EFFECT OF pH ON THE ADSORPTION OF

POTASSIUM CHROMATE AND

CHROMIC ACID ON

ALUMINA


By

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1955


Submitted to the faculty of the Graduate
School of the Oklahoma State University
of Agriculture and Applied Sciences
in partial fulfillment of the
requirements for the
degree of
MASTER OF SCIENCE
August, 1958

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## ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Clarence M. Cunningham, Assistant Professor of Chemistry, for his assistance and guidance throughout the course of these studies.

The author is also pleased to acknowledge the aid of Dr. Tom E. Moore, Associate Professor of Chemistry, by reading this thesis and helping in other ways.

Indebtedness is acknowledged to Halliburton Oil Well Cementing Company and many employees for their sincere interest. Especially to Keith Catto for the flame spectrophotometer analysis and to the Duplicating Department.

The author's wife is due special thanks for her many hours of hard work and patience.

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# PART I

## HISTORY

The capacity possessed by wood charcoal for the sorption of gases was observed by C. W. Scheele in 1773, by the Abbe' F. Fontana in 1777, and others, and the earliest systematic experiments were carried out by T. de Soussure in 1814. de Soussure employed a number of porous materials in conjunction with most of the gases known at the time (1, pg. 106).

The property possessed by charcoal of removing coloring matter from solution was known at least as far back as 1785 (T. Lowitz), and many observations have since been made showing that finely-divided powders are able to take up dyestuffs and other substances from solutions. A general account of the older literature is to be found in Ostwalds' Lehrbuch (2).

Even though adsorption from solution has not yet received any satisfactory theoretical treatment, it is a phenomenon of great practical importance. Every organic chemist is acquainted with the use of activated charcoal as a decolorizing agent. Adsorbents such as diatomaceous earth and kieselguhr are used in refining vegetable oils. Chromotographic adsorption analysis has become one of the most important methods of separating natural products such as amino

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acids, peptides, and plant pigments (3).

In addition, adsorption from solution finds great application in the preparation of certain catalysts, particularly those prepared by impregnation. The impregnated catalyst of chromium oxide on alumina is very important in dehydrogenation catalysis (4).

PART II

INTRODUCTION

Adsorption is a process by which the atoms or mole-
cules of one material become attached to the surface of
another, or more generally speaking, become concentrated at
an interface.

Adsorption at gas-solid inter-faces find very important
applications, as, for example, the adsorption of gases on
activated charcoal in gas masks and in gas chromotography
work. The oldest and most widely used method for determin-
ing the surface area of catalysts involves the adsorption
of nitrogen gas by the catalyst. There is adsorption at
five types of inter-faces but this research is concerned with
only that at solid-liquid inter-faces.

There are two kinds of adsorption, namely physical ad-
sorption and chemisorption or activated adsorption. Physi-
cal adsorption is characterized by having a low heat of ad-
sorption associated with it. The forces which hold the ad-
sorbed atoms or molecules to the surface of the adsorbent
are of the van der Waals type. And in general physical ad-
sorption is easily reversible and the process takes place at
relatively low temperatures.

On the other hand, chemisorption involves rather large
amounts of heat, sometimes on the order of those for chemical

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bonds. Chemisorption is irreversible or reversible only with great difficulty. Although chemisorption does take place to some extent at low temperatures, it is so slow as compared to physical adsorption that it is not important (5). So, chemisorption is usually associated with "high" temperatures.

It has been found experimentally that adsorption is an equilibrium process and that it follows an empirical equation, called the adsorption isotherm (1), one form of which is:

$$\frac{X}{M} = kC^{1/n} \tag{1}$$

where $\frac{X}{M}$ is the grams adsorbed, X, per gram of adsorbent, M, k and n are constants, and C is the final concentration of the solution. If the logarithm of both sides of equation (1) is taken

$$\log \frac{X}{M} = \frac{\log C}{n} + \log k \tag{2}$$

and $\log \frac{X}{M}$ is plotted against $\log C$, a straight line should result. Any deviation from a straight line indicates that effects other than from adsorption are present (1).

The foregoing is the Freundlich isotherm for adsorption from solutions. Other equations have been derived for various other adsorption processes; e.g., Langmuir's equation for the adsorption of gases on solids and Gibbs' equation for the change in surface tension with concentrations due to adsorption at the air-liquid inter-face (6).

In the process of adsorption at solid-liquid interfaces, the presence of a solvent provides a complicating

factor, because it competes with the solute for positions at the inter-face. This difficulty is not present in simple gas-solid systems having only a single component in the gas phase. Perhaps it is for this reason that gaseous adsorption has entertained by far the greatest amount of attention.

Naturally, the simplest case of adsorption from solution is that involving a non-dissociated substance, e.g., alcohol, water, benzene and the other many organic liquids. In the case where there are two non-dissociated substances in solution, the process is somewhat more complicated (7).

The adsorption of strong electrolytes show a number of peculiarities. In the case of single electrolytes or mixtures of the same, we usually have to deal with equilibria which adjust themselves easily and, for the most part, rapidly. The ordinary Freundlich adsorption isotherm holds true for adsorption of electrolytes in solution as well as for gases (6, 8). This is shown in the case of the adsorption of chlorides, thiocynates, and sulfates of the alkali, alkaline-earth and heavy metals by blood charcoal as reported by Rona and L. Michaelis (8).

It is quite obvious that the adsorption process becomes increasingly more complicated as the number of electrolytes in solution is increased.

PART III

MATERIALS

Catalyst

The alumina catalyst was obtained from the Harshaw
Chemical Company. It was necessary to obtain two types
of alumina in the course of the research. The second lot
of alumina differed from the first in that it contained
slightly more iron. A series of experiments were made to
compare the two types; results of these tests are shown in
Figure 1 (curves A and C). The catalyst was in the form of
1/8" pellets and had a BET nitrogen surface area of 99.3 $m^2/g$
as determined by Cunningham (9). The composition stated by
the manufacturer was as follows: $SiO_2$, 0.03%; $Fe_2O_3$, 0.008%;
$TiO_2$, 0.007%; $Na_2O$, 0.4%; and $Al_2O_3$, 99.+%.

The first lot of alumina carried the Harshaw number
Al-0113 T 1/8". The second lot carried the number Al-0104
T 1/8".

Chemicals

The potassium chromate, ferrous ammonium sulfate and
chromic acid used were reagent grade chemicals.

Apparatus

A Photo-volt pH meter was employed using Beckmann

glass electrodes. The pH meter was checked using standard buffer solutions. The results showed a variation of $\pm$ 0.2 of a pH unit.

A constant temperature water-bath, 27.0°C., was equipped with a rotor on which the adsorption vessels were placed. The rotor was driven by means of belts and an electric motor and revolved at a speed of approximately 30-40 rpm.

The adsorption vessels were 8 ounce bottles fitted with ground-glass stoppers.

# PART IV

## EXPERIMENTAL

### General

The alumina catalyst was prepared as follows: Approximately 1 kilogram was placed on a Buchner funnel and washed with four liters of distilled water. After drying for four hours in a drying oven at 110°C., the alumina was placed in a porcelain casserole and calcined in a furnace for 16 hours at 600°C. The alumina was stored in a glass stoppered container until ready for use. The procedure used was very nearly the same as that used in a previous series of experiments by Cunningham (9).

Stock solutions of potassium chromate and chromic acid were prepared and the desired concentrations made by quantitatively diluting these stock solutions. The pH of the diluted solution was measured and then 100 milliliters of the solution was added to the adsorption vessel containing 114.2 grams of the alumina catalyst. The bottle was fitted with a glass stopper and sealed with Apiezon wax. The bottles were then attached to the rotor and placed in the constant temperature water bath.

