Summary

With the aid of a table of ratios of ionic radii, formulas are assigned the oxygen acids of a number of elements in their highest valence states. In most cases these are the accepted ones; the formula $HSb(OH)_6$ for antimonic acid, supported by considerable evidence, has not, however, been suggested before, and its recognition clarifies the chemistry of the antimonates. It is pointed out that the change from an ortho to a meta acid (H_4SiO_4 to $(H_2SiO_3)_x$, H_3BO_3 to $(HBO_2)_x$, $H_2Sn(OH)_6$ to $(H_2SnO_3)_x$, etc.) in general involves polymerization rather than a change in coördination number.

PASADENA, CALIFORNIA

RECEIVED NOVEMBER 23, 1932
PUBLISHED MAY 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Some Properties of Electrolytes in the Solvent Sulfuric Acid[1]

BY LOUIS P. HAMMETT AND ALDEN J. DEYRUP[2]

Among the various evidences that water and organic oxygen compounds are bases in the same sense as are ammonia and its organic derivatives, there is none more convincing than Hantzsch's cryoscopic and conductivity work in the solvent sulfuric acid.[3] It is equally true that either freezing point or conductivity measurements in this solvent offer a most valuable method of investigating the ionic behavior of such weak bases under conditions of extremely high acidity. In the application of this method in the selection of a series of simple mono acid bases for use as indicators under such conditions,[4] we have, however, obtained quantitative results whose values, differing from those of previous workers, lead to a new and surprisingly simple interpretation of the physico-chemical nature of these solutions.

Apparatus, Method and Materials

We have used the familiar Beckmann freezing point method and apparatus with modifications necessary to prevent absorption of moisture. Those more accurate freezing point methods which depend upon the production of equilibrium between solid and liquid phases and the subsequent analysis of the liquid phase are here impossible because there is no method of sufficient precision for the determination of small amounts of water in sulfuric acid or for the recognition of pure sulfuric acid.

To prevent access of moisture from the air the hand operated stirring rod in the Beckmann apparatus passed through a sleeve of rubber tubing, lubricated with vaseline,

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[1] This article is based mainly upon part of a dissertation submitted by Alden J. Deyrup to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, March, 1932.

[2] Gottsberger Fellow, 1931–1932.

[3] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); **62**, 626 (1907); **65**, 41 (1908); **68**, 204 (1909); *Ber.*, **55**, 953 (1922); **B63**, 1782 (1930).

[4] Hammett and Deyrup, THIS JOURNAL, **54**, 2721, 4239 (1932).

and also through a stuffing box of loose cotton to prevent carrying of vaseline into the solution. That there was no significant contamination of the acid during the addition of solute and the inoculation with a crystal of solid acid was demonstrated by an experiment in which a cycle of cooling, inoculation and melting was carried out fifteen times without measurable change in the freezing point of a portion of acid. By taking the usual precautions in reading the thermometer, by inoculation of the cooled solution at a temperature not more than two degrees below the freezing point, by subsequently maintaining the external bath at a temperature 1 ± 0.3° below the freezing point, and by application of the supercooling correction and the necessary thermometric corrections, a reproducibility of 0.001° was obtained on a given portion of solution. A degree of constancy over a period of several hours of the same magnitude was found provided the portion of acid was allowed to stand in the apparatus for twelve hours or longer before the measurements were begun. Supercooling, especially important in this solvent, was corrected for by adding to the observed freezing point a quantity equal to 0.014 times the supercooling times the difference between the freezing point of pure sulfuric acid and that of the solution in question. That this correction, based upon the inaccurate assumption of direct proportionality between concentration and depression, was of sufficient precision was verified both by calculation for the case of the solute water, and in general by the lack of dependence upon the extent of supercooling exhibited by the corrected freezing points. The thermometer was calibrated at the Bureau of Standards, and all temperatures were corrected for errors in the scale, for exposed stem and for the setting factor of the thermometer.

Sulfuric acid was prepared by mixing fuming sulfuric acid (30% SO_3) and 96% acid in a ratio calculated to give slightly less than 100% H_2SO_4, and then adding fuming acid until the freezing point rose to a maximum (about 10.5°) and then dropped a little. This acid, which contained a slight excess of SO_3, was kept in a tightly stoppered bottle. The acids were C. P. samples from well-known sources. The solvent acid used in the experiments with the solute water was the material redistilled in platinum described in a previous paper.[5]

Potassium and sodium sulfates were ignited to a dull red heat.

