volving two uncharged acids or bases and their monovalent salts. For cases in which a chemical reaction goes to completion in the moving boundary with the result that each constituent disappears across it, the mobility values calculated from the boundary velocity and the conductances of the phases separated by the boundary agree with the theoretical constituent mobilities within the experimental error. Thus the moving boundary method can be used for the experimental determination of constituent mobilities as long as a steady state boundary is formed in which the chemical reaction is complete. It should be noted that the theoretical constituent mobilities are obtained by substituting the mobility of the ion and the concentrations of ion and uncharged form into the defining equation (*e. g.*, equation 3 for acetate constituent). This assumes that the mobility of the ion form of the constituent is not affected by the presence of the uncharged molecules.

The conditions under which steady state boundaries are expected may be obtained from the theory. The experimental results agree qualitatively with the theory, although the specific experimental conditions for which the boundary ceases to move in a steady state do not exactly coincide with those predicted theoretically. This is not surprising, since the titration constants are assumed to be independent of concentration and since the theory assumes constant relative ion mobilities.

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Summary

The moving boundary equation for weak electrolytes has been verified for systems containing weak acids and bases which dissociate to give monovalent ions. Depending upon the relative values of the ionization constants and of the ion mobilities concerned, chemical reactions may occur in the moving boundary systems. If these reactions go to completion, the experimentally determined mobilities ($v\kappa$ products) are identical with the constituent mobilities. Thus for the system NaOAc, HOAc(γ)←NaCac, HCac(β)::NaCac(α), the experimental value, $v^{\beta\gamma}\kappa^{\gamma}$, is identical with the acetate constituent mobility given by the equation $\bar{u}^{\gamma}_{\mathrm{OAc}} = u^{\gamma}_{\mathrm{OAc}}c^{\gamma}_{\mathrm{OAc}}/(c^{\gamma}_{\mathrm{OAc}} + c^{\gamma}_{\mathrm{HOAc}})$. In contrast to the strong electrolyte case, the theory predicts and the experimental results confirm that, for weak electrolyte systems, steady state moving boundaries may be obtained even when the boundary is followed by the ion of higher mobility.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Hydrogen Cycle Cation Exchange for Heteropoly Acids and Salts*

BY LOUIS C. W. BAKER, BERNARD LOEV AND THOMAS P. MCCUTCHEON

This investigation was carried out to determine the feasibility of preparing free heteropoly acids from their salts by use of a cation exchange resin. It was expected that the behavior of the heteropoly anions in the presence of a cation exchanger would throw some light on the equilibria existing in the solutions. In addition to their well-known uses[1,2,3] free heteropoly acids are, because of their great solubility, frequently advantageous intermediates in the preparation of heteropoly salts.[3,4,5]

A high capacity sulfonic acid type cation exchange resin was chosen because heteropoly acids are usually strong and often easily reduced. This resin possesses only strongly acidic functional groups, has practically no reducing power, and, if used properly, does not store anions from the regenerant for later release to the solutions being put through the column.

Several well-known heteropoly salts, representative of types suggested by their possible behaviors in the presence of a cation exchange resin, were prepared. Analyses, to establish the identity of the heteropoly ions, were performed in most cases. Following the suggestion of Illingworth and Keggin,[2] powder X-ray patterns of all salts were taken to enable easy identification when they were re-formed in later stages of the work.[6]

Solutions or suspensions of the salts were passed through a column of exchange resin. The *p*H's of the resulting heteropoly acid solutions were determined, and aliquots of the solutions were analyzed for the constituents of the heteropoly anions. In each case an attempt was made to reform the original heteropoly salt from the acid solution by metathesis. The powder X-ray patterns of the salts so formed were compared with those of the parent salts. The general absence of

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* We wish to thank the Committee on Advancement of Research of the University of Pennsylvania for a grant which helped to make this work possible.

(1) H. Wu, *J. Biol. Chem.*, **43**, 189 ff. (1920).

(2) Illingworth and Keggin, *J. Chem. Soc.*, 575 ff. (1935).

(3) M. Jean, *Ann. Chim.*, [12], **3**, 470 ff. (1948).

(4) G. Spacu and V. Nicholaescu, *Bull. Soc. Stiinte Cluj*, **9**, 45 ff. (1938).

(5) *Ibid.*, **9**, 347 ff. (1939).

(6) These X-ray patterns will appear in the third supplement to the A. S. T.M. Powder X-Ray File.

background in the X-ray patterns of the salts formed from the acid solutions indicated that most of them were even more pure than the analyzed samples of the original salts.

