CHAPTER ONE

Introduction

1.1-Transition elements:

Humans have been aware of transition elements for thousands of years. For example the use of copper predate 500 BC and iron 1200 BC, but chromium has been discovered in1797 AC (Chris, 2001). Titanium was discovered in 1791AC. (Bentor, (2015), and zirconium in 1789 AC. (Forrest, (1981).

Transition metals may be strictly defined as those have partly filled d or f orbitals. Here the definition adopted is slightly broader and include also elements that have partly filled d or f shell in one of their commonly occurring oxidation states, this means that the coinage, Cu , Ag and Au treated as transition metals , since Cu^{+2} has $3d^9$ configuration , Ag^{+2} a $4d^9$ configuration and Au^{+3} a $5d^8$ configuration (Cotton & Wilkinson, 1972).

Transition elements are metallic elements that serve as a bridge or transition between the two sides of periodic table S-block and P-block (Petrucci, Harwood & Herring., 2002)

The large number of transition elements is subdivided into three main groups: (a) the main transition elements or d-block elements, (b) the lanthanide elements and (c) the actinide elements (Cotton & Wilkinson, 1972).

The main transition group or d-block includes these elements that have partially filled d-shells only, thus the elements scandium with the outer electronic configuration $4s^2$ $3d^1$ is the lightest member, the eight succeeding elements Ti ,V , Cr , Mn , Fe , Co , Ni and Cu all have partially filled 3d orbilais either in the ground state of the free atom (all except Cu) or in one or more of their chemically important ions (all except Sc) , this group of elements is called the first transition series (Cotton & Wilkinson, 1972). Zr belongs to the second transition series, which begins with Yttrium with ground state outer electronic configuration $5s^2$ $4d^1$ the following eight elements Zr, Nb, Mo, Tc, Ru, Rh, Pd and Ag all have partially filled 4d orbitals either in free elements (all but Ag) or in one or more of the chemically important ions (all but Y) (Petrucci, Harwood & Herring, 2002).

Coordination compounds play an essential role in chemical industry and in life itself. The importance of metal complexes becomes clear when one realizes the chlorophyll, which is vital to photosynthesis in plants is a magnesium complex and that hemoglobin which carries oxygen to animal cells is an iron complex (Fred & Ronald, 1986).

1.1.1-Physical properties of transition metals:

Transition elements are hard, strong, high melting point, form alloys with one another and with other metals, high electrical and thermal conductors, and each transition metal have several readily accessible oxidation states. (William & Jolly, 1991).Their compounds are often colored, many of the compounds are paramagnetic, and their metal ions are often obtained in form of complexes with a wide variety of ligands. The compound, often have a catalytic properties. (William & Jolly, 1991). The two best conductors of electricity are the transition metal (copper) and the main group metal (aluminum). This shows the extent to which the physical properties of main group metals and transition metals overlap. (Boner & Pardue 1996).

1.1.2- Chemical properties of transition metals:

Much of the chemistry of transition metals is the chemistry of complexes or coordination compounds. (William & Jolly, 1991). Transition metals organometalic chemistry is an important part of modern renaissance of inorganic chemistry that began 1950's and 1960's. Transition metal ions (M^{+2}) are lewis acids and the ligands are lewis bases, they join to give coordination compounds or complexes, (ML_n) (Robert, 1988). When transition metals ionized, electrons are removed from the n orbitals before being remove from the valence shell (n-1)d-orbitals and this due to the small difference between the energies of the ns and the (n-1)d- orbitals. For this reason the electronic configuration of chromium and copper differ slightly from the prediction of the aufbau principal. (Boner & Pardue, 1996).

$$\mathrm{Cr} : [\mathrm{Ar}]4s^1 3d^5 .$$

$$\mathrm{Cu} : [\mathrm{Ar}]4s^1 3d^{10} .$$

The sability of transition metals to form organo derivatives only began appreciated properly during 1950's, whereas the organo derivatives of non-transition metals and metalloids had been actively studied for more than hundred years before that (Cotton & Wilkinson, 1972). The main group metals tend to form salts such as NaCl and Mg_3N_2 in which there are just enough negative ions to balance the charge on the positive ions .The transition metals form similar compounds such as $CrCl_3$,

$FeCl_3$ or $Cd(OH)_2$, they are more likely than the main group metals to form complex such as $[FeCl_4]^-$, $[CrCl_4]^-$ or $[Cd(OH)_4]^{-2}$ (Albert *et al*., 1995).

Transition metals have some characteristic chemical properties:-

1/ Forming compounds with several oxidation states. 2/ Strong tendency to form complexes. 3/ Useful as catalyst.

Table (1). Most common oxidation states of first transition series.

Zn	Cu	Ni	Co	Fe	Mn	**Cr**	V	**Ti**	Sc
-	+1	-	-	-	-	-	-	-	-
+2	+2	+2	+2	+2	+2	+2	+2	+2	-
-	+3	+3	+3	+3	+3	+3	+3	+3	3+
-	-	-	-	-	+4	-	+4	+4	-
-	-	-	-	-	-	+5	+5	-	-
-	-	-	-	+6	+6	+6	-	-	-
-	-	-	-	-	+7	-	-	-	-

Copper is the only one element in which the +1ion is important. For the rest of the elements, the sum of the first two ionization energies is low enough for the first two electrons to be removed, (except for scandium where the +2 ions are formed when the 4s electrons have been lost). The first three ionizations are also low enough for three electrons to be removed (except Zn).

The number of successful ionization energies increases from Sc to Mn after which it decreases again. This is because from Sc to Mn the highest oxidation state is simply the sum of the 3d and 4s electron. The metal with higher oxidation state are usually bonded covalently to oxygen or fluorine e.g.$[MnO_4]^{2-}$.

Compounds containing metals in higher oxidation state tend to be oxidizing agent, whereas compounds containing metals in lower oxidations state are usually reducing agent. Higher oxidation states become stable compared to lower ones, across the series. (Varoxidation, 2014).

One striking characteristic of representative elements is that their chemistry markedly changes across a given period as the number of valence electron changes, the chemical similarities occur mainly with vertical groups. In contrast the transition metals show great similarities within a given period as well as within a given vertical group. This differences occurs because the last electrons add for transition metals are inner electrons for the d-block transition metals and f electrons for lanthanides and actinides .These inner d and f electrons cloud participate, as easily in bonding as can the valence s and f electrons, thus the chemistry of transition elements is not affected as greatly by gradual change in the number of electrons as in the chemistry of representative elements. (Steven & Susan, 2002).

Coordination compounds are used extensively in quantitative analysis as a means of separating certain metals ions and as means of positively identifying certain unknown ions. For example experiment may perform, to identify silver ion in solution, if silver ion is present. The addition of chloride ion gives an immediate white precipitate of silver chloride, this precipitate dissolve in excess of aqueous ammonia, but if an excess nitric acid is added to this clear solution the white precipitate forms again, this behavior is due to equilibria (1) and (2). (Fred & Ronald, 1986)

$$Ag^+ + Cl^- \text{—} AgCl\downarrow \text{(white ppt.)} \ldots\ldots\ldots\ldots\ldots(1)$$

$$AgCl + 2NH_3 \text{—} [Ag(NH_3)_2] + Cl^- \text{ (clear solution)}\ldots\ldots\ldots\ldots(2)$$

1.2- Complex formation

It is difficult to state exactly when the first metal complex was discovered. Perhaps the earliest one in record is Prussian blue KCN, $Fe(CN)_2$, or $Fe(CN)_3$ which was obtained by artist's color maker Diesbach in Berlin at the beginning of eighteenth century. However the date usually cited, is that of the discovery of hexaamine cobalt(Ⅲ) chloride $CoCl_3 6NH_3$ by Tassaert (1798).This discovery marks the real beginning of coordination chemistry. Because of existence of the compound of unique properties stimulated a considerable interest, and research on similar system (Dodle & Darl, 1995). Complex compounds have been known for more than 150 years but no satisfactory explanation for their formation was available until the imaginative work of Alfred Werner (William, *et al.*, 1985). From what he observed he, suggested that the transition metal compound has:-.

(i)- Primary valence: number of negative ions that are needed to satisfy the positive charge on the metal ion.

(ii)- Secondary valence: the number of ions or molecules that are coordinated to the metal ion (Boner & Pardue, 1996).

Co(Ⅲ) is six- coordinate and its coordination compounds can written as follows:

$[Co(NH_3)_6]^{+3} (Cl^-)_3$--------------orange-----yellow.
$[Co(NH_3)_5(H_2O)]^{+3}(Cl^-)_3$------------Red.
$[Co(NH_3)_5Cl]^{+2}(Cl^-)_2$----------purple.
$[Co(NH_3)_4Cl_2]^+Cl^-$-----------green.

Brackets [ ] are used to distinguish between ligands that contributed to primary and secondary valencies. The charge on the complex is always the sum of the charges on the ions or molecules that form the complex (Dodle, 1995). For example:-

$$Fe^{+2} + 6CN^{-} \rightarrow Fe(CN)_6^{-4}$$

There are several features of complex or coordination compounds, the first feature is the metal ion, the second is the ligand, the third is the coordination number and the fourth is the geometry (Abbo, 1991).

In formation of $Cu(NH_3)_4^{+2}$ ion the nitrogen atom of each NH_3 molecule contributes a pair of unshared of electrons to form a covalent bond with Cu^{+2} ion, this bond and other like it , where the both electrons contributed by the same atom, is referred to as coordinate covalent bond, there are four such bonds in $Cu(NH_3)_4^{+2}$ ion. The term complex ion indicates the charged species in the metal ion joined by coordinate covalent bond to neutral molecule and/or negative ions (Charles, 1986).

The metal cation in a complex is called the central ion. The molecule or anions bonded directly to it are called ligands. The number of bonds form by the central metal ion is called the coordination number In $Cu(NH_3)_4^{+2}$ the central ion is Cu^{+2} the ligands are NH_3 molecule, coordination number is 4. This molecule cannot exist by itself in the solid state, charge must be balance with total charge -2 typical compound is $[Cu(NH)_3]Cl_2$. Compounds contain a complex ion are referred to as coordination compounds (Cotton, 2006).

1.3-The central metal ion:

The central metal ion is the metal ion to which the ligands are attached at the centre of coordination sphere (Chris, 2001). In a general way it is true that the better complex-forming ions are those for which the ionic potential is relatively large. The comparatively small, highly charged ions of the 3d-transition series for example are much better complex formers than the large univalent alkali metals (Gaafar, 2000).

The bond between the metal ion and a ligand shows high dependency on the properties of the metal atom. The most important of these properties are the size of metal atom, its ionic charge, atomic number, electronic configuration, electronegativity and ionization potential. These properties govern the relative tendencies for various metal to combine with a given donor atom (William *et al.*, 1985). Sedgwick has pointed out that rough division of the metal ions into three groups can be made, based upon the relative tendencies of these ions to form complexes with oxygen as donor atom on one hand or with nitrogen on the other hand . These groups are as follows:

(i)- Those ions which in general , complex more rapidly with oxygen than with nitrogen :Ti^{+4}, Zr^{+4}, Nb^{+5}, V^{+5}, Ta^{+5} , Mo^{+5} , Fe^{+3} and Co^{+3} .

(ii)- Those showing about equally strong tendencies to coordinate with oxygen and nitrogen: Cr^{+3}, Fe^{+2} and Pt^{+2}.

(iii)- Those which complex more rapidly with nitrogen than with oxygen: Cu^{+1}, Cu^{+2}, Au^{+}, V^{+3}, Co^{+2} and Ni^{+2} (Abdalazeem, 2005).

1.4- Ligands:

In principle any molecule or anion with an unshared pair of electrons can donate them to a metal ion to form a coordinate covalent bond. The expected species, such as ammonia molecule, water molecule, hydroxide ion and the chloride ion to act as ligands (Dodle & Darl, 1995). ligands that themselves can both donate or accept electrons, so that their own oxidation state is indistinct, make it difficult if not impossible to attribute unambiguous oxidation number to the metal atom. The extreme examples of such ligands are 1,2 dithiolene ligand, and many others such as NO , CO , CN and various phosphines are also capable of varying their net balance of donor and acceptor behavior toward a given metal atom, because of this the physical significance of the oxidation number assigned to the metal atom surrounded by such ligands becomes vague. Avery cogent example is provided by the pair of ions $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$, the formal oxidation state of the iron atoms are obviously +3 and +2 respectively, but detailed studies of Mossbauer and Esr spectra, coupled with molecular orbital treatment of the bonding, indicate that the effective charge residing on the metal atom is practically the same in the two cases (Cotton & Wilkinson, 1972).

1.4.1-Types of ligands:

Ligands classified, according to the number of electron pair donated.

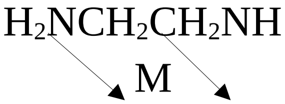
1.4.1.1-monodentate ligands : provide one electron pair per ligand molecule or ion. Monodentate (literally one toothed) because they bite the metal ion in only one place, typical monodentate ligands are:-

$$F^-,\ Cl^-,\ I^-,\ OH^-,\ H_2O,\ NH_3.$$

Such monodentate ligands form no chelate compounds (Cotton, 2006).

1.4.1.2- Bidentate ligands (two toothed) : that ligands furnish two electron pairs per molecule or ion (Charles, 1986).

For example ethylenediamine is bidentate ligand. It attaches to a metal by two nitrogen donor atoms.



Another example of bidentate ligand is carbonate, this an example of a case in which the distance between the potential donors is too short.

O

M C O

O

The carbonato complex is not stable since 4-membered ring is highly strained.5-membered and 6-membered rings are less strained as illustrated by the following examples:-

O

C —O

5-membered ring M Oxalato complex

C —O

O

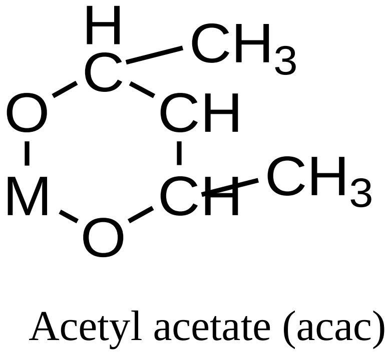
O

C—O

(5-membered ring) M Glycinato complex

CH_2

NH_2



(6-membered ring)

Acetyl acetate (acac)

(M is a metal ion)

1.4.1.3-**Tridentate ligand**: Diethylenetriamine

$H_2NCH_2CH_2NH\ CH_2CH_2NH_2$

1.4.1.4- Hexadentate ligand: EDTA (Ethylenediaminetetraacetate) (Abdalazeem, 2005).The general term polydentate is used for any ligand that supplies more than one pair of electrons. The complex form by polydentate ligands are often called chelate (Greek chela meaning crab's claw).

For ligand to act as chelating agent it must have at least two pairs unshared of electrons, these two pairs must be far enough from one another to form a chelate ring with stable geometry. Chelate formed by ethylenediamine or oxalate ion the ring contains five atoms. Four- membered are less stable, three-membered ring do not occur. (Charles, 1986).Examples

$H_2NCH_2CH_2NH_2$	$H_2NCH_2NH_2$	NH_2NH_2
Ethylenediamine	Methylenediamine	Hydrazine

Methylenediamine is less effective chelating agent than ethylenediamine since it would form four-membered ring opposed 5-membered ring. Hydrazine does not act as chelating agent. To do so it would have to form 3-membered ring with a metal atom, this would required a highly unstable 60^0 angle (Dodle & Darl, 1995). Another important role of ligands is a bridging group. In many cases they serve as monodentate ligands. This means that there is only one ligand atom which is form two (or even three) bonds to different metal atoms. Monoatomic ligands as halides (Cotton & Wilkinson, 1972).

Cl

Pd Pd

Cl

1.4.2-Linkage isomers:

This rise from ambidentate ligands which define as: ligands with two or more different donor cites only one of which is attached to single metal atom at a given time. Examples:-

For NO_2: M-NO_2 nitro attached through N.

: M-ONO nitrito attached through O .

CN^- : Cyano(M-CN) and isocyano (M-NC) .

NCS^- : thiocyanato(M-SCN) and isothiocyanato (M-NCS) .

R_2SO : S-bond and O-bond.

If different donor atoms belong to the same ligand molecule the complex may be termed as mixed donor. If the different donor atoms belong to separate ligand molecules the complex may be termed mix ligand or ternary complex (Hala, 1995).

1.5-Oxidation state and coordination number:

1.5.1-Oxidation state:

An oxidation state (number) is a charge an atom would carry if the molecule or ion was completely ionic (Karen, McArdle & Takats, 2014).

The multiplicity of the oxidation by most transition metals is due to ability of these elements to lose a variable number of d-electron. For example chromium exist in the 0 , +1, +2 , +3 , +4 +5 and +6 oxidation states corresponding to the electronic configuration $3d^5 4s^1$, $3d^5$, $3d^4$, $3d^3$, $3d^2$, $3d^1$ and$3d^0$ respectively. Titanium has four valence electrons $3d^2$ $4s^2$, Ti(Ⅳ) is the most stable and common oxidation state, in lower oxidation states 0, +2 and +3 are quite readily oxidized to titanium Ti(Ⅳ) by air , water and other reagents while Zr has four valence electron $5s^2$ $4d^2$ as same as Ti, as they are in the same group four having the same oxidation states +1 , +2 , +3 and +4 (Cotton & Wilkinson, 1972).

Oxidation reaction involves increase in oxidation state, and reduction reaction occurs when the oxidation state of an atom decreases. Chemical reactions are often divide into two categories, oxidation reduction reaction and metathesis reaction (interchange or position) in which no change in oxidation state of any atom such a reaction is (William, 1991):-

$$NaCl + AgNO_3 \qquad AgCl + NaNO_3$$

1.5.2- Coordination number:

This is the modern terminology for secondary valence which was mentioned first in Alfred Werener's postulates for describing the nature of metal complex which known later as werner's coordination theory (Basol & Ronald, 1986). The coordination number defines as the number of bonds from a ligand to a transition metal ion. Transition metal complexes are characterized with coordination number that range from 1 to 12, but the most common coordination numbers are 2, 4 and 6. Odd coordination number (1, 3, 5, 7, 9) are rare (Abdalazeem, 2005).

1.6- Classification of structure in terms of coordination number

1.6.1- Coordination number (2):

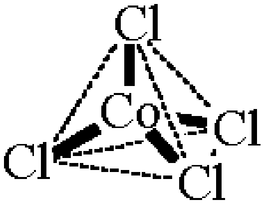
Two-coordinate bond directed at 180^0 angle, the structure is linear. .Examples: $CuCl_2$, $[Ag(NH_3)_2]^+$ and $[Au(CN)_2]^-$ (Struct. 2014).

$$H_3N-Ag-NH_3$$

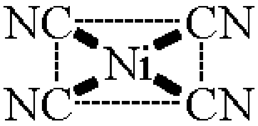
1.6.2- Coordination number (4)

Four-coordinate bond, metal complexes may have either of two different geometries :-

-Tetrahedron : Bonds direct towards the corners of regular tetrahedron. Examples: $[Zn(NH_3)_4]^{+2}$ and $[CoCl_4]^{-2}$.



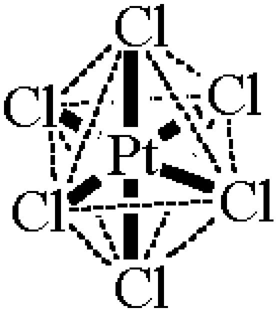
-Square planar : the four bonds direct towards the corners of the square .Examples : $[Pt(NH_3)]^{+2}$ and $[Ni(CN)_4]^{-2}$.(Struct., 2014).



Geometric isomerism (cis and trans) can occur with square planar of the type Ma_2b_2 or Ma_2bc (where M refers to the central metal ion and a, b and c are different ligands). This does not occur in tetrahedral complex because all position of ligands equivalent.

1.6.3- Coordination number (6)

The six ligands surrounding the central metal ion in a complex such as $[Fe(CN)_6]^{-3}$, $[Pt(Cl)_6]^{3-}$ and $[Co(NH_3)]^{+3}$ are located at corners of regular octahedron. Geometric isomerism can occur in octahedral complex such an example is $[Co(NH_3)_4Cl_2]^+$ can exist in cis and trans. These two isomers differ in their physical and chemical properties. The most striking difference is color, the cis complex tend to be violet while trans is green (Charles, 1986).



(Octahedral structure) (Struct, 2014).

1-7- Magnetic properties of transition elements:

These are direct and often sensitive relationship between the magnetic properties of matter in bulk and distribution of unpaired electrons in its various constituent atom and ion. There are several kinds of magnetism, paramagnetism, diamagnetism, ferromagnetism and antiferromagnetism (Cotton & Wilkinson, 1972). Paramagnetism arises whenever the molecule (ion or atom) contains unpaired of electron such as oxygen molecule contain two unpaired of electrons, NO_2 is paramagnetic. Always nature avoids this situation in compound of representative elements, but makes up for it in transition and inner transition metals. Complexes of most transition metals are paramagnetic as a result of presence of unpaired electrons in the splitting d-orbitals (Cotton & Wilkinson, 1972). The actual number of unpaired of electrons can be determined with Gouy balance. Gouy balance is like a normal balance but it has an electromagnet associated with it. A sample of compound is weighed with the magnet off and again with magnet on, a paramagnetic compound attached to the magnet with a force related to the number of unpaired electrons. Calibration with known paramagnetic substance allows determining the number of unpaired electrons in the sample. (Abdalazeem, 2005). Measurement of magnetism of $FeCl_3$ shows that there are five unpaired electrons for each iron(Ⅲ). This shows that the electronic configuration of iron(Ⅲ) is $[Ar]3d^5$ and not $[Ar]4s^2\ 3d^3$. Thus the 4s electrons removed before the 3d electrons when transition metal ion is formed (Dodle & Darl, 1995). Diamagnetic is a property of all forms of matter. In closed shells the electron spin moment and orbital moment balance each other. However when an atom or a molecule placed in magnetic field small moment is induced, so planes of orbital tipped slightly so that small moment set up in opposition to applied field, because of this diamagnetic substances are repelled from magnetic field. A very dilute solution of paramagnetic ion in a diamagnetic solvent such as water may be diamagnetic because of the large ratio of diamagnetic to paramagnetic species therein. Another important feature of paramagnetism is that its magnitude does vary with temperature, this because the moment induced depends only on the size and shapes of orbitals in closed shells and these are not temperature-dependent (Cotton & Wilkinson, 1972).

1.8- Complex ion stability:

In some cases the preference of metal ion for certain ligands is easily understood. It seems reasonable the positive metal ions should preferred anionic ligand, neutral ligand to positive charge ones. However the factor that determine which ligand will coordinate best with a given metal ion, are numerous complicated and not completely understood (Basol & Johnson, 1986).

1.8.1- Stability constant:

The term stable and unstable are often used in general way to describe the reactivity of compounds. In the case of metal complexes these terms have specific meaning, which relate to the thermodynamics of complex formation. Stable complexes might be defined as those which have overall stability constant greater than one, and those unstable would then have overall stability constant less than one (Barrete, 1991). In general an increase in ligand basicity and/or an increase in acidity of the metal ion enhances the stability of complexes formed. The stability of the metal complex $[ML_m]^{n+}$ is usually expressed in the term of formation constant ($ß_m$) . For the reaction: (Quintus, 1982); (William *et al.*, 1985).

$$M^{n+} + mL \rightarrow [ML_m]^{n+}$$

$$\beta_m = \frac{[(ML_m)^{n+}]}{[M^{n+}][L]^m}$$

The generalization about stability is that soft, ligands form stable complexes with soft metal ions and hard ligands-hard metal ions complexes are stable. Mixtures of hard metal ion- soft ligands or soft metal ion- hard ligand complexes are less stable (Petrucci, Harwood & Herring,(2002).The formation constant is the number indicating the extent to which two species combine to form a new complex species in solution. The value of formation constant is the reciprocals of the corresponding dissociation constant values (Barrete, 1991). Determination of stability constants of complexes is an important subject in analytical chemistry. Computer programs such a hyperquad, superquad. sirko and polet have been proposed to obtain their values. However the stability constant of complex is frequently estimated from measurement and treatment of analytical data using a wide selection of traditional methods such as a "Job's method" , continuous variation method, mole ratio method and others. The traditional methods based on graphical representation of curves derived from more or less complicated functions obtained by means of experimental measurement of analytical signals from chemical system in equilibrium (Abel, Kinson, & Stone, 1982). For reaction involving complex ions in water solution we must be concern of two factors:-

(i) The rate of reaction: in which there is exchange of ligands.

$$[Cu(H_2O)_4]^{+2}_{(aq)}+4NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4]^{+2}+4H_2O$$

(ii)-Position of equilibrium involve: This commonly called formation constant. Complex ion that exchange ligands almost instantaneous are referred labile, in which the exchange occur within a half-life of a minute or less or rapidly to be measured, such an example is the substitution of $[Cu(H_2O)_4]^{+2}$ by NH_3. For $[Ni(NH_3)]^{+2}$ the half-life substitution H_2O by NH_3 or other ligands is 0.025s at 25^0 C (Cary, (1986). The complex ions that undergo ligands substitution slowly are called nonlabile or inert, such a complex $[Cr(H_2O)_6]^{3+}$ here the half-life for substitution by NH_3 is 40 h at 25^0C. For illustrated difference between labile and inert, complexes of Fe^{2+} and Fe^{3+} with cyanide, $[Fe(CN)_6]^{-4}$ is inert and nonpoisonous. $[Fe(CN)_6]^{3-}$ labile and poisonous, because CN^- released in water solution are toxic.(Charles, 1986).

The stability of coordination compounds and reaction rate or lability, these two terms relate to different phenomena.The stability of the complex depends on the difference in the free energy between reactants and products, whereas the lability of the compounds depends on the difference in free energy between reactants and activated complex (Cotton, 2006) (Fig.1).

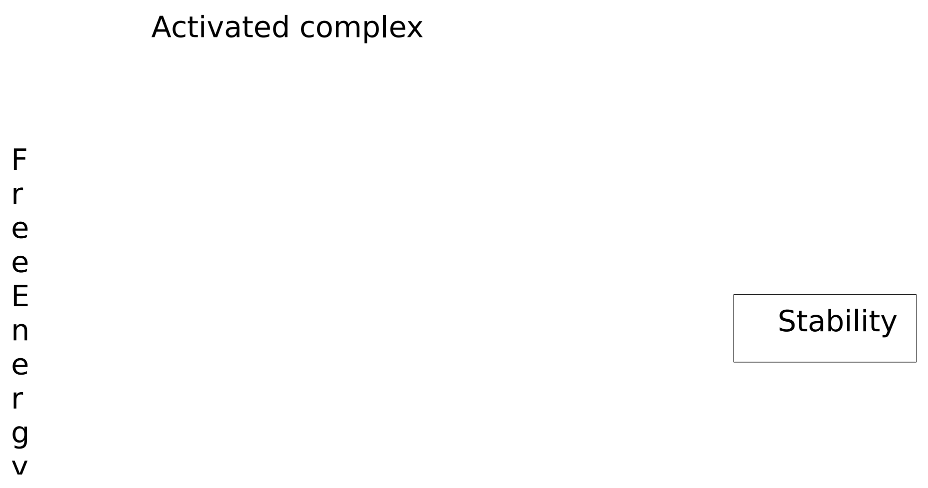


Fig.(1) Stability and lability

1.9- Electronic structure of transition metal complex:

1.9.1- Genealogy of several theories:

The study of Werner and his contemporaries followed by the idea of Lewis and sidgwick on electron pair bonding led to the idea that ligands are groups that can in some way donate electron pairs to metal ion or other acceptors, thus forming the so-called coordinate link. This approach to bonding in complexes was extended by Pauling and developed into the valence bond theory (VBT) of metal-ligand bonding, this theory enjoyed great among chemist (1930's-1940's), but during 1950's it was supplemented by ligand field theory (LFT), the ligand field theory as we have it today evolved out of purely electrostatic theory called crystal field theory (CFT) which was first expounded in 1929 by H. Bethe. CFT treat metal-ligand interaction as purely electrostatic problem, at opposite extreme metal-ligand interaction can be described in terms of molecular orbitals form by overlap of ligands and metal orbitals. CFT modified in certain parameters to allow for the effect of covalence. This modified CFT is sometimes called ligand field theory (LFT). However also LFT used as general name for the whole gradation of theories from CFT to MO formulism, and sometimes called adjusted crystal field theory (ACFT) (Cotton & Wilkinson, 1972).

1.9.2- Concept of effective atomic number:

It has been long recognized that in the compounds in which each atom can share with other atom, gather around itself a number of electrons equal to that found in the corresponding noble gas. Professor Sidgwick of Oxford University applied this to metal complexes and this what he called effective atomic number (EAN) Example: the EAN for cobalt (Ⅲ) in $[Co(NH_3)_6]^{+3}$ is readily calculated as:-

Co: Cobalt atomic number 27 has 27 electrons.

Co^{3+}: 27-3= 24 electrons

$6NH_3$: 6x2 = 12 electrons

EAN: 36 electrons (Kr)

There are many exception to this rule for example $[Ag(NH_3)_2]^+$ and $[Ni(en)_3]^{2+}$ with EAN 50 and 38 respectively. For this unfortunate it would be impossible to estimate the coordination number of metal ion. One class of the compounds that frequently does obey the EAN rule comprises the metal carbonyls and their derivatives (Dodle & Darl, 1995).

1.9.3- Valence bond theory (VBT) "Atomic orbitals":

This theory was developed by Professor Linus Pauling who has been awarded two Nobel prizes. The theory aided coordination chemists for it can account reasonably well for structure and magnetic properties of metal complexes (Cotton & Wilkinson, 1972).This theory starts with simple assumption, it considers that electron pairs donated by ligands enter hybrid orbitals, these electron pairs depend upon the coordination number and geometry of complex. Table (2) below (Charles, 1986)

Table (2). Coordination numbers and geometries.

Example	Hybrid orbitals occupied by ligand electron	Geometry	Coordination number
[Cu(NH3)4]+	sp	Linear	2
[Zn(NH3)6]+2	sp^3	Tetrahedral	4
[Ni(CN)4]-2	dsp^2	Square planar	4
[Cr(NH3)6]+3	d^2sp^3	Octahedral	6

Example: Applying of valence bond theory for $[Co(NH_3)_6]^{+3}$:

The electronic configuration for transition metal ion:

Co^{3+}: $[Ar]3d^6\ 4s^0\ 4p^0$. 4s orbital and three 4p orbitals are empty. To satisfy for the covalent bond theory Co^{3+} needs six empty orbitals to accept six pairs of electrons from the donor atoms (nitrogen), to satisfy for this two orbitals from the five orbitals of 3d should be empty. This leads to pairing of electrons into three orbitals of 3d sub-shell .Now two empty orbitals of the 3d sub-shell plus 4s orbital and three 4p orbitals are empty hybrized to d^2sp^3 .

Co^{3+} :(ཀྵྃ)(ཀྵྃ)(ཀྵྃ)( ) ( ) ( ) ( ) ( ) ( ) 3d 4s 4p Each of these six hybrid orbitals accepted nonbonding pair of electron from NH_3 molecule. $[Co(NH_3)_6]^{3+}$:(ཀྵྃ)(ཀྵྃ)(ཀྵྃ)(ཀྵྃ)(ཀྵྃ) (ཀྵྃ) (ཀྵྃ)(ཀྵྃ)(ཀྵྃ)

……………………. 3d 4s 4p

6 electron pairs from 6 NH_3 (Maxwell, (1988).

Another example to explain bonding in complex $[Ni(NH_3)_6]^{2+}$ on basis of valence bond theory:

The electronic configuration for Ni^{2+} is :[Ar]$3d^8\,4s^0\,4p^0$ or

(↑↓)(↑↓)(↑↓)(↑)(↑) ( ) ( ) ( ) ( )

…… $3d^8$ 4s 4p

If the two unpaired electron in the two 3d orbitals were forced to pair , then there will be one d-orbital empty , plus 4s orbital and three 4p-orbitals , this gives only five empty orbitals in central ion which does not satisfy for d^2sp^3 hybridization ,to solve this, the 4d-orbitals are used to give sp^3d^2 hybridization. The complex ion configuration will be: $[Ni(NH_3)_6]^{2+}$:

(↑↓)(↑↓)(↑↓)(↑)(↑) (↑↓) (↑↓)(↑↓)(↑↓) (↑↓)(↑↓)( )( )( )

………….3d 4s 4p 4d

Six pairs of electrons are donated by six NH_3 molecules. This complex is known as outer-shell complex using sp^3d^2 configuration. Complex of the type d^2sp^3 is known as the inner-shell complex (William, Emil & Conrad 1985).

1.9.4- Crystal field theory (CFT):

The crystal field model interprets the bonding between ligand and metal ion is primary electrostatic in nature. Ligands electron pairs are not donated into orbitals of the central metal ion as the valence bond theory. Instead it assumed that the only effect of ligand to create an electrostatic field around the d-orbitals of the metal ion. The symmetrical field caused by ligands is similar to electrostatic field around ion in ionic crystal, this similarity account for the name crystal field theory. (Charles, 1986).This field changes the relative energy of the different d-orbitals.The degeneracy of the five d-orbitals is partly removed by the electrostatic field (Dodle, 1995). This happens because electrons in the $d_{z^2}\,and..d_{x^2-y^2}$ orbitals will in average spend more time closer to the six regions of ligand electron density than those in the d_{xy}, d_{xz}, d_{yz} orbitals. thus in the energy diagram the first two placed higher energy than the later three orbitals, figure (3). The raised in energy between the two set of orbitals is known as the crystal field splitting or ligand field splitting. And represented by crystal splitting parameter Δ or 10dq. The more specific symbol Δ_o may be used in particular case of an octahedral complex, similarly Δ_t used to donate the value for a tetrahedral complex (Chris, 2001). The two sets of the d-orbitals are given symmetry labels e_g for $d_{z^2} and..d_{x^2-y^2}$ and t_{2g} for $d_{xy}, d_{xz} and..d_{yz}$ orbitals, the energy of e_g increase by (3/5) Δ_o and that of three t_{2g} orbitals will decrease by (2/5) Δ_o ((Schläfer, & Gliemann 1969). In an octahedral complex that contains one d- electron for example $[Ti(H_2O)_6]^{3+}$, the electron will reside in the orbital that has lowest energy i.e t_{2g} orbital that has energy $0.4\Delta_o$ less that of hypothetical degenerate orbitals. Thus the complex will be $0.4\Delta_o$ more stable than a simple electrostatic model predict . $0.4\Delta_o$ called the crystal field stabilization energy (CFSE). For d^5 system is either $3(0.4\Delta_o) +2(-0.6\Delta_o) =0.0\Delta_o$ or $5(0.4\Delta_o) + 0(-0.6\Delta_o) =2.00\Delta_o$ depending in distribution of the five electrons in the t_{2g} and e_g orbitals (Grabtree, 1988) .

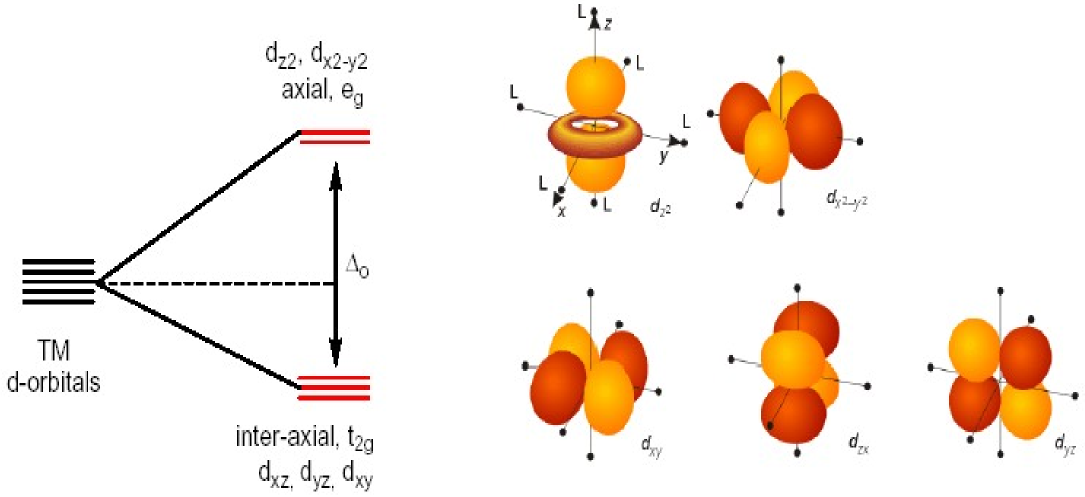


Figure (3) crystal field splitting.

1.9.5-Molecular orbital theory: (MOT):

Molecular orbital theory uses a linear combination of atomic orbitals (LCAO) to represent molecular orbitals involving the whole molecule. These orbitals are often divided into bonding orbitals, anti-bonding orbitals and nonbonding orbitals (Dr.

Paul, 2006).The method for constructing these orbitals specifically for octahedral complexes will take the following steps:

(i)-There are nine valence shell orbital of the metal ion to be considered six of these $d_{z^2}.,d_{x^2-y^2}$, s,P_x,P_y,P_z are suitable for σ-bonding whereas three $d_{xy},d_{xz}and..d_{yz}$ suitable for π-bonding .

(ii)- each of the six ligands possesses one σ-orbital, they must combined into six metal-ion orbitals which are suitable for σ-bonding, to give bonding and anti bonding molecular orbilal.

(iii) If the ligand also possesses π-orbitals , these also combine to overlap effectively with metal ion π-orbital and give bonding and anti bonding MO's then form by overlap (Schläfer,& Gliemann, (1969)

figure (4) Below is the resulting molecular orbital (MO) diagram for an octahedral complex with strong π-acceptor ligands [(Cr)CO)$_6$)]. The Cr^0 centre is a 3d^6 configuration. The 6 CO ligands each donate two electrons to the metal centre via σ bonding. The π bonding symmetry orbitals of the ligands are also populated, but cannot effectively act as π donors to the central metal, partially because of their energies being much lower than the appropriate symmetry metal t$_{2g}$ set, but also because the metal d^6 centre has its t$_{2g}$ set populated by metal based electrons; electron-electron repulsion further hinders any π donor ability from the CO ligand (Landis, & Weinhold, 2007).

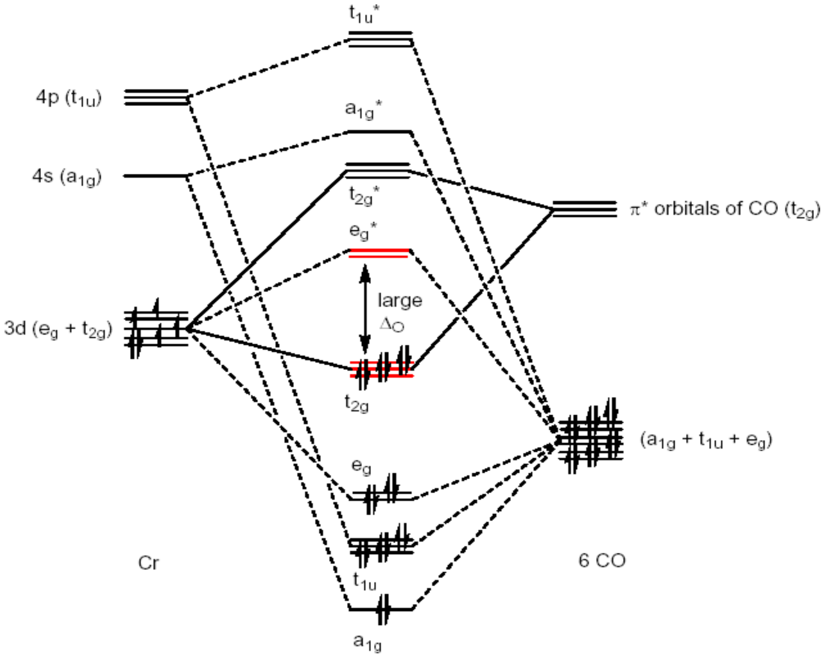


Fig.(4) Molecular orbital diagram. (Chemistry, 2000)

1.10-Titanium:

Titanium latin (titan) the first son of the earth in the mythology. Discovered in 1791, named by Klaproth in 1795. Impure titanium was prepared by Nilson and Pettersson in 1887 AC, however the pure metal (99.9%) was not made until 1910 when Hunter heated $TiCl_4$ with sodium in steel bomb. Titanium is in the first transition series of d-block and has four valence bond electrons $3d^2 4s^2$ (the electronic configuration. [Ar] $3d^2 4s^2$ (Cotton &Wilkinson, 1972).

1.11.1-Physical properties of titanium:-

It is a light, strong, lustrous, corrosion resistance (including resistance towards sea water), transition metal with white silvery metallic color, titanium can be alloyed with other elements such as iron, aluminum, vanadium, molybdenum and others, to produce strong light weight alloys for aerospace (jet engines, missiles and spacecrafts), military industrial processes (chemical and petrochemical), desalination and paper. Pure titanium is insoluble in water but soluble in concentrated acids. (Stwertka, (1998). Nearly 500 kg of Ti alloys is used in each engine of Boeing747 jetliner (Bruce, 1975).

1.11.2-Chemical properties of titanium:-

Titanium is the first member of the d-block transition elements, and has four valence electrons $3d^2 4s^2$. Ti(IV) is the most stable and common oxidation state. Compounds in lower oxidation states -1, 0 , +2 and +3 are quite readily oxidized to Ti(IV) by air, water and other reagents. The energy for removal of electrons is high, so that Ti^{+4} ion does not has real existence, and titanium Ti^{4+} compounds are generally have covalent nature (Cotton & Wilkinson,1972). Compounds of this element and also zirconium are formed with evolution of considerable energy. On the basis of thermodynamic only, the element would be considered very reactive. However it protects itself from chemical attack by very thin layer (TiO_2), and therefore is quite resistant to chemical at ordinary temperature (Bruce1975). Titanium is relatively abundant in the earth's crust (0.6%). The main ores are ilmenite ($FTiO_3$) and rutile one of the several crystalline varieties of (TiO_2). It is not possible to obtain the metal by common reduction with carbon, very stable carbide is produced and moreover the metal is rather reactive towards oxygen and nitrogen at elevated temperature (Cotton & Wilkinson, 1972)

Ilmenite and rutile is treated at red heat with carbon and chlorine to give $TiCl_4$:

$$2TiFeO_3+7Cl_2+6C(900^0C)\rightarrow 2TiCl_4+2FeCl_3+6Co$$

This is fractionated to free form $FeCl_3$. The titanium tetrachloride ($TiCl_4$) is then reduced with molten magnesium at 800^0 C, this gives metallic titanium as sponge mass.

$$TiCl_4+2Mg(800^0C)\rightarrow 2MgCl_2+Ti$$

The excess of magnesium chloride ($MgCl_2$) is removed by volatilization at 1000^0 C. Natural titanium consists of five isotopes with atomic mass from 46-50, all are stable. Eight other unstable isotopes are known (Stwertka, 1998).

There is no particularly strong resemblance between the metal of group 4A and 4 B. The important oxidation state of tin and particularly lead is +2 and not +4 while the reverse is true in titanium family. The tetrachloride of both are however somewhat similar, like $SnCl_4$, $TiCl_4$, $ZrCl_4$ and $HfCl_4$ are relative volatile compounds that exist as discrete covalently bonded molecules (Bruce, 1975).

1.11.3-**Titanium compounds:**

Titanium is a transition metal since it has partially-filled d-orbital. So it is better to consider the chemistry and complexes of titanium according to its several oxidation states. The chief oxidation states of titanium are +4 (d^0), +3 (d^1), +2 (d^2) and +1(d^3) (Mona, 2000).

1.11.4-Chemistry of titanium (IV) (d^0):

This is the important oxidation state.

(A)-Halides : $TiCl_4$ the most well known titanium compounds since it is the usual starting point for preparation of most other titanium compounds, and can be hydrolysed by H_2O : $TiCl_4+2H_2O\rightarrow TiO_2+4HCl$

When HCl present. Roman spectra indicate the present of species $[TiO_2Cl_4]^{4-}$ or $[TiOCl_5]^{3-}$ and not $[TiCl_6]^{2-}$.$TiBr_4$ and TiI_4 are similar to $TiCl_4$, but they are crystalline at room temperature whereas $TiCl_4$ is a liquid (Cotton & Wilkinson, 1972).

$$TiCl_4+Ti\rightarrow 2TiCl_2$$

$$TiCl_4+O_2\xrightarrow{burning}TiO_2+2Cl_{2_{(g)}}$$

(Bruce, 1975)

(B) Oxides: TiO_2 has three crystalline modifications rutile , anatase and brookite , and each of which occur in nature. Considerable number of material called "titanates" are known such that $FeTiO_3$ (ilmenite) and $CaTiO_3$ "perovskite".

(C) Alkoxides : These are much studied and are typically of other transition metal alkoxides (such as V , Fe and U and others) .The compounds can be obtained by reactions as such : (Leslie,1971).

$$TiCl_4+4ROH+4NH_3\rightarrow Ti(OR)_4+4NH_4Cl.$$

$$TiCl_4+3EtOH\rightarrow 2HCl+TiCl_2(OEt)_2.EtOH$$

(D) ß-diketonates: These are made by treating $TiCl_4$ with ß-diketones in an inert solvent. The acetyacetonate [Ti(acac)$_2$] what has cis-Cl groups and is fluxional molecule, and is readily hydrolyzed to an oxo-bridged species where the Ti-O-Ti is almost linear , suggesting some pπ-dπ bonding such as :

$$(C_5H_5)Cl_2Ti\text{-}O\text{-}TiCl_2(C_5H_5)$$

(E) Nitrogen compounds: Nitrogen compounds with N-H bonds appear to react with titanium halides to initially an adduct from, which hydrogen halide is eliminated by base catalysis. Thus the dilute gaseous ammonia gives addition product. But with an excess of ammonia, ammonolysis occurs and up to three Ti-Cl bonds are converted to Ti-NH_2 bonds.

Primary and secondary react in a similar way to give orange and red solids such as $TiCl_2(NHR)_2$ and $TiCl_2NR_2$ (Basol & Ronald, 1986).

1.11.5-Chemistry of titanium (III) d^1 :

The most important compound is the chloride $TiCl_3$ which has several crystalline forms, violet α-form and brown ß-form. The oxide Ti_2O_3 obtained by reducing TiO_2 in 1000^0C in steam of H_2.The addition of OH^- ions to aqueous titanium solution gives purple precipitate of hydrous oxide (Cotton & Wilkinson, 1972).

1.11.6-Chemistry of titanium (∏) d^2 :

The compounds of divalent titanium are few and Ti (Ⅱ) has no aqueous chemistry because of it is oxidation by water. Although it has been reported that the ice-cold solution of titanium oxide (TiO) in dilute HCl contain Ti^{2+} ions which persist for some time. The well-define compounds are $TiCl_2$, $TiBr_2$, TiI_2 and TiO these can be obtained by the reduction of tetrahalides with titanium:

$$TiX_4+Ti \rightarrow 2TiX_2$$

And by disproportional of trihalides [4]:

$$2TiX_3 \rightarrow TiX_2+TiX_4$$

1.12-Zirconium : (Zr)

Zirconium was discovered by Martin Klaproth a German chemist, while analyzing the composition of mineral jarcon or zircon in 1789. Zirconium is Persian word for gold-like Zargum (Forrest, 1981). The primary ore of this element has been known since biblical times, and it has been called by a variety of names including jargon , hyacinth and jacinth. Swedish chemist Jacob Berzlius isolated an impure zirconium metal, was not until 1914 when the pure zirconium was finally produced. (Lide, 2008). Zirconium an element of second transition series, in general the first, second and third transition series of a given group of elements have similar chemical properties but all show pronounced differences from their light congeners (Cotton & Wilkinson, 1972).The radii of Zr^{4+} and Hf^{4+} ions (0.74 and 0.75 respectively) are virtually identical, thus has the effect of making chemical behavior of the two elements extremely similar. The most important difference from titanium is that lower oxidation states are of minor important. Zirconium occurs widely over the earth's crust, but not in very concentrated deposits. The major minerals are baddeleyite a form of ZrO_2 and Zircon $ZrSiO_4$ (Basol and Ronald, 1986).

1.11.1-Physical properties of zirconium:

Zirconium is grayish -white metal, lustrous and exceptionally corrosion resistant. Zirconium is lighter than steel and its hardness is similar to copper. When it is finely divided, the metal can spontaneously ignite in air, especially at high temperature (it is much difficult to ignite the solid). Zirconium zinc alloy becomes magnetic at temperature below 35^0 K. (Forrest, (1981).

1.12.2-Chemical properties:

Zirconium reacts more rapidly with nitrogen than with oxygen, to give mixture of nitride oxide and oxide nitride Zr_2ON_2 (Cotton & Wilkinson, 1972). ZrO_2 is more basic than TiO_2 and is virtually insoluble in an excess of base. Zirconium hydrolysis does not occur, and it is very doubtful indeed if Zr^{4+} aquo ions exist even in strongly acid solutions. The hydrolyzed ion is often referred to as "Zirconyl" ion and written ZrO^{2+}. However there is a little, if any reliable evidence for the existence of such an oxo ion either in solution or in crystalline form (Lide, (2008). Zirconium has nearly equal energy of the 4d and 5s levels, and this allows most of zirconium chemistry to involve the four electrons in these two levels. Zirconium salt dissociated in water at lower pH value, and it hydrated with bonding to eight water molecules, to form square antiprism (Winter,(2007).

$$[Zr(H_2O)_8]^{4+} \rightarrow H_2O \rightarrow [Zr(H_2O)_7(OH)]^{3+} + H_3O^+ \xrightarrow{H_2O} [Zr(H_2O)_6(OH)_2]^{2+} + H_3O^+$$

1.12.3-Compounds of zirconium:

$ZrCl_4$ resembles $TiCl_4$ in chemical properties.

$$ZrCl_4+9H_2O \rightarrow ZrOCl_2.8H_2O+2HCl$$

$ZrCl_4$ combines with donors such as ethers, esters, $PoCl_3$, CH_3CN and with Cl^- to form six coordinate species (Lide, (2008). Zirconium chloride ($ZrCl_4$) reacts with carboxylic acid above 100^0 C to give $Zr(RCO_2)_4$ compound which appear to contains 8-coordinate molecules. $ZrBr_4$ and ZrI_4 are similar to $ZrCl_4$ and ZrF_4 white crystalline subliming at 903^0C which, unlike the other halides, insoluble in donor solvents, it has an eight-coordinate structure. The best known compounds of zirconium is oxide ZrO_2, high melting point (3100^0K), it is not attacked by acids or bases, consequently is used as refractory material in furnace and in manufacture of crucibles. Zirconium oxide is more basic than TiO_2, and thus is less soluble in alkalis and more soluble in acids. This change to basic nature is expected from increased size of Zr^{4+} ions, this makes solution of Zr(Ⅳ) less hydrolyzed than the acidic solution of Ti(Ⅳ) , so the aqueous chemistry of heavier elements is more extensive than that of Ti(Ⅳ). Acidic solution of Zr(Ⅳ) contains polymeric cations as : (Bruce, 1975). $[Zr_3(OH)_4]^{+8}$ and $(Zr_4(OH)_8]^{+8}$

1.13-Chromium:

Chromium has become a subject of much interest in recent years, and the studies about it have continued. Chromium was long thought to be toxic tolerance factor which composes chromium molecule in the trivalent state (+3charge), two niacin molecules, and three amino acids – glycine , systeine and glutamic acid (Fawcett, 1988). Chromium is not found in nature as a free metal, so it must be reduced to its elemental form to make the chromium used in the industry (Fawcett, 1988). Chromium is the earth's 21th most abundant element (about 140ppm) and 6th most abundant transition metal (Brandes, Greenaway, & Stone, 1956).

Principal and commercial available ore is chromite $FeCr_2O_4$ which found mainly in south Africa (with 96% of the world reserve) and in former U.S.S.R and Philippines. less common source include crocoites $PbCrO_4$ and chrome ochre Cr_2O_3.White gemstone, emerald , ruby owe their colors to traces of chromium. (Emsley,2001).Several studies have found that chromium supplementation can improve mild abnormalities in blood sugar control, although one study found no benefit (Kotaś & Stasicka, (2000). Recent evidence suggests that chromium may be effective aid in weight loss. Chromium is redox active transition metal with a wide range (-2 to +6) of possible oxidation states. However only Cr (Ⅲ) and Cr(Ⅵ) are stable. The valence of chromium is important because it control the geochemistry and toxicity of the element. Hexavalent Cr species are strong oxidants which act as carcinogens, mutagens and teratogens in biological system. In contrast Cr(Ⅲ) species has low toxicity, in part because their bioavailability is limited by their low solubility (Haxhillazi, 2003).

1.13.1-Historical background of chromium:-

Chromium was discovered in 1797 by the French chemist Louis Nicolas Vauquenlin, it was named chromium (Greek word chroma color) because of many different colors characteristic of its compounds. [Brandes, Greenaway, & Stone, 1956).). In the mid of 18th century analysis of Siberian red lead ($PbCrO_4$ crocoite) from Siberia showed that a quite a lot of lead, but also a further material, this was eventually identified as chromium oxide. (Guertin, Jacques & Avakian,.2005). A year or two after Vauquenlin's discovery, a German chemist named Tassort working in Paris, found chromium in an ore now called chromite. This ore $Fe(CrO_2)_2$ is now an important source of chromium. In 1822 one of Vauquenlin's pupil (Kurtz) move to England and began producing potassium bichromate and selling to England textile industry at 5 shilling a pound , local manufacture soon followed suit, and competition drove the price down to 8 pence, about an eighth of the original price. This did not give Kurtz a satisfactory profit, so he began producing other chromium compounds, and Kurtz yellow still in British color catalogues. Unlike other metals chromium had no ancient or prehistoric uses (Dennis, & Such, (1993).

1.13.2-Physical properties of chromium:

Chromium is a silver-white metal, it is hard and malleable, fairly good electrical and thermal conductor, its density 7.19g/cm^3, m.p. 1920^{0}C, B.P. 2300^{0}C. (Haxhillazi, 2003). Its compounds are toxic (Hukeey *et al*., 1993). Cr^{2+}(aq) is sky blue , Cr^{+3} is violet . The atomization energy of chromium is 95j/mol which indicate it is hard , strong and with high melting point (Basol & Ronald, 1986).

1.13.3-Chemical properties of chromium:

Apart from stoichiometries, chromium resembles group (6) elements (Albert. et al.,1995). Chromium does not corrode in air at normal temperature, but it forms chromic oxide (Cr_2O_3) when heated strongly.

$$4Cr_{(s)} + 3O_{2_{(g)}} \rightarrow 2Cr_2O_3$$

It is not attacked by water under normal condition , but react slightly with steam , when red hot, to give chromic oxide and hydrogen (Kotaś & Stasicka, 2000).

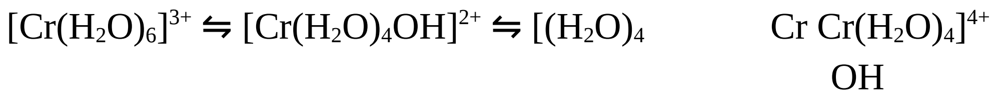
$$2Cr + 3H_2O \rightarrow Cr_2O_3 + 3H_{2_{(g)}}$$

One of the obvious characteristics of Cr(Ⅲ) is that it is acidic i.e. it has the tendency to hydrolyze and form poly nuclear complexes containing OH^- bridge in a process known as olation. This is thought to occur by loss of proton from coordinated water, followed by coordination of OH^- to the second cation (Emsley, (2001).

$$[Cr(H_2O)_6]^{+3} \rightarrow [Cr(H_2O)_5(OH)]^{+2} \rightarrow [(H_2O)_4CrOHCr(H_2O)_4]^{+4}$$

In another attempt to explain this reaction it is suggest that it takes place as follows: (William et al., 1985).

OH



$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_4OH]^{2+} \rightleftharpoons [(H_2O)_4 \underset{OH}{Cr\ Cr}(H_2O)_4]^{4+}$$

The metal dissolves in dilute mineral acids to give chromous salt and hydrogen (Basol & Ronal, 1986). $Cr + 2H^{2+} \rightleftharpoons Cr^{2+} + H_2$

Dilute nitric acid has very little reaction with metallic chromium. Concentrated hydrochloric and sulphuric acids react with the metal more vigorously than the dilute acids. Hot sulphuric acid attacks the metal to give chromic sulphate. Chromium combine with several elements for example chlorine when hot (Guertin, Jacques & Avakian, 2005).

$$2Cr + 3Cl_2 \rightleftharpoons 2CrCl_3$$

1.13.4-Electronic configuration of chromium:

Cr(Ⅱ)d^4 , Cr(Ⅲ) d^3, Cr (Ⅳ)d^2, Cr (V) d^1, Cr(V1) d^0

The atomic number of chromium 24 and the electronic configuration of it, is [Ar] $3d^5\ 4s^1$, instead of the expected configuration (aufbau principle) [Ar] $3d^4\ 4s^2$, due to electron sub-shells which are half filled according to its electronic structure (Chris, 2001).

