ratio is constant with a relative mean deviation of less than 2%. This accounts for the apparent linearity of the lower curve of Fig. 1.

From the concentration quotients evaluated, Fig. 3 was constructed to represent the relative quantities of Fe(II) species in sulfuric acid in the indicated concentration range. The assumption is made here that the concentration of Fe(II) is small enough not to alter the hydrogen ion concentration appreciably and that ionic strength effects need not be considered.

**Complex Formation between Ti(IV) and Fe(II) in $H_2SO_4$.**—Various investigators in the authors' laboratories have reported spectrophotometric evidence for complex formation between Ti(IV) and Fe(II) in sulfuric acid solutions. For example when a solution 1 *M* in $H_2SO_4$ and 0.2 *M* in Ti(IV) is mixed with an equal volume of a solution 1 *M* in $H_2SO_4$ and 0.2 *M* in Fe(II), both of which are colorless, a pale yellow color develops. Spectrophotometric analysis, using the method of continuous variations, indicates that this color is due to the formation of a complex in which the mole ratio of Fe(II) to Ti(IV) is 2.0. The possibility that this color arises from the products of an oxidation-reduction reaction has been eliminated. In the previous publication[5] the nature of Ti(IV) species in perchloric and sulfuric acids has been elucidated. The distribution ratios of Ti(IV) in perchloric and sulfuric acids have been reproduced here as curves C and D, respectively, in Fig. 2.

An attempt was made to study the nature of this complex by eluting samples containing both Ti(IV) and Fe(II) in $H_2SO_4$ with sulfuric acid eluents. Had these cations, when eluted from a mixture, displayed distribution ratios different from that obtained individually, this would have been evidence for complexing.

That the data for such elutions (square points in Fig. 1) coincide with the corresponding predicted curves for the individual elements, indicates that either no complex exists or, more likely, a complex exists but it is so highly dissociated as not to alter the normal elution behavior of its components. The lack of observable adsorption of either Ti(IV) or Fe(II) from mixtures in sulfuric acid by a strong-base anion exchanger is considered as indicative of the absence of negatively-charged complexes of any appreciable stability.

The difficulty here may lie with the fact that only small quantities of Fe(II) and Ti(IV), 0.05 to 2.0 mmole of each, were taken for elution. Greater quantities would have overloaded the column. Furthermore, most of these quantities existed in the resin phase rather than in solution, so that the net effect is a shift in equilibrium away from complex formation. This, of course, implies a complex with a relatively high dissociation constant.

**Analytical Separations of Ti(IV) and Fe(II).**—It is quite apparent from an inspection of Fig. 2 that ion-exchange chromatography can be used as the basis for a quantitative separation of iron and titanium provided that the iron is maintained in the oxidation state of two. With a proper choice of perchloric acid concentration, either cation can be made to precede the other. For example, an eluent of about 2.5 *M* $HClO_4$ will elute titanium first, whereas an eluent of about 5 *M* $HClO_4$ will elute ferrous ion first. The respective elution curves, obtained when 0.1 mmole of each were eluted, were sufficiently narrow that no overlapping of elution curves is anticipated. With the three sulfuric acid elutions of actual mixtures these two cations were quantitatively separated (no overlapping), in which case titanium was eluted first.

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[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY, TITANIUM DIVISION, RESEARCH LABORATORY, SAYREVILLE, N. J.]

# Ion-Exchange Investigation of the Nature of Titanium(IV) in Sulfuric Acid and Perchloric Acid

BY JOHN BEUKENKAMP AND KERMIT D. HERRINGTON

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Ion-exchange elution techniques have been employed to elucidate the nature of Ti(IV) ions in $HClO_4$ and $H_2SO_4$ solutions. In $HClO_4$ up to about 1.5 *M*, Ti(IV) is shown to exist in two ionic forms as follows: $Ti(OH)_3^+ + H^+ \rightleftarrows Ti(OH)_2^{++}$ for which the concentration quotient is 2.0. In $H_2SO_4$ solutions up to about 2.0 *M* the same ions exist, but in addition each accepts a $HSO_4^-$ ligand to form $Ti(OH)_3HSO_4$ and $Ti(OH)_2HSO_4^+$, respectively. The concentration quotients for these association reactions have been determined to be 11.3 and 0.64 respectively. The data point to monomeric titanium species in dilute acid. At high $HClO_4$ concentrations, the distribution ratio goes through a minimum. It is possible to interpret this behavior in terms of complexing of Ti(IV) with $ClO_4^-$.

There is very little information in the literature regarding the nature of titanium (IV) in solution and the extent and type of complexing encountered in sulfuric acid solutions. For example, in a rather comprehensive compilation of stability constants of metal-ion complexes by Bjerrum, *et al.*,[1] no mention is made of interaction between titanium(IV) and ligands derivable from sulfuric acid. With regard to equilibria with hydroxide, other than that involving a solid phase, Delafosse[2] claims the coexistence of $Ti(OH)^{+3}$ and $TiO^{++}$, the former existing at $pH < 0.3$ and the latter at $pH > 0.4$. The titanium(IV) species indicated by Barksdale[3] are speculative.

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(1) J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants of Metal-ion Complexes, with Solubility Products of Inorganic Substances. Part II: Inorganic Ligands," The Chemical Society, London, 1958.

(2) D. Delafosse, *Compt. rend.*, **240**, 1991 (1955).

