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The chelation of Cu(II) with 1, 3-bis(tris(hydroxymethyl)methylamino)-2-propanol and 1, 3-bis (2-hydroxyethylamino)-2-propanol

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"The Chelation of Cu(II) with 1, 3-bis(tris(hydroxymethyl)methylamino)-2-propanol and 1, 3-bis(2-hydroxyethylamino)-2-propanol"

by

David Andrew Jackson, Jr.

THESIS

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ABSTRACT

The chelating agent 1, 3-bis(2-hydroxyethylamino)-2-propanol dihydrochloride was prepared and preliminary examinations of the Cu(II) and Fe(III) complexes were carried out spectrophotometrically. This dihydrochloride as well as 1, 3 bis(tris(hydroxymethyl)methylamino)-2-propanol dihydrochloride, were converted from the chloride salts to their corresponding ammonium bases. The conversion was carried out by passing an aqueous solution of each chloride salt through an ion exchange column containing Amberlite XE-78 resin. Solutions of these bases were standardized for use in potentiometric titrations. Each ammonium base was titrated with standard perchloric acid at 20°C, 30°C, and 40°C. The dissociation constants were calculated using these data. Aqueous solutions of Cu(II) at low pH were titrated with the standardized ammonium bases at 20°C, 30°C and 40°C. These data were used to calculate the stability constants of the Cu(II) complexes.

Comparisons of the two copper chelates were made with respect to their thermodynamic properties calculated from the stability constants. Possible structures of the copper (II) complexes are proposed.

INTRODUCTION

It is the purpose of this study to determine the factors influencing the chelation of Cu(II) with 1, 3-bis(2-hydroxyethylamino)-2-propanol. To determine these factors, potentiometric measurements were made in order to calculate 1) the equilibrium constants of the chelating agent, 2) the stability constant of the complex, and 3) the associated thermodynamic properties. Copper solutions were used because copper ions are strongly chelated, while at the same time a highly colored complex is formed thus facilitating spectrophotometric studies.

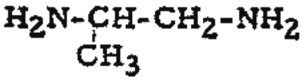
The chelating agent 1, 3-bis(2-hydroxyethylamino)-2-propanol, which we have given the trivial name "Bismon", is the first member in a series of substituted 1, 3-diamino-2-propanols. Beginning with CH_3-NH-CH_2-CHOH-CH_2-NH-CH_3, if one hydrogen atom from each of the terminal methyl groups were substituted by hydroxymethyl groups, then the resulting compound (HO-CH_2)-CH_2-NH-CH_2-CHOH-CH_2-NH-CH_2-(CH_2OH) is Bismon. Subsequent substitution of a hydrogen atom from each of these same carbon atoms by another hydroxymethyl group yields the second member in the series which has not yet been prepared. Finally, if the last hydrogens on these two carbon atoms were replaced by hydroxymethyl groups, the resulting compound (HO-CH_2)$_3$ C-NH-CH_2-CHOH-CH_2-NH-C(CH_2OH)$_3$ is 1, 3 bis(tris(hydroxymethyl)methylamino)-2-propanol. The trivial name for the latter compound is Disec(26)(27) since the reagent is a diamino secondary alcohol.

In order to understand the behavior of Bismon and Disec, we have reviewed the chelating properties of the aliphatic diamines and hydroxydiamines with Cu(II). Because substitution in a chelating agent directly influences the stability of the chelate, correlation of stability and structure is important. A comparison of the Cu(II) chelates having various diamino ligands is desirable in that the values for the stability constants are direct measurements of the effect of substitution within the structure of the chelating agent.

It is to be expected that the diamines have been studied extensively. In a series of papers concerning the steric effects and stability of Cu(II) complexes, Basolo and Murmann(3) have found that alkyl or aryl substitution on the carbon atoms of ethylenediamine, had a relatively small effect on the ligand's coordination tendency toward Cu(II). A single alkyl substitution seemed to increase the stability of the Cu(II) complexes to some extent.

log $K_{0°C}$ ethylenediamine = 21.29 $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$

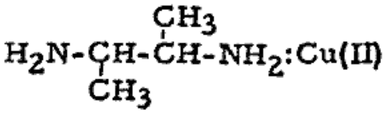
log $K_{0°C}$ propylenediamine = 21.77



$H_2N\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}NH_2$

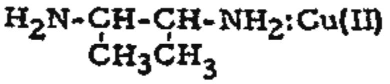
However, a second alkyl substitution seemed to result in an appreciable increase of stability only if there was a racemic mixture formed.

log K



$H_2N\text{-}\underset{CH_3}{CH}\text{-}\overset{CH_3}{CH}\text{-}NH_2\text{:Cu(II)}$ = 22.87 @ 0°C (dl-buen) *

log K



$H_2N\text{-}\underset{CH_3}{CH}\text{-}\underset{CH_3}{CH}\text{-}NH_2\text{:Cu(II)}$ = 21.55 @ 0°C (meso-buen) *

The methyl groups of the dl-buen-Cu(II) complex are on opposite sides of the chelate ring. For the meso-buen-Cu(II) complex both methyl groups are on the same side of the chelate ring, resulting in a crowding of the adjacent groups. This apparent internal strain was noted by a smaller increase in the stability

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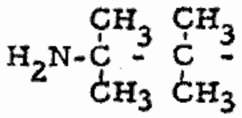
* en = ethylenediamine
buen = butylethylenediamine

constants of the two forms.

To test this hypothesis, the chelating tendencies of tetramethylethylenediamine and isobutylethylenediamine with Cu(II) were studied.

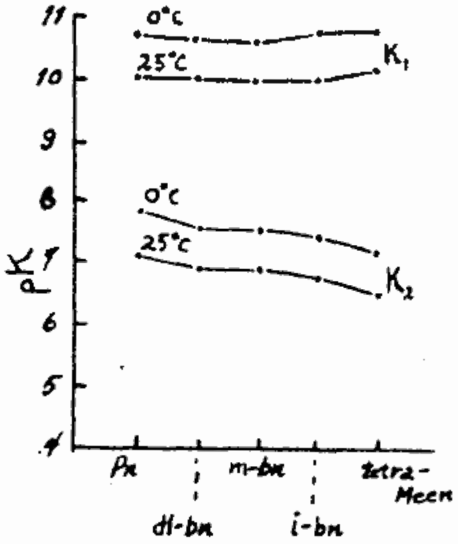


$$\log K \quad H_2N\text{-}C(CH_3)_2\text{-}C(CH_3)_2\text{-}NH_2\text{:Cu(II)} = 23.85 \text{ @ } 0°C$$

$$\log K \quad H_2N\text{-}CH_2\text{-}C(CH_3)_2\text{-}NH_2\text{:Cu(II)} = 21.19 \text{ @ } 0°C$$

It was noted that the tetrameen[*]-Cu(II) complex was more stable than the i-buen[*]-Cu(II) complex. Therefore, the apparent internal strain must not have been the most important factor.

Consideration of the basicities(2)(4) of the ligands did not seem to be the determining factor for the unusually high stability of tetrameen-Cu(II) complex, for tetrameen was found to be a weaker base than all other bases studied in aqueous solution.



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[*] tetrameen = tetramethyethylenediamine
i-buen = isobutylethylenediamine

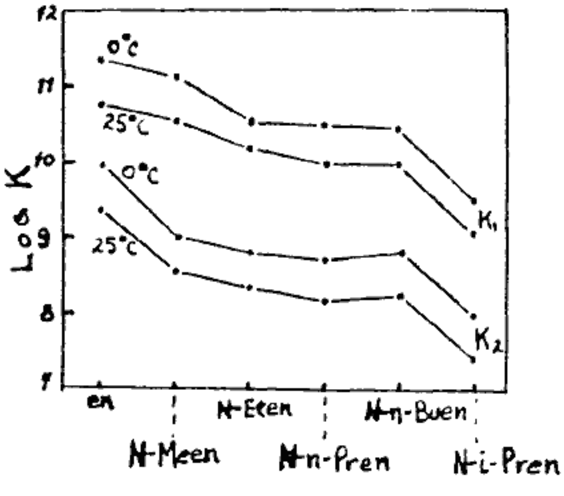
An increase in the number of carbon atoms between the amine groups appeared to decrease stability of the Cu(II) complexes. In comparing the stability constants of various Cu(II) diamine complexes, it was found(14) that the log K for the Cu(II)-ethylenediamine complex had a value 19.60, whereas the log K for trimethylenediamine-Cu(II) was smaller. No value was listed for the Cu(II)-tetramethylenediamine complex.

log K $H_2N\text{-}CH_2CH_2\text{-}NH_2\text{:}Cu(II) = 19.60$ @ 0°C

log K $H_2N\text{-}CH_2CH_2CH_2\text{-}NH_2\text{:}Cu(II) = 16.62$ @ 0°C

log K $H_2N\text{-}CH_2CH_2CH_2CH_2\text{-}NH_2\text{:}Cu(II) =$ ———

A similar decrease in stability is noted when substitution is at the amine groups. A study(6) of N-alkylethylenediamine-Cu(II) complexes makes this apparent by subsequent substitution of methyl, ethyl, n-propyl, n-butyl, and i-propyl groups on a single amine group of ethylenediamine.



Two very interesting facts exist concerning the general trend of the stabilities in going from N-n-Pren*, N-n-Buen to N-i-Pren* derivatives. It was first

* Pren = n-propylethylenediamine
i-Pren = isopropylethylenediamine

noticed that the N-n-butylethylenediamine-Cu(II) complex was more stable than the N-n-propylethylenediamine-Cu(II) complex.

log K $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}C_3H_7:Cu(II) = 19.19$ @ 0°C

log K $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}C_4H_9:Cu(II) = 19.29$ @ 0°C

The authors attribute this to the coiling of the four carbon chain around the central copper ion thus shielding it from the solvent.

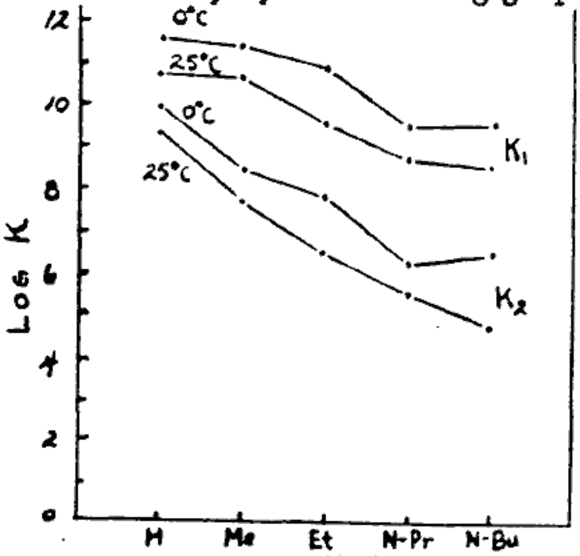
It was also noticed that straight-chain N-alkylethylenediamine-Cu(II) complexes had only slight differences in stabilities. However, if the alkyl substituent was branched, the stability of the complex was greatly reduced. This was the case for the Cu(II)-N-i-propylethylenediamine complex where the log $K_{0°C} = 17.46$. It was assumed that the branched propyl group prevented the close association of the central metal ion and ligand, thus causing steric hindrance.

Examination(5) of the N, N'-dialkylethylenediamine-Cu(II) complexes makes it apparent that alkyl substitution on the second amine group causes a further over-all decrease in chelate stability. For instance:

log K_T $CH_3\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_3 : Cu(II) = 19.53$ @ 0°C

log K_T $C_2H_5\text{-}NH\text{-}CH_2CH_2\text{-}NH\text{-}C_2H_5 : Cu(II) = 18.69$ @ 0°C

This may be seen more clearly by the following graph:



Again, the N, N'-dibutylethylenediamine derivative shows a greater stability compared with the N, N'-dipropylethylenediamine derivative.

log K $C_3H_7\text{-NH-}CH_2CH_2\text{-NH-}C_3H_7\text{:Cu(II)} = 15.54$ @ 0°C

log K $C_4H_9\text{-NH-}CH_2CH_2\text{-NH-}C_4H_9\text{:Cu(II)} = 15.98$ @ 0°C

Continued alkyl substitution (14) on the same amine group resulted in still a further decrease in stability of the N, N-dialkylethylenediamine-Cu(II) complex. For instance:

log K $H_2N\text{-}CH_2\text{-}CH_2\text{-N(}CH_3)_2\text{:Cu(II)} = 16.34$ @ 25°C

log K $H_2N\text{-}CH_2CH_2\text{-N(}C_2H_5)_2\text{:Cu(II)} = 13.84$ @ 25°C

Consideration of stability constant values therefore, indicates a definite trend with substitution. In general, the following statements may be assumed to be true:

1. Alkyl substitution on carbon atoms connecting the two amines results either in an increase of stability, or no appreciable change.
2. An increase in the length of the hydrocarbon chain between the amine groups results in a decrease of stability of the complex due to internal strain within the chelate ring.
3. Alkyl substitution on the amine groups decreases stability proportionately to the number of alkyl groups substituting, as well as the size of the alkyl groups.

Steric hindrance is only one of several factors (23) influencing chelate stability. More than one factor may be in operation at one time. For instance, the basicity of the ligand is indicated by consideration of the dissociation constants of the ligand. The values of the dissociation constants vary with different alkyl substitutions, and the influence of substituted alkyl groups on basicity should be in agreement with results obtained for the stability of the Cu(II) chelates,(7)(4) i.e. the stronger the base the greater the stability of the Cu(II) chelate. This is not always the case, however. For instance, ethylene diamine is a weaker base than 1,3 diaminopropane.(8)

pK_d ethylenediamine = 17.67 @10°C

pK_d 1,3 diaminopropane = 19.97 @10°C

Yet, the stability of the Cu(II)-ethylenediamine complex is greater than the stability of the Cu(II) 1,3 diaminopropane complex. The reason for the apparent disregard of ligand basicity, is due to an increase in the internal strain with the formation of a six membered ring by 1,3 diamino propane. It has been demonstrated that, in general, five membered chelate rings are ~~the most rings occ~~ the most stable for the complexes having aliphatic ligands.(24)

The ability of ethylenediamine to form stable five membered rings with Cu(II) has been emphasized recently by studies(19) on hexacoordinate Cu(II) in trisethylenediamine sulfate. The compound was studied by infrared as well as by visible spectrophotometric methods. Optical rotation studies also were conducted. Mention should be made that $Cu(en)_3SO_4 . H_2O$ crystals had to be grown in an 80% solution of ethylenediamine. An octahedral structure is proposed for the compound.

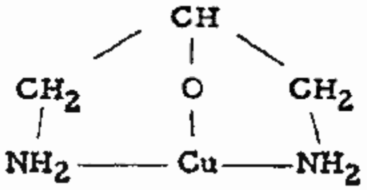
Very little work, up to this time, has been done on aliphatic hydroxy diamine-Cu(II) complexes. In a study of metal complexes with 1,3 diamino-2-propanol, Fernelius(18) et. al. found that 1,3 diamino propanol was a weaker base than 1, 3 diamino propane or 2, 2-dimethyl-1, 3-propane diamine.

pK_d $(H_2NCH_2)_2CHOH$ = 19.79 @ 0°C

pK_d $(H_2NCH_2)_2CH_2$ = 21.55 @ 0°C

pK_d $(H_2NCH_2)C(CH_3)_2$ = 20.29 @ 0°C

All metal complexes so far discussed, except the Cu(II) complex of 1, 3 diamino-2-propanol approached the expected value of $\bar{n} = 2$* . The value obtained Cu(II) complex was $\bar{n} = 1.5$. In a separate study of the Cu(II) - 1, 3 diamino-2-propanol system, the authors suggest that this anomalous value for $\bar{n}$ arises from the ligand acting as a terdentate complexing agent. In this case the hydroxyl group takes an active part in the chelation of the metal, but in so doing, the structure is non-planar.



This forced non-planar configuration meant that the copper ion was held more weakly than if it were in a planar configuration which is normal for most copper complexes.

The value for the entropy change should have increased since the number of rings in the chelate was increased. However, it is stated that this increase was offset by the entropy decrease caused by the forced non-planar structure.

It is of interest to inspect several substituted 1, 3 diamino-2-propanol-Cu(II) complexes in order to understand more fully the importance of the secondary alcohol group in chelate formation. With this question in mind,

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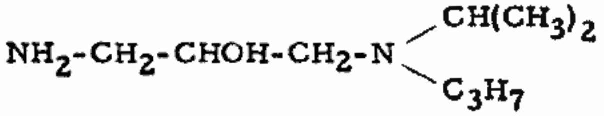
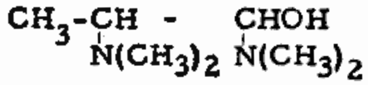
* $\bar{n}$ = average number of ligand molecules bound per metal ion

studies on Disec and Bismon have been carried out. Further studies are desirable with Cu(II)-polyhydroxy diamines. Listed below are a number of compounds which may be of future interest.

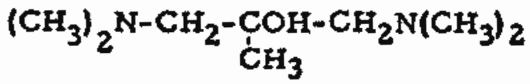
$C_2H_5\text{-}NH\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}NH_2$ (31)

$(R)_2N\text{-}CH_2\text{-}CHOH\text{-}CH_2N(R)_2$
$R = (C_nH_{2n-1})$ from n = 1 to 10 (17),(25)



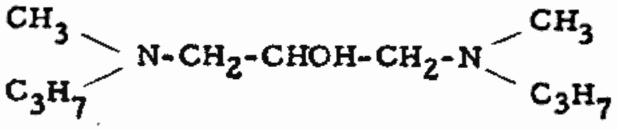


$CH_3\text{-}\underset{N(CH_3)_2}{CH}\text{ - }\underset{N(CH_3)_2}{CHOH}$ (17)

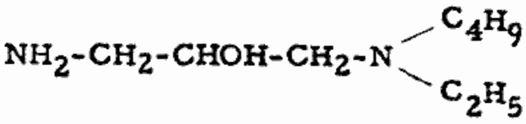


$(CH_3)_2N\text{-}CH_2\text{-}\underset{CH_3}{COH}\text{-}CH_2N(CH_3)_2$ (17)

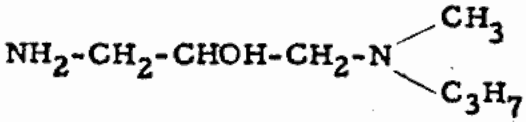
$(CH_3)_2\text{-}N\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}N(CH_3)_2$ (17)



$(HO\text{-}C_2H_4)_2N\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}N(C_2H_4\text{-}OH)$ (26)



(29)



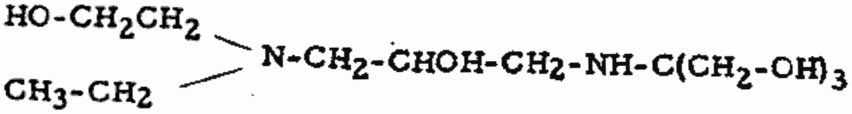
(29)

$(C_2H_5)_2N\text{-}CH_2\text{-}CHOH\text{-}CH_2N(C_2H_5)_2$ (1)

$C_3H_7\text{-}NH\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}NH\text{-}C_3H_7$ (27)

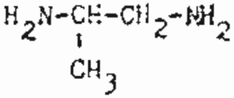
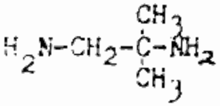
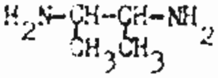
$(HO\text{-}CH_2CH_2)_2N\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}NH\text{-}C(CH_2OH)_3$ (26)

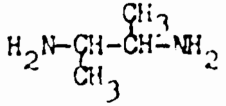
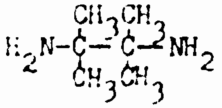
$((HO\text{-}CH_2CH_2)_2N\text{-}CH_2)_2CHOH$ (26)



(26)

Diamine	Dissocia. Constants		Cu(II) Chelate Stability Constants			Thermodynamic Properties						t°C	μ	Ref.
	pk_1	pk_2	Form	log k_1	log k_2	$-\Delta F_1$	$-\Delta F_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2			
ethylenediamine $H_2N-CH_2CH_2-NH_2$	7.98	10.73	MA_2	11.34	9.95	14.16	12.43	8.6	8.6	21	14	0		
	7.47	10.18		10.76	9.37							25	0.5	6+7
N-Methyl-en $H_2N-CH_2CH_2-NH-CH_3$	8.00	10.83	MA_2	11.12	9.03	13.89	11.28	8.5	7.0	20	16	0	0.5	"
	7.56	10.40		10.55	8.56							25		
N-Ethyl-en $H_2N-CH_2CH_2-NH-C_2H_5$	8.16	11.11	MA_2	10.55	8.81	13.18	11.00	5.4	6.4	29	17	0	0.5	"
	7.63	10.56		10.19	8.38							25		
N-n-Propyl-en $H_2N-CH_2CH_2-NH-C_3H_7$	8.24	11.04	MA_2	10.49	8.70	13.10	10.87	7.6	8.0	20	11	0	0.5	"
	7.54	10.34		9.98	8.16							25		
N-n-Butyl-en $H_2N-CH_2CH_2-NH-C_4H_9$	8.11	10.93	MA_2	10.47	8.82	13.08	11.02	8.0	8.2	19	12	0	0.5	"
	7.53	10.30		9.94	8.27							25		
N-i-Propyl-en $H_2N-CH_2CH_2-NH-CH(CH_3)_2$	8.30	11.15	MA_2	9.46	8.00	11.82	9.99	5.8	8.2	22	7	0	0.5	"
	7.70	10.62		9.07	7.45							25		
NN'-dimethyl-en $CH_3-NH-CH_2-CH_2-NH-CH_3$	8.30	10.89	MA_2	11.22	8.31	-	-	-	-	-	-	0	0.5	4+5
	7.47	10.29		10.47	7.63							25		
NN'-diethyl-en $C_2H_5-NH-CH_2CH_2-NH-C_2H_5$	8.53	11.06	MA_2	10.84	7.85	23.30		17.5		21		0	0.5	"
	7.70	10.46		9.30	6.32							25		
NN'-di-n-Propyl-en	8.14	10.97	MA_2	7.39	6.15	-	-	-	-	-	-	0	0.5	"
	7.53	10.27		8.79	5.55							25		

Diamine	Dissocia. Constants		Cu(II) Chelate Stability Constants			Thermodynamic Properties						t°C	μ	Ref.
	pk_1	pk_2	Form	$\log k_1$	$\log k_2$	$-\Delta F_1$	$-\Delta F_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2			
NN'-di-i-Propyl-en	8.26 7.59	11.12 10.40	MA_2	-	-	-	-	-	-	-	-	0 25	0.5	4+5
NN'-di-n-Butyl-en	8.13 7.46	10.93 10.19	MA_2	9.44 8.67	6.54 4.84	-	-	-	-	-	-	0 25	0.5	"
N,N-dimethyl-en $H_2N-CH_2CH_2-N(CH_3)_2$	6.63	9.53	MA_2	9.69	6.65	-	-	-	-	-	-	25	0.1	"
N,N-diethyl-en $H_2N-CH_2-CH_2-N(C_2H_5)_2$	7.07	10.02	MA_2	8.17	5.67	-	-	-	-	-	-	25	0.1	"
Propylenediamine  $H_2N-CH(CH_3)-CH_2-NH_2$	7.00	9.78	MA_2	10.58	9.08	-	-	-	-	-	-	30	0.5	13
(as above)	7.81 7.13	10.76 10.00	MA_2	11.55 10.78	10.12 9.28	-	-	-	-	-	-	0 25	0.5	3+4
2,2-Dimethyl-1,2-diaminoethane  $H_2N-CH_2-C(CH_3)_2-NH_2$	7.41 6.79	10.74 10.00	MA_2	11.31 10.53	9.88 9.05	-	-	-	-	-	-	0 25	0.5	"
Meso-2,3-diaminobutane  $H_2N-CH(CH_3)-CH(CH_3)-NH_2$	7.55 6.92	10.63 9.97	MA_2	11.50 10.72	10.05 9.34	-	-	-	-	-	-	0 25	0.5	"