Chromium is a transition metal since it has partially –filled d-orbital. So it is better to consider the chemistry and complexes of chromium according to its several oxidation states, the chief oxidation state of chromium are +2, +3, +4. A few compounds of cr^{+4} and Cr^{+5} are known but they are unstable [(Guertin, Jacques., & Avakian.,2005)

1.14-Chemistry of chromium

1.14.1-Chromium (Ⅱ) (d^4):

Aqueous solution of the blue chromium(Ⅱ) ions are best prepared by dissolving electrolytic Cr metal in dilute mineral acid. The solution must be protected from air (Holleman, Wiberg, & Wiberg, 1985); (Karen, Patrick & Takats, 2014). because it is readily oxidized to Cr^{+3}, so it can only be preserved in the presence of an inert atmosphere (Guertin, Jacques., & Avakian.,(2005).

Chromium (Ⅱ) acetate $Cr(O_2CCH_3)_4(H_2O)_2$ is precipitated as red solid when a Cr^{2+} solution is added to a solution of sodium acetate (Cotton, *et al.*, 1995).

1.14.11-Chromium (Ⅲ), (d^3):

Chromium (Ⅲ) salts are usually purple in color. Solutions of chromium salts give green precipitate of hydroxide or ammonia solution (Holleman, Wiberg, & Wiberg, 1985).

There are thousands of chromium (Ⅲ) of which few complexes are six coordinated. The principal characteristic is their relative kinetic inertness in aqueous solution, because of this so many complex species can be isolated, and this why of the classical complex chemistry studied by workers, notably S.M. Jorgenson and A. Werner, involved chromium. (Cotton et al., 1995) The most numerous complexes are those of amine ligands, these ligands provide examples of virtually all the kinds of isomerism in octahedral complexes. In addition to mononuclear species for example $[Cr(NH_3)_5Cl]^{2+}$, there are many polynuclear complex species in which two and sometimes more metal atoms are bridged by hydroxo groups or less commonly oxygen in linear Cr-O-Cr group. A representative example is $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ (Cotton et al.,1995). Chromium (Ⅲ) ion form many stable complexes and since they are inert, they capable of exhibiting various types of isomerism .$CrCl_3.6H_2O$ exist as hydrate isomer including Trans $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (green dark) (Emsley,2001). $[Cr(H_2O)_6Cl_2]Cl$ (Violet) and $[Cr(H_2O)_6Cl]Cl_2$ (pale green) (Jones, 2001). $CrCl_3$ anhydrous reacts with pyridine only in the presence of zinc powder, this allows small amount of chromium (Ⅲ) ion to be form which is very labile (Brandes, Greenaway, & Stone, 1956); (Emsley, 2001).

$$CrCl_3 + 3pyr/Zn \rightarrow CrCl_3pyr_3$$

1.14.12-Chromium(Ⅳ) (d^2) :

Chromium (Ⅳ) compounds are perhaps slightly more numerous and stable than of chromium(Ⅴ) but still relatively rare. The most common compounds are peroxo compounds (Cotton & Wilkinson, 1972). The most unusual Cr^{4+} compounds are the species with Cr-C, Cr-N and Cr-O bonds (Cotton, et al. 1995).

1.14.13-Chromium (Ⅴ) (d^1):

This oxidation state is not well known in simple compounds, but electron-spin resonance spectra suggest that many oxide lattices containing may, when suitably oxidized or reduced , contain Cr^{5+} (Cotton & Wilkinson, 1972).

The only evidence for persisting Cr^{5+} species in solution was obtained by dissolution of chromate (Ⅳ) in 65% oleum. The quantity of O_2 evolved and the magnetic properties of the blue solution were consistent with the formation of Cr^{5+}, but the nature of the species is uncertain (Boner & Pardue, 1996).

1.14.14-Chromium (Ⅵ) (d^0):

Chromate and dichromate ions: In basic solution above pH 6 CrO_3 forms the tetrahedral yellow chromate ion CrO_4^{2-} , between pH 2 and pH 6 $HCrO_4^-$ and the orange red dichromate ion $Cr_2O_7^{2-}$ are in equilibrium. At pH values below 1 the main species is H_2CrO_4 (Chris, 2001).

The equilibrium as follows:

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \quad K = 10^{-5.9}$$
$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \quad K = 4.1$$
$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \; K = 10^{-2.2}$$

The pH-dependent equilibria are quite labile and on addition of cations that form insoluble chromate e.g.Ba^{2+}, Pb^{2+}, Ag^+ the chromate and not dichromate are precipitated (Cotton & Wilkinson, 1972). Chromium (Ⅵ) oxide is very soluble in water forming chromic (Ⅵ) oxide and is used for cleaning laboratory glassware (Guertin, Jacobs, & Avakian, 2005). Another compound is chromyl chloride (CrO_2Cl_2) a deep-red liquid which formed by the action of HCl on chromium (Ⅵ) oxide :

$$CrO3+2HCl \rightarrow CrO2Cl2+H2O$$

Or in warming dichromate with an alkali metal chloride in concentrated sulphuric acid.

$$K_2Cr_2O_7+4KCl+3H_2SO_4 \rightarrow 2CrO_2Cl_2+3K_2SO_4+3H_2O$$

CrO_2Cl_2 is photosensitive, rather stable vigorously oxidizes organic matter and it hydrolyzed by water to CrO_4^{2-}. (Chris, 2001).

1.15-Ligands:

Aliphatic carboxylic acids are compounds which contain a carboxyl group. Their general formula is R-COOH. Carboxylic acid boil higher than alcohols of corresponding molecular weight, indicating the greater strength of the hydrogen bonds. Molecular weight determination of the lower carboxylic acids by vapor-density method gives twice a formula weight because they exist as dimer (Alebert *et al*., 1973).

1.15.1- Acetic acid:

Systematically named ethanoic acid, is an organic compound with formula CH_3COOH, colorless liquid that when concentrated is called glacial acetic acid, with distinctive sour taste, and pungent odor (smell).

The global demand of acetic acid is around 6.5 million tons per year (mt/a), 1.5mt/a met by recycling, the remainder is manufactured from petrochemical, the biological sources is not competitive. These can be produce by fermentation and oxidation of ethanol.

Use in manufacture as cellulose acetate for photographic film, and as polyvinyl acetate for wood glue.

1.15.2-Oxalic acid is chemical organic compounds, specifically carboxylic acid, with a formula $H_2C_2O_4$. This carboxylic acid is better described with the formula HOOCCOOH. It is relatively strong organic acid, being about 10,000 times stronger than acetic acid, the anion oxalate (OOCCOO) or $(COO)_2$ is a reducing agent.(Cohen, 1930). The other name (synonym) is ethanedoic acid (Alebert, Eberhard & Gunther,1973).

Physical properties : Oxalic acid is white crystals, density 1.90g/cm^3 (anhydrous) or 1.653g/cm^3 (dihydrate), solubility in water 9.5g/100ml at 15^{0}C, 14.3g/100ml at 25^{0}C, 120g/100ml at 100^{0}C, odourless, melting point 101.6^{0}C, boiling point loses $2H_2O$ 111.11^{0}C sublimes 148.88/160^{0}C, pH(1%solution) 1.3 stable in an ordinary conditions, decomposition products carbon dioxide and carbon monoxide may formed when heated, and also formic acid may be of the products. pK_a at 25^{0}C pK_1= 1.23 , pK_2= 4.19 (Dutton &Evans, 1996).

Chemical properties: Oxalic acid (oxalate ion) is versatile since it can act as mono-, bi-, tri-, tetradentate ligand capable of forming polynuclear complexes. Much interesting exist in oxalate ligand as bridging unit for preparing polynuclear complexes and extending molecular assemblies figure (5). With tripositive transition metal ions the tris chelate anions $[M^{3+}(C_2O_4)_3]^{3-}$ are formed. This polynuclear complexes and molecular assemblies, not only owing to their potential magneto structure properties, but also due to the fact that polynuclear oxalate systems are excellent candidates to improve our still limited understanding of the way that molecules and ions organized in the solid state to form materials with a given physical and chemical properties (Wells, 1948). Oxalic acid also combines with metals such as calcium, potassium, iron, magnesium and sodium in the body to form the corresponding oxalates, which irritate the gut and kidneys, especially calcium oxalate known as kidney stones obstruct the kidney tubules (Cohen, 1930).

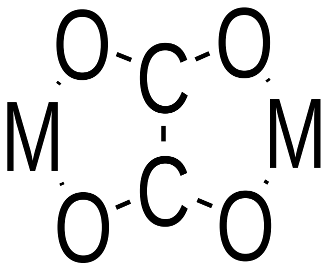


Fig. (4)

1.15.3-Oxaloacetic acid: formula $HOOCCH_2COCOOH$.($C_4H_4O_5$). First known 1896, white crystalline dicarboxylic. Synonyms: 2-oxo succinic acid , oxaloacetic acid, 2-oxo butanoic acid, keto succinic acid, acid 2-oxo succinque. (Wells, 1948). Oxaloacetic acid produces in the body as an intermediate in citric acid cycle, genetic mutation in genes produces pyruvate carboxylase renders some individual unable to produce oxaloacetic, the lack of which effects metabolism in three ways: (i)prevent citric acid cycle from proceeding (ii) oxaloacetic acid requires for producing body fuel during fasting (iii) the breakdown products of oxaloacetic acid is aspartic acid which is required for urea cycle, reduces level of aspartic acid led to an increase in serum ammonia levels (Marrian, (2000).

1.15.4- Propanoic acid:

Also known as propionic acid from Creek words protos meaning first and pion meaning fat. It is a naturally occurring carboxylic acid with chemical formula CH_3CH_2COOH. It is clear liquid with pungent odor.

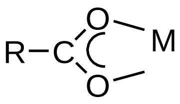
Propanoic acid was first described in 1844 by Johnn Gottlieb (Austrian chemist) who found it among degradation products of sugar. Propanoic acid has physical properties intermediate to those of smaller carboxylic acid formic and acetic and the largest fatty acid (Bebthamscience, 2003).

1.15.5-Citric acid: It is weak organic acid with formula $C_6H_8O_7$ a white crystalline powder with molar mass 192.124. It is a natural preservative and it is also used to sour taste to foods and drinks. The conjugate citrate is important as intermediate in citric acid cycle. It consists of three carboxylic groups. Citric acid is commodity chemical, and more than million tones are produced every year by fermentation (Wikipedia, (2003).

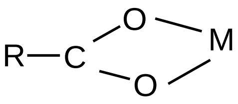
1.16- Literature review:

As indicated by (Al-hazmi, 2005) work entitled “synthesis, characterization and application of zirconia drived from single source precursors” submitted to

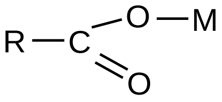
Oklahoma state university, that a variety of zirconium carboxylate complexes were utilized as precursors for synthesis of zirconium oxide. Zirconium carboxylate can be prepared easily by the reaction of sodium carboxylate with and aqueous solution of zirconium salt. Zirconium cations in aqueous solution of zirconium oxychloride for instance, , carboxylate groups displace water in tetrameric cation $[Zr_4 (OH)_8]^{8+}$, to form monocaboxylate zirconium species. As more carboxylate ligands coordinate to zirconium, more water molecules will be displaced from zirconium complex. The bond formed between zirconium atom and carboxylate ligand should be stronger and more stable than the zirconium-water bond. The increase of carboxylate chain length, the hydrophilic nature of zirconium carboxylate reduced. Zirconium metal possibly coordinates to the carboxylate ligands in four different modes: free ion, a monodentate ligand, bidentate bridging ligand and bidentate chelating ligand as follows:



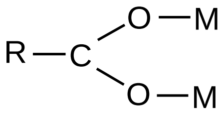
ionic



Chelating



unidentate



possibility of M-M bonding

Another work has been done by (Pienaar, 2005), the work entitled "Metal carboxylate complexes relevant to the fischer-tropsch synthesis". Submitted to university of Stellenbosch (South Africa), determined the molecular structure of copper (п) allyl acetate , Zinc(п) acetate, Zinc(п) isovaleroate, Yttrium (ш) acetate and Lanthanum propionate has been established, zinc has preferred tetrahedral coordination in carboxylate complexes compare to octahedral coordination of copper, lanthanum and yttrium complexes considered. The carboxylate O-C-O angle in these complexes range between 119 and 125^0 and the conformation of the carbon chain is anti in all cases except for copper(п) allyl acetate where gauche conformation adopted. The characterization techniques adopted were infrared spectroscopy, x-ray diffractometry (powder diffraction , single crystal diffraction) and thermal analysis (TGA and DSC) .

Study also has been carried out by (Csilla, 2005) at university of Debrecen entitled "Transition metal complexes of amino acid and peptide derivatives containing caboxylate and imidazole side chain." He has investigated the copper(п)and nickel(п) complexes of di-, tri- and tetra-peptides containing two or more spartic and/or glutamic acids, and he has studied the influence of ß- and ϒ- carboxylate group as well as the effect of increased negative charge of complexes. The result, ligands contain two to five carboxylate functions enhanced metal binding ability of the peptides. It is also important to note that the presence of side chain carboxylate functions results in the formation of carboxylato-bridge polynuclear complexes in medium pH range. The characterization technique adopted were potentiometric titration for determination of protonation constants of the ligands and stability constants of the metal complexes (T= 5^0C, I=0.2mol.dm^{-3} KCl). The evaluation of the titration curves were performed by PSEQUAD and SUPERQUAD computation programs. In order to determine the protonation microconstants NMR technique was used. For characterization of binding modes in the complexes UV- visible spectrophotometer and electron paramagnetic resonance (EPR) spectroscopic method were used.

Many studies have been made for characterization of complexes using potentiometric titration method, one of that, (Nayan & Dey, 1978) studied the acid dissociation constant of iminodiacetic $NH(CH_2COOH)_2$ and iminodipropanoic acid $NH(CH_2CH_2COOH)_2$ and the chelate stability constant of corresponding anions with Cu^{2+}, Ni^{2+} and Cd^{2+}. In this method no mineral acid was added to mixture of titration. The method was modified by adding mineral acid to the titration mixture before titrating against standard alkali solution, as this modified method was applied by to several systems and the results were encouraging. (Chaberek,1952).

The modified method applied by (Ali, 1987), for determination of stoichiometries and stability constants of complexes of ß-alanine with Cu^{2+}, Ni^{2+} and Co^{2+}. The result obtained showed that the modified method would be promising if carefully applied.

The method was also applied by (Abbo, 1991), for determination of stoichiometries and stability constants of complexes of propanoic, ß-chloropropanoic, succinic and ß- aminopropanoic acids, with Cu^{2+}, Ni^{2+} and Co^{2+}.

The same method was also adopted by (Gaafar, 2000), for determination of stoichiometries and stability constants of complexes of three amino acids iso-leucine, serine and tyrosine with Co^{2+} and Ni^{2+}.

Most of these three later studies, their authors confirmed the results obtained with some spectrophotometry method.

done. The work is also aims to study the effect of carbon chain length on the stability of these complexes.

1.17-Charaterization techniques

1.17.1-Potentiometric titration:

Volumetric titrations are usually most conveniently performed with visual indicators. In cases where indicator is unavailable, potentiometric indication of end point can often be used. Potentiometric titrations are among the most accurate known, because the potential follows actual change in activity and therefore the end point coincide with the equivalent point (Louis, 1981) ; (Gurdeep, 1986).

The pH of the solution is directly affected by the complex formation, since all complexing agents are either base or acid. All metal complexes or chelates may be considered as being formed by displacement of one or more usually weakly acidic protons of the complexing or chelating agent by a metal ion in a solution, which result in pH drop (Cotton, 2006).

When stability constants are determined from the pH data the experiment can be carried out in one of the following ways: the change of pH can be measured as function of the ligand concentration, or measured as a function of concentration of acid or alkali added to constant total metal and total ligand concentration. Although pH measurement has been widely used to determine stability constants there are number of limitation to the method:

(i) It cannot used under conditions of extreme pH, at high pH the concentration of the free ligand is insensitive to pH change.

(ii)The method is inapplicable at very low total concentrations.

(iii)The method is inapplicable for very stable complexes such as those formed by transition metal ion and EDTA, because the protons are unable to compete effectively with such metal ions for the ligand.

The composition of the predominant complexes is determined in various pH intervals and at various concentration ratios by comparison of titration curves recorded in the presence and absence of the metal ion. The difference between the titration curves has limiting value that equivalent to quantitative complex formation (Hala, 1995).

1.17.2- potentiometric determination of stability constants

A large number of techniques of great diversity are now being employed for determination of stepwise stability constants. The generally utilized and probably the most accurate and reliable method for determination of stability constant is based on potentiometric measurement of hydrogen ion concentration (Gurdeep, 1986). This depends on the fact that pH of the solution is directly affected by complex formation, which combined by displacement of proton from the acidic ligand (Vogel,1978). The magnitude of the observed pH changing may be employed to determine the stability constant of the metal complex by Calvin, Wilson or Bjerrum's method.

Numerous experimental studies of equilibrium in solution have been made in the last fifteen years, and some of the method used to calculate the stability constants, have been reviewed recently by Sullivan and Hindman (Rossotti & Rossotti, 1955). The fundamental assumption that the complex formation is stepwise process, if this true then the ratios of various stability constants could in theory is predicted by statistical considerations (Hartley & Alcock, 1980).

The study of metal-ligand complexes in a solution would be interesting which throw a light on the mode of storage and transport of metal ion in biological kingdom with a view to understand the bi-inorganic chemistry of the metal ions (Maldhure *et al*., 2012).

The work of coordination chemistry was first begun in the twentieth century; it was mostly related to stepwise formation of complexes (Praveen, et al., 2009).

The stability of compounds means in most general sense, the compounds exist under suitable conditions may be stored for long period of time. However the formation of complexes in solution studied two types of stabilities, thermodynamic and kinetic stabilities are considered (Hartley & Alcock, 1980).

1.17.3-Importance of stability constant: The stability constant of reaction between metal and ligand has found to be greater than zero, is perhaps one of most convincing evidence for the existence of the complex species ML_n in solution. Moreover if all the possible stability constants for a given system have been determined, it is possible in principle to calculate the equilibrium concentration or activity of each species present, under a known set of experimental conditions (Abdulbaset et al., 2012).

There are so many factor affecting the stability of complex, without details that are: solvent, nature of the ligand, steric factor within complex, effect of substituent and nature of the donor atom (Abdulbaset et al., 2012).

1.17.4- Determination of stability constant of binary complex:

It was shown by Calvin and Wilson that pH measurement done during titration with alkali, solution of ligand in presence and absence of metal ion could be used to calculate the formation functions n^-, n_A and pL (Hartley, Burgess & Alcock,1980) (where n_A average number of proton associated with ligand, n^- the average number of ligand attached with metal ion and PL is the free ligand exponential function) (Ashwini, Ashok & Malik, 2007); (Anjani *et al*., 2011).

Irving and Rossotti titrated the three sets of the following solutions against carbonate free standard alkali solution keeping the total volume constant (Minaxi & Shah, 2011); (Avinash & Marutil, 2013)

(i)-Free acid.(A)
(ii)-Free acid +ligand. (A+L).
(iii)-Free acid +ligand +metal. (A+L+M).

On plotting the observed pH against the volume of alkali added, the result is different trends in the titration curves, the acid curve (A), the ligand curve (A+L) lies below the acid curve indicating the dissociation of ligand in the reaction medium and metal complex (A+L+M), lies below the ligand curve indicating the complex formation.

From the titration curves the average number of the proton associated with ligand (n_A) (in some where called proton ligand stability constant, or degree of formation, and others called it proton ligand formation number) at different pH can be calculated utilizing the titration curve of acid in presence or absence of the ligand, can be calculated from the following equation: (Anjani, *et al*., 2011).

$$\bar{n}_A = y - \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)T_L^0} \text{-------------} (1)$$

Where y= the number of dissociable protons, N^0 is the concentration of the alkali, E^0 is the concentration of the free acid, T_L^0 is the total ligand concentration V^0 is the total volume of titration solution,$V_1$and V_2 the volume of alkali added to acid and acid +ligand respectively bring any of them to same pH value.

The average number of the ligand to metal or metal ligand formation number at various pH values determined according to Irving and Rossotti by the following equation: (Ashwini, Ashok & Malik, 2007).

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0} \text{-------------------------}(2)$$

Where V_2 and V_3 the volume of alkali required to the mixture of (acid + ligand) and (acid+ligand +metal) to bring them to same pH, T_m is the total concentration of the metal and other significances as in equation (1).

A free ligand exponent (PL) was calculated using equation (3) (Santosh, 2011).

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti \log \text{pH}]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\}\text{.........................}(3)$$

where V_3 = the volume of alkali required to bring the solution of the complex to same pH in titration curve.

Fairy large number of methods for computing stability constant of complex from experimental data has been used by number of authors. Some of the more generally applicable computational methods are as follows:

1.18-Generally applicable computational methods:

1.18.1 Point-wise calculation method:

This method is used to calculate K_1 and K_2…etc values of the proton ligand formation by using the following expression:

For monobasic acid:-

The ratio of concentration of two consecutive complexes is given by:

$$\frac{[ML_n]}{[ML_{n+1}]} = \frac{n^- + 1 - n}{n - n^-} \quad \text{if } n > n^- > n + 1\text{...........................}(4)$$

or

$$K_n = \left[\frac{(n^- + 1 - n)}{(n - n^-)}\right]\frac{1}{[L]} \quad \text{............................}(5)$$

Hence for a system where n=2

$$K_1 = \left[\frac{n^-}{(1 - n^-)}\right]\frac{1}{[L]} \quad \text{for } 1 > n^- > 0 \quad \text{............................}(6)$$

$$K_2 = \left[\frac{(\bar{n}-1)}{(2-\bar{n})}\right]\frac{1}{[L]} \quad \text{for } 2 > \bar{n} > 1 \text{ ....(7)}$$

By taking logarithm for two sides:

$$\log K_1 = \text{pL} + \log\frac{\bar{n}}{1-\bar{n}} \text{.........................(8)}$$

For dibasic acid:

$$\log K_2 = pL + \log\frac{\bar{n}-1}{2-\bar{n}} \text{...........................(9)}$$

For $2>\bar{n}>1$ (Hartley, Burgess & Alcock,1980) ; (Gharib, Shamel & Mohajeri, 2006).
Generally:

$$\log K_n = \log\frac{\bar{n}+1-n}{n-\bar{n}} + PL \text{.....................(12)} \quad (n > \bar{n} > n-1)$$

(Gharib, Shamel & Mohajeri 2006)

In general the $\bar{n}$ values chosen should lie ideally in the following range:

$0.2<\bar{n}_1<0.8$
$1.2<\bar{n}_2<1.8$
$2.2<\bar{n}_3<2.8$ …. etc.

1.18.2-Half integral method of calculation:

If the value of $\bar{n}$ were put equal 0.5 in equation (8) the obtained value is:
$\log K_1 = pL$.

Similarly putting of value of $\bar{n}$ equal to 1.5 in equation (9) the obtained value is:
$\log K_2 = pL$.

It follows that if a graph is plotted between $\bar{n}$ and pL, then the corresponding values of pL at $\bar{n}$ equal to 0.5 and 1.5 gives $\log K_1$ and $\log K_2$ respectively.

Similarly if the graph plotted n_A against pH the values of pK_1, pK_2 …etc can be calculated in same way. (Lonibala & Rao. Devi 2006).

generally for $\log K_n$ the value of pL at which $\bar{n}= n-0.5$ (Hartley, Burgess, & Alcock.1980). Other expression for this:

$$K_n = \left(\frac{1}{[\mathrm{L}]}\right)_{\mathrm{at}\ n^- = n-0.5}$$

1.18.3- Method of least squares:

Irving and Rossotti showed that the problem of calculating the better set of stability constants from different experimental data can be solved by a least squares method. Moreover when the difference between log K_1 and log K_2 was less than 1.8, the exact values were evaluated by this method.

For a system consisting of (1:1) and (1:2) complex species, the following expression was employed:

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)}.K_1K_2 - K_1 \text{.......................(13)}$$

$$\frac{\bar{n}}{(\bar{n}-1)[L]} \text{ against } \frac{(2-\bar{\mathrm{n}})[\mathrm{L}]}{(\bar{\mathrm{n}}-1)}$$

A plot of

gives the best straight line with slope K_1 K_2 and intercept K_1.(Rossotti. & Rossotti, 1955).

Two other forms of linear treatment are available when N=2 namely extrapolation and elimination and all can be deduced from the basic following equation:

$$n^- = (1-\mathrm{n}^-)[\mathrm{L}]\mathrm{K}_1 + (2-\mathrm{n}^-)[\mathrm{L}]^2\mathrm{K}_1\mathrm{K}_2 \qquad \text{..................(14)}$$

Divide by n^- without rearranging

$$1 = \frac{(1-\bar{n})[L]}{\bar{n}}K_1 + \frac{(2-n^-)[L]^2}{\bar{n}}.K_1K_2 \text{........................(15)}$$

The equation takes the form:

$$F_1x + F_2y = 1----------(16)$$

Where $F_1$and F_2 are function of n^- and [L] , whilst x and y are K_1 and K_1K_2 respectively. This type of equation can be solved graphically by plotting $1/F_1$against $1/F_2$, the point of intersection yielding $K_1$and K_1K_2 by inspection. This method is known as elimination. The sharpness of point of intersection gives an indication of the order of the experimental error in the data set.

The most important form is by rearrangement of equation (14) and division by (2-n$^-$) the resulting form:

$$\left[\frac{(1-n^-)}{(2-n^-)[L]}\right]=\left[\frac{n^-}{(2-n^-)[L]^2}\right]\frac{1}{K_1}-K_2 \quad ....(17)$$

If the left hand side of equation (17) is plotted against n/(2-n)[L]^2, straight line result. An interesting point to note is that whilst the y-intercept gives –K_2 and the slope 1/K_1, the x intercept gives K_1K_2 which is a useful check on the consistency of the data, this called extrapolation (Hartley, Burgess &Alcock,1980).

This is verified by equating the left hand side of equation above to zero and then solving for K_1K_2.

Up till now we have only considered a system where N≤ 2 and hence linear method apply. If system considered for N≥ 3 then rearrangement of the expression will be as such below: (Rossotti & Rossotti, 1955).

$$\left(\frac{N-n^-}{N-1-n^-}\right)[L]+\frac{\beta_{N-1}}{\beta_N}+\frac{\beta_{N-2}}{\beta_N}\left(\frac{n^- -N+2}{N-1-n^-}\right)[L]^{-1}+\sum_{n=0}^{n=N-3}\frac{n^- -n}{N-1-n^-}\frac{\beta_n}{\beta_N}[L]^{n-N+1} ..(18)$$

$$[L]=\frac{T_{CL}-n^- T_{CM}}{\sum_{i=0}^{n}\beta_i^H[H]^i} \quad ....(19)$$

[L]-Concentration of ligand not bonded to metal ion,- can be calculated from the expression:

For monoprotonic equation (19) can be transform to: (Hartley, Burgess &Alcock, 1980).

$$[L]=\frac{T_{CL}-n^- T_{CM}}{1+K_1[H]} \quad ....(20)...$$

Although equation (19) is somewhat alarming equation is non-linear, a plot of the left hand side against (n-N+2)/(N-1-n)[L] will have intercept β_{N-1}/β_N and a limiting slope of β_{N-2}/β_N as [L] tends to zero. Hence all the values of the various K values (via β's) can be found. It should be stressed, however that with an approach of this type errors will accumulate as $K_1$to K_n. calculated (Santosh, *et al*., 2011).

1.18.3.1-Limitation of linear least-squares:

Linear equations derived from a general case for that when only two complexes are present, for calculating stability constants. Examples are equations (13, 14, 15, and 17) using the complex formation function n$^-$ for calculating the stability constants.

These equations do not conform to conditions necessary for the simple linear least-squares procedure to valid and erroneous stability constants may be calculated for the following reasons:

(i)-The independent variable, the x-coordinate, is not exact and cannot be considered error free.

(ii)-Since both the independent and dependent variables, x- and y-coordinates, are function of the same quantity, [L], the errors are correlated.

Rigorous statistics have been developed for this situation and they should therefore be used (Hartley, Burgess & Alcock,1980).

The linear equations that mentioned are perhaps more useful for graphical representation of the data, as no more objective criterion that the eye is used for deciding on the values of stability constants in any case.

For that, we should plot the graphical representation only and give the numerical value of the stability constants (Hartley, Burgess & Alcock,1980).

2.2.4-linear plot method:

This can be utilized for detecting $\log K_1$ by plotting $\log(n^{-}/n^{-} -1)$ versus pL and for $\log K_2$ plotting $\log(n^{-} -1)/(2-n^{-})$ versus pL and so on (Anjani, et al., 2011).

CHAPTER TWO

Materials and Methods

2.1- : Preparation of stock solution:

All material used in this investigation were chemically pure brand and hence were used without further purification. The solutions used throughout the experiment were prepared in doubly distilled water.

2-1-1-Sodium hydroxide solution :(NaOH)

Sodium hydroxide, pellets, fulka, percentage >97.00% .

Concentrated solution of sodium hydroxide (equal weights of solid and water) is prepared, (50gm of sodium hydroxide in 50ml of doubly distilled water) , carbonate remain insoluble and the clear supernatant solution (carbonate free),17M was utilized to prepare the desired concentration by pipetting 6ml in litre volumetric flask and then made up to mark by doubly distilled water, the solution was standardized versus standard hydrochloric acid by titration method, the resulting molarity is 0.10355M. And other solution of carbonate free sodium hydroxide solution is prepared (0.522M)

2-1-2-Hydrochloric acid solution: (HCl)

The percentage is ~36%, molecular weight 36.46 D= 1.18gm/ml, the calculated molarity is 11.65 M. 10ml of concentrated acid transferred to litre volumetric flask and made up to mark with distilled water, the solution standardized against sodium carbonate (0.1M), the resulting molarity of the acid has calculated to be 0.1092M.and other concentration of hydrochloric acid 0.1 is prepared.

2-1-3-Sodium chloride solution :(NaCl)

Interchem (INC) metrocare ltd units, molecular weight 58.44, percentage 99.50% .Since sodium chloride is primary standard substance does not need standardization, the calculated weight is 58.733g, this weight dissolve in litre volumetric flask and completed with distilled water to mark to give 1M solution. It used to maintain the ionic strength constant.

2-1-4-Sodium carbonate solution: (Na_2CO_3)

Brixworth (U.K), molecular weight 105.99, percentage 99.50%. Since sodium carbonate is primary standard substance, the calculated weight 2.653 was transferred to 25ml volumetric flask to give 0.1M solution.

2-1-5-Oxalic acid dihydrate solution: ($H_2C_2O_4.2H_2O$).

Nice chemical laboratory reagent, molecular weight 126.07. Since this acid is primary standard substance the calculated weight is 12.3g transferred into litre volumetric flask, already containing water and then made to mark with distilled water to give 0.1M solution used as stock solution utilized for preparing of dilute ones.

2-1-6-Chromium (ш) chloride solution : ($CrCl_3.6H_2O$)

Extra pure scharlau molecular weight 266.45. Calculated weight 13.322gm was transferred to 500ml volumetric flask to give 0.1M solution, used as stock solution for preparing other dilute concentrations.

2-1-7-Titanium(Ш) chloride solution: ($TiCl_3$)

Acros organics, New Jersey, molecular weight 132.07, titanium chloride 20% solution 2N in hydrochloric acid. To change the normality to molarity, or M= N/3, M=0.6667 by dilution 37.5 gives 0.1M solution.

2-1-8-Acetic acid: (CH_3COOH)

Glacial analytical grade, made in Spain, Mwt. 60.05 density 1.05, purity 99.8%, the calculated molarity of acid is 17.45M, the solution diluted by measuring 2.57ml in 500ml beaker already containing water, then completed to graduation mark by double distilled water to give a solution 0.1M.

2-1-9-Zirconium(1V) chloride: ($ZrCl_4$)

Molecular weight 233.03, Acros organics nitrogen flushed purity 98%, appropriate weight 11.42 g dissolve in 500 ml distilled water to give 0.1M solution, used as stock solution.

2-1-10-Nitric acid :(HNO_3)

Nitric acid (U.K), percentage 69%, density 1.42g/ml, molecular weight 63.01, the calculated molarity is equal to 15.5499M, 6.43≈ 6.5 was transfered to one litre volumetric flask and then made up to graduated mark with double distilled water, and then standardized to 0.1M with sodium carbonate by titration method, then standardized to 0.1M.

2-1-11-Potassium nitrate: (KNO_3):

Interchem.(U.K), purity 99%, molecular weight 70.11, since potassium nitrate is primary standard substance the molecular weight calculated in grams (70.11g), transfer to one litre volumetric flask containing distilled water, after it was dissolved, completed to mark with double distilled water to prepare 1M solution. The solution was used to maintain the ionic strength constant.

2-1-12-**Propanoic acid: ($C_3H_6O_2$).**

Product of USA, purity 99%, density 0.99, molecular weight=74.08. calculated molarity 13.23, an appropriate volume 3.77 introduced in 500ml beaker already contained water, then made up with double distilled water to mark, the prepared solution give a solution of 0.1M.

2-1-13-Oxalacetic acid: ($C_4H_4O_5$).

Molecular weight 132.07, purity 98%, product of HU, New Jersey USA, an appropriate weight =0.47g dissolved in 500ml beaker, then completed to graduation mark with double distilled water to give a solution of 0.1M.

2.2-Apparatus

pH-meter denver instrument ultra basic pH/mVmeter with combine electrode at 29 ± 1^0C, the sensitivity of the pH-meter is 0.01 unit, the instrument could read pH in range 0.00 to 14.00 in step 0.01.The pH-meter was switched on before half an hour for warm up before starting titration. The instrument was calibrated before each set of titration using two buffer solutions of pH 4 and 10. The electrode was washed with distilled water and dried with tissue paper. The readings were recorded only when the instrument registered a steady value for at least one minute.

Startorius analytical balance, maximum weighing capacity 220 grams and increments in 0.0001 grams graduations, (4 decimal places).

Thermo scientific hot plate combined with magnetic stirrer, to stir the solution mixture, during titration course.

CHATER THREE

Results and discussions

The present investigation is based upon reaction of some organic reagent, carboxylic acids and β-substituent carboxylic acid with some transition metals chromium, titanium and zirconium, in purpose of developing a sensitive and selective method for determination of stoichiometries and stability constants of these complexes. These stability constants were evaluated assuming that the formation of hydrolysed products, polynuclear complexes, hydrogen and hydroxyl bearing complexes were absent.

Dissociation of organic acid and their interactions with metal ions (complex formation) may be extremely sensitive to ionic strength of the medium. If charges in the reacting species are opposite then here is a decrease in the reaction rate with increasing ionic strength whereas if the charges are identical, an increase in the reaction rate will occur and if one of the reactant is charge less the reaction rate will not affected by ionic strength of the medium. (Santosh et al., 2011). So many trials had been made for detection of the best ionic strength of the medium to be in concordant with the mentioned in literature, and this conclude that the reactants are oppositely charged, that there was decrease in rate of reaction with increasing ionic strength. This related to the concentration of electrolytes and indicates that how effectively the charge on a particular ion is shielded or stabilized by other ions in an electrolyte. For that volume of potassium nitrate minimize to one milliliter ($1cm^3$) for maintained only the ionic strength of medium.

On plotting the observed pH against the volume of alkali added, different trends have shown, acid curve (A), a ligand curve (A+L) lies below the acid curve indicating the dissociation of ligand in the titration medium, and metal complex curve lies below the ligand titration curve indicating the complex formation.

This investigation represents a comparative study of three graphical methods and two algebraic methods for overall stability constant determination techniques including point-wise calculation method, half integral method, linear plot method, least squares method and Henderson or Hasselbalch's equation in purpose to select the most sensitive and accurate method aiming also to determine the parameters that affect the precision of the methods under investigation.

Titration procedure:

Three sets of solutions Total volume of each (V^0) 200cm^3 were prepared for titration against free carbonate sodium hydroxide solution. The change in pH of solution with each addition of alkali was recorded for each of the following mixtures, to calculate the formation function $\bar{n}_A$, $\bar{n}$ and PL.

A/ 10cm^3 HCl 0.12293M + 1cm^3 KNO_3 1M.

B/ A + 10 cm^3 acetic acid 0.1M.

C/ B + 2.5 cm^3 $CrCl_6.6H_2O$. 0.1M

All solution were completed with distilled water to 200 cm^3 after addition of 1cm^3 of KNO_3 0.1M. The titrations were carried out in 250 cm^3 beaker with magnet bar inside, for stirring the solution.

The ionic strength was maintained constant by using KNO_3 (u = 0.005).

Chromium carboxylates complexes

3/Results and discussion

3.1-Chromium- acetic acid system.

The pH titration reading of acid, acid + ligand (acetic acid) and acid + ligand + metal ion (Cr^{+3}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}$ M , $T_{Cl} = 5\times10^{-3}$ M , $T_{cm} = 1.25\times10^{-3}$ M , $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$ $t = 36.5^0 C$.

Table (3.1.1)

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.24	2.28	2.28	3.6	11.82	5.73	4.93
0.1	2.26	2.29	2.29	3.7	11.85	6.11	5.03
0.2	2.28	2.31	2.30	3.8	11.87	7.60	5.13
0.3	2.30	2.32	2.32	3.9	11.90	10.46	5.25
0.4	2.32	2.35	2.34	4.0	11.92	10.83	5.37
0.5	2.35	2.37	2.36	4.1	11.94	11.04	5.52
0.6	2.38	2.40	2.39	4.2	11.94	11.18	5.67
0.7	2.41	2.43	2.41	4.3	11.98	11.28	5.82
0.8	2.44	2.46	2.44	4.4	12.00	11.36	5.95
0.9	2.48	2.49	2.47	4.5	12.02	11.43	6.07
1.0	2.52	2.53	2.51	4.6	12.03	11.50	6.18
1.1	2.56	2.57	2.55	4.7	12.05	11.55	6.25
1.2	2.61	2.61	2.59	4.8	12.06	11.59	6.36
1.3	2.66	2.66	2.63	4.9	12.08	11.64	6.55
1.4	2.77	2.72	2.68	5.0	12.09	11.68	6.97
1.5	2.78	2.79	2.74	5.1	12.10	11.71	9.53
1.6	2.87	2.87	2.80	5.2	12.12	11.74	10.43
1.7	2.98	2.97	2.88	5.3	12.13	11.78	10.76
1.8	3.12	3.09	2.97	5.4	12.14	11.80	10.96
1.9	3.34	3.25	3.07	5.5	12.15	11.83	11.10
2.0	3.76	3.43	3.19	5.6	12.17	11.85	11.21
2.1	9.65	3.65	3.32	5.7	12.18	11.88	11.30
2.2	10.65	3.85	3.46	5.8	12.19	11.90	11.37
2.3	10.95	4.03	3.60	5.9	12.20	11.92	11.43
2.4	11.12	4.18	3.74	6.0	12.21	11.94	11.49
2.5	11.24	4.31	3.87	6.1	12.22	11.96	11.53
2.6	11.34	4.42	3.98	6.2	12.23	11.98	11.58
2.7	11.42	4.53	4.10	6.3	12.24	12.00	11.62
2.8	11.49	4.64	4.20	6.4	12.25	12.01	11.65
2.9	11.55	4.74	4.30	6.5	12.25	12.03	11.69
3.0	11.60	4.84	4.39	6.6	12.26	12.04	11.72
3.1	11.64	4.94	4.49	6.7	12.27	12.06	11.74
3.2	11.68	5.05	4.58	6.8	12.27	12.07	11.77
3.3	11.72	5.18	4.66	6.9	12.28	12.09	11.80
3.4	11.76	5.32	4.75	7.0	12.29	12.10	11.82
3.5	11.79	5.50	4.84	7.1	12.30	12.11	11.84

Amatlab program have been created for plotting the graph for volume of alkali solution versus pH of three sets of solutions (acid, acid+ligand, acid+ligand+metal ion) and secondly to find the volume of alkali required for bringing the three sets of solutions to reach the same pH. This program written in matlab as follows:

plot (x,y1,x,y2,x,y3)

```
yii=2.5;
disp(['        y ','     x1  ',   '     x2          x3  '])
while yii<12

disp( [yii,        polyxpoly(x,y1,[0,45],[yii,yii])  ,
polyxpoly(x,y2,[0,45],[yii,yii]) , polyxpoly(x,y3,[0,45],[yii,yii])
yii=yii+0.1000001;
end
```

yii means the chart start from pH 2.5 and can be change as it requires.

Yii+0.1000001means the gradually increase from the starting may be 0.1. also the rate of successive increase can be changed to any number as it requires.Y X1 X2 X3 means display should be in columns and X1, X2, X3 represent the volume of alkali needed to bring the solutions of acid, acid+ligand and acid+ligand+metal ion respectively to the facing pH (Y).

As a conclusion this program plotted the graph and determined the volume of alkali required to bring the three set of solutions to the same pH. The result has been as follows:

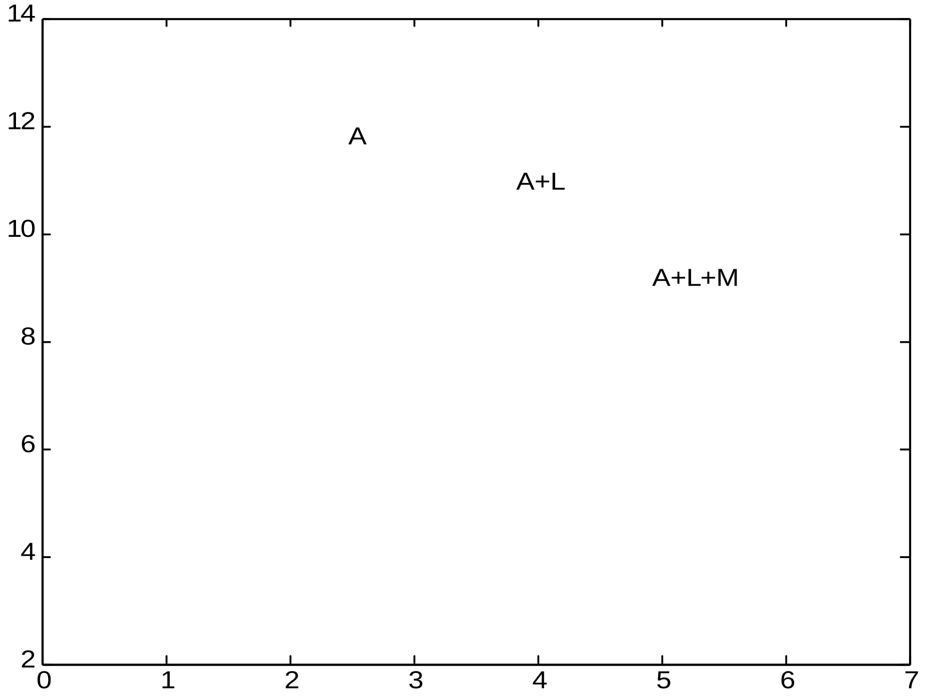


Fig. (3.1.1) Titration curves of three set of solutions against pH

Table (3.1.2). Alkali volume required for bringing the three sets of solutions to the same pH (B).

B	V1	V2	V3	B	V1	V2	V3
2.5	0.9500	0.9250	0.9750	7.3	2.0601	3.7799	5.0101
2.6	1.1800	1.1750	1.2250	7.4	2.0618	3.7866	5.0141
2.7	1.3667	1.3667	1.4333	7.5	2.0635	3.7933	5.0181
2.8	1.5222	1.5125	1.600	7.6	2.0652	3.8000	5.0222
2.9	1.6273	1.6300	1.7222	7.7	2.0669	3.8035	5.0262
3.0	1.7143	1.7250	1.8300	7.8	2.0686	3.8070	5.0302
3.1	1.7157	1.8063	1.9250	7.9	2.0703	3.8105	5.0343
3.2	1.8364	1.8688	2.0077	8.0	2.0720	3.8140	5.0383
3.3	1.8818	1.9278	2.0846	8.1	2.0737	3.8175	5.0423
3.4	1.9143	1.9833	2.1571	8.2	2.0754	3.8210	5.0464
3.5	1.9381	2.0318	2.2286	8.3	2.0771	3.8245	5.0504
3.6	1.9619	2.0773	2.3000	8.4	2.0788	3.8280	5.0544
3.7	1.9857	2.1250	2.3714	8.5	2.0805	3.8315	5.0585
3.8	2.0007	2.1750	2.4462	8.6	2.0822	3.8350	5.0625
3.9	2.0024	2.2278	2.5273	8.7	2.0839	3.8385	5.0665
4.0	2.0041	2.2833	2.6167	8.8	2.0856	3.8420	5.0706
4.1	2.0058	2.3467	2.7000	8.9	2.0873	3.8455	5.0746
4.2	2.0075	2.4154	2.8000	9.0	2.0890	3.8490	5.0786
4.3	2.0092	2.4923	2.9000	9.1	2.0907	3.8524	5.0827
4.4	2.0109	2.5818	3.0100	9.2	2.0924	3.8559	5.0867
4.5	2.0126	2.6727	3.1111	9.3	2.0941	3.8594	5.0907
4.6	2.0143	2.7636	3.2250	9.4	2.0958	3.8629	5.0948
4.7	2.0160	2.8600	3.3444	9.5	2.0975	3.8664	5.0988
4.8	2.0177	2.9600	3.4556	9.6	2.0992	3.8699	5.1078
4.9	2.0194	3.1286	3.5667	9.7	2.1050	3.8734	5.1189
5.0	2.0211	3.1762	3.6700	9.8	2.1150	3.8769	5.1300
5.1	2.0228	3.2385	3.7583	9.9	2.1250	3.8804	5.1411
5.2	2.0244	3.3143	3.8500	10.0	2.1350	3.8839	5.1522
5.3	2.0261	3.3857	3.9417	10.1	2.1450	3.8874	5.1633
5.4	2.0278	3.4444	4.0200	10.2	2.1550	3.8909	5.1744
5.5	2.0295	3.5000	4.0867	10.3	2.1650	3.8944	5.1856
5.6	2.0132	3.5435	4.1533	10.4	2.1750	3.8979	5.1967
5.7	2.0329	3.5870	4.2200	10.5	2.1850	3.9108	5.2212
5.8	2.0346	3.6184	4.2867	10.6	2.1950	3.9378	5.2515
5.9	2.0363	3.6447	4.3615	10.7	2.2167	3.9649	2.2818
6.0	2.0380	3.6711	4.4417	10.8	2.2500	3.9919	5.3200
6.1	2.0397	3.6974	4.6118	10.9	2.2833	4.0333	5.700
6.2	2.0414	3.7060	4.6706	11.0	2.3294	4.0810	5.4286
6.3	2.0431	3.7128	4.7455	11.1	2.3882	4.1429	5.5000
6.4	2.0448	3.7195	4.8211	11.2	2.4667	4.2200	5.5909
6.5	2.0465	3.7262	4.8737	11.3	2.5600	4.3250	5.7000
6.6	2.0482	3.7329	4.9100	11.4	2.6750	4.4572	5.8500
6.7	2.0499	3.7396	4.9300	11.5	2.8167	4.6000	6.0250
6.8	2.0516	3.7463	4.9500	11.6	3.0000	4.8200	6.2500
6.9	2.0533	3.7530	4.9700	11.7	3.2500	5.0667	6.5334
7.0	2.0550	3.7597	4.9900	11.8	3.5334	5.4000	6.9000
7.1	2.0567	3.7664	5.0020	11.9	3.9000	5.8000	-
7.2	2.0584	3.7732	5.0060	-	-	-	-

B is the pH-meter reading.

V1, **V2** and **V3** are volumes of alkali added to bring the solutions of acid, acid+ ligand and acid+ligand+metal ion respectively to the same pH value.

3.1.1-Practical proton-ligand stability constant:

3.1.1.1-Point-wise calculation method:

Since the ligand used is monobasic acid, the calculation of free ligand exponent function (pL) of metal complexes requires a prior knowledge of the practical proton-ligand stability constant. Using excel program on personal computer the values of n_A at various pH reading (B) were calculated from the acid and ligand titration curve, table (3.1.1). The ligand titration curve is well separated from the free acid titration curve at pH 2.9 indicating the dissociation of the ligand in the titration medium, figure (3.1.1) and table (3.1.2). The formation curve for the ligand extends $0<n_A<1$ in n_A scale Table (3.1.3). The pK_a taken as an average from $n_A = 0.2$ to $n_A = 0.8$ the value found, $pK_a = 4.8365$.This value is further being verified by half integral method.

$$pk_1 = \log \frac{n_A}{1-n_A} + pH -----(1.1)$$

Table (3.1.3) Proton-ligand stabilityconstant.(acetic acid) pKa average value =4.8365

pKa	$\log\left(\frac{n_A}{(1-n_A}\right)$	.n_A	V2	V1	pH
5.7463	2.8463	0.9986	1.6300	1.6273	2.9
5.2466	2.2466	0.9943	1.7250	1.7143	3.0
4.4001	1.3001	0.9523	1.8063	1.7157	3.1
4.9607	1.7607	0.9829	1.8688	1.8364	3.2
4.9054	1.6054	0.9758	1.9278	1.8818	3.3
4.8240	1.4240	0.9637	1.9833	1.9143	3.4
4.7852	1.2852	0.9507	2.0318	1.9381	3.5
4.7896	1.18962	0.9393	2.0773	1.9619	3.6
4.8020	1.1020	0.9267	2.1250	1.9857	3.7
4.7960	0.9960	0.9083	2.1750	2.0007	3.8
4.7713	0.8713	0.8815	2.2278	2.0024	3.9
4.7642	0.7642	0.8532	2.2833	2.0041	4.0
4.7606	0.6606	0.8207	2.3467	2.0058	4.1
4.7637	0.5637	0.7855	2.4154	2.0075	4.2
4.7678	0.4678	0.7459	2.4923	2.0092	4.3
4.7675	0.3675	0.6998	2.5818	2.0109	4.4
4.7743	0.2743	0.6529	2.6727	2.0126	4.5
4.7869	0.1869	0.6060	2.7636	2.0143	4.6
4.7980	0.0980	0.5562	2.8600	2.016	4.7
4.8078	0.0078	0.5045	2.9600	2.0177	4.8
4.7540	-0.1459	0.4167	3.1286	2.0194	4.9
4.8104	-0.1895	0.3926	3.1762	2.0211	5.0
4.8515	-0.2484	0.3608	3.2385	2.0228	5.1
4.8761	-0.3238	0.3217	3.3143	2.0244	5.2
4.9007	-0.3992	0.2851	3.3857	2.0261	5.3
4.9351	-0.4648	0.2553	3.4440	2.0278	5.4
4.9673	-0.5326	0.2267	3.5000	2.0295	5.5
4.9850	-0.6149	0.1953	3.5435	2.0132	5.6

3.1.1.2-Half integral method (acetic acid)

In case of half integral method the proton-ligand stability constant can be calculated from ligand formation curve by plotting n_A against pH. The value of pH where $n_A= 0.5$ corresponds to value of pK_a, figure (3.1.2), the value was found to be, $pK_a=4.815$. This value was in a good agreement with the value obtained by point-wise method.

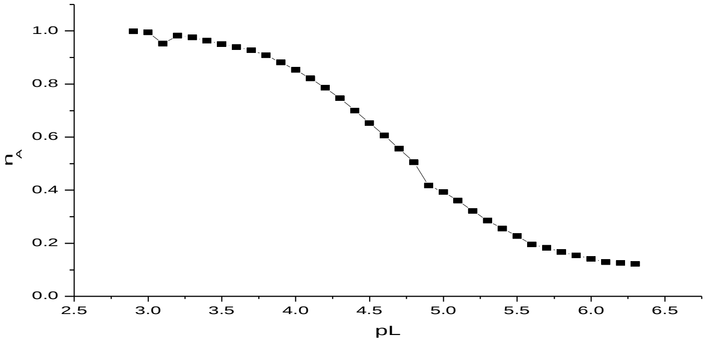


Fig. (3.1.2) half integral method (acetic acid) pK_a =4.815

3.1.2-Metal-ligand stability constant :(chromium acetate)

3.1.2.1-Point-wise calculation method

Metal-ligand titration curve crossed over ligand titration curve at pH 2.5 table (3.1.2) figure (3.1.1). n^- range from 0.1044 to 2.1991, table (3.1.4) indicating the formation of ML and ML_2 complex species. The formation of complex species extends from pH 2.5 to pH 5.2, showed that complexes are stable in acidic medium, after that the pL cannot be calculated that means [L] tends to zero. Metal-ligand stability constant for 1:1and 1:2 complex spieces were calculated by point-wise method using equation (1.2), and equation (1.3).

$$\log K_1 = \mathrm{pL} + \log\frac{\bar{n}}{1-\bar{n}} \text{ ------------ } (3.1.2)$$

$$\log K_2 = pL + \log\frac{\bar{n}-1}{2-\bar{n}} \text{ --------- } (3.1.3)$$

All calculations were done using excel program in personal computer table (3.1.4) and table (3.1.5) for evaluation of n^- and pL. Linear equations (1.1) and (1.2) were solved for determination of $\log K_1$and $\log K_2$. The average values were taken as correct value of $\log K_1$ and $\log K_2$.The values of the metal-ligand formation number (n^-) were selected in the range 0.2 to 0.8 and 1.2 to 1.8 for $\log K_1$and $\log K_2$

respectively. These values were found, logK_1= 3.6175, logK_2=3.0439The unappreciable difference between logK_1 and logK_2 indicates that the complex species were form simultaneously and not in step-wise manner.(Minaxi & Shah 2011), (Sayyed, Abdul Rahim, & Mazahar 2011) K_1>K_2 this indicates no steric effect in the addition of second ligand. (Lonibala, 2006). These values were further corroborated by the method of half integral.

Table: (3.1.4). Point-wise method logK_1(Average value =3.6175)

Log K_1	$\log\left(\frac{n^-}{(1-n^-)}\right)$	pL	n^-	V3	V2
3.6040	-0.9291	2.3146	0.1053	1.225	1.1750
3.6517	-0.7864	4.5331	0.1405	1.4333	1.3667
3.6961	-0.6481	4.4382	0.1836	1.6000	1.5125
3.6299	-0.6169	4.3443	0.1946	1.7222	1.6300
3.6081	-0.5436	4.2469	0.2224	1.8300	1.7250
3.6094	-0.4487	4.1516	0.2625	1.9250	1.8063
3.5913	-0.3733	4.0582	0.2974	2.0077	1.8688
3.5805	-0.2917	3.9645	0.3381	2.0846	1.9278
3.5668	-0.2137	3.8722	0.3794	2.1571	1.9833
3.5787	-0.1129	3.7806	0.4354	2.2286	2.0318
3.6022	-0.0025	3.6916	0.4985	2.3000	2.0773
3.6217	0.1029	3.6047	0.5589	2.3714	2.1250
3.6622	0.2265	3.5188	0.6275	2.4462	2.1750
3.7541	0.3972	3.4357	0.7139	2.5273	2.2278
3.9446	0.6611	3.3569	0.8209	2.6167	2.2833

Table: (3.1.5). Point-wise method logK_2 (Average value = 3.0439)

Log K_2	$\log\left(\frac{n^- -1}{(2-n^-)}\right)$	pL	n^-	V3	V2
1.6025	1.6025	3.1456	1.0278	2.8	2.4154
2.3210	2.3210	3.0850	1.1469	2.9	2.4923
2.6293	2.6293	3.0320	1.2835	3.01	2.5818
2.8207	2.8207	2.9827	1.4078	3.1111	2.6727
3.1191	3.1191	2.9509	1.5956	3.225	2.7636
3.6064	3.6064	2.9351	1.8243	3.3444	2.86

3.1.2.2-Half integral method: (Chromium acetate)

For determination of log K_1 and log K_2 according to this method n^- should be plotted versus pL, table (3.1.6), From the formation curve figure (3.1.3) the values of pL at which n^-= 0.5 and n^-=1.5 corresponds to values of logK_1 and logK_2 respectively. For this purpose graph is elongated and broaden. The values found, logK_1=3.6 and logK_2=2.958, the values were in a good agreement with values of point-wise calculation method. These values were further verified by linear plot method.

