

# THE ISOELECTRIC POINTS OF SOLID OXIDES, SOLID HYDROXIDES, AND AQUEOUS HYDROXO COMPLEX SYSTEMS

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## I. INTRODUCTION

Solid oxides in aqueous suspension are generally electrically charged as may be observed most directly in electrophoresis experiments. The charge has long been attributed to one of two apparently indistinguishable mechanisms (5-7, 36, 56, 81, 87, 129): (a) amphoteric dissociation of surface MOH groups; and (b) adsorption of metal hydroxo complexes derived from the hydrolysis products of material dissolved from the solid, *i.e.*, from amphoteric dissociation of  $M^{z+}(\text{OH})_z$ - (aq).

Both mechanisms explain qualitatively the pH dependence of surface charge and the existence of a pH resulting in zero net charge, called the isoelectric point (IEP) or zero point of charge (ZPC). The term "isoelectric point" is variously used to represent both the pH at which an immersed solid oxide surface has zero net charge and the pH resulting in (electrically) equivalent concentrations of positive and negative complexes, *i.e.*

$$\Sigma(z - n)M^{z+}(\text{OH})_n^{z-n} = 0$$

in a system of hydroxo complexes,  $M^{z+}(\text{OH})_n^{z-n}$ .

The term "IEPS" will be used when referring to solids and "IEP" when referring to dissolved species. The IEPS and the ZPC are identical by definition.

Based primarily on data for the W(VI) and Fe(III) systems it was proposed in 1962 (87) that the IEPS was identical with the IEP of the corresponding hydroxo complexes. The evidence readily available at that time was convincing but meager. A much more extensive collection of IEPS's and IEP's has been compiled to serve as a reference list and to test whether or not the two are indeed equal.

This paper is concerned first with the isoelectric points of solid oxides and an analysis of the dependence of the IEPS on the properties of the cation, its coordination, the hydration state of the solid, and its purity. The second major concern of the paper is comparison of the IEPS's with the isoelectric points of appropriate hydroxo complex systems and a discussion of the relationship between the two.

## II. THE ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

### A. SELECTION AND PRESENTATION OF DATA

#### 1. General

Many methods have been used to estimate the IEPS. Electrokinetic methods, including electroosmosis, streaming potential, and electrophoresis, are used commonly enough to require no further description. Direct measurement of potential-determining ion adsorption by potentiometric titration (19, 83a, 87) and study of the pH dependence of nonspecific adsorption are important, less commonly used methods. The IEPS may be inferred from a great variety of other measurements because much of the behavior of near-colloidal suspensions depends upon the structure of the electrical double layer which is absent or collapsed at the IEPS (83a, 129).

All of the IEPS data available to the author are summarized in Table I. The entries listed under each element are arranged chronologically, the most recent first. Whenever possible, details of sample preparation and characterization, measurement method, and experimental conditions are given. In one case details are sufficiently complex to merit special mention. Mattson and Pugh (72) prepared hydrous oxides by mixing appropriate metal salts, usually the chloride, and HCl or NaOH as necessary to vary pH in resulting suspensions. Electrophoretic velocities were measured in the same suspension after aging for approximately 12 hr. Thus the material for which the IEPS is reported has been precipitated at the IEPS and still contains whatever coprecipitated anions were present during precipitation. No attempt was made to identify the solid by X-ray diffraction. Only in the case of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were the solids chemically analyzed.

IEPS's considered questionable for any reason are set off in parentheses. In general, all of the IEPS's listed in Table I are used in the analyses to follow. However, the most basic IEPS's for  $\text{ZrO}_2$  and  $\text{ThO}_2$  are omitted because of the high probability that specific adsorption of cations has occurred in these cases. The IEPS's of  $\text{Mn}(\text{OH})_2$  and  $\text{Sn}(\text{OH})_2$  are omitted because special precautions should be taken to prevent oxidation of the hydroxides, and no such precautions are mentioned by the experimenter.

Many IEPS citations were found for the four oxide systems Al(III), Fe(III), Si(IV), and Ti(IV). When the frequency of recurrence of an IEPS among independent citations for each well-characterized material was studied ("citation frequency analysis"), several clusters of values were observed. Although, by definition, one IEPS characteristic of each different material would be expected, the average of each cluster (which includes two or more independent citations) is taken as a significant apparent IEPS for the material. This is done

because the high frequency of recurrence of the "cluster values" seems to indicate that each does indeed have real meaning. Detailed citations for each system are given in Tables II, III, IV, and V.

#### 2. Aluminum Oxides and Hydroxides

IEPS's for "amorphous"  $\text{Al}(\text{OH})_3$ , "hydrous"  $\text{Al}_2\text{O}_3$ , and for well-characterized  $\alpha$  and  $\gamma$  forms of  $\text{Al}_2\text{O}_3$ ,  $\text{AlOOH}$ , and  $\text{Al}(\text{OH})_3$  are given in Table II. A citation frequency analysis of the IEPS reported for each material was made. Replicate measurements on one material in the same laboratory were considered once. Measurements on one material in one laboratory but by several methods were considered independent.

Robinson, Pask, and Fuerstenau (103) have shown that heat treatment of synthetic  $\alpha$ - $\text{Al}_2\text{O}_3$  decreases the IEPS to a value near pH 6.7. Subsequent aging for 7 days under water led to values near 9.2. Holmes (86) found an intermediate value after an indefinite water-aging time ( $\leq 1$  day); hence, his value was rejected as failing to represent any equilibrium state of the solid. The observations on natural minerals by Schuylenborgh and Sanger (111, 112) have not been reproduced by any other group, hence are questioned but not rejected, because their method is valid (1) and IEPS's for many of their synthetic materials agree with observations by others.

IEPS determinations on amorphous materials are accepted only with reservation owing to the uncertainty of structure and to the very high probability of anion coprecipitation (124). When first precipitated, cold amorphous aluminum hydroxide is probably hydrous  $\gamma$ - $\text{AlOOH}$ . On aging cold, transition from  $\gamma$ - $\text{AlOOH}$  to  $\alpha$ - $\text{AlOOH}$  and to  $\alpha$ - $\text{Al}(\text{OH})_3$  occurs. On aging hot ( $\sim 100^\circ$ ),  $\gamma$ - $\text{AlOOH}$  crystals grow and lose adsorbed water. Thus amorphous materials are probably mixtures of hydrous  $\gamma$ - and  $\alpha$ - $\text{AlOOH}$  and  $\alpha$ - $\text{Al}(\text{OH})_3$  (124).

The average IEPS's (cluster averages) for each oxide and hydroxide of aluminum are summarized in Table I. Further discussion of these materials will appear under "Hydration" and "Effects of Impurities" below.

#### 3. Quartz and Silica Gels

IEPS citations for  $\text{SiO}_2$  are listed in Table IV. Excluding citations stating that the IEPS is less than "X" pH, natural quartz has an average IEPS of pH 2.2 and gels and sols an average of pH 1.8. The difference is probably not significant, hence an IEPS less than or equal to  $\text{pH } 2.0 \pm 0.2$  should be assumed.

### B. VARIABLES AFFECTING THE ISOELECTRIC POINT

#### 1. Gross Effects of Cationic Charge

Broad probable IEPS ranges characteristic of the cation oxidation state may be selected from Table I as shown in Chart I.

TABLE I  
 ISOELECTRIC POINTS OF OXIDES AND HYDROXIDES<sup>a,b</sup>

Material	IEPS	Comment	Investigator	Ref.
Aluminum				
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	5, 6.6, 9.2	See Table II		
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	(8.0)			
$\alpha$ -AlOOH	(7.7), 9.1			
$\alpha$ -Al(OH) <sub>3</sub>	5.0			
$\gamma$ -Al(OH) <sub>3</sub>	9.25			
Antimony				
Sb <sub>2</sub> O <sub>3</sub>	(<0.4)	un, IEPS by eo	Michaelis	75
Beryllium				
BeO (hydrous)	(10.2)	un, IEPS by eo	Michaelis	75
Cadmium				
Cd(OH) <sub>2</sub>	(>10.5)	un, ppt. from CdCl <sub>2</sub> + KOH, w, a, product Cd(OH) <sub>2</sub> or CdO(hyd), IEPS by mep.	Holmes	86
CdO	(10.4 ± 0.2)	Cd(OH) <sub>2</sub> , ig., x (contains ~5% Cd <sub>3</sub> SiO <sub>3</sub> ·2H <sub>2</sub> O), IEPS by mep.	Holmes	86
Cerium				
CeO <sub>2</sub> (hydrous)	(6.75)	un, ppt CeCl <sub>4</sub> + NaOH, IEPS by mep, in $\mu$ est. = 0.02 M	Mattson and Pugh	72
Chromium				
Cr <sub>2</sub> O <sub>3</sub> (hydrous)	(7.0)	ppt CrCl <sub>3</sub> + NaOH as descr. IEPS by mep. If 10% excess NaOH: w, IEPS = 6.49; w, a (4 mo. at room temp.), IEPS = 6.96; w, a (temp > room temp.), IEPS = 7.18. If stoichio. NaOH: w, IEPS = 6.68; w, a (4 mo. at room temp.), IEPS = 6.96; w, a (temp. > room temp.), IEPS = 7.18. If 10% deficient NaOH: w, IEPS = 7.10; w, a (4 mo. at room temp.), IEPS = 7.29; w, a (temp. > room temp.), IEPS = 7.40	Tewari and Ghosh	119
Cobalt				
Co(OH) <sub>2</sub>	(~11.4)	un, ppt CoCl <sub>2</sub> + NaOH, IEPS by mep. in $\mu$ est. = 0.01 M	Mattson and Pugh	72
Copper				
1.		Blue ppt from Cu(NO <sub>3</sub> ) <sub>2</sub> + NaOH (0°) identified by color only, w (0°), a (0°)	Holmes	86
Cu(OH) <sub>2</sub>	(9.4 ± 0.4)	un, IEPS by mep. (0°)		
CuO	9.5 ± 0.4	x, w, a (100°), a, IEPS by mep. (room temp.)		
2.		un, ppt CuCl <sub>2</sub> + NaOH, IEPS by mep. in $\mu$ est. ≤ 0.01 M	Mattson and Pugh	72
Cu(OH) <sub>2</sub> (hydrous)	(7.6)			
Iron				
1. Fe(OH) <sub>2</sub>	(12 ± 0.5)	un, IEPS by eo	Krause and Borkowska	64
2. Fe <sub>3</sub> O <sub>4</sub>	6.5 ± 0.2	Natural magnetite (Port Henry, N. Y.), dry ground only, IEPS by mep.	Iwasaki, Cooke, and Kim	54
3. Fe <sub>3</sub> O <sub>4</sub>	6.5 ± 0.2	Synth. by reduction natural Fe <sub>2</sub> O <sub>3</sub> in CO-CO <sub>2</sub> , IEPS by mep.	Iwasaki, Cooke, and Kim	54
4.		See Table III		
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	5.2, 6.7, 8.6			
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	6.7 ± 0.2			
$\alpha$ -FeOOH	6.7 ± 0.2			
$\gamma$ -FeOOH	7.4			
"Fe(OH) <sub>3</sub> " (amorph)	8.5			
Lanthanum				
La <sub>2</sub> O <sub>3</sub> (hydrous)	(10.4)	un, ppt LaCl <sub>3</sub> + NaOH, IEPS by mep. at $\mu$ est. = 0.01 M	Mattson and Pugh	72

TABLE I (Continued)