(3) J. Barksdale, "Titanium," Ronald Press Co., New York, N. Y., 1949.

Hixson and Fredrickson[4] indicate in aqueous solutions of $TiOSO_4 \cdot 2H_2O$ complexes with a mole ratio of titanium to sulfur equal to 2:1 and point out that about half of the total dissolved titanium will react rapidly with peroxide, whereas the remainder does so only slowly.

The purpose of this investigation was to elucidate the nature of titanium(IV) species in sulfuric acid by means of ion-exchange elution techniques. With the expectation that this cation would not form complexes with perchloric acid, the change in distribution between resin and perchloric acid solutions was to have been measured and compared with that obtained with sulfuric acid solutions. Differences between these two acid systems could then be attributed to the formation of sulfate and/or bisulfate complexes. That the possibility of complexing with perchlorate did exist became evident when a reversal of distribution ratio, $C$, was observed. Reversals of this type have been attributed by various investigators as possibly due to any of a number of effects, one of which is the formation of cationic complexes.

## Experimental

**General.**—The techniques used for all elutions are essentially the same as those appearing in the current literature on ion-exchange chromatography. Briefly this technique is: A Pyrex column, containing the resin, is suspended vertically and fitted with a stopcock at the bottom. A solution containing the ions to be studied is introduced at the top of the resin bed (with minimal disturbance) with the aid of a pipet. Eluent solution then flows through the column from a reservoir placed above. Flow rates (usually 4 ml. per min.) are maintained by adjusting the stopcock. The eluent solution emerging from the column passes into a siphon pipet which in turn delivers a definite volume into a receiver, usually a volumetric flask. Receivers are changed after each siphoning or after a definite number of siphonings. The concentration of ions being eluted then is determined in the receivers.

Curves of concentration of ion eluted *versus* volume of eluent are then plotted. These curves should be Gaussian in shape. $U_m$ is defined as the volume, in ml., eluted at the point where the elution curve reaches a maximum. $C$, the distribution ratio is calculated from the equation, $C = (U_m/V) - 1$ where $V$ is the interstitial volume, *i.e.*, the volume of resin bed *not* occupied by resin particles. A discussion of this equation, which is of fundamental importance to ion-exchange chromatography, can be found in the literature.[5]

In this work, 0.050 mmole of Ti(IV), as titanyl sulfate solution, was carefully introduced at the top of the resin bed with the aid of a 5-ml. pipet. With $HClO_4$ elutions, qualitative tests of the eluted fractions showed that the sulfate from the sample passed through the columns, unsorbed. Thus the sulfate was separated from Ti(IV) at the commencement of each $HClO_4$ elution and the behavior of Ti(IV) was not influenced by the sulfate of the sample.

To each fraction of eluent, one ml. of 3% $H_2O_2$ was added. The titanium concentration was determined by measuring the intensity of any yellow color which developed.

**Determination of *W*, *V* and *Q*.**—The dry weight of resin in a column, $W$, was determined as follows: Several hundred grams of the product as received from the manufacturer was washed repeatedly with water. Very fine particles were removed by repeated decantation. This batch then was air dried by exposing to the laboratory atmosphere for approximately one week. The air-dried resin now was homogenized and stored in an airtight bottle. A small portion of this was removed for a moisture determination by heating to constant weight at 105°. From the moisture content thus determined, and the weight of air-dried resin taken for a column, the oven-dry weight in a column is readily computed. It is this oven-dry weight which is given the symbol $W$.

Interstitial volumes, $V$, were determined as described: A standard $HClO_4$ solution was eluted until the solution emerging from the column had the same molarity as that entering. Then the column was drained until the level of liquid above the resin bed coincided with the upper level of the resin bed. At this point, the liquid in the interstices was removed by employing water as eluent. Enough water was used to require a volume of approximately three to four times the anticipated interstitial volume. The eluted interstitial acid was collected and titrated with standard 0.25 $M$ NaOH. In certain cases, aliquots were titrated. By dividing the total number of mmoles of acid collected by the molarity of the acid, $V$ is obtained.

Subsequent to the determination of $V$, the capacity of the entire column, $QW$, and the capacity of one gram of resin $Q$, then were determined as follows: The column, being in the acid form, and containing water in the interstices, is completely converted to the sodium form by employing 2 $M$ NaCl as an eluent. The acid thus removed from the column was collected and titrated with standard alkali. In certain cases aliquots were titrated. The total meq. of acid removed from the column equals $QW$ and, since $W$ has been determined, $Q$ can be evaluated.

**Reagents and Chemicals. Resin.**—AG 50W × 8, 100 to 200 mesh.[6] This resin is a cation exchanger of the polystyrene–divinylbenzene type containing nuclear sulfonate groups. It is Dowex 50 which has been further screened.

**Standard Alkali and Acids.**—Standard 0.25 $M$ NaOH was made from reagent-grade 18 $M$ NaOH and was stored in polyethylene containers, protected from $CO_2$ with Ascarite tubes and automatic burets. It was standardized against N.B.S. potassium acid phthalate. $H_2SO_4$ and $HClO_4$ solutions were made by diluting reagent grade materials and were standardized with this 0.25 $M$ NaOH.

**Titanium Sulfate Solutions.**—$TiOSO_4 \cdot 2H_2O$ was prepared from butyl titanate by precipitation from hot 45% $H_2SO_4$. Analysis of this product confirmed the stoichiometry of this formula. Solutions of this compound were made by dissolving it in the appropriate acid of the same concentration as the eluent to be used during elution. These solutions contained sufficient dissolved Ti(IV) so that a 5-ml. aliquot taken for elution would contain 0.050 mmole Ti(IV).

