across the gradient of a strong and weak magnetic field. A sample with a paramagnetic compound will be pulled down towards the magnetic, and provide a positive difference in apparent mass mb – ma. Diamagnetic compounds can either exhibit no apparent change in weight or a negative change as the sample is slightly repelled by the applied magnetic field. With a paramagnetic sample, the magnetic induction is stronger than the applied field and magnetic susceptibility is positive. A diamagnetic sample has a magnetic induction much weaker than the applied field, and a respective negative magnetic susceptibility. The following mathematical equation relates the apparent change in mass to the volume susceptibility of the sample:

**Force = (mb – ma)g =  (K2 – K1)AH2**

* mb – ma = apparent difference in mass
* g = gravitational acceleration
* K1 = volume susceptibility of sample
* K2 = volume susceptibility of medium, usually air and of negligible value
* H = applied magnetic field
* A = area of the sample tube

## Instrument

In a practical device, the whole assembly of balance and magnet is enclosed in a glass box to ensure that the weight measurement is not affected by air currents. The sample can also be enclosed in a thermostat in order to make measurements at different temperatures. Since it requires a large and powerful electromagnet, the Gouy balance is a stationary instrument permanently set up on a bench. The apparatus is often placed on a marble balance table in a non-ventilated room to minimize the vibrations and disruption from the environment. The stationary magnetic of a Gouy balance is often an electromagnet connected to a power source since balance recordings with and without the applied magnetic field are required of the procedure.

**Complexes of transition metal ions**

The effective magnetic moment for a compound containing a transition metal ion with one or more unpaired electrons depends on the total orbital and spin angular momentum of the unpaired electrons, and, respectively. "Total" in this context means "vector sum". In the approximation that the electronic states of the metal ions are determined by Russell-Saunders coupling and that spin-orbit coupling is negligible, the magnetic moment is given by

\mu_{\text{eff}} = \sqrt{\vec{L}(\vec{L}+1)+ 4\vec{S}(\vec{S}+1)} \mu_B

### Spin-Only Formula and Orbital Contribution To Magnetic Moment:

Orbital angular momentum is generated when an electron in an orbital of a degenerate set of orbitals is moved to another orbital in the set by rotation. In complexes of [high symmetry](https://en.wikipedia.org/wiki/Molecular_symmetry), certain rotations are not possible. In that case, the orbital angular momentum is said to be "quenched" and \vec{L} is smaller than might be expected (partial quenching), or zero (complete quenching). There is complete quenching in the following cases. Note that an electron in a degenerate pair of dx2–y2 or dz2orbitals cannot rotate into the other orbital because of symmetry.

**Quenched orbital angular momentum**

|  |  |  |
| --- | --- | --- |
| dn | Octahedral | Tetrahedral |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  |  | High spin | Low spin |  |
| d1 |  |  |  | e1 |
| d2 |  |  |  | e2 |
| d3 | t2g3 |  |  |  |
| d4 |  | t2g3eg1 |  |  |
| d5 |  | t2g3eg2 |  |  |
| d6 |  |  | t2g6 | e3t23 |
| d7 |  |  | t2g6eg1 | e4t23 |
| d8 | t2g6eg2 |  |  |  |
| d9 | t2g6eg3 |  |  |  |

t2g, t2 = (dxy, dxz, dyz). eg, e = (dx2–y2, dz2).

When orbital angular momentum is completely quenched,  the paramagnetism can be attributed to electron spin alone. The total spin angular momentum is simply half the number of unpaired electrons and the spin-only formula results.

