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Some properties of some rare-earth and transition metal dihydroxycarboxylates

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Some properties of some rare-earth and transition metal dihydroxycarboxylates

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Santi Kulprathipanja

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I. INTRODUCTION

Because the rare earths (those elements of atomic number 57 through 71, as well as 21 and 39) all exist as trivalent ions in solution and have a great affinity for water, their ions are protected by a tightly adhering hydrated layer. This layer makes the properties of the rare-earth ions even more alike; so, the separation of the pure individual rare-earth elements is very difficult. A great deal of research on separating these elements by fractional means was done over 140 years (1794 to 1940). During that period, all the naturally occurring rare earths were isolated, and a great deal about their basic properties was learned. During World War II, ion-exchange methods were developed at the Ames and Oak Ridge Laboratories for separating rare earths, and better than 99.99% pure rare earths have become commercially available since that time.

Although pure rare-earth elements have been isolated readily the past 20-30 years, much of their chemistry is still in question compared to the chemistry of the transition metals. Chemistry of rare earths in solution is one of the least understood subjects. Complex ion formation is highly important with these cations, but the governing principles are not as clearly decipherable as is the case with the transition metals. There are several reasons for this. In the first place, the well-shielded (by 5s and 5p electrons) 4f electrons of lanthanides precludes the probability of hybrids that would lead to covalent bonding involving 4f orbitals. A further reason lies in the relatively large sizes of the cations. Attractions that the cations have for anions to yield complexes by any kind of ionic association are sharply reduced. The number of known complexes is limited, because only species that can attract these cations as a result of their own small size, large charge, or chelating ability will give strong complexes.

Because of the lanthanide contraction, one should expect a decrease in basicity across the series from lanthanum to lutetium. If only electrostatic character and the lanthanide contraction are considered in the complex formation of rare earths, a monotonic increase in formation constants across the series from lanthanum to lutetium would appear to be axiomatic (the bond strength should increase linearly, or nearly so, from lanthanum to lutetium). In nearly all complex systems which have been studied, this is not strictly the case. Although other factors, such as crystal field effects, thermodynamic considerations and Bjerrum's statistical ratio theory have been invoked to account for the perturbations observed, none satisfactorily elucidates all factors of the various stability trends extant.

Two ligands (α, β-dihydroxyisobutyrate and α, β-dihydroxy-β-methylisobutyrate) are studied in this dissertation. Complex formation between these two chelates and rare-earth cations have been investigated. Hopefully, some questions concerning the dentate character of these ligands, as well as inductive and steric effects of the added functional groups in these two chelates (compared to α-hydroxyisobutyrate and ethylmethylglycolate) why the effects of the lanthanide contraction and bonding character of the why the effects of lanthanide contraction and bonding character of the ligand in rare-earth complexes alone do not explain the observed stability trends. The formation constant data obtained from studies in this research fill some holes in the literature regarding the solution chemistry of lanthanons. Such data are of particular importance in predicting the separability of the lanthanons by ion-exchange chromatographic techniques.

The well-known Irving-Williams order of stabilities and a linear relationship between the acidity of the donor group and chelate stability have been found to hold for most data for divalent transition metals found in the literature. It was intended to further test these two theories using the α-hydroxyisobutyrate, α,β-dihydroxyisobutyrate and α,β-dihydroxy-β-methylisobutyrate ligands. Consequently, complex formation between some divalent transition metals and these three chelates was also studied. It was hoped that formation constants obtained from this study might shed light on the molecular structures of these complexes in solution.

II. REVIEW OF PREVIOUS WORK

A. Transition Metal Hydroxycarboxylates

1. The Irving-Williams order of stabilities

Mellor and Maley (1, 2) pointed out that the stability of complexes of bivalent transition metal ions with ammonia, ethylenediamine, propylenediamine or salicyladehyde follows the order

$$Cu > Ni > Co > Zn > Cd > Fe > Mn$$

They were not yet certain what factor or factors determined the order of chelate stability for metals in this series. The electronegativity or basicity of the metal was thought to have something to do with species stability (the more basic the metal, the less stable its complexes). If this were so, one should expect to find a correlation between the covalent radii of bivalent transition metals and the stability of the various complexes formed by them. Because the extreme members of the series were concerned, they concluded that the above stability order held, irrespective of the nature of the ligands involved. Their extended sequence has, however, little generality and it fails with, e.g., glycine, alanine, glycylglycine, and several carboxylic acid anions, for which the order is

$$Cu > Ni > Zn > Co > Mn$$

Irving and Williams (3, 4) later showed, however, that the Mellor and Maley order of stability does not hold for some systems. The previously published and current data on complexes formed by bivalent ions of the first transition series were collected and examined critically by Irving and Williams and the order $Mn < Fe < Co < Ni < Cu > Zn$ was found to hold for the stabilities of nearly all such complexes (irrespective of the nature of the coordinated ligand or of the number of ligand molecules involved). This order is now known as "the Irving-Williams order of stabilities." Some of the ligands cited in this case are ethylenediamine, propylenediamine, 1,3-diaminopropane, 1,2,3-triaminopropane, diethylenetriamine, triaminotriethylamine, triethylenetetramine, a great variety of α- and β-aminoacids, nitrilotriacetic acid, ethylenediaminetetraacetic acid, tropolone, 4-hydroxypteridine, and many mono- and dicarboxylic acids. Thus, the Irving-Williams order remains valid for "nitrogen-type", "nitrogen-oxygen-type", and "oxygen-type" ligands.

Irving and Williams suggested that both ionic bonds and covalent bonds were controlling factors in the stability order of metal complexes. Because, if complexes between cations and ligand anions were purely electrostatic in character, a simple relation should exist between their association constants, K, and the radius, r, of the unhydrated ion and its valency, Z. But, from the experimental and calculated values of K for hydroxy-complexes of the bivalent transition metals, it was revealed that these were much more stable than could be accounted for by purely electrostatic forces of attraction. That the increments in stability should increase monotonically along the Irving-Williams series can only mean that some additional stabilizing factor is in operation which increases in extent as one moves along the series; this must be the tendency towards the formation of a covalent bond between metal and ligand. The point was made (by the plots in figure 1) that, while the stability sequence follows the Irving-Williams order for all the ligands represented, the stability increment from metal to metal is greatest for the most polarizable ligand. The respective increments decrease with bidentate

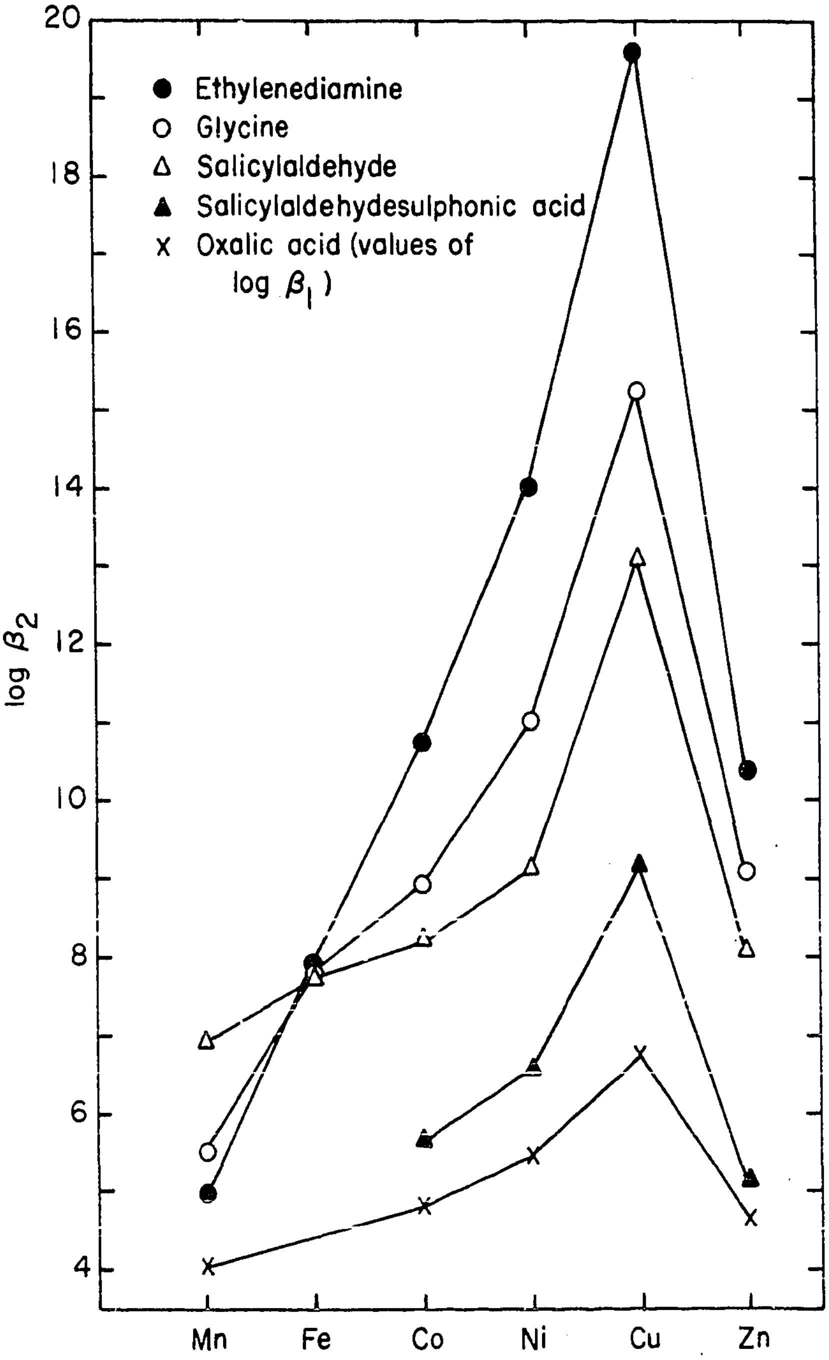


Figure 1. Divalent transition-metal complexes with various types of ligand

ligands as the donor atoms change from N to O (e.g., ethylenediamine) > nitrogen-oxygen-type ligands (e.g., glycine), and > oxygen-oxygen-type ligands (e.g., salicylaldehyde and oxalic acid). Furthermore, the more electropositive the coordinating atom of the ligand, the greater the stability increment from metal to metal. This emphasizes the significance of covalent bonding in determining the stability of complexes. The magnitudes of the electrostatic and covalent interactions were suggested to be dependent upon the reciprocal of the ionic radius (Z^2/r) and the second ionization potential as ($M(gas) \rightarrow M^{+2}(gas) + 2e$) both increase monotonically throughout the series from manganese to copper.

2. The influence of the donor group in complex stability

The linear relationship between the basicity of the donor group (pK_a) and the chelate stability ($\log K_n$) has been found to hold in a large portion of the literature reported so far. Thus, the weaker the acidity of the ligand, the more stable is the chelate compound. Thus, Guns and Verbeek (5) suggested that the stability constants of the α-hydroxyisobutyrate bivalent metal complexes being higher than those for the corresponding lactate complexes could be attributed to the increased inductive effect of the 2-methyl group in α-hydroxyisobutyrate. This effect becomes quite evident in the acid dissociation constants: $K_a = 2.30 \times 10^{-4}$ for lactic acid, $K_a = 1.73 \times 10^{-4}$ for α-hydroxyisobutyric acid. Filipović, et al. (6,7) reported the stability constant of bivalent metal complexes with lactate are greater than for the corresponding glycolate complexes, and again the increased inductive effect of the methyl group in lactate makes the acidity of lactic acid lower than in glycolic acid.

At this point one can see that the values of stability constants of bivalent metal complexes increase in the series glycolate < lactate < α-hydroxyisobutyrate, and the acidity of the three acids considered change in the reverse sequence.

Murakami, et al. (8) found linear relationships between the acidities of the donor groups in four catechols and the stabilities of their chelates with copper(II) and zinc(II). In this case the acidity of both hydroxyl groups in the ligand molecule should be taken into consideration, since both groups are involved in chelate ring formation. The value of ($pK_{H_2L} + pK_{HL}$), as a measure of ligand basicity, decreases in the order: catechol > 4-carboxycatechol > catechol-4-sulfonate > Tiron. The stability order, however, is antiparallel to this order and is found to be in the sequence: Tiron > catechol-4-sulfonate > 4-carboxycatechol > catechol. Substituent groups were considered to play an important role in this case.

Filipović, et al.(6,7) reported the stability constants between divalent transition metals and some monocarboxylate ligands. The ligand acidity, decreases in the order: formic acid > acetic acid > propionic acid, and all the metal complex stabilities considered changed in the reverse sequence.

Steric hindrance influences on formation of metal complexes by a ligand can be overwhelming, by causing a less favorable positioning of the basicity of the donor groups with respect to the available coordinations sites. Roletto, et al. (9) and Ostacoli, et al.(10) illustrated this situation in a case of dicarboxylic acids (cyclopropane-1,1-dicarboxylic, cyclobutane-1,1-dicarboxylic, cyclopentane-1,1-dicarboxylic and cyclohexane-1,1-dicarboxylic acids) with some bivalent transition metal ions.

In this case a bigger ring bearing the donor groups tended to decrease the stability of the complexes. Here the increased inductive effect of the added methylene group in a bigger ring did not increase the stabilities of the metal complexes.

Warnke and Kwiatkowski (11) reported the stability constants of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with propionate, β-hydroxypropionate and α-hydroxypropionate. They showed that the values of the stability constants increased in the series propionate $<$ β-hydroxypropionate $<$ α-hydroxypropionate. From this sequence it follows that the presence of a hydroxyl group in a carbon chain raises appreciably the stability of the compounds being formed. The basicity of the donor ligands changes in the reverse sequence. Both phenomena may be ascribed to the availability of the hydroxyl group in the carbon chain. Situating an -OH at α or β position allows five- or six-membered rings to form, respectively. The former is characterized by a higher stability than the latter. The increase in the values of the observed stability constants clearly points to chelate ring formation involving bidentate ligands.

Patel and co-workers (12, 13) reported some non-relationships between the basicity or steric hindrance of the donor group (see Table 1, in which: 3MeOHAO, 4MeOHAO and 5MeOHAO stand for the 3-methyl, 4-methyl and 5-methyl derivatives of 2-hydroxyacetophenone oxime; and 3MeOHB, 4MeOHB and 5MeOHB stand for the 3-methyl, 4-methyl and 5-methyl derivatives of 2-hydroxybutyrophenone , respectively) and the complex stabilities of divalent transition metal ions (Ni, Cu, Zn). No explanation was given.

Table 1: Metal-ligand stability constants ($\log K_1$) of metal complexes
[Temp. = 40 ± 0.1°C, μ = 0.1M(KNO_3)]

Ligand	Metal			H^+
	Cu	Ni	Zn	
3MeOHAO	11.26	7.53	7.98	11.86
4MeOHAO	10.92	7.50	7.86	11.71
5MeOHAO	11.18	7.49	7.83	11.97
OHB	7.87	5.28	6.00	11.43
3MeOHB	8.55	6.01	7.10	12.19
4MeOHB	7.54	5.88	6.68	11.63
5MeOHB	8.31	5.53	6.38	11.70

3. The ratios of stepwise stability constants

Bjerrum (14) has described this topic in detail, but a brief summation will be given here in order to elucidate the material in this section and elsewhere.

The successive formation constants are defined as

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\ [L]}$$

where M and L are metal and ligand ions, respectively. The ratio of the successive formation constants, or the "total effect":

$$T = \frac{K_1}{K_2}$$

depends on three factors, the statistical term (S), the ligand repulsion effect (E) and the "rest" (everything else) effect (R). The relationship between these factors is

$$T = S \times E \times R.$$

The statistical factor, S, can be estimated from the number of cation association sites and ligand bonding groups, since each formation constant is equal to the rate constant of the forward step over the rate constant of the reverse step. The rate constant of the forward step, in each case, is proportional to the number of sites at which the ligand can bond to the pre-existing complex. The rate constant of the reverse step, in each case, is proportional to the number of ways in which the product complex can lose a ligand to reform the original complex.

If the ligand is monodentate, the coordination number of the cation is N, and n is the number of sites capable of losing a ligand, one can see that the ratio of first formation constant to the second formation constant or S is:

$$S = \frac{(N - n + 1)}{n} \Big/ \frac{(N - n)}{(n + 1)}.$$

If the ligand is polydentate, in order to find the factors proportional to the forward rate constants, one must examine the geometry of each reactant complex to determine the number of sites available to the ligand. This step is facilitated by the use of structural models. The reverse rate constants are always proportional to the number of ligands present in the product complex. Such statistical ratios have been calculated for square planar and tetrahedral models, and together with ratios for higher coordination which were calculated by Powell (15), are listed in Table 2.

Table 2: Statistical ratios of stepwise formation constants

Coordination number	Geometry configuration	dentate charactor	S
10	square antiprism (D_4d)	tridentate	4.92
		bidentate	3.13
		monodentate	2.22
9	trigonal prism (D_3h)	tridentate	4.92
		bidentate	3.27
		monodentate	2.25
8	cube (Oh)	tridentate	7.33
		bidentate	3.43
		monodentate	2.29
8	dodecahedral (D_2d)	tridentate	7.11
		bidentate	3.64
		monodentate	2.29
8	square antiprism (D_4d)	tridentate	5.33
		bidentate	3.56
		monodentate	2.29
7	pentagonal bipyramid (D_5h)	tridentate	10.00
		bidentate	4.09
		monodentate	2.33
6	octahedral (Oh)	tridentate	16.00
		bidentate	4.80
		monodentate	2.40
4	square planar (D_4h)	tridentate	----
		bidentate	8.00
		monodentate	2.67
4	tetrahedral (Td)	tridentate	----
		bidentate	12.00
		monodentate	2.67

The ligand repulsion effect: A ligand that is about to associate with a 1:1 or 1:2 species is repelled electrostatically by the already bound ligands, since all ligands are either negatively charged or possess dipoles. That is $E > 1.0$. The "rest" effect, R, is generally ignored because it is obsure and usually equals about 1. R is only taken into consideration when such factors as steric hindrance, due to very large ligands are obvious.

Manning (16) summarized the stability constant data of divalent copper with acetate and glycolate ligands from Kolat and Powell (17), Fronaeus (18) and Lundquist (19) and found that E values in both ligands are about 1.6, and that T values are 4.7 ± 0.2 and 12.0 ± 2.5 for acetate and glycolate, respectively. His conclusions were that the respective species were comprised of monodentate acetate in square planar array about copper and bidentate glycolate in a square planar configuration about copper (in both cases R was assumed to be 1).

Powell and Rowlands (20) reported T values of 3.5 ± 1.0 in a case of divalent Co, Ni, Zn and Cd with 1-hydroxycyclopentanecarboxylate complexes, and 10.5 ± 0.6 for the copper complex. The conclusions were that, in tetragonally distorted octahedral complexes, coordination probably involves a mixture of monodentate and bidentate linkages in the cases of Co^{+2}, Ni^{+2}, Zn^{+2}, and Cd^{+2}, and a combination of bidentate and tridentate in a case of Cu^{+2}.

The steriochemistry of divalent transition metal complexes involves tetrahedral, square planar and octahedral structures, but some structures are more favored than others (21). Octahedral and tetrahedral coordination are the most common for divalent cobalt, which forms more tetrahedral complexes than any other transition metal ion. Divalent nickel forms mainly the structural types: octahedral, tetrahedral, and square planar.

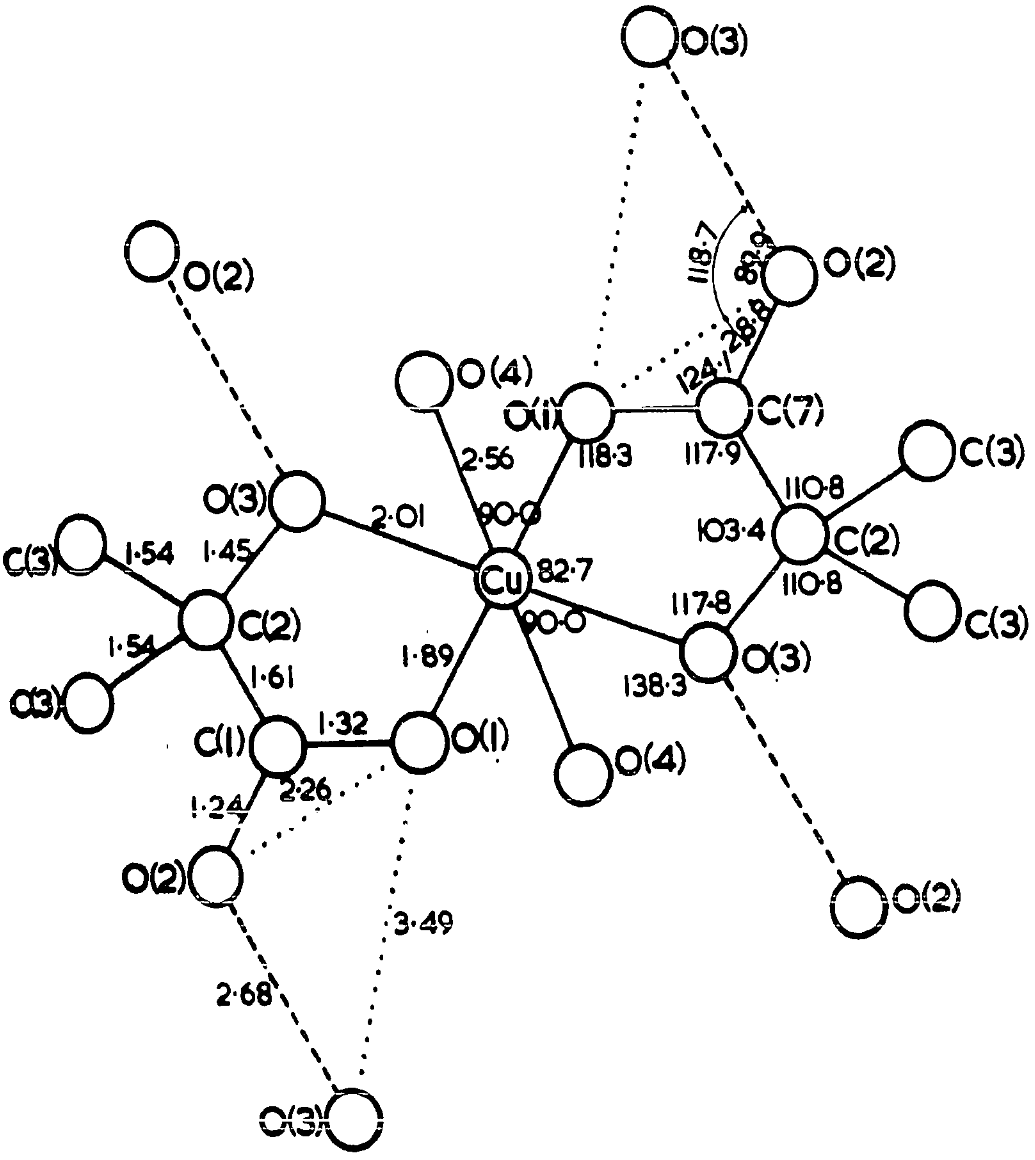


Figure 2. Structure of Diaquobis(α-hydroxyisobutyrato)copper(II)

The crystal structure of (3,3-dimethyl-1,5,8,11-tetraazacyclotridecane) nickel(II) diperchlorate, for example, is square planar (22). Because of the Jahn-Teller effect in the d^9 configuration of divalent copper, the tetragonally distorted octahedron (in which two trans metal-ligand distances are greater than the other four) is the most common structure. Prout, *et al.* (23) reported the crystal structures of bis(glycolato) copper(II), aquobis(DL-lactato)copper(II)hemihydrate, diaquobis(α-hydroxyisobutyrato)copper(II), diaquobis(methoxyacetato)copper(II), and diaquobis(phenoxyacetato)copper(II). All these complexes contain trans-chelate rings which (apart from the bow-shaped lactate) are coplanar. The copper ions are in elongated tetragonally distorted octahedral environments with two exceptions: in the lactate copper ions are in a nearly square-pyramidal five-coordinate environment; and in the methoxyacetate the octahedron is compressed. Figure 2 shows the crystal structure of diaquobis(α-hydroxyisobutyrato)copper(II). The coordination configuration of the copper is distorted octahedral with the copper-water contact Cu-O(4) 2.56 , copper-hydroxyl group Cu-O(3) 2.01 , and the copper-carboxyl-oxygen Cu-O(1) 1.89 . The individual complexes are joined by hydrogen-bonding of the hydroxyl group O(3) to O(2) of another molecule in the mirror plane, and the resulting sheets are held together by hydrogen-bonding through the water molecules. Divalent zinc and cadmium often have coordination numbers of six; but four, such as in the case of the tetrahedral structure, is more common. The crystal structure of zinc(II)dithizonate, for example, has been determined by single crystal X-ray analysis to be tetrahedral by Mawby and Irving (24).

4. Formation constants

The stabilities of metal chelates increase with the effective polydentate nature of the chelating agents (25), so one should observe a stability constant increase in the order of metal-monocarboxylate < metal-dicarboxylate < metal-tricarboxylate. It is also expected to find that the stability constants of metal-hydroxycarboxylates fall between those of metal-monocarboxylates and metal-dicarboxylates. Complexes of divalent transition metals with ligands containing oxygen atoms as potential donors, such as carboxylates and hydroxycarboxylates, will be reviewed here. Sillen and Martell (26) have published an extensive compilation of stability data which includes transition metal species formed with many other kinds of ligands.

Because only weak complexes form between monodentate carboxylate ligands and divalent metal ions, few data regarding these have been reported in the literature so far, and as a matter of fact, those reported do not agree with each other very well. The stability constants in Table 3 were collected from data reported by Filipović, et al. (6, 7), Mihailov, et al. (27), Hershenson, et al. (28), Kolat and Powell (17), Yasuda, et al. (29), Tanaka (30), Sandell (31) and Mihailov, et al. (32). With regard to the values of stability constants in Table 3 (taking into consideration the lower accuracy in the case of formate) one can see that the Irving-Williams order of stabilities holds for these systems.

Table 3: The stability constants for the monocarboxylates of some bivalent metals.

metal	K_1	K_2	K_a	Temp.	μ	Ref.
1. Formate:						
Co	5.4	2.8		25	2	7
Ni	2.9	0.9		25	2	7
Cu	25.0	8.0		25	2	6
	38.0	2.9		25	2	27
	37.0	4.5		25	2	28
Zn	5.0	2.4		25	2	7
	3.2	1.7		25	2	27
	4.0	2.3		25	2	28
Cd	7.0	1.0		25	2	7
	4.4	4.1		25	2	27
	3.0	4.3		25	2	28
2. Acetate:						
Co	4.6	1.3		25	2	7
Ni	5.5	2.5		25	2	7
	10.0		2.95×10^{-5}	25	1	29
Cu	78.0	15.8	2.80×10^{-5}	20	0.1	17
	50.0	9.0		25	2	6
	63.1		2.95×10^{-5}	25	1	29
Zn	19.0	6.5	2.80×10^{-5}	20	0.1	17
	5.0	2.4		25	2	7
	10.0		2.95×10^{-5}	25	1	29
Cd	41.0	11.7	2.80×10^{-5}	20	0.1	17
	6.7	1.3		25	2	7
	31.6		2.95×10^{-5}	25	1	29
3. Propionate:						
Co	5.0	0.8		25	2	7
	5.3			25	1	11
Ni	5.5	2.5		25	2	7
	6.0			25	1	11
Cu	40.0	11.0		25	2	6
	46.0	9.1		25	1	11
Zn	9.6	2.5		25	2	7
	7.0	2.4		25	1	11
Cd	16.0	3.9		25	2	7
	15.5	4.7		25	1	11
4. Butyrate:						
Co	4.6	1.7		25	2	7
Ni	5.4	1.2		25	2	7
Cu	35.0	8.6		25	2	6
Zn	9.6	0.5		25	2	7
Cd	16.0	6.7		25	2	7

Table 3: (continued)

metal	K_1	K_2	K_a	Temp.	μ	Ref.
5. Benzoate:						
Ni	7.9		9.98×10^{-5}	25	.1	29
Cu	39.8		9.98×10^{-5}	25	.1	29
Zn	7.9		9.98×10^{-5}	25	.1	29
Cd	25.1		9.98×10^{-5}	25	.1	29
6. Ethoxyacetate:						
Ni	11.5	2.0		25	1	32
	10.5	3.0		25	1	31
Cu	74.6	6.9		25	1	32
	62.0	12.0		25	1	31
Zn	14.5	3.3		25	1	32
	13.5	5.5		25	1	31
Cd	12.8	2.8		25	1	32
	11.7	4.2		25	1	31

Some stability constants for some dicarboxylate chelate species of bivalent metals are summarized in Table 4. More details can be found in the publication of Powell and Johnson (33), Yasuda, et al.(29), Tanaka (30), and Roletto, et al. (34) from which these data were taken. Data in Table 4 show that the size of the chelate ring is the main factor influencing the stability of the complexes. The stability is highest for oxalate which forms a five-membered ring, and it decreases as the size of the chelate ring increases. The Irving Williams order of stabilities holds for these systems very well.

Table 4: The stability constants for the dicarboxylates of some bivalent metals.

	metal	K_1	K_2	K_{a_1}	K_{a_2}	Temp.	μ	Ref.
1.	Oxalate							
	Co	$5.0x10^4$		$4x10^{-2}$	$1.55x10^{-4}$	25	.1	26
	Ni	$2x10^5$		$4x10^{-2}$	$1.55x10^{-4}$	25	.1	26
	Cu	$1.6x10^6$	$1.1x10^4$	$4x10^{-2}$	$1.55x10^{-4}$	25	0	26
	Zn	$8.0x10^4$		$4x10^{-2}$	$1.55x10^{-4}$	25	.1	26
	Cd	$3.31x10^3$	59	$4x10^{-2}$	$1.55x10^{-4}$	25	0	26
2.	Malonate							
	Co	$9.0x10^2$	30			25	.1	33
	Ni	$1.88x10^3$	47			25	.1	33
		$1.60x10^3$		$1.74x10^{-3}$	$5.13x10^{-6}$	25	.1	29
	Cu	$1.04x10^5$	840			25	.1	33
		$1.0x10^5$		$1.74x10^{-3}$	$5.13x10^{-6}$	25	.1	29
	Zn	$9.3x10^2$	30			25	.1	33
		$5.0x10^2$		$1.74x10^{-3}$	$5.13x10^{-6}$	25	.1	29
	Cd	$2.0x10^2$		$1.74x10^{-3}$	$5.13x10^{-6}$	25	.1	29
3.	Succinate							
	Ni	40		$1x10^{-4}$	$6.17x10^{-6}$	25	.1	29
	Cu	398		$1x10^{-4}$	$6.17x10^{-6}$	25	.1	29
	Zn	40		$1x10^{-4}$	$6.17x10^{-6}$	25	.1	29
	Cd	120		$1x10^{-4}$	$6.17x10^{-6}$	25	.1	29
4.	Glutarate							
	Ni	40		$7.24x10^{-5}$	$9.97x10^{-6}$	25	.1	29
	Cu	251		$7.24x10^{-5}$	$9.97x10^{-6}$	25	.1	29
	Zn	40		$7.24x10^{-5}$	$9.97x10^{-6}$	25	.1	29
	Cd	100		$7.24x10^{-5}$	$9.97x10^{-6}$	25	.1	29
5.	1,1-cyclopropanedicarboxylate							
	Co	$3.16x10^3$		$2.09x10^{-2}$	$7.6x10^{-8}$	25	.1	34
	Ni	$7.76x10^3$		$2.09x10^{-2}$	$7.6x10^{-8}$	25	.1	34
	Cu	$9.77x10^5$		$2.09x10^{-2}$	$7.6x10^{-8}$	25	.1	34
	Zn	$3.16x10^3$		$2.09x10^{-2}$	$7.6x10^{-8}$	25	.1	34
6.	1,1-cyclobutanedicarboxylate							
	Co	$1.6x10^2$	10			25	.1	33
		$1.7x10^2$		$1x10^{-3}$	$2.82x10^{-6}$	25	.1	34
	Ni	$2.2x10^2$	10			25	.1	33
		$1.58x10^2$		$1x10^{-3}$	$2.82x10^{-6}$	25	.1	34
	Cu	$1.03x10^5$	$1.3x10^3$			25	.1	33
		$1.05x10^5$		$1x10^{-3}$	$2.82x10^{-6}$	25	.1	34
	Zn	$3.4x10^2$	30			25	.1	33
		$3.02x10^2$		$1x10^{-3}$	$2.82x10^{-6}$	25	.1	34

In Table 5, are collected the stability constants for hydroxycarboxylate species of some bivalent metals, which were reported by Thun, et al. (5), Filipović, et al. (7), Warnke and Kwiatkowski (11), Powell and Rowlands (20), Tanaka (30), and Folkesson and Larsson (35). If one compares the stability constants data in Table 5 with Tables 3 and 4, one will see that the stability constant values of divalent metal hydroxycarboxylates are higher than in the case of monocarboxylates, but lower than in the case of dicarboxylates. In this situation, the presence of the hydroxyl group in the carbon chain appreciably raises the stability of the complex species being formed. Thus, bonding between oxygen in hydroxyl groups and a metal ion should be taken into account, although it is less important than the bonding between a carboxyl group and the metal ion. Formation of chelate rings is considered certain in such systems. Figure 3 shows a plot of $\log K_1$ versus atomic number of some divalent transition metal ions which form complexes with butyrate, α-hydroxyisobutyrate and oxalate.

Table 5: The stability constants for hydroxycarboxylates of some bivalent metals

Metal	K_1	K_2	K_a	Temp	μ	Ref.
1. Glycolate						
Co	30	6.5		25	2	7
	94			25	0	36
Ni	49	10.2		25	2	7
Cu	250			25	2	7
	646	59		25	0	36
	229	22		25	1	30

Table 5: (continued)

Metal	K_1	K_2	K_a	Temp	μ	Ref.
1. Glycolate (continued)						
Zn	52	14.5		25	2	7
Cd	32	2.2		25	2	7
	73			25	0	36
2. Lactate						
Co	23.5	8.9	$2.30\text{x}10^{-4}$	25	1	5
	24.7	8.2		25	1	11
Ni	39	12	$2.30\text{x}10^{-4}$	25	1	5
	43.4	15.5		25	1	11
Cu	310	31	$2.30\text{x}10^{-4}$	25	1	5
	228	68		25	1	11
Zn	40.7	17	$2.30\text{x}10^{-4}$	25	1	5
	28.8	10		25	1	11
Cd	16.2	7.4	$2.30\text{x}10^{-4}$	25	1	5
	24.9	7.4		25	1	11
3. β-hydroxypropionate						
Co	10.6	4.2		25	1	11
Ni	15.6	3.8		25	1	11
Cu	73.1	21.5		25	1	11
	309	31		25	1	30
Zn	12.5	4.9		25	1	11
4. α-hydroxysiobutyrate						
Co	28.8	9.3	$1.73\text{x}10^{-4}$	25	1	5
Ni	46.4	13.5	$1.73\text{x}10^{-4}$	25	1	5
Cu	550	39.8	$1.73\text{x}10^{-4}$	25	1	5
Zn	51.3	30.0	$1.73\text{x}10^{-4}$	25	1	5
Cd	17.4	8.3	$1.73\text{x}10^{-4}$	25	1	5
5. Mandelate						
Co	16.5	3.3		20	2	35
Ni	25.5	7.1		20	2	35
Zn	32	11.8		20	2	35
6. 1-hydroxycyclopentanecarboxylate						
Co	37	10	$1.13\text{x}10^{-4}$	25	.1	20
Ni	66	20	$1.13\text{x}10^{-4}$	25	.1	20
Cu	630	60	$1.13\text{x}10^{-4}$	25	.1	20
	631	60		25	.1	30
Zn	77	20	$1.13\text{x}10^{-4}$	25	.1	20
Cd	28	8.2	$1.13\text{x}10^{-4}$	25	.1	20

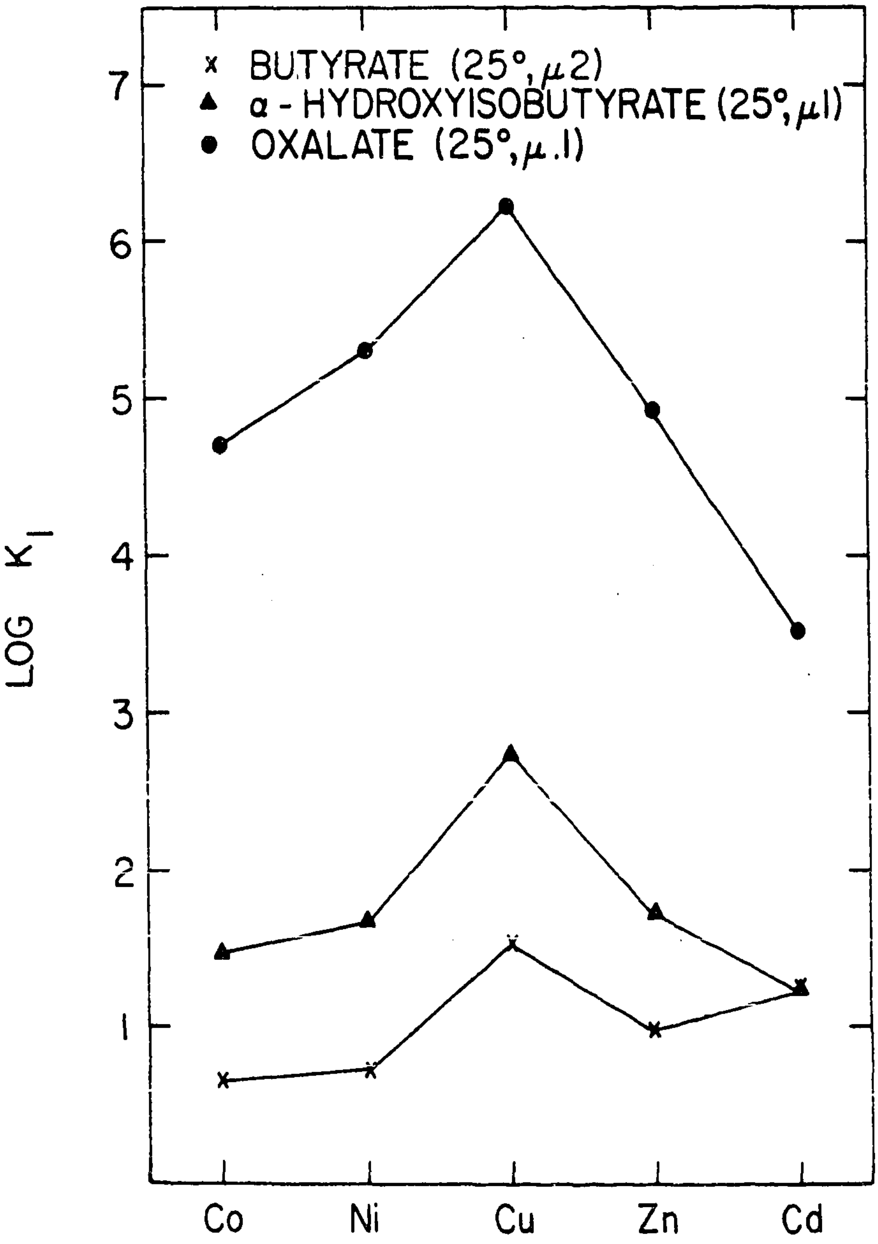


Figure 3. Divalent transition-metal complexes with 3 types of ligand

B. Rare-Earth Hydroxycarboxylates

1. Bonding in lanthanide complex species

The coordination chemistry of the rare-earth metal ions can, with profit, be contrasted and compared with that of the d-type transition metal ions. The stabilities of coordination compounds of the d-type transition metal ions are related to participation of the d electrons in the metal-ligand bond through hybridization of metal electronic orbitals and overlaps of these hybrid orbitals with appropriate ligand orbitals which one knows as covalent bonds. Because electrons in the 4f orbitals in the rare-earth metal ions are effectively shielded from interaction with ligand orbitals by electrons in the 5s and 5p orbitals, hybridization does not occur. Significant cation-ligand attractions are thus largely electrostatic in character (ionic bonds). The absence of significant interactions between ligand and 4f orbitals is supported by a wealth of experimental evidence, especially magnetic and spectral data.

Paramagnetic behavior among the tripositive rare-earth metal ions is due to the presence of unpaired 4f electrons. Since these electrons are well shielded from external influences, both their spin and orbital motions are significant in determining the overall observed susceptibility or moment of a complex containing such a species should indicate clearly whether or not these 4f electrons are involved in bond formation. Moeller and Horwitz (37) compared the magnetic susceptibility of complexes LnL (where Ln refers to Nd(III), Sm(III), Eu(III), Gd(III), or Y(III); and, L is ethylenediaminetetraacetate, N-hydroxyethylethylenediaminetriacetate or 1,2-diaminocyclohexanetetraacetate) with those calculated for the free gaseous ions by Van Vleck and Frank (38), and surmised that the 4f electrons could not be of great significance in bond formation in these chelates. Fritz, et al. (39, 40) also observed only small effects in the magnetic susceptibility in complexes LnL (where Ln refers to lanthanide(III) cations and L is ethylenediaminetetraacetate or acetylacetone) at low temperature. Axtmann (41) concluded from proton nuclear magnetic resonance spectra that a hydrated trivalent lanthanide cation in aqueous solution involved ion-dipole electrostatic bonding with water molecules. His argument was based on the linearity between the logarithms of the acidity constants of the hydrated cations and the chemical shift.

The sharply defined absorption bands, characteristic of all the tripositive lanthanide ions except lanthanum and lutetium ions, are associated with forbidden transitions among the 4f orbitals that are permitted, because of the electric effects of fields imposed by the surrounding anions (42). The overall spectrum of a given ion, therefore, is altered only in the intensities of certain absorption peaks and in altered resolution of complex bands as the anion environment is altered. However, this situation is not the same as with d-transition elements where the d electrons (being external) take an active part in bonding, producing a change in the environment of the central metal ion that frequently causes a substantial variation in absorption spectra. Shielding of the 4f electrons by a complete $5s^2 5p^6$ octet makes such effects much less drastic in the lanthaide series. Moeller and Horwitz (37) found no new bands in different parts of the spectrum in complex species of LnL (where Ln was Pr(III), Nd(III), Sn(III) or Er(III) and L was ethylenediaminetetraacetate, N-hydroxyethylethylenediaminetriacetate or 1,2-diaminocyclohexanetetraacetate) when compared with the spectrum of $LnCl_3$. This is a further indication that the 4f electrons are not involved in bond formation in such chelates; and no correlation exists between alterations in absorption characteristics and chelate stabilities.

Further evidence for the ionic model mentioned above is the absence of π-bonding interactions in the cyclopentadiene derivatives of these ions shown by Wilkinson and Birmingham (43,44). On the other hand, Jorgensen, et al. (45,46) pointed out that the possibility of covalent interactions cannot be completely excluded, because there is evidence based upon nephelauxetic effects of some degree of covalency in some of the complex species. Ephraim and Block (47,48) also found a red shift of the bands in absorption spectra for the anhydrous lanthanide (Pr^{+3}, Nd^{+3}, Sm^{+3}) acetylacetone chelates compared to the aquo ions. The anhydrous fluorides showed some blue shift with respect to the aquo ion. The phenomenon of red shift was explained by Ephraim partly as the expansion of the lanthanide orbital radius due to covalent bonding and partly as contraction due to highly electrostatic bonding. Jorgensen named this effect the nephelauxetic effect.

2. Interpretation of trends in complex stabilities

Some useful data for the rare earth metals and trivalent rare earth cations are presented in Table 6 (49), they are useful for the review in this section and elsewhere. One can see from Table 6 that only the electronic configuration of the cation and its radius are important at this moment for evaluating the effects of progressive changes in complex-ion formation.

Table 6: Numerical data for rare-earth metals and trivalent rare-earth cations

Symbol	Z	Elec. Conf.		$-E^o$ (V)	Electronegativity	Met. Rad. Ln(Å)	Cry. Rad. Ln^{+3}(Å)
		Ln	Ln^{+3}				
La	57	$4f^05d^16S^2$	$4f^0$	2.52	1.1	1.89	1.061
Ce	58	$4f^2\ 6S^2$	$4f^1$	2.48	1.1	1.83	1.034
Pr	59	$4f^3\ 6S^2$	$4f^2$	2.47	1.1	1.84	1.013
Nd	60	$4f^4\ 6S^2$	$4f^3$	2.44	1.2	1.83	0.995
Pm	61	$4f^5\ 6S^2$	$4f^4$	2.42	1.2	----	0.979
Sm	62	$4f^6\ 6S^2$	$4f^5$	2.41	1.2	1.81	0.964
Eu	63	$4f^7\ 6S^2$	$4f^6$	2.41	1.1	1.99	0.950
Gd	64	$4f^75d^16S^2$	$4f^7$	2.40	1.2	1.81	0.938
Tb	65	$4f^9\ 6S^2$	$4f^8$	2.39	1.2	1.80	0.923
Dy	66	$4f^{10}\ 6S^2$	$4f^9$	2.35	1.2	1.80	0.908
Ho	67	$4f^{11}\ 6S^2$	$4f^{10}$	2.32	1.2	1.79	0.894
Er	68	$4f^{12}\ 6S^2$	$4f^{11}$	2.30	1.2	1.78	0.881
Tm	69	$4f^{13}\ 6S^2$	$4f^{12}$	2.28	1.2	1.77	0.869
Yb	70	$4f^{14}\ 6S^2$	$4f^{13}$	2.27	1.1	1.94	0.858
Lu	71	$4f^{14}5d^16S^2$	$4f^{14}$	2.25	1.2	1.75	0.848
Y	39	$4d^1\ 5S^2$	----	2.37	1.3	1.78	0.880

Ionic bonds between rare-earth cations and ligand anions were suggested in the previous section. If this type of bonding is significant, then in terms of an extension of the Born relationship (50, 51)

$$E = \frac{Z^2}{2r}\left(1 - \frac{1}{D}\right)$$

where E is the energy change on solvation (complexation) of a gaseous ion of charge Z and radius r in a medium of dielectric constant D, a generalized increase in the stabilities of such chelates with decreasing crystal radii and stabilities of yttrium complexes comparable with those of the analogous erbium and holmium species may be expected. Because of the "lanthanide contraction" (due to the not quite perfect screening effect of the f electrons) one should expect to see the bond strength increase linearly with increasing ionic potential Z^2/r and a slight discontinuity at gadolinium.

In nearly all complexes which have been studied, this is precisely what is found for the values of $\log K_1$ for complexes of the lighter rare earths, lanthanum through samarium or europium. This simple relationship is, however, not always found when the heavier rare earths, terbium to lutetium, are considered. The trends in the formation constant data for the heavier rare earths can be divided qualitatively into three groups. The first group contains those ligands for which there is a regular increase in the chelate formation constants (glycolate, lactate, iminodiacetate, α-hydroxyisobutyrate, nitrilotriacetate, ethylenediamine-N,N'-diacetate, ethylenediaminetetraacetate and 1,2-diaminocyclohexanetetraacetate). The second group is comprised of ligands for which the chelate formation constants of the heavier rare earths have very nearly the same values. Such ligands include acetate, methoxyacetate, acetylacetone, dipicolinate and N-hydroxyethylethylenediaminetriacetate. The last group is represented by the 2,2'-bis [di(carboxymethyl)amino]diethyl ether ligand and diethylenetriamine-N,N,N',N',N"-pentaacetate. The lanthanide chelate formation constants of this last group increase at first and then show a slight decrease to lutetium.

An example of each group will be discussed here. Aminopolycarboxylates have been chosen instead of hydroxycarboxylates, because considerable thermodynamic data is available for aminopolycarboxylates. Formation constants and thermodynamic functions of rare-earth metal N-hydroxyethylethylenediaminetriacetate (HEDTA) (52, 53, 54), ethylenediaminetetraacetate (EDTA) (55); and diethylenetriaminepentaacetate (DTPA) (56, 57) species are summarized in Table 7. LogK versus ionic potential data for these three compounds have been plotted in Figure 4.

Figure 4 shows a fairly linear relationship between logK and Z^2/r for the lighter rare earths in each case (so the electrostatic bond picture is not unreasonable); but other factors must be involved in the cases of the heavy rare-earth species for which non-linear relationships are seen. It can be argued that the gadolinium break is related to the corresponding discontinuity in crystal radius at gadolinium, however, this discontinuity appears too small to account for the substantial anomalies in formation constants observed at this point.

Table 7: Thermodynamic functions of formation of rare earth-aminopolycarboxylate complexes

Complexes	logK	ΔG^0 (Kcal/mole)	ΔH^0 (Kcal/mole)	ΔS^0 (e.u.)	$\Delta S^0 + \bar{S}^0_{Ln}$ (e.u.)
Ln-HEDTA					
La	13.46	-18.38	-2.28	54.2	20
Ce	14.11	-19.27	-3.06	54.2	19
Pr	14.61	-19.95	-4.45	52.0	15
Nd	14.86	-20.29	-4.25	53.8	15
Sm	15.28	-20.87	-4.65	54.4	15
Eu	15.35	-20.96	-4.81	54.1	14
Gd	15.22	-20.78	-4.66	54.1	12
Tb	15.32	-20.92	-3.39	58.8	16
Dy	15.30	-20.89	-2.12	62.6	19
Ho	15.32	-20.92	-1.14	66.3	21
Er	15.42	-21.06	-0.32	69.4	25
Tm	15.59	-21.29	0.92	74.5	29
Yb	15.88	-21.68	0.36	74.0	27
Lu	15.88	-21.68	0.22	73.4	26
Y	14.65	-20.00	-0.29	66.1	19
Ln-EDTA					
La	15.19	-20.72	-0.80	66.8	32.1
Ce	15.45	-21.07	-0.47	69.1	32.8
Pr	15.76	-21.49	-0.80	69.4	31.9
Nd	16.05	-21.89	-0.80	70.7	32.2
Sm	16.53	-22.54	-0.80	72.9	32.6
Eu	16.66	-22.72	-0.16	75.7	34.6
Gd	16.82	-22.94	0.43	78.4	36.6
Tb	17.32	-23.62	1.50	84.3	41.6
Dy	17.78	-24.25	1.50	86.3	42.7
Ho	18.04	-24.61	1.25	86.7	42.2
Er	18.37	-25.06	1.50	89.1	43.8
Tm	18.64	-25.44	1.58	90.6	44.5
Yb	18.99	-25.91	1.32	91.3	44.5
Lu	19.14	-26.11	0.64	89.7	42.2
Y	18.09				
Ln-DTPA					
La	19.48	-26.57	-5.7	70	35.3
Ce	20.50				
Pr	21.07	-28.74	-7.1	72.0	34.5
Nd	21.06	-29.47	-5.8	79.4	40.9
Sm	22.34	-30.48	-8.2	74.7	34.4
Eu	22.39	-30.55	-8.1	75.3	34.2
Gd	22.46	-30.65	-7.5	77.6	35.8
Tb	22.71	-30.99	-7.7	78.1	35.4

Table 7: (continued)

Complexes	logK	ΔG^0 (Kcal/mole)	ΔH^0 (Kcal/mole)	ΔS^0 (e.u.)	$\Delta S^0+\bar{S}^0_{Ln}$ (e.u.)
Ln-DTPA (continued)					
Dy	22.82	-31.14	-8.0	77.6	34.0
Ho	22.78	-31.08	-7.6	78.7	34.2
Er	22.74	-31.02	-7.3	79.6	34.3
Tm	22.72	-31.00	-5.5	85.5	39.4
Yb	22.62	-30.87	-5.5	85.1	38.3
Lu	22.44	-30.61	-4.6	87.2	40.7
Y	22.05	-30.08	-5.2	83.4	36.2

Staveley and Randall (58) and Choppin and Chopoorian (59) suggested a possible existence of crystal-field effects in rare-earth metal chelates in the EDTA type ligand, since a change in the logK values with increasing atomic number is observed as in the d-type transition elements. There is indeed a break at the gadolinium ion, for which there should be no crystal-field stabilization, that is possibly why the yttrium chelates do not quite fall in the place predicted from the radius of the yttrium ion. Since both gadolinium and yttrium have zero crystal-field stabilization, however, it would be expected on the basis of size that the yttrium complex of a given ligand would always be more stable than the corresponding gadolinium complex. Such is not the case. In addition, it is seen that, when the chelates of two other ligand types (HEDTA and DTPA) are considered, the crystal-field modification of the electrostatic argument does not hold, since there is no regular increase in logK values.

