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1st Status Report

Under

NASA Grant NSG 1204

Chemistry of the System:

$\text{Al}_2\text{O}_3$  (c)-HCl·aq.

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## ABSTRACT

The vapor pressure of water over 2:1 by weight mixtures of 3-M hydrochloric acid and  $\text{Al}_2\text{O}_3$  is reported as a function of time over a 180 minute reaction period at  $31^\circ\text{C}$ . The  $\text{Al}_2\text{O}_3$  sample is one of high surface area furnished by NASA Langley Research Center.

## I. INTRODUCTION

### Brief Review of Aqueous Aluminum Chemistry

The various oxides of aluminum have been studied in minute detail with extensive results, especially since the Hall Process rendered the most abundant metal in the earth's crust a commodity at ca. 25¢ per pound. (1) The gibbsite form of the trihydrate,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , is the most common crystalline form of hydrated alumina. It is soluble in aqueous sodium hydroxide or aqueous strong acid, yielding solutions of sodium aluminate,  $\text{Na}^+ [\text{Al}(\text{OH})_4]^-$  and aluminum salts,  $[\text{Al}(\text{OH}_2)_6]^{3+} 3\text{X}^-$ , respectively.

Anhydrous alumina,  $\text{Al}_2\text{O}_3$ , exists in several crystalline forms, the most common being the  $\alpha$  form, known as alundum. In massive form, that is, large crystals formed from molten  $\text{Al}_2\text{O}_3$ , it is hard enough to scratch glass easily. It is the matrix of such ornamental gems as ruby and sapphire, the colors being imparted to the gem by trace impurities of other metal oxides. Alundum is not soluble in ordinary aqueous acid or base, although it is dissolved slowly by aqueous hydrofluoric acid or alkali metal salts thereof. It is much more slowly dissolved by hot, aqueous NaOH. Alundum is attacked somewhat more rapidly by anhydrous, fused sodium hydroxide.

Hydrous alumina is the ill-defined substance obtained by the rapid and complete neutralization of an aqueous solution of either  $[\text{Al}(\text{OH}_2)_6]^{3+}$  salts or  $[\text{Al}(\text{OH})_4]^-$  salts. Its composition is  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , where  $x$  is a large number, impossible to reproduce precisely. Sometimes called "aluminum hydroxide", hydrous

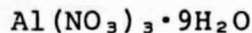
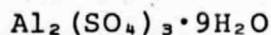
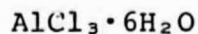
alumina is amorphous and of very low density. It loses water easily, in fact does so upon standing in the aqueous environment from which it precipitated. The aging process is accompanied by a decrease in  $x$ , an increase in density, and a slow ordering of the solid, as seen by broad x-ray powder diffraction lines. Freshly precipitated hydrous alumina is very easily soluble in aqueous sodium hydroxide or in aqueous strong acid. All oxides of aluminum in the 3+ oxidation state are white, if pure.

Sodium aluminate,  $\text{Na}^+[\text{Al}(\text{OH})_4]^-$ , is soluble in water, and is the all important "solution" step in the Bayer Process, by which alumina is produced as the feed material for Hall Process cells. Alumina is leached from bauxite ore into solution by sodium hydroxide. Upon cooling and standing, the solutions of aluminate deposit gibbsite, which is heated to give the anhydrous alumina. Note that the sodium hydroxide is regenerated and the solution from which the gibbsite is deposited is recycled to dissolve more alumina, after appropriate makeup.

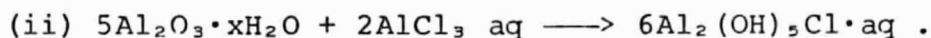
$\text{Na}^+[\text{Al}(\text{OH})_4]^- + \text{H}_2\text{O} \longrightarrow \text{Na}^+ \text{OH}^- + 1/2 \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{O} .$

The stability of aluminate solutions is a complicated function of at least three variables, excess sodium hydroxide, aluminum concentration, and temperature. As well the  $[\text{Al}(\text{OH})_4]^-$  ion is not monomeric. Its degree of aggregation,  $N$ , in the formula  $[\text{Al}(\text{OH})_4]_N^{N-}$ , is a function of unknown variables. Solutions of aluminate at ordinary concentration levels, are stable only at very high pH, i.e., 12 and greater.

