Predominance Area Diagram Of The Fifth Oxidation State Of Uranium

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ABSTRACT

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The predominance area diagram of uranium (V) was determined. Generation of the species was accomplished by electrolytic reduction of uranyl (VI) ion. Measurement of the ratio of the sixth, fifth and other oxidation states of uranium was carried out by polarographic techniques. The results define a larger area of predominance of uranium (V) than was previously believed, but support the extremely short lifetime of the species.

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Introduction:

Uranium, the heaviest naturally occuring element, owes much of its study to one isotope whose relative abundance is less than one percent. One pound of U^{235} can theoretically produce 6.2×10^{10} calories of heat through nuclear fission.

Much early investigation was concerned with extraction and isolation of uranium from mixed oxides. Because the tremendous differences in physical properties between compounds of different oxidation states promised possibilities of easier separation techniques, a large amount of information on the descriptive chemistry of uranium has been collected.

Uranium in its ground state un-ionized configuration has the noble gas radon structure plus three 5f, one 6d and two 7s electrons. Energy tables show that the 7s is the lowest energy level of the three. The 5f level drops below 6d at about actinium. element 90. However, all three levels are situated in a band only one electron volt wide.

With these facts what can be said about hypothetically stable oxidation states? Removing three f electrons and one d electron, the +4 configuration would yield a radon plus $7s^2$ configuration which by classical rules would be a relatively stable oxidation state. Six fold ionization would yield the radon electronic configuration which would also be expected to be stable. The other possibilities are more complex. The order of electron removal is not certain and has been shown[21] to vary with the physical state under study and other factors.

The first three electrons removed, however, are the 6d and two 7s electrons although some claims[36] are made for a $5f^2 6d$ U(III) configuration. This +3 state and the $5f^1$ U(V) state should be less stable than the U(IV) and U(VI) states as no half-filled or filled subshells exist. It is known from spectroscopic and magnetic susceptibility

data that the 5f electrons become relatively more tightly-bound as the positive charge on the nucleus increases.[36] The increasing positive charge of the nucleus must, by the third ionization, render the ion considerably more stable than the U(II) ion which contains a less affected d or s electron.

The oxidation states of uranium actually observed are +3, +4, +5 and +6. Uranium (III) oxidizes in water with the evolution of hydrogen, but is relatively stable in strong acid. Uranium (V) disproportionates very quickly to the (IV) and (VI) states however. The solid compounds of uranium (V) are more stable than their aqueous solutions, and so these will now be examined.

The earliest compound reported[16] was UCl_5-PCl_5, followed in 1874 by the characterization of UCl_5. This latter compound can be formed from the tetrachloride and chlorine at elevated

temperature but decomposes rapidly over 100°C back to the reagents. UCl_5 under vacuum and at elevated temperature disproportionates to the tetrachloride and hexachloride. The compound may also be formed[35] by liquid phase chlorination of UO_3 with carbon tetrachloride as follows:

$$2UO_3 + 6CCl_4 \xrightarrow{250^\circ C} 2UCl_5 + 6COCl_2 + Cl_2$$

or by a similar procedure, but starting with U_3O_8:

$$2U_3O_8 + 16CCl_4 \xrightarrow{250^\circ C} 6UCl_5 + 16COCl_2 + Cl_2$$

The first preparation[61] of UF_5 was accomplished by a displacement reaction involving UCl_5 and hydrogen fluoride. Later it was prepared as follows[35]:

$$2UCl_6 + 10HF\ (anhydrous) \longrightarrow 2UF_5 + 10HCl + Cl_2$$

and

$$UF_4 + \tfrac{1}{2}F_2 \xrightarrow{200^\circ} UF_5$$

An interesting reaction[36] involving UF_4 and UF_6 produces two crystallographically different forms of UF_5 and two mixed oxidation state compounds. Another method, involving a continuous gas phase procedure[70], is:

$$2UF_6 + 2HBr \xrightarrow{650^\circ C} 2UF_5 + 2HF + Br_2$$

All UF_5 compounds violently disproportionate upon hydrolysis. The pentabromide prepared by Prigent[57] in 1954 is very unstable and difficult to isolate unless addition compounds are formed. The pentaiodide has never been obtained in pure compound form.

Compared to the halides, a group which may be referred to as halo complexes is definitely more stable.

Addition of a singly charged cation M to the hexachlorouranate ion (UCl_6^-) results in formation of $MUCl_6$ compounds. Oxidation of UCl_6 in CH_3NO_2 solution by Cl_2 at approximately 85°C results[62] in the preparation of tetraethyl ammonium hexachlorouranate $(CH_3 - CH_2)_4NUCl_6$ and tetraphenyl arsenic hexachlorouranate $(C_6H_6)_4AsUCl_6$. The preparation of $CsUCl_6$, $(Me_2H_2N)UCl_6$, Me_4NUCl_6, Pr_4NUCl_6 and $RbUCl_6$ was carried out by the addition of the chloro salt (i.e. Me_2H_2NCl) to a thionyl chloride solution of uranium (V).[5]

Although sensitive to moisture, these compounds are much less sensitive to heat and some, such as $(C_6H_5)_4AsUCl_6$, have sharp melting points.

Bagnall, Brown and Preez[5] isolated tetramethyl ammonium hexachlorouranate which is sufficiently stable so that decomposition does not occur until 245°C.

The fluorocompounds of uranium are easier to isolate because of better crystal packing. Compounds of the form MUF_6 where M is lithium, sodium, potassium, rubidium, cesium, ammonium, silver or thallium have been prepared[4,54,55,7,58,53] using an appropriate salt such as LiF and UF_5 in HF. The ammonium salt can also be synthesized[72] using NH_4F and UF_6 at 120°C. If a solution of U(V) saturated with HF is cooled,[24] two hydrates of HUF_6 precipitate. Subjecting $(C_6H_6)_4AsUCl_6$ to 40% HF produces $(C_6H_6)_4AsUF_6$.[63] The following types of compounds have also been isolated;[58,23,25,22] $(NH_3OH)UF_6$, $NOUF_6$, $N_2H_6(UF_6)_2$ and the heptafluoro

compound $M_2H_6UF_7$. Cobalt, nickel or copper difluorides dissolved in HF react with[52] UF_5 to yield $MU_2F_{12}.xH_2O$ where M is the metal.

Ryan[63] oxidized UBr_6^{2-} with Br_2 in CH_3NO_2 to obtain UBr_6^- and prepared the tetraethyl ammonium and tetraphenyl arsene UBr_6 from this. Condensation[63] of HI with $(C_6H_6)_4AsUCl_6$ followed by evaporation results in $(C_6H_6)_4AsUI_6$ which is much more stable than UI_6^-.

In addition to these ionic types of compounds, products can be formed by the addition of another neutral molecule to the entity UX_5. The resultant molecules are probably best represented as $M^+.UX_6^-$ [28,9] as in most cases coordination to uranium by the molecule is unlikely. The reactions[36,34]

$$UO_3 + 4PCl_5 \longrightarrow UCl_5 \cdot PCl_5 + 3POCl_3 + \tfrac{1}{2}Cl_2$$

$$2UO_3 + 8SOCl_2 \text{ (excess)} \xrightarrow[\Delta]{} 2UCl_5 \cdot SOCl_2 + 6SO_2 + Cl_2$$

result in products which exhibit greater stability to heat, although rapid hydrolysis and resultant disproportionation occur. Two other known[5] compounds of this class are $UCl_5(C_6H_6)_3PO$ and $UCl_5(C_8H_{17})_3PO$. The molecule $UCl_5(Cl_2C{=}CClCOCl)$ has been isolated[65] and this differs from the above types in that a coordinate metal-oxygen bond exists. Like all other compounds of this class, however, rapid hydrolysis occurs. Both UCl_5 and UBr_5 addition compounds have been formed[12,65] using phosphorous, and arsenic containing ligands such as $(C_6H_6)_3P$, $(C_6H_6)_2AsCH_2CH_2As(C_6H_6)_2$, where the metals can co ordinate with uranium.

The largest group of uranium (V) compounds prepared are those of the form $U(OR)_5$ where R= alkyl or mixed alkyl, fluoroalkyl, amino alkyl or sulfide alkyl. The basic reactions fall into the following types[9,34] where R and Et are alkyl and (C_2H_5) respectively:

1. $UX_4 + 4NaOR \xrightarrow[-4NaX]{} U(OR)_4 \xrightarrow[NaOR]{O_2 \text{ or } Br_2} U(OR)_5$

2. $UX_4 + 4ROH + 4NH_3 \xrightarrow[-4NH_4X]{} U(OR)_4 \xrightarrow[NaOR]{O_2 \text{ or } Br_2} U(OR)_5$

3. $UX_5 + 5ROH + 5NH_3 \xrightarrow[-5NH_4X]{} U(OR)_5$

4. $U(OEt)_5 + 5ROH \longrightarrow 5EtOH + U(OR)_5$

5. $(C_5H_6N)_2UOCl_2 + 5NH_3 + 3ROH$

$\longrightarrow UO(OR)_3 + 5NH_4Cl + 2C_5H_5N$

$2UO(OR)_3 \longrightarrow U(OR)_5 + UO_2(OR)$

TABLE I

Alkoxy Compounds of U(V),[5,10,11,34,68]

	State	M.P. or B.P.
$U(OMe)_5$	1	145
$U(OEt)_5$	1	180
$U(OPr)_5$	1	181
$U(OiPr)_5$	1	150
$U(OBr)_5$	1	206
$U(OiBu)_5$	1	192
$U(OsBu)_5$	1	175
$U(OtBu)_5$	1	120
$U(OAm)_5$	1	246
$U(OCH_2CH_2iPr)_5$	1	225
$U(OCH_2CHEtMe)_5$	1	220
$U(OCH_2iBu)_5$	1	165
$U(OCHEt_2)_5$	1	180
$U(OCHPrMe)_5$	1	175
$U(OCHiPr)_5$	1	160
$U(OCMe_3)_5$	1	125
$U(OCMe_2Et)_5$	1	130
$U(OCMeEt_2)_5$	1	200
$U(OCEt_3)_5$	1	210
$U(OCMe_2Pr)_5$	1	200
$U(OCMe_2iPr)_5$	1	-

Table I Cont'd. Alkoxy Compounds of U(V).

	State	M.P. or B.P.
$U(OCMeEtiPr)_5$	1	-
$U_2(OEt)_5(OtBu)_5$	1	150
$U_2(OEt)_4(OtBu)_6$	1	150
$U(OEt)(OtBu)_4$	1	-
$U(OCH_2CH{=}CH_2)_5$	1	178
$U(OCH_2CH_2NEt_2)_5$	1	-
$U(OCH_2CH_2SCH_2CF_3)_5$	1	-
$U(OCH_2CF_3)_5$	1	125

where:

Abbreviation	Chemical Species
Me	CH_3-
Et	C_2H_5-
Pr	C_3H_7-
iPr	$(CH_3)_2CH$-
Bu	C_4H_9-
iBu	$(CH_3)_2CH_2CH$-
tBu	$(CH_3)_3C$-
Am	C_5H_{11}-

Table I summarizes the known[34,10,11,5,68] compounds.

These compounds once again demonstrate increased thermal stability over the corresponding simple alkyl entities, but are very sensitive to moisture. They are relatively volatile, are soluble in organic solvents and exist predominantly as dimers and trimers.

Similar to the above, but more ionic are three hexaethoxy U(V) compounds.[33]

$NaU(OEt)_6$

$Ca(U(OEt)_6)_2$

$Al(U(OEt)_6)_3$

By reacting penta-alkoxides with arylhalides in dry benzene, compounds of the form $U(OR)_{5-n}X_n$ have been obtained.[33,11,5,6] Table II lists these although few conclusions can be drawn from the sparse data.

TABLE II

Alkoxyhalo Compounds of U(V) [5,6,11,33]

	Melting Point
$U(OEt)_4Cl$	160°C
$U(OEt)_3Cl_2$	-
$U(OEt)_2Cl_3$	-
$U(OEt)Cl_4CH_3COOEt$	-
$U(OPr)_4Cl$	185°C
$U(OiPr)_4Cl$	-
$U(OiPr)_3Cl_2$	-
$U(OiPr)_2Cl_3$	-
$U(OiPr)Cl_4$-$CH_3COOiPr$	-
$U(OAm)_4Cl$	-
$U(OEt)_4Br$	-
$U(O\ Et)_3Br_2$	-
$U(O\ Et)_2Br_3$	-
$U(O\ Et)Br_4CH_3COOEt$	-
$U(O\ Am)_4Br$	-
$U(O\ Am)_2Br_3$	-
$U(O\ Am)Br_4$ - CH_3COOAm	-

where the abbreviations are as in Table I.

Four rather interesting compounds have been isolated[11] for which physical data are available. Uranium (V) trimethyl silyloxide is the lowest boiling (140°C) and most polymerized. The ethyl dimethyl silyloxide boils next (155°C) and is significantly less polymerized. Diethyl methyl silyloxide U(V) boils higher still (160°C) and is only slightly dimerized. Finally the triethyl compound exists as a monomer and boils at 170°C. Boiling points seem in contradiction to densest packing, which implies that the electron density increase on oxygen due to the higher inductive effects of the ethyl group compared to methyl, is the most significant factor in cohesiveness. This is partially confirmed by the higher boiling point and dimerization of $U(OSi\ Me_3)_5$ versus $U(OCMe_3)_5$ where of course carbon is more electronegative than silicon.

It is also known that it is possible to coordinate ligands with the penta-alkoxide

U(V) group. The molecules $U(OtBu)_5.tBuOH$ and $U(OtBu)_5.Py$ where Py is pyridine, were isolated by Bradley et al.[11] A group of less stable amine complexes which may be represented as $U(OCH_2CF_3)_5.N$, where

$N = 2Me_2N$, $2PrNH_3$, $2iPrNH_3$, $2Pr_2NH$

$= 3Me_2NH$ and $3CH_2$——CH_2 (N, H)

has been characterized.[33]

By dissolving $U(OEt)_5$ in benzene and adding molar amounts of various diketones, the compounds listed in Table III have been synthesized.[6]

TABLE III

Diketone Derivatives of U(V) Pentaethoxide [6]

		B.P.
$U(OEt)_4$	acac	118
$U(OEt)_3$	$acac_2$	drc
$U(OEt)_2$	$acac_3$	drc
$U(OEt)_4$	bezac	110
$U(OEt)_3$	$bezac_2$	drc
$U(OEt)_2$	$bezac_3$	drc
$U(OtBu)_4$	acac	-
$U(OtBu)_3$	$acac_2$	195
$U(OtBu)_2$	$acac_3$	-
$U(OtBu)_4$	bezac	210
$U(OtBu)_2$	$bezac_3$	215

where acac and bezac are acetylacetonate and benzoylacetonate respectively.

The butoxide compounds were formed by refluxing the ethoxy compounds with t-butyl alcohol until exchange occurred. As a general rule the tetraethoxy or tetrabutoxy complexes are thermally more stable than the more substituted compounds, probably due to the more symmetrical and stronger U-OEt bonds.

Finally β-ketoesters have been formed[6] using the aforementioned technique to produce the compounds of Table IV.

TABLE IV

Ethoxy-β-Ketoester Compounds of U(V)[6]

		B.P.
$U(OEt)_4$	Meacac	140
$U(OEt)_3$	$(Meacac)_2$	152
$U(OEt)_2$	$(Meacac)_3$	-
$U(OEt)_4$	Etacac	-
$U(OEt)_3$	$(Etacac)_2$	-
$U(OEt)_2$	$(Etacac)_3$	-

where Meacac and Etacac are methyl and ethyl acetylacetonates.

These, from the limited data available, appear more thermally stable than the acetylacetonate complexes.

Pentavalent uranium oxide U_2O_5 was the subject of a thorough crystallographic study after it was first made by Rundle et al.[62] The violet crystals can be prepared by thermal decomposition of UO_2Cl_2 at 900° or by the action of dilute sulfuric acid on U_3O_8 or UO_5 [47,50], but the temperature must be kept below 160° or UO_2 is formed. Oxidation at room temperature yields U_5O_{13} but decomposition occurs into U_3O_8 and U_4O_9 above 250°. Many crystal studies have been carried out in order to properly identify the great number of apparent oxides reported. For example the species $UO_2^+ O_{0.5}^{2-}$ is proposed[50] for U_2O_5 and this occurence of UO_2^+ is probable in many non-stoichiometric oxides such as U_3O_8, U_5O_{13} and U_4O_9.

Five types of oxide compounds that exist are composed of UO^{3+}, UO_2^{+}, UO_3^{-}, $U_2O_6^{2-}$ and UO_4^{3-} and the required positive or negative ions.

Mixed metal oxides are very common, but little physical data have been reported. The group MUO_3, where M is Li^+, Na^+, K^+ or Rb^+ is prepared[26,17] by heating M_2UO_4 with UO_2 at 700°C. The following reaction has also been reported:[64]

$$BaUO_3 + UO_3 \xrightarrow[M_2]{550^\circ C} Ba(UO_3)_2 \longrightarrow BaUO_4 + UO_2$$

These UO_3^{-} compounds, dissolved in water, are sufficiently stable that they are not affected by hydrochloric or sulfuric acid and do not cause alkaline reactions with water.

Another type of mixed oxide is represented by MUO_4 where $M=Se^{3+}$, Y^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Yb^{3+}. These may be synthesized by the following reactions:[60]

$$M_2O_3 + UO_2 + UO_3 \xrightarrow{1000^oC} 2MUO_4$$

or for[59,20]

$$M = Bi^{3+}, Cr^{3+} \text{ or } Fe^{3+}$$

$$2M_2O_3 + U_3O_8 + UO_2 \xrightarrow{1000^oC} 2MUO_4$$

Unlike the univalent metal types these are oxidized by acids.

Compounds of the form MU_2O_6 are produced as the result of thermal decomposition of diuronates ($U_2O_7^{2-}$) or by thermal reduction of the +6 diuronates at 600° with ammonia. The compounds with $M=Co^{2+}$, Ni^{2+}, Mg^{2+}, Cd^{2+}, Ni^{+}, K^{+}, Ca^{2+}, Sr^{2+}, Ba^{2+} have been reported.[38,8]

The compound UO_2Br, with an infra-red spectrum expected of a UO_2^+ compound (much like UO_2^{2+}), has been synthesized[51] utilizing the following technique:

$$UO_3 + 2HBr \xrightarrow{250^oC} UO_2Br + \tfrac{1}{2}Br_2 + H_2O$$

This compound, stable to 500°C, is the only UO_2^+ type yet reported.

By the reactions:

$$MoCl_5 + UO_3 \longrightarrow UO_2Cl_2 + MoOCl_5$$

$$UO_2Cl_2 + MoOCl_3 \longrightarrow UOCl_3 + MoO_2Cl_2$$

oxychlorides and oxybromides have been prepared. They have also been prepared by heating[46] UCl_4 and UO_2Cl_2

The reaction[57] of carbon tetrabromide and uranium triamide at 110° under dry nitrogen yields $UOBr_3$.

The reaction of UCl_5, $SOCl_2$ and pyridine in alcoholic solution yields[9] $(pyH)_2UOCl_5$. The compounds $(Et_4N)_2UOCl_5$, $(Ph_4As)_2UOCl_5$ and $(Et_4N)_2UOBr_3$ have also been reported.[63] As with all U(V) compounds, they are unstable to moisture despite good thermal stability.

U(V) compounds in molten chlorides have also been studied. Adams et al[1] found characteristic bands, especially the predominant one at 1500 mμ, for melts containing UO_2Cl_2, U_3O_8 and UO_3 with various $MgCl_2$, LiCl and KCl ratios. They attribute the band to UO_2^+ by analogy with the similar spectrum of iso electronic NpO_2^{+2} which also possesses a single 5f electron. The reaction pathways proposed are:

$$UO_2Cl_2 \rightleftharpoons UO_2Cl + \tfrac{1}{2}Cl_2 \quad \text{for} \quad UO_2Cl_2$$

and for UO_3:

$$2UO_3 + MgCl_2 \longrightarrow MgUO_4 + UO_2Cl_2$$

$$MgUO_4 + MgCl_2 \longrightarrow UO_2Cl_2 + MgO$$

followed by

$$UO_2Cl_2 \rightleftharpoons UO_2Cl + \tfrac{1}{2}Cl_2$$

Subsequently,[69] the equilibrium constant for the reaction $Cl^- + UO_2^{2+} \rightleftharpoons UO_2^+ + \tfrac{1}{2}Cl_2$ was measured using the chlorine pressure of the cell and the value was found to vary from 5.6×10^{-7} to 2.1×10^{-6}.