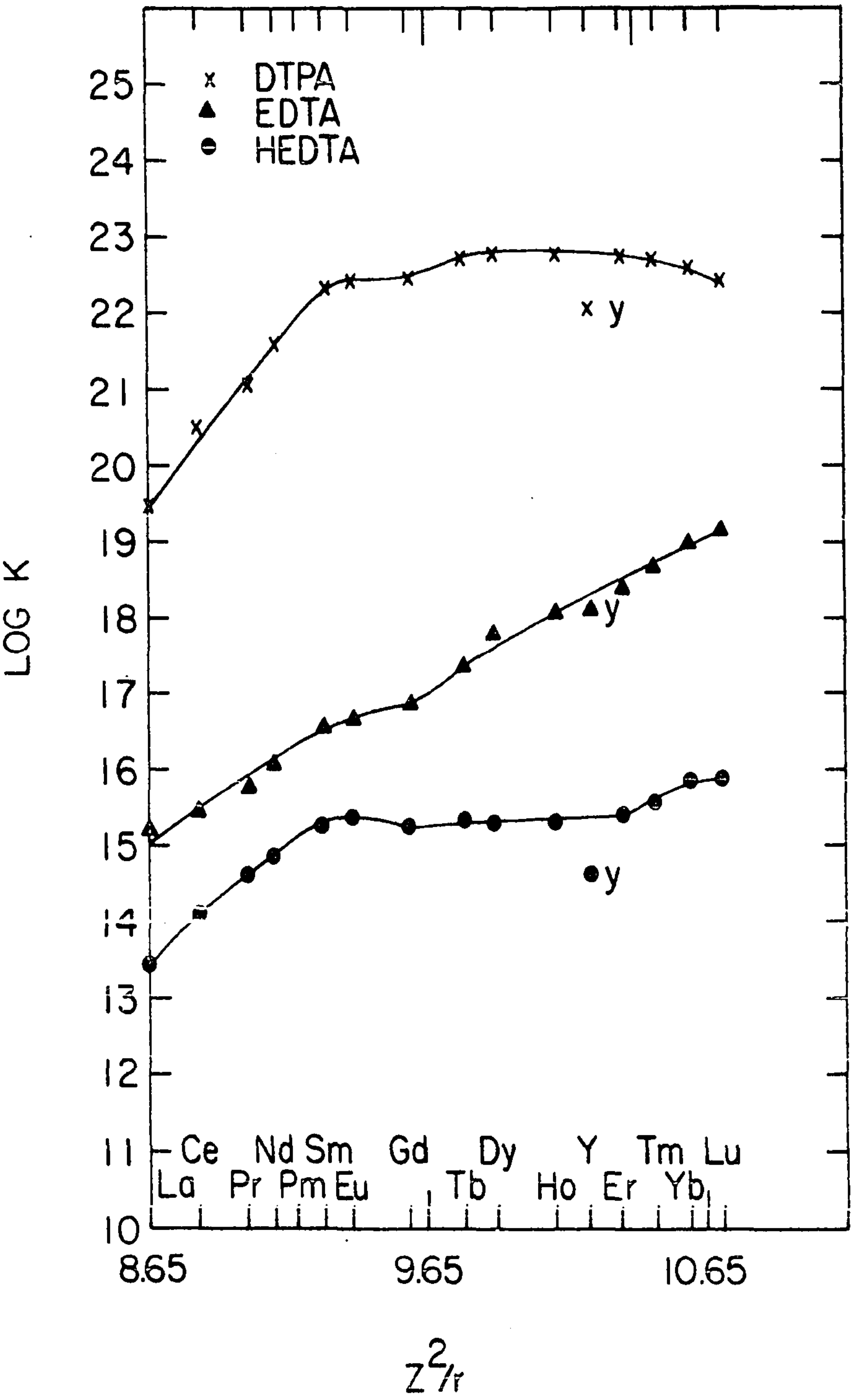


Figure 4. LogK as a function of Z^2/r for various rare-earth complexes

Both the coordination number of the rare-earth metal ions and the number of coordination sites occupied by each ligand involved seem to play a role when one considers thermodynamic and statistical ratio data. However, the interpretation of the trends observed in such data is at most only partly satisfactory. The trends in the formation constants of the 2:1 and higher complexes are much more difficult to systematize since in many of these species there is good evidence for assuming that steric effects are important, and also, for the simple complexes, the errors in the measurements are so large that it is difficult to decide which trends are real. Without a doubt, the rare-earth metal ions coordinate predominantly to oxygen donors, and very little work has been done with nitrogen donors, since the basicity of most of these compounds is such that rare-earth metal hydroxides precipitate before coordination extensively occurs (60).

Wheelwright, et al. (61) found the formation constants of the trivalent lanthanide ions with EDTA to increase generally with atomic number; however, a "plateau" occurs in the region Eu-Gd. These authors suggested as an explanation for this plateau, that the progressively smaller radii of the lanthanide ions in the series from La to Lu imposes increasing steric hindrance on the interaction between EDTA and the ions. They also suggested that all six donor atoms of EDTA are coordinated to the lanthanons La to Gd; but that after Gd, only five of the six could fit around the central ion, leaving one molecule of water still attached. From absorption spectra of protonated Nd and Y-EDTA complexes, Moeller, et al. (62) suggested that Nd is probably pentacoordinated by EDTA rather than 6-coordinated. The change in coordination after Gd would then be from pentacoordinated to tetracoordinated, rather than from 6- to 5- as proposed by Wheelwright.

Betts and Dahlinger (55) obtained ΔH^0, ΔG^0, and ΔS^0 values of formation of chelate species from EDTA and rare earths (Table 7). The major contribution to stability is seen to be the entropy change. Of more interest, however, is the partial molal entropy of the chelate, $\bar{S}^0_{LnY^-}$. The authors obtained this value by approximation in terms of $\Delta S^0 + \bar{S}^0_{Ln^{+3}}$ ($\Delta S^0 = \bar{S}^0_{LnY^-} - \bar{S}^0_{Ln^{+}} - \bar{S}^0_{Y^-}$). The entropy of a simple hydrated ion is determined primarily by its charge and radius, while the entropies of complex ions have additional contributions arising from structural factors (63). Table 7 indicates that $\bar{S}^0_{LnY^-}$ for EDTA chelates in the La-Gd region and in the Tb-Lu region differs by 6-10 eu. Constancy within each region was interpreted as indicating constancy of structure in that region, and the difference between the two regions was ascribed to alteration in the polydentate character of EDTA. Entropy data correlated quite well with a change from pentadentate to tetradentate in those two regions.

However, one can see from Table 7 that, the thermodynamic data in the HEDTA (52, 54) and DTPA (54, 56, 57) cases suggested no comparable explanation for the trends in stability. On the other hand, it must be emphasized that the errors in evaluation of ΔH^0 and ΔS^0 from formation-constant data by the methods used are substantial, and small differences which might be significant are thus covered up. Exact thermodynamic interpretations that can reflect steric effects must thus await more accurate evaluation of enthalpy changes.

Powell and Burkholder measured the ion-exchange separation factors for the rare-earths with EDTA (64) and HEDTA (65) as eluent at 92°C and suggested that at room temperature EDTA chelates form a nine-coordinated chelate species $[Ln(OH_2)_3Ch]^-$ from La to Nd (perhaps Pm) in which a number of hydrogen bonds form between uncoordinated carboxyl oxygen atoms and coordinated water molecules, and tend to enhance the chelate stability above that expected to be due to a simple hexadentate attachment. For the heavy rare earths (Tb to Lu) and Y, an uncomplicated nine-coordinated chelates species $[Ln(OH_2)_3Ch]^-$ receives no stability contribution at all from hydrogen bonding. A gradual change in the number of existing hydrogen bonds from Sm to Gd was suggested, accompanied by progressive reduction in the nominal dentate character of the ligand anion to a minimum value of six. In the HEDTA chelate case, it was suggested that the HEDTA ligand always bonds pentadentately to the heavy lanthanons (Lu to Er), but that it attaches hexadentately to all lighter lanthanons larger than Eu (the 6th donor atom of HEDTA is the oxygen of the hydroxyethyl group). The intermediate lanthanon (Ho-Eu) chelates comprise a transitional set in which the character of the HEDTA anion increases gradually from pentadentate to hexadentate. At 92^{o} it may be presumed that both the hydrogen bonds in the case of EDTA and the bond of hydroxyethyl group in the case of HEDTA are broken, lowering the formation constants of the lighter lanthanons at this temperature for both cases.

Besides the ion-exchange separation which showed that, as lanthanons decrease in radius from La to Lu, the coordination number of the ligand tends to decrease by one due to strains introduced, other data exist which suggest that a change in ligand dentate character occurs somewhere between Sm and Ho depending on the chelating agent. Powell also invoked Bjerrum's statistical ratio theory to explain trends in the formation constants of the 2:1 and higher complexes which are much more difficult to systematize than are the 1:1 complexes because of the weak complexes represented. This subject will be discussed more extensively in a later section.

Spedding, et al. (66-69) studied the properties of dilute aqueous solutions of ordinary rare-earth electrolytes, and strongly suggests that the basic coordination number of the lanthanide cation does increase by one unit as the radius of the cation increases from that of Dy^{+3} to that of Nd^{+3}. Spedding has suggested that the smaller cations (Dy^{+3} to Lu^{+3}) exhibit an 8 coordination number, and that a 9 coordination number is probable in the larger cations (La^{+3} to Nd^{+3}). Powell and Burkholder (65) proposed that the change in coordination number of the freely hydrated rare-earth cation with radius is more likely to be from 9 to 10 than from 8 to 9, because the X-ray crystallographic data of Fitzwater and Rundle (70) reveals 9 nearest-neighbor oxygen atoms (all donated by water molecules) about the lanthanon in crystalline $Er(C_2H_5OSO_3)_3 \cdot 9H_2O$, as well as in $Pr(C_2H_5OSO_3)_3 \cdot 9H_2O$, $Y(C_2H_5OSO_3)_3 \cdot 9H_2O$ and $La(C_2H_5OSO_3)_3 \cdot 9H_2O$.

Bertha and Choppin (71) studied the entropies of hydration (ΔS_h^o) of Ln^{+3} in the lanthanide iodates, and found the values of ΔS_h^o of -81 eu for La-Pr and -96 for Dy-Lu. The authors concluded that this would be consistent with a model of two differently sized hydration spheres, one associated with the La-Pr ions and a larger one with the Dy-Lu ions. The ions from Nd through Gd form a transition group.

3. Bjerrum's statistical ratio theory

Although it can be misleading to infer too much about structures in solution from crystallographic data, such information gives some idea of the possible structures and coordination numbers of the rare-earth complexes in solution as well as the number of donor sites of the ligands utilized in bonding. Consequently, the structures of known crystalline complexes will be reviewed before speculating further.

10-coordinate lanthanide chelate $HLa(H_2O)_4EDTA$ and 9-coordinate lanthanide chelates $MLa(H_2O)_3EDTA$ (M = ammonium, sodium or potassium) have been studied by X-ray analysis (72-74). Both $HLa(H_2O)_4EDTA$ and $MLa(H_2O)_3EDTA$ tend to exhibit the eight vertices of a dodecahedron structure. In the second chelate type, the authors predicted that if they replaced La^{+3} by smaller Ln^{+3} ions, a transition from 9-coordinate $MLn(OH_2)_3EDTA$ (La-Sm) to 8-coordinate $MLn(OH_2)_2EDTA$ (Tb-Lu) would occur. They suggested that the chelates of Eu^{+3} and Gd^{+3} would be transitional in coordination type between a 9-coordinate and 8-coordinate. Martin and Jacobson studied the crystal structure of nitrilotriacetatodiaquopraseodymium(III) monohydrate ($Pr(H_2O)_2NTA \cdot H_2O$) (75) and nitrilotriacetatodiaquodysprosium(111)dihydrate $Dy(H_2O)_2(NTA) \cdot 2H_2O$ (76). The authors found that in the first case, Pr is 9-coordinate with 6 carboxylate oxygen atoms, 2 waters, and one nitrogen in the coordination sphere, the structure can be described as either a distorted, tricapped, trigonal prism or a distorted, capped, square antiprism. For $Dy(H_2O)_2NTA \cdot 2H_2O$, Dy is 8-coordinate with 5 acetate oxygen atoms, 2 waters and one nitrogen atom in the coordination sphere, the eight donor atoms reside at the corners of a distorted dodecahedron with triangular faces.

The structure of trichlorotris(hexamethylphosphoramide)praseodymium (III) (77) consists of discrete monomeric units comprising a Pr(III) ion coordinated to 3 hexamethylphosphoramide molecules via the oxygen atoms

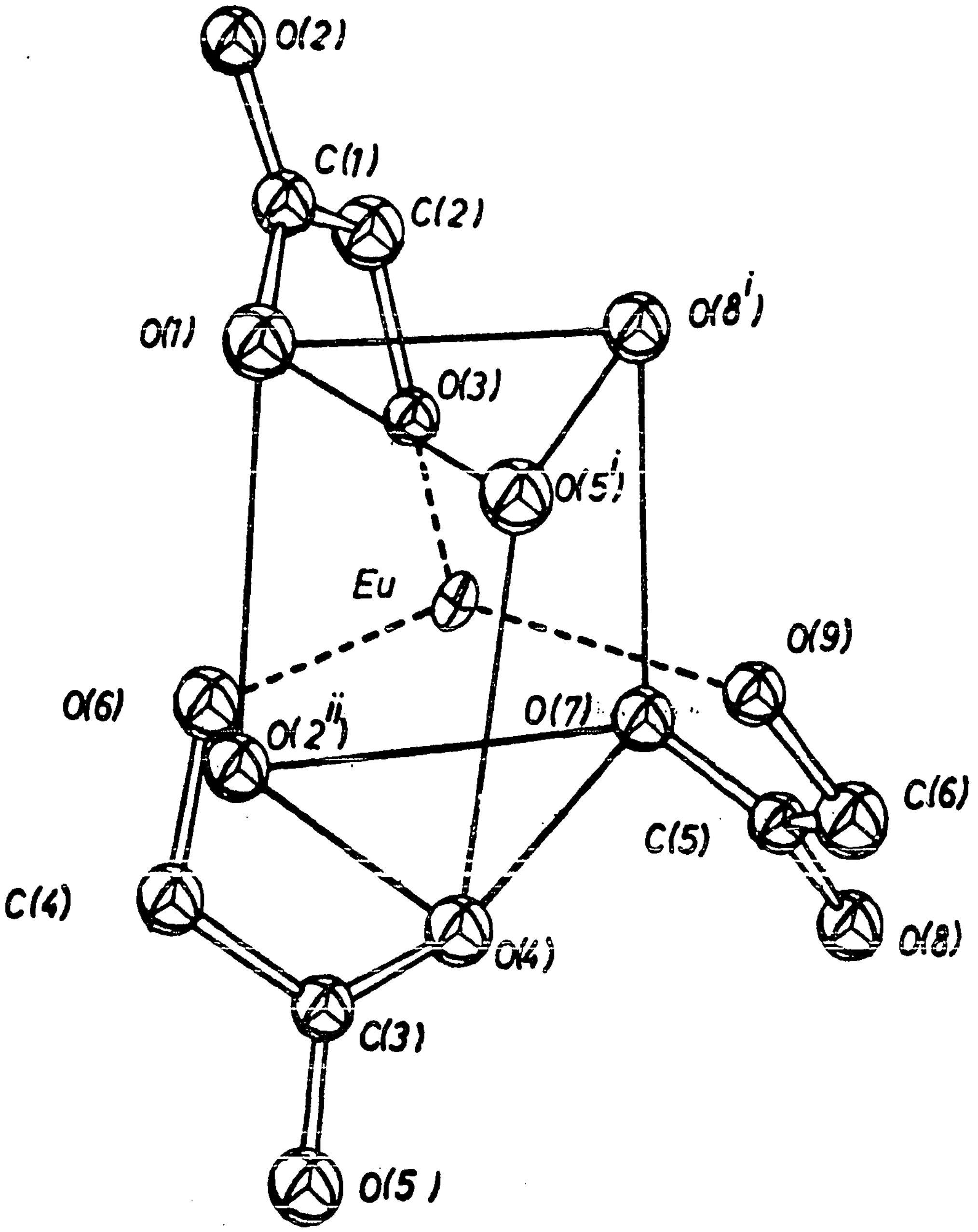


Figure 5. Structure of tris(hydroxyacetate)europium(III), Eu(HOCH$_2$COO)$_3$

and to 3 chloride ions forming an octahedral coordination sphere (C_{2v}).

Grenthe determined the structures of $Ln(HOCH_2COO)_3$ from X-ray intensity data and found that in the structure of the heavy rare-earth (Tb-Lu) chelates such as $Er(HOCH_2COO)_3 \cdot 2H_2O$ (78), there are two non-equivalent metal atoms in the structure. They are located on two-fold axes and are each coordinated by 8 oxygen atoms forming distorted dodecahedra. One metal ion is coordinated by four hydroxyacetate ligands forming a discrete anionic complex, the other by two hydroxyacetate and four waters forming a discrete cationic complex. The complexes are joined by hydrogen bonds.

Identical structures are obtained in the cases of $Gd(HOCH_2COO)_3$ (79) and $Eu(HOCH_2COO)_3$ (80). The structure of $Eu(HOCH_2COO)_3$ is shown in Figure 5. The metal ion is 9-coordinate with a coordination polyhedron of the tri-capped trigonal prism type. All ligands are bonded as chelates with the hydroxy oxygen in the equatorial and one of the carboxylate oxygens at a corner position of the prism. The three remaining corners are occupied by carboxylate oxygens from ligands which are chelated to neighboring europium atoms.

One can see that the coordination number of lanthanide chelates varies between 6-10 in crystals. The coordination number of the central metal ion changes in some chelates series, but remains constant across the series (from Lu to La) in others. Powell and Burkholder (65) proposed from these X-ray crystallographic data and ion exchange separation data that in solution the change in coordination number of the freely hydrated rare-earth cation with radius ought to be from 10(La^{+3}-Nd^{+3}) to 9(Dy^{+3}-Lu^{+3}).

Powell and Rowlands (81) measured the stability constants of rare earths with 1-hydroxycyclopentanecarboxylic acid (HCPC), and found that K_1/K_2

are 4.93 and 3.29 for larger rare-earths (La-Nd) and smaller rare-earths (Tb-Lu), respectively. The authors compared their data with a 9-coordinated trigonal prism (D_3h) model for the rare-earth metal ions, S values of which are shown in Table 2, being 4.92 and 3.27 for the tridentate and bidentate ligand cases, respectively. They concluded that in this system HCPC bonded tridentately with lighter rare-earths (La-Nd) and changed to bidentate in a heavier rare-earths (Tb-Lu).

Lanthanide 2-hydroxy-2-methylbutanoate(EMG) chelate stabilities were studied by Powell, et al. (82), and K_1/K_2 values were found to be 6 for La to Nd and 4 for Sm to Lu. The conclusions drawn were that, EMG also functions tridentately in bonding to larger lanthanons but only bidentately to the smaller ones. Powell also calculated E and R values in these two systems and found that $1.0 < E < 1.5$ for the process $Ln^{+3} \rightarrow LnL^{+2} \rightarrow LnL_2^{+}$ (L are HCPC and EMG), that $1.0 < R < 1.5$ in the case of HCPC, and that $1.22 < R < 1.83$ with EMG. In both systems, the values of $f(\mu)$ at $\mu = 0.1$ (the activity correction to the K_1/K_2 ratio) was estimated to be about 0.67 via Bjerrum's equation ($K_1/K_2 = T = SERf(\mu)$).

4. Formation constants

The most strong lanthanide complexes are formed between lanthanides and aminopolycarboxylates. Carboxylates or hydroxycarboxylates are expected to form but weak complexes with lanthanides (25, 83). Because of the imprecise nature of most data on lanthanide aminopolycarboxylate chelates stability constants found in the literature, one should not expect to find more agreeable data in cases of carboxylates or hydroxycarboxylates. Rare-earth hydroxycarboxylate chelate stability constant data will be reviewed here, together with those of some species formed by mono and dicarboxylate ligands. Sillen and Martell (26) and Moeller, et al. (84) have published an extensive compilation of stability data which includes much of the information on rare-earth stability constants.

Formation constants of lanthanides with acetate, propionate and isobutyrate in Table 8, reported by Kolat and Powell (17), Powell, et al. (85), and Stagg and Powell (86) show that the ligand affinity for rare-earth ions decreases in the order acetate>propionate> isobutyrate. As one can see, the linnear relationship between the basicity of the donor group and the chelate stability, which has been found to hold in a large portion for most transition metal chelates, does not hold for these simple carboxylates of trivalent lanthanides. Choppin and Graffeo (87) found almost the same values for the formation of the lanthanide propionate and isobutyrate complexes at 25° and ionic strength of 2.0, but the values of Δ S and Δ H for the complex formation of isobutyrate were reported to be higher than with propionate. The authors concluded that the bulkier isobutyrate ion should disrupt the inner hydration sphere of metal ions more than propionate would. Grenthe (88) shown from his thermodynamic data that acetate ion acts as a unidentate ligand in the same way as thioglycolate.

Some formation constants for the dicarboxylates of trivalent lanthanides are summarized in Table 9. One should expect to see the most stable complex five-membered ring formed between oxalate anion and lanthanide cations in such systems, and as a matter of fact, the oxalate ion has been used for the precipitation of the rare-earths in a gravimetric method of analysis. In complex species formed between 1:1 malonate homologues and lanthanons, the formation constants for the heavy lanthanons (Er^{+3}-Lu^{+3})

Table 8. The stability constants for the monocarboxylates of trivalent lanthanides.

Metal	Acetate		Propionate		Isobutyrate	
	K_1	K_2	K_1	K_2	K_1	K_2
La	105	17.2	78	15	43.8	3.3
Ce	124	27.5	112	17	61.1	3.4
Pr	150	28.1	132	22	82.9	18.1
Nd	166	34.8	157	21	95.4	13.1
Sm	201	38.4	161	31	112	18.5
Eu	202	39.7	168	33	94.6	7.7
Gd	146	39.8	122	30	73.7	25.8
Tb	118	39.3	99	39	65.5	10.5
Dy	108	40.4	85	33	55.1	6.7
Ho	101	39.3	90	32	49.7	16.9
Er	102	38.8	87	35	49.3	7.8
Tm	104	38.9	81	33	49.5	3.9
Yb	107	43.3	85	28	60.7	20.8
Lu	111	43.6	100	34	65.1	3.2
Y	94	42.7	75	15	39.8	13.0

acetate (17) : K_a 2.80 x 10^{-5}, 20° and $\mu = 0.1$

propionate (85) : K_a 2.21 x 10^{-5}, 20° and $\mu = 0.1$

isobutyrate (86) : K_a 2.30 x 10^{-5}, 25° and $\mu = 0.5$

increase in the sequence: 1,1-cyclopentanecarboxylate $<$ malonate $<$ diethylmalonate $<$ di-n-propylmalonate. Powell and Johnson (91) and Powell, et al. (92) suggested that the steric effect of the alkyl groups is more important than the inductive effect, because the -OOC-C-COO- bond angle is important in the complex formation.

Table 9. The stability constants for the dicarboxylates of trivalent lanthanides

Metal	Oxalate		Diglycolate		1,1-cyclopentanecarboxylate	
	$K_1 x10^{-6}$	K_2	$K_1 x10^{-5}$	$K_2 x10^{-4}$	$K_1 x10^{-4}$	$K_2 x10^{-2}$
La	0.45		0.85	0.30		
Ce	0.78		1.44	0.58		
Pr	2.00		2.16	0.78		
Nd	3.32		2.82	1.13		
Sm	4.17		3.54	2.21		
Eu	9.12		3.35	3.28	1.49	3.38
Gd	4.90		2.53	3.36	1.51	3.10
Tb	3.80		2.11	4.51	1.82	3.29
Dy	3.55		2.05	4.68	1.92	3.31
Ho	3.80		1.90	4.71	1.77	3.11
Er			2.20	4.77	1.75	3.33
Tm	3.63		3.11	5.37	1.76	3.76
Yb	4.27		3.56	6.49	1.84	4.16
Lu			4.34	8.16	1.65	4.42
Y			1.75	3.32		

oxalate (89) : K_{a_1} 6.45×10^{-2}, K_{a_2} 6.17×10^{-5}, at 25^{0} and $\mu = 0.5$

diglycolate (90) : K_{a_1} 1.60×10^{-3}, K_{a_2} 1.82×10^{-4}, at 20^{0} and $\mu = 1.0$

1,1-cyclopentanecarboxylate (91) : K_{a_1} 9.0×10^{-4}, K_{a_2} 1.56×10^{-6}, at 25^{0} and $\mu = 0.1$

Table 9. (Continued)

Metal	malonate		diethylmalonate		di-n-propylmalonate	
	$K_1 x10^{-4}$	$K_2 x10^{-2}$	$K_1 x10^{-4}$	$K_2 x10^{-2}$	$K_1 x10^{-4}$	$K_1 x10^{-2}$
La	0.49	1.6	0.41	2.2	0.46	
Ce	0.68	2.2	0.61	3.4	0.92	4.5
Pr	0.82	2.5	0.81	3.8	1.04	8.2
Nd	0.88	3.0	1.03	4.1	1.14	10.0
Sm	1.56	4.5	2.13	3.9	2.83	7.8
Eu	2.03	4.9	2.92	3.9	3.72	7.1
Gd	2.09	4.4	3.09	3.6	3.82	5.2
Tb	2.74	5.1	4.28	4.1	5.39	5.7
Dy	3.00	5.0	4.87	4.0	6.02	4.9
Ho	2.45	3.8	4.30	3.4	5.25	3.6
Er	2.63	4.2	4.60	3.9	5.41	4.2
Tm	2.65	3.9	5.00	4.1	5.71	4.3
Yb	3.40	5.6	5.70	4.9	6.52	5.6
Lu	2.82	4.8	4.87	5.2	6.08	5.6
Y	2.51	4.4	4.00	2.8	5.16	4.5

malonate (92) : K_{a_1} 2.47×10^{-3}, K_{a_2} 5.34×10^{-6}, at 25° and $\mu = 0.1$

diethylmalonate (92) : K_{a_1} 1.10×10^{-2}, K_{a_2} 1.05×10^{-7}, at 25° and $\mu = 0.1$

di-n-propylmalonate (92) : K_{a_1} 1.50×10^{-2}, K_{a_2} 7.12×10^{-7}, at 25° and $\mu = 0.1$

Some of the stability constants of the lanthanide hydroxycarboxylate complexes are summarized in Table 10. The data have been collected under the same conditions (25° and μ 0.1) if available. The most work has been done on α-hydroxyisobutyric acid (59, 86, 93, 94, 95, 96), lactic and glycolic acids (59, 94, 96, 97, 98, 99,). Eeckhaut, et al. (100), and Thun and Verbeek (101) reported some stability constants of the lanthanide dialkyl-substituted glycolate homologous complexes, but the data are not complete.

The monoalkylsubstituted glycolates, such as methylglycolate (MG), ethylglycolate (EG), isopropylglycolate (PG) and t-butylglycolate (BG) together with 1-hydroxycyclopentanecarboxylate (HCPC) are plotted in Figure 6. The stability constants increase as BG $<$PG$<$EG$<$HCPC$<$MG, the steric effect of alkyl group is considered to be much greater than the inductive effect in those systems.

Table 10. Stability constants for the hydroxycarboxylates of trivalent lanthanides

Metal	G		MG		EG	
	K_1	K_2	K_1	K_2	K_1	K_2
La	355	49	400	55	212	66
Ce	495	71	570	93	284	78
Pr	600	80	705	113	388	85
Nd	780	92	740	126	438	91
Sm	820	126	760	162	566	129
Eu	860	137	890	169	593	133
Gd	620	116	780	141	605	144
Tb	600	123	790	203	722	175
Dy	840	111	1020	220	824	202
Ho	980	112	1050	250	875	248
Er	1010	153	1460	288	995	267
Tm	1135	188	1550	329	1110	298
Yb	1350	174	1700	388	1290	342
Lu	1400	214	1875	405	1390	365
Y	610	123	1040	216	724	210

glycolate·G (94): K_a 2.72 x 10^{-4}, at 20° and μ 0.1

methylglycolate·MG (94): K_a 2.33 x 10^{-4}, at 20° and μ 0.1

ethylglycolate·EG (102): K_a 2.13 x 10^{-4}, at 25° and μ 0.1

Table 10. (Continued)

Metal	PG		BG		HCPC	
	K_1	K_2	K_1	K_2	K_1	K_2
La	149	58	120	39	238	48
Ce	197	71	156	48	324	67
Pr	237	89	164	37	402	83
Nd	270	93	210	54	463	91
Sm	380	104	300	83	615	140
Eu	427	115	330	94	636	170
Gd	433	122	390	82	698	167
Tb	520	151	420	126	792	230
Dy	616	166	500	140	958	293
Ho	654	182	520	164	1050	302
Er	740	200	600	173	1163	381
Tm	830	217	620	207	1288	409
Yb	948	246	720	211	1497	474
Lu	1027	253	740	235	1663	528
Y	541	153	421	126	995	273

isopropylglycolate - PG (102) : K_a 2.03 x 10^{-4}, at 25° and μ 0.1

t-butylglycolate - BG (102) : K_a 1.37 x 10^{-4}, at 25° and μ 0.1

1-hydroxycyclopentanecarboxylate - HCPC (81) : K_a 1.13 x 10^{-4}, at 25° and μ 0.5

Table 10. (Continued)

Metal	HIBA		EMG		EEG	
	K_1	K_2	K_1	K_2	K_1	K_2
La	290	62	220	38	102	29
Ce	367	96	320	53	111	44
Pr	507	92	350	59	167	52
Nd	579	102	450	69	204	70
Sm	771	165	630	140	485	99
Eu	946	209	800	200	687	111
Gd	991	230	880	220	822	110
Tb	1239	302	1200	299	1060	142
Dy	1360	332	1450	350	1250	150
Ho	1592	409	1720	429	1340	158
Er	1756	540	2090	539	1440	181
Tm	2009	553	2320	577	1530	197
Yb	2280	652	2690	669	1740	204
Lu	2565	734	2790	703	1790	223
Y	1333	355	1600	385	1100	138

α-hydroxyisobutyrate - HIBA (93): K_a 1.63 x 10^{-4}, at 25^{o} and μ 0.1

ethylmethylglycolate - EMG (82) : K_a 1.86 x 10^{-4}, at 25^{o} and μ 0.1

diethylglycolate - EEG (102): K_a 2.38 x 10^{-4}, at 25^{o} and μ 0.1

Table 10. (Continued)

Metal	THIB		BHMP		HP	
	K_1	K_2	K_1	K_2	K_1	K_2
La	249	30	114	30	36	
Ce	409	69			37	
Pr	559	88	201	39	42	
Nd	646	65	236	39	46	
Sm	720	164	299	47	56	
Eu	631	158	288	49	44	
Gd	486	200	236	43	41	
Tb	519	145	201	40	35	
Dy	454	164	186	44	28	
Ho	511	153	191	44	30	
Er	619	110	188	40	21	
Tm	711	130	202	42	28	
Yb	789	148	197	41	32	
Lu	874	176	217	43	25	
Y	451	104	147	36	27	

α,β,β'-trihydroxyisobutyrate - THIB (86) : K_a 5.15 x 10^{-4}, at 25° and μ0.5

bis-hydroxymethyl-2,2-popionates - BHMP (103) : K_a 4.07 x 10^{-5}, at 25° and μ 0.1

β-hydroxypropionate - HP (104) : at 25° and μ 2.0

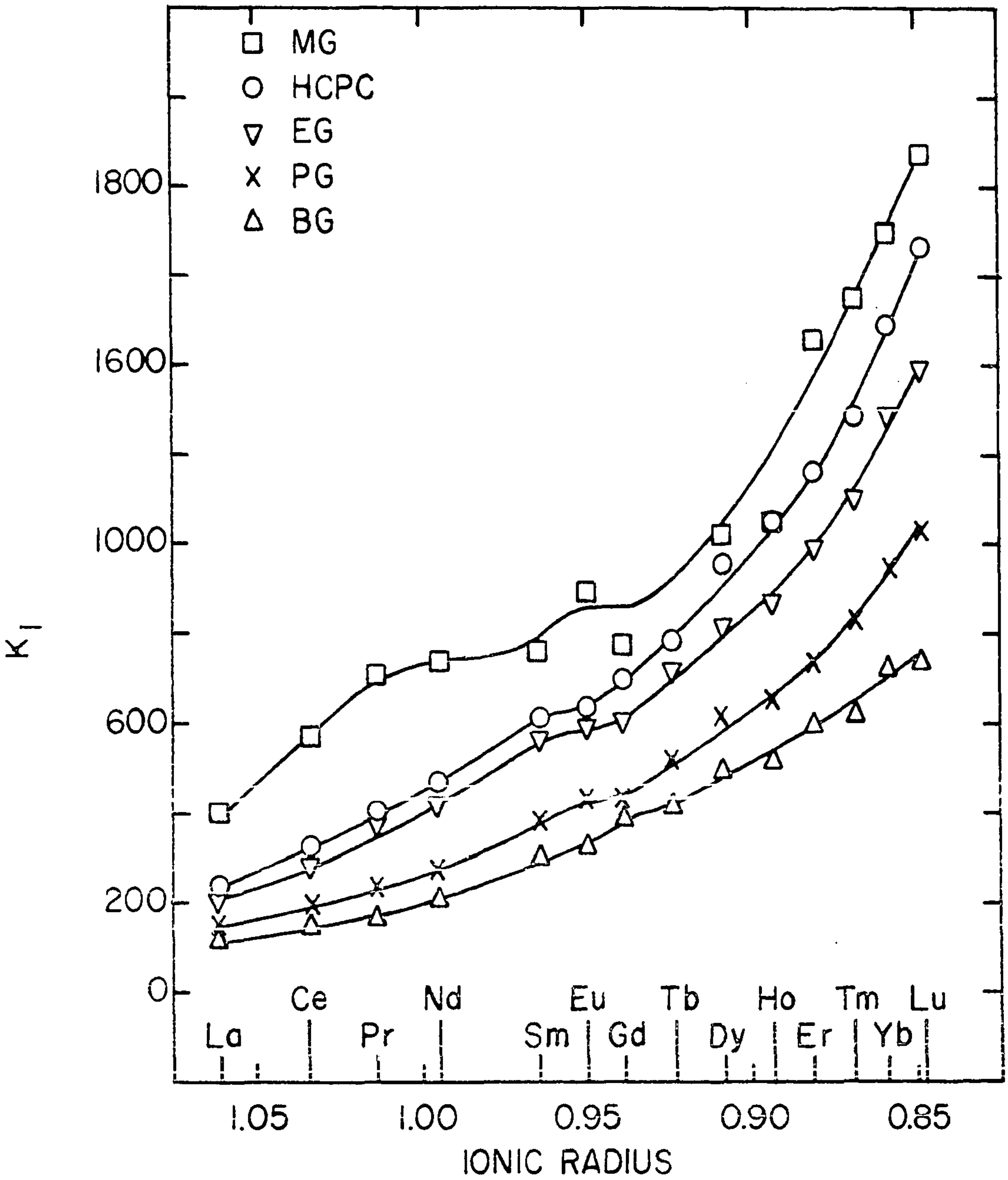


Figure 6. K_1 as a function of ionic radius for hydroxycarboxylate rare-earth complexes

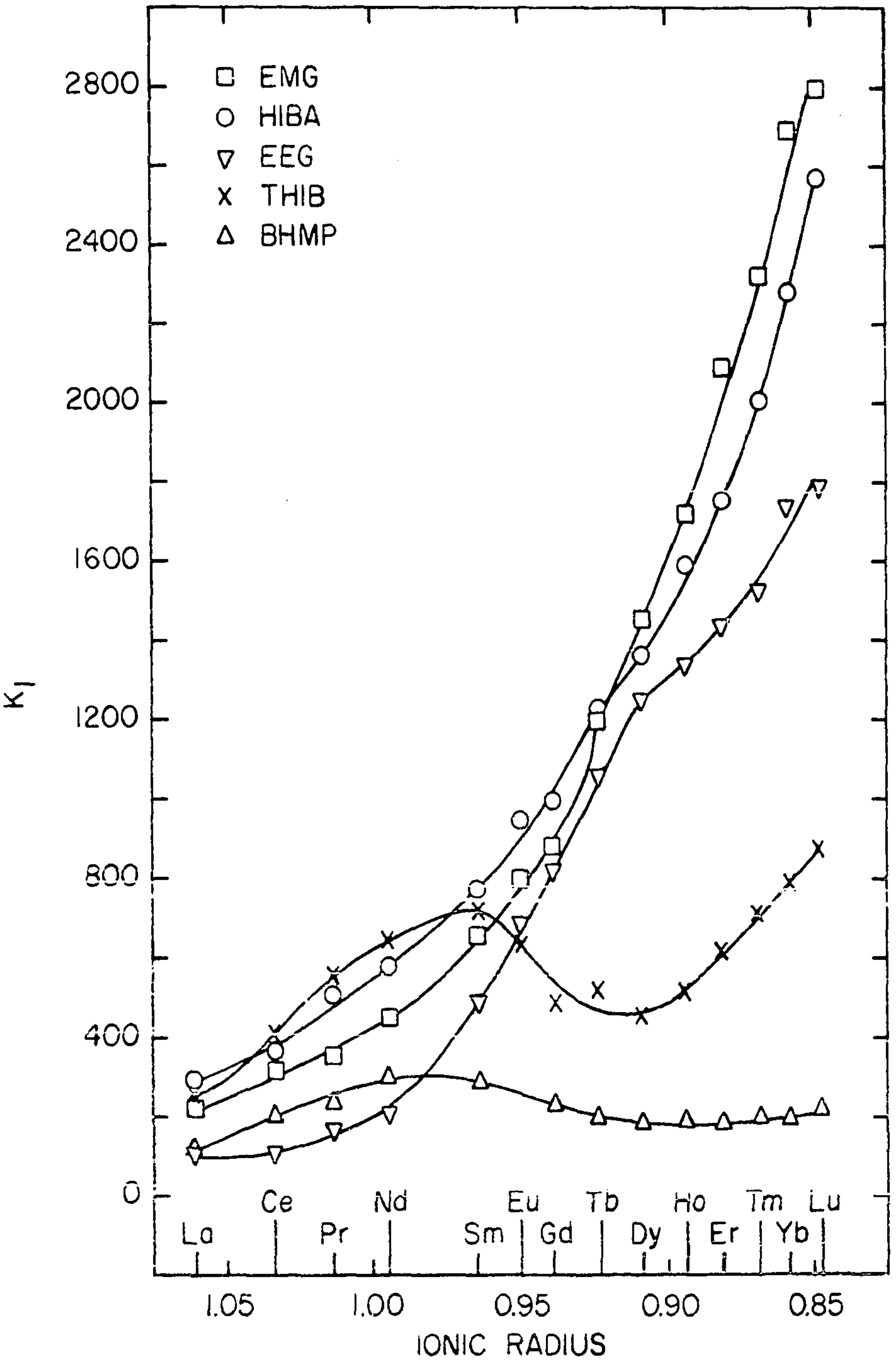


Figure 7. K_1 as a function of ionic radius for hydroxycarboxylate rare-earth complexes

Figure 7 shows a plot of the dialkylsubstituted glycolates, such as α-hydroxyisobutyrate (HIBA), ethylmethylglycolate (EMG) and diethylglycolate (EEG). The trends of the stability constants in this system are very interesting, because the stability constants increase as EEG < EMG < HIBA in the lighter lanthanides, but increase in the order EEG < HIBA < EMG for the heavier lanthanides. Powell's argument (81, 91, 92) on dicarboxylate and 1-hydroxycyclopentanecarboxylate systems can be used in explaining in this system. When the steric effect is increased by increasing the bulk of the alkyl groups from methyl-methyl < ethyl-methyl < ethyl-ethyl, this steric effect will make the bond angle -OOC-C-OH decrease in the order HIBA > EMC > EEG. The smaller ionic radius of the heavier lanthanides will then fit the smaller -OOC-C-OH bond angle better compared to the lighter lanthanides. In the case of EEG, one is led, therefore, to hypothesize that, the -OOC-C-OH bond angle is too small even in the case of the heavier lanthanides.

The plot of α, β, β'-trihydroxyisobutyrate (THIB) and bis-hydroxymethyl-2,2-propionates (BHMP) in Figure 7 shows that the hydroxy groups of β-carbon atoms are not bonded to the heavier lanthanides. Jones and Choppin (104) studied the formation constants and thermodynamic parameters in β-hydroxypropionate lanthanides complexes and indicated that the hydroxyl group is not involved in a chelate ring.

III. MATHEMATICAL METHOD

A. Acid Dissociation Constants

1. General considerations

In aqueous solution a carboxylic acid exists in equilibrium with the carboxylate anion and hydronium ion.

$$H_nA + H_2O = H_{n-1}A^- + H_3O^+$$

where H_nA represents the undissociated carboxylic acid, H_2O the water molecule, $H_{n-1}A^-$ the carboxylate anion, and H_3O^+ the hydronium ion. Since the acids used in this research are dihydroxymonocarboxylic acids and the hydroxyl group is a weaker acid than water (the pK_a value is 16 for methyl alcohol (105) and 19 for tertiary butyl alcohol (106)), the dissociation of hydrogen ion of the hydroxyl group can be neglected in comparison to the dissociation of the hydrogen ion of the carboxyl group. Only one hydrogen ion in homologous series is dissociated, therefore n in above equilibrium reaction is equal to one. The charges on the hydronium ion and the carboxylate ion will be presumed understood, hereafter, and the hydronium ion will be represented simply as H.

The thermodynamic dissociation constant K_a is defined by the equations,

$$K_a = \frac{[H][A]}{[HA]} \frac{\gamma_H \gamma_A}{\gamma_{HA}}$$

$$K_a = K_c \cdot \frac{\gamma_A \gamma_A}{\gamma_{HA}}$$

where K_c is the stoichiometric dissociation constant, the brackets denote molar concentrations, and γ_i represents the activity coefficient of the ith species. For a given system, the thermodynamic dissociation constant is a function only of temperature and is directly related to the free energy of acid dissociation by means of the equation

$$\Delta G^o = -RT\ln K_a \qquad (1)$$

At all finite concentrations, the stoichiometric dissociation constant will be related to the thermodynamic dissociation constant as:

$$K_c = K_a \frac{\gamma_{HA}}{\gamma_H \gamma_A} = K_a F(\gamma) = K_a F(I) \qquad (2)$$

At the solute standard state, the activity coefficients approach one as the concentrations of all the species approach zero. Thus, in the limiting case of the infinitely dilute solution, the stoichiometric dissociation constant will equal the thermodynamic dissociation constant.

Activities or activity coefficients can not be measured in the multicomponent systems, such as the ones studied in this research. Consequently, the thermodynamic dissociation constants cannot be obtained experimentally, but one can obtain the stoichiometric dissociation constant directly, because the molar concentrations of all the species can be measured.

At this point, three theories which were defined by Lewis and Randall (107), Debye and Hückel (108), and Harned (109) and Harned and Owen (110) should be introduced. Lewis and Randall pointed out that the activity coefficient of a given ion is the same in all solutions of identical ionic strength. The ionic strength, I, is defined by

$$I = \tfrac{1}{2}\Sigma \ Z_i^2C_i \tag{3}$$

where Z_i and C_i represent the charge and molar concentration of the ith ions respectively. The summation is carried out over all the ions present in solution. Later Debye and Hückel pointed out that the relationship between activity coefficients and ionic strength is

$$\log\gamma_i = -\left[\frac{AZ_i^2I^{\frac{1}{2}}}{1-B\overset{\circ}{a}I^{\frac{1}{2}}}\right] \tag{4}$$

where the constants A and B depend on the temperature and the properties of the solvent, and $\overset{\circ}{a}$ is the ion-size parameter of each individual ion. In practice, the ion-size parameter is usually treated as a semiempirical constant, because its exact value is difficult to determine. This theory is valid only for relatively dilute solutions. So, according to the Debye-Hückel theory, the activities of ionic species in a solution are primarily a function of the ionic strength of the solution. The last theory is Harned's theory of ionic interactions. Harned's equation is in the following form:

$$\Delta \log \gamma_A = \frac{C\Delta[A]}{I} \qquad (5)$$

where $\Delta \log \gamma_A$ is the difference in $\log \gamma_A$ for two solutions of the same ionic strength which differs in free ligand concentration by $\Delta[A]$. The constant C depends upon the ionic strength and the specific electrolytes under study. It will be shown later that for the systems studied in this research, the only major concentration differences in a given series of solutions are in the values of $[A]$, the free ligand concentration, and in $[NO_3^-]$ the concentration of background electrolyte anion. It can be seen from this equation that $\Delta \log \gamma_A$ may be rendered almost negligible if the ionic strength is several orders of magnitude greater than the values of free ligand concentration. This fact suggests using as large a value of ionic strength as is consistent with the validity of equation 4. Harned's equation can provide a quantitative relationship between these concentration changes and the activity coefficient changes which result therefrom.

Stoichiometric dissociation constants in this dissertation are determined from a wide range of equilibrium constant data. These data have all been obtained from dilute solutions of identical ionic strength in which equation 4 is presumed valid, so all the relevant activity coefficients should have remained constant. The term F(I), in equation 2 should be constant; consequently, the value of the stoichiometric dissociation constant should be a constant for all solution of the same ionic strength, and this type of dissociation constant is called a conditional dissociation constant. Once conditional dissociation constants have been measured, one can estimate the values of the thermodynamic dissociation constants in a number of ways. The most famous way is by obtaining conditional dissociation constants at several ionic strengths and extrapolating the results to zero ionic strength. At zero ionic strength, F(I) will equal one, and K_a will equal K_c.

Powell, et al. (81, 82, 111, 112) and Devine (93) have applied the Debye-Hückel theory in determination of the acid dissociation constants in the last ten years, and they found that the value of K_c decreased slightly as the concentration of ligand increased. This idea was also examined by Ellilä (113) who found that the acid dissociation constant of acetic acid depended upon the nature and concentration of the background electrolyte even in solutions of identical ionic strength. Kilpatrick (114) also found that the acid dissociation constant of benzoic acid depended on the nature and concentration of the supporting electrolyte in solutions of identical ionic strength. So, application of the Debye-Hückel theory to acid dissociation constants is in question.

Powell has applied Harned's theory of ionic interactions to the acid dissociation constants of carboxylic acids system, and found a variation in K_c with [A]. According to Harned's theory of ionic interactions, if the composition of the ionic medium changes substantially, the value of K_c will vary slightly with concentration even when the ionic strength remains constant. For many purposes a slight variation in K_c with changes in [A] could be ignored. However, Powell showed that this variation should be taken into account in the calculation of rare-earth and transition metal complexes stability constants. The use of a variable K_c resulted in lower standard deviations and improved consistency of the results. Consequently, a variable K_c was used to calculate the stability constants reported in this dissertation.

2. The methods of calculation

The preparation of the sample solutions used in the determination of the conditional ionization constants will be described in the next chapter. The pH_c readings and stoichiometric data on these solutions were used to calculate K_c, the conditional ionization constant, for each sample solution.

The following definitions must now be introduced:

V_T = total volume of each sample;

V_{B_i} = volume of buffer solution added to the ith sample;

V_{S_i} = volume of KNO_3 supporting electrolyte added to the ith sample;

C_{HA} = concentration of unneutralized acid in the buffer solution;

C_A = concentration of carboxylate anion in buffer solution;

C_S = concentration of KNO_3 supporting electrolytes;

pH_{C_i} = pH_C of the ith sample solution.

From a monobasic acid,

$$HA + H_2O = A^- + H_3O^+$$

the values of K_{c_i} were then calculated by the equation

$$K_{c_i} = \frac{[H]_i[A]_i}{[HA]_i} \qquad (6)$$

The concentration of undissociated acid in each sample, $[HA]_i$ and the concentration of free carboxylate ion in each sample, $[A]_i$, were calculated by means of the equations

$$[HA]_i = \frac{V_{B_i} C_{HA}}{V_T} - [H]_i,$$

$$[A]_i = \frac{V_{B_i} C_A}{V_T} + [H]_i,$$

and $[H]_i$, the hydrogen ion concentration of each sample, was calculated from the pH_{C_i} of the sample by means of the equation

$$[H]_i = 10^{-pH_{C_i}} .$$

The correct amount of KNO_3 supporting electrolyte for the desired ionic strength in each sample, V_{S_i}, was calculated from the equation

$$V_{S_i} = \frac{(I - [A]_i)V_T}{C_S}$$

The calculated values of V_{S_i} were then compared with the original estimates. If the difference of these two values is greater than one percent for a given set of concentration data, that set can be dropped from consideration, or the experiment may be repeated using the calculated values of V_{S_i} .

The slight variation in K_c with changes in the [A] value obtained from an ordinary least squares calculation was used to calculate the formation constants in this dissertation. The experimental K_c from equation (6) was compared with the least squares K_c. If the percentage difference between these two values exceeded one percent for a given set of concentration data, that set was dropped from consideration, and a new, more precise, least squares calculation was made with the remaining data.

An ordinary least squares calculation of the conditional ionization constant K_c can be rationalized by means of Harned's theory of ionic interactions. From equation 2 it can be seen that the variation of K_c must be due to variations of the activity coefficient F(I), because the thermodynamic ionization constant K_a is a function only of temperature as in equation 1.

If the undissociated acid is a non-ionic species, then γ_{HA} should be independent of changes in the ionic composition of the solution and should remain constant at any constant ionic condition.

Harned's theory predicts that γ_H will change as the supporting electrolyte cation is replaced by hydrogen ions. However, in all the solutions studied, the concentration of potassium ion remained constant at 9.80×10^{-2} molar at a constant ionic strength of 0.100 molar. The variation in hydrogen ion concentration was very small over the series of solutions studied as from 2.262×10^{-4} to 2.882×10^{-4} molar in the case of 2,3-dihydroxy-2-methylisobutyric acid, so the variation of K_c caused by γ_H can be ruled out in this case.

