39. *Polyanion Equilibria in Aqueous Solution. Part II.*[1] *A Thermodynamic Study of the Paratungstate A Anion.*

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The equilibrium between the normal tungstate ion WO_4^{2-} and the paratungstate A ion $HW_6O_{21}^{5-}$ has been studied by using paper chromatography with ^{185}W tracer as the method of analysis. The thermodynamic equilibrium constant and enthalpy and entropy changes for the condensation have been evaluated and are discussed.

IT is possible to determine quantitatively the species present in acidified tungstate solutions by using paper chromatography with ^{185}W as tracer.[1] We report here a detailed study of the effect of pH, concentration, and temperature on the equilibrium between the normal tungstate ion WO_4^{2-} and its first chromatographically separable condensation product, the paratungstate A ion $HW_6O_{21}^{5-}$, formed by the reaction:

$$7H^+ + 6WO_4^{2-} \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O \qquad (1)$$

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[1] Part I, *J.*, 1961, 5317.

EXPERIMENTAL

The preparation of solutions, chromatographic technique, and measurement of activity have been described previously.[1]

Control of pH.—All experimental work was carried out in a temperature-controlled glove box through which carbon dioxide-free air was continually passed. The pH of each solution was measured by means of a Cambridge glass–calomel meter standardised with a 0·050M-potassium hydrogen phthalate buffer and a 0·010M-borax buffer. On no occasion was the difference between the buffers greater than $0{\cdot}00_5$ of a pH unit from that expected from published values [2] in the temperature range 18—35°. The buffer solutions were prepared weekly from carbon dioxide-free distilled water and kept under a carbon dioxide-free atmosphere.

Method.—Aliquot parts (5·00 ml.) of sodium ^{185}W-tungstate containing a 10% molar excess of sodium hydroxide were titrated potentiometrically against hydrochloric acid. Up to four 1 ml. samples were removed at suitable volume intervals during each titration. The solutions were left overnight to allow the pH to become constant before measurement. The pH was then accurately determined (±0·01 pH) and the species present were quantitatively separated by paper chromatography.

The experimental conditions for each series of titrations are shown in Table 1.

TABLE 1.

Experimental conditions for titration.

Expt. no.	HCl (N)	Na_2WO_4 (M)	Temp.	Expt. no.	HCl (N)	Na_2WO_4 (M)	Temp.
1	0·1080	0·1900	25°	4(a)	2·39	0·2982	25°
2	2·005	0·0192	25	4(b)	2·39	0·2982	35
3	2·39	1·178	25	4(c)	2·39	0·2982	17

Heat of Reaction.—The heat of reaction of 215 ml. of 0·100M-sodium tungstate and 10·0 ml. of 2·39N-hydrochloric acid was determined calorimetrically by mixing in a Dewar flask. The temperatures of the solutions were measured for 10 min. before and after mixing and extrapolated to time of mixing (±0·002°). The observed temperature rise ($1{\cdot}00_5$°) was due to the heat of reaction plus the heat of dilution of the hydrochloric acid. The latter can be estimated from known values.[3] The water equivalent of the calorimeter was determined by mixing batches of water of different temperatures and by measuring the heat of dilution of hydrochloric acid under similar conditions to those used above.

RESULTS

The results of the chromatographic analyses of the above solutions are given in Fig. 1 as a plot of $x[=a_X/(a_X + a_Y)]$ against pH, where a_X and a_Y are the atom percent of tungsten as WO_4^{2-} and $HW_6O_{21}^{5-}$, respectively. In addition, about 10% of the tungsten was present as paratungstate B, $W_{12}O_{41}^{10-}$. As expected, the concentration of WO_4^{2-} decreases as the pH is decreased and it increases with increasing dilution at constant pH. At constant pH and total concentration, the concentration of $HW_6O_{21}^{5-}$ decreases with increasing temperature, confirming that polymerisation is exothermic.

The results are also plotted as a radiometric titration curve (Fig. 2). The solid line is the theoretical curve for reaction (1) for sodium tungstate containing 10% molar excess of sodium hydroxide. This plot shows clearly that the endpoint of the titration which forms the condensed species corresponds to a $H^+ : WO_4^{2-}$ ratio of 7 : 6 (1·17). It therefore confirms that the reaction takes place in the form written in (1), to give $HW_6O_{21}^{5-}$. The reaction cannot lead to $W_2O_7^{2-}$, $W_3O_{10}^{2-}$, $W_3O_{11}^{4-}$, $W_6O_{21}^{6-}$, $H_2W_6O_{21}^{4-}$, or $H_3W_6O_{21}^{3-}$.

