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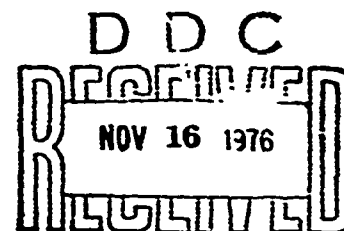
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THE ADSORPTION OF CHROMIUM (VI) AT THE OXIDE/WATER INTERFACE

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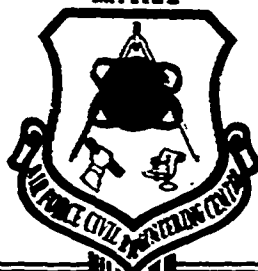
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ITEM 20. (CONCLUDED):

In this report data on adsorption of chromium and phosphate are compared at the water interface of various metal oxides. The conclusions of this investigation are: (1) for Al_2O_3 both chromium and phosphate adsorb at low pH's; however, upon increasing pH, there is a decrease in the percentage adsorption; (2) chromium adsorption decreases with increasing ionic strength; (3) phosphate exhibits a higher specific adsorption energy than does chromium; (4) adsorption of both chromium and phosphate is low for solids which have isoelectric points at low pH's; (5) with a more valid method of determining the surface potential other than the Nernst equation, the simple electrical double layer model can be used to give reasonable predictions of the pHi and surface charge response for adsorption of anions.

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PREFACE

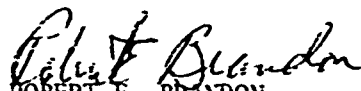
This report was prepared by the Air Force Civil Engineering Center, OL-AA, Kirtland AFB, New Mexico, under Job Order Number 21034C41. This report summarizes work done between 1 July 1974 and 30 June 1975. Captain Michael G. MacNaughton was the project officer and author.

This report has been reviewed by the Information Officer (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


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SECTION I

INTRODUCTION

The fate and transport of pollutants in the natural environment are controlled by many complex physical, chemical, and biological mechanisms. It is necessary, however, to attempt to understand those significant processes which either increase or decrease the environmental impact of these pollutants in order to accurately establish effluent standards and/or develop control strategies.

Chromium is a documented heavy metal contained in numerous electroplating solutions, corrosion inhibitors for cooling systems, paint stripping, and corrosion-resistant coatings.

The toxicity of chromium to aquatic organisms has been demonstrated for fish, *Daphnia*, invertebrates, and algae in concentrations varying from 0.03 to 118 mg/lit with the lower trophic level organisms exhibiting the more sensitive reactions⁽¹⁾.

Although in many cases other chemical, physical, or biological processes may be important in the aquatic chemistry of metals, adsorption to inorganic suspended or deposited sediments has been reported to be a significant controlling mechanism for the transport of many metals^(2, 3, 4, 5).

Considerable research has been conducted on the reactions of hydrolyzable metal ions at the oxide/solution interface; however, there have been few studies on the surface chemical reactions of anionic metal complexes such as chromate. Studies of the adsorption of anions at the oxide/aqueous solution interface have in the past been limited mainly to phosphate^(6, 7, 8, 9, 10, 11, 12, 13) and molybdenum^(14, 15, 16, 17).

Huang⁽¹¹⁾ was able to model the adsorption of phosphate at the aluminum oxide/solution interface using a modification of the James and Healy⁽¹⁸⁾ model for hydrolyzable metal ion adsorption. After James and Healy, Huang assumes the total free energy of adsorption is equal to the individual coulombic, solvation, and specific chemical-free energies. Although included in the model, the solvation interactions of large anionic species would be expected to be minor in contrast to those found for smaller high charged metal ions. Hingston, Posner, and Quirk⁽¹⁰⁾ investigated the competitive adsorption of phosphate, arsenate, and selenite on gibbsite and goethite and found that at lower pH's phosphate was adsorbed on sites which were not common to arsenate but that all of the anions were specifically adsorbed. Muljadi, Posner, and Quirk⁽⁷⁾ measured the adsorption of phosphate on kaolinite, gibbsite, and pseudoboehmite and proposed that the adsorption occurs in three different regions. For the first two regions exchange takes place between phosphate and OH on the edge faces of the oxide or clay crystals with the first type having the highest affinity. In contrast to

the other regions which obey a Langmuir isotherm, region III is linear and occurs at higher concentrations (10^{-5} to 10^{-1} M).

Bache (8) also interpreted the removal of phosphate from solution in the presence of gibbsite and ferric hydroxide as occurring in three stages: (1) a high energy chemisorption, (2) precipitation of a phosphate phase, and (3) a low energy sorption of phosphate on the precipitate.

Exchange with OH is proposed by Low and Black (13), while Kuo and Lotse (12) modeled the removal of phosphate on kaolinite by assuming replacement of H_2O at the surface and the formation of a covalent bond between Al and the O of the phosphate. It was hypothesized that the phosphate ions form an octahedral complex of aluminum phosphate.

In this study, an attempt has been made to show that the adsorption of chromate at the oxide/solution interface can be modeled reasonably well using a simple electrical double layer interpretation of the interface. In addition to chromate, evidence is also presented that the model holds equally well for another anion of environmental significance, phosphate, and is applicable to oxides of varying surface characteristics. Although not representative of all surfaces found in natural waters, the oxides used here have isoelectric points varying from 2.0 for SiO_2 to 9.0 for Al_2O_3 .

SECTION II

EXPERIMENTAL

REAGENTS

Reagents used in this study were of analytical reagent (AR) grade quality, and water used was deionized, singly distilled from an all-Pyrex® still and stored in a Pyrex® container. This water had a conductivity of 1.1 megohm cm^{-1} or better at 25°C. The stock solutions of chromium were generated from AR potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and phosphate from AR potassium dihydrogen phosphate (KH_2PO_4). Control of pH and ionic strength was accomplished using AR nitric acid and carbonate free potassium hydroxide (DILUT-IT 9689).

PREPARATION OF SOLIDS

α - Quartz, SiO_2 α - Quartz was prepared by heating min-u-sil 5 (Pennsylvania Glass Sand Corporation) at 500°C for 24 hours to oxidize any organic matter present in the commercial product. This treatment was followed by refluxing in boiling 4M HCl for 24 hours to remove substantial quantities of iron oxide impurities. The α - Quartz was subsequently treated by careful washing with distilled water until the pH of the supernatant was approximately 6. No chloride could be detected with AgNO_3 . The cleaned quartz was vacuum dried at 80°C. X-ray diffraction identified the silica as α - Quartz. The Brunauer, Emmett and Teller (B.E.T.) gas adsorption surface area was $5 \pm 1.0 \text{ m}^2/\text{gm}$, and the isoelectric point was at pH 2.0 ± 0.2 .

