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THE ELECTROCHEMICAL PROPERTIES OF MOLYBDENUM AND TUNGSTEN

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Molybdenum and tungsten find widespread application in the manufacture of high-grade steels, electrical engineering electroplating, and other fields. These metals play an important part in improving processes of chemical technology, where they are employed as catalysts. Their compounds will probably also find application in semiconductor technology. The preparation of the metals in an extremely pure state therefore acquires great significance. Electrochemical methods occupy a prominent place in solving this problem. At the same time, it becomes necessary to determine traces of molybdenum and tungsten in various materials and industrial products. Electrochemical methods of analysis have an important role in this connection also.

A systematic account of the large amount of published information which has accumulated on the electrochemistry of molybdenum and tungsten will considerably ease the labour of researach workers in this field.

1. POTENTIALS OF REDOX SYSTEMS

The peculiar structure of the electron shells of molybdenum and tungsten is responsible for the variety of types of compounds, in which the metals exhibit a valency varying from two to six. Compounds with hydrogen, which are so typical of elements of the sulphur subgroup, are unknown with molybdenum and tungsten[1]. These metals form a series of redox systems, characterised by definite potentials. Owing, however, to the instability of several compounds in aqueous solution, the redox potentials of these systems have not been evaluated. In particular, no data have been published for the systems M^V/M^{IV}, M^{IV}/M^{III}, and M^{III}/M^{II} in aqueous solution. Quadrivalent compounds of molybdenum and tungsten are extremely unstable in aqueous solution, undergoing disproportionation with the formation of trebly charged and quintuply charged ions.

The potentials of other redox systems have been studied quite thoroughly. Thermodynamic calculations of potentials yield the values[2,3]

$Mo^{III}/Mo_{solid} - 0.20$ V; $Mo^{V}/Mo^{III} \sim 0.0$ V;

$WO_4^{2-}/W_{solid} \sim -1.1$ V; $W^{III}/W_{solid} > -0.05$ V;

$WO_2/W^{III} < -0.05$ V; $WO_2/WO^{2+} + 0.26$ V.

Careful measurements of the potentials of various systems containing molybdenum were made by Foerster and his coworkers[4], a selection of whose results is given in Table 1.

Table 1 shows the potential of the Mo^{VI}/Mo^{V} system depends on the relative concentrations of oxidised and reduced forms. This relationship should be consistent with the formula

$$\varphi = \varphi_0 + 0.058 \log \frac{[M^{VI}]\,[H^+]^2}{[M^V]}, \quad (1)$$

in conformity with the potential-determining process

$$MO_2Cl_3^- + 2H^+ + 2Cl^- + e \rightarrow MOCl_5^{2-} + H_2O. \quad (2)$$

The measured potentials differ somewhat from those calculated theoretically by means of Eqn. (1). The theoretical shift in potential produced by doubling the hydrochloric acid concentration should be $0.058 \times 2 \log 2 = 0.035$ V. The changes in potential found experimentally on passing from 2 *N* to 4 *N* and 8 *N* HCl were respectively 0.039 V and 0.190 V. The potentials of this system in 4 *N* and 8 *N* HCl should be +0.628 V and +0.663 V.

The discrepancy between theoretical and experimental values was attributed partly to variation in the activity of hydrochloric acid with change in its concentration. On the other hand, these workers postulated the formation of more stable chloride complexes of quinquevalent molybdenum, which would have inevitably produced a positive shift in the potential with increase in concentration of the chloride ion.

The normal oxidation potential of this system was found to be +0.400 V.[3] The material of the indicator electrode (platinum, iridium, gold) had practically no effect on the potential.

The potential of the Mo^{V}/Mo^{III} system was calculated by means of the equation

$$\varphi = \varphi_0 + 0.029 \log \frac{[Mo^V]\,[H^+]^2}{[Mo^{III}]}, \quad (3)$$

in conformity with the reaction

$$MoO^{3+} + 2H^+ + 2e \rightleftarrows Mo^{3+} + H_2O. \quad (4)$$

The data in Table 2 show that the potentials of this system are more negative than those of the previous system. The

TABLE 1. Potentials (on standard hydrogen scale) of the Mo^{VI}/Mo^{V} system in hydrochloric-acid solutions.