Diamine	Constants		Stability Constants											
	pk_1	pk_2	Form	log k_1	log k_2	$-F_1$	$-F_2$	$-H_1$	$-H_2$	S_1	S_2			
Racemic-2,3-diaminobutane	7.60	10.69	MA_2	12.22	10.65	-	-	-	-	-	-	0	0.5	3+4
 $H_2N-CH(CH_3)-CH(CH_3)-NH_2$	6.91	10.00		11.39	9.82							25		
Tetramethyl-en	7.18	10.73	MA_2	12.22	10.88	29.9		24.4		19		0	0.5	〃
 $H_2N-C(CH_3)_2-C(CH_3)_2-NH_2$	6.56	10.13		11.63	10.24							25		
Trimethylene-diamine $H_2N-(CH_2)_3-NH_2$	9.69 @0°C	11.5 @0°C	MA_2	10.52 @0°C	7.94 @0°C	13.2	9.71	12.5	12.3	2.3	-8.7			15
	8.21@ 49.1°C	9.95@ 49.1°C		9.00@ 49.1°C	6.45@ 49.1°C	±.02	±.04	±.5	±.5	±1.7	±1.7	25	.15	
(as above)	9.0	10.7	MA_2	9.8	7.1	-	-	-	-	-	-			21
(as above)	9.95	11.60	MA_2	10.74	8.05	13.3	9.7	14	13	-3	-12	0	1.0	20
	8.95	10.54		9.62	7.00							30		
2,2-dimethyl 1,3 diamino-	9.07	11.22		10.95	8.25							0		〃
propane	8.18	10.22	MA_2	9.94	7.45	13.8	10.3	12	12	7	- 7	30	1.0	
$H_2N-CH_2-C(CH_3)_2-CH_2-NH_2$	7.55	9.65		9.41	6.86							50		

Diamine	Dissocia. Constants		Cu(II) Chelate Stability Constants			Thermodynamic Properties						t°C	μ	Ref.
	pk_1	pk_2	Form.	$\log k_1$	$\log k_2$	$-\Delta F_1$	$-\Delta F_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2			
1,3 diamino-2-propanol $H_2N-CH_2CHOHCH_2-NH_2$	8.12 ±.04	9.96 ±.05	MA	3.72 ±.03	-	4.9	-	5.2	-	-1	-	10	-	9
	7.93 ±.02	9.69 ±.03		3.64 ±.03								20		
	7.68 ±.02	9.42 ±.06		3.57 ±.17								30		
	7.38 ±.05	9.14 ±.00		3.34 ±.07								40		
1,3 bis(2-hydroxyethyl amino)-2-propanol $(HOCH_2CH_2-NH-CH_2)_2$ CHOH	7.10 ±.12	8.80 ±.01	MA	13.51	-	18.12		22.4		-14.6		20	-	This Paper
	6.90 ±.12	8.77 ±.01		13.37		18.54				-12.7		30		
	6.63 ±.04	8.51 ±.03		12.44		17.83				-14.6		40		
1,3 bis(tris(hydroxymethyl) methylamino)-2-propanol $[(HOCH_3)C-NH-CH_2]_2$ CHOH	6.15 ±.01	8.15 ±.08	MA	11.62	-	15.58		14.68		3.07		20	-	"
	5.89 ±.03	7.94 ±.10		11.23		15.58				2.97		30		
	5.67 ±.09	7.72 ±.12		10.91		15.63				3.04		40		

EXPERIMENTAL

Preparation of Chelating Agents

(A) Reagents:

Sodium Hydroxide - Reagent grade, Carbon dioxide-free solution, standardized against potassium acid phthalate primary analytical reagent, Mallinckrodt.

Ethanol Amine - Eastman Organic Chemicals, # Distillation Products Industries.

Acetone - Analytical Reagent grade, Mallinckrodt Chemical Products.

Acetic Anhydride - Analytical Reagent grade, Mallinckrodt Chemical Products.

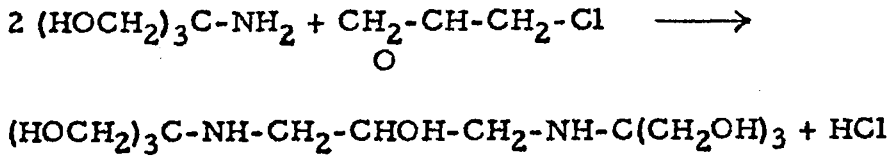
Epichlorohydrin - Shell Chemical Corporation.

Hydrochloric acid - Reagent grade, "Baker Analyzed" reagent, J. T. Baker Chemical Co.

Pyridine - Reagent grade, "Baker Analyzed reagent, J. T. Baker Chemical Co.

(B) Procedure

Disec: The method for preparing Disec was followed exactly as Pierce and Wotiz (26) described. The procedure involved the reaction of epichlorohydrin with tris (hydroxymethyl) methylamine in alcohol. The dihydrochloride was separated from solution by precipitation with HCl. Recrystallization from hot alcohol was necessary for the pure compound. The Disec used for this experiment was from the third recrystallization. The melting point of the recrystallized compound was exactly 188° C, compared to the listed value of 184-186° C.

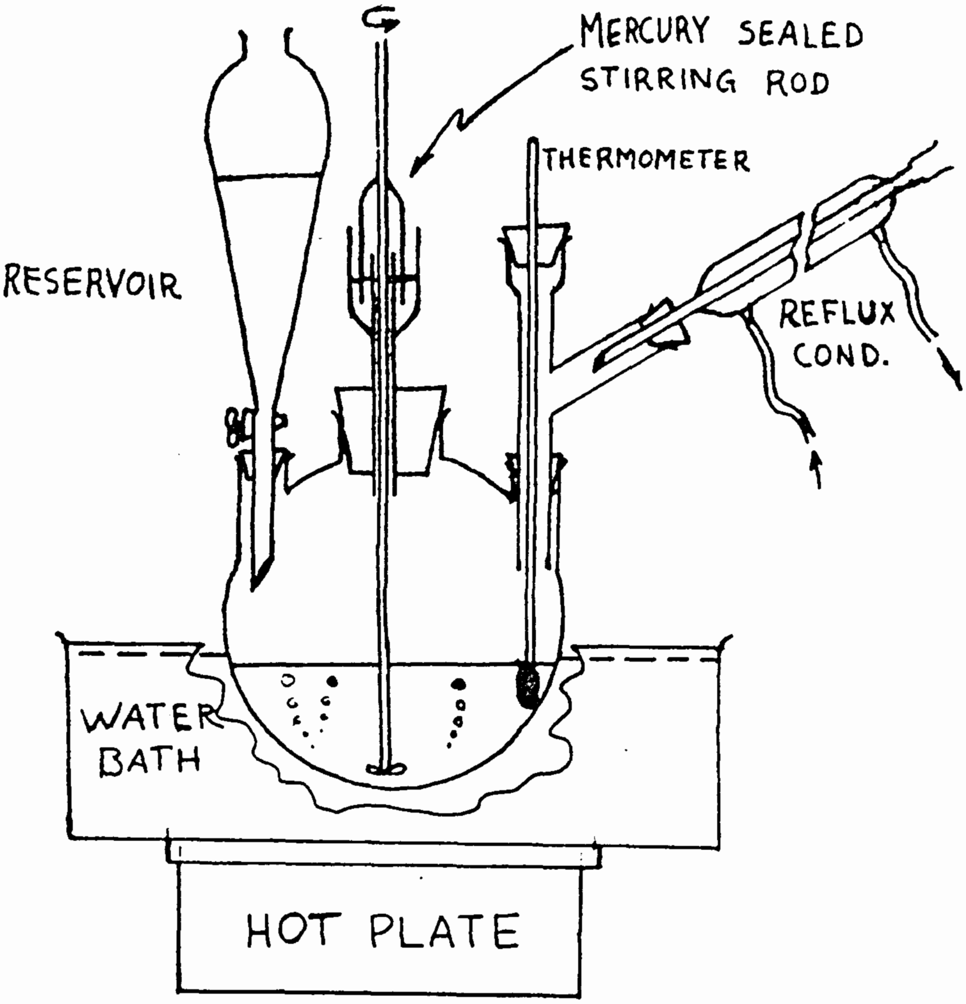


$$2\ (HOCH_2)_3C\text{-}NH_2 + \underset{O}{CH_2\text{-}CH}\text{-}CH_2\text{-}Cl \longrightarrow$$

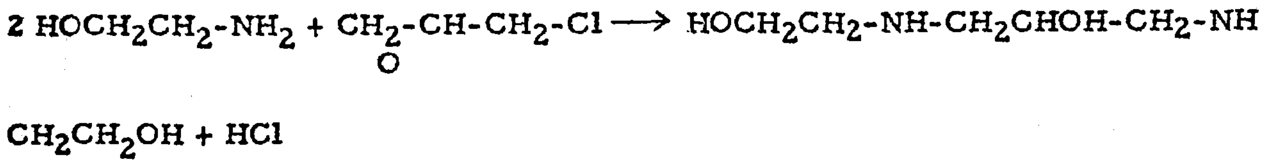
$$(HOCH_2)_3C\text{-}NH\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}NH\text{-}C(CH_2OH)_3 + HCl$$

Bismon: 122 grams of ethanolamine and 100 ml of 95% ethanol were placed in a 3 neck 500 ml round bottom flask. The center neck was fitted with a mercury sealed stirring rod. One neck was fitted with a separatory funnel which served as a reservoir for the epichlorohydrin. The remaining neck was fitted with a combination reflux condenser and thermometer, (see diagram on the following page). The flask was immersed in cold water during the addition of the epichlorohydrin since the reaction was greatly exothermic. The entire apparatus was placed under a hood because of the toxicity of epichlorohydrin. The epichlorohydrin was added slowly from the separatory funnel while the reaction mixture was stirred vigorously. The temperature was kept between 20° C and 30° C throughout this addition by adding ice to the water bath. On complete addition of the epichlorohydrin, the mixture was allowed to remain at room temperature overnight. The mixture was then refluxed in a water bath for six hours, allowed to cool, and transferred to a one liter beaker. To the mixture were added slowly, with stirring, 160 ml of 95% ethanol and 160 ml of reagent grade concentrated HCl. The dihydrochloride separated as a viscous oil; the supernatant liquid was decanted and discarded.

Crystallization was slow, therefore the oil was allowed to stand for four to five days. Separation of the crystals from the oil was carried out by filtering with suction. Washing the crystals with Reagent grade acetone was necessary,


MERCURY SEALED
STIRRING ROD
THERMOMETER
RESERVOIR
REFLUX
COND.
WATER
BATH
HOT PLATE

because the crystals were to some extent soluble in 95% ethanol. The impure crystals were dried over P_2O_5 under reduced pressure. M. P. = 103-120°C



$$2\ HOCH_2CH_2\text{-}NH_2 + \underset{O}{CH_2\text{-}CH}\text{-}CH_2\text{-}Cl \longrightarrow HOCH_2CH_2\text{-}NH\text{-}CH_2CHOH\text{-}CH_2\text{-}NH$$

$$CH_2CH_2OH + HCl$$

(C) Purification

Bismon was purified by successive recrystallization. The crystals were dissolved in the minimum quantity of hot water, and absolute ethanol was added. On cooling, the product separated as a very viscous white syrup. The supernatant liquid was discarded. The white syrup was treated with hot absolute ethanol which partially dissolved the syrup, and the supernatant liquid was added to one liter of acetone. Repeated treatment of the syrup with small portions of absolute ethanol followed by addition of the dissolved portion to acetone, eventually dissolved all of the white syrup. The pure crystals of Bismon formed in the acetone-ethanol mixture within three to four days. The purified crystals were filtered with suction, washed with acetone, and dried over P_2O_5 under reduced pressure. Second and third recrystallizations were carried out. Loss of about half the original amount of impure crystals was caused by the extreme solubility of Bismon in water. The samples were stored in a desiccator with P_2O_5 under reduced pressure. M. P. 139-44° C.

(D) Proof of Purity

Three samples of Bismon were analyzed for carbon and hydrogen by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, New York. The results are as follows:

	Calculated	Found		
		(1)	(2)	(3)
% C = $^{84}/251$ =	33.4	33.2	34.14	34.19
% H = $^{20}/251$ =	7.98	8.27	8.48	8.55

The recrystallized Disec samples were used directly, and assumed to be pure from the melting point data.

(E) Proof of Structure of Bismon

Acetylation procedure of Bismon was carried out according to the method outlined by Ogg, Porter and Willets.(30) The results are as follows:

NaOH = .4869 Normal

Weight of Bismon crystals

Sample #1 = 0.569 gm
Sample #2 = 0.507 gm

Volume of NaOH needed for titrations:

Sample #1,	40.90 ml
Sample #2,	42.00 ml
Blank,	53.30 ml

Calculations:

$$\% \text{ OH} = \frac{\text{A(NaOH)(OH)(100)}}{\text{Gm sample (1000)}}$$

Sample #1

A = 53.3 - 40.9 = 12.4 ml

$$\% \text{ OH} = \frac{(12.4)(.487)(17)(100)}{(.569)\,(1000)} = 18.1\%$$

Sample #2

A = 53.3 - 42.0 = 11.3 ml

$$\% \text{ OH} = \frac{(11.3)(.487)(17)(100)}{(.507)\,(1000)} = 18.4\%$$

$$\text{Theoretical value} = \frac{3\,(OH)}{MW} = \frac{51}{251} = 20.3\%$$

These experimental values are of the same order of magnitude as the theoretical value, and can only serve as an approximate indication of the number of hydroxyl groups within the formula of Bismon. Since the Bismon crystals were hydroscopic it was impossible to keep them dry while weighing. The error due to the amount of water absorbed during this time was large enough to alter the OH percentages greatly. The values were close enough to the theoretical to assume three hydroxyl groups per ligand molecule. Knowing the nature of the reagents used in preparing Bismon and the number of hydroxyl groups per ligand, it was assumed that the reaction for preparing Bismon took place as desired, and that the structure is symmetrical.

Preparation of Solutions

(A) Reagents

Cupric Nitrate - Reagent grade, Baker and Adamson Co., General Chemical Division of Allied Chemical and Dye Corp.

Sodium Hydroxide - Reagent grade, CO_2 free solution standardized against potassium acid phthalate primary standard analytical reagent, Mallinckrodt Chemical Products.

Perchloric Acid - Reagent grade 70% assay, Mallinckrodt Chemical Products.

(B) Standardization

Copper Nitrate - a stock solution of copper nitrate was made up approximately to 0.1 Molar, and standardized by electrodeposition(28) of the copper. Platinum electrodes were used; a current of 0.5 amperes was used overnight since the electrodes remained stationary. The average molarity of the stock solution was 0.1042 Molar.

Perchloric acid - Concentrated $HClO_4$ (70%) was diluted to approximately 0.2 M and 0.02 M and standardized with standard NaOH. The stock solutions used had the following concentrations:

$$M_{HClO_4} = 0.2090$$

$$M_{HClO_4} = 0.0211$$

Stock Solution of Cu^{++}-H^+ mixture - the Cu^{++}-H^+ mixture was made by mixing the following amounts of each stock solution, and diluting to 500 ml final volume.

$$\left.\begin{array}{l}50\text{ ml of }0.0104\text{ N Cu }(NO_3)_2\\ 50\text{ ml of }0.0211\text{ N }HClO_4\end{array}\right\}\begin{array}{c}\text{diluted}\\ \text{to}\\ 500\text{ ml}\end{array}\left\{\begin{array}{l}1.04\times10^{-3}\text{ M }Cu^{++}\\ 2.11\times10^{-3}\text{ M }H^{+}\end{array}\right.$$

Disec Free Base - Approximately 18.55 gm of Disec dihydrochloride was weighed out and dissolved in 500 ml carbon dioxide-free water. This weight of crystals made approximately a 0.1 Molar solution.

MW Disec : 2 HCl = 371
371 gm/l = 1 Molar
37.1 gm/l = 0.1 Molar
18.55 gm/500 ml = 0.1 Molar

The solution was passed through an ion exchange column containing Amberlite XE-78 strong anion exchange resin. After the conversion from chloride to free base took place, the solution was diluted to 1000 ml final volume by passing 500 ml carbon dioxide-free water through the column to wash through any base which remained. The final solution of Disec free base should have been approximately 0.05 M. The exact concentration was determined by a potentiometric titration with standard 0.209 $HClO_4$. The end-point for the titration was found by plotting a differential curve of $\frac{\Delta pH}{\Delta V}$ vs. V ml acid. An example of this is shown on the next page.

Sample calculation for Disec standardization:

N acid = 0.209

V base = 50.0 ml

V acid = 24.0 ml . . . from differential titration curve.

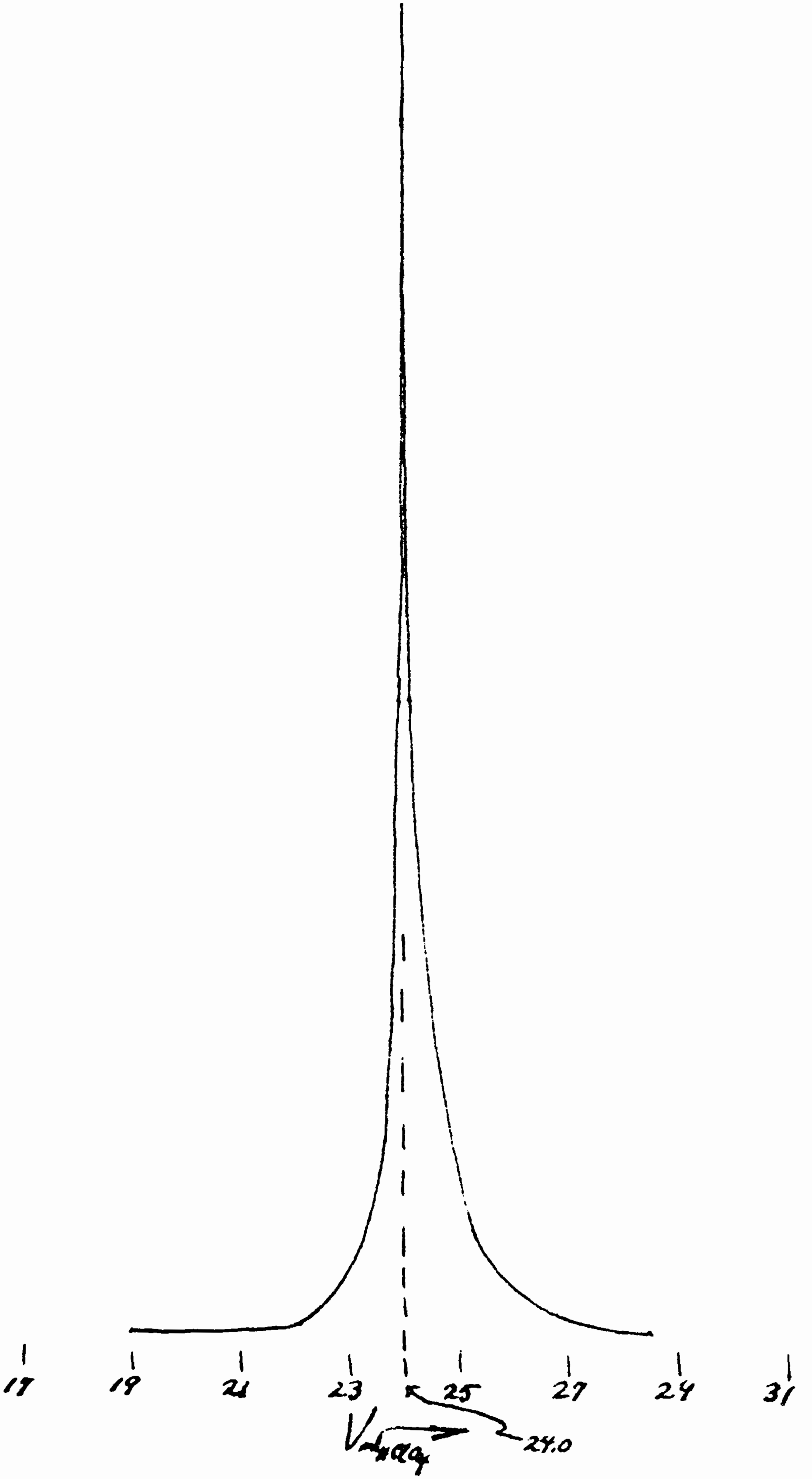
$$N_A V_A = N_B V_B \text{ ; } N_B = \frac{N_A V_A}{V_B} = \frac{(0.209)(24.0)}{50.0} = 0.1003 \text{ Normal}$$

Since there are two amine groups per ligand molecule, then the molarity of the base is one half the normality, i.e. $M = \frac{0.1003}{2} = 0.0501$

Bismon Free Base - the same procedure as that for Disec was followed except that the original weight of Bismon dihydrochloride was approximately 2.513 gms. in 500 ml solution.

M. W. Bismon : 2 HCl = 251
251 gm/l = 1 Molar
25.1 gm/l = 0.1 Molar
2.51 gm/l = 0.01 Molar
2.51 gm/500 ml = 0.02 Molar

Conversion of dyhydrochloride to free base, and dilution to one liter final volume resulted in a solution approximately 0.01 Molar. The exact concentration was determined, as before, by potentiometric titration with standard 0.209 M $HClO_4$. The exact concentration of Bismon free-base was found to be 9.24×10^{-3} Molar. Subsequent preparations of Bismon free base were approximately 0.01 M. The exact concentrations were determined by the same procedure as above


17
19
21
23
25
27
24
31
24.0
V

Potentiometric Titrations

In all cases the titrations were carried out in a nitrogen atmosphere with the temperature varying no more than 0.05 degree. The nitrogen gas was saturated with carbon dioxide-free water vapor before it entered the titration vessel. The temperatures of the solutions being titrated were regulated by circulating water from a constant temperature bath through a water jacket surrounding the titration vessel. For temperature below those of the room, ice water from a reservoir was pumped through the coils of the constant temperature bath. The rate at which the ice water flowed through these coils was regulated by connecting the pump to a Powerstat. A magnetic mixer was used to stir the solutions in the titration vessel, and therefore a concentration gradient was avoided.

It should be pointed out that grounding of all equipment was necessary. Any small charge built up by the electrical pumps, heaters, or mixer caused abnormal deflections of the galvanometer, and inaccuracies in the pH readings The ringstand which held the buret was grounded, as well as the solution itself. The solution was grounded through a piece of platinum wire which was coiled around the thermometer in the titration vessel. A diagram of the apparatus appears at the end of the discussion of potentiometric titrations.

A list of the individual pieces of apparatus follows:

1) Beckman Model G pH meter equipped with a saturated calomel electrode and a Beckman Model E No. 1190-80 glass electrode.