DISCUSSION

The thermodynamic equilibrium constant K_a for reaction (1) will be the product of the mass product K_c and the activity coefficient product K_f.

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[2] Gold, " pH Measurements," Methuen, London, 1956, p. 118.

[3] " International Critical Tables," McGraw-Hill, New York, 1929, Vol. V, p. 212.

Mass Product K_c.—In the expression

$$K_c = \frac{[HW_6O_{21}^{5-}][H_2O]^3}{[H^+]^7[WO_4^{2-}]^6},$$

$$[HW_6O_{21}^{5-}] = a_Y C_{WO_3}/6$$

and

$$[WO_4^{2-}] = a_X C_{WO_3},$$

where C_{WO_3} is the stoicheiometric concentration of tungsten in the solution expressed as moles of WO_3 per litre. Thus K_c may be evaluated from the analytical results (Figs. 3 and 4a). Errors have been calculated by using a ±5% uncertainty in the quantitative measure of the tungsten present in each form, a 0·01 uncertainty in the pH, and a ±5% uncertainty in C_{WO_3}. Results have been evaluated only for $0{\cdot}10 < a_X < 0{\cdot}80$ and $0{\cdot}10 < a_Y < 0{\cdot}80$; outside these limits the errors of analysis are too great for reliability. The variation of K_c with concentration (Fig. 4a) is typical for an equilibrium constant in which activity coefficients have been ignored.

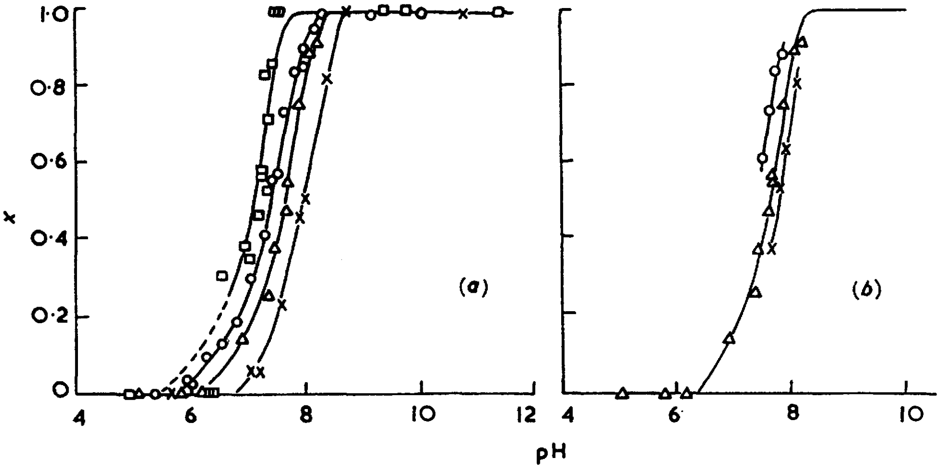

Fig. 1. (*a*) Dependence of composition x [$= a_X/(a_X + a_Y)$] upon pH and concentration. □ Expt. no. 2. ○ Expt. no. 1. △ Expt. no. 4(a). × Expt. no. 3. (*b*) Dependence of composition upon pH and temperature. ○ Expt. no. 4(b). △ Expt. no. 4(a). × Expt. no. 4(c).

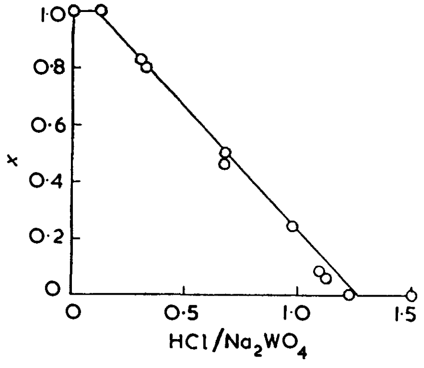

Fig. 2. Radiometric titration of hydrochloric acid against sodium tungstate (expt. no. 3).

A polarographic investigation of this reaction was carried out by Souchay[4] using

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[4] Souchay, *Ann. Chim.* (*France*), 1943, **18**, 73.