**0.2 *M* $Ba(ClO_4)_2$ Solution.**—This was prepared by dissolving 0.100 mole reagent-grade $Ba(OH)_2 \cdot 8H_2O$ in sufficient $HClO_4$ so that, when diluted to 500 ml., the $[H^+]$ was 0.2009 as determined by titration with 0.25 $M$ NaOH to the phenolphthalein end-point.

**Hydrogen Ion Concentrations.**—Throughout this work, the concentrations of hydrogen ion corresponding to given molarities of sulfuric acid were calculated from the Raman spectra data of Young,[7] as also described by Brubaker.[8] Hydrogen ion concentrations for perchloric acid were calculated from the proton magnetic resonance data of Hood, *et al.*[9]

**Evaluation of the Charge per Atom in Perchloric Acid.**—Two methods were employed for determining the charge per titanium atom, as contrasted with the charge per species obtained from elution data.

**Method 1.**—A given quantity of resin, $QW$, in the hydrogen form is completely converted (while in a column) to the titanium form by eluting with a standard titanium (IV) solution. Then the titanium(IV) is displaced from the column with excess acid and collected in a suitable receiver, the contents of which are analyzed for the total mmoles of titanium(IV). The charge, $n$, on the cation is then equal to $QW$ divided by the number of mmoles of titanium(IV) retained by the resin. When determining the mmoles retained, it is necessary to correct for the quantity of titanium (IV) initially present in the interstices of the column.

**Method 2.**—Through a column containing $QW$ meq. of HR, there is passed, very slowly, a standard titanium(IV) solution of concentration equal to [Ti]. This alters the hydrogen ion concentration of the effluent so that the acidity is appreciably different from that of the influent

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[4] A. W. Hixson and R. E. C. Fredrickson, *Ind. Eng. Chem.*, **37**, 678 (1945).

[5] J. Beukenkamp, W. Rieman and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954).

[6] Purchased from Bio Rad Labs., Berkeley, Calif.

[7] T. F. Young, *Record Chem. Progress*, **12**, 81 (1951).

[8] C. H. Brubaker, Jr., *J. Chem. Ed.*, **34**, 325 (1957).

[9] G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **22**, 2067 (1954).

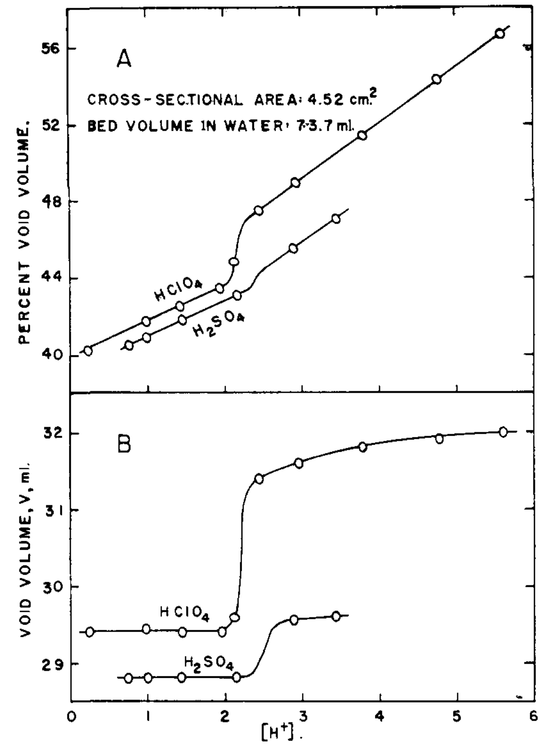

Fig. 1.—Effect of acid on the apparent interstitial volume of a column containing AGW50X8, 100-200 mesh.

solution. When all of the resin has been converted, the acidity of the effluent solution rather abruptly changes and becomes identical to that of the influent solution. By measuring the volume, *v*, of effluent (corrected for the interstitial volume) to reach the midpoint of the inflection of the hydrogen ion concentration, the mmoles of titanium (IV) needed to convert the column can be obtained from the product [Ti]*v*. Then, the ratio, *QW*/[Ti]*v*, can be identified with the charge per atom.

The perchloric acid eluents used for these methods were prepared by dissolving in perchloric acid freshly-prepared hydrated titania, which in turn was obtained by hydrolyzing isopropyl titanate. The sulfuric acid eluents were prepared by dissolving $TiOSO_4 \cdot 2H_2O$ in the appropriate concentration of this acid.

These methods were tested by determining the charge per atom of barium in an eluent containing barium perchlorate. A small column, constructed for these methods, had a cross-sectional area of approximately 0.8 cm.$^2$ and contained sufficient resin to yield *QW* = 10.3 meq.

## Results

**Interstitial Volume,** *V*.—The results for *V* obtained with the method described indicate that a constant value is obtained only with a given acid and only over a limited range of hydrogen ion concentration. Fig. 1B demonstrates this effect. The lack of agreement obtained between these two acids is as yet unexplained. Throughout this work, the values of *V* used were those obtained with acid concentrations below 2.0 *M*. The somewhat arbitrary choice then was made to apply the *V* obtained with a given acid to all elutions with that particular acid and apply the other *V* to elutions with the other acid. Thus the concept of a given column with a variable interstitial volume is tentatively accepted for this work.

