# Formation of heteropolyanions as a result of acid-base reactions in nitrate melts\*

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Titration curves for acid-base titrations between  $K_2CrO_4$ ,  $Na_2MOO_4$ ,  $Na_2WO_4$ ,  $K_3PO_4$ ,  $Na_3VO_4$  (in function of bases) and  $I_2O_5$  (in function of acid) were determined using potentiometric method. On the basis of obtained values of acid-base formal potentials the conjugated Lux pairs were arranged in acid-base series. Further it was observed that in the course of titration of a mixture of anions of the type  $XO_4^{-1}$  (or  $X_2O_7^{-1}$ ) (X = P, As, V) and anions of the type  $ZO_4^{2-1}$  (Z = Mo, W) in suitable ratios with  $I_2O_5$  complex anions  $[X_2Z_{24}O_{87}]^{20-1}$  were formed. In the course of further titration unsoluble salts having anion  $[X(Z_3O_{10})_4]^{3-1}$  appear.

Методом потенциометрии кислотно-основного титрования был найден ход кривых  $K_2CrO_4$ ,  $Na_2MOO_4$ ,  $Na_2WO_4$ ,  $K_3PO_4$ ,  $Na_3VO_4$  в качестве оснований и  $I_2O_5$  в качестве кислоты. По измеренным значениям формальных кислотно-основных потенциалов были сопряженные льюксовские пары расположены в кислотно-основной ряд. Было также обнаружено, что при титровании смесей анионов типа  $XO_4^{3-}$  или  $X_2O_7^{4-}$  (X = P, As, V) с анионами типа  $ZO_4^{2-}$  (Z = Mo, W) в подходящем отношении пятиоксидом иода образуются комплексные анионы  $[X_2Z_{24}O_{87}]^{20-}$  и при дальнейшем титровании образуются нерастворимые соли с анионом  $[X(Z_3O_{10})_4]^{3-}$ 

The principle of acid-base reactions in the melts of oxo salts is described by the Lux equation [1]

base 
$$\rightleftharpoons$$
 acid +  $O^{2^{-}}$ 

In the melt of nitrate of alkali metal the acid-base dissociation of the type

$$NO_{3}^{-} = NO_{2}^{+} + O^{2-}$$

takes place [2] and, therefore, the mutual reactions of the Lux acids and bases in the nitrate melts can be indicated potentiometrically using the electrode changing reversibly its potential with the change of activity of oxide ions  $a(O^{2^{-}})$ .

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Using oxygen indicator electrode and silver reference electrode series of reactions of the Lux acids with Na<sub>2</sub>O<sub>2</sub> or Na<sub>2</sub>CO<sub>3</sub> as bases have been studied in nitrate melts [3—6] and from the course of titration curves the conclusions on the formation of intermediate and final products have been drawn. However, there is no accord of views of different authors on the formation of intermediate product  $Mo_2O_7^{2-}$  [7, 8] or  $Mo_3O_{10}^{2-}$  [5] during titration of MoO<sub>3</sub> with the Lux base. Open to discussion is also the question if during titration of WO<sub>3</sub> the intermediate anion  $W_2O_7^{2-}$  is [9] or is not [5] formed. On the basis of potentiometric measurements the equilibrium constants  $K = a(acid) \cdot a(O^{2-})/a(base)$  which characterize the relative strength of the Lux acids and bases were estimated as well [3—5, 8, 9]. The values of equilibrium constants could be determined only if the values of  $E^0$  in the Nernst equation were known

$$E = E^{0} - (2.303 \ RT/2F) \log a(O^{2-})$$

The value of  $E^{\circ}$  can be found on the basis of series of E data at different values of  $a(O^{2^{-}})$ . However, it is necessary to assume that  $a(O^{2^{-}})$  equals concentration of Na<sub>2</sub>CO<sub>3</sub> [10] or Na<sub>2</sub>O<sub>2</sub> [11] added. Results of some papers indicate that these assumptions are not always fulfilled [12-14].