Salts in which aluminum forms a part of the cation(s) are much more common. A few examples of such common salts are:



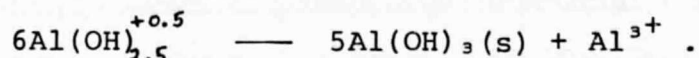
All are white, easily soluble in water, yielding acid solutions. The first hydrolysis constant of the  $[\text{Al}(\text{OH}_2)_6]^{3+}$  ion is  $10^{-5}$ . Thus a 0.10-M  $\text{Al}^{3+}$  salt solution results in a pH of 3. As the pH of  $\text{Al}^{3+}$  solution is raised aluminum solute isopolycondensations result,  $p\text{Al}^{3+} + q\text{H}_2\text{O} \rightleftharpoons [\text{Al}_p(\text{OH})_q]^{3p-q} + q\text{H}^+$ . As  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  or other effective aqueous base is added to  $\text{Al}^{3+}$  solutions,  $[\text{Al}(\text{OH})_{\tilde{n}}]_N^{3-\tilde{n}}$  results, such that the pH does not increase sensibly up to  $\tilde{n} \approx 3.0$ , at which point hydrous alumina precipitates. Further addition of base results in large increases of pH into the basic region and the dissolution of the precipitate as  $[\text{Al}(\text{OH})_4]^-$ . It is actually possible to add base to  $\text{Al}^{3+}$  solution up to  $\tilde{n} \approx 2.5$  without obtaining a precipitate, although the stability of the resulting solutions varies enormously. A white, solid substance of the empirical composition  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot x\text{H}_2\text{O}$  ( $x \approx 2$ ) is obtained upon evaporation of such solutions. Identical or similar substances are obtained in at least two other ways:



The resultant white solid, or solutions thereof, are commodity chemicals, used in at least two practical applications, as anti-perspirants (3) and as clay-stabilization reagents in oil wells. (4) The details of just what solute particles exist in solutions are not agreed upon as yet. However a number of facts about such solutions have been established. Thus 2-M solutions of

$\text{Al}_2(\text{OH})_5\text{Cl}$  are stable at room temperature indefinitely.

Upon simple dilution to ca. 0.1-M or less the solutions deposit, slowly, crystals of gibbsite with a concomitant lowering of pH. These facts are best described by the reaction:



That such solutions are not at true equilibrium is certain.

Some idea of how far from equilibrium these isopolycation salt solutions are may be shown as follows. At room temperature the  $K_{\text{sp}}$  for gibbsite is  $\sim 10^{-34} = [\text{Al}^{3+}][\text{OH}^-]^3$ . At pH = 4, the concentration of hexaquoaluminum ion should be  $\sim 10^{-4}$ -M. Yet 2-M solutions of the basic aluminum salt persist for long periods of time. The rates at which such polymeric solutions change and the nature of the ultimate products are influenced profoundly by temperature, ionic strength, total aluminum concentration, and the nature of the anion present.

Booster rocket propellants will be  $\text{Al} + \text{NH}_4\text{ClO}_4 + \text{binder}$  with resulting exhaust of  $\text{Al}_2\text{O}_3 + \text{N}_2 + \text{HCl} + \text{water} + \text{traces of several other substances.}$ (2) The possibility of chemical reaction among the  $\text{Al}_2\text{O}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{O}$  need be considered. Were the  $\text{Al}_2\text{O}_3$  massive  $\alpha\text{-Al}_2\text{O}_3$ , little chemical change would be expected. However the  $\text{Al}_2\text{O}_3$  is high surface area, very small particle size, and its reactivity, as such, will not be negligible. The particles serve as nuclei for the condensation of liquid water, in which  $\text{HCl}$  is very soluble.  $\text{HCl}\cdot\text{aq}$  in contact with high surface  $\text{Al}_2\text{O}_3$  is expected to result in chemical reactions.

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Sequential possible reactions are:

1.  $\text{H}_2\text{O}(\text{g}) + \text{Al}_2\text{O}_3(\text{s}) \longrightarrow \text{Al}(\text{OH})_3$  surface reaction
2.  $\text{Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$  (on the  $\text{Al}_2\text{O}_3(\text{s})$ )
3.  $\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{HCl}\cdot\text{aq}$
4.  $\text{HCl}\cdot\text{aq} + \text{Al}(\text{OH})_3(\text{s}) \longrightarrow \text{AlCl}_3\cdot\text{aq}$
5.  $\text{AlCl}_3\cdot\text{aq} + \text{Al}(\text{OH})_3(\text{s}) \longrightarrow \text{Al}(\text{OH})_{\tilde{n}}\text{Cl}_{3-\tilde{n}}\cdot\text{aq}$  .
6.  $\text{Al}(\text{OH})_{\tilde{n}}\text{Cl}_{3-\tilde{n}}\cdot\text{aq} \longrightarrow \text{Al}(\text{OH})_3(\text{gibbsite}) + \text{AlCl}_3\cdot\text{aq}$  .