The bed volume of a column was found to decrease linearly as a function of hydrogen ion concentration for both $H_2SO_4$ and $HClO_4$. The change in bed volume for the resin indicated in Fig. 1 was −4.2% per unit of hydrogen ion concentration for the range indicated. This gives rise to the curves shown in Fig. 1A, where these changes are expressed in terms of the per cent. of the bed volume which is void of resin.

**Other Column Parameters.**—The ratio *QW*/*V* was determined for two different columns. For one column, *W* = 20.9 g., *QW* = 104.7 meq., *V* = 21.4 ml. and *QW*/*V* = 4.89. For the other column, *W* = 64.5 g., *QW* = 323.1 meq., *V* = 66.0 ml. and *QW*/*V* = 4.90.

**Graphical Presentation of Data.**—For reasons to be given subsequently, the data obtained with $HClO_4$ and $H_2SO_4$ elutions are plotted in two ways. First, a plot of log *C versus* log [H$^+$], where [H$^+$] refers to that in the eluent, is shown in Fig. 2.

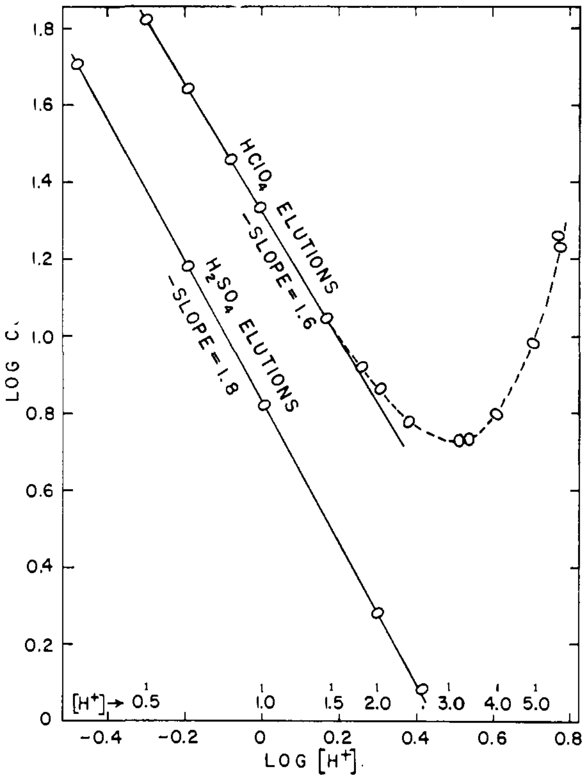

Fig. 2.—Evaluation of net charge for Ti(IV) in $HClO_4$ and $H_2SO_4$.

With $HClO_4$ eluents, a straight line of negative slope equal to approximately 1.6 occurs below [H$^+$] = 1.5. Above this, the curve deviates from linearity and then reverses. With $H_2SO_4$ eluents, a straight line of negative slope equal to approximately 1.8 occurs over the entire range studied.

A second type of plot is shown in Fig. 3 where *C*[H$^+$] is plotted *versus* *C*[H$^+$].$^2$ Linearity is obtained at lower concentrations of acid, and the extrapolated ordinate intercept of these curves are identical.

**Evaluation of the Charge per Atom.**—The first line in Table I shows that the two methods described give in $HClO_4$, a charge per barium ion of 2.0. This, of course, agrees with the anticipated value.

TABLE I

CHARGE PER ATOM AND DEGREE OF POLYMERIZATION OF TITANIUM(IV) IONS

Column = 0.8 cm.$^2$ × 5 cm. for which $QW$ = 10.3 meq. and $V$ = 2 ml.

| | Data from Method 1 | | Data from Method 2 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Eluent | Mmoles on resin | $n$ = $QW$/ mmoles on resin | Ml. to reach inflection = $v$ | [M]$v$ | $n$ = $QW$/ [M]$v$ | $n$, ave. | [H$^+$] in eluent | Net charge per species from $K_1$ | Degree poly., Method 1 | Degree poly., Method 2 |
| 0.200 $M$ $Ba(ClO_4)_2$ in 0.2009 $M$ $HClO_4$ | 5.15 | 2.0 | 26 | 5.20 | 2.0 | 2.0 | 0.2009 | .. | .. | .. |
| 0.095 $M$ Ti in 0.500 $M$ $HClO_4$[a] | 6.35 | 1.6 | 77 | 7.31 | 1.4 | 1.5 | .365[c] | 1.4 | 0.9 | 1.0 |
| 0.045 $M$ Ti in 0.600 $M$ $HClO_4$[a] | 6.00 | 1.7 | 135 | 6.08 | 1.7 | 1.7 | .532[c] | 1.5 | 0.9 | 0.9 |
| 0.050 $M$ Ti in 0.1733 $M$ $H_2SO_4$[b] | 7.52 | 1.3 | 152 | 7.60 | 1.3 | 1.3 | .225[c] | 0.7 or 1.3[d] | 1.0 | 1.0 |

[a] Refers to initial [$HClO_4$] used to dissolve indicated quantity of titania. [b] Refers to initial [$H_2SO_4$] used to dissolve indicated quantity of $TiOSO_4 \cdot 2H_2O$. [c] Calculated with successive approximations to account for acid neutralized by dissolved titania or by dissolved $TiOSO_4 \cdot 2H_2O$. [d] Calculated from various constants reported here. 1.3 obtained by excluding contribution of complexes with zero charge, 0.7 obtained by considering all species. 1.3 is assumed applicable here.

