1st Status Report

Under

NASA Grant NSG 1204

Chemistry of the System:

$Al_2O_3(c)-HCl \cdot aq.$

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ABSTRACT

The vapor pressure of water over 2:1 by weight mixtures of 3-M hydrochloric acid and Al_2O_3 is reported as a function of time over a 180 minute reaction period at 31°C. The Al_2O_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, $Al_2O_3 \cdot 3H_2O$, 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, $Na^+[Al(OH)_4]^-$ and aluminum salts, $[Al(OH_2)_6]^{3+}\ 3X^-$, respectively.

OXIDES

Anhydrous alumina, Al_2O_3, exists in several crystalline forms, the most common being the α form, known as alundum. In massive form, that is, large crystals formed from molten Al_2O_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 $[Al(OH_2)_6]^{3+}$ salts or $[Al(OH)_4]^-$ salts. Its composition is $Al_2O_3 \cdot xH_2O$, 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.

SALTS

Sodium aluminate, $Na^+[Al(OH)_4]^-$, 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.

$$Na^+[Al(OH)_4]^- + H_2O \longrightarrow Na^+\ OH^- + 1/2\ Al_2O_3 \cdot 3H_2O + H_2O\ .$$

The stability of aluminate solutions is a complicated function of at least three variables, excess sodium hydroxide, aluminum concentration, and temperature. As well the $[Al(OH)_4]^-$ ion is not monomeric. Its degree of aggregation, N, in the formula $[Al(OH)_4]_N^{N-}$, 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:

$AlCl_3 \cdot 6H_2O$

$Al_2(SO_4)_3 \cdot 9H_2O$

$Al(NO_3)_3 \cdot 9H_2O$

All are white, easily soluble in water, yielding acid solutions. The first hydrolysis constant of the $[Al(OH_2)_6]^{3+}$ ion is 10^{-5} Thus a 0.10-M Al^{3+} salt solution results in a pH of 3. As the pH of Al^{3+} solution is raised aluminum solute isopolycations result, $pAl^{3+} + qH_2O \rightleftarrows [Al_p(OH)_q]^{3p-q} + qH^+$. As OH^-, CO_3^{2-}, HCO_3^- or other effective aqueous base is added to Al^{3+} solutions, $[Al(OH)_{\tilde{n}}]_N^{(3-\tilde{n})N}$ results, such that the pH does not increase sensibly up to $\tilde{n} \cong 3.0$, 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 $[Al(OH)_4]^-$. It is actually possible to add base to Al^{3+} solution up to $\tilde{n} \cong 2.5$ without obtaining a precipitate, although the stability of the resulting solutions varies enormously. A white, solid substance of the empirical composition $Al_2(OH)_5Cl \cdot xH_2O$ ($x \cong 2$) is obtained upon evaporation of such solutions. Identical or similar substances are obtained in at least two other ways:

(i) $5Al(s) + AlCl_3 \cdot aq \;\text{——}\; 3Al_2(OH)_5Cl \cdot aq$., and

(ii) $5Al_2O_3 \cdot xH_2O + 2AlCl_3\ aq \longrightarrow 6Al_2(OH)_5Cl \cdot aq$.

The resultant white solid, or solutions thereof, are commodity chemicals, used in at least two practical applications, as antiperspirants (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

$Al_2(OH)_5Cl$ 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:

$$6Al(OH)_{2.5}^{+0.5} \;—\; 5Al(OH)_3(s) + Al^{3+}\ .$$

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_{sp} for gibbsite is ~ $10^{-34} = [Al^{3+}][OH^-]^3$. At pH = 4, the concentration of hexaaquoaluminum ion should be ~ 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.

IMPACT UPON SHUTTLE

Booster rocket propellants will be Al + NH_4ClO_4 + binder with resulting exhaust of Al_2O_3 + N_2 + HCl + water + traces of several other substances.(2) The possibility of chemical reaction among the Al_2O_3, HCl, and H_2O need be considered. Were the Al_2O_3 massive α-Al_2O_3, little chemical change would be expected. However the Al_2O_3 is high surface area, very small particle size, and its reactivity, as such, will not be negligible. The particles serve as nucleii for the condensation of liquid water, in which HCl is very soluble. HCl·aq in contact with high surface Al_2O_3 is expected to result in chemical reactions.

Sequential possible reactions are:

1. $H_2O(g) + Al_2O_3(s) \longrightarrow Al(OH)_3$ surface reaction
2. $Al_2O_3(s) + H_2O(g) \longrightarrow Al_2O_3(s) + H_2O(l)$ (on the $Al_2O_3(s)$)
3. $HCl(g) + H_2O(l) \longrightarrow HCl \cdot aq$
4. $HCl \cdot aq + Al(OH)_3(s) \longrightarrow AlCl_3 \cdot aq$
5. $AlCl_3 \cdot aq + Al(OH)_3(s) \longrightarrow Al(OH)_{\tilde{n}}Cl_{3-\tilde{n}} \cdot aq$.
6. $Al(OH)_{\tilde{n}}Cl_{3-\tilde{n}} \cdot aq \longrightarrow Al(OH)_3$(gibbsite) $+ AlCl_3 \cdot aq$.