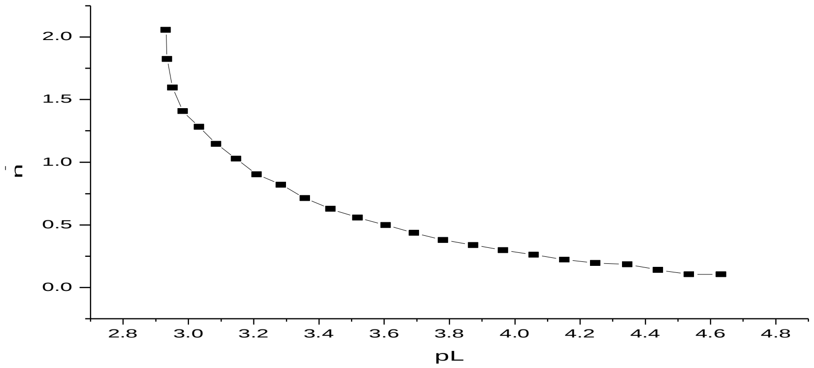


Fig.(31.3). Cr-acetate formation curve $\log K_1$=3.6 &$\log K_2$=2.958

3.1.2.3- Linear plot method :(Chromium acetate)

To estimate the stability constants of chromium acetate by this method log n^- /(1-n^-) and log(n^- -1)/(2-n^-) were plotted against corresponding pL for determination of $\log K_1$, and $\log K_2$ respectively (Anjani et al., 2011). It is obviously that from figure (3.1.4) and figure (3.1.5) log K_1= 3.6 and log K_2=2.96, these values were in a good agreement with values deduced by two previous methods. The values were further corroborated by least squares method.

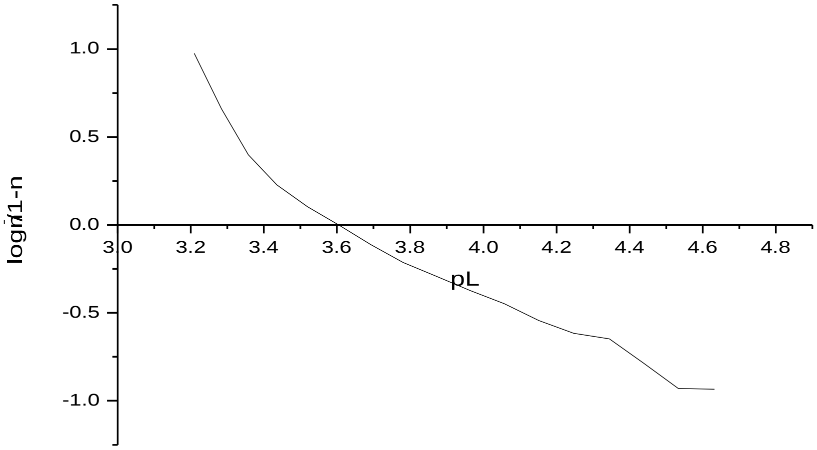


Fig. (31.4) Linear plot method $\log K_1$= 3.6

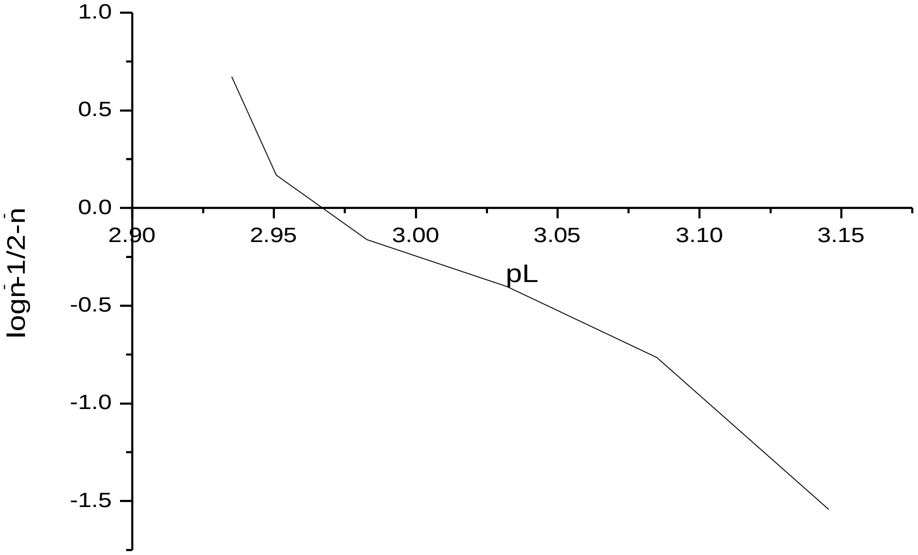


Fig. (3.1.5) Linear plot method $\log K_2 = 2.96$

3.1.2.4-Method of least squares: (chromium acetate)

Irrving and Rossotti showed that the problem of calculating the better set of stability constants from different experimental data can be solved by a least squares method. Moreover when a difference between the values $\log K_1$ and $\log K_2$ was less than 1.8, such as the case under investigation the exact values can be evaluated by this method. (Gurdeep, 1986)

Least squares method one of the most popular graphical methods as they make use of all data. Two forms of linear treatment are available when N=2, namely extrapolation and elimination. (N is all possible coordination sites) as the present case, the following expression was employed.

$$n^- = (1-n^-)[L]K_1 \ + (2-n^=)[L]^2 K_1 K_2 ....(3.1.3)$$

$$\frac{n^-}{(1-n^-)[L]} = \left(\frac{(2-n^-)[L]}{(1-n^-)}\right) K_1 K_2 + K_1$$

---------- (3.1.4)

$$\frac{n^-}{(1-n^-)[L]} \times \frac{1}{K_1 K_2} \ - \ \frac{1}{K_2} = \left(\frac{(2-n^-)[L]}{(1-n^-)}\right)$$

---------- (3.1.5)

A plot of the left hand side (equation'1.4') against $(2-n^{-})[L]/(n^{-}-1)$ give a straight line equation. An interesting point to note is that whilst the y-intercept gives K_1 and the slope $K_1 K_2$, the x-intercept is $-1/K_1$and the slope $1/K_1K_2$ which is a useful check on the consistency of the data.(Vogel, 1978). In this way error accumulated on K_{n-1}.

By plotting equation (3.1.4), $\log K_1=3.3768$ and $\log K_1=2.9242$ fig (3.1.6). However with an approach of this type, errors will accumulate as we calculate $K_1$to K_n. (Rossotti & Rossotti,1955). For plotting of equation (3.1.5), values obtained $\log K_1=3.1029$, and $\log K_2= 3.00$, fig. (3.1.7).

The method can be also utilized to confirm the presence and absence of 1:2 complex species. Nayan and Dey have also attempted to simplify the approach for calculating various parameters required for stability constant. (Gurdeep, 1986). The R squared (R^2) on figure (3.1.6) and figure (3.1.7) is an excel label, names as coefficient of determination, it is a famous number, people quote to prove how good the fit is, it is quite useless for evaluating a working curve unless you count the number of nines you get. (0.978 is a pretty bad working curve, 0.999 is probably a good one). In the figures fitted, R^2=0.983, that means the working curves are good.

Table (3.1.6) Least squares method for confirmation of $\log K_1$= and $\log K_2$

$\frac{(2-n^{-})[L]}{(1-n^{-})}$	$\frac{n^{-}}{(1-n^{-})[L]}$	[L]	n^{-}	pL
4.9E-05	4992.5923	2.3E-05	0.1044	4.6319
6.2E-05	4017.9331	2.9E-05	0.1053	4.5331
7.9E-05	4484.8425	3.6E-05	0.1405	4.4382
0.0001	4967.5484	4.5E-05	0.1836	4.3443
0.0001	4265.1598	5.7E-05	0.1946	4.2469
0.0002	4055.8009	7.1E-05	0.2224	4.1516
0.0002	4068.3161	8.7E-05	0.2625	4.0582
0.00023	3901.7738	0.0001	0.2974	3.9645
0.00034	3806.1331	0.0001	0.3381	3.8722
0.00043	3688.3915	0.0002	0.3794	3.7806
0.00056	3790.6599	0.0002	0.4354	3.6916
0.00074	4000.9270	0.0002	0.4985	3.6047
0.00099	4184.9108	0.0003	0.5589	3.5188
0.00135	4593.6042	0.0004	0.6275	3.4357
0.00198	5676.3636	0.0004	0.7139	3.3569
0.00343	8801.5979	0.0005	0.8209	3.2835
0.00704	15259.7411	0.0006	0.9040	3.2098
-0.0250	-51624.2899	0.0007	1.0278	3.1456
-0.00458	-9494.4212	0.0008	1.1469	3.0850
-0.00235	-4874.2900	0.0009	1.2835	3.0320

-0.00151	-3317.6648	0.0010	1.4078	2.9827
-0.00076	-2392.3013	0.0011	1.5956	2.9509

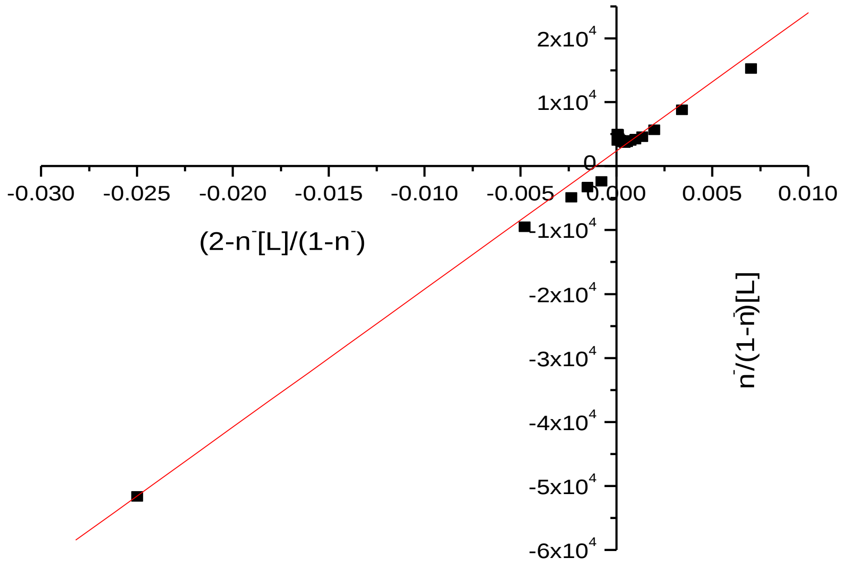


Fig. (3.1.6) least squared Method (equation 1.4) $\log K_1=3.3768$& $\log K_2=2.9242$

Linear Regression for Data

Parameter	Value	Error	R^2
Intercept	2381.38229	360.54328	0.99163
Slope	2.15881E6	62833.38787	

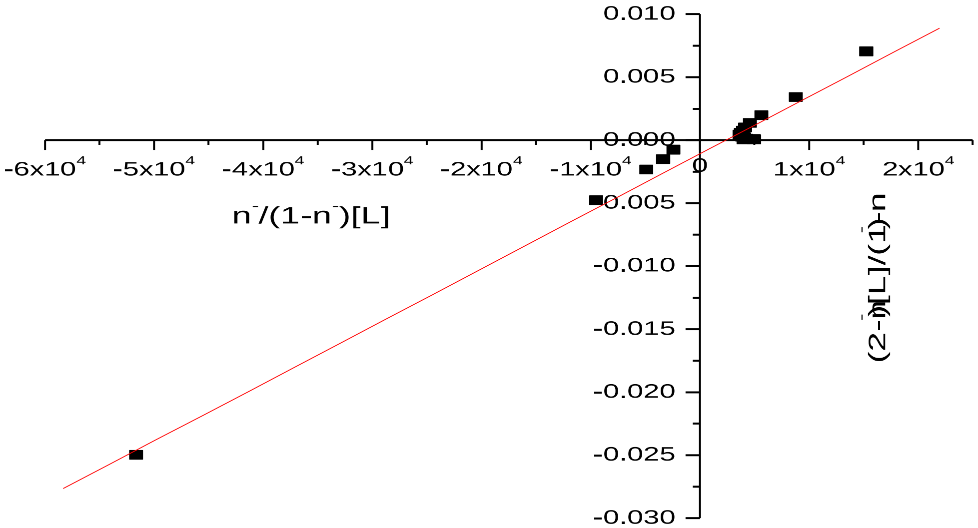


Fig. (3.1.7) least squares method (equation 1.5) logK_1 =3.1029 & logK_2=3.00

```
                    Linear Regression for Data

Parameter                  Value                Error              R^2
----------------------------------------------------------------------------------------
     Intercept            -0.0011             0.00016           0.99163
     Slope                 4.555E-7           1.32576E-8
----------------------------------------------------------------------------------------
```

Table (3.1.7) Summary for chromium acetate stability constants

Method	logK_1	logK_2	Logβ_2
Point wise calculation method	3.6175	3.0439	6.6614
Half integral method	3.6	2.958	6.558
Linear plot method	3.6	2.96	6.56
Least squares method eq. (1.4)	3.3455	2.9242	6.2697
Least squares method eq. (1.5)	3.1029	3.00	6.1029

3.2-Chromium-oxalic acid system

Table (3.2.1). The pH - titration reading of acid, acid + ligand(oxalic acid) and acid + ligand + metal ion (Cr^{+3}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}$ M , $T_{Cl} = 5\times10^{-5}$ M , $T_{cm} = 1.25\times10^{-5}$ M , $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$, $t = 36.5^0 C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.22	2.02	2.01	4.1	11.90	3.72	3.37
0.1	2.24	2.02	2.02	4.2	11.92	3.82	3.45
0.2	2.26	2.03	2.03	4.3	11.94	3.91	2.54
0.3	2.29	2.04	2.04	4.4	11.95	4.01	3.63
0.4	2.31	2.06	2.05	4.5	11.97	4.09	3.71
0.5	2.34	2.07	2.06	4.6	11.99	4.19	3.79
0.6	2.37	2.08	2.07	4.7	12.01	4.29	3.88
0.7	2.40	2.09	2.08	4.8	12.02	4.41	3.96
0.8	2.43	2.11	2.10	4.9	12.04	4.53	4.04
0.9	2.47	2.12	2.11	5.0	12.05	4.67	4.12
1.0	2.51	2.14	2.12	5.1	12.06	4.85	4.21
1.1	2.56	2.15	2.14	5.2	12.08	5.09	4.30
1.2	2.61	2.17	2.15	5.3	12.09	5.54	4.39
1.3	2.67	2.19	2.17	5.4	12.10	7.29	4.50
1.4	2.74	2.20	2.19	5.5	12.11	10.31	4.61
1.5	2.82	2.22	2.20	5.6	12.13	10.72	4.74
1.6	2.92	2.24	2.22	5.7	12.14	10.93	4.89
1.7	3.04	2.26	2.24	5.8	12.15	11.08	5.10
1.8	3.21	2.28	2.26	5.9	12.16	11.19	5.33
1.9	3.51	2.31	2.28	6.0	12.17	11.28	5.61
2.0	4.44	2.33	2.31	6.1	12.18	11.36	5.86
2.1	10.16	2.36	2.33	6.2	12.19	11.42	6.06
2.2	10.70	2.39	2.35	6.3	12.20	11.48	6.26
2.3	10.94	2.42	2.38	6.4	12.21	11.52	6.48
2.4	11.10	2.45	2.41	6.5	12.21	11.57	6.76
2.5	11.21	2.48	2.44	6.6	12.22	11.60	7.18
2.6	11.30	2.52	2.47	6.7	12.23	11.64	7.62
2.7	11.38	2.56	2.50	6.8	12.24	11.67	8.18
2.8	11.45	2.61	2.54	6.9	12.25	11.70	8.97
2.9	11.50	2.66	2.58	7.0	12.26	11.73	9.61
3.0	11.55	2.71	2.62	7.1	12.27	11.76	10.07
3.1	11.60	2.77	2.67	7.2	12.28	11.78	10.42
3.2	11.64	2.84	2.72	7.3	12.29	11.80	10.67
3.3	11.68	2.91	2.77	7.4	12.30	11.83	10.86
3.4	11.71	3.00	2.83	7.5	12.31	11.85	11.00
3.5	11.74	3.09	2.90	7.6	12.32	11.87	11.11
3.6	11.77	3.19	2.96	7.7	12.33	11.89	11.25
3.7	11.80	3.30	3.04	7.8	12.34	11.91	11.27
3.8	11.83	3.41	3.12	7.9	12.35	11.93	11.34
3.9	11.85	3.52	3.20	8.0	12.36	11.95	11.39
4.0	11.87	3.62	3.28	-	-	-	-

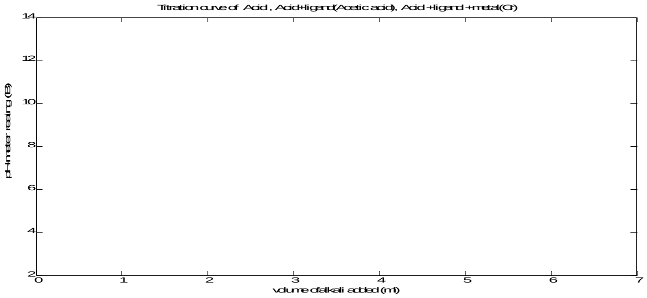


Fig.(3.2.1). Alkali volume against pH of three sets of solutions.

Table (3.2.2) Volume of alkali required to bring three set of solutions to same pH

B	V1	V2	V3	B	V1	V2	V3
2.1	0.7500	0.800	-	6.8	2.0413	5.3720	6.5096
2.2	1.400	1.500	-	6.9	2.0430	5.3777	6.5334
2.3	0.3500	1.8667	1.9667	7.0	2.0448	5.3835	6.5573
2.4	0.7000	2.2334	2.3667	7.1	2.0465	5.3892	6.5811
2.5	0.9751	2.5501	2.7001	7.2	2.0483	5.3949	6.6047
2.6	1.1801	2.7801	2.9501	7.3	2.0500	5.4003	6.6274
2.7	1.3429	2.9801	3.1601	7.4	2.0518	5.4037	6.6501
2.8	1.4751	3.1429	3.3501	7.5	2.0535	5.4070	6.6728
2.9	1.5801	3.2858	3.5001	7.6	2.0553	5.4103	6.6956
3.0	1.6667	3.4001	3.6501	7.7	2.0570	5.4136	6.7144
3.1	1.7353	3.5101	3.7751	7.8	2.0588	5.4169	6.7322
3.2	1.7942	3.6092	3.9001	7.9	2.0605	5.4202	6.7501
3.3	1.8300	3.7001	4.0223	8.0	2.0622	5.4235	6.7680
3.4	1.8634	3.7910	4.1376	8.1	2.0640	5.4268	6.7858
3.5	1.8967	3.8819	4.2557	8.2	2.0657	5.4302	6.8026
3.6	1.9097	3.9801	4.3668	8.3	2.0675	5.4335	6.8153
3.7	1.9204	4.0801	4.4877	8.4	2.0695	5.4368	6.8279
3.8	1.9312	4.1802	4.6113	8.5	2.0710	5.4401	6.8406
3.9	1.9420	4.2891	4.7252	8.6	2.0727	5.4434	6.8532
4.0	1.9527	4.3902	4.8502	8.7	2.0742	5.4467	6.8659
4.1	1.9635	4.5102	4.9752	8.8	2.0762	5.4500	6.8786
4.2	1.9742	4.6102	5.0891	8.9	2.0780	5.4533	6.8912
4.3	1.9850	4.7085	5.2002	9.0	2.0797	5.4566	6.9048
4.4	1.9957	4.7918	5.3093	9.1	2.0815	5.4600	6.9204
4.5	2.0011	4.8752	5.4002	9.2	2.0832	5.4633	6.9360
4.6	2.0028	4.9502	5.4911	9.3	2.0850	5.4666	6.9517
4.7	2.0045	5.0168	5.5694	9.4	2.0867	5.4699	6.9673
4.8	2.0063	5.0724	5.6402	9.5	2.0885	5.4732	6.9829
4.9	2.0082	5.1209	5.7049	9.6	2.0902	5.4765	6.9986
5.0	2.0098	5.1626	5.7525	9.7	2.0920	5.4798	7.0197
5.1	2.0115	5.2023	5.8001	9.8	2.0937	5.4831	7.0415
5.2	2.0133	5.2245	5.8436	9.9	2.0955	5.4864	7.0632
5.3	2.0150	5.2467	5.8871	10.0	2.0972	5.4898	7.0849
5.4	2.0168	5.2690	5.9251	10.1	2.0990	5.4931	7.1088
5.5	2.0185	5.2912	5.9608	10.2	2.1076	5.4964	7.1374
5.6	2.0203	5.3034	5.9965	10.3	2.1261	5.4997	7.1659
5.7	2.0220	5.3092	6.0361	10.4	2.1446	5.5221	7.1945
5.8	2.0238	5.3149	6.0761	10.5	2.1631	5.5465	7.2323
5.9	2.0255	5.3206	6.1202	10.6	2.1816	5.5709	7.2723
6.0	2.0273	5.3263	6.1702	10.7	2.2003	5.5953	7.3162
6.1	2.0290	5.3320	6.2202	10.8	2.2420	5.6385	7.3689
6.2	2.0308	5.3377	6.2702	10.9	2.2837	5.6861	7.4292
6.3	2.0325	5.3435	6.3184	11.0	2.3380	5.7472	7.5008
6.4	2.0343	5.3492	6.3638	11.1	2.4008	5.8190	7.5917
6.5	2.0360	5.3549	6.4073	11.2	2.4917	5.9121	7.6649
6.6	2.0378	5.3606	6.4430	11.3	2.6011	6.0261	7.8441
6.7	2.0395	5.3663	6.4787	-	-	-	-

B is the pH-meter readings.**V1**, **V2** and **V3** volumes of alkali needed for acid, acid+ ligand and acid +ligand + metal ion.

3.2.1-Proton-ligand stability constant:

3.2.1.1-pointwise calculation method:

Since the ligand used is Diprotonic, the calculation of free ligand exponent function (pL) of metal complexes requires a prior knowledge of the practical proton-ligand stability constant. The values of n_A at various pH readings (B) were calculated from the acid and ligand titration curves table (3.2.3) using excel program on personal computer. The ligand titration curve is well separated from the acid titration curve at pH 2.1 indicating the dissociation of the ligand in the titration medium table (3.2.2) and figure (3.2.1). The formation curve for the ligand in the range $0<n_A<2$, indicating the dissociation constants pKa_1 and pKa_2. .The accurate values of pk_1 and pk_2 were determined using equations (3.2.1) & (3.2.2): (Abdulbast, 2012)

$$pk_1 = \log \frac{n_A - 1}{2 - n_A} + pH \qquad \text{-------- (3.2.1)}$$

$$pk_2 = \log \frac{n_A}{1 - n_A} + pH \qquad \text{------- (2.2)}$$

The correct values of $pka_1$and pka_2 were taken as average of values of n^- in range 0.2-0.8 and 1.2-1.8 respectively. The values were found, pka_2=4.5708 and pka_1=1.7799 table (3.2.3) and table (3.2.4).

Table (3.2.3). Dissociation constant of oxalic acid pKa_1.(Average value=1.7799)

pKa_1	$\log\left(\frac{(n_A-1)}{(2-n_A)}\right)$	.n_A	V2	V1	pH
1.6865	-0.6143	1.1958	1.8667	0.3500	2.3
1.7657	-0.6343	1.1884	2.2334	0.7000	2.4
1.8036	-0.6964	1.1675	2.5501	0.9751	2.5
1.8640	-0.7360	1.1552	2.7801	1.1801	2.6
1.8978	-0.8022	1.1362	2.9801	1.3429	2.7
1.9373	-0.8627	1.1206	3.1429	1.4751	2.8
1.9516	-0.9488	1.1011	3.2858	1.5801	2.9
1.9786	-1.0214	1.0869	3.4001	1.6667	3.0
1.9452	-1.1548	1.0654	3.5101	1.7353	3.1

1.8685	-1.3315	1.0445	3.6092	1.7942	3.2
1.5030	-1.7970	1.0157	3.7001	1.8300	3.3

Table (3.2.4) Dissociation constant of oxalic acid pKa_2 (Average value 4.5708)

pKa_2	$\log\left(\frac{n_A}{(1-n_A}\right)$	$.n_A$	V2	V1	pH
4.8316	1.3316	0.9555	3.8819	1.8967	3.5
4.6086	1.0086	0.91071	3.9801	1.9097	3.6
4.5022	0.8022	0.8638	4.0801	1.9204	3.7
4.4494	0.6494	0.8169	4.1802	1.9312	3.8
4.4134	0.5134	0.7653	4.2891	1.942	3.9
4.4056	0.4056	0.7178	4.3902	1.9527	4.0
4.3889	0.2890	0.6605	4.5102	1.9635	4.1
4.4008	0.2008	0.6136	4.6102	1.9742	4.2
4.4182	0.1182	0.5676	4.7085	1.985	4.3
4.4514	0.0514	0.5295	4.7918	1.9957	4.4
4.4801	-0.0199	0.4886	4.8752	2.0011	4.5
4.5129	-0.0871	0.4500	4.9502	2.0028	4.6
4.5525	-0.1475	0.4159	5.0168	2.0045	4.7
4.6014	-0.1986	0.3876	5.0724	2.0063	4.8
4.6560	-0.2440	0.3631	5.1209	2.0082	4.9
4.7159	-0.2841	0.3421	5.1626	2.0098	5.0
4.7768	-0.3232	0.3221	5.2023	2.0115	5.1
4.8553	-0.3447	0.3114	5.2245	2.0133	5.2
4.9333	-0.3667	0.3006	5.2467	2.015	5.3

3.2.2 -Metal-ligand stability constants: (chromium oxalate)

3.2.2.1-point-wise calculation method

Metal ligand titration curve cross over the ligand titration curve at pH 2.3 table (3.2.2) indicating starting point of formation of the chelates. n^- extended between 0.1334 to 2.0856 indicating the formation of chelate species ML , ML_2, table (3.2.4) the ML complex type is major one in the solution medium, for it extends from pH 2.3 to nearly 4. Since the ligand is bidentate making a chelate, ML_2 formation beyond pH 4 till pH 4.7 table (2.5), two molecules attached to ligand in four places, with two water molecules. At a very narrow range of pH the ML_3 begins formation from pH 4.8 to 5 which can be neglected after that the free ligand exponential function (pL) cannot be calculated or [L] tends to zero. Equation (3.1.2), (3.1.3) and (3.2.1) were employed.

The correct values of $\log k_1$ and $\log k_2$ were taken as an average for the values of n^- from 0.2 to 0.8 and 1.2 to 1.8 respectively. The values found were $\log K_1 = 3.7762$ and $\log K_2 = 2.9479$. These values were further corroborated by half integral method.

In general $K_1 > K_2 > K_3$ etc. any reversal of this order implies specific electronic or steric phenomenon. (Vogel, 1978)

Table (3.2.5). $\log K_1$ Cr-oxalate (Average value =3.7762)

Log K_1	$\log\left(\frac{n^-}{(1-n^-)}\right)$	pL	n^-	V3	V2
3.9179	-0.8128	0.1334	2.3248	1.9667	1.8667
3.9423	-0.6748	0.1745	2.3319	2.3637	2.2334
3.9147	-0.5908	0.2042	2.3372	2.7001	2.5501
3.8809	-0.5159	0.2336	2.3422	2.9501	2.7801
3.8150	-0.4742	0.2512	2.3454	3.1601	2.9801
3.8054	-0.3826	0.2930	.35241	3.3501	3.1429
3.7335	-0.3512	0.3082	2.3551	3.5001	3.2858
3.7476	-0.2423	0.3640	.36446	3.6501	3.4001
3.7047	-0.1880	0.3934	2.3695	3.7751	3.5101
3.6959	-0.1042	0.4403	2.3776	3.9001	3.6092
3.7141	0.0023	0.5013	2.3882	4.0223	3.7001
3.7211	0.0968	0.5555	2.3979	4.1376	3.791
3.7487	0.2084	0.6177	409173	4.2557	3.8819
3.7646	0.3077	0.6700	2.4189	4.3668	3.9801
3.8440	0.4640	0.7443	2.4331	4.4877	4.0801

Table (3.2.6) $\log K_2$ Cr-oxalate (Average value =2.9479)

pKa_2	$\log\left(\frac{(n^- -1)}{(2-n^-)}\right)$	n^-	pL	V3	V2
2.2063	-0.9162	1.1082	3.1224	4.9752	4.5102
2.5470	-0.5299	1.2280	3.0769	5.0891	4.6102
2.7960	-0.2458	1.3621	3.0418	5.2002	4.7085
3.0891	0.0629	1.5362	3.0262	5.3093	4.7918
3.3593	0.3443	1.6884	3.0150	5.4002	4.8752
3.9312	0.8985	1.8878	3.0326	5.4911	4.9502

3.2.2.2-Half integral method:

From below formation curve, the stability constants were determined from the values of pL at which $n^- = 0.5$ and $n^- = 1.5$ corresponds to $\log K_1$ and $\log K_2$ respectively, figure (3.2.2) $\log K_1 = 3.71$, $\log K_2 = 3.04$. These values were in a good concordance with the values obtained by point-wise method. Since the difference between the stability constants less than 1.8 then these complexes were occurred simultaneously. These values were further verified by linear plot method.

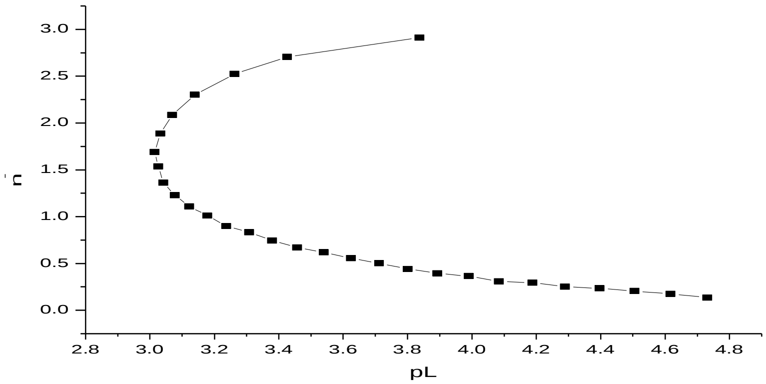


Fig. (3.2.2). Metal-ligand formation curve of Cr-oxalate. Average values of $\log K_1$and $\log K_2$ were 3.71 and 3.04 respectively.

3.2.2.3-Linear plot method: (chromium oxalate)

In this method log (n)/(1-n) and log(n-1)/(2-n) were plotted against corresponding pL, for determination of $\log K_1$ and log K_2 respectively, figures (3.2.3) and (3.2.4), values were found to be $\log K_1$=3.72 and $\log K_2$=3.0296

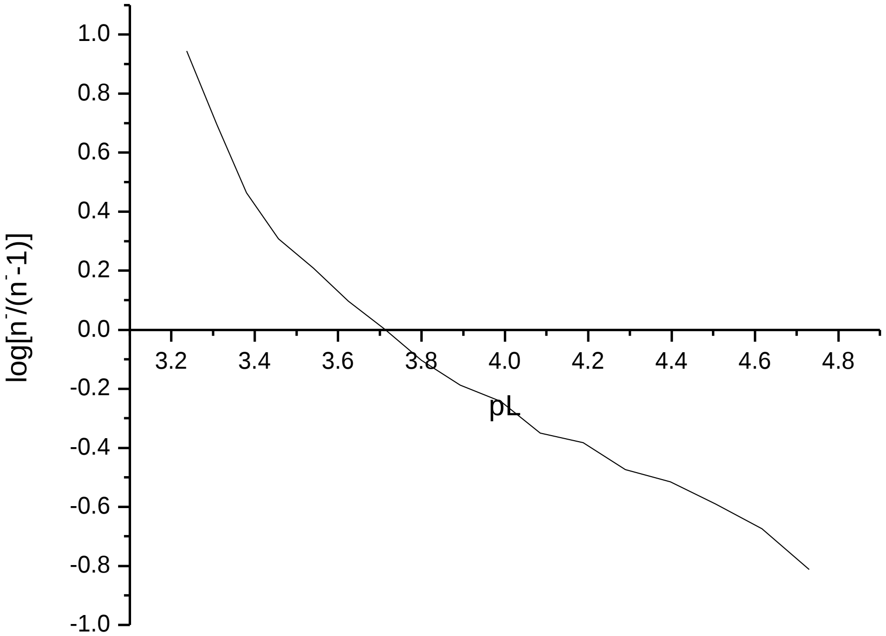


Fig.(3.2.3) logK_1 of Cr-oxalate by linear plot method =3.71

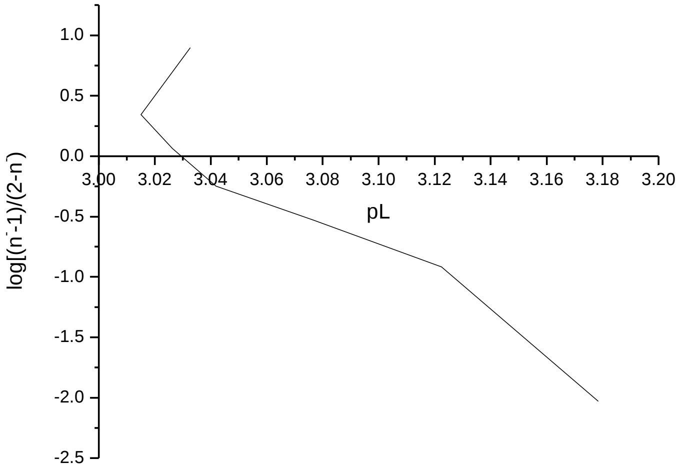


Fig. (3.2.4) linear plot method Cr-oxalate logK_2=3.03

3.2.2.4-Method of least squares: (chromium oxalate)

For this system chromium oxalate the possible coordination sites N =2, the complex species ML and ML_2 can be characterizing by the equations (2.3) or (2.4).

$$\frac{n^-}{(1-n^-)[L]} = \frac{(2-n^-)[L]}{(1-n^-)} \times K_1K_2 + K_1$$

------(2.3)

Thus plotting $n^-/(1-n^-)[L]$ against $(2-n^-)[L]/(1-n^-)$ tends to straight line of intercept K_2 and slope K_1K_2. logK_1=3.5525 and logK_2=2.8221.

Another form of equation (2.3) can take the form:

$$\frac{n^-}{(1-n^-)[L]} \times \frac{1}{K_1K_2} - \frac{1}{K_2} = \frac{(2-n^-)[L]}{(1-n^-)}$$

------(2.4)

According to this form logK_1= 3.6785 and logK_2=3.0. As mentioned before this form matching very well the values obtained by other three methods, we explained before how these values have been obtained.

Equation (2.4) can check also consistency of data.

Table (3.2.7) Determination of log $K_1$and logK_2 (least squares method)

$\frac{(2-n^-)[L]}{(1-n^-)}$	$\frac{n^-}{(1-n^-)[L]}$	[L]	pL	n^-
4.0E-05	8277.1137	1.9E-05	4.7307	0.1334
5.3E-05	8755.4615	2.4E-05	4.6171	0.1745
7.0E-05	8215.9900	3.1E-05	4.5054	0.2042

9.2E-05	7602.3711	4.0E-05	4.3969	0.2336
0.0001	6531.9544	5.1E-05	4.2893	0.2512
0.0002	6388.8863	6.5E-05	4.1880	0.2930
0.0002	5413.5482	8.2E-05	4.0847	0.3082
0.0003	5591.8902	0.0001	3.9899	0.3640
0.0003	5065.8480	0.0001	3.8927	0.3934
0.0004	4965.2124	0.0001	3.8001	0.4403
0.0006	5177.3200	0.0002	3.7119	0.5013
0.0008	5261.5272	0.0002	3.6243	0.5555
0.0010	5606.4351	0.0003	3.5403	0.6177
0.0014	5815.0831	0.0003	3.4568	0.6700
0.0020	6982.2099	0.0004	3.3800	0.7443
0.0034	10086.0936	0.0005	3.3088	0.8320
0.0063	15170.2124	0.0006	3.2369	0.8979
-0.0711	-164698.197	0.0007	3.1785	1.0092
-0.0062	-13580.1085	0.0008	3.1224	1.1082
-0.0028	-6430.6010	0.0008	3.0769	1.2279
-0.0016	-4141.6134	0.0009	3.0418	1.3621
-0.0008	-3043.5104	0.0009	3.0262	1.5362
-0.0004	-2538.5804	0.0010	3.0150	1.6884
-0.0001	-2292.2096	0.0009	3.0326	1.8879

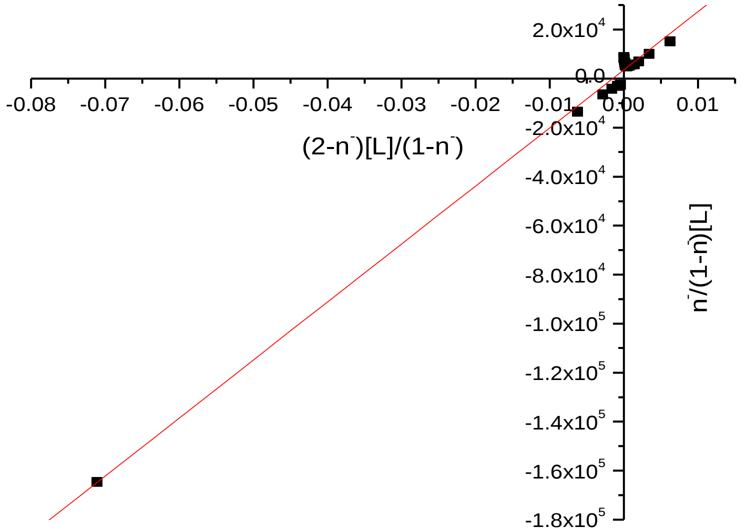


Fig (3.2.5) least squares method logK$_1$=3.5525&logK$_2$=2.8221[equation 2.3]

Linear Regression

```
Parameter          Value              Error              R^2
   ------------------------------------------------------------------------------------------
  Intercept        3569.26285         647.38547          0.99652
   Slope           2.36902E6          43212.15133
```

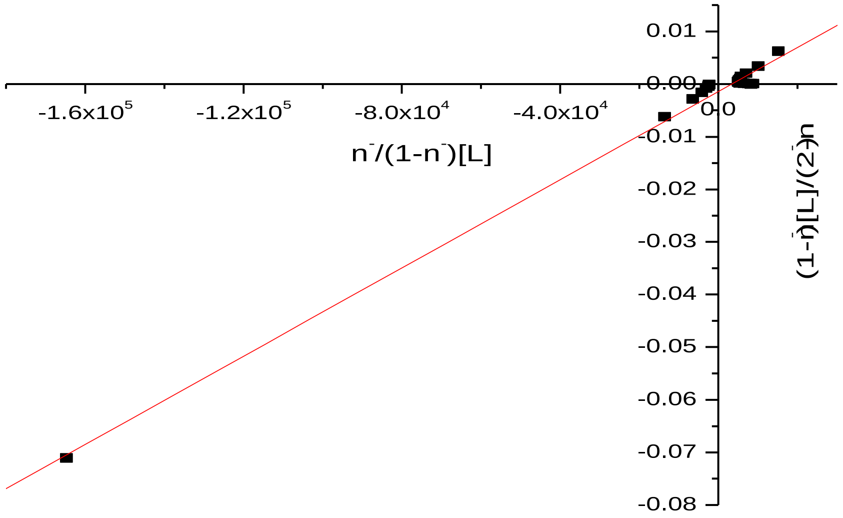


Fig. (3.2.6) least squares method logK_1=3.8247 &logK_2= 2.8539[equation 2.4]

```
                         Linear Regression for:

     Parameter                Value            Error           R2
------------------------------------------------------------------------------------------
     Intercept               -0.00142          0.00028         0.99599
   Slope                     4.19259E-7        8.02693E-9
------------------------------------------------------------------------------------------
```

Table (3.2.7) Stability constants of chromium oxalate by four graphical method

Method	logK_1	logK_2	Logβ_2
Point wise method	3.7762	2.9479	6.7241
Half integral method	3.71	3.03	6.75
Linear plot method	3.72	3.0296	6.7496
Least squares method equ.[2.3]	3.5525	2.8221	6.3746
Least squares method equ.[2.3]	3.8247	2.8539	6.6786

3.3/Chromium-oxalacetic acid system:

Table (3.3.1). The pH - metric readings of acid, acid + ligand and acid + ligand + metal ion $(\mathrm{Cr}^{+3})N^0 = 0.522M$, $\mathrm{E}^0 = 5\times10^{-3}\mathrm{M}$, $\mathrm{T}_{\mathrm{Cl}} = 1.5\times10^{-3}\mathrm{M}$, $\mathrm{T}_{\mathrm{cm}} = 5\times10^{-4}\mathrm{M}$, $\mathrm{V}^0 = 200cm^3$ $\mathrm{u}^0 = 5\times10^{-3}$, $\mathrm{t} = 22.5^0C$.

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.33	2.22	2.24	3.1	11.92	11.59	10.88
0.1	2.35	2.24	2.26	3.2	11.94	11.66	11.07
0.2	2.38	2.27	2.28	3.3	11.97	11.71	11.21
0.3	2.40	2.30	2.31	3.4	11.99	11.76	11.32
0.4	2.44	2.33	2.33	3.5	12.01	11.80	11.41
0.5	2.47	2.36	2.36	3.6	12.04	11.83	11.48
0.6	2.51	2.39	2.39	3.7	12.06	11.86	11.55
0.7	2.56	2.43	2.42	3.8	12.08	11.90	11.60
0.8	2.62	2.47	2.46	3.9	12.10	11.93	11.65
0.9	2.68	2.51	2.50	4.0	12.11	11.95	11.70
1.0	2.75	2.56	2.54	4.1	12.13	11.97	11.74
1.1	2.84	2.62	2.58	4.2	12.15	12.00	11.77
1.2	2.96	2.69	2.63	4.3	12.16	12.02	11.81
1.3	3.17	2.75	2.69	4.4	12.17	12.04	11.84
1.4	3.39	2.84	2.75	4.5	12.19	12.06	11.87
1.5	4.16	2.94	2.82	4.6	12.20	12.08	11.90
1.6	10.00	3.06	2.91	4.7	12.22	12.10	11.92
1.7	10.73	3.21	3.01	4.8	12.23	12.12	11.95
1.8	11.03	3.44	3.13	4.9	12.24	12.14	11.97
1.9	11.21	3.78	3.29	5.0	12.25	12.15	11.99
2.0	11.33	4.35	3.49	5.1	12.27	12.17	12.01
2.1	11.44	5.46	3.78	5.2	12.28	12.18	12.03
2.2	11.51	6.90	4.16	5.3	12.29	12.19	12.05
2.3	11.58	9.64	4.72	5.4	12.30	12.21	12.07
2.4	11.64	10.48	5.53	5.5	12.31	12.22	12.09
2.5	11.69	10.85	6.20	5.6	12.32	12.23	12.10
2.6	11.74	11.08	6.87	5.7	12.33	12.25	12.12
2.7	11.78	11.24	8.00	5.8	12.34	12.26	12.13
2.8	11.82	11.36	9.51	5.9	12.35	12.27	12.15
2.9	11.85	11.45	10.22	6.0	12.36	12.28	12.16
3.0	11.89	11.53	10.62	6.1	12.37	12.29	12.17

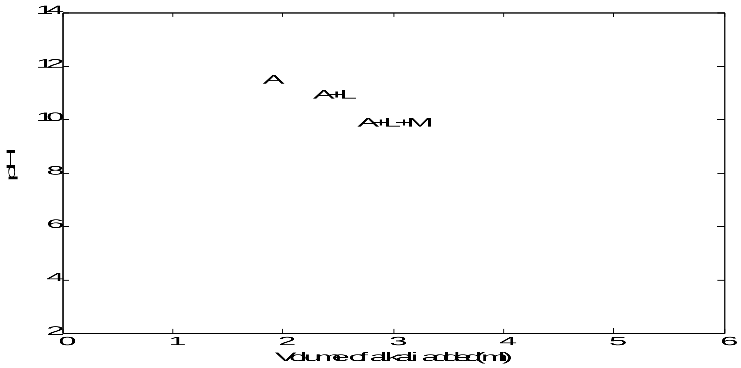


Fig. (3.3.1) Titration curve of three sets of solutions

Table (3.3.2). Alkali volume required to bring three sets of solutions to same pH

B	V1	V2	V3	B	V1	V2	V3
2.3	0.3000	0.2667	-	7.2	1.5521	2.2110	2.6292
2.4	0.3000	0.6250	0.6333	7.3	1.5538	2.2146	2.6381
2.5	0.5750	0.8750	0.9000	7.4	1.5555	2.2183	2.6469
2.6	0.7667	1.0667	1.1400	7.5	1.5572	2.2219	2.6558
2.7	0.9286	1.2167	1.3167	7.6	1.5589	2.2255	2.6646
2.8	1.0556	1.3556	1.4714	7.7	1.5606	2.2292	2.6735
2.9	1.1500	1.4600	1.5889	7.8	1.5623	2.2328	2.6823
3.0	1.2267	1.5500	1.6900	7.9	1.5640	2.2365	2.6912
3.1	1.2933	1.6267	1.7750	8.0	1.5658	2.2401	2.7000
3.2	1.3321	1.6933	1.8438	8.1	1.5675	2.2438	2.7066
3.3	1.3679	1.7391	1.905	8.2	1.5692	2.2474	2.7132
3.4	1.4013	1.7826	1.9550	8.3	1.5709	2.2511	2.7199
3.5	1.4143	1.8177	2.0035	8.4	1.5726	2.2547	2.7265
3.6	1.4273	1.8471	2.0379	8.5	1.5743	2.2584	2.7331
3.7	1.4403	1.8765	2.0724	8.6	1.5760	2.2620	2.7397
3.8	1.4532	1.9035	2.1053	8.7	1.5777	2.2657	2.7464
3.9	1.4662	1.9211	2.1316	8.8	1.5795	2.2693	2.7530
4.0	1.4792	1.9386	2.1579	8.9	1.5812	2.2730	2.7596
4.1	1.4922	1.9561	2.1842	9.0	1.5829	2.2766	2.7662
4.2	1.5007	1.9737	2.2071	9.1	1.5846	2.2803	2.7729
4.3	1.5024	1.9912	2.2250	9.2	1.5863	2.2839	2.7795
4.4	1.5041	2.0045	2.2429	9.3	1.5880	2.2879	2.7861
4.5	1.5058	2.0135	2.2607	9.4	1.5897	2.2912	2.7927
4.6	1.5075	2.0225	2.2786	9.5	1.5914	2.2949	2.7993
4.7	1.5092	2.0315	2.2964	9.6	1.5932	2.2985	2.8127
4.8	1.5110	2.0405	2.3099	9.7	1.5949	2.3072	2.8268
4.9	1.5127	2.0496	2.3222	9.8	1.5966	2.3191	2.8409
5.0	1.5144	2.0586	2.3346	9.9	1.5983	2.3310	2.8549
5.1	1.5161	2.0676	2.3469	10.0	1.6000	2.3429	2.8690
5.2	1.5178	2.0766	2.3593	10.1	1.6137	2.3548	2.8831
5.3	1.5195	2.0856	2.3716	10.2	1.6274	2.3667	2.8972
5.4	1.5212	2.0946	2.3840	10.3	1.6411	2.3786	2.9200
5.5	1.5229	2.1028	2.3963	10.4	1.6548	2.3905	2.9450
5.6	1.5247	2.1097	2.4105	10.5	1.6685	2.4054	2.9700
5.7	1.5264	2.1167	2.4254	10.6	1.6822	2.4325	2.9950
5.8	1.5281	2.1236	2.4403	10.7	1.6959	2.4595	3.0308
5.9	1.5298	2.1306	2.4552	10.8	1.7234	2.4865	3.0693
6.0	1.5315	2.1375	2.4702	10.9	1.7567	2.5218	3.1106
6.1	1.5332	2.1444	2.4851	11.0	1.7900	2.5653	3.1632
6.2	1.5349	2.1514	2.5000	11.1	1.8389	2.6126	3.2215
6.3	1.5366	2.1583	2.5149	11.2	1.8945	2.6751	3.2929
6.4	1.5384	2.1653	2.5299	11.3	1.9751	2.7501	3.3819
6.5	1.5401	2.1722	2.5448	11.4	2.0637	2.8445	3.4890
6.6	1.5418	2.1792	2.559	11.5	2.1859	2.9626	3.6287
6.7	1.5435	2.1861	2.5746	11.6	2.3335	3.1144	3.8002
6.8	1.5452	2.1931	2.5896	11.7	2.5202	3.2802	4.0002
6.9	1.5469	2.2000	2.6027	11.8	2.7502	3.5003	4.2752
7.0	1.5486	2.2037	2.6115	11.9	3.0337	3.8005	4.6005
7.1	1.5503	2.2073	2.6204	12.0	-	-	-

B is the pH-meter reading.

V1, **V2** and **V3** are the volumes of alkali employed to bring the solutions of acid, acid+ ligand and acid+ligand+metal ion respectively to the same pH value.

3.3.1-Dissociation constant of oxalacetic acid:

3.3.1.1- point-wise calculation method:

The free ligand titration curve displaced to right side of acid titration curve at pH=2.3 indicates the dissociation of protons from oxalacetic acid. The values of n_A extend between 1.4267 and 0.6656 table (3.3.2) showed that there were two dissociable protons pK_1 and pK_2. According to point-wise calculation method the values of dissociation constants can be evaluated table (3.3.3), and table (3.3.4). Values of proton-ligand formation constant were selected in range 0.2 to 0.8 and 1.2 to 1.8 (on n_A scale) for pK_1 and pK_2 respectively. The values found pK_1= 2.9252, pK_2=10.5172.

Fig.(3.3.3) pKa_1 of oxalacetic acid (Average value=2.9252)

B	V1	V2	n_A	$\log\left(\frac{(n_A-1)}{(2-n_A}\right)$	pK_1
2.4	0.3000	0.625	1.4267	-0.1283	2.2717
2.5	0.5750	0.875	1.4715	-0.0495	2.4505
2.6	0.7667	1.0667	1.4720	-0.0487	2.5513
2.7	0.9286	1.2167	1.4934	-0.0115	2.6885
2.8	1.0556	1.3556	1.4728	-0.0473	2.7527
2.9	1.1500	1.4900	1.4028	-0.1711	2.7289
3.0	1.2267	1.5500	1.4323	-0.1183	2.8817
3.1	1.2933	1.6267	1.4148	-0.1495	2.9505
3.2	1.3321	1.6933	1.3661	-0.2384	2.9616
3.3	1.3679	1.7391	1.3487	-0.2714	3.0286
3.4	1.4013	1.7826	1.3311	-0.3055	3.0945
3.5	1.4143	1.8177	1.2923	-0.3840	3.1160
3.6	1.4273	1.8471	1.2636	-0.4461	3.1539
3.7	1.4403	1.8765	1.2349	-0.5129	3.1871
3.8	1.4532	1.9035	1.2102	-0.5749	3.2251
3.9	1.4662	1.9211	1.2022	-0.5961	3.3039

Fig. (3.3.4) Determination of log pK_2 average value 10.5172

B	V1	V2	n_A	$\log\left(\frac{(n_A)}{(1-n_A}\right)$	pK_2
8.5	1.5743	2.2584	0.8009	0.6044	9.1044
8.7	1.5777	2.2657	0.7940	0.5861	9.2861
8.9	1.5812	2.2730	0.7874	0.5687	9.4687
9.1	1.5846	2.2803	0.7806	0.5512	9.6512
9.3	1.5880	2.2876	0.7738	0.5341	9.8341
9.5	1.5914	2.2949	0.7670	0.5173	10.0174
9.7	1.5946	2.3072	0.7510	0.4795	10.1795
9.9	1.5983	2.331	0.7158	0.4012	10.3012
10.1	1.6137	2.3548	0.7012	0.3705	10.4705
10.3	1.6411	2.3786	0.7077	0.3840	10.6840
10.5	1.6685	2.4054	0.7089	0.3866	10.8866
10.7	1.6959	2.4595	0.6623	0.2926	10.9926
10.9	1.7567	2.5218	0.6601	0.2882	11.1882
11.1	1.8389	2.6126	0.6456	0.2604	11.3604
11.3	1.9751	2.7501	0.6442	0.2579	11.5579
11.5	2.1859	2.9626	0.6427	0.2549	11.7549
11.7	2.5202	3.2802	0.6740	0.3155	12.0155

3.3.2-Metal-ligand stability constants: (chromium oxalacetate)

3.3.2.1-point-wise calculation method:

Metal titration curve showed a displacement with respect to the ligand titration curve along the volume axis at pH 2.4 table (3.3.2) and figure (3.3.1).The values of n^- extends from 0.0305 to 2.9997 indicate the formation of complex species ML_1 and ML_2. To calculate the complex stability constants for chelates, expressions (1.2) and (1.3) were used. $\log K_1=10.2385$, $\log K_2=6.0183$, tables (3.3.5) and (3.3.6). As it has seen that there is appreciable difference between $\log K_1$ and $\log K_2 > 1.8$, what indicates the complex species were formed, in stepwise manner and not simultaneously. (Sayyed, 2011). The higher values of $\log K_1$ and $\log K_2$ showed that the ligand is stronger chelating agent (Anil, 2008).These values were further verified by half integral method.

Table (3.3.5) metal-ligand stability constants Cr-oxalacetate $\log K_1$ average value = 10.2385

Log K_1	$\log\left(\frac{n^-}{(1-n^-)}\right)$	n^-	pL	V3	V2
10.6551	-0.4531	0.2605	11.1082	1.1400	1.0667
10.6544	-0.2687	0.3501	10.9230	1.3167	1.2167
10.5767	-0.1567	0.4107	10.7334	1.4714	1.3556
10.4769	-0.0655	0.4624	10.5424	1.5889	1.4600
10.3683	0.0174	0.5100	10.3509	1.6900	1.5500
10.2388	0.0813	0.5467	10.1575	1.7750	1.6267
10.0924	0.1299	0.5742	9.96256	1.8438	1.6933
10.0264	0.2516	0.6409	9.77481	1.9050	1.7391
9.89785	0.3167	0.6746	9.58116	1.9550	1.7826
9.86902	0.4737	0.7485	9.39529	2.0035	1.8177
9.76732	0.5647	0.7859	9.20263	2.0379	1.8471

Table. (3.3.6) metal-ligand stability constants Cr-oxalacetate $\log K_1$ average value = 6.0183

Log K_2	$\log\left(\frac{(n^- -1)}{(2-n^-)}\right)$	n^-	pL	V3	V2
6.7269	-0.5692	1.2124	7.2961	2.2786	2.0225
6.6750	-0.4350	1.2686	7.1100	2.2964	2.0315
6.5619	-0.3574	1.3051	6.9193	2.3099	2.0405
6.4329	-0.2947	1.3366	6.7275	2.3222	2.0496
6.3044	-0.2319	1.3696	6.5363	2.3346	2.0586
6.1745	-0.1709	1.4029	6.3454	2.3469	2.0676
6.0459	-0.1092	1.4375	6.1551	2.3593	2.0766
5.9173	-0.0479	1.4725	5.9652	2.3716	2.0856
5.7914	0.0153	1.5088	5.7760	2.384	2.0946
5.6712	0.0831	1.5477	5.5881	2.3963	2.1028
5.5821	0.1770	1.6005	5.4051	2.4105	2.1097
5.5092	0.2843	1.6581	5.2249	2.4254	2.1167
5.4504	0.4037	1.7170	5.0467	2.4403	2.1236

5.4127	0.5417	1.7768	4.8710	2.4552	2.1306

3.3.2.2-Half integral method: (chromium oxalacetate)

In method of interpolation at half n^- values, the average number of ligand attached to metal (n^-) was plotted against the ligand exponential function (pL), $\log K_1$and $\log K_2$ were calculated from formation curve, figure (3.3.2), by known values of pL at which n^-=0.5 and 1.5 respectively. The values were found to be $\log K_1$=10.232and $\log K_2$ =5.76. These values were in agreement with the values obtained by point wise calculations method. The values were further corroborated by linear plot method.