The next two lines show the charge per titanium (IV) atom in dilute $HClO_4$ varies from 1.4 to 1.7, while in dilute $H_2SO_4$ the charge is approximately 1.3. The significance of the last three columns of this table will be discussed subsequently.

## Discussion

**Interstitial Volume,** $V$.—The constancy of $V$ below [H$^+$] = 2 (see Fig. 1B) is interpreted to mean that resin invasion (sometimes called Donnan penetration or entrance of non-exchanging electrolyte) is negligible in this acidity region. The method employed for the determination of $V$ is expected to be sensitive to resin invasion effects.

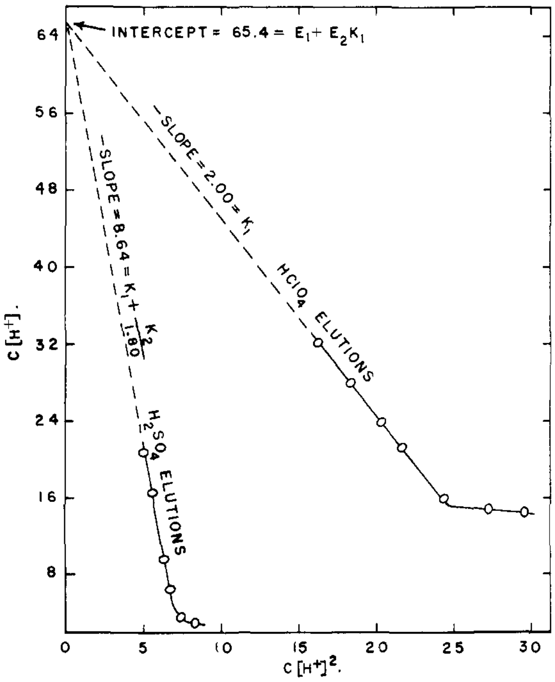

Fig. 3.—Evaluation of certain constants for elution equations.

**Determination of the Charge per Species in $HClO_4$. General Treatment.**—The reaction of an uncomplexed metal ion, $M^{+n}$, with the hydrogen form of a cation exchanger, HR, can be represented as

$$M^{+n} + n\text{HR} \rightleftharpoons \text{MR}_n + n\text{H}^+$$

for which the exchange constant is defined as

$$E = \frac{[\text{MR}_n][\text{H}^+]^n}{[\text{M}^{+n}][\text{HR}]^n}$$

where the concentrations of resin species are expressed as mole fractions and the concentrations of species in solution as molarities. If the quantity of $M^{+n}$ undergoing exchange is quite small in comparison with $QW$, then the assumption that [HR] = 1.00 yields only a negligible error. Then [MR$_n$] = $E$ [M$^{+n}$]/[H$^{+n}$]. Since the product of mole fraction and total number of mmoles in the system yields the number of mmoles of species in question, the mmoles of metal ion in the resin phase is equal to $QW$ [MR$_n$] = $QWE$ [M$^{+n}$]/[H$^+$]$^n$. The mmoles of metal ion in solution is simply the product $V$[M$^{+n}$]. The distribution ratio, $C$, being defined as the ratio of the quantity in the resin phase to that in the solution phase, becomes $C = (QW/V)(E/[\text{H}^+]^n)$, or in logarithmic form, $\log C = -n \log [\text{H}^+] + \log (QWE/V)$.

With column techniques, $C$ is determined readily from $C = (U_m/V) - 1$, and the ratio $QW/V$ is determined as described above. A plot of log $C$ *versus* log [H$^+$] (where [H$^+$] pertains to that in the eluent) should then yield a straight line whose negative slope can be identified with the charge on the cationic species. Should the curve be nonlinear or the slope not an integer, a mixture of ions could be indicated. Since the exchange constant, $E$, can be evaluated from the intercept, an equation can be obtained which describes $C$ as a function of hydrogen ion concentration.

Kraus and Nelson[10] have derived an equation for the slope of a log $C$ *vs.* log [H$^+$] curve in which they take into consideration the effect of variations in the activity coefficient quotient, $G$. Their equation, as applied to cation exchange with a univalent ion such as H$^+$, and written with nomenclature consistent with this work is

$$\frac{\text{d} \log C}{\text{d} \log [\text{H}^+]} = -n + \frac{n \, \text{d} \log [\text{HR}]}{\text{d} \log [\text{H}^+]} - \frac{\text{d} \log G}{\text{d} \log [\text{H}^+]}$$

It is pointed out by Kraus and Nelson that d log [HR]/d log [H$^+$] will be negligibly small if resin invasion is small and if [HR] >> [TiR$_n$]. In the present work, it is believed that, below [H$^+$] = 2, resin invasion is indeed small. Furthermore, [HR] varied between 0.9990 and 0.9998 for all

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(10) K. A. Kraus and F. Nelson, "The Structure of Electrolytic Solutions," edited by W. J. Hamer, John Wiley and Sons, Inc., New York, N. Y., 1959, chapter 23.

elutions, which corresponds to a ratio of [HR] to $[TiR_n]$ of the order of 1000. It is therefore concluded that the second term on the right of this equation is negligible.