Material	IEPS	Comment	Investigator	Ref.
Lead				
1. Pb(OH) <sub>2</sub>	(9.8 ± 0.5)	un, white ppt dil. Pb(NO <sub>3</sub> ) <sub>2</sub> + NaOH, w, a, Pb(OH) <sub>2</sub> + tr PbCO <sub>3</sub> ·2Pb(OH) <sub>2</sub> (x), gave ZPC = 11.6 ± 0.2, IEPS by mep.	Holmes	86
2. Pb(OH) <sub>2</sub>	(11.0)	un, ppt Pb(NO <sub>3</sub> ) <sub>2</sub> + NaOH, IEPS by mep. at μ est. <0.01 M	Mattson and Pugh	72
Magnesium				
1. MgO	12.4 ± 0.3	Optical grade MgO (Magnovite, Norton Co.) w, d, IEPS by sp	Robinson, Pask, and Fuerstenau	103
2. Mg(OH) <sub>2</sub>	(~12)	un, ppt MgCl <sub>2</sub> + NaOH, IEPS by mep. in μ est. <0.01 M	Mattson and Pugh	72
3. Mg(OH) <sub>2</sub>	(~12)	un, IEPS by eo	Michaelis	75
Manganese				
1. Mn(OH) <sub>2</sub>	(7.0)	un, ppt MnCl <sub>2</sub> + NaOH, IEPS by mep. at μ est. <0.01 M	Mattson and Pugh	72
2. MnO <sub>2</sub>	(4-4.5)	Synth. ig. Mn(NO <sub>3</sub> ) <sub>2</sub> in air, c (HNO <sub>3</sub> ), w, d (160°) mole ratio O/Mn = 2.06, tetrag. MnO <sub>2</sub> (x), IEPS by drift	Rao	98
Mercury				
HgO	7.3 ± 0.3	ppt Hg(NO <sub>3</sub> ) <sub>2</sub> + NaOH, x, w, IEPS by mep.	Holmes	86
Nickel				
1. NiO	10.3 ± 0.4	Baker and Adamson reagent, NiO, IEPS by mep.	Holmes	86
2. Ni(OH) <sub>2</sub>	11.1 ± 0.4	ppt Ni(NO <sub>3</sub> ) <sub>2</sub> + NaOH, w, x, IEPS by mep.	Holmes	86
3. Ni(OH) <sub>2</sub>	(~12)	un, ppt NiCl <sub>2</sub> + NaOH, IEPS by mep. in μ est. = 0.01 M	Mattson and Pugh	72
Platinum				
PtO?	(≥14)	Supposed oxide film on Pt in 1 atm. O <sub>2</sub> , IEPS est. from pH dependence of Pt-O <sub>2</sub> electrode.	Kruyt	83b
Plutonium				
1. PuO <sub>2</sub>	9.0	Sulfate ig. (850°), IEPS by mep.	Sowden and Francis	118
2. PuO <sub>2</sub>	8.6-8.9	Oxalate ig. (500-900°), ground, IEPS by mep.	Sowden and Francis	118
Silicon				
1. SiO <sub>2</sub>	2.2	Natural α-SiO <sub>2</sub> (quartz) }	See Table IV	
2. SiO <sub>2</sub> (hydrous)	1.8	SiO <sub>2</sub> sols and gels }		
Thorium				
1. ThO <sub>2</sub>	9.0-9.3	ppt oxalate from nitrate at room temp. to 70°, ig. (900-1100°), grind, IEPS by mep.	Sowden and Francis	118
2. ThO <sub>2</sub>	(8.5-11)	un, ppt Th(NO <sub>3</sub> ) <sub>4</sub> + NaOH, w, d (100°), IEPS est. ads. (Na <sup>+</sup> , Cl <sup>-</sup> )	Amphlett, MacDonald, and Redman	3
3. ThO <sub>2</sub>		ppt oxalate from nitrate, ig. (20 hr. at 400° then 70 hr. at 900°), store CO <sub>2</sub> free, IEPS by mep. in μ indic.	Anderson	6
	(9.5)	μ = 10 <sup>-4</sup> M KCl, uncertain only because IEPS est. by scaling figure		
	(8)	μ = 10 <sup>-3</sup> M KCl		
	(4.2)	μ = 10 <sup>-2</sup> M KCl		
4. ThO <sub>2</sub>	(6.85)	un, ppt Th(NO <sub>3</sub> ) <sub>4</sub> + NaOH, IEPS by mep. in est. μ ~ 0.04 M	Mattson and Pugh	72
Tin				
1. SnO (hydrous)	(6.6)	un, ppt SnCl <sub>2</sub> + NaOH, IEPS by mep.	Mattson and Pugh	72
2. SnO <sub>2</sub>	7.3	Mineral cassiterite, c, w, d (120°), IEPS by mep.	Johansen and Buchanan	56
3.		SnO <sub>2</sub> synth. HNO <sub>3</sub> + Sn(metal) 80°, product w	Johansen and Buchanan	56

TABLE I (Continued)

Material	IEPS	Comment	Investigator	Ref.
SnO <sub>2</sub> (hydrous)	4.5	IEPS by mep., material as descr.		
SnO <sub>2</sub>	5.5	SnO <sub>2</sub> (hyd) ig. (850°, 2 hr. in air), IEPS by mep.		
4. SnO <sub>2</sub>	(8.5)	Mineral cassiterite, c, w, d (120°), IEPS by sp	Johansen and Buchanan	55
5. SnO <sub>2</sub>		Three natural cassiterites g, w, d (110°), IEPS by sp	O'Connor and Buchanan	79
	4.7	74.6% Sn, low Fe		
	(9.5)	75.8% Sn, high Fe, "soluble base" present		
	4.7	75.4% Sn, low Fe		
6. SnO <sub>2</sub> (hydrous)	(3.9)	un, ppt SnCl <sub>4</sub> + NaOH, IEPS by mep. in est. $\mu \sim 0.01 M$	Mattson and Pugh	72
Titanium				
1. TiO <sub>2</sub>	(3.5), 4.7	Natural rutile	} See detailed citations in Table V	
2. TiO <sub>2</sub>	4.7, 6.2	Synthetic rutile, anatase		
Tungsten				
1. WO <sub>3</sub> (hydrous)	(0.5)	ppt Na <sub>2</sub> WO <sub>4</sub> + HCl, IEPS by mep.	El Wakkad and Rizk	27
2. WO <sub>3</sub> (hydrous)	(<0.3)	un, IEPS by eo	Michaelis	75
Uranium				
1. UO <sub>2</sub> -U <sub>3</sub> O <sub>8</sub>		Samples synth. thermal decomp. ammonium diuranate + H <sub>2</sub> -H <sub>2</sub> O(g) mixt. at temp. indic., ground, w, IEPS by sp.	Pravdic and Sotman	96
	5.8 ± 0.2	ig. (600°), cool in 3 hr., oxygen to uranium mole ratio (O/U) = 2.00, str. cubic by x		
	4.7 ± 0.2	ig. (600°), water quenched, O/U = 2.00		
	6.6 ± 0.3	ig. (600°), O/U = 2.08, cubic by x		
	6.0 ± 0.2	ig. (600°), O/U = 2.33, inhomogeneous		
	3.5 ± 0.2	ig. in air to U <sub>3</sub> O <sub>8</sub> then in H <sub>2</sub> -H <sub>2</sub> O to O/U = 2.45		
2. UO <sub>2</sub> -U <sub>3</sub> O <sub>8</sub>	3.0 ± 0.2 and 4.5 ± 0.5	Two samples of natural uraninite, O/U ~2.3, ground, w, a, IEPS by sp (see also Figure 1)	Parreira and Ottewill	88
3. U <sub>3</sub> O <sub>8</sub>	(4)	Synth. w, a, IEPS by sp	Parreira and Ottewill	88
Yttrium				
Y <sub>2</sub> O <sub>3</sub> (hydrous)	(8.95)	un, ppt Y(NO <sub>3</sub> ) <sub>3</sub> + NaOH, IEPS by mep.	Mattson and Pugh	72
Zinc				
1. ZnO		ppt ZnCl <sub>2</sub> + NaOH at 100°, refluxed with H <sub>2</sub> O 10 days, w, x, tr SiO <sub>2</sub> major impurity, IEPS by ti	Ray and de Bruyn	101
	9.2	$\mu \leq 10^{-2} M NaCl$		
	8.7	$\mu \leq 10^{-2} M NaNO_3$		
2. ZnO	(9.0 ± 0.3)	Oxidized zinc metal, IEPS by drift	Herczyńska and Prószyńska	48
3. ZnO	9.3 (9.2-9.7)	ppt Zn(NO <sub>3</sub> ) <sub>2</sub> + NaOH, w, a, x, IEPS by mep.	Holmes	86
4. ZnO (hydrous)	(10.3)	un, ppt ZnCl <sub>2</sub> + NaOH, IEPS by mep.	Mattson and Pugh	72
Zirconium				
1. ZrO <sub>2</sub>	(10-11)	un, ppt ZrO(NO <sub>3</sub> ) <sub>2</sub> + NaOH, w, d (100°), IEPS est. ads. (Na <sup>+</sup> , Cs <sup>+</sup> , Cl <sup>-</sup> )	Amphlett, Macdonald and Redman	3
2. ZrO <sub>2</sub>	(4)	un, natural mineral, IEPS by eo	Verwey	123
3. ZrO <sub>2</sub> (hydrous)	(6.7)	un, ppt Zr(NO <sub>3</sub> ) <sub>4</sub> + NaOH, IEPS by mep. in est. $\mu \sim 0.02 M$	Mattson and Pugh	72

<sup>a</sup> Abbreviations: ads., IEPS estimated as pH at which adsorption of indifferent positive ions equals that of negative ions (48, 83a); a, aged or stored in distilled water for period indicated (if known); c, sample cleaned by leaching in concentrated HCl or other acid indicated; co, IEPS estimated as pH of maximum rate of coagulation of a suspensoid (129); d, sample dried  $\leq 100^\circ$  or as indicated, stored dry; di, sample cleaned by dialysis; drift, IEPS estimated as pH at which suspension pH does not drift from that at which it was made. Usually oxide is precipitated at initial pH of test (83a); eo, electroendosmosis or electroosmosis (83a); ig., sample ignited at temperature indicated; un, exact identification of solid missing. Structure or composition inferred from author's statement or sample history; mep., microelectrophoresis (1, 83a); ppt, sample prepared by precipitation using solutions of salts indicated; sp, IEPS estimated as pH of zero streaming potential or current; sub, IEPS estimated as pH of maximum subsidence rate of a coagulated suspension (129); ti, IEPS estimated as pH at which adsorption of H<sup>+</sup> is equal to that of OH<sup>-</sup> as determined by potentiometric titration of a suspension;  $\mu$ , total salt concentration during IEPS measurement; w, sample washed in water, usually by decantation, until free of Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>, etc.; x, sample identified by X-ray diffraction; ( ), citations in parentheses are estimates based on insufficient or inadequately reported data or reports of experiments using poorly characterized solids. <sup>b</sup> Unless otherwise noted, the only foreign ions present in the systems reported are either Na<sup>+</sup> or K<sup>+</sup> and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>.

TABLE II  
ISOELECTRIC POINTS OF ALUMINUM OXIDES AND HYDROXIDES<sup>a</sup>

IEPS	Description	Investigator	Ref.
$\alpha\text{-Al}_2\text{O}_3$			
1. 9.1-9.2	Synth. $\alpha\text{-Al}(\text{OH})_3$ ig. (1000-1350°), x, w, di, a (>2 days, 0.1 M KCl), w, IEPS by sp in $\mu = 10^{-8}$ M KCl	Koz'mina, Belova, and Sannikov	63
2. 6.4-6.7 9.1-9.5	$\alpha\text{-Al}_2\text{O}_3$ , Linde A abrasive (Linde Air Products Co.) ig. (600-1400°), a ( $\leq 1$ day)	Robinson, Pask, and Fuerstenau	103
3. 7.7	All non-ig. and ig. ( $\leq 1000^\circ$ ) samples after a ( $\text{H}_2\text{O}$ , 7 days), x, c, w, IEPS by sp, $\mu \leq 10^{-2}$ M KCl	Yopps and Fuerstenau	129
9.1	ig. (1400°), a ( $\text{H}_2\text{O}$ , 7 days), etc.		
9.0-9.1	Same basic material as 2		
9.1	x, c, w, a (7 days), IEPS by ti, $\mu = 10^{-3}$ - $10^{-1}$ M KCl		
4. 7.5-8.2	x, c, w, a (7 days), IEPS by sub, $\mu = 10^{-3}$ - $10^0$ M KCl	Holmes	86
9.1	x, c, w, a (7 days), IEPS by mep., $\mu = 10^{-3}$ M KCl, $\text{KNO}_3$ , and $\text{KClO}_4$ separately		
5. 10 9.8 $\pm$ 0.2	Flame-fused synthetic sapphire, ground in mullite ware, not cleaned, a ( $\leq 1$ day), x, IEPS by mep.	Herczyńska and Prószyńska	48
6. 6.7	"Chromatographic $\text{Al}_2\text{O}_3$ used as received"	Dobiáš, Spurný, and Freudlová	24
7. 8.4	IEPS by ads. $\text{H}^+$ , $\text{OH}^-$		
8. (9.4)	IEPS by drift	Johansen and Buchanan	56
9. a. 2.3 b. 3.0	Synthetic sapphire, c, w, d (120°), IEPS by eo	Johansen and Buchanan	55
	Natural corundum, c, w, d (120°)	Modi and Fuerstenau	76
	IEPS by mep.	Schuylenborgh and Sängner	112
	0.94% $\text{SiO}_2$ , IEPS by sp		
	Flame-fusion sapphire (Linde Air Products Co.), c, w, a, IEPS by sp		
$\gamma\text{-Al}_2\text{O}_3$			
1. 7.4-8.6	Synth. $\alpha\text{-Al}(\text{OH})_3$ ig. (300-800°), x, w, di, a (>2 days, 0.1 M KCl), w, IEPS by sp in $\mu = 0.001$ M KCl	Koz'mina, Belova, and Sannikov	63
2. (8.0)	$\gamma\text{-Al}_2\text{O}_3$ prepared by thermal treatment and aging of the hydrolysis product of Al ethylate, IEPS by mep.	Fricke and Keefer	31
$\alpha\text{-AlOOH}$ (Boehmite)			
1. 7.7	Synth. $\text{Al}(\text{OH})_3$ ig. (300°), di, a (>2 days in 0.1 M KCl), w, IEPS by sp in $\mu = 0.001$ M KCl, x	Koz'mina, Belova, and Sannikov	63
2. (<2)	Natural bauxite, x, di, d, IEPS by mep.	Schuylenborgh and Sängner	112
3. 8.8	Synthetic $\alpha\text{-AlOOH}$ , x, w, di, d, IEPS by mep.	Schuylenborgh	111
4. 9.4	Synth. from $\text{AlCl}_3 + \text{NH}_4\text{OH}$ at 18°	Fricke and Keefer	31
	Synth. from $\text{Na}_3\text{AlO}_3$ ( $c_1$ and $c_2 = 100c_1$ ) + $\text{CO}_2$		
	Synth. boehmite, prepared by thermal treatment and aging of the hydrolysis product of purified Al ethylate, IEPS by mep.		
$\gamma\text{-AlOOH}$ (Diaspore)			
1. (<2)	Natural diaspore, x, di, d, IEPS by mep.	Schuylenborgh and Sängner	112
2. 7.5	Synthetic diaspore, x, di, d, IEPS by mep.	Schuylenborgh	111
	Synth. at 70° from $\text{AlCl}_3 + \text{NH}_4\text{OH}$ , product $\alpha\text{-AlOOH} + \text{tr } \gamma\text{-Al}(\text{OH})_3$		
	Synth. from $\text{Na}_3\text{AlO}_3 + \text{CO}_2(\text{g})$		
$\alpha\text{-Al}(\text{OH})_3$ (Gibbsite, Hydrargillite)			
1. 3.8-5.0	Synth. $\alpha\text{-Al}(\text{OH})_3$ (3.8) and same ig. (200°) (5.0), di, a (>2 days in 0.1 M KCl), x, w, IEPS by sp	Koz'mina, Belova, and Sannikov	63
2. 5.0, 5.2	Natural gibbsite (two samples), di, d, IEPS by mep.	Schuylenborgh and Sängner	112
3. 4.9	Synth. by aging $\text{Na}_3\text{AlO}_3(\text{aq})$ , di, d, x, IEPS by mep.	Schuylenborgh	111
$\gamma\text{-Al}(\text{OH})_3$ (Bayerite)			
1. 9.3 $\pm$ 0.2	$\gamma\text{-Al}(\text{OH})_3$ , synth. by hydrolysis of purified $\text{Al}(\text{OC}_2\text{H}_5)_3$ , x, w, a, IEPS by mep.	Korpi and Holmes	86
2. 7.5	Synthetic materials, x, w, di, d, IEPS by mep.	Schuylenborgh	111
	Synth. from $\text{AlCl}_3 + \text{NH}_4\text{OH}(\text{aq})$ at 70°		
3. 9.2	Synth. from $\text{Na}_3\text{AlO}_3(\text{aq}) + \text{CO}_2(\text{g})$	Fricke and Keefer	31
	$\gamma\text{-Al}(\text{OH})_3$ , synth. by hydrolysis of purified $\text{Al}(\text{OC}_2\text{H}_5)_3$ or related compounds, IEPS by mep.		