The solid acids were prepared by evaporation of their solutions. The stability of the acid solutions upon standing for several weeks was observed. The effects of letting the solutions stand for prolonged periods in contact with separate portions of exchange resin were also noted. In two cases new salts of the heteropoly anions were prepared from the acids by metathesis, analyzed, and X-rayed.

After each run, the exchange material was washed until the water gave no tests for any of the ions involved. Following an additional thorough washing, the resin was regenerated, using upflow technique. The used regenerant solution in each case was concentrated and tested qualitatively for the constituents of the heteropoly salt. A washed but unregenerated portion of the resin was extracted with sodium hydroxide solution. This solution was then tested for the presence of molybdates or tungstates, depending upon which had been involved in the experiment.

Experimental Results and Discussion

Apparatus.—The X-ray patterns were taken on a North American Phillips Geiger counter X-ray spectrometer with automatic recording device. A Leeds and Northrup No. 7662 *p*H Meter was used.

Preliminary Experiment.—Since it has been shown[7] that certain artificial cation exchange materials are incapable of producing pure acids from their salts because the resulting solutions are always contaminated with anions of the acid which was used to regenerate the exchanger, an experiment was performed to show that such was not the case with the exchange resin used in this study. A column of the resin was washed thoroughly with distilled water and upflow regenerated with a large volume of 2 *N* hydrochloric acid. The resin bed was then washed until water could stand in it for two days and still give no reaction with silver nitrate. A 2 *N* solution of sodium sulfate was thereupon passed slowly through the resin bed. The strongly acidic effluent was tested for sodium ion by the flame test, and for chloride ion, with negative results in both cases. A similar regenerating and washing procedure was used before all runs made with heteropoly compounds.

Heteropoly Compounds.—(I) The bright yellow, soluble ammonium salt of the 9-molybdophosphate anion was prepared[1] and X-rayed. This anion may be variously formulated.[1,8] *Anal.* Calcd. for $(NH_4)_6H_6[P_2O_2(Mo_2O_7)_9]\cdot 7H_2O$ or $(NH_4)_6[P_2Mo_{18}O_{62}]\cdot 10H_2O$: P, 2.02; Mo, 56.2. Found: P, 2.00; Mo, 56.5; atomic P:Mo ratio, 1:9.06. This substance, especially when in the solid state, is readily reduced by metals, dust, etc., to deep blue-green substances.[1] However, if a few drops of dilute hydrogen peroxide are added to a solution of this compound, it can be kept for long periods without reduction.

When a solution of this salt was passed through the exchange column (45 cm. high by 4 cm. in diam.), no reduction by the resin occurred, although no hydrogen peroxide had been added. The effluent had the same yellow color as the influent, gave no Nessler test for ammonium ion, and had a *p*H of 1.4. A molarity of 0.015 on the basis of the above formulas,[9] and an average atomic P:Mo ratio of 1:8.95 were revealed by analysis of aliquots of the acid. Evaporation produced the very soluble solid orange acid which has been prepared previously by other methods.[1] The acid solution did not decompose on long standing. Some of the solution, containing a little hydrogen peroxide, was allowed to stand overnight in contact with a separate portion of the resin; and no decomposition was noticeable. When the hydrogen peroxide was omitted, overnight standing with the resin reduced some of the heteropoly ion and thereby produced in the solution a green color, which was readily dispelled by addition of hydrogen peroxide. The resin was washed and regenerated as described above. The used regenerant contained much ammonium ion, but no phosphorus or molybdenum. The sodium hydroxide wash contained no molybdenum. The ammonium salt was re-formed by dissolving solid ammonium chloride in the acid solution until the concentration was just beneath that at which the ammonium heteropoly salt would precipitate; after which, saturated ammonium chloride solution was added. The powder X-ray pattern of the recrystallized precipitate was identical with that of the original ammonium salt.

These experiments show that production of an acid which is easily reduced is possible. To avoid reduction, hydrogen peroxide may be added to the influent and removed from the effluent by boiling. The slight change in atomic P:Mo ratio is within the error of the analyses. The presence of a cation exchange resin does not decompose this anion, presumably because the equilibria in which it is involved in solution cannot produce any cations other than hydrated protons.