In the case of γ_A, the data from 2,3-dihydroxy-2-methylisobutyric acid showed that, [A] varied from 1.714×10^{-3} to 2.260×10^{-2} molar, while $[NO_3^-]$ varied from 9.829×10^{-2} to 7.740×10^{-2} molar. According to Harned's theory, γ_A will vary as the supporting electrolyte NO_3^- anion is replaced by carboxylate anion and these concentration changes are significant. So, it is reasonable to conclude that the variation of K_c in equation 2 due to variation of γ_A and Harned's equation, as shown in equation 5, must be applied to obtain a quantitative relation between K_c and $[A]$.

The term $K_a\gamma_{HA}/\gamma_H$ in equation 2 was assumed to be constant in this system; if this constant is designated K_{a_1}, the equation may be rewritten

$$K_c = \frac{K_{a_1}}{\gamma_A}$$

or

$$\log K_c = \log K_{a_1} - \log\gamma_A.$$

If the values of K_c at two different ligand concentrations $[A]_1$ and $[A]_2$, are compared,

$$\log K_{c_2} - \log K_{c_1} = -[\log\gamma_{A_1} - \log\gamma_{A_2}]$$

Harned's equation can be introduced into the above equation, if $[A]_1$ equal zero and $[A]_2$ equal any finite ligand concentration,

$$\log K_{c_i} - \log K_{c_0} = -\frac{C[A]_i}{I}$$

K_{c_0} at zero ligand concentration and constant ionic strength will be defined as K_{a_2}. The above equation can then be rewritten

$$\log K_{c_i} = \log K_{a_2} - \frac{C[A]_i}{I}$$

or

$$K_{c_i} = K_{a_2} 10^{-C[A]_i/I}$$

From the exponential equation

$$a^x = e^{x\ln a} = 1 + x\ln a + \frac{(x\ln a)^2}{2!} + \frac{(x\ln a)^3}{3!} + \ldots.$$

The $10^{-C[A]_i/I}$ can be expanded to give:

$$10^{-C[A]_i/I} = 1 - 2.3\frac{C[A]_i}{I} + 2.65\frac{C^2[A]_i^2}{I^2} - 2.03\frac{C^3[A]_i^3}{I^3} + \ldots.$$

The above equation can then be written

$$K_{c_i} = K_{a_2} - 2.3\frac{C[A]_i}{I}K_{a_2} + 2.65\frac{C^2[A]_i^2}{I^2}K_{a_2} - 2.03\frac{C^3[A]_i^3}{I^3}K_{a_2} + \ldots.$$

or

$$K_{c_i} = a - b[A]_i + c[A]_i^2 - d[A]_i^3 + \ldots. \qquad (7)$$

where $a = K_{a_2}$

$b = 2.3CK_{a_2}/I$

$c = 2.65C^2K_{a_2}/I^2$

$d = 2.03C^3K_{a_2}/I^3$

One can see that equation 7 is rationalized from Harned's theory of ionic interactions. If γ_{HA} and γ_{H} are assumed to be constant and the higher powers of anion concentration are assumed to be small compared to the first two terms. In practice equation 7 is used to find the best fit between the experimental conditional ionization constant from equation 6 and the variable conditional ionization constant from this equation. Sometimes this theory has been ignored in order to obtain the best fit of K_c in using the least-square method of calculation.

Powell, et al. (81, 82, 111, 112) and Devine (93) assumed that $[A]_i$ is always much larger than $[A]^2_i$, then the equation was rewritten to get a good fit by least square method,

$$K_{c_i} = a - b[A]_i \qquad (8)$$

Farrell, a former chemist in professor Powell's research group minimized the coefficient b in equation 8 by plotting K_{c_i} versus $[A]^{\frac{1}{2}}_i$, and his equation was written as

$$K_{c_i} = a - b[A]^{\frac{1}{2}}_i \qquad (9)$$

It would be surprising if anyone paid any attention to the third term in equation 7, but it was nevertheless of interest to see how the more rigorous K_c experimental fit compared to the less exact version, using a least square calculation. In this dissertation, this idea was tried for

$$K_{c_i} = a - b[A]_i + c[A]^2_i \qquad (10)$$

The methods of least square calculation (115) were applied to equations 8, 9, and 10 in order to determine the coefficient a, b, and c. A computer program used for this purpose had been written by James Farrell, and later Don Johnson modified the program for the case of equation 10. These three simple least squares treatments have been compared in this dissertation for 2,3-dihydroxy-2-methylisobutyric acid. For equation 8

$$K_c = 0.30593 \times 10^{-3} - 0.52157 \times 10^{-3}[A] \tag{11}$$

with equation 9

$$K_c = 0.3104 \times 10^{-3} - 0.10135 \times 10^{-3}[A]^{\frac{1}{2}} \tag{12}$$

and with equation 10

$$K_c = 0.29791 \times 10^{-3} + 0.17424 \times 10^{-3}[A] - 0.15620 \times 10^{-1}[A]^2 \tag{13}$$

The sample output tables of equations 11, 12, and 13 are shown in Appendix A.

B. Formation Constants

1. General considerations

If the two species $M(H_2O)_n^{+q}$ and $A(aq)^{-p}$ coexist in aqueous solution, they may react to form one or more complexes in accord with the general equilibrium equation

$$xM(H_2O)_n^{+q} + yA(aq)^{-p} = M_x(H_2O)_{nx-y}A_y^{+qx-py} + yH_2O \qquad (14)$$

where M^{+q} and A^{-p} stand for the metal cation and ligand anion, respectively. Since the metal cations used in this research are the trivalent lanthanide ions and the divalent transition metal ions, and oxidation-reduction reactions are not being considered due to the existing conditions, the charges on the metal cations will be presumed always to be three for lanthanide ions and two for transition metal ions. The charge on the ligand anion will be always be presumed to be one, because the hydroxyl hydrogen atoms of the dihydroxymonocarboxylic acids used in this research do not dissociate (at least not in the pH range utilized). Hydrolysis is assumed not to occur with either the metal cations or the ligand anions since all equilibrated solutions in this work were in the pH range 3-4; and at such low pH values, hydrolysis of tripositive lanthanons and divalent transition metal cations is negligible (116, 117). For the reasons mentioned above, the charges on metal cations, ligand anions and complex ions will be omitted here and elsewhere.

The metal cations, ligand anions and complexes will all usually be solvated appreciably, but the number of associated solvent molecules in solution cannot be determined; hence the associated water molecules will also be omitted from the formulas of these species.

Although many examples of the existence of polynuclear complexes for which $x > 1$ and $y \geq 0$ have been reported, it has been found that only mononuclear complexes, for which $x = 1$ and $y \geq 1$, are formed in a large number of analogous systems, especially in dilute solution. In the particular conditions of this research and others, only mononuclear complexes appear to form, and polynuclear complexes will not be considered further. In a system which contains only mononuclear species, M may be considered the central group of the complex MA_n, and A is usually referred to as the ligand. The maximum number of ligands that can combine with one central group is commonly denoted by N.

Now, equation 14 can be represented specifically as various equilibria between a metal ion M and a ligand anion A:

$$M + A = MA$$

$$MA + A = MA_2$$

$$MA_2 + A = MA_3$$

$$MA_{n-1} + A = MA_n$$

The equations above give rise to a set of equilibrium expressions

$$K_1 = \frac{[MA]}{[M][A]}$$

$$K_2 = \frac{[MA_2]}{[MA][A]}$$

$$K_3 = \frac{[MA_3]}{[MA_2][A]}$$

$$K_n = \frac{[MA_n]}{[MA_{n-1}][A]} \qquad (15)$$

Another way of expressing the set of equilibrium relationships is as follows:

$$M + A = MA$$

$$M + 2A = MA_2$$

$$M + 3A = MA_3$$

$$M + nA = MA_n$$

for which

$$\beta_1 = \frac{[MA]}{[M][A]}$$

$$\beta_2 = \frac{[MA_2]}{[M][A]^2}$$

$$\beta_3 = \frac{[MA_3]}{[M][A]^3}$$

$$\beta_n = \frac{[MA_n]}{[M][A]^n} \qquad (16)$$

Since there can be only N independent equilibria is such a system, it is clear that the K_i's and the β_i's are related. It is not difficult for one to see that the relationship is:

$$\beta_N = K_1 K_2 K_3 \cdots K_N = \prod_{i=1}^{N} K_i$$

The K_i's are called the stepwise formation constants (or stepwise stability constants and stepwise equilibrium constants), and β_i's are called the over-all formation constants (or over-all stability constants and over-all equilibrium constants).

The stoichiometric formation constant, β_n in equation 16 can be rewritten to get the thermodynamic formation constant, $*\beta_n$

$$*\beta_n = \beta_n \frac{\gamma_{MA_n}}{\gamma_M \gamma_A^n} \tag{17}$$

or

$$\beta_n = *\beta_n \frac{\gamma_M \gamma_A^n}{\gamma_{MA_n}} = *\beta_n F(\gamma) = *\beta_n F(I) \tag{18}$$

For a given system, the thermodynamic stability constant is a function only of temperature; it is directly related to equation 1 (which replaces K_a in equation 1 by $*\beta_i$). Equations 17 and 18 are referred to systems involving finite concentrations. At the solute standard state, the activity coefficients approach one as the concentrations of all the species approach zero. Thus, in the limiting case of the infinitely dilute solution, the stoichiometric formation constant will equal the thermodynamic formation constant.

Essentially the same general considerations by Lewis and Randall (107), Debye and Hückel (108), Harned (109), and Harned and Owen (110) theory are applied to the complex-ion formation constants. The thermodynamic formation constants cannot be obtained directly, although stoichiometric formation constants can easily be measured. According to Debye and Hückel's theory, the value of β_n will be constant for all dilute solutions of the same ionic strength. According to Harned's theory of ionic interactions, if the composition of the ionic medium changes, the values of β_n will vary slightly with concentration even when the ionic strength remains constant.

Stoichiometric formation constants are determined from a wide range of equilibrium constant data obtained from dilute solutions of identical ionic strength in which equation 4 is presumed valid, as all the relevant activity coefficients should have remained very nearly constant. $F(\gamma)$ or $F(I)$ in equation 18 should be constant; consequently, the value of the stoichiometric formation constant should be a constant for all solution of the same ionic strength, and this type of formation constant is called a conditional formation constant (or conditional stability constant and conditional equilibrium constant). Once conditional formation constants have been measured, one can estimate the values of the thermodynamic formation constants by obtaining conditional formation constants at several ionic strengths and extrapolating the results to zero ionic strength. At zero ionic strength, $F(\gamma)$ or $F(I)$ will equal one, and β will equal $*\beta$.

Powell used an application of the Harned's theory to calculate the acid dissociation constants. He used this slight variation in K_c with changes in $[A]$ to obtain the formation constant in order to correct the β_i values. He showed that when this variation K_c with changes in $[A]$ was taken into account, it resulted in lower standard deviations and improved consistency of the results. Consequently, a variable K_c was used to calculate the formation constants reported in this dissertation.

Approximately the same range of ligand concentration was used in the study of the rare-earth and transition metal complex stability constants as was used in the study of the acid dissociation constants. Since the activity coefficient of one of the species was not held strictly constant during the measurement of the acid dissociation constant, one must assume that the same behavior will be found during the measurement of the formation constants. As in Harned's theory, the formation constant values should vary slightly over the range of ligand concentrations employed. Unfortunately, because of the computational difficulties involved, the functional dependence of β_i on $[A]$ cannot be determined as one does in the case of acid dissociation constants. But by using a variable K_c, the variation in β_i with increasing $[A]$ should be kept relatively small, and the formation constant values presented in this dissertation can be considered to be the average values over the ligand concentration range employed.

2. The methods of calculation

Prior to discussing formation constant calculation methods, some necessary definitions should be introduced. In the next section, the experimental aspects of the formation constant determinations will be described. C_A and C_M are the total concentrations of the ligand and metal ions, respectively, and are known from the analytical compositions of the initial solutions. These terms are defined by

$$C_A = [A] + [MA] + 2[MA_2] + 3[MA_3] + \ldots n[MA_n]$$

and

$$C_M = [M] + [MA] + [MA_2] + [MA_3] + \ldots [MA_n]$$

Where $[A]$ and $[M]$ are free ligand and free metal concentrations respectively. The solution of these equations generally involves the use of the average number of ligands bound per metal ion $\bar{n}$, which is defined as:

$$\bar{n} = \frac{C_A - [A]}{C_M} \tag{19}$$

$\bar{n}$ was first introduced by Niels Bjerrum (118, 119) in 1915 and has been defined as "the degree of formation of the system" or "the ligand number" by Jannik Bjerrum (14). The ligand number is also given as:

$$\bar{n} = \frac{[MA] + 2[MA_2] + 3[MA_3] + \cdots n[MA_n]}{[M] + [MA_2] + [MA_3] + \cdots [MA_n]}$$

from

$$K_1 = \frac{[MA]}{[M][A]}$$

$$K_2 = \frac{[MA_2]}{[MA][A]}$$

$$K_3 = \frac{[MA_3]}{[MA_2][A]}$$

$$K_n = \frac{[MA_n]}{[MA_{n-1}][A]}$$

it is seen that

$$[MA] = K_1[M][A] = \beta_1[M][A]$$

$$[MA_2] = K_1K_2[M][A]^2 = \beta_2[M][A]^2$$

$$[MA_3] = K_1K_2K_3[M][A]^3 = \beta_3[M][A]^3$$

$$[MA_n] = K_1 \dots K_n [M][A]^n = \beta_n [M][A]^n$$

One can replace the terms $[MA]$, $[AM_2]$, $[AM_3] \cdots [AM_n]$ appropriately, and factor out $[M]$ to get:

$$\bar{n} = \frac{K_1[A] + 2K_1K_2[A]^2 + 3K_1K_2K_3[A]^3 + \dots NK_1 \dots K_N[A]^N}{1 + K_1[A] + K_1K_2[A]^2 + K_1K_2K_3[A]^3 + \dots K_1 \dots K_N[A]^N}$$

$$= \frac{\sum_{n=1}^{N} n\beta_n [A]^n}{\sum_{n=0}^{N} \beta_n [A]^n} \qquad (20)$$

This interesting result shows that the ligand number $\bar{n}$ depends only on the conditional formation constants and the concentration of the free ligand $[A]$ in solution. If one knows N different values of $\bar{n}$ at N values of $[A]$, one can determine N constants (either $\beta_1, \beta_2, \beta_3, \dots, \beta_N$ or K_1, K_2, $K_3, \dots, K_N$). For the calculation of these constants graphical or numerical methods are widely used (14, 120, 121, 122) though the use of computers is replacing these methods to a large extent (123).

Equation 20 is the basic equation for the formation constant calculation. The methods to be considered consist of two types: (a) those methods useful only or primarily where one complex is present at a time; (b) those methods designed to take step-wise formation of the complexes into consideration without worrying about whether all of the possible complexes are actually present in the solution or not. The systems studied in this research are complex, so the focus of this section will be on the second type, but some idea of the first type should be introduced here.

The slope-ratio method was described by Harvey and Manning (124) and Meyer and Ayres (125) for the case in which one complex predominates at a time. Beer's law can be used to determine the molar concentration of the complex species. Once the extinction coefficient of the complex has been established, the formation constant can be determined. Another spectrophotometric method used to determine the formation constant is the method of isomolar solutions. It was described by Job (126), Jones (127) and Watkins and Jones (128). The last method for the single complex that will be mentioned is the solubility method. This method is applicable only where solubility changes are due to formation of a single new complex. Vosburgh and Beckmann (129) studied the formation of cadmium oxalate in cadmium perchlorate solutions; and a somewhat more complicated instance where solubility studies were used to determine complexity constants (the Yb^{+3} - $C_2O_4^=$ system) was studied by Crouthamel and Martin (130).

Equation 20 is the basis for calculating the formation constants in a system wherein more than one complex is present at a time. The methods that have been used to calculate the stability constants can be divided into three categories: successive approximation methods, graphical integration techniques, and least squares computations. Although a least squares method was used in this research, the basic concepts of the other two methods will be briefly discussed. The descriptions of these two methods given below are intended to illustrate the general nature of the methods rather than their most sophisticated mathematical formulation.

a) J. Bjerrum's Potentiometric Method (14). This publication presented a very complete survey of the problems involved in the determination of successive stability constants of metal ammines and related complexes. By using a medium which contained a large amount of an ammonium salt, such as ammonium nitrate, ammonia and the metal ammines could be generated by the addition of a strong base. For any solution:

$$[NH_3] = K_{NH_4^+} \frac{[NH_4^+]}{[H^+]}$$

where $K_{NH_4^+}$ is the acid dissociation constant of the NH_4^+ ion. The ammonia concentration could thus be determined from the pH_c, while the total available ammonia, C_{NH_3}, and the ionic strength remained constant due to the experimental conditions. From these quantities, $\bar{n}$ can be calculated by either the exact expression:

$$\bar{n} = \frac{C_{NH_3} + [H^+] - [NH_3]}{C_M}$$

or by the approximation $$\bar{n} = \frac{C_{NH_3} - [NH_3]}{C_M}$$

From the various equilibria in which $M(NH_3)_x$ species are formed one can then determine the successive stability constants using at least N expressions of the type:

$$\bar{n} = \frac{K_1[NH_3] + 2K_1K_2[NH_3]^2 + 3K_1K_2K_3[NH_3]^3 + \ldots NK_1\ldots K_N[NH_3]^N}{1 + K_1[NH_3] + K_1K_2[NH_3]^2 + K_1K_2K_3[NH_3]^3 + \ldots K_1\ldots K_N[NH_3]^N}$$

Martell and Calvin (131) present a variety of approximate and graphical methods for obtaining solutions for such sets of equations. Specific solutions have not been published for all numbers of complexes but are available for cases where up to three ligands are coordinated. Block and McIntyre (132) have given exact algebraic solutions for the formation constants for N = 1, 2, and 3 which are useful in the treatment of most complexation reactions involving polydentate ligands; Randall, Martin, and Moeller (133) used a digital computer to calculate successive formation constant for N = 3. The disadvantages of Bjerrum's methods are the limiting use of N and one cannot use data for which $\bar{n}$ is greater than N, or data for which $\bar{n}$ is very close to N. Consequently, K_1 is calculated from data for which $\bar{n}$ is between the limits of 0.3 and 0.7, K_2 is calculated from data for which $\bar{n}$ has the limits of 1.3 and 1.7, and K_3 is established between the $\bar{n}$ values 2.3 and 2.7.

b) Ion-exchange Methods (134, 135). Cation exchange chromatography has been used to study complexes in solution for systems containing either a single complex or systems in which several complexes are present. The basic principle is the relationship which exists between the amount of metal absorbed on the ion exchange resin and the concentration of metal ion in solution. The amount of metal absorbed on the cation exchange resin ideally depends only on the concentration of free metal ion in solution. The amounts of resin, the ionic strength, the pH, and the temperature must all be held constant in such experiments.

Ion exchange techniques have been applied to the determination of successive stability constants by several people. Fronaeus (136, 137, 138) has illustrated his study of the cupric acetate system. The sodium form of the resin was used in a medium kept at unit ionic strength by the addition of sodium perchlorate. His equations are developed as follows: C_M and C_A are the total concentrations of metal ion M and ligand ion A in the solution in equilibrium with the ion-exchanger. $[MR_2]$, $[MAR]$, and $[NaR]$ are the moles of M^{+2}, MA^+, and Na^+ contained in a unit weight of the exchanger at equilibrium. Then

$$C_{MR} = [MR_2] + [MAR]$$

$$\phi = \frac{C_{MR}}{C_M}$$

In practice, ϕ values are obtained at different C_A values but ideally C_{MR} should be kept constant. For a rough approximation one may use:

$$\bar{n} = -\frac{C_A}{\phi}\left(\frac{\partial \phi}{\partial C_A}\right)_{C_{MR}}$$

Where $[A^-]$ values may be calculated from equation 19

$$[A^-] = C_A - \bar{n} \cdot C_M$$

If the denominator of Equation 20 is denoted by x, then it is apparent that

$$x = 1 + \sum_{n=1}^{N} \beta_n [A^-]^n$$

To obtain the β_n, the product $\phi \cdot x$ is differentiated twice with respect to $[A^-]$ and using the equation for ϕ to get:

$$\phi'' \cdot x + 2\phi' \cdot x' + \phi \cdot x'' = 0$$

Substitution of the expressions for x, x', and x" leads to:

$$\phi'' + \sum_{n=1}^{N}([A^-]^n\cdot\phi'' + 2n[A^-]^{n-1}\cdot\phi' + n(n-1)[A^-]^2\cdot\phi)\beta_n = 0$$

A graph of ϕ vs. $[A^-]$ allows ϕ' to be evaluated and a graph of ϕ' vs. $[A^-]$ allows ϕ'' to be obtained. When ϕ, ϕ', and ϕ'' terms are known at N discrete values of $[A^-]$ the complexity constants β_N can be computed. Mahan and Dey (139) used this method for nickel(II)-Nitroso-R-Salt complexes.

c) A Graphical Method. Equation 20 has been modified by several people to get a suitable form such that, if 2 functions in the modified equation are plotted, some other function such as complexity constants β_i can be obtained from the graph. One useful method has been reported by Rossotti and Rossotti (140) who rearranged equation 20 to get:

$$\frac{\bar{n}}{a(\bar{n}-1)} + \beta_1 + \beta_2 a\frac{(\bar{n}-2)}{(\bar{n}-1)} = \sum_{n=3}^{N}\frac{(n-\bar{n})}{(\bar{n}-1)}\beta_n a^{n-1}$$

Plotting $\bar{n}/a(\bar{n}-1)$ vs. $a(\bar{n}-2)/(\bar{n}-1)$ give β_1 as an intercept and β_2 as a limiting slope.

d) The Least Squares Method. The least squares method used in this dissertation is based on the method of Sullivan, Rydberg, and Miller (123). This method was first adapted by Stagg (141), Stagg and Powell (142). The method has been further modified by Powell and several of his co-workers.

Equations 19 and 20 can be rearranged to get

$$\sum_{n=0}^{N}(\bar{n}-n)\beta_n[A]^n = \sum_{n=0}^{N}(C_A - [A] - nC_M)\beta_n[A]^n = 0$$

A program was developed for the I.B.M. 360 computer to calculate the best values for the β_n from the equation:

$$0 = \sum_{n=0}^{N} (y - x - nz)\beta_n x^n$$

The input data are $y = C_A$, $x = [A]$ and $z = C_m$. The residual for a given set of data (x_i, y_i, z_i) will be given by the equation

$$U_i = \sum_{n=0}^{N} (y_i - x_i - nz_i)\beta_n x_i^n \qquad (21)$$

A weighting factor was introduced in applying the method of least squares to equation 21, because of the small random errors in the dependent variables (x, y, z) that one cannot avoid. The weighting factor weights those data expected to exhibit smaller errors more heavily than data prone to larger errors. When the dependent variable is subject to random errors, the weighted least squares method requires that a set of β_n be determined which minimizes the residuals. Therefore in equation 21, while one ideally should have each $U_i = 0$, one can determine that set of β_n values which best relates I data sets (x_i, y_i, z_i) in the least squares sense by minimizing

$$S = \sum_{i=1}^{I} w_i U_i^2 \qquad (22)$$

Where w_i is the weighting factor for the ith data set and I is the total number of data sets (x_i, y_i, z_i).

When S is minimized with respect to each of the parameters in the β_n, N equations of the form $dS/d\beta_n$ are obtained. These N equations are set equal to zero and solved by matrix algebra. Each of these N equations is of the form

$$Y(n) + W(n,1)\beta_1 + W(n,2)\beta_2 + \dots + W(n,N)\beta_N = 0$$

or in matrix form

$$\begin{bmatrix} W(1,1) & W(1,2) & \dots & W(1,N) \\ W(2,1) & & & \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ W(N,1) & W(n,2) & \dots & W(N,N) \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \cdot \\ \cdot \\ \cdot \\ \beta_N \end{bmatrix} = \begin{bmatrix} -Y_1 \\ -Y_2 \\ \cdot \\ \cdot \\ \cdot \\ -Y_N \end{bmatrix}$$

where $$W(N,N) = \sum_{i=1}^{I} w_i(y_i - x_i - nz_i)(y_i - x_i - Nz_i)x_i^{2N}$$

$$Y(N) = \sum_{i=1}^{I} w_i(y_i - x_i)(y_i - x_i - nz_i)x_i^{N}$$

using a matrix notation $WA = -Y$

A can be solved by inverting W as

$$A = W^{-1}(-Y) \tag{23}$$

The computer program is set up to calculate the values of $\beta_0, \beta_1 \dots \beta_N$

from the data sets (x_i, y_i, z_i) using equation 23. The minimum value of S in equation 22 is then calculated using the best values of the $\beta_0, \beta_1, \ldots \beta_N$. The standard deviation of each of the parameters $\delta\beta_i$, may be computed from the diagonal elements of the inverse of the matrix as

$$\delta\beta_i^{2} = W_{ii}^{-1} \frac{S_{min}}{(I-N)}$$

where W_{ii}^{-1} is the i th diagonal element of the inverse of W, and (I-N) is the degrees of freedom for the Chi-squared distribution χ^2 of S_{min}, where I is the number of data points used and N is the number of parameters.

The weighting factor should be determined prior to the calculation of equation 23. The weighting factor is related to the errors in the measurements by the expression

$$w_i = \frac{1}{\delta U^2} \tag{24}$$

where δU is the standard error in the residual U which reflects the errors in the data x, y and z. Sullivan, Rydberg, and Miller (123) assumed that most of the variation in U is due to variation in x_i, then

$$\delta U = \frac{\partial U}{\partial x} \delta x$$

where δx is the standard deviation in the quantity x. Devine (93) revised the computer program to include the variation in y and z in the weighting factor:

$$\delta U = \frac{\partial U}{\partial x}\delta x + \frac{\partial U}{\partial y}\delta y + \frac{\partial U}{\partial z}\delta z \qquad (25)$$

This complete weighting factor gave a better fit of the data, and showed smaller standard deviations in the calculated β_n values than when the shorter weighting factor was used. The complete weighting factor was also used in this research instead of the original shorter one.

Since one needs to know the β_n in order to calculate the weighting factor, an iterative procedure was employed. One must first estimate the values of the desired stability constants and feed them into the computer program to calculate the first set of weighting factors from equations 24 and 25. Then an improved set of βs are calculated from equation 23, and this improved set of β's is used to calculate a new set of weighting factors. The process is repeated until convergence is obtained to within acceptable limits. Generally three to ten such iterations sufficiently yields a consistent set of solutions in this research.

The best stability constants, calculated from the last iterative process, were used to obtain a number of quantities. The sample output tables of this program is shown in Appendices B, C, D, E, and F. The experimental $\bar{n}$ was obtained from the experimental quantities x_i, y_i, and z_i, using equation 19, and equation 20 was used to obtain a calculated $\bar{n}$ from stability constants and the x_i values. The percentage difference between the two values of $\bar{n}$ was then calculated for each individual data set. The percentage differences in the two values of $\bar{n}$ provide a means of checking the consistency of each data point with respect to the whole series of measurements.

The weighted least squares method had several advantages. It provided a number of statistical checks on the results of the computations, such as the calculation of the standard deviation of each parameter and the percentage difference or apparent errors between the two values of $\bar{n}$.

IV. EXPERIMENTAL DETAILS

A. Preparation of the Organic Ligands

1. α,β-dihydroxy-β-methylisobutyric acid (DHMIBA)

Melikoff (143), Melikoff and Petrenko-Kritschenko (144) had difficulty in synthesizing this acid, because the two asymmetric carbon atoms caused four optical isomers or two pairs of enantiomorphic modifications. One of the dl-mixtures melts at 110-111° and the other at 88° (145). The high-melting diastereomer has been prepared successfully from tiglic acid (trans-2-methyl-2-butenoic acid) via treatment with HOCl followed by alcoholic KOH and subsequent hydrolysis (143) and from tiglic acid by hydroxylating via peracetic acid (trans-addition) (146) and from angelic acid (cis-2-methyl-2-butenoic acid) by hydroxylating with aqueous alkaline $KMnO_4$ (cis-addition) (145). The lower-melting diastereomer has been obtained from tiglic acid via the hydroxylating action of alkaline $KMnO_4$ at 0° (145, 146). Because of the low yield and the high cost of angelic and tiglic acids as intermediates in the methods mentioned above, a new method (147) was developed in this laboratory using a procedure similar to that used in the case of α,β-dihydroxyisobutyric acid (148).

a. *Experimental procedure* Ninety-four grams (3.5 moles) of freshly prepared anhydrous liquid HCN (0°) was added in an efficient hood to 259 g (2.5 moles) of 85% 3-hydroxy-2-butanone (acetoin) at 0° contained in a 2-l, three-neck, round-bottom flask, fitted with an ice-water-cooled reflux condenser, a thermometer and a stirrer. After thoroughly mixing the reactants, the flask was raised just out of the ice-bath, and solid

KCN catalyst was added in 0.1-g portions to initiate and sustain the reaction. After adding a total of 0.8 g of KCN, the temperature was observed to rise, slowly at first and then rapidly. When the temperature reached 40°, the reaction was quenched and maintained between 30 and 32°, either by judiciously dipping the reaction flask momentarily into the ice-bath or by adding a bit more KCN. In all, 2.0 g of solid KCN catalyst was used. After the reaction subsided and the temperature had dropped to 25° (2.5 h), the mixture was allowed to stand overnight at room temperature.

The mixture was then cooled to 2° and treated with 282 ml of chilled 12N HCl, (3.5 moles), whereupon the temperature rose rapidly. The temperature was again controlled by means of the ice-bath between 30 and 32° and (after about an hour) the solution was saturated with respect to HCl by bubbling in anhydrous HCl at such a rate that the temperature of the mixture did not exceed 30° while being stirred in the ice-bath. After 5 h of such treatment, the mixture was allowed to stand overnight at room temperature.

After 20 h, the light-brown reaction mixture was diluted to a volume of 4.5 l, then passed into and eluted (with distilled water) through an ion-exchange column system (comprised of six 6-in.-diameter X 48-in.-long cylindrical beds of 40-50 mesh Dowex 50W-X8 (H^+form) cation-exchange resin) as shown in Figure 8, at a rate of 1.2 l/h. The effluent solution was collected in a series of fifty-five 1.2 l fractions and the pH of each solution was measured to monitor the separation achieved. The strong acid (HCl) was observed to pass through the system (at pH 0.9) in fractions 19-36, and 2,3-dihydroxy-2-methylbutanamide was detected (accompanied by some formic and 2,3-dihydroxy-2-methylbutanoic acids) in fractions 40-49 (which had a pH of about 2.4).

When the HCl-free amide-bearing fractions(40-49) were combined and evaporated to a small volume (at 98°) and allowed to cool, large crystals of 2,3-dihydroxy-2-methylbutanamide separated from the aqueous medium. The crystals were filtered off, washed with a small portion of cold acetone and dried. The recovered amide, weighing 288 g (86% yield), melted at 139-140° and was found to contain 45.25% C, 8.20% H and 10.50% N (theoretical analysis: 45.11% C; 8.27% H; 10.53% N; 36.09% O). On two prior occasions, when the temperature was controlled less carefully, the amide was obtained in yields of 53 and 71%.

Two moles (266 g) of the amide were dissolved in 2.5 l of water and treated with 100 g (2.5 moles) of NaOH pellets. The solution was simmered at 98° (while water was added occasionally) until evolution of NH_3 ceased; then it was cooled and passed into and eluted (with distilled water) through an ion-exchange column system (comprised of three 6-in.-diameter X 48-in.-long cylindrical beds of 40-50 mesh Doxex 50W-X8 (H^+ form) cation-exchange resin) at a rate of about 1.2 l/h. The effluent solution was collected in a series of thirty 1.2-l fractions. Fractions 18 through 25 (pH 2.13) were found to contain the bulk of the 2,3-dihydroxy-2-methylbutanoic acid. These were concentrated by vacuum evaporation (under 40°) to a thick syrup, which was dissolved in hot ethyl acetate and allowed to cool; whereupon, 2,3-dihydroxy-2-methylbutanoic acid separated in crystalline form and was recovered by filtration. This crude acid product was recrystallized from a warm mixture of acetone and carbon tetrachloride, yielding 204 g (76% yield) of 2,3-dihydroxy-2-methylbutanoic acid melting at 109-110° and having an equivalent weight of 135.39 (calculated 134.14). The product was found to contain 44.54% C and 7.50% H (theoretical analysis: 44.71% C; 7.46% H; 47.83% O).

2. α,β-dihydroxyisobutyric acid (DHIBA)

Because of the difficulty in the synthesis of this acid reported by Melikoff (143), Glattfeld and Sherman (149), Powell developed a new method of preparation using ion-exclusion and ion-exchage techniques. The α,β-dihydroxyisobutyric acid used in this research was synthesized using the method described by Powell, et al. (148); and full details are reiterated here in order to compare the method with that described above in the case of α,β-dihydroxy-β-methylisobutyric acid.

a. Experimental procedure 124 g (4.6 moles) of freshly prepared anhydrous liquid HCN (0°) was added in an efficient hood to 296 g (3.61 moles) of 90.6% acetol at 0° contained in a 2-l, 3-neck, round-bottom flask, fitted with an icewater-cooled reflux condenser, a thermometer and a stirrer. After thoroughly mixing the reactants, the flask was raised just out of the ice-bath and solid KCN catalyst was added in 0.2 g portions to initiate and sustain the reaction. After adding 0.4 g of catalyst, the temperature of the reaction mixture was observed to rise, slowly at first and then rapidly, until the mixture began to boil and HCN began to return from the condenser. The temperature was maintained between 45-50° by judicious dipping of the reaction flask momentarily into the ice-bath or by adding catalyst, as needed. In all, 2 g of catalyst were added to the mixture to ensure establishment of equilibrium within a reasonable time.

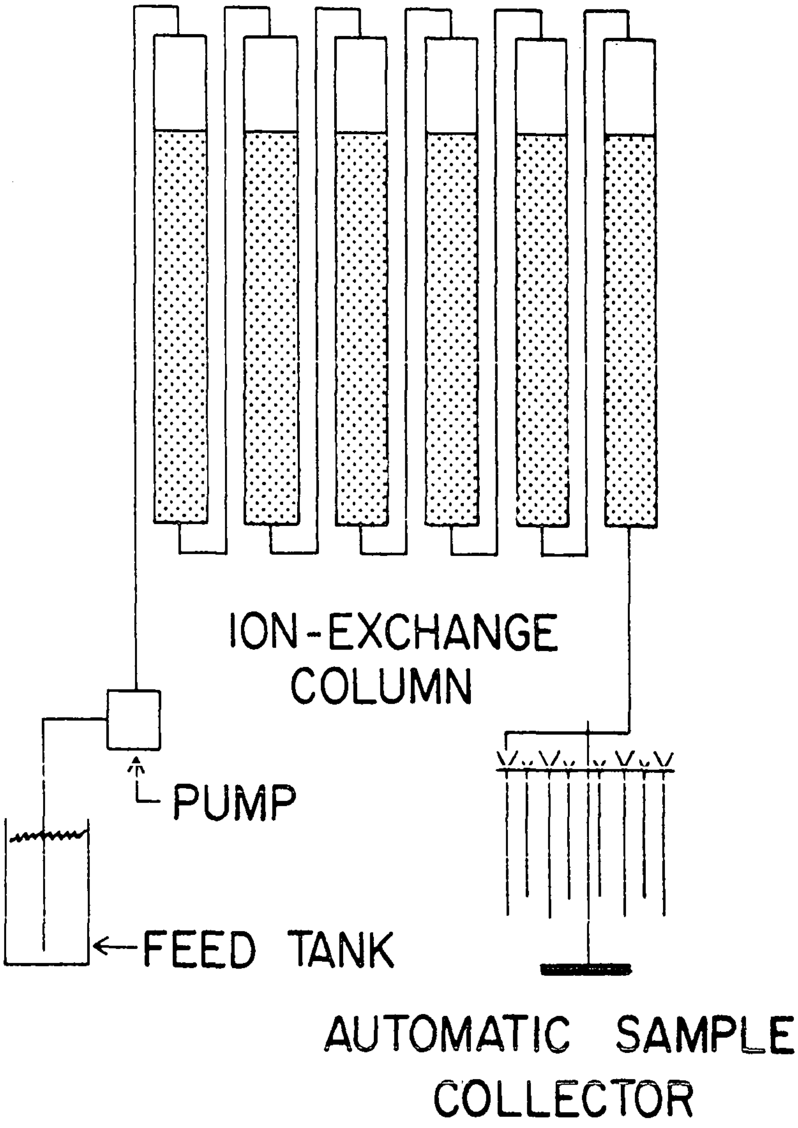
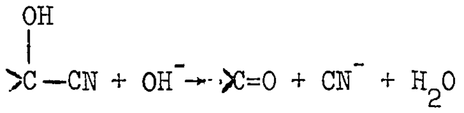


Figure 8. An ion-exchange column system

After the reaction had subsided and the temperature returned to 25° (about 2 h), the flask assembly with reaction mixture was weighed (the assembly had been weighed alone previously) and about a gram of the mixture was weighed into a 100-ml volumetric flask containing 2 ml of concentrated nitric acid and about 50 ml of distilled water and finally diluted to volume. This procedure "froze" the reaction and permitted an analysis for the constituents HCN and acetol cyanohydrin present at equilibrium. HCN was estimated in one aliquot of the diluted reaction mixture by adding a known amount of silver nitrate, filtering off and rinsing the AgCN precipitate, and finally titrating the soluble silver in the filtrate plus rinse water with standard potassium thiocyanate solution. The acetol cyanohydrin content was determined by the difference between the CN^- titers in this aliquot and an identical portion which was first made strongly basic to convert the cyanohydrin to the original ketone and CN^- and then added with vigorous stirring to a known amount of excess silver nitrate solution containing sufficient nitric acid to neutralize all of the base. The reaction



$$>\overset{\displaystyle OH}{\overset{|}{C}}-CN + OH^- \rightarrow\; >C{=}O + CN^- + H_2O$$

was found to occur instantaneously and quantitatively. By virtue of these analyses it was established that 3.41 moles out of 3.61 moles of acetol originally present were converted to acetol cyanohydrin, and that only 0.81 moles of HCN and 0.20 moles of acetol remained unreacted.

The reaction mixture was then cooled to 0°, treated with 400 ml of cold concentrated hydrochloric acid, and saturated with respect to HCl by bubbling in anhydrous HCl at such a rate that the temperature of the mixture did not exceed 40° while being stirred in an ice bath. Within an hour a large amount of NH_4Cl had formed and the reaction was allowed to proceed at room temperature overnight with no further addition of HCl. After 16 h of hydrolysis, the mixture was sampled and analyzed again for cyanohydrin. The same technique was used to determine the concentration of cyanohydrin in the presence of chloride as was used to estimate cyanohydrin in the presence of excess cyanide. At this point only 0.06 moles of cyanohydrin remained. Analysis for nitrogen (Kjeldahl), after removing ammonium ion from an aliquot by cation exchange and correcting for cyanohydrin, revealed that the reaction mixture contained 2.86 moles of α,β-dihydroxyisobutyramide at this point.

The reaction mixture was then diluted to a volume of 8 l, passed into and eluted (with distilled water) through an ion-exchange column system (consisting of three 6-in. diameter x 48-in. long beds of H^+-form, 40-50 mesh, Dowex 50W X8, cation-exchange resin) as shown in Figure 8, at a rate of about 1.8 l/h. The effluent solution was collected in a series of 80, 900-ml fractions. The individual samples were analyzed for total acidity, chloride (HCl), displaceable NH_3 (amide), and volatile weak acid (formic acid). The first strong acid (HCl) appeared in the 27th fraction, peaked at about the 45th fraction and then fell off sharply (see Fig. 9). Amide and weak acids were detected in samples 50 through 76. Samples 50 through 60 contained varying proportions of HCl, amide and α,β-dihydroxyisobutyric acid, but only a little formic acid. Most of the formic acid (from hydrolysis of HCN) eluted in fractions 61 through 75.

Elution curves for the several constituents of the mixture are somewhat irregular. The occurrence of shoulders was unexpected, but reproducible, and remains to be explained. Integration of the areas under these analytical curves revealed a total of 2.55 moles of α,β-dihydroxyisobutyramide, 0.84 moles of α,β-dihydroxyisobutyric acid and 0.76 moles of formic acid. Since 3.41 moles of acetol cyanohydrin and 0.81 moles of HCN were indicated before hydrolysis, material balances reveal that virtually all of the excess HCN ended up as formic acid and 3/4 and 1/4 of the acetol cyanohydrin intermediate yielded amide and acid respectively.

When the HCl-free amide-bearing solutions (61 through 73), containing 233 g of amide, were evaporated to near dryness and allowed to cool, large crystals of α,β-dihydroxyisobutyramide separated from the aqueous medium. These crystals were filtered off subsequently and rinsed with a small portion of cold acetone. The recovered amide, melting at 123-127° weighed 202 g. When recrystallized from water, the pure amide melted at 128.5-129.5°. It is clear, of course, that additional ion-exclusion operations performed on the HCl-containing samples, 50 through 61, as well as appropriate retreatment of the mother liquor from amide recovery, would have enhanced the yield of α,β-dihydroxyisobutyramide. Subsequently, 155 g of the recovered amide was dissolved in a liter of water and treated with 60 g of NaOH pellets. The solution was boiled (while water was added occasionally) until evolution of NH_3 ceased; then it was cooled and passed through a 2-in., H^+-form, 40-50 mesh, Dowex 50W X8, cation-exchange resin bed, 4 ft. long, to obtain a dilute solution of α,β-dihydroxyisobutyric acid which was subsequently concentrated to a thick syrup by vacuum evaporation below 30°. The syrup was dissolved in 3 parts of warm ethyl acetate and allowed to cool. Crystallization of α,β-dihydroxy-

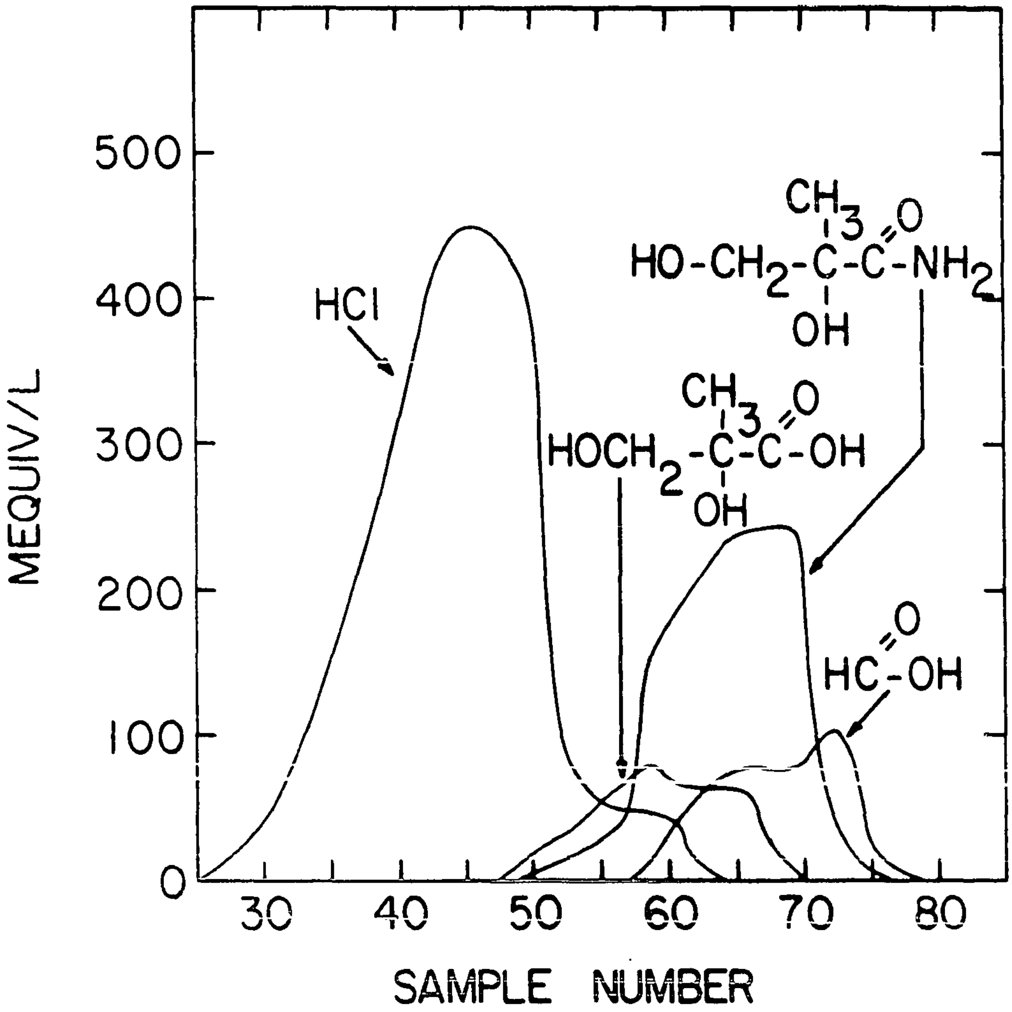


Figure 9. Ion exclusion separation of mineral acid from reaction products

isobutyric acid was induced and the mixture was cooled in ice before filtering. Two crops of crystals totalling 115.4 g and melting at 104-104.5° were obtained. The melting point noted by Glattfeld and Sherman (149) was 104°.

3. α-hydroxyisobutyric acid (HIBA)

α-hydroxyisobutyric acid from the Aldrich Chemical Co., Inc., was purified by recrystallizing it from hot carbon tetrachloride solution. The recrystallized acid was found to melt at 83.5° and have an equivalent weight of 104.70 (calculated 104.12).

B. Preparation of Reagents

1. Trivalent rare-earth nitrate solutions

Approximately 0.1 M rare-earth nitrate solutions were prepared by dilution of concentrated stock solutions of rare-earth nitrates. These concentrated stock solutions were prepared originally from rare-earth oxides of 99.99% purity supplied by Powell's rare-earth separation group at the Ames Laboratory of the U. S. Atomic Energy Commission by Mr. James Farrell, using the method described by Adolphson (150). They were found to have a 3:1 anion to cation ratio, within experimental error. The diluted solutions were standardized by precipitation of aliquots with oxalic acid and ignition of the rare-earth oxalates to their corresponding oxides (all rare-earth oxides are Ln_2O_3, except CeO_2, Pr_6O_{11} and Tb_4O_7) at 800° (83). As a check of these standardizations, complexometric EDTA titrations of the type described by Fritz and Schenk (151) were used.

2. Divalent transition metal nitrate solutions

Approximately 0.1 M transition metal nitrate solutions were prepared from crystalline transition metal nitrates, which were obtained from J. T. Baker Chemical Co., without further purification. These solutions were standardized by passing aliquots through a well-washed hydrogen-form cation exchanger (Dowex-50) and titrating the effluent and rinsings with standard base.

3. Potassium hydroxide solution

Approximately 0.1 M and 1.0 M potassium hydroxide solutions were prepared by diluting concentrated, carbonate-free, potassium hydroxide purchased from Anchemia Chemicals, Ltd. in boiled, deionized water. The resulting solutions were kept in large containers and Ascarite (NaOH), 8 to 20 mesh, and Drierite ($CaSO_4$), 8 mesh, were used to protect the solutions from carbonate contamination and dilution errors, respectively. The solutions were standardized by titration against primary standard grade potassium acid phthalate.

4. Potassium nitrate solution

About 1.5 M potassium nitrate solution was prepared from J. T. Baker reagent-grade potassium nitrate, dissolved in boiled, deionized water. The solution was standardized by passing aliquots through a well-washed, hydrogen-form, cation exchanger (Dowex-50) and titrating the effluent and rinsings with standard base.

5. Nitric acid solution

Approximately 0.05 M nitric acid solution was prepared from concentrated, reagent-grade acid. The solution was standardized by titration against standard base.

6. Buffer solutions

Approximately 0.1 M solutions of α,β-dihydroxyisobutyric acid, α,β-dihydroxy-β-methylisobutyric acid and α-hydroxyisobutyric acid were prepared by dissolution of the recrystallized reagents and standardized; then they were partially neutralized with standard CO_2-free potassium hydroxide. The free acid concentration in each buffer was confirmed by subsequent titration of aliquots with standard base.

C. Experimental Apparatus

The apparatus for the potentiometric experiments is shown in Figure 10. Either a Beckman Research pH meter or a Corning Model 101 Digital Electrometer was used to measure hydrogen ion concentrations of the solutions. These pH meters were each equipped with a Beckman sleeve-type calomel reference electrode and a Beckman (or Corning) glass electrode. Most of the experiments were done using the Corning Model 101 Digital Electrometer, because this instrument has a number of modes of operation, including a direct pH readout which was used in this research. This instrument was better than the currently available electrodes in terms of accuracy, stability, and reproducibility. The Corning 101 Electrometer will read pH values to within ± 0.001 pH units with comparable linearity and repeatability. High quality glass and reference electrodes deliver comparable performance only when in perfect operating condition, a state much more easily discussed than attained.

A pair of constant temperature water baths, equipped to circulate through a jacketed titration cell were used. The titration cell was prepared by the Ames Laboratory glass shop. The temperatures of the baths were maintained at 25.00° ± .05° by Philadelphia Micro-set thermoregulators and Precision Scientific electronic relays. Beside reference and glass electrodes, the titration cell was also equipped with a solution ground, a tube for bubbling nitrogen through the solution, a filling funnel and a drain. Since a separate solution was prepared for each experimental point, this cell was not a titration cell in the true sense of the word, but was rather designed to make highly reproducible pH determinations of successive prepared solutions of known stoichiometry.

The solution ground was simply a platinum wire, immersed in the solution and connected electrically to the ground terminal of the potentiometer. The solution ground and the sleeve-type reference electrode were incorporated into the system in order to alleviate some rather persistent problems of instability and irreproducibility. It was also found that the stability of the glass electrode was improved substantially by storing it in strong acid solutions during periods of disuse.