α - Alumina, Corundum, Al_2O_3 α - alumina was prepared by the repeated washing of 0.5 micron Liade A alumina abrasive (Union Carbide) with distilled water. X-ray diffraction identified the alumina as α - alumina. The B.E.T. gas adsorption surface area was $17 \pm 2.0 \text{ m}^2/\text{gm}$, and the isoelectric point was at pH 9.1 ± 0.2 .

Anatase, TiO_2 Titanium dioxide was obtained as the AR powder from J. T. Baker Company. It was necessary to first wash the oxide in 1M KOH to remove residual phosphate contamination. This treatment was followed by 1N HNO_3 and repeated washing with distilled water until the pH of the supernatant was 7.0. X-ray diffraction identified the titania as anatase. The B. E. T. gas adsorption surface area was $7 \pm 0.5 \text{ m}^2/\text{gm}$, and the isoelectric point was at pH 7.2 ± 0.2 .

ADSORPTION EXPERIMENTS

Adsorption experiments were conducted in 35-ml Pyrex® centrifuge tubes with Teflon®-lined screw caps. The experimental procedure involved addition of a known amount of solid in 23 ml of the electrolyte solution, addition of 2 ml of the Cr (VI) or phosphate stock solutions and equilibration for 24 hours. Mixing was achieved by gently rotating the tubes end-over-end at 10 rpm during the experiments.

After centrifugation at 300 rpm for 30 minutes a sample was carefully withdrawn and analyzed. Chromium was analyzed using a Perkin Elmer 403 Atomic Absorption Spectrophotometer with deuterium background corrector and automatic averaging. Nitrous oxide was used as the oxidant gas. Phosphate was analyzed using the ammonium molybdate colorimetric method (19).

The pH of the equilibrated solutions was measured subsequent to withdrawal of the samples for analysis.

The amount of chromium or phosphate adsorbed was calculated by subtracting the residual solution concentration from the initially added concentration. Control experiments indicated that adsorption to the centrifuge tubes and caps was undetectable.

SECTION III

AQUATIC CHEMISTRY OF CHROMIUM

The chemistry of chromium in natural waters is complicated by the possibilities of at least two oxidation states, Cr (III) and Cr (VI). Under conditions of pH and pE found for most oxygenated waters the theoretical log ratio of Cr (VI)/Cr (III) would be 20.5 (20, 21). This does not imply that this is the actual ratio since non-equilibrium conditions are common in marine and fresh water systems (22). Measurements of the Cr (VI)/Cr (III) ratio in marine waters reveal a significant concentration of Cr (III). This implies that either organic material is responsible for the Cr (III) content or the oxidation reaction is kinetically unfavorable (23). In this investigation, measured values of Cr (VI) and total chromium were the same, confirming the predominance of Cr (VI) in oxidizing environments.

Cr (VI) is the highest oxidation state of chromium and exists in aqueous solutions as oxo compounds. Unlike some of the other high valent oxo compounds such as V (V), Mo (VI), and W (VI), chromium (VI) does not exist in numerous polyacid and anionic forms (20, 25). The only aqueous species which are important are those formed from the hydrolysis of chromate, CrO_4^{-2} . These are shown in Table 1 along with the hydrolysis constants selected from Sillen (21) and Arnek (25). The hydrolytic speciation of Cr (VI) is shown in Figures 1 and 2 for total chromium concentrations of 10^{-1} M and 10^{-4} M. The change in the speciation with a change in total chromium concentration at a constant pH is due to the dinuclear species $\text{Cr}_2\text{O}_7^{-2}$. As can be seen in these figures, the predominant species for concentrations of chromium which might exist in natural water are CrO_4^{-2} and HCrO_4^{-} . Only in those instances of heavy industrial pollution would $\text{Cr}_2\text{O}_7^{-2}$ become important. The hydrolysis of phosphate is shown in Figure 3.

TABLE 1. EQUILIBRIUM DATA (21, 25)

<u>Chromate</u>	
<u>Reaction</u>	<u>Log Constant</u>
$\text{H}^+ + \text{CrO}_4^{=2} \rightleftharpoons \text{HCrO}_4^-$	$*K_1 = 6.50$
$\text{H}^+ + \text{HCrO}_4^- \rightleftharpoons \text{H}_2\text{CrO}_4$	$*K_{12} = -0.8$
$2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{=2} + \text{H}_2\text{O}$	$K_{22} = 1.53$
$\text{K}^+ + \text{CrO}_4^{=2} \rightleftharpoons \text{KCrO}_4^-$	$K = 0.51$
<u>Phosphate</u>	
$\text{H}^+ + \text{PO}_4^{=3} \rightleftharpoons \text{HPO}_4^{=2}$	$*K_1 = -2.1$
$\text{H}^+ + \text{HPO}_4^{=2} \rightleftharpoons \text{H}_2\text{PO}_4^-$	$*K_2 = -7.2$
$\text{H}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_3\text{PO}_4$	$*K_3 = -11.8$