(II) A recrystallized sample of the pink, moderately soluble ammonium salt of the very stable 6-molybdochromic ion[10,11,12] was then subjected to identical treatment (except that no use of hydrogen peroxide was necessary). *Anal.* Calcd. for $(NH_4)_3H_6[Cr(MoO_4)_6]\cdot 4H_2O$: Cr, 4.54; Mo, 50.4. Found: Cr, 4.63; Mo, 50.6; atomic Cr:Mo ratio, 1:5.94. The acid solution gave no Nessler test and had a *p*H of 1.4 at a molarity of 0.021. The pink solution, upon evaporation to dryness, gave a green solid which could be redissolved to re-form the pink solution. This behavior identifies the acid with that previously prepared by other methods.[11] Analysis of aliquots of the acid solution showed an average atomic Cr:Mo ratio of 1:6.13. The solution did not decompose on 2 months' standing. The used regenerant solution contained much ammonium ion, traces of chromium, and no molybdenum. The sodium hydroxide wash contained no molybdenum. If the heteropoly salt solution was allowed to stand in contact with the resin overnight, the pink color was completely destroyed. The effluent then contained much molybdenum, but only a small amount of chromium. The used regenerant for this portion of resin contained much ammonium ion, a moderate amount of chromium, and no molybdenum. The ammonium salt of the heteropoly anion was reprepared from the free acid by addition of ammonium chloride solution. It was recrystallized. Its powder X-ray pattern was identical with that of the parent salt.

The monomethylammonium salt of the anion was prepared by adding monomethylammonium chloride solution to the solution of the free acid. This new, moderately soluble, beautifully crystalline, pink compound was recrystallized and X-rayed. *Anal.* Calcd. for $[(CH_3)NH_3]_3H_6[Cr(MoO_4)_6]\cdot 8H_2O$: N, 3.36; Cr, 4.14; Mo, 45.5. Found: N, 3.40; Cr, 4.16; Mo, 45.8.

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(7) Mathers and Yancy, *Proc. Indiana Acad. Sci.*, **51**, 132 (1941).

(8) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y., 1945, p. 344.

(9) Extraordinary efficiencies, in terms of grams of solute converted, are achieved with exchange resins operating on solutions of the high molecular weight heteropoly compounds, because their solutions, concentrated in terms of weight per cent. of solute, are dilute in terms of molarity.

(10) Struve, *J. prakt. Chem.*, **61**, 449 (1854).

(11) R. D. Hall, THIS JOURNAL, **29**, 695 ff. (1907).

(12) Rosenheim and Schwer, *Z. anorg. Chem.*, **89**, 226 ff. (1914).

Magnetic measurements made by Rây, *et al.*,[13] indicate that this heteropoly ion is an octahedral coördination complex of the penetration type with d^2sp^3 bonds. The decreased proportion of chromium in the effluent, the presence of chromium in the used regenerant, and the decomposition of the complex upon standing with the resin, all indicate that there is, nevertheless, a very small equilibrium concentration of chromic ions in solutions containing this heteropoly anion, even at low *p*H. This effect is so small, however, that production of the free acid, containing only minute traces of excess molybdate, is practical by ion exchange if the solution is not kept in contact with the resin longer than necessary.

(III) The insoluble, colorless ammonium salt of the 6-molybdoferric ion was prepared.[11,12,13] On warming in water, the insoluble compound decomposed to form an orange-brown solution. On rapid cooling, the colorless complex reformed, thereby enabling it to be recrystallized. The recrystallized material was pure white. The compound was not analyzed quantitatively, but its crystallization in colorless square plates identified it with $(NH_4)_3H_6[Fe(MoO_4)_6]\cdot 7H_2O$ analyzed previously.[11,12,13] It was X-rayed.

Since this salt is insoluble, it was pulverized; and a suspension of it was passed through the exchange column. The insoluble particles were completely transposed, during passage through the column, into the free acid and the even more insoluble ammonium form of the resin. The colorless effluent contained no ammonium ion, produced no Tyndall cone, and had a *p*H of 2.4 at a molarity of approximately 0.003. The addition of ammonium chloride solution produced an immediate precipitate, the crystal form and X-ray pattern of which were identical with those of the parent ammonium salt. When heated, the free acid decomposed irreversibly to form an orange-brown solution. The acid did not decompose upon two months of standing at room temperature. The used regenerant contained a small amount of iron, much ammonium ion, and no molybdenum. The sodium hydroxide wash contained no molybdenum.

In contrast with the 6-molybdochromic ion discussed above, magnetic measurements made by Rây, *et al.*,[13] indicate the 6-molybdoferric ion in the solid state to be a complex anion of the associated type with sp^3d^2 octahedral bonds, which might resonate with ionic bonds. The above experiments indicate that the concentration of the cation of the central atom in equilibrium with the complex was extremely small and of an order of magnitude comparable with the case of the 6-molybdochromic ion.

