POTENTIOMETRIC DETERMINATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE

SIMULTANEOUS DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND VANADIUM^{IV} AT ROOM TEMPERATURE

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Summary—The use of orthophosphoric acid as a catalyst has enabled the potentiometric titration of vanadium^{IV} to be carried out with cerium^{IV} sulphate in 1 0–2 0N sulphuric acid medium at room temperature Using the same catalyst a method has also been developed for the simultaneous differential potentiometric titration of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate in a sulphuric acid medium; this method is more satisfactory than the procedure described by Furman[1] because the first potential break is quite marked and it is more convenient because it avoids the high temperature required for the second stage of the titration in the Furman procedure Chromium^{III} and iron^{III} do not interfere in these titrations.

FURMAN[1] attempted the potentiometric determination of vanadium^{IV} in sulphuric acid medium with cerium^{IV} sulphate. When the titration was carried out at room temperature, he observed that it required several min for the potential to become constant in the neighbourhood of the equivalence point and therefore recommended the titration to be carried out at 50–60°. He observed that the potential break at the equivalence point varied from 25 to 100 mv per 0·05 ml of 0·05N cerium^{IV} solution when the initial volume of the titration mixture was varied from 200 to 25 ml. Almost simultaneously Willard and Young[2] reported that vanadium^{IV} can be determined potentiometrically at 70–75° with cerium^{IV} sulphate in sulphuric, hydrochloric or perchloric acid media.

We have observed that potentiometric titrations in 0·5 to 2·0N hydrochloric acid medium give much higher titres than the theoretical, the error increasing with increasing concentration of hydrochloric acid. During the earlier part of the titration the potential rises, then remains steady for a long interval until the equivalence point is passed when the potential shows a sudden jump. We[3] have shown that the need for a high temperature arises from the fact that the reaction between vanadium^{IV} and cerium^{IV} is slow in a sulphuric acid medium at room temperature. Various catalysts were tried to see if the reaction could be accelerated sufficiently well to enable the titration to be carried out at room temperature and it was found that orthophosphoric acid has a pronounced accelerating effect on the reaction. This observation has now been utilised for the potentiometric determination of vanadium^{IV} with cerium^{IV} sulphate at room temperature and for the differential potentiometric titration of iron^{IV} and vanadium^{IV} in mixtures.

EXPERIMENTAL

Reagents

Iron^{II} *ammonium sulphate solution, approx.* 0 05N   Prepared by dissolving about 20 g of the substance in 1 litre of water, sufficient sulphuric acid being added before dilution to give an overall acidity of 1 0N   The solution is standardised against cerium^{IV} sulphate solution.

The preparation of 0 05N cerium^{IV} sulphate and 0 05N vanadium^{IV} sulphate solutions and the source of phosphoric acid have already been described.[3]

Apparatus

The potentiometric titration assembly consisted of a Junior potentiometer and a Taut suspension galvanometer (both manufactured by W. G. Pye & Co , England), a saturated calomel electrode as reference electrode and a bright platinum rod electrode as indicator electrode   The salt bridge consisted of a U-tube (with porous end plates) filled with saturated potassium chloride solution. The titration mixture was stirred during the titration by means of a B T L. magnetic stirrer.

RESULTS AND DISCUSSION

About 5·0 ml of 0·05N vanadium^{IV} solution is taken in a 150-ml Pyrex beaker and diluted to 80 ml with 1·0N sulphuric acid.   When the mixture is titrated at room temperature (28°), the potentials attain stable values quickly after each addition of the cerium^{IV} sulphate solution in the initial stages.   As the equivalence point is approached, however, the potentials show considerable drift with time, reaching steady values in about 3 min, then just before the equivalence point, it takes 4 min for the potential to reach a constant value.   After the equivalence point is reached, the potentials again attain steady values quickly.   This behaviour is exemplified by the results presented in Table I.   The results also show that in the presence of phosphoric acid (1·0 ml of syrupy phosphoric acid for 80 ml of titration mixture) the potentials do not show any drift with time even in the neighbourhood of the equivalence point.