The extent to which 3, 4, 5, and 6 take place will determine the vapor pressure of water in the system. Since the vapor pressure of  $\text{H}_2\text{O}$  is a parameter in the cloud stability, a detailed knowledge of the chemical behavior of the  $\text{Al}_2\text{O}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$  exhaust cloud system is desirable.

It is likely that thorough understanding of the chemical details outlined in steps 1-6 will emerge slowly, i.e., over years, if not decades. Thus it is considered expedient to undertake experiments designed to obtain direct measurements of the vapor pressure of water over ranges of  $\text{Al}_2\text{O}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$  mixtures such as might be expected in the exhaust cloud.



## II. EXPERIMENTAL PROCEDURE

A Hewlett Packard Model 302B Vapor Pressure Osmometer was available in the Chemistry Department. It had never been used. Actually it was a replacement for an earlier H-P VPO which had been destroyed in a fire during the summer of 1972. The VPO was placed in operation in accordance with the operating and service manual. Routine performance checks were made and spare parts were ordered, but no thorough check of the operation characteristics was undertaken until we moved into the new building, on or about 1 September 1976.

Reproducible data on standard solutions from week to week, even from day to day, were not possible unless the instrument operating temperature was several degrees above the lab temperature. Similar limitations have been reported by others.<sup>(5)</sup> Accordingly for the data reported herein, the operating temperature was 31°. The Variable Temperature Controller 18575A, an option on the VPO Model 302B - not available on the original VPO 302, made it possible to set our operating temperature at any desired temperature rather than the individual fixed temperature thermostat probes used with the 302.

New Rogers Hall (the new chemistry building at William and Mary) uses deionized water rather than distilled water, the former being piped from a central supply to each lab. Standard solutions prepared from deionized water were found to give different VPO readings from replicate solutions prepared using distilled water. All data reported herein are for solutions prepared using distilled water.

The VPO output is microvolts of bridge imbalance and is proportional to  $\Delta T$ , the difference in temperature between two thermistor beads. In our case the reference bead is always wet with water and the sample bead with the sample solution.

The usual protocol for a sample reading is as follows:

1. Both reference and sample beads washed with 4-5 drops of solvent.
2. Leave one drop of solvent on each bead to check zero of bridge balance.
3. Sample bead washed with 3-5 drops of sample.
4. Place drop of sample on sample bead.
5. Record VPO readings at 2, 3, 4, and 5 min. intervals from the time the drop was placed on the sample bead.
6. Wash sample bead with 3-5 drops of solvent.
7. Repeat steps 3, 4, 5 to get 2nd set of values.
8. Wash sample bead with 3-5 drops of solvent.
9. Repeat steps 3, 4, 5 to get 3rd set of values.
10. Repeat step 1.

A thorough check of instrument performance was undertaken using 3 series of standard solutions:

- KCl ca. 0.10, 0.25, 0.50, and 1 molal
- NaCl ca. 0.10, 0.25, 0.50, and 1 molal
- HCl ca. 0.10, 0.25, 0.50, 1 and 3 molal.

The standard solutions were prepared gravimetrically, using c. p. samples of KCl and NaCl, dried at 100°C. The HCl solutions were prepared to approximate strength from c. p. conc.

HCl and standardized by titration.

Large scale plots of  $m$  (molality) vs.  $a_w$  (activity of water) were made for the NaCl and KCl solutions, using data from Stokes and Robinson. (6) From these graphs  $a_w$  values were read for the individual solutions. 4 significant figures were carried although we believe they are good to 3 only.