Equilibria of Oxidation States

The aqueous chemistry of uranium is more complex than that of most elements because of the occurrence of four oxidation states and compounds with coordination numbers up to and even exceeding 8.

Oxidation state (III) exists principally in acid solution, but is rapidly oxidized by water to U(IV). The U(IV) oxidation state is first formed as an unhydrated ion, for instance on dissolution of UCl_4. According to Kraus and Betts,[43,49] this quickly forms a monomeric species according to the reaction:

$$U^{4+} + H_2O \rightleftharpoons U(OH)^{3+} + H^+$$

followed by $U(UOOH)_n^{n+y}$ polymerization.[36] The higher polymers or polynuclear complexes, $U(OH)_4$ and UO_2 which exist at higher pH, are all solids.

The most stable oxidation state (VI) has been the most extensively studied and provides a basis for estimates of the behaviour of U(V). Data from x-ray crystallography[18], infra-red[13] and Raman spectra[18,13] and oxygen exchange with water[15] confirm the O - U - O structure and

this leads to UO_2^{2+} as the most commonly accepted species, at least at lower pH. Except at very low uranium concentrations or at high pH, species such as $UO_2(OH)^+$ or $UO_2(OH)_2$ are not judged to be very significant.[42]

As with U(IV), polymer formation is important and has been the subject of much research.[19,3,31,32] Sutton[6] proposed the following scheme:

$$2UO_2^{2+} + H_2O \rightleftharpoons UO_2(UO_3)^{2+} \qquad K = 1.1 \times 10^{-6}$$

$$U_2O_5^{2+} + UO_2^{2+} \rightleftharpoons U_3O_8^{2+} + 2H^+ \qquad K = 5 \times 10^{-9}$$

$$U_3O_8^{2+} + H_2O \rightleftharpoons U_3O_8(OH)^+ + H^+ \qquad K = 2.8 \times 10^{-4}$$

However, Ahrland et al[2] concluded that sheet-like complexes with two OH bridges per repeating unit of the structure $UO_2\left[(OH)_2UO_2\right]_n^{2+}$, where n

is not known, occur.

Knowledge of the redox relationships of the four oxidation states provides more insight into the stability of U(V). The reversible U(III) / U(IV) couple has been measured[45] and found to have a formal potential of 0.631 volts (versus SHE) which shifts due to complexing. With chloride ion for instance, the potential increases slightly. The U(IV) / U(VI) equilibrium is said[35] to occur as follows:

$$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$$

with a potential of -0.334 volts (versus SHE). This reaction will be discussed subsequently, but for now, the potential of the U(IV) / U(V) irreversible couple calculated as $E_{46} + E_{56}$, where E_{46} and E_{56} are the half cell potentials for the U(IV) / U(VI) and for the U(V) / U(VI) couples respectively, is approximately -0.607 volts (versus SHE) and is strongly influenced by complexing.

With the above facts in mind, what can be said of the species of U(V) that exist? Herasymenko[29] first found a polarographic wave attributable to a UO_2^{2+} reduction to U(V), and noted that it was independent of hydrogen ion concentration. After Corruthers[14] confirmed its dependence on uranium concentration only, and Kolthoff and Cohn[40] showed that it existed significantly only in strongly acid solution, Harris and Kolthoff[27] showed that the reduction was a one electron, reversible change occurring at -0.18 volts (vs SCE). By analogy to the accepted uranyl (VI) species at that acidity, the fact that no acid-base equilibrium is involved, and that the reaction is reversible and rapid, implying no strong metal oxygen bonds are broken or formed, the latter authors concluded that the species was UO_2^{+}. This was later supported by measurement of the diffusion coefficient[39] which

was almost exactly the same as that for UO_2^{2+}. In addition the absorbance spectrum of UO_2^{+} is very similar to that of isoelectronic NpO_2^{2+} and indeed to UO_2^{2+}.[44]

The reaction therefore is represented as:

$$UO_2^{2+} + 1e^- \rightleftharpoons UO_2^{+} \qquad E^o = +0.062$$

where the equilibrium shifts more to the left with increasing pH.[43]

Probably because the speed of one electron transfers discourages investigation, most kinetic and mechanistic studies have been carried out on the disproportionation of U(V) into U(IV) and U(VI). Kern and Orlemann[39] followed, kinetically, the disproportionation of uranium (V) perchlorate in sodium perchlorate-perchloric acid solution. After reduction by electrolysis,

various amounts of oxygen-free perchloric acid were added and the diffusion current measured as a function of time. Second order kinetics were identified, and the following values are given for the expression:

$$\frac{d\,(UO_2^+)}{dt} = k''/\ a_{H^+}.(UO_2^+)^2$$

$k''/\ a_{H^+} = 130$ (at ionic strength from 0.02 to 0.4)

In another set of data,[39] shown in Table V, the Brønsted theory requirement of rate dependence on ionic strength is confirmed. This requires formation of an outer sphere complex or ion pair.

TABLE V

Effect of Ionic Strength

on Disproportionation Rate.[39]

u	a_{H^+}	k' / a_{H+}
0.119	0.0214	78
0.137	0 0383	80
0.156	0.0577	80
0.174	0.0725	88
0.192	0.0852	97
0.281	0.158	120
0.40	0.2 - 0.3	130

Kern and Orlemann[39] proposed:

$$UO_2^{2+} + H^+ \rightleftharpoons UOOH^{2+}$$

$$UO_2^+ + UOOH^{2+} \longrightarrow UO_2(UOOH)^{3+} \qquad \text{Rate Determining}$$

$$UO_2(UOOH)^{3+} \longrightarrow UO_2^{2+} + UOOH^+$$

$$UOOH^+ \longrightarrow U(IV) \text{ species}$$

although they did not attempt to identify the U(IV) species.

In a subsequent paper on the disproportionation of U(V), Nelson and Kraus[53] using the Debye - Hückel theory and the following equation:

$$2UO_2^+ + 4H_3O^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 6H_2O$$

postulated the U(VI) species as being UO_2^{2+} and UO_2Cl^+, the U(V) species as being UO_2^+ and the U(IV) species as being U^{4+} and $U(OH)^{3+}$. Using polarographic, spectrophotometric and potentiometric methods independently, equilibrium constants

were derived and all were approximately equal, thus justifying the above species. Agreement with the Debye-Hückel theory was shown by straight line dependence of log K_{eq} versus

$$\mu^{\frac{1}{2}} / (1+0.3286\, a^{o}\mu^{\frac{1}{2}})$$

The formation of U(V) in solution can be attempted by many methods, but in fact few work. The attempt[49] to reduce a solution of U(VI) with hydrogen using platinized platinum as a catalyst failed because it was too difficult to control the hydrogen input and reduction to the U(IV) state occurred.

Reduction of uranyl chloride with zinc amalgam has also been tried[49] but, despite initial and specific reduction to U(V), rapid disproportionation occurred due to contact with the amalgam.

The dissolution of a U(V) compound of

course would apparently be the simplest method except for the multiplicity of oxidation states of uranium. The hydrolysis of UCl_5 in acidic, aqueous solution has been followed[43] polarographically yielding the following curves of Figure 1. The anodic diffusion current rises slowly until a plateau value is found when the uranium U(V) concentration becomes constant. Simultaneously the cathodic diffusion current decays from the initially high value to a stable U(VI) concentration. It was also found that the half-wave potential did not change and that the sum of twice the cathodic diffusion current and the anodic diffusion current was constant. The former point indicates that no new U(V) species has been formed. In the latter case, if one assumes that uranium exists only in the fourth, fifth or sixth oxidation states, then because the fourth and sixth state concentrations are always equal, they may be measured from the U(VI) value.

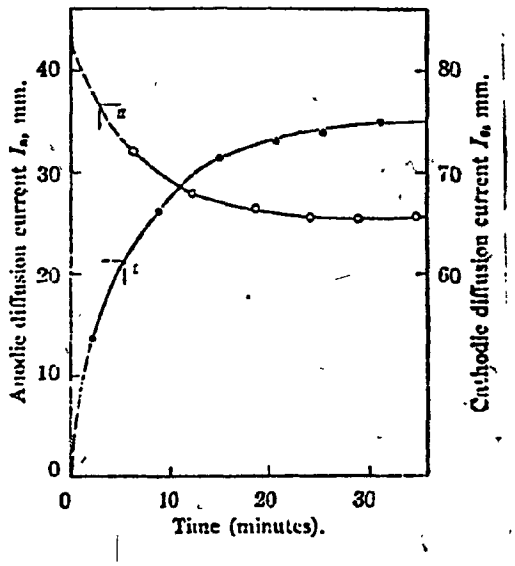
FIGURE 1

Dissolution of UCl_5

Anodic and Cathodic

Diffusion Currents Versus Time.

(After K. Kraus and F. Nelson Jour. Amer. Chem. Soc., 71, 2518(1949)).



Where Ia = anodic diffusion current due to:-

$$UO_2^{+} - e \rightleftharpoons UO_2^{2+}$$

where Ic = cathodic diffusion current due to:-

$$UO_2^{2+} + e^{-} \rightleftharpoons UO_2^{+}$$

These facts are consistent with the proposed mechanism:

$$2UCl_5 + 8H_2O \longrightarrow U(OH)^{3+} + UO_2^{2+} + 10Cl^- + 5H_3O^+$$

$$UO_2^{2+} + U(OH)^{3+} + 4H_2O \longrightarrow 2UO_2^{+} + 3H_3O^+$$

By measuring the hydrogen ion activity during the course of the dissolution,[43] the above mechanism has been further substantiated.

There are two possible explanations as to why the rapid and complete disproportionation of UCl_5 to U(IV) and U(VI) in media in which U(V) is most stable occurs. The possibility of UCl_5 being a U(IV) - U(VI) solid matrix is ruled out by the fact that all uranium atoms are geometrically equivalent according to x-ray data,[71] and hence

the compound is truly U(V). The dissolution process therefore must involve formation of the metastable $U(H_2O)_n^{+5}$ species which rapidly disproportionates into U(IV) and U(VI).

Another method, based on the above knowledge, is the mixing of U(IV) and U(VI) solutions in order to carry out reverse disproportionation. As with UCl_5 dissolution, however, a mixture of 3 oxidation states would result and, as will be discussed below, this is not advantageous. The most successful method to date has been the electrochemical reduction of uranyl perchlorate and chloride solutions. This yields high proportions of U(V) which are quite stable to disproportionation.

The possibility of oxidation of U(IV) to U(V) might be considered for a moment. Solutions of uranium containing three oxidation states are known[43] to be meta stable with disproportionation proceeding quite slowly. A point is reached,

however, at which the rate increases rapidly. Kraus et al[44] believe that this is due to an autocatalytic effect caused by a U(IV) polymer which exists only in traces immediately after hydrolysis. In order to reduce polymerization of U(IV), the pH would have to be too high for U(V) stability. In addition, any oxidizing agent sufficiently strong to convert U(IV) to U(V) would also be strong enough to force the reversible U(V) / U(VI) couple towards its most stable equilibrium where U(VI) is predominant. Hence, except for the case of rapid oxidation immediately after hydrolysis of a U(IV) salt and the use of some as yet unknown oxidizing agent, the method is not a possibility.

As mentioned earlier, the electronic structures of the oxidation states of uranium are not absolutely certain, but f electron removal and transuranic contraction definitely occur

starting at uranium. The so-called actinide series may or may not start with actinium, but by the time U(III) is reached there is no doubt that lanthanide type behaviour is followed. As a result uranium, neptunium and plutonium are very similar chemically and all exist in acid solution with oxidation states (III), (IV), (V) and (VI) as:

$M(H_2O)_8^{3+}$	U(III)
$M(H_2O)_8^{4+}$	U(IV)
$M(OH)(H_2O)_7^{3+}$	"
$MO_2(H_2O)_6^{+}$	U(V)
$MO_2(H_2O)_6^{2+}$	U(VI)

The relative stability to disproportionation in solution will be primarily due to differences in redox potentials of the different metal couples. Thermodynamically a process is spontaneous if the free energy change is less than zero. For the reactions:

$$MO_2^{+} \rightleftharpoons MO_2^{2+} + e^{-} \qquad E_{56}$$

$$M^{4+} + 6H_2O \rightleftharpoons MO_2^+ + 4H_3O^+ + e^-$$

knowing that free energy is proportional to potential, the criterion for stability is that difference in half-cell potentials be negative or:

$$E = E_{56} - E_{45} < 0$$

Table No. VI summarizes the values[48] versus the standard hydrogen electrode for the elements under consideration. Only Np(V) would be stable according to these results, however, the voltages as given by the Nernst equation are functions of pH, and E_{45} becomes greater by a factor of 0.059 x 4 pH. The value of E therefore diminishes and the M(V) stability increases as long as the postulated reactions apply.

TABLE VI

Redox Potential Difference

for U, Np and Pu [48]

Element	E_{45}	E_{56}	E
Uranium	-0.60	-0.06	+0.54
Neptunium	-0.737	-1.135	-0.398
Plutonium	-1.20	-0.93	+0.27

The hydrolytic behaviour of uranium (IV) has been mentioned and for M(IV) near pH 1, it is known that the reaction:

$$M^{4+} + 2H_2O \rightleftharpoons MOH^{3+} + H_3O^+$$

occurs. The pK values[43] are 1.45 for uranium and 1.55 for plutonium. At approximately pH 1.5, Pu (IV) polymerizes[43] with the rate proportional to Pu (IV) concentration and pH while for U(IV), polymerization is not significant even at pH 2[43], although the same general behaviour can be expected. From the reactions:

$$MO_2^+ + 2H_2O \rightleftharpoons MO_2OH + H_3O^+$$

$$K_a = \frac{[MO_2OH][H_3O^+]}{[MO_2^+][H_2O]^2}$$

the MO_2^+ species were found[43] to have pK_a values of 8.9 and 9.7 for neptunium and plutonium respectively. Although the pK_a for the similar

UO_2^+ reaction has not been measured, it would logically be around 8. As with Np and Pu, where between pH 9 and 10 $MO_2(OH)_2^-$ forms, $UO_2(OH)_2^-$ would form above pH 8.

Although known to be very complex (see preceding discussion of uranyl hydrolysis), MO_2^{2+} solutions are 50% hydrolyzed[43] at pH 4 for U(VI), at pH 4.7 for Np (VI) and at pH 5.4 for Pu (VI). Above this the major species becomes $MO_2(OH)_2$ and probably $MO_2(OH)_3^-$ between pH 8 and 10.

In their paper, Kraus, Nelson and Johnson[44] plotted pH - potential curves for uranium, plutonium and neptunium. The equations used were, unlike most diagrams, based on practical hydrolytic and potential data. With uranium for example, four parts were used:

1) At low pH the reaction between U^{4+} and UO_2^+ was considered to be most important

in determining stability.

The reaction is:

$$UO_2^+ + 4H^+ + 1e^- \rightleftharpoons U^{4+} + 2H_2O$$

for which $E = E^{\circ} - 0.059\ (4)\ pH$

$= +0.60 - 0.236\ pH$

2) From pH 2 to 4, the U(V) / U(VI) couple was used:

$$UO_2^{2+} + 1e^- \rightleftharpoons UO_2^+$$

$E = 0.052$ volts.

3) Around pH 4, hydrolysis of UO_2^+ begins, resulting in a modification of the preceding equation. This is represented by the curvature of figure 1.

4) From pH 4 to 8, hydrolysis of UO_2^+ takes place with the unhydrolysed U(V) / U(VI) couple being replaced by:

$$UO_2^+ + 4H_2O \rightleftharpoons UO_2(OH)_2 + 2H_3O^+ + 1e^-$$

The Nernst type equation for the preceding reaction is unknown and, as the reaction has never been rigorously studied, the only knowledge about the behaviour is that the pK value is "around 8". In order to use the potential-pH diagram technique of Pourbaix, Delahay and Van Rysselberghe[56], the chemical potentials (partial molal free energies) must be known for all species. This could not be found for the compound $UO_2(OH)_2$ so that a best guess is derived as follows:

$$G = -RT \ln K = -1.98 \times 298 \times 2.3 \times 8$$
$$= -10856 \text{ calories}$$

$$\Delta G^o = \mu^o_{UO_2(OH)_2} + 2\mu^o_{H_3O^+} - \mu^o_{UO_2^+} - 4\mu^o_{H_2O}$$

$$-10856 = \mu^o_{UO_2(OH)_2} + 2\,(0) + 237600 - 4\,(-56,690)$$

$\mu^{o}_{UO_2(OH)_2}$ = -453,504 calories.

Using the Pourbaix equation for the reaction, and neglecting activity terms as the concern is with unit activity at the boundries, the result is:

$$E = \frac{\mu^{o}_{UO_2(OH)_2} - \mu^{o}_{UO_2^{+}} - 4\,\mu^{o}_{H_2O}}{23070\ (\ 1\ )} - 0.059\ (1)\ pH$$

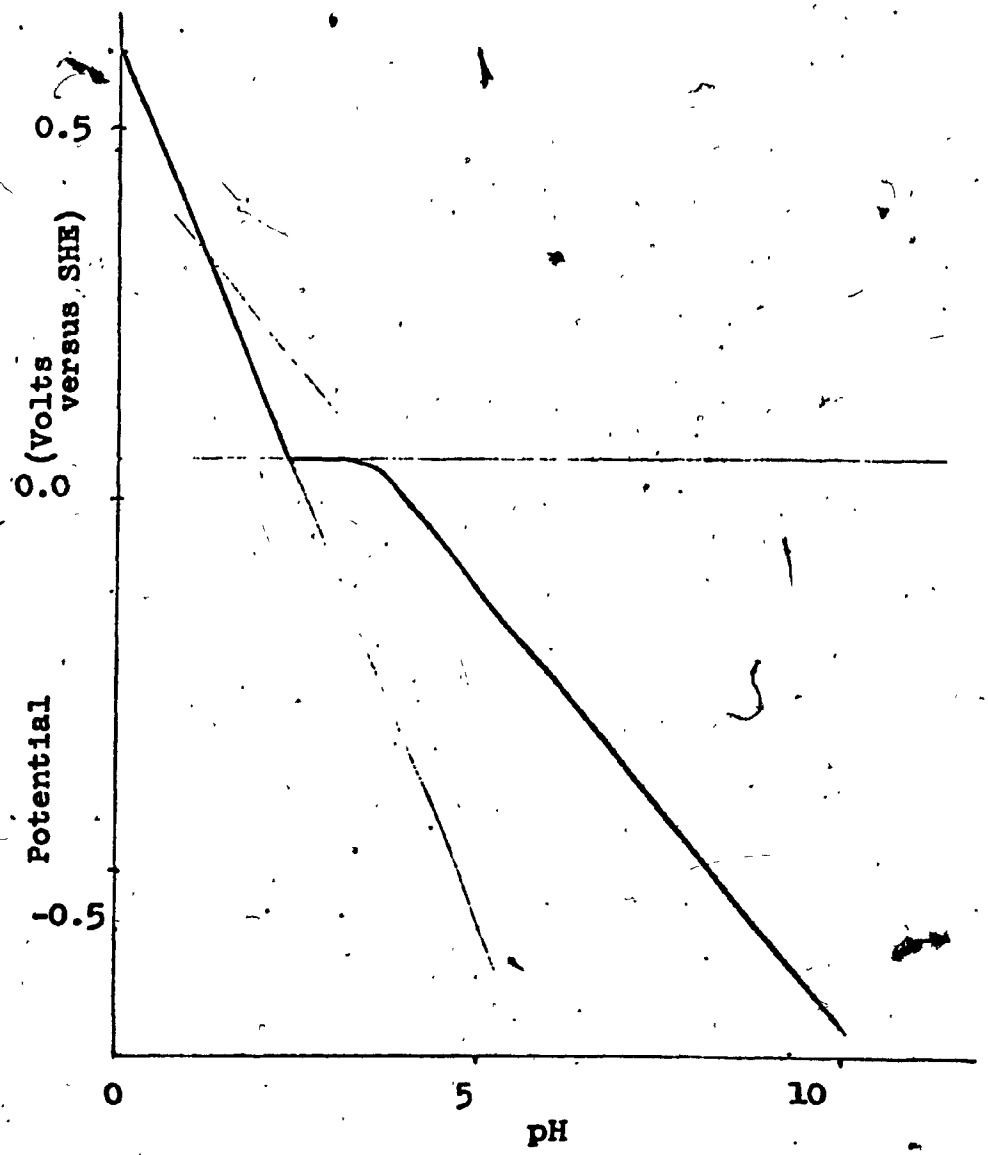
$$= \frac{-\ 453,504 \ +\ 237,600 \ +\ 4\ (56,690\ )}{23070} - 0.118\ pH$$

$$= 0.471 - 0.118\ pH$$

Plotting these equations yields Figure 2.