**\mu_{\text{eff}}= \sqrt{n(n+2)} \mu_B**

where n is the number of unpaired electrons. The spin-only formula is a good first approximation for high-spin complexes of first-row transition metals

.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Ion | Ti3+ | V4+ | Cu2+ | V3+ | Ni2+ | V2+ | Cr2+ | Co2+ | Mn4+ | Cr2+ | Fe2+ | Mn2+ | Fe3+ |
| No.of.unpaired electrons | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 3 | 4 | 4 | 5 | 5 |
| Spin only/μB | 1.73 |  |  | 2.83 |  | 3.87 |  |  |  | 4.90 |  |  | 5.97 |
| observed | 1.73 | 1.68-1.78 | 1.70-2.20 | 2.75-2.85 | 2.8-3.5 | 3.80-3.90 | 3.70-3.90 | 5.3-5.0 | 3.80-4.0 | 4.75-4.90 | 5.1-5.7 | 5.65-6.1 | 5.7-6.0 |

The small deviations from the spin-only formula may result from the neglect of orbital angular momentum or of spin-orbit coupling. For example, tetrahedral d3, d4, d8 and d9 complexes tend to show larger deviations from the spin-only formula than octahedral complexes of the same ion, because "quenching" of the orbital contribution is less effective in the tetrahedral case.

**Example**

**Account for the magnetic moments of (Et4N)2[NiCl4] recorded at 80 and 300 K, 3.25B.M. & 3.89 B.M. respectively**

Ni2+ is a d8 metal ion.

The formula suggests a 4 coordinate complex and we can assume that the complex is tetrahedral with a d electron configuration of e4 t2 4 therefore the spin-only magnetic moment can be calculated as 2.83 BM Why did we ignore the possibility of it being square-planar?

The free ion Russell-Saunders ground term is 3F (L=3 and S=1) which will give rise to the lowest energy T term in a tetrahedral field and hence the resultant magnetic moment is expected to be temperature dependent and have a direct orbital contribution.

The observed values may be quite different then to the calculated spin-only magnetic moment.

The value of µS+L can be calculated as: µS+L = √ 4S(S+1)+L(L+1) = √8+12 = √20 = 4.47 B.M.

If you use the spin-only formula µs = √ n(n+2) = √ 8 = 2.8 BM

**Given that the spin-only magnetic moment for the complex [Cr(en)3]Cl3**

The spin-only magnetic moment is given by quantum mechanics as μ = √[n(n+2)] BM =

μ = √15 = 3.87 BM

**The Observed Magnetic Moment of [Mn(NCS)6]4- Is 6.06 B.M. Predict The Electronic Configurations.**

Mn in this complex is Mn(II) d5. There are two possibilities of an electronic configuration for this octahedral species, namely low-spin t2g5 with one unpair electron & t2g3eg2 with five unpaid electrons. The observed magnetic moment is close to the spin-only value

Therefore, the configuration should be t t2g3eg2 (high spin)

**Thermodynamic and Kinetic Aspect of Meta Complexes**

The metal complex is called as stable complex. This means that complex exists and under suitable conditions it may be stored for a longer time. Further it can be generalized that, a complex may be quite stable to one reagent and it may decompose readily in presence of another regent. The stability also depends upon the action of heat or light on a compound. While studying the formation of complexes in solution, there exist two types of stability of complex.

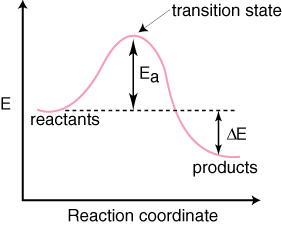
* 1. **Thermodynamic Stability**
  2. **Kinetic Stability**

1. **Thermodynamic Stability:**

It can be defined as the measure of the extent to which the complex will form or it will be transformed into another species under certain conditions when the system has reached equilibrium. This type of stability deals with metal-ligand bond energies, stability constant etc.

1. **Kinetic Stability:**

It deals with the speed with which transformation leading to the attaining the equilibrium take place, this is concerned with the rates and mechanisms of chemical reaction such as substitution, racemisation, electron or group transfer reactions etc. According to the kinetic view, we may use the terms inert or labile complexes instead of stable or unstable.