### Experimental

#### Chemicals

Equimolar mixture NaNO<sub>3</sub> + KNO<sub>3</sub> was prepared from anal. grade reagents (Lachema, Brno) which were purified by recrystallization from aqueous solution and dried by melting at 573 K in atmosphere of dry nitrogen and finally filtered through glass wool and after solidification pulverized. Almost all other chemicals were anal. grade (Lachema, Brno; Reanal, Hungary; BDH-Chemicals Ltd., England). Na<sub>2</sub>O<sub>2</sub>, KIO<sub>3</sub>, TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and Ta<sub>2</sub>O<sub>5</sub> were used without preliminary treating. Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CrO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> were dried at ~400 K before use. By thermal dehydration of their hydrates I<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>MoO<sub>4</sub>, Na<sub>2</sub>WO<sub>4</sub>, WO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, Na<sub>4</sub>As<sub>2</sub>O<sub>7</sub> were prepared. MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> were prepared by thermal decomposition of their ammonium salts. By neutralization of respective oxide or more acidic salt with Na<sub>2</sub>CO<sub>3</sub> the following substances were prepared: Na<sub>3</sub>VO<sub>4</sub>, Na<sub>3</sub>AsO<sub>4</sub>, Na<sub>3</sub>NbO<sub>4</sub>, and Na<sub>3</sub>TaO<sub>4</sub>. Traces of moisture and CO<sub>2</sub> were removed from gaseous oxygen and nitrogen in columns filled with silica gel and potassium hydroxide. 0.1 M solution of AgNO<sub>3</sub> in the equimolar melt (KNO<sub>3</sub> + NaNO<sub>3</sub>) (for silver reference electrode) was prepared by melting the components at 573 K during 3 h.

The electrolytic cell (Fig. 1) consisted of ground joint pair NZ 60 mm. Its jacket was prolonged in a big test tube with the diameter about 60 mm which was slightly smaller than the inner diameter of the used heating element (product of Lachema, Brno, max. power 440 W). Inner ground joint serves as a movable head which bears 4 ground joints NZ 14.5 mm for mercury thermometer, for sample filling, and for oxygen and silver electrodes. The oxygen electrode consisted of a platinum plate covered with platinum black.



Fig. 1. Electrolytic cell.
 A — head; B — test tube; C — oxygen electrode; D — silver electrode.

It was saturated with oxygen at normal pressure. The silver electrode consisted of a silver rod immersed in 0.1 M-AgNO<sub>3</sub> in the NaNO<sub>3</sub> + KNO<sub>3</sub> melt and it was separated from the titrated melt by a glass membrane having low resistivity (63.3 k $\Omega$ ). The whole cell can be described by the scheme

Pt, O<sub>2</sub> | titrated melt | glass membrane | 0.1 M-AgNO<sub>3</sub> in KNO<sub>3</sub> + NaNO<sub>3</sub> | Ag

The titrations were carried out at the temperature 533 K in 250 g of equimolar mixture of nitrates. Load of the titrated Lux bases as well as the consumption of titrating agent  $(I_2O_5)$  was in units of millimoles.

#### Results

#### Preliminary experiments

During preliminary experiments it was found that substances which were studied by means of potentiometric titration may be divided on the basis of their behaviour with respect to equimolar nitrate melt into four groups:

- substances with good solubility: K2CrO4, K2Cr2O7, Na2MoO4, Na2WO4, KIO3;
- substances less soluble: K<sub>3</sub>PO<sub>4</sub>, Na<sub>3</sub>VO<sub>4</sub>, Na<sub>3</sub>AsO<sub>4</sub>, Na<sub>4</sub>As<sub>2</sub>O<sub>7</sub>;
- insoluble substances: MoO<sub>3</sub>, WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, Na<sub>3</sub>NbO<sub>4</sub>, Na<sub>3</sub>TaO<sub>4</sub>;
- substances which react with the nitrate melt with formation of  $NO_2$ :  $CrO_3$ ,  $P_2O_5$ ,  $I_2O_5$ .

From this survey it follows that the substances which act as the Lux acids are usually in the melt of nitrates insoluble while the Lux bases are usually soluble. Therefore, it was more advantageous to investigate acid-base behaviour by means of titration of solutions of the Lux bases by acids than to do the titration in opposite way. Insoluble Lux bases (Na<sub>3</sub>NbO<sub>4</sub> and Na<sub>3</sub>TaO<sub>4</sub>) were not further studied. Strong Lux acid is to be used as titrating agent. (One of the substances which react with the nitrate melt — CrO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, I<sub>2</sub>O<sub>5</sub>.) The most advantageous seems to be I<sub>2</sub>O<sub>5</sub> because it reacts with bases (in contrast to CrO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>) without formation of intermediate products and forms iodate

 $I_2O_5 + O^{2-} = 2IO_3^{-}$ 

Besides that it was found that the EMF values corresponding to the equivalent ratio of different conjugated Lux acid-base pairs are reproducible and do not depend on the concentration of  $IO_3^-$  ions. It allows to compare the strength of acid-base couples according to the values of formal potentials at the presence of anions  $IO_3^-$ 

Acid-base properties of oxo compounds of phosphorus, arsenic, vanadium, chromium, molybdenum, and tungsten in their highest oxidation numbers



- Fig. 2. Curves for potentiometric titration of phosphate by iodine pentoxide.
- 1. 2.522 mmol of  $K_3PO_4$  titrated by  $I_2O_5$ ;
- 2. 3.816 mmol of  $K_3PO_4$  titrated by  $I_2O_5$ .