TABLE II (Continued)

IEPS	Description	Investigator	Ref.
	In buffers IEPS shifts as follows: glyco coll (9.00), borate (6.78), acetate (5.59), phosphate (4.05), citrate (2.4). Buffer concentrations not given	Fricke and Leonhardt	32
	Amorphous $Al_2O_3$		
1.	ppt $AlCl_3(aq) + NaOH$ as described, IEPS by mep., IEPS given in parentheses. If 10% excess NaOH; w (5.08), a (4 mo. room temp.) (5.78); a (temp. > room temp.) (6.79); if stoichio. NaOH, w (6.63), a (4 mo., room temp.) (7.06); a (temp. > room temp.) (7.28); if 10% deficient NaOH, w (7.29), a (4 mo., room temp.) (7.32); a (temp. > room temp.) (7.43)	Tewari and Ghosh	120
2. 8.0	Unaged product of hydrolysis of very pure aluminum ethylate, IEPS by mep.	Fricke and Keefer	31
3.	ppt from $AlCl_3$ or $Al_2(SO_4)_3$ with NaOH adjusted to fix final pH. IEPS by mep. without washing (see text)	Mattson	71
8.0 ± 0.2	In solid, mole ratio $Cl/Al_2O_3$ ca. 0.005		
7.5 ± 0.2	In solid, mole ratio $SO_4/Al_2O_3$ ca. 0.074		

\* For meaning of abbreviations see footnotes, Table I.

 TABLE III  
 ISOELECTRIC POINTS OF IRON(III) OXIDES AND HYDROXIDES<sup>a</sup>

IEPS	Description	Investigator	Ref.
	Natural $\alpha$ - $Fe_2O_3$ (Hematite)		
1.	Hematite	Joy, Watson, and Cropton	58
5.7	IEPS by sp		
5.4	IEPS by ti		
2. (4.5-5.0)	c, w, a, IEPS by ti and suspension effect (83a)	Chwastiak	20
3. 6.6 ± 0.2	Specular hematite (Labrador), <sup>b</sup> c, then ground in mullite ware, w, a, IEPS by mep., two independent observations: 6.6, 6.7	Holmes and Feeney	86
4. 6.7 ± 0.1	Mineral selected, ground, w, IEPS by mep.	Iwasaki, Cooke, and Choi	51
5. 6.9 ± 0.2	Same sample described under 3, <sup>b,c</sup> c, w, a, IEPS by sp, $\mu = 10^{-4} M KNO_3$	Korpi	59
6. (4.2)	Mineral c, w, d (120°), IEPS est. from sp data	Johansen and Buchanan	55
7. 6.7	Mineral c, w, d (120°), IEPS by mep.	Johansen and Buchanan	56
8. (2.2)	Mineral x, c, w, di, d, IEPS by mep.	Schuylenborgh and Sanger	112
	Synthetic $\alpha$ - $Fe_2O_3$		
1.	All materials synth. by 100° hydrolysis and aging under reflux conditions of $Fe(NO_3)_3$ solution, w, a, x, IEPS by ti ( $H^+$ , $OH^-$ ) unless otherwise noted		
a. 8.7 ± 0.1	$\mu \leq 1.0 M$ , 4 determinations, once each in $NaNO_3$ , $NaCl$ , $NaClO_4$ , $Na_2SO_4$ , 25°	Albrethson	2
8.85 ± 0.2	0.005 M $NaNO_3$ , IEPS by suspension effect (83a)		
b. 9.04 ± 0.05	$\mu = 0.001-0.10 M KNO_3$ , 25°	Korpi	59
c. 9.03 ± 0.05	$\mu \leq 0.01 M KNO_3$ , 21°	Parks and de Bruyn	85, 87
8.77	$\mu = 1.0 M KNO_3$ , 21°		
8.7 ± 0.2	$\mu = 0.01-0.10 M KNO_3$ , 38°		
2.	Baker and Adamson reagent grade <sup>d</sup> $Fe_2O_3$ (synth. by ignition of $Fe(SO_4)_3$ in air or $O_2$ ), w, a, x		
8.4 ± 0.1	IEPS by ti at 21°, $\mu \leq 0.1 M KNO_3$	Parks	85
8.0 ± 0.2	IEPS by mep.	Miaw	74
3.	Starting materials synth. $FeNH_4(SO_4)_2 + NH_4OH$ , w (5% $NH_4NO_3$ ), w, IEPS by mep.	Johansen and Buchanan	56
8.0	ppt as described		
6.5	ppt, d, ig. (850°, 2 hr.)		
4. 1.9	Synth, x, w, di, d (105°), IEPS by mep.	Schuylenborgh and Sanger	112
5. 8.3	$Fe_2O_3$ sol synth. $FeCl_3 + NH_4OH$ , w, a ( $H_2O$ , 150-160° at ~5 atm.), IEPS by mep.	Toelstra and Kruyt	121
	$\gamma$ - $Fe_2O_3$		
1. 6.7 ± 0.2	Synth. by ppt $FeOOH$ , ig. to $Fe_2O_3$ , x (tr. $\gamma$ - $FeOOH$ ), w, IEPS by mep.	Iwasaki, Cooke, and Kim	54

TABLE III (Continued)

IEPS	Description	Investigator	Ref.
$\alpha$ -FeOOH (Goethite)			
1. 6.1 $\pm$ 0.1	Samples, w (H <sub>2</sub> O only), x, IEPS by sp, analyzed <sup>a</sup>	Flaningham	30
2. 6.7 $\pm$ 0.2	w (H <sub>2</sub> O <sub>2</sub> ), w (H <sub>2</sub> O), analyzed, <sup>f</sup> IEPS by sp	Iwasaki, Cooke, and Colombo	52
3. 3.2	Mineral, x, w, di, d (105°), IEPS by mep.	Schuylenborgh and Sanger	112
4. 6.7	Colloidal $\alpha$ -FeOOH, synth. by aging hydroxide from FeCl <sub>3</sub> + NaOH in 3 M NaClO <sub>4</sub> , IEPS by mep.	Lengweiler, Buser, and Feitknecht	67
5.	Samples synth. several ways involving different reagents, concentrations, and rates. Histories leading to more ordered structures (X-ray diffraction) lead to more acid IEPS, x, w, di, d, IEPS by mep. Analyses and DTA given in original paper	Schuylenborgh, Arens, and Kok	110, 113
5.9-7.2	Sample not dried after washing		
6.0-6.8	d (60°)		
4.2-6.8	d (105°)		
$\gamma$ -FeOOH (Lepidocrocite)			
1. 7.4 $\pm$ 0.2	Natural lepidocrocite, w (H <sub>2</sub> O <sub>2</sub> ), w (H <sub>2</sub> O) anal, <sup>g</sup> IEPS by mep.	Iwasaki, Cooke, and Kim	54
2.	Samples synth. in several ways. Details same as item 5, under " $\alpha$ -FeOOH." More ordered structures give more acid IEPS	Schuylenborg, Arens, and Kok	110, 113
5.4-7.3	Samples not dried before study		
6.6	d (60°)		
5.3-5.7	d (105°)		
Hydrous or Poorly Characterized Fe <sub>2</sub> O <sub>3</sub> and "Amorphous Hydroxides"			
1. (7)	"Hydroxide" IEPS est. by ads. (Zn <sup>2+</sup> , Co <sup>2+</sup> )	Zhabrova and Egorov	131
2.	Synth. Fe(NO <sub>3</sub> ) <sub>3</sub> + NH <sub>4</sub> OH, IEPS by mep.	Schuylenborg, Arens, and Kok	110, 113
8.5	w, di, not dried		
6.0	w, di, d (60°)		
4.3	w, di, d (105°)		
3. 8.6	Fe <sub>2</sub> O <sub>3</sub> sol by hydrolysis FeCl <sub>3</sub> , di (5 days, 90°), a, IEPS by mep.	Hazel and Ayres	47
4.	ppt from FeCl <sub>3</sub> or Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> with NaOH adjusted to fix pH, IEPS by mep. without washing (see text)	Mattson	72
7.2	Mole ratio Cl/Fe <sub>2</sub> O <sub>3</sub> in solid is 0.005		
7.0	Mole ratio SO <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub> in solid is 0.014		
5. (8.8 $\pm$ 0.5)	IEPS by eo	Michaelis	75

<sup>a</sup> See footnotes, Table I, for abbreviations. <sup>b</sup> 99.77% Fe<sub>2</sub>O<sub>3</sub>, 0.05% FeO, 0.09% SiO<sub>2</sub>, same material used by Korpi (59). <sup>c</sup> Washed in hot alcoholic KOH, hot H<sub>2</sub>O, HNO<sub>3</sub> in Soxhlet extractor for 3 hr., H<sub>2</sub>O in Soxhlet for 3 days, stored in dist. H<sub>2</sub>O. <sup>d</sup>  $\leq$ 0.2% insol.,  $\leq$ 0.2% SO<sub>4</sub><sup>2-</sup>,  $\leq$ 0.005% Cu, Zn. <sup>e</sup> 2.4% SiO<sub>2</sub>, 1.7% Al<sub>2</sub>O<sub>3</sub>, 1.3% P<sub>2</sub>O<sub>5</sub> (30). <sup>f</sup> 58.73% Fe, 2% SiO<sub>2</sub>, 0.46% Mn, 10.25% H<sub>2</sub>O (400°), 11.24% H<sub>2</sub>O (800°). <sup>g</sup> 56.62% Fe, 10.5% H<sub>2</sub>O, 0.93% insol.

CHART I

M <sub>2</sub> O	IEPS > pH 11.5
MO	8.5 < IEPS < 12.5
M <sub>2</sub> O <sub>3</sub>	6.5 < IEPS < 10.4
MO <sub>2</sub>	0 < IEPS < 7.5
M <sub>2</sub> O <sub>3</sub> , MO <sub>2</sub>	IEPS < 0.5

The ranges include oxides, hydrous oxides, oxyhydroxides, hydroxides, and superficially hydrated or hydrous oxides. The term "hydrous" will be used in a generic sense to include any or all of these materials except "anhydrous" oxides.

Several factors help to explain the broad range of IEPS in each group. Among these are differences in hydration state, purity, and cation radius. The role of each of these factors in fixing the IEPS will be discussed in the paragraphs to follow and an equation will be developed relating the IEPS to the charge to radius ratio of the cation in the pure solid.

## 2. Effects of Hydration

Several groups (55, 56, 80, 103, 110-113) have independently studied the relationship between IEPS and sample history and agree in their conclusions that treatment likely to lead to bulk or surface dehydration results in a more acid IEPS than is observed for materials likely to be hydrated. The data from Table I which most clearly involve materials of differing hydration state are summarized in Table VI.

The average IEPS increase accompanying hydration for the materials listed in Table VI is about two pH units. This conclusion is in apparent conflict with the results of Koz'mina, Belova, and Sannikov (63). However, their samples were aged for several days in 0.1 M KCl, and the more acid IEPS observed with increasing hydration probably reflects increasing replacement of OH<sup>-</sup> by Cl<sup>-</sup> as well. The effects of impurities on IEPS will be discussed in the next section.