****

**Stepwise formation constants and overall formation constant**

Jannik Bjerrum developed the first general method for the determination of stability constants of metal-ammine complexes in 1941. The reasons why this occurred at such a late date, nearly 50 years after Alfred Werner had proposed the correct structures for coordination complexes, have been summarised by Beck and Nagypál. The key to Bjerrum's method was the use of the then recently developed glass electrode and pH meter to determine the concentration of hydrogen ionsin solution. Bjerrum recognised that the formation of a metal complex with a ligand was a kind of acid-base equilibrium: there is competition for the ligand, L, between the metal ion, Mn+, and the hydrogen ion, H+. This means that there are two simultaneous equilibria that have to be considered. In what follows electrical charges are omitted for the sake of generality. The two equilibria are

H + L  HL

M + L  ML

The formation of a complex between a metal ion, M, and a ligand, L, is in fact usually a substitution reaction. For example, in aqueous solutions, metal ions will be present as aqua-ions, so the reaction for the formation of the first complex could be written as

\mathrm{[M(H_{2}O)_n] + L \leftrightharpoons [M(H_{2}O)_{n-1}L] + H_{2}O}

\beta'=\mathrm{\frac{[M(H_2O)_{n-1}L] [H_2O]} {[M(H_2O)_n] [L] }}

[L] Should be read as "the concentration of L" and likewise for the other terms in square brackets. The expression can be greatly simplified by removing those terms which are constant. The number of water molecules attached to each metal ion is constant. In dilute solutions the concentration of water is effectively constant. The expression becomes.

\beta =\mathrm{\frac{[ML] } {[M] [L] }}.

Following this simplification a general definition can be given, For the general equilibrium

In the laboratory course, it will have been pointed out that the "stability of a complex in solution" refers to the degree of association between the two species involved in the state of equilibrium. Qualitatively, the greater the association, the greater the stability of the compound. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have are action of the type:

M    +  4L    ⇄     ML4

Then the larger the stability constant, the higher the proportion of ML4 that exists in the solution. Free metal ions rarely exist in solution so that M, will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

1. M + L ⇄ ML               K1 = [ML [L]] / [M]   
2. ML + L ⇄ ML2           K2 = [ML2] / [ML] [L]   
3. ML2 + L ⇄ ML3         K3 = [ML3] / [ML2] [L]   
4. ML3 + L ⇄ ML4         K4 = [ML4] / [ML3] [L] 

where K1, K2 etc. are referred to as "stepwise stability constants".   
Alternatively, we can write the "Overall Stability Constant" denoted by βn thus:

M   +  4L   ⇄   ML4           β4 = [ML4]/ [M] [L]4

***Relationship between The stepwise and overall stability constants are as follows:***

β4=K1.K2.K3.K4 or more generally,  
βn=K1.K2.K3.K4--------------Kn

Or

This equation evident that overall stability constants is equal to stepwise stability constants.

**Consider the four steps involved in the formation of the cuprammonium ion Cu(NH3)42+:**

**STEP 1:**     Cu2++NH3 ⇄  Cu(NH3)2+   
where K1   =     [Cu(NH3)2+]

                          [Cu2+][NH3]  
**STEP 2:**     Cu(NH3)2+ + NH3 ⇄  Cu(NH3)2+2  
where K2  =       [Cu(NH3)22+]  
                        [Cu(NH3)2+][NH3]  
**STEP 3:**     Cu(NH3)22+ + NH3  ⇄  Cu(NH3)32+  
where K3  =       [Cu(NH3)32+]  
                       [Cu(NH3)22+][NH3]  
**STEP 4:**     Cu(NH3)32+ + NH3 ⇄  Cu(NH3)42+  
where K4  =       [Cu(NH3)42+]  
                        [Cu(NH3)32+][NH3]  
  
where the {K} constants are the stepwise stability constants.  
In terms of overall stability constant:  
  
β4   =     [Cu(NH3)42+]  
              [Cu2+][NH3]4

Hence

β4=K1.K2.K3.K4

The addition of the four ammine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

logK1 =4.0, logK2 =3.2, logK3 =2.7, logK4 =2.0 or logβ4 =11.9

## Main Factors Affecting Stability of Complexes:

The main factors affecting stability of complexes  are:

1. Charge on the metalion.
2. Principal quantum number.
3. Nature of ligands
4. Chelation
5. Macro cyclic ligands
6. Hardness and softness
7. Surrounding conditions

**1. Charge on the metal ion:**

The effect of this factor on stability of complexes can be explained on the basis of crystal field theory. For a given ligand, greater the charge on the metal ion greater is the magnitude of crystal field splitting which ultimately affects the stability of the complex.