1. 3.867 mmol of  $Na_2MoO_4$  titrated by  $I_2O_5$ ; 2. 4.760 mmol of  $Na_2MoO_4$  titrated by  $I_2O_5$ .

The Lux bases of composition  $K_3PO_4$ ,  $Na_3VO_4$ ,  $K_2CrO_4$ ,  $Na_2MoO_4$ , and Na<sub>2</sub>WO<sub>4</sub> were titrated in solution of nitrate melt by jodine pentoxide. An attempt to titrate also Na<sub>1</sub>AsO<sub>4</sub> in the same way resulted in conclusion that  $I_2O_5$  does not react with arsenate(V) and that it reacts with the melt as if no arsenate ions were present. Titrating the other Lux bases the first potential step appeared after consumption of I<sub>2</sub>O<sub>5</sub> corresponding to the following acid-base reaction

or

or

$$2MO_4^{3-} + I_2O_5 = M_2O_7^{4-} + 2IO_3^{-}$$
 (M = P, V)  
 $2MeO_4^{2-} + I_2O_5 = Me_2O_7^{2-} + 2IO_3^{-}$  (Me = Cr, Mo, W)

After the first potential step the second reaction between dianions  $M_2 O_2^{4-}$  (resp.  $Me_2O_2^{2-}$ ) and  $I_2O_5$  follows but it is disturbed by the reaction of  $I_2O_5$  with the nitrate melt. As it follows from potentiometric curves this reaction influences the consumption of I<sub>2</sub>O<sub>5</sub> (if the next potential step appears at all) and also constant potential of oxygen electrode is established in much slower way. In Figs. 2 and 3 the curves for titration of  $K_3PO_4$  and  $Na_2MoO_4$  by jodine pentoxide are presented. Dash parts of the curves correspond to the region in which a stable value of electrode potential is achieved very slowly. The second potential step is apparent only by titration of phosphate (Fig. 2); consumption of agent between the first and the second potential step corresponds to the stoichiometry of reaction

$$P_2O_7^{4-} + I_2O_5 = 2PO_3^{-} + 2IO_3^{-}$$

By titrating vanadates, molybdates, and tungstates(VI) the second potential step is distorted (Fig. 3) and only the appearance of dark red  $(V_2O_5)$ , white (MoO<sub>3</sub>) or light yellow ( $WO_3$ ) precipitate after the first potential step shows that the reactions follow the scheme

> $V_2 O_2^{4-} + 2I_2 O_5 = V_2 O_5 + 4IO_3^{-}$  $Me_2O_7^{2-} + I_2O_5 = 2MeO_3 + 2IO_3^{-}$  (Me = Mo, W)

By titrating chromate by iodine pentoxide this agent reacts with the nitrate melt immediately after the first potential step and therefore, the second potential step cannot be observed at all. In order to make it possible to compare the strength of the Lux acids and bases the values of EMF of the cell corresponding to the plateau on the potentiometric curves (*i.e.* at mole ratios  $I_2O_5$ : Lux base = 1 4 or 3 4) were determined. In the system  $Na_3AsO_4/Na_4As_2O_7$  the value of EMF was obtained so that the mixture  $Na_3AsO_4$ :  $Na_4As_2O_7$  (mole ratio 2 : 1) was added to

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the nitrate melt (solvent) and when an equilibrium was achieved the EMF value was read. The measurement was repeated three times, always with a new solvent. The most important data are summarized in Table 1.