At the end of 24 hours, the bottles were removed from the bath; the wax was carefully removed and the contents

analyzed for dichromate by the method described by Engelder
(10) and Olson, Orlemann, and Koch (11). All adsorption
measurements followed this general procedure.

## Analytical

An acid solution was made by slowly adding 120 ml. of
concentrated sulfuric acid and 35 ml. of concentrated (85%)
phosphoric acid to 850 ml. of distilled water. The solution
was cooled to room temperature before using.

Since the ferrous ammonium sulfate is oxidized by air,
it was necessary to standardize the solution daily or when
used. This ease of oxidation is greatly decreased by the
addition of a small amount of concentrated sulfuric acid to
the stock solution of the ferrous ammonium sulfate.

To a 250 ml. Erlenmeyer flask was added 100 ml. of the
sulfuric-phosphoric acid mixture. Ten milliliters of the
ferrous ammonium sulfate was added and 2 drops of barium
diphenylamine sulfonate solution. This was then titrated
with a standard solution of potassium chromate. From the
volumes of the solutions used, the concentration of the
ferrous ammonium sulfate was calculated.

## Analysis of Test Solutions

Essentially, the same procedure was followed as that
described above, but the small volume of solution recovered
from the adsorption bottle, required a slight modification.
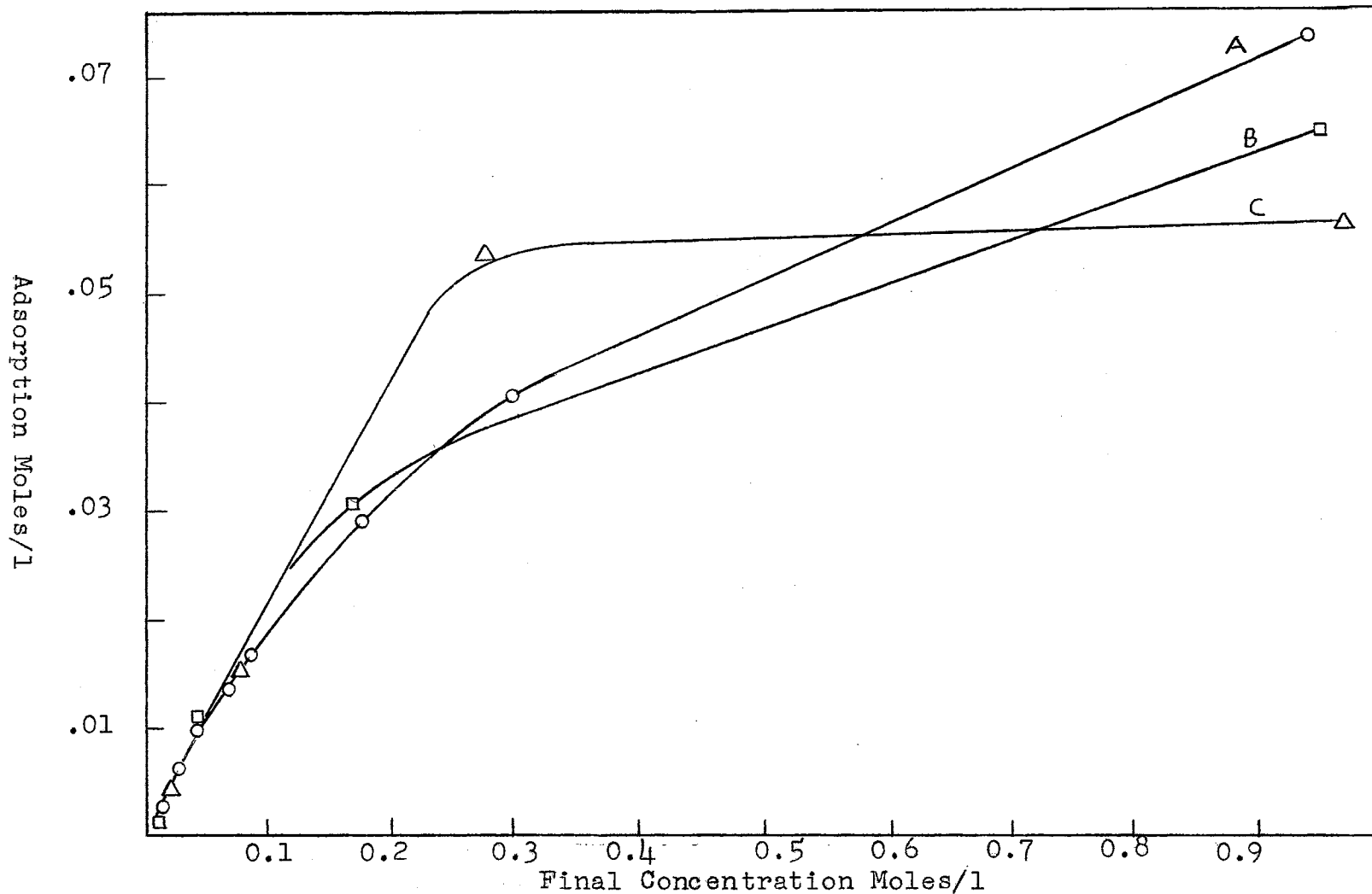To the sulfuric-phosphoric acid mixture was added a 5 ml.

Figure 1 - Plot of final concentration in moles/l against apparent adsorption in moles/l for the adsorption of $K_2CrO_4$ on alumina at 27.0°C. A, o, after 24 hours - first catalyst; B, □ , after 12 hours - first catalyst; C, △ , after 24 hours - new catalyst.

aliquot of the test solution. Two drops of the barium di-
phenylamine sulfonate was added and then an excess of fer-
rous ammonium sulfate. This was then back-titrated with a
standard potassium chromate solution. The molarity of the
test solution was calculated as follows:

$$\frac{\text{m.e. } Fe(NH_4)_2(SO_4)_2 \quad - \quad \text{m.e. } K_2CrO_4}{V \times 3} = \text{Molarity of test}$$

solution, where m.e. is the milliequivalents used and V is
the volume of the test solution.

## Preparation of Indicator

The indicator for the titration was a 0.2% solution of
barium dephenylamine sulfonate. The aqueous solution was
made by adding 0.35 grams of barium diphenylamine solfonate
to 100 ml. of distilled water containing 1 ml. of concen-
trated sulfuric acid. This solution was prepared fresh week-
ly. A good discussion on the chemistry of the indicator may
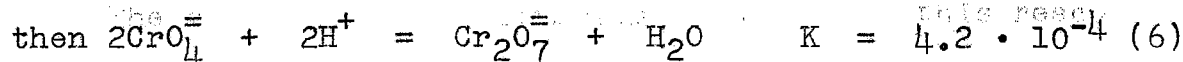be found in Olson, Orlemann, and Koch (11).

PART V

DISCUSSION AND RESULTS

There has been previous indication that a change in
pH had a definite effect on the adsorption of chromic acid
on activated alumina (9). In this previous work, atten-
tion was devoted mostly to the adsorption of chromic acid
from very dilute solutions.