Example,

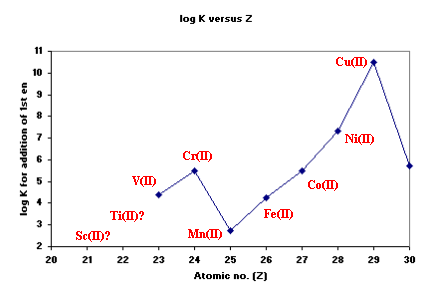
**Ions                            Ligands                                 CFSE (∆oin cm-1)**

     V2+                              6H2O                                      12600

            V3+                              6H2O                                      17700

# Irving–Williams series

# The Irving-Williams Series refers to the relative stabilities of complexes formed by transition metals. In 1953 [Harry Irving](https://en.wikipedia.org/wiki/Harry_Irving_(chemist)) and [Robert Williams](https://en.wikipedia.org/wiki/Robert_Williams_(chemist)) observed that the [stability](https://en.wikipedia.org/wiki/Stability_constants_of_complexes) of complexes formed by [divalent](https://en.wikipedia.org/wiki/Divalent) first-row [transition metal](https://en.wikipedia.org/wiki/Transition_metal) ions generally increase across the period to a maximum stability at copper : Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)



## Explanation

Three explanations are frequently used to explain the series:

1. The [ionic radius](https://en.wikipedia.org/wiki/Ionic_radius) is expected to decrease regularly from Mn(II) to Zn(II). This is the normal periodic trend and would account for the general increase in stability.
2. The [Crystal Field Stabilization Energy](https://en.wikipedia.org/wiki/Crystal_Field_Stabilization_Energy) (CFSE) increases from zero for Mn(II) to a maximum at Ni(II). This makes the complexes increasingly stable. CFSE for Zn(II) is zero.
3. Although the CFSE of Cu(II) is less than that of Ni(II), octahedral Cu(II) complexes are subject to the [Jahn-Teller effect](https://en.wikipedia.org/wiki/Jahn-Teller_effect" \o "Jahn-Teller effect), which affords octahedral Cu(II) complexes additional stability.

However, none of the above explanations can satisfactorily explain the success of the Irving–Williams series in predicting the relative stabilities of transition metal complexes. A recent study of metal-thiolate complexes indicates that interplay between covalent and electrostatic contributions in metal-ligand binding energies might result in Irving–Williams series

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Some actual CFSE values for octahedral complexes of first-row transition metals (∆oct) are 0.4Δ (4 Dq) for iron, 0.8Δ (8 Dq) for cobalt and 1.2Δ (12 Dq) for nickel. When the stability constants are quantitatively adjusted for these values they follow the trend that is predicted, in the absence of crystal field effects, between manganese and zinc. This was an important factor contributing to the acceptance of crystal field theory, the first theory to successfully account for the thermodynamic, spectroscopic and magnetic properties of complexes of the transition metal ions and precursor to [ligand field theory](https://en.wikipedia.org/wiki/Ligand_field_theory).

**2. Principal quantum number.**

Even though the metal ions have same charge, if the principal quantum numbers are different, then the magnitude of CFSE will be different and hence stability will be different.

Example,

**Principal Q.No.        Ions                     Ligands                                 CFSE(∆oin cm-1)**

           d6                  d6-Co3+                       6H2O                                      18600

           d6                 d6-Rh3      6H2O                                      20600

**3.  Nature of ligands:**

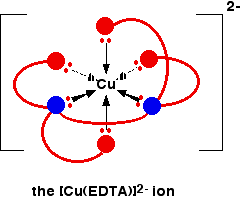
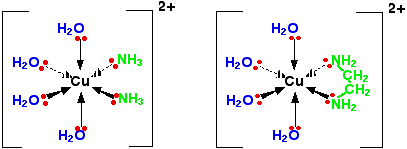
Properties of ligands like size, charge, dipole moment, polarizability and π-bonding capacity will affect the CFSE and stability of complexes. Smaller the size of the ligand, greater is the approach of the ligand with the metal ion and greater is the crystal field splitting. Larger the charge on the anion, greater the polarizability and greater is the magnitude of crystal field splitting.