D. Experimental Procedure

The difficulty of this experiment was the instability of the pH measurements. Reference electrode, glass electrode, battery and solution

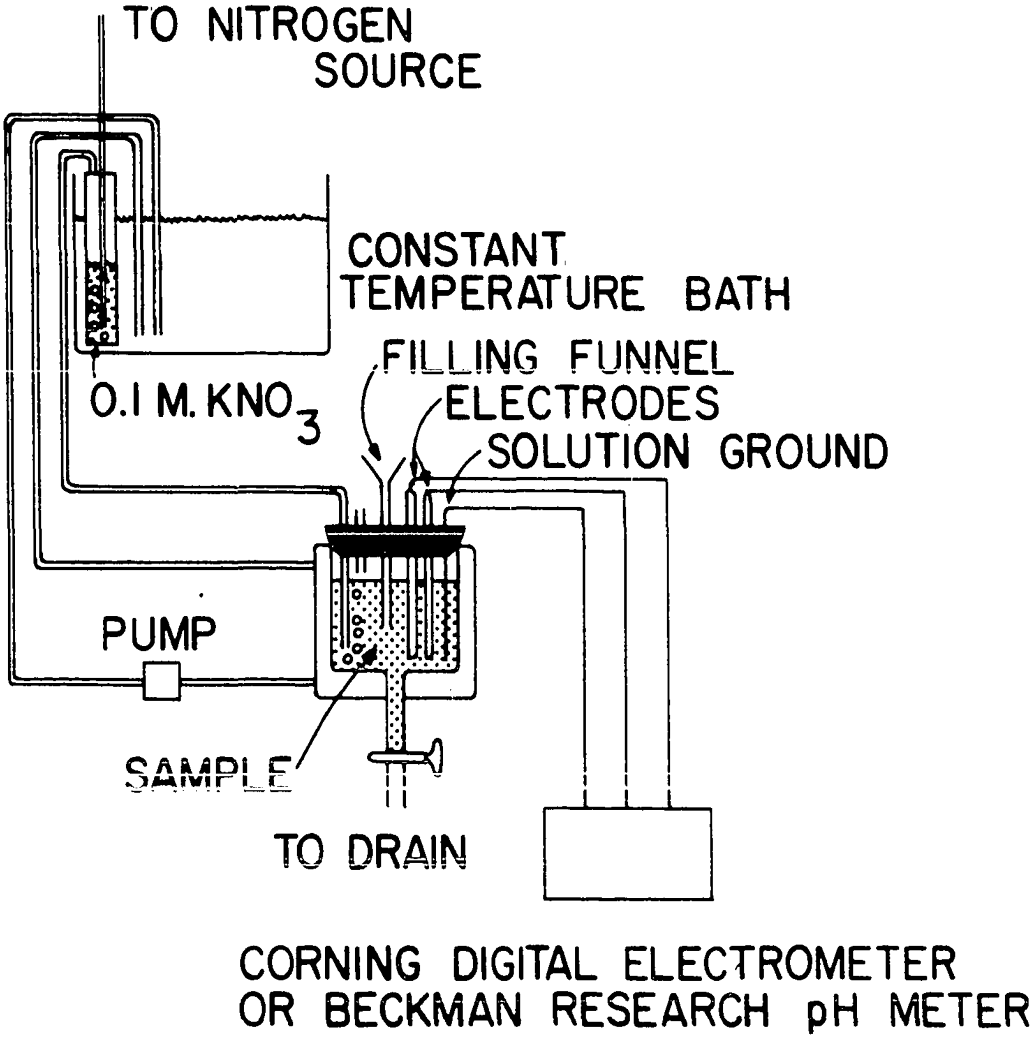


Figure 10. Apparatus for pH measurements

ground were thought to cause this difficulty. The solution ground (Fig. 10) and a Beckman sleeve-type calomel reference electrode were suggested by Mr. Harvey Burkholder in this research group, and it improved the measurements. The mercury batteries were checked every month.

The main problem resulted from surface adsorption effects at the tip of the glass electrode, because it was quite sensitive to changes in its ionic environment. After the electrodes were removed from the standard solution and placed in a sample solution containing rare-earth ions, a wait of twenty minutes was necessary before a steady pH reading could be obtained. Also, if the electrodes were washed with distilled water after each measurement, about ten or fifteen minutes was needed for the surface of the glass electrode to equilibrate with the new ionic environment. The following procedures were developed for standardizing the pH meter and measuring the samples in order to overcome this difficulty.

After internal calibration of the pH meters (Beckman Research or Corning Electrometer), the instruments were standardized against a known nitric acid solution (the pH of the standard was close to the pH range of the subsequent measurements) with its ionic strength adjusted to 0.10 M. A standard nitric acid solution was used instead of standard pH buffer in order to yield readings in terms of hydrogen ion concentration rather than activity. The electrodes were soaked in a portion of the standard for at least an hour before standardization was begun, and at least three samples of the buffer were read each time the instrument was standardized.

The sample readings were made in a similar fashion after the pH meter had been standardized. Each sample solution was divided into three portions. The first portion was used to rinse the electrodes, which were then soaked in the second portion. The final reading was taken on the third portion. Three minutes were allotted to allow the surface of the electrodes to equilibrate with each new ionic sample before the pH was measured.

Since a concentration standard rather than an activity standard was employed, the pH meter read the hydrogen ion concentration directly.

1. Formation constant measurements

As shown in Appendices B, C, D, E, and F, different volumes of buffer (VB) were added to a series of 23 to 45(I), 100 or 200-ml (final solution volume), volumetric flasks together with 2.00 or 4.00 ml of standard metal nitrate solution, and a constant ionic strength of 0.100 was maintained in all cases by adding calculated volumes of standard potassium nitrate solution prior to diluting to volume. All solutions were equilibrated overnight in a 25.0°C water bath, and the pH_c (pH) of each was determined to 0.001 units by means of the Beckman Research pH meter or Corning Model 101 Digital Electrometer.

The computer program used to calculate the formation constants also calculated the volume of standard potassium nitrate solution (Vol. KNO_3) that should have been added to each sample solution to achieve the desired ionic strength. These calculated values were used to check the original estimates and, if the calculated values (Vol. KNO_3) were significantly different from the original estimates, the measurements were repeated on new sample solutions which contained the correct amounts of potassium nitrate.

2. Acid dissociation constant measurements

The same procedure used in formation constant measurements was used in acid dissociation constant determinations, except no metal nitrate solution was added. Vacid and Vbase, as shown in Appendix A are the volumes of buffer added to each sample. Again, if the calculated values of potassium nitrate solution from the computer ($VKNO_3$) were significantly different from the original estimates, the measurements were repeated on new sample solutions which contained the correct amounts of potassium nitrate.

V. EXPERIMENTAL RESULTS

All the acid dissociation constants and chelate formation constants studied in this dissertation are stoichiometric values obtained at an ionic strength of 0.1 M (with potassium nitrate as the supporting electrolyte) and a temperature of 25°C. All the results from computer printouts are shown in Appendices A, B, C, D, E, and F. Only the computed acid dissociation constants from Appendix A and the formation constants from Appendices B, C, D, E, and F, together with the calculated standard deviations of the formation constants will be reported in this section. Some graphs will also be plotted from these data.

A. Acid Dissociation Constants

One can see from Harned's theory of ionic interaction (109, 110) as discussed in the Mathematical Method section that the value of K_c should vary slightly with the anion concentration even at constant ionic strength. The variable acid dissociation constant and the range of anion concentration in each system from Appendix A are summarized in Table 11. The variation of K_c up to $[L] = 0.02$ M. were calculated to be about 3, 1.5 and 3% for HIBA, DHIBA, and DHMIBA, respectively. Although this variation is small, it was taken into account in the calculation of metal complex stability constants in order to improve consistency of the results.

The variation of K_c for HIBA, DHIBA, and DHMIBA versus the anion concentration is shown in Figure 11. One can obtain similar linear be-

Table 11. The variable acid dissociation constant K_c of α-hydroxyisobutyric (HIBA), α,β-dihydroxyisobutric (DHIBA) and α,β-dihydroxy-β-methylisobutyric acids (DHMIBA) as a function of anion concentration $[L^-]$

Acid	Variable K_c	$[L^-] \times 10^2$ range (moles/liter)
HIBA	$(1.596 - 2.616[L])10^{-4}$	0.416 - 1.015
DHIBA[a]	$(2.654 - 1.407[L])10^{-4}$	0.035 - 1.247
	$(2.650 - 0.600[L]^{\frac{1}{2}})10^{-4}$	0.035 - 2.468
DHMIBA	$(3.059 - 5.218[L])10^{-4}$	0.171 - 2.260
	$(3.084 - 0.907[L]^{\frac{1}{2}})10^{-4}$	0.222 - 2.260
	$(2.979 + 1.742[L] - 156.20[L]^2)10^{-4}$	0.171 - 2.260

[a] Farrell, James, Department of Chemistry, Iowa State University.

havior, if a plot of K_c versus the square root of the anion concentration is made. The acid dissociation constants of these three acids decrease slightly as the anion concentration increases, and as the anion concentration approaches zero, K_c values equal 1.596×10^{-4} ($pK_c = 3.80$), 2.654×10^{-4} ($pK_c = 3.57$), and 3.059×10^{-4} ($pK_c = 3.52$) for α-hydroxyisobutyric, α,β-dihydroxyisobutyric and α,β-dihydroxy-β-methylisobutyric acids, respectively.

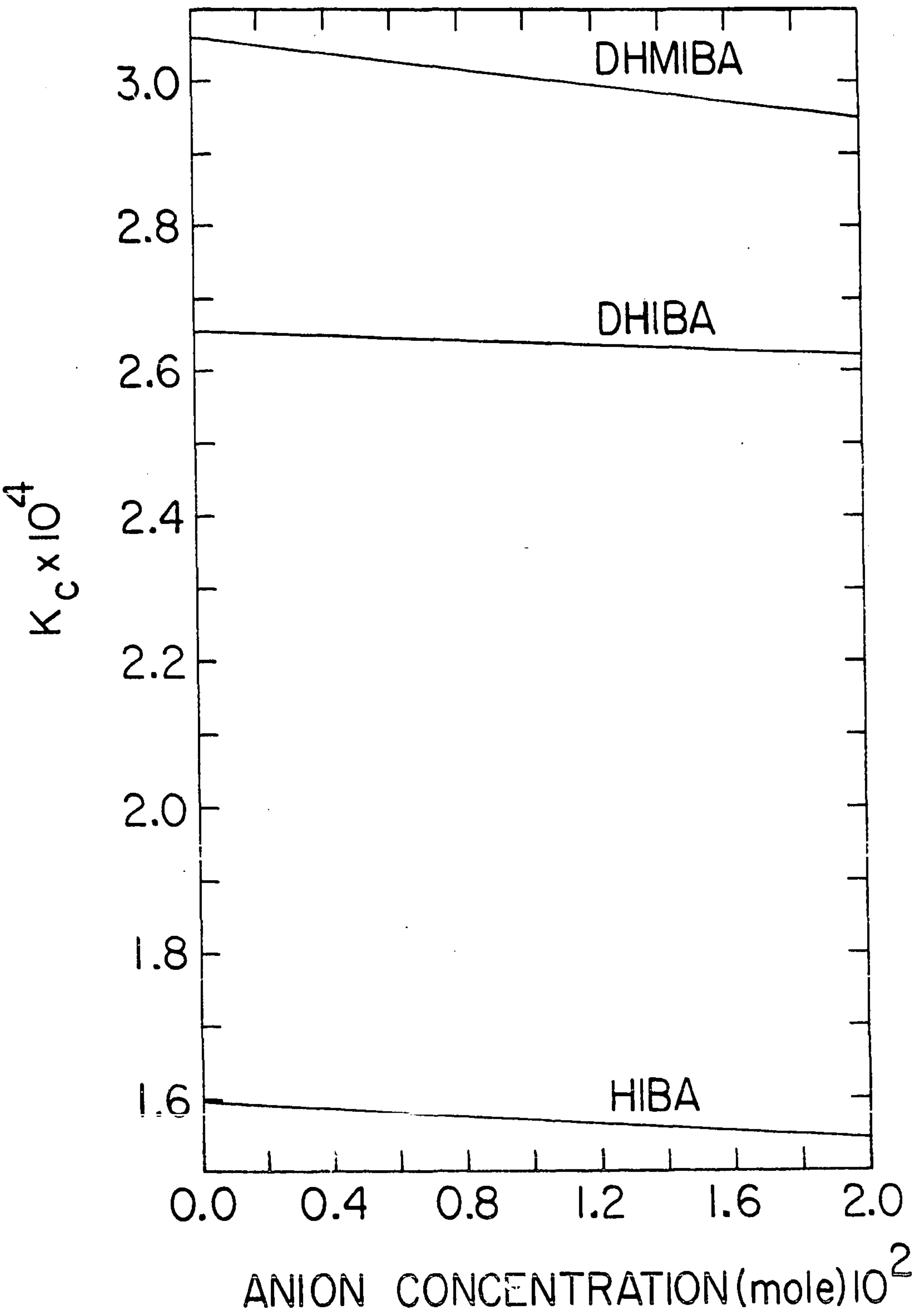


Figure 11. The variable K_c of α-hydroxyisobutyric (HIBA), α,β-dihydroxyisobutyric (DHIBA) and α,β-dihydroxy-β-methylisobutyric acids (DHMIBA) as a function of anion concentration

B. Formation Constants

1. Rare-earth(III) α,β-dihydroxyisobutyrate complexes

The formation constants of the rare-earth(III) DHIBA complexes from Appendix B are summarized in Table 12. The first three stepwise formation constants (K_1, K_2, and K_3) have been determined. Some values of K_4 have also been reported where calculable.

The formation constants of the rare-earth DHIBA chelate species have been studied previously by Mr. James Farrell of this research group. The experimental method and computer program used by Farrell is similar to the one used in this work with one significant exception: all pH readings were taken by a Beckman Research pH meter. The data otherwise were obtained under the same conditions as those employed in this research (25° and $\mu = 0.1\underline{M}$). The preliminary results obtained by Farrell are listed in Table 13. Comparison of these values with the author's results in Table 12 shows good agreement.

Figure 11 shows a plot of the first and second formation constants (K_1, K_2) of the rare-earth(III) DHIBA complexes as a function of ionic radius. One can see from this plot that, both values of K_1 and K_2 from Tables 12 and 13 agree very well to each other, and as a matter of fact, the standard deviations for the K_1 and K_2 values in both Table 12 and 13 are very small.

The ratios of the successive formation constants (K_1/K_2) in Table 12 can be divided into three groups, La to Nd, Sm to Tb, and Dy to Lu (including Y). The average values of K_1/K_2 are 5.97, 4.66, and 4.62 for La to Nd, Sm to Tb, and Dy to Lu (including Y), respectively. The values

Table 12. Formation constants of rare-earth(III) α,β-dihydroxyisobutyrate complexes

Ln(III)	K_1	K_2	K_3	K_4	K_1/K_2	K_2/K_3
La	445.6±0.7	73.9±1.4	15.6±11.9		6.03	4.75
Ce	682.5±0.6	112.4±0.5	23.7±5.5		6.07	4.75
Pr	886.9±0.6	154.4±0.7	26.6±5.2		5.74	5.81
Nd	922.4±0.9	152.4±0.3	30.8±4.1	5.4±25.1	6.05	4.95
Sm	1115.0±0.1	217.6±0.5	43.8±1.1		5.12	4.97
Eu	1123.0±0.7	253.8±0.2	46.4±3.3	61.4±0.1	4.50	5.53
Gd	1067.0±0.1	234.6±0.7	48.3±2.6	16.8±6.0	4.55	4.86
Tb	1084.0±0.1	241.8±0.6	43.1±1.5		4.48	5.62
Dy	1165.0±0.7	251.2±0.5	47.2±4.3	19.4±8.4	4.64	5.32
Ho	1299.0±0.4	279.1±0.5	61.4±2.0	16.2±6.8	4.66	4.55
Er	1479.0±0.6	322.5±0.3	64.7±2.5	19.4±5.7	4.59	4.99
Tm	1657.0±0.4	363.4±0.4	67.3±2.5	49.3±1.2	4.56	5.40
Yb	1848.0±0.4	384.0±0.2	65.6±1.8	20.8±4.1	4.81	5.85
Lu	1984.0±0.4	401.7±0.3	71.1±2.1	21.4±5.7	4.94	5.65
Y	1134.0±0.8	276.1±0.5	53.5±3.9	36.6±1.9	4.11	5.16
		average from La to Nd			5.97	5.07
		average from Sm to Tb			4.66	5.25
		average from Dy to Y			4.62	5.28

Table 13. Formation constants of rare-earth α,β-dihydroxyisobutyrate complexes (data from Mr. James Farrell) same conditions as in Table 12.

Ln(III)	K_1	K_2	K_3	K_4	K_1/K_2	K_2/K_3
La	441.4±0.3	80.7±0.8	12.4±4.9		5.47	6.49
Ce	689.8±0.2	112.8±0.5	26.6±1.7		6.12	4.24
Pr	864.0±0.3	154.1±0.4	28.6±2.1		5.61	5.40
Nd	994.5±0.2	169.6±0.5	31.7±3.0	10.8±8.2	5.86	5.35
Sm	1157.0±0.3	220.7±0.4	40.5±2.5	2.9±33.1	5.24	5.45
Eu	1146.0±0.3	232.5±0.4	33.9±3.0	7.3±15.8	4.93	6.86
Gd	1046.0±0.3	234.5±0.3	47.4±1.7	11.0±9.6	4.46	4.95
Tb	1108.0±0.4	238.4±1.1	52.4±3.0	13.1±8.3	4.65	4.55
Dy	1205.0±0.3	266.0±0.3	46.7±1.9	11.2±6.0	4.53	5.70
Ho	1263.0±0.2	273.4±0.3	52.6±1.7	5.9±12.5	4.62	5.20
Er	1428.0±0.2	309.3±0.4	61.3±1.7	13.7±6.6	4.62	5.04
Tm	1624.0±0.2	353.6±0.2	71.5±1.4	23.0±2.2	4.59	4.95
Yb	1828.0±0.4	377.2±0.5	65.9±2.6	10.0±12.0	4.85	5.73
Lu	1925.0±0.6	394.4±0.4	77.8±2.6	5.7±26.0	4.88	5.07
Y	1037.0±0.2	223.4±0.3	46.5±1.5	10.1±5.9	4.64	4.81
		average from La to Nd			5.77	5.37
		average from Sm to Tb			4.82	5.45
		average from Dy to Y			4.68	5.23

of K_2/K_3 are not significantly different as shown in the case of K_1/K_2, and as a matter of fact, the standard deviations of K_3 values are large compared to the values of K_3. If the values of K_2/K_3 are separated into three regions as in the case of K_1/K_2, they are 5.07, 5.25, and 5.28 for La to Nd, Sm to Tb, and Dy to Lu (including Y), respectively. Also, K_1/K_2 and K_2/K_3 from Table 12 agree very well with Farrell's data in Table 13. His average K_1/K_2 values are 5.77, 4.82, and 4.68 for La to Nd, Sm to Tb,

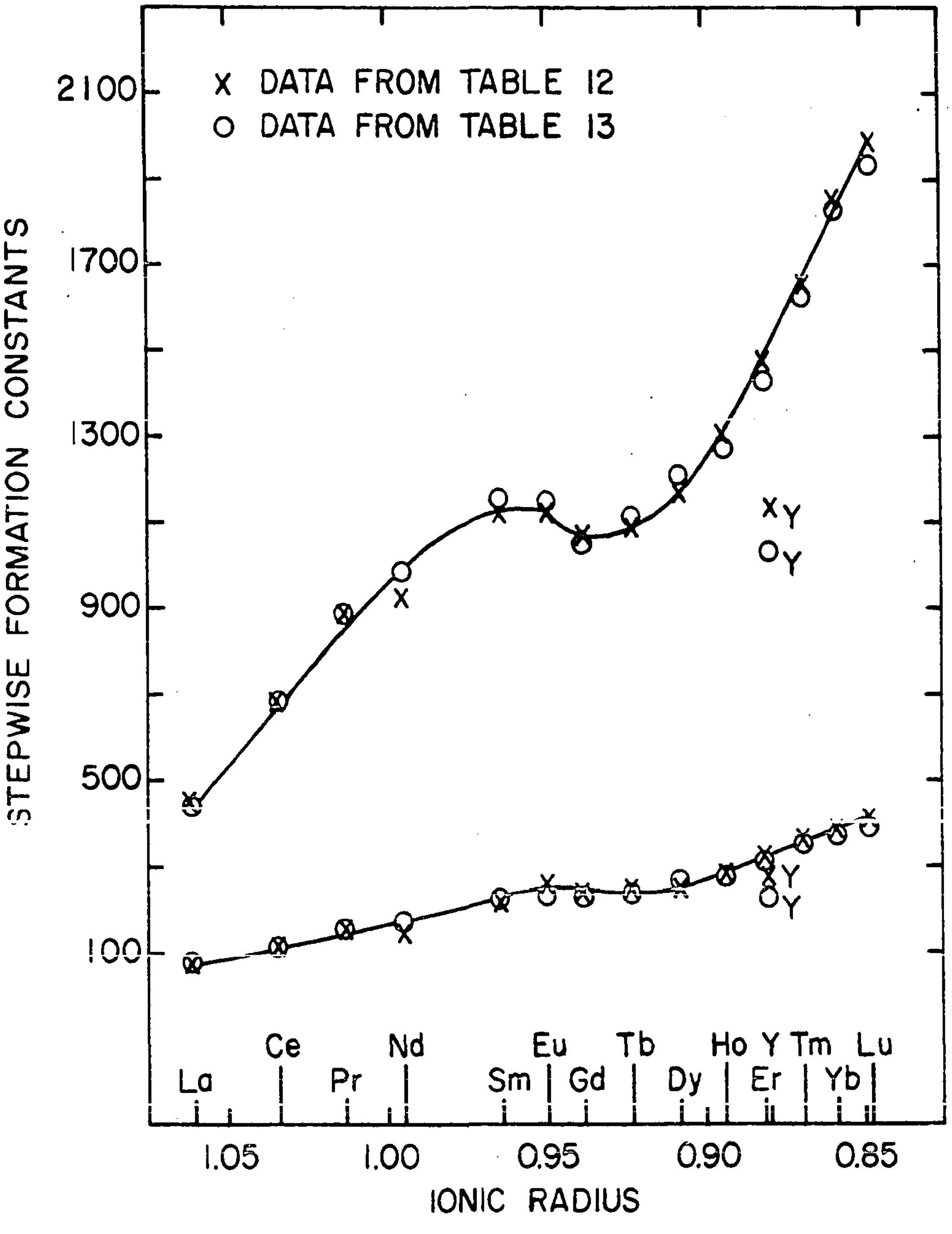


Figure 12. First and second formation constants (K_1(upper), K_2(lower)) of rare-earth(III) α, β-dihydroxyisobutyrate complexes as a function of ionic radius

and Dy to Lu (including Y), respectively, and K_2/K_3, are 5.37, 4.45, and 5.22 for the same order as in the case of K_1/K_2.

The variations in K_1 and K_2 with decreasing ionic radius of the trivalent rare-earth ions as shown in Figure 12 are very similar to each other, that is, they increase from La to Sm and Eu, then decrease to Gd. Beyond Tb, they increase smoothly to the maximum at Lu, while Y values lie below the lines. The lesser variation in the case of K_2 compared to K_1 is not surprising if the smaller magnitude of the K_2 values are taken into account. It is likewise not surprising that, if one tried to plot the values of K_3 and K_4, the trends would be difficult to sort out. The standard deviations for K_3 and K_4 are altogether too large to allow any reliable correlations to be made.

2. Rare-earth(III) α,β-dihydroxy-β-methylisobutyrate complexes

The first three stepwise formation constants (K_1, K_2, and K_3) and some values of K_4 (where calculable) from Appendix C, are summarized in Table 14 for the case of the trivalent rare-earth DHMIBA chelate species. The values of K_1/K_2 and K_2/K_3 for these chelate species are also shown in Table 14.

Powell, et al. (102) studied the formation constants of some of the trivalent rare-earth DHMIBA complexes at a higher ionic strength. Their data are summarized in Table 15. No comments or discussion will be made regarding these data, because their data were not obtained under the conditions studied in this research. The potentiometric titration method, in which it is very difficult to obtain high accuracy was used in this early study of this system.

Table 14. Formation constants of rare-earth(III) α,β-dihydroxy-β-methylisobutyrate complexes

Ln(III)	K_1	K_2	K_3	K_4	K_1/K_2	K_2/K_3
La	372.5±0.5	59.8±2.3	9.7±27.0		6.23	6.14
Ce	650.8±0.1	99.5±0.3	13.8±0.3		6.54	7.23
Pr	903.0±0.3	141.6±0.4	21.3±3.6		6.38	6.65
Nd	1082.0±0.2	166.4±0.2	23.5±1.8		6.51	7.08
Sm	1393.0±0.6	210.0±0.5	28.8±5.9	3.3±8.70	6.64	7.29
Eu	1342.0±0.2	299.6±0.1	39.8±0.6	1.5±	4.48	7.52
Gd	1204.0±0.6	226.7±0.9	36.9±6.4	2.3±71.0	5.31	6.15
Tb	1099.0±0.7	223.6±0.3	36.4±2.8		4.92	6.14
Dy	994.9±0.4	228.6±0.3	15.2±4.3		4.35	15.09
Ho	1065.0±0.6	221.7±0.6	21.5±6.4		4.81	10.30
Er	1288.0±0.5	241.1±0.3	38.5±3.5		5.34	6.26
Tm	1401.0±0.2	291.5±0.1	52.8±0.5		4.81	5.53
Yb	1616.0±0.3	355.0±0.1	51.8±0.8		4.55	6.85
Lu	1769.0±0.2	381.9±0.1	60.4±0.7		4.63	6.33
Y	817.3±0.3	174.6±0.4	27.1±2.4		4.68	6.45
		average from La to Sm			6.46	6.88
		average from Eu to Dy			4.77	6.60[a]
		average from Ho to Y			4.80	6.28[b]

[a] Does not include K_2/K_3 of Dy

[b] Does not include K_2/K_3 of Ho

Table 15. Formation constants of rare-earth(III) α,β-dihydroxy-β-methylisobutyrate complexes at 25° and $\mu = 0.5$ M. $NaClO_4$ (data from Powell, et al. (102)

Ln(III)	K_1	K_2	K_3	K_1/K_2	K_2/K_3
La	263	46		5.72	
Ce	471	81	13	5.82	6.22
Pr	614	96		6.40	
Nd	830	120	13	6.91	9.22
Sm	1070	175	12	6.12	14.60
Eu	1060	175	14	6.06	12.50
Gd	780	200	10	3.90	20.00
Tb	700	213	8	3.29	26.60
Dy	710	231		3.07	
Ho	650	217	11	3.00	19.74
Er	720	207	13	3.48	15.93

Figure 13, shows a plot of the first and second formation constants (K_1, K_2) of the rare-earth(III) DHMIBA complexes as a function of ionic radius of the trivalent rare-earth ions. The variations in K_1 and K_2 with decreasing ionic radius of the trivalent rare-earth ions at either ionic strength 0.1 or 0.5 in Figure 13 are similar to each other; that is, they increase from La to Sm and Eu, then decrease to Dy (Ho in the case of K_2). Beyond Dy, they increase to the maximum at Lu. Y falls below the lines. The lesser variation in the case of K_2 compared to K_1 is to be expected because of the smaller K_2 values. The ionic strength difference (0.1 compared to 0.5) of these two data sets (data in Table 14 and 15) accounts for their vertical displacement.

The ratio of the successive formation constants (K_1/K_2) given in Table 14 can be divided into three regions, as in the case of the rare-

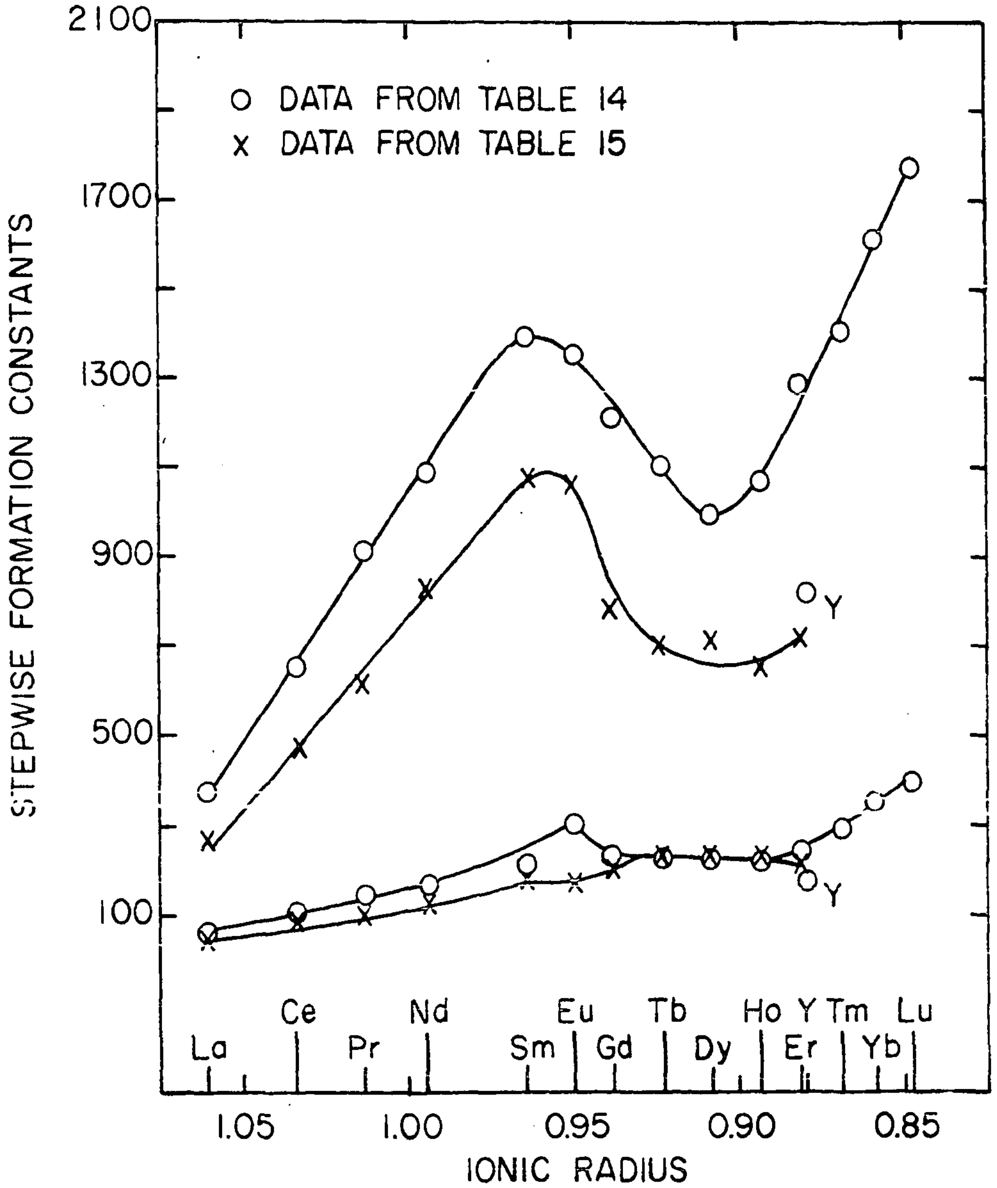


Figure 13. First and second formation constants (K_1(upper), K_2(lower)) of rare-earth(III) α,β-dihydroxy-β-methylisobutyrate complexes as a function of ionic radius

earth(III) DHIBA complexes; but, the extent of each region is different. In this case, three regions are La to Sm, Eu to Dy, and Ho to Lu (including Y). The average values of K_1/K_2 are 6.46, 4.77 and 4.80 for La to Sm, Eu to Dy and Ho to Lu (including Y), respectively. The values of K_2/K_3 are not significantly different, but, if they are divided into the same three regions, the average values of K_2/K_3 are 6.88, 6.60, and 6.28 for La to Sm, Eu to Dy, and Ho to Lu (including Y), respectively.

3. Formation constants of divalent transition metal α,β-dihydroxyisobutyrate complexes

The formation constants of the first two chelate species of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) cations with the DHIBA ligand from Appendix D are summarized in Table 16. The K_1 values decrease in the order Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II). The ratio of the successive formation constant (K_1/K_2) is 9.39 for Cu(II), and is the only ratio in Table 16 that was determined to a sufficient degree of accuracy to be of significance. The standard deviations of K_2 in the case of Co(II), Ni(II), Zn(II) and Cd(II) compared to K_2 were simply too large.

Table 16. Formation constants of divalent transition metal α,β-dihydroxyisobutylate complexes

M(III)	K_1	K_2	K_1/K_2
Co	41.5 ± 0.2	5.8 ± 11.7	7.11
Ni	66.1 ± 0.2	8.9 ± 8.2	7.40
Cu	429.0 ± 0.2	45.8 ± 0.7	9.39
Zn	58.3 ± 1.0	5.6 ± 20.0	10.40
Cd	42.5 ± 0.3	22.6 ± 4.1	1.88

4. Formation constants of divalent transition metal α,β-dihydroxy-β-methylisobutyrate complexes

The first and second formation constants of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with DHMIBA from Appendix E are summarized in Table 17. Their K_1 values also decrease in the order Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II). Because of the large values of the standard deviations of K_2 in the case of Co(II), Ni(II), Zn(II), and Cd(II) compared to K_2 as shown in Table 17, the only K_1/K_2 ratio determined to any degree of accuracy is that for Cu(II).

Table 17. Formation constants of divalent transition metal α,β-dihydroxy-β-methylisobutyrate complexes

M(II)	K_1	K_2	K_1/K_2
Co	38.8 ± 0.7	17.2 ± 6.7	2.26
Ni	64.0 ± 0.2	17.3 ± 1.8	3.70
Cu	414.0 ± 0.2	47.4 ± 1.1	8.77
Zn	56.9 ± 0.6	22.0 ± 4.8	2.58
Cd	41.5 ± 0.1	27.9 ± 10.5	1.49

Figure 14 shows a plot of the first formation constants of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with DHIBA and DHMIBA. Parallel trends are observed for these two ligands.

5. Formation constant of divalent copper α-hydroxyisobutyrate complex

Only the Cu(II) HIBA complex formation constant was studied in this system. The stabilities of the 1:1 and 2:1 HIBA complex species of

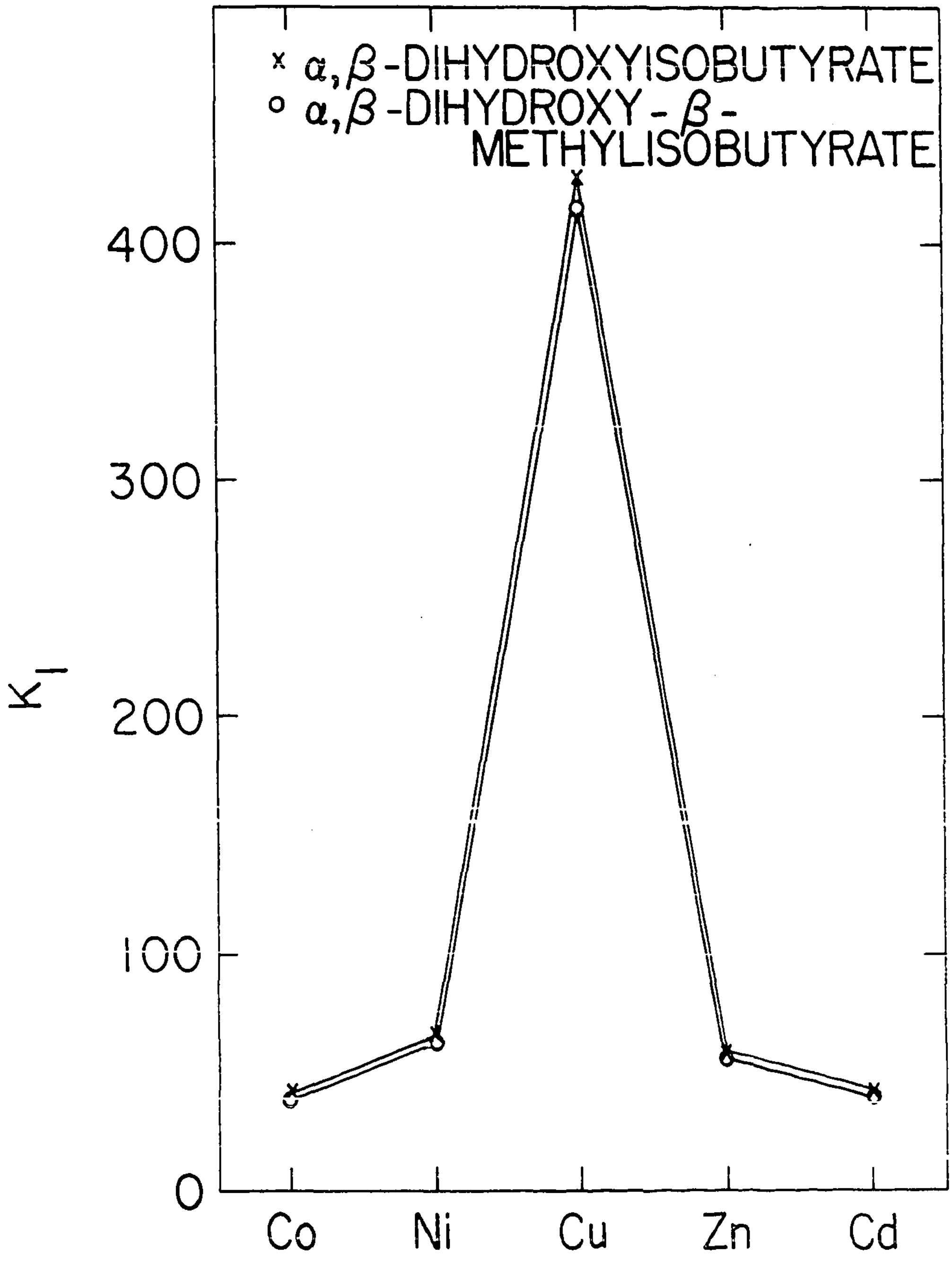


Figure 14. First formation constants of divalent transition metal with α,β-dihydroxyisobutyrate and α,β-dihydroxy-β-methylisobutyrate

divalent copper from Appendix F were reported in Table 18. The ratio of the successive formation constant (K_1/K_2) is 10.51 for this chelate species.

Table 18. Formation constant of copper(II) α-hydroxyisobutyrate complex

M(II)	K_1	K_2	K_1/K_2
Cu	660.0 ± 0.2	62.8 ± 1.0	10.51

The formation constants of divalent transition metal HIBA chelate species have been reported by Thun, et al. (5) at 25° and μ 1.0 M were summarized in Table 5. The potentiometric titration method was used to obtain those data under different conditions than studied in this research; so, no reliable comparison can be made. The first formation constants in Table 5, however, decrease in the order Cu(II) > Zn(II) > Ni(II) > Co(II) > Cd(II).

VI. DISCUSSION AND CONCLUSIONS

A. Transition Metal Dihydroxycarboxylate Complexes

The linear relationship between the basicity of the ligand (pK_c) (or the acidity of the ligand ($\log K_c$)) and the chelate stability ($\log K$) has been found to hold in a large portion of the literature reported so far. Thus, the weaker the acidity of the ligand acid, the more stable is the metal chelate compound. The stabilities of the divalent transition metal α,β-dihydroxyisobutyrate (DHIBA) complexes (Table 16) are higher than for the corresponding divalent transition metal α,β-dihydroxy-β-methylisobutyrate (DHMIBA) complexes (Table 17). Only the copper(II) α-hydroxyisobutyrate (HIBA) complexes were investigated in this research (Table 18), and they exhibited higher consecutive formation constants than either the DHIBA or DHMIBA complexes. From this, it would not be unreasonable to assume that the formation constants of HIBA chelates ought to be higher than those of the other two ligands in the cases of Co(II), Ni(II), Zn(II), and Cd(II) as well. Therefore, the data obtained from this investigation confirms the parallel relationship between the ligand basicity and the stability constant in agreement with past observations, that is, both pK_c and $\log K$ increase in the order DHMIBA < DHIBA < HIBA. The plot in Figure 14 presents good evidence to support these two trends. One would expect to see similar parallel trends in Figure 14 in addition to the ones that already appear, if the formation constants of Co(II), Ni(II) and Zn(II) (perhaps Cd(II)) HIBA chelates were investigated under the same conditions as one studied in this research.

For both dihydroxy ligands (DHIBA and DHMIBA) the sequence of increasing formation constants proved to be the same: Co(II) <Ni(II) < Cu(II) > Zn(II) > Cd(II), which is in agreement with the well-known Irving-Williams order of stabilities (3, 4).

Because both ionic and covalent interactions are involved in these divalent metal complexes, the stability sequence ought to depend on the reciprocal of the ionic radius and the second ionization potential of the transition metals. However, from the ionic radius and second ionization potential values in Table 19, it is clearly very difficult to predict whether the orders for the non-adjacent metals Ni and Zn should be Ni(II) > Zn(II) or Ni(II) < Zn(II). Likewise it is unclear from the opposing trends whether the stability order should be Co(II)> Cd(II) or Co(II) <Cd(II). As a matter of fact both orders in each case are found in the literature (Table 3, 4, and 5). Apparently, the stabilities of these complexes depend also upon the nature of the ligand, thus no invariant order can be expected. For both ligands (DHIBA and DHMIBA) the sequence of non-adjacent metal complex stabilities is Ni(II) >Zn(II) and Co(II) $\cong$ Cd(II).

Table 19. Thermodynamic data of some divalent transition metal (152)

	Co^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}	Cd^{+2}
ionic radius (Å)	0.74	0.72	0.69	0.74	0.92
second ionization potential (Kcal)[a]	577.2	597.6	649	633.8	600.3
hydration energy ΔH_{hy} (Kcal)[b]	-505	-519.5	-516.4	-503.0	-447

[a] $M(gas) \rightarrow M^{+2}(gas) + 2e$

[b] $M^{+2}(gas) \rightarrow M^{+2}(aq)$

For both ligands (DHIBA and DHMIBA) studied in this research, there is an increase in both formal charge and electron-donating power, compared with water; so, both electronic and covalent interactions are important in divalent transition metal complexes. If the percent ionic character in each complex could be calculated, one should be able to predict the stability trends of these complexes. Nevertheless, the relative steric hindrances of the ligands and the coordination geometry of each metal complex must also be taken into account.

Because of the Jahn-Teller effect in the d^9 configuration of divalent copper, the tetragonally distorted octahedron (in which two trans metal-ligand distances are greater than the other four) is the most common structure in copper(II) complexes. The crystal structure of diaquobis(α-hydroxyisobutyrato)copper(II) (Figure 2) is an example of this, having two waters in *trans* positions and two bidentate HIBA ligands which form *trans*-chelate rings in a square planar configuration (23). Bjerrum's statistical ratio theory (14) which was described previously has been applied for this system. The ratio of the successive formation constants (K_1/K_2), or the total effect (T), is equal to the product of a statistical term (S), a ligand repulsion effect (E) and a "rest" effect (R). The S term was calculated, using the configuration of diaquobis(α-hydroxyisobutyrato)copper(II) in Figure 2, to be 8. Because small ligands are involved in this system (HIBA, DHIBA, and DHMIBA), steric hindrance probably can be ignored, so R equals about 1. E values for the copper complexes in Tables 16, 17, and 18 (calculated using these assumptions) are then 1.10, 1.18, and 1.31 for DHMIBA, DHIBA, and HIBA, respectively. Manning (16) summarized the formation constant data on divalent copper chelates, from Kolat and Powell (17) and Fronaeus (18), and found the E value was 1.75 for acetate. One can see then that E increases in the sequence: DHMIBA < DHIBA < HIBA < acetate, with the inductive effects on these ligands changing in the sequence (K_c: 3.06×10^{-4}, 2.65×10^{-4}, 1.60×10^{-4}, and 2.80×10^{-5} for DHMIBA, DHIBA, HIBA and acetate, respectively). This is reasonable, because the E value is determined principally by the magnitude of the effective negative charge on the carboxyl group. K_1/K_2 values of 8.77 for DHMIBA, 9.39 for DHIBA, and 10.51 for HIBA, therefore, do not appear unreasonable, if one assumes that the $Cu(DHMIBA)_2$, $Cu(DHIBA)_2$, and $Cu(HIBA)_2$ species in solution all have the tetragonally distorted octahedron configuration (for which S equals 8) in agreement with the crystal structure of diaquobis(HIBA)copper(II) mentioned above.

No safe conclusions with regard to coordination geometry can be drawn in the cases of DHMIBA and DHIBA chelates of Co(II), Ni(II), Zn(II), and Cd(II). From Appendices D and E one can see that, the maximum $\bar{n}$ achieved was less than 1 in these cases, thus the standard deviations for the K_2 values in Table 16 and 17 are prohibitively large.

The last point that will be considered in this system, before going to the next section, is whether both or only one hydroxyl group in DHIBA and DHMIBA participates in bonding to the metal cation. Warnke and Kwiatkowski (11) studied the stability of divalent transition metal complexes of propionate, α-hydroxypropionate and β-hydroxypropionate (Tables 3 and 5), and observed the stabilities of the chelate species increase in the series propionate < β-hydroxypropionate < α-hydroxypropionate. From this sequence, the author suggested hydroxyl groups in α or β positions allow the formation of five- and six-membered rings, respectively. Jones and Choppin(104) in another paper reported that the β-hydroxy group in β-hydroxypropionate is not involved in a chelate ring with the trivalent rare-earth cations. In the case of ligands studied in this research, the stability of the chelate species increase in the order DHMIBA< DHIBA< HIBA. From this sequence, one is forced to conclude that only one hydroxyl group in either DHIBA or DHMIBA participates in bonding to divalent transition metals. The hydroxyl group in α-position is the one most likely to interact with the metal cations, because it allows formation of a five-member ring as with the more stable HIBA chelates. If both hydroxyl groups interacted with these transition metal ions, one should observe stabilities of the chelate species of DHMIBA and DHIBA to be greater than in the case of HIBA. Since that is not the case, bidentate character (one from the α-hydroxyl and one from the carboxyl group) is suggested for DHIBA and DHMIBA. As a matter of fact, this suggestion agrees very well with Bjerrum's statistical ratio theory discussed above.

B. Rare-earth Dihydroxycarboxylate Complexes

Nearly pure ionic or electrostatic interaction between the donor group and the central atom in the rare-earth chelate species has been supported by a wealth of experimental evidence, especially magnetic (37, 39, 40, 41) and spectral data (37, 42). Assuming ionic character and because of the lanthanide contractions which causes the ionic radius of lanthanons to decrease smoothly as the atomic number increases (Figure 15), one should expect to see the Born relationship to hold true in all rare-

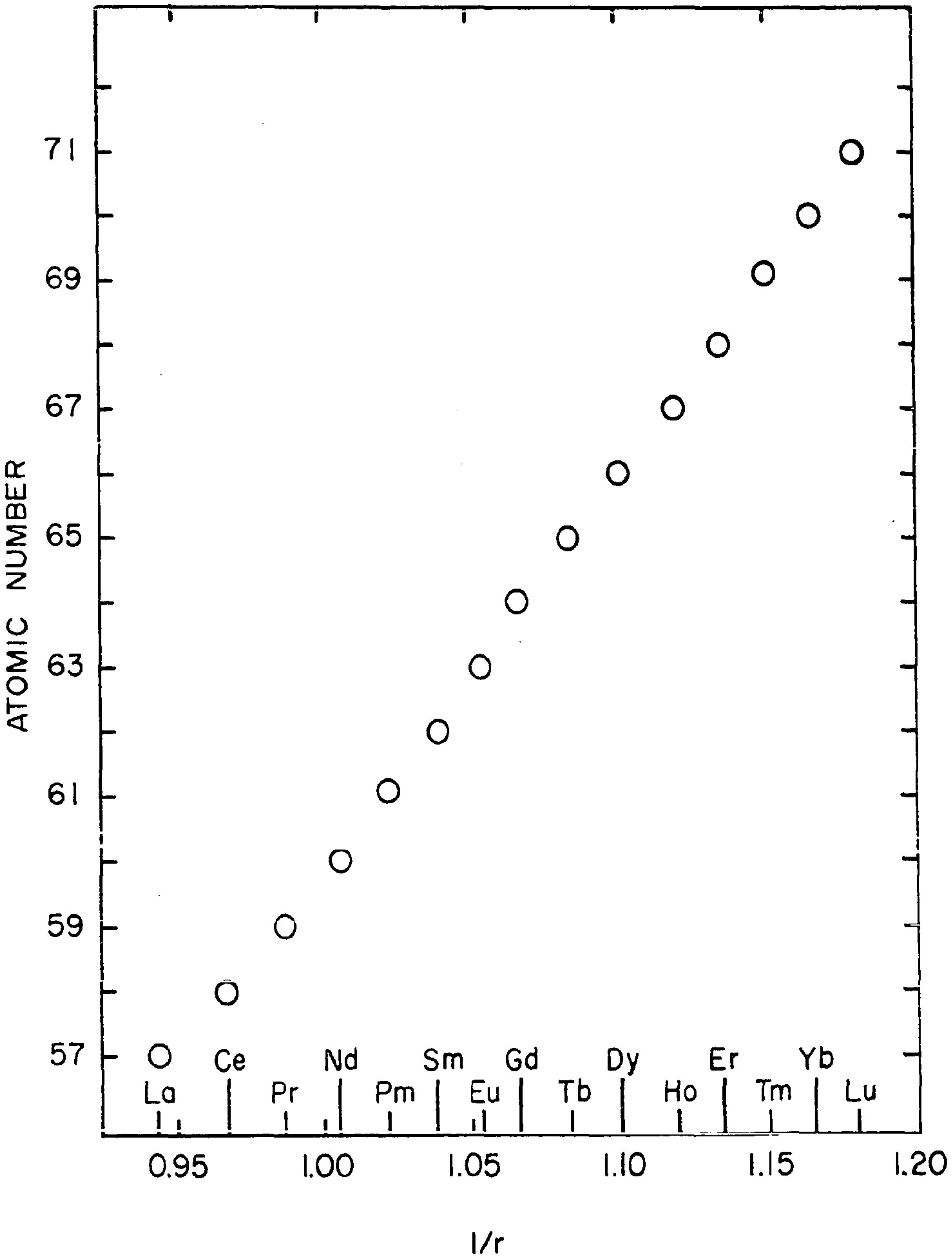


Figure 15. Atomic number versus 1/radius of trivalent rare-earth metals

earth complex systems (50, 51). That is, a linear relationship should predominate between logK and Z^2/r (or more generally $1/r$) (K = formation constant, r = ionic radius and Z = charge). Some of the monohydroxycarboxylate ligands seem to behave principally in this fashion in forming complexes with the rare-earth cations. Some of the aminopolycarboxylates such as ethylenediaminetetraacetate, 1,2-diaminocyclohexanetetraacetate and nitrilotriacetate also show this expected trend. Recently, the rare-earth N'-methylethylenediamine-N',N,N-triacetate (MEDTA) complexes were studied by Johnson (153), Powell, et al. (154), and the complex stabilities were found to increase quite regularly across the series from lighter rare-earths to heavier rare-earths. The authors (153) suggested that MEDTA acts as a pentadentate ligand across the entire series.

Both $\log K_1$ of the lanthanon-DHIBA and the lanthanon-DHMIBA chelate species as a function of $1/r$ are plotted in Figure 16. A non-linear behavior is obtained in this plot, in contrast to the corresponding data for monohydroxycarboxylates complexes. Electrostatic interaction in the complexes alone fails to explain this behavior. Crystal-field effects and thermodynamic data failed to explain this in some other complexes (52-59); and, as a matter of fact, both crystal-field stabilization energies and thermodynamic data are not available for DHIBA and DHMIBA lanthanon complexes. The statistical ratios of the formation constants of the complexes formed between DHIBA and DHMIBA and rare earths are therefore considered the best way to obtain an explanation of this non-linear behavior.