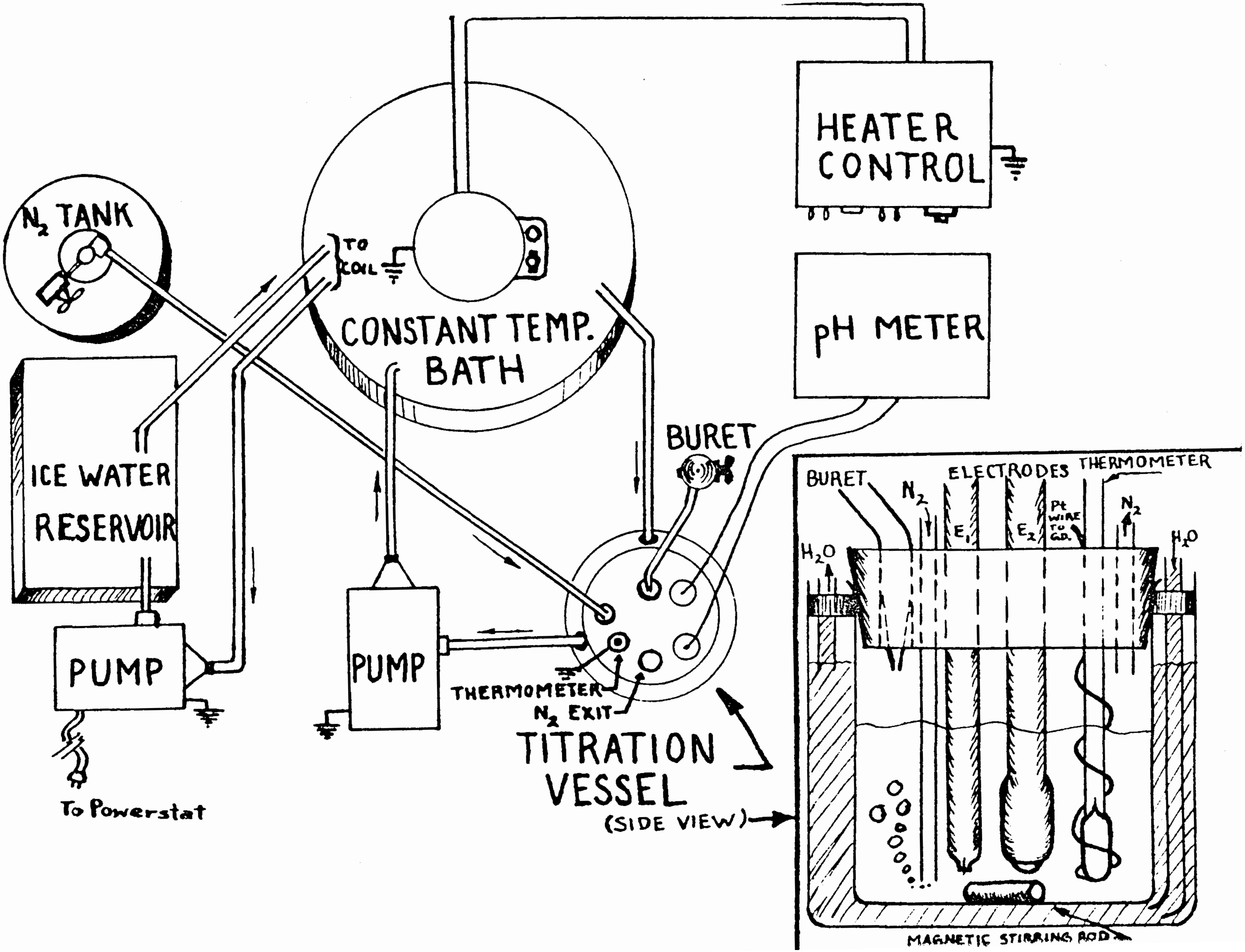
2) Sargent Constant Temperature Water Bath, S-84805, accurate to ± 0.01°C

3) Powerstat-116, Superior Electric Co.

4) Mag-mix magnetic stirrer

5) Eastern Industries water pump, model B-1, type 100, regulated by the Powerstat.

6) Gormann-Rupp water pump, No. 16R1-A8BC8F558, with constant flow.


N$_2$ TANK
TO COIL
CONSTANT TEMP. BATH
HEATER CONTROL
pH METER
ICE WATER RESERVOIR
PUMP
To Powerstat
PUMP
BURET
THERMOMETER
N$_2$ EXIT
TITRATION VESSEL
(SIDE VIEW)
BURET
N$_2$
ELECTRODES
THERMOMETER
E$_1$
E$_2$
Pt WIRE TO GD.
N$_2$
H$_2$O
H$_2$O
MAGNETIC STIRRING ROD

Determination of pK values for the ligands

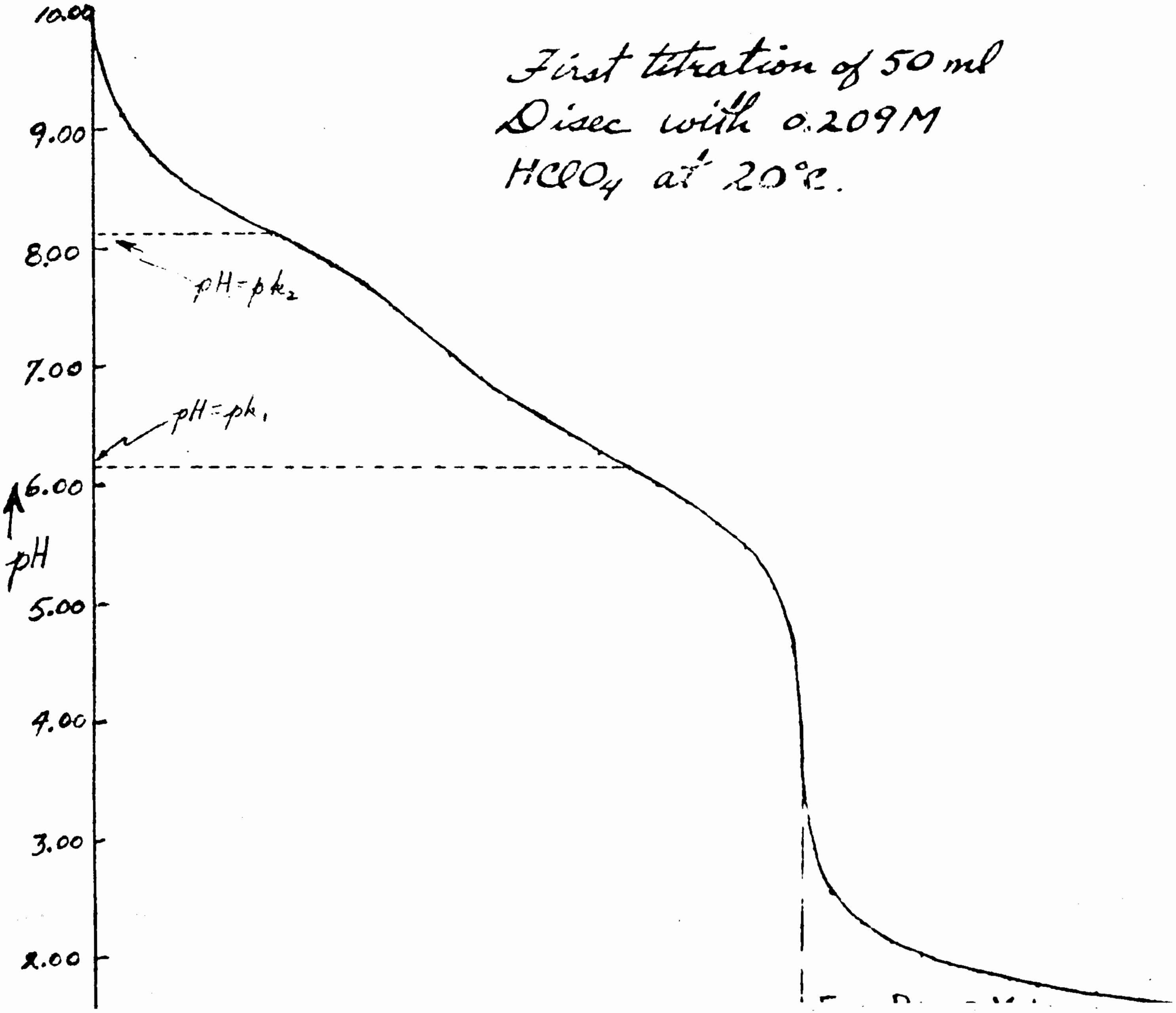
The general procedure for determining the pK values for the two ligands involved the potentiometric titration of 50 ml of the free base with standard perchloric acid. The titrations were run in triplicate at 20°C, 30°C and 40°C; the end-points were determined by plotting the differential curve of V_{HClO_4} vs. $\frac{\Delta pH}{\Delta V}$. The equilibrium constants for the ligands were determined graphically [redacted]e titration curves, and reading the values for k_1, and k_2 directly from the graph. The following equilibria exist, since dissociation takes place in two steps:

$$H_2A^{++} \rightleftharpoons H^+ + HA^+ \text{ [redacted] } ; \; k_2 = \frac{(H^+)\;(HA^+)}{(H_2A^{++})}$$

$$HA^+ \rightleftharpoons H^+ + A \; ; \; k_1 = \frac{(H^+)\;(A)}{(HA^+)}$$

where (A) stands for the free ligand; (HA^+) and (H_2A^{++}) are the protonated species. At the end-point, essentially all the base had been neutralized. At one-fourth the end-point volume $HA^+ = H_2A^{++}$, and $H^+ = k_2$. At three-fourths the end-point volume, $HA^+ = A^+$ and $H^+ = k_1$. By reading the pH values at points one-fourth and three-fourths of the volume of perchloric acid at neutralization, the values for pk_2 and pk_1 were obtained. An example of graphical determination of pk_1 and pk_2 for Disec is given on the next page. From the pH values at 6 ml and 18 ml, pk_2 and pk_1 were obtained.

The following charts summarize the determinations for the constants.



First titration of 50 ml
Disec with 0.209M
$HClO_4$ at 20°c.

EQUILIBRIUM CONSTANTS OF DISEC

SUMMARY OF VALUES OBTAINED FROM GRAPHS

Temp.	Vneut.	V 1/4 neut.	p H (pk$_2$)	log H+	k$_2$=H+
20° C	24.00	6.00	8.12	1.88-10	7.59x10^{-9}
"	24.00	6.00	8.18	1.82-10	6.61x10^{-9}
"	23.98	5.99	8.16	1.84-10	6.92x10^{-9}
30° C	23.95	5.98	8.00	--	1x10^{-8}
"	23.95	5.98	7.92	2.08-10	1.20x10^{-8}
"	23.97	5.99	7.90	2.10-10	1.26x10^{-8}
40° C	23.97	5.99	7.67	2.33-10	2.14x10^{-8}
"	23.96	5.99	7.76	2.24-10	1.74x10^{-8}
"	23.95	5.99	7.74	2.26-10	1.82x10^{-8}

Temp	V 3/4neut.	p H (pk$_1$)	log H+	k$_1$=H+	K$_e$=k$_1$k$_2$	pKe (pk$_1$+pk$_2$)
20°C	18	6.14	3.86-10	7.24x10^{-7}	5.49x10^{-15}	14.26
"	18	6.15	3.85-10	7.08x10^{-7}	4.68x10^{-15}	14.33
"	17.99	6.15	3.85-10	7.08x10^{-7}	4.89x10^{-15}	14.31
30° C	17.96	5.89	4.11-10	1.29x10^{-6}	1.29x10^{-14}	13.89
"	17.96	5.88	4.12-10	1.32x10^{-6}	1.58x10^{-14}	13.80
"	17.98	5.90	4.10-10	1.26x10^{-6}	1.59x10^{-14}	13.80
40° C	17.97	5.62	4.38-10	2.4x10^{-6}	5.14x10^{-14}	13.29
"	17.97	5.69	4.31-10	2.04x10^{-6}	3.55x10^{-14}	13.45
"	17.97	5.69	4.31-10	2.04x10^{-6}	3.71x10^{-14}	13.43

AVERAGE VALUES

	k$_2$	k$_1$	K$_e$
20° C	7.04x10^{-9}	7.13x10^{-7}	5.02x10^{-15}
30° C	1.15x10^{-8}	1.29x10^{-6}	1.49x10^{-14}
40° C	1.90x10^{-8}	2.16x10^{-6}	4.13x10^{-14}

Summary of values for the equilibrium constant of Disec in terms of average deviation and 95% confidence intervals at the three temperatures:. . . following Dean & Dixon as cited in "Elem. Quant. Anal." by Peursem and Imes, pages 174-175. In this instance when n=3, tw=1.3, Q=.94.

	Range w	Ave. Val. $\bar{x}$	Ave. dev.	Wtw	95% confidence interval ($x \pm wtw$)
pk_2 20°C	.06	8.15	±.02	.08	8.15±.08
pk_1 20° C	.01	6.15	±.00	.01	6.15±.01
pk_e 20° C	.07	14.30	±.02	.09	14.30±.09
pk_2 30° C	.08	7.94	±.04	.10	7.94±.10
pk_1 30° C	.02	5.89	±.01	.03	5.89±.03
pK_e 30° C	.09	13.83	±.05	.12	13.83±.12
pk_2 40° C	.09	7.72	±.04	.12	7.72±.12
pk_1 40° C	.07	5.67	±.03	.09	5.67±.09
pK_e 40° C	.16	13.39	±.07	.21	13.39±.21

EQUILIBRIUM CONSTANTS OF BISMON - SUMMARY OF VALUES OBTAINED FROM GRAPHS

Temp.	V neut.	$\frac{V}{4}$ neut.	pH (pk_2)	-log H^+	$k_2=H^+$ x 10^9	V 3/4 neut.	pH (pk_1)	-log H^+	$k_1=H^+$	$Ke=k_1k_2$ x 10^{16}	pKe
20°C	4.40	1.10	8.83	1.17-10	1.48	3.30	7.10	2.90-10	$7.94x10^{-8}$	1.17	15.93
	4.39	1.10	8.80	1.20-10	1.59	3.30	7.14	2.86-10	$7.24x10^{-8}$	1.15	15.94
	4.33	1.08	8.77	1.23-10	1.70	3.25	7.05	2.95-10	$8.91x10^{-8}$	1.51	15.82
30°C	44.12	11.03	8.77	1.23-10	1.70	33.09	6.91	3.09-10	$1.23x10^{-7}$	2.09	15.68
	4.43	1.11	8.77	1.23-10	1.70	3.32	6.94	3.06-10	$1.15x10^{-7}$	1.96	15.71
	4.38	1.10	8.78	1.22-10	1.66	3.29	6.85	3.15-10	$1.41x10^{-7}$	2.54	15.63
40°C	4.29	1.07	8.52	1.48-10	3.02	3.22	6.65	3.35-10	$2.24x10^{-7}$	6.76	15.17
	4.31	1.08	8.50	1.50-10	3.16	3.23	6.62	3.38-10	$2.40x10^{-7}$	7.58	15.12
	4.30	1.08	8.52	1.48-10	3.02	3.23	6.63	3.37-10	$2.34x10^{-7}$	7.06	15.15

Average Values

	k_2	k_1	K_e
20°C	$1.59x10^{-9}$	$8.03x10^{-8}$	$1.28x10^{-16}$
30°C	$1.68x10^{-9}$	$1.26x10^{-7}$	$2.12x10^{-16}$
40°C	$3.06x10^{-9}$	$2.32x10^{-7}$	$7.10x10^{-16}$

Summary of results for Bismon's equilibrium constants in terms of average deviation and 95% confidence intervals at the three temperatures: ...following Dean and Dixon as cited in "Elementary Quantitave Analysis" by Peursem and Imes, pages 174-175. In this instance when n=3, tw$_{0.95}$ = 1.3; Q$_{0.90}$= .94

	Range W	Ave.Val $\bar{x}$	Ave.dev.	Wtw	95% confidence interval ($\bar{x}$ ± wtw)
$_2$20°C	.06	8.80	±.02	.08	8.80 ± .08
$_1$20°C	.09	7.10	±.03	.12	7.10 ± .12
20°C	.12	15.90	±.05	.16	15.90 ± .16
30°C	.01	8.77	±.00	.01	8.77 ± .01
30°C	.09	6.90	±.03	.12	6.90 ± .12
30°C	.08	15.67	±.03	.10	15.67 ± .10
40°C	.02	8.51	±.01	.03	8.51 ± .03
40°C	.03	6.63	±.01	.04	6.63 ± .04
40°C	.05	15.14	±.02	.07	15.14 ± .07

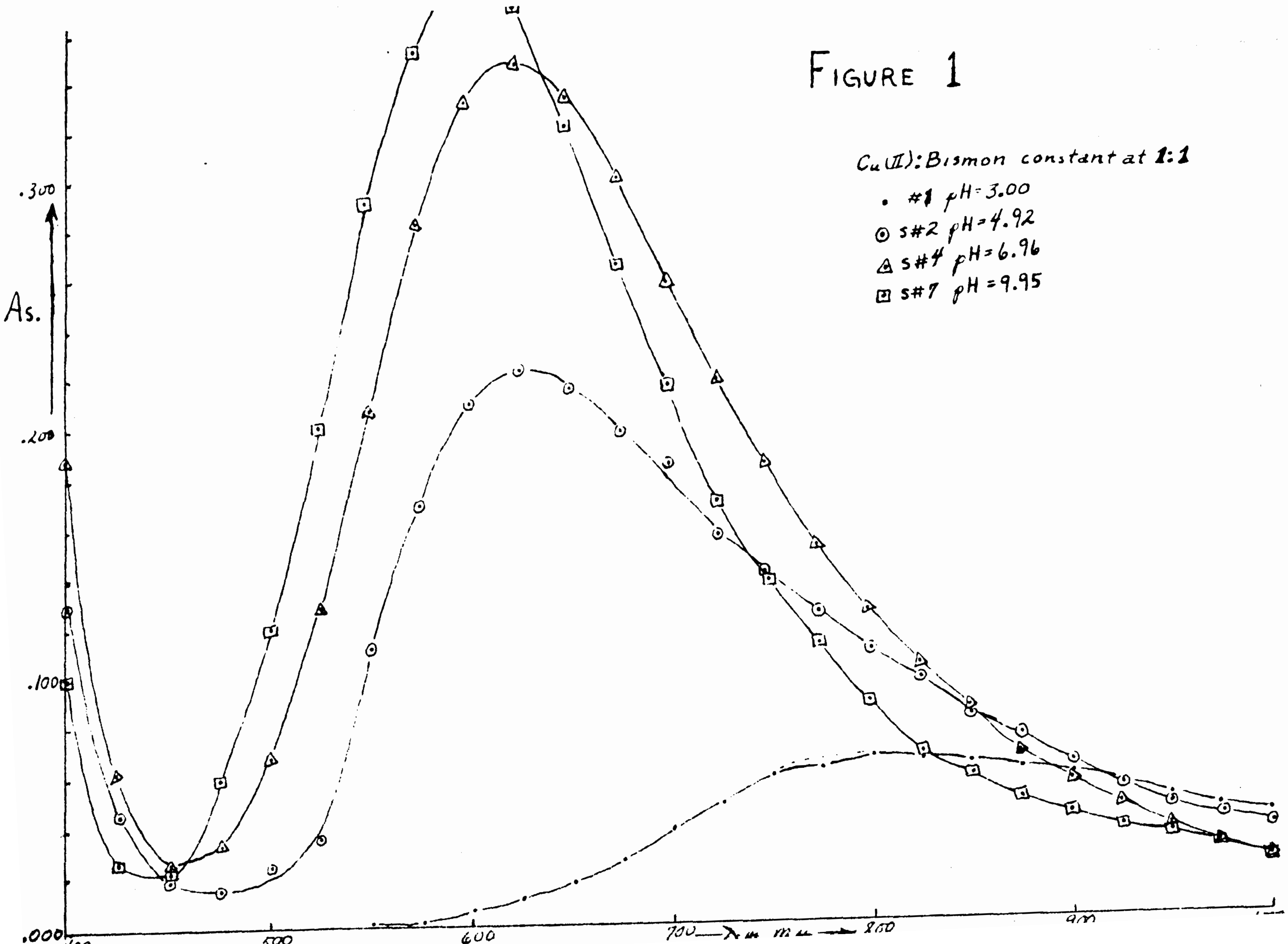
Spectrophotometric Studies

A Beckman Model DU Spectrophotometer and 1 cm. Corex cells calibrated against each other were used. Investigation was restricted to the Bismon-Cu (II) chelate, since studies of the Disec-Cu (II) chelate have been reported earlier.(16)

Absorption spectra of eight solutions containing Bismon and Copper nitrate in a molar ratio of 1:1 were determined between 400 and 1000 millimicrons at pH values of 3.00, 3.91, 4.92, 5.90, 6.96, 8.06, 8.88 and 9.95. This is shown in figure (1).

The absorbency maximum shifted from 625 millimicrons to 615 millimicrons as pH was increased. This plot also showed variation of absorbency with pH. Once the wave length allowing maximum absorbency was obtained, it was used in the determination of the molar-ratio of metal ion and ligand in the chelate. It should be mentioned that solutions of Bismon alone showed no measurable absorbency in this range.

FIGURE 1


Cu(II):Bismon constant at 1:1
• #1 pH=3.00
⊙ s#2 pH=4.92
△ s#4 pH=6.96
⊡ s#7 pH=9.95
As.
.300
.200
.100
.000
500
600
700 — λ mμ → 800
900

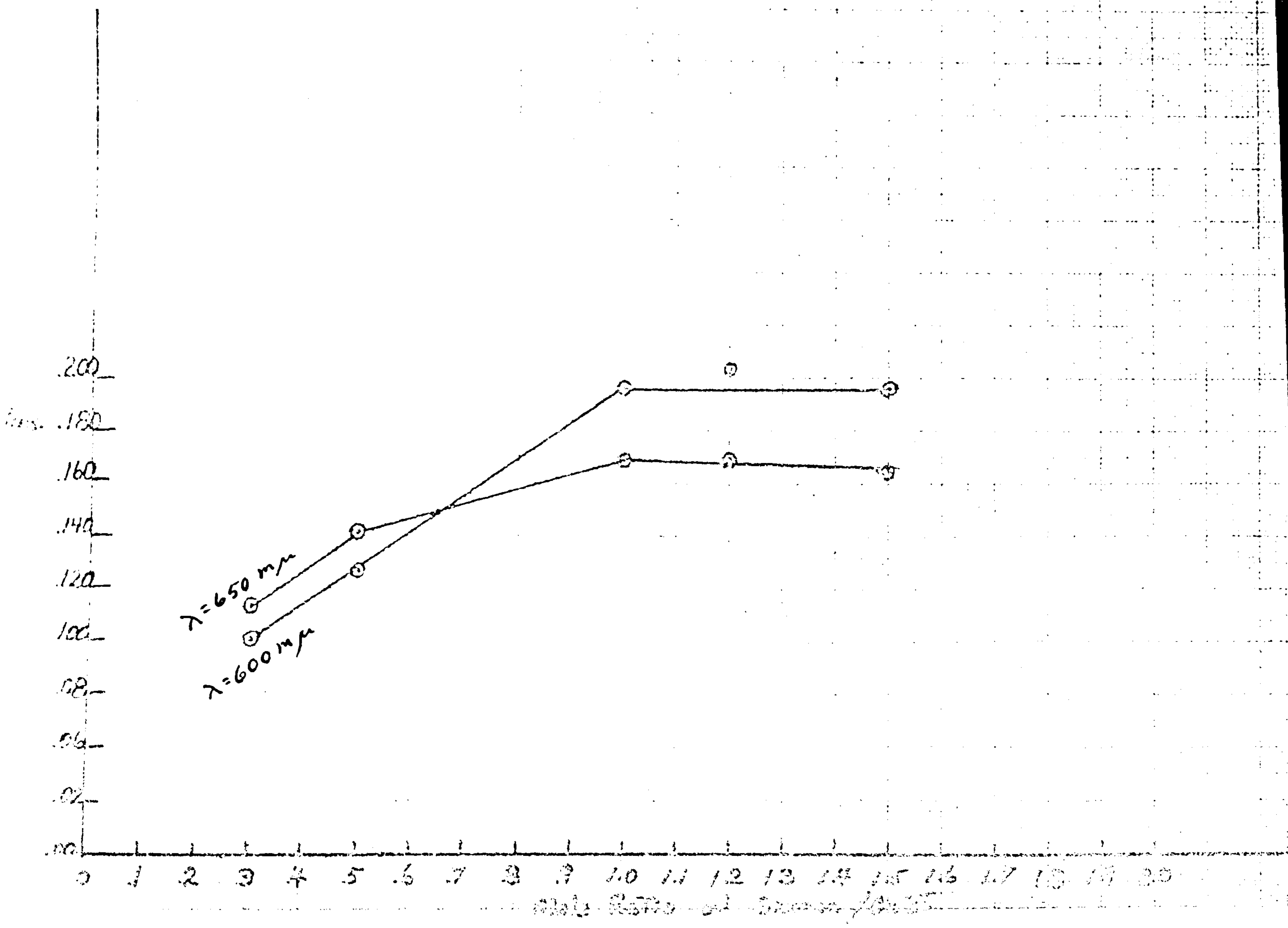
(A) Determination of Ratio of Bismon to Copper (II) in the Chelate:

Method of Yoe and Jones(32)

Solutions at pH 8.5 containing 0.005 molar Cu(II) and increasing concentrations of Bismon free base were inspected at the wave lengths 550, 600, 650 and 700 millimicrons. The absorbency increased with-increase in mole ratio of ligand to metal ion until the point was reached where essentially all the metal was chelated. At this point maximum absorbency occured and a higher mole ratio produced no increase in absorbency. It was previously proved that a pure solution of the ligand did not absorb light significantly in this wave length range. A plot of the mole ratios vs. absorbency showed a plateau region where chelation of the copper ion with Bismon was greatest. It will be observed that the absorbency becomes essentially constant at a molar ratio of one to one.