Mo^{VI}/Mo^{V} ratio	Acid concn., *N*	Potential Pt, V
99:1	8	+0.822
99:1	4	+0.632
99:1	2	+0.593
97:3	2	+0.576
50:50	2	+0.532
3:97	2	+0.484
1:99	2	+0.470

TABLE 2. Potentials (on standard hydrogen scale) of the Mo^{V}/Mo^{III} system in hydrochloric-acid solutions.

Mo^{V}/Mo^{III} ratio	Acid concn., N	Potential Pt, V
97:3	8	+0.322
97:3	4	+0.258
97:3	2	+0.188
50:50	2	+0.114
3:97	2	+0.054
1:9	2	+0.054

same features were observed in the variation of the potential with the concentration ratio of oxidised and reduced forms, and also with the concentration of hydrochloric acid.

Doubling the hydrochloric acid concentration should produce a shift in potential of $0.029 \times 2 \log 2 = 0.017$ V. For a concentration ratio of 100 between oxidised and reduced forms, the corresponding potentials should be +0.205 V (4 N HCl) and +0.232 V (8 N HCl). The measured values were more positive, +0.258 and +0.322 V. Thus the changes in potential accompanying increase in concentration of hydrochloric acid considerably exceeded the theoretical values.

The redox potentials of systems involving molybdenum had been measured by Chilesotti[5] before Foerster's investigations. The measurements were made in the titration of tervalent molybdenum with potassium permanganate. The results obtained by the two workers differ considerably.

The Mo^{VI}/Mo^{V} system has been studied also by other workers[6,7], who explained the variation in potential with the concentration of hydrochloric acid not only by the influence of the hydrogen-ion concentration but also by the occurrence of two different forms of quinquevalent molybdenum.

Syrokomskii studied the potentials of redox systems as functions of the concentrations of complexing agents[8,9]. He showed the effect of the concentration of the anions PO_4^{3-}, $C_2O_4^{2-}$, and $C_4H_4O_6^{2-}$ on the potential, which becomes more negative on addition of the complexing agent. The shift in potential produced by the different anions varies in the above sequence.

The effect of thiocyanate on the redox potential of the Mo^{VI}/Mo^{V} system was studied by Tarayan and Ekimyan[10], who found that the potential becomes more positive with increase in the thiocyanate concentration.

The potential of the W^{VI}/W^{V} system was first measured by Collenberg and Guthe[11], who obtained a value of +0.26 V, differing from that calculated by means of Eqn. (1). The experimental results have been reproduced by Chernikhov and Goryushina[12,13] in the potentiometric titration of sexivalent tungsten with bivalent chromium. Some lack of reproducibility in the potentials of systems containing quinquevalent tungsten has been explained by its rapid oxidation in air. According to some workers[14], however, solutions of quinquevalent tungsten are stable, and can be employed as working solutions in oxidimetric titration. A systematic study of the redox potentials of tungsten systems in hydrochloric acid solutions has been made by Geyer and Henze[15,16], some of whose results are listed in Table 3.

Tungsten was obtained in lower states of oxidation by electrolysis with platinum, mercury, and amalgamated

TABLE 3. Potentials (on standard hydrogen scale) of redox systems in hydrochloric-acid solutions.

W^{VI}/W^{V} ratio	Potential, V		W^{V}/W^{III} ratio	Potential, V	
	12.5	8.0		12.5	9.5
90:10	+0.42	+0.29	90:10	+0.13	+0.03
50:50	+0.36	+0.20	50:50	+0.05	−0.03
10:90	+0.37	+0.16	10:90	−0.02	−0.11

lead electrodes. With a platinum electrode (at a cathodic current density of 0.01–0.3 A cm^{-2}) quinquevalent tungsten was obtained. A sharp jump in potential occurred only when the quinquevalent state was reached. The subsequent conversion of W^{V} into W^{III} was not accompanied by a sharp change in potential. In phosphate solutions reduction occurred with difficulty to quinquevalent tungsten.