Barium sulfate, 6 g. of C. P. $BaCl_2 \cdot 2H_2O$ was dissolved in 500 cc. of water and added gradually, with stirring, to a solution of 6 g. of concentrated sulfuric acid in 200 cc. of water. Both solutions were kept hot. The precipitate was digested for several hours, filtered, washed free of chloride ion and dried. It was then ignited to a dull red heat in a porcelain crucible.

Alizarine.—"Biological" alizarine was sublimed and the resulting orange crystals were kept in an oven at 120° for twelve hours.

Cinnamalacetophenone was dried for one hour at 90°.

Triphenylcarbinol was recrystallized from benzene and dried at 110°.

s-Trinitrobenzene was recrystallized from alcohol and dried at 100°.

Picric acid was dried at 100°.

Trichloroacetic acid was fractionally distilled *in vacuo* and the supercooled liquid was run into capillary ampoules which were weighed and immediately transferred to the freezing point apparatus.

Other organic solutes were the materials previously described.[4] All solutes were carefully protected in desiccators after drying until used.

The Solutes Water and Sulfur Trioxide

These were investigated by adding small weighed amounts of water to a portion of redistilled sulfuric acid containing initially a little sulfur trioxide,

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(5) Ref. 4, p. 2727.

and determining the freezing point after each addition. The results of two such series are given in Table I in which *W* is the weight of acid, *w* the increment of water, and *T* the corrected freezing point on the Beckmann scale. Figure 1 is a plot of part of these data. For the points representing the first series the abscissas are the moles of water added to 1000 g. of acid of the initial composition; for the second series the same quantities plus 0.043. This arbitrary displacement to give the best coincidence was used because there is no other precise method of intercomparison.

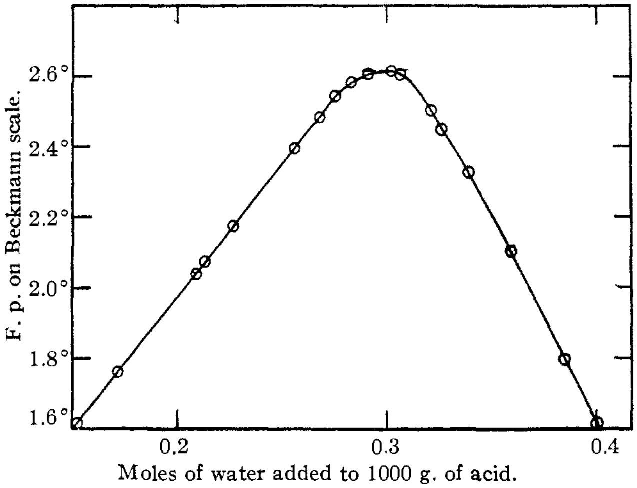

Fig. 1.

TABLE I

W	*w*	*T*	*W*	*w*	*T*
53.7	0	0.438	57.9	0	0.753
	0.0737	1.033		0.0422	1.077
	.0733	1.612		.0497	1.444
	.0595	2.070		.0425	1.755
	.0874	2.617		.0396	2.039
	.0229	2.447		.0183	2.172
	.0310	2.103		.0311	2.392
	.0252	1.799		.0129	2.487
	.0152	1.615		.0074	2.544
	.0188	1.394		.0077	2.585
	.0320	0.984		.0088	2.606
				.0161	2.609
				.0158	2.506
				.0177	2.329
				.0941	1.280

It is in principle extremely probable that the maximum freezing point appears at the composition corresponding to pure H_2SO_4, and this conclusion is verified by the careful experiments of Lichty.[6] The maximum is, however, too flat to make its exact location possible.

The effect of adding water to sulfuric acid is to produce a freezing point depression which, after a short initial curvature, is a linear function of the concentration. That the slope of the linear portion, which we have found from a large scale plot to be 11.85, is very nearly that to be expected from a binary strong electrolyte, appears from the following consideration.