0·1M-sodium tungstate in buffered solutions where the ionic strength, and hence the activity coefficients, would be reasonably constant. In these conditions the polarograph measures concentration rather than activity, and the results obtained should be directly comparable with those obtained chromatographically at the same ionic strength as that of the buffer. From his results a value for the mass product for reaction (1) can be

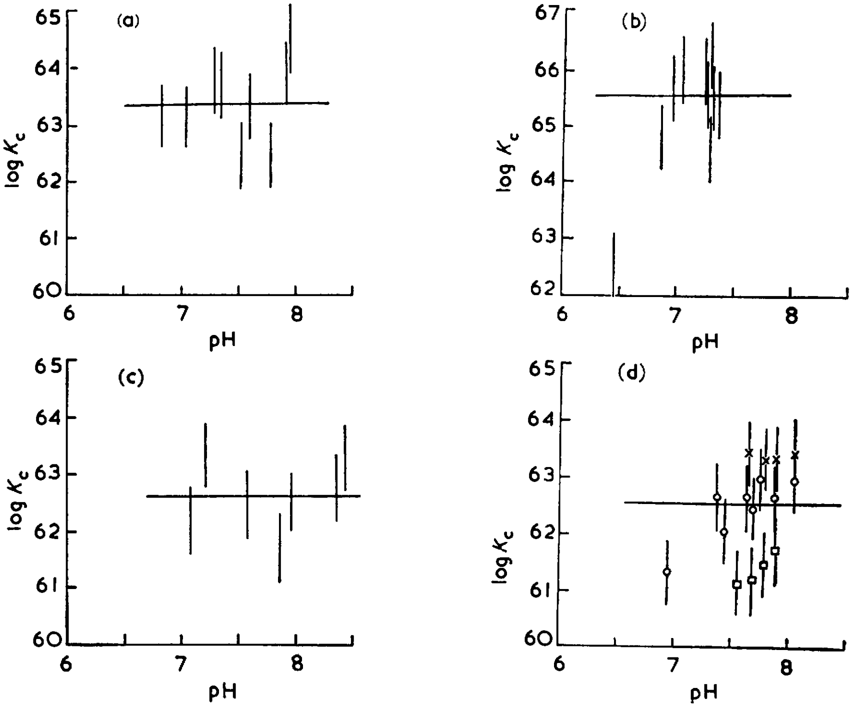

Fig. 3. Mass product K_c. (a) Expt. no. 1. (b) Expt. no. 2. (c) Expt. no. 3. (d) Expt. no. 4: × 17°, ○ 25°, □ 35°.

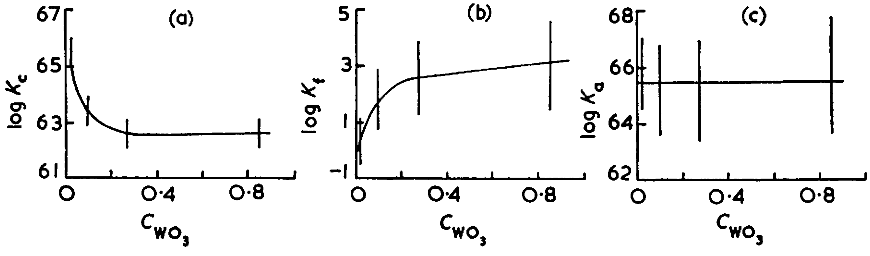

Fig. 4. (a) Mass product K_c. (b) Activity coefficient product K_f. (c) Thermodynamic equilibrium constant K_a.

calculated (see Table 2). The last result in Table 2 could be in considerable error, as at pH 6·64 there is very little of the normal tungstate present. If we neglect this figure, the average value for $\log_{10} K_c$ is 61·9. No error has been quoted, but it is probably of the same order of magnitude as that calculated for $\log K_c$ determined by chromatographic analysis, namely, $\pm 0·5$.

This estimate of K_c agrees, within the estimated errors, with the chromatographic results for $0·2 < C_{WO_3} < 0·9$, showing that the same equilibrium has been studied in both

TABLE 2.

Mass product (K_c) calculated from Souchay's data.

pH	7·66	7·47	7·33	7·08	6·79	6·64
log K_c	62·5	62·3	62·1	60·7	62·0	55·3

cases. The result also confirms indirectly Souchay's finding that paratungstate A and paratungstate B have the same degree of condensation. However, it is known that crystalline sodium paratungstate exists as a 12-fold aggregate[5] and dialysis has shown that when this is dissolved in water the initial product also contains twelve tungsten atoms.[6] Thus there must be more than two paratungstate anions, and this is confirmed by a recent absorption-spectroscopical investigation by Spitsyn and Pirogova.[6]