TABLE IV

ISOELECTRIC POINTS OF SiO <sub>2</sub> <sup>a</sup>				
IEPS	Description	Investigator	Ref.	
α-SiO <sub>2</sub> (Quartz)				
1. 1.5	Brazilian crystal, ground, c (HCl in Soxhlet extractor), w (8 hr., H <sub>2</sub> O in Soxhlet), a, IEPS by mep.	Bhappu	10	
1.8	Crystals from Harding Mine, N. M., ground c, w, a, IEPS by mep.	Bhappu	10	
2. 2.5 ± 0.2	Natural crystals (Mont.), c, w, a, IEPS by mep.	Iwasaki, Cooke, and Choi	53	
3. 2.2-2.8	Quartz from a beach sand (E. H. Sargent Co.), c, w, a, IEPS by sp, IEPS = 2.8 after ample aging at test pH (≤2 days)	Flaningham	30	
4.	All samples Brazilian crystal, ground in a fused quartz disk grinder after c (HCl), w	Li	68	
(2.3)	IEPS by ads. (Na <sup>+</sup> , I <sup>-</sup> )			
2.0	IEPS by sp in HCl only			
(1-2)	IEPS by sp in 10 <sup>-4</sup> M NaCl			
2.7-3	IEPS by ti			
5. <3	Quartz ground, c, w, d (120°), IEPS by mep.	O'Connor and Buchanan	81	
6. 3.7	Brazilian crystal, ground, c, w, a, IEPS by sp	Gaudin and Fuerstenau	36	
SiO <sub>2</sub> Sols and Gels				
1. 2-3	pH of minimum gelation rate	Moulik and Ghosh	78	
2.	Sols synth. Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O (1%) + HCl for precalc. pH (20°)	deBoer, Linsen, and Okkerse	15, 82	
1-2	IEPS by location of viscosity minima. Younger gels IEPS close to pH 2, older closer to pH 1			
1-1.5	1% SiO <sub>2</sub> sols, di, IEPS by mep.			
(2)	pH of minimum gelation rate			
3. 1.3	pH of minimum gelation rate	Sen and Ghosh	114	
4. 2.8-3	pH of minimum gelation rate	Hückel	49	
5. (~0.5)	IEPS by eo	Michaelis	75	

<sup>a</sup> See footnotes, Table I, for abbreviations.

TABLE V

ISOELECTRIC POINTS OF TiO <sub>2</sub> <sup>a</sup>				
IEPS	Description	Investigator	Ref.	
Natural TiO <sub>2</sub> (Rutile)				
1. 4.7 ± 0.2	Sample from N. C., ground, w, x (tr Fe <sub>2</sub> O <sub>3</sub> ), IEPS by mep.	Feeney	86	
2. 3.5 ± 0.2	c (H <sub>2</sub> SO <sub>4</sub> , HCl), w, IEPS by sp	Graham and Madeley	44	
3. 4.8	c (HCl), w, d (120°), IEPS by mep.	Johansen and Buchanan	56	
4. 5.5	c, w, d (120°), IEPS by sp	Johansen and Buchanan	55	
Synthetic TiO <sub>2</sub>				
1. 6.7 ± 0.1	High purity synthetic rutile (National Lead Co.) c (HCl in Soxhlet extractor), w (8 hr., H <sub>2</sub> O in Soxhlet), a (H <sub>2</sub> O), IEPS by sp in μ ≤ 10 <sup>-3</sup> M NaCl	Purcell and Sun	97	
2. 6.0 ± 0.3	Average observed by two operators for several samples including reagent grade TiO <sub>2</sub> (anatase), TiO <sub>2</sub> (hydrous rutile), x, s, w, a, IEPS by mep.	Feeney and Holmes	86	
3.	Samples synth. hydrolysis TiCl <sub>4</sub> at 100° hydrous rutile, w, a, IEPS by mep.	Johansen and Buchanan	56	
6.0	As described			
4.7	d, ig. (1000° in air, 2 hr.)			
4. (4.8)	un, synth. TiCl <sub>4</sub> + NaOH, IEPS by mep. in μ est. 0.02 M (see text)	Mattson and Pugh	72	

<sup>a</sup> See footnotes, Table I, for abbreviations.

Lacking direct characterization of the surfaces of oxide materials used for IEPS work, it has been necessary to infer the probable hydration state from sample history.

On exposure to water an anhydrous oxide can become "hydrated" in several ways: (1) physical adsorption of water molecules including hydrogen bonding to surface oxygen ions but not dissociation; (2) chemisorption of water which dissociates, resulting in surface -MOH groups; and (3) reaction resulting in conversion to an oxyhydroxide or hydroxide, *e.g.*, MgO → Mg(OH)<sub>2</sub> (102). Many anhydrous oxides do not

TABLE VI

VARIATION OF IEPS WITH HYDRATION				
Compound	IEPS	Compound	IEPS	ΔIEPS
Fe <sub>2</sub> O <sub>3</sub>	6.7	Fe <sub>2</sub> O <sub>3</sub> (hydrous)	8.6	1.9
Al <sub>2</sub> O <sub>3</sub>	6.7	Al <sub>2</sub> O <sub>3</sub> (hydrous)	9.2	2.5
TiO <sub>2</sub>	4.7	TiO <sub>2</sub> (hydrous)	6.2	1.5

hydrate completely to produce the hydroxide. In some cases the hydroxide is thermodynamically unstable [Hg(OH)<sub>2</sub>, Cu(OH)<sub>2</sub>], and in others the hydrated compound is stable but the reaction rate is very slow (Fe<sub>2</sub>O<sub>3</sub> → FeOOH (117), Al<sub>2</sub>O<sub>3</sub> → α-Al(OH)<sub>3</sub> (124), etc.). Strong ignition reduces the hydration rates by chemi-

sorption for, *e.g.*, SiO<sub>2</sub> (14), and by total reaction for MgO (102) and decreases the solubility. Mechanical disturbance, *e.g.*, by grinding, leads to an amorphous or disturbed layer with increased solubility, *e.g.*, SiO<sub>2</sub> (122), and increased surface hydration, *e.g.*, Al<sub>2</sub>O<sub>3</sub> (55).

If oxide precipitates form by progressive hydrolysis, polymerization, and oxolation (104, 126), it can be expected that they would retain a superficial layer of more hydrous material which would be lost only on drying and ignition. While it is well established that very high temperatures are needed to remove the last MOH groups from silica gels and that persistent MOH groups are present in other oxides (130), direct evidence of persistent hydrous films is lacking in most cases; however, there is at least some evidence for the presence of hydrous films on Fe<sub>2</sub>O<sub>3</sub> (86, 87) and ZrO<sub>2</sub> (21) prepared by hydrolysis. For Fe<sub>2</sub>O<sub>3</sub>, the solid was identified as hematite by X-ray diffraction, yet DTA and infrared absorption experiments yielded evidence for traces of FeOOH (86).

Detailed study of sample preparation for the Al(III) and Fe(III) materials for which IEPS data are summarized in Table I makes possible several generalizations.

All of the oxides and hydrous oxides of aluminum apparently slowly hydrate (in a matter of days) to the extent that at least a film of material with the properties of Al(OH)<sub>3</sub> results. Amorphous Al(OH)<sub>3</sub> has the same characteristics as the crystalline modifications. The IEPS characteristic of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at equilibrium with water is probably about pH 9.2. All other values presently available for this material seem to represent metastable or impure states.

Ignited and natural Fe<sub>2</sub>O<sub>3</sub> samples appear to hydrate quickly to the extent that their surfaces have the properties of  $\alpha$ -FeOOH. The more basic IEPS of  $\gamma$ -FeOOH can probably be attributed to the effect of the less stable structure.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hydrates no further in reasonable time.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> prepared by hydrolysis and not subsequently dried at high temperature has the IEPS of hydrous or amorphous Fe<sub>2</sub>O<sub>3</sub> and apparently retains a coating or film of hydrous material as predicted above. Fe<sub>2</sub>O<sub>3</sub> with IEPS near pH 5 apparently remains hydrated to a lesser extent than FeOOH, perhaps only physically adsorbing water.

The change in IEPS accompanying changes in hydration has been interpreted in terms of the dependence of the acid strength of surface MOH groups on the O<sup>2-</sup>/OH<sup>-</sup> ratio by O'Connor, Johansen, and Buchanan (80) and by Robinson, Pask, and Fuerstenau (103). Similar arguments have been used to interpret the strengths of the oxyacids, MO<sub>m</sub>(OH)<sub>n</sub> (77, 89). In the latter case an increase in the ratio,  $m/n$ , is said to result in an effective increase in  $Z/r$ , the ratio of cationic charge to radius, and consequently in acid strength. Increased acid strength (or decreased IEPS) could equally well be explained in terms of the increased electrostatic

bond strength which must accompany an increase in  $m/n$  (89). The original articles should be consulted for details.

### 3. Effects of Impurities

Purposeful investigations of the effects of impurities on the IEPS are few. Because many systems in which the IEPS is studied provide ample opportunity for contamination by adsorption or reaction, the subject is quite important. Abramson, Moyer, and Gorin (1) pointed out that the "real" IEPS could be measured only in the absence of all ions other than hydrogen, hydroxyl, and those which are components of the solid. In discussing the origin of charge on organic colloids they listed the following charging processes: (1) dissociation, particularly acid-base dissociation of surface groups such as -COOH, -SiOH; (2) specific adsorption of ions onto otherwise neutral sites (tendencies toward ion-pair formation, hydrogen bonding, and "specific interactions" such as are responsible for complex formation in solution were mentioned as possible "driving forces" for specific adsorption); (3) oriented adsorption of polar molecules such as H<sub>2</sub>O with subsequent adsorption of ions by 1 or 2 above; (4) weak specific adsorption of ions by induced polarization of the substrate (image force bonding).

Mechanisms 2-4 may be called specific adsorption, using the term in the sense used by Grahame (45) to denote any tendency toward interaction other than the simplest electrostatic case. It is assumed that perchlorate, nitrate, and chloride ions do not interact with oxide surfaces in any specific sense and that the charging process characteristic of oxides in aqueous suspension is either acid-base dissociation or specific adsorption of metal hydroxo complexes. The effects of other ions will be classified as impurity effects.

Overbeek (83c) has pointed out that specific adsorption of anions would be expected to produce a negative surface charge under conditions otherwise identical with the IEPS. Should this occur on an oxide surface, the pH at which zero surface charge was observed would be lowered; *i.e.*, the apparent IEPS would be shifted to a more acid pH because increased H<sup>+</sup> adsorption would be necessary to neutralize the anion's negative charge. A structural anionic impurity would be expected to produce an acid shift as well because the M-anion-H surface group would in most cases be a stronger acid than -MOH.

Both adsorbed and structural cationic impurities present before measurement of the IEPS would be expected to shift the IEPS in the direction of the IEPS of the impurity hydroxide. Extensive evidence has been given (26) for cation adsorption on silica gel by ion exchange with H<sup>+</sup> from -SiOH sites. In addition to an IEPS shift in the direction of the appropriate oxide, slight nonequivalence of M<sup>+</sup>/H<sup>+</sup> exchange would also

TABLE VII  
 EFFECTS OF IMPURITIES ON IEPS

A. Structural Impurities (Present in Solid before Experiments)				
Substrate	Impurity	Impurity level, mole %	$\Delta$ IEPS <sup>a</sup>	Ref.
Al <sub>2</sub> O <sub>3</sub> (hydrous)	SO <sub>4</sub> <sup>2-</sup>	~7.4	≥ -0.5	72
	Cl <sup>-</sup>	~0.5	~0	72
Fe <sub>2</sub> O <sub>3</sub> (hydrous)	SO <sub>4</sub> <sup>2-</sup>	~1.4	-1.6	72
Fe <sub>2</sub> O <sub>3</sub> (anhydrous)	SO <sub>4</sub> <sup>2-</sup>	~0.3	-0.2 to -0.6	74, 85
Fe <sub>2</sub> O <sub>3</sub> (hydrous)	Cl <sup>-</sup>	~0.5	≤ -1.4	72
SiO <sub>2</sub> (ignited gel)	Al <sub>2</sub> O <sub>3</sub> (coprecip.)	Var., <40% Al <sub>2</sub> O <sub>3</sub>	$\Delta = 0.12$ (mole % Al <sub>2</sub> O <sub>3</sub> )	56
SnO <sub>2</sub> (mineral)	Fe <sub>2</sub> O <sub>3</sub> + "soluble base"	Unknown	<+4.7	79
B. Adsorbed Impurities (Present in Electrolyte before Experiments)				
Substrate	Impurity	Impurity level, M	$\Delta$ IEPS <sup>a</sup>	Ref.
Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	~5 × 10 <sup>-6</sup>	~-4	21
Al <sub>2</sub> O <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	~3 × 10 <sup>-4</sup>	-2.9	76
ThO <sub>2</sub>	Cl <sup>-</sup>	~10 <sup>-3</sup>	-1.2	6
ThO <sub>2</sub>	Cl <sup>-</sup>	~10 <sup>-2</sup>	-5.0	6
TiO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	~10 <sup>-3</sup>	-0.7	97
TiO <sub>2</sub>	Ca <sup>2+</sup>	~10 <sup>-4</sup>	+0.3	97
		> 10 <sup>-4</sup>	>+4.8	97
$\alpha$ -FeOOH	La <sup>3+</sup>	10 <sup>-5 b</sup>	+1.4	30
$\alpha$ -FeOOH	La <sup>2+</sup>	10 <sup>-4 b</sup>	+2.0	30
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Na dodecyl sulfate	~3 × 10 <sup>-5</sup>	Est. -5.4	76
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Na cetyl sulfate	~2 × 10 <sup>-6</sup>	Est. -2	79
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Dodecylamine	2 × 10 <sup>-5</sup>	+0.05	58
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Dodecylamine	6 × 10 <sup>-5</sup>	+0.10	58
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Dodecylamine	10 × 10 <sup>-5</sup>	+0.25	58
$\alpha$ -SiO <sub>2</sub>	DTAB <sup>c</sup>	2 × 10 <sup>-6</sup>	Est. +5	81
$\alpha$ -SiO <sub>2</sub>	<sup>d</sup>	<sup>d</sup>	Est. +4.5 ± ~1.5)	36
$\alpha$ -SnO <sub>2</sub>	Na cetyl sulfate	2 × 10 <sup>-6</sup>	Est. -0.7	79
$\alpha$ -TiO <sub>2</sub> (rutile)	Na oleate	~10 <sup>-3</sup>	-3.7	97