In a solution of chromic acid or a salt of chromic acid
there is present an equilibrium between the chromate and di-
chromate ions which can be represented by the following
equation:

$$2 \, CrO_4^= + 2H^+ = Cr_2O_7^= + H_2O \qquad (3)$$
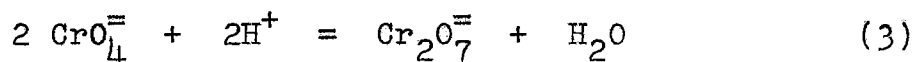
The value of the equilibrium constant for this reac-
tion is calculated as follows (12):

$$HCrO_4^- = CrO_4^= + H^+ \qquad K = 3.2 \cdot 10^{-7} \qquad (4)$$

$$2HCrO_4^- = Cr_2O_7^= + H_2O \qquad K = 43 \qquad (5)$$

then $2CrO_4^= + 2H^+ = Cr_2O_7^= + H_2O \qquad K = 4.2 \cdot 10^{-4}$ (6)
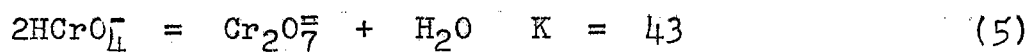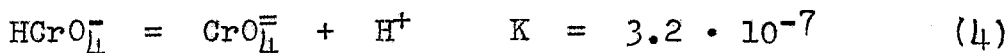
The concentration of either ion is dependent on the pH
of the solution. At a pH of 7 the chromate ion is the pre-
dominate species but, at a pH of 6, this is no longer true.
However, the pH is not the only factor determining the ad-
sorbability of the chromate and dichromate ions. Michaelis
and his co-workers (8) have proved experimentally that com-
pounds having the same cation are specific and regular with

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respect to their adsorbability. That is, of a series of salts possessing common cations the adsorption is an additive property of the cation and anion. Thus, the order of adsorption of a series of sodium salts of various acids is identical with the order for the potassium or ammonium salts. The same is also true with compounds having a common anion. The following series in decreasing adsorptive power on ordinary charcoal from solutions of equivalent ionic strengths was established by Michaelis (8).

Cations - $> H^+ > Ag^+ > Hg^{++} > Cu^{++} > Al^{+++} > Zn^{++}$
$\quad Mg^{++} \quad\quad Ca^{++} \quad\quad NH_4^+ \quad\quad K^+ \quad\quad Na^+$.

Anions - $> OH^- > CN^- > S^= > I^- > NO_3^- > Br^- > Cl^-$
$> HPO_4^= > SO_4^=$.
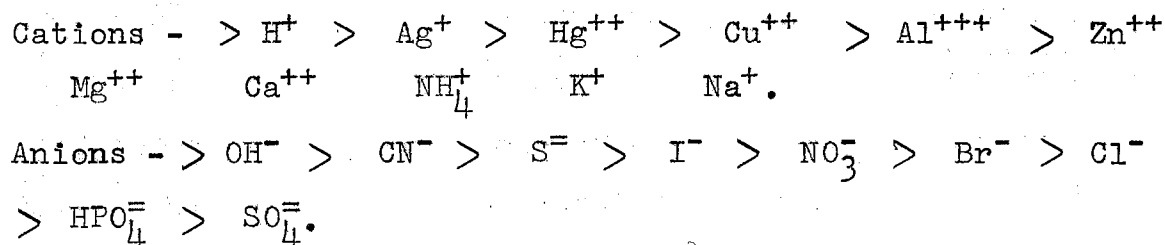
Schilow and his co-workers (13) have shown that a different order is obtained when other types of charcoal are employed.

It is also known that acids and bases are more readily adsorbed than are salts (14). This means that hydrogen and hydroxyl ions are the most easily adsorbed ions from solution as can be seen above.

Also, it can be expected since the hydrogen and hydroxyl ions are the most easily adsorbed components, that there would be an inherent change of pH in any adsorption process from aqueous solutions. This is indeed the case as may be seen from Table I.

The magnitude of this change in pH during adsorption is a function of the pH of the solution before the adsorption takes place, a function of the adsorbent used and a

function of the nature of the chemical constituents pre-
sent in solutions. Naturally, in any series of tests the
adsorbent would ordinarily remain constant.

TABLE I

Effect of Alumina on pH of Nitric Acid and

Sodium Hydroxide Solutions

| (1)<br>Sample | (2)<br>Initial pH | (3)<br>Final pH |
|---|---|---|
| Distilled $H_2O$ | 6.20 | 9.90 |
| 0.1N $HNO_3$ | 1.30 | 5.70 |
| 0.2N $HNO_3$ | 1.10 | 4.72 |
| 0.1N NaOH | 12.32 | 11.10 |

(114.2 grams alumina per 100 ml. solution)

Curves A and B in Figure 1 show a comparison of the
isotherms at 24 hours and 12 hours respectively. As may be
seen for the lower concentrations, equilibrium was reached
at the end of 12 hours. However, there is a slight devia-
tion at the higher concentrations.

## Adsorption of Potassium Chromate

A definite trend was observed in the change of pH in this present investigation. In all cases, the initial solutions varied consistently from high pH values in concentrated solutions to low pH values in dilute solutions. The final pH was nearly constant for a particular initial concentration of nitric acid. As the initial concentration of nitric acid increased, the final pH of the solution decreased. It is apparent that the alumina was acting as a buffer in the solutions. The solutions were all buffered toward a more neutral solution. The pH of the alkaline solution (0.1N with NaOH) didn't change as much as did that of the acidic solutions. (Tables II-V). It is believed that this is due in part to a small amount of $Na_2O$ present in the alumina. This would naturally cause a slight neutralization in acid solution and not effect the basic solutions. A determination of the sodium content of the supernatant liquids from the adsorption of distilled water and 0.1N $HNO_3$ on alumina was made. A Beckmann flame photometer was used for the determination. The solutions were identical with those shown in Table I. The distilled water had a sodium content of 340 ppm and the 0.1N nitric acid, 4200 ppm. The accuracy of the determination was on the order of $\pm$ 5%. The solubility of the alumina in 0.1N $HNO_3$ is negligible. This was determined by gravimetric analysis of the 0.1N $HNO_3$ solution.

The adsorption of the potassium chromate increased with

increasing acid content. The adsorption increased the most at the dilute concentrations before finally leveling off to some extent.

As can be seen from the isotherms in Figure 2, for adsorption from acid media no unexpected effects are observed except that in the final concentration ranging from about 0.4 moles to 0.6 moles there seems to be an unexpected scattering of points. There is no reasonable explanation for this. Figure 3 shows this by plotting the logarithm of the final concentration versus the logarithm of the apparent adsorption in moles/l. Figure 4 shows the low concentration range of Curve A in Figure 2.

The adsorption from 0.1N NaOH solution is distinctly different from the others. In alkaline solutions, the dichromate ions present are almost entirely changed to the chromate ions. As was stated previously the hydroxyl ion is one of the most easily adsorbed ions in solution. Thus, it follows that in alkaline solutions the adsorption of the chromate ion would be secondary as compared to the hydroxyl ion. As can be seen from Figure 2, not until the chromate concentration reaches approximately 0.7 molar does it become adsorbed to any great extent.