DATA FOR METHOD OF YOE AND JONES

	Diluted to 100 ml., and adjusted to pH 8.5				
Molar Ratio	Volume 0.01 M Cu (II)	Volume 0.01 M Bismon	Wave Length	Slit Width	As.
$\frac{0.3}{1.00}$	25 ml	7.5 ml	550	.146	.062
			600	.095	.101
			650	.065	.113
			700	.049	.106
$\frac{0.5}{1.00}$	25 ml	12.5 ml	550	.146	.078
			600	.095	.127
			650	.065	.142
			700	.049	.128
$\frac{1.0}{1.0}$	25 ml	25 ml	550	.146	.144
			600	.095	.196
			650	.065	.169
			700	.049	.107
$\frac{1.2}{1.0}$	25 ml	30 ml	550	.146	.152
			600	.095	.203
			650	.065	.169
			700	.049	.105
$\frac{1.5}{1.0}$	25 ml	37.5 ml	550	.146	.141
			600	.095	.196
			650	.065	.165
			700	.049	.096


Abs.
.200
.180
.160
.140
.120
.100
.08
.06
.04
.00
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
Mole Ratio of
λ=650 mμ
λ=600 mμ

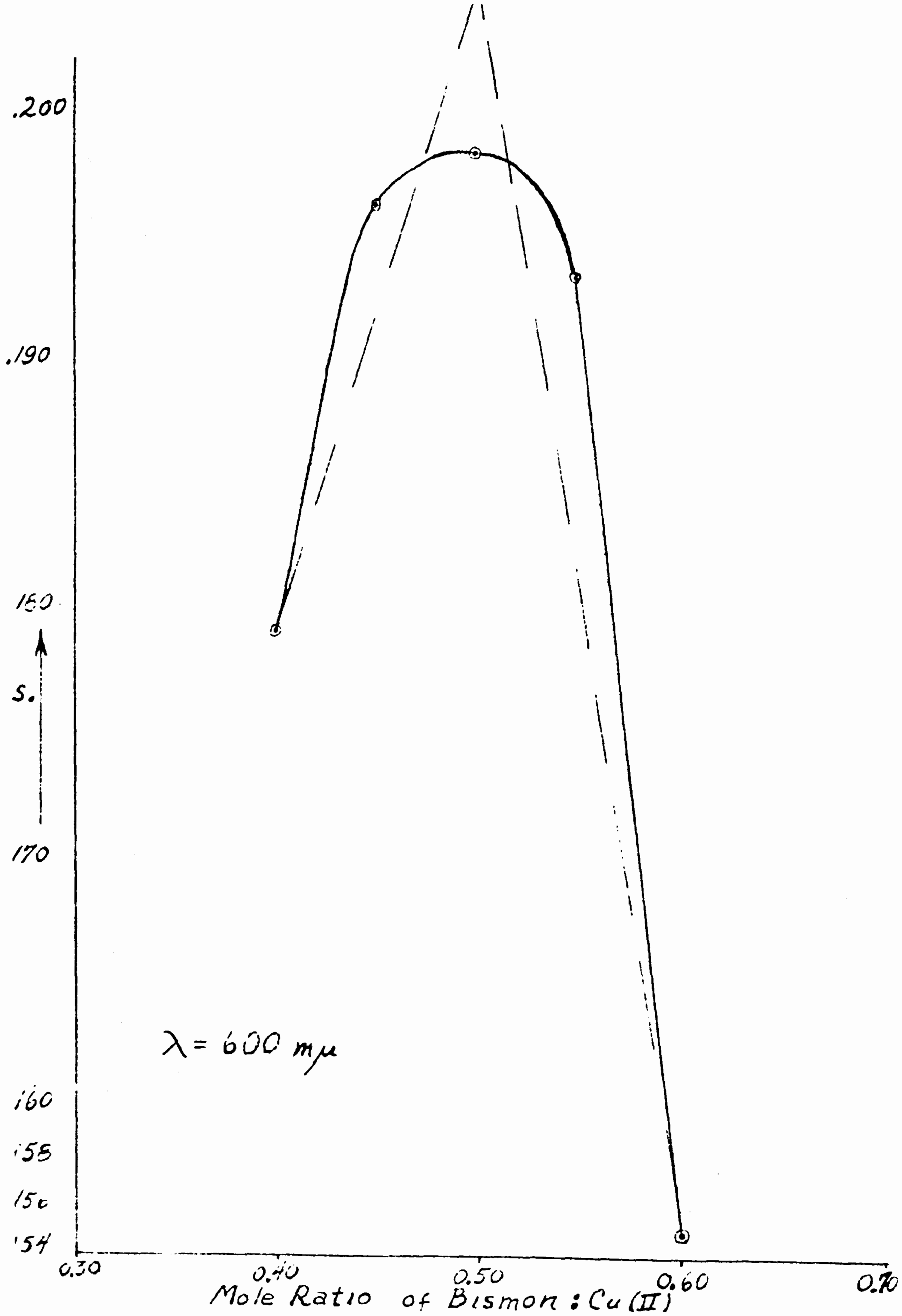
(B) Determination of Ratio of Bismon to Copper (II) in the Chelate:

Job's Method (22)

Whereas in the method of Yoe and Jones the metal ion concentration was held constant, in Job's method the total concentration of metal and ligand was held constant. For a constant total concentration of metal and ligand, the concentration of the chelate is greatest when the metal ion and ligand are present in the same molar ratios in which they exist in the chelate compound. The maximum chelate concentration was determined using wave length 550, 600, 650 and 700 millimicrons. The pH of each solution was adjusted to 8.5 to insure basicity. A plot of absorbence vs. molar ratios of ligand to metal ion showed a peak corresponding to the molar ratio of the chelate. This peak was at a molar ratio of one to one. It may be noted that only when the Cu (II) concentration was in a large excess did any precipitation occur, even after standing several days.

DATA FOR JOB'S METHOD OF CONTINUOUS VARIATIONS

	Diluted to 100 ml.,, and adjusted to pH 8.5				
Molar Ratio Bismon	Volume 0.01 M Bismon	Volume 0.01 M Cu (II)	Wave Length	Slit Width	As.
0.40	20 ml	30 ml	550	.146	.111
			600	.095	.179
			650	.065	.195
			700	.049	.169
0.45	22.5 ml	27.5 ml	550	.146	.139
			600	.095	.196
			650	.065	.193
			700	.049	.151
0.50	25 ml	25 ml	550	.146	.146
			600	.095	.198
			650	.065	.160
			700	.049	.100
0.55	27.5 ml	22.5 ml	550	.146	.146
			600	.095	.193
			650	.065	.159
			700	.049	.096
0.60	30 ml	20 ml	550	.146	.111
			600	.095	.155
			650	.065	.125
			700	.049	.073


.200
.190
180
S.
170
160
158
156
154
λ = 600 mμ
0.30
0.40
0.50
0.60
0.70
Mole Ratio of Bismon : Cu(II)

Determination of Stability Constants

(A) Theoretical Treatment

A thorough account of complexation has been made by Bjerrum(10)(11) in his treatise concerning complex equilibria. In following Bjerrum's method for determining stability constants, it is noted that in the general equilibria between a meatl ion, M, and N donor molecules of ligand A:

$$M + A = MA$$

$$MA + A = MA_2$$

$$MA_2 + A = MA_3$$

$$\ldots . MA_{N-1} + A = MA_N$$

The individual formation (stability) constants are:

$$k_1 = \frac{(MA)}{(M)\ (A)}$$

$$k_2 = \frac{(MA_2)}{(MA)\ (A)}$$

$$k_3 = \frac{(MA_3)}{(MA_2)\ (A)}$$

$$k_N = \frac{(MA_N)}{(MA_{N-1})\ (A)}$$

Rearranging these terms, the concentrations of each species may be found n terms of (M), (A), and the formation constants.

Equations I

$$\left\{\begin{array}{l} (MA) = k_1(M)(A) \\ (MA_2) = k_2\ (MA)(A) = k_1k_2(M)(A)^2 \\ (MA_3) = k_3(MA_2)(A) = k_1k_2k_3(M)(A)^3 \\ (MA_N) = k_N(MA_{N-1})(A) = k_1k_2k_3 \ldots k_N(M)(A)^N \end{array}\right.$$

where (M) and (A) are concentrations of unbound metal ion and ligand respectively.

The quantity $\bar{n}$ is defined as the average number of don~~a~~r groups bound per metal ion present in any form:

$$\bar{n} = \frac{(MA) + 2(MA_2)\ldots.N(MA_N)}{(M) + (MA) + (MA_2)\ldots(MA_N)} = \frac{C_A-(A)}{C_M}$$

where C_A is the total concentration of ligand, C_M the total concentration of metal ion, and (A) the concentration of free ligand.

When Equations I are substituted into the expression for $\bar{n}$, the values of $\bar{n}$ may be found in terms of the stability constants and free ligand concentrations, (A):

$$\bar{n} = \frac{k_1(A) + 2k_1k_2(A)^2 + 3\,k_1k_2k_3\,(A)^3\ldots.}{1 + K_1(A) + k_1k_2(A)^2 + k_1k_2k_3(A)^3\ldots.} = \frac{C_A - (A)}{C_M}$$

Bjerrum named this expression for $\bar{n}$ the "Formation Function" of the system, and the curve obtained by plotting $\bar{n}$ against -log (A) was called the "Formation Function Curve".

Experimentally, values of (A) are directly determined or calculated from the data. From the different concentrations of the unbound ligand (A), various values of $\bar{n}$ may be found from the above equation. Once the values of $\bar{n}$ and (A) have been found, the stability constants may be obtained by 1) graphical determination using the Formation Function Curve, or 2) solution of the simultaneous equations by mathematical calculations.

B) Experimental : Determination of (A) and $\bar{n}$

The stability constants of Bismon and Disec were determined from data obtained by the potentiometric titration of 50 ml of solution 10^{-3} molar in cupric ion and 2×10^{-3} molar in hydrogen ion with 10 ml of standardized base (4.94×10^{-2} molar Disec free base, or 9.24×10^{-3} molar Bismon free base). The titrations were run in triplicate at 20°C, 30°C, and 40°C for each amine. The titration procedure and equipment have been described in an earlier section.

The method of Carlson, McReynolds and Verhoek (13) was used in the determinations of various values of (A) and $\bar{n}$. Beginning with the equation for the Formation Function, expressions for (A) were derived in terms of the hydrogen ion concentration and dissociation constants of the basic ligand.

Since the ligand was basic, allowance had to be made for the fact hat ligand was removed by reaction with hydrogen ion as well as with metal on. For the diamine, the total concentration was expressed:

$$C_A = (A) + (AH^+) + (AH_2^{++}) + \bar{n}C_M$$

and the two dissociation constants of the base:

$$k_{AH} = \frac{(A)(H^+)}{(AH^+)}$$

$$k_{AH_2} = \frac{(AH^+)\,(H^+)}{(AH_2^{++})}$$

The term α, was defined as the fraction of the amine not complex bound which existed as free amine:

$$\alpha = \frac{k_{AH}\,k_{AH_2}}{k_{AH}k_{AH_2} + k_{AH_2}\,(H^+) + (H^+)^2}$$

The term $\bar{n}_A$ was defined as the mean number of hydrogen ions bound to not-complex-bound amine:

$$\bar{n}_A = \frac{(AH^+) + 2(AH_2^{++})}{(A) + (AH^+) + (AH_2^{++})}$$

$$\bar{n}_A = \frac{k_{AH_2}(H^+) + 2(H^+)^2}{k_{AH}k_{AH_2} + k_{AH_2}(H^+) + (H^+)^2}$$

Therefore, by appropriate substitutions in the expression for n̄, it was found that n̄ could be obtained in terms of the known dissociation constants and hydrogen ion concentrations.

$$\bar{n} = \frac{C_A + \frac{(AH^+)}{\bar{n}_A}}{C_M} = \frac{C_A - \frac{C_H - (H^+)}{\bar{n}_A}}{C_M}$$

where C_H was the total concentration of added strong acid. The terms C_A and C_M were directly measured throughout the experiment.

Similarly (A) was obtained in terms of the dissociation constants and ydrogen ion concentrations.

$$(A) = \frac{\alpha (AH^+)}{\bar{n}_A} = \frac{\alpha}{\bar{n}_A} (C_H - H^+)$$

Every set of experimental values of n̄ and (A) therefore fit into the Formation Function, and the corresponding stability constants were obtained y solving a series of equations.

pH	$[H^+]$	k_1	k_2	k_1k_2	$k_2[H^+]$	$[H^+]^2$	Denominator	α
3.00	1×10^{-3}	8.03×10^{-8}	1.59×10^{-9}	1.28×10^{-16}	1.59×10^{-12}	1×10^{-6}	1×10^{-6}	1.28×10^{-10}
3.10	7.943×10^{-4}	″	″	″	1.263×10^{-12}	6.309×10^{-7}	6.309×10^{-7}	2.03×10^{-10}
3.20	6.310×10^{-4}	″	″	″	10.03×10^{-13}	3.982×10^{-7}	3.982×10^{-7}	3.21×10^{-10}
3.30	5.01×10^{-4}	″	″	″	7.97×10^{-13}	2.51×10^{-7}	2.51×10^{-7}	5.09×10^{-10}
3.50	3.16×10^{-4}	″	″	″	5.02×10^{-13}	9.99×10^{-8}	9.99×10^{-8}	1.28×10^{-9}
3.70	1.995×10^{-4}	″	″	″	3.16×10^{-13}	3.98×10^{-8}	3.98×10^{-8}	3.21×10^{-9}
4.00	1.000×10^{-4}	″	″	″	1.59×10^{-13}	1×10^{-8}	1×10^{-8}	1.28×10^{-8}
4.30	5.01×10^{-5}	″	″	″	7.97×10^{-14}	2.51×10^{-9}	2.51×10^{-9}	5.09×10^{-8}
4.50	3.16×10^{-5}	″	″	″	5.02×10^{-14}	9.99×10^{-10}	9.99×10^{-10}	1.28×10^{-7}

$2[H^+]^2$	Numerator	Denominator	$\bar{n}_A$
2×10^{-6}	2×10^{-6}	1×10^{-6}	2.0
1.262×10^{-6}	1.262×10^{-6}	6.309×10^{-7}	″
7.96×10^{-7}	7.96×10^{-7}	3.982×10^{-7}	″
5.02×10^{-7}	5.02×10^{-7}	2.51×10^{-7}	″
2×10^{-7}	2×10^{-7}	9.99×10^{-8}	″
7.96×10^{-8}	7.96×10^{-8}	3.98×10^{-8}	″
2×10^{-8}	2×10^{-8}	1×10^{-8}	″
5.02×10^{-9}	5.02×10^{-9}	2.51×10^{-9}	″
2×10^{-9}	2×10^{-9}	9.99×10^{-10}	″

$$\bar{n}_A = \frac{k_2(H^+) + 2\,(H^+)^2}{k_1k_2 + k_2(H^+) + (H^+)^2}$$

20°C Bismon $A = \frac{\alpha}{\bar{n}_A}(C_H - (H^+))$ At start $\begin{cases} \text{Ave. pH} = 2.9333 = -(.0667-3) \\ \text{Ave. } H^+ = C_{H_o} = 1.166 \times 10^{-3} \end{cases}$

Ave. Vol.Base Added	V total soln. (50 + V base added)	$C_H \times 10^3$ $\left(\frac{50}{v\ tot} \cdot C_{H_o}\right)$	$\frac{\alpha}{\bar{n}_A}$	$(C_H - H^+) \times 10^4$	(A)	log A	pA
1.27	51.27	1.137	6.4×10^{-11}	1.37	8.77×10^{-15}	.9430-15	14.0570
2.87	52.87	1.103	1.015×10^{-10}	3.087	3.1333×10^{-14}	.49596-14	13.5040
3.65	53.65	1.087	1.605×10^{-10}	4.560	7.319×10^{-14}	.86445-14	13.1354
4.15	54.15	1.076	2.55×10^{-10}	5.79	14.76×10^{-14}	1.1691-14	12.8309
4.78	54.78	1.06	6.4×10^{-10}	7.44	47.62×10^{-14}	1.6778-14	12.3222
5.30	55.30	1.05	1.61×10^{-9}	8.50	13.69×10^{-13}	1.1364-13	11.8636
6.13	56.13	1.04	6.4×10^{-9}	9.40	60.16×10^{-13}	1.7793-13	11.2207
7.33	57.33	1.02	2.55×10^{-8}	9.70	24.74×10^{-12}	1.3934-12	10.6066
8.51	58.51	1.00	6.4×10^{-8}	9.68	61.95×10^{-12}	1.7920-12	10.2080

20°C Bismon

$$\bar{n} = \frac{C_A - \frac{\alpha}{\bar{n}A}(C_H - H+)}{C_M} = \frac{C_A - (A)}{C_M}$$

$$C_A = \frac{\text{Vol. base added}}{\text{total vol. soln.}} \cdot M_{Base} \quad \ldots \text{ where } M \approx 9.14 \times 10^{-3}$$

$$C_M = \frac{50}{\text{total vol. soln.}} \cdot M_{Metal} \quad \ldots \text{ where } M = 1.04 \times 10^{-3}$$

$C_A \times 10^4$	$(C_A - A) \times 10^4$	$C_M \times 10^4$	$\bar{n}$
2.264	2.264	10.14	.223
4.962	4.962	9.853	.5045
6.218	6.218	9.692	.6416
7.005	7.005	9.59	.730
7.975	7.975	9.49	.840
8.760	8.760	99.40	.932
9.982	9.982	9.27	1.077
11.686	11.686	9.08	1.287
13.294	13.294	8.89	1.495

30°C Bismon

$$\alpha = \frac{k_1k_2}{k_1k_2+k_2(H^+)+(H^+)^2}$$

pH	(H^+)	k_1	k_2	k_1k_2	$k_2(H^+)$	$(H^+)^2$	Denominator	α
2.85	1.761×10^{-3}	1.26×10^{-7}	1.68×10^{-9}	2.12×10^{-16}	2.958×10^{-12}	3.101×10^{-6}	3.101×10^{-6}	6.84×10^{-11}
3.00	1.00×10^{-3}	"	"	"	1.68×10^{-12}	1×10^{-6}	1×10^{-6}	2.12×10^{-10}
3.30	5.01×10^{-4}	"	"	"	8.417×10^{-13}	2.51×10^{-7}	2.51×10^{-7}	8.45×10^{-10}
3.50	3.16×10^{-4}	"	"	"	5.309×10^{-13}	9.99×10^{-8}	9.99×10^{-8}	2.12×10^{-9}
3.70	1.995×10^{-4}	"	"	"	3.352×10^{-13}	3.98×10^{-8}	3.98×10^{-8}	5.33×10^{-9}
4.00	1.00×10^{-4}	"	"	"	1.68×10^{-13}	1×10^{-8}	1×10^{-8}	2.12×10^{-8}
4.30	5.01×10^{-5}	"	"	"	8.417×10^{-14}	2.51×10^{-9}	2.51×10^{-9}	8.45×10^{-8}

30° C Bismon

$$\bar{n}_A = \frac{k_2(H^+)+2(H^+)^2}{k_1k_2 + k_2(H^+)+(H^+)^2}$$

$2(H^+)^2$	Numerator	Denominator	$\bar{n}A$
$6.202\text{x}10^{-6}$	$6.202\text{x}10^{-6}$	$3.101\text{x}10^{-6}$	2.0
$2.\text{x}0\text{-}^{6}$	$2\text{x}10^{-6}$	$1\text{x}10^{-6}$	2.0
$5.02\text{x}10^{-7}$	$5.02\text{x}10^{-7}$	$2.51\text{x}10^{-7}$	2.0
$19.98\text{x}10^{-8}$	$19.98\text{x}10^{-8}$	$9.99\text{x}10^{-8}$	2.0
$7.96\text{x}10^{-8}$	$7.96\text{x}10^{-8}$	$3.98\text{x}10^{-8}$	2.0
$2\text{x}10^{-8}$	$2\text{x}10^{-8}$	$1\text{x}10^{-8}$	2.0
$5.02\text{x}10^{-9}$	$5.02\text{x}10^{-9}$	$2.51\text{x}10^{-9}$	2.0

30°C Bismon $(A) = \frac{\alpha}{\bar{n}_A} (C_H - H^{+})$ At start $\begin{cases} \text{Ave. pH} = 2.7966 = -(.2034-3) \\ \text{Ave. } H^{+}C_{Ho} = 1.596 \times 10^{-3} \end{cases}$

Ave.Vol.Base Added	V total soln. (50 + V base added)	$C_H \times 10^3$ $\left(\frac{50}{vtot} \bullet C_{Ho}\right)$	$\frac{\alpha}{\bar{n}a}$	$(C_H - H^{+}) \times 10^3$	(A)	log A	pA
1.40	51.40	1.55	3.42×10^{-11}	.209	7.148×10^{-15}	.8542-15	14.1458
3.12	53.12	1.50	1.06×10^{-10}	.50	5.300×10^{-14}	.7243-14	13.2757
4.58	54.58	1.46	4.23×10^{-10}	.959	4.057×10^{-13}	.6082-13	12.3918
5.17	55.17	1.45	1.06×10^{-9}	1.134	1.202×10^{-12}	.0799-12	11.9201
5.70	55.70	1.43	2.67×10^{-9}	1.23	3.284×10^{-12}	.5164-12	11.4836
6.77	56.77	1.41	1.06×10^{-8}	1.31	1.389×10^{-11}	.1427-11	10.8573
8.43	58.43	1.37	4.23×10^{-8}	1.32	5.584×10^{-11}	.7470-11	10.2530

$$\bar{n} = \frac{C_A - \frac{\alpha}{\bar{n}_A}(C_H - H^{+})}{C_M} = \frac{C_A - A}{C_M}$$

$$C_A = \frac{\text{Vol. base added}}{\text{vol. total soln.}} \cdot M_{Base} \text{ ... where } M_{Base} = 9.24 \times 10^{-3}$$

$$C_M = \frac{50}{\text{Vol. total soln.}} \cdot M_{Metal} \text{...Where } M_{Metal} = 1.04 \times 10^{-3}$$

$C_A \times 10^4$	$(C_A - A) \times 10^4$	$C_M \times 10^4$	$\bar{n}$
2.517	2.517	10.1	.249
5.427	5.427	9.79	.554
7.754	7.754	9.53	.814
8.659	8.659	9.43	.918
9.456	9.456	9.34	1.012
11.019	11.019	9.16	1.203
13.331	13.331	8.90	1.498