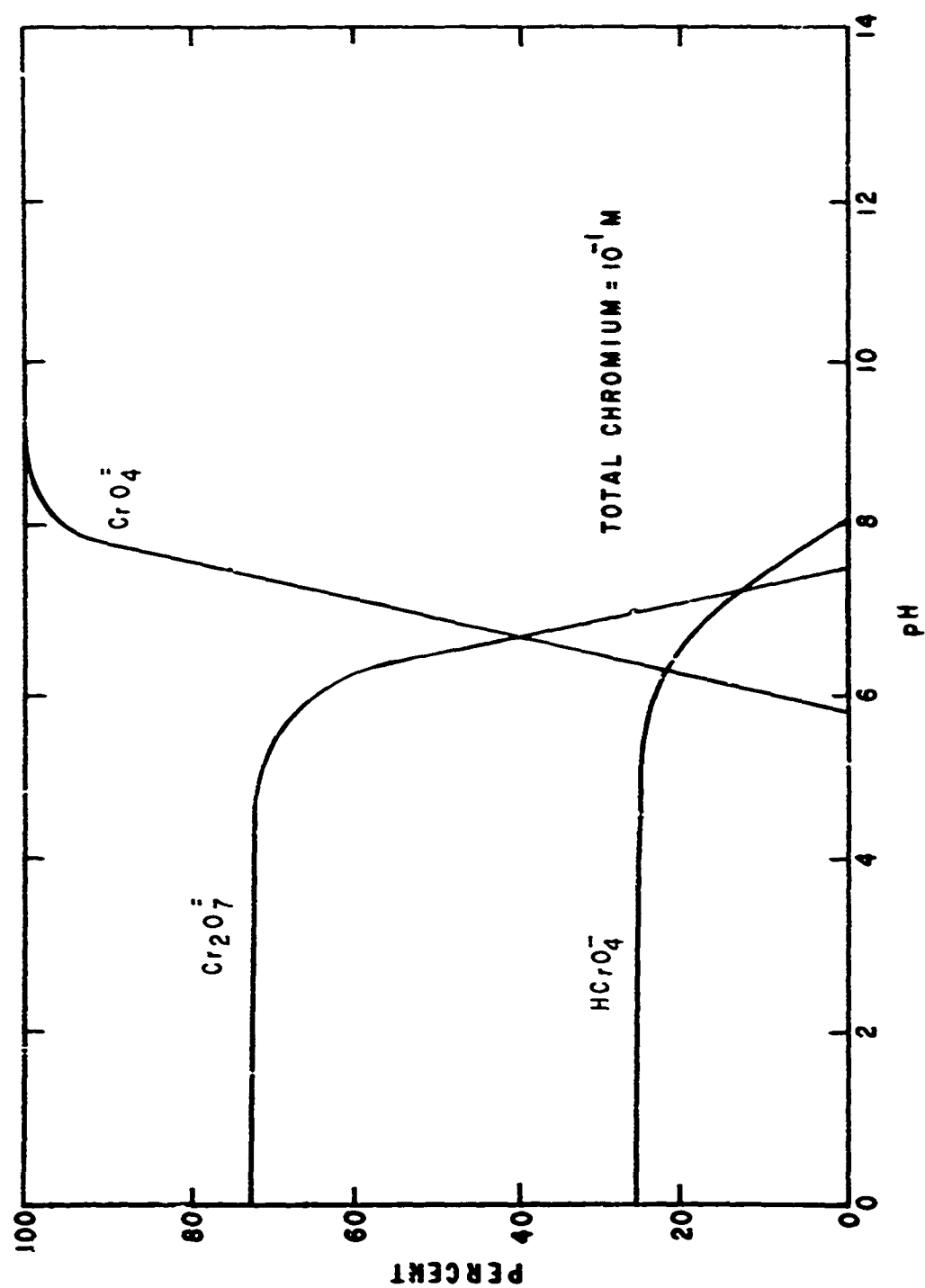


Figure 1. Percentage of Chromium (VI) Species as a Function of pH. Total chromium concentration 1×10^{-1} moles liter $^{-1}$.

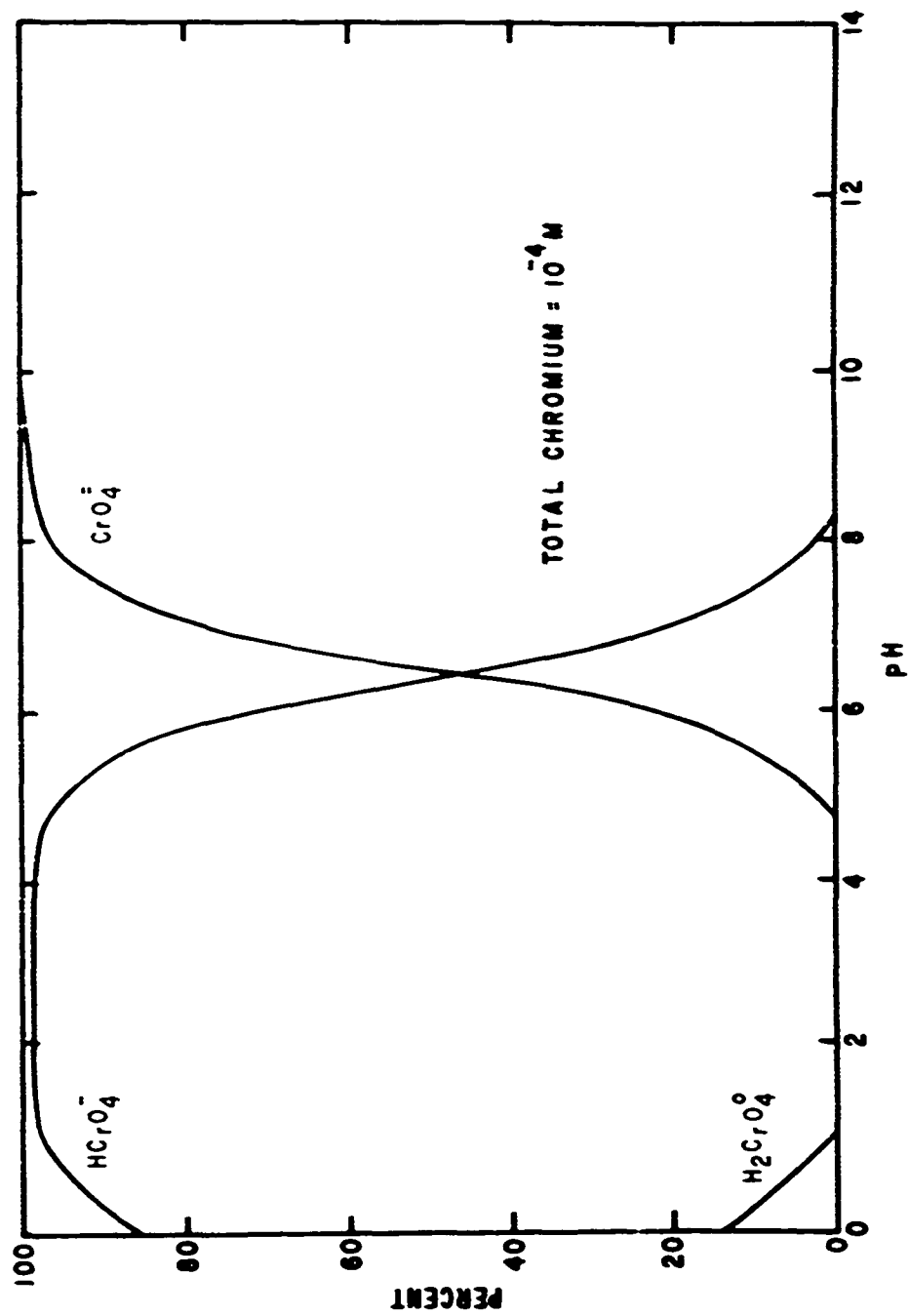


Figure 2. Percentag. of Chromium (VI) Species as a Function of pH. Total chromium concentration 1×10^{-4} moles liter $^{-1}$.