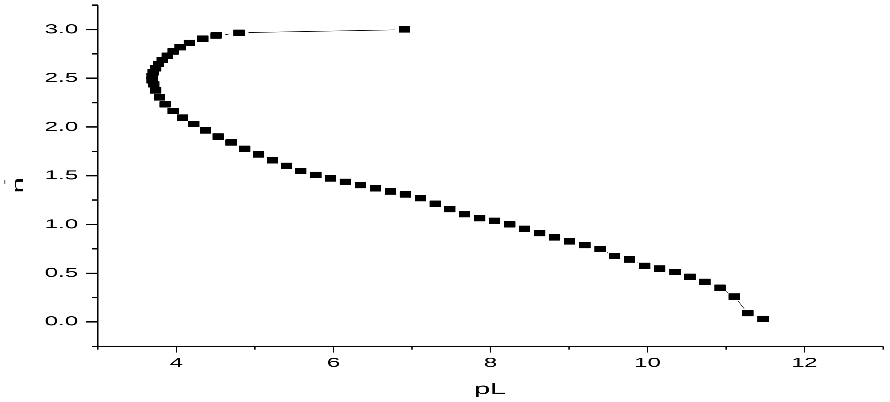


Fig. (3.3.2) Metal-ligand formation curve (Cr-oxalacetate) $\log K_1$=10.4 & $\log K_2$=5.76.

3.3.2.3-Linear plot method:(chromium oxalacetate)

$\log K_1$ and $\log K_2$ were estimated by plotting the corresponding pL against log n^-/ (1-n^-) and log (n^- -1)/(2-n^-) respectively. Results were found to be $\log K_1$=10.2 and $\log K_2$ =5.76, figure (3.3.3) and (3.3.4).

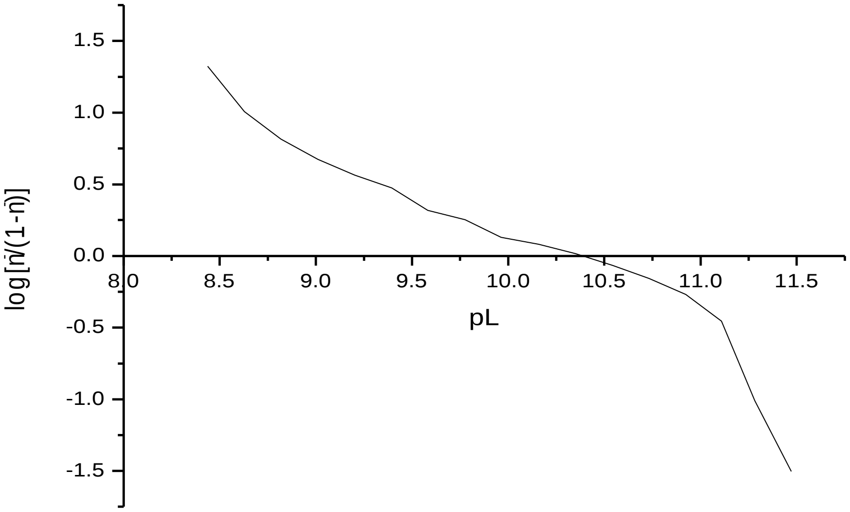


Fig. (3.3.3) linear plot method Cr-oxalacetate logK$_1$= 10.2

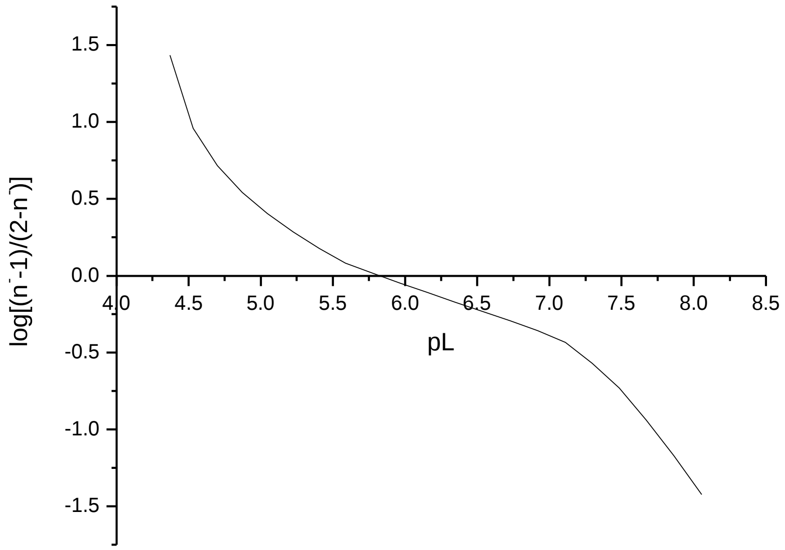


Fig. (3.3.4) Linear plot method Cr-oxalacetic logK$_2$ =5.76

3.3.2.4-Least squares method:

Two forms of linear treatment are available when N=2 namely extrapolation and elimination. (Vogel, 1978).

$$n^{-} = (1-n^{-})[L]K_1 + (2-n^{-})[L]^2 K_1K_2$$

Which on division by (2-n-)[L]2K1K2 and further rearrangement becomes:

$$\frac{n^{-}}{(2-n^{-})[L]^2} = \frac{(1-n^{-})}{(2-n^{-})[L]} \times K_1 - K_1K_2 \text{---------}(3.1)$$

The other deduction can take the form:

$$\frac{(1-n^{-})}{(2-n^{-})[L]} = \left(\frac{n^{-}}{(2-n^{-})[L]^2}\right)\frac{1}{K_1} + K_2 \text{---------}(3.2)$$

Table (3.3.7) Least squares method for determination of logK_1& logK_2

n	pL	[L]	$[L]^2$	$\frac{n^-}{(2-n^-)[L]^2}$	$\frac{(1-n^-)}{(2-n^-)[L]}$
0.0305	11.4721	3.4E-12	1.1E-23	1.36175E+21	1.45987E+11
0.0890	11.2813	5.2E-12	2.7E-23	1.7006E+21	91117104678
0.2605	11.1082	7.8E-12	6.1E-23	1.31711E+22	1.26076E+11
0.3501	10.9230	1.2E-11	1.4E-22	7.75137E+21	75288312112
0.4107	10.7334	1.8E-11	3.4E-22	4.25431E+21	47570713821
0.4624	10.5424	2.9E-11	8.2E-22	2.10974E+21	29287568165
0.5100	10.3509	4.5E-11	2.0E-21	1.00292E+21	17801082543
0.5467	10.1575	7.0E-11	4.8E-21	4.57345E+20	10876382998
0.5742	9.9626	1.1E-10	1.2E-20	2.02664E+20	6699359650
0.6409	9.7748	1.7E-10	2.8E-20	9.74067E+19	3797136406
0.6746	9.5812	2.6E-10	6.9E-20	4.28399E+19	2252186966
0.7485	9.3953	4.0E-10	1.6E-19	2.12032E+19	1196386351
0.7859	9.2026	6.3E-10	3.9E-19	9.40624E+18	672304942.7
0.8254	9.0105	9.7E-10	9.5E-19	4.33832E+18	369440014.1
0.8673	8.8190	1.5E-09	2.3E-18	1.94668E+18	186836958.9
0.9106	8.6280	2.4E-09	5.5E-18	8.77294E+17	84109636.84
0.9547	8.4373	3.7E-09	1.3E-17	3.9694E+17	28561976.94
0.9994	8.2470	5.7E-09	3.2E-17	1.80103E+17	239977.8774
1.0363	8.0551	8.8E-09	7.8E-17	8.05858E+16	-10323711.47
1.0629	7.8611	1.4-08	1.9E-16	3.53781E+16	-11861527.23
1.1032	7.6703	2.1E-08	4.6E-16	1.58577E+16	-13067179.41
1.1569	7.4828	3.3E-08	1.1E-15	7.23847E+15	-13519620.45
1.2124	7.2961	5.1E-08	2.6E-15	3.37167E+1	-12619401.51

				5	
1.2686	7.1100	7.8E-08	6.0E-15	1.60236E+15	-11162840.56
1.3051	6.9193	1.2E-07	1.4E-14	7.3444E+14	-8683576.047
1.3366	6.7275	1.9E-07	3.5E-14	3.34414E+14	-6536550.078
1.3696	6.5363	2.9E-07	8.5E-14	1.49845E+14	-4868643.101
1.4029	6.3454	4.5E-07	2.0E-13	6.69922E+13	-3602622.7
1.4375	6.1551	7.0E-07	4.9E-13	3.02076E+13	-2673890.588
1.4725	5.9652	1.1E-06	1.2E-12	1.36957E+13	-1983795.097
1.5088	5.7760	1.7E-06	2.8E-12	6.27477E+12	-1480598.35
1.5477	5.5881	2.6E-06	6.7E-12	2.9146E+12	-1117470.409
1.6005	5.4051	3.9E-06	1.5E-11	1.42821E+12	-897426.5335
1.6581	5.2247	6.0E-06	3.6E-11	7.27579E+11	-745493.9537
1.7170	5.0467	9.0E-06	8.1E-11	3.91975E+11	-643974.9195
1.7768	4.8710	1.3E-05	1.8E-10	2.24243E+11	-584159.8424
1.8386	4.6992	2.0E-05	4.0E-10	1.41211E+11	-578433.5001
1.9010	4.5320	2.9E-05	8.6E-10	1.0599E+11	-676029.3707
1.9644	4.3714	4.3-05	1.8E-09	1.38019E+11	-1354478.821
2.0293	4.2201	6.0E-05	3.6E-09	-80364620605	1197523.738
2.0954	4.0816	8.3E-05	6.9E-09	-12143409361	269960.1896
2.1629	3.9601	0.0001	1.2E-08	-3658419688	118493.9052
2.2316	3.8599	0.0001	1.9E-08	-1402931180	64163.71844
2.3019	3.7855	0.0002	2.7E-08	-634341574.9	39332.63669
2.3741	3.7395	0.0002	3.3E-08	-332928106.7	26603.12775
2.4365	3.7139	0.0002	3.7E-08	-207818092.1	20079.93824
2.4773	3.6947	0.0002	4.1E-08	-156385595	16989.13288
2.5192	3.6947	0.0002	4.1E-08	-129907719.1	15140.34016
2.5601	3.7088	0.0002	3.8E-08	-112013507.5	13788.57985
2.6026	3.7367	0.0002	3.4E-08	-105857064.8	13166.24197
2.6448	3.7749	0.0002	2.8E-08	-107309881.8	13047.57159
2.6879	3.8244	0.0001	2.2E-08	-116244765.7	13383.20782

2.7308	3.8843	0.0001	1.7E-08	-132516978.9	14103.83045
2.7746	3.9586	0.0001	1.2E-08	-159544023.4	15289.76482
2.8182	4.0502	8.9E-05	7.9E-09	-202127061.9	17023.15621
2.8627	4.1711	6.7E-05	4.5E-09	-274267141.2	19629.61134
2.9064	4.3366	4.6E-05	2.1E-09	-404052655.4	23610.11595
2.9370	4.5084	3.1E-05	9.6E-10	-689158117.5	30652.47593
2.9679	4.8014	1.6E-05	2.5E-10	-1445030624	44136.57121
2.9997	6.9078	1.2E-07	1.5E-14	-3119346815	64494.00717

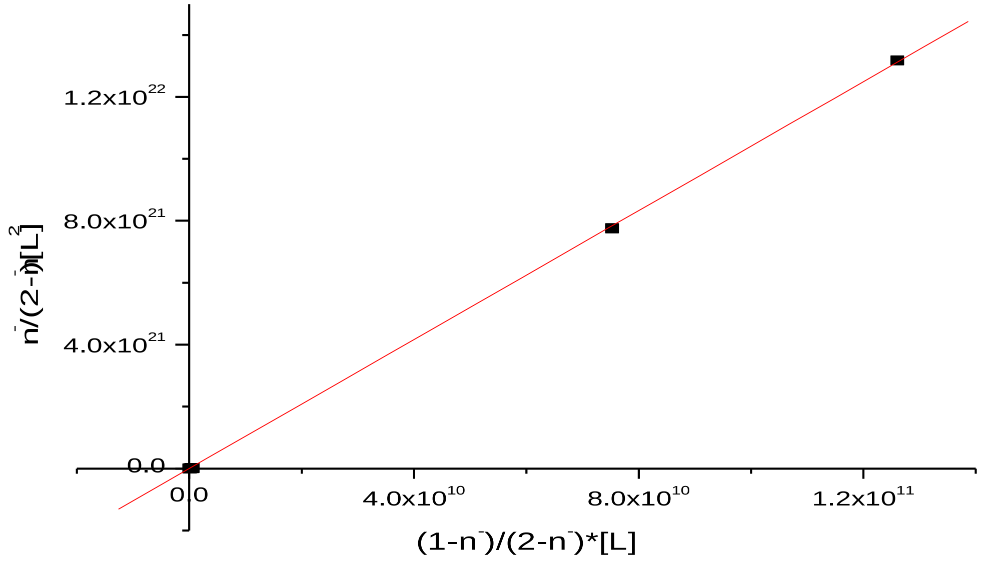


Fig.(3.3.5) Least squares method logK_1= 11.0174 & K_2= 7.4604 (equ. (3.1)

Linear Regression

```
Parameter        Value              Error          R2
        ------------------------------------------------------------
Intercept    -3.00423E18       2.49379E18     0.99997
Slope          1.04097E11      1.20083E8
-----------------------------------------------------------------------------
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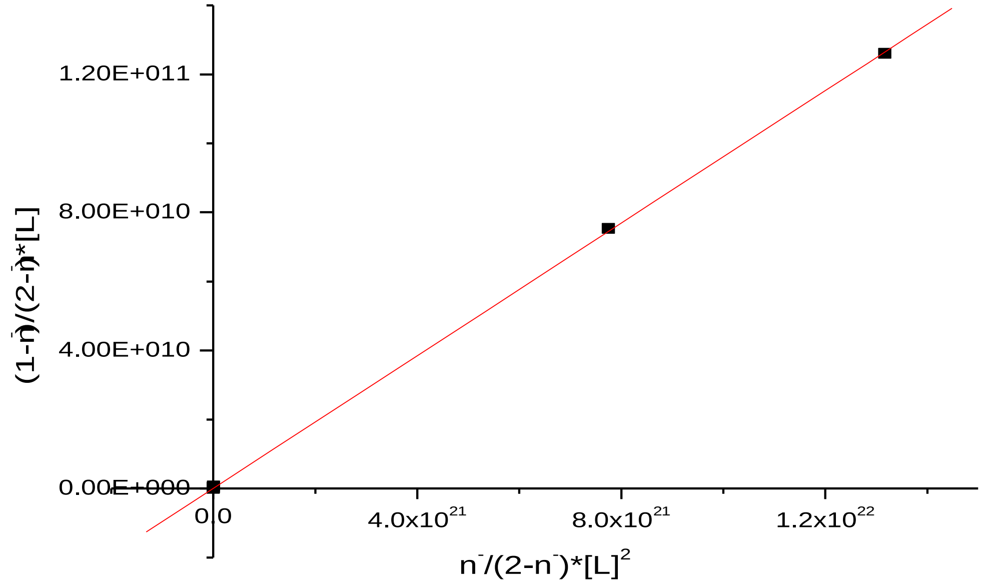


Fig.(3.3.6) Least squares method $\log K_1=11.0175$ &$\log K_2=7.4641$

```
                    Linear Regression
Parameter        Value                Error            R²
  ---------------------------------------------------------------------
Intercept      2.91168E7             2.39491E7      0.99997
Slope          9.60579E-12           1.10809E-14
```

Table (3.3.8) Stability constants chromium oxalacetic by four graphical method

Method	$\log K_1$	$\log K_2$	$\text{Log}\beta_2$
Point wise method	10.2385	6.0183	16.2568
Half integral method	10.232	5.76	15.992
Linear plot method	10.2	5.76	15.96
Least squares method fig.(3.5)	11.0174	7.4604	18.4778
Least squares method fig.(3.6)	11.0174	7.4641	18.4815

3.4/Chromium-propanoic acid system:

Table (3.4.1). pH - metric titration readings of acid, acid + ligand and acid + ligand + metal ion.(Cr^{+3}). $N^0 = 0.522M$, $E^0 = 5\times10^{-3}$ M , $T_{Cl} = 1.5\times10^{-3}$ M , $T_{cm} = 5\times10^{-4}$ M ,
$V^0 = 200 ml u^0 = 5\times10^{-3}$ $t = 22.5^0 C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.33	2.34	2.33	3.1	11.92	11.74	11.38
0.1	2.34	2.34	2.35	3.2	11.95	11.77	11.47
0.2	2.36	2.37	2.37	3.3	11.97	11.81	11.54
0.3	2.39	2.39	2.40	3.4	11.99	11.85	11.61
0.4	2.42	2.42	2.43	3.5	12.02	11.88	11.66
0.5	2.45	2.45	2.46	3.6	12.04	11.91	11.71
0.6	2.49	2.49	2.49	3.7	12.06	11.94	11.76
0.7	2.53	2.54	2.53	3.8	12.08	11.97	11.80
0.8	2.58	2.59	2.58	3.9	12.10	11.99	11.83
0.9	2.64	2.64	2.62	4.0	12.12	12.01	11.87
1.0	2.71	2.71	2.68	4.1	12.13	12.04	11.90
1.1	2.80	2.80	2.76	4.2	12.15	12.06	11.92
1.2	2.92	2.90	2.84	4.3	12.17	12.08	11.95
1.3	3.08	3.04	2.94	4.4	12.18	12.10	11.98
1.4	3.35	3.24	3.07	4.5	12.20	12.11	12.00
1.5	4.24	3.56	3.25	4.6	12.21	12.13	12.03
1.6	9.93	4.07	3.52	4.7	12.22	12.15	12.05
1.7	10.70	4.49	3.84	4.8	12.24	12.16	12.07
1.8	11.02	4.84	4.19	4.9	12.25	12.18	12.09
1.9	11.21	5.19	4.52	5.0	12.26	12.20	12.10
2.0	11.34	5.71	4.80	5.1	12.27	12.21	12.12
2.1	11.44	7.50	5.11	5.2	12.29	12.22	12.14
2.2	11.52	10.42	5.52	5.3	12.30	12.24	12.16
2.3	11.59	10.87	5.96	5.4	12.31	12.25	12.17
2.4	11.65	11.12	6.35	5.5	12.32	12.26	12.19
2.5	11.70	11.28	6.78	5.6	12.33	12.27	12.20
2.6	11.74	11.39	8.83	5.7	12.34	12.28	12.22
2.7	11.78	11.49	10.44	5.8	12.35	12.29	12.23
2.8	11.82	11.57	10.86	5.9	12.36	12.30	12.24
2.9	11.85	11.63	11.11	6.0	12.37	12.32	12.25
3.0	11.89	11.68	11.26	-	-	-	-

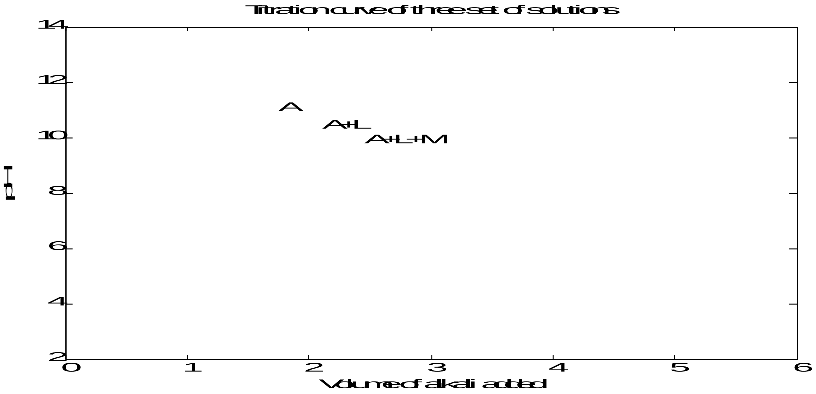


Fig. (3.4.1) titration curve of three sets of solutions against pH

Table (3.4.2) alkali volume required to bring three sets solutions to the same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.3250	0.3333	0.3000	7.2	1.5520	2.0832	2.5205
2.5	0.625	0.6200	0.6250	7.3	1.5538	2.0888	2.5254
2.6	0.8333	0.8200	0.8500	7.4	1.5555	2.0944	2.5302
2.7	0.9857	0.9827	1.0250	7.5	1.5573	2.1000	2.5351
2.8	1.1000	1.1000	1.1500	7.6	1.5591	2.1034	2.5400
2.9	1.1833	1.2000	1.2600	7.7	1.5608	2.1069	2.5449
3.0	1.2500	1.2714	1.3462	7.8	1.5626	2.1103	2.5498
3.1	1.3074	1.3300	1.4167	7.9	1.5643	2.1137	2.5546
3.2	1.3444	1.3800	1.4722	8.0	1.5661	2.1171	2.5595
3.3	1.3815	1.4188	1.5185	8.1	1.5678	2.1206	2.5644
3.4	1.4056	1.4500	1.5556	8.2	1.5696	2.1240	2.5693
3.5	1.4169	1.4813	1.5926	8.3	1.5714	2.1274	2.5741
3.6	1.4281	1.5078	1.6250	8.4	1.5731	2.1308	2.5790
3.7	1.4393	1.5275	1.6563	8.5	1.5749	2.1342	2.5839
3.8	1.4506	1.5471	1.6875	8.6	1.5766	2.1377	2.5888
3.9	1.4618	1.5567	1.7171	8.7	1.5784	2.1411	2.5937
4.0	1.4730	1.5863	1.7457	8.8	1.5801	2.1445	2.5985
4.1	1.4843	1.6071	1.7743	8.9	1.5919	2.1479	2.6044
4.2	1.4955	1.6310	1.8030	9.0	1.5837	2.1514	2.6106
4.3	1.5011	1.6548	1.8333	9.1	1.5854	2.1548	2.6168
4.4	1.5028	1.6786	1.8636	9.2	1.5872	2.1582	2.6230
4.5	1.5046	1.7029	1.8939	9.3	1.5889	2.1616	2.6292
4.6	1.5063	1.7314	1.9286	9.4	1.5907	2.1651	2.6354
4.7	1.5081	1.7600	1.9643	9.5	1.5924	2.1685	2.6416
4.8	1.5098	1.7886	2.0000	9.6	1.5942	2.1719	2.6478
4.9	1.5116	1.8172	2.0323	9.7	1.5960	2.1753	2.6540
5.0	1.5134	1.8457	2.0645	9.8	1.5977	2.1788	2.6603
5.1	1.5151	1.8743	2.0968	9.9	1.5995	2.1822	2.6665
5.2	1.5169	1.9019	2.1220	10.0	1.6091	2.1856	2.6727
5.3	1.5186	1.9212	2.1463	10.1	1.6351	2.1925	2.6851
5.4	1.5204	1.9404	2.1707	10.2	1.6351	2.1925	2.6851
5.5	1.5221	1.9596	2.1951	10.3	1.6481	2.1959	2.6913
5.6	1.5239	1.9789	2.2182	10.4	1.6610	2.1993	2.6975
5.7	1.5257	1.9981	2.2409	10.5	1.6740	2.2178	2.7143
5.8	1.5274	2.0050	2.2636	10.6	1.6870	2.2400	2.7381
5.9	1.5292	2.0106	2.2864	10.7	1.7000	2.2622	2.7619
6.0	1.5309	2.0162	2.3103	10.8	1.7313	2.2845	2.7845
6.1	1.5327	2.0218	2.3359	10.9	1.7625	2.3120	2.8160
6.2	1.5344	2.0274	2.3615	11.0	1.7938	2.3520	2.8560
6.3	1.5362	2.0330	2.3872	11.1	1.8422	2.3920	2.8960
6.4	1.5380	2.0385	2.4116	11.2	1.8948	2.4501	2.9601
6.5	1.5397	2.0441	2.4349	11.3	1.9693	2.5183	3.0334
6.6	1.5415	2.0497	2.4582	11.4	2.0601	2.6101	3.1223
6.7	1.5432	2.0553	2.4814	11.5	2.1751	2.7126	3.2430
6.8	1.5450	2.0609	2.5010	11.6	2.3168	2.8502	3.3859
6.9	1.5467	2.0665	2.5059	11.7	2.5002	3.0402	3.5802
7.0	1.5485	2.0721	2.5107	11.8	2.7502	3.2752	3.8003
7.1	1.5503	2.0777	2.5156	11.9	3.0337	3.5670	4.1005

B is the pH-meter reading. **V1**, **V2** and **V3** are the volumes of alkali employed to bring the solutions of acid, acid+ ligand and acid+ligand+metal ion respectively to the same pH value.

3.4.1-Dissociation constants of propanoic acid:

3.4.1.1-Point-wise calculation method:

The ligand titration curve is well separated from free acid titration curve at pH 2.9, table (3.4.2) indicating the dissociation of the ligand in the titration medium, figure (3.4.1) and table (3.4.2).Using excel program on personal computer the values of n_A at various pH reading (B) were calculated from the acid and ligand titration curve, table (3.4.3).Calculation has been made according to point-wise method, and the value of dissociation constant has been taken as an average of pKa_1 in range of n_A 0.2 -0.8 that is pKa_1=4.8259.This value is further confirmed by half integral method.

Table (3.4.3) proton-ligand stability constant (propanoic acid) pKa_1 average value =4.8259

pKa_1	$\log\left(\frac{n_A}{(1-n_A}\right)$	$.n_A$	v2	v1	B
4.4223	1.5223	0.9708	1.2000	1.1833	2.9
4.4111	1.4111	0.9626	1.2714	1.2500	3.0
4.4866	1.3866	0.9606	1.3300	1.3074	3.1
4.3789	1.1789	0.9379	1.3800	1.3444	3.2
4.4574	1.1574	0.9349	1.4188	1.3815	3.3
4.4760	1.0760	0.9225	1.4500	1.4056	3.4
4.3977	0.8977	0.8877	1.4813	1.4169	3.5
4.3919	0.7919	0.8610	1.5078	1.4281	3.6
4.4404	0.7404	0.8462	1.5275	1.4393	3.7
4.4939	0.6939	0.8317	1.5471	1.4506	3.8
4.6026	0.7026	0.8345	1.5567	1.4618	3.9
4.6087	0.6087	0.8024	1.5863	1.4730	4.0
4.6647	0.5647	0.7859	1.6071	1.4843	4.1
4.7096	0.5096	0.7637	1.6310	1.4955	4.2
4.7364	0.4364	0.7320	1.6548	1.5011	4.3
4.7546	0.3546	0.6935	1.6786	1.5028	4.4
4.7770	0.2770	0.6543	1.7029	1.5046	4.5
4.7898	0.1898	0.6075	1.7314	1.5063	4.6
4.8062	0.1062	0.5608	1.7600	1.5081	4.7
4.8242	0.0242	0.5139	1.7886	1.5098	4.8
4.8429	-0.0571	0.4672	1.8172	1.5116	4.9
4.8610	-0.1390	0.4206	1.8457	1.5134	5.0
4.8758	-0.2242	0.3737	1.8743	1.5151	5.1
4.8900	-0.3100	0.3288	1.9019	1.5169	5.2
4.9631	-0.4369	0.2678	1.9404	1.5204	5.4
4.9929	-0.5071	0.2373	1.9596	1.5221	5.5

3.4.1.2-Half integral method (propanoic acid)

Value of pKa_1 deduced from metal-ligand curve formation, figure (3.4.2) pKa=4.826 and it is in a good agreement with the value obtained by point-wise calculation method.

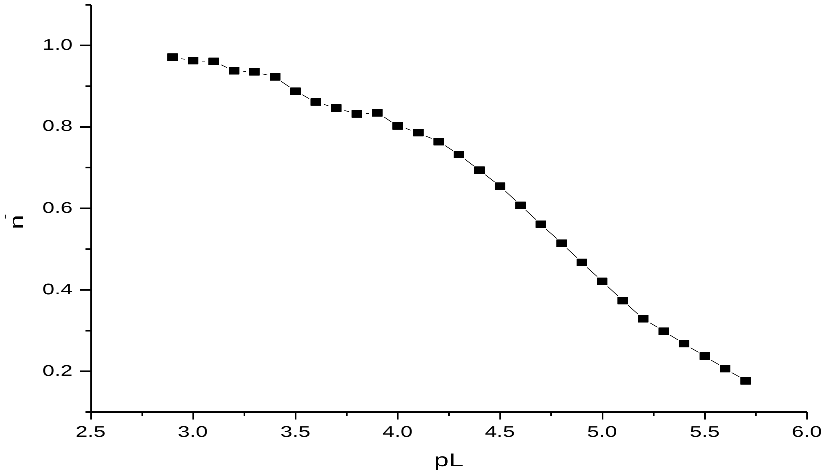


Figure (3.4.2) half integral method (propanoic acid) pKa = 4.826

3.4.2-Metal ligand stability constants: (Chromium propanoiate)

3.4.2.1-Point-wise calculation method:

Metal titration curve showed a displacement with respect to the ligand titration curve along the volume axis at pH 2.5. Table (3.4.2) indicates the affinity of ligand with metal ions which released a protons and produced the volume difference (V_3-V_2), which utilized for calculation of the values n^- and pL and further to evaluate the metal-ligand stability constants. The variation of n^- from 0.0260 to 1.9031 indicates the formation of two complex species ML_1 and ML_2. The values were found to be $\log K_1=4.5499$ and $\log K_2=3.6038$, table (3.4.4), and table (3.4.5).These values were further verified by half integral method.

Table (3.4.4) point-wise method $\log K_1$ (Cr-propanpoiate), average value=4.5499

V2	V3	pL	$.n^-$	$\log\left(\frac{n^-}{(1-n^-)}\right)$	$\log K_1$
0.8200	0.8500	5.0772	0.1539	-0.7403	4.3369
0.9827	1.0250	4.9885	0.2207	-0.5480	4.4406
1.1000	1.1500	4.8962	0.2621	-0.4496	4.4465
1.2000	1.2600	4.8074	0.3238	-0.3199	4.4875
1.2714	1.3462	4.7226	0.4069	-0.1636	4.5589
1.3300	1.4167	4.6355	0.4725	-0.0478	4.5877
1.3800	1.4722	4.5450	0.5145	0.0252	4.5702
1.4188	1.5185	4.4553	0.5580	0.1013	4.5566

1.4500	1.5556	4.3660	0.5989	0.1741	4.5401
1.4813	1.5926	4.2805	0.6559	0.2802	4.5607
1.5078	1.6250	4.1962	0.7120	0.3931	4.5892
1.5275	1.6563	4.1188	0.7961	0.5915	4.7103
1.5471	1.6875	4.0440	0.8828	0.8769	4.9210

Table (3.4.5) point-wise method (Cr-propanoiate) logK_2 average value =3.6038

V2	V3	pL	n	$\log\left(\frac{(n^{-}-1)}{(2-n^{-})}\right)$	logK_2
1.6310	1.8030	3.7624	1.1772	-0.6667	3.0957
1.6548	1.8333	3.7073	1.2745	-0.4220	3.2853
1.6786	1.8636	3.6637	1.3942	-0.1867	3.4770
1.7029	1.8939	3.6304	1.5255	0.04436	3.6748
1.7314	1.9286	3.6185	1.6959	0.35958	3.9780

3.4.2.2-Half integral method: (chromium & propanoic acid)

PL plotted against n^- for construction of formation curve figure (3.4.3). Values were been found, logK_1=4.54and logK_2=3.632. These values were later corroborated by linear plot method.

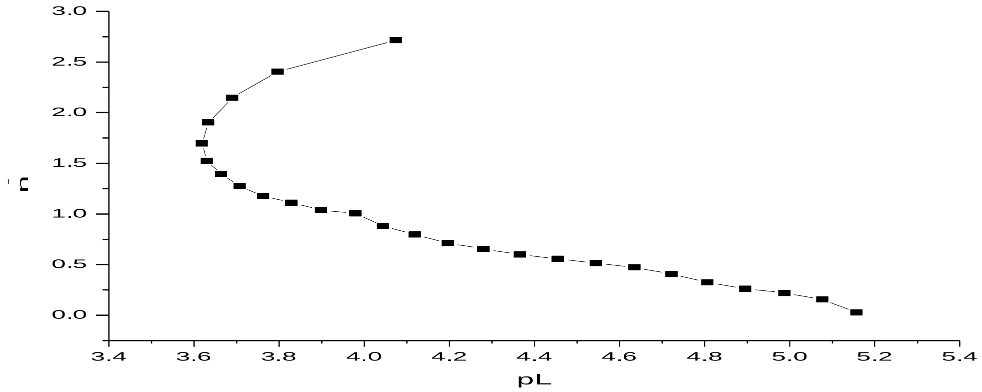


Fig. (3.4.3) Metal-ligand formation curve logK_1= 4.54 & logK_2=3.632

3.4.2.3-Linear plot method: (Cr and propanoic acid)

Plotting of log (n^-/1-n^-) and log(n^- -1)/(2-n^-) versus corresponding pL where curve intersect pL axis the value correspond to logK_1 and logK_2 respectively, figure (3.4.4) and figure (3.4.5). The values were found, logK_1=4.626 and logK_2=3.63. These values were in a good concordance with values obtained by half integral method. The values were further verified by the least squares method.

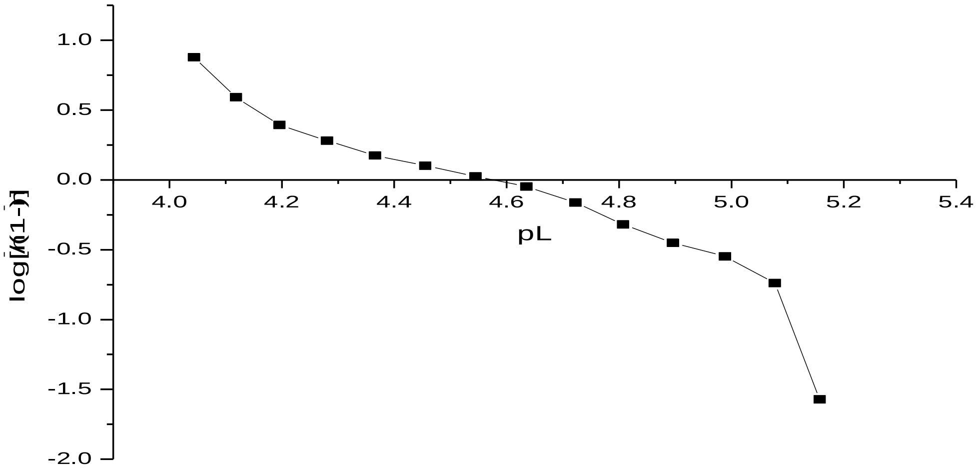


Figure (3.4.4) Linear plot method (Cr-propanoiate) $\log K_1 = 4.626$

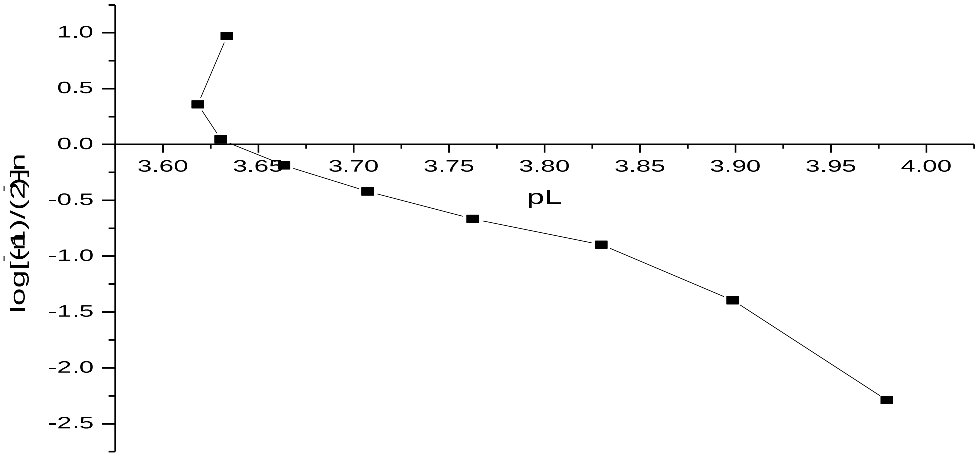


Figure (3.4.5) linear plot method (Cr-propanoiate) $\log K_2 = 3.63$

3.4.2.4-Least squares method: (chromium & propanoate)

For estimation of K_2 and K_3 for chromium propanoiate by this method, linear equation of Rossotti and Rossotti as expressed below has been employed:

$$n^{-} = (1-n^{-})[L]K_1 + (2-n^{-})[L]K_1K_2 ----(4.1)$$

This on division by $(1-n^{-})[L]K_1$ and further rearranging becomes:

$$\frac{n^{-}}{(1-n^{-})[L]} = \frac{(2-n^{-})*[L]}{(1-n^{-})} \times K_1K_2 + K_1 -------(4.2)$$

If the values of n- and [L] were known, plotting of $(2-n^{-})[L]/(1-n^{-})$ V/s $n^{-}/(1-n^{-})[L]$, give straight line equation with y-intercept=K_1 and slope = K_1K_2 . (Gurdeep, 1986).

Table (3.4.6). Least squares method (Cr-propanoiate) $\log K_1 = 4.2198$ & $\log K_2 = 3.7344$

pL	n	[L]	$\frac{(2-\bar{n})[L]}{(1-\bar{n})}$	$\frac{\bar{n}}{(1-\bar{n})[L]^2}$
5.1571	0.0260	6.9647E-06	1.4116E-05	3838.8930
5.0772	0.1539	8.3716E-06	1.8266E-05	21723.1864
4.9885	0.2207	1.0267E-05	2.3442E-05	27579.1226
4.8962	0.2621	1.2701E-05	2.9912E-05	27960.5246
4.8074	0.3238	1.5583E-05	3.8626E-05	30723.2399
4.7226	0.4069	1.8943E-05	5.0881E-05	36218.9184
4.6355	0.4725	2.3148E-05	6.7031E-05	38701.2932
4.5450	0.5145	2.8513E-05	8.7244E-05	37171.0648
4.4553	0.5580	3.5049E-05	0.00014351	36023.8284
4.3660	0.5989	4.3056E-05	0.0002	34678.2783
4.2805	0.6559	5.2416E-05	0.0002	36368.7292
4.1962	0.7120	6.3656E-05	0.0003	38837.3431
4.1188	0.7961	7.6076E-05	0.0004	51320.6695
4.0440	0.8828	9.0363E-05	0.0009	83359.2057
3.9795	1.0051	0.0001	-0.0203	-1870517.592
3.8987	1.0386	0.0001	-0.0031	-212882.0742
3.8297	1.1123	0.0001	-0.0012	-66924.1810
3.7624	1.1772	0.0002	-0.0008	-38434.2168
3.7073	1.2745	0.0002	-0.0005	-23662.7599
3.6637	1.3942	0.0002	-0.0003	-16303.5508
3.6304	1.5255	0.0002	-0.0002	-12394.8823
3.6185	1.6959	0.0002	-0.0001	-10122.9771
3.6337	1.9031	0.0002	-2.4942-05	-9066.0208
3.6895	2.1486	0.0002	2.6452E-05	-9150.3771

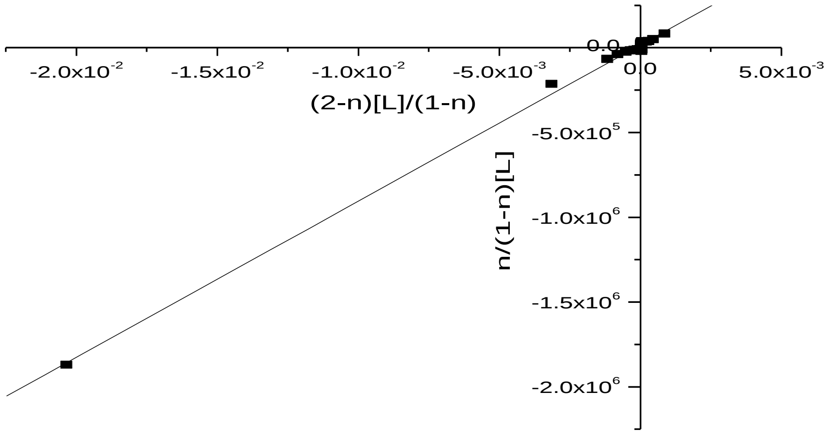


Fig (3.4.6) Least squares method (chromium propanoiate $\log K_1$=4.2198 and $\log K_2$=3.7447)

```
                    Linear Regression:
Parameters            Value            Error          R²
-----------------------------------------------------------------------------------------
   Intercept         16590.2608       4192.90636      0.99849
   Slope              9.2152E7        1.03405E6
   ---------------------------------------------------------------------------------
```

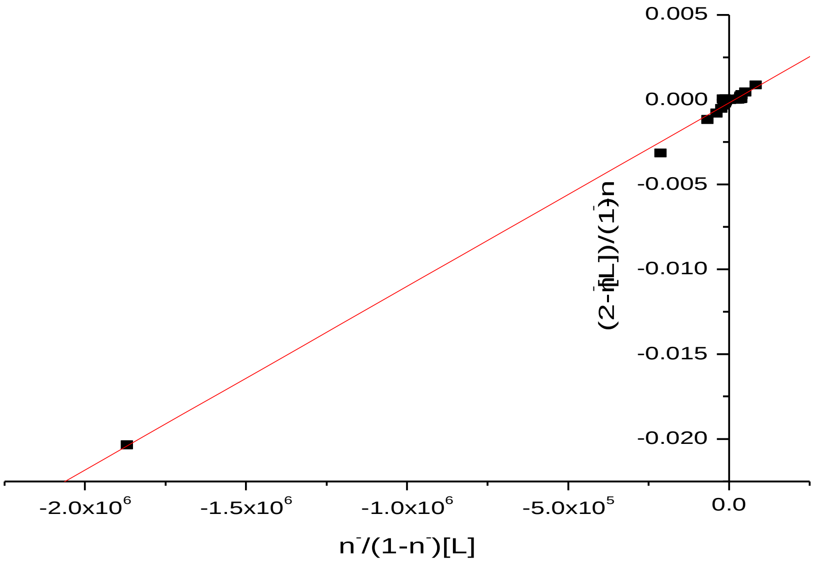


Fig (3.4.7) Least squares method (chromium propanoiate $\log K_1=4.2211$ and $\log K_2=3.7447$)