#### Table 1

Base	Mole ratio $I_2O_5$ : base at potential step	EMF (mV) at mole ratio $I_2O_5$ : base		
		1:4	3:4	
K₃PO₄	0.48 : 1.00	$-210\pm3$	$+330\pm4$	
10. <b>-</b> 21 14-02*	0.97 1.00			
$2Na_3AsO_4 + Na_4As_2O_7$	—	$-255\pm6$		
Na <sub>3</sub> VO <sub>4</sub>	0.49:1.00	$-279 \pm 4$		
K₂CrO₄	0.48:1.00	$+ 42 \pm 7$	_	
Na <sub>2</sub> MoO <sub>4</sub>	0.50:1.00	$+ 89 \pm 4$	(+324±2)*	
Na <sub>2</sub> WO <sub>4</sub>	0.50:1.00	$+100 \pm 0$	$(+249 \pm 1)^*$	

Titration of the Lux bases by iodine pentoxide (potential steps and electrode potentials)

\* Derived by extrapolation from four titration points behind potential step.

## Interaction of oxo anions in acid-base reactions

Titration of mixtures of two Lux bases  $XO_4^{3-}$  and  $ZO_4^{2-}$  (X = P, V, As; Z = = Mo, W) dissolved in an equimolar mixture of nitrates was carried out. Iodine pentoxide was used as titrating agent. Mainly mole ratios  $XO_4^{3-}$   $ZO_4^{2-} = 1$  12 or 1 24 were used. On the potentiometric curves two potential steps occurred. In some cases also the third step appeared, however, in this case  $I_2O_5$  reacted with the melt and NO<sub>2</sub> was liberated.

The consumption of  $I_2O_5$  at the first potential step corresponded to the reaction

$$2XO_4^{3-} + I_2O_5 = X_2O_7^{4-} + 2IO_3^{-} \qquad (X = P, V)$$

while for X = As the potential step did not appear at all. Consumption of  $I_2O_5$  between the first and the second potential step corresponded (for the ratio of components in the mixture  $XO_4^{3-}$ :  $ZO_4^{2-} = 1:12$ ) to the reaction

$$3ZO_4^{2-} + 2I_2O_5 = Z_3O_{10}^{2-} + 4IO_3^{-}$$
 (Z = Mo, W)

If the ratio  $XO_4^{3^-} ZO_4^{2^-}$  in the titrated mixture was greater than 1 12 the consumption of  $I_2O_5$  between the first and the second potential step corresponded also to the formation of trianion  $Z_3O_{10}^{2^-}$ . In this case the second potential step was much less conspicuous than for the ratio X : Z = 1 12. On the other hand if the ratio  $XO_4^{3^-} ZO_4^{2^-}$  in the mixture was smaller than 1 12, the consumption of titrating agent between the first and the second potential step was lower, *i.e.* it was shifted more towards the value corresponding to the formation of dianion  $Z_2O_7^{2^-}$  *E.g.* for the ratio  $XO_4^{3^-} ZO_4^{2^-} = 1$  24 the consumption corresponded to the mean of consumptions observed at the formation of trianion  $Z_3O_{10}^{2^-}$  and dianion  $Z_2O_7^{2^-}$  *i.e.* to the reaction

$$5ZO_4^{2-} + 3I_2O_5 = Z_2O_7^{2-} + Z_3O_{10}^{2-} + 6IO_3^{-}$$

Only in the case of a mixture of bases  $Na_3VO_4 + Na_2MoO_4$  the presence of divanadate anion does not influence the reaction of molybdate and therefore the consumption of  $I_2O_5$  corresponds to the formation of dimolybdate



Fig. 4. Curves for potentiometric titration of a mixture of phosphate—tungstate(VI) by iodine pentoxide.

1. 0.101 mmol of  $K_3PO_4$  plus 2.418 mmol of  $Na_2WO_4$  titrated by  $I_2O_5$ ; 2. 0.200 mmol of  $K_3PO_4$  plus 2.390 mmol of  $Na_2WO_4$ titrated by  $I_2O_5$ .



Fig. 5. Curves for potentiometric titration of a mixture of diarsenate(V)—molybdate by iodine pentoxide.
1. 0.075 mmol of Na<sub>4</sub>As<sub>2</sub>O<sub>7</sub> plus
3.592 mmol of Na<sub>2</sub>MoO<sub>4</sub> titrated by I<sub>2</sub>O<sub>5</sub>;
2. 0.151 mmol of Na<sub>4</sub>As<sub>2</sub>O<sub>7</sub> plus
3.608 mmol of Na<sub>2</sub>MoO<sub>4</sub> titrated by I<sub>2</sub>O<sub>5</sub>;
3. 0.259 mmol of Na<sub>4</sub>As<sub>2</sub>O<sub>7</sub> plus
3.953 mmol of Na<sub>2</sub>MoO<sub>4</sub> titrated by I<sub>2</sub>O<sub>5</sub>.