Brönsted[7] found the heat of solidification of sulfuric acid to be given by

$$\Delta H = -2485 - 6.1\ T_{\text{Cent.}}$$

From this the limiting ratio of depression to molality is 6.154. Using the method of Lewis and Randall,[8] we obtain for an ideal solute in finite concentration

$$\vartheta/m = 6.154\,(1 - 0.0047\,\vartheta)$$

from which the slope of the freezing point–molality curve of a binary electrolyte of constant activity coefficient should be 12.26 in the range of depressions under consideration.[9] The actual slope of the water curve is 97% of this value.

The initial curvature at low concentrations is an effect to be expected, as was indicated by Hantzsch, from a solvent which is largely dissociated to give a product identical with one produced by the ionization of the solute. That sulfuric acid is largely dissociated is indicated both by the high conductivity (about 0.01 r. o.) of the pure acid and by the indicator results previously reported by us (a concentration of bisulfate ion of 0.027 molal in the pure acid). The dissociation might be a simple ionic one

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad \text{(I)}$$

the hydrogen ion being presumably solvated, or a more complex one such as

$$2H_2SO_4 \rightleftharpoons SO_3 + OH_3^+ + HSO_4^- \qquad \text{(II)}$$

In either case bisulfate ion is a product of the dissociation of the solvent. When therefore N moles of a mono acid base such as water are added to this solvent the N moles of bisulfate ion produced by the reaction $H_2O + H_2SO_4 \rightleftharpoons OH_3^+ + HSO_4^-$ repress the solvent dissociation, and the net increase in solute concentration is less than 2 N by an amount equal to the number of moles of dissociation products disappearing through this repression. The result is an apparent incompleteness of ionization at low concentrations. If, however, we add a basic solute to a solution which already contains enough water to make this repression essentially complete and to attain the straight portion of the freezing point curve, the further depression per mole will, in so far as the ions are ideal solutes,

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[6] Lichty, THIS JOURNAL, **30**, 1834 (1908).

[7] Brönsted, *Z. physik. Chem.*, **68**, 693 (1909).

[8] Lewis and Randall, "Thermodynamics," New York, 1923, p. 282ff.

[9] This assumes that the relative partial molal heat content of water in dilute solution in the solvent sulfuric acid is negligible. There are indications in Brönsted's experiments, Ref. 7, that this assumption is essentially correct.

be proportional to the total number of moles produced by the ionization of the solute.

In regard to the nature of the self-ionization, it may be said that there certainly is some dissociation of type II, else there would be a sharp discontinuity of slope at the maximum of the curve in Fig. 1. Nor can the actual course of the curved part of the diagram be accounted for by the application of the law of chemical equilibrium to either of these equations alone, the curvature being too sharp to be represented by equation I and not sharp enough to fit equation II.

Since the slope, 7.55, of the sulfur trioxide branch of the curve lies between that for a non-electrolyte and that for a binary electrolyte, this solute is either a weak electrolyte or one whose more complex ionization depends possibly upon the polymery of sulfur trioxide.

Inorganic Salts

In Table II are given the results of measurements on some inorganic salts. Under *m* is given the molality of the bisulfate, calculated from the weights of sulfuric acid and of neutral sulfate weighed into the apparatus, under ϑ the corrected depression. In these experiments and in the subsequent ones with organic solutes, a measured volume of sulfuric acid containing a slight excess of sulfur trioxide was run into the freezing point apparatus from a buret.[10] Water was then added dropwise until the freezing point rose to a maximum, and then fell a little. In most of our experiments we thus obtained an acid in which the initial repression of ionization of the solvent was no longer a disturbing factor. Under the heading *t* in the table are given approximate values of this initial depression, from which by Fig. 1 the concentration m_H of water may be estimated.

TABLE II

m	ϑ	t	μ	S	i
		$KHSO_4$			
0.0673	0.801	0.5	0.1	6.06	1.96
.0530	0.644		.15	6.00	2.03
.2372	2.852	.1	.25	5.97	2.01
.0484	0.579	.2	.08	6.09	1.97
.0545	.666		.1	6.03	2.03
		$NaHSO_4$			
0.0493	0.584	0.3	0.08	6.08	1.95
.0547	.649	.6	.1	6.05	1.96
.0781	.992	1.2	.2	5.99	2.12
		$Ba(HSO_4)_2$			
.0276	.457	0.1	.09	6.10	2.72
.0476	.854	0.6	.25	6.03	2.98

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(10) This method of measuring sulfuric acid, when a drainage time of thirty minutes is allowed and when the buret is calibrated with the acid, was found by direct weighing to give results accurate to 0.5%.