1. **Chelation:**

**The larger the number of the chelate ring in complex, greater is its stability.**

**The stability of complex is also depends on number of atom present in a ring.**

**It has been proved that the most stable chelate are 5 and 6 – member one. It is found that 5-memerd chelate is frequently more stable than 6-memmberd ring. On the other hand 6-memberd chelates are more stable than 5-memberd chelates of heterocyclic ligand. For example acetyl acetone complexes of the metal ions are more stable than the corresponding ethylene diamine complexes which contain only 5-memberd chelate complex ring.**



Chelation increases stability. This is because the entropy factor is favorable in case of chelate complexes

For example [Cd(en)2]2+ is more stable than [Cd(MeNH2)4]2+ since in the former there is chelation.

**5.  Macro cyclic ligands:**

The increased stability of complexes due to macro cyclic ligands is termed as “macro cyclic effect”. The reason for this effect is mainly entropy and enthalpy factors. The macro cyclic ligands have cavities of particular size and hence selectively form strong complexes with metal ions of corresponding sizes.

For example, 18-crown-6 forms stronger complex with potassium ion than with sodium ion

**6. Hardness and softness:**

Stability of complexes depends also on hardness and softness of the metal and the ligands. As per HSAB theory hard acids prefer hard bases and soft acids prefer soft bases.

For example, Ni2+ is a hard acid and hence it forms stable complex with NH2 and not with soft ligand PH3.But Pd2+ being soft acid forms stable complex with PH3 rather than with NH2.

1. **Surrounding conditions:**

Even though the above factors outline the stability of complexes, many complexes which are stable under particular conditions may not be stable under some other conditions. For example [Co(NH3)6]3+  is unstable in an acidic solution but is stable in water under neutral conditions.

[Co(NH3)6]3+ + 6H3O+ → [Co(H2O)6]3+ + 6NH4+

Hence when somebody says a complex is stable one must always ask, “Under what conditions?” The conditions may be heat, light, acidity or basicity.

**Determination of Composition of Complexes Using Job's Method**

An alternative to the [method of continuous variations](http://community.asdlib.org/imageandvideoexchangeforum/2013/07/29/method-of-continuous-variations/) for determining the stoichiometry of metal-ligand complexes is the mole-ratio method in which the amount of one reactant, usually the moles of metal, is held constant, while the amount of the other reactant is varied. Absorbance is monitored at a wavelength where the metal–ligand complex absorbs. The illustrations below show typical results: (a) the mole-ratio plot for the formation of a 1:1 complex in which the absorbance is monitored at a wavelength where only the complex absorbs; (b) the mole-ratio plot for a 1:2 complex in which all three species—the metal, the

Ligand, and the complex—absorb at the selected wavelength; and (c) the mole-ratio plot for the step-wise formation of ML and ML2.

**Overview**

In this experiment, you prepared nine different mixtures of solutions of iron(III) and 5-sulfosalicylic acid (SSA), and measured the % Transmittance of these mixtures with the Spectronic 20 spectrophotometer (the product of the reaction is colored purple). The mixtures were prepared systematically, from the first mixture (in which there was a small amount of iron and a large amount of SSA present) to the last mixture (in which there was a large amount of iron but only a small amount of SSA present). You calculated the absorbance of each solution (from its % Transmittance) and then made a graph in which you plotted these absorbances versus the mole fraction SSA for each solution. The graph should show a maximum, which represents the molar ratio in which iron(III) and SSA react

When two chemical substances react with each other, they react in a certain fixed, definite mole ratio (the stoichiometry of the reaction. When you prepare the set of systematically-varied mixtures of SSA and iron(III), only one of the mixtures reflects the correct mole ratio for the substances to react to the maximum extent possible. The mixture in which the substances have reacted to the maximum extent possible has the deepest purple color (largest amount of product formed).