FIGURE 2

Practical pH- potential curve for U(V).



In the pH independent region between pH 2.3 and 3.5, the thermodynamic stability of the UO_2^+ species is highest as ΔE is most negative. This optimum stability region[44] is considerably smaller for uranium than for plutonium or neptunium as can be seen from Table VII. This is primarily because of the high hydrolysis of UO_2^+ relative to MO_2^+ for the two succeeding elements.

Method of Pourbaix.

For any redox reaction we may write:

$$a\ Ox + cH^+ + ne \rightleftharpoons b\ Red + d\ H_2O$$

adjusted such that the charge balance:

$$b\ Red - a\ Ox = c\ H^+ + ne$$

is satisfied. Writing all equations with the oxidized species on the left side and hence expressing the half-cell potential as electrode-solution potential by the procedure of Delahay[56] electrochemical equilibrium is satisfied if:

TABLE VII

Optimum Stability Range (pH) of U(V), Np(V), Pu(V).[44]

ELEMENT	O.S.R. (pH)
Uranium	2.3 to 3.5
Neptunium	1.8 to 5.8
Plutonium	0.3 to 5.4

$$Pe - Ps = \frac{1}{nF}(a p_{ox} + c p_{H^+} + n p_{e^-} - b p_{red} - d p_{H_2O})$$

where

Pe, Ps are the electric potentials of the electrode (e) and solution (s) interface.

p_i are the partial molal free energies of the reactants and products

F is the Faraday

Substituting

$$p_i = \mu_i^o + RT \ln a_i$$

where μ_i^o are the standard partial molal free energies and a_i are the corresponding activities,

collecting and grouping terms,

$$Pe - Ps = \frac{1}{nF}(a \mu_{ox}^o + c \mu_{H^+}^o + n \mu_{e^-}^o - b \mu_{red}^o - d \mu_{H_2O}^o)$$

$$+ \frac{RT}{nF} \ln \frac{(a_{ox})^a \quad (a_{H^+})^c}{(a_{red})^b \quad (a_{H_2O})^d}$$

Setting $E = Pe - Ps$ for a standard hydrogen electrode which gives $\mu^o_{H^+} = 0$ and $\mu^o_{e^-} = 0$ by assuming both metallic electrodes are conducting equally, the condition of electrochemical equilibrium becomes:

$$E = \frac{a\mu^o_{ox} - b\mu^o_{red} - d\mu^o_{H_2O}}{23070\ n} - 0.059 \frac{c}{n} pH$$

$$+ 0.059 \log \frac{(a_{ox})^a}{(a_{red})^b}$$

For acid base reactions of the type

$$a\ A + bH^+ \rightleftharpoons c\ B + d\ H_2O$$

where the charge balance

$$c\ B - a\ A = bH^+$$

exists, the equilibrium constants are:

$$K = \frac{(a_B)^c \quad (a_{H_2O})^d}{(a_A)^a \quad (a_{H^+})^b}$$

Again substituting $\mu_i = \mu_i^o + RT \ln a_i$

and $\mu_{H^+}^o = 0$, at equilibrium $u_i = 0$ or

$$- \log a_i = \frac{\mu_i^o}{2.3\ RT}$$

$$\log K = \frac{a\mu_A^o - c\mu_B^o - d\mu_{H_2O}^o}{2.3\ RT}$$

Where A is the hydroxide and B the cation, 2.3 RT = 1363 calories per mole at 25°C and $b = \frac{cd}{a}$

the expression becomes:

$$\log a_B = \frac{1}{c} \frac{a\mu_A^o - c\mu_B^o - d\mu_{H_2O}^o}{1363} - \frac{b}{z\ a}pH$$

Depending on whether a reaction is acid-base or oxidation-reduction in nature, one of the preceding equations may be completed using standard

free energies from tables.[48] The use of this method for iron is included in Appendix I. Applying the method to the uranium system, and starting with the reaction:

$$UO_3 + 2H^+ + 2e^- \rightleftharpoons UO_2 + H_2O$$

we find

$$\mu^o_{UO_3} = -283{,}000 \text{ cal}$$

$$\mu^o_{UO_2} = -257{,}000 \text{ cal}$$

$$\mu^o_{H_2O} = -56690 \text{ cal}$$

$$E = \frac{-283{,}000 - (-257{,}000) - (-56690)}{23070\,(2)} - 0.059\,\frac{2}{2}\text{pH}$$

$$+ \frac{0.059}{2} \log \frac{a_{UO_3}}{a_{UO_2}}$$

$$= +0.665 - 0.059\,\text{pH} + 0.0295 \log \frac{a_{UO_3}}{a_{UO_2}}$$

or for the reaction:

$$UO_2 + 3H^+ \rightleftharpoons UOH^{3+} + H_2O$$

we find

$$\mu^{o}_{UO_2} = -257{,}000 \text{ cal}$$

$$\mu^{o}_{UOH^{3+}} = -193{,}500 \text{ cal}$$

$$\mu^{o}_{H_2O} = -56{,}690 \text{ cal}$$

substituting

$$\log a_{UOH^{3+}} = \frac{-257{,}000 - (-193{,}500) - (-56690)}{1363}$$

$$-\frac{3}{1} pH$$

$$= -5.07 - 3\,pH$$

This procedure can then be used to calculate the electrochemical potential equations for all known reactions at or near the optimum stability range for UO_2^{+}.

For the reaction:

$$U^{4+} + H_2O \rightleftharpoons U(OH)^{3+} + H^+ \qquad \text{A-1}$$

$$\log a_{U^{4+}} = \mu^o_{U(OH)^{3+}} - \mu^o_{U^{4+}} - \mu^o_{H_2O} - pH$$

$$= \frac{-193{,}500 + 138{,}400 + 56690}{1363} - pH$$

$$= 1.166 - pH \qquad \text{E-1}$$

For the simple couple:

$$U^{4+} + e^- \rightleftharpoons U^{3+} \qquad \text{A-2}$$

$$E = \frac{\mu^o_{U^{4+}} - \mu^o_{U^{3+}}}{23070} = \frac{-138{,}400 + 124{,}400}{23070\,(1)}$$

$$E = -0.607 \qquad \text{E-2}$$

For the reaction:

$$U(OH)^{3+} + H^+ + e^- \rightleftharpoons U^{3+} + H_2O \qquad \text{A-3}$$

$$E = \mu^o_{U(OH)^{3+}} - \mu^o_{U^{3+}} - \mu^o_{H_2O} - 0.0591 \frac{(1)}{(1)} pH$$

$$E = \frac{-193,500 + 124,400 + 56690}{23070\ (1)} - 0.059\ pH$$

$$E = -0.538 - 0.059\ pH \qquad E\text{-}3$$

and

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad A\text{-}4$$

$$E = \frac{\mu^o_{UO_2^+} - \mu^o_{U^{4+}} - 2\,\mu^o_{H_2O}}{23070\ (2)} - 0.0591\ \frac{(4)}{(2)}\ pH$$

$$= \frac{-237,600 + 138,400 + 2\ (56690)}{23070\ (2)} - 0.0591\ \frac{(4)}{(2)}\ pH$$

$$= 0.308 - 0.118\ pH \qquad E\text{-}4$$

Another boundary equation is:

$$UO_2^+ + 3H^+ + e^- \rightleftharpoons U(OH)^{3+} + H_2O \qquad A\text{-}5$$

$$E = \frac{\mu^o_{UO_2^+} - \mu^o_{U(OH)^{3+}} - \mu^o_{H_2O}}{23070\ (1)} - 0.0591\ \frac{(3)}{(1)}\ pH$$

$$= \frac{-237,600 + 193,500 + 56,690}{23070\ (1)} - 0.0591\ (3)\ pH$$

$$E = +0.546 - 0.177\ pH \qquad E\text{-}5$$

Less important is:

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad A\text{-}6$$

$$E = \frac{\mu^o_{UO_2^{2+}} - \mu^o_{U^{4+}} - 2\mu^o_{H_2O}}{23070\ (2)} - 0.059\ \frac{(4)}{(2)}\ pH$$

$$= \frac{-236,400 + 138,400 + 2\ (56,690)}{23,070\ (2)} - 0.059\ (2)\ pH$$

$$E = +0.333 - 0.118\ pH \qquad E\text{-}6$$

and

$$UO_2^{2+} + 3H^+ + 2e^- \rightleftharpoons U(OH)^{3+} + H_2O \qquad A\text{-}7$$

$$E = \frac{\mu^o_{UO_2^{2+}} - \mu^o_{U(OH)^{3+}} - \mu^o_{H_2O}}{23,070\ (2)} - 0.059\ \frac{(3)}{(2)}\ pH$$

$$= \frac{-236,400 + 193,500 + 56,690}{23070\ (2)} - 0.059\ \frac{(3)}{(2)}\ pH$$

$$E = +0.298 - 0.0885\ pH \qquad E\text{-}7$$

The best known equation is of course:

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^+ \qquad \text{A-8}$$

$$E = \frac{\mu^o_{UO_2^{2+}} - \mu^o_{UO_2^+}}{23070\ (1)} = \frac{236{,}400 + 237{,}600}{23070\ (1)}$$

$$E = +\ 0.052 \text{ volts} \qquad \text{E-8}$$

Although not listed as an actual equation for uranium, for:

$$UO_2(OH)_2 + 2H_3O^+ + e^- \rightleftharpoons UO_2^+ + 4H_2O \qquad \text{A-9}$$

$$E = +\ 0.471 - 0.118\ pH \qquad \text{E-9}$$

could be calculated, as before.

The only side of the quadrangle not described is the UO_2^+ / $U(OH)_4$ equilibrium. The reaction:

$$U(OH)_4 + e^- \rightleftharpoons UO_2^+ + 2H_2O \qquad \text{A-10}$$

could be assumed and

$$E = \frac{\mu^o_{U(OH)_4} - \mu^o_{UO_2^{2+}} - 2\,\mu^o_{H_2O}}{23070\ (1)}$$

$$= \frac{-351{,}600 + 237{,}600 + 2\ (56{,}690)}{23070\ (1)}$$

$$E = -\ 0.027 \text{ volts} \qquad \text{E-10}$$

By plotting these results on a Pourbaix type pH - potential diagram (Figures 3 and 4) an area from pH 2.80 to 4.30 between the redox couples E-8 and E-10 is obtained.

Research Proposal

It was the intention of this research to attempt a verification of the diagram experimentally. A polarographic technique was used to ascertain the ratio of U(V) and U(VI) after electrolysis of U(VI) solutions. Because nitrate ions are known to interfere with the polargraphic oxidations to be followed, it was decided to convert the uranyl nitrate to uranyl chloride.

FIGURE 3 pH - POTENTIAL DIAGRAM FOR URANIUM

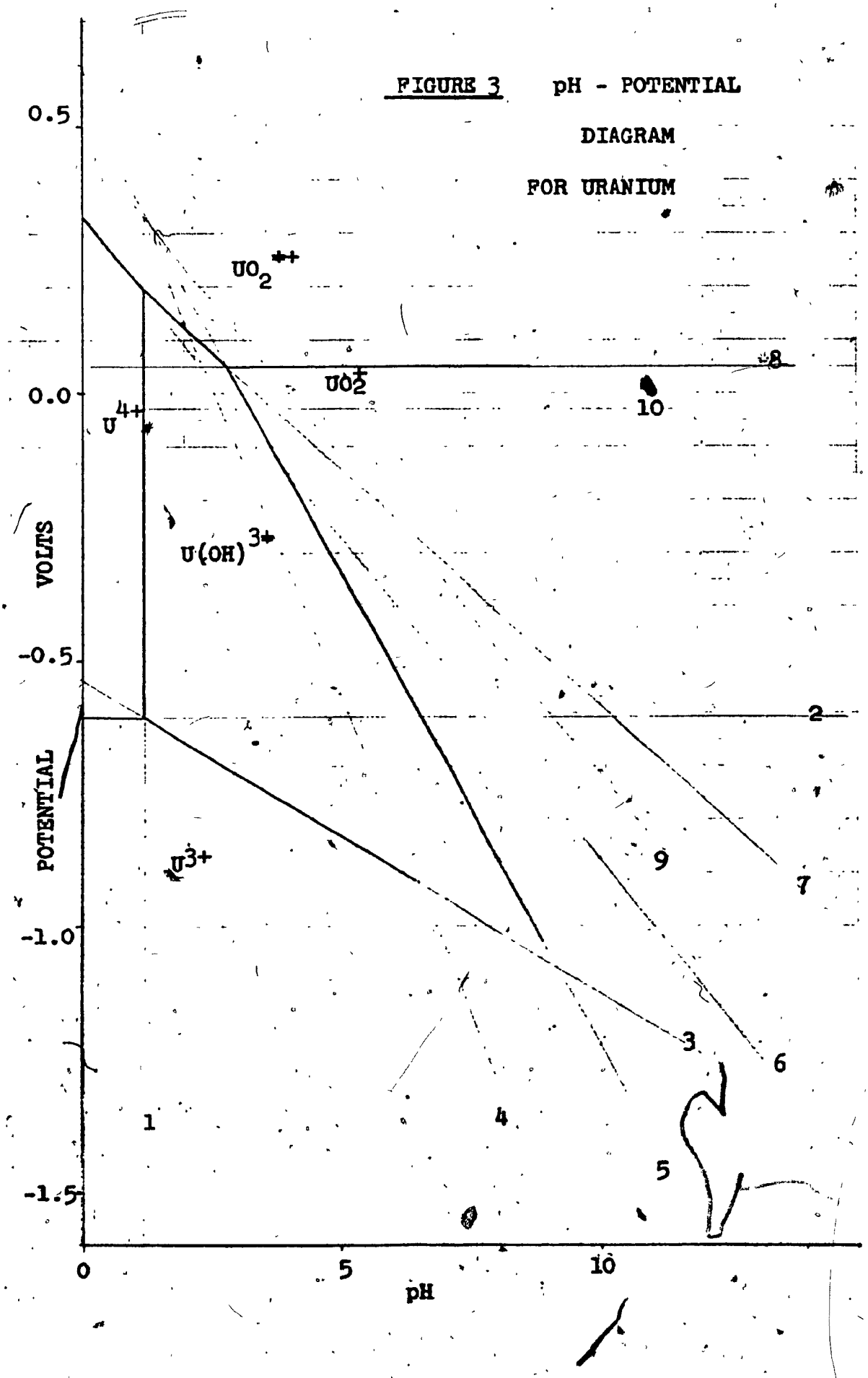
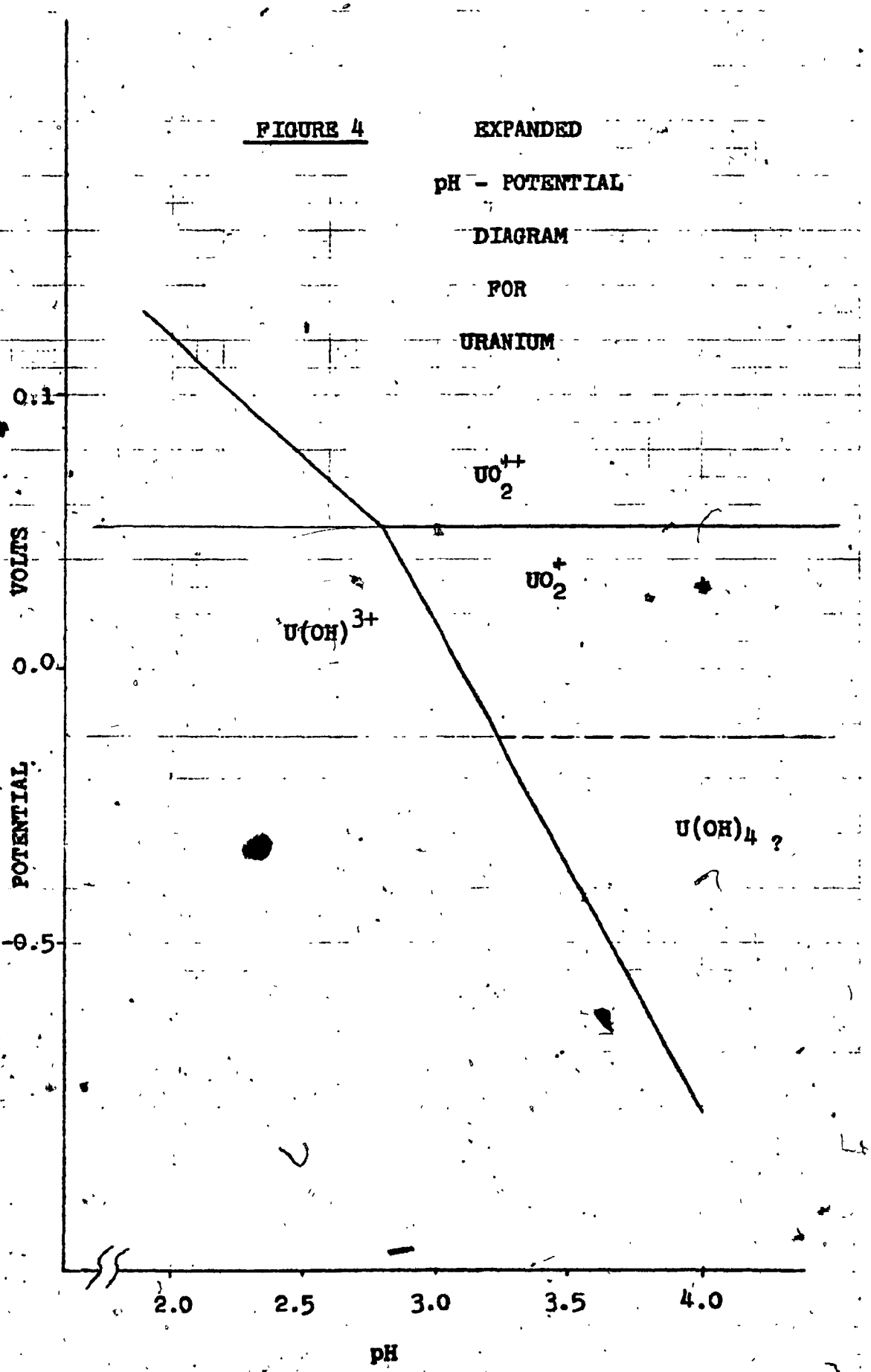


FIGURE 4 EXPANDED pH - POTENTIAL DIAGRAM FOR URANIUM



EXPERIMENTAL

1. Synthesis of Uranyl Chloride.

Uranyl chloride can be synthesized in the following ways:

$$UO_3 + HCl \longrightarrow UO_2Cl_2$$

$$UCl_4 + O_2 \xrightarrow{300^oC} UO_2Cl_2$$

$$U + HCl \longrightarrow UO_2Cl_2$$

$$UO_2(NO_3)_2 + 6H_2O + 2HCl \xrightarrow{\text{dryness}} UO_2Cl_2 + 2NO_2 + O_2 + 6H_2O$$

However, it was felt that none of these methods would result in a product uncontaminated by reaction byproducts. A reaction sequence was used wherein the less expensive and readily available uranyl acetate or nitrate was dissolved in water and the uranium precipated by ammonia.

$$2UO_2(NO_3)_2 \cdot 6H_2O + 2NH_4OH \text{ (excess)} \rightleftharpoons (NH_4)_2U_2O_7 + 4HNO_3 + 9H_2O$$

The voluminous ammonium uranate precipitate was then filtered on a large Buchner funnel and washed with dilute ammonium hydroxide. When the filtrate tested free of nitrate[27] ion by the sulfuric acid/ferrous sulfate test, the uranate was dissolved in concentrated HCl, and the filter was washed with dilute HCl. The ammonia was removed by boiling. The mother liquor was concentrated by boiling and by vacuum distillation of the resultant constant boiling HCl and water mixture. Uranyl chloride precipitated from the cold, concentrated mother liquor. Further concentration and cooling increased the yield to 80%.