The initial and final concentration of the chromate and dichromate ions present in the solutions have been calculated and are shown in Tables VI-VIII. The calculations were made as follows:

No acid - Since the initial pH is above 7 we may assume that

TABLE II

Adsorption of $K_2CrO_4$ – no acid

| (1)<br><br>Sample | (2)<br><br>Initial<br>pH | (3)<br><br>Final<br>pH | (4)<br><br>Initial<br>Conc.<br>(Moles/l) | (5)<br><br>Final<br>Conc.<br>(Moles/l) | (6)<br><br>Apparent<br>Adsorption<br>(Moles/l) |
|---|---|---|---|---|---|
| 1 | 9.20 | 9.20 | 1.002 | 0.9414 | 0.0606 |
| 2 | 9.15 | 9.19 | 0.4981 | 0.4629 | 0.0352 |
| 3 | 9.02 | 9.10 | 0.3982 | 0.3578 | 0.0404 |
| 4 | 8.90 | 9.17 | 0.3333 | 0.2948 | 0.0385 |
| 5 | 8.89 | 9.10 | 0.1999 | 0.1733 | 0.0266 |
| 6 | 8.60 | 9.11 | 0.0983 | 0.0859 | 0.0124 |
| 7 | 8.50 | 9.12 | 0.0667 | 0.0515 | 0.0152 |
| 8 | 8.42 | 9.19 | 0.0404 | 0.0318 | 0.0086 |
| 9 | 8.39 | 9.20 | 0.0198 | 0.0157 | 0.0042 |
| 10 | 8.20 | 9.31 | 0.0097 | 0.0082 | 0.0016 |

TABLE III

Adsorption of $K_2CrO_4$ - 0.1N $HNO_3$

| (1) | (2) | (3) | (4) | (5) | (6) |
|---|---|---|---|---|---|
| Sample | Initial pH | Final pH | Initial Conc. (Moles/1) | Final Conc. (Moles/1) | Apparent Adsorption (Moles/1) |
| 1 | 7.60 | 8.25 | 0.9018 | 0.7841 | 0.1177 |
| 2 | 7.50 | 8.20 | 0.8016 | 0.6897 | 0.1119 |
| 3 | 7.30 | 8.20 | 0.6513 | 0.5668 | 0.0845 |
| 4 | 7.20 | 8.20 | 0.5010 | 0.3959 | 0.1051 |
| 5 | 7.10 | 8.18 | 0.4008 | 0.3144 | 0.0864 |
| 6 | 6.80 | 8.10 | 0.2505 | 0.1734 | 0.0771 |
| 7 | 3.20 | 7.85 | 0.1002 | 0.0448 | 0.0555 |
| 8 | 1.70 | 7.51 | 0.0498 | 0.0120 | 0.0378 |

TABLE IV

Adsorption of $K_2CrO_4$ - $0.2N$ $HNO_3$

| (1) | (2) | (3) | (4) | (5) | (6) |
|:---:|:---:|:---:|:---:|:---:|:---:|
| Sample | Initial pH | Final pH | Initial Conc. (Moles/l) | Final Conc. (Moles/l) | Apparent Adsorption (Moles/l) |
| 1 | 7.00 | 7.50 | 0.8194 | 0.7167 | 0.1027 |
| 2 | 7.00 | 7.40 | 0.7169 | 0.5818 | 0.1351 |
| 3 | 7.00 | 7.50 | 0.6657 | 0.5369 | 0.1288 |
| 4 | 6.90 | 7.50 | 0.5633 | 0.4559 | 0.1074 |
| 5 | 6.90 | 7.40 | 0.5121 | 0.3919 | 0.1202 |
| 6 | 6.90 | 7.35 | 0.4097 | 0.2958 | 0.1139 |
| 7 | 6.40 | 7.15 | 0.3073 | 0.1952 | 0.1121 |
| 8 | 6.20 | 7.10 | 0.2561 | 0.1474 | 0.1086 |
| 9 | 1.40 | 6.90 | 0.1024 | 0.0183 | 0.0841 |
| 10 | 1.20 | 6.10 | 0.0512 | 0.0007 | 0.0505 |

TABLE V

Adsorption of $K_2CrO_4$ - 0.1N NaOH

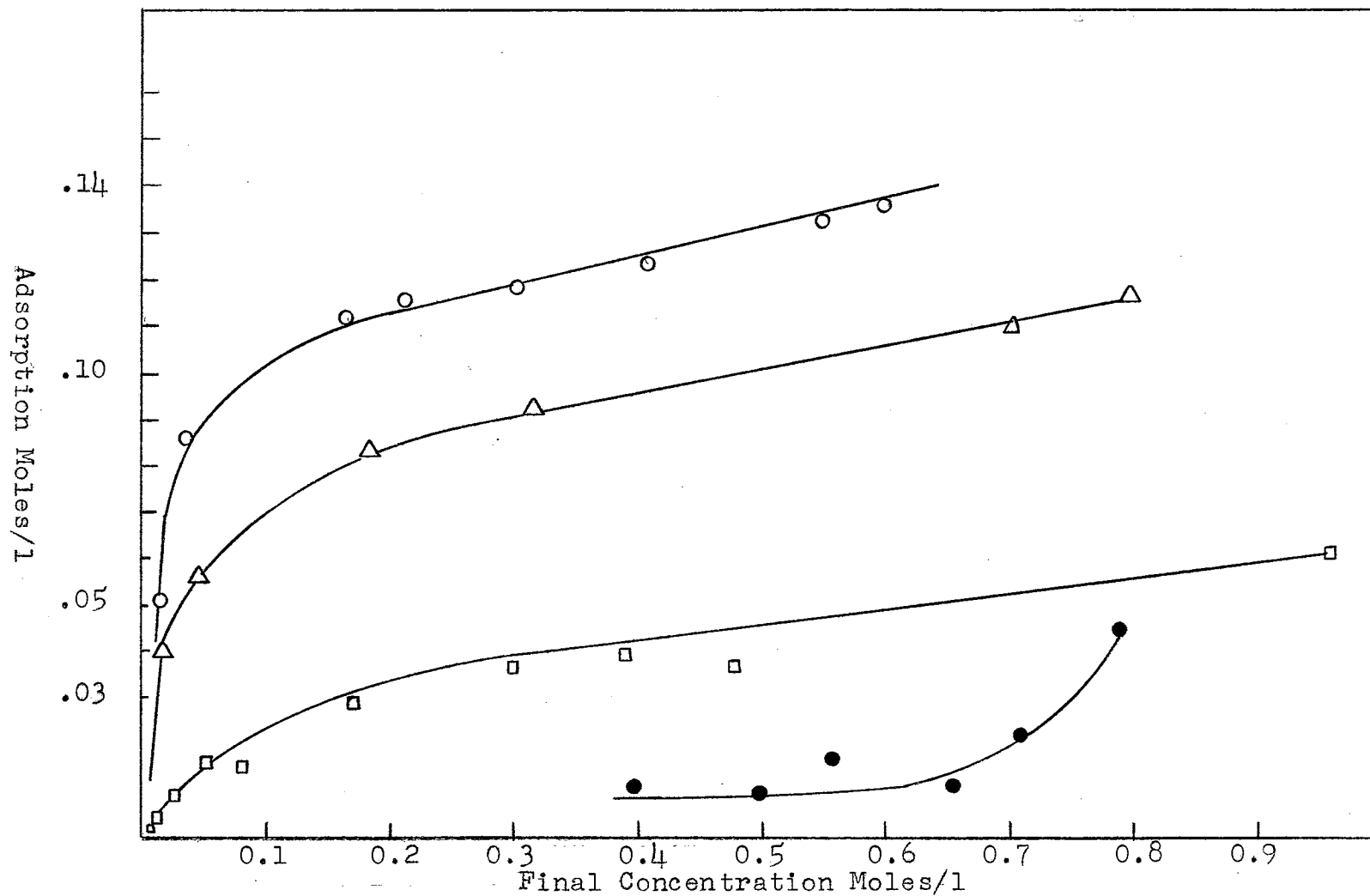| (1) | (2) | (3) | (4) | (5) | (6) |
|-----|-----|-----|-----|-----|-----|
| Sample | Initial pH | Final pH | Initial Conc. (Moles/1) | Final Conc. (Moles/1) | Apparent Adsorption (Moles/1) |
| 1 | 12.4 | 10.8 | 0.8194 | 0.7733 | 0.0461 |
| 2 | 12.5 | 10.8 | 0.7169 | 0.6967 | 0.0202 |
| 3 | 12.6 | 10.8 | 0.6657 | 0.6534 | 0.0123 |
| 4 | 12.6 | 10.9 | 0.5633 | 0.5449 | 0.0184 |
| 5 | 12.5 | 10.8 | 0.5121 | 0.5022 | 0.0099 |
| 6 | 12.5 | 10.8 | 0.4097 | 0.4002 | 0.0095 |