We have calculated and include in our tables the van't Hoff factor, *i*, the ratio of the actual freezing point depression to that produced by an ideal non-electrolyte at the same concentration. The extent to which this quantity approximates an integer is a measure of the ideality of the ionic solutes in the solvent, and in this solvent it offers a more obvious criterion of the nature of the solvent than would activities or activity coefficients. In making this calculation we have taken account both of the variation of the ideal slope with temperature and the deviation from proportionality of molality and mole fraction, both of which are here larger than in aqueous solutions. If we assume that the ions are not solvated, we have as a first approximation for the freezing point depression produced by an ideal strong electrolyte of the type under discussion

$$\frac{\mathrm{d}\,\vartheta}{\mathrm{d}\,m} = 6.154\,i\left[1 - \frac{m_{\mathrm{H}} + im}{10.20} - 0.0047\,\vartheta\right] \qquad (1)$$

The quantity 6.154 times the bracket for values of m and ϑ midway between the initial and final values for the particular experiment is tabulated under S and was used in calculating the values of i given. We have also included in the tables under μ the approximate total ionic strength of the solution.

It is a striking result of these experiments that the values of i lie so near to whole numbers, even at moderately large ionic strengths, and with both 1:1 and 2:1 electrolytes. Unless there is some peculiar compensation, interionic attractions and other factors which might cause changes in ionic activity coefficients with varying concentration have a magnitude too small to be detected by this type of experimentation.

We have thus found an "apparent degree of ionization" of very nearly 100%, and in this we differ from previous workers. Hantzsch obtained an average value of 83% for 1:1 electrolytes, Oddo[11] agreed with Hantzsch for the solute water, but obtained 100% for some nitrogen bases, Poma[12] found 66%. Part of this difference probably lies in the use by previous workers of an initial solvent in which the self-dissociation had not been completely repressed. This would of course give a lower estimate of the degree of ionization of the solute, but there are probably further differences of significance in the actual experimentation. Hantzsch's direct determination of the cryoscopic constant of sulfuric acid with non-electrolytes gave an average value of 7.00, similar experiments of Oddo gave 6.81, whereas Brönsted's heat of solidification predicts 6.15.

Non-electrolytes

Table III contains the results of experiments with three solutes which Hantzsch found by conductivity methods to be non-electrolytes. The

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(11) Oddo and Scandola, *Z. physik. Chem.*, **62**, 243 (1908); **66**, 138 (1909); *Gazz. chim. ital.*, **39**, II, 1 (1909); **39**, II, 44 (1909); **40**, II, 163 (1910); Oddo and Casalino, *ibid.*, **47**, II, 200 (1917); **47**, II, 232 (1917); **48**, I, 17 (1918).

(12) Poma, *J. chim. phys.*, **10**, 177 (1912).

molal freezing point depressions calculated from the dilute solution law and listed under the heading λ agree moderately well with the value predicted from the thermal data. Such a constant difference as thus appears between the results of different workers is, of course, easily possible with the Beckmann method unless extreme care is taken to eliminate errors. In view, however, of the precautions taken by us, especially the application of the supercooling correction and the careful control of the temperature of the outside bath, neither of which is mentioned by the other investigators, we feel that the agreement of our results with the thermal data and the divergence of previous results are not fortuitous.

TABLE III

m	t	ϑ	λ
	s-Trinitrobenzene		
0.0410	0.05	0.260	6.36
.1002	.1	.626	6.25
.1679	.1	1.036	6.17
	Picric Acid		
.0535	.5	0.334	6.24
.1621	.5	.967	5.97
	Trichloroacetic Acid		
.2671	.2	1.601	6.00

Organic Bases

Table IV contains the results of cryoscopic investigations on some organic bases, including our indicators and other substances studied in the search for indicators. The slopes used in the calculation of i and listed under S were obtained from an equation similar to equation 1 but taking account of the disappearance of sulfuric acid in the ionization reaction $B + H_2SO_4 \rightleftarrows BH^+ + HSO_4^-$. The experiments here listed cannot be expected to have the precision of those with the inorganic electrolytes because of the difficulty of obtaining the compounds concerned in a pure and especially in an anhydrous condition. All of the bases listed were found to be recoverable unchanged upon dilution after the determination.