40°C Bismon

$$\alpha = \frac{k_1k_2}{k_1k_2 + k_2\,H^+ + H^{+\,2}}$$

pH	H^+	k_1	k_2	k_1k_2	$k_2(H^+)$	$(H^+)^2$	Denom.	α
2.70	1.995×10^{-3}	2.32×10^{-7}	3.06×10^{-9}	7.10×10^{-16}	6.105×10^{-12}	3.98×10^{-8}	3.98×10^{-8}	1.78×10^{-10}
3.00	1×10^{-3}	2.32×10^{-7}	3.06×10^{-9}	7.10×10^{-16}	3.06×10^{-12}	1×10^{-6}	1×10^{-6}	7.10×10^{-10}
3.30	5.01×10^{-4}	〃	〃	〃	15.33×10^{-13}	2.51×10^{-7}	2.51×10^{-7}	2.83×10^{-9}
3.50	3.16×10^{-4}	〃	〃	〃	9.67×10^{-13}	9.99×10^{-8}	9.99×10^{-8}	7.11×10^{-9}
3.70	1.995×10^{-4}	〃	〃	〃	6.105×10^{-13}	3.98×10^{-8}	3.98×10^{-8}	1.78×10^{-8}
4.00	1×10^{-4}	〃	〃	〃	3.06×10^{-13}	1×10^{-8}	1×10^{-8}	7.10×10^{-8}
4.30	5.01×10^{-5}	〃	〃	〃	15.33×10^{-14}	2.51×10^{-9}	2.51×10^{-9}	2.83×10^{-7}

$$\bar{n}_A = \frac{k_2(H^+) + 2(H^+)^2}{k_1k_2 + k_2(H^+) + (H^+)^2}$$

$2(H^+)^2$	Numerator	Denominator	$\bar{n}_A$
7.96×10^{-6}	7.96×10^{-6}	3.98×10^{-6}	2.0
2×10^{-6}	2×10^{-6}	1×10^{-6}	2.0
5.02×10^{-7}	5.02×10^{-7}	2.51×10^{-7}	2.0
19.98×10^{-8}	19.98×10^{-8}	9.99×10^{-8}	2.0
7.96×10^{-8}	7.96×10^{-8}	3.98×10^{-8}	2.0
2×10^{-8}	2×10^{-8}	1×10^{-8}	2.0
5.02×10^{-9}	5.02×10^{-9}	2.51×10^{-9}	2.0

40°C Bismon $(A) = \frac{\alpha}{\bar{n}_A} (C_H - H^+)$

At start – (Ave. pH = 2.6300 = (.3700-3)
(Ave $H^+ = C_{H_o} = 2.345 \times 10^{-3}$

Ave.Vol.Base Added	V total soln. (50 + V base added)	$C_H \times 10^3$ $(\frac{50}{vtot} \cdot C_{H_o})$	$\frac{\alpha}{\bar{n}_A}$	$(C_H - H^+) \times 10^4$	(A)	log A	pA (-log A)
.89	50.83	2.31	$.89 \times 10^{-10}$	3.15	2.80×10^{-14}	.4478-14	13.5522
3.15	53.15	2.21	3.55×10^{-10}	1.21	4.296×10^{-13}	.6331-13	12.3669
4.43	54.43	2.16	1.415×10^{-9}	16.6	2.357×10^{-12}	.3724-12	11.6276
5.05	55.05	2.13	3.55×10^{-9}	18.1	6.426×10^{-12}	.8079-12	11.1921
5.83	55.83	2.11	$.89 \times 10^{-8}$	19.1	1.700×10^{-11}	.2304-11	10.7696
6.87	56.87	2.07	3.55×10^{-8}	19.7	6.994×10^{-11}	.8445-11	10.1556
8.72	58.72	2.00	1.415×10^{-7}	19.5	$2,759 \times 10^{-10}$	.4408-10	9.5592

40° Bismon

$$\bar{n} = \frac{C_A - \overset{\alpha}{\bar{n}}_A (C_H - H^{+})}{C_M} = \frac{C_A - (A)}{C_M}$$

$$C_A = \frac{\text{Vol. base added}}{\text{total volume}} \cdot M_{\text{Base}} \text{ where } M_{\text{Base}} = 8.99 \times 10^{-3}$$

$$C_M = \frac{50}{\text{total vol.}} \cdot M_{\text{MEtal}} \text{ where } M_{\text{Metal}} = 1.04 \times 10^{-3}$$

$C_A \times 10^4$	$(C_A - A) \times 10^4$	$C_M \times 10^4$	$\bar{n}$
1.468	1.468	10.2	.144
5.328	5.328	9.78	.545
7.317	7.317	9.55	.766
8.247	8.247	9.45	.873
9.388	9.388	9.31	1.008
10.860	10.860	9.14	1.188
13.350	13.350	8.86	1.507

$$\alpha = \frac{k_1 \quad k_2}{k_1\ k_2 + k_2\ (H^+) + (H^+)^2}$$

20° C Disec

pH	(H^+)x 10^3	k_1	k_2	k_1 k_2	$k_2(H^+)$x10^{12}	$(H^+)^2$x10^7	Denom. x 10^7	10^9
2.70	1.995	$7.13\text{x}10^{-7}$	$7.04\text{x}10^{-9}$	$5.02\text{x}10^{-15}$	14.04	39.80	39.80	1.261
2.80	1.585	"	"	"	11.16	25.10	25.10	2.000
2.90	1.259	"	"	"	8.863	15.85	15.85	3.167
3.00	1.000	"	"	"	7.040	10.00	10.0	5.02
3.10	0.7943	"	"	"	5.592	6.309	6.309	7.957
3.20	0.6310	"	"	"	4.442	3.98	3.98	12.61
3.30	0.5012	"	"	"	3.528	2.51	2.51	20.00
3.40	0.3981	"	"	"	2.803	1.585	1.585	31.67

30° C Disec

pH	(H^+)x 10^3	k_1	k_2	k_1 k_2	$k_2(H^+)$x10^{12}	$(H^+)^2$x10^7	Denom. x 10^7	10^9
2.70	1.995	$1.29\text{x}10^{-6}$	$1.15\text{x}10^{-8}$	$1.49\text{x}10^{-14}$	22.94	39.8	39.8	3.744
2.80	1.585	"	"	"	18.23	25.10	25.1	5.936
2.90	1.259	"	"	"	14.48	15.85	15.85	9.401
3.00	1.000	"	"	"	11.50	10.0	10.0	14.90
3.10	0.7943	"	"	"	9.134	6.309	6.309	23.62
3.20	0.6310	"	"	"	7.257	3.98	3.98	37.44
3.30	0.5012	"	"	"	5.764	2.51	2.51	59.36
3.40	0.3981	"	"	"	4.578	1.585	1.585	94.01

$$\bar{n}_A = \frac{k_2 (H^+) + 2 (H^+)^2}{k_1 k_2 + k_2 (H^+) + (H^+)^2}$$

20° C Disec

$2 (H^+)^2 x 10^7$	Numerator x 10^7	Denom. x 10^7	$\bar{n}_A$
79.6	79.6	39.8	2.0
50.2	50.2	25.10	2.0
31.7	31.7	15.85	2.0
20.0	20.0	10.0	2.0
12.62	12.62	6.309	2.0
7.964	7.964	3.98	2.0
5.02	5.02	2.51	2.0
31.67	3.17	1.585	2.0

30° C Disec

79.6	79.6	39.8	2.0
50.2	50.2	25.1	2.0
31.7	31.7	15.85	2.0
20.0	20.0	10.0	2.0
12.62	12.62	6.309	2.0
7.96	7.964	3.98	2.0
5.02	5.02	2.51	2.0
3.17	3.17	1.585	2.0

$(A) = \frac{\alpha}{\bar{n} A} (C_H - (H^+))$

At Start (Ave $p^H = 2.6900 = -(.3100-3)$
20° C (Ave $H^+ = C_{H_o} = 2.042 \times 10^{-3}$

20° C Disec

Ave. Vol. Base Added	Total Vol. Soln' (50+V added)	CH x 10^3 $\frac{50}{V_{tot}} \cdot C_{H_o}$	$\frac{\alpha}{\bar{n}_A} \times 10^9$	$(C_H - H^+) \times 10^3$	(A) x 10^{12}	log A	PA (-log A)
.04	50.04	2.040	.631	0.045	.0284	.45332-14	13.54668
.23	50.23	2.033	1.000	0.448	.4480	.65128-13	12.34872
.40	50.40	2.023	1.584	0.764	1.210	.08279-12	11.91721
.54	50.54	2.020	2.510	1.020	2.560	.40824-12	11.59176
.68	50.68	2.015	3.979	1.221	4.858	.68646-12	11.31354
.79	50.79	2.010	6.305	1.379	8.695	.93927-12	11.06073
.90	50.90	2.006	10.00	1.505	15.05	1.17754-12	10.82246
1.02	51.02	2.001	15.84	1.603	25.39	1.40466-12	10.59534

$(A) = \frac{\alpha}{\bar{n}\ A}\left(C_H - (H^+)\ \right)$

At Start (Ave p^H = 2.6266 = - (.3734-8)
30° C (Ave H^+ = C_{Ho} = 2.362 x 10-3

30° C Disec

Ave. Vol. Base Added	Total Vol. Sol'n. (50+V added)	CH x 10^3 $\frac{50}{V.tot.} \cdot C_{H_o}$	$\frac{\alpha}{\bar{n}_A} \times 10^9$	$(C_H - H^+) \times 10^3$	(A) x 10^{12}	log A	PA (-logA
.16	50.16	2.354	1.872	.359	.672	.82737-13	12.1726_3
.317	50.317	2.347	2.968	.762	2.262	.35449-12	11.6455_1
.487	50.487	2.339	4.700	1.080	5.076	.70552-12	11.2944_8
.63	50.63	2.333	7.45	1.333	9.931	.99699-12	11.0030_1
.773	50.773	2.326	11.81	1.532	18.09	1.25744-12	10.7425_6
.92	50.92	2.319	18.72	1.688	31.60	1.49969-12	10.5003_1
1.07	51.07	2.313	29.68	1.812	53.78	1.73062-12	10.2693_8
1.213	51.213	2.306	47.00	1.908	89.68	1.95274-12	10.0472_6

$$\bar{n} = \frac{C_A - (A)}{C_M}$$

$$C_A = \frac{\text{Vol. Base added}}{\text{Total Vol. Sol'n.}} \cdot M_{\text{Base}} \quad \text{where } M = 4.94 \times 10^{-12}$$

$$C_M = \frac{T\ 50}{\text{Total Vol. Sol'n}} \cdot M_{\text{Metal}} \quad \text{where } M = 1.04 \times 10^{-3}$$

20° C Disso

$(C_A) \times 10^4$	$(C_A - A) \times 10^4$	$(C_M) \times 10^3$	$\bar{n}$
.3949	.3949	1.039	.0380
2.262	2.262	1.035	.2186
3.921	3.921	1.032	.3799
5.278	5.278	1.029	.5129
6.628	6.628	1.026	.6460
7.684	7.684	1.024	.7504
8.735	8.735	1.022	.8547
9.876	9.876	1.019	.9692

30° C Disso

1.576	1.576	1.037	.1520
3.112	3.112	1.033	.3013
4.765	4.765	1.030	.4626
6.147	6.147	1.027	.5985
7.521	7.521	1.024	.7345
8.925	8.925	1.021	.8741
10.35	10.35	1.018	1.017
11.70	11.70	1.015	1.153

40°C Disec

$$\alpha = \frac{k_1\,k_2}{k_1k_2 + k_2\,(H^+) + (H^+)^2}$$

pH	$[H^+]$	k_1	k_2	k_1k_2	$k_2[H^+] \times 10^{11}$	$(H^+)^2 \times 10^6$	Denom. $\times 10^6$	$\alpha \times 10^8$
2.70	1.995×10^{-3}	2.16×10^{-6}	1.90×10^{-8}	4.13×10^{-14}	3.79	3.98	3.98	1.038
2.80	1.585×10^{-3}				3.01	2.51	2.51	1.646
2.90	1.259×10^{-3}				2.39	1.585	1.585	2.606
3.00	1×10^{-3}				1.90	1.00	1.00	4.13
3.10	7.943×10^{-4}				1.509	.6309	.6309	6.546
3.30	5.01×10^{-4}				.952	.251	.251	16.46

$2[H^+]^2 \times 10^6$	Numerater $\times 10^6$	Denominater $\times 10^6$	$\bar{n}$ A
7.96	7.96	3.98	2.0
5.02	5.02	2.51	2.0
3.17	3.17	1.585	2.0
2.00	2.00	1.00	2.0
1.262	1.262	.6309	2.0
.502	.502	.251	2.0

$$\bar{n}_A = \frac{k_2(H^+) + 2\,(H^+)^2}{k_1k_2 + k_2(H^+) + (H^+)^2}$$

40°C Disec

$$[A] = \frac{\alpha}{\bar{n}_A}\left(C_H - [H^+]\right)$$

At Start– (Ave. pH = 2.6033 = −(.3967−3)

(Ave. $H^+ = C_{H_o}$ = 2.492 x 10^{-3}

Ave. Vol. Base Added	Total Vol. Solution	$C_H \times 10^3$ $50/V$ total$\cdot C_{Ho}$	$\frac{\alpha}{\bar{n}_A} \times 10^8$	$[C_H - H^+] \times 10^3$	$[A]$	log A	pA (−log A)
.216	50.216	2.481	.519	.486	2.522 x 10^{-12}	.40175−12	11.5982
.417	50.417	2.471	.823	.886	7.292 x 10^{-12}	.86285−12	11.1371
.593	50.593	2.463	1.303	1.204	1.569 x 10^{-11}	.19562−11	10.8044
.730	50.73	2.456	2.065	1.456	3.007 x 10^{-11}	.47813−11	10.5218
.900	50.90	2.448	3.273	1.654	5.414 x 10^{-11}	.73352−11	10.2665
1.22	51.22	2.433	8.23	1.932	1.59 x 10^{-10}	.2014−10	9.7986

$$\bar{n} = \frac{C_A - [A]}{Cm}$$

$$C_A = \frac{\text{Vol Base added}}{\text{Total Vol. Solution}} \cdot \text{M Base} \;\ldots\; \text{where M} = 4.94 \times 10^{-12}$$

$$C_M = \frac{50}{\text{Total Vol. Soln.}} \cdot \text{M Metal} \;\ldots\; \text{when M} = 1.04 \times 10^{-3}$$

$C_A \times 10^3$	$[C_A - A] \times 10^3$	$C_M \times 10^4$	$\bar{n}$
.2125	.2125	10.35	.2053
.4086	.4086	10.31	.3963
.5790	.5790	10.28	.5632
.7109	.7109	10.25	.6936
.8735	.8735	10.22	.8547
1.1766	1.1766	10.15	1.1592

(C) Graphical Estimation of Stability Constants

(24) (13)

Several authors have made complex equilibrium studies based on Bjerrum's method for approximation of stability constants. At a first approximation, the following relationship holds true when $\bar{n} = 1/2$:

$$k_1 = 1/(A)$$

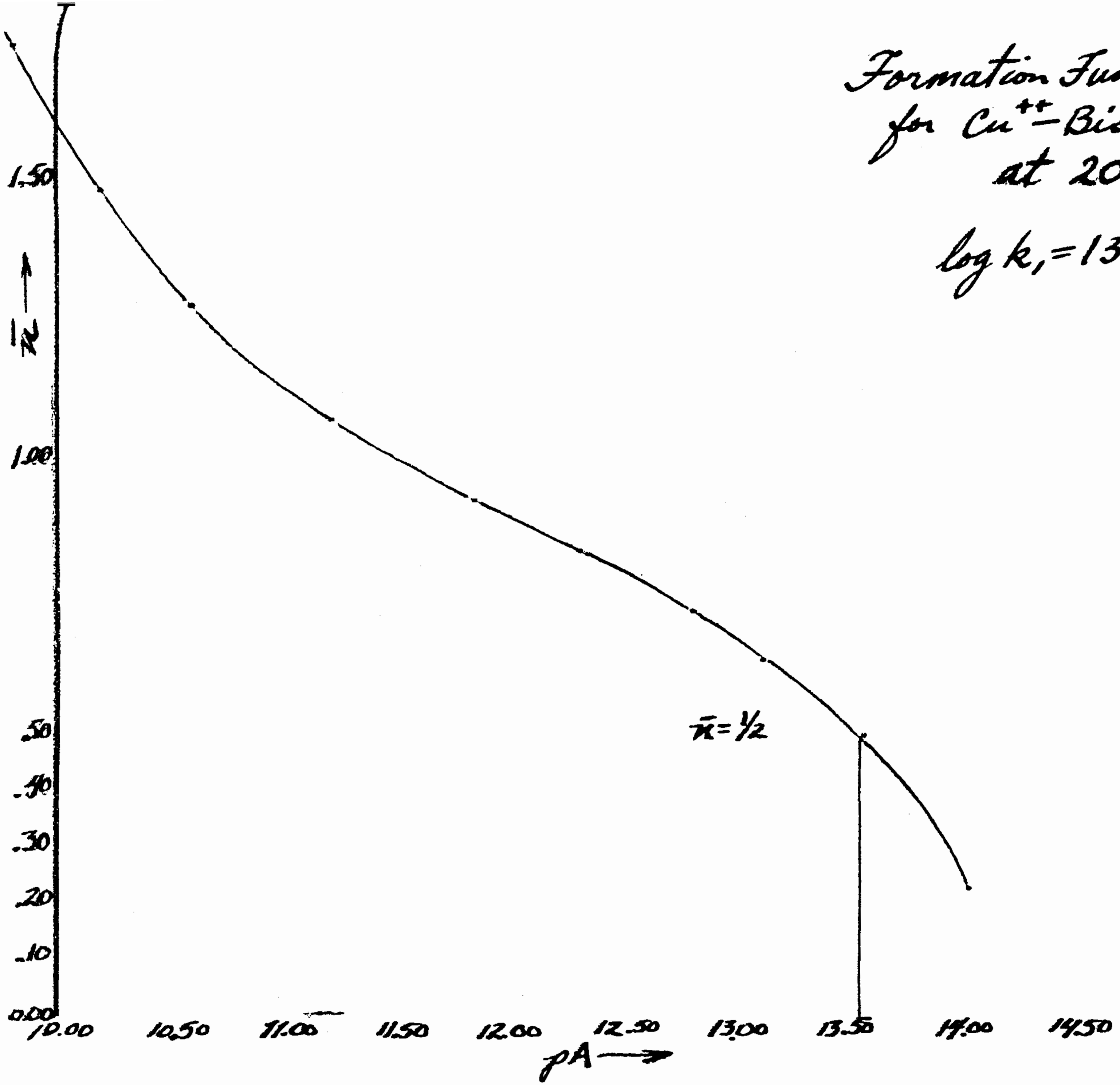
$$\log k_1 = \log 1/(A) = -\log (A)$$

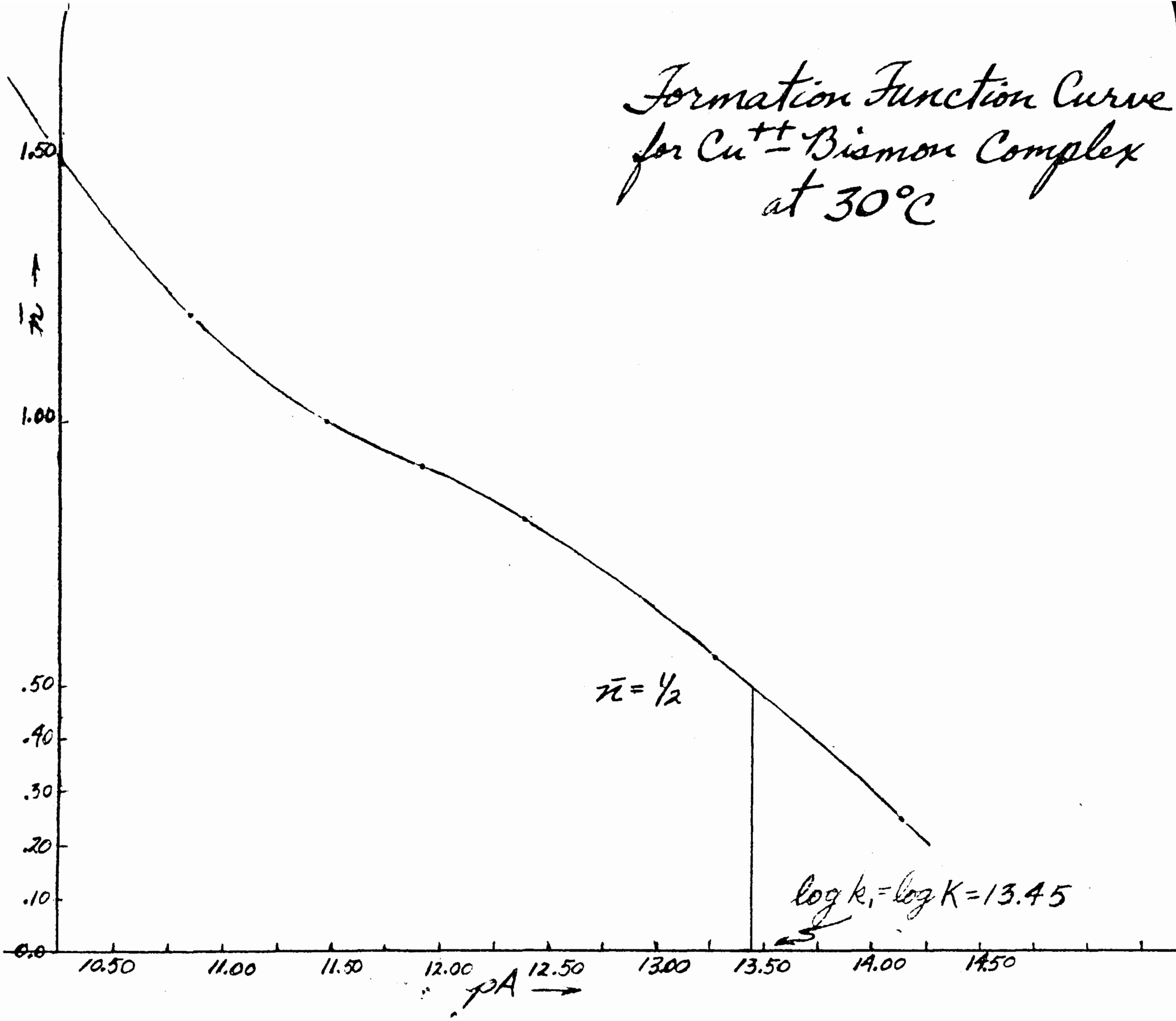
$$\log k_1 = pA$$

Therefore, when $\bar{n}$ was plotted against pA for the Formation Function Curve, the value of $\log k_1$ was read directly from the graph at $\bar{n} = 1/2$. Since it has been found that N = 1 for the copper chelates of both Bismon and Disec, there was only one stability constant associated with each complexation at any particular temperature. The values of these approximations are designated on the various plots of the Formation Function Curves.