In contrast to molybdenum, the potential of the W^{V}/W^{III} system was calculated on the basis of

$$2WOCl_5^{2-} + 4H^+ + 4e \rightleftarrows W_2Cl_9^{3-} + 2H_2O + Cl^-, \quad (5)$$

as the potential-determining process. Consequently the equation

$$\varphi = \varphi_0 + 0{,}029 \log \frac{[W^V]\,[H^+]^4}{[W_2Cl_9^{3-}]}, \quad (6)$$

was used for the calculations.

It is evident from Eqn. (6) that variation in the hydrogen-ion concentration should have a more marked effect on the potential than in the case of the analogous molybdenum system. Measurements of potential for these systems containing different concentrations of hydrochloric acid show that the potential shifts to more positive values with increase in the hydrogen-ion concentration, but no exact relationship is observed. The potentials of both systems are affected by the concentration ratio of oxidised to reduced forms.

Nevertheless, the total concentration of oxidised and reduced forms has hardly any effect on the potential. Addition of phosphoric acid makes the potential more negative[17]. Oxalic acid and other organic complexing agents have the opposite effect. The potentials of the redox systems were not studied in alkaline solutions owing to hydrolysis of the salts with the formation of precipitates. However, the potential of the $W(CN)_8^{3-}/W(CN)_8^{4-}$ system was measured in the presence of potassium cyanide, and found to be +0.57 V. Several authors regard the presence of W^{IV} in these solutions as certain[2,18].

Methods for the oxidimetric determination of molybdenum and tungsten have been developed on the basis of potential measurements in redox systems containing these elements[12,13,19–27].

The potential of metallic molybdenum in solutions of various electrolytes has been measured by Akimov[28], Shatalov[29], and others. A characteristic feature of Akimov's results (Table 4) is their dependence on the previous mechanical treatment of the electrode surface: an electrode having an uncleaned surface shows far more positive potentials than does an electrode which has first been cleaned. This indicates the presence of oxide films on the electrode surface.

The influence of the nature of the electrolyte on the potential is most probably linked in some way with the formation of oxide films. In conformity with this, the potentials are more positive in acid than in alkaline solutions

(dissolution of the film). With time the potential in an alkaline solution becomes more positive, obviously owing to the accumulation of alkali-insoluble oxidation products of molybdenum.

Shatalov[29] considers the concentration of hydrogen ions to be the main potential-determining factor in the case of molybdenum. Potential measurements over the pH range 1–8 have shown a linear relation, which can be expressed by the empirical formula

$$\varphi = \frac{0.35}{0.40} - 0.045\,\mathrm{pH}.$$

Table 5 gives results obtained by Shatalov[29] for the dependence of the potential on the nature of the anion. The results resemble those in Table 4. Chloride and hydroxide ions exert the greatest depolarising effect on molybdenum.

Kruger and Kahlenberg[30] have studied the potentials of molybdenum in solutions of various electrolytes saturated with inert gases (Table 6). It is difficult to compare Table 6 with Table 5 because of differences in the electrolyte concentrations. However, comparison of certain data (for KOH and HCl) indicates considerable negative shifts in potential when a solution is saturated with an inert gas. The reason for these shifts is obscure.

A similar variation in the potential with the nature and concentration of the anion has been obtained by several workers for tungsten[28,29,31-33], results of Korner[31] and Shatalov[29] being listed in Tables 7 and 8 respectively. Table 7 shows the depolarising action of anions on the potential. In the presence of chloride, bromide, iodide, and cyanide ions the potential becomes more negative. A considerable negative shift in the potential is observed also in ammoniacal and alkaline solutions. Shatalov's results (Table 8), obtained for tungsten in the same solutions, differ somewhat from those of Korner. The difference is most probably explained by some irreproducibility in the surface state of the tungsten electrode.

The dependence of the tungsten potential on the pH of the solution was studied by Holven[34]. In view of the direct interdependence of these properties, tungsten was recommended as an indicator electrode for the determination of pH[35].

TABLE 4. Potentials (V, on standard hydrogen scale) of metallic molybdenum in electrolyte solutions.