Although it was considered that precipitation from other than aqueous solvent might increase the yield, it was difficult to find a solvent which would contain considerable hydronium, chloride and ammonium ions and not hydrolyze extensively the uranyl chloride.

The major contaminants would have to be occluded chloride ions and hydronium ions. It is

known that UO_2Cl_2, when dissolved, is hydrolyzed according to:

$$UO_2Cl_2 + xH_2O \rightleftharpoons UO_2(OH)_x^{(2-x)+} + xH^+ + 2Cl^-$$

For the purposes of this research, however, both of these ions are acceptable in low levels, as hydrochloric acid is added to the sample solutions to adjust the pH. As the exact value of x is unknown, direct measurement of pH would not enable calculation of the occluded (H_3O^+).

2. Electrolysis Techniques.

As has been mentioned, uranium (V) is best produced by electrolysis of uranyl (VI) solutions. From the positive value for the free energy difference of the redox couples previously discussed, it would be expected that any potential adequate for the reduction of the stable U(IV) state to U(V) would also be able to continue reduction to +4. However, because the U(IV) / U(V) couple is irreversible, the transition state must have a high energy profile and this apparently results in high overvoltage. The difference

between the half-wave potentials is approximately 0.7 volts, and so the electrolysis must be kept below 0.7 volts to avoid massive U(IV) formation.

It was thought at first that a platinium/platinum electrode system would suffice. One was used and initially in test runs found to be adequate. Under "full load" potentials with proper acidity and supporting electrolyte, however, it was found that the maximum concentration of uranium (V) was about 40%. Although not proven, the cathodic platinum surface which became film coated with black material was probably rendered useless by the reduction of a slight amount of Uranyl (VI) to an insoluble U(IV) species.

To overcome this problem, a stirred-mercury pool with large surface area was used as the cathode. Although it was anticipated that UO_2 would still form, especially at large negative potentials, the much greater electrode surface and agitation of the surface were expected to overcome the problem. The affect of this will be

discussed subsequently. In view of the fact that the solution near the anode would have a depleted chloride concentration as a result of the production of chlorine there, the anodic and cathodic cells were separated by a sintered glass disc. This also kept the reduced uranium in the required area for analysis. Both compartments were filled with the same solution.

Solutions of pH 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 were obtained by the addition of hydrochloric acid to solutions of uranyl chloride and potassium chloride. The attempted measurement with a combination glass electrode did not prove successful. Eventually a simple glass/saturated calomel electrode combination was used. In order to minimize error, the standard buffers used were 1.5, 3.0, and 4.5 pH. Considerable deviation from linearity of:

$$E = K + 0.059\ pH$$

was found but the maximum shift at one end of the range was only 0.4 pH units. By setting the reference at pH 3.0, the uncertainty was decreased to about 0.2 units at each end of the range covered.

3. Polarographic Techniques.

Herasymenko[29] first discovered and identified the U(V) - U(VI) polarographic wave and confirmed that it was a one-electron reversible process. Although the values do vary slightly from author to author and between experimental conditions, there can be no doubt that it is as first described. Compared to the spectrophotometric method, polarographic determination of the amount of each uranium oxidation state is quicker and offers more quantitative results.

For a reversible reaction occuring at an electrode, where no mechanical agitation occurs, the oxidant concentration, near the electrode, becomes much less than that of the bulk solution and a concentration gradient is established. As

electrolysis proceeds, the concentration gradient becomes greater with time. The rate of diffusion of the oxidant to the electrode will depend on the length of the concentration gradient zone, and hence on time of electrolysis. It[41] can be shown that the number of molecules of the oxidant diffusing to the electrode is:

$$N = C_0\sqrt{\frac{D_0}{\pi t}}$$

N = number of oxidant molecules reaching the electrode, per sq.cm. per second.

t = time in seconds.

D_0 = diffusion coefficient, $\frac{cm^2}{sec}$

C_0 = bulk concentration of oxidant in solution in m moles/litre.

If A is the area of the electrode and n the number of electrons transferred per molecule:

$$i_d = n\,N\,A\,F$$
$$= n\,F\,A\,C_0\sqrt{\frac{D_0}{\pi t}}$$

where F = Faraday (96,490 C / equiv.)

i_d = diffusion current in microamperes.

It has been found that because of the negative voltages applied and the likelihood of hydrogen formation, the use of a mercury surface, which results in high overvoltage for the reaction, is best. By the use of a rapid-cycle, short-lived, spherical, charged drop of mercury, t in the diffusion equation can be averaged to a constant value for the half life.

The number of molecules diffusing becomes:

$$N = C_0\left(\sqrt{\frac{D_0}{\pi t}} + \frac{D_0}{r_0}\right)$$

where r_0 = drop radius in mm.

Substituting typical values of

$D_o = 10^{-5}$, t=3 sec. and r_o = 0.5 mm

found in the study[44] of uranyl ions at this pH the equation becomes:

$$N = C_o (10^{-3} + 5 \times 10^{-6})$$

This means that the equation reduces to the simple equation for a plane electrode with only a 0.01% approximation.

For a spherical drop:

$$\text{Area} = 4\pi \left(\frac{3}{4\pi d}\right)^{2/3} m^{2/3} t^{2/3}$$

where d = density of mercury in g/cc.

m = rate of mercury flow in mg/s.

which substituted into the equation, yields

$$i_d = n F A C_0 \sqrt{\frac{D_0}{\pi t}}$$

$$= n F 4\pi \left[\frac{3}{4\pi d}\right]^{2/3} m^{2/3} t^{2/3} C_0 \sqrt{\frac{D_0}{\pi t}}$$

Because of the effect of the drop surface expanding into the solution, the above diffusion current increases by the square root of 7/3. Substituting typical numerical values results in the Ilkovic equation:

$$i_d = 708 \; nm^{2/3} \; t^{1/6} \; C_0 \; D_0^{1/2}$$

where i_d is in μ amps for m in mg per second and C_0 in m moles/liter.

Experimentally, an average value of i_d must be found because during each drop life, the instantaneous diffusion current varies with t, as follows:

$$\bar{i}_d \times \tau = \int_0^{\tau} i_d \, dt$$

where: $\bar{i}_d$ = average diffusion current

τ = drop life

Substituting[30] the previous equation into the above integrand and integrating yields:

$$\bar{i}_d = 607 \, n \, m^{2/3} \, \tau^{1/6} \, D_O^{1/2} \, C_O$$

For a reversible redox relationship in which the reductant is soluble, the Nernst equation is:

$$E_{O/R} = E^o_{O/R} - \frac{0.059}{n} \log \frac{C_O}{C_R} \quad (x=0)$$

where C_O, C_R are the concentrations of oxidant O and reductant R respectfully at the electrode surface (x=0)

$E_{O/R}$ is the cathodic applied potential

and at applied potentials beyond $E^{o}_{O/R}$, the Ilkovic expression becomes:

$$\bar{i} = 607\ n\ m^{2/3} \gamma^{1/6}\ D_O^{1/2}\ (\ C_O - C_O\ (x=0)\ )$$

$$= \bar{i}_d - 607\ n\ m^{2/3} \gamma^{1/6}\ D_O^{1/2}\ C_O\ (x=0)$$

Substituting the mass balance,

$$C_O - C_O\ (x=0) = C_R\ (x=0)$$

$$\bar{i} = 607\ n\ m^{2/3} \gamma^{1/6}\ D_R^{1/3}\ C_R\ (x=0)$$

rearranging the last two Ilkovic expressions for C's and dividing yields:

$$\frac{C_O}{C_R}\ (x=0) = \frac{D_R^{1/2}}{D_O^{1/2}} \cdot \frac{\bar{i}_d - \bar{i}}{\bar{i}}$$

Substituting this in the Nernst relationship gives:

$$E_{O/R} = E_{1/2\ O/R} + \frac{0.059}{n} \log \frac{\bar{i}_d - \bar{i}}{\bar{i}}$$

where

$$E_{1/2\ O/R} = E^{o}_{O/R} + \frac{0.059}{n} \frac{D_R^{1/2}}{D_O^{1/2}}$$

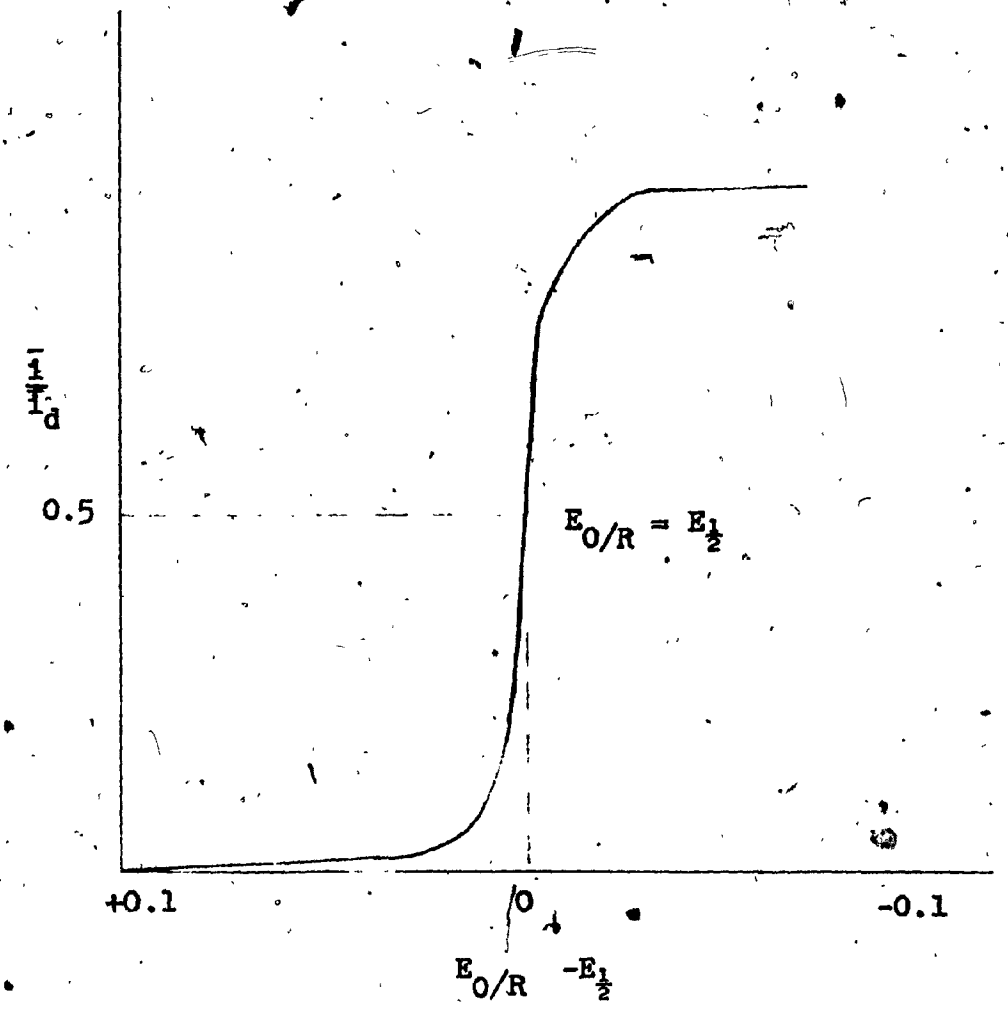
A plot of the potential versus $\bar{i}_d / \bar{i}$ yields the classical polaragraphic wave shown in Figure 5. The plot of log $\frac{\bar{i}_d - \bar{i}}{\bar{i}}$ versus $E_{0/R}$ will yield a straight line if the reversibility (non-hysteresis) criteria of the theory assumptions are valid.

Because the transference of charged cations can also occur by electrostatic attraction to the negative electrode, and this non-diffusion process would upset the assumptions of the Ilkovic operation, the mobility of these ions due to such attraction must be effectively lowered. By adding a large excess of a supporting electrolyte, whose cations are not reduced at the potentials applied, the electrode becomes surrounded by these ions and hence its affect of electrostatic attraction is eliminated. The supporting electrolyte must not of course be reduced in the voltage range under study.

The reduction of UO_2^{2+} to UO_2^{+} results in a polaragraphic wave at the cathodic dropping mercury electrode where the cathodic diffusion current $i_d(c)$ is proportional to UO_2^{2+}. The oxidation of UO_2^{+} produces an

FIGURE 5

Plot of $\bar{i}/i_d$ versus $E_{O/R} - E_{\frac{1}{2}}$

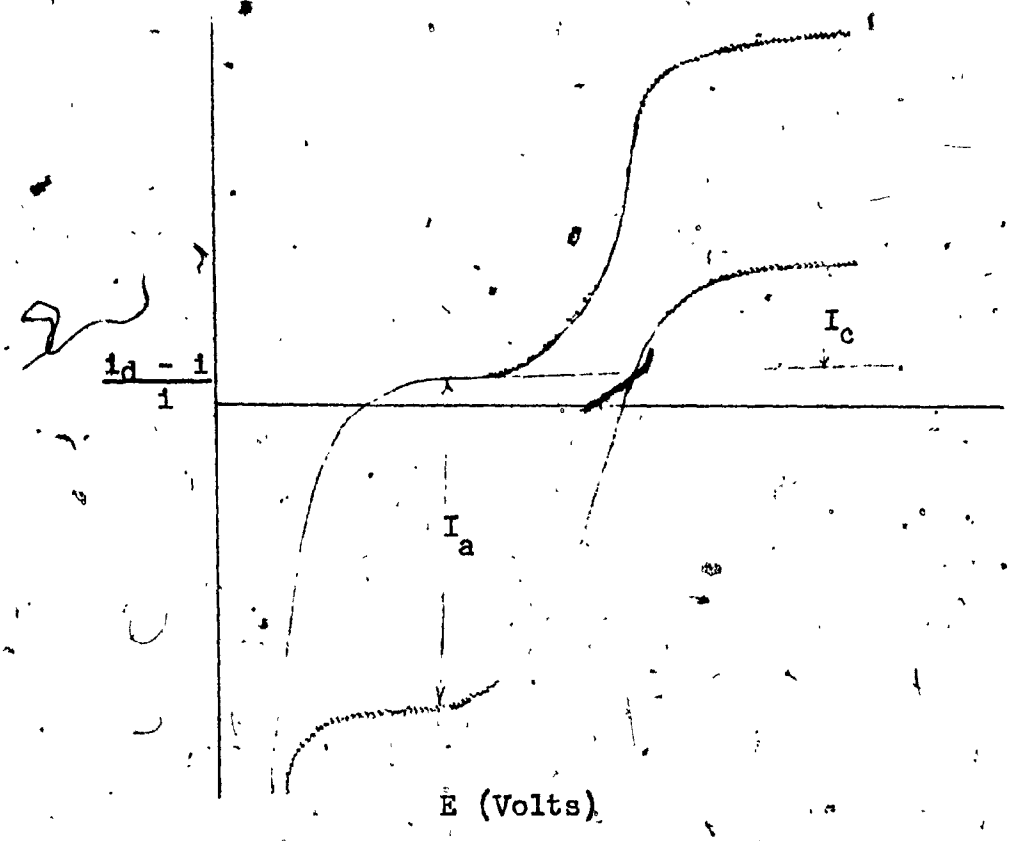


anodic diffusion current proportional to UO_2^+. Both waves occur at the same half-wave potential and differ in their current shift or residual current. As the diffusion coefficients of uranyl (V) and uranyl (VI) are known to be almost exactly equal (Ratios 1.00 to 1.02), the corrected diffusion currents for similar concentration solutions of each species are equal. In most instances a mixture of the two ions exists producing waves with both cathodic and anodic components. A typical series is shown in Figure 6.

Another complication seldom discussed, because other investigators worked at pH levels above 3, was the influence of further reduction to uranium (IV) when large negative voltages were applied during electrolysis. As the UO_2^+ concentration is almost nonexistent before electrolysis and the diffusion coefficients of UO_2^+ and UO_2^{2+} are almost equal, the loss due to U(IV) may be explained using

FIGURE 6

Polarographic Waves of Uranium



Note: The plot of log $\frac{(i_d - i)}{i}$ versus E yields straight lines with slopes of 0.060 for chloride[43] and 0.062 for perchlorate[38] solutions, confirming both reversibility and single electron exchange processes.

$$\Delta \bar{i}_d = i_d^o(c) - (i_d^f(a) + i_d^f(c)) = 0$$

where $\Delta \bar{i}_d$ = diffusion current lost due to conversion of the measurable U(V) and U(VI) states to U(IV).

$i_d^o(c)$ = initial cathodic diffusion current

$i_d^f(a)$ = final anodic diffusion current

$i_d^f(c)$ = final cathodic diffusion current

A very approximate equation would therefore be:

Fractional concentration of U(IV) species =

$$1.00 - \frac{i_d^f(c) + i_d^f(a)}{i_d^o(c)}$$

4. Experimental Conditions.

The conditions of electrolysis and polarographic measurement were fairly standard. The uranyl chloride and potassium chloride concentrations were 1.5×10^{-3} and 0.10 molar respectively. The apparatus as seen in Figure 7, consisted of a dc power source (Hewlett-Packard 6113A)

connected to a stirred mercury cathode and a large platinium anode. Because of the anticipated production of considerable amounts of chlorine, the surface area of the anode had to be large and blown or agitated free of reduced gas. Both anodic and cathodic compartments were swept free of oxygen using N_2 for 60 minutes as the residual current shape was still found to be significant after only 30 minutes.

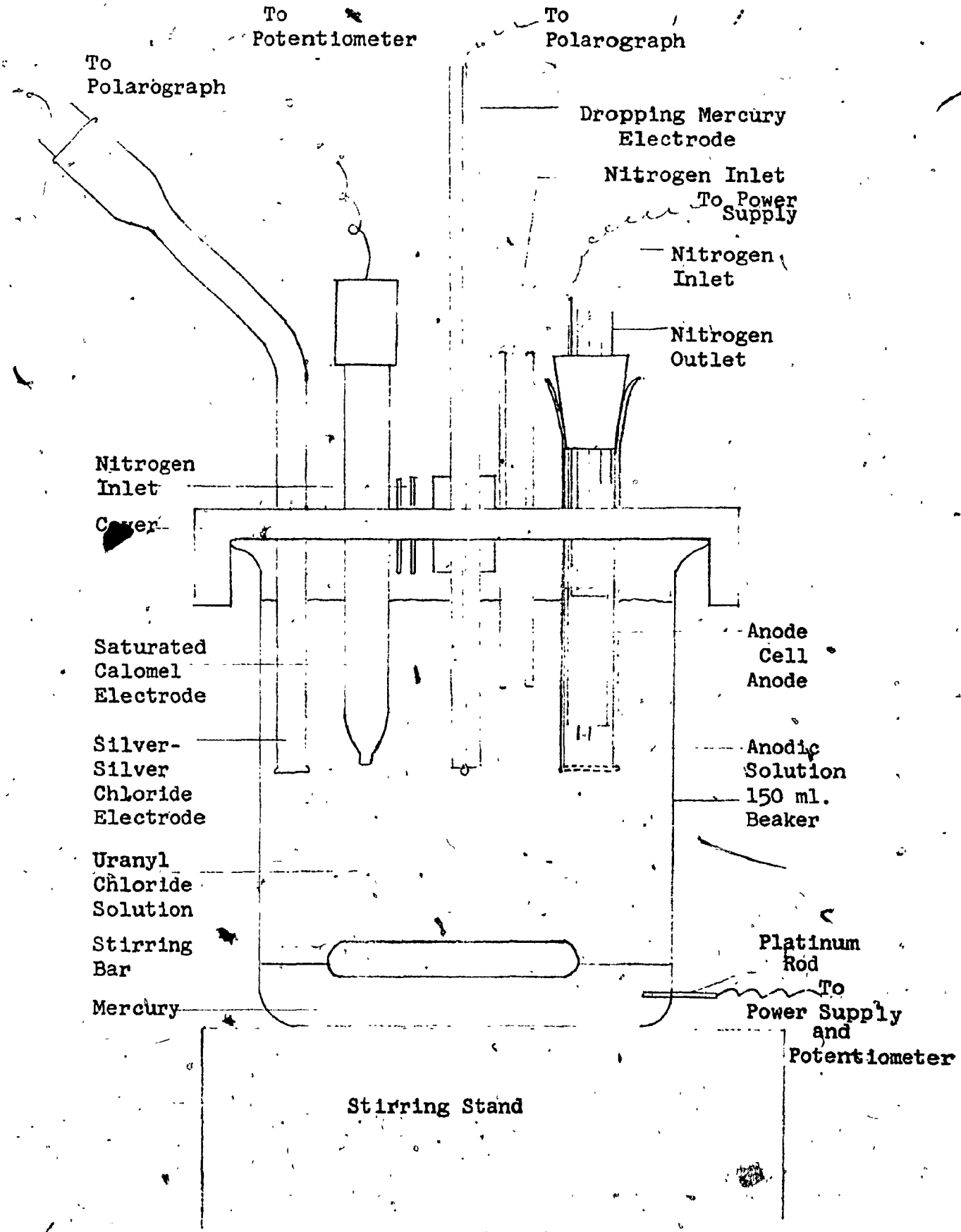
The applied potential was measured and manually controlled by a Metrohm model E 300B potentiometer connected in series between the mercury cathode and a saturated calomel reference electrode. The current-potential polarographic results were obtained using a Metrohm E 354S dropping mercury stand and E 261 Polaricord, using a silver-silver chloride (KCl) reference electrode. Cells were 150 ml pyrex beakers into which rods of platinum were sealed near the bottom. Stirring was accomplished using a 3 cm Teflon-coated magnet on a Metrohm stirring platform. The anodic cell was a pyrex tube

fitted with a medium porosity fritted glass disc and bevelled to permit a tight stoppered fit. Generally the sensitivity was 5×10^{-8} amps/millimeter and the starting voltage and range were +0.25 and -1.0 volts versus SCE respectively. The cell diagram is shown in Figure 7.