Powell and Burkholder (65) proposed that in solution a change in coordination number of the hydrated rare-earth cations with ionic radius occurs

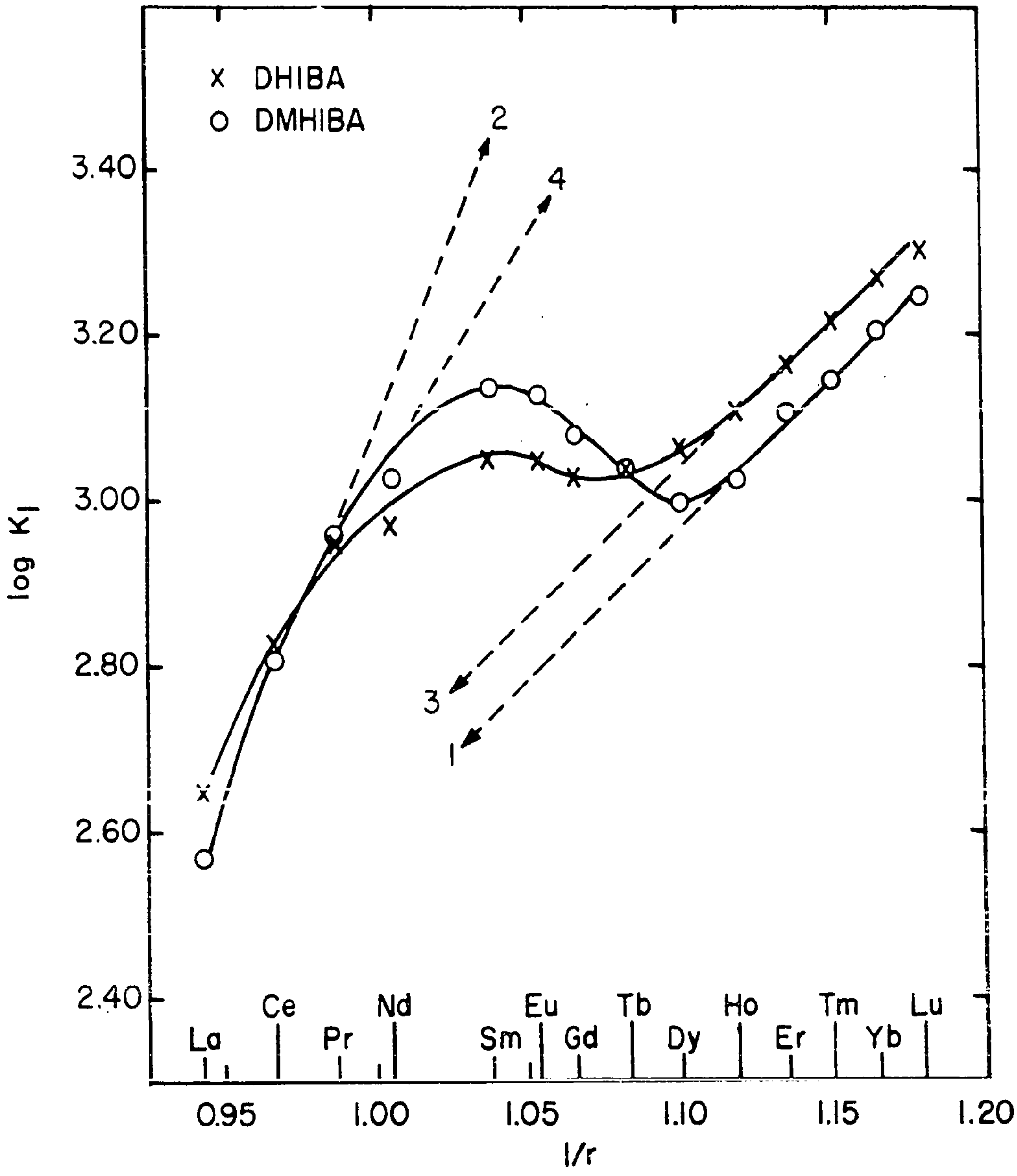


Figure 16. logK_1 of rare-earth(III) DHIBA and DMHIBA complexes as a function of 1/r

from 10(La^{+3} - Nd^{+3}) to 9(Dy^{+3} - Lu^{+3}). Most of the nine-coordinated rare-earth complex crystal structures studied have been characterized as the distorted, tricapped, trigonal prism type by X-ray analysis (e.g., $Pr(H_2O)_2NTA \cdot H_2O$ (75) and $Eu(HOCH_2COO)_3$ (80)). If one assumes that in solution the trivalent rare-earth cations also have a distorted, tricapped, trigonal prism type molecular structure, Figure 5 becomes the model for discussing Bjerrum's statistical ratios.

The theoretical K_1/K_2 and K_2/K_3 ratios (or S terms) were calculated, using the configuration of $Eu(HOCH_2COO)_3$ in Figure 5, to be 4.92 and 4.875, respectively, for a tridentate ligand, and 3.27 and 4.125, respectively, for a bidentate ligand. The computations are summarized in Table 20, together with the corresponding experimented statistical ratios for DHIBA (Table 12) and DHMIBA (Table 14). ER (E = ligand repulsion effect, and R = rest effect values) were calculated only in the case of K_1/K_2.

Table 20. Data for Bjerrum's statistical ratio theory

	Tridentate Case			Bidentate Case		
	K_1/K_2	K_2/K_3	ER	K_1/K_2	K_2/K_3	ER
Theoretical	4.92	4.875	1	3.27	4.125	1
DHIBA	5.97[a]	5.07[a]	1.21	4.62[b]	5.25[b]	1.41
DHMIBA	6.46[c]	6.88[c]	1.31	4.80[d]	6.28[d]	1.47

[a] Average La to Nd.

[b] Average Dy to Lu, including Y.

[c] Average La to Sm.

[d] Average Ho to Lu, including Y.

From the statistical ratios in Table 20, it does not appear unreasonable to assume that DHIBA is attracted to the lighter rare-earth cations (La to Nd) as a tridentate ligand, and that the ligand is attached bidentately rather than tridentately to the heavier rare-earth cations Dy to Lu (including Y). The intermediate lanthanons (Sm-Tb) chelates comprise a transitional set in which the character of the DHIBA anion decreases gradually from tridentate to bidentate. DHMIBA seems to behave in this fashion also, but it slightly changes the regions characteristic of each dentate character. For DHMIBA, the ligand acts tridentately from La to Sm and appears to be attached bidentately to the heavier rare-earth cations Ho to Lu (including Y). The intermediate rare-earth (Eu-Dy) chelates again comprise a transitional set in which the average character of the DHMIBA anion decreases gradually from tridentate to bidentate.

For the first ligand to complex, the hydroxyl group at the β-carbon of the chain in both DHIBA and DHMIBA is free to swing around in the case of a bidentate complex, but in the tridentate case it bonds directly to the metal cation. When free, the hydroxyl group provides both a steric effect (R) and repulsion effect (E) to the second incoming ligand. So, one should expect to see bigger values of ER in the bidentate case when compared to the tridentate case. This effect was found in this research (see Table 20), with both DHIBA and DHMIBA, ER (tridentate) is less than ER (bidentate). Also, a greater R effect is expected, with DHMIBA than with DHIBA in both the tri- and bidentate cases, due to the methyl group in the β-position in DHMIBA. The ER values in Table 20 agree very well with this prediction, that is, ER (DHIBA) < ER (DHMIBA) in both the tri-

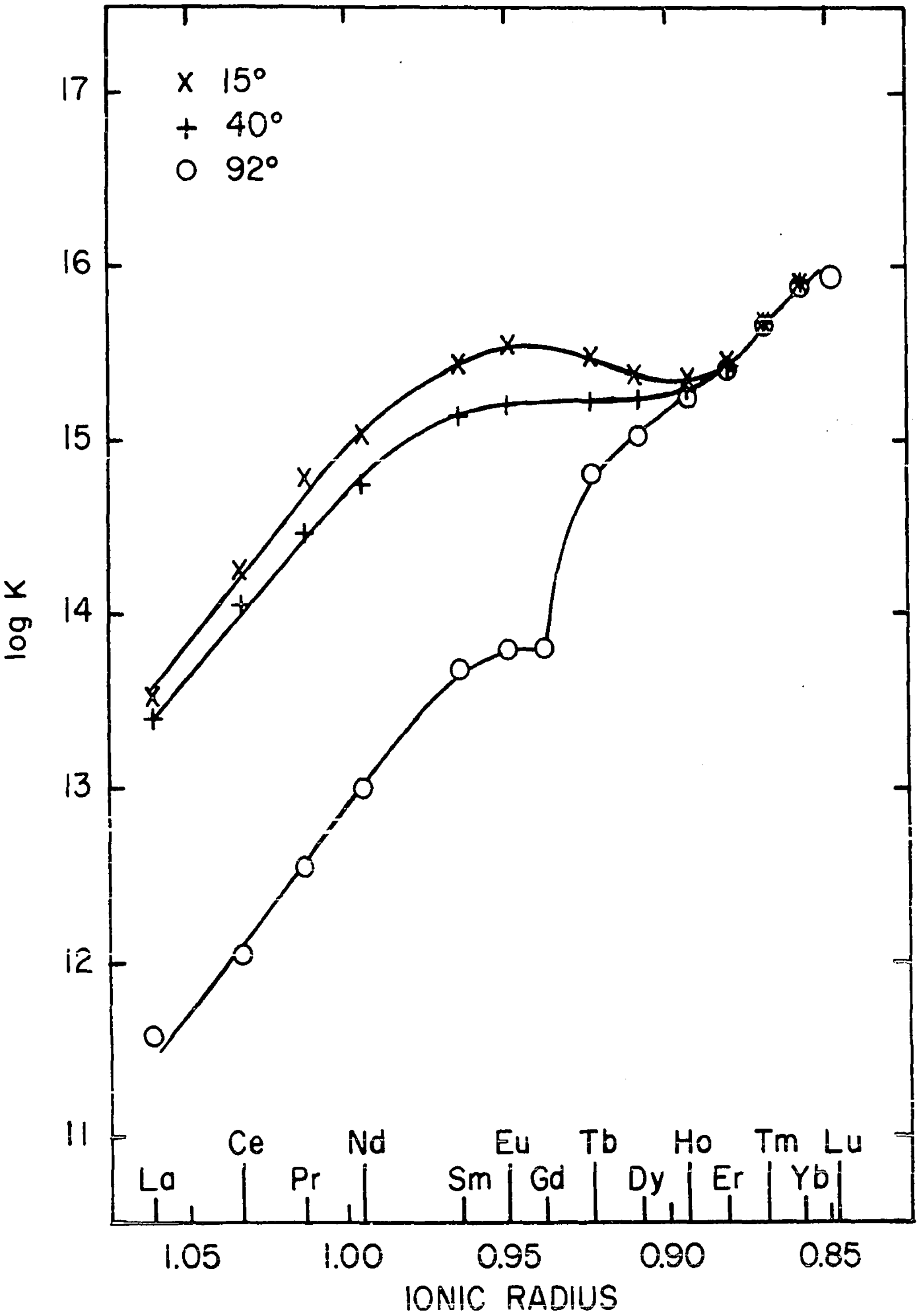


Figure 17. The effect of temperature on the formation constants of rare-earth-HEDTA complexes

and bidentate cases.

From the application of Bjerrum's statistical ratio theory mentioned above, one is forced to conclude that both DHIBA and DHMIBA attach tridentately to the lighter (larger) lanthanons, but bidentately to the heavier (smaller) lanthanons. One should obtain straight lines 2 and 4, in Figure 16, if both DHIBA and DHMIBA behaved as a tridentate ligand across the series, and straight lines 1 and 3 if they behaved as a bidentate ligands across the series. With this picture in mind, one can adequately explain the non-linear relationship between $\log K_1$ and $1/r$ as shown in Figure 16.

More evidence to support the change in dentate character of the ligand can be seen in Figure 17, the plot of logK of HEDTA lanthanon complexes at 15°, 40° (52) and 92°C (65). Powell and Burkholder (65) suggested that HEDTA always bonds pentadentately to the heavy lanthanons (Lu to Er), but that it attaches hexadentately to all the lighter lanthanons larger than Eu (the 6th donor atom of HEDTA is the oxygen of the hydroxyethyl group) at room temperature. At 92°, the bond of the hydroxyethyl group is broken, lowering the formation constants of the lighter lanthanons at this temperature. So, a nearly straight line is obtained at 92° because HEDTA behaves at that temperature purely as a pentadentate ligand across the entire series.

The effect of the hydroxyl group at the β-carbon in both DHIBA and DHMIBA is shown in Figures 18 and 19. The formation constants of DHIBA and α-hydroxyisobutyrate (HIBA) are compared in Figure 18, and the formation constants of DHMIBA and ethylmethylglycolate (EMG) are compared in Figure 19. In both cases, K_1 of the lighter lanthanon (La to Gd) dihy-

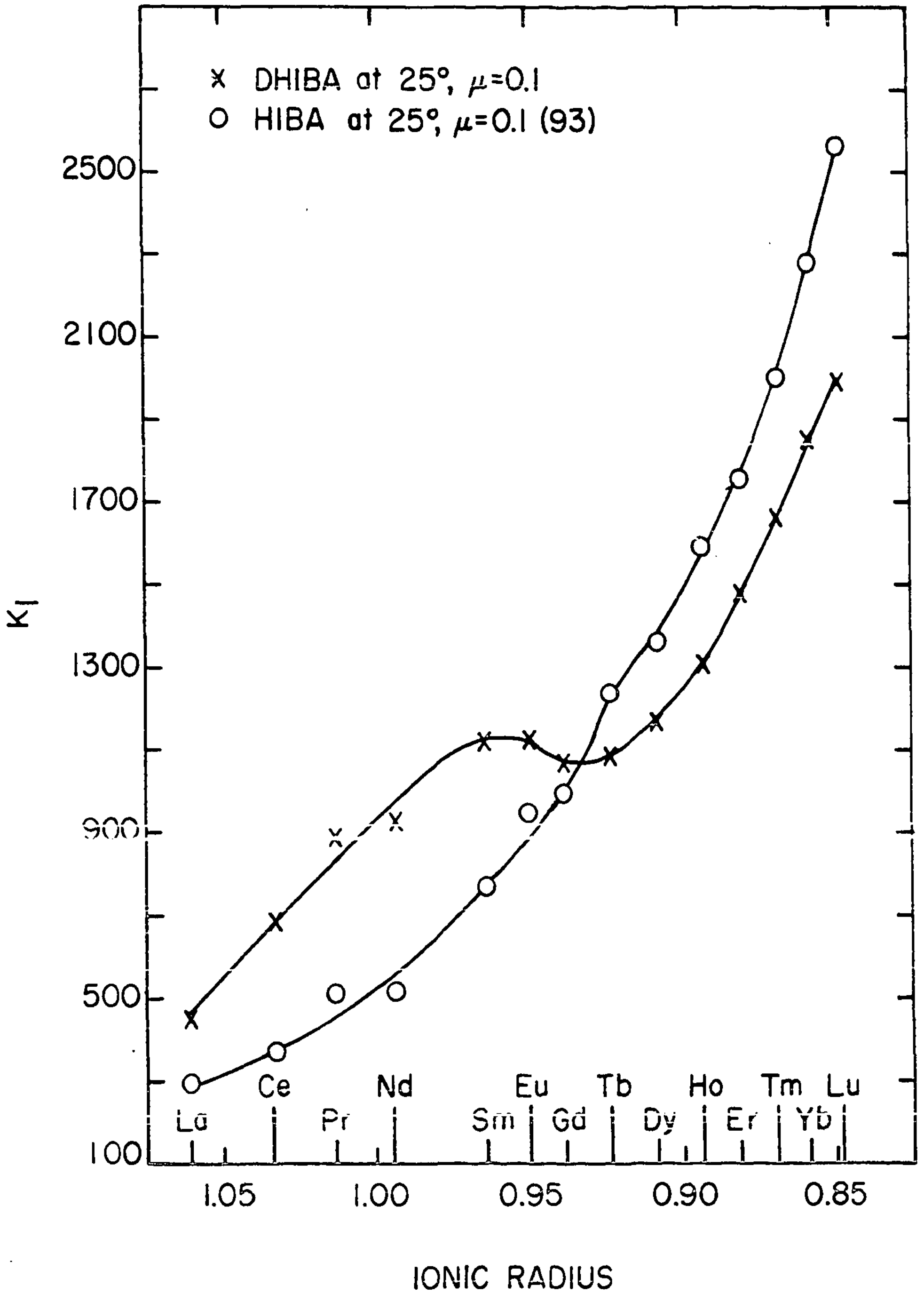


Figure 18. The first formation constants (K_1) of DHIBA and HIBA as a function of ionic radius

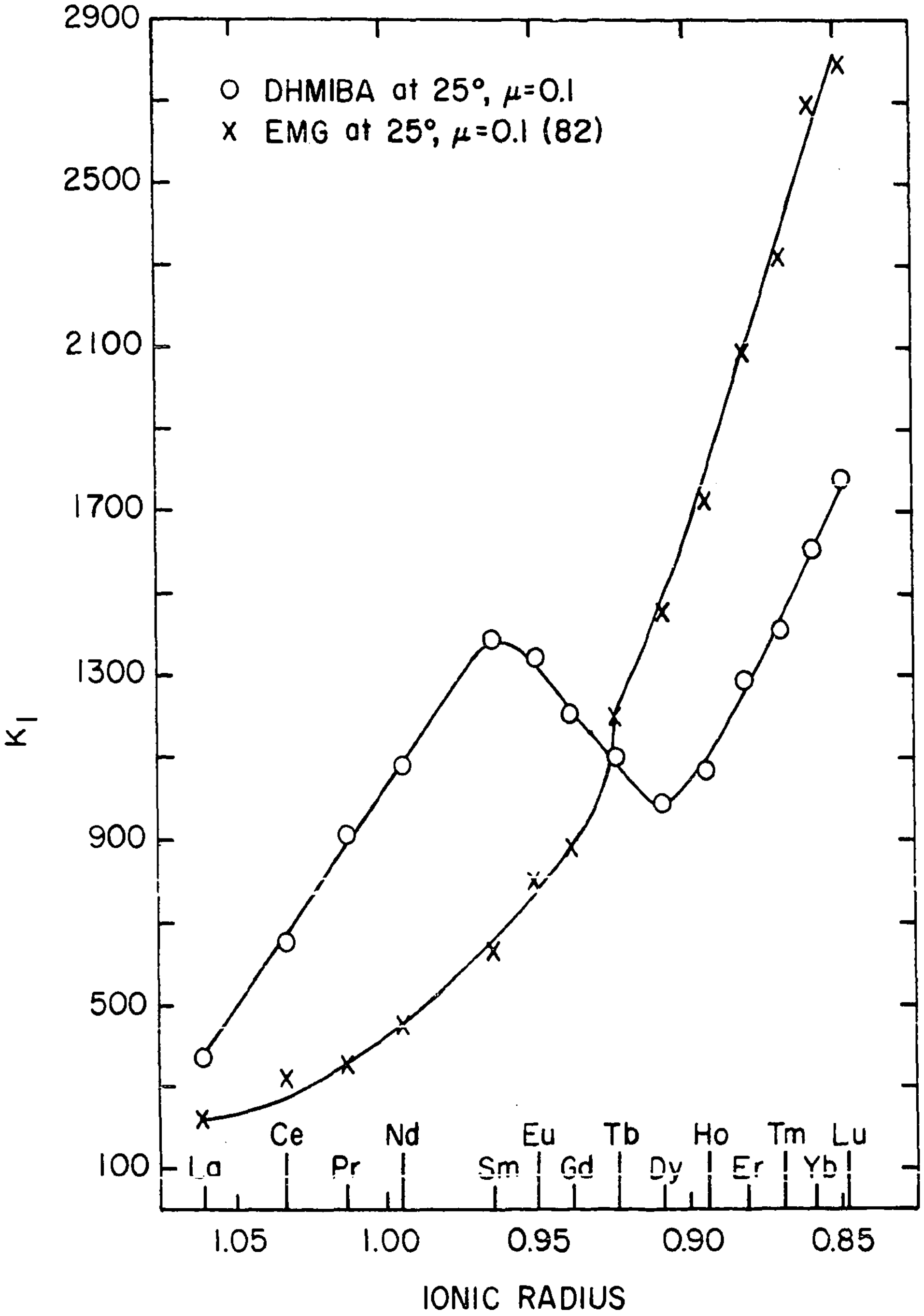


Figure 19. The first formation constants (K_1) of DHMIBA and EMG as a function of ionic radius

droxycarboxylate (DHIBA and DHMIBA) complexes are higher than in the case of the corresponding monohydroxycarboxylates (HIBA and EMG). This clearly suggests that the hydroxyl group at the β-carbon both in DHIBA and DHMIBA participates in bonding to the central atom. The stability relationship reverses for the heavier lanthanons (Tb to Lu) in both cases. In this situation, one is forced to conclude that the hydroxyl group at the β-carbon has nothing to do directly with the bonding of the ligands to smaller cations. The inductive effect of this group now causes weaker lanthanon complexation with DHIBA and DHMIBA than with EMG and HIBA.

The complex stabilities of DHIBA and DHMIBA lanthanon chelates are compared in Figure 20. From La through Sm both ligands appear to function tridentately, but from Eu to Tb the percentage of tridentate bonding decreases. Because of the inductive effect of the methyl group on the β-carbon and the buttressing steric effect of methyl groups on both the α- and β-carbons, the bond angle HOC-COH-COO should be smaller in DHMIBA than in DHIBA, and one should expect to see higher complex stabilities with DHMIBA from La through Tb. It appears that this argument holds only from Pr through Tb. One is led to the conclusion that the bond angle HOC-COH-COO in DHMIBA is now too small to satisfy the larger La^{+3} and Ce^{+3} cations as well as does DHIBA.

From Dy through Lu (and with Y), both DHIBA and DHMIBA attach only bidentately to the cation. The methyl group at β-carbon in DHMIBA donates electrons to the carboxyl group (inductive effect), so that the complex stabilities of DHMIBA should be greater than in the case of DHIBA. But, this is not the case, because the stability curve of DHMIBA in Figure 20 falls below the DHIBA curve. The reason for this is not completely clear.

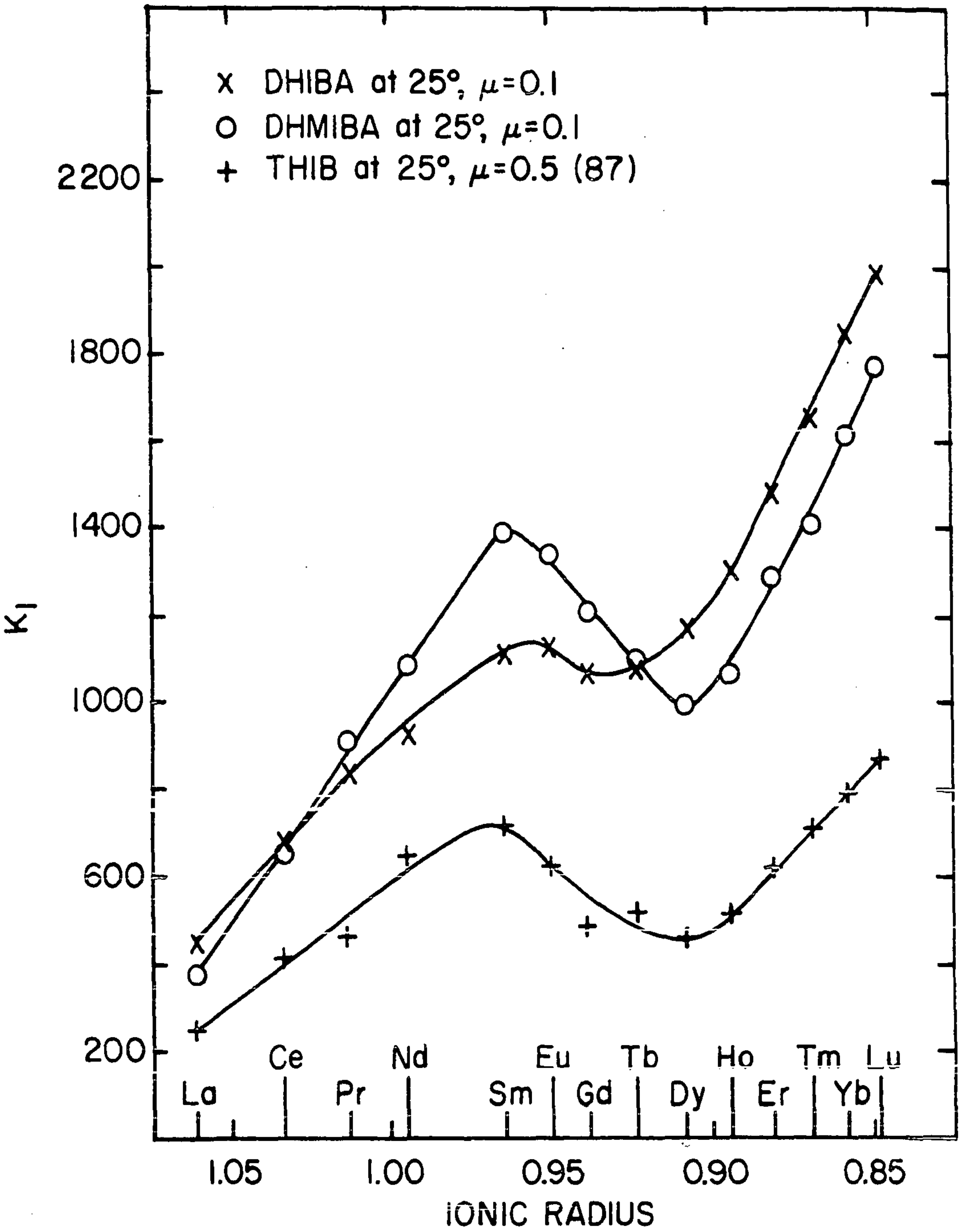


Figure 20. The first formation constant of DHIBA, DHMIBA and THIB as a function of ionic radius

However, if a hydrogen bond between the unbonded hydroxyl group (β-position) and the unbonded oxygen of the carboxyl group occurs in both DHIBA and DHMIBA, the hydrogen bond in DHMIBA should be relatively greater than in DHIBA. This is because the steric effect between the methyl groups at the α- and β-positions in DHMIBA causes the bond distance between the hydroxy group at the β-carbon and oxygen of the carboxyl group to be shorter than in the case of DHIBA. If this is true, the behavior of the complex stabilities from Dy through Lu can be rationalized. As a matter of fact, divalent transition metals also form stronger complexes with bidentate DHIBA than in the case of the bulkier bidentate DHMIBA ligand.

A test of the above argument would be a study of the formation constants of rare-earth complexes with α,β-dihydroxy-β,β-dimethylisobutyrate and α,β,β'-trihydroxyisobutyrate ligands. One more methyl group at the β-carbon compared to DHMIBA should cause even more deviation from linearity in the stability sequence. Hydroxyl groups on both the β and β'-carbons in the later ligand should provide an unfavorable inductive effect that would lower the complex stabilities compared to DHIBA and DHMIBA. The first formation constants of the THIB ligand with lanthanons at 25° and μ 0.5 are plotted in Figure 20. Because of the different conditions studied with this complex no firm conclusions can be drawn, but the trend of these data appears to confirm the above prediction.

VII. SUMMARY

The stoichiometric stepwise formation constants of the complex rare-earth(III) α,β-dihydroxyisobutyrate, rare-earth(III) α,β-dihydroxy-β-methylisobutyrate, transition metal(II) α,β-dihydroxyisobutyrate, transition metal(II) α,β-dihydroxy-β-methylisobutyrate and copper(II) α-hydroxyisobutyrate species were investigated. The stoichiometric acid dissociation constants of α-hydroxyisobutyric and α,β-dihydroxy-β-methylisobutyric acids were also measured. All the stoichiometric formation and acid dissociation constants were studied at an ionic strength of 0.1 $\underline{M}$ with potassium nitrate as the supporting electrolyte and at a temperature of 25°C using the potentiometric method. The pH was measured by a Beckman Research pH meter or a Corning Model 101 Digital Electrometer equipped with a sleeve-type calomel reference electrode and a glass electrode. The stoichiometric formation and acid dissociation constants were calculated by means of a weighted least squares program using an I.B.M. 360 computer.

For both dihydroxy ligands (DHIBA and DHMIBA) the sequence of increasing formation constants proved to be the same: $Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2} > Cd^{+2}$, in agreement with the well-known Irving-Williams series. The stabilities of the divalent transition metal complexes increased in the order DHMIBA < DHIBA < HIBA. The molecular structure in solution of $Cu(DHMIBA)_2$, $Cu(DHIBA)_2$ and $Cu(HIBA)_2$ was predicted to be a tetragonally distorted octahedral configuration from the statistical ratios observed, and in this configuration, bidentate ligands were proposed.

The anomalous trends in the stabilities of both the rare-earth DHIBA and the rare-earth DHMIBA complexes were thought to result from a change in the dentate character of the ligands. Statistical ratios of successive formation constants were studied to predict the dentate character of the ligand in each complex. Both DHIBA and DHMIBA ligands appeared to bond the lighter rare-earth cations tridentately and the heavier rare-earth cations bidentately. The proposed change in dentate character of these ligands was also supported by the observed higher formation constants of the lighter rare-earth DHIBA and DHMIBA complexes compared to the complexes of α-hydroxyisobutyrate and ethylmethylglycolate. This order of stabilities reversed direction with the heavier rare-earth chelates. Both inductive and steric effects of the methyl group at β-carbon position in DHMIBA seem to affect the formation constants. The DHMIBA chelate stabilities were lower than those for DHIBA with La and Ce, markedly higher from Pr through Tb, but then lower again from Dy through Lu.

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IX. APPENDIX A:

ACID DISSOCIATION CONSTANTS OF α,β-DIHYDROXY-β-METHYLISOBUTYRIC AND α-HYDROXYISOBUTYRIC ACIDS

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KC OF DHMIBA-X,          RUN2 NOVEMBER11  1971


ORIG  ACID  CONC. = 0.09930
ORIG   KOH  CONC. = 0.04958
BUFFER ACID CONC. = 0.04972
BUFFER SALT CONC. = 0.04958
FINAL SOLN. VOLUME = 100.00
CONC. SALT ADDED = 1.29010
ST. LINE EQ. FOR KA & ANION DATA IS Y = 0.30594E-03+(-0.52180E-03)*(X)
IONIC STRENGTH= 0.10000

AMPLE     VACID     VBASE      PH        ANION        KA            LSTSQKA      ERROR      VKNO3

  1        3.00      3.00    3.6457   0.17135E-02  0.30614E-03   0.30504E-03   0.36      7.619
  2        4.00      4.00    3.6200   0.22231E-02  0.30492E-03   0.30478E-03   0.05      7.579
  3        5.00      5.00    3.6025   0.27287E-02  0.30475E-03   0.30451E-03   0.08      7.540
  4        6.00      6.00    3.5904   0.32316E-02  0.30439E-03   0.30425E-03   0.05      7.501
  5        8.00      8.00    3.5746   0.42327E-02  0.30374E-03   0.30373E-03   0.00      7.423
  6        9.00      9.00    3.5655   0.47342E-02  0.30634E-03   0.30347E-03   0.95      7.384
  7       10.00     10.00    3.5621   0.52321E-02  0.30526E-03   0.30321E-03   0.68      7.346
  8       12.00     12.00    3.5600   0.62250E-02  0.30127E-03   0.30269E-03  -0.47      7.269
  9       14.00     14.00    3.5561   0.72191E-02  0.30021E-03   0.30217E-03  -0.65      7.192
 10       16.00     16.00    3.5522   0.82132E-02  0.30009E-03   0.30165E-03  -0.52      7.115
 11       18.00     18.00    3.5490   0.92069E-02  0.30008E-03   0.30113E-03  -0.35      7.038
 12       20.00     20.00    3.5462   0.10200E-01  0.30023E-03   0.30061E-03  -0.13      6.961
 13       22.00     22.00    3.5455   0.11192E-01  0.29917E-03   0.30010E-03  -0.31      6.884
 14       24.00     24.00    3.5450   0.12184E-01  0.29824E-03   0.29958E-03  -0.45      6.807
 15       26.00     26.00    3.5440   0.13177E-01  0.29786E-03   0.29906E-03  -0.40      6.730
 16       28.00     28.00    3.5428   0.14169E-01  0.29777E-03   0.29854E-03  -0.26      6.653
 17       30.00     30.00    3.5400   0.15162E-01  0.29895E-03   0.29803E-03   0.31      6.576
 18       32.00     32.00    3.5400   0.16154E-01  0.29823E-03   0.29751E-03   0.24      6.499
 19       35.00     35.00    3.5398   0.17642E-01  0.29744E-03   0.29673E-03   0.24      6.384
 20       40.00     40.00    3.5398   0.20121E-01  0.29621E-03   0.29544E-03   0.26      6.192
 21       45.00     45.00    3.5400   0.22599E-01  0.29511E-03   0.29414E-03   0.33      6.000
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KC OF DHMIBA-SQRT(X)    RUN1+2  NOVEMBER11  1971

ORIG  ACID  CONC. = 0.09930
ORIG   KOH  CONC. = 0.04958
BUFFER ACID CONC. = 0.04972
BUFFER SALT CONC. = 0.04958
FINAL SOLN. VOLUME = 100.00
CONC. SALT ADDED = 1.29010
ST. LINE EQ. FOR KA & ANION DATA IS Y = 0.30835E-03+(-0.90660E-04)*SQRT(X)
IONIC STRENGTH= 0.10000

AMPLE     VACID     VBASE       PH        ANION         KA             LSTSQKA      ERROR       VKNO3

   1       4.00      4.00     3.6200   0.22231E-02   0.30492E-03     0.30407E-03    0.28       7.579
   2       5.00      5.00     3.6025   0.27287E-02   0.30475E-03     0.30361E-03    0.37       7.540
   3       6.00      6.00     3.5904   0.32316E-02   0.30439E-03     0.30319E-03    0.39       7.501
   4       7.00      7.00     3.5865   0.37297E-02   0.30002E-03     0.30281E-03   -0.92       7.462
   5       8.00      8.00     3.5746   0.42327E-02   0.30374E-03     0.30245E-03    0.43       7.423
   6      12.00     12.00     3.5600   0.62250E-02   0.30127E-03     0.30120E-03    0.02       7.269
   7      14.00     14.00     3.5561   0.72191E-02   0.30021E-03     0.30065E-03   -0.15       7.192
   8      14.00     14.00     3.5565   0.72188E-02   0.29991E-03     0.30065E-03   -0.25       7.192
   9      16.00     16.00     3.5522   0.82132E-02   0.30009E-03     0.30013E-03   -0.01       7.115
  10      16.00     16.00     3.5526   0.82130E-02   0.29979E-03     0.30013E-03   -0.11       7.115
  11      18.00     18.00     3.5490   0.92069E-02   0.30008E-03     0.29965E-03    0.14       7.038
  12      18.00     18.00     3.5522   0.92048E-02   0.29774E-03     0.29965E-03   -0.64       7.038
  13      20.00     20.00     3.5462   0.10200E-01   0.30023E-03     0.29919E-03    0.35       6.961
  14      20.00     20.00     3.5490   0.10198E-01   0.29819E-03     0.29919E-03   -0.34       6.961
  15      22.00     22.00     3.5455   0.11192E-01   0.29917E-03     0.29876E-03    0.14       6.884
  16      22.00     22.00     3.5467   0.11192E-01   0.29831E-03     0.29876E-03   -0.15       6.884
  17      24.00     24.00     3.5450   0.12184E-01   0.29824E-03     0.29834E-03   -0.03       6.807
  18      24.00     24.00     3.5460   0.12184E-01   0.29752E-03     0.29834E-03   -0.28       6.807
  19      26.00     26.00     3.5440   0.13177E-01   0.29786E-03     0.29794E-03   -0.03       6.730
  20      26.00     26.00     3.5450   0.13176E-01   0.29714E-03     0.29794E-03   -0.27       6.730
  21      28.00     28.00     3.5428   0.14169E-01   0.29777E-03     0.29756E-03    0.07       6.653
  22      28.00     28.00     3.5440   0.14168E-01   0.29692E-03     0.29756E-03   -0.22       6.653
  23      30.00     30.00     3.5400   0.15162E-01   0.29895E-03     0.29719E-03    0.59       6.576
  24      30.00     30.00     3.5429   0.15160E-01   0.29688E-03     0.29719E-03   -0.10       6.576
  25      32.00     32.00     3.5400   0.16154E-01   0.29823E-03     0.29683E-03    0.47       6.499
  26      32.00     32.00     3.5422   0.16153E-01   0.29666E-03     0.29683E-03   -0.05       6.499
  27      35.00     35.00     3.5398   0.17642E-01   0.29744E-03     0.29631E-03    0.38       6.384
  28      35.00     35.00     3.5420   0.17640E-01   0.29589E-03     0.29631E-03   -0.14       6.384
  29      40.00     40.00     3.5398   0.20121E-01   0.29621E-03     0.29549E-03    0.24       6.192
  30      40.00     40.00     3.5410   0.20120E-01   0.29537E-03     0.29549E-03   -0.04       6.192
  31      45.00     45.00     3.5400   0.22599E-01   0.29511E-03     0.29472E-03    0.13       6.000
  32      45.00     45.00     3.5418   0.22598E-01   0.29386E-03     0.29472E-03   -0.29       6.000
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KC OF CHMIBA-X,X**2      RUN1 NOVEMBER1  1971

 ORIG   ACID  CONC. = 0.09930
 ORIG    KOH  CONC. = 0.04958
 BUFFER ACID CONC. = 0.04972
 BUFFER SALT CONC. = 0.04958
 FINAL SOLN. VOLUME = 100.00
 CONC. SALT ADDED = 1.29010
 ST. LINE EQ. FOR KA & ANION DATA IS Y = 0.29791E-03+( 0.17424E-03)*(X)+(-0.15620E-01)*(X)**2
ONIC STRENGTH =  0.10000

AMPLE      VACID      VBASE        PH         ANION         KA             LSTSQKA     ERROR       VKNO3

   1        3.00       3.00      3.6540    0.17092E-02  0.29859E-03     0.29816E-03    0.14       7.619
   2        4.00       4.00      3.6274    0.22190E-02  0.29853E-03     0.29822E-03    0.11       7.579
   3        5.00       5.00      3.6102    0.27244E-02  0.29833E-03     0.29827E-03    0.02       7.540
   4        6.00       6.00      3.5985    0.32269E-02  0.29781E-03     0.29831E-03   -0.17       7.501
   5        7.00       7.00      3.5865    0.37297E-02  0.30002E-03     0.29834E-03    0.56       7.462
   6        8.00       8.00      3.5833    0.42274E-02  0.29692E-03     0.29836E-03   -0.48       7.424
   7        9.00       9.00      3.5763    0.47275E-02  0.29792E-03     0.29838E-03   -0.16       7.385
   8       10.00      10.00      3.5741    0.52246E-02  0.29605E-03     0.29839E-03   -0.79       7.346
   9       14.00      14.00      3.5565    0.72188E-02  0.29991E-03     0.29835E-03    0.52       7.192
  10       16.00      16.00      3.5526    0.82130E-02  0.29979E-03     0.29828E-03    0.51       7.115
  11       18.00      18.00      3.5522    0.92048E-02  0.29774E-03     0.29819E-03   -0.15       7.038
  12       20.00      20.00      3.5490    0.10198E-01  0.29819E-03     0.29806E-03    0.04       6.961
  13       22.00      22.00      3.5467    0.11192E-01  0.29831E-03     0.29790E-03    0.14       6.884
  14       24.00      24.00      3.5460    0.12184E-01  0.29752E-03     0.29771E-03   -0.06       6.807
  15       26.00      26.00      3.5450    0.13176E-01  0.29714E-03     0.29749E-03   -0.12       6.730
  16       28.00      28.00      3.5440    0.14168E-01  0.29692E-03     0.29724E-03   -0.11       6.653
  17       30.00      30.00      3.5429    0.15160E-01  0.29688E-03     0.29696E-03   -0.03       6.576
  18       32.00      32.00      3.5422    0.16153E-01  0.29666E-03     0.29665E-03    0.01       6.499
  19       35.00      35.00      3.5420    0.17640E-01  0.29589E-03     0.29612E-03   -0.08       6.384
  20       40.00      40.00      3.5410    0.20120E-01  0.29537E-03     0.29509E-03    0.09       6.192
  21       45.00      45.00      3.5418    0.22598E-01  0.29386E-03     0.29387E-03   -0.00       6.000
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KC OF HIBA-X    RUN1  OCTOBER3  1972

CRIG  ACIC  CCNC. = 0.10786
ORIG   KOH  CCNC. = 0.C4987
BUFFER ACID CCNC. = 0.05799
BUFFER SALT CCNC. = 0.C4987
FINAL SOLN. VOLUME = 200.00
CONC. SALT ACDEC = 1.E8800
ST. LINE EQ. FOR KA & ANION DATA IS Y = 0.15962E-03+(-0.26159E-03)*(X)
IONIC STRENGTH= 0.100CC

AMPLE      VACID      VBASE       PH        ANICN          KA              LSTSQKA      ERROR      VKNO3

  1        16.00      16.C0     3.7670    0.41606E-02   0.15923E-03      0.15853E-03    0.44      10.152
  2        16.00      16.00     3.7678    0.41603E-02   0.15891E-03      0.15853E-03    0.24      10.153
  3        17.00      17.C0     3.7668    0.44100E-02   0.15857E-03      0.15846E-03    0.07      10.126
  4        17.00      17.00     3.7665    0.44101E-02   0.15868E-03      0.15846E-03    0.14      10.126
  5        18.00      18.00     3.7660    0.46597E-02   0.15822E-03      0.15840E-03   -0.11      10.100
  6        19.00      19.C0     3.7660    0.49090E-02   0.15763E-03      0.15833E-03   -0.44      10.073
  7        19.00      19.00     3.7660    0.49090E-02   0.15763E-03      0.15833E-03   -0.44      10.073
  8        20.00      20.00     3.7648    0.51589E-02   0.15757E-C3      0.15827E-03   -0.44      10.047
  9        20.00      20.00     3.7640    0.51592E-02   0.15788E-03      0.15827F-03   -0.25      10.047
 10        22.00      22.00     3.7610    0.56591E-02   0.15811E-03      0.15814E-03   -0.01       9.994
 11        22.00      22.00     3.7600    0.56595E-02   0.15850E-03      0.15814E-03    0.23       9.994
 12        23.00      23.00     3.7600    0.59088E-02   0.15810E-03      0.15807E-03    0.02       9.967
 13        24.00      24.00     3.7585    0.61588E-02   0.15830E-03      0.15801E-03    0.19       9.941
 14        25.00      25.C0     3.7583    0.64082E-02   0.15804E-03      0.15794E-03    0.06       9.914
 15        26.00      26.00     3.7573    0.66580E-02   0.15810E-03      0.15787E-03    0.14       9.888
 16        26.00      26.C0     3.7573    0.66580E-02   0.15810E-03      0.15787E-03    0.14       9.888
 17        27.00      27.C0     3.7568    0.69C75E-C2   0.15800E-03      0.15781E-03    0.12       9.861
 18        28.00      28.00     3.7568    0.71569E-02   0.15773E-03      0.15774E-03   -0.01       9.835
 19        28.00      28.C0     3.7564    0.71570E-02   0.15788E-03      0.15774E-03    0.09       9.835
 20        29.00      29.00     3.7564    0.74064E-02   0.15763E-03      0.15768E-03   -0.03       9.809
 21        30.00      30.00     3.7564    0.76557E-02   0.15739E-03      0.15761F-03   -0.14       9.782
 22        30.00      30.C0     3.7565    0.76557E-02   0.15735E-03      0.15761E-03   -0.17       9.782
 23        31.00      31.00     3.7564    0.79051E-02   0.15717E-03      0.15755E-03   -0.24       9.756
 24        32.00      32.00     3.7543    0.81553E-C2   0.15776E-03      0.15748E-03    0.17       9.729
 25        32.00      32.00     3.7542    0.81553E-C2   0.15779E-03      0.15748E-03    0.20       9.729
 26        33.00      33.C0     3.7543    0.84046E-02   0.15756E-03      0.15742E-03    0.09       9.703
 27        34.00      34.00     3.7543    0.86540E-02   0.15738E-03      0.15735E-03    0.02       9.676
 28        34.00      34.00     3.7543    0.86540E-02   0.15738E-03      0.15735E-03    0.02       9.676
 29        35.00      35.00     3.7542    0.89034E-C2   0.15724E-03      0.15729F-03   -0.03       9.650
 30        35.00      35.C0     3.7540    0.89034E-02   0.15732E-03      0.15729E-03    0.02       9.650
 31        36.00      36.00     3.7537    0.91529E-C2   0.15727E-03      0.15722E-03    0.03       9.624
 32        37.00      37.C0     3.7530    0.94025E-02   0.15737E-03      0.15716E-03    0.14       9.597
 33        38.00      38.00     3.7530    0.96519E-02   0.15723E-03      0.15709E-03    0.09       9.571
 34        38.00      38.C0     3.7530    0.96519E-02   0.15723E-03      0.15709F-03    0.09       9.571
 35        40.00      40.C0     3.7537    0.10150E-01   0.15669E-03      0.15696F-03   -0.17       9.518
 36        40.00      40.C0     3.7540    0.10150E-01   0.15658E-03      0.15696E-03   -0.24       9.518
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X. APPENDIX B:

FORMATION CONSTANTS OF RARE-EARTH α,β-DIHYDROXYISOBUTYRATE COMPLEXES

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                                               **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF LA3-OHIBA  RUN 2  NOVEMBER 3 1972

ORIG ACID CONCENTRATION = 0.09359          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05015          POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04344          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05015          CONC. OF  METAL ION SOL.   =  0.10061
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)    VB        ANION CON      N EXP   N CALC    ERROR     PH        KA USED         KA THEO        VOL KNO3

 1    6.000   0.10463E-02    0.358    0.359     -0.42    3.5820    0.26306E-03    0.26229E-03       9.381
 2    8.000   0.13874E-02    0.445    0.445     -0.02    3.5580    0.26276E-03    0.26273E-03       9.383
 3   10.000   0.17373E-02    0.524    0.523      0.32    3.5450    0.26250E-03    0.26301E-03       9.379
 4   11.000   0.19162E-02    0.561    0.559      0.40    3.5410    0.26237E-03    0.26299E-03       9.375
 5   12.000   0.20965E-02    0.597    0.594      0.54    3.5380    0.26225E-03    0.26306E-03       9.370
 6   14.000   0.24690E-02    0.663    0.660      0.34    3.5350    0.26202E-03    0.26249E-03       9.358
 7   16.000   0.28566E-02    0.719    0.723     -0.51    3.5350    0.26179E-03    0.26111E-03       9.342
 8   18.000   0.32438E-02    0.776    0.780     -0.48    3.5350    0.26158E-03    0.26097E-03       9.322
 9   20.000   0.36395E-02    0.828    0.833     -0.57    3.5360    0.26138E-03    0.26069E-03       9.300
10   22.000   0.40365E-02    0.890    0.882     -0.28    3.5370    0.26119E-03    0.26087E-03       9.274
11   25.000   0.46514E-02    0.947    0.952     -0.49    3.5400    0.26091E-03    0.26038E-03       9.233
12   28.000   0.52510E-02    1.017    1.014      0.34    3.5420    0.26065E-03    0.26099E-03       9.187
13   31.000   0.59033E-02    1.071    1.073     -0.24    3.5460    0.26039E-03    0.26016E-03       9.139
14   34.000   0.65251E-02    1.135    1.126      0.80    3.5480    0.26015E-03    0.26088E-03       9.086
15   36.000   0.69532E-02    1.171    1.160      0.96    3.5500    0.26000E-03    0.26083E-03       9.050
16   38.000   0.74022E-02    1.196    1.193      0.22    3.5530    0.25984E-03    0.26002E-03       9.014
17   40.000   0.78382E-02    1.228    1.224      0.30    3.5550    0.25969E-03    0.25993E-03       8.976
18   50.000   0.10071E-01    1.361    1.362     -0.06    3.5650    0.25898E-03    0.25894E-03       8.776
19   60.000   0.12365E-01    1.464    1.477     -0.87    3.5740    0.25833E-03    0.25779E-03       8.562
20   70.000   0.14674E-01    1.561    1.574     -0.84    3.5810    0.25773E-03    0.25726E-03       8.337
21   80.000   0.17008E-01    1.645    1.658     -0.75    3.5870    0.25717E-03    0.25680E-03       8.106

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.4456E 03     2.64890     0.302E 01    0.4456E 03    2.64890         6.032
    2    0.3291E 05     4.51733     0.705E 03    0.7386E 02    1.86842         4.747
    3    0.5121E 06     5.70937     0.665E 05    0.1556E 02    1.19205     *********

    THE NUMBER OF ITERATIONS =   5            SMIN =  0.7931E 01

      NO POINTS ELIMINATED
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                                                ***********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF CE3-DHIBA  RUN 1  NOVEMBER 8 1972

ORIG ACID CONCENTRATION = 0.09359            IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05015            POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04344            VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05015            CONC. OF  METAL ION SOL.   =  0.10150
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)     VB        ANION CON       N EXP   N CALC    ERROR      PH       KA USED       KA THEO     VOL KNO3

 1     4.000    0.60292E-03     0.327    0.325     0.58    3.5780   0.26353E-03   0.26519E-03     9.402
 2     6.000    0.90171E-03     0.442    0.443    -0.27    3.5310   0.26320E-03   0.26249E-03     9.425
 3     8.000    0.12120E-02     0.544    0.547    -0.54    3.5090   0.26291E-03   0.26162E-03     9.437
 4    10.000    0.15299E-02     0.639    0.638     0.19    3.4970   0.26265E-03   0.26308E-03     9.440
 5    11.000    0.17027E-02     0.677    0.683    -0.80    3.4960   0.26252E-03   0.26082E-03     9.441
 6    12.000    0.18609E-02     0.724    0.721     0.46    3.4920   0.26241E-03   0.26336E-03     9.437
 7    14.000    0.22129E-02     0.798    0.799    -0.09    3.4920   0.26218E-03   0.26200E-03     9.429
 8    16.000    0.25708E-02     0.868    0.869    -0.08    3.4930   0.26196E-03   0.26181E-03     9.417
 9    18.000    0.29373E-02     0.934    0.934     0.04    3.4950   0.26175E-03   0.26182E-03     9.400
10    20.000    0.33149E-02     0.994    0.994     0.00    3.4980   0.26155E-03   0.26155E-03     9.380
11    22.000    0.36879E-02     1.057    1.048     0.77    3.5000   0.26136E-03   0.26252E-03     9.356
12    25.000    0.42842E-02     1.131    1.127     0.41    3.5060   0.26107E-03   0.26164E-03     9.317
13    28.000    0.48836E-02     1.205    1.196     0.70    3.5110   0.26081E-03   0.26171E-03     9.273
14    31.000    0.55217E-02     1.259    1.263    -0.35    3.5180   0.26054E-03   0.26011E-03     9.226
15    34.000    0.61489E-02     1.319    1.322    -0.28    3.5230   0.26029E-03   0.25998E-03     9.175
16    36.000    0.65845E-02     1.350    1.360    -0.77    3.5270   0.26013E-03   0.25929E-03     9.140
17    38.000    0.69541E-02     1.394    1.394     0.04    3.5290   0.25998E-03   0.26002E-03     9.102
18    40.000    0.74245E-02     1.428    1.427     0.08    3.5320   0.25983E-03   0.25991E-03     9.064
19    50.000    0.96336E-02     1.571    1.574    -0.21    3.5460   0.25911E-03   0.25893E-03     8.863
20    60.000    0.11914E-01     1.679    1.694    -0.92    3.5580   0.25845E-03   0.25776E-03     8.646
21    70.000    0.14174E-01     1.798    1.792     0.33    3.5660   0.25786E-03   0.25808E-03     8.418
22    80.000    0.16545E-01     1.863    1.878    -0.80    3.5750   0.25728E-03   0.25681E-03     8.184