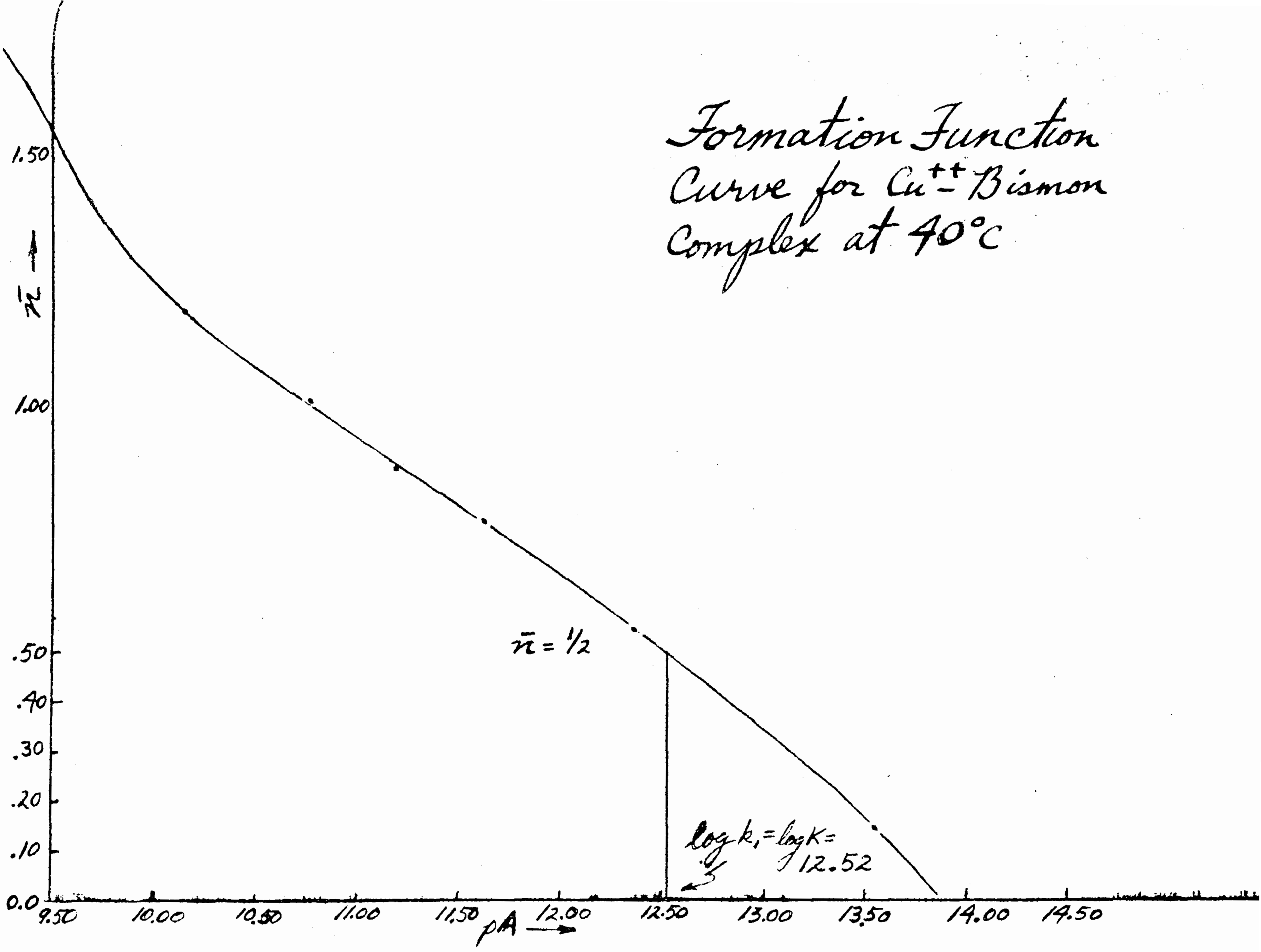
Formation Function Curve
for Cu^{++}–Bismon Complex
at 20°C

$\log k_1 = 13.58$

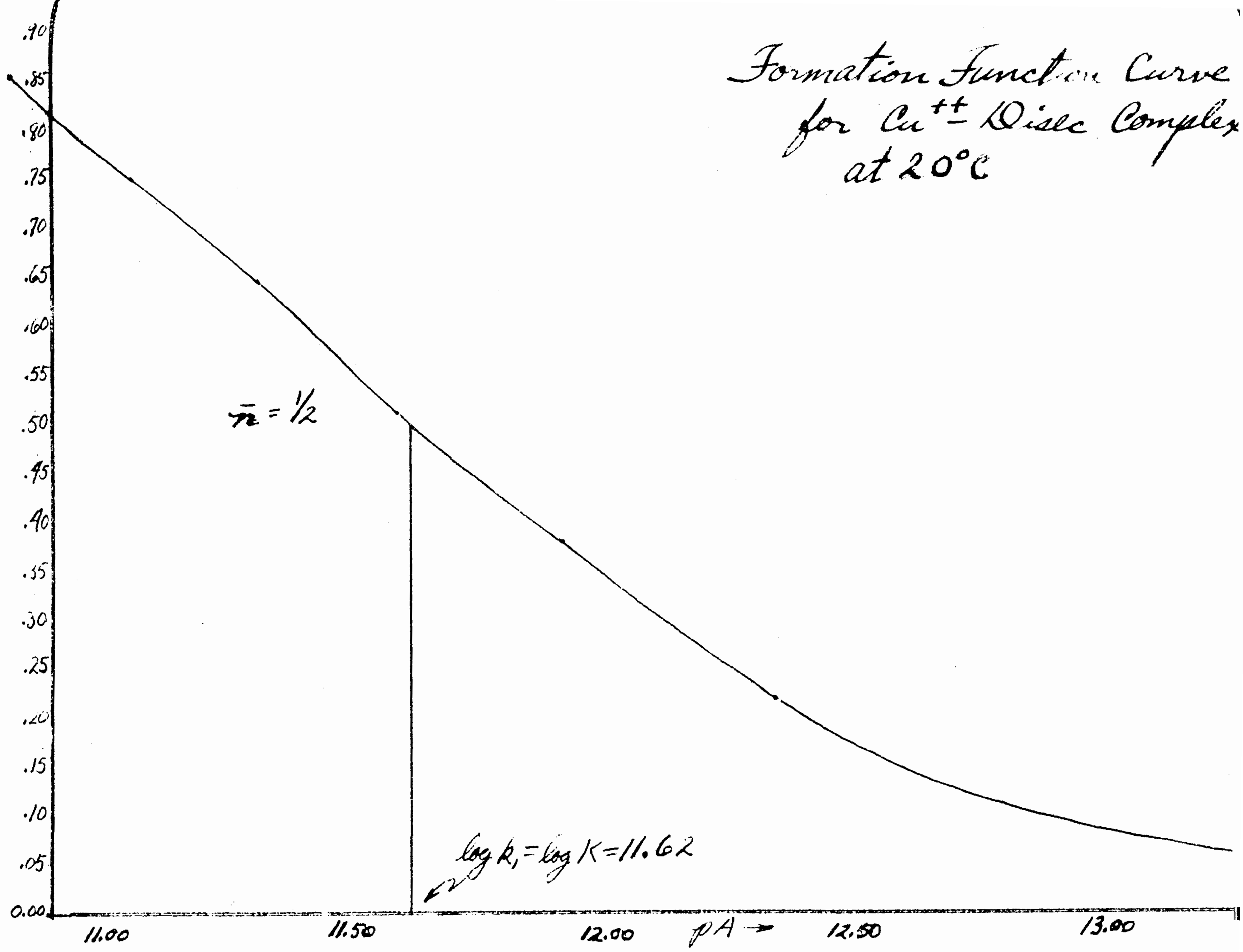




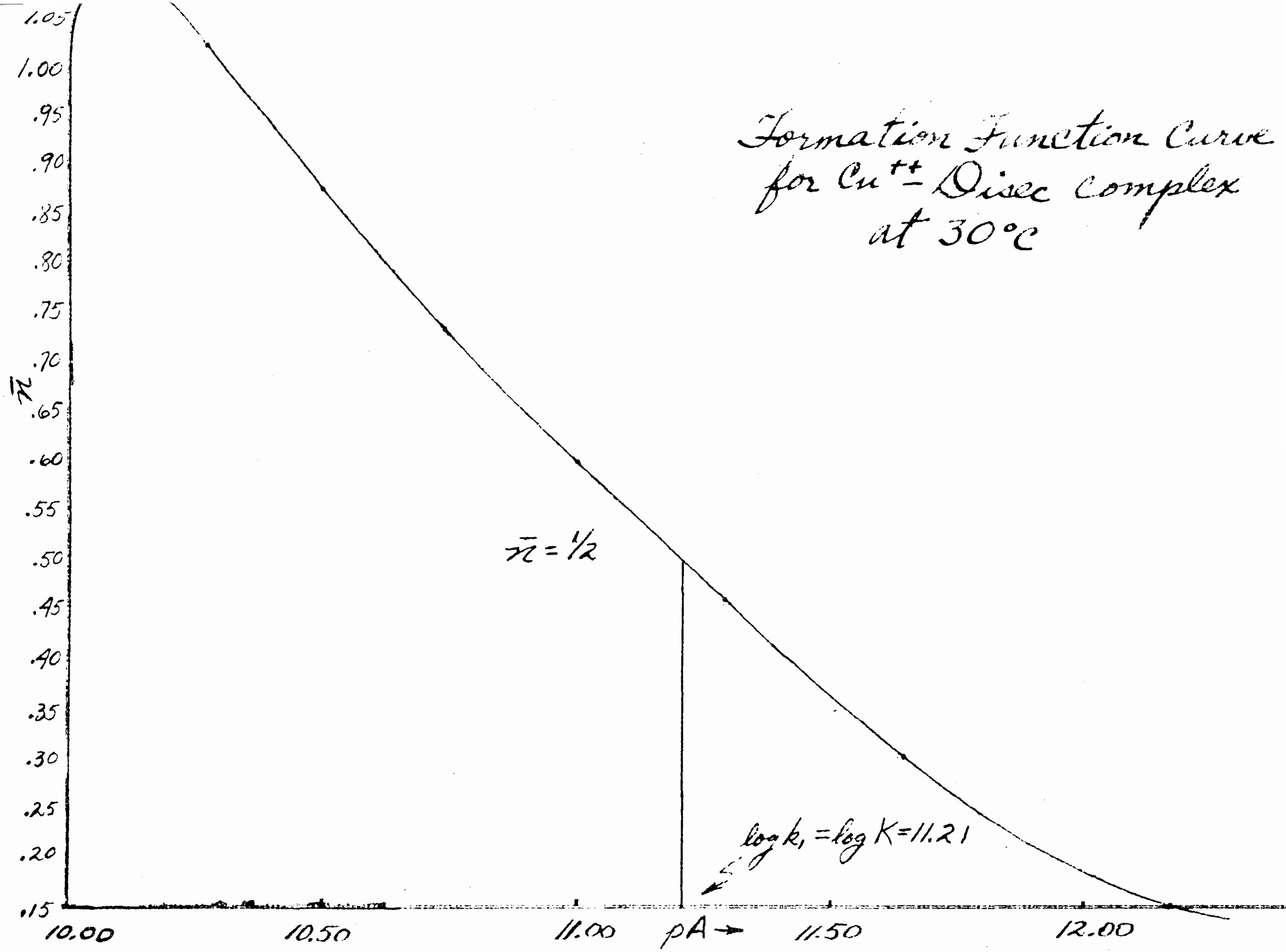
Formation Function Curve
for Cu^{++} - Bismon Complex
at 30°C



Formation Function Curve for Cu^{++}-Bismon Complex at 40°C

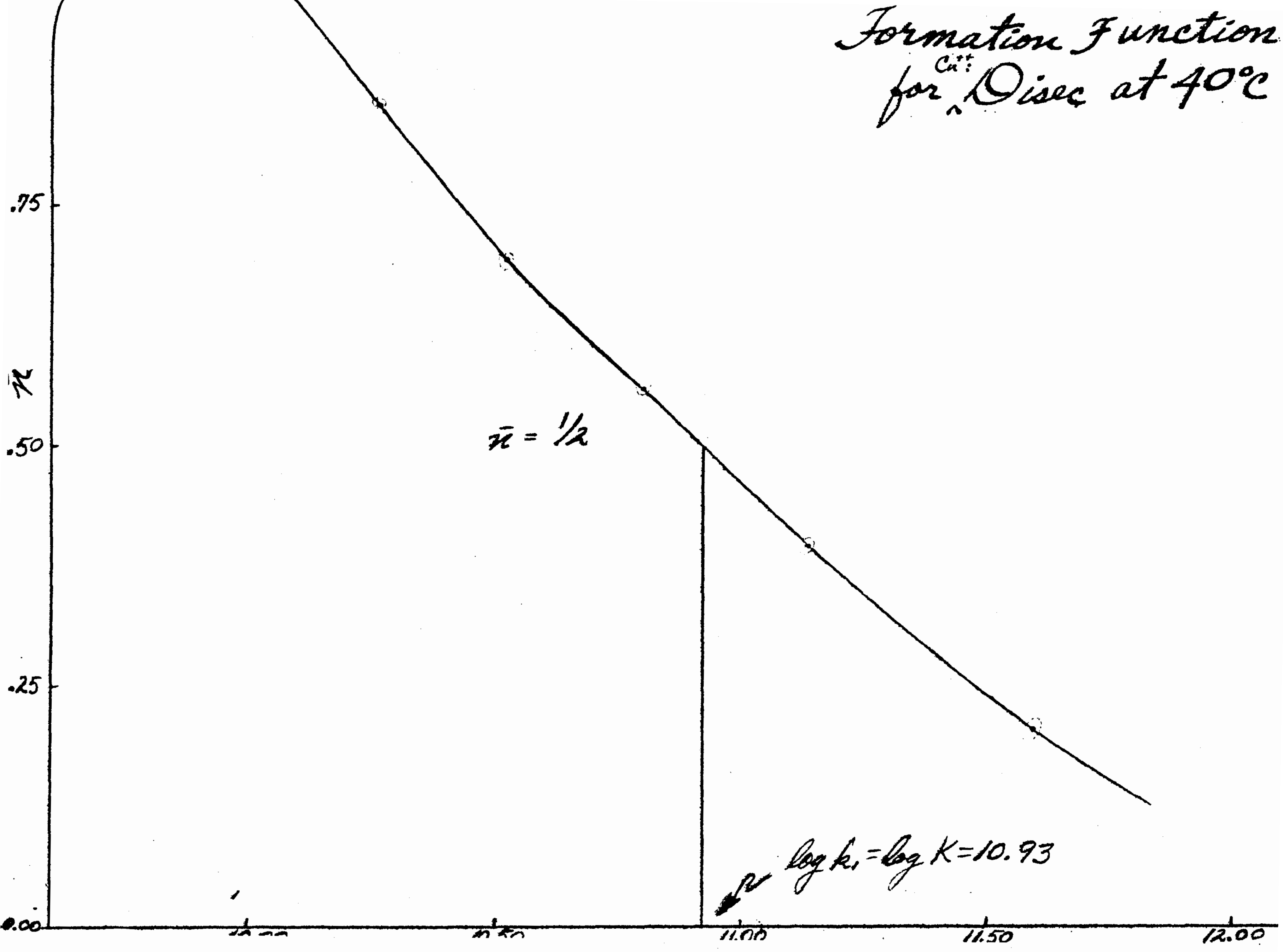


Formation Function Curve for Cu^{++}- Disalc Complex at 20°C



Formation Function Curve for Cu^{++} - Disec complex at 30°C

Formation Function
for $\overset{Cu^{++}}{\wedge}$ Disec at 40°C



(D) Mathematical Evaluation of Stability Constants

Beginning with Bjerrum's Formation Function:

$$\bar{n} = \frac{k_1 (A) + 2k_1k_2(A)^2 + 3k_1k_2k_3(A)^3 \ldots}{1 + k_1(A) + k_1k_2 (A)^2 + k_1k_2k_3 \ \ldots .} = \frac{\sum_1^N nK_n (A)^n}{1 + \sum_1^N K_n(A)^n}$$

where K_n equals the product $k_1k_2k_3 \ldots k_n$, and n equals the actual number of ligands bound to a given metallic ion. Since N = 1 for the copper chelates of both Bismon and Disec, the expression was simplified to the following:

$$\bar{n} = \frac{k_1(A)}{1 + k_1(A)}$$

Therefore, $\bar{n} + \bar{n}k_1(A) = k_1(A)$

$$\bar{n} = k_1(A) - \bar{n}k_1(A) = k_1 \left[(A) - \bar{n}(A)\right]$$

$$k_1 = \frac{\bar{n}}{(A) - \bar{n}(A)} = \frac{\bar{n}}{(A)\ (1-\bar{n})}$$

Block and McIntyre (12) introduced certain simplifying notations* one of which was J_n where $J_n = (n - \bar{n})\,(A)^n$. The specific equation above took the form:

$$k_1 = \frac{\bar{n}}{J_1}$$

The following calculations for the individual stability constants were made using this simplification.

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* It should be stated that even though the simplifying terms used by Block and McIntyre apparently are unnecessary when N = 1 these simplifications have proven very helpful for systems where N = 2 or N = 3. In these systems, the expressions for k_n are more complicated, and any simplification is desirable.

$$J_1 = (1-\bar{n})(A); \; k_1 = \frac{\bar{n}}{J_1}$$

20° Disec $\quad \text{pH} = 3.00; \; \bar{n} = 0.5129; \; (A) = 2.56 \times 10^{-12}$

$$J_1 = (1-0.5129)(2.56 \times 10^{-12}) = (0.4871)(2.56 \times 10^{-12}) = 1.247 \times 10^{-12}$$

$$k_1 = \frac{.5129}{1.247 \times 10^{-12}} = 4.12 \times 10^{11} \; ; \log k_1 = 11.615$$

30° Disec $\quad \text{pH} = 2.90; \; \bar{n} = 0.4626; \; (A) = 5.076 \times 10^{-12}$

$$J_1 = (0.5374)(5.076 \times 10^{-12}) = 2.729 \times 10^{-12}$$

$$k_1 = \frac{0.4626}{2.729 \times 10^{-12}} = 1.695 \times 10^{11} \; ; \log k_1 = 11.2292$$

40° Disec $\quad \text{pH} = 2.90; \; \bar{n} = 0.5632; \; (A) = 1.569 \times 10^{-11}$

$$J_1 = (0.4368)(1.569 \times 10^{-11}) = 0.6853 \times 10^{-11}$$

$$k_1 = \frac{0.5632}{0.6853 \times 10^{-11}} = 8.21 \times 10^{10} \; ; \log k_1 = 10.914$$

20° Bismon $\quad \text{pH} = 3.10; \; \bar{n} = 0.5045; \; (A) = 3.133 \times 10^{-14}$

$$J_1 = (0.4955)(3.133 \times 10^{-14}) = 1.552 \times 10^{-14}$$

$$k_1 = \frac{0.5045}{1.552 \times 10^{-14}} = 3.24 \times 10^{13} \; ; \log k_1 = 13.510$$

30° Bismon $\quad \text{pH} = 3.00; \; \bar{n} = 0.554; \; (A) = 5.300 \times 10^{-14}$

$$J_1 = (0.446)(5.300 \times 10^{-14}) = 2.364 \times 10^{-14}$$

$$k_1 = \frac{0.554}{2.364 \times 10^{-14}} = 2.34 \times 10^{13} \; ; \; \log k_1 \; 13.369$$

40° Bismon $\quad \text{pH} = 3.30; \; \bar{n} = 0.545; \; (A) = 4.296 \times 10^{-13}$

$$J_1 = (0.455)(4.296 \times 10^{-13}) = 1.955 \times 10^{-13}$$

$$k_1 = \frac{(0.545)}{1.995 \times 10^{-13}} = 2.73 \times 10^{12} \; ; \log k_1 = 12.436$$

Thermodynamic Calculations

(A) Theoretical Treatment

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

$$d \ln K = \frac{\Delta H}{R} \quad \frac{dT}{T^2}$$

$$\int d \ln K = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\int d \ln K = \frac{\Delta H}{R} \int T^{-2}\, dT$$

$$\ln K \Big]_{K_1}^{K_2} = \frac{-\Delta H}{R} \left[\frac{1}{T}\right]_1^2$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$-\ln \frac{K_1}{K_2} = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$\left(\frac{T_1 T_2 R}{T_1 - T_2}\right) \ln \left(\frac{K_1}{K_2}\right) = \Delta H$$

$$\Delta H = \frac{T_1 T_2}{T_1 - T_2} (R)(2.3)(\log K_1 - \log K_2)$$ Temp. Range: 20-40°C

(B) Calculations

For Disec

$$\Delta H = \frac{(293)(313)}{293 - 313} (1.987)(2.30)(11.615 - 10.914)$$

$$\Delta H = \frac{91.7 \times 10^3}{-20} (4.57)(.701)$$

$$\Delta H = (-4.58 \times 10^3)(4.57)(.701)$$

$$\Delta H = -14.68 \times 10^3 \text{ cal.}$$

$$\Delta H = -14.68 \text{ kcal.}$$

For Bismon

$\Delta H = (-4.58 \times 10^3)(4.57)(13.510 - 12.436)$

$\Delta H = (-20.7 \times 10^3)(1.074)$

$\Delta H = -22.4 \times 10^3$ cal

$\Delta H = -22.4$ kcal

$$\Delta F = -RT \ln K$$

Disec at 20°C $\Delta F = -(1.987)(293)(2.30)(11.615) = -15580$ cal or -15.58 kcal

Disec at 30°C $\Delta F = -(1.987)(303)(2.30)(11.23) = 15576$ cal or -15.58 kcal

Disec at 40°C $\Delta F = -(1.987)(313)(2.30)(10.91) = -15634$ cal or -15.63 kcal

Bismon at 20°C $\Delta F = -(1.987)(293)(2.30)(13.510) = -18117$ cal or -18.12 kcal

Bismon at 30°C $\Delta F = -(1.987)(303)(2.30)(13.37) = -18544$ cal or -18.54 kcal

Bismon at 40°C $\Delta F = -(1.987)(313)(2.30)(12.44) = -17827$ cal or -17.83 kcal

$$\Delta F = \Delta H - T\,\Delta S \; ; \quad \Delta S = \frac{\Delta H - \Delta F}{T}$$

Disec at 20°C $\Delta S = \frac{(-14.68 \times 10^3 + 15.58 \times 10^3)}{293} = \frac{.90 \times 10^3}{293} = \frac{900}{293} = 3.07$ cal/deg

Disec at 30°C $\Delta S = \frac{(-14.68 \times 10^3 + 15.58 \times 10^3)}{303} = \frac{.90 \times 10^3}{303} = \frac{900}{303} = 2.97$ cal/deg

Disec at 40°C $\Delta S = \frac{(-14.68 \times 10^3 + 15.63 \times 10^3)}{313} = \frac{.95 \times 10^3}{313} = \frac{950}{313} = 3.04$ cal/deg

Bismon at 20°C $\Delta S = \frac{(-22.4 \times 10^3 + 18.12 \times 10^3)}{293} = \frac{-4.28 \times 10^3}{293} = \frac{4280}{293} = -14.6$ cal/deg

Bismon at 30°C $\Delta S = \frac{(-22.4 \times 10^3 + 18.54 \times 10^3)}{303} = \frac{-3.86 \times 10^3}{303} = \frac{-3860}{303} = -12.74$ cal/deg

Bismon at 40°C $\Delta S = \frac{(-22.4 \times 10^3 + 17.83 \times 10^3)}{313} = \frac{-4.57 \times 10^3}{313} = \frac{4570}{313} = -14.6$ cal/deg

(C) Discussion

In the formation of the copper chelates of Bismon and Disec, it is apparent from the log K values that both compounds have high stabilities. Inspection of the associated thermodynamic quantities is significant even when the log K values are given entirely in terms of concentrations. It is seen that the $-\Delta F$ and $-\Delta H$ values are in agreement with the corresponding stabilities of the compounds. The high $-\Delta H$ values signify the relative bond strengths between metal and ligand, and are in accord with the respective basicities of the ligand.(8) On the other hand, the values for the change in entropy upon formation of the two compounds are very different. Whereas the formation of the copper-Disec chelate is accompanied by a favorable entropy change (approximately +3 e. u.), formation of the copper-Bismon chelate is accompanied by a negative entropy change (approximately -14. 5 e. u.). According to other workers,(8) this may mean that the structure of the ring is under strain. At first glance, one might assume this strain to arise from the presence of a 6-membered ring in a system where 5-membered rings are usually more stable.(24) However, the copper-Disec chelate also may have the same ring structure. Therefore, this seems not to be the significant factor since the entropy change is favorable in the case of the copper-Disec compound.

Regardless of the cause of this negative entropy change, it is assumed that the enthalpy $(-\Delta H)$ effect is favorable enough so as not to be significantly offset by the unfavorable entropy effect.