<sup>a</sup>  $\Delta$ IEPS > 0 indicates basic shift of IEPS. <sup>b</sup> FeOOH equilibrated with La(NO<sub>3</sub>)<sub>3</sub> solution then rinsed once before mep. <sup>c</sup> DTAB = dodecyltrimethylammonium bromide. <sup>d</sup> Each of the alkylamine acetates, C<sub>8</sub> (~10<sup>-1</sup> M), C<sub>10</sub> (~3 × 10<sup>-3</sup> M), C<sub>12</sub> (3 × 10<sup>-4</sup> M), C<sub>14</sub> (~10<sup>-4</sup> M), and C<sub>16</sub> (2 × 10<sup>-5</sup> M) give the indicated  $\Delta$ IEPS.

be expected to produce a shift by the same mechanism discussed for anions; *i.e.*, should the equivalents of H<sup>+</sup> lost exceed the equivalents of M<sup>2+</sup> adsorbed, the IEPS would shift to a more acid pH.

The effects of various structural or adsorbed impurities on the IEPS's of several oxides are summarized in Table VII. The expected shifts are observed.

Specific adsorption of dissociable species exceeding a monolayer can be expected to shift the IEPS to or toward that of the adsorbate. The best example is the adsorption of proteins (1, 12) which shifts the IEPS completely to that characteristic of the adsorbate in each case.

#### 4. Nonstoichiometry, Defect Structures, and Semiconductors

Pravdic and Sotman (96) reported the only work that has been done on variation of IEPS with reasonably well-defined deviations from stoichiometry. The variation of IEPS with the mole ratio of oxygen to uranium (O/U) in the series UO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> is shown in Figure 1. The data of Parreira and Ottewill (88) with natural pitchblende (intermediate between UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>) have been plotted on the same figure using an O/U ratio (= 2.3) reported (84) for material from the

same source. The IEPS shifts acid as the oxidation state increases, as would be predicted from the change in Z/r ratio. The points marked "calculated" in Figure 2 were obtained using Eq. 2c to be developed below.

It might be expected that simple heat treatment of some oxides, such as TiO<sub>2</sub>, SnO<sub>2</sub>, and MnO<sub>2</sub>, would result in superficial loss of oxygen and, consequently, nonstoichiometry. This has been observed for TiO<sub>2</sub> (34) and interpreted as production of Ti<sub>2</sub>O<sub>3</sub> in the surface. A shift of IEPS in the direction appropriate for the oxidation state produced would be expected quite apart from dehydration effects because the average Z/r changes. There is at present very little evidence in support of this point. However, a preliminary attempt (86) gave the following results which do show the correct trend.

Precipitated TiO <sub>2</sub> (hydrous rutile)	IEPS = 6.0 ± 0.3
Ppt. heated to 975°, 2 hr.	IEPS = 6.3 ± 0.2
Ppt. heated in 10% H <sub>2</sub> , 975°, 0.5 hr.	IEPS = 6.3 ± 0.5
Ppt. heated in 10% H <sub>2</sub> , 975°, 2 hr.	IEPS = 7.4 ± 0.2

The loss of oxygen and IEPS shift could be explained equally well by assuming that oxygen vacancies and n-type semiconductivity result from heat treatment. An n-type semiconductor would be expected to exhibit

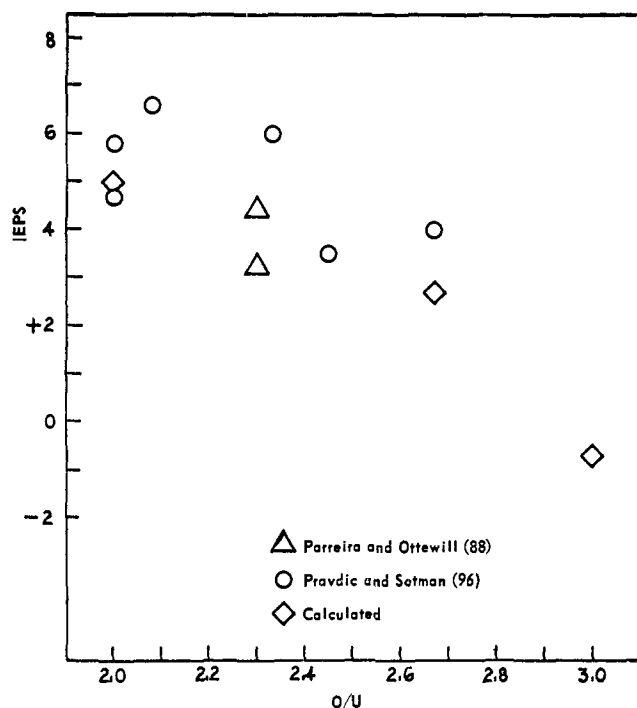


Figure 1.—The effect of composition on the IEPS of uranium oxides.

a more basic IEPS than predicted for the stoichiometric oxide owing to stabilization of adsorbed  $H^+$  by mobile electrons. Similarly p-type semiconductors might be expected to exhibit a more acid IEPS than predicted owing to repulsion of  $H^+$  or stabilization of adsorbed  $OH^-$ . These effects on the IEPS have apparently not been studied to any significant extent.

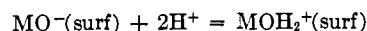
The hydrous oxides precipitated from metal salt solution are defect structures containing a high concentration of structural defects and excess  $H_2O$  in addition to coprecipitated ions (124). Schuylenborgh, Arens, and Sanger (110–113) in a painstaking study of aluminum and iron oxides and hydroxides were able to show that any feature of sample history leading to increased crystal perfection (observed by X-ray diffraction line narrowing) leads to decreased IEPS. As discussed under "Effects of Hydration," substitution of  $H_2O$  for  $O^{2-}$  or  $OH^-$  would be expected to shift the IEPS to a more basic pH. A cation vacancy should have the same effect because hydrogen ions would be accepted to make up the charge deficiency resulting in an increased effective  $OH^-/O^{2-}$  ratio. Presumably, aging results in loss of excess molecular  $H_2O$  and combination of substitutional  $H^+$  with excess  $OH^-$  to form  $H_2O$  which is subsequently lost (122, 124) resulting in the acid shift of IEPS observed.

### C. VARIATION OF IEPS WITH CATIONIC SIZE AND CHARGE

#### 1. An Electrostatic Model

In examining the IEPS data to detect expected trends with cationic size and charge, advantage has

been taken of the postulated analogous dissociation behavior of surface  $-MOH$  groups and dissolved molecular hydroxides and oxyacids. Kossiakoff and Harker (62, 77) found it possible to quantitatively account for the strength of oxyacids using a purely electrostatic model of the acid dissociation process. The important variables are the formal charge of the cation, the number of nonhydroxyl oxygen ions ( $m/n$  or the hydration state), and the geometrical arrangement of the ions (77). A similar but less thoroughly developed analysis based on the amphoteric dissociation model for the origin of surface charge has been found useful. Equilibrium between positive and negative surface sites involving  $2H^+$ , *i.e.*



is assumed to involve primarily the electrostatic work gained by the approach of  $2H^+$  to  $MO^-$ . As a first approximation, each ion (the two hydrogen ions are treated as a doubly positive entity) is assumed a point charge separated from the others by average oxide ionic radii (46) (the radius of  $O^{2-}$  is taken as 1.40 Å.) in a linear array. The free energy involved is then (9a, 62)

$$-\Delta F = \frac{-2Z_H Z_O (e^-)^2}{\epsilon(r_O)} + \frac{2Z_H Z_+ (e^-)^2}{\epsilon(2r_O + r_+)} + \Delta F' = RT \ln K \quad (\text{Eq. 1})$$

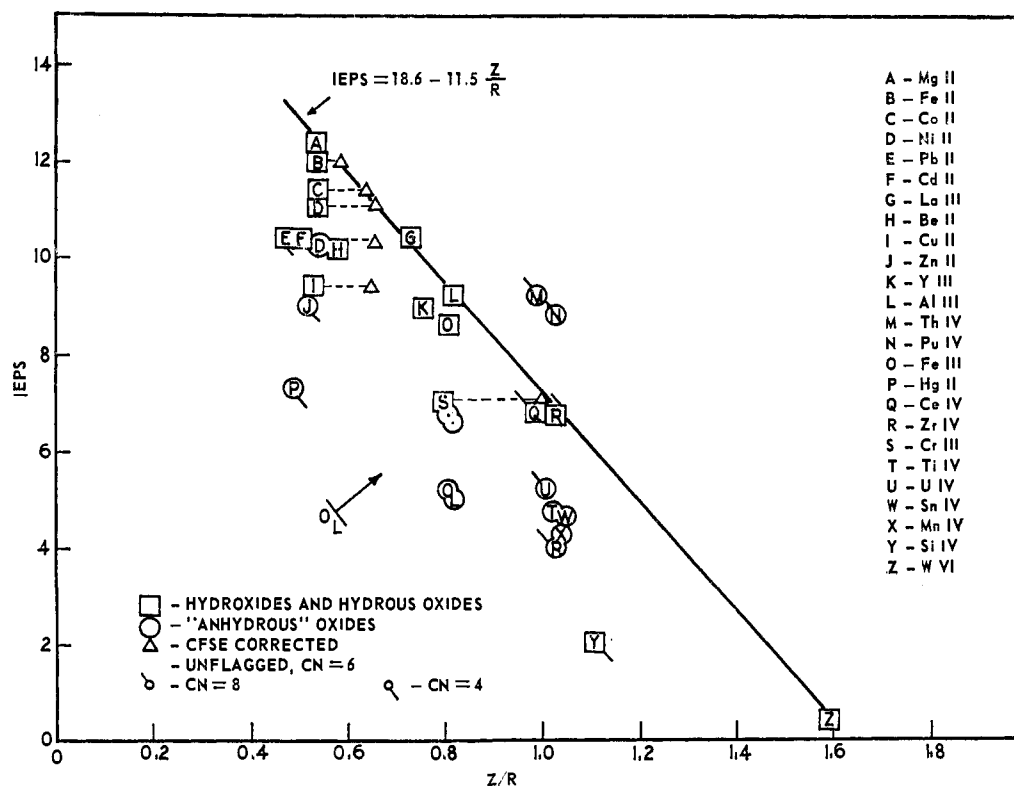
or, since

$$K = \frac{(MOH_2^+)}{(H^+)^2(MO^-)} = \frac{1}{(H^+)^2} \quad (\text{if pH} = \text{IEPS})$$

$$\text{IEPS} = A - B(Z/R) - D\Delta F' \quad (\text{Eq. 2})$$

where  $\Delta F'$  = non-Coulombic contributions to the hydrogen ion binding energy;  $A, B, D$  = constants;  $Z$  = ionic charge of species indicated by subscript  $H = H^+, O = O^{2-}, + = \text{cation}$ ;  $\epsilon$  = appropriate dielectric constant of water;  $e^-$  = electronic charge;  $r$  = ionic radius,  $R = 2r_O + r_+$ ;  $()$  = ionic concentration or activity. Equation 2 predicts that the IEPS should vary linearly with  $Z/R$ , increasing as  $Z/R$  decreases. The prediction is roughly verified in Figure 2, a plot of IEPS *vs.*  $Z/R$ .

Such a simple electrostatic model cannot apply accurately for several reasons: (1) Crystal field effects increase the stability of the  $M-OH$  bond (9b), decreasing the IEPS by reducing the basicity of the group. The crystal field stabilization energy (CFSE) contributes to the term  $\Delta F'$  in Eq. 1. (2) The contributions of additional coordinating anions constitute a different constant term for each coordination number. (3) The value of  $A$  in Eq. 2 is different for each value of the ratio  $m/n$  of nonhydroxyl to hydroxyl oxygens. The exact hydration state of solids for which IEPS's are available is usually not known; hence, it is possible only to consider two extremes, hydrous and anhydrous, using the term "hydrous" in the generic sense described earlier.