```
                    Linear Regression

Parameter          Value                Error          R²
     ------------------------------------------------------------
 Intercept       -0.00018             0.00005         0.9984
   Slope           1.08189E-8         1.21401E-10
     ------------------------------------------------------------
```

Table (3.4.7) Stability constants of (cr-propanoate) obtained by four graphical methods

Method	$\log K_1$	$\log K_2$	$\log\beta_2$
Point wise method	4.5499	3.6038	8.1537
Half integral method	4.54	3.632	8.172
Linear plot method	4.626	3.63	8.256
Linear squares method fig (4.6)	4.2198	3.7344	7.9542
Least squares method fig (4.7)	4.2211	3.7447	8.2676

3.5/ Chromium-citric acid system

Table (3.5.1). The pH titration readings of acid, acid + ligand and acid + ligand + metal ion (Cr^{+3}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}$ M , $T_{Cl} = 5\times10^{-5}$ M , $T_{cm} = 1.25\times10^{-5}$ M ,
$V^0 = 200ml u^0 = 5\times10^{-3}$, $t = 3.65^0 C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.38	2.39	2.36	2.7	11.88	6.14	5.40
0.1	2.40	2.40	2.38	2.8	11.91	6.50	5.67
0.2	2.42	2.42	2.39	2.9	11.94	6.95	5.93
0.3	2.44	2.44	2.41	3.0	11.97	9.26	6.20
0.4	2.47	2.46	2.41	3.1	12.00	10.39	6.48
0.5	2.50	2.48	2.47	3.2	12.02	10.85	6.81
0.6	2.53	2.51	2.49	3.3	12.05	11.14	7.32
0.7	2.57	2.54	2.52	3.4	12.07	11.32	8.45
0.8	2.62	2.58	2.56	3.5	12.09	11.46	9.75
0.9	2.68	2.62	2.60	3.6	12.11	11.56	10.39
1.0	2.75	2.66	2.65	3.7	12.13	11.64	10.79
1.1	2.84	2.72	2.70	3.8	12.15	11.70	11.05
1.2	2.95	2.78	2.76	3.9	12.17	11.76	11.23
1.3	3.13	2.85	2.82	4.0	12.18	11.81	11.37
1.4	3.45	2.93	2.89	4.1	12.20	11.85	11.47
1.5	5.50	3.03	2.98	4.2	12.22	11.89	11.56
1.6	10.40	3.15	3.08	4.3	12.23	11.93	11.64
1.7	10.82	3.29	3.20	4.4	12.24	11.96	11.70
1.8	11.13	3.47	3.33	4.5	12.26	11.99	11.76
1.9	11.31	3.70	3.49	4.6	12.27	12.02	11.80
2.0	11.45	3.97	3.68	4.7	12.28	12.05	11.85
2.1	11.54	4.26	3.90	4.8	12.29	12.07	11.89
2.2	11.62	4.55	4.12	4.9	12.31	12.10	11.92
2.3	11.69	4.83	4.36	5.0	12.32	12.12	11.95
2.4	11.74	5.18	4.60	5.1	12.33	12.14	11.99
2.5	11.79	5.50	4.85	5.2	12.34	12.16	12.01
2.6	11.84	5.82	5.11	5.3	12.35	12.18	12.04

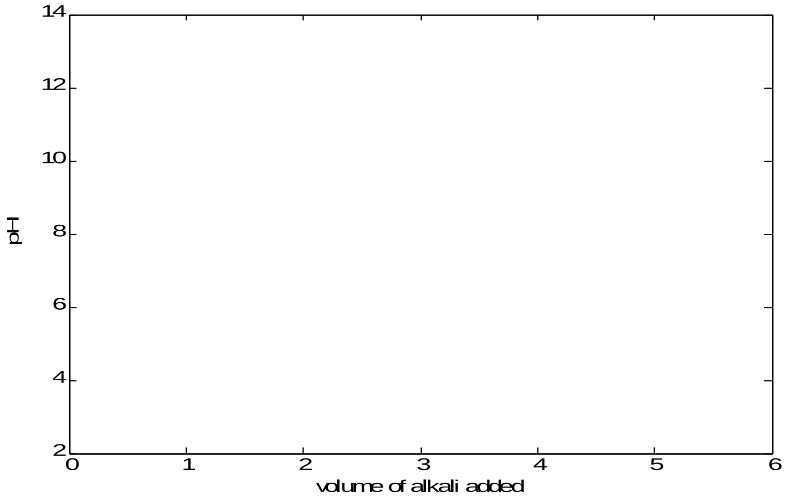


Fig. (3.5.1) Plotting of three sets of solutions (Cr-citrate) against pH

Table (3.5.2) Alkali volume required to bring three sets of solutions to same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.1000	0.1000	0.2500	7.2	1.5366	2.9108	3.2765
2.5	0.5000	0.5667	0.6333	7.3	1.5388	2.9152	3.2961
2.6	0.7600	0.8500	0.9000	7.4	1.5409	2.9195	3.3071
2.7	0.9286	1.0667	1.1000	7.5	1.5431	2.9238	3.3159
2.8	1.0556	1.2286	1.2667	7.6	1.5453	2.9281	3.3248
2.9	1.1546	1.3625	1.4111	7.7	1.5474	2.9325	3.3336
3.0	1.2278	1.4700	1.5200	7.8	1.5496	2.9368	3.3425
3.1	1.2833	1.5583	1.6167	7.9	1.5517	2.9411	3.3513
3.2	1.3219	1.6357	1.7000	8.0	1.5539	2.9455	3.3602
3.3	1.3531	1.7056	1.7769	8.1	1.556	2.9498	3.3690
3.4	1.3844	1.7611	1.8438	8.2	1.5582	2.9541	3.3779
3.5	1.4024	1.8130	1.9053	8.3	1.5603	2.9584	3.3867
3.6	1.4073	1.8565	1.9579	8.4	1.5625	2.9628	3.3956
3.7	1.4122	1.9000	2.0091	8.5	1.5647	2.9671	3.4039
3.8	1.4171	1.9370	2.0546	8.6	1.5668	2.9714	3.4115
3.9	1.4220	1.9741	2.1000	8.7	1.5690	2.9758	3.4192
4.0	1.4268	2.0104	2.1455	8.8	1.5711	2.9801	3.4269
4.1	1.4317	2.0448	2.1909	8.9	1.5733	2.9844	3.4346
4.2	1.4366	2.0793	2.2333	9.0	1.5754	2.9887	3.4423
4.3	1.4415	2.1138	2.2750	9.1	1.5776	2.9931	3.4500
4.4	1.4463	2.1483	2.3167	9.2	1.5797	2.9974	3.4577
4.5	1.4512	2.1828	2.3583	9.3	1.5819	3.0035	3.4654
4.6	1.4561	2.2179	2.4000	9.4	1.5841	3.0124	3.4731
4.7	1.4610	2.2536	2.4400	9.5	1.5862	3.0212	3.4808
4.8	1.4659	2.2893	2.4800	9.6	1.5884	3.0301	3.4885
4.9	1.4707	2.3200	2.5192	9.7	1.5905	3.0389	3.4962
5.0	1.4756	2.3486	2.5577	9.8	1.5927	3.0478	3.5078
5.1	1.4805	2.3772	2.5962	9.9	1.5948	3.0566	3.5234
5.2	1.4854	2.4063	2.6310	10.0	1.5970	3.0655	3.5391
5.3	1.4902	2.4375	2.6655	10.1	1.5991	3.0743	3.5547
5.4	1.4951	2.4688	2.7000	10.2	1.6088	3.0832	3.5703
5.5	1.5000	2.5000	2.7370	10.3	1.6235	3.0920	3.5860
5.6	1.5022	2.5313	2.7741	10.4	1.6382	3.1022	3.6025
5.7	1.504		2.811	10.5			

3.5.1-Practical proton ligand stability constant: (citric acid)

3.5.1.1-Point-wise calculation method:

The ligand used is triprotonic, or tribasic acid. The ligand titration curve is well separated from the acid titration curve at pH 2.5 table (3.5.2), indicating the dissociation of the ligand in the titration medium figure (5.1). n_A extends from 0.4384 to 2.8833 as the ligand is triprotonic. The values obtained were, pKa_1= 3.1459, pKa_2=4.8270 and pKa_3=8.3813, table (3.5.3), table (3.5.4) and table (3.5.5).

Table (3.5.3) Citric acid pKa_1 by point-wise method, average value=3.1459

pH	$.n_A$	$\log\frac{(n_A-2)}{(3-n_A)}$	pKa_1	pH	n_A	$\log\frac{(n_A-2)}{(3-n_A)}$	pKa_1
2.5	2.8833	0.8789	3.3789	3.1	2.5201	0.0349	3.1349
2.6	2.8426	0.7287	3.3287	3.2	2.4525	-0.0828	3.1172
2.7	2.7587	0.4975	3.1975	3.3	2.3850	-0.2034	3.0966
2.8	2.6978	0.3635	3.1635	3.4	2.3429	-0.2825	3.1175
2.9	2.6370	0.2443	3.1443	3.5	2.2838	-0.4021	3.0979
3.0	2.5772	0.1353	3.1353	3.6	2.2164	-0.5587	3.0413

Table (35.4) Citric acid pKa_2 by point-wise method, average value= 4.8270

pH	**$.n_A$**	$\log\frac{(n_A-1)}{(2-n_A)}$	**pKa_2**	**pH**	**n_A**	$\log\frac{(n_A-1)}{(2-n_A)}$	**pKa_2**
4.3	1.8275	0.5389	4.8389	5.1	1.4364	-0.1865	4.9135
4.4	1.7757	0.4191	4.8191	5.2	1.3943	-0.2722	4.9278
4.5	1.7241	0.3105	4.8105	5.3	1.3483	-0.3633	4.9367
4.6	1.6715	0.2086	4.8086	5.4	1.3023	-0.4624	4.9376
4.7	1.6178	0.1120	4.8120	5.5	1.2564	-0.5867	4.9133
4.8	1.5641	0.0330	4.8330	5.6	1.2057	-0.7365	4.8635
4.9	1.5190	-0.0388	4.8612	5.7	1.1550	-0.9340	4.7660
5.0	1.4777	-0.1111	4.8889	5.8	1.1043	-1.2472	4.5528

Table (3.5.5) Citric acid pKa_3 by point-wise method, average value= 8.3813

pH	$.n_A$	$\log\frac{n_A}{(1-n_A)}$	pKa_3	pH	n_A	$\log\frac{n_A}{(1-n_A)}$	pKa_3
6.4	0.8159	0.6465	7.0465	8.3	0.5630	0.1101	8.4101
6.5	0.7714	0.5279	7.0279	8.4	0.5592	0.1034	8.5034
6.6	0.7362	0.4458	7.0458	8.5	0.5556	0.0970	8.5970
6.7	0.7012	0.3705	7.0705	8.6	0.5518	0.0903	8.6903
6.8	0.6662	0.3001	7.1001	8.7	0.5480	0.0836	8.7836
6.9	0.6314	0.2337	7.1337	8.8	0.5442	0.0769	8.8769
7.0	0.6119	0.1977	7.1977	8.9	0.5405	0.0706	8.9706
7.1	0.6082	0.1910	7.2910	9.0	0.5367	0.0639	9.0639
7.2	0.6044	0.1841	7.3841	9.1	0.5329	0.0573	9.1573
7.3	0.6006	0.1772	7.4772	9.2	0.5291	0.0506	9.2506
7.4	0.5968	0.1703	7.5703	9.3	0.5223	0.0388	9.3388
7.5	0.5932	0.1638	7.6638	9.4	0.5107	0.0186	9.4186
7.6	0.5895	0.1572	7.7572	9.5	0.4990	-0.0017	9.4983

7.7	0.5855	0.1501	7.8501	9.6	0.4874	-0.0219	9.5781
7.8	0.5819	0.1436	7.9436	9.7	0.4757	-0.0422	9.6578
7.9	0.5781	0.1368	8.0368	9.8	0.4641	-0.0625	9.7375
8.0	0.5743	0.1300	8.1300	9.9	0.4524	-0.0829	9.8171
8.1	0.5705	0.1233	8.2233	10.0	0.4408	-0.1033	9.8967
8.2	0.5669	0.1168	8.3168	10.1	0.4292	-0.1237	9.9763

3.5.2Metal-ligand stability constant: (chromium citrate)

3.5.2.1-Pointwise calculation method:

Metal-ligand titration curve crossed over ligand titration curve at pH 2.4 table (3.5.2), but the formation of the complex start at pH=2.7 table (3.5.6). The value of n^- extended between 0.0633 and 2.9925, indicating formation 1:1 chelate logK$_1$=6.1327.This value was further verified by half integral method.

Table (3.5.6). Stability constants determined by point-wise method. Average value of logK$_1$= 6.1327

V2	V3	n^-	pL	$\log \frac{n^-}{(1-n^-)}$	logK$_1$
1.7611	1.8438	0.1844	8.7155	-0.6457	8.0697
1.8130	1.9053	0.2111	8.4197	-0.5726	7.8471
1.8565	1.9579	0.2389	8.1242	-0.5033	7.6209
1.9000	2.0091	0.2650	7.8284	-0.4430	7.3854
1.9370	2.0546	0.2932	7.5330	-0.3820	7.1510
1.9741	2.1000	0.3225	7.2379	-0.3223	6.9156
2.0104	2.1455	0.3556	6.9434	-0.2581	6.6853
2.0448	2.1909	0.3948	6.6500	-0.1856	6.4644
2.0793	2.2333	0.4275	6.3557	-0.1269	6.2288
2.1138	2.2750	0.4600	6.0615	-0.0696	5.9918
2.1483	2.3167	0.4945	5.7678	-0.0096	5.7582
2.1828	2.3583	0.5306	5.4748	0.0533	5.5282
2.2179	2.4000	0.5678	5.1828	0.1186	5.3013
2.2536	2.4400	0.6004	4.8911	0.1769	5.0680
2.2893	2.4800	0.6353	4.6023	0.2410	4.8433
2.3200	2.5192	0.6832	4.3206	0.3337	4.6543
2.3486	2.5577	0.7371	4.0487	0.4477	4.4964
2.3772	2.5962	0.7940	3.7934	0.5861	4.3795

3.5.2.2- Half integral method. (chromium citrate)

Construction of metal-ligand formation curve by plotting n^- against pL, from which the stability constants of the complex deduced. $\log K_1$=5.72. Figure (3.5.2).

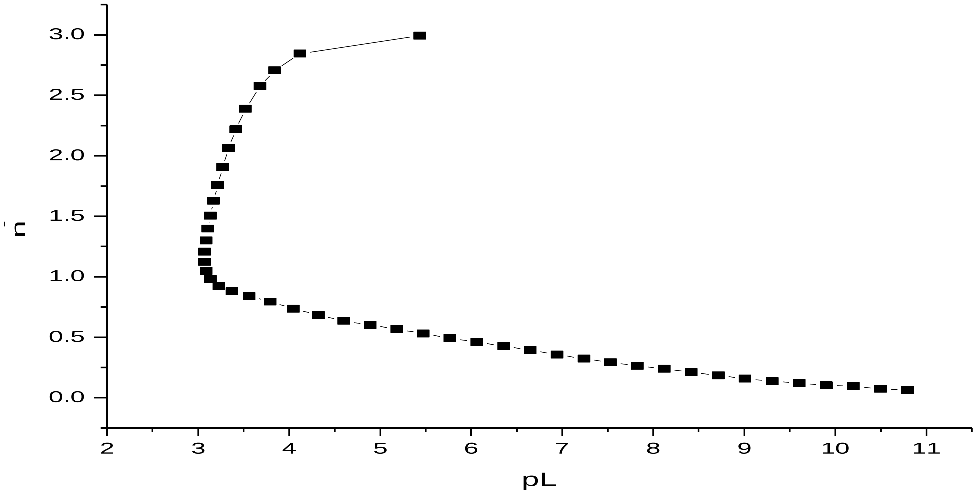


Fig. (3.5.2) Metal-ligand formation curve $\log K_1$=5.72 (half integral method)

3.5.2.3-Linear plot method:

Plotting of log $n^-/(1-n^-)$, versus corresponding pL, the values found was $\log K_1$=5.7. The values were further verified by least squares method. Fig.(3.5.3).

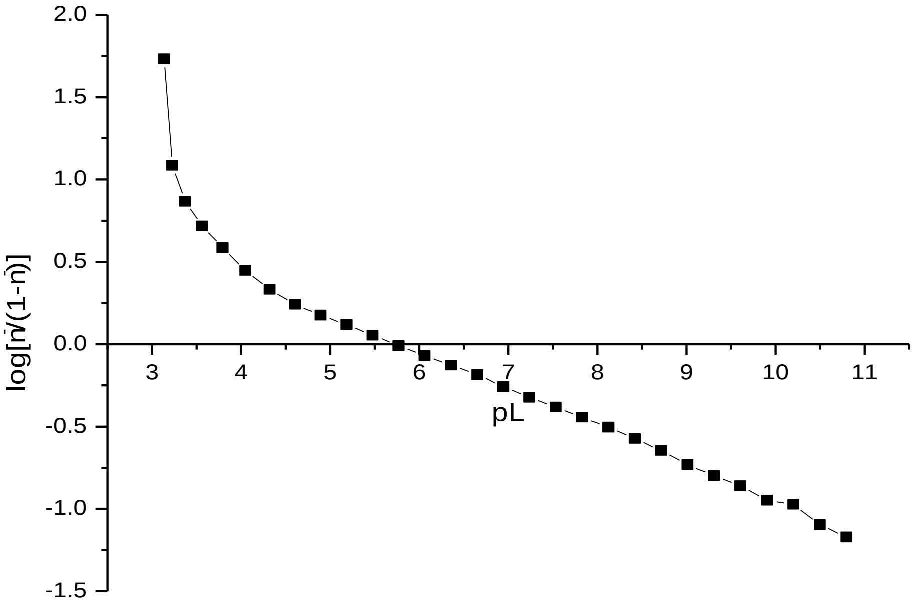


Fig. (3.5.3) Linear plot method (Cr-citrate) $\log K_1$ = 5.7

3.5.2.4 Henderson's or Hasselbalch's equation:(Cr-citrate)

This equation is used when only one complex or chelate is formed.

The equation is familiar as Henderson's or Hasselbalch's equation, and has been widely used for determination of the dissociation constants of monobasic acids. It is also useful for determining constants from n^- and [L] data over a very limited range e.g. if very strong or very weak complexes are formed, or if precipitation occurs at low value of n^-. (Gurdeep,1986).Which is the case. Value was found $\log K_1$= 6.0508. This value was in a good agreement with the value obtained by point-wise calculation method. The equation takes the form as follows:

$$\frac{n^-}{(1-n^-)}=\beta_1[L].$$

or

$$\log\left(\frac{n^-}{(1-n^-)}\right)=\log\beta_1+\log[L].$$

Table (3.5.7) Stability constant of Cr-citrate (Hasselbach’s equation) $\log K_1$ the average value =6.0509)

pL	n^-	$\log[L]$	$\log\frac{n^-}{(1-n^-)}$	$\log\frac{n^-}{(1-n^-)}-\log[L]$
11.7244	0.2634	-11.7244	0.2796	12.0040
11.4032	0.1214	-11.4032	0.2918	11.6950
11.0994	0.0923	-11.0994	0.2941	11.3935
10.7956	0.0633	-10.7956	0.2963	11.0919
10.4975	0.0740	-10.4975	0.2955	10.7930
10.2012	0.0965	-10.2012	0.2938	10.4949
9.9022	0.1015	-9.9022	0.2934	10.1955
9.6053	0.1212	-9.6053	0.2918	9.8971
9.3079	0.1371	-9.3079	0.2905	9.5984
9.0111	0.1562	-9.0110	0.2889	9.2999
8.7155	0.1844	-8.7155	0.2866	9.0020
8.4197	0.2111	-8.4197	0.2843	8.7040
8.1242	0.2389	-8.1242	0.2818	8.4060
7.8284	0.2650	-7.8284	0.2795	8.1079
7.5330	0.2932	-7.5330	0.2768	7.8099
7.2379	0.3225	-7.2379	0.2741	7.5119
6.9434	0.3556	-6.9434	0.2708	7.2142
6.6500	0.3948	-6.6500	0.2668	6.9168
6.3557	0.4275	-6.3557	0.2634	6.6190
6.0615	0.4600	-6.0615	0.2598	6.3213

5.7678	0.4945	-5.7678	0.2559	6.0237
5.4748	-5.4748	-5.4748	0.2517	5.7265
5.1828	-5.1828	-5.1828	0.2471	5.4299
4.8911	-4.8911	-4.8911	0.2430	5.1341
4.6023	-4.6023	-4.6023	0.2384	4.8407
4.3206	-4.3206	-4.3206	0.2318	4.5523
4.0487	-4.0487	-4.0487	0.2238	4.2726
3.7934	-3.7934	-3.7934	0.2149	4.0083
3.5624	-3.5624	-3.5624	0.2073	3.7697
3.3701	-3.3701	-3.3701	0.1999	3.5701
3.2277	-3.2277	-3.2277	0.1917	3.4193
3.1378	-3.1378	-3.1378	0.1800	3.3178
3.0903	-3.0903	-3.0903	0.1653	3.2556
3.0723	-3.0723	-3.0723	0.1469	3.2192
3.0738	-3.0738	-3.0738	0.1228	3.1966
3.0875	-3.0875	-3.0875	0.0914	3.1789
3.1082	-3.1082	-3.1082	0.0520	3.1602
3.1356	-3.1356	-3.1356	-0.0027	3.1328
3.1715	-3.1715	-3.1715	-0.0892	3.0823
3.2149	-3.2149	-3.2149	-0.2356	2.9793
3.2692	-3.2692	-3.2692	-0.5897	2.6795

Table(3.5.8) Stability constants of Cr- citrate estimatedby four methods.

Method	$\log K_1$
Point wise calculation method	6.1327
Half integral method	5.72
Linear plot method	5.70
Least squares method	6.0508

CHAPTER FOUR

Titanium carboxylates complexes

Results and discussion

4.1/Titanium-acetic acid system:

Table (4.1.1). The pH - titration reading of acid, acid + ligand and acid + ligand + metal ion (Ti^{+3}). $N^0 = 0.525M$, $E^0 = 5\times10^{-3}$ M, $T_{Cl} = 1.5\times10^{-3}$ M, $T_{cm} = 5\times10^{-4}$ M, $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$, $t = 36.5^0 C$.

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.34	2.34	2.32	3.4	11.98	11.82	11.62
0.1	2.36	2.36	2.33	3.5	12.00	11.86	11.67
0.2	2.39	2.39	3.34	3.6	12.03	11.89	11.71
0.3	2.42	2.42	2.36	3.7	12.05	11.92	11.75
0.4	2.46	2.45	2.39	3.8	12.07	11.94	11.79
0.5	2.49	2.49	2.41	3.9	12.08	11.97	11.82
0.6	2.54	2.53	2.43	4.0	12.10	11.99	11.85
0.7	2.58	2.57	2.46	4.1	12.12	12.02	11.88
0.8	2.64	2.62	2.50	4.2	12.13	12.04	11.91
0.9	2.69	2.68	2.54	4.3	12.15	12.06	11.93
1.0	2.77	2.75	2.58	4.4	12.17	12.08	11.96
1.1	2.85	2.83	2.63	4.5	12.18	12.10	11.98
1.2	2.96	2.93	2.68	4.6	12.20	12.11	12.00
1.3	3.11	3.06	2.75	4.7	12.21	12.13	12.02
1.4	3.31	3.23	2.82	4.8	12.22	12.15	12.04
1.5	3.74	3.48	2.91	4.9	12.24	12.16	12.06
1.6	9.04	3.87	3.02	5.0	12.25	12.18	12.08
1.7	10.57	4.29	3.17	5.1	12.26	12.19	12.09
1.8	10.94	4.65	3.37	5.2	12.27	12.20	12.11
1.9	11.14	5.00	3.68	5.3	12.28	12.22	12.12
2.0	11.28	5.43	4.11	5.4	12.29	12.23	12.14
2.1	11.39	6.62	4.51	5.5	12.30	12.24	12.15
2.2	11.47	10.39	4.87	5.6	12.31	12.26	12.16
2.3	11.55	10.85	5.30	5.7	12.32	12.27	12.18
2.4	11.61	11.09	6.05	5.8	12.33	12.28	12.19
2.5	11.67	11.25	9.77	5.9	12.34	12.29	12.20
2.6	11.72	11.37	10.60	6.0	12.35	12.30	12.22
2.7	11.76	11.46	10.91	6.1	12.36	12.31	12.23
2.8	11.80	11.53	11.11	6.2	12.37	12.32	12.24
2.9	11.84	11.60	11.25	6.3	12.38	12.33	12.25
3.0	11.87	11.65	11.35	6.4	12.39	12.34	12.26
3.1	11.90	11.70	11.44	6.5	12.40	12.35	12.27
3.2	11.93	11.75	11.51	6.6	12.41	12.36	12.28
3.3	11.96	11.79	11.57	-	-	-	-

Table (4.1.2) Alkali volume that bring the three sets of solutions to the same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.2333	0.2333	0.4500	7.2	1.5653	2.1154	2.4309
2.5	0.5200	0.5250	0.8000	7.3	1.5672	2.1180	2.4336
2.6	0.7333	0.7600	1.0400	7.4	1.5691	2.1207	2.4363
2.7	0.9125	0.9286	1.2286	7.5	1.5709	2.1233	2.4390
2.8	1.0375	1.0625	1.3714	7.6	1.5728	2.1260	2.4417
2.9	1.1455	1.1700	1.4889	7.7	1.5747	2.1286	2.4444
3.0	1.2267	1.2539	1.5818	7.8	1.5766	2.1313	2.4470
3.1	1.2933	1.3235	1.6533	7.9	1.5785	2.1340	2.4497
3.2	1.3450	1.3824	1.7150	8.0	1.5804	2.1366	2.4524
3.3	1.3950	1.4280	1.7650	8.1	1.5823	2.1393	2.4551
3.4	1.4209	1.4680	1.8097	8.2	1.5842	2.1419	2.4578
3.5	1.4442	1.5051	1.8419	8.3	1.5860	2.1446	2.4605
3.6	1.4674	1.5308	1.8742	8.4	1.5879	2.1472	2.4632
3.7	1.4907	1.5564	1.9047	8.5	1.5898	2.1499	2.4659
3.8	1.5011	1.5821	1.9279	8.6	1.5917	2.1525	2.4686
3.9	1.5030	1.6071	1.9512	8.7	1.5936	2.1552	2.4712
4.0	1.5049	1.6310	1.9744	8.8	1.5955	2.1578	2.4739
4.1	1.5068	1.6548	1.9977	8.9	1.5974	2.1605	2.4766
4.2	1.5087	1.6786	2.0225	9.0	1.5992	2.1631	2.4793
4.3	1.5106	1.7028	2.0475	9.1	1.6039	2.1658	2.4820
4.4	1.5125	1.7306	2.0725	9.2	1.6105	2.1684	2.4847
4.5	1.5143	1.7583	2.0975	9.3	1.6170	2.1711	2.4874
4.6	1.5162	1.7861	2.1250	9.4	1.6235	2.1737	2.4901
4.7	1.5181	1.8143	2.1528	9.5	1.6301	2.1764	2.4927
4.8	1.5200	1.8429	2.1806	9.6	1.6366	2.1790	2.4954
4.9	1.5219	1.8714	2.2070	9.7	1.6431	2.1817	2.4981
5.0	1.5238	1.9000	2.2302	9.8	1.6497	2.1844	2.5036
5.1	1.5257	1.9233	2.2535	9.9	1.6562	2.1870	2.5157
5.2	1.5275	1.9465	2.2768	10.0	1.6628	2.1897	2.5277
5.3	1.5294	1.9698	2.3000	10.1	1.6693	2.1923	2.5398
5.4	1.5313	1.9930	2.3133	10.2	1.6758	2.1950	2.5518
5.5	1.5332	2.0059	2.3267	10.3	1.6824	2.1976	2.5639
5.6	1.5351	2.0143	2.3400	10.4	1.6889	2.2022	2.5759
5.7	1.5370	2.0227	2.3533	10.5	1.6954	2.2239	2.5880
5.8	1.5389	2.0311	2.3667	10.6	1.7081	2.2457	2.6000
5.9	1.5408	2.0395	2.3800	10.7	1.7352	2.2674	2.6323
6.0	1.5426	2.0479	2.3933	10.8	1.7622	2.2891	2.6645
6.1	1.5445	2.0563	2.4013	10.9	1.7892	2.3209	2.6968
6.2	1.5464	2.0647	2.4040	11.0	1.8300	2.3625	2.7450
6.3	1.5483	2.0731	2.4067	11.1	1.8800	2.4063	2.7950
6.4	1.5502	2.0815	2.4094	11.2	1.9429	2.4688	2.8644
6.5	1.5521	2.0899	2.4121	11.3	2.0183	2.5417	2.9501
6.6	1.5540	2.0983	2.4148	11.4	2.1112	2.6334	3.0557
6.7	1.5558	2.1021	2.4175	11.5	2.2287	2.7573	3.1859
6.8	1.5577	2.1048	2.4202	11.6	2.3835	2.9002	3.3602
6.9	1.5596	2.1074	2.4229	11.7	2.5602	3.1002	3.5752
7.0	1.5615	2.1101	2.4255	11.8	2.8002	3.3337	3.8337
7.1	1.5634	2.1127	2.4282	11.9	3.1003	3.6337	4.1670

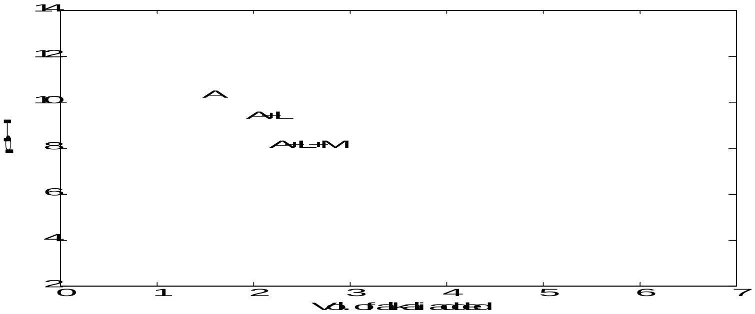


Figure (41.1) Titration curves of the three sets of solutions versus pH

4.1.1-Metal ligand stability constant:

4.1.1.1-Point-wise calculation method: (Titanium acetate)

Metal-ligand titration curve cross over the ligand titration curve at pH 2.4. Table (4.1.2), figure (4.1.1) indicating the formation of the complex. n^- extends between 1.1406 and 2.8823 indicating the formation ML_2 and ML_3 complex species. $\log K_2$ =5.5484 and K_3=4.2895, table (4.1.3), and table (4.1.4). These values were further verified by half integral method.

Table (4.1.3) Stability constants determined by pointwise method $\log K_2$ average value =5.5484

Log K_2	$\log\frac{(n^- -1)}{(2-n^-)}$	pL	n^-	V3	V2
5.4030	-0.0502	5.4532	1.4711	0.8000	0.5250
5.5869	0.2083	5.3786	1.6177	1.0400	0.7600
5.6033	0.3001	5.3032	1.6662	1.2286	0.9286
5.7546	0.5263	5.2283	1.7706	1.3714	1.0625
5.8164	0.6691	5.1473	1.8236	1.4889	1.1700
5.9895	0.9204	5.0691	1.8928	1.5818	1.2539

Table (4.1.4) Stability constants determined by pointwise method $\log K_3$ average value =4.2895

Log K_3	$\log\frac{(n^- -2)}{(3-n^-)}$	pL	n^-	V3	V2
4.0607	-0.5879	4.6487	2.2053	1.8419	1.5051
4.1430	-0.4315	4.5745	2.2702	1.8742	1.5308
4.1767	-0.3211	4.4978	2.3232	1.9047	1.5564
4.3440	-0.0842	4.4283	2.4517	1.9279	1.5821
4.7230	0.3379	4.3851	2.6853	1.9512	1.6071

4.1.1.2- Half integral method:

$\log K_2$ and $\log K_3$ were determined by plotting metal-ligand formation curve, n^- against pL, figure (4.1.2). $\log k_2$= 5.4612 and $\log K_3$= 4.4 and these values were further corroborated with linear plot method.

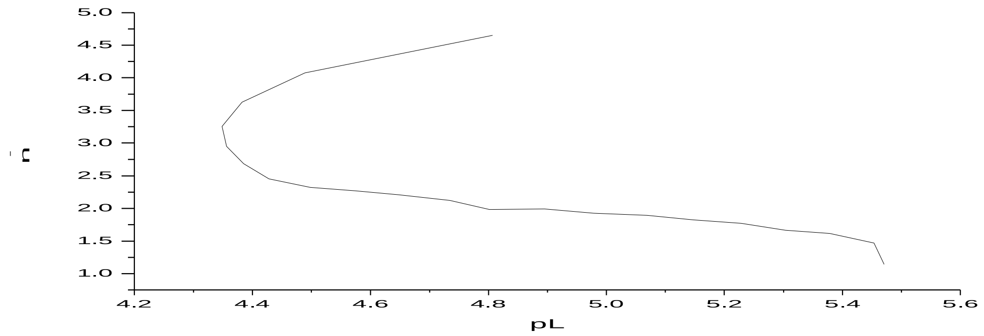


Figure (4.1.2) Metal-ligand formation curve $\log K_2$=5.412 & $\log K_3$=4.352

4.1.1.3 -Linear plot method: (Ti-acetate)

In this method log $(n^{-}-1)/(2-n^{-})$ and log $(n^{-}-2)/(3-n^{-})$ were plotted versus corresponding pL for determination of $\log K_2$ and $\log K_3$ respectively. $\log k_2=5.454$ and $\log K_3=4.386$, figures (4.1.3), and figure (4.1.4) these values were in a good agreement with the two previous methods, and further were verified by least squares method.

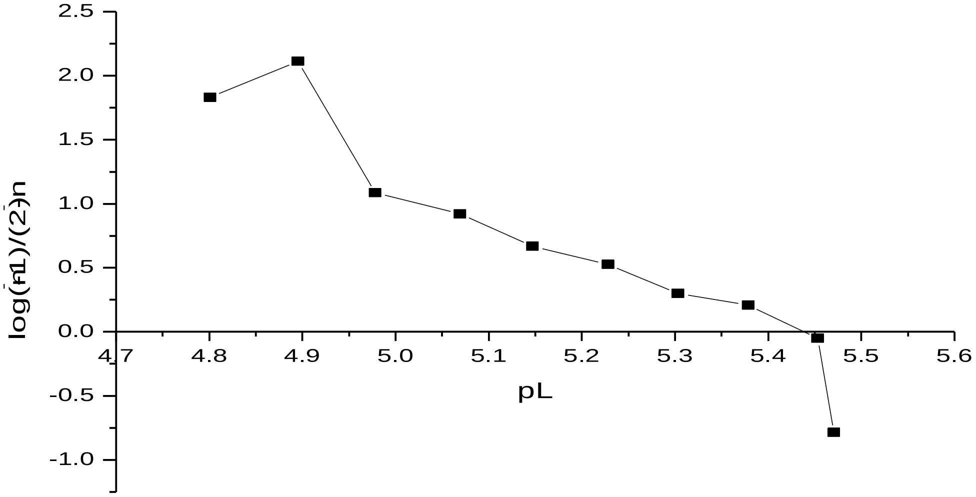


Fig. (4.1.3) linear plot method $\log K_2=5.454$

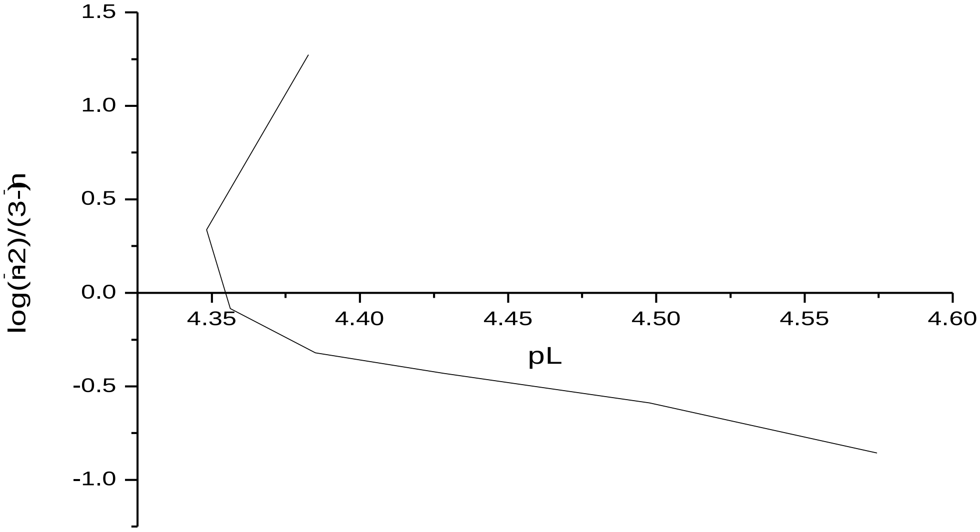


Fig. (4.1.4) linear plot method $\log K_3=4.386$

4.1.1.4-Least squares method:

To calculate the stability constants according to this method the following expression can be used.

$$(n^{-}-1)[L]K_1 = (2-n^{-})[L]^2 K_1K_2 + (3-n^{-})[L]^3 K_1K_2K_3 ----(5.1)$$

On division and rearrangement becomes:

$$\frac{(n^{-}-1)}{(2-n^{-})[L]} = \frac{(3-n)[L]}{(2-n^{-})}K_2K_3 + K_3 ------(5.2)$$

Plotting the right-side equation against the left one, straight line equation is obtained, with intercept K_3 and slope K_2K_3.

Table (4.1.5) Stability constants of Ti-acetate determined by least squares method.

n^-	pL	[L]	$\frac{(3-n^-)[L]}{(2-n^-)}$	$\frac{(n^- -1)}{(2-n^-)[L]}$
1.1407	5.4707	3.34E-06	7.3E-06	48395.90797
1.4582	5.4532	3.5E-06	1.0E-05	252936.3228
1.5421	5.3786	4.2E-06	1.5E-05	386264.8041
1.6193	5.3032	5.0E-06	2.0E-05	401186.9264
1.6933	5.2283	5.9E-06	3.2E-05	568355.9548
1.7455	5.1473	7.1E-06	4.8-05	655221.67
1.8029	5.0691	8.5E-06	8.8E-05	976195.7797
1.8227	4.9781	1.1E-05	0.0001	1157945.494
1.8623	4.8951	1.3E-05	0.0017	10155076.66
1.9476	4.7349	1.8E-05	-0.0001	-499562.992
1.9710	4.6487	2.2E-05	-8.7E-05	-261486.856
2.0192	4.5745	2.7E-05	-7.2E-05	-176466.041
2.0570	4.4978	3.2E-05	-6.7E-05	-128810.752
2.1054	4.4283	3.7E-05	-4.5E-05	-86163.6847
2.1979	4.3851	4.1E-05	-1.9E-05	-59686.7934
2.3010	4.3564	4.4E-05	-2.3E-06	-46646.5877
2.4156	4.3483	4.5E-05	9.1E-06	-40055.531
2.5537	4.3826	4.1E-05	1.6E-05	-38945.9176
2.7090	4.4889	3.2E-05	1.7E-05	-45689.2367
2.8824	4.8070	1.6E-05	9.7E-06	-88317.6359

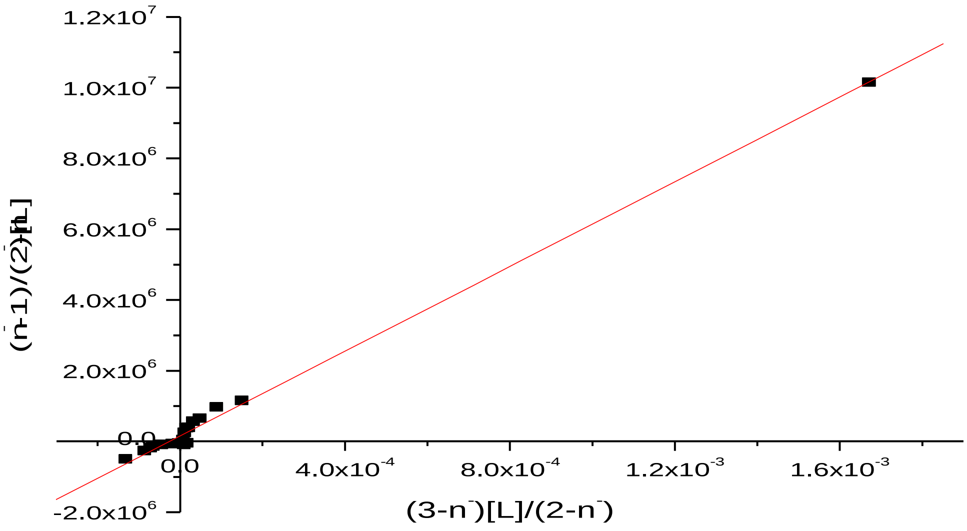


Fig. (4.1.5) plot of the least squares method $\log K_2=5.5807$ &$\log K_3=4.1975$

```
                    Linear Regression
Parameter      Value              Error             R²
          ------------------------------------------------------------
Intercept    157594.55876      44637.31696    0.99652
Slope          5.98402E9         1.17923E8
```

Table (4.1.6) Ti-acetate stability constant estimated by the four methods

Method	$\log K_2$	$\log K_3$	$\log K_2+\log K_3$
Point-wise calculation method	5.5484	4.2895	9.8379
Half integral method	5.412	4.4	9.812
Linear plot method	5.454	4.386	9.84
Least squares method	5.5809	4.1975	9.7784

4.2-Titanium-oxalic acid system:

Table (4.2.1). The pH - titation readings of acid, acid + ligand and acid + ligand + metal ion (Ti^{+3}). $N^0 = 0.522M$, $E^0 = 5\times10^{-3}M$, $T_{Cl} = 1.5\times10^{-3}M$, $T_{cm} = 5\times10^{-4}M$, $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$, $t = 36.5^0C$.

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.33	2.26	2.24	3.1	11.86	11.04	5.88
0.1	2.35	2.26	2.24	3.2	11.89	11.19	9.62
0.2	2.38	2.27	2.25	3.3	11.91	11.31	10.50
0.3	2.41	2.29	2.26	3.4	11.94	11.40	10.86
0.4	2.44	2.31	2.27	3.5	11.96	11.48	11.07
0.5	2.48	2.33	2.29	3.6	11.98	11.55	11.22
0.6	2.52	2.35	2.31	3.7	12.01	11.60	11.33
0.7	2.56	2.38	2.32	3.8	12.03	11.66	11.41
0.8	2.61	2.40	2.34	3.9	12.04	11.70	11.48
0.9	2.67	2.43	2.36	4.0	12.06	11.74	11.54
1.0	2.74	2.46	2.38	4.1	12.08	11.77	11.60
1.1	2.81	2.50	2.41	4.2	12.10	11.81	11.65
1.2	2.91	2.54	2.44	4.3	12.11	11.84	11.69
1.3	3.04	2.58	2.47	4.4	12.13	11.87	11.73
1.4	3.22	2.63	2.50	4.5	12.14	11.89	11.76
1.5	3.53	2.69	2.54	4.6	12.16	11.92	11.79
1.6	5.08	2.75	2.58	4.7	12.17	11.94	11.82
1.7	10.26	2.83	2.62	4.8	12.18	11.96	11.85
1.8	10.81	2.92	2.67	4.9	12.20	11.98	11.88
1.9	11.04	3.02	2.73	5.0	12.21	12.00	11.90
2.0	11.20	3.16	2.80	5.1	12.22	12.02	11.92
2.1	11.33	3.32	2.88	5.2	12.23	12.04	11.95
2.2	11.42	3.52	2.98	5.3	12.24	12.06	11.97
2.3	11.50	3.75	3.10	5.4	12.25	12.05	11.99
2.4	11.56	4.00	3.26	5.5	12.26	12.07	12.01
2.5	11.62	4.26	3.45	5.6	12.27	12.09	12.02
2.6	11.67	4.56	3.67	5.7	12.28	12.10	12.04
2.7	11.72	5.07	3.91	5.8	12.29	12.11	12.06
2.8	11.76	7.17	4.16	5.9	12.30	12.13	12.07
2.9	11.79	10.32	4.48	6.0	12.31	12.14	12.09
3.0	11.83	10.79	4.87	-	-	-	-

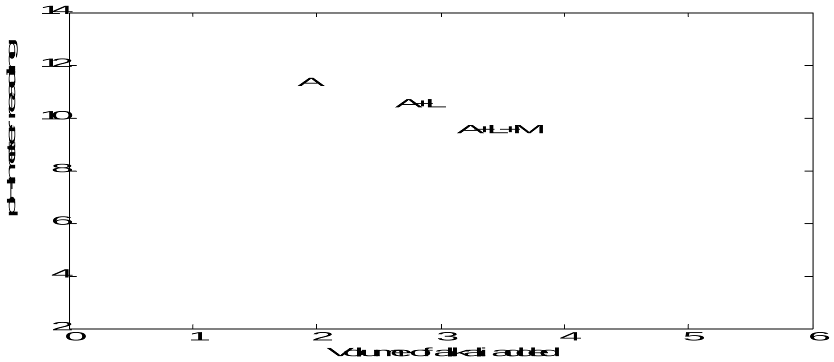


Fig.(4.2.1) Plotting of alkali volume of three set of solution V/s pH

Table (4.2.2) alkali volume required to bring the three sets of solutions to same pH

B	V1	V2	V3	B	V1	V2	V3
2.3	0.3500	0.5500	-	7.2	1.6409	2.8010	3.1353
2.4	0.2667	0.8000	1.0667	7.3	1.6429	2.8041	3.1380
2.5	0.5500	1.1000	1.4000	7.4	1.6448	2.8073	3.1406
2.6	0.7800	1.3400	1.6500	7.5	1.6467	2.8104	3.1433
2.7	0.9429	1.5167	1.8500	7.6	1.6486	2.8136	3.1460
2.8	1.0857	1.6625	2.0000	7.7	1.6506	2.8186	3.1487
2.9	1.1900	1.7778	2.1200	7.8	1.6525	2.8199	3.1513
3.0	1.2692	1.8800	2.2167	7.9	1.6544	2.8231	3.1540
3.1	1.3333	1.9572	2.3000	8.0	1.6564	2.8263	3.1567
3.2	1.3889	2.0250	2.3625	8.1	1.6583	2.8294	3.1594
3.3	1.4258	2.0875	2.4211	8.2	1.6602	2.8326	3.1620
3.4	1.4581	2.1400	2.4737	8.3	1.6622	2.8358	3.1647
3.5	1.4903	2.1900	2.5227	8.4	1.6641	2.8389	3.1674
3.6	1.5045	2.2348	2.5682	8.5	1.6660	2.8421	3.1701
3.7	1.5110	2.2783	2.6125	8.6	1.6680	2.8453	3.1727
3.8	1.5174	2.3200	2.6542	8.7	1.6699	2.8484	3.1754
3.9	1.5239	2.3600	2.6958	8.8	1.6718	2.8516	3.1781
4.0	1.5303	2.4000	2.7360	8.9	1.6737	2.8547	3.1808
4.1	1.5368	2.4385	2.7760	9.0	1.6757	2.8579	3.1834
4.2	1.5432	2.4769	2.8125	9.1	1.6776	2.8611	3.1861
4.3	1.5497	2.5133	2.8438	9.2	1.6795	2.8642	3.1888
4.4	1.5561	2.5467	2.8750	9.3	1.6815	2.8674	3.1914
4.5	1.5626	2.5800	2.9051	9.4	1.6834	2.8706	3.1941
4.6	1.5690	2.6078	2.9308	9.5	1.6853	2.8737	3.1968