Activity-coefficient Product K_f.—Variation in the activity coefficients undoubtedly contributes to the variation of K_c with concentration shown in Fig. 4a. Now

$$K_f = \frac{(f_{HW_6O_{21}^{5-}})(f_{H_2O})^3}{(f_{H^+})^7(f_{WO_4^{2-}})^6}$$

$$\approx \frac{f_{HW_6O_{21}^{5-}}}{(f_{H^+})^7(f_{WO_4^{2-}})^6} \qquad (2)$$

The activity coefficients of single ions may be obtained by expressing them in terms of the mean ionic activity coefficient $f_\pm$ of electrolytes by equations of the type:

$$f_{\pm Na_5HW_6O_{21}} = (f_{Na^+}{}^5 + f_{HW_6O_{21}}{}^{5-})^{1/6}$$

Substituting such expressions in equation (2) and taking logarithms give:

$$\log K_f = 6 \log f_{\pm Na_5HW_6O_{21}} - 18 \log f_{\pm Na_2WO_4} + 14 \log f_{\pm NaCl} - 14 \log f_{\pm HCl} \qquad (3)$$

Equations derived from electrolyte theory for the activity coefficient of a pure electrolyte $f_\pm{}^0$ in dilute solutions, show that $\log f_\pm{}^0$ is approximately proportional to the ion-charge product of the cation and anion, $|Z^+Z^-|$, and also to the square root of the ionic strength I. The best equations, such as that of Davies,[7] can be used to predict the behaviour of a 1 : 1 electrolyte up to ~1M-concentration, but as the ion-charge product of the electrolyte is increased the contribution to the activity coefficients of ion–solvent interactions becomes increasingly important. These interactions cannot be predicted with any accuracy and the activity coefficient becomes increasingly uncertain, making it impossible to predict even the order of magnitude of the activity coefficient of a 0·1M-solution of a polyelectrolyte.

A closer estimate of the activity coefficient of the pure electrolyte ($f_\pm{}^0$) in such a case can be made by comparison with the activity coefficients of electrolytes possessing similar properties. In the present case, for example, the disodium salt of an inorganic oxyacid could be an analogue for sodium tungstate. Suitable salts with known activity coefficients are Na_2CO_3,[8] Na_2CrO_4,[8] Na_2HAsO_4,[8] Na_2HPO_4,[8] Na_2SO_4,[9] and $Na_2S_2O_3$ [8] (see Fig. 5). The activity coefficient of pure sodium tungstate ($f^0{}_{\pm Na_2WO_4}$) would be expected to lie within the extremes of these curves.

There are no activity coefficients known of salts of the same charge type as sodium

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[5] Lindqvist, *Acta Cryst.*, 1952, **5**, 667.

[6] Spitsyn and Pirogova, *Doklady Akad. Nauk S.S.S.R.*, 1957, **115**, 322.

[7] See Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1959, 2nd edn., p. 232.

[8] Ref. 7, pp. 491.

[9] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1958, 3rd edn., p. 553.

paratungstate A ($|Z^+Z^-| = 5$). Fig. 6 shows the variation of activity coefficients with ionic strength for a number of polyelectrolytes having ion charge products of 4 and 6. $|Z^+Z^-| = 4$: $ThCl_4$,[10] $Th(NO_3)_4$,[8] $[Pt(en)_3](ClO_4)_4$,[11] $[Pt(pn)_3]Cl_4$,[12] $K_4[W(CN)_8]$,[12] $K_4[Mo(CN)_8]$,[13] $K_4[Fe(CN)_6]$,[14] $(NMe_4)_4[Mo(CN)_8]$,[12] $[Pt(en)_3]Cl_4$,[13] $BeSO_4$,[8] $MgSO_4$,[8] $MnSO_4$,[8] $NiSO_4$,[8] $CuSO_4$,[8] $ZnSO_4$,[8] UO_2SO_4,[8] $CdSO_4$;[8] and $|Z^+Z^-| = 6$: $Cr_2(SO_4)_3$,[8] $Al_2(SO_4)_3$,[8] $[Co(en)_3]_2(SO_4)_3$.[12] The activity coefficient of pure sodium paratungstate A is reasonably assumed to be within the hatched area.