 Figure 2.—The relationship between IEPS and  $Z/R$ .

It is feasible to account for these effects analytically, but this refinement is unwarranted at present. Instead, the constants  $A$  and  $B$  of Eq. 2 will be evaluated separately for each coordination number and hydration extreme, and the CFSE correction will be evaluated for each transition metal ion by analogy with calculations of simple electrostatic and CFSE terms in the hydration energies of these ions.

## 2. Coordination Number Six and Crystal Field Effects

Among IEPS values for the hydroxides and hydrous oxides with coordination number six (125, 127) the IEPS's of  $\text{Al}_2\text{O}_3(\text{hyd})$  and  $\text{MgO}(\text{hyd})$  are most trustworthy. These two oxides require no crystal field correction and are the least likely to involve important covalent bonding. The constants in Eq. 2, evaluated using these two points are:  $A = 18.6$ ;  $B = 11.5$ . Equation 2 is plotted in Figure 2. The points representing  $\text{La}_2\text{O}_3(\text{hyd})$ ,  $\text{Fe}_2\text{O}_3(\text{hyd})$ , and  $\text{WO}_3(\text{hyd})$  which also involve no large CFSE correction fall very close to the line, indicating that the equation is valid over 12 orders of magnitude in  $\text{H}^+$  concentration.

As expected, the IEPS's of the transition metal hydroxides are not described by Eq. 2 in this form. The crystal field contributions to the hydration energies of these ions have been calculated (9b,c). The CFSE in the hexaquo ions corresponds to a weak crystal field. The field is still weaker if the cation is coordi-

nated with  $\text{OH}^-$  rather than  $\text{H}_2\text{O}$  (9b,d). Hence the relative magnitudes of CFSE should be the same in the hydroxides as in the hexaquo ions. We will assume that the crystal field contribution to the OH binding energy in the hydroxides and hydrous oxides, etc., is proportional to that calculated for the hexaquo ions. The appropriate energies, scaled from figures in Basolo and Pearson (9c), are listed in Table VIII.

Equation 2 may be rewritten to take the CFSE into account as

$$\text{IEPS} = A - B(Z/R) - C(\text{CFSE}) \quad (\text{Eq. 2a})$$

or

$$\text{IEPS} = 18.6 - 11.5 \left[ \frac{Z}{R} + \frac{C}{11.5} (\text{CFSE}) \right] \quad (\text{Eq. 2b})$$

The quantity  $(C/11.5)(\text{CFSE})$  in Eq. 2b may be regarded as an effective change in  $Z/R$  necessary to account for the CFSE contribution to  $\Delta F$ . The constant  $(C/11.5)$  was arbitrarily evaluated using the IEPS for  $\text{Ni}(\text{OH})_2$ . The result,  $(C/11.5) = 0.0029$ , was then used to calculate  $(Z/R)_{\text{eff}}$  for the other transition metals, in some cases making possible predicted values where no measurements are available. The results are summarized in Table VIII. The validity of this approach is amply demonstrated by comparison of columns 6 and 7 in Table VIII and study of Figure 2. In Figure 2, plotting IEPS against  $(Z/R)_{\text{eff}}$  brings the points for all the hydrous transition metal oxides or

TABLE VIII  
 CRYSTAL FIELD CORRECTIONS TO  $(Z/R)_{\text{eff}}$ 

Ion	Approx. CFSE for $M^{2+}(\text{H}_2\text{O})_6$ , kcal. (9c)	$\Delta(Z/R)^a$	$Z/R$ (4b)	$(Z/R)_{\text{eff}}^b$	Predicted IEPS <sup>c</sup> for hydroxide or hydrous oxide	Measured IEPS (hydrous materials)
Mn <sup>2+</sup>	0	0	0.54	0.54	12.4	...
Mn <sup>3+</sup>	42	0.12	0.79	0.91	8.1	...
Fe <sup>2+</sup>	18	0.05	0.54	0.59	11.8	12
Fe <sup>3+</sup>	0	0	0.81	0.81	9.3	8.6 <sup>e</sup>
Co <sup>2+</sup>	33	0.10	0.54	0.64	11.2	11.4
Co <sup>3+</sup>	42	0.12	(0.81) <sup>d</sup>	(0.93)	7.9	...
Ni <sup>2+</sup>	42	0.12	0.54	0.66	[11.0] <sup>f</sup>	[11.1]
Ni <sup>3+</sup>	(30)	0.09	(0.81)	(0.90)	8.6	...
Cu <sup>2+</sup>	39	0.11	0.53	0.64	11.2	9.4
Sc <sup>3+</sup>	0	0	0.77	0.77	11.2	...
Cr <sup>2+</sup>	72	0.20	(0.50)	(0.70)	10.6	...
Cr <sup>3+</sup>	70	0.20	0.80	1.00	7.1	7.0
V <sup>2+</sup>	73	0.21	(0.54)	0.75	10.0	...
V <sup>3+</sup>	39	0.11	0.78	0.89	8.4	...
Ti <sup>2+</sup>	68	0.19	(0.53)	(0.72)	10.3	...
Ti <sup>3+</sup>	30	0.09	0.78	0.87	8.6	...

<sup>a</sup>  $\Delta(Z/R) = 0.0029(\text{CFSE})$ . <sup>b</sup>  $(Z/R)_{\text{eff}} = Z/R + \Delta(Z/R)$ . <sup>c</sup> From Eq. 2b. <sup>d</sup> Entries in parentheses are estimates. <sup>e</sup>  $\sim 9.0$  for  $\text{Fe}_2\text{O}_3$  from nitrate hydrolysis, see Table III. <sup>f</sup> Entries in brackets were used to evaluate constants in Eq. 2b.

hydroxides except that for  $\text{Cu}(\text{OH})_2$  onto the line representing Eq. 2a.

While the coordination number (CN) of Cu(II) in the hydroxide has been assumed to be six in accord with the structures of several oxyhalides (125b), the hydroxide is unstable relative to the oxide in which Cu(II) is found in square-planar oxygen coordination (125b). The CFSE for Cu(II) in square-planar coordination should be larger than has been used for octahedral coordination (9c), hence the failure of this one point to correlate with  $(Z/R)_{\text{eff}}$  can be understood.

We have seen that oxide IEPS's are more acidic than the corresponding hydroxides or hydrous materials. A straight line of slope 11.5 can be fitted to the points representing oxides with CN = 6. Its intercept,  $A = 16.5$ , reflects the average IEPS difference between oxides and hydroxides of about 2 pH units observed in Table VI.

### 3. Coordination Number Four

The hydrous and "anhydrous" materials with CN = 4 can be fairly well represented by Eq. 2a if  $A$  has the values 16.0 and 13.9, respectively. Thus the average IEPS shift due to hydration is about 2.1 pH units as it is for CN = 6. The average difference in IEPS between materials of CN = 6 and those with the same  $Z/R$  but with CN = 4 is about 2.6 pH units.

### 4. Coordination Number Eight

Because additional anions increase the binding energy of  $\text{H}^+$  to the  $-\text{MOH}$  group, a change of CN from 6 to 8 should increase the IEPS. The IEPS's for "anhydrous"  $\text{ThO}_2$  and  $\text{PuO}_2$  can be accounted for by assigning  $A \cong 20.7$ .

The data for  $\text{CeO}_2$ ,  $\text{UO}_2$ , and  $\text{ZrO}_2$  are better described by Eq. 2b if  $A = 18.6$  as for hydrous materials of CN

= 6. Inasmuch as the description of these materials indicates that  $\text{UO}_2$  and  $\text{ZrO}_2$  should be classed among "anhydrous" materials, the assignment of a value to  $A$  for this entire group must remain tentative.

### 5. Summary

In order to make possible a convenient graphical test of the validity of Eq. 1 and 2 they can be expressed in the alternate forms

$$\text{IEPS} = A_{\text{eff}} - 11.5[Z/R + 0.0029(\text{CFSE})] \quad (\text{Eq. 2c})$$

and

$$\text{IEPS} = 18.6 - 11.5[Z/R + 0.0029(\text{CFSE}) + a]$$

or

$$\text{IEPS} = 18.6 - 11.5(Z/R)_{\text{eff}} \quad (\text{Eq. 2d})$$

where

$$(Z/R)_{\text{eff}} = [Z/R + 0.0029(\text{CFSE}) + a]$$

Changes in  $A$  arising from changes in CN or hydration are expressed as an effective change in  $Z/R$  in Eq. 2d.

The IEPS's are plotted vs.  $(Z/R)_{\text{eff}}$  in Figure 3. In roughly 67% of the cases plotted, the experimental IEPS falls within 1 pH unit of the line representing Eq. 2d. In all cases the IEPS predicted with Eq. 2c is within 0.5 pH unit of the maximum observed value.

From the success of Eq. 2d it is concluded that a simple electrostatic model describes quite well the mechanism by which "oxide" surfaces are charged in aqueous solutions and that Eq. 2c, with appropriate values of  $A$ , may be used with reasonable confidence to predict the IEPS of simple oxide materials. Predictions involving CN = 8 should be made with reservations. The values of the constants  $A$  and  $a$  appropriate for each coordination number are summarized in Table IX.

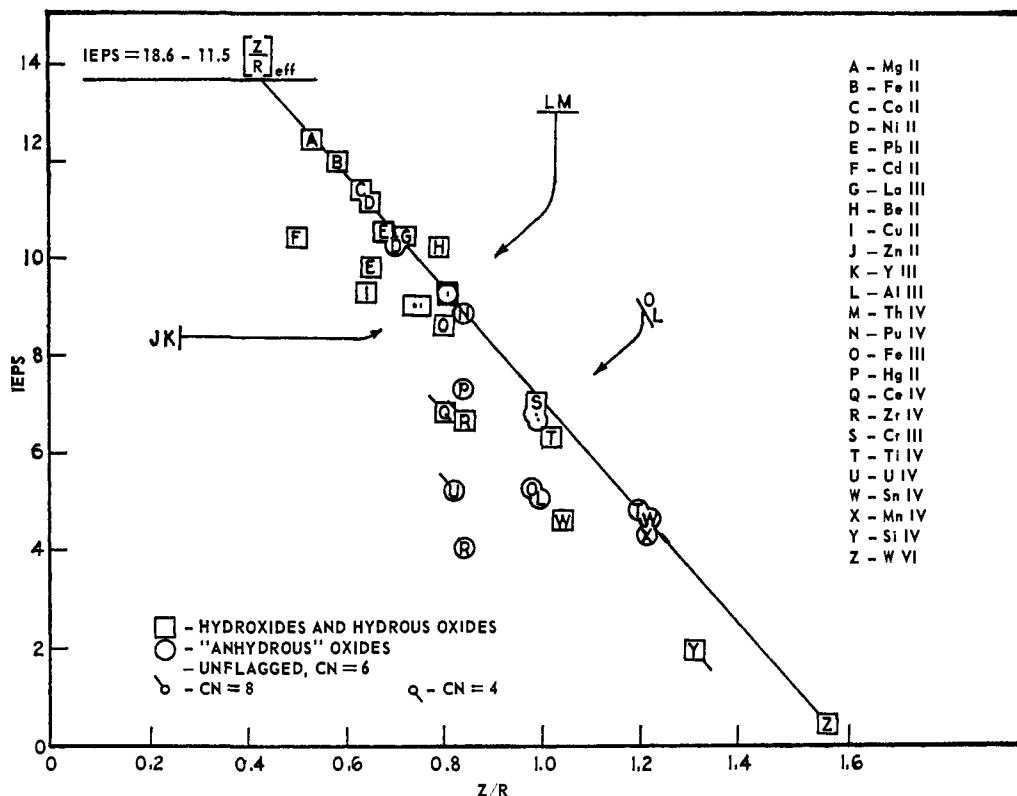


Figure 3.—The relationship between IEPS and  $(Z/R)_{eff}$ , illustrating corrections for crystal field effects, coordination, and hydration.