The derivative d log $G$/d log $[H^+]$ has been plotted by Kraus and Nelson[10] for cations of average size and various charges. This assumes that the Debye–Hückel equation adequately describes activity coefficients for such systems. The *maximum* value of this derivative is 0.2 for a divalent cation and is vanishingly small for a univalent cation. The present work indicates that titanium (IV) exists as a mixture of univalent and divalent cations in the acidity range $[H^+] = 0.2–1.5$. Therefore the derivative in the extreme case will probably lie between 0.1 and 0.2.

Thus, with $HClO_4$ elutions, where d log $C$/d log $[H^+]$ was observed to be approximately $-1.6$, the charge is probably approximately 1.5.

The above considerations lead to the interpretation that a mixture of univalent and divalent titanium(IV) ions governs the ion-exchange behavior of this element in dilute $HClO_4$.

**Evaluation of Species and Equilibria in Perchloric Acid.**—Attempts were made to interpret the data in terms of perchlorate complexes involving a variety of numbers of ligands and a variety of charges per titanium species either individually or in pairs. These attempts failed, with one exception. to yield derived distribution equations which were consistent with the data. The treatment described represents then the only situation which was encountered in this trial and error approach which was consistent.

In dilute perchloric acid the following equilibrium predominates: $Ti(OH)_3^+ + H^+ \rightleftarrows Ti(OH)_2^{++}$. No attempt is made here to show water of hydration or the water molecules needed to satisfy any particular coördination number. The titanium species are not shown in any state of polymerization, other than as monomers, for reasons to be given subsequently. Each of these two ions exchanges with the resin

$$Ti(OH)_3^+ + HR \rightleftarrows Ti(OH)_3R + H^+$$

$$Ti(OH)_2^{++} + 2HR \rightleftarrows Ti(OH)_2R_2 + 2H^+$$

The corresponding concentration quotients are defined as

$$K_1 = \frac{[Ti(OH)_2^{++}]}{[Ti(OH)_3^+][H^+]},\ E_1 = \frac{[Ti(OH)_3R][H^+]}{[Ti(OH)_3^+][HR]},\ E_2 = \frac{[Ti(OH)_2R_2][H^+]^2}{[Ti(OH)_2^{++}][HR]^2}$$

An assumption is made that, since the quantity of titanium taken for elution is very small as compared to $QW$, [HR] is equal to unity. By combination of these three concentration quotients with the definition of $C$, equation 1 is obtained

$$C = (\text{mmoles } Ti(OH)_3R + \text{mmoles } Ti(OH)_2R_2)/(\text{mmoles } Ti(OH)_3^+ + \text{mmoles } Ti(OH)_2^{++})$$

$$C = \frac{QW}{V} \cdot \frac{E_1 + E_2K_1}{[H^+] + K_1[H^+]^2} \qquad (1)$$

Rearranging equation 1 gives $C[H^+] = -K_1C \cdot [H^+]^2 + (QW/V)(E_1 + E_2K_1)$, indicating that a plot of $C[H^+]$ *versus* $C[H^+]^2$ should yield a straight line of slope $= -K_1$. Such a plot (upper curve in Fig. 3) reveals that below a hydrogen ion concentration of 1.5 $M$, *i.e.*, $C[H^+]^2 = 24$, a straight line is obtained whose negative slope equals 2.0. The ordinate intercept has a value of 65.4. Since $QW/V$ is 4.90, $E_1 + E_2K_1 = 13.4$. Further partitioning of $E_1$ and $E_2$ is not necessary. Substitution of these constants in equation 1 yields the following equation which accurately described $C$ as a function of $[H^+]$ for elutions with $HClO_4$ up to 1.5 $M$: $C = 65.4/([H^+] + 2.0\ [H^+]^2)$. The deviation from linearity at hydrogen ion concentrations above 1.5 $M$ indicates that some other effect is becoming appreciable. This will be discussed subsequently.

With this interpretation, and with $K_1 = 2.0$, it can be calculated that $n$ should vary from 1.5 to 1.7 as the hydrogen ion concentration is changed from 0.5 to 1.5. This change in $n$ is too small to be detected in the slope of Fig. 2. A 10% error in $V$ would yield a negligible change in $K_1$ and in the other constants given subsequently.

**Evaluation of the Degree of Polymerization in Perchloric Acid.**—The degree of polymerization of titanium(IV) was calculated by dividing the charge per species, shown in the eighth column of Table I (obtained from the evaluation of $K_1$), by the charge per atom as shown in Table I. The results are given in the last two columns of Table I and indicate that, for the solutions studied, titanium(IV) is monomeric.

These methods for determining the charge per atom (and consequently the degree of polymerization) are subject to certain limitations. The cation being studied must have a high distribution ratio, *i.e.*, only a negligible fraction of the resin can remain in the hydrogen form. This limits the techniques, in the case of titanium(IV), to solvents of low acidity in which case the tendency to precipitate hydrated titania increases. When employing method 2, the elution must be carried out at a very slow flow rate in order to minimize the premature entry of titanium(IV) into the effluent. Since the titanium solutions studied would yield precipitated titania within 8–12 hr. after preparation, it was necessary to employ a very small column so that the experiments could be concluded within the time allotted for one working day. Larger columns would have necessitated longer elutions.

An objection could be raised to method 1, namely, that the result would depend on the relative affinities of the doubly and singly charged titanium (IV) species for the resin. If the relative affinities were grossly different, then the calculated charge would reflect mostly the species with the greatest affinity. Since the results with methods 1 and 2 agree sufficiently well, it is believed that this objection is not serious.