Mixture of bases $K_3PO_4 + Na_2ZO_4$	Mole ratio between substances P: Z $I_2O_5: K_3PO_4$ (1st potential step)	Mole ratio at potential steps			
		Z=Mo		Z = W	
		1 11.95 0.49 : 1	1 : 23.98 0.50 : 1	1 11.93 0.50:1	1 : 23.94 0.50 : 1
	$I_2O_5$ : $Na_2ZO_4$ (1st and 2nd potential step)	0.68 : 1	0.58 : 1	0.66 : 1	0.57 : 1
Na <sub>3</sub> VO <sub>4</sub> + Na <sub>2</sub> ZO <sub>4</sub>	V : Z $I_2O_5 : Na_3VO_4$ (1st potential step)	1 11.99 0.51 1	_	1 : 11.93 0.49 : 1	1 : 23.95 0.50 : 1
	$I_2O_5$ : Na <sub>2</sub> ZO <sub>4</sub> (1st and 2nd potential step)	0.48 : 1	_	0.68 : 1	0.58 : 1
$Na_3AsO_4 + Na_2ZO_4$	As : Z $I_2O_5$ : Na <sub>2</sub> ZO <sub>4</sub> (single potential step)	1 11.93 0.50 : 1	_	1 11.96 0.51 1	_
$Na_4As_2O_7 + Na_2ZO_4$	As : Z $I_2O_5$ : Na <sub>2</sub> ZO <sub>4</sub> (single potential step)	1:7.65 1 11.95 0.67:1 0.67 1	1 : 23.95 0.58 : 1	1 11.78 0.67 : 1	1 : 23.82 0.58 : 1

Table 2
Titration of mixtures of the Lux bases by iodine pentoxide (mole ratio of bases and potential steps)

# $I_2O_5 + 2M_0O_4^{2-} = M_0O_7^{2-} + 2IO_3^{-}$

In the mixture  $AsO_4^{3^-} + ZO_4^{2^-}$  the titration proceeds as if the arsenate(V) anions were not present, *i.e.* the consumption of  $I_2O_5$  at the first (and single) potential step corresponds to the change of  $ZO_4^{2^-}$  into  $Z_2O_7^{2^-}$  On the other hand, in the mixture  $As_2O_7^{4^-} + ZO_4^{4^-}$  (As Z = 1 12) the first (and single) potential step corresponds to the change of  $ZO_4^{2^-}$  into  $Z_3O_{10}^{2^-}$ .

In the course of titration the melt remains between the first and the second potential step clear and colourless in the case of systems P/Mo, P/W, V/Mo, As/Mo (in systems where X = As only before the first step). In the case of system V/W the titrated melt gets yellow and in the system As/W colourless crystals are formed.

After the second potential step (in the case of X = As after the first step) white (P/W, As/Mo) or yellow (P/Mo, V/Mo, V/W, As/W) precipitate occurs. This reaction is however disturbed by the reaction between I<sub>2</sub>O<sub>5</sub> and the nitrate melt.

The most important data on titrations of mixtures consisting of two Lux bases by  $I_2O_5$  are summarized in Table 2. Examples of titration curves are presented in Figs. 4 and 5.

## Discussion

The aim of this work was to determine the strength of the Lux acids and bases. Similar efforts have already appeared [3, 5, 11] but the substances were compared according to the amount of solvent (nitrate) with which the Lux acid can react [5], according to the kinetics of this reaction [5] or according to the change in potential of pure solvent resulting from dissolution of the Lux acid up to final concentration  $10^{-2}$  mol dm<sup>-3</sup> [11]. Also the equilibrium constants of acid-base reactions [3, 5, 11, 15] have been derived on the basis of uncorrect assumptions about the existence of different ions in the melt, mainly  $O^{2-}$  [12–14]. In order to avoid the not completely clear mechanism of reaction of sodium carbonate or peroxide with the nitrate melt titration of the Lux bases by acid was used in this work. An attempt was done to titrate a mixture of two Lux bases by strong Lux acid in order to distinguish the stronger and weaker base. This procedure, however, has two difficulties. The first is that in some cases only one potential step appears on the titration curve which corresponds to simultaneous transition of both bases. The second difficulty is that the mutual reaction of some couples of bases in the course of titration with  $I_2O_5$  results in formation of anions of heteropolyacids.