TABLE IV

m	ϑ	t	μ	S	
		o-Nitraniline			
0.0640	0.812	1.2	0.15	6.11	2.08
		p-Chloro-*o*-nitraniline			
0.0380	0.461	0.4	0.08	6.13	1.98
		2,4-Dichloro-6-nitroaniline			
0.0111	0.134	0.3	0.03	6.15	1.96
		2,4-Dinitroaniline			
0.0199	0.227	0.4	0.05	6.14	1.86
.0237	.282		.15	6.11	1.95

TABLE IV (*Concluded*)

m	ϑ	t	α	S	i
2,6-Dinitro-4-methylaniline					
0.00977	0.125	0.5	0.05	6.14	2.08
N,N-Dimethyl-2,4,6-trinitroaniline					
0.00856	0.107	0.1	0.05	6.15	2.03
6-Bromo-2,4-dinitroaniline					
0.00722	0.095	0.4	0.05	6.14	2.14
2,4,6-Trinitroaniline					
0.0169	0.193	0.5	0.05	6.14	1.86
.0464	.525		.1	6.13	1.85
.0714	.779		.15	6.11	1.79
Azobenzene					
0.0209	0.242	0.2	0.03	6.15	1.88
.0368	.469		.1	6.13	2.08
.0362	.484		.15	6.12	2.18
p-Nitroazobenzene					
0.00911	0.108	0.3	0.03	6.14	1.93
.01152	.142		.04	6.14	1.99
Benzalacetophenone					
0.0219	0.255	0.2	0.04	6.15	1.89
.0624	.803		.1	6.13	2.10
Anthraquinone					
0.0215	0.261	0.3	0.05	6.14	1.98
.0393	.498		.1	6.13	2.07
.0374	.506		.15	6.12	2.21
Cinnamalacetophenone					
0.0223	0.533	0.5	0.09	6.15	3.89
.0218	.527		.14	6.14	3.93
Alizarine					
0.0182	0.312	0.3	0.09	6.15	2.78
.0125	.212		.13	6.15	2.76
.0264	.449		.21	6.15	2.76
Triphenylcarbinol					
0.0202	0.478	0.3	0.06	6.13	3.85
.0358	.888		.15	6.12	4.05
.0205	.531		.19	6.10	4.26
.0195	.464	.9	.1	6.12	3.88
.0361	.910		.15	6.11	4.13

Anthraquinone and triphenylcarbinol have previously been studied by Hantzsch, and our results agree with his in respect to their types of ionization, although not with respect to their extent of ionization. It is interesting to note that Hantzsch has found that dibenzalacetone, like triphenylcarbinol, forms four moles of ionization products, and that we now find cinnamalacetophenone with two differently distributed double bonds behaves similarly, but that benzalacetophenone with one double bond is a simple mono acid base.

The Effect of Water on the Solubility of Barium Sulfate

The picture of sulfuric acid as a solvent in which ions act as nearly ideal solutes is confirmed by our previous indicator measurements, which show that the bisulfate-ion activity is proportional to the concentration of water in the range of water concentrations from 0.1 to 1 molal, and more emphatically by the effect of water upon the solubility of barium sulfate in sulfuric acid. In Table V are given those figures of Trenner and Taylor[13] for the composition of sulfuric acid–water mixtures in equilibrium with solid barium sulfate for which the solid phase was of invariant composition, probably $BaSO_4 \cdot H_2SO_4$ or $Ba(HSO_4)_2$. From these we have calculated the molality of water and barium sulfate and, on the assumption of complete ionization of barium bisulfate and oxonium bisulfate, the solubility product $k_m = m_{Ba^{--}} \times m^2_{HSO_4^-}$. We have also calculated n, the total number of moles in a solution containing 1000 g. of sulfuric acid (on the basis of unsolvated ions), and from this the solubility product in terms of mole fractions k_N.