4.7	1.5755	2.6275	2.9564	9.6	1.6873	2.8769	3.1995
4.8	1.5819	2.6471	2.9821	9.7	1.6892	2.8801	3.2091
4.9	1.5884	2.6667	3.0030	9.8	1.6911	2.8832	3.2205
5.0	1.5948	2.6863	3.0129	9.9	1.6931	2.8864	3.2318
5.1	1.6004	2.7014	3.0228	10.0	1.6950	2.8896	3.2432
5.2	1.6023	2.7062	3.0327	10.1	1.6969	2.8927	3.2546
5.3	1.6042	2.7110	3.0426	10.2	1.6988	2.8959	3.2659
5.4	1.6062	2.7157	3.0525	10.3	1.7073	2.8991	3.2773
5.5	1.6081	2.7205	3.0624	10.4	1.7255	2.9152	3.2886
5.6	1.6100	2.7252	3.0723	10.5	1.7437	2.9370	3.3000
5.7	1.6120	2.7300	3.0822	10.6	1.7618	2.9587	3.3278
5.8	1.6139	2.7348	3.0921	10.7	1.7800	2.9805	3.3556
5.9	1.6158	2.7395	3.1005	10.8	1.7982	3.0040	3.3834
6.0	1.6178	2.7443	3.1032	10.9	1.8392	3.0440	3.4191
6.1	1.6197	2.7490	3.1059	11.0	1.8826	3.0840	3.4667
6.2	1.6216	2.7538	3.1086	11.1	1.9376	3.1401	3.5201
6.3	1.6236	2.7536	3.1112	11.2	2.0001	3.2084	3.5867
6.4	1.6255	2.7633	3.1139	11.3	2.0770	3.2917	3.6728
6.5	1.6274	2.7681	3.1166	11.4	2.1779	3.4001	3.7876
6.6	1.6293	2.7729	3.1193	11.5	2.3002	3.5287	3.9335
6.7	1.6313	2.7776	3.1219	11.6	2.4668	3.7002	4.1002
6.8	1.6332	2.7824	3.1246	11.7	2.6602	3.9002	4.3252
6.9	1.6351	2.7871	3.1273	11.8	2.9252	4.1752	4.6337
7.0	1.6371	2.7919	3.1299	11.9	3.2505	4.5337	5.0005
7.1	1.6390	2.7967	3.1326	12.0	-	-	-

4.2.1-Metal-ligand stability constants :(Titanium and oxalate)

4.2.1.1-pointwise calculation method:

As n^{-} and pL were calculated and hence n^{-} extends between 1.3152 and 2.8983, indicates the formation of 1:2 and 1:3 chelates, the stability constants of chelates were easily found $\log K_2$ =5.0805, and $\log K_3$=4.4069. Tables, (4.2.3) & (4.2.4).

Table (4.2.3) Point-wise method $\log K_2$ average value = 5.0805

Log K_2	$\log\frac{(n^{-}-1)}{(2-n^{-})}$	pL	n^{-}	V3	V2
4.6936	-0.3370	5.0306	1.3152	1.0667	0.8000
5.0120	0.0296	4.9825	1.5170	1.4000	1.1000
5.0620	0.1596	4.9024	1.5909	1.6500	1.3400
5.3277	0.4747	4.8530	1.7489	1.8500	1.5167
5.3072	0.5441	4.7632	1.7778	2.0000	1.6625
5.3933	0.7076	4.6856	1.8361	2.1200	1.7778
5.4815	0.8758	4.6058	1.8825	2.2167	1.8800
5.9605	1.4184	4.5421	1.9632	2.3000	1.9572

Table (4.2.4) Point-wise method $\log K_3$ average value = 4.4069

Log K_3	$\log\frac{(n^{-}-2)}{(3-n^{-})}$	pL	n^{-}	V3	V2
3.1772	-1.2185	4.3957	2.0570	2.4211	2.0875
3.5807	-0.7671	4.3478	2.1460	2.4737	2.1400
3.7601	-0.5405	4.3006	2.2236	2.5227	2.1900
4.1281	-0.1922	4.3202	2.3911	2.5682	2.2348
4.6840	0.2305	4.4535	2.6296	2.6125	2.2783
5.8816	0.9460	4.9357	2.8983	2.6542	2.3200

4.2.1.2-Half integral method: (titanium oxalate)

$\log K_2$ and $\log K_3$ have been determined by plotting formation curve n^{-} versus pL. $\log K_2$=4.987 and $\log K_3$=4.36 figure (4.2.2). The value was in a good concordance with the values of point wise calculation method. The value was further verified by linear plot method.

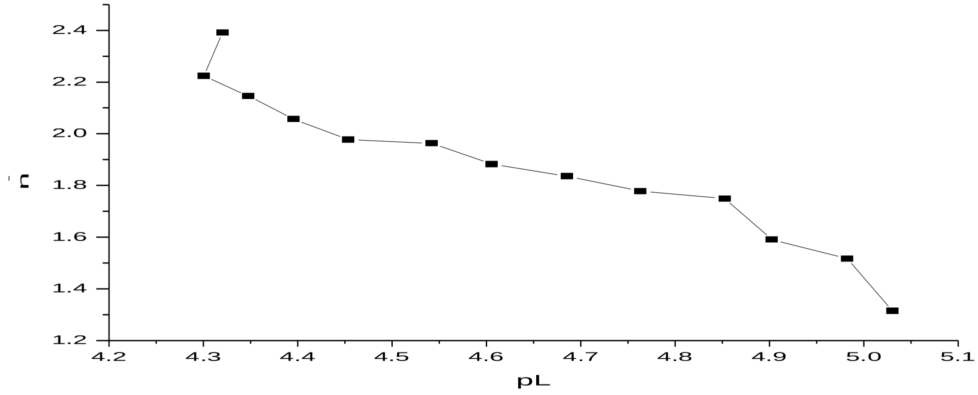


Fig. (42.2).Metal-ligand formation curve $\log K_2$=4.986, &$\log K_3$=4.36

4.2.1.3-Linear plot method: (Titanium oxalate)

In this method the value of $\log K_2$ and $\log K_3$ were calculated by plotting log $(n^- -1)/(2-n^-)$ and $\log(n^- - 2)/(3-n^-)$ against corresponding pL. The values obtained, $\log K_2$=5.00 and $\log K_3$= 4.36 and figure (4.2.3) and figure (4.2.4). This value was in a good agreement with value obtained by half integral method.

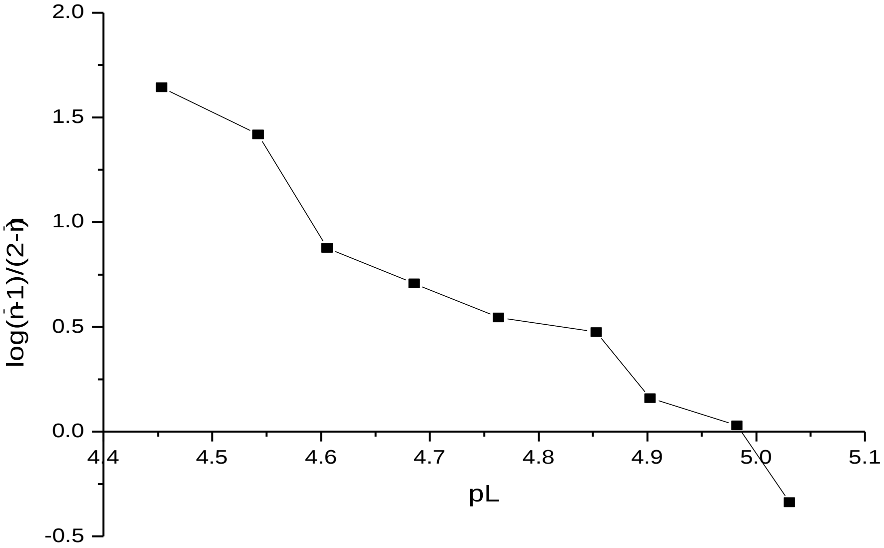


Figure (4.2.3) linear plot method $\log K_2$=5.00

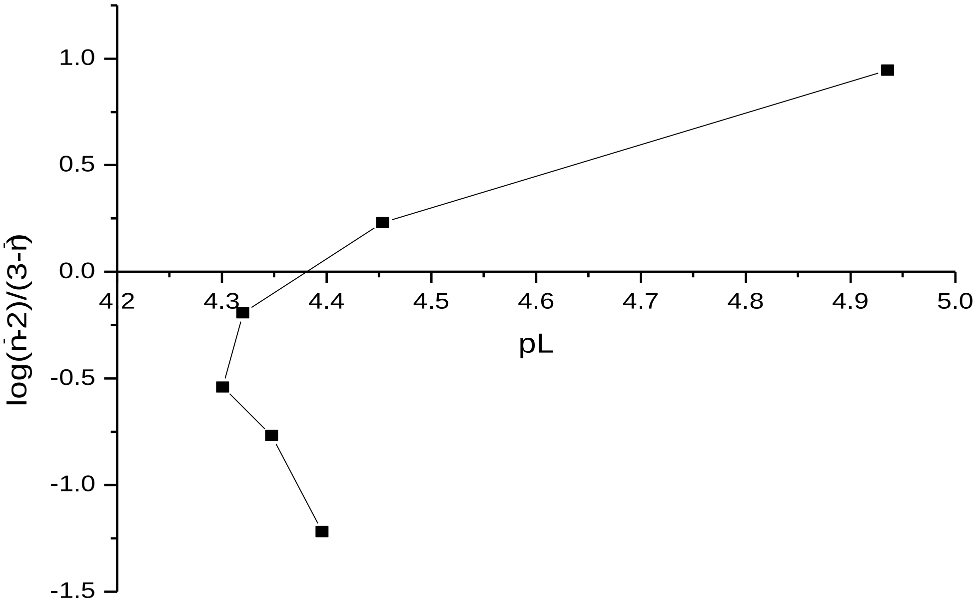


Figure (4.2.4) linear plot method $\log K_2$=5.00

4.2.14-Linear least squares method: (titanium oxalate)

Since there were two complexes, the stability constants can be calculated by the following equation:

$$\frac{(n^- - 1)}{(2 - n^-)[L]} = \frac{(3 - n)[L]}{(2 - n^-)} K_2 K_3 + K_2 \text{------}(4.1.1)$$

Table (4.2.5) Least equation method $\log K_2$ average value = 5.3705

pL	n^-	[L]	$\left(\frac{(3-n^-)}{(2-n^-)}\right)*[L]$	$\left(\frac{(n^- -1)}{(2-n^-)}\right)*\frac{1}{[L]}$
5.0306	1.3152	9.3E-06	2.3E-05	49384.1130
4.9825	1.5170	1.0E-05	3.2E-05	102806.4482
4.9024	1.5909	1.3E-05	4.3E-05	115345.7431
4.8530	1.7489	1.4E-05	7.0E-05	212647.0763
4.7632	1.7778	1.7E-05	9.5E-05	202884.0336
4.6856	1.8361	2.1E-05	0.0001	247329.6142
4.6058	1.8825	2.5E-05	0.0002	303057.8173
4.4536	1.9778	3.5E-05	0.0016	1250331.863
4.3957	2.0570	4.0E-05	-0.0007	-461031.5384
4.3478	2.1460	4.5E-05	-0.0003	-174812.6954
4.3006	2.2236	5.01E-05	-0.0002	-109307.8573
4.3202	2.3911	4.8E-05	-7.4E-05	-74350.72002
4.4535	2.6296	3.5E-05	-2.1E-05	-73532.19782

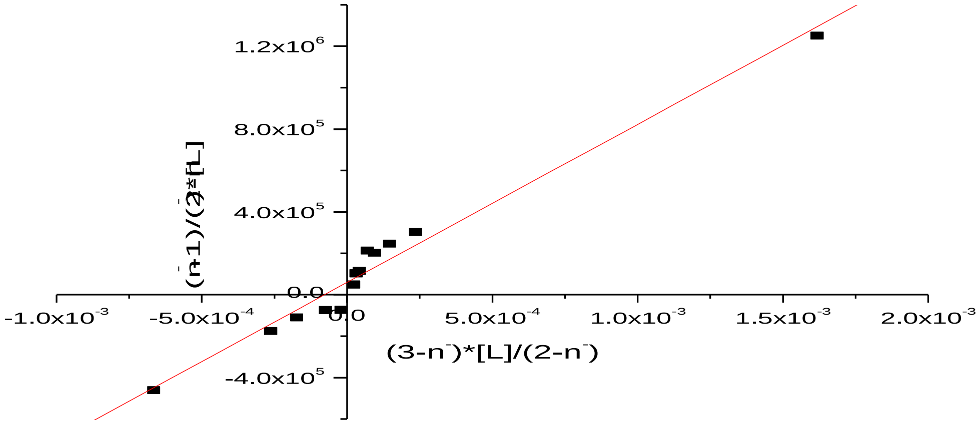


Fig.(4.2.5), least squares method, $\log K_2$=4.7760 & $\log K_3$= 4.1067

Linear Regression

Parameter	Value	Error	R^2
Intercept	59700.14132	19099.17125	0.98655
Slope	7.63329E8	3.81281E7	

Table (4.2.6) Stability constants of Ti-oxalate obtained by the four method

Method	$\log K_2$	$\log K_3$	$\log K_2 + \log K_3$
Point wise calculation method	5.0805	4.4069	9.4874
Half integral method	4.987	4.36	9.347
Linear plot method	5.00	4.36	9.36
Henderson's equation	4.7760	4.1272	8.9032

4.3/Titanium-oxalacetic acid system:

Table (4.3.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ion (Ti^{+3}). $N^0 = 0.522M$, $E^0 = 5\times10^{-3}M$, $T_{Cl} = 1.5\times10^{-3}M$, $T_{cm} = 5\times10^{-4}M$, $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$ $t = 23.5^0C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.28	2.20	2.07	3.1	11.86	11.67	11.36
0.1	2.29	2.21	2.09	3.2	11.89	11.72	11.45
0.2	2.31	2.23	2.11	3.3	11.92	11.76	11.53
0.3	2.33	2.25	2.13	3.4	11.95	11.80	11.59
0.4	2.36	2.27	2.15	3.5	11.97	11.84	11.65
0.5	2.39	2.30	2.17	3.6	12.00	11.87	11.70
0.6	2.42	2.33	2.19	3.7	12.02	11.90	11.74
0.7	2.46	2.36	2.22	3.8	12.04	11.93	11.78
0.8	2.51	2.39	2.25	3.9	12.06	11.96	11.82
0.9	2.56	2.43	2.28	4.0	12.08	11.98	11.86
1.0	2.62	2.47	2.31	4.1	12.10	12.01	11.89
1.1	2.69	2.52	2.35	4.2	12.12	12.03	11.92
1.2	2.79	2.59	2.39	4.3	12.14	12.05	11.95
1.3	2.92	2.65	2.43	4.4	12.15	12.07	11.97
1.4	3.11	2.72	2.48	4.5	12.17	12.09	12.00
1.5	3.49	2.81	2.53	4.6	12.19	12.11	12.02
1.6	6.56	2.93	2.59	4.7	12.20	12.13	12.04
1.7	10.32	3.08	2.66	4.8	12.21	12.15	12.06
1.8	10.82	3.30	2.75	4.9	12.23	12.16	12.08
1.9	11.06	3.69	2.84	5.0	12.24	12.18	12.10
2.0	11.22	4.79	2.96	5.1	12.25	12.20	12.12
2.1	11.34	6.90	3.13	5.2	12.27	12.21	12.13
2.2	11.43	9.87	3.37	5.3	12.28	12.22	12.15
2.3	11.50	10.61	3.89	5.4	12.29	12.24	12.17
2.4	11.57	10.93	5.27	5.5	12.30	12.25	12.18
2.5	11.62	11.12	7.18	5.6	12.31	12.26	12.20
2.6	11.67	11.27	9.91	5.7	12.32	12.28	12.21
2.7	11.72	11.38	10.59	5.8	12.33	12.29	12.22
2.8	11.76	11.47	10.90	5.9	12.34	12.30	12.24
2.9	11.80	11.55	11.10	6.0	12.35	12.31	12.25
3.0	11.83	11.61	11.25	-	-	-	-

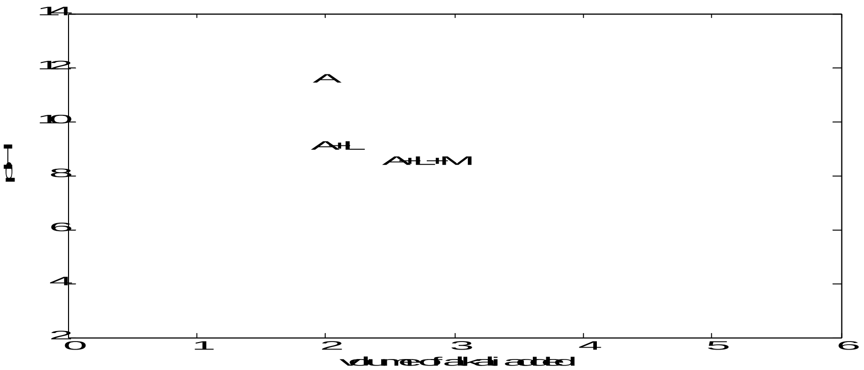


Figure (4.3.1) pH against volume of KOH for the three set of solutions

Table (4.3.2) Alkali volume that bring the three set of solutions to the same pH

B	V1	V2	V3	B	V1	V2	V3
2.3	0.1500	0.5000	0.9667	7.2	1.6170	2.1101	2.5007
2.4	0.5333	0.8250	1.2250	7.3	1.6197	2.1135	2.5044
2.5	0.7800	1.0600	1.4400	7.4	1.6223	2.1168	2.5081
2.6	0.9667	1.2286	1.6143	7.5	1.6250	2.1202	2.5117
2.7	1.1100	1.3714	1.7445	7.6	1.6277	2.1236	2.5154
2.8	1.2077	1.4889	1.8556	7.7	1.6303	2.1269	2.5190
2.9	1.2846	1.5750	1.9500	7.8	1.6330	2.1303	2.5227
3.0	1.3421	1.6467	2.0235	7.9	1.6356	2.1337	2.5264
3.1	1.3947	1.7091	2.0824	8.0	1.6383	2.1370	2.5300
3.2	1.4237	1.7546	2.1292	8.1	1.6410	2.1404	2.5337
3.3	1.4500	1.8000	2.1708	8.2	1.6436	2.1438	2.5374
3.4	1.4763	1.8256	2.2058	8.3	1.6463	2.1471	2.5410
3.5	1.5003	1.8513	2.2250	8.4	1.6489	2.1505	2.5447
3.6	1.5036	1.8769	2.2442	8.5	1.6516	2.1539	2.5484
3.7	1.5068	1.9009	2.2635	8.6	1.6543	2.1572	2.5520
3.8	1.5101	1.9100	2.2827	8.7	1.6569	2.1606	2.5557
3.9	1.5134	1.9191	2.3007	8.8	1.6596	2.1640	2.5593
4.0	1.5166	1.9282	2.3080	8.9	1.6622	2.1673	2.5630
4.1	1.5199	1.9373	2.3152	9.0	1.6649	2.1707	2.5667
4.2	1.5231	1.9464	2.3225	9.1	1.6676	2.1741	2.5703
4.3	1.5264	1.9555	2.3297	9.2	1.6702	2.1774	2.5740
4.4	1.5296	1.9645	2.3370	9.3	1.6729	2.1808	2.5777
4.5	1.5329	1.9736	2.3442	9.4	1.6755	2.1842	2.5813
4.6	1.5362	1.9827	2.3515	9.5	1.6782	2.1875	2.5850
4.7	1.5394	1.9918	2.3587	9.6	1.6809	2.1909	2.5886
4.8	1.5427	2.0005	2.3659	9.7	1.6835	2.1943	2.5923
4.9	1.5459	2.0052	2.3732	9.8	1.6862	2.1976	2.5960
5.0	1.5492	2.0100	2.3804	9.9	1.6888	2.2041	2.5996
5.1	1.5524	2.0147	2.3877	10.0	1.6915	2.2176	2.6132
5.2	1.5557	2.0194	2.3949	10.1	1.6942	2.2311	2.6280
5.3	1.5590	2.0242	2.4016	10.2	1.6968	2.2446	2.6427
5.4	1.5622	2.0289	2.4068	10.3	1.6995	2.2581	2.6574
5.5	1.5655	2.0337	2.4120	10.4	1.7160	2.2716	2.6721
5.6	1.5687	2.0384	2.4173	10.5	1.7360	2.2851	2.6868
5.7	1.5720	2.0431	2.4225	10.6	1.7560	2.2987	2.7033
5.8	1.5752	2.0479	2.4278	10.7	1.7760	2.3282	2.7355
5.9	1.5785	2.0526	2.4330	10.8	1.7960	2.3594	2.7678
6.0	1.5818	2.0573	2.4382	10.9	1.8334	2.3907	2.8000
6.1	1.5850	2.0621	2.4435	11.0	1.8750	2.4369	2.8500
6.2	1.5883	2.0668	2.4487	11.1	1.9251	2.4895	2.9001
6.3	1.5915	2.0716	2.4539	11.2	1.9876	2.5534	2.9667
6.4	1.5948	2.0763	2.4592	11.3	2.0667	2.6274	3.0455
6.5	1.5980	2.0810	2.4644	11.4	2.1668	2.7223	3.1445
6.6	1.6011	2.0858	2.4696	11.5	2.3001	2.8376	3.2626
6.7	1.6037	2.0905	2.4749	11.6	2.4602	2.9835	3.4168
6.8	1.6064	2.0953	2.4801	11.7	2.6602	3.1602	3.6002
6.9	1.6090	2.1000	2.4853	11.8	2.9003	3.4002	3.8502
7.0	1.6117	2.1034	2.4906	11.9	3.2337	3.7003	4.1337
7.1	1.6144	2.1067	2.4958	-	-	-	-

B is the pH-meter reading.

V1, **V2** and **V3** are the volumes of alkali employed to bring the solutions of acid, acid+ ligand and acid+ligand+metal ion respectively to the same pH value

4.3.1-Metal-ligand stability constant: (Ti-oxalacetate)

4.3.1.1-Pointwise calculation method:

Metal titration curve showed a displacement with respect to the ligand titration curve along the volume axis at pH 2.3 indicates the affinity of ligand with metal ions which release a proton and produced the volume difference (V_3-V_2), which utilized for calculation of the values of n^- and pL, in turn to evaluate the metal-ligand stability constants. The variation of n^- from 1.2653 to 2.0556 indicates the formation of 1:2 chelate only since the ligand is dibasic acid. The value of $\log K_2$ was taken as an average for values facing n^- extended from 1.2653 to 1.7987. The value found, K_2=8.6384, table (4.3.3). This value was further verified by half integral method.

What should be mentioned is that, during experimental work, a precipitation occurred at low values of pH, and then disappear at high values of pH.

Titanium-oxalacetic acid form one chelate ML_2, if it compared with titanium-oxalic acid which formed chelate ML_2 and ML_3, one can say this may refer to the longer chain of oxalacetic acid relative to oxalic acid chain, that may leave no room for complex ML_3 (titanium-oxalacetic acid) to be formed. To verify this, x-ray diffraction needed, and also thermal gravimetric analysis can throw a light.

Table (4.3.3) Point-wise calculation method average value of$\log K_2$=8.6384

Log K_2	$\log\frac{(n^- -1)}{(2-n^-)}$	pL	n^-	V3	V2
10.7178	-0.4423	11.1601	1.2653	1.7445	1.3714
10.3010	-0.2807	10.5817	1.3438	2.0824	1.7091
9.9186	-0.1655	10.0841	1.4059	2.2250	1.8513
9.7384	0.0713	9.6671	1.5409	2.3007	1.9191
9.3533	0.1047	9.2486	1.5600	2.3297	1.9555
8.9859	0.1410	8.8449	1.5805	2.3587	1.9918
8.6868	0.2306	8.4562	1.6297	2.3877	2.0147
8.3682	0.3017	8.0666	1.6670	2.4120	2.0337
8.0227	0.3489	7.6738	1.6907	2.4330	2.0526
7.6792	0.3977	7.2815	1.7142	2.4539	2.0716
7.5099	0.4243	7.0856	1.7265	2.4644	2.0810
7.1868	0.4910	6.6958	1.7559	2.4853	2.1000
6.8803	0.5725	6.3077	1.7889	2.5044	2.1135
6.5203	0.6073	5.9130	1.8019	2.5190	2.1269
6.1633	0.6441	5.5192	1.8150	2.5337	2.1404
5.8118	0.6842	5.1276	1.8286	2.5484	2.1539
5.4673	0.7264	4.7409	1.8419	2.5630	2.1673
5.1384	0.7719	4.3664	1.8554	2.5777	2.1808
4.8398	0.8209	4.0189	1.8688	2.5923	2.1943
4.6870	0.8261	3.8609	1.8701	2.5996	2.2041
4.9651	1.2167	3.7484	1.9428	2.6280	2.2311

4.3.1.2-Half integral method: (titanium oxalacetate)

Metal-ligand formation curve was plotted n^- versus pL. log K_2, found to be 9.76 figure (4.3.2). This value was further corroborated by linear plot method. The lengthy of n^- let logK_2 more prone to error. (Gurdeep, 1986)

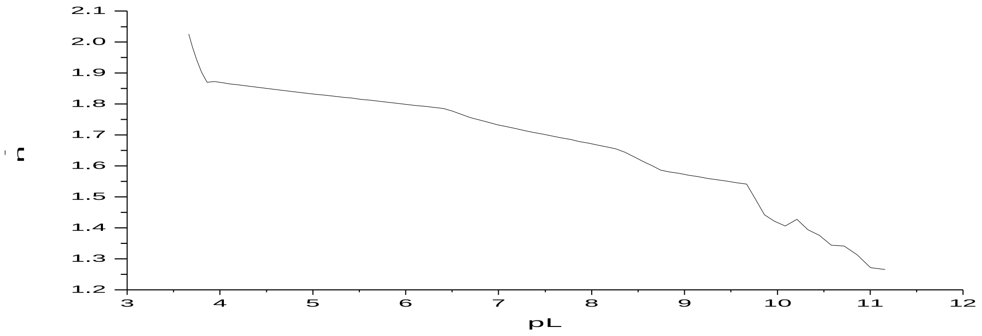


Figure (4.3.2) half integral method logK_2 = 9.76

4.3.1.3-Linear plot method: (titanium oxalacetate)

By plotting pL against log (n-1)/(2-n), the resulting curve at point where pL equal 1.5 should be the value of log K_2. Hence logK_2 =9.821, figure (4.3.3). Thinking may leads to, that, two molecules of this bidentate ligand attached to metal ion as monodentate. The value was further verified by equation familiar as Henderson's or Hasselbalch's equation.

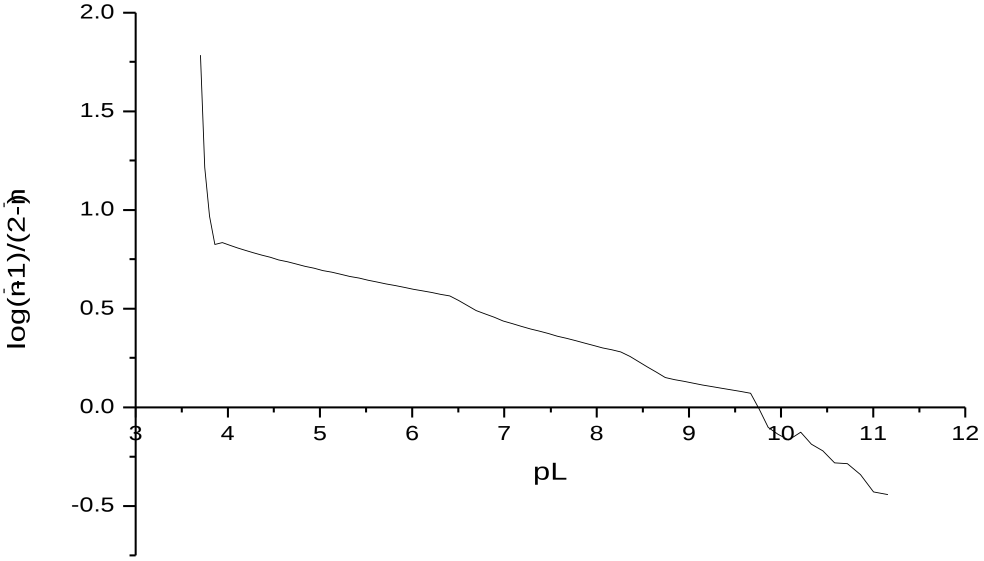


Figure (4.3.3) linear plot method logK_2 =9.821

4.3.1.4-Henderson's or Hasselbalch's equation:(titanium oxalacetate)

Because only one chelate is formed, Henderson's or Hasselbalch's equation can be employed. The lengthy of n^- makes the values of stability constants calculated by these methods more difficult and more prone to error.

$$\log\left(\frac{n^- -1}{(2-n^-)}\right)=\log\beta_1+\log[L].$$

Table (4.3.4) Henderson's or Hasselbalch's equation $\log K_2=7.5696$

pL	n^-	[L]	$\log\frac{(n^- -1)}{(2-n^-)}$	Log[L]	$\log K_2$
11.1601	1.2653	6.92E-12	-0.4423	-11.1601	10.7178
10.8617	1.3132	1.38E-11	-0.3409	-10.8617	10.5207
10.5817	1.3438	2.62E-11	-0.2807	-10.5817	10.3010
10.3286	1.3937	4.69E-11	-0.1875	-10.3286	10.1411
10.0841	1.4059	8.24E-11	-0.1655	-10.0841	9.9186
9.86084	1.4418	1.38E-10	-0.1016	-9.86084	9.7593
9.66712	1.5409	2.15E-10	0.0713	-9.66712	9.7384
9.45522	1.5503	3.51E-10	0.0877	-9.45522	9.5429
9.24861	1.5600	5.64E-10	0.1046	-9.24861	9.3533
9.04559	1.5701	9.00E-10	0.1226	-9.04559	9.1682
8.84485	1.5805	1.43E-09	0.1410	-8.84485	8.9859
8.64871	1.6010	2.25E-09	0.1778	-8.64871	8.8265
8.45618	1.6297	3.50E-09	0.2306	-8.45618	8.6868
8.26357	1.6558	5.45E-09	0.2800	-8.26357	8.5436
8.06659	1.6670	8.58E-09	0.3017	-8.06659	8.3682
7.87011	1.6789	1.35E-08	0.3251	-7.87011	8.1952
7.67379	1.6907	2.12E-08	0.3489	-7.67379	8.0227
7.47763	1.7026	3.33E-08	0.3734	-7.47763	7.8510
7.28145	1.7142	5.23E-08	0.3977	-7.28145	7.6791
7.08561	1.7265	8.21E-08	0.4242	-7.08561	7.5099
6.89054	1.7408	1.29E-07	0.4561	-6.89054	7.34674
6.69584	1.7559	2.01E-07	0.4910	-6.69584	7.1868
6.50323	1.7767	3.14E-07	0.5413	-6.50323	7.0446
6.30773	1.7889	4.92E-07	0.5725	-6.30773	6.8803
6.11028	1.7954	7.76E-07	0.5897	-6.11028	6.7000

Table (4.3.5) Stability constants of Ti-oxalacetate obtained by four methods.

Method	$\log K_2$
Point-wise calculation method	8.6384
Half integral method	9.76
Linear plot method	9.821
Henderson's equation	8.6384

4.4/Titanium-propanoic acid system:

Table (4.4.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ions (Ti^{+3}). $N^0 = 0.522M$, $E^0 = 5\times10^{-3}$ M , $T_{Cl} = 1.5\times10^{-3}$, M , $T_{cm} = 5\times10^{-4}$ M , $V^0 = 200 cm^3$, $u^0 = 5\times10^{-3}$ $t = 22.5^0 C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.33	2.34	2.29	3.1	11.92	11.74	11.59
0.1	2.34	2.34	2.30	3.2	11.95	11.77	11.65
0.2	2.36	2.37	2.31	3.3	11.97	11.81	11.71
0.3	2.39	2.39	2.33	3.4	11.99	11.85	11.76
0.4	2.42	2.42	2.36	3.5	12.02	11.88	11.80
0.5	2.45	2.45	2.39	3.6	12.04	11.91	11.84
0.6	2.49	2.49	2.42	3.7	12.06	11.94	11.88
0.7	2.53	2.54	2.45	3.8	12.08	11.97	11.91
0.8	2.58	2.59	2.48	3.9	12.10	11.99	11.94
0.9	2.64	2.64	2.52	4.0	12.12	12.01	11.97
1.0	2.71	2.71	2.57	4.1	12.13	12.04	11.99
1.1	2.80	2.80	2.62	4.2	12.15	12.06	12.02
1.2	2.92	2.90	2.69	4.3	12.17	12.08	12.04
1.3	3.08	3.04	2.76	4.4	12.18	12.10	12.06
1.4	3.35	3.24	2.85	4.5	12.20	12.11	12.08
1.5	4.24	3.56	2.96	4.6	12.21	12.13	12.10
1.6	9.93	4.07	3.12	4.7	12.22	12.15	12.12
1.7	10.70	4.49	3.36	4.8	12.24	12.16	12.14
1.8	11.02	4.84	3.74	4.9	12.25	12.18	12.15
1.9	11.21	5.19	4.25	5.0	12.26	12.20	12.17
2.0	11.34	5.71	4.65	5.1	12.27	12.21	12.18
2.1	11.44	7.50	4.98	5.2	12.29	12.22	12.20
2.2	11.52	10.42	5.41	5.3	12.30	12.24	12.21
2.3	11.59	10.87	6.12	5.4	12.31	12.25	12.23
2.4	11.65	11.12	9.23	5.5	12.32	12.26	12.24
2.5	11.70	11.28	10.47	5.6	12.33	12.27	12.25
2.6	11.74	11.39	10.88	5.7	12.34	12.28	12.27
2.7	11.78	11.49	11.13	5.8	12.35	12.29	12.28
2.8	11.82	11.57	11.28	5.9	12.36	12.30	12.29
2.9	11.85	11.63	11.41	6.0	12.37	12.32	12.30
3.0	11.89	11.68	11.52	-	-	-	-

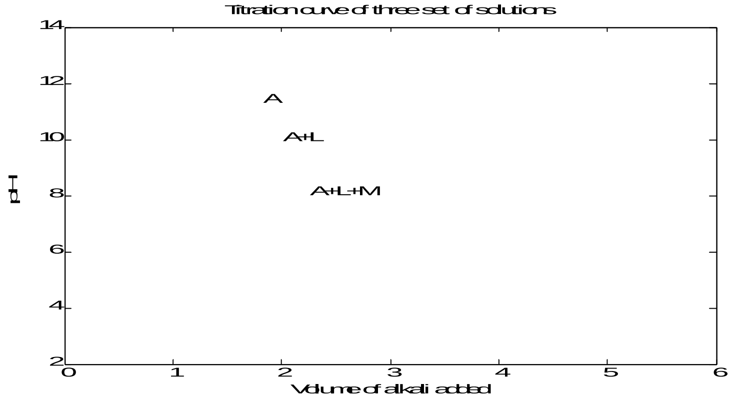


Figure (4.4.1) Titration curves of three sets of solutions versus pH

Table (4.4.2) alkali volume needed to bring the three sets solutions to the same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.3250	0.3333	0.5333	7.2	1.5520	2.0832	2.3347
2.5	0.625	0.6200	0.8500	7.3	1.5538	2.0888	2.3379
2.6	0.8333	0.8200	1.0600	7.4	1.5555	2.0944	2.3412
2.7	0.9857	0.9827	1.2143	7.5	1.5573	2.1000	2.3444
2.8	1.1000	1.1000	1.3445	7.6	1.5591	2.1034	2.3476
2.9	1.1833	1.2000	1.4455	7.7	1.5608	2.1069	2.3508
3.0	1.2500	1.2714	1.5250	7.8	1.5626	2.1103	2.3540
3.1	1.3074	1.3300	1.5875	7.9	1.5643	2.1137	3.3572
3.2	1.3444	1.3800	1.6333	8.0	1.5661	2.1171	2.3605
3.3	1.3815	1.4188	1.6750	8.1	1.5678	2.1206	2.3637
3.4	1.4056	1.4500	1.7105	8.2	1.5696	2.1240	2.3669
3.5	1.4169	1.4813	1.7368	8.3	1.5714	2.1274	2.3701
3.6	1.4281	1.5078	1.7632	8.4	1.5731	2.1308	2.3733
3.7	1.4393	1.5275	1.7895	8.5	1.5749	2.1342	2.3765
3.8	1.4506	1.5471	1.8118	8.6	1.5766	2.1377	2.3797
3.9	1.4618	1.5567	1.8314	8.7	1.5784	2.1411	2.3830
4.0	1.4730	1.5863	1.8510	8.8	1.5801	2.1445	2.3862
4.1	1.4843	1.6071	1.8706	8.9	1.5919	2.1479	2.3894
4.2	1.4955	1.6310	1.8902	9.0	1.5837	2.1514	2.3926
4.3	1.5011	1.6548	1.9125	9.1	1.5854	2.1548	2.3958
4.4	1.5028	1.6786	1.9375	9.2	1.5872	2.1582	2.3990
4.5	1.5046	1.7029	1.9625	9.3	1.5889	2.1616	2.4057
4.6	1.5063	1.7314	1.9875	9.4	1.5907	2.1651	2.4137
4.7	1.5081	1.7600	2.0152	9.5	1.5924	2.1685	2.4218
4.8	1.5098	1.7886	2.0455	9.6	1.5942	2.1719	2.4298
4.9	1.5116	1.8172	2.0758	9.7	1.5960	2.1753	2.4379
5.0	1.5134	1.8457	2.1047	9.8	1.5977	2.1788	2.4460
5.1	1.5151	1.8743	2.1279	9.9	1.5995	2.1822	2.4540
5.2	1.5169	1.9019	2.1512	10.0	1.6091	2.1856	2.4621
5.3	1.5186	1.9212	2.1744	10.1	1.6351	2.1925	2.4702
5.4	1.5204	1.9404	2.1977	10.2	1.6351	2.1925	2.4782
5.5	1.5221	1.9596	2.2127	10.3	1.6481	2.1959	2.4863
5.6	1.5239	1.9789	2.2268	10.4	1.6610	2.1993	2.4944
5.7	1.5257	1.9981	2.2409	10.5	1.6740	2.2178	2.5073
5.8	1.5274	2.0050	2.2549	10.6	1.6870	2.2400	2.5317
5.9	1.5292	2.0106	2.2690	10.7	1.7000	2.2622	2.5561
6.0	1.5309	2.0162	2.2831	10.8	1.7313	2.2845	2.5805
6.1	1.5327	2.0218	2.2972	10.9	1.7625	2.3120	2.6080
6.2	1.5344	2.0274	2.3026	11.0	1.7938	2.3520	2.6480
6.3	1.5362	2.0330	2.3058	11.1	1.8422	2.3920	2.6880
6.4	1.5380	2.0385	2.3090	11.2	1.8948	2.4501	2.7467
6.5	1.5397	2.0441	2.3122	11.3	1.9693	2.5183	2.8155
6.6	1.5415	2.0497	2.3154	11.4	2.0601	2.6101	2.8924
6.7	1.5432	2.0553	2.3187	11.5	2.1751	2.7126	2.9819
6.8	1.5450	2.0609	2.3219	11.6	2.3168	2.8502	3.1165
6.9	1.5467	2.0665	2.3251	11.7	2.5002	3.0402	3.2835
7.0	1.5485	2.0721	2.3283	11.8	2.7502	3.2752	3.5002
7.1	1.5503	2.0777	2.3315	11.9	3.0337	3.5670	3.7670

B is the pH-meter reading.

V1, V2 and V3 are the volumes of alkali employed to bring the solutions of acid , acid+ ligand and acid+ligand+metal ion respectively to the same pH value.

4.4.1-Metal-ligand stability constants: (titanium propanoate)

4.4.1.1-pointwise calculation method:

For calculation of stability constants by this method, n^{-} and pL were calculated at every pH, by the aid of excel program. Complex titration curve pass over the ligand titration curve at pH 2.4, table (4.4.2), and figure (4.4.1), indicating the formation of the complex. The values of n^{-} extends from 1.0835 to 2.8135 indicates the formation ML_2 and ML_3 complex species characterized in table (4.4.3) and table (4.4.4) respectively. The values were found. $\log K_2$=4.7564, and log K_3=4.1015.

Table (4.4.3) point-wise method LogK_2 average value =4.7567

V2	V3	n^{-}	pL	$\log\frac{(n^{-}-1)}{(2-n^{-})}$	logK_2
0.6200	0.8500	1.1875	5.2731	-0.6369	4.6362
0.8200	1.0600	1.2030	5.1779	-0.5938	4.5841
0.9827	1.2143	1.2019	5.0788	-0.5968	4.4820
1.1000	1.3445	1.2815	4.9998	-0.4070	4.5928
1.2000	1.4455	1.3645	4.9228	-0.2415	4.6814
1.2714	1.5250	1.4331	4.8433	-0.1170	4.7263
1.3300	1.5875	1.4610	4.7533	-0.0679	4.6854
1.3800	1.6333	1.5071	4.6692	0.0124	4.6816
1.4188	1.6750	1.5338	4.5803	0.0587	4.6391
1.4500	1.7105	1.6014	4.5050	0.1786	4.6836
1.4813	1.7368	1.6963	4.4406	0.3603	4.8008
1.5078	1.7632	1.8021	4.3837	0.6077	4.9913

Table (4.4.4) point-wise method LogK_3 average value =4.1015

V2	V3	n^{-}	pL	$\log\frac{(n^{-}-2)}{(3-n^{-})}$	logK_3
1.5567	1.8314	2.0627	4.2195	-1.1746	3.0449
1.5863	1.8510	2.1494	4.1760	-0.7554	3.4206
1.6071	1.8706	2.2306	4.2196	-0.5234	3.6962
1.6310	1.8902	2.3229	4.1926	-0.3216	3.8710
1.6548	1.9125	2.5137	4.2574	0.0238	4.2812
1.6786	1.9375	2.8135	4.5987	0.6396	5.2383

4.4.1.2-Half integral method: (titanium propanoate)

The stability constants obtained by construction of complex formation curve, figure (4.4.2). The values of pL at which n^{-} =1.5 and n^{-} = 2.5 corresponds to logK_2 and logK_3 respectively. Values were found, logK_2=4.655 and logK_3= 4.251These values were further verified by linear plot method.

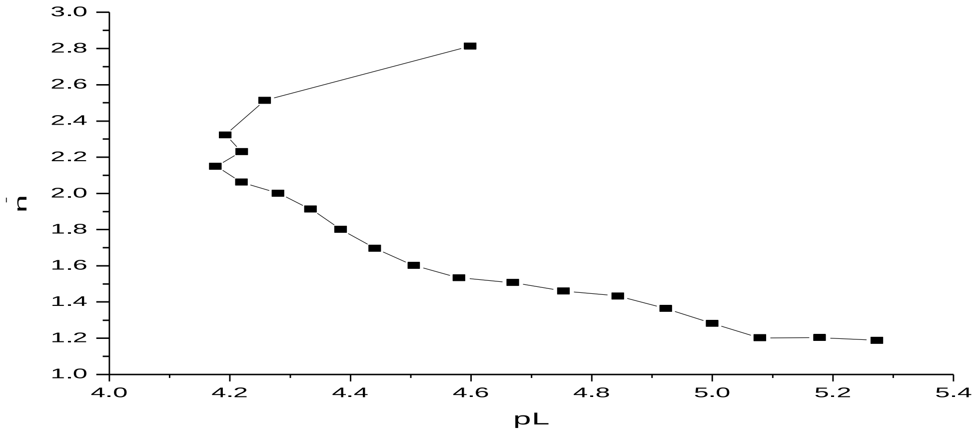


Fig. (4.4.2) Half integral method $\log K_2 = 4.655$ & $\log K_3 = 4.251$

4.4.1.3-Linear plot method: (titanium propanoate)

$\log(\bar{n}-1)/(2-\bar{n})$ and $\log(\bar{n}-2)/(3-\bar{n})$ were plotting against the corresponding pL for determination of $\log K_2$ and $\log K_3$ respectively. $\log K_2 = 4.655$and $\log K_3 = 4.25$. Figures (4.4.3), and (4.4.4).These values were further verified by least squares method.

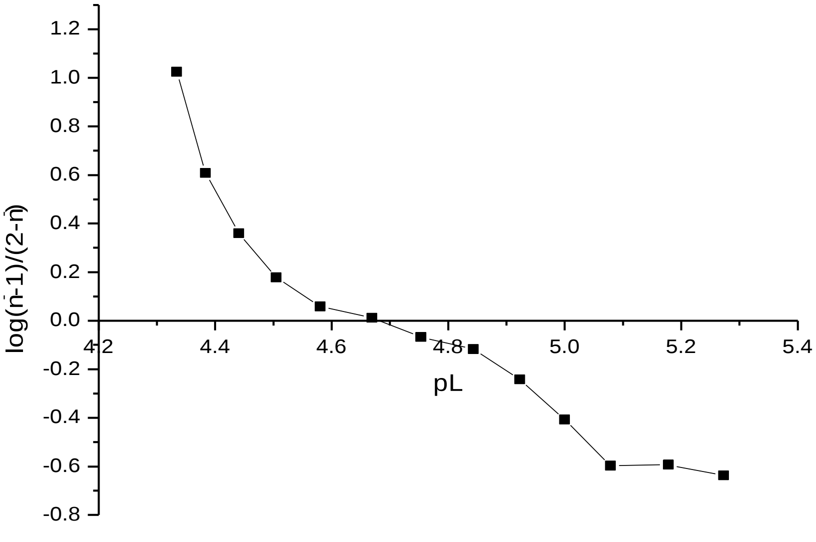


Fig. (4.4.3)Linear plot method $\log K_2 = 4.655$

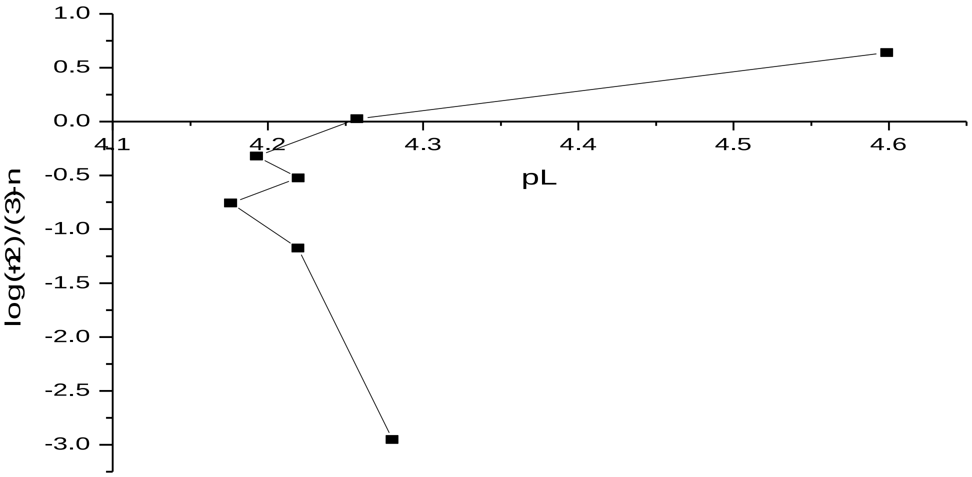


Fig.(4.4.4) . Linear plot method $\log K_3 = 4.25$

4.4.1.4-Least squares method : (titanium propanoate)

Since there are 1:2 and 1:3 complex species the following expression should be used:

$$\left(\frac{n^- -1}{2-n^-}\right)[L]^- = +\left(\frac{3-n^-}{2-n^-}\right)[L]\ K_2K_3 + K_3 -----(4.4.1)$$

The resulting equation is a linear (y=mx+b) y-intercept gives K_3 and the slope K_2K_3.on division by K_2K_3 gives x-intercept $-1/K_2$ and slope $1/K_2K_3$, which is useful check on the consistency of the data. Equation (4.4.1) becomes:

$$\left(\frac{3-n^-}{2-n^-}\right)[L] = \left(\frac{n^- -1}{2-n^-}\right)[L]^- \frac{1}{K_2K_3} - \frac{1}{K_2} -----(4.4.2)$$

Table (4.4.5) $\log K_2$ & $\log K_3$ by least squares method

pL	n^-	[L]	$\frac{(3-n^-)L]}{(2-n^-)}$	$\frac{(n^- -1)}{(2-n^-)[L]}$
5.2731	1.1875	5.3E-06	1.2E-05	43273.7427
5.1779	1.2030	6.6E-06	1.5E-05	38379.4056
5.0788	1.2019	8.3E-06	1.9E-05	30339.0368
4.9998	1.2815	1.0E-05	2.4E-05	39155.6176
4.9228	1.3645	1.2E-05	3.1E-05	48014.1694
4.8433	1.4331	1.4E-05	4.0E-05	53250.2639
4.7533	1.4610	1.8E-05	5.0E-05	48467.1681
4.6692	1.5071	2.1E-05	6.5E-05	48040.9190
4.5803	1.5338	2.6E-05	8.3E-05	43560.2481
4.5050	1.6014	3.1E-05	0.0001	48261.3917
4.4406	1.6963	3.6E-05	0.0002	63217.6627
4.3837	1.8021	4.1E-05	0.0003	98024.2553
4.3340	1.9137	4.6E-05	0.0006	228575.0338
4.2800	2.0011	5.2E-05	-0.0469	-17084838.08

4.2195	2.0627	6.0E-05	-0.0009	-280901.229
4.1760	2.1494	6.7E-05	-0.0004	-115394.9119
4.2196	2.2306	6.0E-05	-0.0002	-88498.5412
4.1926	2.3229	6.4E-05	-0.0001	-63837.9119
4.2574	2.5137	5.5E-05	-5.2E-05	-53301.5501
4.598715796	2.813477727	2.5E-05	-5.8E-06	-88487.5877
5.27307629	1.18748957	5.3E-06	1.2E-05	43273.7427

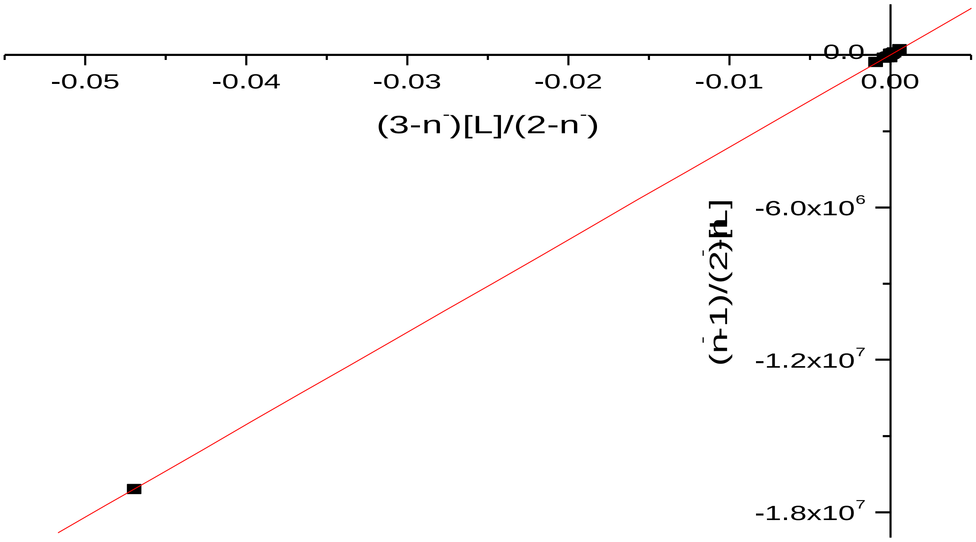


Fig. (4.4.5)Determination of logK$_2$= 4.5257 and logK$_3$ = 4.0763 (y-intercept)