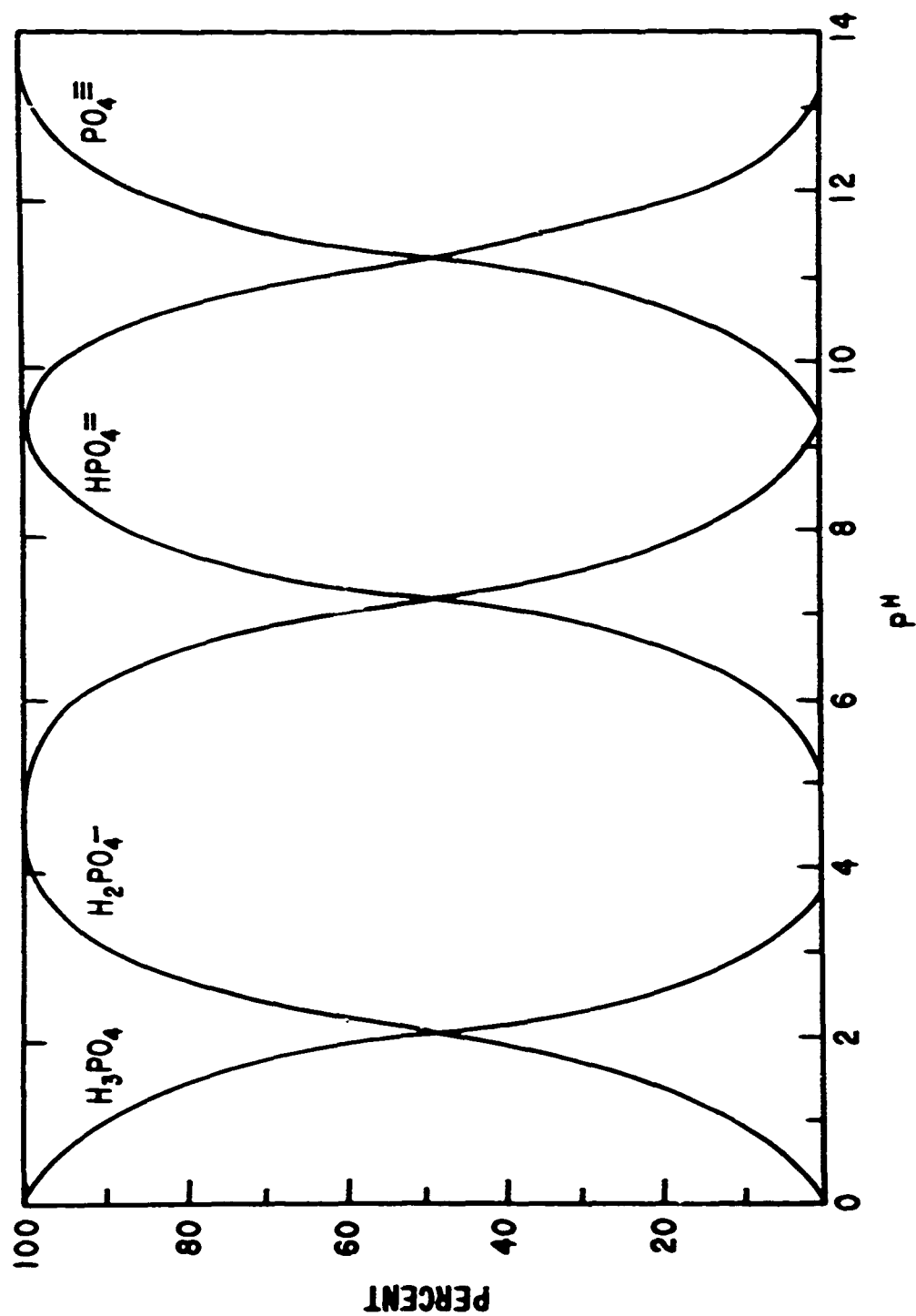


Figure 3. Percentage of Phosphate Species as a Function of pH.

SECTION IV

MODELING

Basically, it is possible to use three models to interpret the interfacial reactions of aqueous ions:

1. Surface reaction or exchange, where the uptake of the species is due to the formation of a surface complex analogous to a mass action reaction in solution.
2. Solubility controls, where precipitation of a solid phase occurs.
3. Electrostatic controls, where the driving force for the uptake is a result of electrical double layer forces.

As has been discussed previously^(26, 27, 28), the experimental differentiation between these models is not possible due to the similarity of their quantitative form.

In this report, the uptake of Cr (VI) and phosphate are interpreted using the simple Grahame-Stern model of the electrical double layer.⁽²⁹⁾ The original model has been modified to account for the adsorption of the anion of interest in a supporting electrolyte of higher concentration and the variation in speciation due to the solution phase hydrolytic reactions.

After Grahame, the charge at the adsorption plane is given by

$$\sigma_s = \frac{z \cdot 1.6 \times 10^{-13} \text{ NS}}{1 + \frac{55.5}{C} \exp (ze \psi_s + \phi)} \quad (1)$$

where z is the charge,

NS is the maximum adsorption density calculated from the hydrated radius,

ψ_s is potential at the adsorption plane,

ϕ is the specific adsorption potential which accounts for all other forces which either retard or enhance adsorption.

This specific adsorption potential is, in fact, a fitting parameter, and the value has no physical significance except for relative comparison of different species and/or surfaces. ϕ is assumed to be zero for the inert electrolyte and acquires a positive or negative value depending on whether a species displays an increased or decreased affinity for the surface as compared to the electrolyte. C is the concentration of all solution species which, for

the work described here, will be the ionic strength. This is necessary because of the changing charge of the hydrolytic species and their varying concentration in solution with changing pH. By using a swamping inert electrolyte which remains constant throughout the pH range of interest, it is assumed that the charge can always be calculated from the ionic strength of the solution. This assumption disregards the influence of the small solution concentration of the species of interest on the surface charge.

The charge in the diffuse layer is given by:

$$\sigma_d = -11.74 \sqrt{C} \sinh (Ze \psi_s/kT) \quad (2)$$

and through electroneutrality the total surface charge σ_o is equal to the sum of the charge at the adsorption plane and that in the double layer. In Equation 2 k is the Boltzmann constant and T is the absolute temperature. Assuming a linear decrease in potential between the two planes and choosing a value for the capacitance (κ) of the inner layer, it is possible to calculate the surface potential, ψ_o :

$$\psi_o = \psi_s + \sigma_o/\kappa \quad (3)$$

In calculations of surface adsorption on oxides, it is necessary to know the concentrations of H^+ and OH^- for two reasons. First, the speciation of many metal ions and weak acids is controlled by hydrolytic reactions and is therefore pH dependent. Second, it has been documented that H^+ and OH^- are potential determining ions for oxide surfaces (30). If the oxide/electrolyte interface acts as a reversible electrode, the pH of the solution is given by the Nernst equation:

$$pH = pH_{zpc} - \psi_o/0.059 \quad (4)$$

where pH_{zpc} is the pH of the zero point of charge.

Since in the experiments described here the majority of the ions in solution were due to the supporting electrolyte (HNO_3 -KOH), the concentration of the species of interest, Cr (VI) and phosphate, at the adsorption plane can be calculated from the electrical potential at the adsorption plane and a specific adsorption potential which gives the best fit to the data.

Since the concentration of any solution species is dependent not only on the hydrolytic reactions which are pH controlled but also on the affinity of the individual species for the surface, the mass balance must take into account both of these reactions:

$$C_{\text{total}} = M^{n+} \left(\sum \frac{\beta_i}{(H^+)^i} \right) (1 + \sum K_i) \quad (5)$$

where n = charge of unprotonated metal

β_i = overall hydrolysis constants

K_i = adsorption constant

Using the potential at the adsorption plane, an appropriate specific adsorption potential ϕ , and assuming the surface coverage is small ($< 25 \mu \text{ coul/cm}^2$), the adsorption constant can be calculated

$$K_i = 2 \cdot S \cdot X_i \cdot \exp(Z_i e (\psi_x + \phi_i)) \quad (6)$$

where S is the surface area in cm^2/lit and X is the hydrated radius of species i .