Figure 2 - Effect of pH on adsorption of $K_2CrO_4$ on alumina at 27.0°C. The curves show adsorption with □ , no acid present; △ , 0.1N with $HNO_3$; o, 0.2N with $HNO_3$; and ● , 0.1N with NaOH.
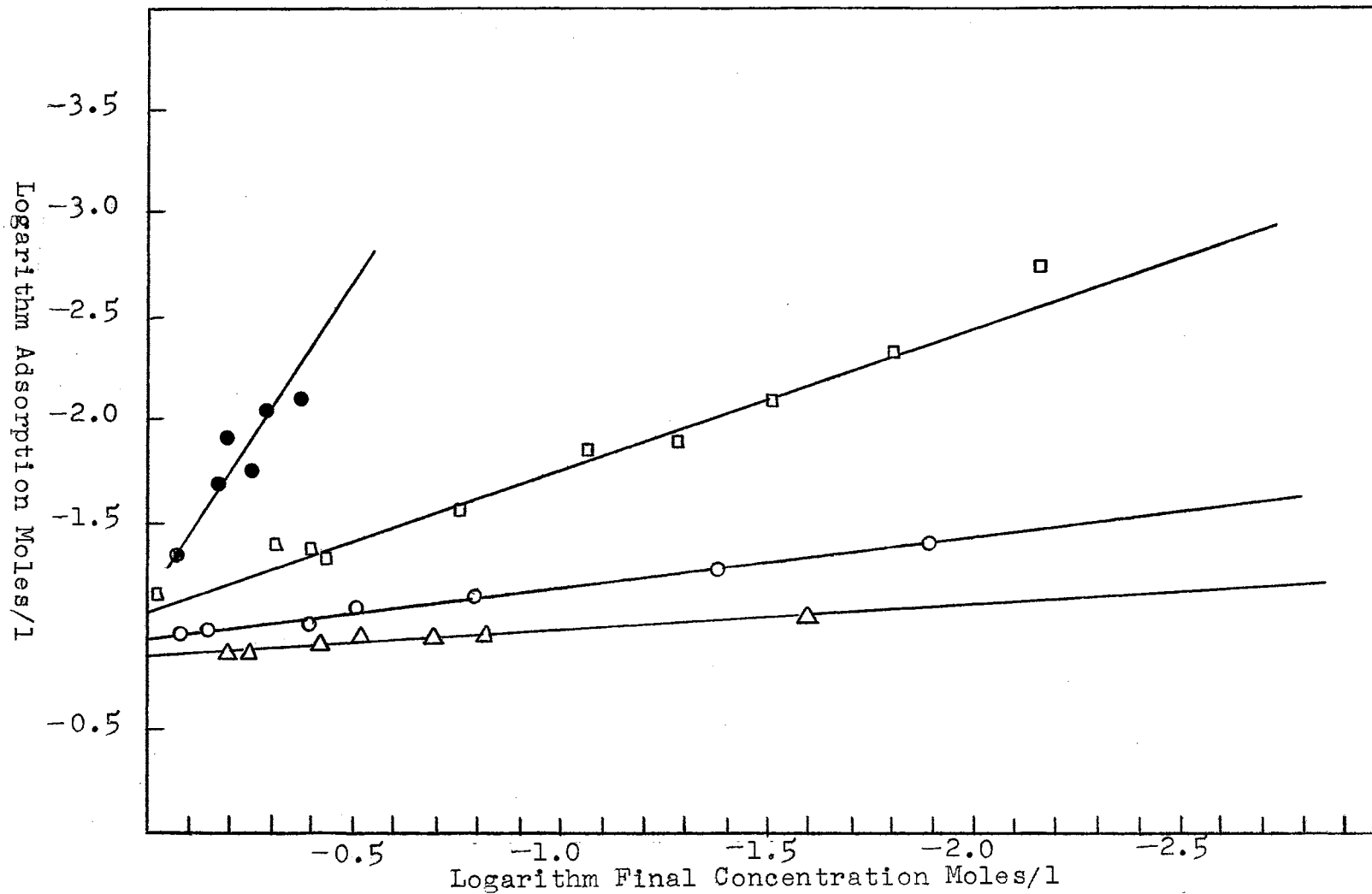
Figure 3 – Plot of logarithm to show linear nature of the adsorption of $K_2CrO_4$ on alumina according to the Freundlich equation. □ , no acid present; o, 0.1N with $HNO_3$; △ , 0.2N with $HNO_3$; ●, 0.1N with NaOH.
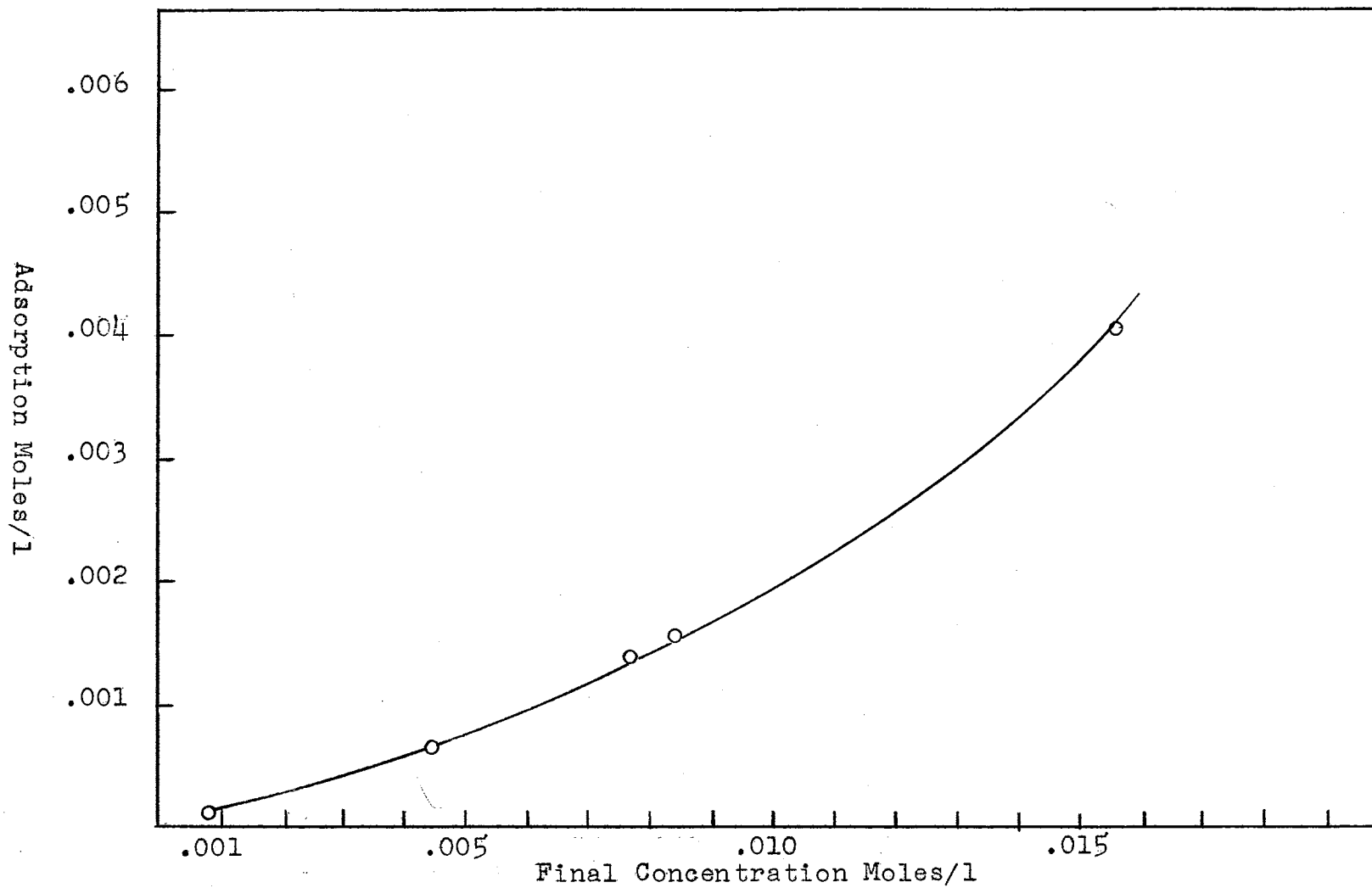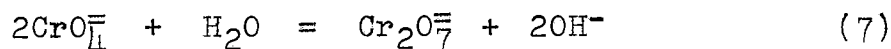
Figure 4 - This curve shows the low concentration range of adsorption of $K_2CrO_4$ on alumina at 27.0°C.