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1   0.6825E 03      2.83412     0.3879E 01    0.6825E 03    2.83412        6.073
    2   0.7671E 05      4.88483     0.1108E 04    0.1124E 03    2.05071        4.749
    3   0.1815E 07      6.25899     0.1203E 06    0.2367E 02    1.37415     *********

   THE NUMBER OF ITERATIONS =    5            SMIN =  0.1828E 02

     NO POINTS ELIMINATED
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                                    **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF PR3-PHIPA  RUN 1+2  JUNE 28 1972

ORIG ACID CONCENTRATION = 0.10268           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982           POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05286           VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982           CONC. OF  METAL ION SOL.   =  0.10209
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)     VB      ANION CON      N EXP    N CALC    ERROR     PH        KA USED        KA THEO       VOL KNO3

 1     1.000  0.29129E-03    0.224    0.222     1.13    3.5998   0.26398E-03   0.25863E-03     6.863
 2     1.000  0.29089E-03    0.225    0.222     1.37    3.5995   0.26398E-03   0.26961E-03     6.863
 3     2.000  0.56220E-03    0.378    0.381    -0.71    3.4718   0.26358E-03   0.26100E-03     6.898
 4     3.000  0.83989E-03    0.506    0.512    -1.24    3.4220   0.26326E-03   0.25921E-03     6.920
 5     3.000  0.83862E-03    0.507    0.512    -0.97    3.4215   0.26326E-03   0.26009E-03     6.919
 6     4.000  0.11232E-02    0.622    0.624    -0.30    3.3967   0.26299E-03   0.26209E-03     6.931
 7     4.000  0.11289E-02    0.619    0.626    -1.21    3.3985   0.26298E-03   0.25938E-03     6.932
 8     5.000  0.14262E-02    0.725    0.726    -0.40    3.3860   0.26273E-03   0.26163E-03     6.937
 9     5.000  0.14254E-02    0.723    0.726    -0.31    3.3858   0.26273E-03   0.26190E-03     6.937
10     6.000  0.17447E-02    0.813    0.818    -0.60    3.3922   0.26249E-03   0.26099E-03     6.938
11     6.000  0.17374E-02    0.817    0.816     0.17    3.3806   0.26250E-03   0.26294E-03     6.937
12     7.000  0.20657E-02    0.900    0.898     0.26    3.3800   0.26227E-03   0.26289E-03     6.933
13     7.000  0.20630E-02    0.902    0.897     0.51    3.3795   0.26227E-03   0.26349E-03     6.932
14     8.000  0.24073E-02    0.976    0.974     0.27    3.3818   0.26206E-03   0.26264E-03     6.925
15     8.000  0.23994E-02    0.981    0.972     0.90    3.3805   0.26206E-03   0.26402E-03     6.924
16     9.000  0.27610E-02    1.046    1.043     0.23    3.3850   0.26185E-03   0.26231E-03     6.914
17     9.000  0.27645E-02    1.044    1.044    -0.01    3.3855   0.26185E-03   0.26181E-03     6.914
18    10.000  0.31031E-02    1.122    1.104     1.63    3.3861   0.26166E-03   0.26475E-03     6.899
19    10.000  0.31240E-02    1.110    1.107     0.27    3.3888   0.26165E-03   0.26216E-03     6.900
20    12.000  0.38654E-02    1.232    1.219     1.00    3.3962   0.26127E-03   0.26294E-03     6.865
21    12.000  0.38672E-02    1.231    1.220     0.89    3.3964   0.26127E-03   0.26277E-03     6.865
22    24.000  0.89260E-02    1.659    1.673    -0.87    3.4460   0.25933E-03   0.25847E-03     6.553
23    26.000  0.98400E-02    1.697    1.726    -1.64    3.4528   0.25905E-03   0.25752E-03     6.491
24    26.000  0.98216E-02    1.707    1.725    -1.04    3.4520   0.25905E-03   0.25808E-03     6.490
25    28.000  0.10717E-01    1.754    1.771    -0.97    3.4572   0.25879E-03   0.25794E-03     6.426
26    28.000  0.10732E-01    1.747    1.772    -1.44    3.4578   0.25878E-03   0.25753E-03     6.427
27    30.000  0.11625E-01    1.795    1.815    -1.07    3.4622   0.25853E-03   0.25765E-03     6.361
28    30.000  0.11615E-01    1.801    1.814    -0.74    3.4618   0.25853E-03   0.25792E-03     6.361
29    35.000  0.13890E-01    1.902    1.908    -0.29    3.4720   0.25793E-03   0.25772E-03     6.193
30    35.000  0.13890E-01    1.902    1.908    -0.29    3.4720   0.25793E-03   0.25772E-03     6.193
31    40.000  0.16251E-01    1.962    1.988    -1.32    3.4820   0.25735E-03   0.25650E-03     6.020
32    40.000  0.16244E-01    1.966    1.998    -1.12    3.4818   0.25735E-03   0.25663E-03     6.020
33    45.000  0.18523E-01    2.067    2.054     0.66    3.4877   0.25683E-03   0.25722E-03     5.843
34    45.000  0.18519E-01    2.070    2.054     0.77    3.4876   0.25683E-03   0.25728E-03     5.843
35    50.000  0.20888E-01    2.127    2.113     0.67    3.4943   0.25633E-03   0.25668E-03     5.663
36    50.000  0.20897E-01    2.122    2.113     0.43    3.4945   0.25633E-03   0.25656E-03     5.663

   (I)    BETA(I)    LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1   0.88695E 03    2.94786    0.493E 01    0.88695E 03    2.94786        5.743
    2   0.13699E 06    5.13656    0.192E 04    0.15445E 03    2.18870        5.806
    3   0.36424E 07    6.56142    0.237E 06    0.26608E 02    1.42496     *********

   THE NUMBER OF ITERATIONS =    5            SMIN =  0.1391E 03

    NO POINTS ELIMINATED
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                                                   **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF NO3-CHIBA  RUN 1+2  JULY 15 1972

ORIG ACID CONCENTRATION = 0.09731           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982           POTASSIUM NITRATE CONC.    =  1.3565
BUFFER ACID CONC.       = 0.04749           VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982           CONC. OF  METAL ION SOL.   =  0.10111
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)    VB       ANION CON      N EXP   N CALC    ERROR     PH      KA USED       KA THEO      VOL KNO3

 1    4.000   0.10973E-02    0.624   0.625    -0.16    3.4350   0.26301E-03   0.26252E-03    6.601
 2    5.000   0.13992E-02    0.726   0.728    -0.36    3.4255   0.26276E-03   0.26176E-03    6.607
 3    6.000   0.17063E-02    0.822   0.818     0.52    3.4203   0.26252E-03   0.26386E-03    6.606
 4    7.000   0.20343E-02    0.906   0.902     0.52    3.4206   0.26229E-03   0.26353E-03    6.602
 5    8.000   0.23786E-02    0.981   0.979     0.24    3.4236   0.26207E-03   0.26259E-03    6.595
 6    9.000   0.27367E-02    1.049   1.050    -0.16    3.4280   0.26186E-03   0.26153E-03    6.585
 7   10.000   0.30983E-02    1.114   1.115    -0.05    3.4320   0.26166E-03   0.26156E-03    6.572
 8   12.000   0.38604E-02    1.226   1.233    -0.56    3.4422   0.26127E-03   0.26033E-03    6.540
 9   12.000   0.38566E-02    1.228   1.232    -0.35    3.4418   0.26127E-03   0.26068E-03    6.540
10   14.000   0.46304E-02    1.335   1.333     0.12    3.4502   0.26092E-03   0.26109E-03    6.500
11   14.000   0.46338E-02    1.333   1.334    -0.05    3.4505   0.26092E-03   0.26084E-03    6.500
12   16.000   0.54465E-02    1.420   1.424    -0.32    3.4598   0.26057E-03   0.26012E-03    6.456
13   18.000   0.62645E-02    1.505   1.504     0.07    3.4673   0.26025E-03   0.26034E-03    6.407
14   18.000   0.62779E-02    1.493   1.505    -0.48    3.4682   0.26025E-03   0.25965E-03    6.408
15   19.000   0.66899E-02    1.540   1.542    -0.15    3.4715   0.26009E-03   0.25991E-03    6.382
16   19.000   0.66899E-02    1.540   1.542    -0.15    3.4715   0.26009E-03   0.25991E-03    6.382
17   20.000   0.71040E-02    1.580   1.577     0.21    3.4746   0.25994E-03   0.26018E-03    6.356
18   20.000   0.71056E-02    1.579   1.577     0.14    3.4747   0.25994E-03   0.26011E-03    6.356
19   22.000   0.79554E-02    1.649   1.643     0.40    3.4812   0.25965E-03   0.26008E-03    6.301
20   22.000   0.79572E-02    1.648   1.643     0.33    3.4813   0.25965E-03   0.26001E-03    6.301
21   24.000   0.88255E-02    1.709   1.704     0.34    3.4876   0.25936E-03   0.25971E-03    6.245
22   24.000   0.88276E-02    1.708   1.704     0.27    3.4877   0.25936E-03   0.25963E-03    6.245
23   26.000   0.97114E-02    1.762   1.760     0.10    3.4937   0.25909E-03   0.25918E-03    6.186
24   26.000   0.97160E-02    1.759   1.760    -0.05    3.4939   0.25909E-03   0.25904E-03    6.186
25   28.000   0.10592E-01    1.817   1.811     0.33    3.4987   0.25882E-03   0.25912E-03    6.126
26   30.000   0.11490E-01    1.864   1.860     0.23    3.5037   0.25857E-03   0.25876E-03    6.065
27   30.000   0.11498E-01    1.860   1.860    -0.01    3.5040   0.25857E-03   0.25856E-03    6.065
28   35.000   0.13745E-01    1.977   1.966     0.55    3.5140   0.25797E-03   0.25837E-03    5.907
29   35.000   0.13777E-01    1.961   1.968    -0.34    3.5150   0.25796E-03   0.25770E-03    5.908
30   40.000   0.16086E-01    2.048   2.060    -0.60    3.5241   0.25739E-03   0.25699E-03    5.745
31   40.000   0.16090E-01    2.046   2.060    -0.70    3.5242   0.25739E-03   0.25692E-03    5.745
32   45.000   0.18416E-01    2.125   2.141    -0.73    3.5317   0.25686E-03   0.25641E-03    5.578
33   50.000   0.20715E-01    2.218   2.211     0.33    3.5372   0.25636E-03   0.25654E-03    5.409
34   50.000   0.20706E-01    2.223   2.210     0.55    3.5370   0.25637E-03   0.25667E-03    5.409

    (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)     K(I)/K(I+1)

     1    0.9224E 03     2.96492     0.844E 01    0.9224E 03    2.96492        6.051
     2    0.1406E 06     5.14798     0.150E 04    0.1524E 03    2.18306        4.946
     3    0.4333E 07     6.63677     0.223E 06    0.3082E 02    1.48879        5.739
     4    0.2326E 08     7.36669     0.704E 07    0.5369E 01    0.72992     *********

     THE NUMBER OF ITERATIONS =  10             SMIN =  0.1715E 02

      NO POINTS ELIMINATED
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                                          **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF SM3-CHIBA  RUN 1+2  JULY 26 1972

ORIG ACID CONCENTRATION = 0.10065            IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982            POTASSIUM NITRATE CONC.    =  1.3565
BUFFER ACID CONC.       = 0.05083            VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982            CONC. OF  METAL ION SOL.   =  0.10123
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)    VB      ANION CON     N EXP   N CALC    ERROR      PH       KA USED       KA THEO      VOL KNO3

 1    2.000   0.49526E-03    0.422    0.419     0.82    3.4520   0.26366E-03   0.26737E-03     6.582
 2    2.000   0.50051E-03    0.418    0.422    -0.89    3.4550   0.26366E-03   0.25965E-03     6.584
 3    3.000   0.74657E-03    0.566    0.566    -0.01    3.4005   0.26336E-03   0.26330E-03     6.609
 4    4.000   0.10098E-02    0.693    0.694    -0.06    3.3765   0.26309E-03   0.26288E-03     6.625
 5    4.000   0.10095E-02    0.693    0.693    -0.01    3.3764   0.26309E-03   0.26304E-03     6.625
 6    5.000   0.12877E-02    0.807    0.807     0.02    3.3657   0.26285E-03   0.26292E-03     6.634
 7    5.000   0.12859E-02    0.808    0.806     0.24    3.3652   0.26285E-03   0.26366E-03     6.634
 8    6.000   0.15828E-02    0.909    0.910    -0.09    3.3625   0.26261E-03   0.26235E-03     6.638
 9    6.000   0.15828E-02    0.909    0.910    -0.09    3.3625   0.26261E-03   0.26235E-03     6.638
10    7.000   0.18912E-02    1.003    1.003    -0.03    3.3630   0.26239E-03   0.26229E-03     6.636
11    7.000   0.18892E-02    1.004    1.002     0.22    3.3624   0.26239E-03   0.26302E-03     6.636
12    8.000   0.22130E-02    1.088    1.088     0.05    3.3658   0.26218E-03   0.26230E-03     6.631
13    8.000   0.22141E-02    1.088    1.088    -0.04    3.3660   0.26218E-03   0.26208E-03     6.631
14    9.000   0.25507E-02    1.165    1.166    -0.09    3.3705   0.26197E-03   0.26175E-03     6.622
15    9.000   0.25410E-02    1.171    1.164     0.56    3.3690   0.26198E-03   0.26334E-03     6.621
16   10.000   0.28972E-02    1.238    1.238    -0.02    3.3755   0.26177E-03   0.26172E-03     6.610
17   10.000   0.29037E-02    1.234    1.239    -0.42    3.3764   0.26177E-03   0.26082E-03     6.611
18   12.000   0.36253E-02    1.365    1.366    -0.12    3.3870   0.26139E-03   0.26115E-03     6.580
19   12.000   0.36173E-02    1.369    1.365     0.29    3.3861   0.26139E-03   0.26198E-03     6.579
20   14.000   0.43845E-02    1.477    1.477     0.02    3.3981   0.26103E-03   0.26107E-03     6.541
21   14.000   0.43845E-02    1.477    1.477     0.02    3.3981   0.26103E-03   0.26107E-03     6.541
22   16.000   0.51886E-02    1.567    1.574    -0.50    3.4100   0.26068E-03   0.25988E-03     6.498
23   16.000   0.51899E-02    1.566    1.575    -0.55    3.4101   0.26068E-03   0.25980E-03     6.498
24   18.000   0.59794E-02    1.665    1.657     0.48    3.4182   0.26036E-03   0.26107E-03     6.448
25   18.000   0.59836E-02    1.662    1.657     0.32    3.4185   0.26036E-03   0.26083E-03     6.448
26   19.000   0.64227E-02    1.689    1.698    -0.53    3.4248   0.26019E-03   0.25946E-03     6.423
27   19.000   0.64257E-02    1.687    1.698    -0.64    3.4250   0.26019E-03   0.25930E-03     6.423
28   20.000   0.68226E-02    1.736    1.732     0.21    3.4280   0.26004E-03   0.26032E-03     6.395
29   20.000   0.68388E-02    1.728    1.734    -0.35    3.4290   0.26004E-03   0.25956E-03     6.396
30   22.000   0.76850E-02    1.798    1.800    -0.09    3.4370   0.25974E-03   0.25962E-03     6.340
31   22.000   0.76941E-02    1.794    1.801    -0.39    3.4375   0.25974E-03   0.25925E-03     6.340
32   24.000   0.85387E-02    1.866    1.859     0.36    3.4440   0.25946E-03   0.25987E-03     6.282
33   24.000   0.85407E-02    1.865    1.859     0.30    3.4441   0.25945E-03   0.25979E-03     6.282
34   28.000   0.10307E-01    1.971    1.963     0.42    3.4575   0.25891E-03   0.25933E-03     6.160
35   28.000   0.10305E-01    1.972    1.963     0.49    3.4574   0.25891E-03   0.25940E-03     6.160
36   30.000   0.11208E-01    2.016    2.008     0.40    3.4635   0.25865E-03   0.25902E-03     6.097
37   30.000   0.11206E-01    2.017    2.008     0.47    3.4634   0.25865E-03   0.25909E-03     6.097
38   35.000   0.13516E-01    2.102    2.106    -0.21    3.4772   0.25802E-03   0.25785E-03     5.936
39   35.000   0.13522E-01    2.098    2.106    -0.37    3.4774   0.25802E-03   0.25772E-03     5.936
40   40.000   0.15789E-01    2.205    2.184     0.98    3.4865   0.25746E-03   0.25816E-03     5.768
•41  50.000   0.20517E-01    2.325    2.307     0.74    3.5035   0.25641E-03   0.25684E-03     5.425
42   50.000   0.20541E-01    2.313    2.308     0.21    3.5040   0.25640E-03   0.25652E-03     5.425

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)       K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.1115E 04     3.04725     0.437E 01    0.1115E 04    3.04725        5.124
    2    0.2426E 06     5.38492     0.130E 04    0.2176E 03    2.33767        4.965
    3    0.1063E 08     7.02665     0.166E 06    0.4383E 02    1.64173    *********

    THE NUMBER OF ITERATIONS =   4           SMIN =  0.3950E 02

     NO POINTS ELIMINATED
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                                      **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF LU3-CHIBA  RUN 1+2  AUGUST 14 1972

ORIG ACID CONCENTRATION = 0.09554          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982          POTASSIUM NITRATE CONC.    =  1.3565
BUFFER ACID CONC.       = 0.04572          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982          CONC. OF  METAL ION SOL.   =  0.10104
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)     VB       ANION CON      N EXP   N CALC    ERROR      PH       KA USED        KA THEO       VOL KNO3

 1     3.000   0.71258E-03     0.570    0.567     0.63    3.4316   0.26340E-03   0.26606E-03      6.612
 2     3.000   0.71437E-03     0.569    0.568     0.23    3.4324   0.26340E-03   0.26437E-03      6.613
 3     4.000   0.96895E-03     0.700    0.702    -0.27    3.4083   0.26313E-03   0.26209E-03      6.632
 4     4.000   0.96951E-03     0.700    0.702    -0.36    3.4085   0.26313E-03   0.26174E-03      6.632
 5     5.000   0.12390E-02     0.818    0.823    -0.62    3.3978   0.26289E-03   0.26068E-03      6.643
 6     5.000   0.12328E-02     0.821    0.820     0.16    3.3960   0.26289E-03   0.26346E-03      6.642
 7     6.000   0.15212E-02     0.926    0.931    -0.55    3.3937   0.26266E-03   0.26088E-03      6.649
 8     6.000   0.15146E-02     0.930    0.929     0.13    3.3921   0.26266E-03   0.26310E-03      6.648
 9     7.000   0.18174E-02     1.026    1.031    -0.48    3.3938   0.26244E-03   0.26101E-03      6.650
10     7.000   0.18117E-02     1.030    1.029     0.03    3.3926   0.26245E-03   0.26253E-03      6.649
11     8.000   0.21217E-02     1.121    1.122    -0.01    3.3954   0.26224E-03   0.26220E-03      6.646
12     8.000   0.21140E-02     1.126    1.119     0.57    3.3940   0.26224E-03   0.26385E-03      6.645
13     9.000   0.24444E-02     1.206    1.207    -0.09    3.3957   0.26203E-03   0.26179E-03      6.639
14     9.000   0.24444E-02     1.206    1.207    -0.09    3.3957   0.26203E-03   0.26179E-03      6.639
15    10.000   0.27626E-02     1.294    1.284     0.80    3.4025   0.26185E-03   0.26381E-03      6.628
16    10.000   0.27730E-02     1.288    1.286     0.16    3.4040   0.26194E-03   0.26223E-03      6.629
17    12.000   0.34582E-02     1.438    1.430     0.56    3.4138   0.26147E-03   0.26269E-03      6.602
18    12.000   0.34665E-02     1.432    1.432     0.03    3.4150   0.26147E-03   0.26153E-03      6.603
19    14.000   0.41981E-02     1.560    1.563    -0.21    3.4262   0.26111E-03   0.26070E-03      6.569
20    14.000   0.41910E-02     1.563    1.562     0.11    3.4255   0.26112E-03   0.26133E-03      6.569
21    16.000   0.49380E-02     1.683    1.680     0.18    3.4354   0.26078E-03   0.26110E-03      6.529
22    16.000 . 0.49404E-02     1.681    1.680     0.08    3.4356   0.26078E-03   0.26092E-03      6.529
23    18.000   0.57225E-02     1.783    1.791    -0.42    3.4458   0.26046E-03   0.25976E-03      6.485
24    18.000   0.57116E-02     1.789    1.789    -0.02    3.4450   0.26047E-03   0.26043E-03      6.485
25    19.000   0.61127E-02     1.835    1.842    -0.39    3.4500   0.26031E-03   0.25968E-03      6.462
26    19.000   0.60982E-02     1.842    1.840     0.12    3.4490   0.26031E-03   0.26050E-03      6.461
27    20.000   0.64911E-02     1.893    1.890     0.16    3.4530   0.26017E-03   0.26042E-03      6.437
28    20.000   0.64911E-02     1.893    1.890     0.16    3.4530   0.26017E-03   0.26042E-03      6.437
29    22.000   0.73065E-02     1.979    1.987    -0.38    3.4616   0.25987E-03   0.25932E-03      6.387
30    22.000   0.73030E-02     1.981    1.986    -0.27    3.4614   0.25987E-03   0.25948E-03      6.386
31    24.000   0.81102E-02     2.072    2.075    -0.16    3.4681   0.25960E-03   0.25938E-03      6.333
32    24.000   0.80968E-02     2.079    2.074     0.24    3.4674   0.25960E-03   0.25992E-03      6.332
33    26.000   0.89477E-02     2.148    2.161    -0.62    3.4752   0.25932E-03   0.25854E-03      6.277
34    28.000   0.97567E-02     2.239    2.239    -0.01    3.4800   0.25907E-03   0.25906E-03      6.219
35    28.000   0.97567E-02     2.239    2.239    -0.01    3.4800   0.25907E-03   0.25906E-03      6.219
36    30.000   0.10586E-01     2.319    2.314     0.25    3.4850   0.25883E-03   0.25911E-03      6.160
37    35.000   0.12755E-01     2.474    2.489    -0.58    3.4982   0.25822E-03   0.25763E-03      6.006
38    35.000   0.12749E-01     2.477    2.488    -0.45    3.4980   0.25823E-03   0.25777E-03      6.005
39    40.000   0.14907E-01     2.638    2.638     0.02    3.5076   0.25767E-03   0.25769E-03      5.843
40    40.000   0.14904E-01     2.640    2.638     0.10    3.5075   0.25766E-03   0.25776E-03      5.843
41    45.000   0.17085E-01     2.790    2.768     0.82    3.5156   0.25716E-03   0.25785E-03      5.675
42    45.000   0.17089E-01     2.798    2.768     0.74    3.5157   0.25716E-03   0.25778E-03      5.675
43    50.000   0.19360E-01     2.895    2.884     0.36 .  3.5242   0.25665E-03   0.25693E-03      5.504

   (I)     BETA(I)      LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)     K(I)/K(I+1)

    1    0.1123E 04      3.05037     0.857E 01     0.1123E 04     3.05037        4.424
    2    0.2850E 06      5.45488     0.254E 04     0.2538E 03     2.40451        5.472
    3    0.1322E 08      7.12121     0.554E 06     0.4638E 02     1.66633        0.755
    4    0.8116E 09      8.90933     0.249E 08     0.6139E 02     1.78812     *********

    THE NUMBER OF ITERATIONS =    5           SMIN =  0.4595E 02

     NO POINTS ELIMINATED
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                                               **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF GD3-DHIPA  RUN 2  NOVEMBER 20 1972

ORIG ACID CONCENTRATION = 0.09599            IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262            POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04337            VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262            CONC. OF  METAL ION SOL.   =  0.08388
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)     VB       ANION CON      N EXP    N CALC    ERROR      PH       KA USED        KA THEO      VOL KNO3

 1    4.000    0.56460E-03    0.455    0.456    -0.24    3.5590   0.26357E-03   0.26273E-03      9.652
 2    6.000    0.85022E-03    0.618    0.617     0.17    3.5120   0.26325E-03   0.26378E-03      9.677
 3    8.000    0.11533E-02    0.759    0.757     0.35    3.4920   0.26296E-03   0.26396E-03      9.690
 4   10.000    0.14775E-02    0.883    0.882     0.05    3.4850   0.26269E-03   0.26281E-03      9.693
 5   11.000    0.16464E-02    0.939    0.940    -0.09    3.4840   0.26257E-03   0.26234E-03      9.692
 6   12.000    0.18190E-02    0.993    0.995    -0.18    3.4840   0.26244E-03   0.26201E-03      9.689
 7   14.000    0.21696E-02    1.097    1.095     0.23    3.4850   0.26221E-03   0.26271E-03      9.677
 8   16.000    0.25405E-02    1.188    1.188     0.06    3.4890   0.26198E-03   0.26210E-03      9.660
 9   18.000    0.29321E-02    1.266    1.274    -0.62    3.4950   0.26175E-03   0.26056E-03      9.639
10   20.000    0.33172E-02    1.348    1.349    -0.09    3.4990   0.26154E-03   0.26139E-03      9.613
11   22.000    0.37179E-02    1.421    1.420     0.04    3.5040   0.26134E-03   0.26142E-03      9.595
12   25.000    0.43396E-02    1.517    1.518    -0.03    3.5120   0.26105E-03   0.26100E-03      9.537
13   28.000    0.49701E-02    1.609    1.605     0.27    3.5190   0.26077E-03   0.26115E-03      9.484
14   31.000    0.56323E-02    1.682    1.686    -0.25    3.5270   0.26050E-03   0.26017E-03      9.427
15   34.000    0.62863E-02    1.760    1.758     0.12    3.5330   0.26024E-03   0.26039E-03      9.367
16   36.000    0.67313E-02    1.807    1.803     0.22    3.5370   0.26008E-03   0.26033E-03      9.325
17   38.000    0.71835E-02    1.849    1.846     0.18    3.5410   0.25991E-03   0.26012E-03      9.283
18   40.000    0.76430E-02    1.887    1.887     0.01    3.5450   0.25975E-03   0.25977E-03      9.239
19   50.000    0.99609E-02    2.068    2.066     0.10    3.5610   0.25901E-03   0.25910E-03      9.010
20   60.000    0.12345E-01    2.210    2.213    -0.14    3.5740   0.25833E-03   0.25823E-03      8.768
21   70.000    0.14753E-01    2.340    2.337     0.12    3.5840   0.25771E-03   0.25780E-03      8.517
22   80.000    0.17217E-01    2.436    2.445    -0.37    3.5930   0.25713E-03   0.25690E-03      8.260

   (I)      BETA(I)      LOG BETA(I)   SIGMA(I)       K(I)        LOG K(I)     K(I)/K(I+1)

    1    0.1067E 04      3.02832     0.547E 01    0.1067E 04     3.02832          4.550
    2    0.2504E 06      5.39867     0.196E 04    0.2346E 03     2.37035          4.859
    3    0.1209E 08      7.08243     0.407E 06    0.4828E 02     1.68377          2.875
    4    0.2031E 09      8.30763     0.190E 08    0.1680E 02     1.22520      *********

    THE NUMBER OF ITERATIONS =    5              SMIN =  0.7131E 01

      NO POINTS ELIMINATED
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                                        **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF TB -DHIBA  RUN 1

ORIG ACID CONCENTRATION = 0.09079           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04883           POTASSIUM NITRATE CONC.    =  1.5523
BUFFER ACID CONC.       = 0.04196           VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.04883           CONC. OF  METAL ION SOL.   =  0.09744
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26540E-03+(-0.14070E-03)*X

(I)     VB        ANION CON      N EXP    N CALC     ERROR      PH       KA USED       KA THEO      VOL KNO3

 1     2.000    0.29789E-03    0.276    0.275      0.19     3.4030   0.26536E-03   0.26722E-03     5.079
 2     2.500    0.37011E-03    0.331    0.330      0.13     3.3585   0.26535E-03   0.26651E-03     5.105
 3     3.000    0.44465E-03    0.382    0.384     -0.28     3.3275   0.26534E-03   0.26286E-03     5.129
 4     6.000    0.91988E-03    0.660    0.659      0.26     3.2491   0.26527E-03   0.26717E-03     5.235
 5     7.000    0.11005E-02    0.741    0.742     -0.09     3.2438   0.26525E-03   0.26459E-03     5.261
 6     8.000    0.12944E-02    0.817    0.821     -0.59     3.2435   0.26522E-03   0.26133E-03     5.284
 7     9.000    0.14908E-02    0.891    0.894     -0.31     3.2439   0.26519E-03   0.26325E-03     5.301
 8    10.000    0.16997E-02    0.962    0.964     -0.20     3.2470   0.26516E-03   0.26397E-03     5.315
 9    10.500    0.17979E-02    0.999    0.994      0.50     3.2470   0.26515E-03   0.26802E-03     5.319
10    11.000    0.19060E-02    1.034    1.027      0.70     3.2490   0.26513E-03   0.26901E-03     5.323
11    12.000    0.21527E-02    1.093    1.094     -0.16     3.2580   0.26510E-03   0.26428E-03     5.334
12    13.000    0.23915E-02    1.155    1.154      0.06     3.2642   0.26506E-03   0.26534E-03     5.339
13    14.000    0.26541E-02    1.210    1.214     -0.33     3.2730   0.26503E-03   0.26348E-03     5.343
14    15.000    0.28984E-02    1.271    1.265      0.48     3.2780   0.26499E-03   0.26717E-03     5.340
15    17.500    0.36250E-02    1.391    1.395     -0.32     3.3010   0.26489E-03   0.26363E-03     5.334
16    22.500    0.52120E-02    1.599    1.606     -0.48     3.3408   0.26467E-03   0.26313E-03     5.286
17    25.000    0.60346E-02    1.697    1.690      0.37     3.3560   0.26455E-03   0.26563E-03     5.248
18    27.500    0.69378E-02    1.774    1.769      0.26     3.3730   0.26442E-03   0.26510E-03     5.205
19    30.000    0.75685E-02    1.845    1.839      0.29     3.3882   0.26429E-03   0.26498E-03     5.157
20    35.000    0.98756E-02    1.949    1.962     -0.67     3.4175   0.26401E-03   0.26265E-03     5.051
21    45.000    0.13983E-01    2.140    2.140     -0.01     3.4570   0.26343E-03   0.26341E-03     4.803
22    50.000    0.16142E-01    2.209    2.209      0.01     3.4730   0.26313E-03   0.26314E-03     4.670

   (I)    BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1   0.1084E 04      3.03505    0.439E 01    0.1084E 04    3.03505        4.484
    2   0.2621E 06      5.41845    0.183E 04    0.2418E 03    2.38340        5.605
    3   0.1131E 08      7.05329    0.277E 06    0.4314E 02    1.63484    *********

   THE NUMBER OF ITERATIONS =   4          SMIN =  0.5171E 02

     NO POINTS ELIMINATED
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                                           ***********FOUR PARAMETER PROGRAM USED***********

 STABILITY CONSTANT OF DY3-DHIBA  RUN 1  OCTOBER 19 1972

CRIG ACID CONCENTRATION = 0.09210           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982           POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04228           VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.04982           CONC. OF  METAL ION SOL.   =  0.10177
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03-(-0.60000E-04)*SQ        RT(X)

(I)    VB      ANION CON      N EXP   N CALC     ERROR      PH       KA USED        KA THEO       VOL KNO3

 1    4.000   0.45955E-03    0.415    0.415      0.12     3.5110   0.26371E-03   0.26429E-03     9.456
 2    4.000   0.45955E-03    0.415    0.415      0.12     3.5110   0.26371E-03   0.26429E-03     9.456
 3    8.000   0.94301E-03    0.697    0.698     -0.13     3.4330   0.26316E-03   0.26264E-03     9.524
 4   10.000   0.12057E-02    0.817    0.816      0.14     3.4220   0.26292E-03   0.26341E-03     9.540
 5   10.000   0.12091E-02    0.815    0.818     -0.29     3.4230   0.26291E-03   0.26186E-03     9.541
 6   11.000   0.13446E-02    0.872    0.872      0.07     3.4200   0.26280E-03   0.26304E-03     9.545
 7   11.000   0.13483E-02    0.870    0.873     -0.35     3.4210   0.26280E-03   0.26158E-03     9.546
 8   12.000   0.14820E-02    0.928    0.923      0.57     3.4180   0.26269E-03   0.26459E-03     9.547
 9   14.000   0.17901E-02    1.020    1.025     -0.55     3.4220   0.26246E-03   0.26079E-03     9.550
10   16.000   0.20979E-02    1.112    1.115     -0.25     3.4250   0.26225E-03   0.26155E-03     9.545
11   16.000   0.21033E-02    1.109    1.116     -0.65     3.4260   0.26225E-03   0.26040E-03     9.546
12   18.000   0.24095E-02    1.202    1.195      0.63     3.4280   0.26205E-03   0.26373E-03     9.533
13   20.000   0.27456E-02    1.280    1.272      0.61     3.4340   0.26186E-03   0.26335E-03     9.518
14   20.000   0.27456E-02    1.280    1.272      0.61     3.4340   0.26186E-03   0.26335E-03     9.518
15   22.000   0.31054E-02    1.344    1.346     -0.11     3.4420   0.26166E-03   0.26140E-03     9.501
16   25.000   0.36498E-02    1.440    1.444     -0.29     3.4520   0.26137E-03   0.26076E-03     9.467
17   25.000   0.36498E-02    1.440    1.444     -0.29     3.4520   0.26137E-03   0.26076E-03     9.467
18   28.000   0.42066E-02    1.530    1.532     -0.13     3.4610   0.26111E-03   0.26085E-03     9.427
19   31.000   0.47726E-02    1.616    1.611      0.30     3.4690   0.26085E-03   0.26139E-03     9.382
20   31.000   0.47841E-02    1.610    1.613     -0.17     3.4700   0.26085E-03   0.26055E-03     9.382
21   34.000   0.53572E-02    1.693    1.684      0.50     3.4770   0.26061E-03   0.26144E-03     9.332
22   36.000   0.57531E-02    1.741    1.730      0.65     3.4820   0.26045E-03   0.26149E-03     9.298
23   36.000   0.57531E-02    1.741    1.730      0.65     3.4820   0.26045E-03   0.26149E-03     9.298
24   38.000   0.61569E-02    1.786    1.774      0.69     3.4870   0.26029E-03   0.26134E-03     9.262
25   40.000   0.66002E-02    1.810    1.819     -0.46     3.4940   0.26013E-03   0.25945E-03     9.226
26   40.000   0.66159E-02    1.802    1.820     -0.99     3.4950   0.26012E-03   0.25868E-03     9.227
27   50.000   0.87362E-02    1.977    2.003     -1.33     3.5160   0.25939E-03   0.25779E-03     9.027
28   60.000   0.10887E-01    2.139    2.152     -0.63     3.5310   0.25874E-03   0.25808E-03     8.810
29   60.000   0.10913E-01    2.126    2.154     -1.30     3.5320   0.25873E-03   0.25738E-03     8.810
30   70.000   0.13079E-01    2.282    2.279      0.12     3.5430   0.25814E-03   0.25825E-03     8.582
31   70.000   0.13049E-01    2.297    2.278      0.86     3.5420   0.25815E-03   0.25893E-03     8.582
32   80.000   0.15306E-01    2.408    2.390      0.79     3.5530   0.25758E-03   0.25822E-03     8.347
33   80.000   0.15306E-01    2.408    2.390      0.79     3.5530   0.25758E-03   0.25822E-03     8.347

    (I)    BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

     1   0.1165E 04      3.06623     0.861E 01    0.1165E 04     3.06623        4.636
     2   0.2926E 06      5.46631     0.352E 04    0.2512E 03     2.40007        5.323
     3   0.1381E 08      7.14026     0.758E 06    0.4720E 02     1.67395        2.437
     4   0.2675E 09      8.42728     0.371E 08    0.1937E 02     1.28702    *********

     THE NUMBER OF ITERATIONS =    5            SMIN =  0.6761E 02

      NO POINTS ELIMINATED
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                                    **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF HO3-DHIPA  RUN 2  NOVEMBER 22 1972

ORIG ACID CONCENTRATION = 0.09599          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04337          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.09840
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)    VB      ANION CON     N EXP   N CALC    ERROR     PH      KA USED       KA THEO      VOL KNO3

 1    2.000   0.23701E-03    0.263   0.263     0.00    3.6410   0.26408E-03   0.26409E-03    9.447
 2    4.000   0.46632E-03    0.457   0.457     0.09    3.5040   0.26370E-03   0.26415E-03    9.509
 3    6.000   0.70919E-03    0.621   0.620     0.07    3.4530   0.26340E-03   0.26371E-03    9.550
 4    8.000   0.97116E-03    0.764   0.765    -0.15    3.4320   0.26313E-03   0.26251E-03    9.577
 5   10.000   0.12504E-02    0.893   0.894    -0.09    3.4240   0.26288E-03   0.26253E-03    9.593
 6   11.000   0.13972E-02    0.952   0.953    -0.10    3.4230   0.26276E-03   0.26239E-03    9.597
 7   12.000   0.15474E-02    1.010   1.010    -0.00    3.4230   0.26264E-03   0.26263E-03    9.598
 8   14.000   0.18621E-02    1.116   1.116     0.04    3.4260   0.26241E-03   0.26254E-03    9.597
 9   16.000   0.21976E-02    1.210   1.213    -0.25    3.4320   0.26219E-03   0.26148E-03    9.589
10   18.000   0.25350E-02    1.304   1.300     0.32    3.4370   0.26198E-03   0.26283E-03    9.574
11   20.000   0.28868E-02    1.390   1.380     0.73    3.4430   0.26178E-03   0.26358E-03    9.555
12   22.000   0.32797E-02    1.454   1.460    -0.43    3.4530   0.26156E-03   0.26058E-03    9.535
13   25.000   0.38521E-02    1.560   1.562    -0.15    3.4630   0.26128E-03   0.26096E-03    9.495
14   28.000   0.44483E-02    1.654   1.655    -0.05    3.4730   0.26100E-03   0.26090E-03    9.448
15   31.000   0.50569E-02    1.742   1.738     0.24    3.4820   0.26073E-03   0.26115E-03    9.397
16   36.000   0.61215E-02    1.864   1.863     0.03    3.4970   0.26031E-03   0.26035E-03    9.303
17   38.000   0.65655E-02    1.904   1.910    -0.32    3.5030   0.26014E-03   0.25966E-03    9.263
18   40.000   0.69871E-02    1.955   1.951     0.23    3.5070   0.25998E-03   0.26031E-03    9.221
19   50.000   0.92644E-02    2.127   2.139    -0.55    3.5300   0.25922E-03   0.25857E-03    9.001
20   60.000   0.11569E-01    2.288   2.287     0.04    3.5460   0.25855E-03   0.25858E-03    8.764
21   70.000   0.13956E-01    2.407   2.413    -0.25    3.5600   0.25791E-03   0.25769E-03    8.516
22   80.000   0.16329E-01    2.535   2.517     0.71    3.5700   0.25733E-03   0.25789E-03    8.260

   (I)     BETA(I)      LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.1299E 04      3.11361     0.458E 01    0.1299E 04    3.11361        4.655
    2    0.3625E 06      5.55934     0.273E 04    0.2791E 03    2.44572        4.549
    3    0.2224E 08      7.34712     0.641E 06    0.6135E 02    1.78778        3.798
    4    0.3592E 09      8.55539     0.349E 08    0.1615E 02    1.20826     *********

    THE NUMBER OF ITERATIONS =    4           SMIN =  0.1445E 02

      NO POINTS ELIMINATED
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                                          **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF ER3-CHIBA  RUN 1  NOVEMBER 28 1972

ORIG ACID CONCENTRATION = 0.09599          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04337          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10546
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)     VB       ANION CON      N EXP    N CALC     ERROR      PH       KA USED       KA THEO      VOL KNO3

 1     4.000   0.41458E-03     0.462     0.462      0.13     3.4720   0.26378E-03   0.26460E-03     9.443
 2     6.000   0.63409E-03     0.629     0.629     -0.07     3.4180   0.26349E-03   0.26312E-03     9.493
 3     8.000   0.87069E-03     0.776     0.776     -0.05     3.3950   0.26323E-03   0.26296E-03     9.527
 4    10.000   0.11241E-02     0.909     0.907      0.24     3.3860   0.26299E-03   0.26405E-03     9.548
 5    11.000   0.12622E-02     0.969     0.970     -0.11     3.3860   0.26287E-03   0.26239E-03     9.556
 6    12.000   0.14040E-02     1.026     1.029     -0.29     3.3870   0.26275E-03   0.26156E-03     9.561
 7    14.000   0.16984E-02     1.134     1.137     -0.31     3.3910   0.26253E-03   0.26138E-03     9.564
 8    16.000   0.20029E-02     1.237     1.234      0.19     3.3960   0.26231E-03   0.26296E-03     9.559
 9    18.000   0.23374E-02     1.324     1.327     -0.28     3.4050   0.26210E-03   0.26123E-03     9.550
10    20.000   0.26645E-02     1.416     1.407      0.57     3.4110   0.26190E-03   0.26357E-03     9.533
11    22.000   0.30222E-02     1.492     1.486      0.41     3.4200   0.26170E-03   0.26282E-03     9.514
12    25.000   0.35882E-02     1.592     1.593     -0.09     3.4340   0.26141E-03   0.26120E-03     9.479
13    28.000   0.41665E-02     1.687     1.688     -0.05     3.4460   0.26113E-03   0.26102E-03     9.436
14    31.000   0.47502E-02     1.781     1.772      0.50     3.4560   0.26086E-03   0.26189E-03     9.386
15    34.000   0.53836E-02     1.850     1.852     -0.13     3.4680   0.26060E-03   0.26035E-03     9.334
16    36.000   0.58090E-02     1.895     1.902     -0.34     3.4750   0.26043E-03   0.25982E-03     9.297
17    38.000   0.62314E-02     1.942     1.947     -0.26     3.4810   0.26026E-03   0.25981E-03     9.258
18    40.000   0.66640E-02     1.985     1.991     -0.34     3.4870   0.26010E-03   0.25955E-03     9.217
19    50.000   0.88819E-02     2.172     2.181     -0.40     3.5120   0.25935E-03   0.25881E-03     9.001
20    60.000   0.11145E-01     2.340     2.332      0.37     3.5300   0.25867E-03   0.25909E-03     8.765
21    70.000   0.13511E-01     2.461     2.460      0.01     3.5460   0.25803E-03   0.25804E-03     8.519
22    80.000   0.15883E-01     2.580     2.568      0.45     3.5580   0.25744E-03   0.25783E-03     8.265

   (I)     BETA(I)     LOG BETA(I)    SIGMA(I)        K(I)      LOG K(I)    K(I)/K(I+1)

    1    0.1479E 04      3.16987     0.922E 01    0.1479E 04    3.16987         4.585
    2    0.4769E 06      5.67839     0.395E 04    0.3225E 03    2.50852         4.987
    3    0.3084E 08      7.48909     0.101E 07    0.6467E 02    1.81071         3.337
    4    0.5977E 09      8.77649     0.546E 08    0.1938E 02    1.28741     *********

   THE NUMBER OF ITERATIONS =    5            SMIN =  0.2003E 02

    NO POINTS ELIMINATED
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                                        ***********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF TM3-CHIPA  RUN 1  NOVEMBER 10 1972

ORIG ACID CONCENTRATION = 0.09359           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05015           POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04344           VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05015           CONC. OF  METAL ION SOL.   =  0.09781
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)     VB        ANION CON       N EXP    N CALC     ERROR       PH        KA USED        KA THEO       VOL KNO3

 1     2.000    0.20009E-03     0.280    0.281     -0.13     3.6070    0.26415E-03    0.26318E-03      9.466
 2     4.000    0.39568E-03     0.498    0.486      0.41     3.4590    0.26381E-03    0.26638E-03      9.535
 3     6.000    0.60709E-03     0.660    0.661     -0.05     3.4040    0.26352E-03    0.26325E-03      9.583
 4     8.000    0.83408E-03     0.812    0.812      0.02     3.3800    0.26327E-03    0.26335E-03      9.614
 5    10.000    0.10824E-02     0.946    0.948     -0.30     3.3720    0.26303E-03    0.26169E-03      9.634
 6    11.000    0.12130E-02     1.007    1.011     -0.35     3.3710    0.26291E-03    0.26142E-03      9.640
 7    12.000    0.13466E-02     1.067    1.070     -0.24     3.3710    0.26280E-03    0.26183E-03      9.643
 8    14.000    0.16222E-02     1.182    1.178      0.32     3.3730    0.26258E-03    0.26378E-03      9.644
 9    16.000    0.19248E-02     1.280    1.281     -0.06     3.3800    0.26237E-03    0.26217E-03      9.640
10    18.000    0.22307E-02     1.377    1.372      0.39     3.3860    0.26217E-03    0.26341E-03      9.628
11    20.000    0.25573E-02     1.463    1.458      0.33     3.3940    0.26197E-03    0.26294E-03      9.613
12    22.000    0.29019E-02     1.539    1.539     -0.04     3.4030    0.26177E-03    0.26166E-03      9.595
13    25.000    0.34219E-02     1.652    1.649      0.26     3.4140    0.26149E-03    0.26213E-03      9.559
14    28.000    0.39754E-02     1.749    1.750     -0.07     3.4260    0.26122E-03    0.26106E-03      9.518
15    31.000    0.45451E-02     1.837    1.843     -0.33     3.4370    0.26095E-03    0.26027E-03      9.473
16    34.000    0.51034E-02     1.933    1.926      0.35     3.4450    0.26071E-03    0.26139E-03      9.421
17    36.000    0.55077E-02     1.980    1.982     -0.11     3.4520    0.26055E-03    0.26035E-03      9.387
18    38.000    0.59093E-02     2.028    2.034     -0.28     3.4580    0.26039E-03    0.25989E-03      9.350
19    40.000    0.63055E-02     2.080    2.083     -0.13     3.4630    0.26024E-03    0.26001E-03      9.312
20    50.000    0.83896E-02     2.287    2.305     -0.80     3.4870    0.25950E-03    0.25838E-03      9.109
21    60.000    0.10483E-01     2.493    2.486      0.25     3.5030    0.25886E-03    0.25916E-03      8.886
22    70.000    0.12683E-01     2.644    2.644      0.01     3.5180    0.25824E-03    0.25826E-03      8.652
23    80.000    0.14879E-01     2.800    2.775      0.88     3.5290    0.25768E-03    0.25851E-03      8.408

   (I)      BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1     0.1657E 04      3.21937    0.693E 01     0.1657E 04    3.21937        4.560
    2     0.6022E 05      5.77974    0.471E 04     0.3634E 03    2.56037        5.396
    3     0.4055E 08      7.60801    0.132E 07     0.6734E 02    1.82827        1.367
    4     0.1998E 10      9.30053    0.896E 08     0.4926E 02    1.69252     *********

    THE NUMBER OF ITERATIONS =    4           SMIN =  0.2336E 02

      NO POINTS ELIMINATED
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                                            **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF Y93-DHIBA  RUN 1  OCTOBER 25 1972

CRIG ACID CONCENTRATION = 0.09251            IONIC STRENGTH OF SOLUTION =  0.1000
CRIG BASE CONCENTRATION = 0.04987            POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04264            VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.04987            CONC. OF  METAL ION SOL.   =  0.05988
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)     VB       ANION CON      N EXP   N CALC    ERROR      PH       KA USED        KA THEO       VOL KNO3

 1    4.000   0.36740E-03    0.494    0.494    -0.01    3.4480   0.26385E-03   0.26376E-03      9.520
 2    4.000   0.36740E-03    0.494    0.494    -0.01    3.4480   0.26385E-03   0.26376E-03      9.520
 3    6.000   0.56597E-03    0.669    0.669     0.02    3.3910   0.26357E-03   0.26369E-03      9.570
 4    8.000   0.78227E-03    0.822    0.821     0.14    3.3670   0.26332E-03   0.26408E-03      9.603
 5   10.000   0.10189E-02    0.957    0.956     0.13    3.3590   0.26308E-03   0.26371E-03      9.624
 6   11.000   0.11466E-02    1.019    1.019    -0.09    3.3590   0.26297E-03   0.26254E-03      9.632
 7   12.000   0.12777E-02    1.077    1.079    -0.12    3.3600   0.26286E-03   0.26232E-03      9.636
 8   14.000   0.15540E-02    1.186    1.187    -0.15    3.3650   0.26263E-03   0.26205E-03      9.638
 9   14.000   0.15540E-02    1.186    1.187    -0.15    3.3650   0.26263E-03   0.26205E-03      9.638
10   16.000   0.18458E-02    1.286    1.286     0.01    3.3720   0.26242E-03   0.26247E-03      9.633
11   16.000   0.18458E-02    1.286    1.286     0.01    3.3720   0.26242E-03   0.26247E-03      9.633
12   18.000   0.21517E-02    1.378    1.374     0.28    3.3800   0.26222E-03   0.26317E-03      9.622
13   20.000   0.24804E-02    1.459    1.458     0.06    3.3900   0.26201E-03   0.26221E-03      9.607
14   22.000   0.28298E-02    1.528    1.536    -0.49    3.4010   0.26181E-03   0.26046E-03      9.588
15   22.000   0.28228E-02    1.532    1.534    -0.12    3.4000   0.26181E-03   0.26147E-03      9.587
16   25.000   0.33381E-02    1.643    1.634     0.58    3.4120   0.26153E-03   0.26302E-03      9.550
17   28.000   0.39579E-02    1.732    1.727     0.27    3.4260   0.26125E-03   0.26187E-03      9.508
18   28.000   0.39074E-02    1.726    1.728    -0.12    3.4270   0.26125E-03   0.26097E-03      9.508
19   31.000   0.44788E-02    1.910    1.911    -0.06    3.4390   0.26098E-03   0.26085E-03      9.460
20   34.000   0.50659E-02    1.886    1.886     0.00    3.4500   0.26073E-03   0.26073E-03      9.408
21   34.000   0.50659E-02    1.886    1.886     0.00    3.4500   0.26073E-03   0.26073E-03      9.408
22   36.000   0.54413E-02    1.945    1.929     0.83    3.4550   0.26057E-03   0.26211E-03      9.371
23   38.000   0.58662E-02    1.979    1.975     0.19    3.4630   0.26040E-03   0.26073E-03      9.334
24   40.000   0.63044E-02    2.006    2.020    -0.68    3.4710   0.26024E-03   0.25911E-03      9.295
25   40.000   0.63044E-02    2.006    2.020    -0.68    3.4710   0.26024E-03   0.25911E-03      9.295
26   50.000   0.84079E-02    2.192    2.200    -0.35    3.4960   0.25950E-03   0.25902E-03      9.086
27   50.000   0.83882E-02    2.202    2.198     0.18    3.4950   0.25950E-03   0.25975E-03      9.086
28   60.000   0.10579E-01    2.346    2.346     0.03    3.5150   0.25883E-03   0.25886E-03      8.862
29   70.000   0.12829E-01    2.463    2.470    -0.29    3.5310   0.25820E-03   0.25791E-03      8.627
30   70.000   0.12829E-01    2.463    2.470    -0.29    3.5310   0.25820E-03   0.25791E-03      8.627
31   80.000   0.15084E-01    2.578    2.575     0.12    3.5430   0.25763E-03   0.25774E-03      8.386
32   80.000   0.15049E-01    2.596    2.574     0.87    3.5420   0.25764E-03   0.25840E-03      8.385