TABLE V

% by wt.			Molality					
H_2SO_4	H_2O	$BaSO_4$	$BaSO_4$	H_2O	HSO_4	k_m	n	k_N
84.11		15.89	0.8093	0.000	1.619	2.121	11.82	1.284×10^{-3}
84.05	0.21	15.74	.8023	.139	1.744	2.440	11.94	1.434
84.22	.17	15.61	.7939	.112	1.700	2.295	11.90	1.362
84.84	.46	14.70	.7422	.301	1.785	2.365	11.99	1.372
85.27	.90	13.83	.6949	.586	1.976	2.713	12.18	1.501
85.49	.89	13.62	.6825	.578	1.943	2.576	12.14	1.440
85.80	.95	13.25	.6615	.614	1.937	2.481	12.14	1.387
85.57	1.26	13.17	.6593	.817	2.136	3.008	12.34	1.602
86.00	1.21	12.79	.6371	.782	2.056	2.693	12.26	1.462
86.06	1.65	12.29	.6118	1.063	2.287	3.200	12.49	1.642
86.54	1.78	11.68	.5782	1.141	2.297	3.050	12.50	1.562
87.22	1.83	10.95	.5378	1.164	2.240	2.700	12.44	1.402
88.45	3.02	8.53	.4131	1.893	2.719	3.053	12.92	1.416
88.86	3.63	7.05	.3399	2.266	2.946	2.949	13.15	1.297
89.13	3.58	7.29	.3504	2.229	2.930	3.009	13.13	1.330
89.28	3.86	6.86	.3292	2.399	3.057	3.075	13.26	1.319
89.68	4.53	5.79	.2765	2.802	3.355	3.112	13.55	1.251
90.40	4.97	4.63	.2194	3.051	3.490	2.672	13.69	1.042

In view of the constancy of these figures, it appears that the decrease in the solubility of barium sulfate in sulfuric acid produced by water is a common ion effect and arises from the fact that both barium sulfate and water are bases in the sulfuric acid system and have in common the char-

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(13) Trenner and Taylor, *J. Phys. Chem.*, **35**, 1336 (1931).

acteristic basic ion of the system, bisulfate ion. The simplicity of the nature of electrolyte solutions in sulfuric acid appears clearly from the fact that we are thus able to apply the solubility product principle to an electrolyte of an initial solubility of 0.8 molal and over a range of concentrations of added electrolyte from zero to nearly three molal.

Summary

Cryoscopic measurements on various ionized solutes in the solvent sulfuric acid may be simply interpreted by taking account of the large dissociation of the solvent. Within the best precision of the Beckmann method, ionic activity coefficients are constant over a wide range of concentrations.

In agreement with this it is found possible to apply the solubility product principle to the effect of water upon the solubility of barium sulfate in sulfuric acid.

NEW YORK CITY

RECEIVED NOVEMBER 28, 1932
PUBLISHED MAY 6, 1933

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 347]

The Reduction Potential of Vanadic Acid to Vanadyl Ion in Hydrochloric Acid Solutions

BY CHARLES D. CORYELL AND DON M. YOST

Introduction

Earlier investigations of cells involving pentavalent and tetravalent vanadium gave values of -0.92 volt[1] and -1.0 volt[2] for the molal reduction potential in sulfuric acid solutions. Abegg, Auerbach and Luther[3] base their figure of -1.20 volts on the first mentioned determination. Uncertain liquid junction potentials diminish the reliability of these determinations, and the undetermined part that the acid concentration plays in the cell reactions introduces uncertainty in the interpretation of the published values.

In this paper are presented the results of measurements on cells in which the potentials due to liquid junctions are practically eliminated. Hydrochloric acid solutions of the vanadium compounds were used rather than sulfuric acid solutions because it is in chloride solutions that a knowledge of the reduction potential is most often desired. This is, for example, the case in applications to qualitative analysis.[4]

(1) Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

(2) Foerster and Böttcher, *Z. physik. Chem.*, [A] **151**, 321 (1930).

(3) Abegg, Auerbach and Luther, "Messungen elektromotorische Kräfte galvanische Ketten," Halle A.S., Wilhelm Knapp, 1911, p. 199.

(4) See, for example, Noyes and Bray, "Qualitative Analysis of the Rare Elements," Macmillan Co., New York, 1927.