That these results indicate one atom per species is the justification for writing equations involving monomers.

**Evaluation of Charges, Species and Equilibria in Sulfuric Acid.**—The displacement of the $H_2SO_4$ curve in Fig. 2 indicates different types of ions than in perchloric acid. The similarity of the two curves of Fig. 2 indicates that, for comparable acidities, an equation for $C$ applicable to sulfuric acid should be of essentially the same form as equation 1 which applies to dilute perchloric acid. Thus, equation 2 was tentatively written for application to sulfuric acid elutions

$$C = \frac{QW}{V} \cdot \frac{E_1' + E_2'K_1'}{[H^+] + K_1'[H^+]^2} \qquad (2)$$

where the primed constants have analogous significance.

Equation 2 requires that a plot of $C[H^+]$ *versus* $C[H^+]^2$ yields a straight line of slope equal to $K_1'$ and intercept equal to $QW/V(E_1' + E_2'K_1')$. Such a plot is shown by the lower curve in Fig. 3 where the negative slope was found to be 8.6 and the ordinate intercept yields the same value for $E_1' + E_2'K_1'$ that was obtained for $E_1 + E_2K_1$ with perchloric acid systems. This indicates that both acid systems have the same cations in common, namely, $Ti(OH)_3^+$ and $Ti(OH)_2^{++}$. This is to be expected since the ligand concentration is zero at the intercept. Hence $E_1$, $E_2$ and $K_1$ are identical with their primed counterparts.

The excellent adherence to linearity of the two curves in Fig. 3, along with the observation that both curves extrapolate to the same ordinate intercept, lends support to the belief that the second and third terms on the right side of the equation of Kraus and Nelson have an insignificant effect on the interpretations thus far given.

The different negative slopes, 8.6 and 2.0, indicate that the cations undergo different equilibria in the two acid systems. This difference can only be due to complexing with ligands from the sulfuric acid.

A number of different equilibria, involving both $HSO_4^-$ and $SO_4^=$ ligands adding in various numbers to either or both of the proposed cations, was considered. In each case, distribution equations were derived and tested, both for fit with the data, and for internal consistency with all interpretations made during this work. In some cases negative concentration quotients were needed to obtain equations that would fit data. These were immediately ruled out. This was especially prevalent when the ligand was considered to be $SO_4^=$ or if negatively charged complexes were formed. The interpretation given below is the best that can be derived from the evidence obtained. The equilibria and mass action expressions thus proposed are

$$\begin{array}{ll}
\text{In solution only} \left\{ \begin{array}{l} Ti(OH)_3^+ + H^+ \rightleftarrows Ti(OH)_2^{++} \\ Ti(OH)_3^+ + HSO_4^- \rightleftarrows Ti(OH)_3HSO_4 \\ Ti(OH)_2^{++} + HSO_4^- \rightleftarrows Ti(OH)_2HSO_4^+ \end{array} \right. & \begin{array}{l} K_1 = [Ti(OH)_2^{++}]/[Ti(OH)_3^+][H^+] \\ K_2 = [Ti(OH)_3HSO_4]/[Ti(OH)_3^+][HSO_4^-] \\ K_3 = [Ti(OH)_2HSO_4^+]/[Ti(OH)_2^{++}][HSO_4^-] \end{array} \\
\text{Between solution and resin} \left\{ \begin{array}{l} Ti(OH)_3^+ + HR \rightleftarrows Ti(OH)_3R + H^+ \\ Ti(OH)_2^{++} + 2HR \rightleftarrows Ti(OH)_2R_2 + 2H^+ \\ Ti(OH)_2HSO_4^+ + HR \rightleftarrows Ti(OH)_2HSO_4R + H^+ \end{array} \right. & \begin{array}{l} E_1 = [Ti(OH)_3R][H^+]/[Ti(OH)_3^+] \\ E_2 = [Ti(OH)_2R_2][H^+]^2/[Ti(OH)_2^{++}] \\ E_3 = [Ti(OH)_2HSO_4R][H^+]/[Ti(OH)_2HSO_4^+] \end{array}
\end{array}$$

A derivation of a distribution equation from these equilibria yields

$$C = \frac{QW}{V} \cdot \frac{E_1 + E_2K_1 + E_3K_1K_3[H^+][HSO_4^-]}{[H^+] + K_1[H^+]^2 + K_2[H^+][HSO_4^-] + K_1K_3[H^+]^2[HSO_4^-]}$$

The data of Young[7,8] show that for sulfuric acid concentrations of the range studied in this work, $[H^+] = 1.80[HSO_4^-]$. Substitution of this yields

$$C = \frac{QW}{V} \cdot \frac{1.80(E_1 + E_2K_1) + E_3K_1K_3[H^+]^2}{1.80[H^+] + (1.80K_1 + K_2)[H^+]^2 + K_1K_3[H^+]^3} \qquad (3)$$

The three parameters $K_2$, $K_3$ and $E_3$ then were obtained by solving three simultaneous equations obtained from the data of three elutions with sulfuric acid. This yielded $E_3 = 0.77$, $K_2 = 11.3$ and $K_3 = 0.64$.

Substitution of numerical values for all pertinent parameters in equation 3 results in an equation which quite accurately describes $C$ as a function of either $[H^+]$ or $[H_2SO_4]$. When such an equation is plotted, the curve accurately coincides with the points shown in Fig. 2.