only chromate is present, so that the concentration of the solution is the same as that of the chromate. Even though this assumption is made the initial concentration of dichromate can be calculated,

$$2CrO_4^= + H_2O = Cr_2O_7^= + 2OH^- \qquad (7)$$

if we let x equal the amount of dichromate present, 2x the hydroxyl ion concentration and C - 2x the chromate present where C is the concentration measured,

$$k = \frac{(2x)^2 \, x}{(C - 2x)^2} = 4.2 \times 10^{-14}. \qquad (8)$$

Since x is small it may be neglected in the denominator. The same assumption is made in calculating the final concentrations.

Nitric acid - When acid is present an entirely different situation exists. No longer is only chromate present but also considerable amounts of dichromate and if the solution is very acid, possibly all the chromate is converted to dichromate. The concentration of $H^+$ or $OH^-$ must be taken into account here. Thus,

$$2CrO_4^= + 2H^+ = Cr_2O_7^= + H_2O, \qquad (9)$$
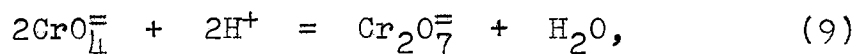
letting x be the dichromate and C - 2x the chromate

$$k = \frac{x}{(C - 2x)^2 \, (H^+)^2} = 4.2 \times 10^{14} \qquad (10)$$

the initial concentration of both ions may be calculated. However, in very dilute solutions in $0.1N$ $HNO_3$ the effect of hydrolysis must be considered,

$$2CrO_4^= + H_2O = Cr_2O_7^= + 2OH^-. \qquad (11)$$
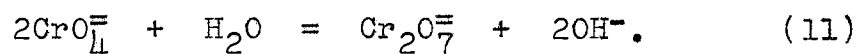
Using equation (9) the concentration of dichromate present disregarding hydrolysis can be calculated. In the

TABLE VI

Concentration of chromate and dichromate ions - no acid

| (1) | (2) | (3) | (4) | (5) |
|-----|-----|-----|-----|-----|
| Sample | Initial Chromate (Moles/l) | Final Chromate (Moles/l) | Initial Dichromate (Moles/l) | Final Dichromate (Moles/l) |
| 1 | 1.002 | 0.9414 | $2.19 \cdot 10^{-5}$ | $1.47 \cdot 10^{-4}$ |
| 2 | 0.4981 | 0.4629 | 1.37 " | 0.372 " |
| 3 | 0.3982 | 0.3578 | 1.18 " | 0.349 " |
| 4 | 0.3333 | 0.2948 | 1.05 " | 0.166 " |
| 5 | 0.1999 | 0.1733 | 0.747 " | 0.079 " |
| 6 | 0.0983 | 0.0859 | 0.466 " | 0.019 " |
| 7 | 0.0667 | 0.0515 | 0.360 " | 0.006 " |
| 8 | 0.0404 | 0.0318 | 0.258 " | 0.002 " |
| 9 | 0.0198 | 0.0157 | 0.158 " | 0.001 " |
| 10 | 0.0097 | 0.0082 | 0.100 " | 0.000 " |

TABLE VII

Concentration of chromate and dichromate ions - 0.1N $HNO_3$

| (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|
| Sample | Initial Chromate (Moles/l) | Final Chromate (Moles/l) | Initial Dichromate (Moles/l) | Final Dichromate (Moles/l) |
| 1 | 0.8018 | 0.7678 | 0.05 | $8.14 \cdot 10^{-3}$ |
| 2 | 0.7016 | 0.6739 | 0.05 | 7.91 " |
| 3 | 0.5513 | 0.5561 | 0.05 | 5.35 " |
| 4 | 0.4010 | 0.3907 | 0.05 | 2.60 " |
| 5 | 0.3008 | 0.3108 | 0.05 | 1.80 " |
| 6 | 0.1505 | 0.1718 | 0.05 | 0.795 " |
| 7 | 0.0002 | 0.0444 | 0.05 | 0.168 " |
| 8 | 0.0000 | 0.0119 | 0.025 | 0.061 " |

## TABLE VIII

Concentration of chromate and dichromate ions - $0.2N$ $HNO_3$

| (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|
| Sample | Initial Chromate (Moles/l) | Final Chromate (Moles/l) | Initial Dichromate (Moles/l) | Final Dichromate (Moles/l) |
| 1 | 0.6194 | 0.3767 | 0.1 | 0.170 |
| 2 | 0.5169 | 0.2598 | 0.1 | 0.161 |
| 3 | 0.4657 | 0.4009 | 0.1 | 0.068 |
| 4 | 0.3633 | 0.3479 | 0.1 | 0.054 |
| 5 | 0.3121 | 0.2779 | 0.1 | 0.057 |
| 6 | 0.2097 | 0.2166 | 0.1 | 0.040 |
| 7 | 0.1073 | 0.1274 | 0.1 | 0.034 |
| 8 | 0.0561 | 0.0975 | 0.1 | 0.025 |
| 9 | $5.7 \cdot 10^{-8}$ | 0.0161 | 0.051 | 0.001 |
| 10 | $2.7 \cdot 10^{-8}$ | 0.0005 | 0.026 | 0.000 |

concentrated solutions this value is 0.05 moles/1 which is
the amount of dichromate present before hydrolysis. The to-
tal dichromate present after hydrolysis would then be
(.05 + x), where x is that produced by hydrolysis. The chro-
mate present would be equal to the total concentration, C,
minus the dichromate, 2(.05 + x) or (C - 0.1 - 2x).