As a direct comparison of the stabilities of the two compounds, the following reaction may be written:

$$\mathrm{Cu(Disec)^{++} + Bismon \rightleftharpoons Cu(Bismon)^{++} + Disec}$$

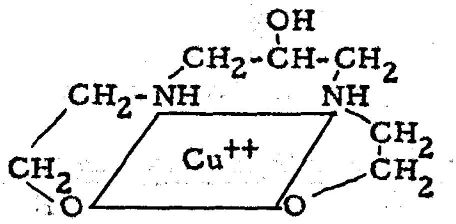
The associated thermodynamic quantities for the reaction are therefore:

t°C	Δ F	Δ H	Δ S
20	-2.62		-17.67
30	-2.96	-7.72	-15.67
40	-2.20		-17.64

Formation of the copper-Bismon chelate is in harmony with the relative strengths of the ligands, as seen by the favorable ΔF and ΔH values. The small value for (- ΔH) in this case is expected since the reaction involves a more negative entropy value. Replacement of Disec molecules by Bismon in the chelates, apparently causes an increase in strain upon ring formation. Even with this increase, the copper-Bismon chelate is more stable than the copper-Disec chelate. This is primarily an enthalpy effect due to the greater basicity of Bismon.

STRUCTURE OF BISMON : Cu(II) CHELATE

It has been shown that the mole ratio of Bismon to copper ion is 1:1. Since Cu(II) is usually considered as having a coordination number of four, and the copper chelates as having a square planar configuration,(19) it is assumed that for the 1:1 mole ratio of Bismon: Cu(II) the Bismon is quadridentate. This being the case, a structure may be proposed whereby both the nitrogen atoms and the two primary alcohol groups take part in chelate formation.



The secondary alcohol group appears not to take part in the chelation, since the resulting compound would be non-planar. This secondary alcohol group does have a tendency to contribute to the chelation of Cu(II) as this was demonstrated in the chelation of Cu(II) by 1, 3-diamino-2-propanol.(9) The ligand in that case, was apparently terdentate, whereas for the copper chelates of Bismon and Disec it is quadridentate. No indication of polynucleation or polymerization was noted.

SUMMARY

Two polyhydroxyamines, 1,3-bis(tris(hydroxymethyl)methylamino)-2-propanol dihydrochloride and 1,3-bis(2-hydroxyethylamino)-2-propanol dihydrochloride, have been prepared; and the melting points of the compounds were found to be 188°C and 139-44°C respectively. These hydrochlorides were converted to their corresponding ammonium bases by passing aqueous solutions of each salt through an ion exchange column containing Amberlite XE-78 resin. Standardized solutions of the bases were potentiometrically titrated with 0.209 N perchloric acid at 20°C, 30°C and 40°C, and the equilibrium constants were determined from the data. The pk values for the bases are listed in the following table:

1,3 bis(tris(hydroxymethyl)methylamino)-2-propanol

	20°C	30°C	40°C
pk_1	6.15	5.89	5.67
pk_2	8.15	7.94	7.72

1,3-bis(2-hydroxyethylamino)-2-propanol

	20°C	30°C	40°C
pk_1	7.10	6.90	6.63
pk_2	8.80	8.77	8.51

The molar ratio of ligand to Cu(II) ion for Bismon was found to be 1:1 by applying Job's Method of Continuous Variations and the method of Yoe and Jones. Stability constant values were determined for the Cu(II) chelates of both bases by means of potentiometric titration measurements at 20°C, 30°C and 40°C. The log K values are listed in the following table:

Cu(II) : 1, 3-bis(tris(hydroxymethyl)methylamino)-2-propanol

	20°C	30°C	40°C
log K	11.62	11.23	10.91

Cu(II) : 1, 3-bis(2-hydroxyethylamino)-2-propanol

	20°C	30°C	40°C
log K	13.51	13.37	12.44

Thermodynamic considerations supported the relative stability of the two chelates. It was found that 1, 3-bis(2-hydroxyethylamino)-2-propanol formed the more stable chelate with Cu(II). This was in accord with the more basic characteristics of the ligand. The negative values of the entropy change upon chelation with Cu(II) are, in both chelates, attributed to the strain within the structure upon ring formation. Each chelate appeared to involve two 5-membered rings and one 6-membered ring. No apparent chelation was found to exist involving the secondary alcohol group of the ligands.

APPENDIX

TABLES OF DATA

Disec Standardization

Maximum λ

Bismon Equilibrium Constant

Disec Equilibrium Constant

Cu (II): Bismon Stability Constant

Cu (II): Disec Stability Constant

#1

DISEC STANDARDIZATION

V $HClO_4$	pH	ΔpH	ΔV	$\frac{\Delta pH}{\Delta V}$
0.00	9.92			
2.00	8.57			
5.00	8.03			
7.00	7.75			
9.00	7.43			
10.00	7.27			
12.00	6.83			
14.00	6.43			
16.00	6.13			
18.00	5.85			
19.05	5.69			
20.00	5.54			
21.00	5.36			
22.00	5.11			
22.50	4.90	.21	.50	.42
23.10	4.50	.40	.60	.66
23.30	4.29	.21	.20	1.05
23.60	3.50	.79	.30	2.63
23.80	3.13	.37	.20	1.85
23.90	3.00	.13	.10	1.30
24.00	2.88	.12	.10	1.20
24.10	2.81	.07	.10	.70
24.20	2.73	.08	.10	.80
24.40	2.62	.11	.20	.55
24.60	2.54	.08	.20	.40
24.80	2.48	.06	.20	.30
25.02	2.40	.08	.22	.36
26.00	2.19			
27.03	2.03			
28.00	1.93			

#2

V $HClO_4$	pH	ΔpH	ΔV	$\frac{\Delta pH}{\Delta V}$
0.00	9.99			
2.00	8.60			
5.00	8.05			
7.00	7.78			
9.00	7.47			
10.00	7.29			
12.00	6.87			
14.00	6.45			
16.00	6.13			
18.00	5.86			
20.00	5.57			
21.00	5.37			
21.50	5.11			
22.50	4.92	.19	.50	.38
23.00	4.62	.30	.50	.60
23.20	4.41	.21	.20	1.05
23.30	4.25	.16	.10	1.60
23.40	4.18	.17	.10	1.70
23.50	3.95	.23	.10	2.30
23.60	3.65	.30	.10	3.00
		.28	.10	2.8

2 cont'd.

HClO$_4$	pH	ΔpH	ΔV	$\frac{\Delta pH}{\Delta V}$
3.70	3.37	.18	.10	1.8
3.80	3.19	.17	.10	1.7
3.90	3.02	.12	.10	1.2
4.00	2.90	.15	.20	.75
4.20	2.75	.12	.20	.60
4.40	2.63	.10	.20	.50
4.60	2.53			
5.00	2.40			
6.00	2.20			
7.00	2.03			
8.00	1.93			
9.00	1.85			

3

HClO$_4$	pH	ΔpH	ΔV	$\frac{\Delta pH}{\Delta V}$
0.00	9.99			
2.00	8.59			
5.05	8.07			
7.00	7.78			
9.00	7.47			
0.02	7.28			
2.00	6.87			
4.00	6.44			
6.02	6.13			
8.00	5.87			
0.00	5.56			
1.00	5.36			
1.50	5.26			
2.00	5.11	.20	.50	.40
2.50	4.91	.31	.50	.62
3.00	4.60	.22	.20	1.10
3.20	4.38	.16	.10	1.60
3.30	4.22	.21	.10	2.10
3.40	4.01	.29	.10	2.90
3.50	3.72			
3.60	3.55	.26	.10	2.60
3.70	3.29	.18	.10	1.80
3.80	3.11	.12	.10	1.20
3.90	2.99	.10	.10	1.00
4.00	2.89	.17	.20	.85
4.20	2.72	.11	.20	.55
4.40	2.61	.09	.20	.45
4.60	2.52			
5.00	2.41			
6.00	2.19			
7.00	2.05			
8.00	1.93			
9.00	1.85			

Determination of Wavelength for Greatest Absorbency . . . Variation of Absorbency with pH

Sample of Bismon crystals made up to a 1:1 ratio with Cu^{++} (5 ml .1 N Cu^{++} diluted to 100 ml with H_2O and/or NaOH soln. for pH adjustment.)

#1	31.5245	S#1	29.8758	S#2	30.0069	S#3	29.7476
	31.3987		29.7476		29.8758		29.6192
	.1258 gm		.1282 gm		.1311 gm		.1284 gm

S#4	30.2813	S#5	29.6030	S#6	29.4746	S#7	29.3457
	30.1546		29.4746		29.3457		29.2193
	.1267 gm		.1284 gm		.1289 gm		.1264 gm

#1 pH = 3.00
S#1 " = 3.91
S#2 " = 4.92
S#3 " = 5.90
S#4 " = 6.96
S#5 " = 8.06
S#6 " = 8.88
S#7 " = 9.95

Abs. #1	λ	Slit Width
----	400	.405
----	425	.335
----	450	.299
----	475	.255
----	500	.210
----	525	.170
.002	550	.135
.002	575	.110
.006	600	.086
.010	625	.071
.016	650	.057
.024	675	.050
.036	700	.042
.046	725	.040
.057	750	.036
.060	775	.032
.065	800	----
.063	825	.029
.062	850	.026
.059	875	.026
.056	900	.025
.052	925	.027
.046	950	.031
.042	975	.036
.040	1000	.041

Cell 1 : distilled H_2O; Cell 2 : S#1; Cell 3 : S#2; Cell 4 : S#3

Abs. S#1	Abs. S#2	Abs. S#3	λ	Slit Width
.085	.129	.096	400	.420
.032	.046	.028	425	.368
.013	.019	.006	450	.308
.011	.016	.010	475	.255
.009	.025	.028	500	.213
.014	.056	.073	525	.169
.024	.111	.146	550	.135
.035	.168	.219	575	.109
.047	.209	.270	600	.086
.056	.222	.283	625	.070
.063	.214	.265	650	.059
.067	.197	.231	675	.050
.074	.183	.202	700	.045
.077	.154	.162	725	.039
.082	.133	.131	750	.037
.083	.108	.097	800	.030
.078	.096	.082	825	.029
.072	.080	.064	850	.028
.067	.072	.056	875	.026
.062	.062	.046	900	.025
.056	.051	.037	925	.026
.052	.044	.028	950	.031
.049	.039	.025	975	.037
.045	.034	.021	1000	.041

Cell 1: distilled H_2O; Cell 2: S#4

Abs. S#4	λ	Slit Width
.188	400	.422
.062	425	.373
.027	450	.313
.034	475	.259
.068	500	.213
.127	525	.170
.206	550	.139
.281	575	.110
.331	600	.088
.345	625	----
.332	650	.059
.299	675	.050
.256	700	.045
.217	725	.040
.183	750	.036
.150	775	.033
.124	800	.032
.102	825	.030
.083	850	.028
.067	875	.027
.055	900	.026
.044	925	.027
.036	950	.031
.028	975	.039
.023	1000	.044

Cell 1: distilled H_2O; Cell 2: S#5; Cell 3: S#6; Cell 4: S#7

Abs. S#5	Abs. S#6	Abs. S#7	λ	Slit Width
.139	.121	.101	400	.435
.050	.039	.027	425	.380
.028	.027	.023	450	.318
.046	.052	.060	475	.260
.090	.115	.119	500	.212
.164	.179	.201	525	.171
.253	.268	.290	550	.138
.326	.337	.351	575	.110
.370	.379	.385	600	.089
.375	.382	.386	615	.076
.370	.376	.370	625	.070
.335	.337	.320	650	.059
.287	.285	.264	675	.050
.236	.236	.215	700	.044
.185	.185	.168	725	.040
.146	.148	.136	750	.035
.116	.122	.110	775	.034
.093	.095	.086	800	.032
.069	.073	.066	825	.030
.056	.060	.058	850	.028
.047	.050	.048	875	.026
.036	.040	.041	900	.025
.030	.033	.036	925	.026
.025	.029	.033	950	.032
.020	.023	.027	975	.038
.017	.021	.024	1000	.042

DATA FOR BISMON EQUILIBRIUM CONSTANT

sing 50 ml of Bismon free base (.01 M) and titrating with .0211 N $HClO_4$ at
° C - 1st run

i	ΔpH	V ml $HClO_4$	ΔV	ΔpH/ΔV
.04		0.00		
.61		2.00		
.37		4.00		
.26		5.00		
.91		9.00		
.77		11.00		
.62		13.00		
.40		16.00		
.23		18.00		
.04		20.00		
.85		22.00		
.76		23.00		
.67		24.00		
.58		25.00		
.48		26.00		
.39		27.00		
.30		28.00		
.22		29.00		
.06	.16	31.00	2.0	.08
.90	.16	33.00	2.0	.08
.74	.20	35.00	2.0	.10
.54	.19	37.00	2.0	.095
.35	.34	39.00	2.05	.17
.01		41.05		

pH	ΔpH	Vml$HClO_4$	ΔV	ΔpH/ΔV
5.80	.21	42.00	.95	.22
5.64	.16	42.50	.50	.32
5.40	.24	43.00	.50	.48
5.08	.32	43.50	.50	.64
4.68	.40	44.00	.50	.80
4.32	.36	44.50	.50	.72
4.06	.26	45.00	.50	.52
3.82	.24	45.50	.50	.48
3.66	.16	46.00	.50	.32
3.40	.26	47.00	1.00	.26
3.21	.19	48.05	1.00	.19
3.10		49.00		
3.00		50.00		

Using 50 ml Bismon free base (.01 M) and titrating with .209 N $HClO_4$ at 30° C - 2nd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ΔV
10.08		0.00		
9.69		.20		
9.37		.40		
9.20		.60		
9.02		.80		
8.85		1.00		
8.70		1.20		
8.59		1.40		
8.41		1.60		
8.27		1.80		
8.09		2.00		
7.88		2.20		
7.68		2.42		
7.50		2.60		
7.37		2.80		
7.20		3.00		
7.02		3.20		
6.86		3.40		
6.72		3.60		
6.51		3.80		
6.30	.21	4.00	.20	1.05
5.83	.47	4.20	.20	2.35
5.48	.35	4.30	.10	3.50
4.79	.69	4.40	.10	6.90
4.10	.69	4.50	.10	6.90

pH	ΔpH	ΔV	Vml$HClO_4$	ΔpH/ΔV
3.61	.49	.10	4.60	4.9
3.18	.43	.10	4.70	4.3
3.00	.18	.10	4.80	1.8
2.87	.13	.10	4.90	1.3
2.76	.11	.10	6.00	1.1
2.61			5.20	
2.50			5.40	
2.40			5.60	
2.31			5.80	
2.27			6.00	
2.13			6.50	
2.04			7.00	
1.90			8.00	
1.80			9.00	
1.71			10.04	

Using 50 ml Bismon free base (.01 M) and titrating with (.209 N) $HClO_4$
at 30° C - 3rd run

pH	ΔpH	ml $HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
10.20		0.00		
9.83		.21		
9.41		.41		
9.20		.60		
9.01		.80		
8.85		1.00		
8.69		1.20		
8.52		1.40		
8.44		1.60		
8.26		1.80		
8.08		2.00		
7.82		2.20		
7.61		2.40		
7.41		2.60		
7.24		2.80		
7.12		3.00		
6.91		3.20		
6.77	.20	3.40	.20	1.00
6.57	.23	3.60	.20	1.15
6.34	.35	3.80	.20	1.75
5.99	.27	4.00	.10	2.70
5.72	.44	4.10	.10	4.40
5.28	.79	4.22	.12	6.58
4.49	.64	4.30	.08	8.00
3.85		4.40		

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
3.44	.41	4.50	.10	4.10
3.20	.24	4.60	.10	2.40
3.03	.17	4.70	.10	1.70
2.80	.15	4.81	.11	1.36
2.80	.08	4.90	.09	1.13
2.73	.07	5.00	.10	.70
2.64		5.21		
2.58		5.40		
2.50		5.60		
2.46		5.80		
2.41		6.00		
2.32		6.50		
2.25		7.00		
2.14		8.02		
2.07		9.00		
2.00		10.00		

ing 50 ml Bismon free base .01M and titrating with .209N $HClO_4$ at
° - 1st run

	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
70		0.00		
32		.20		
.		-		
13		.60		
.02		.80		
.88		1.00		
.73		1.20		
.63		1.40		
.48		1.60		
.40		1.82		
.25		2.00		
.00		2.20		
.83		2.40		
.66		2.60		
.43		2.85		
.36		3.00		
.15		3.21		
.03		3.40		
.81	.18	3.60	.20	.90
.63	.39	3.80	.20	1.95
.24	.26	4.00	.10	2.60
.98	.49	4.10	.10	4.90
.49		4.20		
:	1.62	:	.20	8.10
.87		4.40		

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
	.43		.10	4.30
3.44	.24	4.50	.10	2.40
3.20	.14	4.60	.10	1.40
3.06	.10	4.70	.10	1.00
2.96	.09	4.80	.10	.90
2.87		4.90		
2.81		5.00		
2.60		5.50		
2.50		6.00		
2.43		6.50		
2.39		7.01		

Using 50 ml Bismon free base .01M and titrating with .209 N$HClO_4$ at 20° C - 2nd run

pH	ΔpH	ml$HClO_4$	ΔV	ΔpH/ΔV
9.68		0.00		
-		.20		
9.45		.40		
9.34		.60		
9.12		.80		
9.00		1.00		
8.82		1.20		
8.72		1.40		
8.60		1.60		
8.46		1.80		
8.27		2.00		
8.10		2.20		
7.88		2.40		
7.73		2.60		
7.54		2.80		
7.40		3.00		
7.27		3.30		
7.10		3.40		
6.89		3.60		
6.67	.22	3.81	.21	1.05
6.36	.31	4.00	.19	1.63
6.01	.35	4.10	.10	3.50
5.50	.51	4.20	.10	5.10
4.76	.74	4.30	.10	7.40
4.18	.58	4.40	.10	5.80

pH	ΔpH	ml$HClO_4$	ΔV	ΔpH/ΔV
	.67		.10	6.70
3.51	.23	4.50	.10	2.30
3.28	.15	4.66	.11	1.36
3.13	.10	4.71	.09	1.11
3.03	.09	4.80	.10	.90
2.94		4.90		
2.87		5.00		
2.67		5.50		
2.57		6.00		
2.47		6.50		
2.37		7.02		

sing 50 ml .01M Bismon free base and titrating with .209 $NHClO_4$ at
0° C - 3rd run

H	ΔpH	ml $HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
.78		0.00		
.48		.20		
.30		.40		
.10		.60		
.96		.80		
.81		1.00		
.11		1.20		
.57		1.41		
.42		1.60		
.30		1.80		
.14		2.00		
.92		2.20		
.77		2.40		
.60		2.60		
.43		2.80		
.27		3.00		
.10		3.21		
.96	.18	3.40	.20	.90
.78	.20	3.60	.20	1.00
.58	.34	3.80	.20	1.70
.24	.24	4.00	.10	2.40
.00	.42	4.10	.10	4.20
.58	.75	4.20	.10	7.50
.83	.72	4.30	.10	7.20
.11	.51	4.40	.10	5.10
.60		4.50		

pH	ΔpH	ml $HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
	.31		.10	3.10
3.29	.25	4.60	.11	2.27
3.04	.10	4.21	.09	1.11
2.94	.07	4.80	.10	.70
2.87	.07	4.90	.10	.70
2.81		5.00		
2.60		5.50		
2.49		6.00		
2.40		6.50		
2.32		7.00		

Using 50 ml of .01 M Bismon free base and titrating with .209 N $HClO_4$ at 40° C - 1st run

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
9.77		0.00		
9.32		.22		
9.09		.40		
8.90		.60		
8.72		.80		
8.58		1.00		
8.40		1.20		
8.27		1.40		
8.10		1.60		
7.93		1.80		
7.74		2.01		
7.53		2.22		
7.38		2.40		
7.18		2.60		
7.00		2.80		
6.82		3.00		
6.68		3.20		
6.50	.18	3.40	.20	.90
6.32	.24	3.60	.20	1.20
6.08	.35	3.80	.20	1.75
5.73	.26	4.00	.11	2.36
5.47	.48	4.11	.09	5.33
4.99	.75	4.20	.10	7.50
4.24	.42	4.30	.10	4.20
3.82		4.40		

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
3.24	.58	4.50	.10	5.80
3.03	.21	4.60	.10	2.10
2.90	.13	4.70	.10	1.30
2.78	.12	4.80	.10	1.20
:	.19	:	.20	.95
2:59	.26	5:00	.51	.51
2.33		5.51		
2.17		6.00		
2.04		6.50		
1.95		7.02		
1.82		8.00		
1.72		9.00		
1.65		10.00		

Using 50 ml .01 M Bismon free base and titrating with .209 N $HClO_4$ at 40° C - 2nd run

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
9.76		0.00		
9.34		.20		
9.07		.40		
8.90		.60		
8.72		.80		
8.58		1.00		
8.39		1.20		
8.26		1.40		
8.09		1.60		
7.90		1.80		
7.72		2.00		
7.53		2.20		
7.36		2.40		
7.13		2.60		
6.99		2.80		
6.81		3.00		
6.64		3.20		
6.50		3.40		
6.28	.18	3.60	.20	.90
6.10	.34	3.80	.20	1.70
5.76	.26	4.00	.10	2.60
5.50	.39	4.10	.10	3.90
5.11	.73	4.20	.10	7.30
4.38	.60	4.30	.10	6.00
3.78		4.40		

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
3.38	.40	4.50	.10	4.00
3.00	.38	4.61	.11	3.45
2.89	.11	4.70	.09	1.22
2.78	.11	4.80	.10	1.10
2.69	.09	4.90	.10	.90
2.58	.11	5.00	.10	1.10
2.31		5.50		
2.16		6.00		
2.04		6.50		
1.96		7.00		

sing 50 ml .01 M Bismon free base and titrating with .209 N $HClO_4$ at
0° C - 3rd run

H	ΔpH	ml $HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
.76		0.00		
.38		.20		
.10		.40		
.90		.60		
.73		.80		
.58		1.00		
.42		1.20		
.25		1.40		
.09		1.60		
.92		1.80		
.73		2.00		
.58		2.20		
.34		2.40		
.14		2.60		
.99		2.80		
.81		3.00		
.64		3.20		
.50		3.40		
.32	.21	3.60	.20	1.05
.11	.35	3.80	.20	1.75
.76	.32	4.00	.10	3.20
.44	.48	4.10	.10	4.80
.96	.74	4.20	.10	7.40
.22	.53	4.30	.10	5.30
.69		4.40		

pH	ΔpH	ml$HClO_4$	ΔV	$\frac{\Delta pH}{\Delta V}$
	.38		.10	3.80
3.31	.24	4.50	.10	2.40
3.07	.17	4.60	.10	1.20
2.90	.11	4.70	.10	1.10
2.79	.09	4.80	.10	.90
2.70	.09	4.90	.10	.90
2.61		5.00		
2.32		5.50		
2.15		6.00		
2.04		6.50		
1.94		7.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 20° - 1st run

pH	ml $HClO_4$
9.92	0.00
9.63	0.20
9.42	0.40
9.29	0.61
9.20	0.80
9.11	1.00
9.01	1.20
8.96	1.40
8.90	1.60
8.83	1.80
8.79	2.00
8.73	2.20
8.70	2.40
8.66	2.60
8.62	2.80
8.59	3.00
8.44	3.80
8.41	4.00
8.32	4.50
8.29	5.00
8.20	5.50
8.12	6.00
8.05	6.50
7.99	7.00
7.91	7.50
7.85	8.00
7.78	8.50
7.69	9.01
7.60	9.50
7.51	10.01
7.42	10.50
7.31	11.00
7.20	11.50
7.10	12.00
7.00	12.50
6.90	13.03
6.80	13.50
6.71	14.00
6.63	14.50
6.56	15.00
6.48	15.53
6.41	16.00
6.32	16.50
6.28	17.00
6.20	17.50
6.14	18.00