Experimentally the entire pH-potential diagram from pH 2.0 to 4.5 and from 0 to perhaps ±1300 milli-volts should be examined. If pH is adjusted in increments of 0.5 and potential in steps of 100 mv, 84 combined electrolysis-polarographic experiments would be required for each duplicate series. Initial tests were made to attempt to reduce the range of potential required.

The treatment of the data obtained to calculate U(V), U(VI) and U(IV) fractions should enable calculation of the complete pH potential diagram.

FIGURE 7 CELL DIAGRAM



RESULTS

TABLE VIII

Results of Electrolysis and Polarography.

pH	-E(mv)	It (uA)	Ia (uA)	Ic (uA)	% U(V)	% U(VI)	% U(IV)	Polarogram
1.5	100	1.75	0.05	1.70	2.8	97.1	0.1	1
1.5	250	1.35	0.10	1.20	7.4	88.9	3.7	2
1.5	300	1.30	0.10	1.15	7.7	88.5	3.8	3
1.5	550	1.35	0.30	0.90	22.2	66.7	11.1	4
1.5	650	1.50	0.50	0.75	33.3	50.0	16.7	5
1.5	650	1.80	0.40	0.95	26.7	63.3	10.0	6
1.5	800	1.40	0.45	0.75	32.1	53.9	14.3	7
1.5	950	1.45	0.35	0.65	24.1	44.8	31.1	8
1.5	1000	1.20	0.20	0	16.7	0	83.3	9
1.5	1100	1.60	0.15	-0.15	9.4	0	90.6	10
1.5	1160	1.50	0.10	-0.45	6.7	0	93.3	11
2.0	500	1.70	0.52	1.04	30.6	61.2	8.2	12
2.0	650	1.92	0.58	1.22	30.2	63.5	6.3	13
2.0	850	1.70	0.74	0.64	43.5	37.6	18.9	14
2.0	950	1.74	0.74	0.76	42.5	43.7	13.8	15
2.0	1200	1.74	0.24	-0.52	13.8	0	86.2	16
2.5	400	1.78	0.08	1.74	4.5	97.8	0	17
2.5	400	2.02	0.48	1.50	23.8	74.3	1.9	18
2.5	550	1.96	0.92	0.88	46.9	44.9	8.2	19
2.5	550	2.06	1.00	0.74	48.5	35.9	15.6	20

TABLE VIII (Cont'd):

pH	-E(mv)	It (uA)	Ia (uA)	Ic (uA)	% U(V)	% U(VI)	% U(IV)	Polar-ogram
2.5	700	2.00	0.98	0.68	49.0	34.0	17.0	21
2.5	700	1.96	1.00	0.78	51.0	39.8	9.2	22
2.5	750	1.70	0.88	0.68	51.8	40.0	8.2	23
2.5	950	1.88	0.92	0.80	48.9	42.6	8.5	24
2.5	1050	2.02	0.96	0.62	47.5	30.7	21.8	25
2.5	1200	2.04	0.82	-0.08	40.2	0	59.8	26
2.5	1300	2.14	0.46	0.30	21.5	14.0	64.5	27
3.0	350	1.42	0.42	0.88	29.6	62.0	8.4	28
3.0	400	1.42	0.42	0.78	29.6	54.9	15.5	29
3.0	500	1.56	0.42	1.06	26.9	67.9	5.2	30
3.0	520	1.78	0.80	0.60	44.9	33.7	21.4	31
3.0	600	1.46	0.44	1.04	30.1	71.2	0	32
3.0	750	1.48	1.00	0.32	67.6	21.6	10.8	33
3.0	1000	1.52	0.78	0.52	51.3	32.9	15.8	34
3.0	1100	1.48	0.54	0.68	36.5	45.9	17.6	35
3.0	1100	1.42	0.52	0.70	36.6	49.3	14.1	36
3.5	350	1.26	0.16	1.22	12.7	96.8	0	37
3.5	400	1.94	0.02	1.84	1.0	94.8	4.2	38
3.5	500	1.58	0.28	1.34	17.7	84.8	0	39
3.5	500	1.38	0.36	0.82	26.1	59.4	14.5	40
3.5	600	1.80	1.04	0.52	57.7	28.9	13.4	41

TABLE VIII (Cont'd):

pH	-E(mv)	It (uA)	Ia (uA)	Ic (uA)	% U(V)	% U(VI)	% U(IV)	Polarogram
3.5	600	1.62	0.62	1.98	38.3	60.5	1.2	42
3.5	650	1.40	0.40	1.98	28.6	70.0	1.4	43
3.5	750	1.72	1.00	0.56	58.1	32.6	9.3	44
3.5	750	1.68	1.26	0.24	75.0	14.3	10.7	45
3.5	750	1.72	1.36	0.00	79.1	0	20.9	46
3.5	800	1.40	1.00	0.20	71.4	14.3	14.3	47
3.5	900	1.96	1.48	0.16	75.5	8.2	16.3	48
3.5	1000	1.54	1.42	-0.32	93.5	0	6.5	49
3.5	1100	1.38	1.16	-0.14	84.0	0	16.0	50
3.5	1200	1.50	0.24	-0.18	16.0	0	84.0	51
3.9	400	1.04	0.38	0.34	36.5	32.7	30.8	52
3.9	500	1.04	0.48	0.16	46.2	15.4	38.4	53
3.9	700	0.92	0.62	0.10	67.4	10.9	26.1	54
3.9	850	0.92	0.68	-0.20	73.9	0	26.1	55
3.9	1100	1.20	0.78	-0.04	65.0	0	35.0	56
3.9	1200	1.08	0.34	-0.06	31.5	0	68.5	57
4.5	550	0.98	0.26	-0.70	26.5	0	73.5	58
4.5	700	0.84	0.42	-0.20	50.0	0	50.0	59
4.5	750	0.66	0.16	-0.32	24.2	0	75.8	60