The activity coefficient of an electrolyte in a mixed electrolyte solution, $f_\pm$, can be calculated from the values of the activity coefficients of the individual electrolytes $f_\pm{}^0$ by using Guggenheim's equation,[15] namely (with changed terminology):

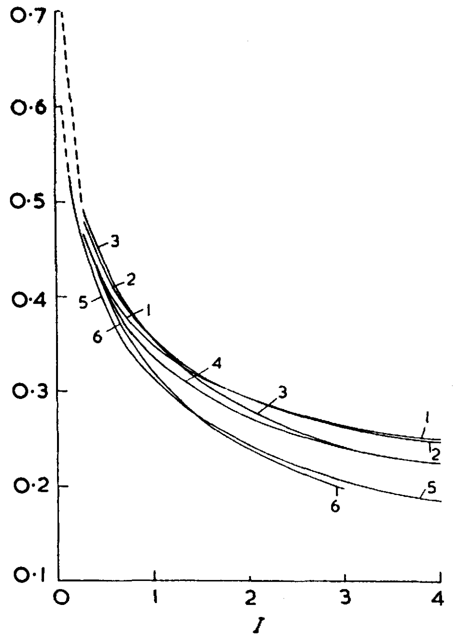

FIG. 5. Activity coefficients of Na_2WO_4-like electrolytes.

1, Na_2CO_3. 2, Na_2CrO_4. 3, Na_2HAsO_4. 4 $Na_2S_2O_3$. 5, Na_2SO_4. 6, Na_2HPO_4.

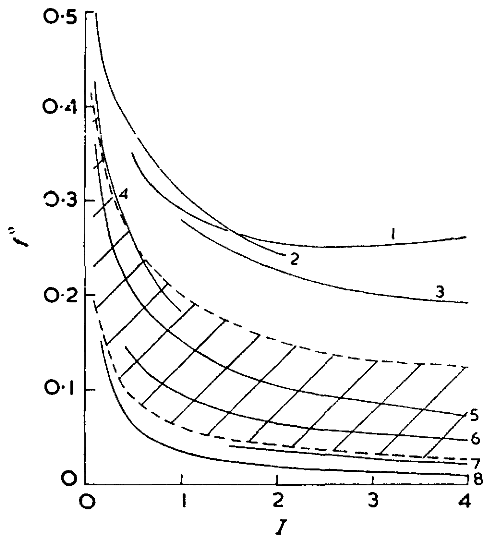

FIG. 6. Activity coefficients of $Na_5HW_6O_{21}$-like electrolytes.

1, $ThCl_4$. 2, $[Pt(en)_3](ClO_4)_4$. 3, $Th(NO_3)_4$. 4, $[Pt(pn)_3]Cl_4$. 5, $K_4[W(CN)_8]$, $K_4[Mo(CN)_8]$, $K_4[Fe(CN)_6]$, $[Pt(en)_3]Cl_4$, $(NMe_4)_4[Mo(CN)_8]$. 6, $BeSO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, $ZnSO_4$, UO_2SO_4, $CdSO_4$. 7, $Cr_2(SO_4)_3$, $Al_2(SO_4)_3$. 8, $[Co(en)_3]_2(SO_4)_3$.

$$\log f_{\pm X_1Y_1}^{(X_2Y_2)} = -\frac{0{\cdot}5|Z_1{}^+Z_1{}^-|I^{1/2}}{1 + I^{1/2}} + \frac{|Z_1{}^+|}{|Z_1{}^+| + |Z_1{}^-|}\sum_X \lambda_{XY_1}[X] + \frac{|Z_1{}^-|}{|Z_1{}^+| + |Z_1{}^-|}\sum_Y \lambda_{X_1Y}[Y] \qquad (4)$$

where λ is a constant for any electrolyte XY. The λ terms can be evaluated by Glueckauf's procedure,[16] provided $f_\pm{}^0$ is known for a solution of the *same ionic strength* as the mixture.

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[10] Robinson, *J. Amer. Chem. Soc.*, 1955, **77**, 6200.
[11] Braubaker, *J. Amer. Chem. Soc.*, 1957, **79**, 4274.
[12] Wynveen, Dye, Groves, and Braubaker, *J. Amer. Chem. Soc.*, 1960, **82**, 4441, 4445.
[13] Braubaker, *J. Amer. Chem. Soc.*, 1956, **78**, 5762.
[14] Robinson, *J. Amer. Chem. Soc.*, 1937, **59**, 84.
[15] Guggenheim, *Phil. Mag.*, 1935, **19**, 606.
[16] Glueckauf, *Nature*, 1949, **163**, 414.