TABLE I.—POTENTIOMETRIC TITRATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE
AT ROOM TEMPERATURE (28°)

Volume of cerium^{IV} sulphate added, ml	Addendum	e m f (v) observed after							
		30 sec	60 sec	90 sec	120 sec	150 sec	180 sec	210 sec	240 sec
5·70	Nil	0 869	0 867	0 866	0 865	0 865	0 865	—	—
	1 0 ml of H$_3$PO$_4$	0 864	0 864	0·864	—	—	—	—	—
5 80	Nil	0 905	0 885	0 881	0 880	0 880	0 880	—	—
	1 0 ml of H$_3$PO$_4$	0 879	0 877	0 877	0 877	0 877	—	—	—
5 90	Nil	0 960	0 950	0 945	0 930	0 927	0 920	0 914	0 911
	1 0 ml of H$_3$PO$_4$	0 907	0 904	0 904	0 904	0 904	—	—	—
6 00	Nil	1 081	1 080	1 080	1 080	1 080	1·080	—	—
	1 0 ml of H$_3$PO$_4$	1 004	1 004	1 004	1 004	1 004	1 004	—	—
6 10	Nil	1 127	1 128	1 128	1 128	—	—	—	—
	1 0 ml of H$_3$PO$_4$	1 075	1 075	1 075	—	—	—	—	—

5 0 ml of vandium^{IV} solution ≡ 5 98 ml of cerium^{IV} sulphate solution

The value of the potential break obtained in a titration carried out (in the presence of phosphoric acid) at room temperature is about 20 mv lower than the potential break obtained during a titration carried out at 60° in the absence of phosphoric acid. This is evident from the data in Table II.

Although the potential break in the presence of phosphoric acid is lower than that obtained in its absence, the potential break is still sufficiently high to enable the equivalence point to be detected easily.   The potential break increases as the sulphuric

acid concentration decreases, but there is a risk of cerium phosphate being precipitated when the concentration of sulphuric acid is below 1·0N. Several titrations of vanadium^{IV} have also been carried out keeping the concentration of sulphuric acid at 2·0N, but varying the amount of syrupy phosphoric acid from 0·5 to 2·5 ml. The results in Table III show that the potential break decreases as the phosphoric acid concentration increases. Moreover, when the amount of syrupy phosphoric acid is increased beyond 2·5 ml precipitation of cerium phosphate begins. In view of these findings, the optimum amount of syrupy phosphoric acid is fixed as

TABLE II

Conditions of titration	Potential break at the equivalence point per 0 1 ml of 0 04N cerium^{IV} sulphate, mV
0 5N H$_2$SO$_4$ at 60°	153
0 5N H$_2$SO$_4$ + 1 0 ml of H$_3$PO$_4$ at 28°	129
1 0N H$_2$SO$_4$ at 60°	147
1 0N H$_2$SO$_4$ + 1 0 ml of H$_3$PO$_4$ at 28°	108
2 0N H$_2$SO$_4$ at 60°	107
2 0N H$_2$SO$_4$ + 1 0 ml of H$_3$PO$_4$ at 28°	96

1·0 ml for 80 ml of the titration mixture and the optimum concentration of sulphuric acid precsribed as 1·0 to 2·0N. When 5·0 ml of syrupy phosphoric acid is used, the titration can be made in 4·0N sulphuric acid medium without any risk of cerium phosphate being precipitated. The potential break under these conditions is 84 mv per 0·1 ml of 0·04N cerium^{IV} solution as compared with the break of 96 mv obtained in titrations in 2·0N sulphuric acid (using 1·0 ml of syrupy phosphoric acid) and a break of 108 mv observed in titrations in 1·0N sulphuric acid (using 1·0 ml of syrupy phosphoric acid). These results can be understood when we take into account the facts that the vanadium^V/vanadium^{IV} potential increases with increase in the acid concentration, and that the cerium^{IV}/cerium^{III} potential does not change very much with an increase in the concentration of sulphuric acid.

TABLE III —EFFECT OF PHOSPHORIC ACID ON THE POTENTIOMETRIC TITRATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE IN 2·0N SULPHURIC ACID AT ROOM TEMPERATURE

Amount of phosphoric acid added, ml	Break in potential at the equivalence point per 0 10 ml of 0 04N cerium^{IV} sulphate, mV
0 50	109
1 00	96
2·50	91

Recommended procedure for potentiometric titration of vanadium^{IV} with cerium^{IV} sulphate

An aliquot volume of vanadium^{IV} solution taken in a 150-ml Pyrex beaker is diluted to 80 ml with 1 0 to 2·0N sulphuric acid, then treated with 1 0 ml of syrupy phosphoric acid The titration is carried out with 0 05N cerium^{IV} sulphate solution using the electrometric titration assembly described above The cerium^{IV} sulphate is added while stirring the solution and the stirring is continued for about 15 sec after each addition. The stirring is then stopped and the potential noted. Towards the close of the titration, the potentials are noted 1 min after each addition of cerium^{IV} sulphate The break in potential at the end-point per 0 05 ml of 0 05N cerium^{IV} sulphate corresponds to about 50–60 mv.