FIGURE 8

PLOT OF PERCENT U(V)
vs.
APPLIED POTENTIAL
at
pH 1.5

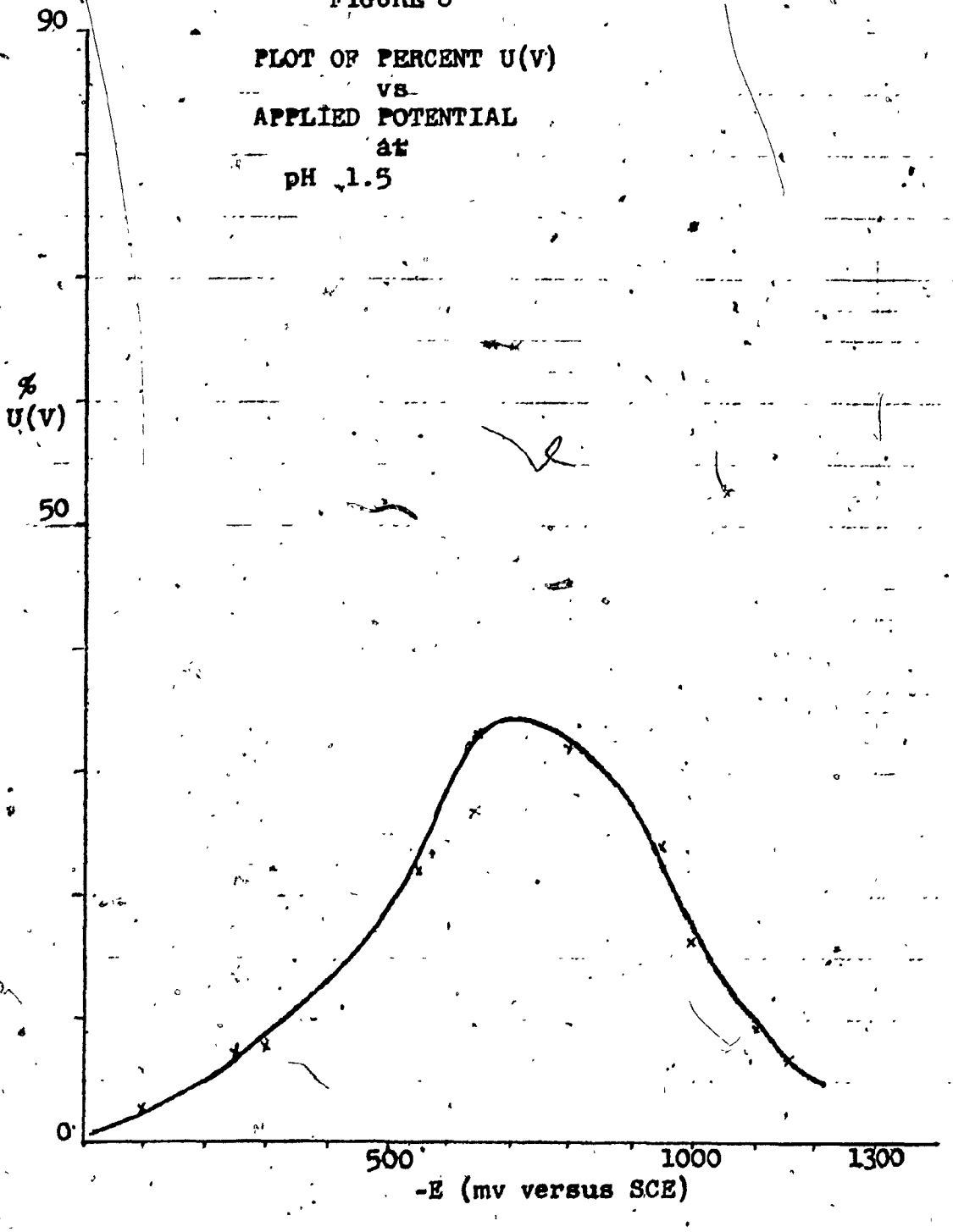


FIGURE 9 PLOT OF PERCENT U(V)
versus
APPLIED POTENTIAL AT pH 2.5

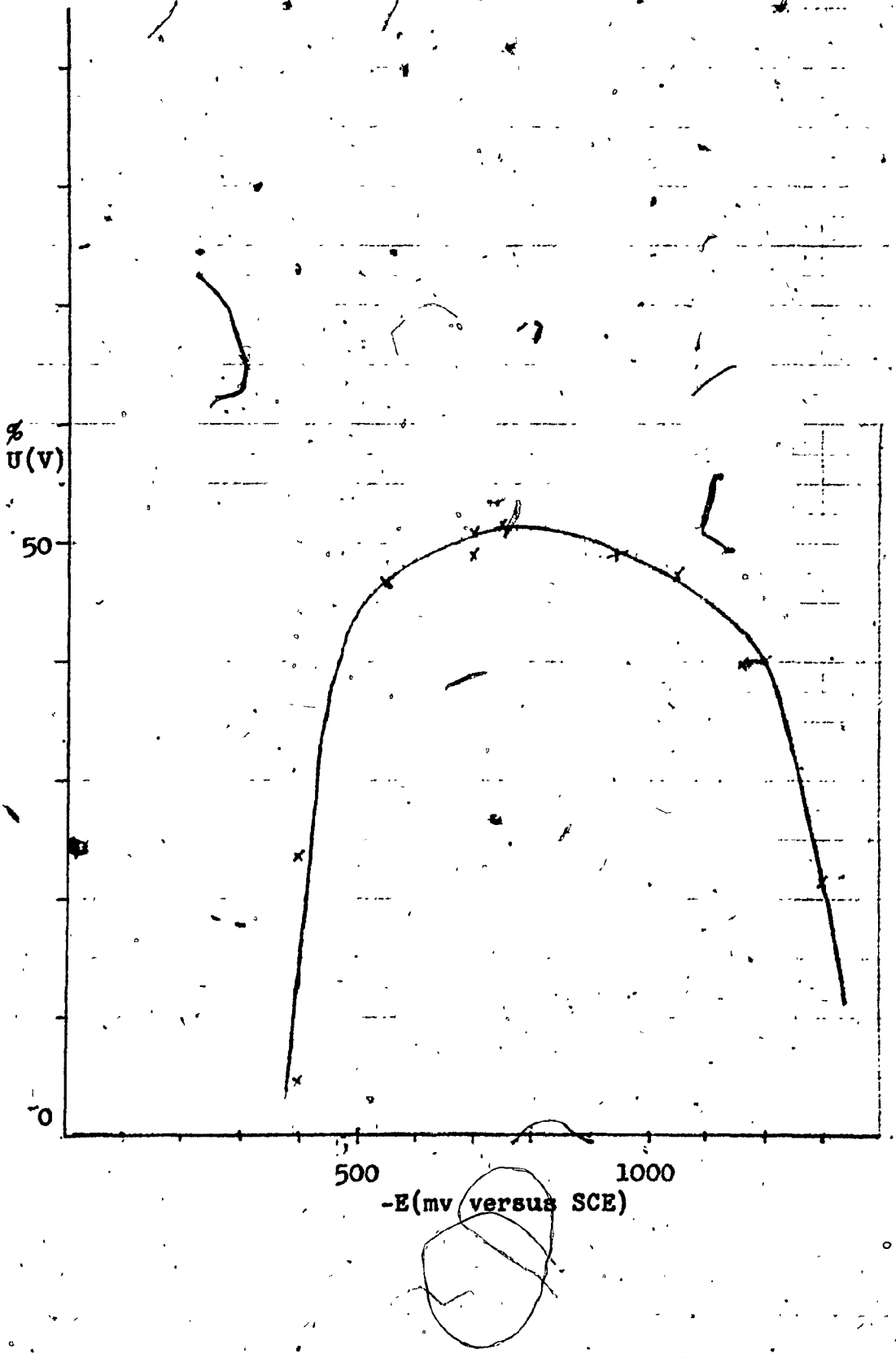


FIGURE 10

PLOT OF PERCENT U(V)
versus
APPLIED POTENTIAL
at
pH 2.0

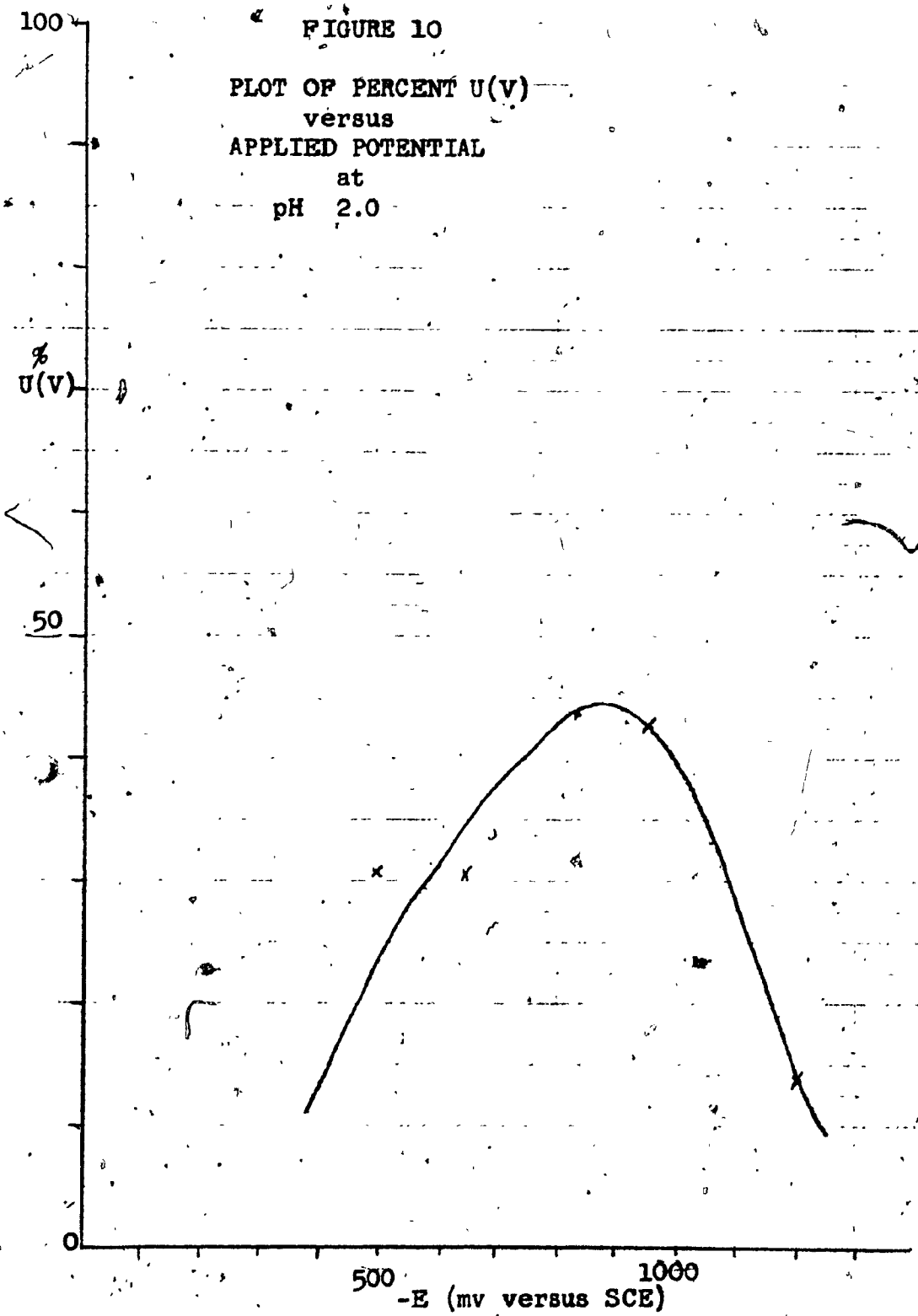


FIGURE 11

PLOT OF PERCENT U(V)
versus
APPLIED POTENTIAL at pH 3.9

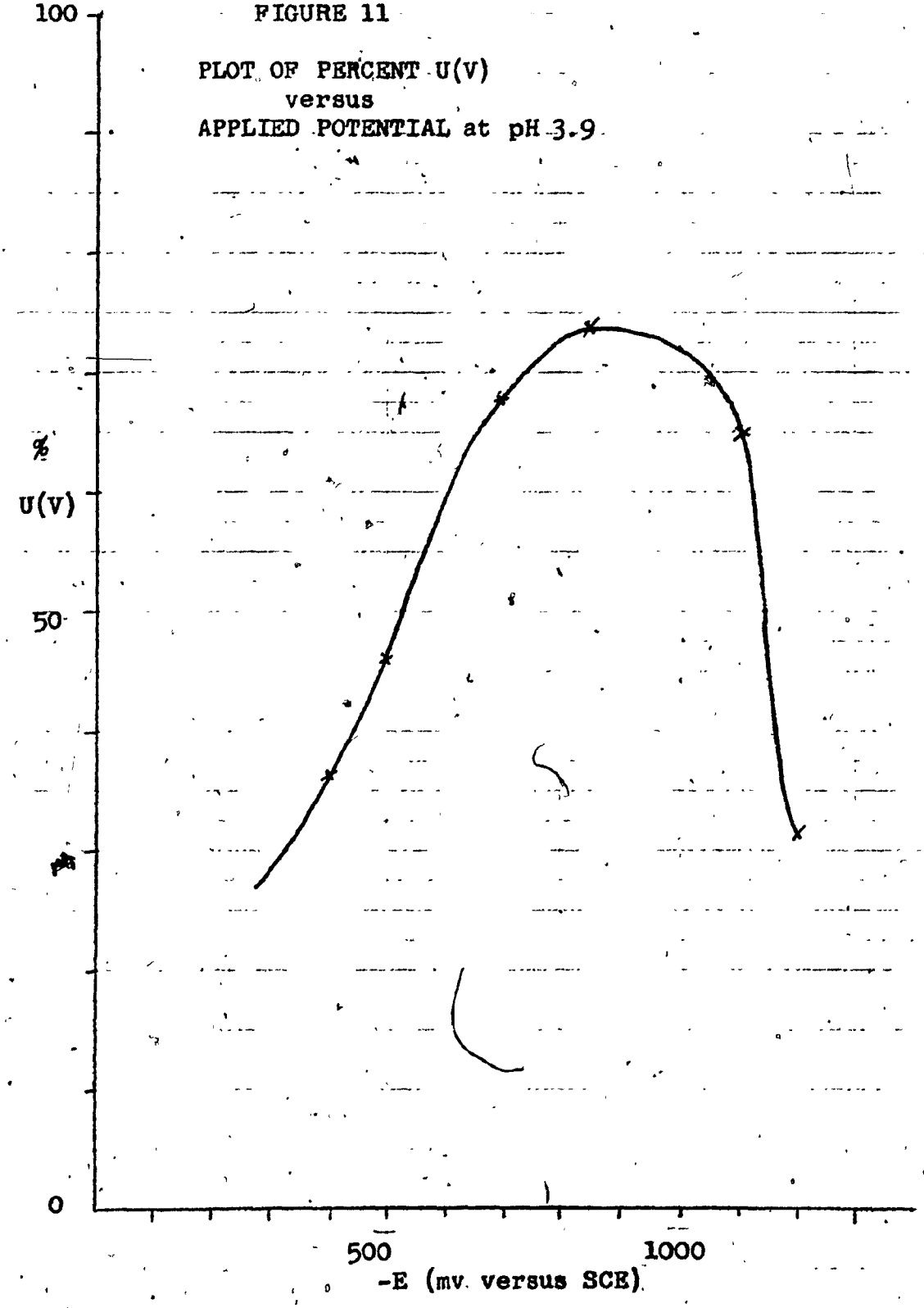


FIGURE 12 PLOT OF PERCENT U(V)
versus
APPLIED POTENTIAL at pH 3.5

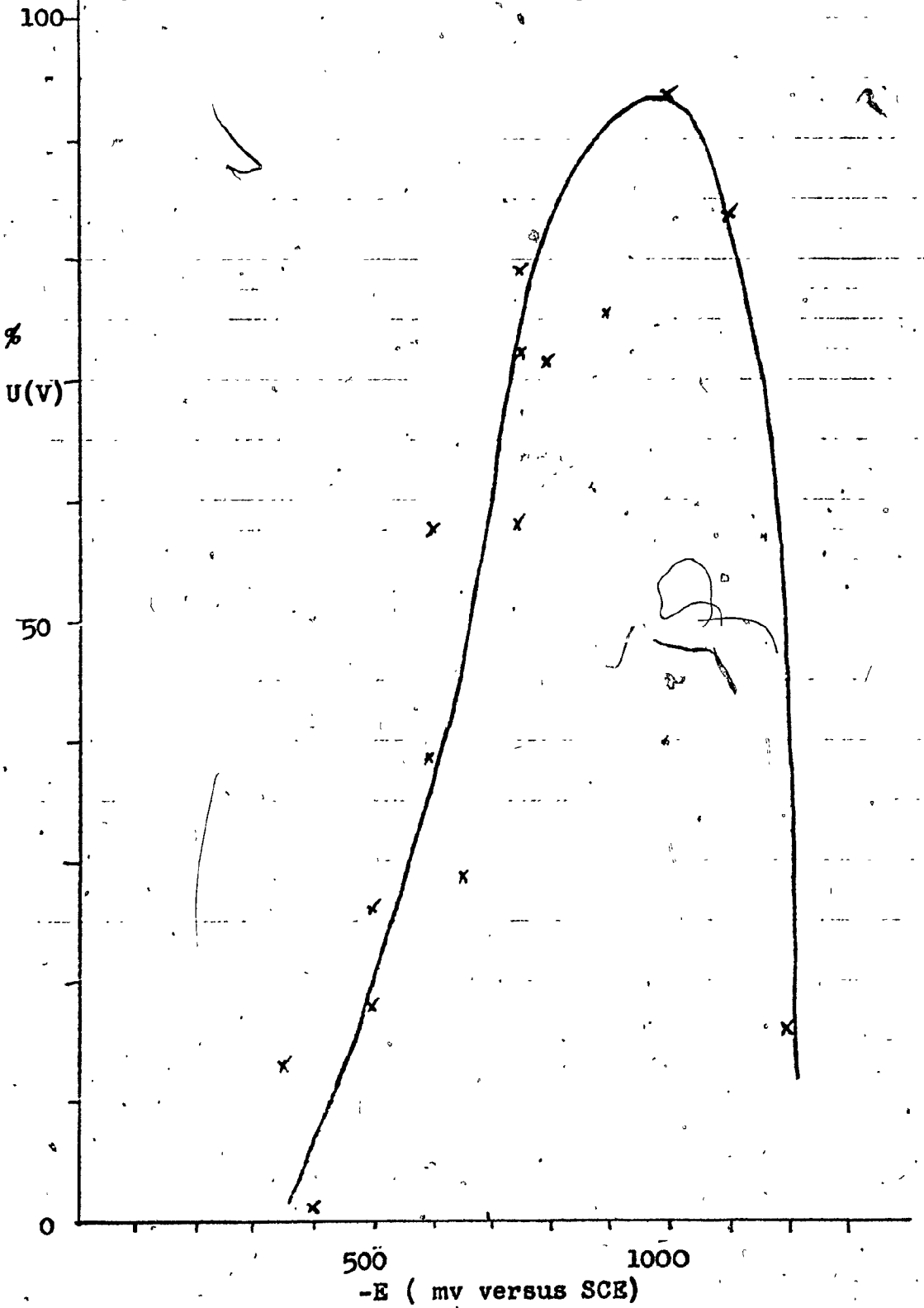


FIGURE 13
PLOT OF PERCENT U(V)
versus
APPLIED POTENTIAL at pH 3.0

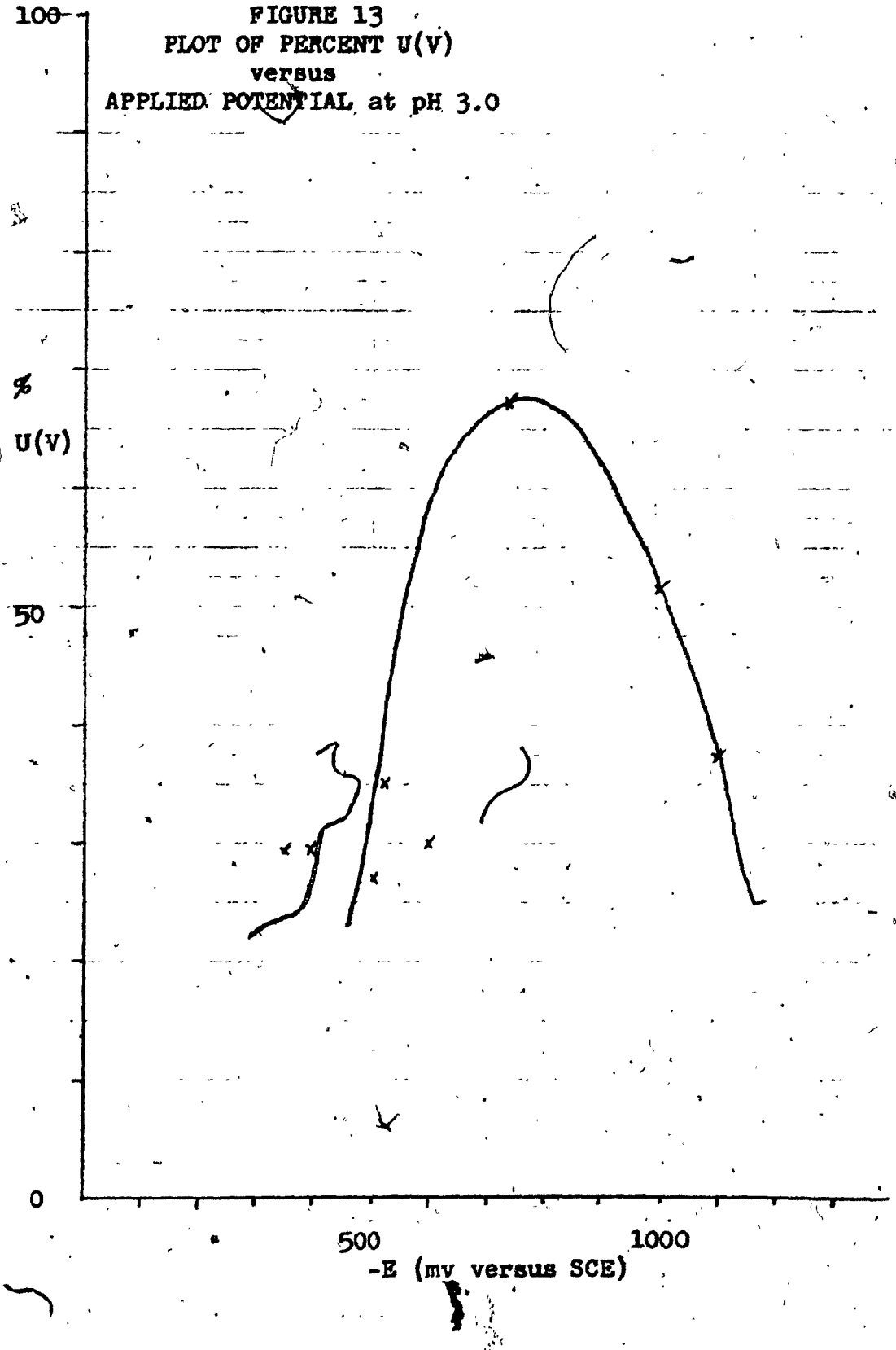


FIGURE 14

PLOT OF PERCENT U(V)
versus
APPLIED POTENTIAL at pH 4.5

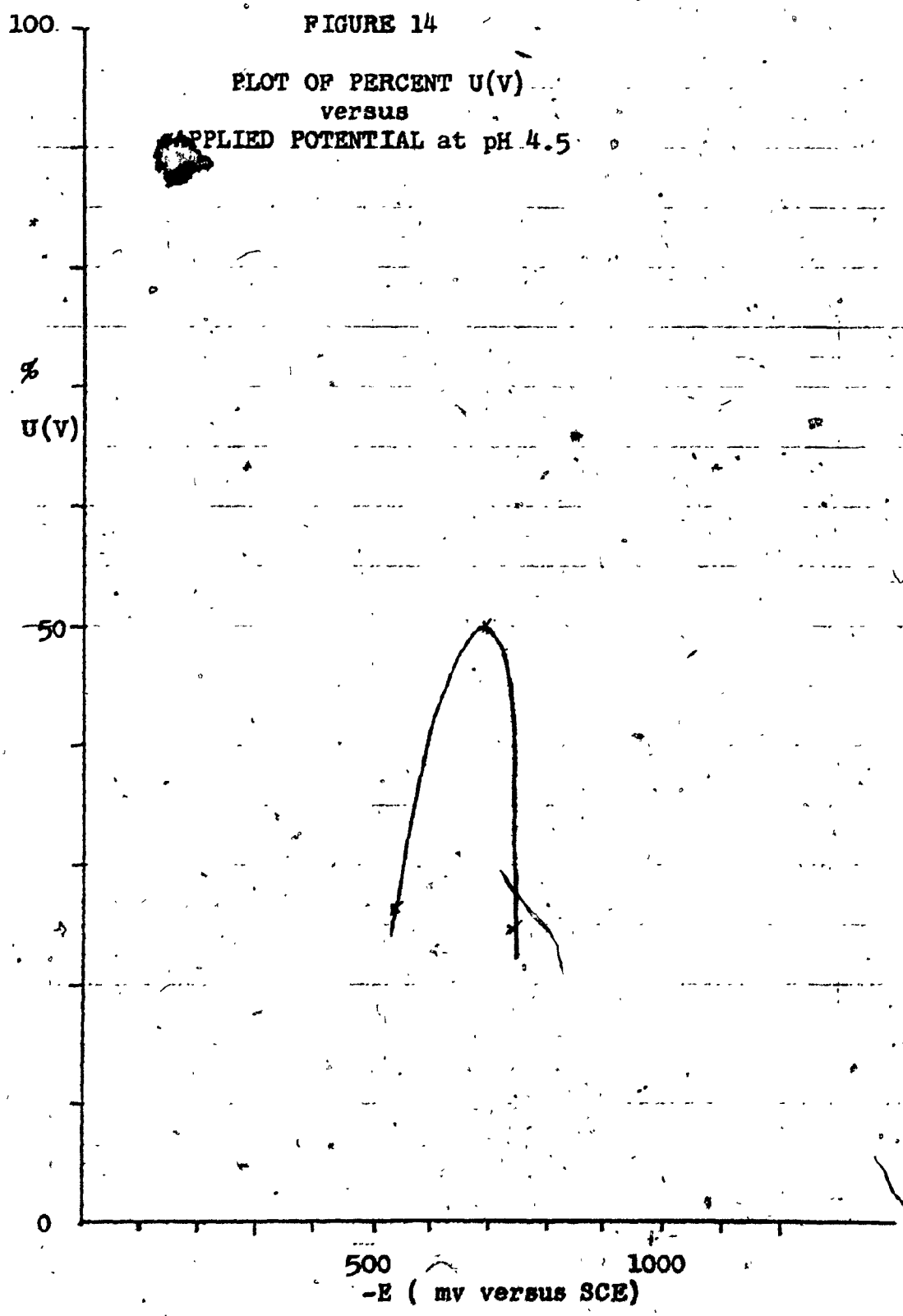


FIGURE 15 PLOT OF PERCENT U(IV) versus APPLIED POTENTIAL

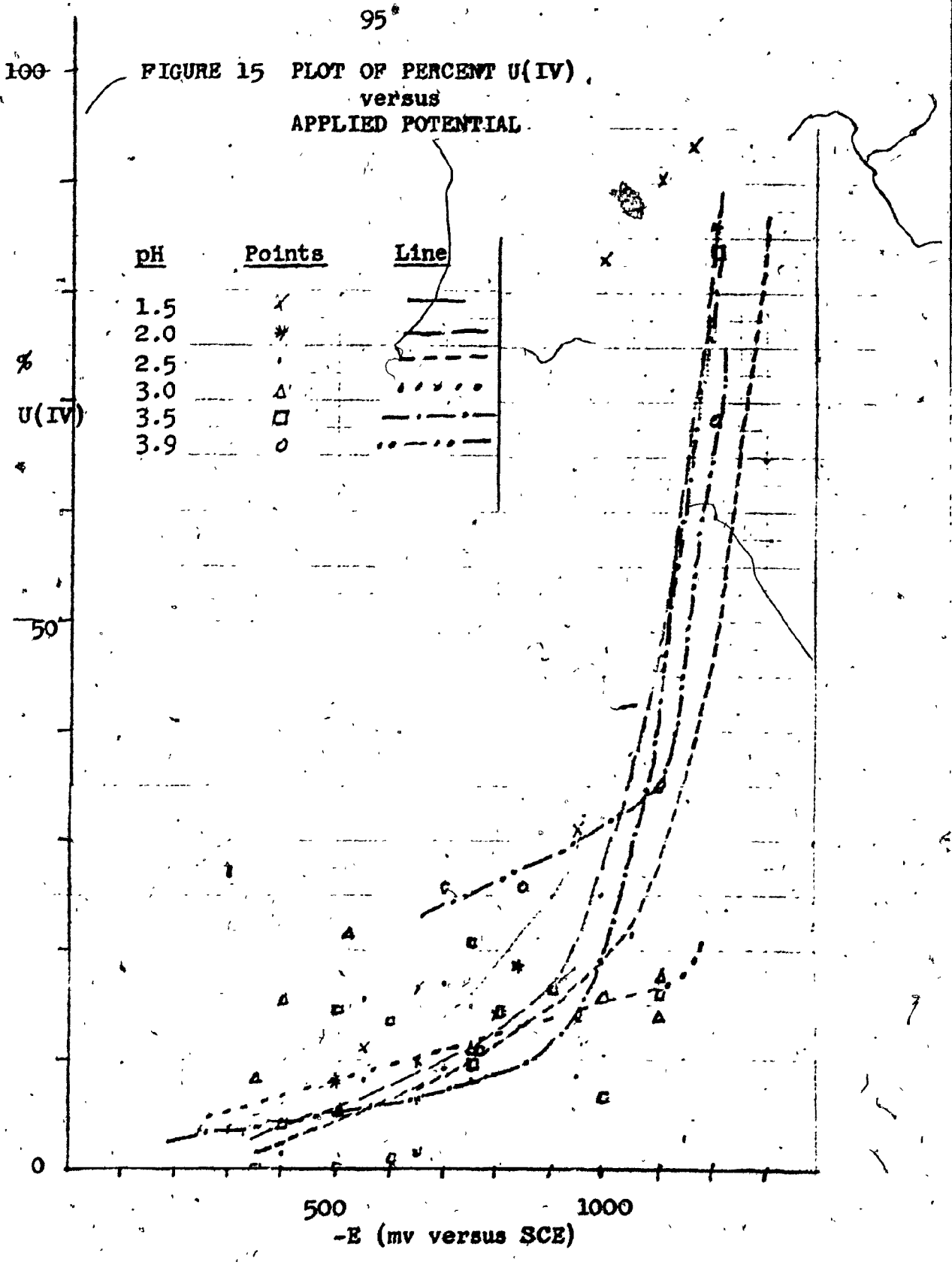


FIGURE 16

PLOT OF PERCENT U(VI)
versus
APPLIED POTENTIAL

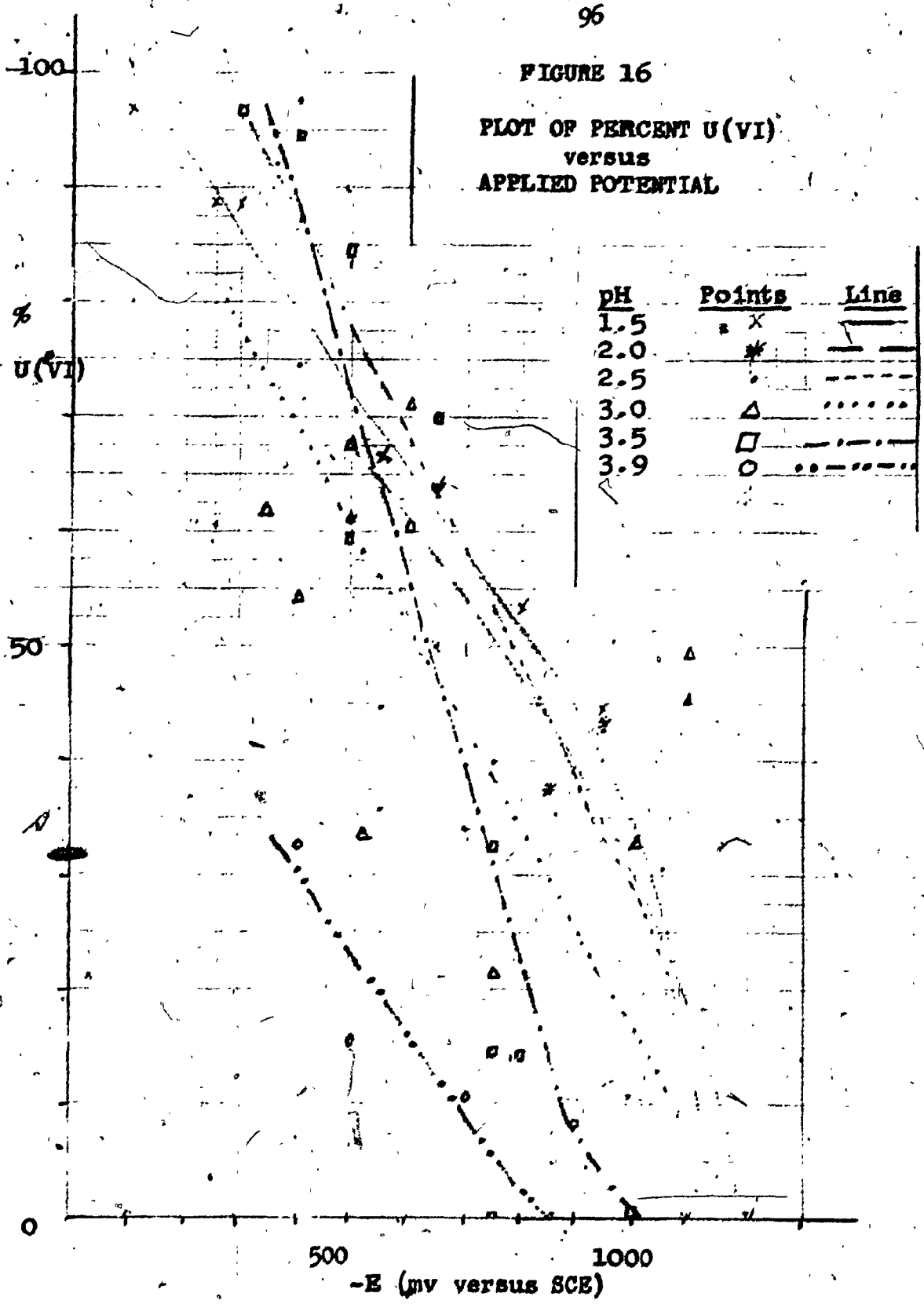


FIGURE 17 PLOT OF PERCENT U(V)
versus
pH

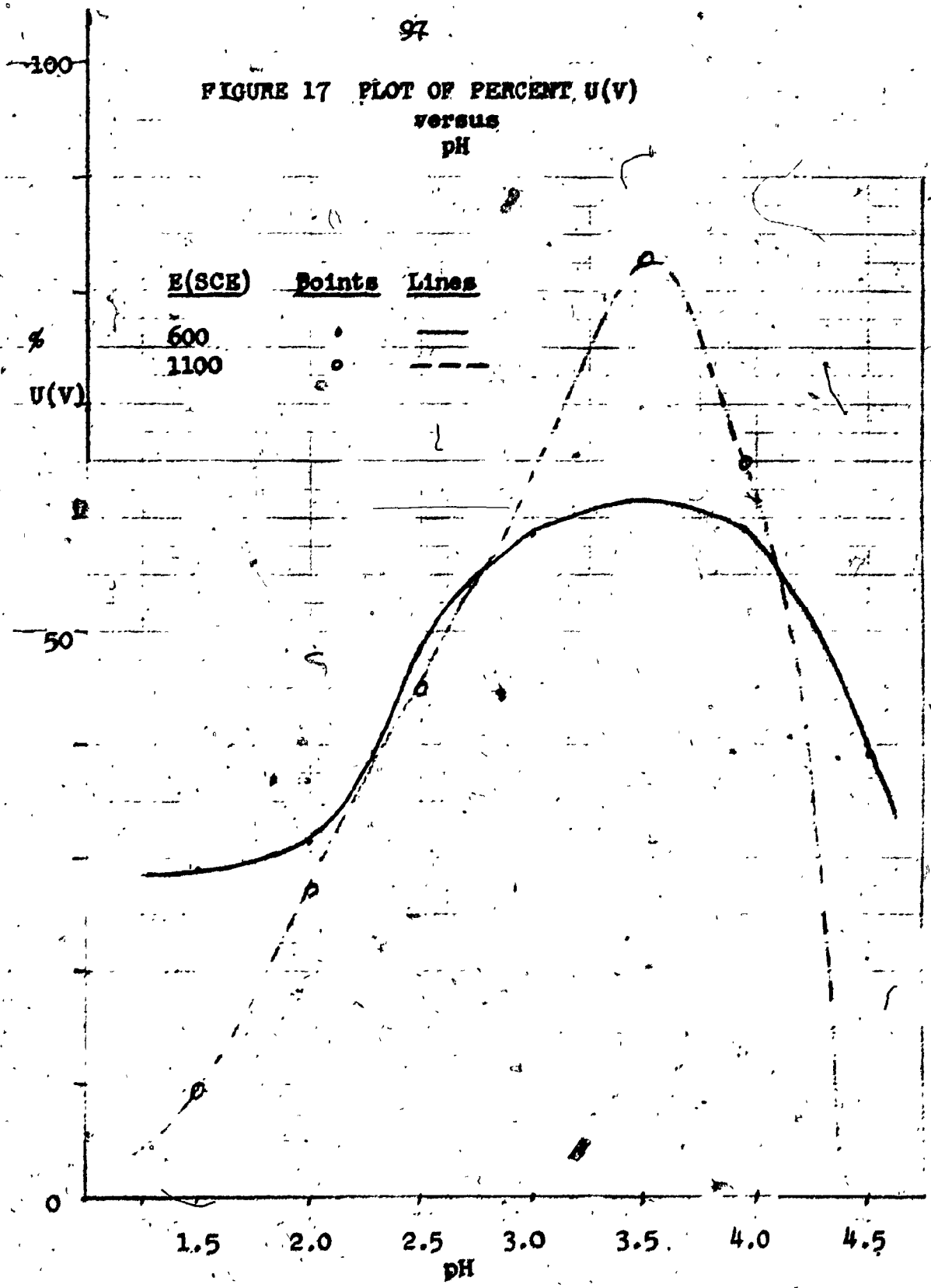


FIGURE 18

PLOT OF APPLIED POTENTIAL
versus
pH for U(V) =50%

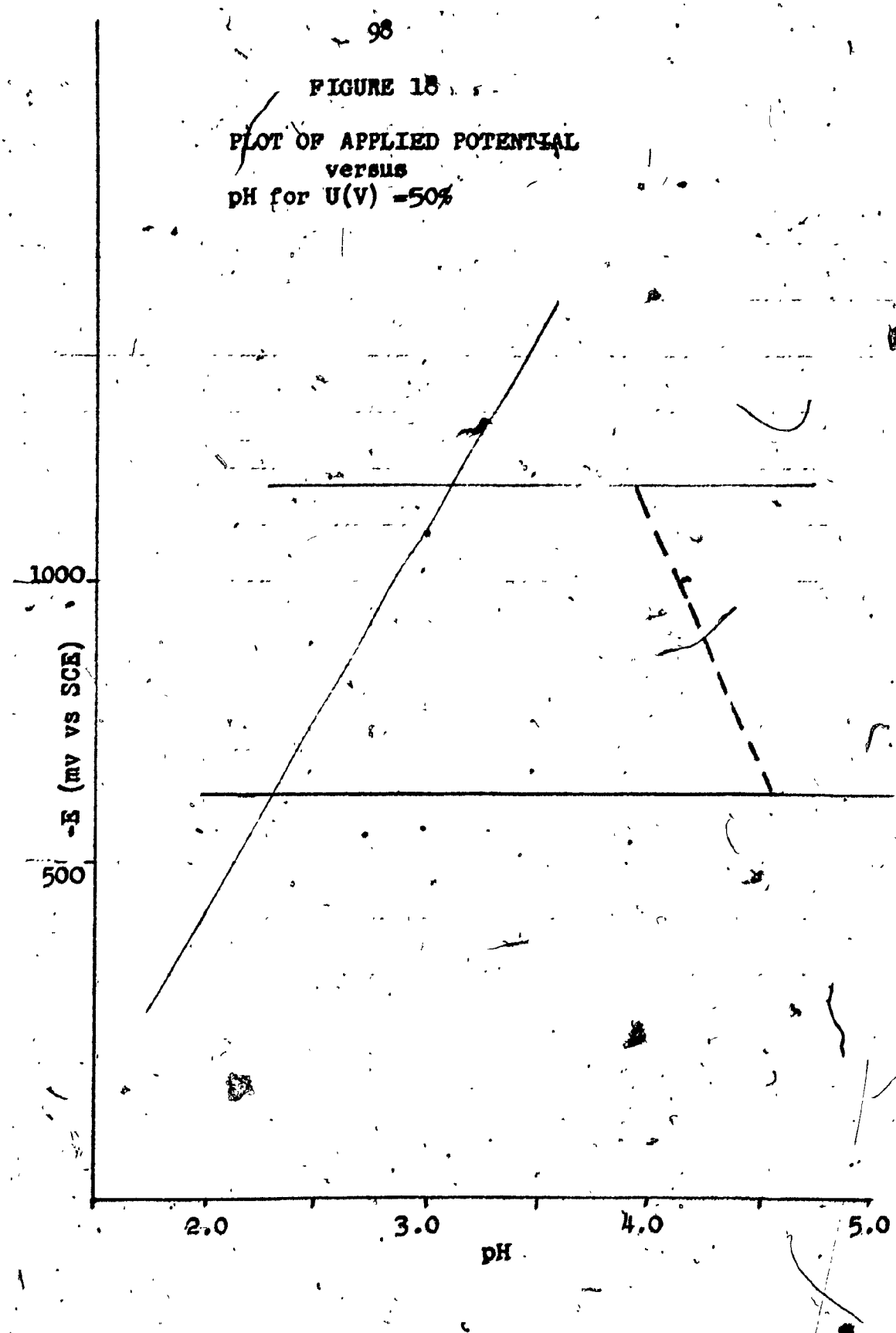
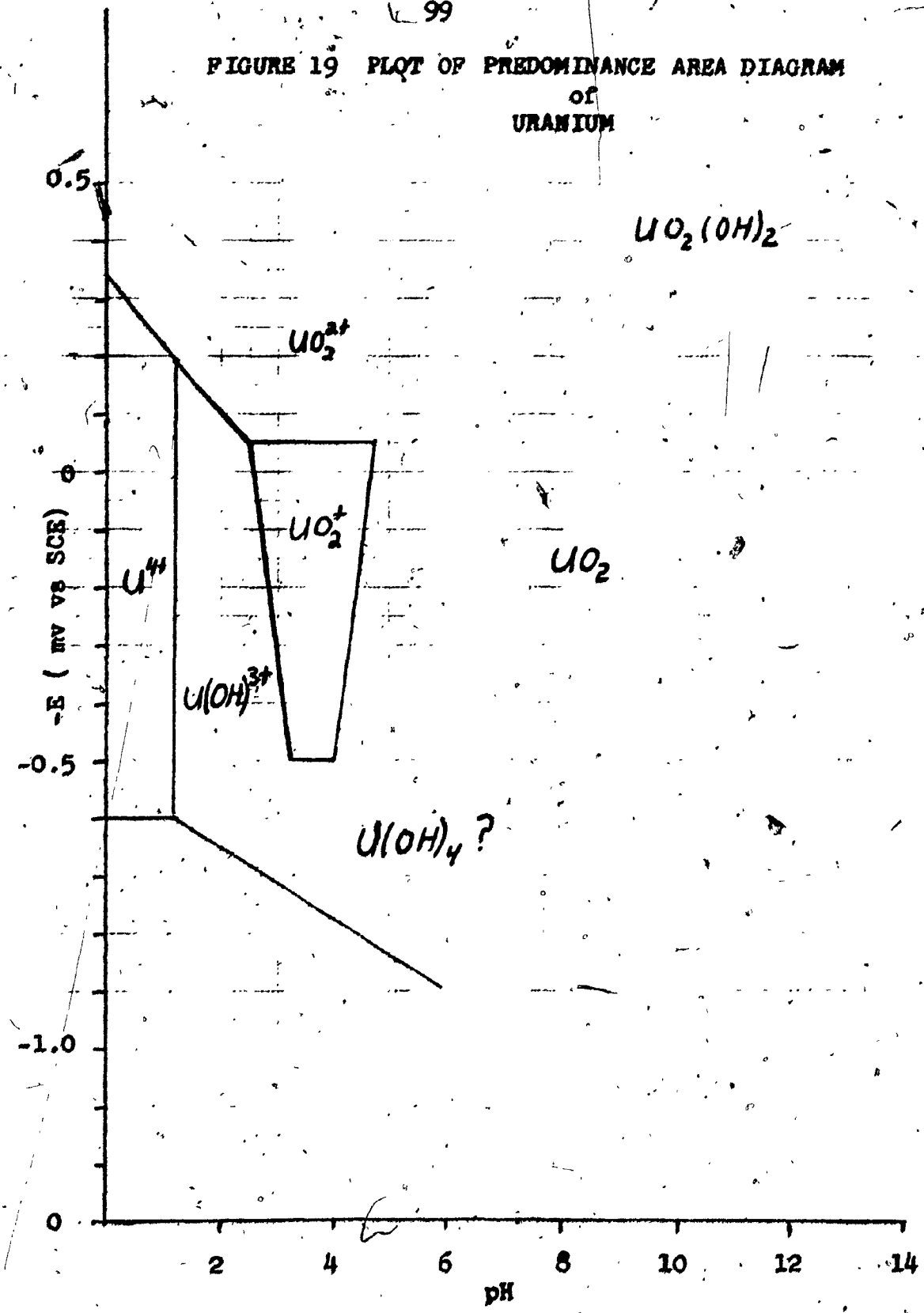


FIGURE 19 PLOT OF PREDOMINANCE AREA DIAGRAM
OF
URANIUM



Sample Calculations:

The method[44] normally used to calculate the percentage of U(V) is to divide the anodic diffusion current by the sum of the anodic and cathodic diffusion currents after electrolysis. This procedure was used until the results produced U(V) values greater than 100 percent. The data were re-examined using the following solutions:

$$\% \, U(V) = \frac{i_d^f(a)}{i_d^o(c)} \times 100$$

$$\% \, U(VI) = \frac{i_d^f(c)}{i_d^o(c)} \times 100$$

$$\% \, U(IV) = 100 - \% \, U(V) - \% \, U(VI)$$

For pH 3.5 at - 600 mv, these results are:

$$\% \, U(V) = \frac{31}{81} \times 100 = 38.27$$

$$\% \, U(VI) = \frac{49}{81} \times 100 = 60.49$$

$$\% \, U(IV) = 100 - 38.27 - 60.49 = 1.2$$

Complications arose when dealing with negative values of the final cathodic diffusion current. The percentage of U(VI) was set equal to zero for these cases.

Graphically all values were used irrespective of deviation from norm, except where it was known beforehand that the experiment failed because of inadequate control of potential, loss of solution during degassing, very irregular polarograms, inhibitive coating of electrodes by deposited or precipitated U(IV) species or similar procedural problems. In all cases the resultant lines were drawn through the average of the values.

The upper and lower potential values for 50% U(V) at each pH were derived graphically and plotted to yield the predominance area diagram for U(V). Once again averages were used for each line.

The final potential values were calculated by adding 0.66 volts to the observed potentials. This included 0.242 volts to correct the saturated calomel electrode values to those for the standard hydrogen electrode and overvoltage for evolution of a gaseous oxidation product at the anode.

DISCUSSION

Discussion

As with all work previously reported in the literature, no maximum suppressor was used and the concentration was kept at approximately 1.5 x 10^{-3} M UO_2Cl_2. This was acceptable for all but the solution of pH 3.5 in which maximum reduction occurred. Even for this series the plateau peak was only about 5% of the initial cathodic diffusion current and readings were taken at more negative potential values to eliminate this perturbation.

It was discovered early in the work that the final percentage of UO_2^+ found depended exponentially on the time span of electrolysis. After 30 minutes approximately 68% of the amount reduced after one hour of electrolysis was found. Further electrolysis had little effect, probably due to increased disproportionation as suggested by the rate laws. The problem was that the predominance area should indicate maximum stability and therefore all reductions were carried out for 60 minutes as the best approximation to this.

The problem of disproportionation or simple oxidation of $(UO_2)^+$ to U(IV) and U(VI) caused concern because of its effect on accuracy of results. For pH 2.5 and 3.0, the decrease in anodic diffusion current was followed. In the former case, the reduction was approximately 3% in 5 minutes while in the latter the loss was 50% in 20 minutes and 57% in 30 minutes. Although a half life of 20 minutes would have normally seemed to be very short, the experimental setup allowed for final measurement in less than 1½ minutes.