Substitution of equations of type (4) in equation (3) leads to the following equation for the activity coefficient product:

$$\log K_f = 9\frac{[\mathrm{Na^+}]}{I}\log f_{\pm}{}^{0}{}_{\mathrm{Na_5HW_6O_{21}}} - \tfrac{3}{8}\frac{[\mathrm{Na^+}]}{I}\log f^{0}{}_{\pm\mathrm{Na_2WO_4}} - 7\frac{[\mathrm{Cl^-}]}{I}\log f^{0}{}_{\pm\mathrm{HCl}} + \left(6 + 44\frac{[\mathrm{Na^+}]}{I} - 7\frac{[\mathrm{Cl^-}]}{I}\right)\frac{0{\cdot}5I^{1/2}}{1+I^{1/2}} \qquad (5)$$

It is important that the activity coefficient of sodium paratungstate B, $f^0{}_{\pm\mathrm{Na_{10}W_{12}O_{41}}}$, the values of which are unknown, has been eliminated from this equation. By inserting the derived values of $f^0{}_{\pm\mathrm{Na_5HW_6O_{21}}}$ and $f^0{}_{\pm\mathrm{Na_2WO_4}}$, the known values[8] of $f^0{}_{\pm\mathrm{HCl}}$, and the experimental values for the concentrations in equation (5), K_f can be evaluated for any set of experimental conditions. It is then found that K_f is relatively insensitive to the proportion of the tungsten in each of the three chromatographic forms $WO_4{}^{2-}$, $HW_6O_{21}{}^{5-}$, and $W_{12}O_{41}{}^{10-}$ and is constant within the limits of error for any value of $C_{\mathrm{WO_3}}$. Values for K_f have therefore been estimated at each of the concentrations at which K_c has been determined and are shown in Fig. 4b. The error quoted is due entirely to the uncertainty in $f^0{}_{\pm\mathrm{Na_5HW_6O_{21}}}$.

Activity coefficient equations of type (4) oversimplify the interactions occurring between the components of the mixture, and therefore we should not expect very close agreement between these calculated values and those obtained by different empirical equations,[7] or between these and experiment. In the present case, the reasonableness of the calculations can at present be checked only by reference to the limited experimental results of Robinson and Sinclair.[17] Cross-differentiation relations of the type[18]

$$0{\cdot}018\left[\frac{\partial \ln a_{\mathrm{Na_5HW_6O_{21}}}}{\partial \ln [\mathrm{HW_6O_{21}{}^{5-}}]}\right]_{\substack{\mathrm{Na_5HW_6O_{21}}\\ \mathrm{Na_2WO_4}\\ \mathrm{NaCl}\\ \mathrm{HCl}}} = -\left[\frac{\partial \ln a_{\mathrm{H_2O}}}{\partial [\mathrm{HW_6O_{21}{}^{5-}}]}\right]_{\substack{\mathrm{Na_2WO_4}\\ \mathrm{NaCl}\\ \mathrm{HCl}}}$$

are used, where $a_{\mathrm{H_2O}}$ is the water activity. By using the integrated forms of these equations with data interpolated from Robinson and Sinclair's results, $f_{\pm}/f^0{}_{\pm}$ can be estimated for the various electrolytes. Combining the values calculated with those previously obtained for $f^0{}_{\pm}$ enables $\log K_f$ to be evaluated for any set of experimental conditions. For example, at unit ionic strength, $\log K_f = 2 \pm 7$. Although the precision is poor, this value is in agreement with that derived from more empirical equations.

Although we cannot obtain precise absolute values for $\log K_f$, we believe the variation of $\log K_f$ with ionic strength shown in Fig. 4b (and 4c) is much smaller, perhaps only 25% of that shown.

Thermodynamic-equilibrium Constant K_a.—Values for $\log_{10} K_a$, which is equal to the sum of $\log_{10} K_c$ and $\log_{10} K_f$, are shown in Fig. 4c. It can be seen that, within the uncertainty of estimation of activity coefficients, a constant value of $\log_{10} K_a = 65{\cdot}5 \pm 1$ is obtained. This constant value which is more reliable than could have been obtained by extrapolation to infinite dilution, and is in accordance with equation (1) describing the reaction that takes place, for which there is other supporting evidence (see above). It is fairly pointed out, however, that constant values of K_a could be obtained with some, but not many, other reactions. Thus K_c, K_f, and K_a have also been calculated by assuming that the first separable condensation product (form Y^1) is, not the paratungstate A ion $HW_6O_{21}{}^{5-}$, but some other plausible tungstate anion. The calculations are sufficiently precise to show a meaningful variation in the estimated thermodynamic equilibrium constant if Y was assumed to be $HWO_4{}^-$, $W_2O_7{}^{2-}$, $W_3O_{10}{}^{2-}$, $W_3O_{11}{}^{4-}$, $W_6O_{21}{}^{6-}$, $H_2W_6O_{21}{}^{4-}$, or $H_3W_6O_{21}{}^{3-}$, which can thus be eliminated as possible formulæ for the condensed

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[17] Robinson and Sinclair, *J.*, 1934, 642.
[18] McKay, *Nature*, 1952, **169**, 464.

species. However, within the uncertainties of such calculations, these results are consistent with its being $W_7O_{24}^{6-}$ or $HW_6O_{21}^{5-}$.