It is assumed that all species of the same metal exhibit the same specific adsorption potential regardless of the extent of hydrolysis. In the case where other ligands are present, this would not necessarily be the case. As has been shown previously for Hg (II), the chloro complexes are weakly adsorbed as compared to the hydroxo complexes (26). The total adsorption of the metal is then the summation of the adsorption of the individual species.

$$\text{Total Adsorbed} = \sum_i K_i \quad (7)$$

SECTION V

RESULTS AND DISCUSSION

The absorption of 2×10^{-4} M Cr (VI) from aqueous solutions of 0.1, 0.01, and 0.001 M KNO_3 onto α - alumina along with that predicted by the

EDL model are shown in Figure 4. It can be seen that adsorption below pH 4.0 is relatively pH independent. However, as the pH is increased above 4.0, there is a large decrease in percentage adsorption, reaching approximately zero in the pH range 7 to 8.5. It is also apparent from this figure that there is a decreasing percentage adsorption as the concentration of the supporting nitrate electrolyte is increased. The calculated adsorption isotherms for Cr (VI) are shown by the solid lines in Figure 4. The model predicts minimal adsorption of chromate for 0.1 M ionic strength and therefore this line is not shown in the figure. While reproducing the pH response reasonably well, the electrostatic model predicts a more substantial decrease in the percentage adsorption with increasing ionic strength than observed. This same observation has been made by Hunter and Wright (31), who concluded of the Nernstian prediction that the surface potential as a function of pH as given in Equation (4) gives too high a value. Table 2 shows the measured adsorption of Cr (VI) on Al_2O_3 as a function of ionic strength at pH 4.0 compared with that calculated using the Nernst equation and that calculated using a potential which gives the best fit to the data. The 140 mv found is close to the 120 mv found by Hunter and Wright (31) to give the best fit to the Al_2O_3 zeta potential data of Modi and Fuerstenau (32).

Using a zeta potential of 84 mv as found by Modi at pH 4.0, an ionic strength of 10^{-3} , and the surface charge measured by Sadek et al (33) of $14.3 \mu \text{ coul/cm}^2$, it is possible to calculate a surface potential for comparison. Using a capacity of $140 \mu \text{ f/cm}^2$ for the inner Helmholtz plane and a value of $20 \mu \text{ f/cm}^2$ for the outer Helmholtz plane, as found by Yates et al (34) for oxide surfaces, the calculated surface potential is 142 mv which is in close agreement with the 140 mv found in Table 2. Therefore, in order to model the adsorption of solution species at the oxide/water interface using an electrostatic model, a more complex model of calculating surface potential such as proposed by Yates et al must be used.

The adsorption of phosphate onto α - alumina from 0.1 and 0.01 M potassium nitrate solutions is shown in Figure 5. Although exhibiting the same generalized shape adsorption isotherm as chromate, the decrease in percentage adsorption does not occur until a pH of ~7 is reached. The response to increasing electrolyte, while measurable, is not nearly as significant as found for chromate. Also, the maximum percentage adsorption measured for phosphate at the same concentration and solution conditions is much higher than chromate, indicating a stronger specific adsorption energy.

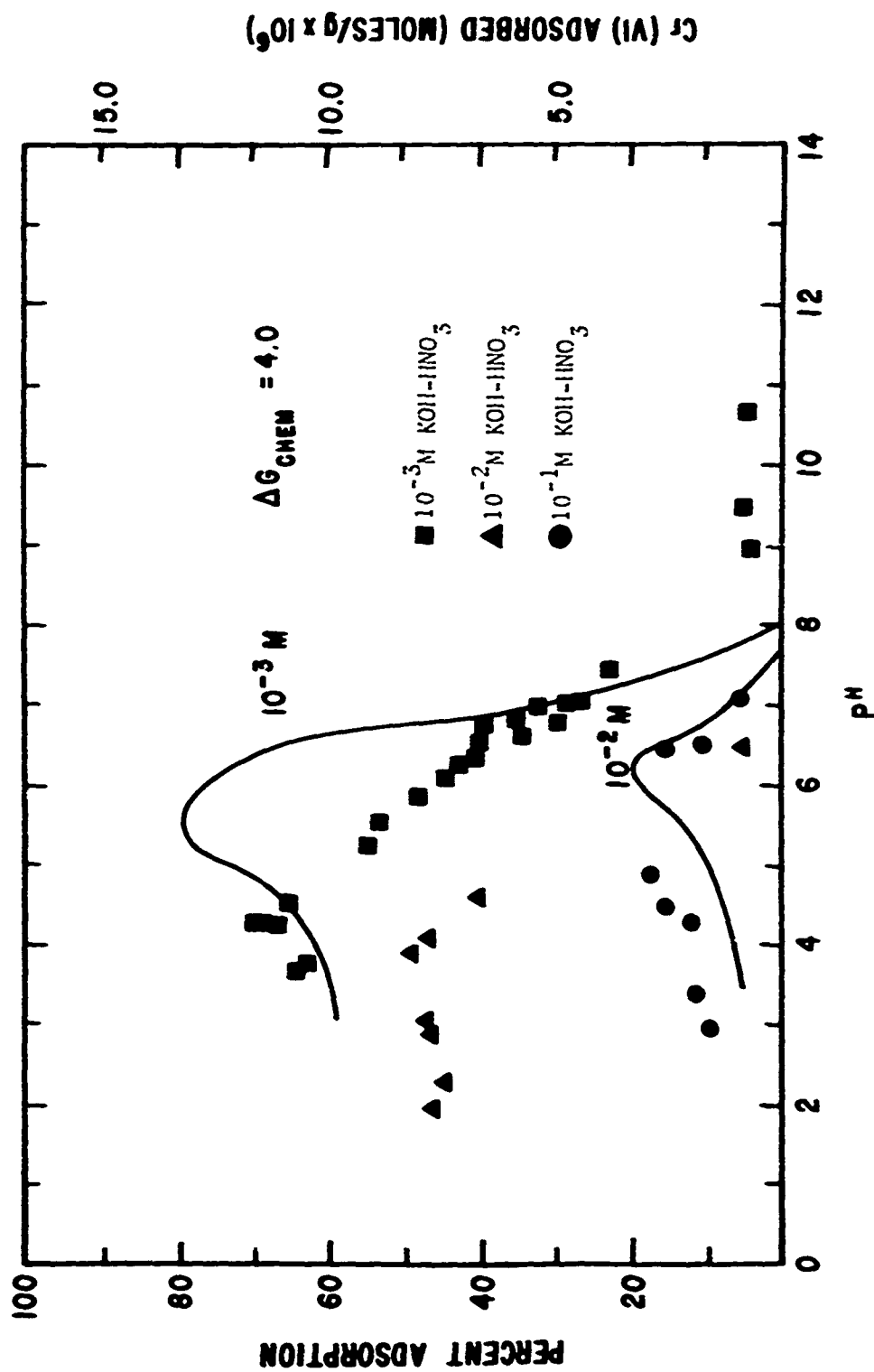


Figure 4. Percentage Adsorption of Cr (VI) on Al_2O_3 as a Function of pH and Ionic Strength. Total Cr (VI) concentration 2×10^{-4} moles liter⁻¹. Solid concentration 12 gm liter^{-1} ($204 \text{ m}^2 \text{ liter}^{-1}$).