Another problem known in advance was the extreme susceptibility of uranium (V) species to oxidation. In this research, degassing the samples initially and maintaining the samples free from oxygen as much as possible was considered important both from oxygen contribution to residual current and stability of the reduced species. It was found that after a degassing period of 10 minutes with nitrogen, the residual current varied by as much as 15%. For solutions of pH 2.5, 30 minutes of nitrogen flushing reduced the cathodic diffusion

current by 11% and little reduction to U(V) occurred thereafter. For this reason, a period of at least 30 minutes degassing was decided upon.

The electrode system used by others [44,39] was a source of extreme frustration throughout the project. To ensure maximum reduction, sufficient current density had to be used. Coiled platinum wire anodes simply did not offer sufficient surface area for the gaseous evolution at the rates applied. A large platinum sheet offering one hundred times more area was finally decided upon. The stirred mercury cathode proved even more of a problem. The mercury became contaminated quickly with uranium (IV) hydroxide and/or oxide especially at higher pH and potential. The agitation required was finally achieved with a magnetic stirring bar of length only 25% less than the cell diameter. This caused excessive vibration of the cell and varying contact of the mercury, resulting in fluctuation of the applied potential. It seemed

logical to substitute a platinum plate for the stirred mercury cathode maintaining the stirring with a much smaller bar to avoid polarization of the surface. The results, shown in Table VIII indicated that the platinum-platinum electrode system would never achieve 50% reduction. In addition a zero shift on the potentiometer of as much as 400 mv between successive reductions was observed. Only at higher pH was the film coating on the plate finally observed. An experiment was carried out to determine only the effect of the stirred mercury versus the platinum cathode with all other factors constant. The reduction was double with the former. The apparent ability of mercury to continually present new surface justifies its use. It must be remembered that the contaminated mercury will, however, require changing, especially at higher pH and potential.

One of the most confusing phenomena observed was the shift to more positive values of the half-wave potential for certain polarograms.

TABLE IX

Results Obtained Using a Platinum Anode and Cathode Combination

pH	-E(mV)	% U (V)	% U (IV)
2.5	400	3.2	0
2.5	600	4.0	7
2.5	750	21.5	4
3.0	400	3.7	0.6
3.0	500	27.3	5
3.0	600	26.4	0
3.0	700	29.7	3
3.0	740	33.7	2
3.0	800	7.2	5
3.5	400	0	5
3.5	500	0	0
3.5	600	0	0
3.5	750	21.6	2
3.5	850	15.0	6.5
3.5	950	8.8	11

As this shifted upwards in one case (-750 mv, pH 3.0) by 128 mV, it became necessary to ascertain its cause. The anode reaction is known to be:

$$Cl^- \qquad \tfrac{1}{2}Cl_2 \quad +1e$$

According to Kolthoff and Lingane,[41] the half-wave potential becomes more positive as the concentration of the supporting electrolyte increases. It would appear, therefore, that the loss of the species under study via electrolysis results in an effective increase of the potassium chloride molarity and the subsequent upward shifting of $E_{\frac{1}{2}}$.

In all previous papers concerned with the polarography of uranyl (V), the percentage of U(V) was obtained by dividing the anodic diffusion current by the sum of the anodic and cathodic diffusion currents after electrolysis. The logic is acceptable up to pH 3.5 and/or an applied potential of -700 mv (versus SCE). It is of course, based on the assumption that all uranium exists as either UO_2^+ or UO_2^{2+}. The rapid precipitation of U(IV) species at higher pH and potential negates the assumption and

produces erroneously high values for percent U(V) as the cathodic diffusion current after electrolysis becomes negative. A legitimate assumption is that all uranium before electrolysis exists as uranyl (VI) ion. The anodic diffusion current after electrolysis, divided by the cathodic diffusion current before electrolysis, should therefore yield the true concentration. Experimentally it was found that low pH, low potential data yielded the same results for both methods. At higher pH and potential, however the new method yielded satisfactory results whereas the older method yielded concentrations greater than 100% of all uranium found.