The production of an acid from an insoluble salt, where no soluble salt is available, emphasizes the versatility of the method.

(IV) The soluble, light greenish-blue ammonium salt of the 6-molybdocobaltic ion was prepared by the method of Friedheim and Keller.[14] It was also prepared in good yield by a new method, from a complex cobaltic cation, without the use of an oxidizing agent; 500 ml. of solution, containing 15 g. of carbonatotetramminecobaltinitrate, was added in small portions to 500 ml. of a boiling solution which contained 72 g. of ammonium paramolybdate. The solution was evaporated to 150 ml. and filtered. Addition of ammonium chloride produced a precipitate which contained much ammonium 6-molybdocobaltiate and some ammonium 5-molybdocobaltiate (dark olive-green). These were easily separated owing to the greater solubility of the latter. The yield was about 70%. *Anal.* Calcd. for $(NH_4)_3H_6[Co(MoO_4)_6]\cdot 7H_2O$: Co, 4.89; Mo, 47.8. Found, when prepd. by method of Friedheim and Keller: Co, 4.74; Mo, 47.7; atomic Co:Mo ratio, 1:6.19. Found, when prepd. from carbonatotetramminecobaltinitrate: Co, 4.74; Mo, 47.8.

A solution of this compound was passed through the exchange column. An effluent of the same blue-green color as the influent was produced, which contained no ammonium ion. It had a *p*H of 1.7 at a molarity of 0.019. Aliquots of this solution were analyzed and revealed an atomic Co:Mo ratio of 1:6.24. The solution showed no decomposition after several weeks of standing. The new, extremely soluble, green solid acid was made by evaporation. The used regenerant contained much ammonium ion, some cobalt, and no molybdenum. The sodium hydroxide wash contained no molybdenum. A solution of the acid was decolorized when it was allowed to stand in contact with the resin for three days. The used regenerant for this portion of resin contained much cobalt and ammonium ion, but no molybdenum. The ammonium salt of the anion was prepared from the acid by addition of ammonium chloride solution. It was recrystallized. Its powder X-ray pattern was identical with that of the original ammonium salt.

The monomethylammonium salt of the anion was prepared by adding monomethylammonium chloride to the acid. This new, moderately soluble, beautifully crystalline, light blue compound was X-rayed. *Anal.* Calcd. for $[(CH_3)NH_3]_3H_6[Co(MoO_4)_6]\cdot 6H_2O$: N, 3.42; Co, 4.81; Mo, 47.0. Found: N, 3.53; Co, 4.80; Mo, 46.7.

This heteropoly ion is of the same valence type as the 6-molybdochromic ion.[13] The results indicate an analogous case with respect to behavior in the presence of a cation exchanger. The cobalt was probably removed as cobaltous cation after reduction by the resin.

(V) The soluble, dark olive-green ammonium salt of the 5-molybdocobaltic ion was prepared, using the method of Friedheim and Keller[14] except that 3% hydrogen peroxide solution was used. The product was recrystallized by dissolving excess ammonium chloride in its solution. The composition of the resulting salt corresponded to the triammonium 5-molybdocobaltiate reported by N. S. Kurnakow,[15] who used bromine as oxidizing agent, rather than to the diammonium 5-molybdocoaltiate prepared by Friedheim and Keller. The compound was X-rayed. *Anal.* Calcd. for $(NH_4)_3H_5[Co(OH)(MoO_4)_5]\cdot 3H_2O$: Co, 5.97; N, 4.25; Mo, 48.6. Found: Co, 5.96; N, 4.42; Mo, 48.3; atomic Co:Mo ratio, 1:4.97. This salt is stable in the solid state, but decomposed upon prolonged standing in solution. When the solution was passed through the exchange column, the clear effluent had the same color as the influent, contained no ammonium ion, and had a *p*H of 1.7 at a molarity of 0.019. Immediate addition of ammonium chloride resulted in the precipitation of impure ammonium 5-molybdocobaltiate, which was identified by its X-ray pattern. Upon standing, the acid solution deposited molybdic oxide. After standing for several hours, the heteropoly ion was apparently completely converted to the 6-molybdocobaltic ion; and addition of ammonium chloride then produced a precipitate which consisted principally of ammonium 6-molybdocobaltiate, the identity of which was verified by its X-ray pattern. The decomposition and conversion of the heteropoly ion is caused by the low *p*H, since addition of a mineral acid to a solution of ammonium 5-molybdocobaltiate brought about the same effects. The used regenerant contained much ammonium ion, some cobalt, and no molybdenum. The sodium hydroxide wash contained no molybdenum. When

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[13] P. Rây, A. Bhaduri and B. Sarma, *J. Indian Chem. Soc.*, **25**, 51-56 (1948).