Assuming  $p = p_0 \cdot a_w$  it is first necessary to know  $p_0$ . It was obtained by interpolation between values at 30 and 35° given on p. 457 of ref. 6. The figure used is  $p_0 = 33.8952$  mm Hg (31°C).  $\Delta p$  values for individual solutions were calculated as  $p_0 - p$ . A large scale plot of  $\Delta p$  vs. VPO readings was made to use as the standard curve from which to convert VPO readings to  $\Delta p$  values for experimental solutions. A point on the  $\Delta p$  vs. VPO plot was obtained for the ca. 3-M HCl solution by reference to other data. (7) The data were available for 10% and 14% HCl by weight (our sample was 10.42%) and  $H_2O$  v.p. at 30 and 35°C. The  $\Delta p$  value for that solution was calculated by dual interpolation.

The first sample of  $Al_2O_3$  to be studied was received on October 2, 1975 from Mr. W. R. Cofer, III of the Space Applications Technology Division of Langley Research Center, NASA. It was packaged in a T 34/12 weighing bottle, labelled " $Al_2O_3$  #5, prepared 7-25-74." We used the sample as it was received. Into each of nine small, rubber capped vials was weighed accurately ca. 1 gm. of  $Al_2O_3$ . At time zero ca. 2 ml of ca. 3-M HCl was added to each vial, and each vial was stoppered and reweighed. The vials were shaken vigorously and allowed to

stand. At 20 minute intervals ca. 0.5 ml of the liquid was sampled from a different vial for VPO measurement. The standing samples were swirled every 20 minutes. Thus sample one had been swirled once and represented the results of  $\text{Al}_2\text{O}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$  contact for 20 min., sample two had been swirled twice and represented 40 min. contact, etc. Readings were taken by the following protocol:

1. 3 successive drops of 3-M HCl on sample bead.
2. 4th drop of 3-MHCl on sample bead.
3. Read VPO at 5 min. after addition of 4th drop.
4. Wash sample bead with 3-5 drops of solvent.
5. Add 3 successive drops of sample 1 solution to sample bead.
6. Add 4th drop of sample 1 sol'n. to sample bead.
7. Read VPO at 5 min. after 4th drop.
8. Repeat 5-7 using sample 2.
9. Check VPO for 3-M HCl (blank)
10. Repeat 5-7 for sample 3, etc.

$\Delta p$  values for each of the nine vials were read from the large scale graph of  $\Delta p$  vs. VPO.

Two additional experiments were conducted. 10th and 11th sample vials were prepared. For No. 11, after zeroing the instrument with solvent on sample bead, a drop of 3-MHCl was placed on the sample bead, followed by 3 drops of sample solution, then the 4th drop. VPO readings were recorded on that drop for ca. 30 min. For No. 10 the regular sample protocol was followed, that is, the sample bead was washed with 3-5 drops of solvent

prior to making the sample reading, which in this case was the 4th drop of sample and readings recorded for ca. 30 min.

### III. RESULTS

- A. The reproducibility of VPO measurements from time to time is shown in Table I, in which are listed the actual solution molalities and VPO readings. The VPO readings are usually the average of the 5 readings.
- B. The  $\Delta p$  vs.  $m$  calculations for the average values of each molality of each standard (NaCl, KCl, and HCl) are shown in Table II. The data plotted in Figure 1.
- C. Vapor pressure lowerings,  $\Delta p$  values, for the nine  $Al_2O_3 \cdot HCl \cdot aq$  samples were read from a large scale plot similar to Figure 1, using the VPO readings. Blank readings were made using 2.999-M HCl approximately every third sample. The results appear in Table III, and are plotted in Figure 2.
- D. The VPO readings on Samples 10 and 11 follow:

<u>Sample 10</u>		<u>Sample 11</u>	
<u>time (min.)</u>	<u>VPO(<math>\mu V</math>)</u>	<u>time (min.)</u>	<u>VPO(<math>\mu V</math>)</u>
7.8	160.9 x 100	8.5	177.3 x 100
10.3	169.0 x 100	10.8	179.9 x 100
13.2	167.9 x 100	13.2	178.5 x 100
16.2	167.7 x 100	15.5	177.3 x 100
19.0	168.8 x 100	17.8	175.0 x 100
21.7	168.8 x 100	20.2	176.8 x 100
22.7	169.1 x 100	23.5	172.9 x 100
27.0	170.0 x 100	26.3	174.3 x 100
29.3	169.7 x 100	31.0	176.8 x 100

#### IV. CONCLUSIONS

- A. The vapor pressure osmometer is well-suited to the task of measuring the vapor pressures of the reacting systems  $\text{Al}_2\text{O}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ .
- B. For the one sample of  $\text{Al}_2\text{O}_3$  tested thus far, the reaction with 2.999-M HCl (ca. 10% HCl by weight) is such as to result in an increase in water pressure from ca. 28.2 mm Hg (2.999-M HCl) to ca. 29.2 mm Hg.
- C. The first sample data point in Figure 2 and Table III is an artifact of the protocol used in light of results reported under D. The obvious explanation is that the sample bead requires more time (in terms of conditioning drops) to give a correct response when being changed from a pure solvent wash to a sample in which the solvent activity differs so much from unity.