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 H_2O is a parameter in the cloud stability, a detailed knowledge of the chemical behavior of the $Al_2O_3 \cdot HCl \cdot H_2O$ 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 $Al_2O_3 \cdot HCl \cdot H_2O$ 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.(5) 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 ΔT, 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 $p = p_0 \cdot a_w$ is 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). Δp values for individual solutions were calculated as $p_0 - p$. A large scale plot of Δp vs. VPO readings was made to use as the standard curve from which to convert VPO readings to Δp values for experimental solutions. A point on the Δp 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 Δp 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 $Al_2O_3 \cdot HCl \cdot H_2O$ 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 rop 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.

Δp values for each of the nine vials were read from the large scale graph of Δp 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 Δp 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, Δp 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:

Sample 10		Sample 11	
time (min.)	VPO(μV)	time (min.)	VPO(μV)
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 $Al_2O_3 \cdot HCl \cdot H_2O$.

B. For the one sample of Al_2O_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 Al_2O_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 Al_2O_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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TABLE I

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

KCl molality ↓	DATE →	9-19-75	9-22-75	9-25-75	9-26-75	10-9-75	11-24-75	AVG.
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 molality ↓	DATE →	9-23-75	9-24-75	AVG.
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-HCl ↓	DATE →	9-23-75	9-24-75	9-25-75	9-26-75	10-9-75	11-24-75	11-25-75	AVG.
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
2.999-M 3.190-m		—	—	—	—	196.9 x 100	193.2 x 100	193.5 x 100	194.5 x 100

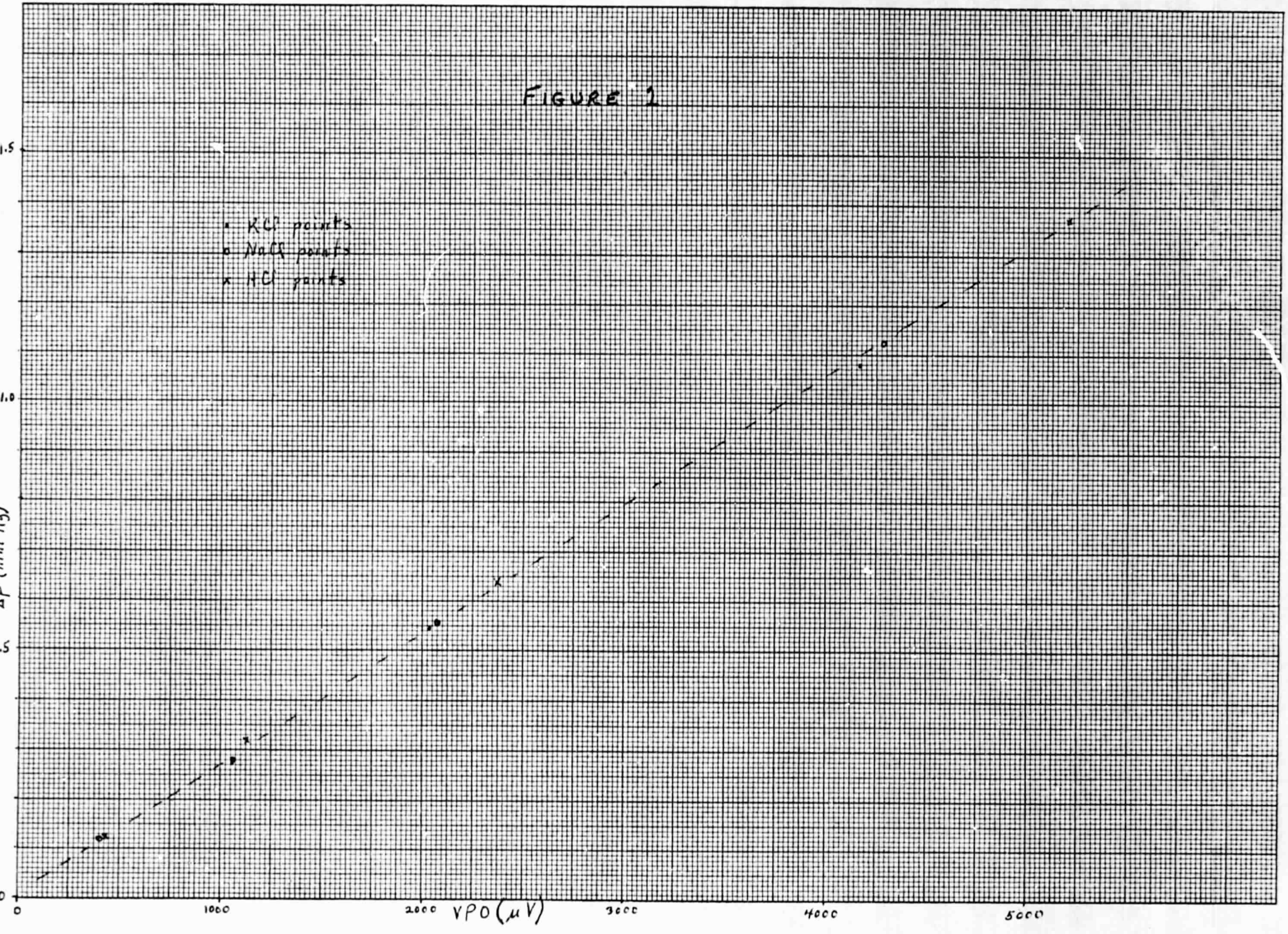
TABLE II

KCl molality	Δp calc. mm. Hg	Avg. VPD μV x 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