Some typical results are given in Table IV.

TABLE IV

Amount of vanadium[IV], *millimoles*	
Taken	Found
0 3030	0 3018
0 3310	0 3315
0 4417	0 4402
0 6061	0 6046
1 0200	1·0170

Interferences

Iron[III] and chromium[III] do not interfere with the determination of vanadium[IV] by the proposed method. The presence of these salts does not even effect the value of the break in potential.

Titration in a hydrochloric acid medium

Titration of vanadium[IV] with cerium[IV] sulphate in hydrochloric acid medium at room temperature using phosphoric acid as a catalyst gave slightly higher titres than the theoretical values (about 1·5% higher in 1·0N hydrochloric acid and 2·0% higher in 2·0N hydrochloric acid).

Titration in a perchloric acid medium

In the titration of vanadium[IV] with cerium[IV] sulphate solution in 0·5 to 2N perchloric acid medium the potential jumps are higher than in a sulphuric acid medium, but the titres are still slightly higher (about 0·5 to 1·0%) than the theoretical values.

Differential titration of iron[II] and vanadium[IV] in mixtures

Furman[1] reported the potentiometric titration of a mixture of iron[II] and vanadium[IV] with cerium[IV] sulphate in the following manner. The mixture is first titrated at room temperature, then at 50–60°. The first jump in potential corresponds to complete oxidation of iron[II] and the second jump corresponds to complete oxidation of vanadium[IV]. The method is not satisfactory because the first jump in potential is very small. The correct equivalence point corresponding to the complete oxidation of iron[II] can be obtained only from the curve showing the relation between $\dfrac{\Delta E}{\Delta V}$ and V. The equivalence point cannot be obtained from the simple curve showing the relation between E and V. Smith and Getz[4] carried out the differential potentiometric titration of a mixture of iron[II] and vanadium[IV] perchlorates in 8N perchloric acid medium with ammonium nitratocerate. They found that the potential break at either of the stages is about 300 mv. Obviously this method is not of much practical interest because it would be very tedious indeed to get both of the metals in the form of perchlorates.

We have been able to carry out the simultaneous differential titration of iron[II] and vanadium[IV] in 1·0–2·0N sulphuric acid medium at room temperature using a small quantity of orthophosphoric acid as a catalyst for the oxidation of vanadium[IV] by cerium[IV].

When a mixture of iron^{II} and vanadium^{IV} is titrated with cerium^{IV} sulphate, iron^{II} will be oxidised first and even if a little vanadium^{IV} is oxidised, the vanadium^{V} formed will, in turn, oxidise iron^{II} and itself be reduced to vanadium^{IV}, so that in effect vanadium^{IV} will not be oxidised until iron^{II} is completely oxidised. After all of the iron^{II} is oxidised the slight excess of cerium^{IV} oxidises vanadium^{IV} to vanadium^{V} and there will be a sudden jump in potential. This break in potential corresponds to the one obtained during the electrometric titration of iron^{II} with vanadium^{V}. Moreover, the presence of phosphoric acid helps to increase the value of this break in potential; under our experimental conditions the first break has been found to have a value of 60–70 mv per 0·05 ml of 0·05N cerium^{IV} sulphate solution. The second break in potential has been observed to have a value of 55–65 mv per 0·05 ml of 0·05N cerium^{IV} sulphate solution.
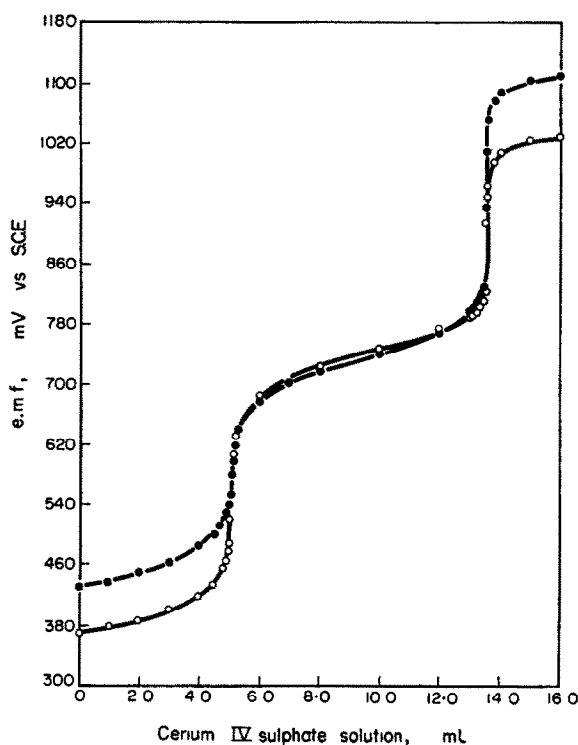