#### V. FURTHER WORK

- A. Different samples of  $\text{Al}_2\text{O}_3$  and different concentrations of HCl will be investigated for chemical interaction using the same technique.
- B. Electron microscopy will be used to attempt the detection of changes in the  $\text{Al}_2\text{O}_3$  concomitant with the chemical interaction.

Experimental work done by Mrs. Ann Grinnalds and recorded in NASA Grant A-37 research notebook No. 1.

Respectfully submitted,

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S. Y. Tyree, Jr.  
Professor of Chemistry

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TABLE I

AVERAGE VPO READINGS,  $\mu V \times$  RANGE

KCl molarity ↓	DATE →	AVERAGE VPO READINGS, $\mu V \times$ RANGE					AVG.	
		9-19-75	9-22-75	9-25-75	9-26-75	10-9-75		11-24-75
0.09647		401.5 x 1	404.3 x 1	410.3 x 1	397.35 x 1	—	397.2 x 1	402.1 x 1
0.2453		107.6 x 10	106.6 x 10	104.5 x 10	105.0 x 10	—	105.8 x 10	105.9 x 10
0.4948		198.85 x 10	200.05 x 10	207.35 x 10	202.4 x 10	205.8 x 10	206.85 x 10	203.6 x 10
1.004		395.5 x 10	416.85 x 10	428.55 x 10	418.85 x 10	423.35 x 10	417.65 x 10	416.8 x 10
NaCl molarity ↓	DATE →	AVERAGE VPO READINGS, $\mu V \times$ RANGE					AVG.	
		9-23-75	9-24-75	9-25-75	9-26-75	10-9-75		11-24-75
0.09669		410.25 x 1	408.5 x 1	409.4 x 1	—	—	—	—
0.2453		108.1 x 10	—	108.1 x 10	—	—	—	—
0.4986		205.9 x 10	205.1 x 10	205.5 x 10	—	—	—	—
1.007		434.85 x 10	423.1 x 10	429.0 x 10	—	—	—	—
m-HCR ↓	DATE →	AVERAGE VPO READINGS, $\mu V \times$ RANGE					AVG.	
		9-23-75	9-24-75	9-25-75	9-26-75	10-9-75		11-24-75
0.1037	432.45 x 1	43.3 x 10	436.2 x 1	434.3 x 1	—	—	—	434.0 x 1
0.2671	113.9 x 10	111.5 x 10	113.1 x 10	114.35 x 10	—	—	—	113.2 x 10
0.5397	237.3 x 10	240.9 x 10	238.2 x 10	235.05 x 10	—	—	—	237.9 x 10
1.091	518.3 x 10	522.4 x 10	521.2 x 10	516.8 x 10	—	522.0 x 10	—	520.1 x 10
3.999-M	—	—	—	—	196.9 x 100	193.2 x 100	193.5 x 100	194.5 x 100
3.190-M	—	—	—	—	—	—	—	—



TABLE II

KCl molality	$\Delta p$ calc. mm. Hg	Avg. VPD $\mu V \times Range$
0.09647	0.1119	402.1 x 1
0.2453	0.2746	105.9 x 10
0.4948	0.5457	203.6 x 10
1.004	1.0779	416.8 x 10

NaCl molality		
0.09669	0.1119	409.4 x 1
0.2453	0.2779	108.1 x 10
0.4986	0.5593	205.5 x 10
1.007	1.1253	429.0 x 10

HCl molality		
0.1037	0.1220	434.0 x 1
0.2671	0.3220	113.2 x 10
0.5397	0.6406	237.9 x 10
1.091	1.3728	520.1 x 10