Therefore the equilibrium equation can be set up and
the initial dichromate concentration in dilute solution in
0.1N $HNO_3$ can be calculated.

$$k = \frac{(2x)^2 \ (.05 + x)}{(C - 0.1 - 2x)^2} = 4.2 \times 10^{-14} \quad (12)$$

The final concentrations can be calculated using equation
(11), taking into account the pH of the solutions.

In dilute potassium chromate solutions in 0.2N $HNO_3$ the
amount of acid removed by conversion of chromate to dichromate
must be taken into account. Thus in equation (9) if 2x is
the amount of chromate present then the dichromate can be
represented by $\frac{1}{2}$(C - 2x) and the acid content would be the
amount of acid added, 0.2N, minus that removed by conver-
sion of chromate to dichromate (C - 2x). Thus, the equili-
brium equation is

$$k = \frac{\frac{1}{2}(C - 2x)}{(0.2 - C + 2x)^2 \ (2x)^2} = 4.2 \times 10^{14}. \quad (13)$$

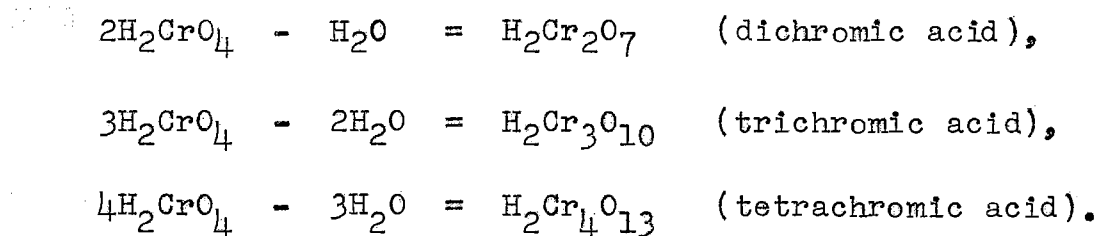The final concentration can be calculated using equation (11).

## Adsorption of Chromic Acid

Adsorption from chromic acid solution increased much
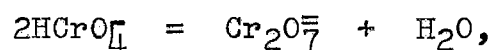more sharply initially than did adsorption from potassium

chromate solution. This can be explained on the basis of a lower initial pH. However, instead of the gradual leveling effect noted in the potassium chromate curves, a maximum adsorption is reached after which a very pronounced decrease in the apparent adsorption takes place (Figure 5). At a first glance this was most unexpected.

Addition of nitric acid to the chromic acid solutions resulted in an even steeper initial slope of the adsorption isotherm. The maximum peak was reached sooner and the resulting decrease in the apparent adsorption was greater than before.

This can be explained from the fact that in solutions of chromic acid there are several poly-acids formed (15). Chromic acid shows a marked tendency to form poly-acids by elimination of water, as in the following examples:

$$2H_2CrO_4 - H_2O = H_2Cr_2O_7 \quad \text{(dichromic acid)},$$

$$3H_2CrO_4 - 2H_2O = H_2Cr_3O_{10} \quad \text{(trichromic acid)},$$

$$4H_2CrO_4 - 3H_2O = H_2Cr_4O_{13} \quad \text{(tetrachromic acid)}.$$

The reaction,

$$2HCrO_4 = Cr_2O_7^= + H_2O,$$

takes place spontaneously, and it may be supposed that there are many $HCrO_4^-$ ions in the solution, for it becomes redder on acidifying, indicating the formation of ions of a different structure (15). It is thus likely that the various chromate ions, $CrO_4^=$, $Cr_2O_7^=$, and $Cr_4O_{13}^=$, exist

together in equilibrium in solution. There is not much
evidence for the existence of the tri- and tetra- chromate
ions in dilute solution; for the addition of water prob-
ably occurs,

$$H_2Cr_2O_7 + H_2O = 2H_2CrO_4,$$
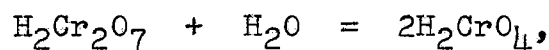
resulting in the ionic change

$$Cr_2O_7^= = 2HCrO_4^-.$$

In dilute solutions this condensation effect does
not occur, but in concentrated solutions there is appa-
rently considerable condensation. This results in de-
creasing the number of dichromate ions available for ad-
sorption so that the apparent adsorption decreases with
an increase in concentration. The fact that an increase
in the acid content would tend to shift this equilibrium
even more, accounts for the effect of nitric acid upon
the adsorption at higher concentrations.

If this line of reasoning is correct, then it fol-
lows that a similar effect should result if concentrated
acid were added to potassium dichromate solutions. That
this is indeed the case may be seen in Figure 6. This
isotherm of potassium dichromate solution, 2 Molar with
$HNO_3$, shows a very steep initial adsorption, then a maxi-
mum and a slight decrease in adsorption.

Thus, it has been shown that by the addition of acid
to dilute solutions of potassium chromate and chromic acid,