FIG. 1.—Electrometric titration of a mixture of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate:
●—1·0N sulphuric acid, according to Furman's procedure
○—1·0N sulphuric acid in the presence of 1 ml of phosphoric acid, at room temp.

Recommended procedure for potentiometric titration of a mixture of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate

The mixture of iron^{II} and vanadium^{IV} taken in a 150-ml Pyrex beaker is diluted with 1 0–2 0N sulphuric acid to 50 ml and 1·0 ml of syrupy phosphoric acid is added. It is then titrated with cerium^{IV} sulphate solution at room temperature using the potentiometric equipment already described.

Some typical results are presented in Table V.

Fig. 1 gives a typical curve showing the relation between the observed e.m.f. and the volume of cerium^{IV} sulphate solution added. The results show that the method now

developed is precise and more convenient than those of previous investigators. The method is likely to prove of great value in the analysis of vanadium steels and chrome vanadium steels.

We have attempted to use ferroin in the phosphoric acid catalysed system. If the titration is made in a $1 \cdot 0N$ sulphuric acid medium the indicator shows the colour change when both iron^{II} and vanadium^{IV} are oxidised, but the colour transition is not sharp on account of the diminishing intensity of the ferroin red colour as the end-point is approached. This determination can be made very satisfactorily by carrying out

TABLE V

Amount of iron^{II}, *millimoles*		Amount of vanadium^{IV}, *millimoles*	
Taken	Found	Taken	Found
0 2939	0 2947	0 3988	0 3988
0 3000	0 2996	0 5000	0 4983
0 3515	0 3530	0 3843	0 3843
0 4000	0 3985	0 4000	0 3985
0 6000	0 5991	0 4000	0 3992

the titration in a $1 \cdot 5 - 2 \cdot 5N$ sulphuric acid medium using Rhodamine 6G as a fluorescence indicator, in the presence of $1 \cdot 0 - 1 \cdot 5$ ml of syrupy phosphoric acid per 50 ml of the titration mixture. Iron^{II} alone can be determined by carrying out the titration with cerium^{IV} sulphate in $10 - 12N$ sulphuric acid, because any vanadium^{V} formed by oxidation of vanadium^{IV} will oxidise ferroin in $10 - 12N$ sulphuric acid. ·

Zusammenfassung—Die Verwendung von Phosphorsaure als Kalalysator ermoglicht die potentiometrische Titration von Vanadin(IV) mit Cer(IV) in 1–2 n Schwefelsaure bei Zimmertemperatur Mit dem gleichen Katalysator wurde ein Methode entwickelt zur simultanen, differential-potentiometrischen Titration von Eisen(II) und Vanadin-(IV) mit Cer(IV) in schwefelsaurem Medium. Diese Methode arbeitet besser als die von Furman, da der erste Potentialsprung besser ausgepragt ist. Ein weitere Vorteil ist, dass fur den zweiten Teil der Titration keine erhohte Temperatur benotigt wird Chrom(III) und Eisen(III) storen nicht

Résumé—L'utilisation de l'acide orthophosphorique comme catalyseur permet le titrage potentiométrique du vanadium(IV) par le sulfate de cérium(IV) en milieu acide sulfurique 1,0 à 2,0 N, à la température ordinaire En utilisant le même catalyseur, une méthode est proposée pour le titrage simultané par potentiométrie différentielle du fer(II) et du vanadium(IV) par le sulfate de cérium(IV) en milieu acide sulfurique; cette méthode est meilleure que celle de Furman pour deux raisons. le premier saut de potentiel est plus marqué et, de plus, la méthode est d'une mise en oeuvre plus commode en n'imposant pas d'opérer à haute température pour la deuxième partie du titrage Le chrome(III) et le fer(III) ne gênent pas dans ces dosages

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