A thermodynamic equilibrium constant can also be calculated from the early work of Bhagwat and Dhar[19] who measured the solubility of benzoic acid in 0·02—1·0M-sodium tungstate. They incorrectly explained their results in terms of a dissociation constant $K = 7{\cdot}3 \times 10^{-5}$ for the reaction $H^+ + WO_4^{2-} \rightleftharpoons HWO_4^-$. In benzoic acid solutions, the medium would be acidic (pK_a for benzoic acid $= 4{\cdot}2$). If we assume the reaction is as shown by equation (1), Bhagwat and Dhar's figures yield a value for log K_a of 46·0 (standard deviation $\sigma = 0{\cdot}4$) at 30°. The validity of this argument is confirmed by the same workers' results on the solubility of benzoic acid in sodium molybdate solutions. If the reaction $8H^+ + 7MoO_4^{2-} \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O$ is used instead of $H^+ + MoO_4^{2-} \rightleftharpoons HMoO_4^-$, a value for log K_a of 55·6 ($\sigma = 0{\cdot}1$) at 30° is obtained. This value compares with the value of log $K = 57{\cdot}7 \pm 0{\cdot}3$ obtained potentiometrically at 25° and in 3M-sodium perchlorate by Sasaki, Lindqvist, and Sillén.[20]

The large difference in the equilibrium constant for reaction (1) between that obtained from solubility measurements and that obtained from chromatographic or polarographic analysis (a factor of 10^{20}) cannot be due to experimental errors or to activity coefficient errors. It could be due to formation of an intermediate between the mono- and the hexa-tungstate or to complex formation between the benzoate anion and one of the tungstate anions. In this regard it should be noted that complexes have been reported between tungstate and phosphate,[21] arsenate,[19] oxalate,[22] and other organic anions.[23]

Thermodynamic Quantities of the Condensation.—The effect of temperature on the equilibrium between WO_4^{2-} and $HW_6O_{21}^{5-}$ is shown in Figs. 1b and 3d. From these results the enthalpy and entropy changes have been calculated as −47,000 ± 20,000 cal. per mole of $HW_6O_{21}^{5-}$ and 140 ± 70 entropy units per mole of $HW_6O_{21}^{5-}$, respectively. In calculating these figures the reasonable assumption has been made that within the limits of error the activity coefficient product K_f is independent of temperature.

The experimental heat of reaction leads to an enthalpy change of −64,500 ± 1000 cal. per mole of $HW_6O_{21}^{5-}$, which when combined with the chromatographic results leads to an entropy change of 82 ± 9 entropy units per mole of $HW_6O_{21}^{5-}$. The two methods thus agree within experimental error.

The entropy change [$\Delta S = 23 \pm 12$ (chromatographic) and $\Delta S = 14 \pm 2$ (calorimetric) per mole of WO_4^{2-}] show a more disordered arrangement for the polyanion. This is difficult to understand unless water of hydration is lost during the condensation, *i.e.*, unless six normal tungstate ions are hydrated more than the polytungstate.

Mechanism of Formation of Polyanions.—The ability to condense or polymerise at low pH is a property of all oxyanions of the transition metals of Groups V and VI of the Periodic Classification ($M^VO_4^{3-}$ and $M^{VI}O_4^{2-}$, respectively). There has been remarkably little discussion as to the mechanism of condensation. It is often assumed that the first step in the aggregation is formation of the acid ion, for example, HWO_4^-. It is known that both $HCrO_4^-$ (ref. 24) and $HMoO_4^-$ (ref. 20) exist at that pH where condensation begins. Freedman[24] suggested that addition of a proton would weaken the tetrahedral complex so that expansion of covalency takes place with the co-ordination of two water molecules to complete the octahedral structure. That the normal tungstate ion is a dihydrate follows from the conductometric titration of alkali against sodium tungstate

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[19] Bhagwat and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 807.

[20] Sasaki, Lindqvist, and Sillén, *J. Inorg. Nuclear Chem.*, 1959, **9**, 93.