TABLE IX  
CORRELATION CONSTANTS  $A_{eff}$  AND  $a$

State of hydration	Coordination number of corresponding oxide		
	4	6	8
Hydroxides, oxyhydroxides, hydroxy oxides, superficially hydrated or hydroxy oxides	$A_{eff} = 16.2$ $a = 0.21$	$A_{eff} = 18.6$ $a = 0.0$	...
"Anhydrous" oxides	$A_{eff} = 14.1$ $a = 0.39$	$A_{eff} = 16.5$ $a = 0.18$	$A = 20.7$ $a = -0.18$

### III. THE ISOELECTRIC POINTS OF AQUEOUS HYDROXY COMPLEX SYSTEMS

The stability constants for a number of metal hydroxy complexes were collected and used to calculate the complex isoelectric points (IEP) and several other equivalence points (EP) for each system. An equivalence point (EP) is the pH at which any selected pair of positive and negative ions have equivalent concentrations. The selected ions, if hydroxy complexes, are indicated simply by a pair of numbers in parentheses, the first indicating the ionic charge of the positive ion, the second the charge of the negative ion. EP(1,1) or EP(+,-) is the pH at which  $(M^{z+}(OH)_{z-1}^+) = (M^{z+}(OH)_{z+1}^-)$  and, because the concentrations of other species are small, is usually essentially equal to the IEP. The pH of minimum solubility, the pHMS, is identical with the IEP. The EP(4,1) is the pH at

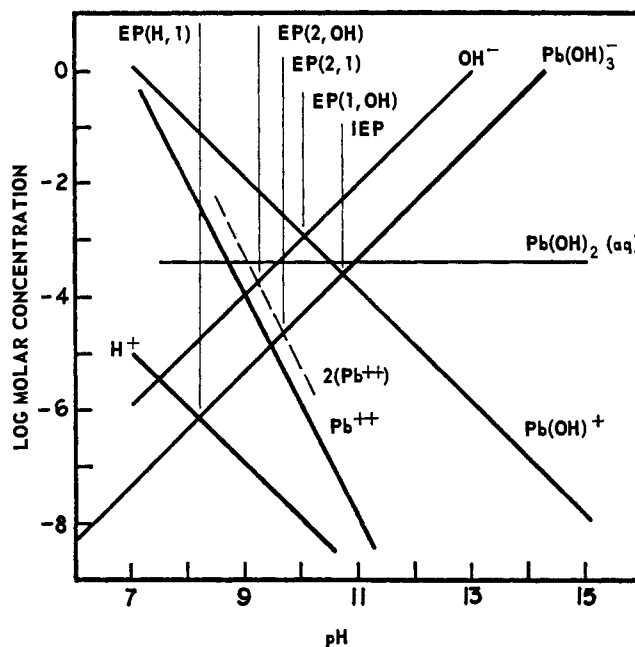


Figure 4.—pH dependence of the concentrations of lead hydroxy complexes in equilibrium with solid PbO (red) and definition of several equivalence points (EP).

which  $4(M^{z+}(OH)_{z-4}^{+4}) = (M^{z+}(OH)_{z+1}^-)$ . The EP(3,OH) is the pH at which  $3(M^{z+}(OH)_{z-3}^{+3}) = (OH^-)$ . The relationships among the IEP's and the various EP's are illustrated in Figure 4 where the concentrations of mononuclear hydroxy complexes in equilibrium

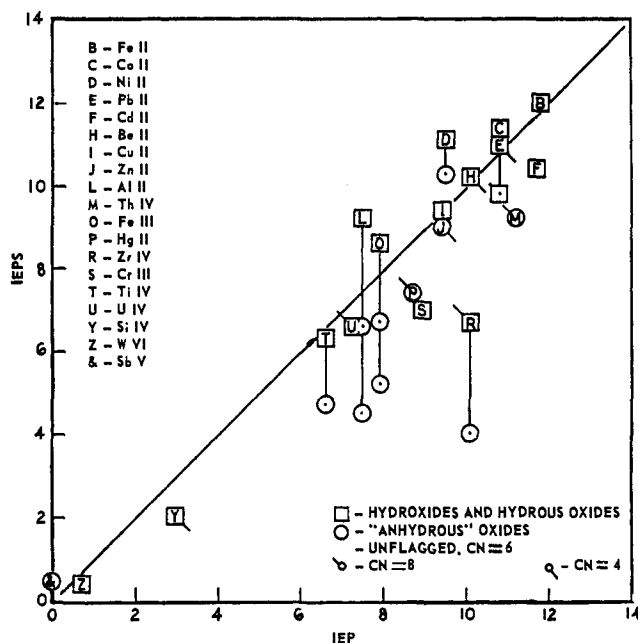


Figure 5.—The relationship between IEPS and IEP.

with PbO are plotted as functions of pH. The IEP's and EP's are collected in Table X. In the first and second columns the IEP and EP(2,1) extremes resulting from consideration of all cited literature are given as the lower entry for each element. A preferred value is given as the upper entry. These were selected by assuming Feitknecht and Schindler (29) standard and selecting additional data where necessary from authors they had chosen. Failing in this, an author was chosen who reported a  $K$  very near one selected by Feitknecht and Schindler as well as one sought, usually  $K_s(z_{+1})$ . In other columns the meaning of multiple entries is the same unless indicated otherwise.

#### IV. COMPARISON OF THE ISOELECTRIC POINTS OF SOLIDS WITH THOSE OF HYDROXO COMPLEX SYSTEMS

##### A. GENERAL OBSERVATIONS

The IEPS's are compared with corresponding IEP's in Figure 5. It is obvious that the two quantities are related, especially for the hydrous oxides and hydroxides; however, detailed comparison of each IEPS and all of the corresponding EP's immediately reveals that in many cases the IEPS is more closely approximated by an EP other than the IEP. Table XI lists the materials studied in groups according to the EP which most closely matches the IEPS. Where several IEPS's are reported in Table I, the value selected for comparison in Table XI is given in parentheses.

After study of the properties of the materials in each group several trends emerge: (a) all materials for which  $IEPS = IEP$  are hydrous and most have  $CN = 6$  (those in this group with  $CN \neq 6$  have  $CN = 4$  and  $r_+ < 1.0 \text{ \AA.}$ ); (b) with the exception of HgO, the

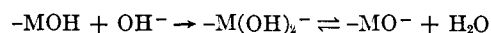
materials for which  $IEPS = EP(1,OH)$  are either hydrous with  $CN = 4$  and  $r_+ > 1.0 \text{ \AA.}$  or are "anhydrous" oxides which rehydrate very slowly once thoroughly dehydrated; (c) materials for which  $IEPS \approx EP(2,OH)$  are all "anhydrous" oxides which in most cases exhibit at least one other IEPS.

##### B. ADSORPTION AND IDENTIFICATION OF POTENTIAL-DETERMINING SPECIES

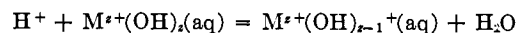
The observations of the previous paragraph can be explained if it is postulated that: (a)  $H^+$ ,  $OH^-$ , and all hydroxo complexes present play important roles in establishing surface charge and are potential-determining ions (PDI) (45); (b) all hydroxo complexes adsorb onto oxide materials physically with about equal equilibrium constants in each case; and (c)  $H^+$  and  $OH^-$  adsorb physically or nondissociatively on some materials and chemically or dissociatively on others. Dissociative adsorption involves dissociation of surface  $-MOH$  groups, e.g.



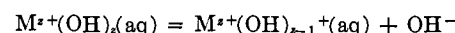
and



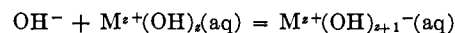
with equilibrium constants determined by the cation  $M$  and assumed nearly equal to those for the analogous reactions



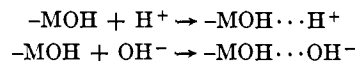
or



and

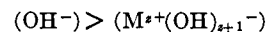


Nondissociative or physical adsorption involves no dissociation of surface  $-MOH$  groups and is assumed to be governed by equilibrium constants nearly equal to those for adsorption of hydroxo complexes and the same for  $H^+$  and  $OH^-$ . The adsorption reactions can be represented by



The IEPS is thus equal to the IEP if the PDI, as determined by relative concentrations, is any pair among  $H^+$ ,  $OH^-$ ,  $M^{z+}(OH)_{z-1}^+$ , and  $M^{z+}(OH)_{z+1}^-$ , provided  $H^+$  and  $OH^-$  adsorb dissociatively. The equivalence of  $H^+$  and  $M^{z+}(OH)_{z-1}^+$  as PDI arises because development of a positive site by surface dissociation or by formation in solution and subsequent adsorption of a monopositive complex are indistinguishable processes.

The near equality of IEPS and IEP for materials in column 1, Table XI, and the fact that for most systems



and

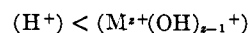




TABLE X

## ISOELECTRIC POINTS AND EQUIVALENCE POINTS FOR SEVERAL HYDROXO COMPLEX SYSTEMS

	IEP or EP(1,1)	EP(2,1)	EP(1,OH)	EP(2,OH)	EP(3,1) and others	Ref.
Al(III) <sup>a</sup>	7.5 (6.2-7.7)	6.2	7.2 $\alpha$ -Al(OH) <sub>3</sub> and Al-OOH 7.7 amorph	5.8	5.9	4, 8, 13, 17, 23 25, 29, 33, 42, 65 73, 94, 105, 107 37, 93
Sb(III)	6-6.5	.....	.....	.....	.....	93
Sb(V)	~0	.....	.....	.....	.....	13, 29, 65
Be(II)	10.1 (9.9-10.4)	(6.6-7.9)	9.8 (inact.) 10.2 (act.)	6.6 7	.....	13, 29, 41, 70, 128
Cd(II)	11.7 (11.4-12.3)	11.1 (10.8-11.3)	9.3 (act.)	9.4 (inact.) 9.6 (act.)	.....	13, 28, 29, 65
Cr(III) <sup>b</sup>	8.4 (8.2-9.3)	8.1 (7.8-8.6)	8.2	7.8	6.5-7.0	13, 29, 116
Co(II) <sup>b,c</sup>	10.8 (8.9-11.8)	10.5 (7.8-11.3)	8.2 (pink Co(OH) <sub>2</sub> ) 9.0 (blue)	8.9 9.4	.....	13, 29, 65, 90, 128
Cu(II)	9.4 (9.4-10.1)	9.0 (8.9-9.3)	7.6	7.3 (CuO) 7.9 (Cu(OH) <sub>2</sub> )	.....	13, 29, 40, 65
Fe(II) <sup>d</sup>	12.4 (11.3-12.4)	10.8 (10.5-11.5)	9.9 (inact.) 10.4 (act.)	9.1 9.5	.....	11, 29, 40, 66, 109, 128
Fe(III) <sup>e</sup>	8.0 (7.4-8.4)	6.4 (5.6-6.7)	4.7 ( $\alpha$ -FeOOH) 5.7 ("act. Fe(OH) <sub>3</sub> ")	4.8-4.9	3.5 ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> ) 4.0 ( $\alpha$ -FeOOH) 4.5 ("act. Fe(OH) <sub>3</sub> ")	13, 29, 65, 94, 128
Pb(II) <sup>f</sup>	10.8 (10.6-11.1)	9.5 (9.4-9.8)	10.0 (red PbO) 10.1 (yw PbO) 10.3 (Pb(OH) <sub>2</sub> )	8.9 9.0 9.1	.....	13, 29
Mn(II)	11.8	11.3	9.6	9.7	.....	13, 29
Hg(II)	8.6 (8.4-9.4)	7.1 (6.8-7.2)	(6.3-7.1)	5.6	.....	49, 95, 115
Mo(VI) <sup>g,h</sup>	(0.9-1.5)	.....	.....	.....	.....	13, 16, 29, 94, 95, 116
Ni(II) <sup>i</sup>	9.4 (7.9-10.3)	9.8 (8.8-10.4)	8.6 (act.) 7.4 (inact.)	8.4 9.2	.....	13, 14, 18 29, 57
Si(IV) <sup>k</sup>	(2.8-3.2)	.....	.....	.....	EP(H,1) = 5.2-5.7	60
Ag(I)	12.1 (12-12.2)	.....	.....	.....	.....	50
Sr(II) <sup>i</sup>	12.9	.....	.....	.....	.....	13, 29, 38
Te(IV) <sup>k</sup>	(3.8-4.2)	.....	.....	.....	.....	13, 22, 29, 35
Th(IV)	~11.2	~8.9	~7.8	~6.4	.....	18, 29, 65, 69, 94
Sn(II)	7.3 (6.4-7.3)	5.8 (5.2-5.8)	7.1	5.4	.....	13, 39, 43
Ti(IV) <sup>k</sup>	6.6 (6.6-7.1)	5.6 (5.5-5.8)	-0.8 (rutile) 4.7 (amorph.)	0.4 3.7	.....	27, 106
U(VI) <sup>l</sup>	(9.0-9.8)	(7.3-7.8)	(7.7-8.0)	6.7	.....	27, 49
V(V) <sup>o,m</sup>	(1.0-2.5)	.....	.....	.....	.....	13, 29, 91, 92, 108
W(VI) <sup>o,m</sup>	(0.4-1.0)	.....	.....	.....	.....	13, 29, 61, 65, 94
Zn(II) <sup>n</sup>	10.0 (8.7-10.6)	9.4 (8.6-9.8)	8.6 (ZnO) 9.5 (Zn(OH) <sub>2</sub> amorph.)	8.5 (ZnO) 9.0 (Zn(OH) <sub>2</sub> amorph.)	.....	13, 29, 61, 65, 94
Zr(IV) <sup>o</sup>	(9.8-10.5)	(7.2-7.6)	7.5	5.5	.....	