TABLE 2. PERCENTAGE ADSORPTION OF Cr (VI) AS A FUNCTION OF IONIC STRENGTH

<u>Ionic Strength</u>	<u>Experimental</u>	<u>Calculated* Nernst Equation</u>	<u>Calculated** $\psi = 140$ mv</u>
10^{-1} M	12	0	10
10^{-2} M	49	6	41
10^{-3} M	67	67	70

*Chemical potential = 4.0 Kcal/mole.

**Chemical potential = 1.6 Kcal/mole.

The results for phosphate shown in Figure 5 are interesting in that the predicted increase in adsorption with increasing ionic strength above the isoelectric point is observed in the data. This occurs because of the reduction in the repulsive electrostatic charge of the negative surface at the higher electrolyte concentration.

It has been proposed that the adsorption of phosphate on alumina is the result of complexation with the central metal cation (12). Since, unlike phosphate, Cr (VI) forms no known aluminum coordination there should be minimal competition for adsorption sites.

In Figure 6 the influence of increasing phosphate concentration on the percentage Cr (VI) adsorption is illustrated. This implies that either both anions are specifically adsorbed into the adsorption plane and compete for space or that they are adsorbed at the same sites on the surface. Conversely, the presence of chromate results in little or no decrease in phosphate adsorption up to Cr (VI) concentrations of 10^{-3} M, again confirming the higher specific adsorption of phosphate. As shown in Figures 7 and 8 the model does duplicate the response to changing the surface charge properties of the solid. Neither chromate (Figure 7) nor phosphate (Figure 8) adsorb strongly on SiO_2 (IEP ~ 2.0) which has a negative surface charge at all but the lowest pH values, but both adsorb to Al_2O_3 (IEP ~ 9.0) which exhibits a positive surface charge below pH ~ 9.0 . TiO_2 with an isoelectric point of ~ 7.0 gives minimal adsorption for Cr (VI) but does adsorb the phosphate species even at low surface potentials.

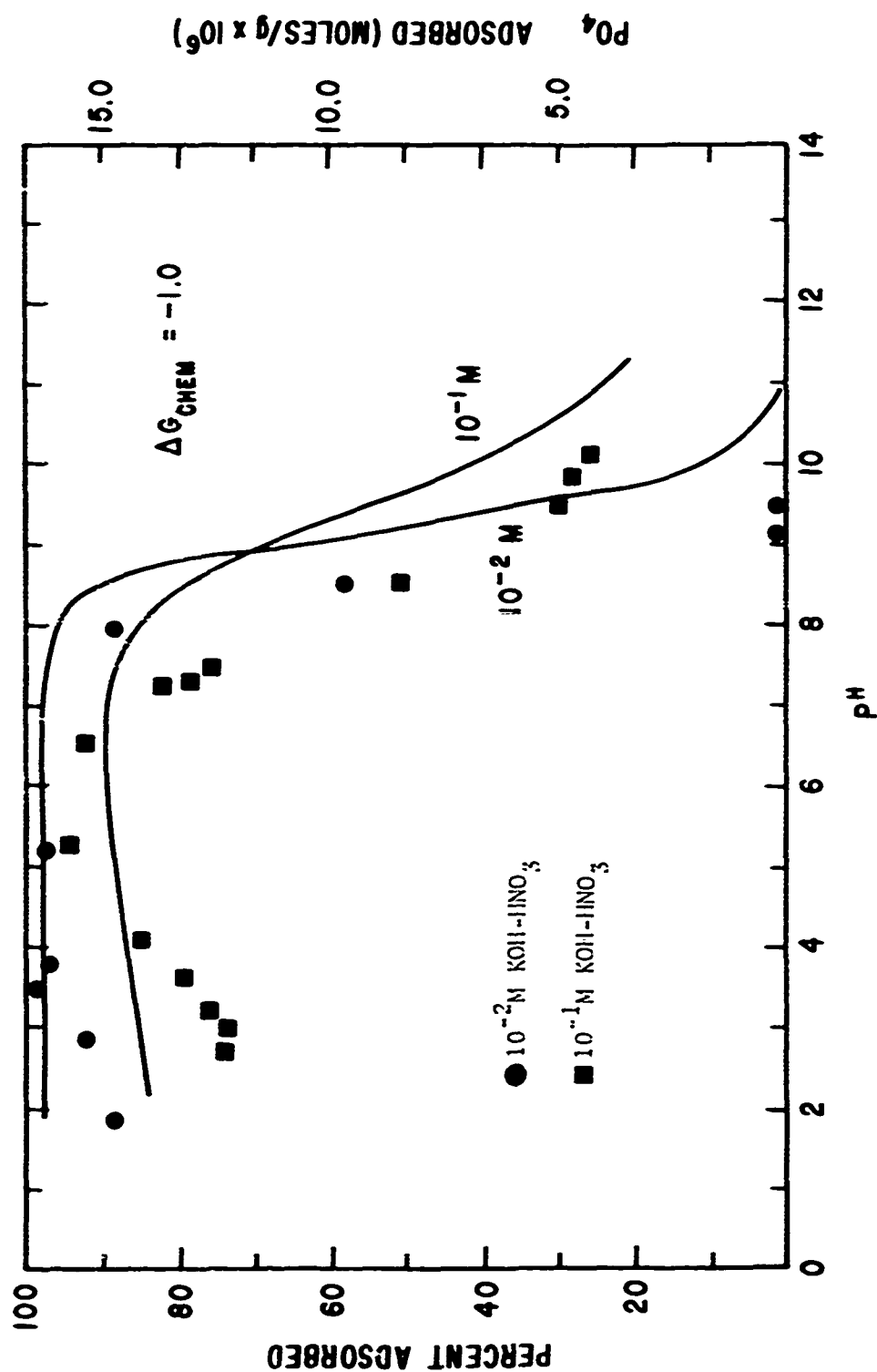


Figure 5. Percentage Adsorption of Phosphate on Al₂O₃ as a Function of pH and Ionic Strength. Total phosphate concentration 2×10^{-4} moles/liter⁻¹. Solid concentration 12 gm liter⁻¹ (204 m² liter⁻¹).