```
                         Linear Regression
  Parameter        Value                Error            R2
                 -----------------------------------------------------------
 Intercept        11922.4635        7295.98938     0.99997
 Slope            3.64165E8         694782.83118       -
                 -----------------------------------------------------------
```

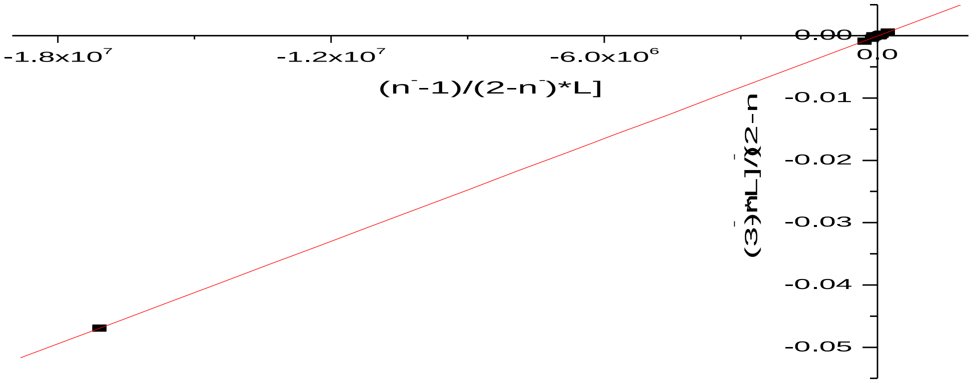


Fig.(4.4.6) Determination of logK$_2$ =4.5229& logK$_3$ = 4.0364(x-intercept)

```
                    Linear Regression

Parameter      Value           Error           R^2
           ------------------------------------------------------------
 Intercept    -0.00003       0.00002       0.99997
 Slope         2.74583E-9    5.2387E-12
           ------------------------------------------------------------
```

Table (4.4.6) Stability constants of Ti-propanoate obtained by four methods

Method	$\log K_2$	$\log K_3$	$\log K_2+\log K_3$
Pointwise method	4.7567	4.1015	8.8582
Half integral method	4.655	4.251	8.9060
Linear plot method	4.655	4.25	8.9050
Least squares method (y-intercept)	4.5257	4.0763	8.6020
Least squares method (x-intercept)	4.5229	4.0384	8.5613

4.5/ Titanium-citric acid system

Table (4.5.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ions (Ti^{+3}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}M$, $T_{Cl} = 5\times10^{-5}M$, $T_{cm} = 1.25\times10^{-5}M$, $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$, $t = 3.65^0 C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.38	2.39	2.31	2.7	11.88	6.14	4.87
0.1	2.40	2.40	2.31	2.8	11.91	6.50	5.18
0.2	2.42	2.42	2.33	2.9	11.94	6.95	5.53
0.3	2.44	2.44	2.34	3.0	11.97	9.26	5.84
0.4	2.47	2.46	2.35	3.1	12.00	10.39	6.13
0.5	2.50	2.48	2.37	3.2	12.02	10.85	6.45
0.6	2.53	2.51	2.39	3.3	12.05	11.14	6.83
0.7	2.57	2.54	2.42	3.4	12.07	11.32	7.67
0.8	2.62	2.58	2.44	3.5	12.09	11.46	9.95
0.9	2.68	2.62	2.47	3.6	12.11	11.56	10.58
1.0	2.75	2.66	2.50	3.7	12.13	11.64	10.94
1.1	2.84	2.72	2.53	3.8	12.15	11.70	11.18
1.2	2.95	2.78	2.57	3.9	12.17	11.76	11.34
1.3	3.13	2.85	2.62	4.0	12.18	11.81	11.47
1.4	3.45	2.93	2.67	4.1	12.20	11.85	1.57
1.5	5.50	3.03	2.72	4.2	12.22	11.89	11.64
1.6	10.40	3.15	2.78	4.3	12.23	11.93	11.71
1.7	10.82	3.29	2.86	4.4	12.24	11.96	11.77
1.8	11.13	3.47	2.94	4.5	12.26	11.99	11.82
1.9	11.31	3.70	3.04	4.6	12.27	12.02	11.87
2.0	11.45	3.97	3.15	4.7	12.28	12.05	11.91
2.1	11.54	4.26	3.29	4.8	12.29	12.07	11.95
2.2	11.62	4.55	3.48	4.9	12.31	12.10	11.98
2.3	11.69	4.83	3.73	5.0	12.32	12.12	12.01
2.4	11.74	5.18	4.00	5.1	12.33	12.14	12.03
2.5	11.79	5.50	4.29	5.2	12.34	12.16	12.06
2.6	11.84	5.82	4.58	5.3	12.35	12.18	12.09

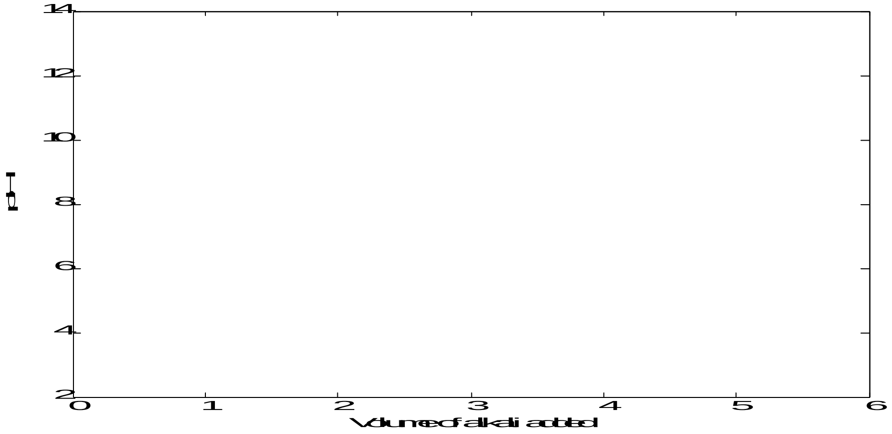


Fig. (4.5.1) Plotting of three sets of solutions versus pH

Table (4.5.2) Alkali volume used for bringing three sets of solutions to the same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.1000	0.1000	0.6333	7.2	1.5366	2.9108	3.3441
2.5	0.5000	0.5667	1.0000	7.3	1.5388	2.9152	3.3560
2.6	0.7600	0.8500	1.2600	7.4	1.5409	2.9195	3.3679
2.7	0.9286	1.0667	1.4600	7.5	1.5431	2.9238	3.3798
2.8	1.0556	1.2286	1.6250	7.6	1.5453	2.9281	3.3917
2.9	1.1546	1.3625	1.7500	7.7	1.5474	2.9325	3.4013
3.0	1.2278	1.4700	1.8600	7.8	1.5496	2.9368	3.4057
3.1	1.2833	1.5583	1.9546	7.9	1.5517	2.9411	3.4101
3.2	1.3219	1.6357	2.0357	8.0	1.5539	2.9455	3.4145
3.3	1.3531	1.7056	2.1053	8.1	1.556	2.9498	3.4189
3.4	1.3844	1.7611	2.1579	8.2	1.5582	2.9541	3.4232
3.5	1.4024	1.8130	2.2080	8.3	1.5603	2.9584	3.4276
3.6	1.4073	1.8565	2.2480	8.4	1.5625	2.9628	3.4320
3.7	1.4122	1.9000	2.2880	8.5	1.5647	2.9671	3.4364
3.8	1.4171	1.9370	2.3259	8.6	1.5668	2.9714	3.4408
3.9	1.4220	1.9741	2.3630	8.7	1.5690	2.9758	3.4452
4.0	1.4268	2.0104	2.4000	8.8	1.5711	2.9801	3.4496
4.1	1.4317	2.0448	2.4345	8.9	1.5733	2.9844	3.4540
4.2	1.4366	2.0793	2.4690	9.0	1.5754	2.9887	3.4583
4.3	1.4415	2.1138	2.5035	9.1	1.5776	2.9931	3.4627
4.4	1.4463	2.1483	2.5379	9.2	1.5797	2.9974	3.4671
4.5	1.4512	2.1828	2.5724	9.3	1.5819	3.0035	3.4715
4.6	1.4561	2.2179	2.6069	9.4	1.5841	3.0124	3.4759
4.7	1.4610	2.2536	2.6414	9.5	1.5862	3.0212	3.4803
4.8	1.4659	2.2893	2.6759	9.6	1.5884	3.0301	3.4847
4.9	1.4707	2.3200	2.7097	9.7	1.5905	3.0389	3.4890
5.0	1.4756	2.3486	2.7410	9.8	1.5927	3.0478	3.4934
5.1	1.4805	2.3772	2.7742	9.9	1.5948	3.0566	3.4978
5.2	1.4854	2.4063	2.8057	10.0	1.5970	3.0655	3.5079
5.3	1.4902	2.4375	2.8343	10.1	1.5991	3.0743	3.5238
5.4	1.4951	2.4688	2.8629	10.2	1.6088	3.0832	3.5397
5.5	1.5000	2.5000	2.8914	10.3	1.6235	3.0920	3.5556
5.6	1.5022	2.5313	2.9226	10.4	1.6382	3.1022	3.5714
5.7	1.5043	2.5625	2.9549	10.5	1.6530	3.1239	3.5873
5.8	1.5065	2.5938	2.9871	10.6	1.6677	3.1457	3.6056
5.9	1.5086	2.6250	3.0207	10.7	1.6824	3.1674	3.6334
6.0	1.5108	2.6563	3.0552	10.8	1.6971	3.1891	3.6611
6.1	1.5129	2.6875	3.0897	10.9	1.7258	3.2173	3.6889
6.2	1.5151	2.7167	3.1219	11.0	1.7581	3.2518	3.7250
6.3	1.5172	2.7445	3.1531	11.1	1.7904	3.2862	3.7667
6.4	1.5194	2.7722	3.1844	11.2	1.8389	3.3334	3.8126
6.5	1.5216	2.8000	3.2132	11.3	1.8945	3.3889	3.8751
6.6	1.5237	2.8222	3.2395	11.4	1.9644	3.4572	3.9462
6.7	1.5259	2.8445	3.2658	11.5	2.0557	3.5401	4.0301
6.8	1.528	2.8667	3.2621	11.6	2.1751	3.6501	4.1430
6.9	1.5302	2.8889	3.3083	11.7	2.3202	3.8002	4.2859
7.0	1.5323	2.9022	3.3202	11.8	2.5202	3.9802	4.4602
7.1	1.5345	2.9065	3.3321	11.9	2.7670	4.2252	4.6752

Table (4.5.3). Calculation of proton attached to lignd and ligand attached to metal.

B	V1	V2	V2	n_A	n^-	pL
2.4	0.1000	0.1000	0.6333	3.0000	0.3121	2.8730
2.5	0.5000	0.5667	1.0000	2.8833	0.2739	11.4386
2.6	0.7600	0.8500	1.2600	2.8426	0.2663	11.1369
2.7	0.9286	1.0667	1.4600	2.7587	0.2709	10.8381
2.8	1.0556	1.2286	1.6250	2.6978	0.2853	10.5407
2.9	1.1546	1.3625	1.7500	2.6370	0.2917	10.2420
3.0	1.2278	1.4700	1.8600	2.5772	0.3072	9.9447
3.1	1.2833	1.5583	1.9546	2.5201	0.3263	9.6481
3.2	1.3219	1.6357	2.0357	2.4525	0.3476	9.3517
3.3	1.3531	1.7056	2.1053	2.3850	0.3672	9.0551
3.4	1.3844	1.7611	2.1579	2.3429	0.3776	8.7569
3.5	1.4024	1.8130	2.2080	2.2838	0.3955	8.4510
3.6	1.4073	1.8565	2.2480	2.2164	0.4161	8.1635
3.7	1.4122	1.9000	2.2880	2.1491	0.4385	7.8674
3.8	1.4171	1.9370	2.3259	2.0932	0.4633	7.5717
3.9	1.4220	1.9741	2.3630	2.0370	0.4891	7.2762
4.0	1.4268	2.0104	2.4000	1.9821	0.5174	6.9813
4.1	1.4317	2.0448	2.4345	1.9307	0.5454	6.6863
4.2	1.4366	2.0793	2.4690	1.8791	0.5757	6.3917
4.3	1.4415	2.1138	2.5035	1.8275	0.6085	6.0980
4.4	1.4463	2.1483	2.5379	1.7757	0.6442	5.8049
4.5	1.4512	2.1828	2.5724	1.7241	0.6833	5.5129
4.6	1.4561	2.2179	2.6069	1.6715	0.7257	5.2222
4.7	1.4610	2.2536	2.6414	1.6178	0.7722	4.9336
4.8	1.4659	2.2893	2.6759	1.5641	0.8234	4.6484
4.9	1.4707	2.3200	2.7097	1.5190	0.8799	4.3690
5.0	1.4756	2.3486	2.7410	1.4777	0.9360	4.0982
5.1	1.4805	2.3772	2.7742	1.4364	1.0021	3.8453
5.2	1.4854	2.4063	2.8057	1.3943	1.0699	3.6192
5.3	1.4902	2.4375	2.8343	1.3483	1.1365	3.4323
5.4	1.4951	2.4688	2.8629	1.3023	1.2097	3.2965
5.5	1.5000	2.5000	2.8914	1.2564	1.2905	3.2129
5.6	1.5022	2.5313	2.9226	1.2057	1.4008	3.1787
5.7	1.5043	2.5625	2.9549	1.1550	1.5306	3.1710
5.8	1.5065	2.5938	2.9871	1.1043	1.6780	3.2069
5.9	1.5086	2.6250	3.0207	1.0536	1.8544	3.2592
6.0	1.5108	2.6563	3.0552	1.0028	2.0629	3.3414
6.1	1.5129	2.6875	3.0897	0.9521	2.3071	3.4699
6.2	1.5151	2.7167	3.1219	0.9051	2.5718	3.6778
6.3	1.5172	2.7445	3.1531	0.8603	2.8701	4.1950

4.5.1-Metal-ligand stability constants: (titanium citrate)

4.5.1.1-pointwise calculation method:

n^- and pL were calculated at every pH, by the aid of excel program. Complex titration curve pass over the ligand titration curve at pH 2.6, table (4.5.3) and figure (4.5.1), indicating the formation of the complex. The values of n^- extend from 0.26626 to 2.8701 and since the ligand is a tridentate this indicates the formation ML chelate species characterized in table (4.5.4). The value was found, $\log K_1=7.8351$

Table (4.5.4) Point-wise method (Ti-citrate) $\log K_1$ average value =7.8351

V2	V3	n^-	pL	$\log \frac{n^-}{(1-n^-)}$	$\log K_2$
0.8500	1.2600	0.2663	11.1369	-0.4402	10.6967
1.0667	1.4600	0.2709	10.8381	-0.4300	10.4081
1.2286	1.6250	0.2853	10.5407	-0.3989	10.1418
1.3625	1.7500	0.2917	10.2420	-0.3853	9.8570
1.4700	1.8600	0.3072	9.9444	-0.3532	9.5915
1.5583	1.9546	0.3263	9.6481	-0.3148	9.3332
1.6357	2.0357	0.3476	9.3517	-0.2734	9.0783
1.7056	2.1053	0.3672	9.0551	-0.2364	8.8186
1.7611	2.1579	0.3776	8.7569	-0.2170	8.5399
1.8130	2.2080	0.3955	8.4600	-0.1842	8.2758
1.8565	2.2480	0.4161	8.1635	-0.1471	8.0164
1.9000	2.2880	0.4385	7.8674	-0.1073	7.7601
1.9370	2.3259	0.4633	7.5717	-0.0639	7.5078
1.9741	2.3630	0.4891	7.2762	-0.0189	7.2573
2.0104	2.4000	0.5174	6.9813	0.0303	7.0115
2.0448	2.4345	0.5454	6.6863	0.0791	6.7654
2.0793	2.4690	0.5757	6.3919	0.1324	6.5243
2.1138	2.5035	0.6085	6.0980	0.1916	6.2896
2.1483	2.5379	0.6442	5.8049	0.2579	6.0628
2.1828	2.5724	0.6833	5.5129	0.3339	5.8468
2.2179	2.6069	0.7257	5.2222	0.4226	5.6448
2.2536	2.6414	0.7722	4.9336	0.5301	5.4637
2.2893	2.6759	0.8234	4.6484	0.6685	5.3169
2.3200	2.7097	0.8799	4.3690	0.8648	5.2338

4.5.1.2-Half integral method: (titanium citrate)

The stability constants obtained by construction of complex formation figure (4.5.2). The values of pL at which $n^-=0.5$, Value was found, hence $\log K_1=7.26$.This value was further verified by linear plot method.

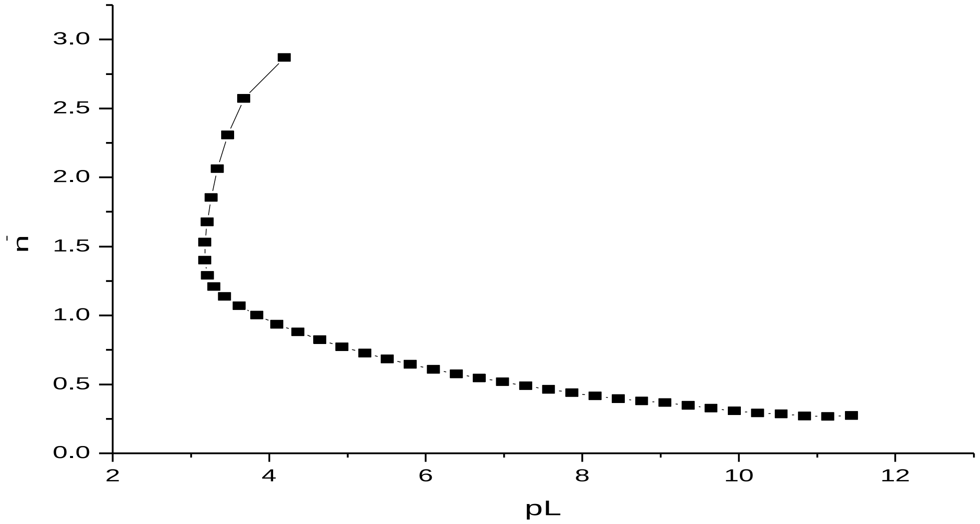


Fig.(4.5.2) Metal-ligand titration curve $\log K_1 = 7.26$

4.5.1.3- Linear plot method: (Ti-citrate)

In this method pL plotted versus log $n^-/(1-n^-)$, where the resulting curve cross pL axis is the value of $\log K_1 = 7.26$. figure (4.5.3).

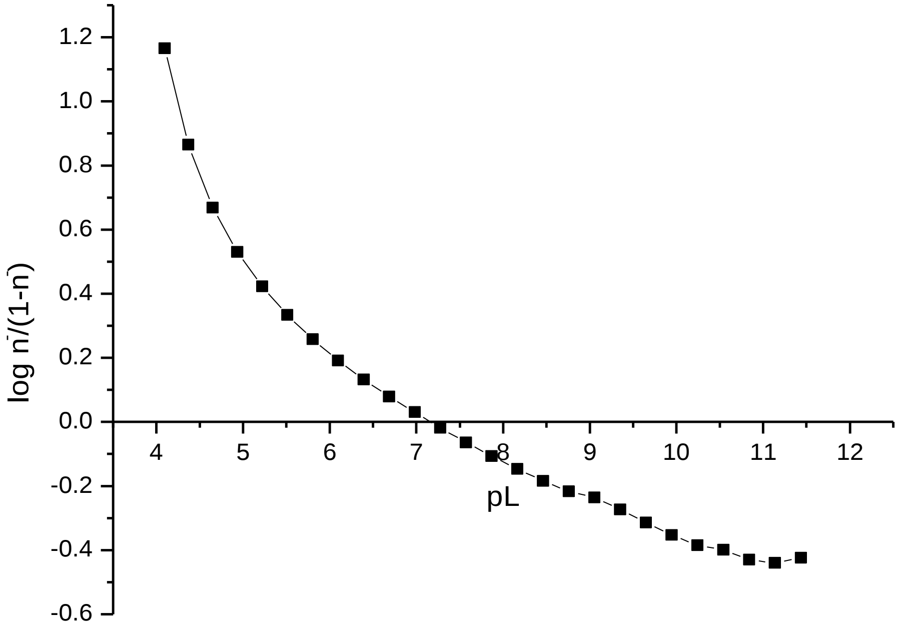


Fig.(4.5.3) Metal-ligand titration curve $\log K_1 = 7.26$

4.5.1.4- Hinderson-Hasselbalch's equation: (Ti-citrate)

Table (4.5.5) Henderson’s equation (Ti-citrate) $\log K_1$ average value 7.6282

pL	[L]	n^{-}	$\log\frac{n^{-}}{(1-n^{-})}$	logL]	$\log K_1$
11.1369	7.3E-12	0.2663	-0.4402	-11.1369	10.6967
10.8381	1.5E-11	0.2709	-0.4300	-10.8381	10.4081
10.5407	2.9E-11	0.2853	-0.3989	-10.5407	10.1418
10.2420	5.7E-11	0.2917	-0.3853	-10.2420	9.8567
9.9447	1.1E-10	0.3072	-0.3532	-9.9447	9.5915
9.6481	2.2E-10	0.3263	-0.3148	-9.6481	9.3332
9.3517	4.4E-10	0.3476	-0.2734	-9.3517	9.0783
9.0551	8.8E-10	0.3672	-0.2364	-9.0551	8.8186
8.7569	1.8E-09	0.3776	-0.2170	-8.7569	8.5399
8.4600	3.5E-09	0.3955	-0.1842	-8.4600	8.2758
8.1635	6.9E-09	0.4161	-0.1471	-8.1635	8.0164
7.8674	1.4E-08	0.4385	-0.1073	-7.8674	7.7601
7.5717	2.7E-08	0.4633	-0.0639	-7.5717	7.5078
7.2762	5.3E-08	0.4891	-0.0189	-7.2762	7.2573
6.9813	1.0E-07	0.5174	0.0303	-6.9813	7.0115
6.6863	2.1E-07	0.5454	0.0791	-6.6863	6.7654
6.3919	4.1E-07	0.5757	0.1325	-6.3919	6.5243
6.0980	8.0E-07	0.6085	0.1916	-6.0980	6.2896
5.8049	1.6E-06	0.6442	0.2579	-5.8050	6.0628
5.5129	3.1E-06	0.6833	0.3339	-5.5129	5.8468
5.2222	6.0E-06	0.7257	0.4226	-5.2222	5.6448
4.9336	1.2E-05	0.7722	0.5301	-4.9336	5.4637
4.6484	2.2E-05	0.8234	0.6685	-4.6484	5.3169
4.3690	4.3E-05	0.8799	0.8648	-4.3690	5.2338
4.0982	8.0E-05	0.9360	1.1654	-4.0982	5.2636

Table (4.5.6) Stability constants of Ti- Citrate obtained by four methods

Method	$\log K_1$
Point-wise method	7.8351
Half integral method	7.26
Linear plot method	7.26
Hinderson’s equation	7.4337

CHAPTER FIVE

Zirconium carboxylate complexes

5.1/ Zirconium-acetic acid system

Table (5.1.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ions (Zr^{+4}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}$ M, $T_{Cl} = 5\times10^{-5}$ M, $T_{cm} = 1.25\times10^{-5}$ M, $V^0 = 200cm^3$. $u^0 = 5\times10^{-3}$, $t = 3.65^0 C$.

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.24	2.26	2.12	4.1	11.97	11.23	4.66
0.1	2.26	2.29	2.13	4.2	11.99	11.32	4.75
0.2	2.28	2.31	2.14	4.3	12.01	11.40	4.86
0.3	2.31	2.33	2.15	4.4	12.02	11.46	4.98
0.4	2.33	2.36	2.16	4.5	12.04	11.52	5.09
0.5	2.36	2.38	2.17	4.6	12.05	11.57	5.21
0.6	2.39	2.42	2.18	4.7	12.07	11.61	5.35
0.7	2.42	2.45	2.20	4.8	12.08	11.65	5.54
0.8	2.46	2.48	2.21	4.9	12.10	11.69	5.78
0.9	2.51	2.52	2.23	5.0	12.11	11.73	6.12
1.0	2.55	2.56	2.25	5.1	12.12	11.76	6.93
1.1	2.60	2.61	2.27	5.2	12.14	11.79	9.24
1.2	2.66	2.65	2.29	5.3	12.15	11.81	10.30
1.3	2.72	2.71	2.31	5.4	12.16	11.84	10.67
1.4	2.79	2.78	2.33	5.5	12.17	11.86	10.89
1.5	2.88	2.85	2.35	5.6	12.18	11.89	11.05
1.6	2.99	2.94	2.37	5.7	12.19	11.91	11.17
1.7	3.14	3.06	2.40	5.8	12.20	11.93	11.27
1.8	3.36	3.21	2.42	5.9	12.21	11.95	11.34
1.9	3.91	3.40	2.45	6.0	12.22	11.97	11.41
2.0	10.01	3.62	2.48	6.1	12.23	11.98	11.47
2.1	10.37	3.83	2.52	6.2	12.24	12.00	11.52
2.2	10.98	4.01	2.55	6.3	12.25	12.02	11.56
2.3	11.15	4.17	2.60	6.4	12.26	12.03	11.61
2.4	11.27	4.31	2.64	6.5	12.27	12.05	11.65
2.5	11.36	4.44	2.69	6.6	12.28	12.06	11.68
2.6	11.45	4.55	2.74	6.7	12.28	12.07	11.72
2.7	11.51	4.66	2.80	6.8	12.29	12.09	11.75
2.8	11.56	4.76	2.88	6.9	12.30	12.10	11.77
2.9	11.61	4.87	2.96	7.0	12.31	12.11	11.79
3.0	11.66	4.98	3.06	7.1	12.32	12.12	11.82
3.1	11.70	5.11	3.19	7.2	12.32	12.14	11.85
3.2	11.74	5.24	3.33	7.3	12.33	12.15	11.87
3.3	11.77	5.40	3.51	7.4	12.34	12.16	11.89
3.4	11.80	5.59	3.70	7.5	12.34	12.17	11.91
3.5	11.83	5.87	3.88	7.6	12.35	12.18	11.92
3.6	11.85	6.42	4.02	7.7	12.36	12.19	11.94
3.7	11.88	10.00	4.17	7.8	12.36	12.20	11.96
3.8	11.90	10.65	4.31	7.9	12.37	12.21	11.98
3.9	11.93	10.93	4.43	8.0	12.38	12.22	11.99
4.0	11.95	11.10	4.54	-	-	-	-

Table (5.1.2). Alkali volume required to bring three sets of solutions to same pH

B	V1	V2	V3	B	V1	V2	V3
2.2	0.7000	-	-	7.0	1.9507	3.6162	5.1030
2.3	0.2667	0.1500	1.2500	7.1	1.9523	3.6190	5.1074
2.4	0.6333	0.5500	1.7000	7.2	1.9539	3.6218	5.1117
2.5	0.8800	0.8500	2.0500	7.3	1.9556	3.6246	5.1100
2.6	1.1000	1.0800	2.3000	7.4	1.9572	3.6274	5.1203
2.5	0.8800	0.8500	2.0500	7.5	1.9589	3.6302	5.1247
2.6	1.1000	1.0800	2.3000	7.6	1.9605	3.6330	5.1290
2.7	1.2667	2.2833	2.5200	7.7	1.9621	3.6358	5.1333
2.8	1.4111	1.4286	2.7000	7.8	1.9638	3.6385	5.1377
2.9	1.5182	1.5556	2.8250	7.9	1.9654	3.6413	5.1420
3.0	1.6067	1.6500	2.9400	8.0	1.9670	3.6441	5.1463
3.1	1.6733	1.7267	3.0308	8.1	1.9687	3.6469	5.1506
3.2	1.7273	1.7933	3.1071	8.2	1.9703	3.6497	5.1550
3.3	1.7727	1.8474	3.1786	8.3	1.9720	3.6525	5.1593
3.4	1.8073	1.9000	3.2389	8.4	1.9736	3.6553	5.1636
3.5	1.8255	1.9455	3.2944	8.5	1.9752	3.6581	5.1680
3.6	1.8436	1.9909	3.3474	8.6	1.9769	3.6609	5.1723
3.7	1.8618	2.0381	3.4000	8.7	1.9785	3.6637	5.1766
3.8	1.8800	2.0857	3.4556	8.8	1.9802	3.6665	5.1810
3.9	1.8982	2.1389	3.5143	8.9	1.9818	3.6693	5.1853
4.0	1.9015	2.1944	3.5857	9.0	1.9834	3.6721	5.1896
4.1	1.9031	2.2563	3.6533	9.1	1.9851	3.6749	5.1939
4.2	1.9048	2.3214	3.7214	9.2	1.9867	3.6777	5.198
4.3	1.9064	2.3929	3.7929	9.3	1.9884	3.6804	5.2057
4.4	1.9080	2.4692	3.8750	9.4	1.9900	3.6832	5.2151
4.5	1.9097	2.5545	3.9636	9.5	1.9916	3.6860	5.2245
4.6	1.9113	2.6455	4.0500	9.6	1.9933	3.6888	5.2340
4.7	1.9130	2.7400	4.1444	9.7	1.9949	3.6916	5.2434
4.8	1.9146	2.8364	4.2455	9.8	1.9966	3.6944	5.2528
4.9	1.9162	2.9273	4.3333	9.9	1.9982	3.6972	5.2623
5.0	1.9179	3.0154	4.4182	10.0	1.9998	3.7000	5.2717
5.1	1.9195	3.0923	4.5083	10.1	2.0125	3.7154	5.2811
5.2	1.9211	3.1692	4.5917	10.2	2.0264	3.7308	5.2906
5.3	1.9228	3.2375	4.6643	10.3	2.0403	3.7462	5.3000
5.4	1.9244	3.3000	4.7263	10.4	2.0542	3.7615	5.3270
5.5	1.9261	3.3526	4.7789	10.5	2.0681	3.7769	5.3541
5.6	1.9277	3.4036	4.8250	10.6	2.0819	3.7923	5.3811
5.7	1.9293	3.4393	4.8667	10.7	2.0958	3.8179	5.4136
5.8	1.910	3.4750	4.9059	10.8	2.1280	3.8536	5.4519
5.9	1.9326	3.5055	4.935	10.9	2.1680	3.8893	5.5063
6.0	1.9343	3.5236	4.9647	11.0	2.2118	3.9412	5.5688
6.1	1.9359	3.5418	4.9941	11.1	2.2766	4.0000	5.6417
6.2	1.9750	3.5600	5.0099	11.2	2.3417	4.0769	5.7300
6.3	1.9392	3.5782	5.0222	11.3	2.4333	4.1778	5.8429
6.4	1.9408	3.5964	5.0346	11.4	2.5445	4.3000	5.9857
6.5	1.9425	3.6022	5.0469	11.5	2.6833	4.4667	6.1600
6.6	1.9441	3.6050	5.0593	11.6	2.8800	4.6750	6.3800
6.7	1.9457	3.6078	5.0716	11.7	3.1000	4.9250	6.6500
6.8	1.9474	3.6106	5.0840	11.8	3.4000	5.2500	7.0334
6.9	1.9490	3.6134	5.0963	11.9	3.8000	5.6500	7.4500

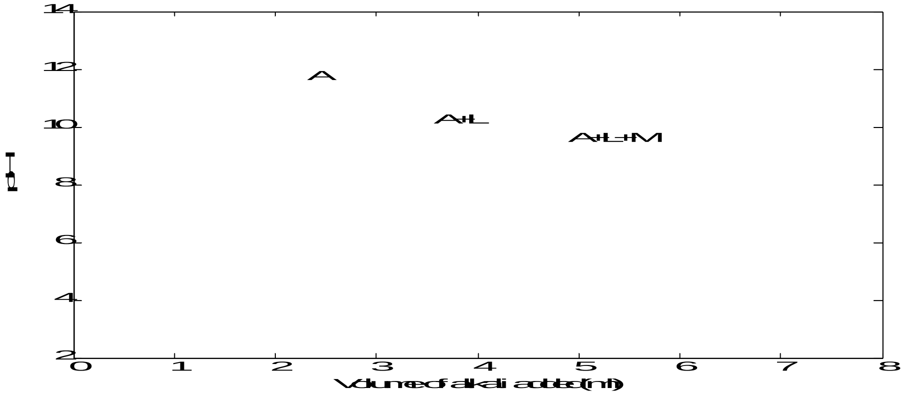


Fig. (5.1.1)Titration curves of three sets of solutions versus pH

5.1.1-Practical proton ligand stability constant:

5.1.1.1-Point-wise calculation method:

ligand used is monoprotonic. The ligand titration curve is well separated from the acid titration curve at pH 2.7 table (5.1.2), indicating the dissociation of the ligand in the titration medium figure (5.1.1). Number of proton attached to ligand extends $0<n_A<1$ table (5.1.3).pKa_1 values calculated on table (5.1.3), the value taken as average of n_A 0.2 - 0.8. pK_a= 4.87707 This value was further corroborated by half integral method.

Table (5.1.3). Dissociation constant of acetic acid, average value of pKa=4.8770

pK_1	$\log\frac{n_A}{(1-n_A)}$	n_A	pH	pKa_1	$\log\frac{n_A}{(1-n_A)}$	n_A	pH
4.7416	0.6416	0.8142	4.1	4.7536	2.0536	0.9912	2.7
4.7517	0.5517	0.7808	4.2	4.8308	2.0308	0.9908	2.8
4.7634	0.4634	0.7440	4.3	4.5966	1.6966	0.9803	2.9
4.7778	0.3778	0.7047	4.4	4.6317	1.6317	0.9772	3.0
4.7895	0.2895	0.6608	4.5	4.6385	1.5385	0.9719	3.1
4.8011	0.2011	06137	4.6	4.6436	1.4436	0.9652	3.2
4.8134	0.1134	0.5649	4.7	4.6879	1.3879	0.9607	3.3
4.8261	0.0261	0.5150	4.8	4.6899	1.2898	0.9512	3.4
4.8444	-0.0556	0.4680	4.9	4.6712	1.1712	0.9368	3.5
4.8645	-0.1355	0.4226	5.0	4.6755	1.0755	0.9225	3.6
4.8929	-0.2071	0.3829	5.1	4.6903	0.9903	0.9072	3.7
4.9185	-0.2815	0.3434	5.2	4.7159	0.9159	0.8918	3.8
4.9492	-0.3508	0.3084	5.3	4.7386	0.8386	0.8734	3.9
4.9819	-0.4181	0.2763	5.4	4.7395	0.7395	0.8459	4.0

5.1.1.2-Half integral method

Proton-ligand stability constant calculated by plotting n_A against pH, figure (5.1.2). The value of pH where n_A= 0.5 corresponds to value of pKa_1. pKa_1= 4.836, the value was in a good agreement with the value obtained by point-wise method.

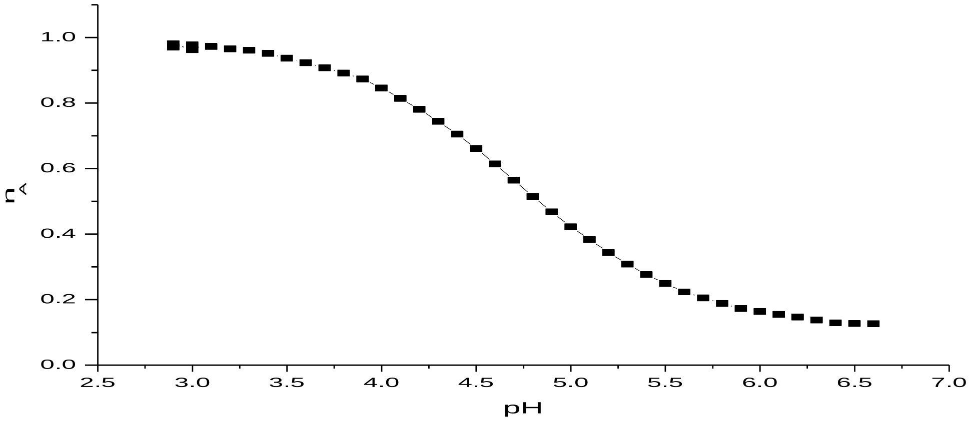


Fig. (5.1.2). Half integral Method (Zr-acetate) pK_a =4.836

5.1.2-Metal-ligand stability constants: (zirconium acetate)

5.1.2.1-Point-wise calculation method:

Metal-ligand titration curve crossed over ligand titration curve at pH 2.3, table (5.1.2), Figure (5.1.1). The value of n^- extended between 2.1992 and 3.9504, table (5.1.4) since the ligand is monobasic acid this indicates the existance of ML_3 and ML_4 complex species. The value [L] represented the quantity of free ligand in the solution decrease gradually with the increase of pH of the solution and attained almost zero, so pL cannot be calculated after pH=4.3, this suggests that with increasing pH the ligand distributed in complex species. $\log K_3$=5.1050 and K_4=4.1095 table (5.1.4) and table (5.1.5). The complexes were formed simultaneously. These values were further verified by half integral method.

Table (5.1.4) Point-wise method stability constants, (Zr-acetate) $\log K_3$ average value =5.1050

Log K_3	$\log\frac{(n^- - 2)}{(3-n^-)}$	pL	n^-	V2	V3
4.6242	-0.6043	5.2285	2.1992	0.1500	1.2500
4.8631	-0.3004	5.1635	2.3336	0.5500	1.7000
5.1084	-0.0016	5.1100	2.4991	0.8500	2.0500
5.1155	0.0891	5.0264	2.5511	1.0800	2.3000
5.1912	0.2382	4.9530	2.6338	1.2833	2.5200
5.2606	0.3826	4.8780	2.7070	1.4286	2.7000
5.2188	0.4319	4.7870	2.7299	1.5556	2.8250

5.2606	0.5541	4.7065	2.7818	1.6500	2.9400
5.3022	0.6778	4.6244	2.8265	1.7267	3.0308
5.3521	0.8107	4.5413	2.8661	1.7933	3.1071
5.5076	1.0438	4.4638	2.9171	1.8474	3.1786
5.7934	1.4081	4.3853	2.9624	1.9000	3.2389

Table (5.1.5). Point-wise method (Zr-acetate) $\log K_4=4.1095$

Log K_3	$\log\frac{(n^{-}-3)}{(4-n^{-})}$	pL	n^{-}	V2	V3
3.2653	-0.9870	4.2523	3.0934	1.9909	3.3474
3.4605	-0.7293	4.1897	3.1572	2.0381	3.400
3.6114	-0.5246	4.1361	3.2301	2.0857	3.4556
3.7462	-0.3465	4.0927	3.3105	2.1389	3.5143
4.0311	-0.0757	4.1068	3.4565	2.1944	3.5857
4.3432	0.18485	4.1583	3.6048	2.2563	3.6533
4.8155	0.51425	4.3013	3.7657	2.3214	3.7214

5.1.2.2-Half integral method: (zirconium acetate)

The metal-ligand stability constants calculated by plotting n^{-} against pL figure (5.1.3). From the formation curve of complex, log K_3 = 5.11 and K_4= 4.113. These values were in a good agreement with values obtained by point-wise method. These values were further corroborated with linear plot method.

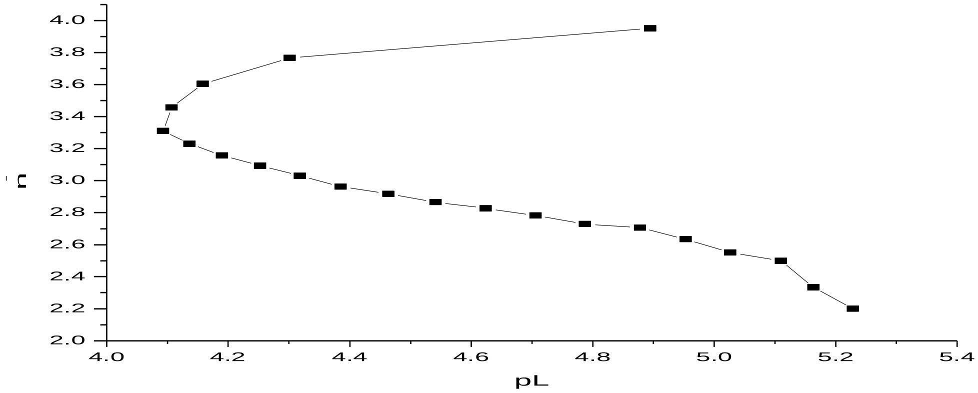


Fig. (5.1.3) Zr-acetate formation curve $\log K_3$= 5.11& $\log K_4$=4.113

5.1.2.3-Linear plot method: (zirconium acetate)

log (n-2)/(3-n) and log(n-3)/(4-n) were plotted against corresponding pL, for determination of $\log K_3$ and log K_4 respectively figure (5.1.4) and figure (5.1.5) the values obtained were, K_3= 5.115and K_4=4.125.

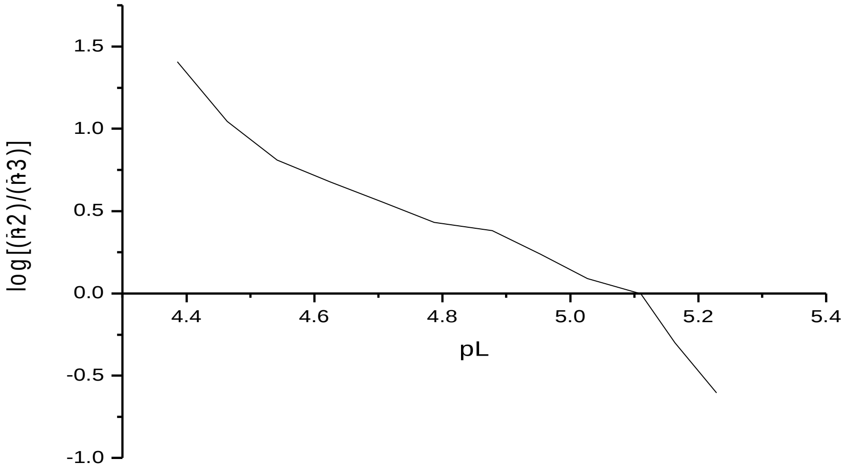


Fig. (5.1.4) Linear plot method Zr-acetate logK_3=5.11

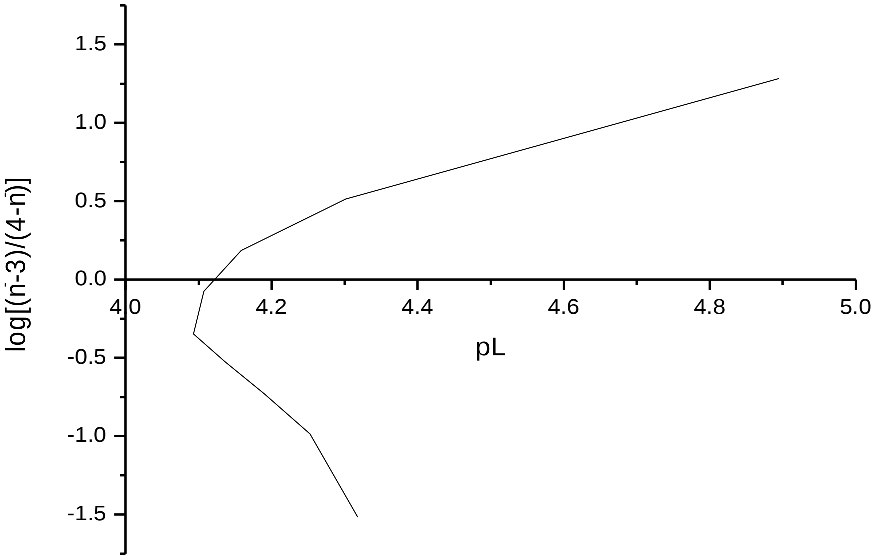


Fig. (5.1.5) Linear plot method Zr-acetate logK_4=4.125

5.1.2.4-Least squares method: (zirconium acetate)

For evaluation of K_3 and K_4 by this method, one can adopt F. J. C. Rossotti and H. S. Rossotti expression:

$$\frac{(2-n^{-})}{(4-n^{-})[L]} = \frac{(3-n^{-})[L]}{(4-n^{-})[L]^2} \times K_3 + K_3 K_4$$

------------(5.1.1)

Or

$$\frac{(n^- - 2)}{(3 - n^-)[L]} \times \frac{1}{K_3 K_4} - \frac{1}{K_4} = \frac{(4 - n^-)[L]}{(3 - n^-)}$$

--------------(5.1.2)

Plotting left-hand side against right-hand side of equation (5.1.1) or (5.1.2) resulting is straight line equation, Figure (5.1.6) and figure (5.1.7) respectively, and stability constant deduced from intercept and slope, as elucidated on the captions below figure (5.1.6).logK_3=5.1974, logK_4=4.3259, and figure (5.1.7) logK_3= 5.000, logK_4=4.3056. As we mentioned before it seen obviously that equation (5.1.2) gives more accurate result than equation (5.1.1) if the sign is omitted.

Table (5.1.6) Least squares method (Zr-acetate) logK_3 &logK_4

pL	n^-	[L]	[L]2	$\frac{(n^- - 2)}{(3 - n^-)[L]^2}$	$\frac{(4 - n^-)}{(3 - n^-)[L]}$
5.2285	2.1992	5.9082E-06	3.49077E-11	-3168154624	75267.94602
5.1635	2.3336	6.8626E-06	4.70945E-11	-4251591258	58270.89193
5.1100	2.4991	7.7616E-06	6.0243E-11	-5519385379	42999.65109
5.0264	2.5511	9.4106E-06	8.85594E-11	-4295168382	32921.50111
4.9530	2.6338	1.1144E-05	1.24186E-10	-3735630269	24052.88107
4.8780	2.7070	1.3243E-05	1.75375E-10	-3118012864	17110.18085
4.7870	2.7300	1.6331E-05	2.66701E-10	-2155027679	13019.7581
4.7065	2.7818	1.9657E-05	3.86385E-10	-1660799718	9113.736722
4.6244	2.8265	2.3747E-05	5.63923E-10	-1248830469	6227.214559
4.5413	2.8661	2.8753E-05	8.26737E-10	-923878633	4107.304541
4.4638	2.9171	3.4374E-05	1.1816E-09	-716716452	2227.384731
4.3853	2.9624	4.1177E-05	1.69554E-09	-547030201	880.2094545
4.3182	3.0296	4.8066E-05	2.31038E-09	-459232830	-634.5479486
4.2523	3.0934	5.5935E-05	3.12872E-09	-385479641	-1841.946744
4.1897	3.1572	6.4606E-05	4.17397E-09	-328955306	-2887.096637
4.1361	3.2301	7.3103E-05	5.34411E-09	-298940988	-4087.174953
4.0927	3.3105	8.0777E-05	6.52487E-09	-291288743	-5574.760497
4.1068	3.4565	7.8194E-05	6.11429E-09	-438331485	-10743.06672
4.1583	3.6048	6.9448E-05	4.82301E-09	-842032342	-22039.0563
4.3013	3.7657	4.9972E-05	2.49716E-09	-3017653618	-65392.72221
4.8950	3.9504	1.2736E-05	1.62199E-10	-2.425E+11	-1504943.635

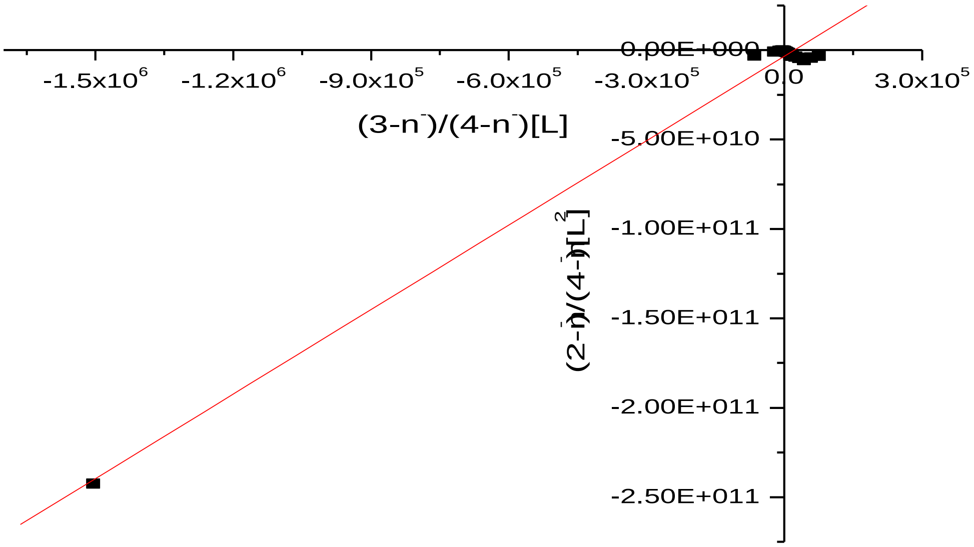


Fig. (5.1.6) least squares method (equation ‘5.1.1’) $\log K_3=5.1974$ & $\log K_4=4.3259$

Linear Regression

Parameter	Value	Error	R_2
Intercept	-3.33637E9	1.28213E9	0.9943
Slope	157541.99547	3888.59382	

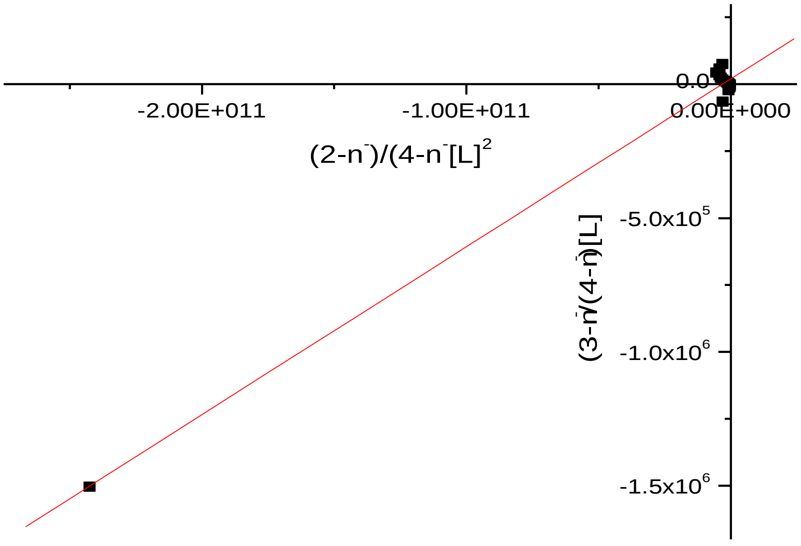


Fig. (5.1.7) least squares method (equation ‘5.1.2’) $\log K_3=5.00$ & $\log K_4=4.3056$

Linear Regression