<sup>a</sup> Several values of IEP are available as pHMS data estimated graphically. For  $\gamma$ -Al(OH)<sub>3</sub>, 7.7 (42); for "amorph. Al(OH)<sub>3</sub>," 7.3 (73); for  $\alpha$ -Al(OH)<sub>3</sub>, 6.3 (127); for "bauxite," 7.2 (73); for  $\gamma$ -AlOOH, 6.5-7 (89); for a "hydrous oxide," 7.2 (101). If surface structure changes from amorphous on acid side to boehmite on basic side, the IEP can be as basic as 8.4 (29, 73). <sup>b</sup>  $K_{s0}$  (93);  $K_{s1}$ ,  $K_{s2}$  (28, 29),  $K_{s4}$  (29). <sup>c</sup>  $\log *K_{s1} = 9.82$  (116). <sup>d</sup>  $\log *K_{s1} = -8.2$  (13). <sup>e</sup> If surface structure changes from amorphous on acid side to  $\alpha$ -FeOOH on basic side, IEP  $\rightarrow$  9.0. <sup>f</sup>  $\log *K_{s1} = -7.59$  (13, 29). <sup>g</sup> pHMS data. <sup>h</sup> pHMS data supplemented by hydrolysis data. <sup>i</sup> pHMS in 0.1 M LiCl<sub>2</sub>, 20<sup>o</sup>av. <sup>j</sup>  $\log *K_{s1} = 10.12$  (16, 29, 119). <sup>k</sup> pHMS data estimated graphically and supplemented by hydrolysis data. <sup>l</sup> IEP: (UO<sub>2</sub>OH<sup>+</sup>) = (UO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup>). <sup>m</sup> EP(2,1): 2(UO<sub>2</sub><sup>2+</sup>) = (UO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup>), etc. <sup>n</sup>  $\log *K_{s1} = -8.94$  (13, 91). <sup>o</sup>  $\log K_{s0} = 52$  (13, 29, 61), Zr<sup>3+</sup> dominant (13, 29, 65).

imply that all hydrous materials with CN = 6 or CN = 4 if  $r_+ < 1.0$  Å. involve as PDI the ions  $M^{2+}(\text{OH})_{z-1}^+$  and OH<sup>-</sup> and that OH<sup>-</sup> adsorbs dissociatively. Because H<sup>+</sup> and  $M^{2+}(\text{OH})_{z-1}^+$  are equivalent and the two negative PDI for these materials, OH<sup>-</sup> and  $M^{2+}(\text{OH})_{z+1}^-$ , are also equivalent, the IEPS is equal to IEP regardless of whether or not hydroxo complexes are present.

Materials listed in column 2 of Table XI have IEPS's equal to EP(1, OH), implying that the PDI are again  $M^{2+}(\text{OH})_{z-1}^+$  and OH<sup>-</sup> but that OH<sup>-</sup> adsorbs nondissociatively. In this case the absence of hydroxo complexes will change the apparent IEPS to a value near pH 7 if H<sup>+</sup> also adsorbs nondissociatively. Hydroxo complexes are likely to be absent in suspensions of ignited oxides such as Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> which are

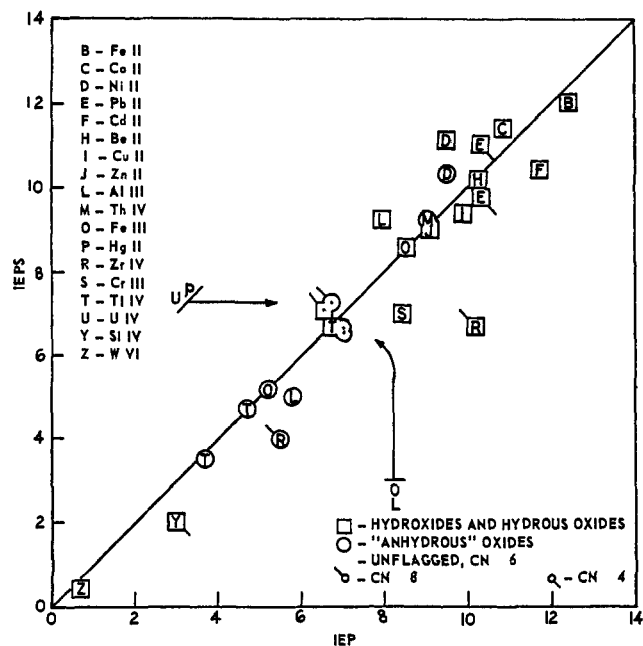


Figure 6.—The relationship between IEPS and selected EP.

TABLE XI

EQUIVALENCE POINTS MOST CLOSELY APPROXIMATING THE ISOELECTRIC POINT OF A SOLID OXIDE MATERIAL

(1) IEPS ~ IEP	(2) IEPS ~ EP(1,OH)	(3) IEPS ~ EP(2,OH)	(4) IEPS > IEP <sup>a</sup>
Fe(OH) <sub>3</sub>	Be(OH) <sub>2</sub>	ThO <sub>2</sub> (9.2)	Al <sub>2</sub> O <sub>3</sub> (hydrous) (9.2)
Co(OH) <sub>2</sub>	PbO (hydrous)	HgO (7.0)	Fe <sub>2</sub> O <sub>3</sub> (hydrous) (8.6)
Ni(OH) <sub>2</sub> , NiO	ZnO (hydrous)	TiO <sub>2</sub> (3.5)	
Cu(OH) <sub>2</sub> , CuO	HgO (7.0)	ZrO <sub>2</sub> (4.0)	
CdO (hydrous)	Al <sub>2</sub> O <sub>3</sub> (6.6)	Al <sub>2</sub> O <sub>3</sub> (5.0)	
Fe <sub>2</sub> O <sub>3</sub> (hydrous) (8.6)	Fe <sub>2</sub> O <sub>3</sub> (5.2)	Fe <sub>2</sub> O <sub>3</sub> (5.2)	
Cr <sub>2</sub> O <sub>3</sub> (hydrous)	TiO <sub>2</sub> (4.7)	Fe <sub>2</sub> O <sub>3</sub> (6.7)	
TiO <sub>2</sub> (hydrous) (6.2)			
WO <sub>3</sub> (hydrous)			
SiO <sub>2</sub>			

<sup>a</sup> In general, IEP > EP(+,OH) > EP(2,OH).

both only slightly soluble and very slow to come to equilibrium. Both of these materials have one reported IEPS near pH 7. Unfortunately, no experimenter has reported even the total metal concentration in solution during measurement of IEPS.

Table XII summarizes the probable PDI and IEPS-IEP relationships for the two classes of materials in the

first and second columns of Table XI. The IEPS's are compared in Figure 6 with EP's selected using the "rules" of Table XII.

### C. ALTERNATE MECHANISMS FOR POTENTIAL-DETERMINING ION ADSORPTION

#### 1. Adsorption onto Hydrogen-Bonded Water

Another possible adsorption mechanism may prove useful in the explanation of the postulated nondissociative adsorption. It is well established, particularly for SiO<sub>2</sub> gels (4, 73), that the first layer of adsorbed water is present as -MOH groups and that the second layer is hydrogen bonded to the first. Thus arrays such as -MOHO<sub>H</sub> should be present on immersed surfaces.

Dissociative adsorption of H<sup>+</sup> or OH<sup>-</sup> onto this group, because interactions with M<sup>2+</sup> in this case is a second-order effect, should reflect the charge and size of M<sup>2+</sup> only slightly, hence be nearly indistinguishable from the postulated physical or nondissociative adsorption onto -MOH groups.

#### 2. Nonequivalence of Potential-Determining Species

It is conceivable that hydroxo complex ions other than those which are most concentrated near the IEPS could usurp the dominant potential-determining role.

Raupach's (99) study of the solubility of aluminum oxyhydroxides and hydroxides led him to believe that the predominant ion in equilibrium with α-Al(OH)<sub>3</sub> and α-AlOOH is AlOH<sup>2+</sup> and that in equilibrium with "bauxite" and γ-AlOOH or "precipitated Al(OH)<sub>3</sub>" is Al(OH)<sub>2</sub><sup>+</sup>. Without giving physical reasons, he proposed a mechanism by which the solution is depleted in Al<sup>3+</sup>, leaving AlOH<sup>2+</sup> the predominant potential-determining ion in the appropriate systems.

Each element listed below has at least one IEPS (reported by more than one author) which is more closely approximated by EP(2,OH) or EP(2,1) than by the IEP or EP(1,OH).

Al(III) IEPS = 5	EP(2,OH) = 5.8	IEP = 7.5
Fe(III) IEPS = 6.7	EP(2,OH) = 6.4 (5.6-6.7)	IEP = 8.0
Th(IV) IEPS = 9.4	EP(2,1) = 8.9	IEP = 11.7

TABLE XII

SUMMARY OF PROBABLE POTENTIAL-DETERMINING IONS AND EQUIVALENCE POINT-ISOELECTRIC POINT RELATIONSHIPS FOR TWO CLASSES OF SOLIDS

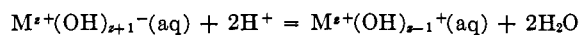
Description of solid	Hydroxo complexes present	Hydroxo complexes absent
A. Hydroxides, oxyhydroxides, hydrous oxides, and superficially hydrated or hydrous oxides. CN = 6 and CN = 4 if $r_+ < 1.0 \text{ \AA}$ .	PDI are M <sup>2+</sup> (OH) <sub>n-1</sub> <sup>+</sup> or H <sup>+</sup> and M <sup>2+</sup> (OH) <sub>n+1</sub> <sup>-</sup> or OH <sup>-</sup> IEP = IEPS (dissociative adsorption)	PDI are H <sup>+</sup> , OH <sup>-</sup> IEP = IEPS (dissociative adsorption)
P. "Anhydrous" oxides and class "A" materials with CN = 4 and $r_+ > 1.0 \text{ \AA}$ .	PDI are same as class "A" and EP(+,OH) or EP(+,-) = IEPS (nondissociative adsorption)	PDI are H <sup>+</sup> , OH <sup>-</sup> IEPS ~ pH 7 (nondissociative adsorption)

Ti(IV)	IEPS = 3.5	EP(2,OH) = 3.7	IEP = 6.6
Zr(IV)	IEPS = 4.0	EP(2,OH) = 5.5	IEP = 10.2
Zr(IV)	IEPS = 6.7	EP(2,1) = (7.2-7.6)	IEP = 10.2

Of these, the IEPS's of Al(III), Th(IV), and Zr(IV) also fail to correlate with  $(Z/R)_{eff}$ . This point and the coincidence that this particular IEPS = EP(2,OH) or EP(2,1) do seem to indicate that a different mechanism is operating to establish equilibrium between the solid and the liquid in these cases. However, neither realistic justification for the fact nor physical reasoning upon which to base selection of the exclusive potential-determining role of  $M^{z+}(\text{OH})_{z-2}^{2+}$  has yet been found.

### 3. pH-Dependent Surface Modification

Raupach (99, 100) also found that the acid solubility of the oxyhydroxides and hydroxides of aluminum was characteristic of  $\alpha\text{-Al}_2\text{O}_3$  or amorphous  $\text{Al}(\text{OH})_3$  ( $\alpha\text{-AlOOH}$ ?) while the solubility in basic solutions was characteristic of  $\alpha$ - or  $\gamma\text{-Al}(\text{OH})_3$ . This may reflect recrystallization of the surface accompanying the change in pH. (The relative stability of  $\text{FeOOH}$  and  $\text{Fe}_2\text{O}_3$  is pH dependent. The reaction is slow in bulk but presumably occurs quickly at the solid-solution interface (117).) Normally the IEP is independent of the state of hydration or crystalline modification of the solid phase because the free energy terms representing the solid cancel in calculation of the equilibrium constant for the net reaction



However, if the structure or composition of the solid or its surface change with pH, the change must be reflected either in the ionic concentrations used with the equilibrium constant for this reaction or in calculation of the constant itself by taking into account the free energy involved in the solid change. For the Al(III) system, the IEP is pH 8.2 if calculated on the assumptions that  $\text{Al}(\text{OH})_2^+$  is produced through equilibration of the solution with an amorphous hydroxide surface and that  $\text{Al}(\text{OH})_4^-$  is produced through equilibration with an  $\alpha\text{-Al}(\text{OH})_3$  surface. This value is in considerably better agreement with the observed IEPS for  $\text{Al}_2\text{O}_3$  (hyd) (IEPS = 9.2) than is the nominal IEP (pH 7.5). The most basic IEP calculable in this way for  $\text{Fe}_2\text{O}_3$  assumes that the surface is amorphous hydroxide when acid and  $\text{FeOOH}$  when basic. The result, IEP = 9.0, is in excellent agreement with the most basic observed IEPS = 9.0. In spite of the moderate success in these two cases, no physical reason upon which to base prediction of circumstances leading to pH-dependent surface modification nor any direct evidence of such modification is immediately apparent.

## V. SUMMARY AND CONCLUSIONS

Extensive lists of isoelectric points of solid oxide materials (IEPS's) and of metal hydroxo complex systems (IEP's) have been compiled. The IEPS reflects the chemical composition of the solid and the electrolyte in which it is immersed. Structural or adsorbed anionic impurities shift the IEPS to more acid values, cationic impurities to more basic values or toward the IEPS characteristic of the impurity oxide. Oxidation and reduction resulting in nonstoichiometry may be expected to shift the IEPS toward that characteristic of the oxidation state produced. Hydration increases the IEPS; dehydration and increased structural perfection decrease the IEPS. The IEPS's of pure oxide materials can be quantitatively accounted for in most cases by an electrostatic model involving the charge to radius ratio and the coordination number with crystal field and hydration corrections.

The IEPS and IEP are definitely related and are equal for many hydrous materials; however, for a significant number of materials there are other EP's which more closely approximate the IEPS. There appear to be several mechanisms by which  $\text{H}^+$ ,  $\text{OH}^-$ , and all hydroxo complexes present determine the surface charge on immersed oxide materials. Further work is needed to clarify the factors deciding which mechanism predominates in a given case, but it appears that for some materials adsorption of  $\text{OH}^-$  and  $M^{z+}(\text{OH})_{z-1}^+$  can be distinguished from amphoteric dissociation of bound MOH groups.

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