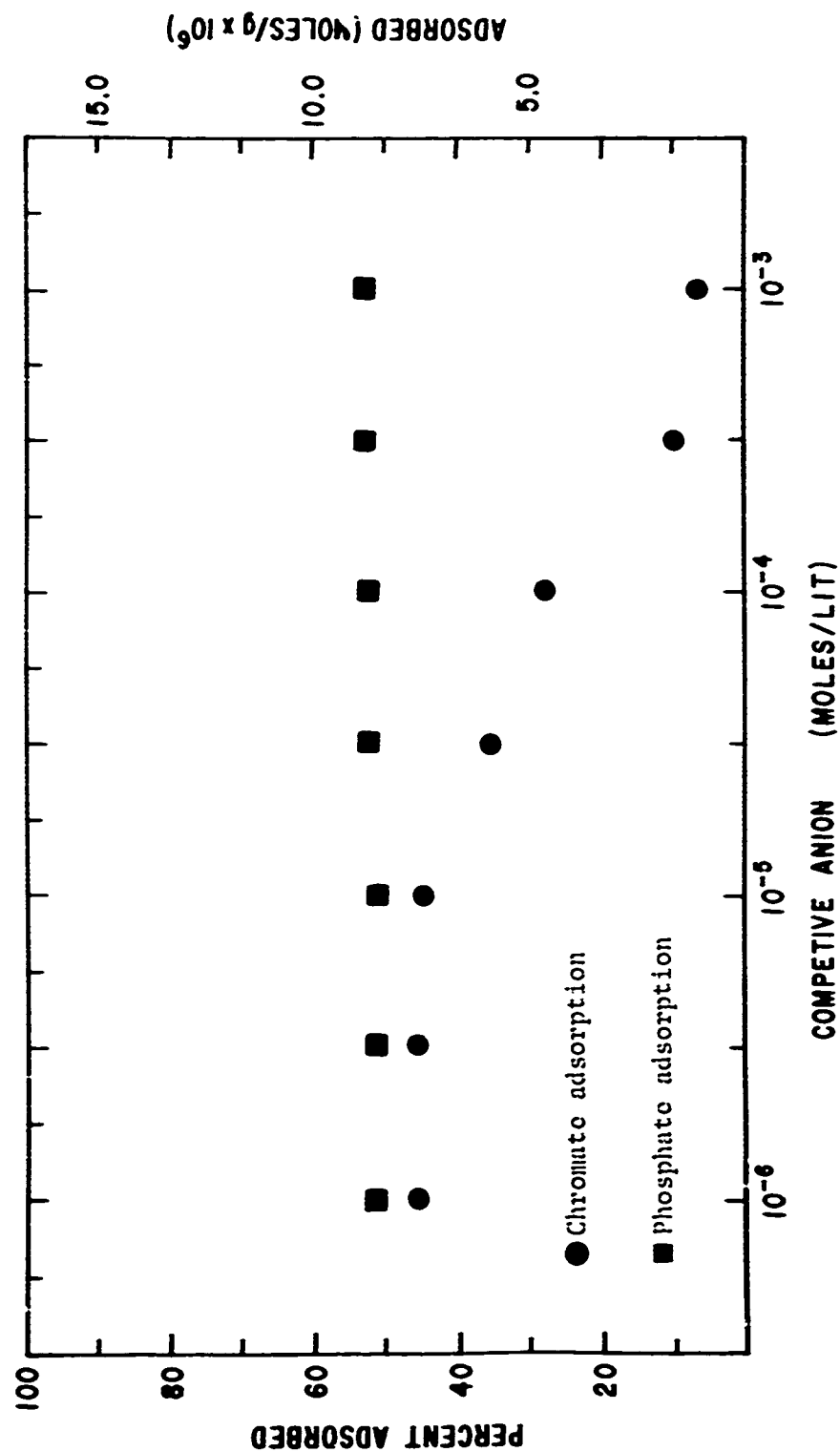


Figure 6. Percentage Adsorption of Chromate and Phosphate on Al_2O_3 as a Function of the Concentration of the Other Anion. Initial Concentration 2×10^{-4} moles liter $^{-1}$.