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 20° - 1st run (continued)

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
6.08		18.50		
6.00		19.00		
5.93		19.50		
5.87		20.00		
5.77		20.50		
5.69		21.00		
5.58		21.55		
5.49		22.00		
5.33	.20	22.50	.50	.40
5.13	.16	23.00	.30	.533
4.97	.31	23.30	.30	1.033
4.66	.55	23.60	.30	1.833
4.11	.40	23.90	.10	4.00
3.71	.31	24.00	.10	3.1
3.40	.29	24.10	.13	2.23
3.11	.16	24.23	.17	.94
2.95	.16	24.40	.20	.80
2.79	.11	24.60	.20	.55
2.68	.10	24.80	.21	.476
2.58		25.01		
2.49		25.30		
2.46		25.50		
2.38		25.80		
2.32		26.00		
2.23		26.50		
2.17		27.00		
2.11		27.50		
2.05		28.00		
1.98		29.00		
1.90		30.00		
1.87		30.50		
1.83		31.05		
1.80		32.00		
1.72		34.00		
1.65		36.05		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 20° - 2nd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ΔV
9.60		.01		
8.50		3.30		
8.00		6.70		
7.50		10.25		
7.00		12.51		
6.50	.50	15.40	3.63	.137
6.00	.60	19.03	3.10	.193
5.40	.10	22.13	.37	.270
5.30	.20	22.50	.50	.400
5.10	.20	23.00	.30	.666
4.90	.34	23.30	.30	1.133
4.56	.55	23.60	.20	2.750
4.01	.45	23.80	.20	2.250
3.46	.36	24.00	.20	1.800
3.10	.20	24.20	.20	1.000
2.90	.13	24.40	.20	.650
2.77	.08	24.60	.20	.400
2.69	.09	24.80	.20	.450
2.60	.33	25.00	2.00	.165
2.27		27.00		
2.09		29.00		
1.90		33.00		
1.85		37.00		
1.78		40.00		

Using 50 ml of .05 Disec free base and titrating with .209 N $HClO_4$ at 20°C - 3rd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ΔV
9.92		0.00		
8.31		5.00		
8.02		7.00		
7.72		9.00		
7.54		10.00		
7.12		12.00		
6.73		14.03		
6.42		16.00		
6.16		18.00		
5.86		20.00		
5.47		22.02		
5.30	.21	22.50	.48	.437
5.09	.18	23.00	.30	.60
4.91	.31	23.30	.30	1.033
4.60	.46	23.60	.20	2.300
4.14	.33	23.80	.10	3.3
3.81	.35	23.90	.11	3.181
3.46	.31	24.01	.13	2.384
3.15	.07	24.14	.06	1.166
3.08	.18	24.20	.20	.900
2.90	.17	24.40	.20	.850
2.73	.10	24.60	.20	.500
2.63	.06	24.80	.20	.300
2.57		25.00		
2.29		26.00		
2.13		22.00		
2.01		28.03		
1.92		29.00		
1.87		30.00		
1.75		32.00		
1.63		35.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 30°C - 1st run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
9.76		.00		
8.51		2.32		
8.00		5.50		
7.70		7.62		
7.20		10.68		
6.80		12.49		
6.50		14.02		
6.20		15.71		
6.00		17.22		
5.70		19.31		
5.49		20.65		
5.41		21.00		
5.37		21.30		
5.30		21.60		
5.20		22.00		
5.07	.06	22.50	.20	.300
4.93	.23	22.80	.30	.766
4.87	.24	23.00	.30	.800
4.64	.13	23.30	.10	1.300
4.40	.20	23.60	.10	2.000
4.27	.27	23.70	.10	2.700
4.07	.31	23.80	.10	3.100
3.80	.24	23.90	.10	2.400
3.49	.16	24.00	.10	1.600
3.25	.12	24.10	.10	1.200
3.09	.09	24.20	.10	.900
2.97	.08	24.30	.10	.800
2.88	.12	24.40	.20	.600
2.80	.14	24.50	.30	.466
2.68		24.70		
2.54		25.00		
2.40		25.50		
2.28		26.00		
2.19		26.50		
2.11		27.00		
2.00		28.00		
1.83		30.00		
1.69		33.00		
1.60		35.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 30°C - 2nd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
9.77		0.00		
8.07		5.00		
7.79		7.00		
7.48		9.00		
7.30		10.00		
6.89		12.00		
6.49		14.00		
6.18		16.00		
5.88		18.03		
5.59		20.03		
5.22		22.00		
5.07		22.50		
	.22		.50	.11
4.85		23.00		
	.17		.30	.566
4.68		23.30		
	.26		.30	.866
4.42		23.60		
	.31		.20	1.55
4.11		23.80		
	.60		.20	3.00
3.51		24.00		
	.41		.20	2.05
3.10		24.20		
	.21		.20	1.05
2.89		24.40		
	.17		.20	.85
2.72		24.60		
	.10		.20	.50
2.62		24.80		
	.07		.20	.35
2.55		25.00		
	.27		1.00	.27
2.28		26.00		
2.10		27.00		
1.99		28.00		
1.90		29.00		
1.82		30.00		
1.72		32.00		
1.60		35.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 30°C
3rd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
9.74		0.00		
8.06		5.00		
7.78		7.00		
7.47		9.00		
7.30		10.00		
6.88		12.00		
6.48		14.00		
6.16		16.00		
5.89		18.00		
5.59		20.00		
5.20	.17	22.00	.50	.34
5.03	.22	22.50	.50	.44
4.81	.16	23.00	.30	.533
4.65	.35	23.30	.30	1.166
4.30	.30	23.60	.20	1.50
4.00	.30	23.80	.10	3.00
3.70	.28	23.90	.10	2.80
3.42	.21	24.00	.10	2.10
3.21	.14	24.10	.10	1.40
3.07	.20	24.20	.20	1.00
2.87	.15	24.40	.20	.75
2.72	.11	24.60	.20	.55
2.61	.08	24.80	.20	.40
2.53	.26	25.00	1.00	.26
2.27		26.00		
2.10		27.00		
1.99		28.00		
1.90		29.00		
1.82		30.00		
1.72		32.00		
1.60		35.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 40°C
1st run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
9.48		0.00		
8.12		3.00		
7.65		6.00		
7.38		8.00		
7.03		10.00		
6.61		12.00		
6.20		14.00		
5.89		16.00		
5.60		18.00		
5.31		20.00		
4.91		22.00		
4.77	.20	22.50	.50	.40
4.57	.17	23.00	.30	.566
4.40	.28	23.30	.30	.933
4.12	.31	23.60	.20	1.55
3.81	.21	23.80	.10	2.10
3.60	.24	23.90	.10	2.40
3.36	.20	24.00	.10	2.00
3.16	.15	24.10	.10	1.50
3.01	.12	24.20	.10	1.20
2.89	.12	24.30	.20	.60
2.77	.14	24.50	.20	.70
2.63	.14	24.70	.30	.466
2.49	.17	25.00	.50	.34
2.32		25.50		
2.21		26.00		
2.05		27.00		
1.93		28.00		
		29.00		
1.77		30.00		
1.68		32.00		
1.54		35.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 40°C
2nd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
9.60		0.00		
8.20		3.00		
7.74		6.00		
7.46		8.00		
7.12		10.00		
6.69		12.00		
6.29		14.00		
5.94		16.03		
5.68		18.00		
5.38		20.00		
4.99		22.00		
4.82	.21	22.50	.50	.42
4.61	.18	23.00	.30	.60
4.43	.34	23.30	.30	1.133
4.09	.27	23.60	.20	1.35
3.82	.23	23.80	.10	2.30
3.59	.22	23.90	.10	2.20
3.37	.20	24.00	.10	2.00
3.17	.15	24.10	.10	1.50
3.02	.11	24.20	.10	1.10
2.91	.17	24.30	.20	.85
2.74	.11	24.50	.20	.55
2.63	.12	24.70	.30	.40
2.51	.14	25.00	.50	.28
2.31		25.50		
2.23		26.00		
2.09		27.00		
1.98		28.00		
1.88		29.00		
1.80		30.00		
1.71		32.00		
1.58		35.00		

Using 50 ml of .05 Disec free base and titrating with .2090 N $HClO_4$ at 40°C
3rd run

pH	ΔpH	ml $HClO_4$	ΔV	ΔpH/ ΔV
9.59		0.00		
7.88		5.00		
7.10		10.00		
6.09		15.00		
5.37		20.00		
4.95		22.00		
4.80	.22	22.50	.50	.44
4.58	.17	23.00	.30	.566
4.41	.31	23.30	.30	1.033
4.10	.39	23.60	.20	1.950
3.71	.22	23.80	.10	2.20
3.49	.23	23.90	.10	2.30
3.26	.17	24.00	.10	1.70
3.09	.13	24.10	.10	1.30
2.96	.08	24.20	.10	.80
2.88	.16	24.30	.20	.80
2.72	.13	24.50	.20	.65
2.59	.10	24.70	.30	.333
2.49	.28	25.00	1.00	.28
2.21		26.00		
2.06		27.00		
1.93		28.05		
-		30.00		
1.68		32.06		
1.56		35.05		

Using 50 ml of Cu^{++}-H^{+} soln. and titrating with .01M Bismon free base at 20°C - 1st run

pH	ml base
2.82	0.00
2.85	1.00
2.90	2.00
3.00	3.00
3.16	4.00
3.30	4.50
3.50	5.00
3.70	5.50
3.89	6.00
4.07	6.50
4.19	7.00
4.30	7.50
4.39	8.00
4.54	9.00
4.70	10.00
4.92	11.00
5.03	11.30
5.20	11.60
5.53	12.00
5.73	12.21
5.85	12.40
5.98	12.60
6.10	12.80
6.20	13.00
6.41	13.50
6.58	14.00
6.72	14.50
6.85	15.00
6.97	15.50
7.08	16.00
7.26	17.00
7.42	18.00
7.59	19.00
7.74	20.00

Using 50 ml of Cu^{++}-H^{+} soln. and titrating with .01M Bismon free base at 20°C - 2nd run.

pH	ml base
2.98	0.00
3.01	1.00
3.07	2.00
3.13	3.00
3.29	4.00
3.41	4.50
3.61	5.02
3.79	5.50
3.97	6.00
4.12	6.50
4.24	7.00
4.33	7.50
4.42	8.00
4.56	9.00
4.70	10.00
4.92	11.00
5.04	11.30
5.22	11.60
5.33	11.80
5.52	12.00
5.72	12.20
5.84	12.40
5.98	12.60
6.10	12.82
6.20	13.02
6.40	13.50
6.57	14.00
6.71	14.50
6.84	15.00
6.94	15.50
7.05	16.00
7.25	17.03
7.41	18.00
7.56	19.00
7.71	20.00
7.84	21.00

Using 50 ml of Cu^{++}-H^{+} soln. and titrating with .01M Bismon free base at 20°C - 3rd run

pH	ml base
3.00	0.00
3.03	1.00
3.08	2.00
3.17	3.00
3.32	4.00
3.46	4.50
3.64	5.00
3.81	5.50
3.99	6.00
4.13	6.50
4.25	7.00
4.34	7.50
4.43	8.00
4.58	9.00
4.72	10.00
4.95	11.00
5.06	11.30
5.22	11.60
5.36	11.80
5.54	12.00
5.73	12.20
5.87	12.40
6.00	12.60
6.10	12.80
6.18	13.00
6.40	13.52
6.57	14.00
6.71	14.50
6.83	15.00
6.94	15.50
7.04	16.00
7.23	17.00
7.40	18.00
7.56	19.02
7.71	20.06
7.84	21.00
7.97	22.00
8.08	23.00
8.20	24.00

Using 50 ml Cu^{++}-H^{+} solution, and titrating with 0.01 M Bismon free base at 30°C - 1st run:

pH	ml base
2.80	0.00
2.83	1.00
2.89	2.00
2.98	3.00
3.14	4.00
3.27	4.50
3.43	5.00
3.60	5.50
3.78	6.00
3.92	6.60
4.03	7.00
4.13	7.50
4.20	8.00
4.37	9.00
4.51	10.00
4.75	11.00
4.93	11.50
5.30	12.00
5.50	12.20
5.64	12.40
5.73	12.60
5.84	12.80
5.94	13.00
6.15	13.50
6.31	14.00
6.47	14.52
6.57	15.00
6.68	15.50
6.79	16.02
6.99	17.00
7.14	18.00
7.29	19.00
7.44	20.00
7.58	21.00
7.72	22.07
7.81	23.00
7.92	24.00
8.01	25.00
8.09	26.00
8.20	28.00
8.30	30.00

Using 50 ml Cu^{++}- H^{+} solution, and titrating with 0.01 M Bismon free base at 30° C - 2nd run:

pH	ml base
2.83	0.00
2.86	1.00
2.90	2.00
3.00	3.00
3.18	4.00
3.32	4.50
3.48	5.00
3.64	5.50
3.81	6.00
3.96	6.50
4.07	7.00
4.16	7.50
4.24	8.00
4.40	9.00
4.55	10.03
4.75	11.00
4.94	11.50
5.29	12.00
5.49	12.20
5.59	12.40
5.73	12.60
5.84	12.80
5.95	13.00
6.14	13.50
6.32	14.00
6.45	14.50
6.57	15.00
6.70	15.50
6.79	16.00
6.99	17.00
7.14	18.00
7.30	19.00
7.45	20.02
7.58	21.00
7.71	22.00
7.82	23.01
7.93	24.05
8.00	25.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.01 M Bismon free base at 30° C - 3rd run:

pH	ml base
2.75	0.00
2.79	1.00
2.84	2.00
2.94	3.00
3.10	4.00
3.26	4.51
3.43	5.00
3.60	5.50
3.80	6.00
3.94	6.50
4.05	7.00
4.14	7.50
4.23	8.00
4.39	9.00
4.53	10.00
4.76	11.00
4.93	11.50
5.31	12.00
5.46	12.20
5.60	12.40
5.74	12.60
5.84	12.80
5.96	13.00
6.15	13.52
6.30	14.00
6.46	14.50
6.58	15.00
6.69	15.50
6.80	16.00
6.99	17.00
7.13	18.00
7.30	19.00
7.44	20.00
7.58	21.00
7.71	22.00
7.82	23.00
7.93	24.00
8.01	25.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.01 M Bismon free base at 40° C - 1st run:

pH	ml base
2.63	0.00
2.82	2.00
2.96	3.00
3.15	4.00
3.46	5.00
3.60	5.50
3.74	6.01
3.90	6.50
4.00	7.00
4.10	7.50
4.19	8.00
4.32	9.00
4.46	10.00
4.66	11.00
5.07	12.00
5.27	12.30
5.48	12.60
5.60	12.80
5.69	13.00
5.90	13.52
6.04	14.00
6.20	14.50
6.32	15.02
6.42	15.50
6.52	16.00
6.62	16.50
6.70	17.00
6.87	18.00
7.03	19.00
7.17	20.00
7.31	21.00
7.44	22.00
7.56	23.00
7.67	24.00
7.76	25.00
7.84	26.00
7.91	27.00
7.98	28.00
8.03	29.00
8.08	30.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.01 M Bismon free base at 40° C - 2nd run:

pH	ml base
2.62	0.00
2.72	1.00
2.83	2.00
2.99	3.00
3.34	4.50
3.50	5.00
3.64	5.50
3.80	6.00
3.93	6.50
4.03	7.00
4.12	7.50
4.20	8.00
4.34	9.00
4.50	10.00
4.70	11.02
4.89	11.50
5.19	12.00
5.39	12.30
5.57	12.60
5.68	12.80
5.77	13.00
5.96	13.50
6.11	14.01
6.23	14.50
6.35	15.00
6.48	15.50
6.57	16.00
6.66	16.52
6.74	17.00
6.90	18.00
7.07	19.00
7.21	20.00
7.34	21.00
7.48	22.00
7.59	23.00
7.70	24.00
7.79	25.00
7.87	26.00
7.94	27.02
8.00	28.00
8.05	29.00
8.10	30.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.01 M Bismon free base at 40° C -3rd run:

pH	ml base
2.63	0.00
2.72	1.00
2.82	2.00
2.99	3.00
3.20	4.00
3.33	4.50
3.50	5.00
3.64	5.50
3.81	6.00
3.94	6.50
4.03	7.00
4.12	7.50
4.20	8.00
4.34	9.00
4.50	10.00
4.72	11.00
5.19	12.00
5.33	12.20
5.48	12.40
5.59	12.60
5.69	12.80
5.77	13.00
5.96	13.50
6.11	14.00
6.24	14.50
6.36	15.00
6.48	15.50
6.57	16.00
6.74	17.00
6.90	18.00
7.07	19.00
7.21	20.00
7.36	21.00
7.48	22.00
7.60	23.00
7.70	24.01
7.79	25.00
7.87	26.00
7.94	27.00
8.00	28.00
8.06	29.05
8.11	30.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.0494 M Disec free base at 20° C - 1st run:

pH	ml base
2.68	0.00
2.79	0.20
2.90	0.40
3.02	0.60
3.20	0.80
3.38	1.00
3.52	1.20
3.68	1.40
3.82	1.60
3.97	1.80
4.05	1.90
4.18	2.00
4.40	2.10
4.73	2.20
5.03	2.30
5.24	2.40
5.44	2.50
5.57	2.60
5.69	2.70
5.79	2.80
5.90	2.90
6.02	3.00
6.20	3.20
6.39	3.40
6.56	3.60
6.73	3.80
6.89	4.00
7.06	4.20
7.23	4.40
7.33	4.60
7.44	4.80
7.54	5.00
7.72	5.50
7.83	6.00
7.94	6.50
8.00	7.00
8.12	8.00
8.22	9.00
8.31	10.00

Using 50 ml Cu^{++} - H^{+} solution , and titrating with 0.0494 M Disec free base at 20°C -2nd run:

pH	ml base
2.70	0.00
2.78	0.20
2.90	0.40
3.05	0.60
3.21	0.80
3.39	1.00
3.54	1.20
3.69	1.40
3.82	1.60
3.99	1.80
4.09	1.90
4.18	2.00
4.39	2.10
4.72	2.20
5.02	2.30
5.24	2.40
5.48	2.50
5.60	2.60
5.71	2.70
5.82	2.80
5.90	2.90
5.99	3.00
6.18	3.20
6.35	3.40
6.51	3.60
6.70	3.80
6.90	4.00
7.06	4.20
7.21	4.40
7.32	4.60
7.43	4.80
7.50	5.00
7.68	5.50
7.80	6.00
7.90	6.50
7.99	7.03
8.10	8.00
8.20	9.00
8.27	10.00

Using 50 ml Cu^{++}-H^{+} solution and titrating with 0.0494 M Disec free base at 30° C - 1st run:

pH	ml base
2.64	0.00
2.79	0.20
2.88	0.40
3.03	0.60
3.19	0.80
3.33	1.00
3.46	1.20
3.60	1.40
3.73	1.60
3.90	1.80
4.29	2.00
4.60	2.10
4.87	2.20
5.03	2.30
5.20	2.40
5.32	2.50
5.48	2.60
5.56	2.70
5.66	2.80
—	2.90
5.84	3.00
6.02	3.20
6.18	3.40
6.39	3.60
6.56	3.80
6.71	4.00
6.90	4.20
7.03	4.40
7.16	4.60
7.25	4.80
7.32	5.00
7.48	5.50
7.60	6.00
7.70	6.50
7.78	7.00
7.90	8.00
7.99	9.00
8.05	10.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.0494 Diseo free base at 30°C - 2nd run:

pH	ml base
2.62	0.00
2.70	0.20
2.82	0.41
2.92	0.60
3.10	0.80
3.24	1.00
3.38	1.20
3.51	1.40
3.65	1.60
3.80	1.80
3.90	1.90
4.05	2.00
4.25	2.10
4.53	2.20
4.81	2.30
5.01	2.40
5.15	2.50
5.34	2.61
5.47	2.71
5.56	2.80
5.65	2.90
5.72	3.00
5.91	3.20
6.10	3.40
6.27	3.60
6.44	3.80
6.63	4.00
6.79	4.20
6.97	4.40
7.09	4.60
7.19	4.80
7.27	5.00
7.44	5.50
7.57	6.00
7.67	6.52
7.73	7.00
7.87	8.00
7.97	9.00
8.03	10.00

Using 50 ml Cu^{++} - H^{+} solution , and titrating with 0.0494 M Disec free base at 30°C - 3rd run:

pH	ml base
2.62	0.00
2.70	0.20
——	0.40
2.95	0.60
3.10	0.80
3.27	1.00
3.40	1.20
3.50	1.40
3.66	1.60
3.81	1.80
——	1.90
4.01	2.00
4.23	2.10
4.55	2.20
4.82	2.30
5.03	2.40
5.20	2.50
5.33	2.60
5.45	2.70
5.56	2.80
5.65	2.90
5.75	3.00
5.96	3.20
6.12	3.40
6.28	3.60
6.46	3.80
6.63	4.00
6.81	4.20
6.93	4.40
7.09	4.60
7.19	4.80
7.29	5.00
7.44	5.50
7.58	6.00
7.68	6.50
7.76	7.00
7.89	8.02
7.99	9.00
8.05	10.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.0494 M Disec free base at 40°C - 1st run:

pH	ml base
2.60	0.00
2.70	0.20
2.80	0.40
2.90	0.60
3.04	0.80
3.18	1.00
3.29	1.20
3.40	1.41
3.54	1.60
3.68	1.80
3.79	1.90
3.93	2.00
4.14	2.11
4.42	2.20
4.67	2.30
4.84	2.40
4.99	2.50
5.10	2.60
5.21	2.70
5.31	2.80
5.45	2.90
5.50	3.00
5.69	3.20
5.87	3.40
6.02	3.60
6.21	3.80
6.39	4.00
6.53	4.20
6.69	4.40
6.83	4.60
6.93	4.80
7.02	5.00
7.20	5.50
7.32	6.00
7.43	6.50
7.50	7.00
7.63	8.00
7.73	9.03
7.80	10.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.0494 M Disec free base at 40°C - 2nd run:

pH	ml base
2.61	0.00
2.69	0.21
2.80	0.43
2.92	0.60
3.06	0.80
3.19	1.00
3.29	1.20
3.43	1.42
3.56	1.60
3.68	1.80
3.82	1.90
3.99	2.00
4.20	2.10
4.49	2.20
4.72	2.30
4.90	2.40
5.03	2.50
5.17	2.60
5.25	2.70
5.34	2.80
5.44	2.90
5.53	3.00
5.75	3.20
5.99	3.40
6.04	3.60
6.22	3.80
6.42	4.00
6.59	4.20
6.73	4.40
6.87	4.60
6.97	4.80
7.05	5.00
7.22	5.50
7.34	6.00
7.44	6.50
7.51	7.00
7.63	8.00
7.73	9.04
7.82	10.00

Using 50 ml Cu^{++} - H^{+} solution, and titrating with 0.0494 M Disec free base at 40°C - 3rd run:

pH	ml base
2.60	0.00
2.67	0.20
2.77	0.40
2.92	0.62
3.02	0.80
3.17	1.01
3.29	1.20
3.40	1.40
3.53	1.60
3.67	1.80
3.77	1.90
3.90	2.00
4.11	2.10
4.39	2.20
4.63	2.30
4.82	2.40
4.98	2.50
5.11	2.60
5.21	2.70
5.31	2.80
5.40	2.90
5.50	3.00
5.68	3.20
5.83	3.40
6.00	3.60
6.19	3.80
6.36	4.00
6.53	4.20
6.69	4.40
6.81	4.60
6.94	4.80
7.03	5.00
7.20	5.50
7.32	6.00
7.42	6.51
7.50	7.00
7.62	8.00
7.72	9.02
7.79	10.00

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