[21] Spitsyn and Koneva, *Zhur. neorg. Khim.*, 1956, **1**, 2488; Spitsyn, *ibid.*, 1957, **2**, 502; Spitsyn, Spiridinov, and Kolli, *Zhur. fiz. Khim.*, 1958, **32**, 1143; *Chem. Abs.*, 1957, **51**, 12,722, 17,562, 1958, **52**, 19,650.

[22] Rae and Bannerjee, *Saugar Univ. J. (India)*, 1957, **6**, 17; *Chem. Abs.*, 1959, **53**, 14651; Ripan, Duca, and Ceteanu, *Studii si Cercetari Chim. (Fil. Cluj)*, 1959, **10**, 31.

[23] Gmelin's " Handbuch der anorganischen Chemie," S.N. 54, Wolfram, Berlin, 1933, pp. 332.

[24] Freedman, *J. Amer. Chem. Soc.*, 1958, **80**, 2072.

solutions which gives end-points[25] at $OH^- : WO_4^{2-} = 2:1$ and $4:1$, so that the normal tungstate ion should be written as $H_4WO_6^{2-}$. Similar behaviour was reported with sulphate, tellurate, chromate, and molybdate.

As in the solid state, we might expect the structure of ions to be governed by the radius ratio $r_M^{V} : r_O^{II}$(or $r_M^{VI} : r_O^{II}$). If this ratio is below 0·414 : 1, the anion would be expected to be tetrahedrally co-ordinated; if above 0·414 : 1, octahedrally co-ordinated.[26] Those oxyanions of the transition metals which exist in monomeric form at high pH but are condensed in acid solution, namely, vanadate, chromate, molybdate, and tungstate, all have a radius ratio equal to or below 0·44 : 1 (Table 3). In contrast, the oxyanions of uranium, niobium, and tantalum are always condensed, even in highly alkaline solutions. These have larger radius ratios (0·48—0·52 : 1) and would probably exist in the octahedrally co-ordinated state under all conditions, while the former do not appear to expand to octahedral form until the addition of a proton weakens the metal–oxygen bond. Again the oxyanions of the elements in the B Groups of the Periodic Classification (except germanium), irrespective of their radius ratios, form polyanions only when heated, and this is by linking of tetrahedra and not octahedra. Thus it appears that polyanion formation is relatively easy with a transition-metal ion, perhaps because vacant *d*-orbitals are available to allow hybridisation to the d^2sp^3 or sp^3d^2 octahedral states. Also, if the radius ratio is small, protonation of the oxygen seems to occur, weakening the metal–oxygen bond sufficiently for expansion to the octahedral state to occur. Size and easily accessible vacant *d*-orbitals are, however, not the only prerequisites for polyanion formation, as is shown by dichromate. This is tetrahedrally co-ordinated, even though it apparently has the properties necessary for octahedral co-ordination. Likewise the germanate ion GeO_3^{2-} (a B group oxyanion), which has no easily accessible vacant *d*-orbitals, forms polyanions ($Ge_5O_{11}^{2-}$ and $HGe_7O_{16}^{3-}$)[27] in acid conditions in a similar manner to vanadate, molybdate, and tungstate.

TABLE 3.

Radius ratios, (r_M^{V} or $r_M^{VI} : r_O^{II}$), in polyanion formation.

Ion	W^{VI}	Cr^{VI}	V^{V}	Mo^{VI}	U^{VI}	Nb^{V}	Ta^{V}
Radius ratio	0·36	0·37	0·42	0·44	0·48	0·50	0·52

In the case of tungstate, the tungsten–oxygen octahedra so formed condense, sharing an edge with one another to form the ditungstate. Further condensation either takes place linearly or the third octahedron condenses across the ditungstate to form a "limiting" tritungstate.[24] These condensations, involving elimination of water, account for the experimentally observed increase in entropy. The unit cell of crystalline sodium paratungstate contains two of each type of tritungstate,[5] while the metatungstate anion consists of four limiting tritungstate groups.[28] Further condensation would be complex, particularly in concentrated solutions, and would be expected to lead to an almost infinite number of mixed limiting-linear types. However, tungsten is like all other polyanion-forming elements in that under any one set of conditions a single species predominates, for example, $Mo_7O_{24}^{6-}$, $HW_6O_{21}^{5-}$, $Ge_5O_{11}^{2-}$, $V_2O_7^{2-}$ $Nb_5O_{16}^{7-}$ or $Nb_6O_{19}^{8-}$, and $Ta_5O_{16}^{7-}$ or $Ta_6O_{19}^{8-}$. A sound foundation to the chemistry of polyanion formation will only be laid when the central fundamental problems of explaining why these particular species should be so stable have been solved by detailed work on a variety of systems.

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