The assignment of zero percent U(VI) to all negative values of final cathodic diffusion current might well be challenged. A negative $I_d^f(c)$ is indicative of (1) large slope, (2) too much residual current, (3) a combination of a very large anodic current and a small loss of the U(V)/U(VI) couple to U(IV) or (4) of a large conversion

to U(IV). It is assumed that the first possibility was eliminated by the long degassing periods used. The second two cases involve two known and one or two unknown species. It is felt that the U(V) percentage is correct. As less than zero percent U(V) cannot exist, the difference between 100% and U(V) must therefore be the other specie(s). For this reason it is felt that the assumption is justified.

The variation of results seem quite substantial. Many points fell well off the averages which constitute the curves. The 4d rule might well have been applied to those points to improve the appearance of the graphs. However, that would also lead the observer to believe that the obtaining of data was without problems and nothing could be less correct. Each test run took slightly over two hours, and as many were rejected on the basis of experimental difficulties as were used in calculating results. For those used, the variability is an honest witness to the effects of precipitation of a solid on electrode surfaces and to the impossibility of accurately controlling a

rapid and irregularly changing potential manually over long periods of time.

Two recommendations could be made: (1) The use of a larger diameter cell with a platinum wire ring to ensure greater contact with the stirred mercury and (2) an automatic controlling device capable of reducing the potential of a power source from 12 volts down to 3 volts as required to maintain the required millivolt applied potential on the cell.

The half cell reactions are:

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^{+} \qquad E^o = + 0.06v$$

$$2Cl^- \rightleftharpoons Cl_2 + 2e^- \qquad E^o = - 1.359$$

The overall potential therefore is -1.359 + 2(0.06) or - 1.239 volts versus SHE. As the saturated calomel electrode was used for potential measurement, this would become -0.997 volts versus SCE. The values found normally were at maximum

around -800 mv (vs SCE) and so approximately -0.200 V is apparently unexplained. As with many gaseous evolution products on platinum electrodes, it must be assumed that overvoltage is the cause.

Theoretical predictions of the lower pH predominance of uranium (V) were quite accurate. At pH 1.5, a maximum of approximately 35% of UO_2^+ was found at an applied voltage of -700 mv. The more or less Gaussian distribution was as expected, although the peak center occurred slightly lower than the experimental average. As the predominant species is UO_2^{2+} except at very high potential, the higher reduction than expected may be explained by the low energy requirements of the U(V) - U(VI) couple.

At pH 2.0, the peak center shifted to higher negative potentials very close to the average for maximum reduction and a Gaussian distribution was maintained. The approximately 45% maximum obtained was slightly higher than expected and the ease of the U(V) - U(VI) couple is probably responsible.

At pH 2.5, a Gaussian distribution disappears although the maximum occurs near the experimental average. The unusually wide spread only 6% below the peak must be attributed to chance as no other such distributions were attained. The 52% reduction was obtained 0.3 pH units below the theoretical value for initial predominance. As will be shown later this results in an even lower experimental pH for initial predominance.

The expected bell curve was obtained at pH 3.0 with a maximum reduction of 67.5% and values for pH 3.5 are 93% and -1000 mv. Although the pH 3.5 curve tails to lower pH values, the spread of points might well allow for a true Gaussian plot. The 870 mv, 74% reduction at pH 3.9 tails even more than the previous set, but more data at highly negative potentials might have altered this. Because the optimum stability range[44] was estimated to end at pH 4.0, a reduction of perhaps 50 to 60% was expected for this acidity. This high conversion can be explained by the combination of a rapid fall off of UO_2^{2+}

concentration and a delayed rapid increase of U(IV) concentration at this combination of pH and potential. It would appear that the reluctance of U(IV) to polymerize is indeed a fact, although the system was definitely autocatalytic. Precipitation often did not start until 55 minutes after electrolysis started, but was very extensive 5 minutes later.

The 50%, -700 mv peak for pH 4.5 extended the theoretical expectation of predominance by half a pH unit. It also introduced a problem with respect to the closing of the diagram boundries. Because the bulk of the area under both pH 3.5 and 3.9 curves lay on the low potential side of the peak maximum ordinate and the 4.5 maximum occurred at -700 mv which is on the low potential side also, a three dimensional examination of the E versus pH vs % U(V) plot between pH 4.0 to 4.5 would indicate greater predominance on the low mv side. As -700 mv is very close to the UO_{2+}/UO_2^{2+} line, it was assumed that the line sloped from this point to the UO_2^{+}/U(IV) boundary.

Several additional plots are included for information. Although not without exceptions, solutions of lower pH contain more UO_2^{2+} at any potential than those of higher pH. The ion probably never exists as a predominant species at pH 4.5.

The variation of results renders the U(IV) curve much more difficult to analyze. The exponential increase in U(IV) concentration could very well be the autocatalytic formation of polymerized species. The rapid increase in concentration of U(IV) in this area renders attempts to produce U(V) at this potential futile.

A final plot is the variation of U(V) content with pH at several potentials. Roughly Gaussian and skewed distributions were obtained. The peak centers coincide at pH 3.5 as expected, but once again most of the area, or the greater predominance of U(V), lies on the low pH side. It is felt that this is due to the ease of reduction of UO_2^{2+} to UO_2^{+} and to the irreversible removal of UO_2^{+} when disproportionation to U(IV) and U(VI) occurs which alters the distribution to the side where UO_2^{2+} is most stable.

SUMMARY

Summary:

The concentration of Uranyl (V) ion has been examined as a function of applied potential and pH. The position of maximum concentration, 93%, was found to be at pH 3.5 and applied potential -0.360 volts versus SHE. Assumptions, based on previous information, would have placed this maximum at a lower pH and higher potential.

The pH range found, from 2.35 to 4.7, was considerably larger than the theoretically calculated one which extended from pH 2.8 to approximately 4. The 0.59 volt applied potential band where predominance was found also exceeds expectations although no figures are available for comparison. This greater area of stability is attributed to formation of uranium (IV) polymers at even higher pH than expected and to the fact that the equilibrium:

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$$

favors the reductant slightly more than previous data indicated.

Boundary lines for the hypothetical UO_2^+/UO_2 and $UO_2^+/U(OH)_4$ equilibria have been drawn for the first time. The longer and shorter lines of contact respectively may be explained by the relative ease of polymer formation as compared to the overall energetics of the irreversible one electron transfer.

The half life of UO_2^+ was found to be only 20 minutes. This explains why the species, with such a large area of predominance, was not known until 30 years ago. Maintenance of experimental conditions within the area of predominance, will result in the formation of uranium (V) compounds only when the bonds formed are sufficient to prevent disproportionation into the much more stable U(IV) and U(VI) states. In order to achieve this, multiple bonding with the vacant orbitals of uranium will most certainly be required.

Appendix 1

The Development of a Potential-pH Diagram for Iron from the Delahay-Pourbaix-Van Rysselberghe Equations.

The equations required for the development of the iron diagram can easily be derived from general chemical reactions and thermodynamic data using the procedure developed in the text.

For the reduction of the ferrous state to metallic iron of activity 1;

$$Fe^{2+} + 2\,e^- \rightleftharpoons Fe$$

we get[55]

$$E = -0.440 + 0.0295 \log a_{Fe^{2+}} \qquad (1)$$

The other reactions and equations with which we are concerned are:

$$Fe(OH)_2 + 2H^+ \rightleftharpoons Fe^{2+} + 2H_2O$$

$$\log a_{Fe^{2+}} = 13.23 - 2pH \qquad (2)$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

$$E = 0.771 + 0.0591 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \quad (3)$$

$$Fe(OH)_3 + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O$$

$$\log a_{Fe^{3+}} = 4.62 - 3\,pH \quad (4)$$

$$Fe(OH)_2 + 2H^+ + 2e^- \rightleftharpoons Fe + 2H_2O$$

$$E = -0.049 - 0.0591\,pH \quad (5)$$

$$Fe(OH)_3 + H^+ + e^- \rightleftharpoons Fe(OH)_2 + H_2O$$

$$E = 0.262 - 0.0591\,pH \quad (6)$$

$$Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$$

$$E = 1.044 - 0.177\,pH - 0.0591 \log a_{Fe^{2+}} \quad (7)$$

$$HFeO_2^- + H^+ \rightleftharpoons Fe(OH)_2$$

$$\log a_{HFeO_2^-} = -18.30 + pH \quad (8)$$

$$HFeO_2^- + 3H^+ + 2e^- \rightleftharpoons Fe + 2H_2O$$

$$E = 0.591 - 0.0886\,pH + 0.0295 \log a_{HFeO_2^-} \quad (9)$$

$$Fe(OH)_3 + e^- \rightleftharpoons HFeO_2^- + H_2O$$

$$E = -0.839 - 0.0591 \log a_{HFeO_2^-} \qquad (10)$$

For the purposes of these diagrams, equal activity of two species is considered as equal concentration or predominance. The ratio of activities is therefore unity and the log becomes zero. Solids are assigned unit activity by convention and in order to limit the number of lines, either unit or some other designated activity is assigned.

It is common to start drawing the diagram using the equations of 0 or 90° slope. Solving the equations (1) to (4) as follows:

$$E = -0.440 + 0.0295 \log (1)$$

or

$$E = -0.440 \qquad (1)$$

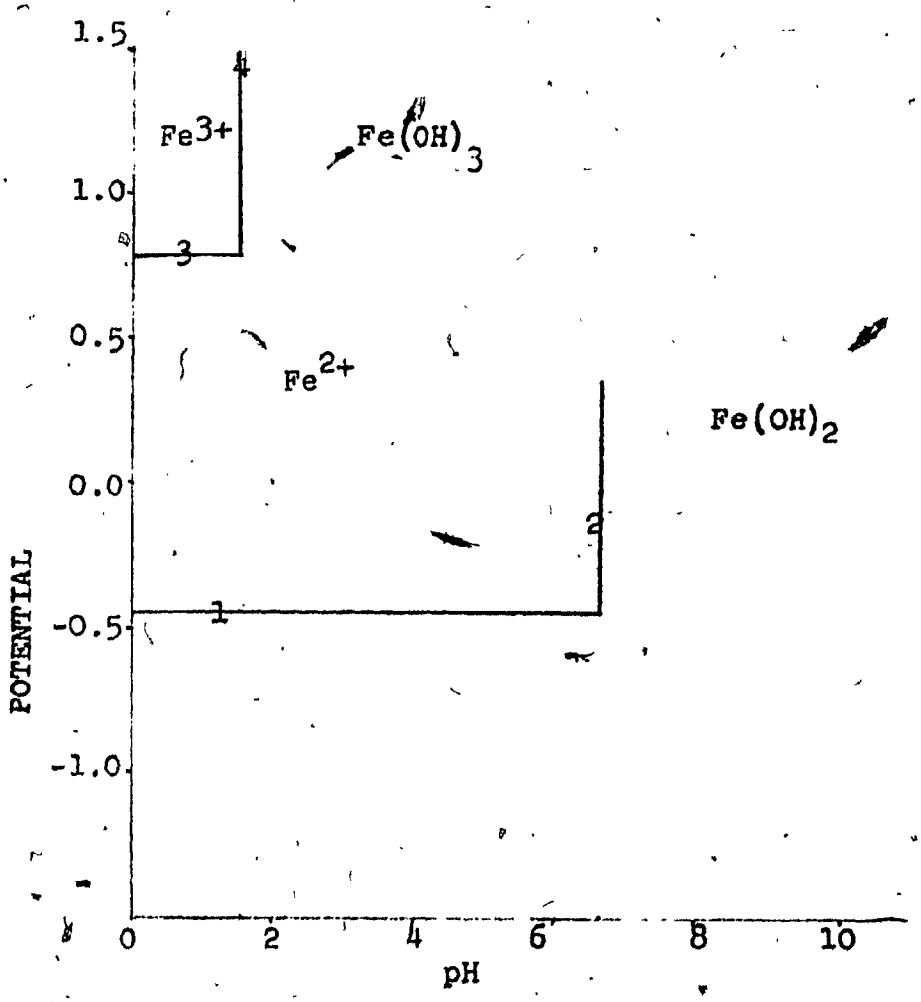
and

$$pH = 6.61 \qquad (2)$$

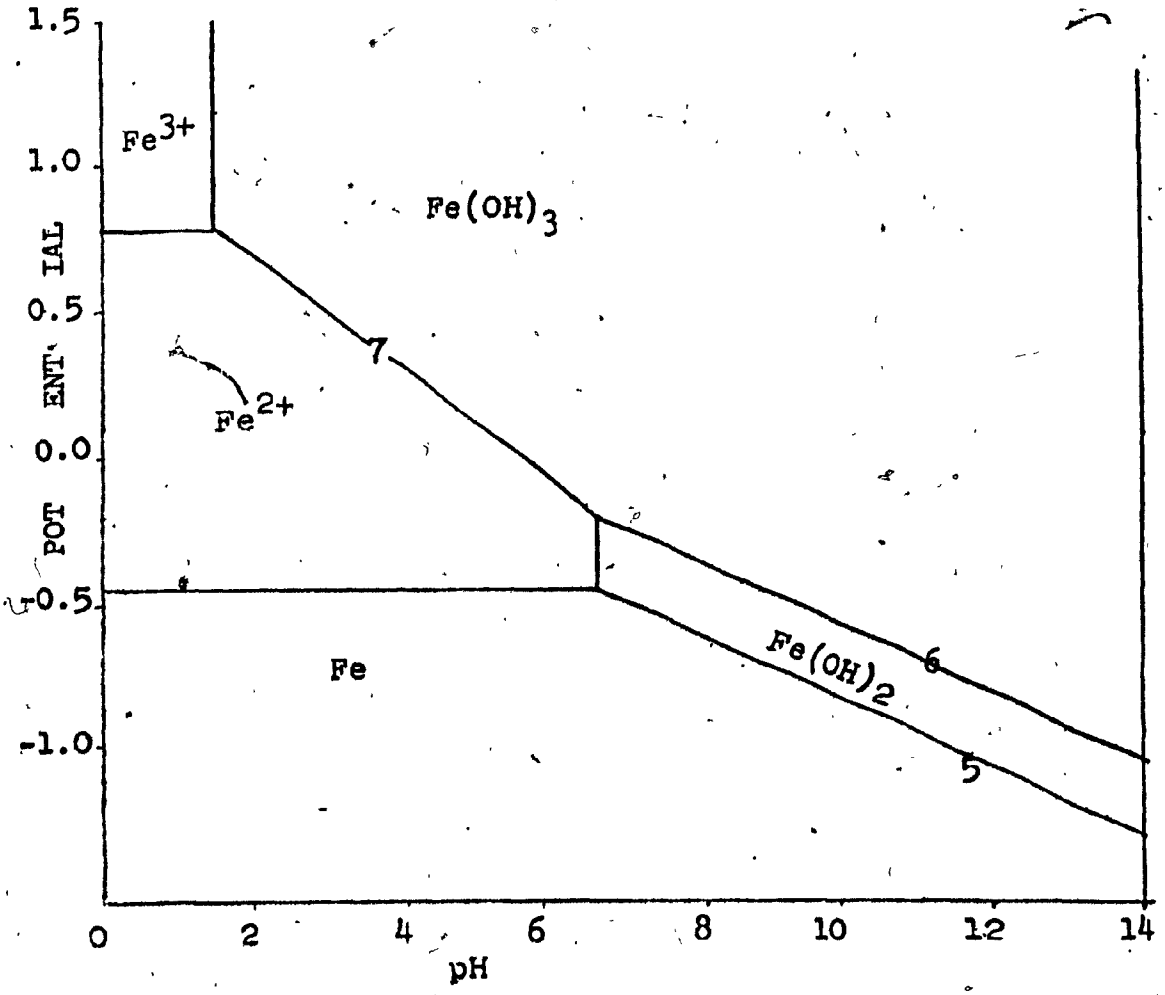
$$E = 0.771 \qquad (3)$$

$$pH = 1.54 \qquad (4)$$

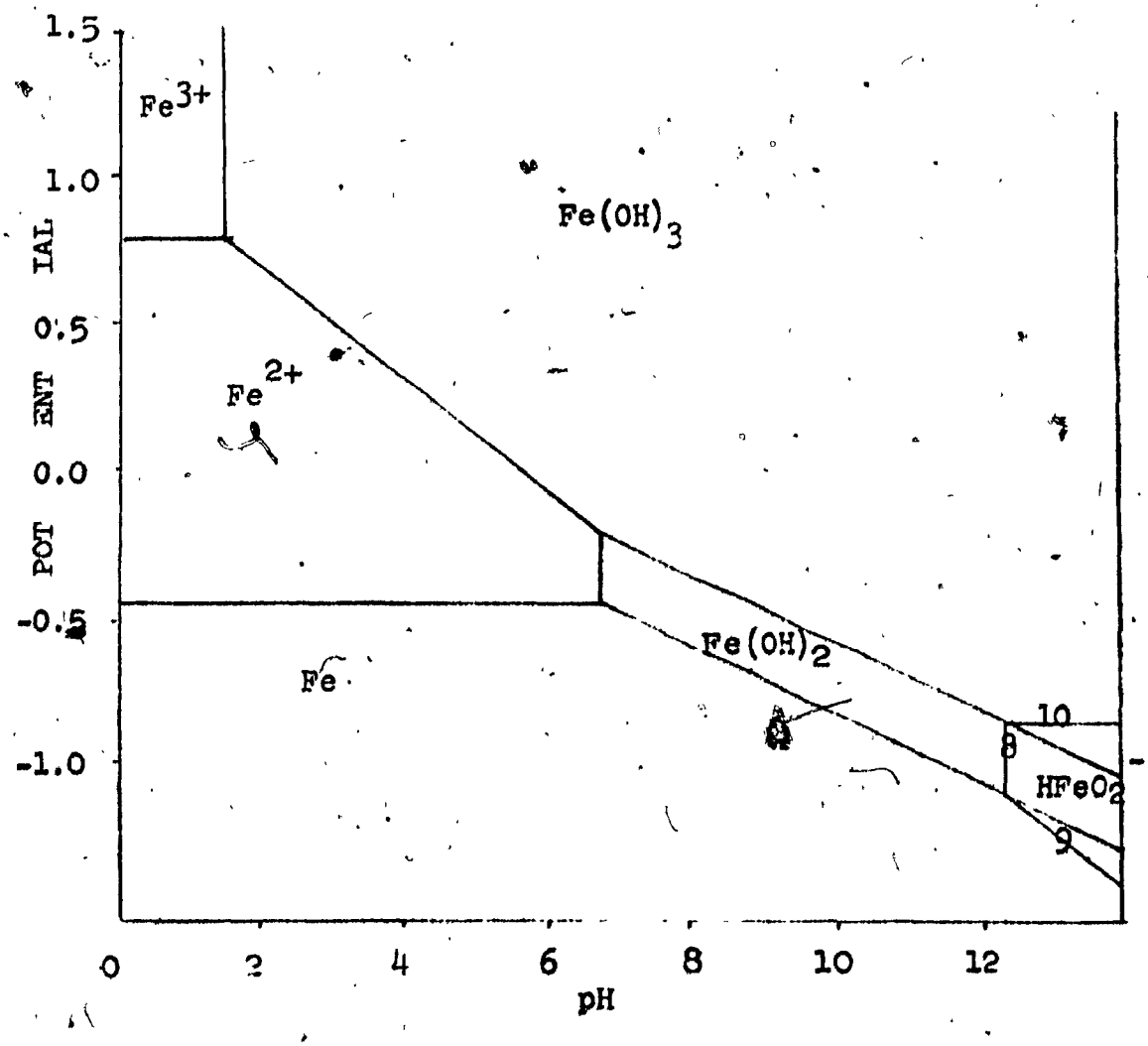
we can draw:


1.5
1.0
0.5
0.0
-0.5
-1.0
POTENTIAL
Fe3+
Fe(OH)3
Fe2+
Fe(OH)2
1
2
3
4
0
2
4
6
8
10
pH

Equation (5) is drawn by calculating two values of E corresponding to two pH's from equation (5). The potentials corresponding to pH 0 and 10 are - 0.049 and - 0.640. Equations (6) and (7) are handled in a similar manner except that unit activity is assigned to the ferrous ion in equation (7). The diagram becomes therefore:



The activity of the $HFeO_2^-$ ion is known to be very low so an activity of 10^{-6} is assigned for use in equations 9 and 10. The final form of the diagram becomes:



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