```
  Parameter              Value                 Error                R²
------------------------------------------------------------------------------------
  Intercept            20209.53103            8204.4937          0.9943
  Slope                0.00001                1.54882E-7            -
------------------------------------------------------------------------------------
```

Table (5.1.7) Stability constants of zirconium acetate obtained.by four methods

Method	$\log K_3$	$\log K_4$	$\log K_3+\log K_4$
Point wise calculation method	5.0803	4.1095	9.1898
Half integral method	5.11	4.113	9.223
Linear plot method	5.11	4.125	9.235
Least squares method fig..(1.6)	5.1974	4.3259	9.5233
Least squares method fig.(1.7)	5.00	4.3056	9.3055

5.2/ Zirconium-oxalic acid system

Table (5.2.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ions (Zr^{+3}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}\,\mathrm{M}$, $T_{Cl} = 5\times10^{-5}\,\mathrm{M}$, $T_{cm} = 1.25\times10^{-5}\,\mathrm{M}$, $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$ $t = 36.5^0 C$.

Table

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.26	2.01	1.87	4.1	11.96	3.85	2.66
0.1	2.28	2.03	1.88	4.2	11.98	3.95	2.71
0.2	1.31	2.04	1.88	4.3	12.00	4.05	2.77
0.3	2.33	2.05	1.89	4.4	12.02	4.14	2.84
0.4	2.35	2.06	1.90	4.5	12.04	4.25	2.93
0.5	2.38	2.07	1.91	4.6	12.05	4.35	3.03
0.6	2.41	2.09	1.92	4.7	12.07	4.47	3.13
0.7	2.45	2.10	1.93	4.8	12.09	4.60	3.26
0.8	2.48	2.11	1.94	4.9	12.10	4.75	3.41
0.9	2.52	2.13	1.94	5.0	12.11	4.94	3.58
1.0	2.56	2.15	1.95	5.1	12.13	5.24	3.78
1.1	2.61	2.17	1.97	5.2	12.14	5.87	4.01
1.2	2.66	2.18	1.98	5.3	12.15	9.36	4.23
1.3	2.73	2.20	1.99	5.4	12.16	10.45	4.46
1.4	2.80	2.22	2.00	5.5	12.17	10.80	4.71
1.5	2.88	2.24	2.01	5.6	12.19	11.00	5.20
1.6	2.99	2.26	2.02	5.7	12.20	11.15	5.66
1.7	3.14	2.28	2.04	5.8	12.21	11.25	6.06
1.8	3.35	2.31	2.05	5.9	12.22	11.34	6.30
1.9	3.78	2.33	2.07	6.0	12.23	11.42	6.48
2.0	9.07	2.36	2.08	6.1	12.24	11.48	6.64
2.1	10.51	2.39	2.09	6.2	12.25	11.53	6.69
2.2	10.88	2.42	2.11	6.3	12.26	11.58	6.78
2.3	11.08	2.45	2.13	6.4	12.27	11.62	6.90
2.4	11.21	2.48	2.14	6.5	12.28	11.66	7.05
2.5	11.33	2.52	2.16	6.6	12.28	11.70	7.28
2.6	11.41	2.56	2.19	6.7	12.29	11.73	8.43
2.7	11.48	2.60	2.20	6.8	12.30	11.76	9.54
2.8	11.54	2.65	2.22	6.9	12.31	11.79	10.28
2.9	11.59	2.71	2.25	7.0	12.32	11.82	10.64
3.0	11.64	2.77	2.28	7.1	12.32	11.84	10.86
3.1	11.68	2.83	2.30	7.2	12.33	11.86	11.03
3.2	11.72	2.91	2.33	7.3	12.34	11.89	11.15
3.3	11.75	3.00	2.35	7.4	12.35	11.91	11.25
3.4	11.79	3.09	2.38	7.5	12.35	11.93	11.33
3.5	11.82	3.20	2.41	7.6	12.36	11.95	11.40
3.6	11.85	3.31	2.44	7.7	12.36	11.97	11.46
3.7	11.88	3.43	2.47	7.8	12.37	11.98	11.51
3.8	11.90	3.54	2.52	7.9	12.38	12.00	11.55
3.9	11.92	3.65	2.57	8.0	12.38	12.02	11.60
4.0	11.94	3.75	2.61	-	-	-	-

(5.2.2) Alkali volume required for three set of solutions to reach the same pH

[B]	V1	V2	V3	B	V1	V2	V3
2.3	0.1669	1.7667	3.1000	6.3	1.9476	5.2123	5.9000
2.4	0.5667	2.1333	3.4667	6.4	1.9495	5.2152	5.9556
2.5	0.8500	2.4500	3.7600	6.5	1.9514	5.2181	6.0125
2.6	1.0800	2.7000	3.9750	6.6	1.9533	5.2209	6.0750
2.7	1.2571	2.8833	4.1800	6.7	1.9552	5.2238	6.2111
2.8	1.4000	3.0500	4.3429	6.8	1.9571	5.2266	6.3167
2.9	1.5182	3.1875	4.4667	6.9	1.9590	5.2295	6.4000
3.0	1.6067	3.3000	4.5700	7.0	1.9609	5.2324	6.4667
3.1	1.6733	3.4091	4.6700	7.1	1.9628	5.2352	6.5217
3.2	1.7286	3.5000	4.7538	7.2	1.9647	5.2381	6.5652
3.3	1.7762	3.5909	4.2670	7.3	1.9665	5.2410	6.6017
3.4	1.8116	3.6750	4.8933	7.4	1.9684	5.2438	6.6104
3.5	1.8349	3.7636	4.9529	7.5	1.9703	5.2467	6.6191
3.6	1.8581	3.8545	5.0100	7.6	1.9722	5.2496	6.6278
3.7	1.8814	3.9500	5.0600	7.7	1.9741	5.2524	6.6365
3.8	11.900	4.0500	5.1087	7.8	1.9760	5.2553	6.6452
3.9	1.9023	4.1500	5.1522	7.9	1.9779	5.2582	6.6539
4.0	1.9042	4.2500	5.1957	8.0	1.9798	2.2610	6.6626
4.1	1.9060	4.3556	5.2409	8.1	1.9817	5.2639	6.6713
4.2	1.9079	4.4545	5.2864	8.2	1.9836	5.2668	3.6800
4.3	1.9098	4.5500	5.3304	8.3	1.9854	5.2696	6.6887
4.4	1.9117	4.6417	5.3739	8.4	1.9873	5.2725	6.6974
4.5	1.9136	4.7231	5.4160	8.5	1.9892	5.2754	6.7063
4.6	1.9155	4.8000	5.4560	8.6	1.9911	5.2782	6.7153
4.7	1.9174	4.8667	5.4960	8.7	1.9930	5.2811	6.7243
4.8	1.9193	4.9263	5.5184	8.8	1.9949	5.2840	6.7333
4.9	1.9212	4.9789	5.5388	8.9	1.9968	5.2868	6.7423
5.0	1.9231	5.0200	5.5592	9.0	1.9987	5.2897	6.7514
5.1	1.9250	5.0533	5.5796	9.1	2.0021	5.2926	6.7604
5.2	1.9268	5.0867	5.6000	9.2	2.0090	5.2954	6.7694
5.3	1.9287	5.1095	5.6217	9.3	2.0160	5.2983	6.7784
5.4	1.9306	5.1254	5.6435	9.4	2.0229	5.3037	6.7874
5.5	1.9325	5.1413	5.6652	9.5	2.0299	5.3128	6.7964
5.6	1.9344	5.1571	5.6870	9.6	2.0368	5.3220	6.8081
5.7	1.9363	5.1730	5.7105	9.7	2.0438	5.3312	6.8216
5.8	1.9382	5.1889	5.7368	9.8	2.0507	5.3404	6.8351
5.9	1.9401	5.2009	5.7632	9.9	2.0576	5.3495	6.8486
6.0	1.9420	5.2037	5.7895	10.0	2.0646	5.3587	6.8622
6.1	1.9439	5.2066	5.8231	10.1	2.0715	5.3679	6.8757
6.2	1.9457	5.2095	5.8615	****	****	****	****

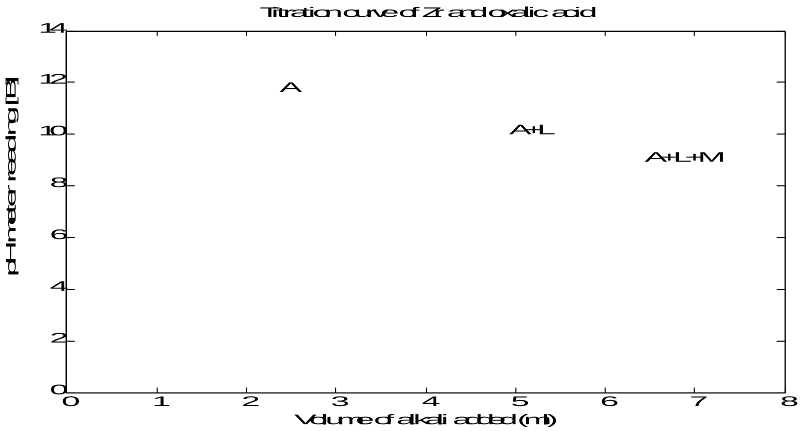


Figure (52.1) Plotting of Alkali volume of the three sets of solutions versus pH

5.2.1-Metal-ligand stability constant: (zirconium oxalate)

5.2.1.1-Point-wise calculation method:

Since the ligand is dibasic and n^- values lies between 2.3360 and 3.9128 this indicates the formation of complex 1:2 only. Metal-ligand stability constant $\log K_2$ was calculated, table (5.2.3). The average value was taken as correct value for $\log K_2=3.3953$. This value was further corroborated by half integral method.

Table (5.2.3) Point-wise method (Zr-oxalate) $\log K_2$ average value=3.4985

Log K_3	$\log\frac{(n^- - 2)}{(4-n^-)}$	n^-	pL	V3	V2
3.9826	-0.6179	2.3884	4.6005	4.4667	3.1875
3.8911	-0.6073	2.3962	4.4984	4.5700	3.3000
3.8364	-0.5675	2.4261	4.4039	4.6700	3.4091
3.7769	-0.5332	2.4532	4.3101	4.7538	3.5000
3.7010	-0.5137	2.4691	4.2147	4.8267	3.5909
3.6390	-0.4842	2.4939	4.1232	4.8933	3.6750
3.5767	-0.4564	2.5181	4.0331	4.9529	3.7636
3.5077	-0.4353	2.5370	3.9430	5.0100	3.8545
3.4140	-0.4351	2.5372	3.8491	5.0600	3.9500
3.3219	-0.4353	2.5370	3.7571	5.1087	4.0500
3.2530	-0.4188	2.5520	3.6719	5.1522	4.1500
3.1896	-0.4004	2.5691	3.5900	5.1957	4.2500
3.1317	-0.3801	2.5884	3.5118	5.2409	4.3556
3.0922	-0.3486	2.6189	3.4408	5.2864	4.4545
3.0613	-0.3139	2.6536	3.3752	5.3304	4.5500
3.0458	-0.2716	2.6971	3.3174	5.3739	4.6417
3.0536	-0.2166	2.7557	3.2702	5.4160	4.7231
3.0748	-0.1570	2.8212	3.2318	5.4560	4.8000
3.1326	-0.0774	2.9111	3.2100	5.4960	4.8667
3.1150	-0.0548	2.9370	3.1699	5.5184	4.9263
3.1071	-0.0298	2.9657	3.1369	5.5388	4.9789
3.1308	0.0123	3.0142	3.1185	5.5592	5.0200
3.1824	0.0684	3.0786	3.1140	5.5796	5.0533
3.2511	0.1311	3.1498	3.1200	5.6000	5.0867
3.3693	0.2203	3.2483	3.1491	5.6217	5.1095
3.5277	0.3284	3.3611	3.1992	5.6435	5.1254
3.7231	0.4525	3.4785	3.2705	5.6652	5.1413
3.9795	0.6052	3.6023	3.3743	5.6870	5.1571
4.3875	0.8333	3.7440	3.5542	5.7105	5.1730

5.2.1.2-Method of interpolation at half n^- values:(half intedral method)

$\log K_2$ was calculated from metal-ligand formation curve by plotting n^- against pL, figure (5.2.2), $\log K_2=3.3$. This value in a good concordance with the value obtained by point-wise calculation method. The value was further verified by linear plot method.

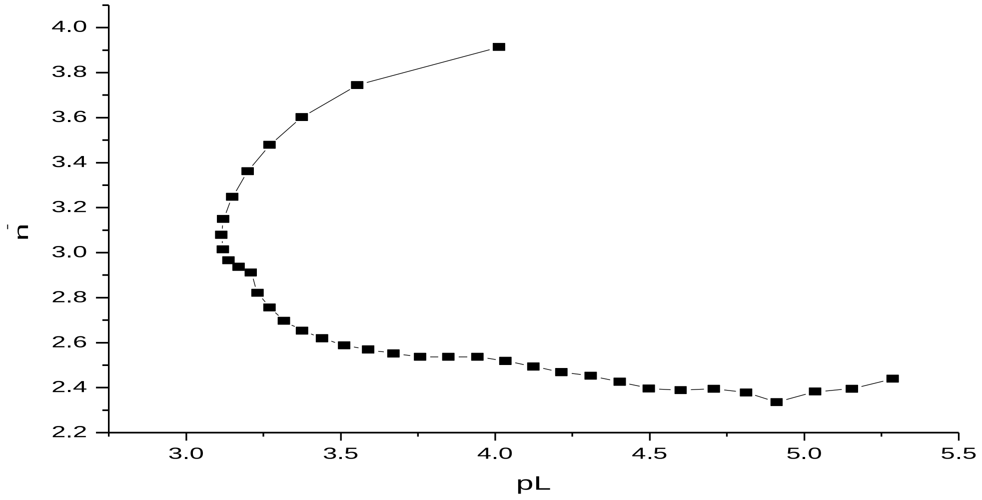


Fig. (5.2.2) Metal-ligand formation curve (zirconium oxalate) $\log K_2 = 3.3$

5.2.1.3-Linear plot method: (Zirconium oxalate)
$\log K_2$ calculated by plotting log $(n-2)/(4-n^-)$ v/s corresponding pL. $\log K_2 = 3.126$ (5.2.3) this value was in a good agreement with the two previous methods.

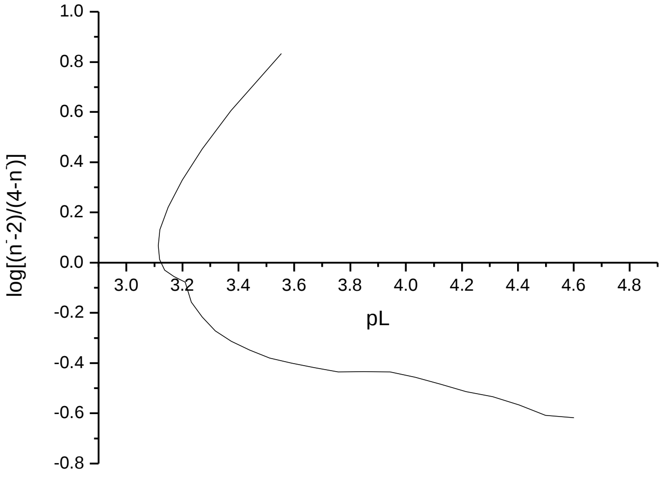


Fig. (5.2.3). Linear plot method Zr-oxalate $\log K_3 = 3.126$

5.2.1.4- Hinderson or Hasselbalch's equation: (zirconium oxalate**).**
Because only one chelate is form and the ligand is dibasic Hinderson's equation can taken the following form.

$$\log K_4 = \log\left(\frac{(n^- - 2}{(4 - n^-)}\right) - \log[L]$$

Table(5.2.4) Zr-oxalate stability constant, logK_2 average value =3.4768

Log K_2	$\log\frac{(\bar{n}-2)}{(4-\bar{n})}$	Log[L]	pL	$\bar{n}$
3.8911	-0.6073	-4.4984	5.2858	2.4396
3.8364	-0.5675	-4.4039	5.1546	2.3952
3.7769	-0.5332	-4.3101	5.0357	2.3831
3.7010	-0.5137	-4.2147	4.9105	2.3360
3.6390	-0.4842	-4.1232	4.8117	2.3788
3.5767	-0.4562	-4.0331	4.7082	2.3950
3.5077	-0.4353	-3.9430	4.6005	2.3884
3.4140	-0.4351	-3.8491	4.4984	2.3962
3.3219	-0.4352	-3.7571	4.4039	2.4261
3.2530	-0.4188	-3.6719	4.3101	2.4532
3.1896	-0.4004	-3.5900	4.2147	2.4691
3.1317	-0.3801	-3.5118	4.1232	2.4939
3.0922	-0.3486	-3.4408	4.0331	2.5181
3.0613	-0.3139	-3.3752	3.9430	2.5370
3.0458	-0.2716	-3.3174	3.8491	2.5372
3.0536	-0.2166	-3.2702	3.7571	2.5370
3.0748	-0.1570	-3.2318	3.6719	2.5520
3.1326	-0.0774	-3.2100	3.5900	2.5691
3.1150	-0.0548	-3.1699	3.5118	2.5884
3.1071	-0.0298	-3.1369	3.4408	2.6189
3.1308	0.0123	-3.1185	3.3752	2.6536
3.1824	0.0684	-3.1140	3.3174	2.6971
3.2511	0.1311	-3.1200	3.2702	2.7557
3.3693	0.2203	-3.1491	3.2318	2.8212
3.5277	0.3284	-3.1992	3.2100	2.9111
3.7231	0.4525	-3.2705	3.1699	2.9370
3.9795	0.6052	-3.3743	3.1369	2.9657
4.3875	0.8333	-3.5542	3.1185	3.0142
5.3544	1.3414	-4.0130	3.1140	3.0786
3.8911	-0.6079	-4.4984	3.1200	3.1498
3.8364	-0.5675	-4.4039	3.1491	3.2483
3.7769	-0.5332	-4.3101	3.1992	3.3611
3.7010	-0.5137	-4.2147	3.2705	3.4785
3.6390	-0.4842	-4.1232	3.3743	3.6023
3.5767	-0.4564	-4.0331	3.5542	3.7440

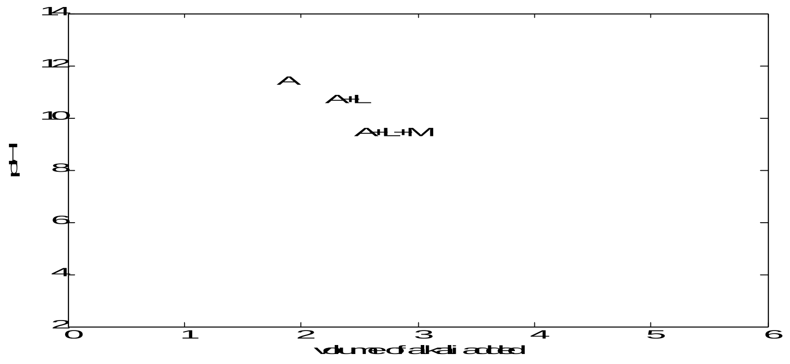
Table (5.2.5). Stability constants of zr-oxalate, obtained by four methods.

Method	logK_2
Point wise calculation method	3.4985
Half integral method	3.3
Linear plot method	3.126
Hinderson’s equation	3.4768

5.3/Zirconium and oxalacetic acid system:

Table (5.3.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ions (Zr^{+4}). $N^0 = 0.522M$, $E^0 = 5\times10^{-3}$ M , $T_{Cl} = 1.5\times10^{-3}$ M , $T_{cm} = 5\times10^{-4}$ M , $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$ $t = 22.5^0 C$.

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.31	2.25	2.02	3.1	11.95	11.62	11.04
0.1	2.34	2.27	2.03	3.2	11.98	11.68	11.17
0.2	2.37	2.29	2.05	3.3	12.01	11.73	11.29
0.3	2.40	2.31	2.06	3.4	12.03	11.77	11.37
0.4	2.44	2.33	2.08	3.5	12.05	11.82	11.45
0.5	2.48	2.36	2.12	3.6	12.08	11.85	11.51
0.6	2.53	2.40	2.15	3.7	12.09	11.88	11.57
0.7	2.58	2.43	2.17	3.8	12.11	11.91	11.62
0.8	2.63	2.46	2.20	3.9	12.13	11.94	11.66
0.9	2.70	2.50	2.23	4.0	12.15	11.97	11.71
1.0	2.78	2.55	2.26	4.1	12.17	11.99	11.75
1.1	2.89	2.60	2.30	4.2	12.19	12.02	11.78
1.2	3.01	2.66	2.33	4.3	12.20	12.04	11.81
1.3	3.19	2.71	2.37	4.4	12.22	12.06	11.84
1.4	3.48	2.78	2.42	4.5	12.23	12.08	11.87
1.5	4.50	2.87	2.47	4.6	12.24	12.10	11.90
1.6	10.02	2.98	2.52	4.7	12.26	12.12	11.92
1.7	10.74	3.12	2.58	4.8	12.27	12.14	11.94
1.8	11.04	3.31	2.65	4.9	12.28	12.16	11.97
1.9	11.23	3.60	2.73	5.0	12.29	12.18	11.99
2.0	11.36	4.19	2.83	5.1	12.31	12.19	12.01
2.1	11.46	5.77	2.95	5.2	12.32	12.20	12.03
2.2	11.55	7.56	3.11	5.3	12.33	12.32	12.04
2.3	11.61	9.99	3.35	5.4	12.34	12.23	12.06
2.4	11.68	10.60	3.82	5.5	12.35	12.25	12.08
2.5	11.73	10.92	5.39	5.6	12.36	12.26	-
2.6	11.78	11.13	7.04	5.7	12.37	12.27	-
2.7	11.82	11.28	9.33	5.8	12.38	12.28	-
2.8	11.86	11.39	10.32	5.9	12.39	12.30	-
2.9	11.89	11.48	10.55	6.0	12.40	12.31	-
3.0	11.93	11.56	10.84	6.1	-	-	-



Fig(5.3.1) Titration curves of three sets of solution versus pH.

Fig. (5.3.2) Alkali volume required for the three set solutions to reach the same pH

B	V1	V2	V3	B	V1	V2	V3
2.1	0.4500	-	-	7.1	1.5471	2.1743	2.6026
2.2	0.8000	-	-	7.2	1.5489	2.1799	2.6070
2.3	0.2500	1.1000	-	7.3	1.5507	2.1855	2.6114
2.4	0.3000	0.6000	1.3600	7.4	1.5525	2.1911	2.6157
2.5	0.5400	0.9000	1.5600	7.5	1.5543	2.1967	2.6201
2.6	0.7400	1.1000	1.7286	7.6	1.5562	2.2016	2.6245
2.7	0.9000	1.2800	1.8625	7.7	1.5580	2.2058	2.6288
2.8	1.0182	1.4222	1.9700	7.8	1.5598	2.2099	2.6332
2.9	1.1083	1.5273	2.0583	7.9	1.5616	2.214	2.6376
3.0	1.1917	1.6143	2.1313	8.0	1.5634	2.2181	2.6419
3.1	1.2500	1.6857	2.1938	8.1	1.5652	2.2222	2.6463
3.2	1.3035	1.7421	2.2375	8.2	1.5670	2.2263	2.6507
3.3	1.3379	1.7947	2.2792	8.3	1.5688	2.2305	2.655
3.4	1.3724	1.8310	2.3106	8.4	1.5707	2.2346	2.6594
3.5	1.4020	1.8655	2.3319	8.5	1.5725	2.2387	2.6638
3.6	1.4118	1.9000	2.3532	8.6	1.5743	2.2428	2.6681
3.7	1.4216	1.9170	2.3745	8.7	1.5761	2.2469	2.6725
3.8	1.4314	1.9339	2.3957	8.8	1.5779	2.251	2.6769
3.9	1.4412	1.9509	2.4051	8.9	1.5797	2.2551	2.6812
4.0	1.451	1.9678	2.4115	9.0	1.5815	2.2593	2.6856
4.1	1.4608	1.9847	2.4178	9.1	1.5833	2.2634	2.6900
4.2	1.4706	2.0006	2.4242	9.2	1.5851	2.2675	2.6943
4.3	1.4804	2.0070	2.4306	9.3	1.5870	2.2716	2.6987
4.4	1.4902	2.0133	2.4369	9.4	1.5888	2.2757	2.7071
4.5	1.5000	2.0196	2.4433	9.5	1.5906	2.2798	2.7172
4.6	1.5018	2.0260	2.4497	9.6	1.5924	2.2840	2.7273
4.7	1.5036	2.0323	2.4561	9.7	1.5942	2.2881	2.7374
4.8	1.5054	2.0386	2.4624	9.8	1.5960	2.2922	2.7475
4.9	1.5072	2.0449	2.4688	9.9	1.5978	2.2963	2.7576
5.0	1.5091	2.0513	2.4752	10.0	1.5996	2.3017	2.7677
5.1	1.5109	2.0576	2.4815	10.1	1.6111	2.3180	2.7778
5.2	1.5127	2.0639	2.4879	10.2	1.6250	2.3344	2.7879
5.3	1.5145	2.0703	2.4943	10.3	1.6389	2.3508	2.7980
5.4	1.5163	2.0766	2.5006	10.4	1.6528	2.3672	2.8348
5.5	1.5181	2.0829	2.5067	10.5	1.6667	2.3836	2.8783
5.6	1.5199	2.0892	2.5127	10.6	1.6806	2.4000	2.9173
5.7	1.5217	2.0956	2.5188	10.7	1.6945	2.4313	2.9518
5.8	1.5236	2.1017	2.5249	10.8	1.7200	2.4625	2.9862
5.9	1.5254	2.1073	2.5309	10.9	1.7534	2.4938	3.0300
6.0	1.5272	2.1129	2.5370	11.0	1.7867	2.5381	3.0800
6.1	1.5290	2.1184	2.5430	11.1	1.8316	2.5858	3.1462
6.2	1.5308	2.124	2.5491	11.2	1.8843	2.6467	3.2251
6.3	1.5326	2.1296	2.5552	11.3	1.9539	2.7183	3.3126
6.4	1.5344	2.1352	2.5612	11.4	2.0401	2.8112	3.4376
6.5	1.5362	2.1408	2.5673	11.5	2.1446	2.9251	3.5835
6.6	1.538	2.1464	2.5733	11.6	2.2835	3.0668	3.7602
6.7	1.5399	2.1520	2.5794	11.7	2.4402	3.2402	3.9802
6.8	1.5417	2.1575	2.5855	11.8	2.6502	3.4602	4.2670
6.9	1.5435	2.1631	2.5915	11.9	2.9252	3.7670	4.6005
7.0	1.5453	2.1687	2.5976	12.0	-	-	-

5.3.1-Metal-ligand stability constant:(zirconium oxalacetate)

5.3.1.1-Point-wise calculation method

Metal-ligand titration curve cross over the ligand titration curve at pH 2.4, table (5.3.2) and figure (5.3.1), indicating the formation of a complex. n^{-} extended between 2.0206 to 2.9607 Table (5.3.3) indicating the formation of ML_3 chelate only. logK_3= 4.4584.This value was further verified by half integral method.
It was noticed during the titration course; a precipitate appeared at lower pH (2.4) and disappeared at higher pH.

Table (5.3.3) Zr-oxalacetate stability constant logK_3 average value =4.4584

logK_3	$\log\frac{(n^{-}-2)}{(3-n^{-})}$	n^{-}	pL	V3	V2
6.0802	-1.6775	2.0206	7.7578	2.4433	2.0196
6.1295	-1.4351	2.0354	7.5644	2.4497	2.0260
6.0984	-1.2729	2.0506	7.3713	2.4561	2.0323
6.0246	-1.1537	2.0656	7.1783	2.4624	2.0386
5.9323	-1.0534	2.0813	6.9857	2.4688	2.0449
5.8224	-0.9706	2.0967	6.7931	2.4752	2.0513
5.7028	-0.8980	2.1123	6.6008	2.4815	2.0576
5.5782	-0.8308	2.1287	6.4090	2.4879	2.0639
5.4474	-0.7702	2.1451	6.2175	2.4943	2.0703
5.3109	-0.7154	2.1615	6.0263	2.5006	2.0766
5.1679	-0.6672	2.1771	5.8351	2.5067	2.0829
5.0211	-0.6230	2.1924	5.6441	2.5127	2.0892
4.8744	-0.5798	2.2083	5.4542	2.5188	2.0956
4.7272	-0.5382	2.2245	5.2655	2.5249	2.1017
4.5818	-0.4970	2.2415	5.0787	2.5309	2.1073
4.4388	-0.4559	2.2593	4.8947	2.5370	2.1129
4.2969	-0.4170	2.2769	4.7139	2.5430	2.1184
4.1603	-0.3782	2.2951	4.5385	2.5491	2.1240
4.0304	-0.3403	2.3136	4.3707	2.5552	2.1296
3.9091	-0.3041	2.3318	4.2132	2.5612	2.1352
3.8031	-0.2674	2.3508	4.0705	2.5673	2.1408
3.7137	-0.2321	2.3695	3.9458	2.5733	2.1464
3.6461	-0.1969	2.3885	3.8430	2.5794	2.1520
3.6032	-0.1608	2.4085	3.7640	2.5855	2.1575
3.5813	-0.1260	2.4280	3.7073	2.5915	2.1631
3.5811	-0.0900	2.4484	3.6712	2.5976	2.1687
3.5815	-0.0649	2.4627	3.6464	2.6026	2.1743
3.5853	-0.0456	2.4738	3.6309	2.6070	2.1799
3.5981	-0.0260	2.4850	3.6241	2.6114	2.1855
3.6155	-0.0072	2.4958	3.6228	2.6157	2.1911
3.6390	0.0129	2.5074	3.6261	2.6201	2.1967
3.6660	0.0336	2.5193	3.6324	2.6245	2.2016
3.6968	0.0556	2.5320	3.6412	2.6288	2.2058
3.7311	0.0791	2.5454	3.6521	2.6332	2.2099
3.7670	0.1029	2.5589	3.6641	2.6376	2.2140
3.8025	0.1260	2.5720	3.6765	2.6419	2.2181
3.8409	0.1507	2.5858	3.6903	2.6463	2.2222
3.8806	0.1757	2.5998	3.7050	2.6507	2.2263
3.9195	0.2000	2.6131	3.7195	2.6550	2.2305
3.9602	0.2252	2.6268	3.7350	2.6594	2.2346
4.0040	0.2520	2.6411	3.7520	2.6638	2.2387
4.0474	0.2784	2.6550	3.7690	2.6681	2.2428
4.0945	0.3067	2.6696	3.7878	2.6725	2.2469

4.1436	0.3360	2.6843	3.8076	2.6769	2.2510
4.1927	0.3650	2.6986	3.8277	2.6812	2.2551
4.2461	0.3964	2.7135	3.8498	2.6856	2.2593
4.3026	0.4292	2.7287	3.8734	2.6900	2.2634
4.3596	0.4620	2.7434	3.8976	2.6943	2.2675
4.4201	0.4965	2.7583	3.9236	2.6987	2.2716
4.6073	0.6017	2.7999	4.0056	2.7071	2.2757
4.9030	0.7635	2.8530	4.1395	2.7172	2.2798
5.3233	0.9869	2.9066	4.3364	2.7273	2.2840
6.1018	1.3887	2.9607	4.7130	2.7374	2.2881

5.3.1.2-Half integral method: (zirconium oxalacetate)

$\log K_3$ was estimated from metal-ligand formation curve, that constructed by plotting n^- v/s pL fig(5.3.2).$\log K_3$ is the value of pL at which $n^-=2.5$. $\log K_3=3.616$. The value was further verified by linear plot method.

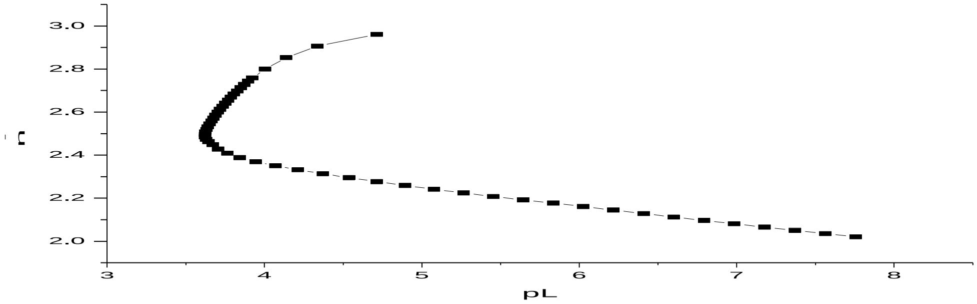


Fig. (5.3.2) Zr-oxalacetate curve log $K_3=3.616$

5.3.1.3-Linear plot method: (zirconium oxalacetate)

pL plotted against $\log(n^- -2)/(3-n^-)$, where curve intersect pL should be $\log K_3$. $\log K_3=3.7$, figure (5.3.3), this value was in a good agreement with the half integral method value. The value was further verified by least squares method.

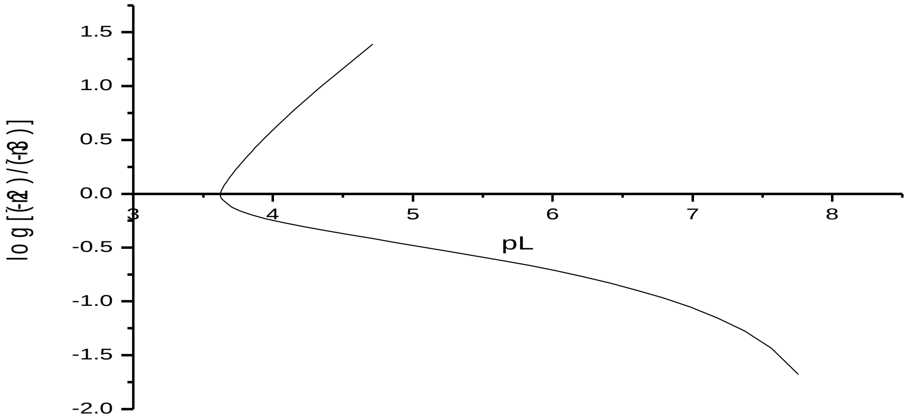


Figure (5.3.3) linear plot method, Zr-oxalacetic $\log K_3 =3.64$

5.3.1.4-Henderson's or Hasselbalch's equation: (zirconium oxalacetate)

Since only one chelate 1:3 is formed, so the following expression of Henderson's equation is employed.

$$\frac{n^{-}-2}{(3-n^{-})}=\beta_1[L].$$

By taking logarithm it becomes:

$$\log\left(\frac{(n^{-}-2)}{(3-n^{-})}\right)=\log K_3+\log[L].$$

Value was found, $\log K_3$= 4.4584, table (5.3.4). The value obtained agreed very much with the value point-wise calculation method than other two methods.

Table (5.3.4) Henderson's Hasselbalch's equation, $\log K_3$ average value =4.4584

pL	n^{-}	[L]	$\log\left(\frac{(n^{-}-2)}{(3-n^{-})[L]}\right)$	Log[L]	$\log K_3$
7.7578	2.0206	1.7E-08	-1.6775	-7.7578	6.0802
7.5644	2.0354	2.7E-08	-1.4351	-7.5644	6.1294
7.3713	2.0506	4.3E-08	-1.2729	-7.3713	6.0984
7.1783	2.0656	6.6E-08	-1.1537	-7.1783	6.0246
6.9857	2.0813	1.0E-07	-1.0534	-6.9857	5.9323
6.7931	2.0967	1.6E-07	-0.9706	-6.7931	5.8224
6.6008	2.1123	2.5E-07	-0.8980	-6.6008	5.7028
6.4090	2.1287	3.9E-07	-0.8308	-6.4090	5.5782
6.2175	2.1451	6.1E-07	-0.7702	-6.2175	5.4474
6.0263	2.1615	9.4E-07	-0.7154	-6.0263	5.3109
5.8351	2.1771	1.5E-06	-0.6672	-5.8351	5.1679
5.6441	2.1924	2.3E-06	-0.6230	-5.6441	5.0211
5.4542	2.2083	3.5E-06	-0.5798	-5.4542	4.8744
5.2655	2.2245	5.4E-06	-0.5383	-5.2655	4.7272
5.0787	2.2415	8.3E-06	-0.4970	-5.0787	4.5818
4.8947	2.2593	1.3E-05	-0.4559	-4.8947	4.4388
4.7139	2.2769	1.9E-05	-0.4170	-4.7139	4.2969
4.5385	2.2951	2.9E-05	-0.3782	-4.5385	4.1603
4.3707	2.3136	4.3E-05	-0.3403	-4.3707	4.0304
4.2132	2.3318	6.1E-05	-0.3041	-4.2132	3.9091
4.0705	2.3508	8.5E-05	-0.2674	-4.0705	3.8031
3.9458	2.3695	0.0001	-0.2321	-3.9458	3.7137
3.8430	2.3885	0.0001	-0.1969	-3.8430	3.6461
3.7640	2.4085	0.0002	-0.1608	-3.7640	3.6032
3.7073	2.4280	0.0002	-0.1260	-3.7073	3.5813
3.6712	2.4484	0.0002	-0.0900	-3.6712	3.5811

3.6464	2.4627	0.0002	-0.0649	-3.6464	3.5815
3.6309	2.4738	0.0002	-0.0456	-3.6309	3.5853
3.6241	2.4850	0.0002	-0.0260	-3.6241	3.5981
3.6228	2.4958	0.0002	-0.0072	-3.6228	3.6155
3.6261	2.5074	0.0002	0.0129	-3.6261	3.6390
3.6324	2.5193	0.0002	0.0336	-3.6324	3.6660
3.6412	2.5320	0.0002	0.0556	-3.6412	3.6968
3.6521	2.5454	0.0002	0.0791	-3.6521	3.7311
3.6641	2.5589	0.0002	0.1029	-3.6641	3.7670
3.6765	2.5720	0.0002	0.1260	-3.6765	3.8025
3.6903	2.5858	0.0002	0.1506	-3.6903	3.8409
3.7049	2.5998	0.0002	0.1757	-3.7049	3.8806
3.7195	2.6131	0.0002	0.2000	-3.7195	3.9195
3.7350	2.6268	0.0002	0.2252	-3.7350	3.9602
3.7520	2.6411	0.0002	0.2520	-3.7520	4.0040
3.7690	2.6550	0.0002	0.2784	-3.7690	4.0474
3.7878	2.6696	0.0002	0.3067	-3.7878	4.0945
3.8076	2.6843	0.0002	0.3360	-3.8076	4.1436
3.8277	2.6986	0.0001	0.3650	-3.8277	4.1927
3.8498	2.7135	0.0001	0.3964	-3.8498	4.2461
3.8734	2.7287	0.0001	0.4292	-3.8734	4.3026
3.8976	2.7434	0.0001	0.4620	-3.8976	4.3596
3.9236	2.7583	0.0001	0.4965	-3.9236	4.4201
4.0056	2.7999	9.9E-05	0.6017	-4.0056	4.6073
4.1395	2.8530	7.3E-05	0.7635	-4.1395	4.9030
4.3364	2.9066	4.6E-05	0.9869	-4.3364	5.3234

Table (5.3.5) Stability constants of Zi-oxalacetate obtained.by four methods

Method	$\log K_3$
Point wise method	4.4584
Half integral method	3.616
Linear plot method	3.70
Hasselbalch’s equation	4.4584

5.4/Zirconium-propanoic acid system:

Table (5.4.1). The pH - titration readings of acid, acid + ligand and acid + ligand + metal ions (Zr^{+4}). $N^0 = 0.522M$, $E^0 = 5\times10^{-3}M$, $T_{Cl} = 1.5\times10^{-3}M$, $T_{cm} = 5\times10^{-4}M$, $V^0 = 200cm^3$, $u^0 = 5\times10^{-3}$ $t = 22.5^0C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.33	2.34	2.23	3.1	11.92	11.74	11.10
0.1	2.34	2.34	2.25	3.2	11.95	11.77	11.26
0.2	2.36	2.37	2.27	3.3	11.97	11.81	11.38
0.3	2.39	2.39	2.28	3.4	11.99	11.85	11.47
0.4	2.42	2.42	2.30	3.5	12.02	11.88	11.55
0.5	2.45	2.45	2.32	3.6	12.04	11.91	11.61
0.6	2.49	2.49	2.35	3.7	12.06	11.94	11.67
0.7	2.53	2.54	2.37	3.8	12.08	11.97	11.72
0.8	2.58	2.59	2.40	3.9	12.10	11.99	11.76
0.9	2.64	2.64	2.43	4.0	12.12	12.01	11.80
1.0	2.71	2.71	2.47	4.1	12.13	12.04	11.84
1.1	2.80	2.80	2.50	4.2	12.15	12.06	11.87
1.2	2.92	2.90	2.54	4.3	12.17	12.08	11.90
1.3	3.08	3.04	2.59	4.4	12.18	12.10	11.93
1.4	3.35	3.24	2.65	4.5	12.20	12.11	11.96
1.5	4.24	3.56	2.71	4.6	12.21	12.13	11.98
1.6	9.93	4.07	2.78	4.7	12.22	12.15	12.10
1.7	10.70	4.49	2.87	4.8	12.24	12.16	12.03
1.8	11.02	4.84	2.98	4.9	12.25	12.18	12.05
1.9	11.21	5.19	3.13	5.0	12.26	12.20	12.07
2.0	11.34	5.71	3.34	5.1	12.27	12.21	12.09
2.1	11.44	7.50	3.67	5.2	12.29	12.22	12.11
2.2	11.52	10.42	4.07	5.3	12.30	12.24	12.13
2.3	11.59	10.87	4.44	5.4	12.31	12.25	12.14
2.4	11.65	11.12	4.75	5.5	12.32	12.26	12.16
2.5	11.70	11.28	5.06	5.6	12.33	12.27	12.18
2.6	11.74	11.39	5.41	5.7	12.34	12.28	12.19
2.7	11.78	11.49	6.06	5.8	12.35	12.29	12.20
2.8	11.82	11.57	8.90	5.9	12.36	12.30	12.22
2.9	11.85	11.63	10.44	6.0	12.37	12.32	12.23
3.0	11.89	11.68	10.85	-	-	-	-

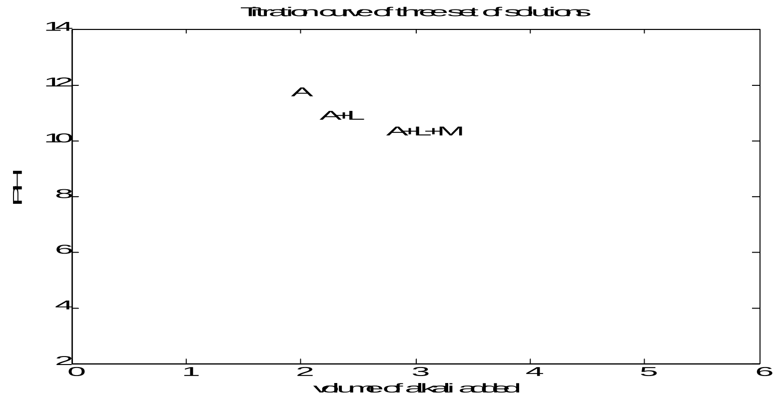


Figure (5.4.1) Plotting of three sets of solutions of alkali volume against pH

Table (5.4.2) alkali volume required for the three components to reach the same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.3250	0.3333	0.8000	7.2	1.5520	2.0832	2.7401
2.5	0.6250	0.6200	1.1000	7.3	1.5538	2.0888	2.7437
2.6	0.8333	0.8200	1.3167	7.4	1.5555	2.0944	2.7472
2.7	0.9857	0.9827	1.4833	7.5	1.5573	2.1000	2.7507
2.8	1.1000	1.1000	1.6222	7.6	1.5591	2.1034	2.7542
2.9	1.1833	1.2000	1.7273	7.7	1.5608	2.1069	2.7577
3.0	1.2500	1.2714	1.8133	7.8	1.5626	2.1103	2.7613
3.1	1.3074	1.3300	1.8800	7.9	1.5643	2.1137	2.7648
3.2	1.3444	1.3800	1.9333	8.0	1.5661	2.1171	2.7683
3.3	1.3815	1.4188	1.9810	8.1	1.5678	2.1206	2.7718
3.4	1.4056	1.4500	2.0182	8.2	1.5696	2.1240	2.7754
3.5	1.4169	1.4813	2.0485	8.3	1.5714	2.1274	2.7789
3.6	1.4281	1.5078	2.0788	8.4	1.5731	2.1308	2.7824
3.7	1.4393	1.5275	2.1075	8.5	1.5749	2.1342	2.7859
3.8	1.4506	1.5471	2.1325	8.6	1.5766	2.1377	2.7894
3.9	1.4618	1.5567	2.1575	8.7	1.5784	2.1411	2.7930
4.0	1.4730	1.5863	2.1825	8.8	1.5801	2.1445	2.7965
4.1	1.4843	1.6071	2.2081	8.9	1.5919	2.1479	2.8000
4.2	1.4955	1.6310	2.2351	9.0	1.5837	2.1514	2.8065
4.3	1.5011	1.6548	2.2622	9.1	1.5854	2.1548	2.8130
4.4	1.5028	1.6786	2.2892	9.2	1.5872	2.1582	2.8195
4.5	1.5046	1.7029	2.3194	9.3	1.5889	2.1616	2.8260
4.6	1.5063	1.7314	2.3516	9.4	1.5907	2.1651	2.8325
4.7	1.5081	1.7600	2.3839	9.5	1.5924	2.1685	2.8390
4.8	1.5098	1.7886	2.4161	9.6	1.5942	2.1719	2.8455
4.9	1.5116	1.8172	2.4484	9.7	1.5960	2.1753	2.8520
5.0	1.5134	1.8457	2.4807	9.8	1.5977	2.1788	2.8584
5.1	1.5151	1.8743	2.5114	9.9	1.5995	2.1822	2.8649
5.2	1.5169	1.9019	2.5400	10.0	1.6091	2.1856	2.8714
5.3	1.5186	1.9212	2.5686	10.1	1.6351	2.1925	2.8779
5.4	1.5204	1.9404	2.5972	10.2	1.6351	2.1925	2.8844
5.5	1.5221	1.9596	2.6139	10.3	1.6481	2.1959	2.8909
5.6	1.5239	1.9789	2.6292	10.4	1.6610	2.1993	2.8974
5.7	1.5257	1.9981	2.6446	10.5	1.6740	2.2178	2.9147
5.8	1.5274	2.0050	2.6600	10.6	1.6870	2.2400	2.9390
5.9	1.5292	2.0106	2.6754	10.7	1.7000	2.2622	2.9634
6.0	1.5309	2.0162	2.6908	10.8	1.7313	2.2845	2.9878
6.1	1.5327	2.0218	2.7014	10.9	1.7625	2.3120	3.0200
6.2	1.5344	2.0274	2.7049	11.0	1.7938	2.3520	3.0600
6.3	1.5362	2.0330	2.7085	11.1	1.8422	2.3920	3.1001
6.4	1.5380	2.0385	2.7120	11.2	1.8948	2.4501	3.1626
6.5	1.5397	2.0441	2.7155	11.3	1.9693	2.5183	3.2334
6.6	1.5415	2.0497	2.7190	11.4	2.0601	2.6101	3.3223
6.7	1.5432	2.0553	2.7225	11.5	2.1751	2.7126	3.4376
6.8	1.5450	2.0609	2.7261	11.6	2.3168	2.8502	3.5835
6.9	1.5467	2.0665	2.7296	11.7	2.5002	3.0402	3.7602
7.0	1.5485	2.0721	2.7331	11.8	2.7502	3.2752	4.0002
7.1	1.5503	2.0777	2.7366	11.9	3.0337	3.5670	4.3003

B is the pH-meter reading.**V1**, **V2** and **V3** are the volumes of alkali employed to bring the solutions of acid , acid+ ligand and acid+ligand+metal ion respectively to the same pH value.

5.4.1-Metal-ligand stability constants:

5.4.1.1-Point-wise calculation method: (zirconium propanoate)

Metal titration curve showed a displacement with respect to the ligand titration curve along the volume axis at pH 2.4 indicate the affinity of ligand with metal ions which release a proton, figure (5.4.1) and table (5.4.2). This deviation used for calculation of stability constants by point-wise method, n^- extends in the range 2.4881 to 2.9968 indicates the formation complex of 1:3 only, the value of stability constants is found, $\log K_3$=11.5165, table (5.4.3)

Table (5.4.3) point-wise method $\mathrm{Log}K_3$ average value =11.5165

V2	V3	.n^-	.pL	$\log\frac{(n^- -2)}{(3-n^-)}$	$\log K_3$
0.3333	0.8000	2.4881	11.4807	-0.0207	11.4661
0.6200	1.1000	2.4974	11.3885	-0.0045	11.3883
0.820	1.3167	2.5456	11.3325	0.0795	11.4156
0.9827	1.4833	2.6101	11.2990	0.1944	11.4962
1.1000	1.6222	2.7356	11.3686	0.4443	11.8160

5.4.1.2-Half integral method: (zirconium propanoate)

Metal-ligand formation curve was plotted n^- against pL figure (5.4.2). $\log K_3$corresponds to value of pL where n^-=2.5. The value was found, $\log K_3$=11.382. This value was further verified by linear plot method.

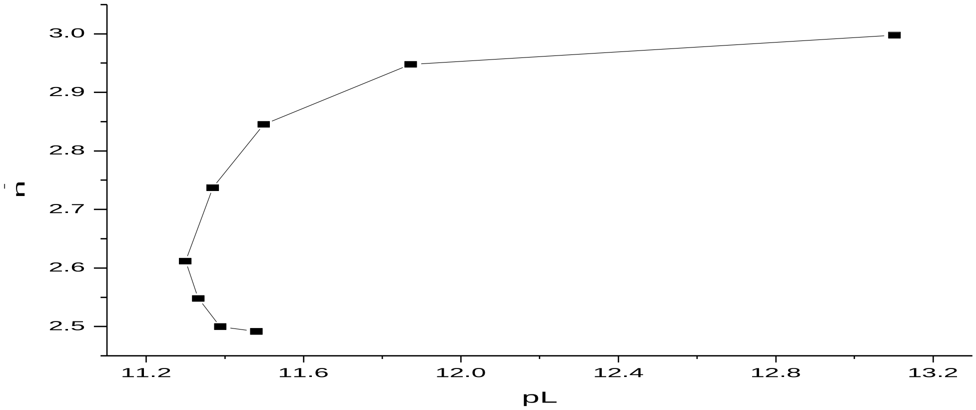


Fig.(5.4.2)Metal-ligand formation curve $\log K_3$=11.382

5.4.1.3-Linear plot method:

Plotting of pL versus log (n^- -2)/(3-n^-), $\log K_3$ equal to point of intersect of the curve with x-axis (pL) figure (5.4.3). The value found, $\log K_3$=11.382 the value was in a good agreement with the value obtained by point-wise calculation method. This value was further verified by Henderson's Hasselbalch's equation.

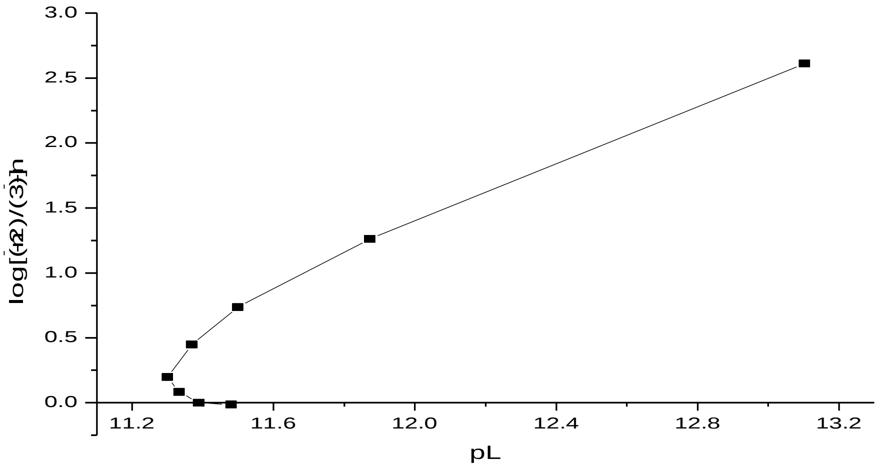


Figure (5.4.3) linear plot method $\log K_3$ = 11.382

5.4.1.4-Henderson's Hasselbalch's equation: (zirconium propanoate)

This equation is used if there is only one complex exists in a solution, in addition to its other limitations. When N=3 the equation becomes:

$$\log(\frac{n^{-}-2)}{(3-n^{-})} = \log K_3 + \log[L]$$

The value of $\log K_3$ has taken as an average of the left hand side values of the equation. The value found, $\log K_3$=11.5125 table (5.4.4).

Table (5.4.4) Henderson's equation $\log K_3$ average value=11.5125

pL	n^{-}	log[L]	$\log\frac{(n^{-}-2)}{(3-n^{-})}$	logK3
3.5936	2.4881	-11.4807	-0.0207	11.4600
3.6022	2.4974	-11.3885	-0.0045	11.3840
3.6465	2.5456	-11.3325	0.0795	11.4120
3.7132	2.6101	-11.2990	0.1944	11.4934
3.8822	2.7356	-11.3686	0.4443	11.8129
4.1123	2.8442	-11.4992	0.7340	12.2332

Table (5.4.5) Stability constants of Zr-propanoic acid obtained.by four methods

Method	$\log K_3$
Pointwise method	11.5165
Half integral method	11.382
Linear plot method	11.382
Henderson' equation	11.5125

5.5/ Zirconium-citric acid system.

Table (5.5.1). The titration resdings of acid, acid + ligand and acid + ligand + metal ions (Zr^{+4}). $N^0 = 0.525M$, $E^0 = 6.1465\times10^{-3}$ M , $T_{Cl} = 5\times10^{-5}$ M , $T_{cm} = 1.25\times10^{-5}$ M , $V^0 = 200 cm^3$, $u^0 = 5\times10^{-3}$, $t = 3.65^0 C$

Vol. of alkali added	Acid	Acid +ligand	Acid+ligand +metal ion	Volume of alkali added	Acid	Acid+ligand	Acid+ligand+ metal ion
0.0	2.38	2.39	2.31	2.7	11.88	6.14	4.38
0.1	2.40	2.40	2.29	2.8	11.91	6.50	4.71
0.2	2.42	2.42	2.31	2.9	11.94	6.95	5.06
0.3	2.44	2.44	2.32	3.0	11.97	9.26	5.46
0.4	2.47	2.46	2.33	3.1	12.00	10.39	5.82
0.5	2.50	2.48	2.35	3.2	12.02	10.85	6.14
0.6	2.53	2.51	2.37	3.3	12.05	11.14	6.89
0.7	2.57	2.54	2.39	3.4	12.07	11.32	6.93
0.8	2.62	2.58	2.41	3.5	12.09	11.46	7.95
0.9	2.68	2.62	2.43	3.6	12.11	11.56	9.81
1.0	2.75	2.66	2.46	3.7	12.13	11.64	10.44
1.1	2.84	2.72	2.48	3.8	12.15	11.70	10.83
1.2	2.95	2.78	2.51	3.9	12.17	11.76	11.08
1.3	3.13	2.85	2.55	4.0	12.18	11.81	11.25
1.4	3.45	2.93	2.58	4.1	12.20	11.85	11.38
1.5	5.50	3.03	2.63	4.2	12.22	11.89	11.48
1.6	10.40	3.15	2.67	4.3	12.23	11.93	11.56
1.7	10.82	3.29	2.72	4.4	12.24	11.96	11.63
1.8	11.13	3.47	2.78	4.5	12.26	11.99	11.69
1.9	11.31	3.70	2.85	4.6	12.27	12.02	11.74
2.0	11.45	3.97	2.93	4.7	12.28	12.05	11.78
2.1	11.54	4.26	3.03	4.8	12.29	12.07	11.83
2.2	11.62	4.55	3.14	4.9	12.31	12.10	11.86
2.3	11.69	4.83	3.29	5.0	12.32	12.12	11.90
2.4	11.74	5.18	3.47	5.1	12.33	12.14	11.93
2.5	11.79	5.50	3.74	5.2	12.34	12.16	11.96
2.6	11.84	5.82	4.06	5.3	12.35	12.18	11.99

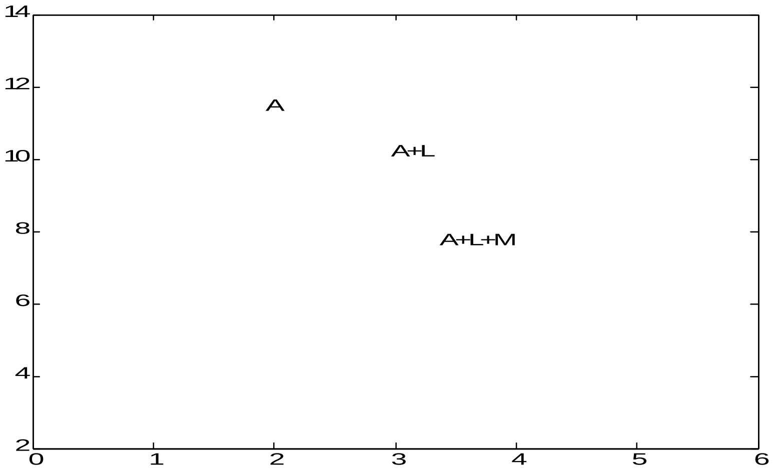


Fig. (5.5.1) plotting of three sets of solutions versus pH

Table (5.5.2) Alkali volume required to bring three sets of solutions to same pH

B	V1	V2	V3	B	V1	V2	V3
2.4	0.1000	0.1000	0.7500	7.2	1.5366	2.9108	3.4265
2.5	0.5000	0.5667	1.1667	7.3	1.5388	2.9152	3.4363
2.6	0.7600	0.8500	1.4400	7.4	1.5409	2.9195	3.4461
2.7	0.9286	1.0667	1.6600	7.5	1.5431	2.9238	3.4559
2.8	1.0556	1.2286	1.8286	7.6	1.5453	2.9281	3.4657
2.9	1.1546	1.3625	1.9625	7.7	1.5474	2.9325	3.4755
3.0	1.2278	1.4700	2.0700	7.8	1.5496	2.9368	3.4853
3.1	1.2833	1.5583	2.1636	7.9	1.5517	2.9411	3.4951
3.2	1.3219	1.6357	2.2400	8.0	1.5539	2.9455	3.5027
3.3	1.3531	1.7056	2.3056	8.1	1.556	2.9498	3.5081
3.4	1.3844	1.7611	2.3611	8.2	1.5582	2.9541	3.5134
3.5	1.4024	1.8130	2.4111	8.3	1.5603	2.9584	3.5188
3.6	1.4073	1.8565	2.4482	8.4	1.5625	2.9628	3.5242
3.7	1.4122	1.9000	2.4852	8.5	1.5647	2.9671	3.5296
3.8	1.4171	1.9370	2.5188	8.6	1.5668	2.9714	3.5349
3.9	1.4220	1.9741	2.5500	8.7	1.5690	2.9758	3.5403
4.0	1.4268	2.0104	2.5813	8.8	1.5711	2.9801	3.5457
4.1	1.4317	2.0448	2.6125	8.9	1.5733	2.9844	3.5511
4.2	1.4366	2.0793	2.6438	9.0	1.5754	2.9887	3.5565
4.3	1.4415	2.1138	2.6750	9.1	1.5776	2.9931	3.5618
4.4	1.4463	2.1483	2.7061	9.2	1.5797	2.9974	3.5672
4.5	1.4512	2.1828	2.7364	9.3	1.5819	3.0035	3.5726
4.6	1.4561	2.2179	2.7667	9.4	1.5841	3.0124	3.5780
4.7	1.4610	2.2536	2.7970	9.5	1.5862	3.0212	3.5833
4.8	1.4659	2.2893	2.8257	9.6	1.5884	3.0301	3.5887
4.9	1.4707	2.3200	2.8543	9.7	1.5905	3.0389	3.5941
5.0	1.4756	2.3486	2.8829	9.8	1.5927	3.0478	3.5995
5.1	1.4805	2.3772	2.9100	9.9	1.5948	3.0566	3.6143
5.2	1.4854	2.4063	2.9350	10.0	1.5970	3.0655	3.6302
5.3	1.4902	2.4375	2.9600	10.1	1.5991	3.0743	3.6460
5.4	1.4951	2.4688	2.9850	10.2	1.6088	3.0832	3.6619
5.5	1.5000	2.5000	3.0111	10.3	1.6235	3.0920	3.6778
5.6	1.5022	2.5313	3.0389	10.4	1.6382	3.1022	3.6937
5.7	1.5043	2.5625	3.0667	10.5	1.6530	3.1239	3.7154
5.8	1.5065	2.5938	3.0945	10.6	1.6677	3.1457	3.7410
5.9	1.5086	2.6250	3.1250	10.7	1.6824	3.1674	3.7667
6.0	1.5108	2.6563	3.1563	10.8	1.6971	3.1891	3.7923
6.1	1.5129	2.6875	3.1875	10.9	1.7258	3.2173	3.8280
6.2	1.5151	2.7167	3.2172	11.0	1.7581	3.2518	3.8680
6.3	1.5172	2.7445	3.2457	11.1	1.7904	3.2862	3.9118
6.4	1.5194	2.7722	3.2743	11.2	1.8389	3.3334	3.9706
6.5	1.5216	2.8000	3.3023	11.3	1.8945	3.3889	4.0385
6.6	1.5237	2.8222	3.3250	11.4	1.9644	3.4572	4.1201
6.7	1.5259	2.8445	3.3477	11.5	2.0557	3.5401	4.2251
6.8	1.528	2.8667	3.3705	11.6	2.1751	3.6501	4.3573
6.9	1.5302	2.8889	3.3932	11.7	2.3202	3.8002	4.5202
7.0	1.5323	2.9022	3.4069	11.8	2.5202	3.9802	4.7402
7.1	1.5345	2.9065	3.4167	11.9	2.7670	4.2252	5.0003

5.5.1-Metal-ligand stability constant: (zirconium citrate)

5.5.1.1-Point-wise calculation method:

Metal-ligand titration curve crossed over ligand titration curve at pH 2.4 table (5.5.2). The values of n^- extended between 1.1649 and 2.8752 indicating formation of 1:2 complex only, since ligand is tribasic and n^-s value start with value ≥1. The value of $\log K_2$ deduced from table (5.5.3) and the correct value taken as an average. This value was further verified by half integral method.

Table (5.5.3) Stability constants of Zr-citrate $\log K_2$ average value = 7.5441

V2	V3	n^-	.pL	$\log\frac{(n^- -1)}{(2-n^-)}$	$\log K_2$
0.8500	1.4400	1.0892	11.2928	-1.0092	10.2837
1.0667	1.6600	1.1274	11.0021	-0.8357	10.1664
1.2286	1.8286	1.1649	10.7112	-0.7045	10.0067
1.3625	1.9625	1.1910	10.4177	-0.6270	9.7907
1.4700	2.0700	1.2179	10.1245	-0.5549	9.5696
1.5583	2.1636	1.2560	9.8341	-0.4633	9.3708
1.6357	2.2400	1.2880	9.5423	-0.3930	9.1492
1.7056	2.3056	1.3146	9.2492	-0.3383	8.9109
1.7611	2.3611	1.3378	8.9554	-0.2922	8.6631
1.8130	2.4111	1.3678	8.6634	-0.2353	8.4281
1.8565	2.4482	1.3939	8.3705	-0.1871	8.1834
1.9000	2.4852	1.4215	8.0781	-0.1375	7.9406
1.9370	2.5188	1.4508	7.7863	-0.0858	7.7005
1.9741	2.5500	1.4754	7.4933	-0.0428	7.4505
2.0104	2.5813	1.5028	7.2013	0.0049	7.2062
2.0448	2.6125	1.5339	6.9105	0.0590	6.9695
2.0793	2.6438	1.5669	6.6206	0.1169	6.7375
2.1138	2.6750	1.6014	6.3314	0.1787	6.5101
2.1483	2.7061	1.6379	6.0432	0.2459	6.2891
2.1828	2.7364	1.6739	5.7555	0.3152	6.0708
2.2179	2.7667	1.7113	5.4692	0.3917	5.8609
2.2536	2.7970	1.7504	5.1850	0.4781	5.6631
2.2893	2.8257	1.7868	4.9026	0.5672	5.4698
2.3200	2.8543	1.8324	4.6284	0.6962	5.3246
2.3486	2.8829	1.8834	4.3653	0.8794	5.2447
2.3772	2.9100	1.9318	4.1175	1.1356	5.2531
2.4063	2.9350	1.9746	3.8942	1.5845	5.4786

5.5.1.2-Half integral method

Construction of metal-ligand formation curve by plotting n^- against pL, from which the stability constant of the chelate is deduced. $\log K_2$= 7.16, figure (5.5.2). This value was further verified by linear plot method.

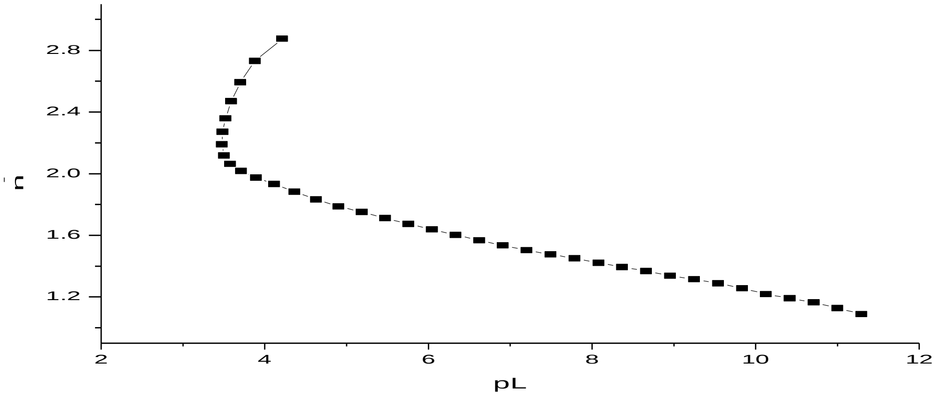


Figure (5.5.2) Metal-ligand formation curve $\log K_2=7.16$

5.5.1.3-Linear plot method:

Plotting of log $(n^- -1)/(2-n^-)$ versus corresponding pL, value found was, $\log K_2=7.16$, figure (5.5.3). The value was in good agreement with the values obtained by two previous methods. The value was further verified by Hinderson's equation.

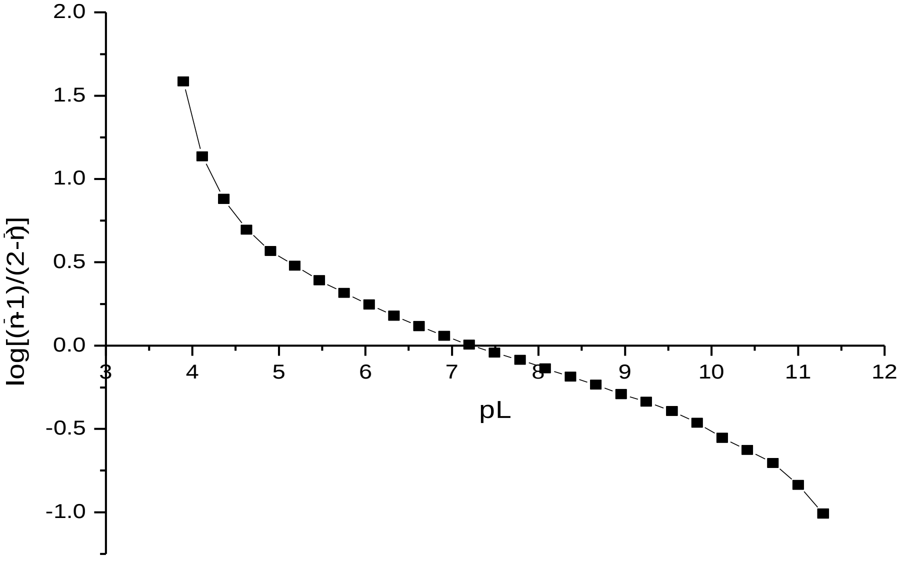


Fig. (5.5.3) Stability constant of Zr-Citrate $\log K_2 =7.16$

5.5.1.4-Henderson and Hesselbalch's equation:

Table (5.5.4) Stability constants of Zr-citrate, $\log K_2$ average value = 7.5441

pL	L	n^{-}	Log[L]	$\log\frac{(n^{-}-1)}{(2-n^{-})}$	$\log K_2$
11.2928	5.1E-12	1.0892	-11.2928	-1.0092	10.2837
11.0021	10.0E-12	1.1274	-11.0021	-0.8357	10.1664
10.7112	1.9E-11	1.1649	-10.7112	-0.7045	10.0067
10.4177	3.8E-11	1.1910	-10.4177	-0.6270	9.7907
10.1245	7.5E-11	1.2180	-10.1245	-0.5549	9.5696
9.8341	1.5E-10	1.2560	-9.8341	-0.4633	9.3708
9.5423	2.9E-10	1.2880	-9.5423	-0.3930	9.1492
9.2492	5.6E-10	1.3146	-9.2492	-0.3383	8.9109
8.9554	1.1E-09	1.3378	-8.9554	-0.2922	8.6631
8.6634	2.2E-09	1.3678	-8.6634	-0.2353	8.4281
8.3705	4.3E-09	1.3939	-8.3705	-0.1871	8.1834
8.0781	8.4E-09	1.4215	-8.0781	-0.1375	7.9406
7.7863	1.6E-08	1.4508	-7.7863	-0.0858	7.7005
7.4933	3.2E-08	1.4754	-7.4933	-0.0428	7.4505
7.2013	6.3E-08	1.5028	-7.2013	0.0049	7.2062
6.9105	1.2E-07	1.5339	-6.9105	0.0590	6.9695
6.6205	2.4E-07	1.5669	-6.6205	0.1169	6.7375
6.3314	4.7E-07	1.6014	-6.3314	0.1787	6.5101
6.0432	9.1E-07	1.6379	-6.0432	0.2459	6.2891
5.7555	1.8E-06	1.6739	-5.7555	0.3152	6.0708
5.4692	3.4E-06	1.7113	-5.4692	0.3917	5.8609
5.1850	6.5E-06	1.7504	-5.1850	0.4781	5.6631
4.9026	1.3E-05	1.7868	-4.9026	0.5672	5.4698
4.6284	2.4E-05	1.8324	-4.6284	0.6962	5.3246
4.3653	4.3E-05	1.8834	-4.3653	0.8794	5.2447
4.1175	7.6E-05	1.9318	-4.1175	1.1356	5.2531
3.8942	0.00013	1.9746	-3.8942	1.5845	5.4786

Table (5.5.5) Stability constants of Zr-citrate obtained by four methods.

Method	$\log K_2$
Point wise calculation method	7.5441
Half integral method	7.16
Linear plot method	7.16
Hesselbalch’s equation	7.5441

CHAPTER SIX

Conclusion and Recommendation

Conclusion

The three graphical methods, half integral method, linear plot method and least squares method in addition to the two algebraic ones (point-wise and Henderson's equation) give nearly the same results for each chromium, titanium and zirconium carboxylates systems, and no appreciated difference between the stability constants except in least squares method, the difference is very small and always ≤ 0.3, specially in K_{n-1}, where the error accumulated. This method has many restrictions which can be found in literature.

Chromium with these carboxylic acid ligands forms 1:1and 1:2 complexes except with citric acid, it forms 1:1 complex only. The values of stability constants were always in order of $\log K_1 > \log K_2$ this indicates that the complexes form simultaneously, and may implies no specific electronic or steric phenomenon. The difference between $\log K_1$ and $\log K_2$ of chromium acetate complexes is lesser than of propanoate complexes, this smaller difference may be due to that chromium acetate 1:2 forms trans structure with water, and chromium propanoate may be in cis structure with water. The difference of stability constants values of 1:1 and 1:2 chromium oxalate complexes nearly as same as chromium acetate complexes (0.5). In chromium oxalacetate the difference between $\log K_1$ and $\log K_2$ bigger enough (4.2201), ($\log K_2$=10.2385 and $\log K_2$=6.0183), this indicates the steric hindrance to the linking of the secondary ligand to the metal ion, which make me thought of the long carbon chain of oxalacetic acid in respect to acetic acid, oxalic acid and propanoic acid, and this elucidate why chromium ion forms 1:1complex only with citric acid.

The strongest chelating agent of these ligands with chromium as it was found were oxalacetic acid and citric acid respectively, the first is bidentate as the second is tridentate ligand.

Metal ion solutions used in present study were very dilute; hence there was no possibility of formation of polynuclear complexes.

Titanium forms 1:2 and 1:3 complexes with the ligands acetic acid, oxalic acid and propanoic acid. The difference between stability constants of these complexes was ≤1 this implies that 1:2 and 1:3 complexes found in the same time in the solution.

But with comparative long carbon chain ligands, oxalacetic acid and citric acid titanium forms only 1:1 chelates.

The strongest chelating agents of these ligands under the study with titanium were oxalacetic acid and citric acid.

Zirconium ion forms only one complex with all ligands under investigation, except with acetic acid forms two 1:3 and 1:4 complexes, the difference between the values of stability constants was unity in all methods employed; this indicates the complexes formed simultaneously and not in step-wise manner. Zirconium forms only 1:3 complexes with propanoic acid and oxalacetic acid, with two remained ligands oxalic acid and citric acid forms only 1:2 complexes. Since oxalacetic acid attached to zirconium metal ion as same as propanoic acid, this implies that oxalacetic acid attached to zirconium as monodentate ligand.

The strongest chelating agent of ligand under study to zirconium were propanoic acid ($\log K_3=11.5165$) and citric acid ($\log K_2=7.5441$).

Now the maximum numbers of ligands under investigation attached to chromium and titanium were two, but zirconium accommodated four ligands as maximum number. Zirconium is a second series transition element.

Always if the complex is alone in the solution would be very stable or the value of stability constant will be high, in addition the chelation will increase the stability of interaction. I stating out of this investigation that, the bidentate ligands is high stable than tridentate ones, example for this, titanium oxalacete $\log K_1= 9.76$, and titanium citrate $\log k_1= 7.26$

The question should be asked "what method should be use, and which should give the most accurate value". Each of these methods employed above seen satisfactorily to give the answer, with difference ≤ 0.3, for a system where $N \leq 3$ (N is the possible coordination sites).

The most important thing in this work is that, matlab program used for determination of the volume of alkali that required to bring the three sets of solutions to the same pH, which is important for determination of formation functions n_A, n^- and pL.

Interaction of metal ion with carboxylic acid shows high dependency on the salt that added to maintain the ionic strength of the medium, so potassium nitrate with nitric acid as free acid is found adequate after many trials, for nitrate ion has very slight complexing tendency, and the competition between nitrate ion and the ligands under study is of minor importance.

Half integral method and linear plot method, give nearly unique answer for K_n values, whereas common fault is that, as n- increases, K_n becomes more prone to error.

Differences in magnitude between K_n values obtained by five methods, are due solely to errors inherent in the experimental data or non-rigorous data treatment, that is, least squares and other graphical methods fit to curves with correlated errors.

In half integral method and least squares method, one treat all data gained from the experiment, that allow one to say the output of these methods is more accurate than others.

In least squares method the slope and intercept obtained by adding trend line and display equation on chart is less accurate than that obtained by LINEST in excel program, or that obtained from origin program (view- result log or fit linear).

Recommendation:

Potentiometic titration is the most reliable technique for determination of stiochiometries and stability constants of complexes, if the external factors are well adjusted, such that temperature, ionic strength, concentration. Spectrophotometric methods, such as continuous variations method, mole ratio method, can applied for the same purpose, but colored transition metal that formed colored complexes, in need of special treatment for to calculate the absorbance of the complex only. Spectrophotometric methods better to be use as confirmation experiments. In each of these two techniques a very dilute solutions must be used.

Potentiometric titration, having more than ever methods for determination of stability constants,

The apparatus and tools for performing the potentiometic titration experiments are cheaper and obtainable, than that of spectrophotometric experiments.

Potentiometric methods give convincing results, if the data derived rigorously.

References

Abdalazeem, Abdeen, Omar. (2005) Determination of Stoichiometries and Stability Constants of Chromium with Nitrogen Containing Ligands. Thesis submitted in fulfillment of requirement of Khartuom University for degree of M.Sc.Khartoum. U of K.

Abdulbaset, A. Zaid, Mazahar. Farooqui, D.M. Janrao. (2012) Study of stability constant of biological active molecules (drug) using potentiometric titration technique. J. of chem. boil. phys. Sc. 2 (1). P. 67-81.

A.K. Maldhure. S.S. Agarkar. R.K. Taywade. R.S. Wankhade. (2012) Metal-ligand stability constants of Co(Ⅱ), Ni(Ⅱ) and Cu(Ⅱ) metal ion complexes with N-(5-methyl-hydroxyacetophenone)-N-(2-hydroxyacetophenone). J. Chem. pharm. Res. 4 (8). P.3865-3868.

Alebert, Zlatkis. Eberhard, Breitmale. Gunther, Jung. (1973) A concise Introduction to Organic Chemistry. United States of America: McGraw Hill..

A. Leslie, Neal. (1971) Chemistry and Biochemistry a Comprehensive Introduction. United States of America: McGraw-Hill book company.

Ali, Hamoud, Ali. (1987) determination of stoichiometries and stability constants of complexes of propanoic, ß-chloropropanoic, succinic and ß- aminopropanoic acids, with Cu^{2+}, Ni^{2+} and Co^{2+}. Thesis submitted in fulfillment of requirement of Khartuom University for degree of Doctor of Philosophy. Khartoum: U of K.

Andrew, pienaar. (2005) Metal Carboxylate Complexes Relavant to the Fischer-Tropsch synthesis. Thesis submitted in fulfillment of requirement of Stellenbosch University for degree Ms.C. Stellenbosch: Stellenbosch university

Anil, B. Naik. Maroti, Narwade. (2008) Studies on influence of dielectric constants on complex equilibria between substituted pyrazalines and lanthanide metal ions pH-metrically. Amer.-Euras. scient. Res. 3(2). P. 212-216.

Anjani, Kumar, Mishra. Prem, Mohan, Mishra. Sunil, K., Misra. (2011). Equilibrium studies on bivalent transition metal chelates with biologically active schiff's base of heterocyclic aldehydes. Ras. J. Chem. 4(2). P. 303-319.

Ashwini, kumar, Ashok. Kumar, Malik. (2007) Potentiometric studies on the complexes of Cu(Ⅱ), Cd(Ⅱ), Co(Ⅱ), Ni(Ⅱ), Pb(Ⅱ), and Zn(Ⅱ) with Gabapentin. Euras. analy. Chem. 2(2). P. 1-6.

Avinash, Ramteke. Marutil, Narwade. (2013) Studies of stability constants of complexes of chlorosubstituted pyrazoles and pyrazoline with Cu(Ⅱ), Ni(Ⅱ), Co(Ⅱ) and Nd(Ⅱ) metal ions in 70% dioxane- water mixture at 0.1 ionic strength. Arch. of appl. Sc. 5 (1). P. 231-237.

BENTHAMSCIENCE. (2003) Propanoic Acid. [Online]. Avalable from: http://benthamscience-com10pen/tolsj/articles,pdf. [Accessed: 2013].

Bentor, Yinon. (2015). Chemical Element.com - Titanium.[Online]. [Online]. Modified 31 march 2007. Available from www.chemicalelements.com/elements/**ti**.html, [Accessed: 2013]

Boner, George,M. & Pardue, Harry,L. (1996). Chemistry An Experimental Science. 2nd edition. John wiley & sons Inc.

Brandes, E. A. Greenaway, H. T. & Stone, H. E. N. (1956). Ductility in Chromium. Nature

Bruce, H. Mahan. (1975) University Chemistry. 3rd edition. Addison-Wesley publishing.

Cary, D. Christian. (1986) Analytical Chemistry. 4th. New York. John Wiley and Sons.

Charles E. Mortimers. (1986). Chemistry. 6th edition. U.S.A. Wadsworth Inc.

CHEMISTRY 3211 COORDINATION CHEMISTRY PART 3. (2000). Molecular Orbt- tal Diagram for CO**.** [Online]. Available from: www.chem.mun.ca/homes/cmkhome/Chemistry%203211%20Pt3.pdf. [Accessed: 2012].

Chris, J. Jones. (2001) D and F Block Chemistry. Royal Society Chemistry.

CLASSIFICATION OF STRUCTURE IN TERMS OF COORDINATION NUMBER. (2005)

Coordination number (2). [Online]. Available From:
www.chem.purdue.edu/gchelp/cchem/struct2.html. [Accessed: 2014]

Cotton, Simon. (2006) Lanthanide and Actinide Chemistry. John Wiley & Sons Ltd.

C. R. Landis, & F. Weinhold. (2007) Valence and extra-valence orbitals in main group and transition metal bonding. Journal of Computational Chemistry 28 (1). P. 198–203.

Dennis, J. K. & Such, T. E. (1993) History of Chromium Plating. Nickel and Chromium Plating. Woodhead. P. 9–12.

Dodle, Douglas. Darl H. Daniel. (1995) Concept and Model of Inorganic Chemistry. 2nd edition. united states. Xerox college.

Dr. Paul, G. Hages. (2006) M.O. diagrams for O_2 and N_2. University of Lethbrige

Emsley, John. (2001) Chromium Nature's Building Blocks. An A-Z Guide to the Elements. Oxford, England, UK. Oxford University Press. P. 495–498

E.W. Abel, G.W. Kinson. F.G.A.Stone. (1982) Comprehensive Organometalic Chemistry Sir Geoffrey Wikinson, FRS.

Fawcett, Eric. (1988) Spin-density-wave antiferromagnetism in chromium. Reviews of Modern Physics.

F. Albert, Cotton. & Geoffrey, Wilkinson. (1972) Advanced Inorganic Chemistry 3rd edition. John wiley & sons.

F. Albert, Cotton., et al. (1995). Basic Inorganic Chemistry. 3rd edition. John Wiley and sons Inc.

F. Gharib. A. Shamel. S. Mohajeri. (2010) Russ. J. Inorg. Chem. Vol. 55. P. 1651

Figgis, B.N., Lewis, J. Lewis, J. & Wilkins, R.G. ((1960) The Magnetochemistry of Complex Compounds. Modern Coordination Chemistry. New York: Wiley Interscience.

Forrest, A. L. (1981) Effects of Metal Chemistry on Behavior of Titanium in Industrial Applications. Industrial Applications of Titanium and Zirconium. p. 112

Fred, Basol. & Ronald, C. Johnson. (1986). Coordination Chemistry. 2nd edition. British Library Cataloguing in Publication Data.

F.R.,‘Hartley. C. Burgess, R.M. Alcock. (1980) Solution equilibria. New York. John Wiley and sons.

F. J. C. Rossotti. H. S. Rossotti. (1955) Graphical methods for determining equilibrium constants.1- system of mononuclear complexes. Ac. chem. scandinavica. Vol.9, 1166-1176.

Gaafar, Abd Elatief, Hamid. (2000) Determination of Stoichiometries and Stability Constants of Copper (Ⅱ) and Nickel (Ⅱ) Complexes with some Amino Acids. Tthesis submitted in fulfillment of requirements of Khartoum University for degree M.Sc. Khartoum: Uof K.

Guertin, Jacques, Jacobs. James, Alan. & Avakian, Cynthia. (2005). Chromium (VI) Handbook: CRC Press. P. 7–11

Gurdeep, Raj. (1986) Advance inorganic chemistry-Ⅱ. [Online]. Ninth thoroughly revised 2004. Twelfth edition. Satyendra Rastogi “Mitra” p.67.(E- book). Available from: Book code : 277-12 . [Accessed ed. 2010]

Hala, Ali, Shuwail. (1995) Study in Mixed Ligand Complexes. A thesis submitted in partial fulfillment of the requirements for King Abdul Aziz University for the degree of M.Sc. Jadda: King Abdul Aziz University.

Holleman, Arnold, F. Wiberg, Egon. & Wiberg, Nils. (1985) Chromium. Lehrbuch der Anorganischen Chemie. German. Walter de Gruyter. P. 1081–1095.

Haxhillazi, Gentiana. (2003) Preparation, Structure and Vibrational Spectroscopy of

Tetraperoxo Complexes of Cr^{V+}, V^{V+}, Nb^{V+} and Ta^{V+}. Thesis submitted in fulfillment of requirement of University of Siegen. For degree of Doctor of Philosophy. Siegen: University of Siegen.

Jack, Barrete. (1991), understanding inorganic chemistry. Ellis harwood limited.

Julius, B. Cohen. (1930). Practical Organic Chemistry. New York: Macmillan

Kalleey, Csilla. (2005) Transition Metal Complexes of Amino Acid and Peptide Derivatives containing Caboxylate and Imidazole side chains. Thesis submitted in fulfillment of requirement of University of Debrecen. for degree of Doctor of Philosophy. Debrecen: University of Debrecen.

Karen, Pavel. McArdle, Patrick. & Takats, Josef. (2014) Toward a comprehensive definition of oxidation state, (IUPAC Technical Report). *Pure and* Applied Chemistry 86 (6).

Kotaś, J. & Stasicka, Z. (2000) Chromium occurrence in the environment and methods of its speciation. Environmental Pollution 107 (3). P.263–283.

Lames E. Hukeey et al. (1993) Inorganic Chemistry Principle of Structure and Reactivity. 4th edition. Harber Collins colledge.

Lide, David, R. (2008) Zirconium. CRC Handbook of Chemistry and Physics 4. New York: CRC Press.

Louis, Meites. (1981) An Introduction to Chemical Quilibrium and Kinetics. Pergamon series in analytical chemistry. Vol. 1. Hungary. Franklin printing house.

MARRIAN. (2000) Oxalacetic Acid. [Online]. Available from: http://www.marrian-websTer.com. [Accessed: 2014].

Martin, V. Dutton, Christine, S. Evans. (1996) Oxalate Production by fungi, it's role in pathogenicity and ecology in soil environment. Canadian journal of microbiology. Vol.42. P. 881-895.

M. Abbo. (1991) The interaction of some β-substitued carboxylic acids with Cu (Ⅱ), Ni(Ⅱ) and Co(Ⅱ).Thesis submitted in fulfillment of requirement of Khartuom University for degree of Doctor of Philosophy. Khartoum: U of K.

Maxwell J. C. (1988) An Elementary Treatise on Electricity, 2nd Oxford, England: Clarendon Press.

METAL PROGRAM. (2003) Physical Properties of Chromium. [Online]. Last revised Tuesday 07/Jan./2003. Available from: http://www.toxic. [Accessed: 2012].

Minaxi, Maru. M.K. Shah. (2011) Synthesis and physic-chemical studies of some divalent transition metal complexes of 2-(2'-chloro-6'-substituted quinoliny)-1H-benzo[d]imidazole ligands. J. Chem. Res. 2 (2). P. 14-27.

Mohammed.H.Al-hazmi. (2005) Synthesis and Characterization and Application of Zirconia and Sulfated Zirconia from Single source and Precursors. Thesis submitted in patial fulfillment of requirement of College of the Oklahoma State University for degree of Doctor of Philosophy. Oklahoma: Oklahoma state university.

Mona. (2000) Chromium Complexes. Thesis Submitted in Fulfillments of the Requirements of Khartoum University for degree of Master. Khartoum: (U of K).

Praveen P. Singh et al. J. Indian Soc. (2009) Determination of stability constants of metal-Methionine & and metal-methionine NTA complexes. Vol.86. P.83-86.

Quintus, Fernando. & Michael, D. Ryan. (1982) Calculation in Analytical Chemistry. New York: Harcourt Brace Jovanovich.

Ram, Nayan. & Arun, K. Dey. (1978) pH-metric titration technique for Study of metal complexes in solution. J. of inorganic& nuclear Chemistry 40(2). P. 289-293.

R.H. Petrucci, W.S. Harwood & F.G. Herring. ((2002). General Chemistry.8th edition, Prentice-Hall.
R. K. Lonibala. T. R. Rao. R. K. B. Devi. J. (2006) Chem. Sci., , 118(4). P. 227-334
Robert Grabtree. (1988) Organometalic Chemistry Of Transition Metal. John Wiley and sons Inc.
Santosh, D. Deosarkar. Ashok, B. Kalambe. Vijay, J. Thakare. Shivraj, G. Wanale. Vinay, V. Hiwase. (2011) Potentiometric studies of electrolyte effects on complex equilibria of some substituted 5-(2-hydroxy phenyl) Pyrazoles. Der pharma chemic. 3 (6). P. 75-83.
Sayyed, Hussain, Abdul Rahim, Mazahar, Farooqui. (2011) Studies of binary complexes of metal ions with mandelic acid by potentiometry. Chem. J. 02 (6). P. 206-209.
S.Chaberek Jr. & A. E. Martell (1952) Stability of Metal Chelates Iminodiacetic and Iminodipropionic acids . J. Amer. Chemical Soc. 74(20). P. 5052-5056
Schläfer, H. L.& Gliemann, G. (1969) Basic Principles of Ligand Field Theory. New York. Wiley Interscience.
Steven, S. Zumdah. & Susan, A. Zumdah. (2003) Chemistry, 6th edition. New York: Houghton mifflim company.
Stwertka, Albert. (1998). Titanium. Guide to the Elements . Oxford University Press
TRANSITION ELEMENTS. (2007) Oxidation states. [Online]. Last modified 2011. Available from: www.4college.co.uk/a/ss/varoxidation.php. (Accessed: 2014)
Vogel, A.I. (1978) A text Book of Quantitative Inorganic Analysis. 4th edition. London: Longman.
Wells, A.F. (1948) Structural Inorganic Chemistry. Oxford Canadian press.
WIKIPEDIA. (2003) Citric Acid.[Online]. Available from:
http://en.wikipedia.org/wiki/Citric_acid. [Accessed: 2013].
Winter, Mark. (2007) Electronegativity (Pauling). University of Sheffield. Retrieved
2008-03-05.
William, L. Masterton. Emil J. Slowinski. Conrad L. Stanitski. (1985) Chemical Principles. 6th edition. U.S: CBS college publishing.
William, L. Jolly. (1991). Modern Inorganic Chemistry. 2nd edition. Singapore: Mc.Graw-Hill co.