The magnitudes of the terms in equation 3 are such that, in the more dilute sulfuric acid regions, the last term in the numerator and the last term in the denominator contribute little to the value of $C$. Hence, at low concentrations, equation 3 reduces to the form of equation 1, and the slope of Fig. 3, − 8.6, corresponds to $-(1.80K_1 + K_2)/1.80$. Insertion here of $K_1 = 2.0$ yields then a value for $K_2$ of 12.0 which compares favorably with 11.3 obtained from solving simultaneous equations.

Fig. 4 shows the relative quantities of each of the species believed to be present in sulfuric acid up to acid concentrations slightly greater than 2 *M*. Fig. 4 is valid only for solutions in which the concentration of titanium is not large enough to appreciably affect the acidity of the solution. These relative quantities were calculated from the corresponding values of $K_1$, $K_2$ and $K_3$ under the assumption that ionic strength effects need not be considered.

It is interesting to note that the predominant species in sulfuric acid is $Ti(OH)_3HSO_4$. Stoichiometrically, this is identical to the formula $TiOSO_4 \cdot 2H_2O$, which has been assigned to solid titanyl sulfate. The solid, although written as a dihydrate, does not exhibit the properties customarily associated with hydrates, namely, an equilibrium vapor pressure. It thus appears likely that $Ti(OH)_3HSO_4$ comes closer to a true representation of the solid.

A hydrogen ion concentration of 0.5 corresponds roughly to *p*H of 0.3 which agrees remarkably well with the claim of Delafosse[2] that one of two possible species predominates just above, or just below, this *p*H. However, the interpretation given here is different. Whereas Delafosse claims $Ti(OH)^{+++}$ and $TiO^{++}$ exist at acidities just above and below this point, respectively, this work indicates $Ti(OH)_2^{++}$ and $Ti(OH)_3^+$, respectively.

Inspection of Fig. 4 shows that at the lower end of the range of sulfuric acid concentration studied, about half of the titanium(IV) is uncomplexed and the other half is complexed with $HSO_4^-$ in a ratio of 1:1. Thus, when considering the status of all the titanium(IV), a mole ratio of titanium to sulfur of 2:1 can be deduced. This is in substantial agreement with the results of Hixson and Fredrickson[4] who point out that only about half of the total titanium(IV) reacts rapidly with peroxide, the remainder only slowly. Their techniques of *p*H measurement and conductivity point to a mole ratio of titanium to sulfur of 2:1.

**Titanium (IV)–Perchlorate Complexes at High Concentrations of Perchloric Acid.**—With perchloric acid elutions, Fig. 2 indicates *via* a reversal in *C*, that some other phenomenon is becoming effective. This reversal could mean that at higher perchloric acid concentrations a fundamental change in the nature of the cations is taking place.

It could also be due to other factors. Reversals of this type have been considered by others as possibly due to activity coefficient effects,[11] a change in hydration number of the exchanging ion,[12] resin shrinkage,[12] resin invasion,[12] as well as cationic complexes.[12] Recently Kraus, *et al.*,[13] have shown that reversal could be due to adsorption by the cation exchanger of anionic complexes. This latter phenomenon could conceivably be related to that studied by Sargent and Rieman[14] who give the name "salting-out chromatography" to chromatographic separations based on such effects. It is not believed that a salting-out process explains the reversal of *C* in the case of titanium(IV), since this element is not particularly amenable to solvent extraction, a criterion apparently necessary for this phenomenon.

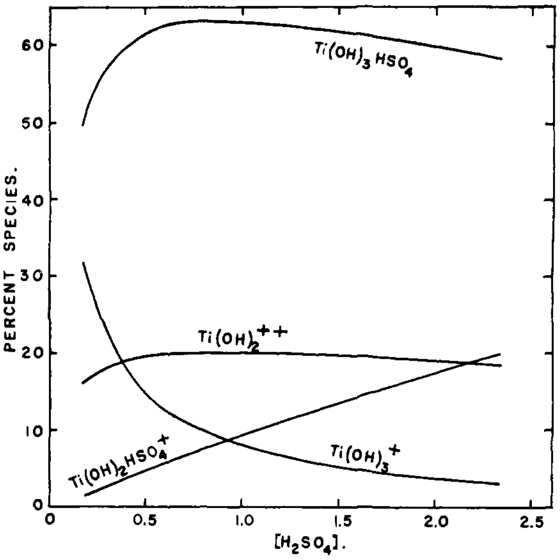

Fig. 4.—Relative concentrations of various species in $H_2SO_4$,

It can be shown that if reactions are considered in which the two hydroxyl groups of $Ti(OH)_2^{++}$ are neutralized in a stepwise fashion and that if each of the resulting trivalent and tetravalent titanium (IV) species combine with perchlorate ions to give positively charged complexes, a distribution equation can be derived

$$C = \frac{k_1 + k_2[H^+]^4 + k_3[H^+]^6}{[H^+] + k_4[H^+]^2 + k_5[H^+]^3} \tag{4}$$

After having evaluated all of the pertinent constants from elution data at high perchloric acid concentrations, equation 4 accurately fits the data over the entire perchloric acid concentration range studied. The constants are concentration quotients, or products of concentration quotients; their constancy implies that activity coefficient quotients are constant over the acid range studied.

It is the purpose here merely to show that, at perchloric acid concentrations above 2 *M*, the formation of titanium(IV)–perchlorate complexes should not be overlooked, especially since evidence for perchlorate complexes of other polyvalent cations has been reported.[15–19]

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