For these reasons the course of titration of each base with  $I_2O_5$  was studied separately and formal electrode potentials corresponding to equimolar mixture of acid-base pairs were considered to be the criterion characterizing position of the pair in acid-base series. The behaviour of anion  $AsO_4^{3^-}$  with respect to  $I_2O_5$  is surprising. From potentiometric measurements it follows that anion  $AsO_4^{3^-}$  is rather a strong base (Table 1). Despite of that it does not react in acid-base reaction with  $I_2O_5$  (it reacts however with anion  $Cr_2O_7^{2^-}$ ). It is probably due to the very slow corresponding acid-base reaction and so  $I_2O_5$  added reacts primarily with the nitrate melt.

Conjugated acid-base pairs studied in this work are arranged according to the values of formal electrode potentials (E') (as a matter of fact according to EMF of the cell) in the following series

This acid-base series differs in most cases from the series which follows for the strength of conjugated acid-base pairs from literature data on equilibrium constants [3, 5, 8, 9, 11, 15].

Our measurements confirm formation of anions  $Mo_2O_7^{2^-}$  in the nitrate melt in agreement with [7, 8] but disagree with [5] where formation of anions  $Mo_3O_{10}^{2^-}$  is assumed. We identified this trimolybdate anion only in connection with the formation of heteropolyanions.

By titrating a mixture of oxo anions of the type  $ZO_4^{2^-}$  (Z = Mo, W) and oxo anions of the type  $XO_4^{3^-}$ , resp.  $X_2O_7^{4^-}$  (X = P, V, As) with I<sub>2</sub>O<sub>5</sub> it was observed that in most cases the presence of the latter anions influences the course of titration of molybdate or tungstate(VI) in such way that after the formation of anions  $X_2O_7^{4^-}$  it is not formed the anion  $Z_2O_7^{2^-}$  (as in the case of titration of  $ZO_4^{2^-}$ ) but the anion  $Z_3O_{10}^{2^-}$ . From this influence of anion  $X_2O_7^{4^-}$  it may be assumed that in the melt a complex is formed in which each dianion  $X_2O_7^{4^-}$  bonds eight trianions  $Z_3O_{10}^{2^-}$ . Therefore, it may be assumed that complex anion of the summary composition  $[X_2Z_{24}O_{87}]^{20^-}$  is formed according to the equation

$$X_2O_7^{4-} + 24ZO_4^{2-} + 16I_2O_5 = [X_2Z_{24}O_{87}]^{20-} + 32IO_3^{-}$$

The formation of this anion is apparent mainly in the system V/W because the heteropolyanion is vellow, which is manifested by the increasing intensity of colour of solution. This effect begins at potential step corresponding to the change of  $VO_4^{3-}$  into  $V_2O_7^{4-}$ . Also in the case of the pair As/Mo the formation of the complex is good accessible to observation because at certain concentration transparent crystals appear in the melt. Shift of potential step from consumption corresponding to the formation of  $Z_2 \Omega_2^{4-}$  to consumption corresponding to the formation of  $Z_2 \Omega_2^{2-}$ is observed in all studied systems with the exception of combination V/Mo. In this system the shift of potential was not observed. From this fact it may be assumed that in this case ionic radii are not suitable for the formation of heteropolyanion. In the case of arsenic the complex is formed only if titration starts from  $As_2O_2^{4-}$  while the anions  $AsO_4^{3-}$  behave inertly. After potential step which corresponds to the formation of the above complex a precipitate is formed in the course of further acidification of the complex anion. The precipitate is vellow or white, which depends on the element. From appearance and mole ratio X : Z it can be judged that the precipitate contains known anions of heteropolyacid of composition  $[X(Z_3O_{10})_4]^{3-}$  which are formed according to the reaction

$$[X_2 Z_{24} O_{87}]^{20^-} + 7 I_2 O_5 = 2 [X (Z_3 O_{10})_4]^{3^-} + 14 IO_3^-$$

Formation of this substance is manifested markedly by colour in the case of couples in which X = P, V (but also in the case of couple V/Mo when the complex  $[V_2Mo_{24}O_{87}]^{20-}$  is not formed).

While substances with anion  $[X(Z_3O_{10})_4]^{3-}$  are apparently known salts of heteropolyacids (even if from aqueous solutions they are usually isolated in hydrated form) the anion of composition  $[X_2Z_{24}O_{87}]^{20-}$  is a species which is probably formed only by reactions occurring in melts and it has not yet been prepared from aqueous solution.

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