[14] Friedheim and Keller, *Ber.*, **39**^{4}, 4301 ff. (1907).

[15] Gmelin, "Handbuch der anorg. Chem.," 8th ed., **53**, 392 (1935).

a solution of the acid was allowed to stand in contact with resin for 3 days, it was almost completely decolorized; and a large amount of molybdic oxide precipitated in the resin bed. The used regenerant for this portion of resin contained much ammonium ion and cobalt.

In this case also, the cobalt which is removed by the resin is apparently first reduced by it. The formation, even in an impure condition, of so unstable an acid demonstrated the usefulness of the ion exchange method.

(VI) The soluble, dark orange-red ammonium phospho-vanadio tungstate was prepared according to Rogers,[16] who assigned to it the formula $13(NH_4)_2O \cdot 2P_2O_5 \cdot 8V_2O_5 \cdot 34WO_3 \cdot 86H_2O$. The compound was analyzed qualitatively. The crystal form corresponded to that described in the literature.

A solution of this compound, approximately 0.002 molar on the basis of the above formula, was passed through the exchange column. The effluent was slightly lighter in color than the influent, contained no ammonium ion, and produced no Tyndall cone. It did not decompose upon standing for several months. Its *p*H was 1.6. It gave positive qualitative tests for phosphorus, tungsten, and vanadium. Evaporation produced a very soluble, reddish-orange, crystalline solid which completely redissolved to form a very acidic solution. The used regenerant contained much ammonium ion and a moderate amount of vanadium, but no phosphorus or tungsten. The sodium hydroxide wash contained no tungsten. Addition of ammonium chloride to the acid solution produced a crystalline orange precipitate which was proved by X-ray to be different from the original salt.

The structure of this reproducible compound is unknown, as is the precise significance of the formula ascribed by Rogers. The results indicate that ammonium ion is held to one or more complex anions containing phosphorus, vanadium, and/or tungsten. A new acid containing these elements was apparently produced. The partial reduction and removal of pentavalent vanadium from solutions by ion exchange resins has been noted previously.[17]

(VII) The soluble, very dark brown ammonium phospho-vanadico tungstate was prepared according to Rogers,[16] who assigned it the formula $15(NH_4)_2O \cdot 2P_2O_5 \cdot 6V_2O_3 \cdot 44WO_3 \cdot 106H_2O$. The compound was analyzed qualitatively. The crystal form corresponded to that described. Upon heating with concd. hydrochloric acid, no chlorine was evolved, thus proving that no pentavalent vanadium was present.

A solution of this substance, approximately 0.002 molar on the basis of the above formula, was passed through the exchange column. The color of the effluent was more orange than that of the influent. The solution contained no ammonium ion, produced no Tyndall cone, and had a *p*H of 1.6. It contained phosphorus, vanadium and tungsten. It had not decomposed after standing for two months. Evaporation to dryness produced soluble, orange crystals. Addition of ammonium chloride caused the solution to darken, and then to precipitate a crystalline substance of nearly the same color as the original salt. X-Ray evidence, however, proved this to be a different substance. The used regenerant contained much ammonium ion and some vanadium but no phosphorus or tungsten. The quantity of vanadium in the regenerant was approximately one third as much as that found in the case of a similar size run on ammonium phospho-vanadio tungstate (VI). The sodium hydroxide wash contained no tungsten.

This case is analogous to that of the preceding compound. Vanadium-containing cations must be in equilibrium to a limited extent with some complex in the solution.

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Summary

1. A new and convenient method for the preparation of heteropoly acids has been presented, with an investigation of some of the limits of its applicability.

2. A new method for the preparation of 5-molybdocobaltiate and 6-molybdocobaltiate ions from a complex cobaltic cation has been described.

3. Two new heteropoly salts and 5 new heteropoly acids have been reported.

4. It has been indicated that solutions of certain heteropoly ions of different valence types contain small equilibrium concentrations of the cations of their central atoms even at low *p*H and that vanadium in its +3 and +5 valence states is partially removed from certain heteropoly compounds by a cation exchange resin.

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[16] A. Rogers, THIS JOURNAL, **25**, 299 ff. (1903); see also: W. E. Henderson and W. C. Fernelius, "A Course in Inorganic Preparations," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 121-122.

[17] Devlin, McNabb and Hazel, *J. Franklin Inst.*, **248**, [3] 251-253 (1949).