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1   0.1848E 04     3.26681     0.313E 01    0.1848E 04     3.26681        4.814
    2   0.7098E 06     5.85114     0.413E 04    0.3840E 03     2.58433        5.854
    3   0.4656E 08     7.66801     0.110E 07    0.6559E 02     1.81687        3.151
    4   0.9691E 09     8.98638     0.623E 08    0.2082E 02     1.31838     *********

    THE NUMBER OF ITERATIONS =    4            SMIN =  0.2833E 02

     NO POINTS ELIMINATED
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                                                    ***********FOUR PARAMETER PROGRAM USED***********

 STABILITY CONSTANT OF LU3-DHIPA  RUN 1  OCTOBER 26 1972

CRIG ACID CONCENTRATION = 0.09251            IONIC STRENGTH OF SOLUTION =  0.1000
CRIG BASE CONCENTRATION = 0.04987            POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04264            VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.04987            CONC. OF  METAL ION SOL.   =  0.10434
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)    VB      ANION CON     N EXP   N CALC    ERROR      PH        KA USED       KA THEO      VOL KNO3

 1    2.000   0.17007E-03    0.282   0.282    -0.22    3.5960   0.26422E-03   0.26216E-03     9.396
 2    2.000   0.16907E-03    0.283   0.281     0.54    3.5850   0.26422E-03   0.26919E-03     9.395
 3    4.000   0.34183E-03    0.492   0.491     0.20    3.4300   0.26389E-03   0.26547E-03     9.475
 4    4.000   0.34322E-03    0.491   0.493    -0.32    3.4310   0.26389E-03   0.26137E-03     9.476
 5    6.000   0.52873E-03    0.668   0.667     0.14    3.3710   0.26362E-03   0.26459E-03     9.530
 6    6.000   0.53055E-03    0.666   0.668    -0.29    3.3720   0.26362E-03   0.25162E-03     9.531
 7    8.000   0.73765E-03    0.817   0.822    -0.55    3.3480   0.26337E-03   0.26002E-03     9.569
 8    8.000   0.73765E-03    0.817   0.822    -0.55    3.3480   0.26337E-03   0.26002E-03     9.569
 9   10.000   0.95579E-03    0.957   0.954     0.39    3.3370   0.26314E-03   0.26528E-03     9.591
10   11.000   0.10772E-02    1.019   1.017     0.15    3.3370   0.26303E-03   0.26380E-03     9.600
11   11.000   0.10741E-02    1.021   1.016     0.49    3.3360   0.26303E-03   0.26560E-03     9.599
12   12.000   0.12053E-02    1.076   1.078    -0.22    3.3390   0.26292E-03   0.26184E-03     9.607
13   14.000   0.14607E-02    1.191   1.185     0.49    3.3420   0.26271E-03   0.26489E-03     9.611
14   14.000   0.14607E-02    1.191   1.185     0.49    3.3420   0.26271E-03   0.26489E-03     9.611
15   16.000   0.17421E-02    1.291   1.285     0.44    3.3500   0.26250E-03   0.26426E-03     9.609
16   18.000   0.20542E-02    1.375   1.381    -0.45    3.3620   0.26228E-03   0.26061E-03     9.603
17   18.000   0.20489E-02    1.378   1.379    -0.13    3.3610   0.26228E-03   0.26182E-03     9.602
18   20.000   0.23577E-02    1.464   1.462     0.18    3.3700   0.26209E-03   0.26270E-03     9.588
19   22.000   0.27051E-02    1.531   1.543    -0.79    3.3830   0.26188E-03   0.25941E-03     9.573
20   22.000   0.26983E-02    1.535   1.542    -0.45    3.3820   0.26198E-03   0.26046E-03     9.572
21   25.000   0.32087E-02    1.642   1.645    -0.17    3.3960   0.26160E-03   0.26112E-03     9.538
22   28.000   0.37485E-02    1.736   1.739    -0.16    3.4100   0.26133E-03   0.26092E-03     9.497
23   28.000   0.37393E-02    1.741   1.737     0.20    3.4090   0.26133E-03   0.26184E-03     9.496
24   31.000   0.43087E-02    1.820   1.823    -0.15    3.4230   0.26106E-03   0.26072E-03     9.451
25   34.000   0.48865E-02    1.897   1.900    -0.16    3.4350   0.26081E-03   0.26047E-03     9.401
26   34.000   0.48748E-02    1.903   1.899     0.24    3.4340   0.26081E-03   0.26132E-03     9.400
27   36.000   0.52745E-02    1.947   1.947     0.02    3.4420   0.26064E-03   0.26067E-03     9.365
28   38.000   0.56599E-02    1.999   1.990     0.44    3.4480   0.26049E-03   0.26132E-03     9.327
29   38.000   0.56599E-02    1.999   1.990     0.44    3.4480   0.26049E-03   0.26132E-03     9.327
30   40.000   0.60835E-02    2.032   2.035    -0.15    3.4560   0.26032E-03   0.26004E-03     9.290
31   50.000   0.81549E-02    2.224   2.219     0.24    3.4830   0.25958E-03   0.25994E-03     9.084
32   50.000   0.81549E-02    2.224   2.219     0.24    3.4830   0.25958E-03   0.25994E-03     9.084
33   60.000   0.10311E-01    2.378   2.368     0.42    3.5040   0.25891E-03   0.25943E-03     8.861
34   70.000   0.12564E-01    2.498   2.495    -0.31    3.5220   0.25827E-03   0.25794E-03     8.628
35   70.000   0.12593E-01    2.473   2.497    -0.94    3.5230   0.25827E-03   0.25726E-03     8.629
36   80.000   0.14809E-01    2.603   2.601     0.06    3.5350   0.25770E-03   0.25776E-03     8.388
37   80.000   0.14808E-01    2.603   2.601     0.06    3.5350   0.25770E-03   0.25776E-03     8.388

   (I)     BETA(I)      LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)     K(I)/K(I+1)

    1    0.1984E 04     3.29747     0.741E 01    0.1984E 04    3.29747        4.938
    2    0.7969E 06     5.90138     0.570E 04    0.4017E 03    2.60390        5.650
    3    0.5666E 08     7.75327     0.160E 07    0.7110E 02    1.85199        3.330
    4    0.1210E 10     9.08269     0.103E 09    0.2135E 02    1.32942     *********

   THE NUMBER OF ITERATIONS =   5           SMIN =  0.8140E 02

     NO POINTS ELIMINATED
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                                                   **********FOUR PARAMETER PROGRAM LSEC**********

 STABILITY CONSTANT OF Y3-DHIBA  RUN1+2  JUNE 14 1972

ORIG ACID CONCENTRATION = 0.09962          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.04980          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982          CONC. OF  METAL ION SOL.   =  0.09698
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SC        RT(X)

(I)     VB      ANION CON      N EXP   N CALC    ERROR     PH        KA USED        KA THEO       VOL KNO3

 1     2.000   0.49197E-03    0.439    0.439      0.38   3.4590   0.26367E-03   0.26540E-03      6.961
 2     2.000   0.49284E-03    0.439    0.438      0.09   3.4595   0.26367E-03   0.26408E-03      6.961
 3     3.000   0.73397E-03    0.592    0.596     -0.65   3.4061   0.26337E-03   0.25069E-03      6.990
 4     4.000   0.98896E-03    0.733    0.730      0.42   3.3782   0.26311E-03   0.26470E-03      7.007
 5     4.000   0.99702E-03    0.729    0.734     -0.88   3.3810   0.26311E-03   0.25980E-03      7.008
 6     5.000   0.12578E-02    0.858    0.854      0.49   3.3661   0.26287E-03   0.26456E-03      7.017
 7     6.000   0.15443E-02    0.969    0.967      0.24   3.3622   0.26264E-03   0.26340E-03      7.022
 8     7.000   0.18487E-02    1.068    1.071     -0.25   3.3632   0.26242E-03   0.26167E-03      7.023
 9     8.000   0.21509E-02    1.169    1.162      0.60   3.3636   0.26222E-03   0.26386E-03      7.017
10     9.000   0.24770E-02    1.256    1.250      0.48   3.3678   0.26201E-03   0.26325E-03      7.009
11    12.000   0.35402E-02    1.469    1.481     -0.79   3.3862   0.26143E-03   0.25976E-03      6.968
12    12.000   0.35384E-02    1.470    1.480     -0.70   3.3860   0.26143E-03   0.25995E-03      6.968
13    14.000   0.42641E-02    1.605    1.606     -0.07   3.3955   0.26108E-03   0.26094E-03      6.929
14    14.000   0.42661E-02    1.604    1.606     -0.17   3.3957   0.26108E-03   0.26076E-03      6.929
15    16.000   0.50149E-02    1.727    1.719      0.50   3.4047   0.26075E-03   0.26161E-03      6.883
16    18.000   0.58095E-02    1.826    1.823      0.17   3.4150   0.26043E-03   0.26069E-03      6.834
17    18.000   0.58109E-02    1.826    1.824      0.12   3.4151   0.26043E-03   0.26061E-03      6.834
18    20.000   0.66252E-02    1.915    1.919     -0.21   3.4245   0.26012E-03   0.25981E-03      6.781
19    20.000   0.66457E-02    1.904    1.922     -0.91   3.4258   0.26011E-03   0.25879E-03      6.781
20    22.000   0.74093E-02    2.022    2.003      0.96   3.4304   0.25984E-03   0.26115E-03      6.723
21    22.000   0.74268E-02    2.013    2.005      0.40   3.4314   0.25983E-03   0.26038E-03      6.724
22    24.000   0.82491E-02    2.100    2.085      0.71   3.4382   0.25955E-03   0.26046E-03      6.664
23    24.000   0.82549E-02    2.096    2.085      0.54   3.4385   0.25955E-03   0.26023E-03      6.665
24    25.000   0.86972E-02    2.123    2.126     -0.11   3.4430   0.25940E-03   0.25927E-03      6.635
25    25.000   0.87176E-02    2.112    2.127     -0.71   3.4440   0.25940E-03   0.25853E-03      6.635
26    26.000   0.91154E-02    2.163    2.162      0.05   3.4460   0.25927E-03   0.25933E-03      6.604
27    28.000   0.99739E-02    2.222    2.233     -0.07   3.4523   0.25901E-03   0.25893E-03      6.541
28    28.000   0.99785E-02    2.229    2.234     -0.20   3.4525   0.25901E-03   0.25878E-03      6.541
29    30.000   0.10392E-01    2.290    2.301     -0.45   3.4585   0.25875E-03   0.25827E-03      6.477
30    30.000   0.10844E-01    2.294    2.300     -0.25   3.4582   0.25875E-03   0.25848E-03      6.476
31    35.000   0.12997E-01    2.464    2.447      0.68   3.4692   0.25816E-03   0.25880E-03      6.309
32    35.000   0.13021E-01    2.451    2.449      0.10   3.4700   0.25815E-03   0.25825E-03      6.309
33    40.000   0.15260E-01    2.577    2.580     -0.09   3.4806   0.25759E-03   0.25751E-03      6.136
34    45.000   0.17545E-01    2.680    2.695     -0.55   3.4900   0.25705E-03   0.25663E-03      5.959

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.11345 04      3.05476    0.917E 01    0.11345 04    3.05476         4.109
    2    0.31328 06      5.49589    0.4167 04    0.27615 03    2.44112         5.164
    3    0.16752 08      7.22403    0.976  06    0.53473 02    1.72814         1.462
    4    0.61287 09      8.78730    0.4346 09    0.36587 02    1.56327     ********

    THE NUMBER OF ITERATIONS =    5            SMIN =  0.51653 02

     NO POINTS ELIMINATED
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XI. APPENDIX C:

FORMATION CONSTANTS OF RARE-EARTH α,β-DIHYDROXY-β-METHYLISOBUTYRATE COMPLEXES

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                                              **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF LA3-DHMIBA  RUN 1  FEBRUARY 15 1973

ORIG ACID CONCENTRATION = 0.09780          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04518          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10061
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)    VB       ANION CON     N EXP   N CALC    ERROR     PH       KA USED       KA THEO      VOL KNO3

 1    2.000   0.42585E-03    0.144    0.143     0.19    3.7240   0.30571E-03   0.30609E-03     9.343
 2    6.000   0.11766E-02    0.339    0.341    -0.70    3.5540   0.30532E-03   0.30407E-03     9.359
 3    8.000   0.15547E-02    0.421    0.422    -0.28    3.5280   0.30512E-03   0.30465E-03     9.356
 4   11.000   0.21293E-02    0.535    0.528     1.24    3.5070   0.30482E-03   0.30670E-03     9.339
 5   12.000   0.23315E-02    0.566    0.562     0.78    3.5040   0.30471E-03   0.30587E-03     9.332
 6   14.000   0.27476E-02    0.622    0.625    -0.58    3.5010   0.30450E-03   0.30368E-03     9.316
 7   16.000   0.31576E-02    0.681    0.682    -0.24    3.4980   0.30428E-03   0.30397E-03     9.294
 8   18.000   0.35788E-02    0.733    0.736    -0.34    3.4970   0.30406E-03   0.30364E-03     9.270
 9   20.000   0.40073E-02    0.782    0.786    -0.48    3.4970   0.30384E-03   0.30326E-03     9.243
10   22.000   0.44351E-02    0.831    0.832    -0.10    3.4970   0.30362E-03   0.30350E-03     9.214
11   25.000   0.50880E-02    0.898    0.895     0.29    3.4980   0.30328E-03   0.30359E-03     9.166
12   28.000   0.57700E-02    0.950    0.956    -0.55    3.5010   0.30292E-03   0.30236E-03     9.116
13   31.000   0.64289E-02    1.015    1.008     0.64    3.5020   0.30258E-03   0.30319E-03     9.061
14   36.000   0.75900E-02    1.090    1.091    -0.11    3.5070   0.30197E-03   0.30187E-03     8.965
15   38.000   0.80413E-02    1.127    1.120     0.58    3.5080   0.30174E-03   0.30222E-03     8.924
16   40.000   0.85140E-02    1.152    1.149     0.29    3.5100   0.30149E-03   0.30172E-03     8.883
17   50.000   0.10903E-01    1.269    1.277    -0.58    3.5190   0.30024E-03   0.29984E-03     8.667
18   60.000   0.13307E-01    1.380    1.381    -0.07    3.5260   0.29899E-03   0.29895E-03     8.438
19   70.000   0.15728E-01    1.432    1.469     0.87    3.5320   0.29773E-03   0.29822E-03     8.198

   (I)     BETA(I)     LOG BETA(I)    SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.3725E 03      2.57113     0.194E 01    0.3725E 03    2.57113        6.226
    2    0.2229E 05      4.34802     0.615E 03    0.5983E 02    1.77689        6.143
    3    0.2170E 06      5.33654     0.642E 05    0.9739E 01    0.98853      *********

   THE NUMBER OF ITERATIONS =    5            SMIN =  0.1120E 02

     NO POINTS ELIMINATED
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                                          **********THREE PARAMETER PROGRAM USED**********

STABILITY CONSTANT OF CE3-DHMIPA  RUN 3  AUGUST 18 1973

ORIG ACID CONCENTRATION = 0.09759            IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262            POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04497            VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262            CONC. OF  METAL ION SOL.   =  0.10539
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB       ANION CON      N EXP    N CALC     ERROR      PH       KA USED       KA THEO      VOL KNO3

 1     2.000   0.33737E-03    0.191    0.191     -0.01    3.6700   0.30575E-03   0.30571E-03    11.654
 2     4.000   0.64741E-03    0.329    0.329      0.05    3.5400   0.30559E-03   0.30576E-03    11.699
 3     8.000   0.12967E-02    0.546    0.546     -0.01    3.4650   0.30525E-03   0.30522E-03    11.738
 4    10.000   0.16416E-02    0.637    0.636      0.08    3.4530   0.30507E-03   0.30526E-03    11.740
 5    11.000   0.18210E-02    0.677    0.678     -0.08    3.4500   0.30498E-03   0.30480E-03    11.738
 6    12.000   0.20030E-02    0.717    0.718     -0.12    3.4480   0.30489E-03   0.30460E-03    11.734
 7    14.000   0.23737E-02    0.791    0.791      0.06    3.4460   0.30469E-03   0.30483E-03    11.720
 8    16.000   0.27616E-02    0.856    0.858     -0.22    3.4470   0.30449E-03   0.30405E-03    11.701
 9    18.000   0.31507E-02    0.921    0.919      0.24    3.4480   0.30429E-03   0.30473E-03    11.676
10    20.000   0.35587E-02    0.976    0.976     -0.01    3.4510   0.30407E-03   0.30406E-03    11.647
11    22.000   0.39716E-02    1.029    1.028      0.01    3.4540   0.30386E-03   0.30388E-03    11.614
12    25.000   0.46059E-02    1.100    1.100     -0.00    3.4590   0.30353E-03   0.30352E-03    11.559
13    28.000   0.52528E-02    1.166    1.165      0.09    3.4640   0.30319E-03   0.30331E-03    11.498
14    31.000   0.59126E-02    1.225    1.224      0.15    3.4690   0.30285E-03   0.30305E-03    11.431
15    36.000   0.70357E-02    1.314    1.311      0.24    3.4770   0.30226E-03   0.30255E-03    11.312
16    38.000   0.75089E-02    1.338    1.343     -0.43    3.4810   0.30201E-03   0.30152E-03    11.263
17    50.000   0.10311E-01    1.500    1.503     -0.19    3.4970   0.30055E-03   0.30037E-03    10.939
18    80.000   0.17624E-01    1.766    1.770     -0.26    3.5260   0.29674E-03   0.29657E-03    10.035

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.6508E 03      2.81346     0.748E 00    0.6508E 03    2.81346        6.542
    2    0.6474E 05      4.81120     0.272E 03    0.9948E 02    1.99774        7.234
    3    0.8903E 06      5.94954     0.327E 05    0.1375E 02    1.13834    *********

    THE NUMBER OF ITERATIONS =    5            SMIN =  0.1109E 01

      NO POINTS ELIMINATED
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                                    **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF ER3-DHMIBA  RUN 3  JULY 17 1973

ORIG ACID CONCENTRATION = 0.10164          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04902          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10012
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB      ANION CON      N EXP   N CALC    ERROR      PH       KA USED        KA THEO       VOL KNO3

 1     2.000   0.30484E-03    0.233   0.232     0.28     3.6100   0.30577E-03   0.30707E-03    11.760
 2     4.000   0.59302E-03    0.396   0.397    -0.18     3.4770   0.30562E-03   0.30487E-03    11.818
 3     6.000   0.89253E-03    0.530   0.532    -0.35     3.4260   0.30546E-03   0.30420E-03    11.851
 4     8.000   0.12053E-02    0.647   0.647     0.03     3.4020   0.30530E-03   0.30540E-03    11.867
 5    10.000   0.15349E-02    0.750   0.748     0.29     3.3910   0.30513E-03   0.30598E-03    11.872
 6    11.000   0.17091E-02    0.796   0.795     0.03     3.3890   0.30504E-03   0.30511E-03    11.871
 7    12.000   0.18866E-02    0.839   0.840    -0.13     3.3880   0.30495E-03   0.30460E-03    11.868
 8    14.000   0.22504E-02    0.920   0.922    -0.19     3.3880   0.30476E-03   0.30428E-03    11.855
 9    16.000   0.26272E-02    0.994   0.996    -0.20     3.3900   0.30456E-03   0.30409E-03    11.835
10    18.000   0.30070E-02    1.066   1.062     0.41     3.3920   0.30436E-03   0.30524E-03    11.809
11    20.000   0.34151E-02    1.123   1.125    -0.19     3.3970   0.30415E-03   0.30377E-03    11.780
12    22.000   0.38128E-02    1.185   1.180     0.46     3.4000   0.30394E-03   0.30481E-03    11.745
13    25.000   0.44454E-02    1.260   1.258     0.21     3.4070   0.30361E-03   0.30397E-03    11.688
14    28.000   0.50960E-02    1.327   1.328    -0.08     3.4140   0.30327E-03   0.30314E-03    11.626
15    31.000   0.57511E-02    1.391   1.390     0.07     3.4200   0.30293E-03   0.30304E-03    11.557
16    34.000   0.64219E-02    1.447   1.447     0.05     3.4260   0.30258E-03   0.30264E-03    11.485
17    36.000   0.68780E-02    1.481   1.482    -0.10     3.4300   0.30234E-03   0.30222E-03    11.435
18    38.000   0.73411E-02    1.511   1.516    -0.35     3.4340   0.30210E-03   0.30166E-03    11.383
19    50.000   0.10155E-01    1.674   1.683    -0.50     3.4530   0.30063E-03   0.30013E-03    11.051

    (I)      BETA(I)      LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)     K(I)/K(I+1)

     1    0.9030E 03      2.95567    0.234E 01     0.9030E 03     2.95567         6.376
     2    0.1279E 06      5.10679    0.918E 03     0.1416E 03     2.15112         6.649
     3    0.2724E 07      6.43517    0.116E 06     0.2130E 02     1.32838     *********

     THE NUMBER OF ITERATIONS =    5            SMIN =  0.7105E 01

       NO POINTS ELIMINATED
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                                        **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF ND3-DHMIBA  RUN 2  AUGUST 18 1973

ORIG ACID CONCENTRATION = 0.09759          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04497          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10800
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB       ANION CON      N EXP   N CALC     ERROR      PH      KA USED        KA THEO       VOL KNO3

 1    2.000    0.25960E-03     0.236    0.236     -0.07     3.6140   0.30579E-03    0.30536E-03    11.655
 2    4.000    0.51128E-03     0.406    0.405      0.20     3.4730   0.30566E-03    0.30672E-03    11.727
 3    6.000    0.77862E-03     0.546    0.546      0.05     3.4200   0.30552E-03    0.30575E-03    11.773
 4    8.000    0.10649E-02     0.667    0.667     -0.06     3.3970   0.30537E-03    0.30514E-03    11.801
 5   10.000    0.13716E-02     0.773    0.774     -0.24     3.3880   0.30521E-03    0.30430E-03    11.815
 6   11.000    0.15304E-02     0.822    0.823     -0.15     3.3860   0.30513E-03    0.30462E-03    11.818
 7   12.000    0.16922E-02     0.869    0.868      0.08     3.3850   0.30505E-03    0.30531E-03    11.817
 8   14.000    0.20347E-02     0.953    0.954     -0.08     3.3870   0.30487E-03    0.30461E-03    11.811
 9   16.000    0.23860E-02     1.033    1.030      0.28     3.3900   0.30469E-03    0.30547E-03    11.797
10   18.000    0.27627E-02     1.100    1.101     -0.17     3.3960   0.30449E-03    0.30405E-03    11.777
11   20.000    0.31409E-02     1.166    1.165      0.10     3.4010   0.30429E-03    0.30454E-03    11.751
12   22.000    0.35357E-02     1.224    1.224      0.04     3.4070   0.30409E-03    0.30417E-03    11.721
13   25.000    0.41463E-02     1.303    1.304     -0.05     3.4160   0.30377E-03    0.30367E-03    11.669
14   28.000    0.47679E-02     1.378    1.374      0.23     3.4240   0.30344E-03    0.30388E-03    11.609
15   31.000    0.54057E-02     1.443    1.438      0.30     3.4320   0.30311E-03    0.30362E-03    11.544
16   34.000    0.60721E-02     1.498    1.497      0.09     3.4400   0.30276E-03    0.30290E-03    11.474
17   38.000    0.69772E-02     1.563    1.567     -0.30     3.4500   0.30229E-03    0.30185E-03    11.375
18   40.000    0.74255E-02     1.597    1.599     -0.10     3.4540   0.30206E-03    0.30192E-03    11.323
19   50.000    0.97500E-02     1.732    1.735     -0.18     3.4730   0.30084E-03    0.30064E-03    11.048
20   70.000    0.14584E-01     1.921    1.932     -0.58     3.5010   0.29832E-03    0.29783E-03    10.448

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)      K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.1082E 04      3.03434    0.180E 01    0.1082E 04    3.03434        6.505
    2    0.1801E 06      5.25542    0.730E 03    0.1664E 03    2.22109        7.079
    3    0.4232E 07      6.62652    0.946E 05    0.2350E 02    1.37109    *********

    THE NUMBER OF ITERATIONS =    4          SMIN =  0.4252E 01

      NO POINTS ELIMINATED
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                                          **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF SM3-CHMIBA  RUN 1  APRIL 11 1973

ORIG ACID CONCENTRATION = 0.09647          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04385          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10060
RATIO OF THE VKCH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)    VB       ANION CON      N EXP   N CALC    ERROR      PH      KA USED       KA THEO      VOL KNO3

 1    4.000   0.47234E-03    0.459    0.459    -0.01    3.4630   0.30568E-03   0.30561E-03    9.487
 2    6.000   0.73000E-03    0.615    0.615    -0.07    3.4110   0.30555E-03   0.30516E-03    9.525
 3    8.000   0.10095E-02    0.747    0.748    -0.12    3.3900   0.30540E-03   0.30486E-03    9.547
 4   10.000   0.13076E-02    0.864    0.862     0.26    3.3820   0.30525E-03   0.30631E-03    9.555
 5   11.000   0.14655E-02    0.915    0.915    -0.00    3.3820   0.30516E-03   0.30515E-03    9.557
 6   12.000   0.16293E-02    0.966    0.963     0.25    3.3820   0.30508E-03   0.30598E-03    9.556
 7   14.000   0.19714E-02    1.055    1.054     0.12    3.3860   0.30490E-03   0.30529E-03    9.549
 8   16.000   0.23313E-02    1.135    1.136    -0.04    3.3920   0.30471E-03   0.30459E-03    9.535
 9   18.000   0.27073E-02    1.207    1.209    -0.23    3.3990   0.30452E-03   0.30389E-03    9.517
10   20.000   0.30865E-02    1.277    1.275     0.17    3.4050   0.30432E-03   0.30476E-03    9.493
11   22.000   0.34924E-02    1.333    1.337    -0.27    3.4130   0.30411E-03   0.30347E-03    9.467
12   25.000   0.41164E-02    1.410    1.420    -0.65    3.4240   0.30378E-03   0.30241E-03    9.422
13   28.000   0.47454E-02    1.486    1.492    -0.36    3.4330   0.30345E-03   0.30276E-03    9.371
14   31.000   0.53843E-02    1.558    1.556     0.12    3.4410   0.30312E-03   0.30334E-03    9.315
15   34.000   0.60583E-02    1.611    1.616    -0.26    3.4500   0.30277E-03   0.30234E-03    9.256
16   36.000   0.64745E-02    1.665    1.649     0.94    3.4530   0.30255E-03   0.30401E-03    9.214
17   38.000   0.69284E-02    1.699    1.684     0.90    3.4580   0.30232E-03   0.30364E-03    9.172
18   40.000   0.74263E-02    1.710    1.719    -0.51    3.4650   0.30206E-03   0.30134E-03    9.131
19   50.000   0.97284E-02    1.867    1.855     0.63    3.4830   0.30086E-03   0.30158E-03    8.903
20   60.000   0.12163E-01    1.958    1.967    -0.45    3.5000   0.29959E-03   0.29914E-03    8.664
21   70.000   0.14619E-01    2.040    2.058    -0.89    3.5130   0.29830E-03   0.29755E-03    8.415
22   80.000   0.17035E-01    2.144    2.134     0.45    3.5220   0.29704E-03   0.29738E-03    8.160
    (I)      BETA(I)      LOG BETA(I)    SIGMA(I)         K(I)        LOG K(I)     K(I)/K(I+1)

     1    0.1393E 04      3.14402     0.857E 01     0.1393E 04     3.14402        6.635
     2    0.2925E 06      5.46619     0.302E 04     0.2100E 03     2.32216        7.290
     3    0.8426E 07      6.92562     0.596E 06     0.2880E 02     1.45944        8.674
     4    0.2798E 08      7.44683     0.264E 08     0.3321E 01     0.52121     *********

     THE NUMBER OF ITERATIONS =  10           SMIN =  0.2104E 02

       NO POINTS ELIMINATED
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                                                    **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF EU3-DHMIBA  RUN 2  AUGUST 5 1973

ORIG ACID CONCENTRATION = 0.10213          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04951          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10104
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB        ANION CON       N EXP    N CALC      ERROR       PH        KA USED         KA THEO       VOL KNO3

 1     2.000    0.24264E-03     0.277     0.277       0.01     3.5590   0.30580E-03    0.30585E-03      11.782
 2     4.000    0.47553E-03     0.477     0.477      -0.04     3.4120   0.30568E-03    0.30543E-03      11.865
 3     6.000    0.71986E-03     0.644     0.642       0.24     3.3540   0.30555E-03    0.30685E-03      11.918
 4     8.000    0.98474E-03     0.786     0.788      -0.16     3.3290   0.30542E-03    0.30463E-03      11.953
 5    10.000    0.12663E-02     0.913     0.914      -0.09     3.3180   0.30527E-03    0.30485E-03      11.971
 6    11.000    0.14152E-02     0.971     0.972      -0.15     3.3160   0.30519E-03    0.30456E-03      11.976
 7    12.000    0.15669E-02     1.027     1.027      -0.01     3.3150   0.30511E-03    0.30509E-03      11.977
 8    16.000    0.22231E-02     1.219     1.218       0.12     3.3210   0.30477E-03    0.30517E-03      11.961
 9    18.000    0.25771E-02     1.301     1.300       0.12     3.3270   0.30459E-03    0.30497E-03      11.941
10    20.000    0.29474E-02     1.375     1.374       0.05     3.3340   0.30439E-03    0.30453E-03      11.915
11    22.000    0.33285E-02     1.443     1.441       0.12     3.3410   0.30419E-03    0.30453E-03      11.884
12    25.000    0.39258E-02     1.532     1.531       0.07     3.3520   0.30388E-03    0.30406E-03      11.830
13    28.000    0.45500E-02     1.608     1.611      -0.13     3.3630   0.30356E-03    0.30327E-03      11.768
14    31.000    0.51899E-02     1.678     1.680      -0.15     3.3730   0.30322E-03    0.30293E-03      11.699
15    34.000    0.58406E-02     1.742     1.742      -0.01     3.3820   0.30288E-03    0.30287E-03      11.625
16    36.000    0.62876E-02     1.778     1.780      -0.09     3.3880   0.30265E-03    0.30249E-03      11.574
17    38.000    0.67292E-02     1.818     1.814       0.19     3.3930   0.30242E-03    0.30272E-03      11.520
18    40.000    0.71964E-02     1.844     1.848      -0.22     3.3990   0.30218E-03    0.30183E-03      11.467
19    50.000    0.95198E-02     1.987     1.985       0.08     3.4210   0.30096E-03    0.30106E-03      11.179

   (I)      BETA(I)      LOG BETA(I)    SIGMA(I)         K(I)        LOG K(I)      K(I)/K(I+1)

    1    0.1342E 04       3.12782      0.219E 01      0.1342E 04     3.12782          4.480
    2    0.4021E 06       5.60438      0.107E 04      0.2996E 03     2.47656          7.521
    3    0.1602E 08       7.20467      0.155E 06      0.3984E 02     1.60030      *********

    THE NUMBER OF ITERATIONS =   4            SMIN =  0.3124E 01

      NO POINTS ELIMINATED
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                                         **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF GD3-DHMIBA  RUN 1  APRIL 11 1973

ORIG ACID CONCENTRATION = 0.09647          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.04385          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.08388
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB       ANION CON      N EXP    N CALC     ERROR      PH       KA USED        KA THEO       VOL KNO3

 1    2.000    0.28087E-03    0.282    0.281      0.58    3.6410   0.30578E-03   0.30874E-03      9.615
 2    4.000    0.55775E-03    0.490    0.482     -0.34    3.5080   0.30564E-03   0.30413E-03      9.661
 3    6.000    0.85084E-03    0.641    0.645     -0.70    3.4590   0.30549E-03   0.30276E-03      9.687
 4   10.000    0.14873E-02    0.904    0.904      0.04    3.4280   0.30515E-03   0.30529E-03      9.698
 5   11.000    0.16616E-02    0.958    0.960     -0.19    3.4270   0.30506E-03   0.30450E-03      9.696
 6   12.000    0.18398E-02    1.008    1.012     -0.35    3.4270   0.30497E-03   0.30399E-03      9.691
 7   14.000    0.21959E-02    1.110    1.105      0.46    3.4270   0.30478E-03   0.30596E-03      9.676
 8   16.000    0.25713E-02    1.198    1.189      0.75    3.4300   0.30459E-03   0.30635E-03      9.656
 9   18.000    0.29662E-02    1.274    1.267      0.55    3.4350   0.30438E-03   0.30559E-03      9.632
10   20.000    0.33778E-02    1.339    1.338      0.09    3.4410   0.30417E-03   0.30435E-03      9.604
11   22.000    0.37902E-02    1.404    1.401      0.23    3.4460   0.30395E-03   0.30439E-03      9.573
12   25.000    0.44301E-02    1.490    1.487      0.16    3.4540   0.30362E-03   0.30390E-03      9.521
13   28.000    0.50910E-02    1.562    1.564     -0.09    3.4620   0.30327E-03   0.30314E-03      9.465
14   31.000    0.57732E-02    1.622    1.633     -0.62    3.4700   0.30292E-03   0.30202E-03      9.406
15   34.000    0.64618E-02    1.679    1.694     -0.88    3.4770   0.30256E-03   0.30139E-03      9.343
16   36.000    0.69041E-02    1.728    1.730     -0.12    3.4800   0.30233E-03   0.30217E-03      9.299
17   38.000    0.73689E-02    1.763    1.765     -0.14    3.4840   0.30209E-03   0.30191E-03      9.254
18   40.000    0.78410E-02    1.793    1.799     -0.30    3.4880   0.30184E-03   0.30149E-03      9.209
19   50.000    0.10217E-01    1.938    1.939     -0.01    3.5040   0.30060E-03   0.30059E-03      8.972
20   60.000    0.12650E-01    2.051    2.049      0.10    3.5170   0.29933E-03   0.29941E-03      8.724
21   70.000    0.15095E-01    2.157    2.137      0.93    3.5270   0.29806E-03   0.29871E-03      8.468

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)       K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.1204E 04     3.08071     0.707E 01    0.1204E 04    3.08071        5.313
    2    0.2729E 06     5.43607     0.399E 04    0.2267E 03    2.35536        6.147
    3    0.1006E 08     7.00280     0.815E 06    0.3687E 02    1.56673       24.240
    4    0.1531E 08     7.18498     0.426E 08    0.1521E 01    0.18219     *********

   THE NUMBER OF ITERATIONS =  10            SMIN =  0.2830E 02

     NO POINTS ELIMINATED
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                                           **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF TB3-CHMIPA  RUN 1  MAY 22 1973

ORIG ACID CONCENTRATION = 0.09827          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04565          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10582
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB       ANION CON      N EXP   N CALC    ERROR      PH       KA USED        KA THEO       VOL KNO3

 1     4.000   0.50291E-03    0.423    0.421     0.39    3.4620   0.30567E-03   0.30777E-03    11.766
 2     6.000   0.76013E-03    0.572    0.571     0.23    3.4060   0.30553E-03   0.30665E-03    11.817
 3     8.000   0.10385E-02    0.700    0.704    -0.60    3.3820   0.30539E-03   0.30276E-03    11.851
 4    10.000   0.13242E-02    0.819    0.819     0.11    3.3690   0.30524E-03   0.30568E-03    11.867
 5    11.000   0.14827E-02    0.869    0.875    -0.58    3.3680   0.30516E-03   0.30293E-03    11.874
 6    12.000   0.16403E-02    0.920    0.926    -0.66    3.3670   0.30507E-03   0.30266E-03    11.876
 7    14.000   0.19582E-02    1.019    1.018     0.02    3.3660   0.30491E-03   0.30496E-03    11.872
 8    16.000   0.22921E-02    1.108    1.103     0.50    3.3680   0.30473E-03   0.30628E-03    11.860
 9    18.000   0.26490E-02    1.186    1.182     0.34    3.3730   0.30455E-03   0.30553E-03    11.844
10    20.000   0.30132E-02    1.260    1.253     0.55    3.3780   0.30436E-03   0.30584E-03    11.820
11    22.000   0.34020E-02    1.322    1.321     0.08    3.3850   0.30416E-03   0.30435E-03    11.793
12    25.000   0.39916E-02    1.413    1.411     0.14    3.3940   0.30385E-03   0.30417E-03    11.744
13    28.000   0.45917E-02    1.498    1.489     0.64    3.4020   0.30354E-03   0.30487E-03    11.685
14    31.000   0.52367E-02    1.562    1.562     0.02    3.4120   0.30320E-03   0.30323E-03    11.622
15    34.000   0.58933E-02    1.621    1.627    -0.38    3.4210   0.30286E-03   0.30219E-03    11.554
16    36.000   0.63139E-02    1.670    1.665     0.25    3.4250   0.30264E-03   0.30306E-03    11.504
17    38.000   0.67733E-02    1.699    1.704    -0.30    3.4310   0.30240E-03   0.30192E-03    11.455
18    40.000   0.72263E-02    1.731    1.739    -0.44    3.4360   0.30216E-03   0.30149E-03    11.403
19    50.000   0.95365E-02    1.875    1.886    -0.62    3.4570   0.30096E-03   0.30017E-03    11.127
20    60.000   0.11926E-01    1.983    2.001    -0.92    3.4740   0.29971E-03   0.29873E-03    10.830

    (I)     BETA(I)      LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

     1    0.1099E 04      3.04107     0.816E 01    0.1099E 04     3.04107        4.916
     2    0.2458E 06      5.39050     0.249E 04    0.2236E 03     2.34943        6.142
     3    0.8945E 07      6.95159     0.344E 06    0.3640E 02     1.56109     *********

    THE NUMBER OF ITERATIONS =    5             SMIN =  0.3153E 02

      NO POINTS ELIMINATED
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                                        **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF DY3-OHMIBA  RUN 2  JULY 5 1973

ORIG ACID CONCENTRATION = 0.10160          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.09262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04398          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10397
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)    VB      ANION CON     N EXP   N CALC    ERROR     PH       KA USED      KA THEO     VOL KNO3

 1    2.000   0.27959E-03    0.242    0.242    -0.25   3.5920   0.30578E-03  0.30442E-03   11.714
 2    6.000   0.80664E-03    0.565    0.565    -0.02   3.3940   0.30551E-03  0.30544E-03   11.831
 3    8.000   0.10875E-02    0.696    0.693     0.35   3.3670   0.30536E-03  0.30679E-03   11.859
 4   10.000   0.13375E-02    0.810    0.808     0.33   3.3550   0.30521E-03  0.30643E-03   11.874
 5   11.000   0.15435E-02    0.863    0.860     0.39   3.3520   0.30512E-03  0.30651E-03   11.877
 6   12.000   0.17111E-02    0.909    0.912    -0.25   3.3520   0.30504E-03  0.30420E-03   11.880
 7   14.000   0.20460E-02    1.001    1.003    -0.15   3.3520   0.30486E-03  0.30441E-03   11.874
 8   18.000   0.27633E-02    1.159    1.159     0.03   3.3590   0.30449E-03  0.30456E-03   11.839
 9   20.000   0.31495E-02    1.223    1.226    -0.25   3.3650   0.30429E-03  0.30368E-03   11.814
10   22.000   0.35454E-02    1.283    1.287    -0.31   3.3710   0.30408E-03  0.30337E-03   11.782
11   25.000   0.41677E-02    1.359    1.369    -0.74   3.3810   0.30376E-03  0.30222E-03   11.728
12   28.000   0.47923E-02    1.434    1.438    -0.25   3.3890   0.30343E-03  0.30295E-03   11.664
13   31.000   0.54371E-02    1.500    1.499     0.08   3.3970   0.30309E-03  0.30324E-03   11.595
14   34.000   0.61172E-02    1.549    1.555    -0.37   3.4060   0.30274E-03  0.30215E-03   11.521
15   36.000   0.65373E-02    1.595    1.585     0.84   3.4090   0.30252E-03  0.30380E-03   11.468
16   38.000   0.70120E-02    1.621    1.617     0.22   3.4150   0.30227E-03  0.30260E-03   11.416
17   40.000   0.74800E-02    1.647    1.646     0.03   3.4200   0.30203E-03  0.30207E-03   11.362
18   50.000   0.98207E-02    1.778    1.763     0.85   3.4390   0.30081E-03  0.30176E-03   11.074
19   60.000   0.12249E-01    1.870    1.854     0.96   3.4550   0.29954E-03  0.30036E-03   10.769
20   70.000   0.14755E-01    1.924    1.926    -0.12   3.4690   0.29823E-03  0.29814E-03   10.454
21   80.000   0.17271E-01    1.976    1.986    -0.53   3.4800   0.29692E-03  0.29654E-03   10.132

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.9949E 03     2.99780     0.398E 01    0.9949E 03    2.99780        4.353
    2    0.2274E 06     5.35685     0.149E 04    0.2286E 03    2.35906       15.087
    3    0.3446E 07     6.53731     0.171E 06    0.1515E 02    1.18046     *********

    THE NUMBER OF ITERATIONS =    5             SMIN =  0.1674E 02

      NO POINTS ELIMINATED
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                                               **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF HO3-DHMIBA  RUN 2  JUNE 11 1973

ORIG ACID CONCENTRATION = 0.10160          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04898          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.09840
RATIO OF THE VKOH TO VP = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)    VB       ANION CON     N EXP    N CALC    ERROR      PH      KA USED       KA THEO      VOL KNO3

 1    2.000   0.27959E-03    0.255    0.255     0.30    3.5920  0.30578E-03  0.30744E-03    11.801
 2    4.000   0.54601E-03    0.436    0.439    -0.60    3.4540  0.30564E-03  0.30273E-03    11.870
 3    6.000   0.81692E-03    0.590    0.588     0.40    3.3980  0.30550E-03  0.30725E-03    11.910
 4    8.000   0.11133E-02    0.718    0.721    -0.42    3.3750  0.30535E-03  0.30372E-03    11.937
 5   10.000   0.14149E-02    0.839    0.834     0.62    3.3620  0.30519E-03  0.30737E-03    11.945
 6   11.000   0.15778E-02    0.891    0.887     0.43    3.3600  0.30511E-03  0.30655E-03    11.946
 7   12.000   0.17532E-02    0.935    0.939    -0.50    3.3610  0.30502E-03  0.30340E-03    11.947
 8   14.000   0.21005E-02    1.025    1.031    -0.62    3.3620  0.30483E-03  0.30301E-03    11.938
 9   18.000   0.28344E-02    1.183    1.187    -0.32    3.3690  0.30445E-03  0.30366E-03    11.897
10   20.000   0.32134E-02    1.256    1.253     0.29    3.3730  0.30425E-03  0.30492E-03    11.866
11   22.000   0.35986E-02    1.326    1.312     1.10    3.3770  0.30405E-03  0.30644E-03    11.831
12   25.000   0.42399E-02    1.396    1.396    -0.02    3.3880  0.30372E-03  0.30367E-03    11.775
13   28.000   0.48744E-02    1.471    1.467     0.24    3.3960  0.30339E-03  0.30382E-03    11.710
14   31.000   0.55561E-02    1.521    1.533    -0.79    3.4060  0.30303E-03  0.30173E-03    11.641
15   34.000   0.62205E-02    1.581    1.588    -0.47    3.4130  0.30269E-03  0.30196E-03    11.565
16   36.000   0.66630E-02    1.622    1.622    -0.02    3.4170  0.30245E-03  0.30243E-03    11.513
17   38.000   0.71125E-02    1.659    1.653     0.33    3.4210  0.30222E-03  0.30267E-03    11.459
18   40.000   0.75869E-02    1.683    1.684    -0.07    3.4260  0.30197E-03  0.30187E-03    11.404

   (I)    BETA(I)    LOG BETA(I)   SIGMA(I)         K(I)       LOG K(I)    K(I)/K(I+1)

    1   0.1065E 04    3.02746    0.668[illegible] 01   0.1065E 04   3.02746        4.805
    2   0.2362E 06    5.37323    0.294[illegible] 04   0.2217E 03   2.34577       10.299
    3   0.5084E 07    6.70623    0.38[illegible] 06    0.2153E 02   1.33299    *********

   THE NUMBER OF ITERATIONS =   4          SMIN =  0.3750E 02

     NO POINTS ELIMINATED
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                                                  **********FOUR PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF ER3-CHMIBA  RUN 1  APRIL 30 1973

ORIG ACID CONCENTRATION = 0.09605           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262           POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04343           VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262           CONC. OF  METAL ION SOL.   =  0.10546
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB       ANION CON      N EXP    N CALC     ERROR       PH       KA USED       KA THEO       VOL KNO3

 1     4.000   0.46538E-03    0.442    0.442     -0.15     3.4630   0.30569E-03   0.30477E-03    11.789
 2     6.000   0.70837E-03    0.599    0.597      0.33     3.4060   0.30556E-03   0.30733E-03    11.842
 3    10.000   0.12559E-02    0.853    0.852      0.12     3.3720   0.30527E-03   0.30579E-03    11.896
 4    11.000   0.14077E-02    0.907    0.908     -0.19     3.3710   0.30520E-03   0.30439E-03    11.902
 5    12.000   0.15630E-02    0.958    0.961     -0.33     3.3710   0.30511E-03   0.30379E-03    11.905
 6    14.000   0.18834E-02    1.054    1.057     -0.25     3.3730   0.30495E-03   0.30404E-03    11.902
 7    16.000   0.22121E-02    1.147    1.142      0.40     3.3760   0.30478E-03   0.30611E-03    11.890
 8    18.000   0.25711E-02    1.223    1.223     -0.01     3.3830   0.30459E-03   0.30456E-03    11.873
 9    20.000   0.29333E-02    1.298    1.294      0.27     3.3890   0.30440E-03   0.30515E-03    11.849
10    22.000   0.33128E-02    1.364    1.361      0.25     3.3960   0.30420E-03   0.30487E-03    11.821
11    25.000   0.39171E-02    1.447    1.453     -0.41     3.4080   0.30389E-03   0.30291E-03    11.771
12    28.000   0.45179E-02    1.532    1.531      0.08     3.4170   0.30357E-03   0.30375E-03    11.712
13    31.000   0.51532E-02    1.601    1.603     -0.12     3.4270   0.30324E-03   0.30301E-03    11.647
14    34.000   0.57862E-02    1.672    1.666      0.35     3.4350   0.30291E-03   0.30355E-03    11.577
15    36.000   0.62442E-02    1.702    1.707     -0.35     3.4420   0.30267E-03   0.30206E-03    11.529
16    38.000   0.66829E-02    1.741    1.744     -0.18     3.4470   0.30244E-03   0.30214E-03    11.478
17    40.000   0.71302E-02    1.777    1.779     -0.14     3.4520   0.30221E-03   0.30198E-03    11.426
18    50.000   0.94113E-02    1.934    1.926      0.41     3.4730   0.30102E-03   0.30156E-03    11.147
19    60.000   0.11798E-01    2.044    2.044      0.00     3.4910   0.29978E-03   0.29978E-03    10.850
20    70.000   0.14217E-01    2.140    2.138      0.07     3.5050   0.29851E-03   0.29858E-03    10.540
21    80.000   0.16683E-01    2.214    2.217     -0.16     3.5170   0.29723E-03   0.29709E-03    10.222

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.1288E 04     3.10997    0.656E 01     0.1288E 04     3.10997        5.343
    2    0.3106E 06     5.49214    0.251E 04     0.2411E 03     2.38216        6.262
    3    0.1196E 08     7.07760    0.511E 06     0.3850E 02     1.58547       17.115
    4    0.2690E 08     7.42970    0.235E 08     0.2250E 01     0.35209     *********

   THE NUMBER OF ITERATIONS =  10           SMIN =  0.1317E 02

     NO POINTS ELIMINATED
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                                            **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF TM3-DHMIBA  RUN 2  AUGUST 19 1973

ORIG ACID CONCENTRATION = 0.09759           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262           POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04497           VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262           CONC. OF  METAL ION SOL.   =  0.10109
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB        ANION CON       N EXP   N CALC    ERROR      PH        KA USED        KA THEO      VOL KNO3

 1     2.000    0.23045E-03     0.273    0.273     0.07    3.5910    0.30581E-03    0.30635E-03    11.780
 2     4.000    0.45680E-03     0.473    0.473     0.04    3.4430    0.30569E-03    0.30592E-03    11.864
 3     6.000    0.69708E-03     0.639    0.639    -0.01    3.3860    0.30557E-03    0.30553E-03    11.919
 4     8.000    0.95609E-03     0.784    0.784    -0.10    3.3610    0.30543E-03    0.30491E-03    11.955
 5    10.000    0.12350E-02     0.911    0.913    -0.21    3.3510    0.30529E-03    0.30434E-03    11.975
 6    11.000    0.13809E-02     0.970    0.971    -0.16    3.3490    0.30521E-03    0.30453E-03    11.980
 7    12.000    0.15295E-02     1.027    1.026     0.07    3.3480    0.30513E-03    0.30543E-03    11.982
 8    14.000    0.18442E-02     1.131    1.129     0.14    3.3500    0.30497E-03    0.30548E-03    11.979
 9    16.000    0.21784E-02     1.223    1.223     0.03    3.3550    0.30479E-03    0.30489E-03    11.968
10    18.000    0.25262E-02     1.308    1.307     0.09    3.3610    0.30461E-03    0.30491E-03    11.950
11    20.000    0.28900E-02     1.385    1.384     0.06    3.3680    0.30442E-03    0.30460E-03    11.925
12    22.000    0.32645E-02     1.457    1.454     0.16    3.3750    0.30423E-03    0.30467E-03    11.896
13    25.000    0.38513E-02     1.552    1.549     0.15    3.3860    0.30392E-03    0.30428E-03    11.843
14    28.000    0.44646E-02     1.634    1.634    -0.01    3.3970    0.30360E-03    0.30357E-03    11.783
15    31.000    0.50929E-02     1.709    1.709     0.02    3.4070    0.30327E-03    0.30331E-03    11.717
16    34.000    0.57327E-02     1.779    1.775     0.23    3.4160    0.30294E-03    0.30337E-03    11.644
17    36.000    0.61868E-02     1.811    1.817    -0.30    3.4230    0.30270E-03    0.30216E-03    11.595
18    38.000    0.66217E-02     1.854    1.854     0.01    3.4280    0.30248E-03    0.30250E-03    11.542
19    40.000    0.70919E-02     1.885    1.891    -0.32    3.4340    0.30224E-03    0.30171E-03    11.489
20    50.000    0.93923E-02     2.034    2.040    -0.29    3.4570    0.30103E-03    0.30065E-03    11.204