TABLE III

<u>SAMPLE</u>	<u>TIME (min.)</u>	<u><math>\Delta p</math> (mm. Hg)</u>
2.999-M HCl	0	5.67
# 1	20	4.28
# 2	40	4.62
2.999-M HCl	40	5.57
# 3	60	4.72
# 4	80	4.65
2.999-M HCl	80	5.75
# 5	100	4.72
# 6	120	4.62
# 7	140	4.62
2.999-M HCl	140	5.70
# 8	160	4.34
2.999-M HCl	160	5.60
# 9	180	4.59

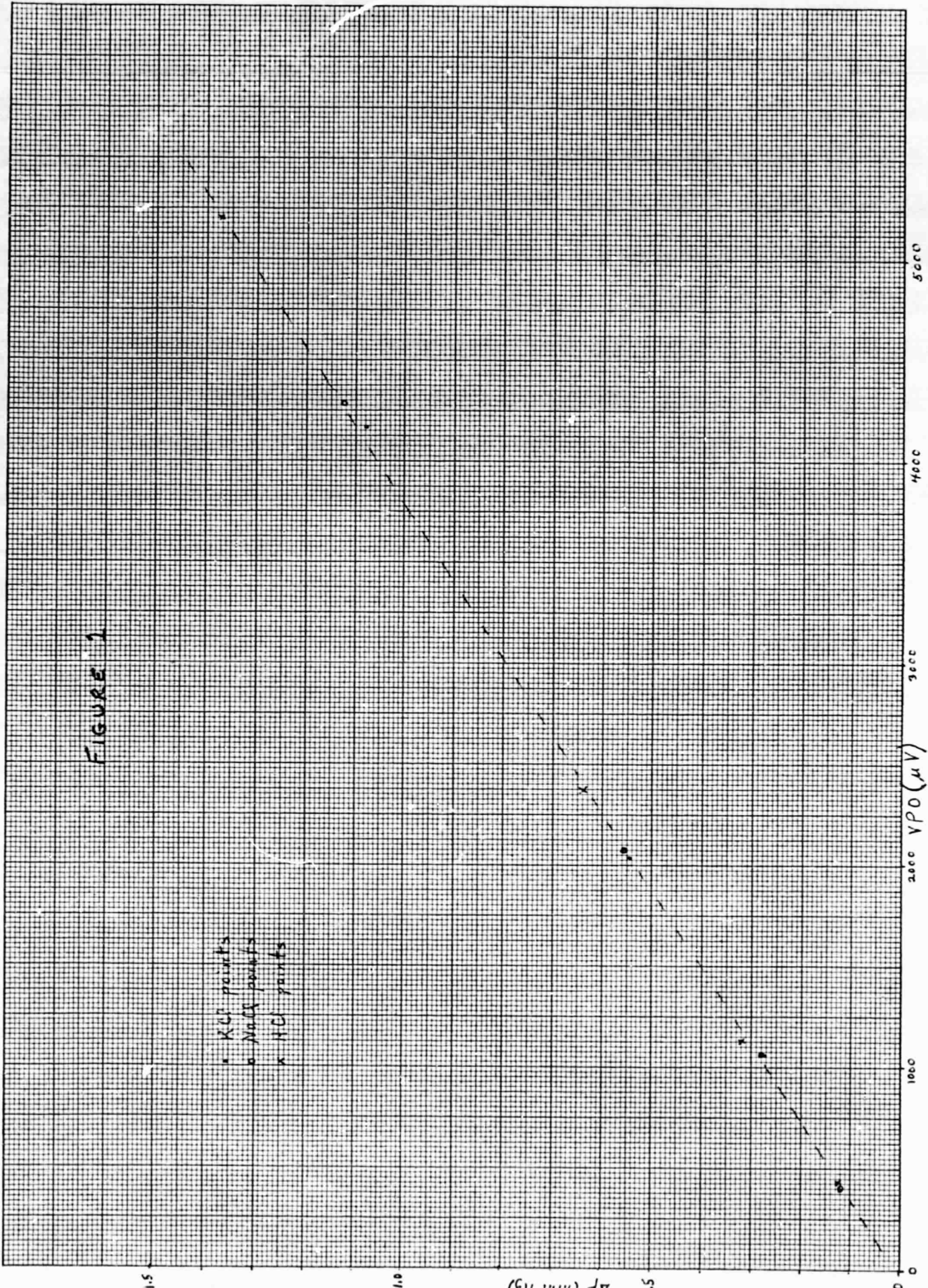


FIGURE 2