the adsorption is greatly enhanced. However, when the concentration of acid becomes too great in concentrated solution of chromates the adsorption process is hindered by the formation of poly-ions.
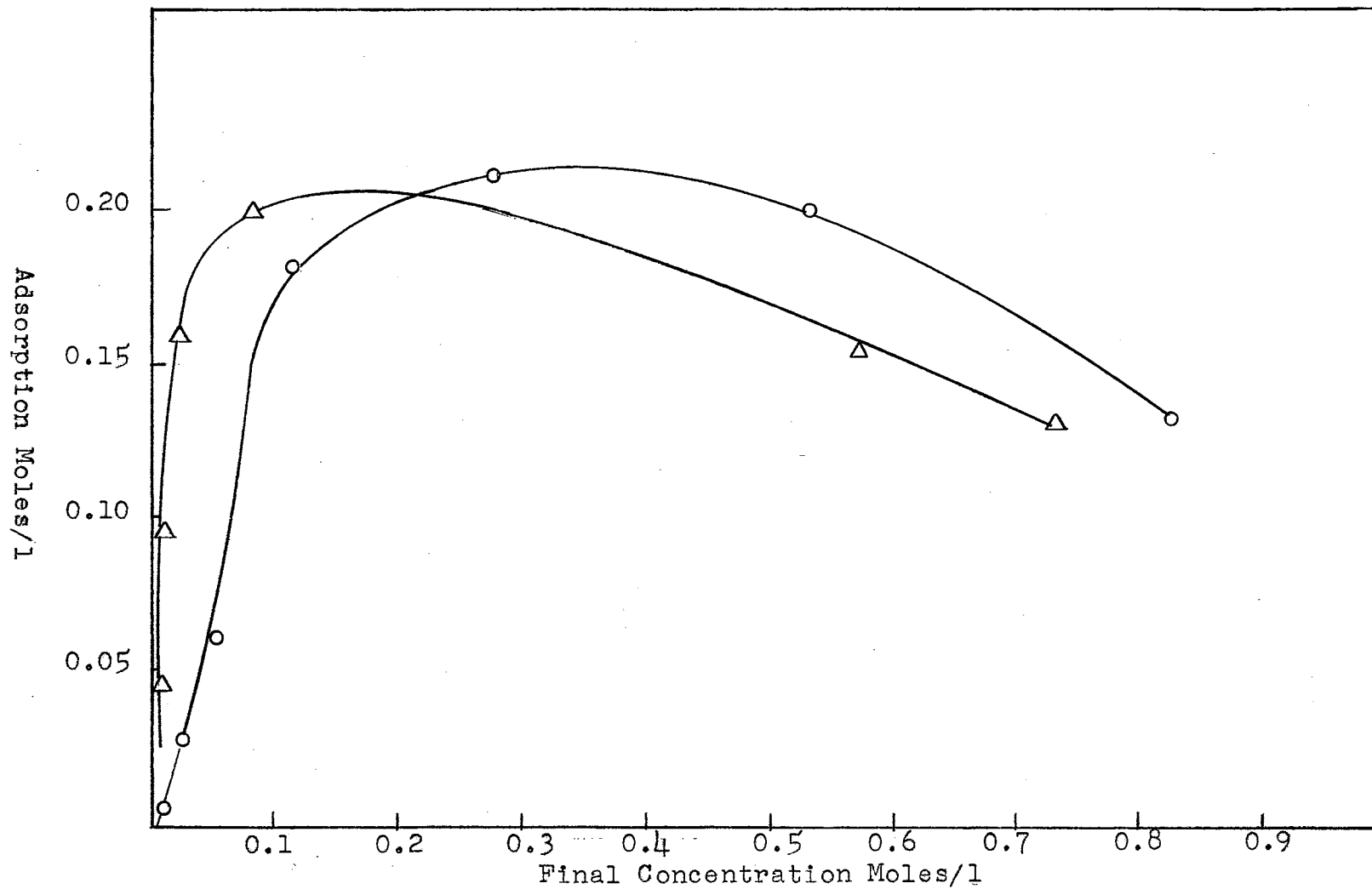
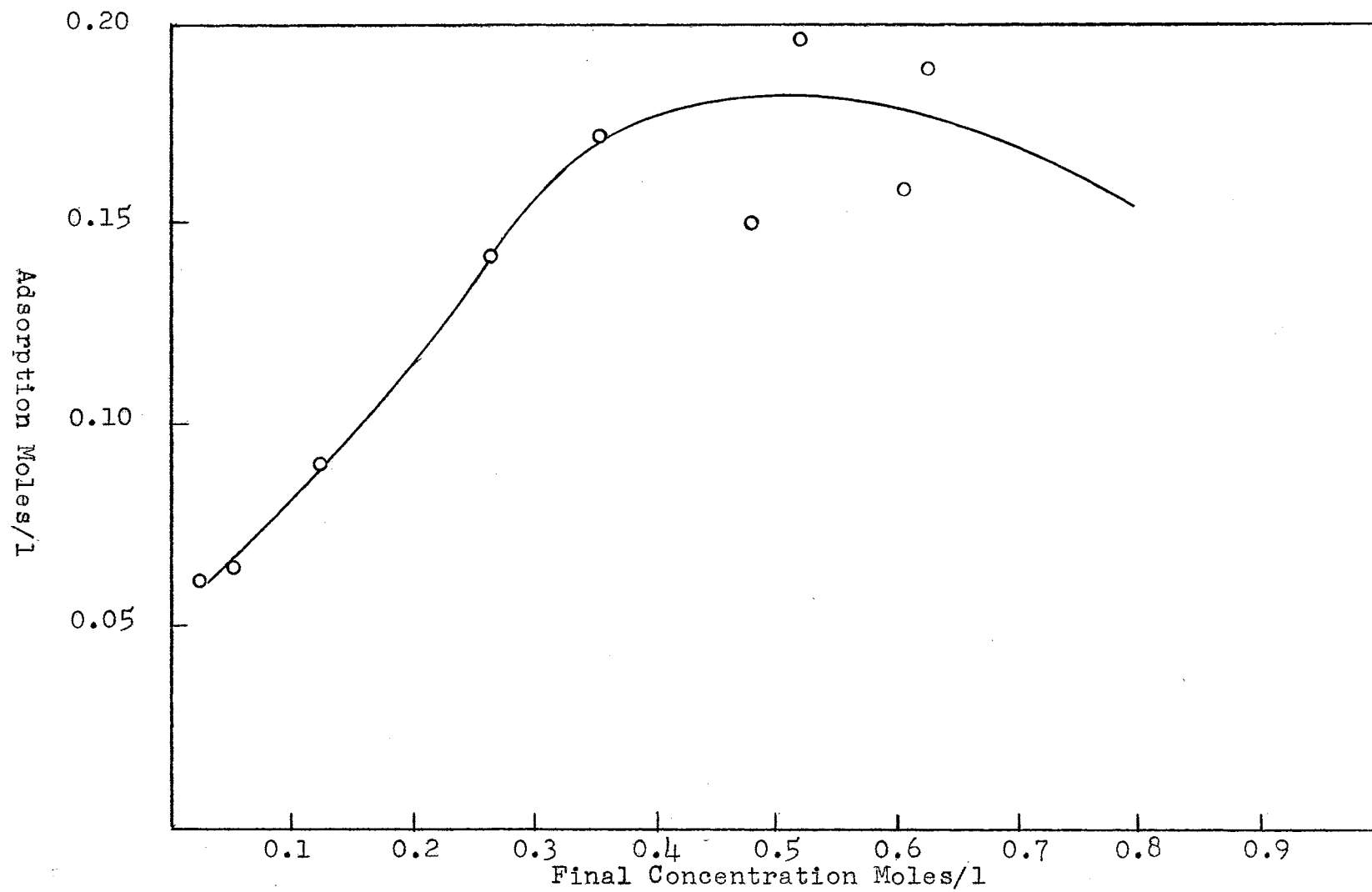Figure 5 - Adsorption of $H_2CrO_4$ on alumina at 27.0°C from solution o, with no acid present; and △, 0.1N with $HNO_3$.

Figure 6 - Adsorption of $K_2CrO_4$ on alumina at 27.0°C from solution 2N with $HNO_3$.

PART VI

SUMMARY

An attempt has been made to determine what effect pH
has on the adsorption of potassium chromate solutions and
chromic acid solutions on ⅋-alumina at constant temperature.
The following is a summary of the conclusions drawn from
the discussion and results presented above:

1. The adsorption of potassium chromate on the alumina
used in the present investigation follows the Freundlich
adsorption isotherm.

2. The adsorption process reaches equilibrium in dilute
solutions after 12 hours and after 24 hours in the more
concentrated solutions, at a temperature of 27.0°C. The
effect of adsorption as a function of temperature was not
followed, although it was noted in a series which was dis-
carded that when the temperature varied about 10°C. that
the adsorption was noticeably decreased.

3. In solutions containing only nitric acid or sodium hy-
droxide, adsorption on alumina caused pH values to change
consistently to higher values when the initial pH was below
7.0. When the initial pH was above 7.0 very little change
was noted. This is interpreted as indicating that the alumi-
na acts as a buffer which is analogous to saying that the
hydrogen and hydroxide ions adsorb on the alumina very readily.

4. When the pH of the potassium chromate solution was decreased by the addition of nitric acid, the adsorption increased very sharply in dilute solutions and then leveled off to some extent.

5. The addition of sodium hydroxide to the potassium chromate solutions suppressed the adsorption to about 80% of that when no acid or base was present.

6. The increase in the adsorption of potassium chromate on alumina is directly proportional to the hydrogen-ion concentration.

7. The adsorption isotherm of chromic acid on alumina is decidedly different than that for potassium chromate. The maximum and subsequent decrease in adsorption of chromic acid on alumina is attributed to the presence of poly-ions of dichromic acid in concentrated solutions. The formation of these poly-ions is enhanced by lowering the pH of the solution. Also, it has been shown that this same effect is obtained in potassium chromate solutions when the concentration of acid is very high, about 2N with nitric acid, corresponding to the formation of poly-ions.

8. Calculations have been made to determine the concentration of chromate and dichromate ions present in solution before and after adsorption. As the pH of the solutions was not held constant an adsorption isotherm may not be drawn for the separate ions.

# PART VII

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