**Calculations**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Test tube | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
| %T | 61.0% | 39.4% | 27.7% | 22.1% | 19.9% | 22.0% | 27.9% | 40.1% | 60.5% |

Suppose the data had been recorded for the experiment 19.9%.  % Transmittance of Solutio

**A. Calculation of Absorbance of Solution in Test tube #3**

It is the absorbance of a colored solution which is directly related to the concentration of the colored species in the solution. The absorbance is calculated from the measured % Transmittance (a derivation follows):**Absorbance = -log (%T/100) = log (100/%T) = log (100) - log (%T) = 2 - log(%T)**

Be very careful how you use your calculator for this calculation. Some calculators require different keystrokes for using the logarithm of a number in a calculation. Absorbance values should come out to be between 0 and 2: if you get any other sort of number, you are using your calculator incorrectly!!

For solution #3, the % Transmittance was 27.7%. The absorbance corresponding to this is

Absorbance = 2- log(%T) = 2 - log(27.7%) = 2 - 1.442 = 0.558

**B. Calculation of the moles of Fe+3 is Test Tube #3**

To calculate the number of moles of iron(III) present in Test tube #3, you need two bits of information. You need to know the volume of the stock Fe(III) taken as well as the concentration of the Fe(III) stock solution. At the bottom is the volume of iron(III) that was to be placed into each of the test tubes. For Test Tube #3, you should have used 3.00 mL of the iron(III) stock solution. You should have recorded the exact concentration of the iron(III) solution from the bottle label on the data page (For my data above, the concentration of iron(III) is 1.65 × 10-3M (M means moles of Fe3+ per liter).Given this, calculate the number of moles of Fe(III) in Test Tube #3,

**C. Calculation of the moles of SSA in Test Tube #3**

This calculation is similar to that in Part B, only for SSA in Test Tube #3 (rather than Fe3+). At a table which indicates the amount of SSA solution you were supposed to have used for each mixture: for Test Tube #3, you should have used 7.00 mL. You should have recorded the concentration of the stock SSA solution in your data: for my table of data above, the concentration of SSA is 1.71 × 10-3 M

Given this, calculate the number of moles of SSA in Test Tube #3,

**D. Calculation of mole fraction of SSA in Test Tube #3**

The mole fraction of a given component in a mixture represents the number of moles present of the component of interest, divided by the total number of moles of all components present. We have a mixture containing 4.95 × 10-6 moles of Fe3+ and 1.20 × 10-5 moles of SSA. Using this data.

**E. Calculation of mole fraction Fe(III) in Test Tube #3**

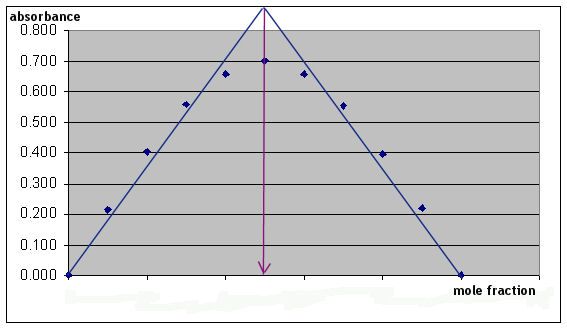
This calculation is based on the same data as in Part D above, only in terms of Fe(III) rather than SSA:

***X*Fe = (1 - *X*SSA) = (1- 0.708) = 0.292.**

**A. Summary of Results**

The table just summarizes all your results for Absorbance and Mole Fraction for each of your solutions. The calculations are done exactly as illustrated above, only substituting the correct volumes of Fe and SSA for the individual solutions.

**B. Results from Graph**

When plotting your graph, When you plot your nine data points, you should notice that there is a group of ascending data points and a group of descending data points. In addition to drawing a smooth curve through the data points, you should plot two lines on your graph: one which encompasses the ascending data points and one which encompasses the descending data points. The intersection of these two lines more easily shows the location of the maximum point on your graph (relative to the mole fraction, horizontal scale).

Here is a crude example of the general shape