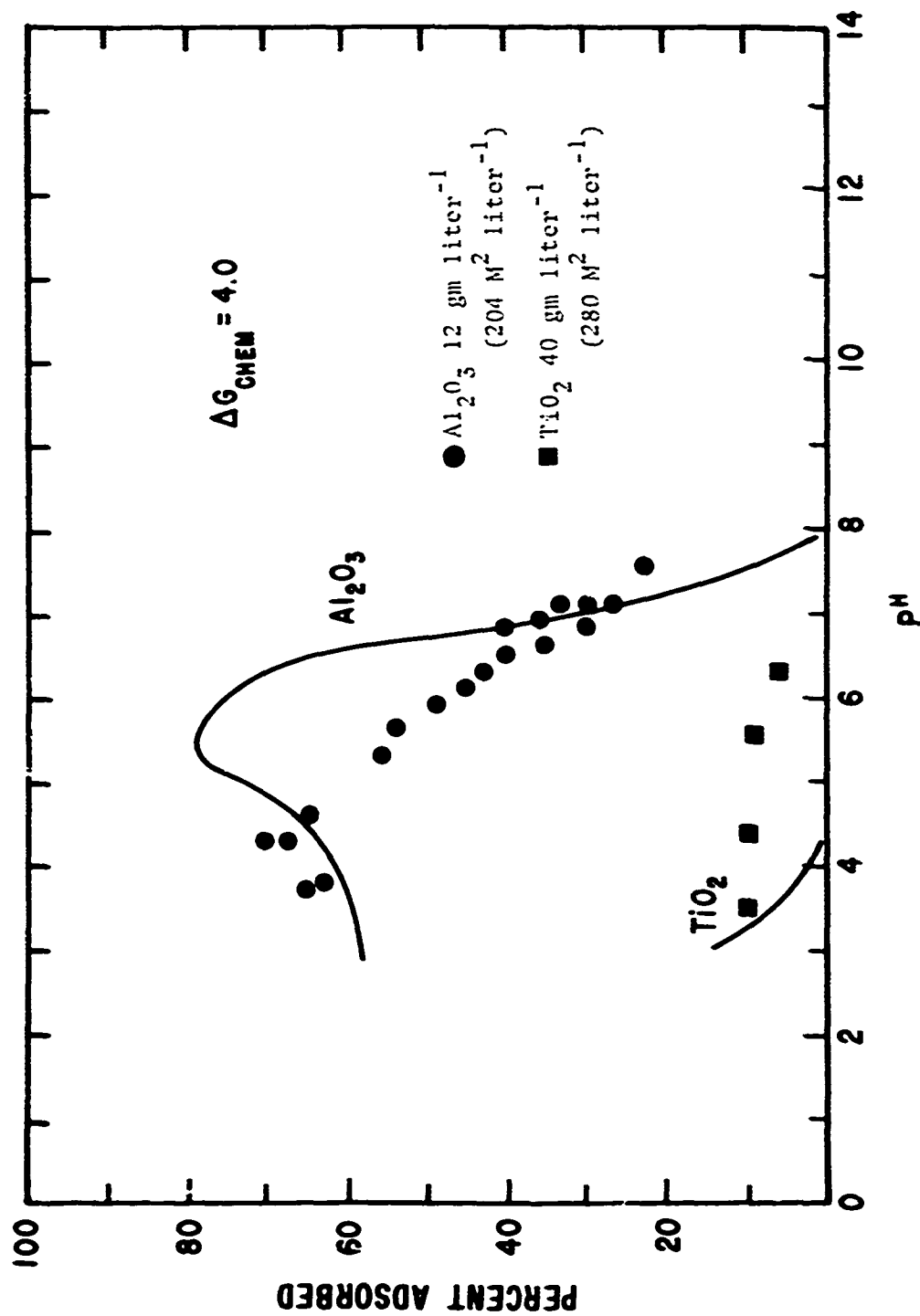


Figure 7. Percentage Adsorption of Chromate as a Function of pH and Solid Substrate. Total chromium concentration 2×10^{-4} moles liter⁻¹, electrolyte 10^{-3} M KOH- HNO_3 .

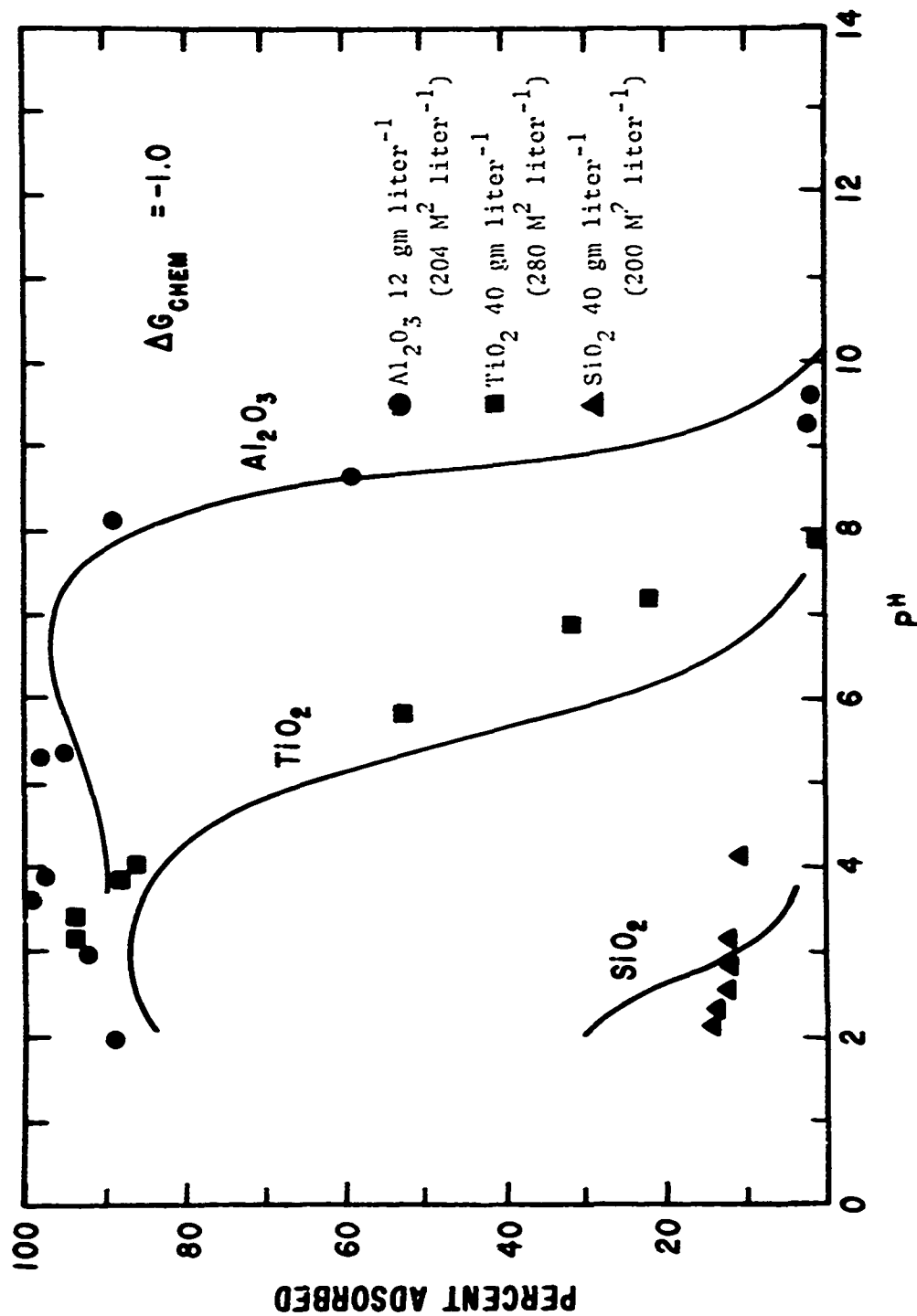


Figure 8. Percentage Adsorption of Phosphate as a Function of pH and Solid Substrate. Total phosphate concentration 2×10^{-4} moles liter⁻¹. 10^{-3}N KOH- HNO_3 .

SECTION VI

CONCLUSIONS

From the adsorption results presented here, it appears that both Cr (VI) and phosphate exhibit the same generalized adsorption behavior on Al_2O_3 : (1) adsorption is appreciable at low pHs, however upon increasing pH there is a decrease in percentage adsorption. Adsorption at low pHs is due to the strong coulombic attraction between the negatively charged anions and the positively charged surface of the Al_2O_3 ; (2) a decrease in percentage adsorption results with increasing electrolyte concentrations. This reduction occurs due to the compression of the electrical double layer at the oxide interface and the resulting decrease in the electrical potential; (3) phosphate exhibits a higher specific affinity for all the oxides than does chromate. This implies that the surface reaction is not dependent on the type of central metal cation of the oxide and that coordination between the anion and the metal is not responsible for the interfacial reaction.

Except for the use of the Nernstian equation in determining surface potential, the simple EDL model of the oxide/solution interface gives reasonable estimates of the pH and surface charge response for adsorption of anions. As has been reported previously, the surface potential must be calculated using a more complex procedure (28, 29).

From the data presented here, indications are that if chromium is in the +6 oxidation state it will be associated predominately with the solution phase except in the presence of particulate matter with high I.E.P.s such as Al_2O_3 , CaCO_3 , and possibly some of the magnesium silicates such as chrysotile (30).

For purposes of pollution control, the use of alumina adsorption columns or alum precipitation would appear to present efficient methods for removal of chromate and phosphate from solution.

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