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1   0.1401E 04     3.14645     0.235E 01    0.1401E 04    3.14645        4.806
    2   0.4084E 06     5.61108     0.115E 04    0.2915E 03    2.46464        5.525
    3   0.2155E 08     7.33340     0.180E 06    0.5276E 02    1.72232    *********

   THE NUMBER OF ITERATIONS =   4           SMIN =  0.3877E 01

     NO POINTS ELIMINATED
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                                                   **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF YB3-DHMIBA  RUN 2  AUGUST 5 1973

ORIG ACID CONCENTRATION = 0.10213          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04951          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10025
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB        ANION CON       N EXP    N CALC     ERROR      PH        KA USED        KA THEO       VOL KNO3

 1     2.000    0.21917E-03     0.297    0.297      0.05     3.5400    0.30582E-03    0.30627E-03     11.808
 2     4.000    0.43564E-03     0.511    0.512     -0.10     3.3890    0.30570E-03    0.30495E-03     11.899
 3     6.000    0.66480E-03     0.689    0.688      0.15     3.3300    0.30558E-03    0.30656E-03     11.957
 4     8.000    0.91549E-03     0.840    0.841     -0.11     3.3050    0.30545E-03    0.30481E-03     11.995
 5    10.000    0.11854E-02     0.974    0.975     -0.10     3.2950    0.30531E-03    0.30479E-03     12.016
 6    11.000    0.13304E-02     1.033    1.037     -0.32     3.2940    0.30524E-03    0.30369E-03     12.022
 7    12.000    0.14706E-02     1.096    1.091      0.42     3.2920    0.30516E-03    0.30709E-03     12.022
 8    14.000    0.17847E-02     1.199    1.198      0.09     3.2960    0.30500E-03    0.30537E-03     12.020
 9    16.000    0.21153E-02     1.293    1.293      0.02     3.3020    0.30483E-03    0.30491E-03     12.008
10    18.000    0.24606E-02     1.380    1.378      0.14     3.3090    0.30465E-03    0.30511E-03     11.988
11    20.000    0.28304E-02     1.453    1.456     -0.23     3.3180    0.30445E-03    0.30374E-03     11.963
12    22.000    0.32059E-02     1.523    1.525     -0.11     3.3260    0.30426E-03    0.30394E-03     11.931
13    25.000    0.37925E-02     1.618    1.617      0.05     3.3380    0.30395E-03    0.30408E-03     11.876
14    28.000    0.44079E-02     1.699    1.699      0.00     3.3500    0.30363E-03    0.30363E-03     11.812
15    31.000    0.50411E-02     1.771    1.770      0.06     3.3610    0.30330E-03    0.30343E-03     11.743
16    34.000    0.56884E-02     1.837    1.833      0.21     3.3710    0.30296E-03    0.30337E-03     11.668
17    36.000    0.61392E-02     1.871    1.872     -0.06     3.3780    0.30273E-03    0.30261E-03     11.616
18    38.000    0.65866E-02     1.907    1.908     -0.03     3.3840    0.30249E-03    0.30245E-03     11.563
19    40.000    0.70445E-02     1.939    1.942     -0.16     3.3900    0.30226E-03    0.30199E-03     11.508

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.1616E 04     3.20839     0.4096E 01    0.1616E 04    3.20839        4.551
    2    0.5737E 06     5.75867     0.2145E 04    0.3550E 03    2.55028        6.852
    3    0.2973E 08     7.47313     0.3666E 06    0.5182E 02    1.71447     *********

    THE NUMBER OF ITERATIONS =    4            SMIN =  0.8079E 01

      NO POINTS ELIMINATED
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                                                  **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF LU3-DHMIBA  RUN 2  JULY 17 1973

ORIG ACID CONCENTRATION = 0.10164          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04902          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.10210
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB      ANION CON      N EXP   N CALC     ERROR      PH       KA USED        KA THEO       VOL KNO3

 1     2.000   0.20450E-03    0.301    0.302     -0.05    3.5320   0.30582E-03    0.30534E-03     11.787
 2     4.000   0.40832E-03    0.521    0.520      0.16    3.3770   0.30572E-03    0.30699E-03     11.883
 3     6.000   0.62905E-03    0.700    0.702     -0.21    3.3180   0.30560E-03    0.30414E-03     11.947
 4     8.000   0.86513E-03    0.858    0.856      0.22    3.2910   0.30548E-03    0.30681E-03     11.987
 5    10.000   0.11240E-02    0.994    0.992      0.23    3.2810   0.30534E-03    0.30662E-03     12.010
 6    11.000   0.12666E-02    1.053    1.057     -0.30    3.2810   0.30527E-03    0.30369E-03     12.019
 7    12.000   0.14092E-02    1.112    1.115     -0.24    3.2810   0.30519E-03    0.30401E-03     12.022
 8    14.000   0.17079E-02    1.222    1.222     -0.01    3.2840   0.30504E-03    0.30497E-03     12.021
 9    16.000   0.20263E-02    1.320    1.319      0.13    3.2900   0.30487E-03    0.30540E-03     12.010
10    18.000   0.23651E-02    1.408    1.406      0.11    3.2980   0.30470E-03    0.30509E-03     11.992
11    20.000   0.27222E-02    1.485    1.485     -0.01    3.3070   0.30451E-03    0.30449E-03     11.968
12    22.000   0.30926E-02    1.557    1.557     -0.02    3.3160   0.30432E-03    0.30425E-03     11.938
13    25.000   0.36695E-02    1.654    1.652      0.11    3.3290   0.30402E-03    0.30431E-03     11.884
14    28.000   0.42771E-02    1.736    1.736      0.01    3.3420   0.30370E-03    0.30373E-03     11.822
15    31.000   0.49047E-02    1.809    1.809     -0.01    3.3540   0.30337E-03    0.30334E-03     11.753
16    34.000   0.55491E-02    1.875    1.874      0.01    3.3650   0.30304E-03    0.30305E-03     11.679
17    36.000   0.59895E-02    1.913    1.914     -0.05    3.3720   0.30281E-03    0.30271E-03     11.628
18    38.000   0.64266E-02    1.954    1.950      0.19    3.3780   0.30258E-03    0.30294E-03     11.574
19    40.000   0.68903E-02    1.981    1.986     -0.22    3.3850   0.30234E-03    0.30195E-03     11.520
20    50.000   0.92063E-02    2.124    2.127     -0.16    3.4110   0.30113E-03    0.30090E-03     11.230

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.1769E 04     3.24769     0.409E 01    0.1769E 04    3.24769        4.631
    2    0.6756E 06     5.82969     0.221E 04    0.3819E 03    2.58200        6.327
    3    0.4078E 08     7.61047     0.387E 06    0.6036E 02    1.78078    *********

    THE NUMBER OF ITERATIONS =   4           SMIN =  0.7871E 01

      NO POINTS ELIMINATED
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                                                   **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF Y3-DHMIBA  RUN 2  JULY 17 1973

ORIG ACID CONCENTRATION = 0.10164          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.05262          POTASSIUM NITRATE CONC.    =  1.5100
BUFFER ACID CONC.       = 0.04902          VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.05262          CONC. OF  METAL ION SOL.   =  0.09698
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB        ANION CON        N EXP    N CALC      ERROR      PH        KA USED         KA THEO        VOL KNO3

 1     2.000    0.32050E-03      0.229     0.228       0.45     3.6210    0.30576E-03    0.30764E-03     11.801
 2     4.000    0.61605E-03      0.393     0.394      -0.43     3.4880    0.30561E-03    0.30396E-03     11.856
 3     6.000    0.91476E-03      0.532     0.532      -0.04     3.4340    0.30545E-03    0.30531E-03     11.888
 4     8.000    0.12298E-02      0.652     0.655      -0.36     3.4090    0.30529E-03    0.30414E-03     11.907
 5    10.000    0.15562E-02      0.761     0.762      -0.15     3.3960    0.30512E-03    0.30469E-03     11.913
 6    11.000    0.17230E-02      0.813     0.812       0.13     3.3920    0.30503E-03    0.30540E-03     11.912
 7    12.000    0.18967E-02      0.860     0.860       0.04     3.3900    0.30494E-03    0.30505E-03     11.909
 8    14.000    0.22504E-02      0.950     0.948       0.24     3.3880    0.30476E-03    0.30535E-03     11.898
 9    16.000    0.26205E-02      1.030     1.028       0.13     3.3890    0.30456E-03    0.30487E-03     11.881
10    18.000    0.29994E-02      1.105     1.102       0.27     3.3910    0.30437E-03    0.30496E-03     11.857
11    20.000    0.33931E-02      1.169     1.171      -0.17     3.3950    0.30416E-03    0.30381E-03     11.830
12    22.000    0.37940E-02      1.234     1.232       0.20     3.3980    0.30395E-03    0.30433E-03     11.797
13    25.000    0.44129E-02      1.319     1.317       0.21     3.4040    0.30363E-03    0.30400E-03     11.741
14    28.000    0.50531E-02      1.390     1.393      -0.25     3.4110    0.30329E-03    0.30289E-03     11.680
15    31.000    0.57098E-02      1.459     1.461      -0.18     3.4170    0.30295E-03    0.30268E-03     11.612
16    34.000    0.63610E-02      1.528     1.522       0.39     3.4220    0.30261E-03    0.30316E-03     11.539
17    36.000    0.68291E-02      1.555     1.561      -0.37     3.4270    0.30237E-03    0.30187E-03     11.490
18    38.000    0.72719E-02      1.597     1.596       0.07     3.4300    0.30214E-03    0.30222E-03     11.438
19    50.000    0.10084E-01      1.766     1.773      -0.42     3.4500    0.30067E-03    0.30024E-03     11.105
20    60.000    0.12488E-01      1.878     1.886      -0.41     3.4630    0.29942E-03    0.29906E-03     10.806

    (I)      BETA(I)     LOG BETA(I)    SIGMA(I)         K(I)        LOG K(I)     K(I)/K(I+1)

     1    0.8173E 03       2.91238     0.242E 01     0.8173E 03     2.91238         4.681
     2    0.1427E 06       5.15446     0.953E 03     0.1746E 03     2.24208         6.447
     3    0.3865E 07       6.58716     0.121E 06     0.2708E 02     1.43270     *********

    THE NUMBER OF ITERATIONS =    5            SMIN =  0.8319E 01

      NO POINTS ELIMINATED
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XII. APPENDIX D:

FORMATION CONSTANTS OF BIVALENT TRANSITION METAL α,β-DIHYDROXYISOBUTYRATE COMPLEXES

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                                              **********TWO PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF CO2-CHIPA  RUN 2  OCTOBER 5 1971

ORIG ACID CONCENTRATION = 0.09945            IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04958            POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.04987            VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04958            CONC. OF  METAL ION SOL.   =  0.10035
RATIO OF THE VKOH TO VP = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)     VB       ANION CON      N EXP   N CALC    ERROR     PH       KA USED        KA THEO       VOL KNO3

 1     1.000   0.59519E-03    0.024    0.024    -0.06    3.8172   0.26353E-03   0.26352E-03     7.244
 2     3.000   0.15751E-02    0.063    0.062     0.70    3.6700   0.26262E-03   0.26276E-03     7.177
 3     5.000   0.25215E-02    0.096    0.097    -1.55    3.6295   0.26199E-03   0.26167E-03     7.111
 4     6.000   0.29849E-02    0.115    0.114     1.27    3.6176   0.26172E-03   0.26198E-03     7.079
 5     7.000   0.34587E-02    0.125    0.130    -1.48    3.6102   0.26147E-03   0.26118E-03     7.046
 6     8.000   0.39264E-02    0.144    0.146    -1.34    3.6040   0.26124E-03   0.26098E-03     7.013
 7     9.000   0.43901E-02    0.161    0.161     0.12    3.5988   0.26102E-03   0.26105E-03     6.980
 8    10.000   0.48581E-02    0.176    0.175     0.07    3.5950   0.26082E-03   0.26083E-03     6.947
 9    16.000   0.76744E-02    0.259    0.260    -0.48    3.5830   0.25974E-03   0.25966E-03     6.745
10    18.000   0.86199E-02    0.293    0.286    -1.04    3.5812   0.25943E-03   0.25925E-03     6.677
11    20.000   0.95470E-02    0.315    0.310     1.61    3.5791   0.25914E-03   0.25941E-03     6.609
12    22.000   0.10494E-01    0.338    0.334     1.13    3.5782   0.25885E-03   0.25904E-03     6.540
13    24.000   0.11435E-01    0.363    0.357     1.77    3.5773   0.25858E-03   0.25887E-03     6.471
14    26.000   0.12382E-01    0.385    0.379     1.70    3.5768   0.25832E-03   0.25859E-03     6.402
15    28.000   0.13332E-01    0.406    0.400     1.48    3.5765   0.25807E-03   0.25830E-03     6.332
16    30.000   0.14283E-01    0.427    0.421     1.38    3.5763   0.25783E-03   0.25804E-03     6.261
17    32.000   0.15235E-01    0.446    0.441     1.30    3.5762   0.25759E-03   0.25779E-03     6.191
18    35.000   0.16665E-01    0.475    0.469     1.17    3.5762   0.25725E-03   0.25742E-03     6.085
19    37.000   0.17622E-01    0.492    0.498     0.98    3.5763   0.25704E-03   0.25717E-03     6.014

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)     K(I)/K(I+1)

    1   0.4145E 02      1.61754     0.741E-01    0.4145E 02     1.61754         7.110
    2   0.2416E 03      2.38318     0.334E 02    0.5830E 01     0.76564      *********

   THE NUMBER OF ITERATIONS =    5             SMIN =  0.2002E-01

     NO POINTS ELIMINATED
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                                         **********TWO PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF NI2-DHIBA  RUN 3  OCTOBER 6 1971

ORIG ACID CONCENTRATION = 0.10017          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04997          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05020          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04997          CONC. OF  METAL ION SOL.   =  0.09664
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)     VB       ANION CON      N EXP   N CALC    ERROR      PH      KA USED       KA THEO      VOL KNO3

 1     1.000   0.59341E-03    0.038    0.037     0.03    3.9063  0.26355E-03  0.26356E-03    7.265
 2     4.000   0.20002E-02    0.120    0.121    -0.75    3.6330  0.26232E-03  0.26209E-03    7.173
 3     5.000   0.24564E-02    0.147    0.145     1.13    3.6163  0.26203E-03  0.26236E-03    7.142
 4     6.000   0.29228E-02    0.167    0.170    -1.47    3.6063  0.26176E-03  0.26132E-03    7.111
 5     7.000   0.33801E-02    0.192    0.193    -0.52    3.5980  0.26151E-03  0.26136E-03    7.080
 6     8.000   0.39314E-02    0.219    0.214     2.00    3.5911  0.26129E-03  0.26185E-03    7.049
 7     9.000   0.42940E-02    0.239    0.236     1.34    3.5868  0.26107E-03  0.26144E-03    7.018
 8    10.000   0.47546E-02    0.260    0.257     1.46    3.5832  0.26086E-03  0.26126E-03    6.986
 9    12.000   0.56318E-02    0.299    0.297     0.96    3.5783  0.26048E-03  0.26073E-03    6.921
10    14.000   0.66122E-02    0.336    0.334     0.63    3.5751  0.26012E-03  0.26028E-03    6.856
11    16.000   0.75464E-02    0.370    0.369     0.33    3.5730  0.25979E-03  0.25987E-03    6.790
12    18.000   0.84937E-02    0.403    0.403     0.11    3.5716  0.25947E-03  0.25950E-03    6.723
13    22.000   0.10375E-01    0.458    0.465    -1.32    3.5705  0.25889E-03  0.25859E-03    6.586
14    24.000   0.11321E-01    0.482    0.493    -2.40    3.5705  0.25861E-03  0.25809E-03    6.517
15    26.000   0.12298E-01    0.498    0.521    -4.46    3.5710  0.25835E-03  0.25740E-03    6.447
16    28.000   0.13242E-01    0.527    0.547    -3.66    3.5707  0.25810E-03  0.25734E-03    6.377
17    30.000   0.14186E-01    0.555    0.571    -2.81    3.5705  0.25785E-03  0.25729E-03    6.307
18    32.000   0.15132E-01    0.583    0.595    -1.96    3.5704  0.25762E-03  0.25723E-03    6.237

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)       K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.6607E 02     1.82002     0.112E 00    0.6607E 02    1.82002        7.398
    2    0.5901E 03     2.77091     0.484E 02    0.8931E 01    0.95089     *********

   THE NUMBER OF ITERATIONS =   4            SMIN =  0.4150E-01

     NO POINTS ELIMINATED
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                                                   **********TWO PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF CU2-CHIFA  RUN 2A  JULY 30 1971

ORIG ACID CONCENTRATION = 0.10007            IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04997            POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05010            VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04997            CONC. OF  METAL ION SOL.   =  0.10261
RATIO OF THE VKOH TO VB = 1.00000            CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ        RT(X)

(I)     VB       ANION CON      N EXP    N CALC    ERROR      PH      KA USED       KA THEO      VOL KNO3

 1     2.000   0.73924E-03    0.255    0.255    -0.03    3.5797  0.26337E-03  0.26330E-03    7.273
 2     4.000   0.14410E-02    0.422    0.422     0.11    3.5100  0.26272E-03  0.26289E-03    7.249
 3     5.000   0.18079E-02    0.491    0.492    -0.06    3.4982  0.26245E-03  0.26237E-03    7.232
 4     6.000   0.21352E-02    0.553    0.554    -0.17    3.4921  0.26220E-03  0.26196E-03    7.213
 5     7.000   0.25640E-02    0.613    0.609     0.66    3.4880  0.26196E-03  0.26280E-03    7.191
 6     8.000   0.29652E-02    0.661    0.662    -0.03    3.4880  0.26173E-03  0.26169E-03    7.167
 7     9.000   0.33683E-02    0.708    0.709    -0.05    3.4883  0.26152E-03  0.26146E-03    7.142
 8    10.000   0.37844E-02    0.749    0.753    -0.54    3.4900  0.26131E-03  0.25073E-03    7.116
 9    12.000   0.46203E-02    0.827    0.829    -0.26    3.4930  0.26092E-03  0.26067E-03    7.059
10    16.000   0.63663E-02    0.947    0.955    -0.82    3.5020  0.26021E-03  0.25955E-03    6.937
11    18.000   0.72597E-02    0.997    1.007    -0.95    3.5063  0.25989E-03  0.25919E-03    6.872
12    20.000   0.81571E-02    1.046    1.053    -0.68    3.5100  0.25958E-03  0.25912E-03    6.805
13    22.000   0.90719E-02    1.086    1.095    -0.83    3.5139  0.25929E-03  0.25875E-03    6.738
14    24.000   0.99693E-02    1.135    1.132     0.29    3.5164  0.25901E-03  0.25918E-03    6.669
15    30.000   0.12763E-01    1.231    1.227     0.30    3.5257  0.25822E-03  0.25837E-03    6.458
16    35.000   0.15134E-01    1.291    1.292    -0.06    3.5324  0.25762E-03  0.25759E-03    6.277
17    40.000   0.17519E-01    1.344    1.346    -0.08    3.5379  0.25706E-03  0.25702E-03    6.093

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)       K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.4293E 03     2.63276    0.6167E 00   0.4293E 03    2.63276        9.384
    2    0.1964? 05     4.29313    0.1695E 03   0.4575E 02    1.66037    *********

    THE NUMBER OF ITERATIONS =   4            SMIN =  0.28265 00

     NO POINTS ELIMINATED
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                                               **********TWO PARAMETER PROGRAM USED***********

 STABILITY CONSTANT OF ZN2-EHIBA  RUN 3A  AUGUST 16 1971

ORIG ACID CONCENTRATION = 0.10017          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04997          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05020          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04997          CONC. OF  METAL ION SOL.   =  0.09839
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ      RT(X)

(I)    VB       ANION CON      N EXP    N CALC    ERROR     PH       KA USED        KA THEO      VOL KNO3

 1    3.000   0.15515E-02    0.084    0.084    -0.20   3.6615  0.26264E-03  0.26258E-03     7.192
 2    4.000   0.20173E-02    0.108    0.107     0.49   3.6363  0.26230E-03  0.26244E-03     7.161
 3    5.000   0.24795E-02    0.132    0.130     1.54   3.6200  0.26201E-03  0.26243E-03     7.130
 4    6.000   0.29558E-02    0.146    0.151    -3.56   3.6108  0.26174E-03  0.26080E-03     7.098
 5    9.000   0.43275E-02    0.217    0.210     3.21   3.5900  0.26105E-03  0.26185E-03     7.003
 6   10.000   0.48099E-02    0.226    0.229    -1.36   3.5880  0.26084E-03  0.26050E-03     6.970
 7   12.000   0.57390E-02    0.254    0.265    -0.37   3.5825  0.26045E-03  0.26037E-03     6.904
 8   14.000   0.66879E-02    0.290    0.298    -2.75   3.5799  0.26009E-03  0.25946E-03     6.837
 9   16.000   0.76090E-02    0.321    0.329     0.57   3.5765  0.25977E-03  0.25989E-03     6.771
10   18.000   0.85396E-02    0.367    0.358     2.27   3.5744  0.25946E-03  0.25994E-03     6.703
11   20.000   0.94861E-02    0.394    0.387     1.86   3.5735  0.25916E-03  0.25954E-03     6.635
12   22.000   0.10417E-01    0.429    0.413     3.88   3.5722  0.25888E-03  0.25966E-03     6.566
13   24.000   0.11370E-01    0.452    0.433     3.22   3.5720  0.25860E-03  0.25923E-03     6.497
14   26.000   0.12321E-01    0.477    0.462     3.20   3.5718  0.25834E-03  0.25895E-03     6.427
15   30.000   0.14252E-01    0.511    0.508     0.70   3.5725  0.25784E-03  0.25796E-03     6.285
16   35.000   0.16672E-01    0.551    0.559    -1.42   3.5735  0.25725E-03  0.25701E-03     6.106
17   50.000   0.23307E-01    0.693    0.685    -0.28   3.5757  0.25572E-03  0.25568E-03     5.562

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)        LOG K(I)    K(I)/K(I+1)

    1    0.58295 02     1.76557     0.5601 00    0.58295 02    1.76557       10.395
    2    0.32685 03     2.51431     0.1274 03    0.56075 01    0.74874     *********

   THE NUMBER OF ITERATIONS =    4            SMIN =  0.70315E-01

     NO POINTS ELIMINATED
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                                        *********TWO PARAMETER PROGRAM USFD**********

 STABILITY CONSTANT OF CD2-CHIBA  RUN 2  MAY 5 1972

ORIG ACID CONCENTRATION = 0.10082          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05100          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982          CONC. OF  METAL ION SOL.   =  0.09979
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.26500E-03+(-0.60000E-04)*SQ       RT(X)

(I)    VB       ANION CON       N EXP    N CALC    ERROR     PH      KA USED       KA THEO       VOL KNO3

 1    2.000   0.10999E-02      0.047    0.047    -0.12    3.7059   0.26301E-03   0.26298E-03     7.213
 2    3.000   0.15778E-02      0.068    0.067     0.83    3.6609   0.26262E-03   0.26280E-03     7.180
 3    4.000   0.20519E-02      0.086    0.087    -1.23    3.6360   0.26228E-03   0.26201E-03     7.148
 4    5.000   0.25179E-02      0.107    0.107    -0.10    3.6192   0.26199E-03   0.26197E-03     7.116
 5    6.000   0.29836E-02      0.126    0.127    -0.22    3.6077   0.26172E-03   0.26167E-03     7.084
 6    7.000   0.34470E-02      0.146    0.146     0.09    3.5991   0.26148E-03   0.26150E-03     7.052
 7    8.000   0.39085E-02      0.167    0.166     0.72    3.5924   0.26125E-03   0.26141E-03     7.020
 8    9.000   0.43724E-02      0.185    0.185     0.31    3.5874   0.26103E-03   0.26110E-03     6.989
 9   10.000   0.48351E-02      0.204    0.204     0.25    3.5833   0.26083E-03   0.26088E-03     6.957
10   12.000   0.57592E-02      0.243    0.242     0.38    3.5771   0.26045E-03   0.26053E-03     6.892
11   14.000   0.66842E-02      0.280    0.279     0.31    3.5728   0.26009E-03   0.26016E-03     6.828
12   16.000   0.76094E-02      0.317    0.315     0.53    3.5696   0.25977E-03   0.25988E-03     6.763
13   18.000   0.85329E-02      0.354    0.351     0.79    3.5672   0.25946E-03   0.25962E-03     6.697
14   20.000   0.94543E-02      0.392    0.386     1.61    3.5652   0.25917E-03   0.25951E-03     6.632
15   22.000   0.10380E-01      0.428    0.420     1.89    3.5638   0.25889E-03   0.25928E-03     6.566
16   24.000   0.11317E-01      0.459    0.453     0.98    3.5631   0.25862E-03   0.25882E-03     6.499
17   26.000   0.12258E-01      0.486    0.486    -0.09    3.5627   0.25836E-03   0.25834E-03     6.432
18   28.000   0.13186E-01      0.520    0.518     0.43    3.5620   0.25811E-03   0.25820E-03     6.364
19   30.000   0.14110E-01      0.556    0.548     1.46    3.5613   0.25787E-03   0.25816E-03     6.297
20   35.000   0.16457E-01      0.629    0.622     1.03    3.5610   0.25730E-03   0.25750E-03     6.126
21   40.000   0.18836E-01      0.685    0.692    -1.08    3.5617   0.25677E-03   0.25656E-03     5.951
22   50.000   0.23563E-01      0.812    0.816    -0.48    3.5625   0.25579E-03   0.25571E-03     5.599
23   60.000   0.28327E-01      0.921    0.923    -0.23    3.5640   0.25490E-03   0.25486E-03     5.240

   (I)     BETA(I)     LOG BETA(I)    SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.4249E 02     1.62828      0.140E 00     0.4249E 02    1.62828        1.879
    2    0.9609E 03     2.98265      0.405E 02     0.2261E 02    1.35437     *********

   THE NUMBER OF ITERATIONS =    4            SMIN =  0.2312E-01

    NO POINTS ELIMINATED
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XIII. APPENDIX E:

FORMATION CONSTANTS OF BIVALENT TRANSITION METAL α,β-DIHYDROXY-β-METHYLISOBUTYRATE COMPLEXES

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                                         **********TWO PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF CO2-CHMIBA  RUN 2  JANUARY 14 1972

ORIG ACID CONCENTRATION = 0.09817           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04950           POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.04867           VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04950           CONC. OF  METAL ION SOL.   =  0.10035
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.30835E-03+(-0.90660E-04)*SQ       RT(X)

(I)     VB       ANION CON      N EXP    N CALC    ERROR      PH       KA USED       KA THEO       VOL KNO3

 1    4.000    0.20685E-02     0.080     0.080     0.60     3.6028   0.30423E-03   0.30437E-03     7.142
 2    5.000    0.25406E-02     0.097     0.097    -0.65     3.5852   0.30378E-03   0.30363E-03     7.110
 3    6.000    0.30102E-02     0.113     0.115    -1.63     3.5729   0.30338E-03   0.30300E-03     7.077
 4    7.000    0.34737E-02     0.132     0.132    -0.36     3.5633   0.30301E-03   0.30292E-03     7.045
 5    8.000    0.39377E-02     0.150     0.150     0.04     3.5561   0.30266E-03   0.30267E-03     7.013
 6    9.000    0.43987E-02     0.169     0.166     1.20     3.5502   0.30234E-03   0.30261E-03     6.980
 7   10.000    0.48622E-02     0.186     0.183     1.26     3.5457   0.30203E-03   0.30231E-03     6.948
 8   12.000    0.57836E-02     0.222     0.216     2.68     3.5386   0.30146E-03   0.30206E-03     6.883
 9   14.000    0.67142E-02     0.253     0.249     1.64     3.5342   0.30092E-03   0.30129E-03     6.817
10   16.000    0.76431E-02     0.285     0.281     1.30     3.5309   0.30042E-03   0.30071E-03     6.751
11   18.000    0.85714E-02     0.316     0.312     1.26     3.5284   0.29996E-03   0.30023E-03     6.685
12   20.000    0.95000E-02     0.348     0.343     1.32     3.5265   0.29951E-03   0.29980E-03     6.619
13   22.000    0.10440E-01     0.373     0.373    -0.17     3.5255   0.29909E-03   0.29905E-03     6.552
14   24.000    0.11379E-01     0.398     0.403    -1.15     3.5247   0.29868E-03   0.29843E-03     6.484
15   26.000    0.12308E-01     0.429     0.431    -0.46     3.5237   0.29829E-03   0.29819E-03     6.417
16   28.000    0.13233E-01     0.462     0.459     0.63     3.5228   0.29792E-03   0.29805E-03     6.349
17   30.000    0.14169E-01     0.489     0.487     0.54     3.5224   0.29756E-03   0.29767E-03     6.281
18   32.000    0.15101E-01     0.518     0.513     0.94     3.5220   0.29721E-03   0.29740E-03     6.213
19   35.000    0.16505E-01     0.559     0.552     1.20     3.5217   0.29670E-03   0.29694E-03     6.110
20   37.000    0.17438E-01     0.587     0.577     1.77     3.5215   0.29638E-03   0.29673E-03     6.041

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+I)

    1   0.38911E 02     1.59001     0.2900E 00   0.3891E 02    1.59001        2.260
    2   0.66970E 03     2.82588     0.4945E 02   0.1721E 02    1.23587     *********

    THE NUMBER OF ITERATIONS =    4              SMIN =  0.9634E-02

      NO POINTS ELIMINATED
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                                                    **********THREE PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF NI2-DHMIBA  RUN 3  APRIL 21 1972

ORIG ACID CONCENTRATION = 0.10041          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04981          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05060          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04981          CONC. OF  METAL ION SOL.   =  0.09664
RATIO OF THE VNCH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.30593E-03+(-0.52157E-03)*X

(I)     VB       ANION CON      N EXP    N CALC     ERROR      PH        KA USED        KA THEO      VOL KNO3

 1     3.000   0.15580E-02    0.096     0.096      0.01    3.6045   0.30512E-03   0.30512E-03    7.202
 2     4.000   0.20207E-02    0.123     0.123     -0.05    3.5762   0.30488E-03   0.30486E-03    7.172
 3     5.000   0.24796E-02    0.149     0.149     -0.06    3.5578   0.30464E-03   0.30461E-03    7.142
 4     6.000   0.29356E-02    0.175     0.175      0.22    3.5448   0.30440E-03   0.30447E-03    7.111
 5     7.000   0.33920E-02    0.200     0.200     -0.03    3.5354   0.30416E-03   0.30415E-03    7.081
 6     8.000   0.38466E-02    0.225     0.225      0.11    3.5281   0.30392E-03   0.30396E-03    7.050
 7     9.000   0.43022E-02    0.249     0.249     -0.09    3.5225   0.30369E-03   0.30365E-03    7.020
 8    10.000   0.47575E-02    0.273     0.273     -0.20    3.5180   0.30345E-03   0.30338E-03    6.989
 9    12.000   0.56663E-02    0.320     0.320     -0.04    3.5112   0.30297E-03   0.30296E-03    6.927
10    14.000   0.65761E-02    0.367     0.366      0.06    3.5065   0.30250E-03   0.30252E-03    6.864
11    16.000   0.74193E-02    0.411     0.412     -0.24    3.5033   0.30202E-03   0.30195E-03    6.801
12    18.000   0.83957E-02    0.458     0.456      0.49    3.5006   0.30155E-03   0.30170E-03    6.738
13    20.000   0.93074E-02    0.503     0.500      0.58    3.4988   0.30108E-03   0.30126E-03    6.674
14    22.000   0.10219E-01    0.548     0.543      0.86    3.4974   0.30060E-03   0.30087E-03    6.609
15    24.000   0.11143E-01    0.584     0.586     -0.23    3.4969   0.30012E-03   0.30005E-03    6.544
16    26.000   0.12060E-01    0.626     0.628     -0.37    3.4963   0.29964E-03   0.29953E-03    6.479
17    28.000   0.12981E-01    0.665     0.669     -0.70    3.4960   0.29916E-03   0.29895E-03    6.413
18    37.000   0.17129E-01    0.838     0.849     -1.34    3.4961   0.29700E-03   0.29661E-03    6.112

   (I)     BETA(I)     LOG BETA(I)   SIGMA(I)       K(I)       LOG K(I)     K(I)/K(I+1)

    1    0.6404E 02      1.80642    0.104E 00    0.6404E 02    1.80642        3.703
    2    0.1107E 04      3.04426    0.275E 02    0.1729E 02    1.23783        0.667
    3    0.2871E 05      4.45797    0.226E 04    0.2592E 02    1.41371     *********

    THE NUMBER OF ITERATIONS =  10            SMIN =  0.1731E-01

       NO POINTS ELIMINATED
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                                        **********TWO PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF CU2-DHMIPA  RUN 1  OCTOBER 26 1971

CRIG ACID CONCENTRATION = 0.09878          IONIC STRENGTH OF SOLUTION =  0.1000
CRIG BASE CONCENTRATION = 0.04958          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.04920          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04958          CONC. OF  METAL ION SOL.   =  0.10261
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.30835E-03+(-0.90660E-04)*SQ       RT(X)

(I)     VB      ANION CON      N EXP    N CALC    ERROR      PH      KA USED       KA THEO      VOL KNO3

 1    2.000   0.75514E-03    0.253    0.253    -0.01    3.5472   0.30586E-03   0.30583E-03    7.271
 2    3.000   0.11059E-02    0.342    0.342    -0.07    3.4957   0.30534E-03   0.30520E-03    7.261
 3    4.000   0.14618E-02    0.420    0.419     0.17    3.4690   0.30488E-03   0.30518E-03    7.247
 4    5.000   0.18280E-02    0.488    0.488     0.12    3.4544   0.30447E-03   0.30467E-03    7.230
 5    6.000   0.22027E-02    0.551    0.550     0.17    3.4460   0.30409E-03   0.30436E-03    7.210
 6    7.000   0.25887E-02    0.606    0.606    -0.06    3.4417   0.30374E-03   0.30365E-03    7.189
 7    8.000   0.29756E-02    0.658    0.658     0.08    3.4392   0.30340E-03   0.30352E-03    7.166
 8    9.000   0.33973E-02    0.696    0.707    -1.57    3.4405   0.30307E-03   0.30104E-03    7.141
 9   10.000   0.37995E-02    0.741    0.750    -1.11    3.4400   0.30276E-03   0.30140E-03    7.114
10   12.000   0.46005E-02    0.835    0.824     1.26    3.4390   0.30220E-03   0.30360E-03    7.059
11   14.000   0.54475E-02    0.904    0.891     1.40    3.4420   0.30166E-03   0.30307E-03    7.000
12   16.000   0.63339E-02    0.953    0.952     0.12    3.4470   0.30113E-03   0.30125E-03    6.938
13   18.000   0.72036E-02    1.011    1.004     0.75    3.4500   0.30066E-03   0.30130E-03    6.875
14   20.000   0.81019E-02    1.055    1.051     0.38    3.4540   0.30019E-03   0.30050E-03    6.809
15   22.000   0.89931E-02    1.103    1.093     0.90    3.4570   0.29975E-03   0.30043E-03    6.742
16   24.000   0.98943E-02    1.146    1.131     1.29    3.4600   0.29933E-03   0.30024E-03    6.674
17   26.000   0.10801E-01    1.186    1.166     1.74    3.4628   0.29893E-03   0.30008E-03    6.605
18   28.000   0.11730E-01    1.215    1.199     1.40    3.4661   0.29853E-03   0.29941E-03    6.535
19   30.000   0.12662E-01    1.243    1.229     1.19    3.4691   0.29815E-03   0.29885E-03    6.465
20   32.000   0.13580E-01    1.278    1.256     1.81    3.4713   0.29779E-03   0.29881E-03    6.394

   (I)     BETA(I)     LOG BETA(I)    SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.4149E 03     2.61799     0.9000E 00    0.4149E 03    2.61799        8.765
    2    0.1964E 05     4.29325     0.2570E 03    0.4734E 02    1.67525     *********

   THE NUMBER OF ITERATIONS =    4            SMIN =  0.8262E 00

     NO POINTS ELIMINATED
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                                                  **********TWO PARAMETER PROGRAM USED**********

 STABILITY CONSTANT OF ZN2-DHMIPA  RUN 3  JANUARY 14 1972  .

ORIG ACID CONCENTRATION = 0.09849           IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04982           POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.04867           VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04982           CONC. OF  METAL ION SOL.   =  0.09839
RATIO OF THE VKOH TO VB = 1.00000           CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.30835E-03+(-0.90660E-04)*SQ       RT(X)

(I)     VB       ANION CON       N EXP    N CALC     ERROR      PH        KA USED        KA THEO        VOL KNO3

 1     3.000   0.15614E-02     0.087     0.087      0.26     3.6226    0.30477E-03    0.30485E-03      7.192
 2     4.000   0.20280E-02     0.111     0.112     -0.93     3.5952    0.30427E-03    0.30396E-03      7.161
 3     5.000   0.24365E-02     0.137     0.137      0.20     3.5768    0.30383E-03    0.30389E-03      7.131
 4     7.000   0.33960E-02     0.188     0.184      2.31     3.5542    0.30307E-03    0.30381E-03      7.070
 5     8.000   0.38601E-02     0.208     0.208      0.02     3.5480    0.30272E-03    0.30272E-03      7.039
 6     9.000   0.43243E-02     0.227     0.231     -1.86     3.5432    0.30239E-03    0.30180E-03      7.008
 7    10.000   0.47701E-02     0.255     0.253      0.87     3.5378    0.30209E-03    0.30236E-03      6.977
 8    12.000   0.56929E-02     0.294     0.297     -0.89     3.5320    0.30151E-03    0.30123E-03      6.914
 9    14.000   0.66161E-02     0.333     0.340     -2.02     3.5280    0.30098E-03    0.30036E-03      6.850
10    20.000   0.93566E-02     0.462     0.458      0.90     3.5200    0.29958E-03    0.29984E-03      6.657
11    22.000   0.10300E-01     0.489     0.496     -1.34     3.5197    0.29915E-03    0.29877E-03      6.591
12    24.000   0.11204E-01     0.537     0.531      1.18     3.5180    0.29875E-03    0.29908E-03      6.525
13    26.000   0.12135E-01     0.570     0.565      0.97     3.5176    0.29836E-03    0.29860E-03      6.458
14    28.000   0.13062E-01     0.605     0.599      1.13     3.5172    0.29799E-03    0.29829E-03      6.390
15    30.000   0.13993E-01     0.639     0.631      1.29     3.5170    0.29763E-03    0.29797E-03      6.322
16    32.000   0.14928E-01     0.670     0.662      1.26     3.5170    0.29727E-03    0.29760E-03      6.254
17    35.000   0.16327E-01     0.718     0.706      1.75     3.5170    0.29677E-03    0.29721E-03      6.151
18    37.000   0.17279E-01     0.741     0.735      0.89     3.5175    0.29643E-03    0.29665E-03      6.081
19    40.000   0.18673E-01     0.792     0.775      2.17     3.5175    0.29596E-03    0.29648E-03      5.977

   (I)     BETA(I)      LOG BETA(I)    SIGMA(I)        K(I)        LOG K(I)     K(I)/K(I+1)

    1    0.5693E 02      1.75531     0.3403 00     0.5693E 02     1.75531         2.582
    2    0.1255E 04      3.09861     0.7555 02     0.2204E 02     1.34329      *********

   THE NUMBER OF ITERATIONS =    4            SMIN =  0.3049E-01

     NO POINTS ELIMINATED
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                                                  **********TWO PARAMETER PROGRAM USED**********

STABILITY CONSTANT OF CO2-DHMIPA  RUN 3  APRIL 30 1972

ORIG ACID CONCENTRATION = 0.10041          IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04981          POTASSIUM NITRATE CONC.    =  1.2901
BUFFER ACID CONC.       = 0.05060          VOLUME OF METAL ION SOL.   =  2.00
BUFFER SALT CONC.       = 0.04981          CONC. OF  METAL ION SOL.   =  0.09979
RATIO OF THE VKOH TO VB = 1.00000          CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  100.00
STRAIGHT LINE EQUATION-Y= 0.30835E-03+(-0.90660E-04)*SQ       RT(X)

(I)     VB       ANION CON     N EXP    N CALC    ERROR      PH      KA USED        KA THEO      VOL KNO3

 1     2.000   0.11191E-02    0.047    0.047    -0.02    3.6637   0.30532E-03   0.30531E-03     7.211
 2     3.000   0.16015E-02    0.069    0.068     0.16    3.6150   0.30472E-03   0.30476E-03     7.178
 3     4.000   0.20753E-02    0.088    0.088    -0.07    3.5871   0.30422E-03   0.30420E-03     7.146
 4     5.000   0.25444E-02    0.108    0.108    -0.24    3.5689   0.30378E-03   0.30371E-03     7.114
 5     6.000   0.30108E-02    0.128    0.129    -0.43    3.5561   0.30338E-03   0.30326E-03     7.082
 6     7.000   0.34753E-02    0.148    0.149    -0.52    3.5466   0.30301E-03   0.30287E-03     7.051
 7     8.000   0.39357E-02    0.169    0.169     0.39    3.5390   0.30266E-03   0.30276E-03     7.019
 8     9.000   0.43975E-02    0.190    0.189     0.40    3.5332   0.30234E-03   0.30244E-03     6.987
 9    10.000   0.48586E-02    0.210    0.209     0.47    3.5285   0.30203E-03   0.30215E-03     6.956
10    12.000   0.57793E-02    0.250    0.248     0.67    3.5214   0.30146E-03   0.30163E-03     6.892
11    14.000   0.66982E-02    0.291    0.287     1.08    3.5163   0.30093E-03   0.30121E-03     6.828
12    16.000   0.76213E-02    0.328    0.326     0.69    3.5128   0.30044E-03   0.30061E-03     6.764
13    18.000   0.85370E-02    0.370    0.364     1.50    3.5098   0.29997E-03   0.30038E-03     6.699
14    20.000   0.94643E-02    0.405    0.401     0.87    3.5080   0.29953E-03   0.29975E-03     6.634
15    22.000   0.10387E-01    0.443    0.439     1.04    3.5064   0.29911E-03   0.29937E-03     6.569
16    24.000   0.11311E-01    0.479    0.474     1.13    3.5052   0.29871E-03   0.29899E-03     6.503
17    26.000   0.12242E-01    0.512    0.509     0.58    3.5045   0.29832E-03   0.29846E-03     6.436
18    28.000   0.13174E-01    0.544    0.543     0.13    3.5040   0.29794E-03   0.29798E-03     6.369
19    30.000   0.14113E-01    0.573    0.577    -0.67    3.5038   0.29758E-03   0.29742E-03     6.302
20    35.000   0.16455E-01    0.647    0.657    -1.43    3.5035   0.29672E-03   0.29638E-03     6.131
21    40.000   0.18785E-01    0.728    0.730    -0.29    3.5032   0.29592E-03   0.29586E-03     5.960
22    50.000   0.23471E-01    0.876    0.862     1.57    3.5038   0.29446E-03   0.29480E-03     5.609

   (I)     BETA(I)      LOG BETA(I)    SIGMA(I)        K(I)       LOG K(I)    K(I)/K(I+1)

    1    0.4154E 02      1.61843     0.423E-01    0.4154E 02    1.61843         1.487
    2    0.1160E 04      3.06463     0.123E 02    0.2794E 02    1.44620     *********

   THE NUMBER OF ITERATIONS =   4            SMIN =  0.1969E-02

    NO POINTS ELIMINATED
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XIV. APPENDIX F:

FORMATION CONSTANTS OF THE COPPER(II) α-HYDROXYISOBUTYRATE COMPLEXES

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                                   **********THREE PARAMETER PROGRAM USED**********
STABILITY CONSTANT OF CU2-HIPA   RUN 1+2   OCTOBER 7 1972

ORIG ACID CONCENTRATION = 0.10786             IONIC STRENGTH OF SOLUTION =  0.1000
ORIG BASE CONCENTRATION = 0.04987             POTASSIUM NITRATE CONC.    =  1.8880
BUFFER ACID CONC.       = 0.05799             VOLUME OF METAL ION SOL.   =  4.00
BUFFER SALT CONC.       = 0.04987             CONC. OF METAL ION SOL.    =  0.10150
RATIO OF THE VKOH TO VB = 1.00000             CONC. EXCESS ACID IN METAL =  0.0
FINAL SOLUTION VOLUME   =  200.00
STRAIGHT LINE EQUATION-Y= 0.15962E-03+(-0.26159E-03)*X

(I)    VB       ANION CON     N EXP   N CALC   ERROR     PH       KA USED       KA THEO     VOL KNO3

 1    2.000   0.32198E-03   0.182   0.182    0.02   3.7164   0.15954E-03   0.15958E-03     9.969
 2    4.000   0.61203E-03   0.308   0.306    0.56   3.6203   0.15946E-03   0.16036E-03     9.972
 3    8.000   0.12426E-02   0.500   0.502   -0.31   3.5791   0.15929E-03   0.15889E-03     9.951
 4    8.000   0.12432E-02   0.500   0.502   -0.42   3.5793   0.15929E-03   0.15875E-03     9.951
 5   10.000   0.15825E-02   0.579   0.591   -0.22   3.5767   0.15921E-03   0.15895E-03     9.932
 6   10.000   0.15817E-02   0.580   0.580   -0.11   3.5765   0.15921E-03   0.15908E-03     9.932
 7   12.000   0.19384E-02   0.649   0.650   -0.10   3.5785   0.15911E-03   0.15901E-03     9.907
 8   12.000   0.19351E-02   0.651   0.649    0.28   3.5778   0.15911E-03   0.15942E-03     9.907
 9   14.000   0.23143E-02   0.708   0.712   -0.52   3.5834   0.15901E-03   0.15850E-03     9.878
10   16.000   0.27007E-02   0.762   0.767   -0.61   3.5887   0.15891E-03   0.15835E-03     9.847
11   16.000   0.26967E-02   0.764   0.766   -0.27   3.5881   0.15891E-03   0.15867E-03     9.847
12   18.000   0.30807E-02   0.819   0.814    0.72   3.5920   0.15881E-03   0.15943E-03     9.812
13   20.000   0.34867E-02   0.863   0.858    0.68   3.5978   0.15871E-03   0.15925E-03     9.776
14   20.000   0.34884E-02   0.863   0.858    0.56   3.5980   0.15871E-03   0.15915E-03     9.776
15   22.000   0.39016E-02   0.903   0.897    0.65   3.6035   0.15860E-03   0.15908E-03     9.737
16   24.000   0.43364E-02   0.933   0.934   -0.16   3.6102   0.15849E-03   0.15838E-03     9.696
17   24.000   0.43344E-02   0.934   0.934   -0.02   3.6100   0.15849E-03   0.15847E-03     9.696
18   26.000   0.47619E-02   0.967   0.966    0.12   3.6150   0.15837E-03   0.15845E-03     9.655
19   28.000   0.52026E-02   0.994   0.996   -0.18   3.6204   0.15826E-03   0.15815E-03     9.612
20   28.000   0.51979E-02   0.997   0.996    0.10   3.6200   0.15826E-03   0.15832E-03     9.612
21   30.000   0.56427E-02   1.022   1.023   -0.10   3.6250   0.15814E-03   0.15808E-03     9.568
22   32.000   0.60823E-02   1.050   1.048    0.25   3.6290   0.15803E-03   0.15817E-03     9.523
23   32.000   0.60766E-02   1.053   1.047    0.56   3.6286   0.15803E-03   0.15834E-03     9.524
24   34.000   0.65471E-02   1.065   1.071   -0.50   3.6342   0.15791E-03   0.15764E-03     9.477
25   36.000   0.65954E-02   1.089   1.091   -0.17   3.6378   0.15779E-03   0.15770E-03     9.431
26   36.000   0.65906E-02   1.092   1.091    0.07   3.6375   0.15779E-03   0.15783E-03     9.431
27   38.000   0.74501E-02   1.110   1.110   -0.00   3.6414   0.15767E-03   0.15767E-03     9.384
28   40.000   0.78964E-02   1.135   1.127    0.72   3.6442   0.15755E-03   0.15788E-03     9.338
29   40.000   0.78964E-02   1.135   1.127    0.72   3.6442   0.15755E-03   0.15788E-03     9.338
30   42.000   0.83963E-02   1.138   1.144   -0.50   3.6490   0.15743E-03   0.15721E-03     9.289
31   44.000   0.88484E-02   1.156   1.159   -0.26   3.6520   0.15731E-03   0.15720E-03     9.240
32   46.000   0.93330E-02   1.162   1.173   -0.93   3.6558   0.15718E-03   0.15680E-03     9.191
33   46.000   0.93308E-02   1.163   1.172   -0.84   3.6557   0.15718E-03   0.15684E-03     9.191
34   48.000   0.97884E-02   1.182   1.185   -0.18   3.6580   0.15706E-03   0.15699E-03     9.143
35   50.000   0.10271E-01   1.189   1.196   -0.56   3.6612   0.15693E-03   0.15672E-03     9.093
36   50.000   0.1026[illegible]E-01   1.192   1.196   -0.35   3.6610   0.15693E-03   0.15680E-03     9.093
37   52.000   0.10750E-01   1.199   1.207   -0.66   3.6640   0.15681E-03   0.15657E-03     9.043
38   54.000   0.11213E-01   1.216   1.216   -0.02   3.6660   0.15669E-03   0.15668E-03     8.994
39   54.000   0.11213E-01   1.216   1.216   -0.02   3.6660   0.15669E-03   0.15668E-03     8.994
40   56.000   0.11706E-01   1.218   1.225   -0.58   3.6690   0.15656E-03   0.15636E-03     8.943
41   60.000   0.12690E-01   1.228   1.240   -0.96   3.6740   0.15630E-03   0.15600E-03     8.841
42   62.000   0.13159E-01   1.237   1.246   -0.71   3.6760   0.15618E-03   0.15596E-03     8.790
43   62.000   0.13153E-01   1.240   1.246   -0.46   3.6758   0.15618E-03   0.15604E-03     8.790
44   64.000   0.13609E-01   1.261   1.252    0.72   3.6770   0.15606E-03   0.15627E-03     8.741
45   70.000   0.15072E-01   1.276   1.266    0.80   3.6830   0.15568E-03   0.15589E-03     8.586

    (I)    BETA(I)     LOG BETA(I)   SIGMA(I)       K(I)       LOG K(I)    K(I)/K(I+1)

     1   0.6600E 03     2.81952     0.150E 01    0.6600E 03    2.81952       10.505
     2   0.4146E 05     4.61764     0.404E 03    0.6282E 02    1.79812       -5.139
     3  -0.5069E 06    ********     0.348E 05   -0.1223E 02   ********     *********

    THE NUMBER OF ITERATIONS =  10          SMIN =  0.1700E 02

     NO POINTS ELIMINATED
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