SAMPLE	TIME (min.)	Δp (mm. Hg)
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 1


• KCl points
o NaCl points
x HCl points
1.5
1.0
.5
0
0
1000
2000
3000
4000
5000
VPO (μV)

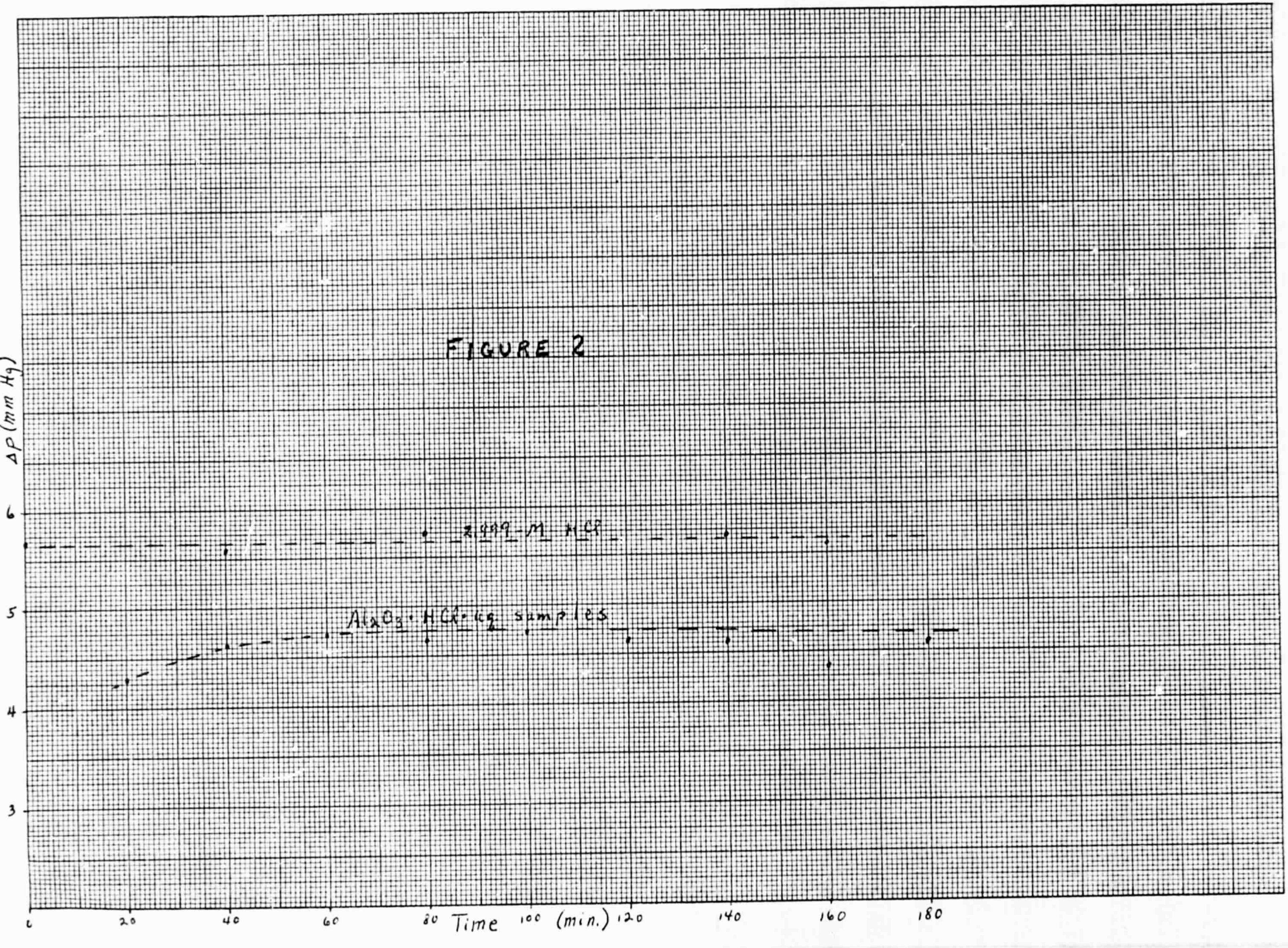


FIGURE 2

2.999 M HCl
Al₂O₃ · HCl · 4g samples
ΔP (mm Hg)
6
5
4
3
0
20
40
60
80
100
120
140
160
180
Time (min.)