3% NaCl			0.1 *N* HCl		
1 min	5 min	cleaned	1 min	5 min	cleaned
+0.103	+0.080	−0.362	+0.338	+0.318	−0.072
0.1% *N* HNO_3			0.1 *N* NaOH		
1 min	5 min	cleaned	1 min	5 min	cleaned
+0.349	+0.323	−0.022	−0.326	−0.242	−0.602

TABLE 5. Potentials (V, on standard hydrogen scale) of metallic molybdenum in solutions of various electrolytes.

Electrolyte concn.	Potential
3% NaCl	+0.105 * −0.362 **
0.1 *N* HCl	+0.330 * −0.092 **
0.1 *N* HNO_3	+0.329 * −0.019 **
0.1 *N* NaOH	−0.228 * −0.660 **
1.0 *N* HCl	+0.372 * +0.305 **
1.0 *N* KOH	−0.320 * −0.400 **

* After 5 min.
** Cleaned.

TABLE 6. Potentials (V, on standard hydrogen scale) of molybdenum in electrolyte solutions saturated with inert gases.

Gas	Electrolyte	Potential
N_2	KCl	−0.246
	KOH	−0.695
	HCl	+0.085
H_2	HCl	−0.228
	KOH	−0.680
	HCl	+0.094
Ar	KCl	−0.245
	KOH	−0.680
	HCl	+0.080
He	KCl	−0.250
	KOH	−0.645
	HCl	+0.074

TABLE 7. Potentials (V, on standard hydrogen scale) of tungsten in electrolyte solutions.

Electrolyte	Potential
H_2SO_4	+0.193
HCl	+0.256
HNO_3	+0.311
KOH	−0.315
NaOH	−0.316
NH_4OH	−0.238
KCN	−0.647
KF	+0.522
KCl	+0 563
KBr	+0.589
KI	+0.733
KNO_3	+0.300
K_2SO_4	+0.719

TABLE 8. Potentials (V, on standard hydrogen scale), of tungsten in electrolyte solutions.

Electrolyte	Potential	Atmosphere	Electrolyte	Potential
HCl	+0.345	H_2	KI	+0.170
	+0.305	N_2	H_2SO_4	+0.193
	+0.311		KCl	0.00
HNO_3	−0.370	H_2	KF	−0.045
KOH	−0.320	N_2	NH_4OH	−0.238

2. COMPOSITION AND SPECTROPHOTOMETRY OF COMPLEX COMPOUNDS

A vast literature exists[36-76] on the composition of compounds formed by sexivalent molybdenum and tungsten with inorganic and organic reagents. The composition is greatly

dependent on the nature and concentration of the ligand. Thus the compound $H_2Mo_4O_{13}$ is assumed[36] to be present in dilute hydrochloric acid solutions. With increasing concentration of the acid, the cationic form $HMo_2O_6^+$ is produced. Further increase in the concentration of hydrochloric acid to 5–6 *N* promotes formation of the complex MoO_2Cl_2 by the reaction

$$HMo_2O_5^+ + 3H^+ + 4Cl^- \rightarrow 2MoO_2Cl_2 + 2H_2O.$$

The formulae WCl_6, $WOCl_4$, and WO_2Cl_2 have been attributed[11,77] to the chloride complexes of sexivalent tungsten. In aqueous solution the complexes are unstable, undergoing hydrolysis to form a precipitate of tunstic acid. The chloride complexes of sexivalent molybdenum and tungsten have their maximum light absorption in the ultraviolet. The complex $H^+[MoO_3.H_2SO_4]$ can be formed in sulphuric-acid solution.

Numerous heteropolyacids of molybdenum and tungsten are known, and a fair amount of information has been published[37-39, 50-53] on their composition and structure. The composition of the heteropolycompounds is represented by the general formula $H_3[El^1(M_3O_{10})_4].nH_2O$ or $H_4[El^2(M_3O_{10})_4].nH_2O$, where El^1 = P, As, Sb, etc. and El^2 = Si, Ge, Sn, etc.

Sexivalent molybdenum and tungsten form many complex compounds with organic reagents. Some of these are brightly coloured, and are used for the absorptiometric determination of molybdenum. In several cases the composition of the compounds which are formed has not been established[40-48, 54-76].

The chloride complexes of quinquevalent tungsten possess a blue colour and their maximum absorption lies in the range 600–700 nm. These compounds, and the corresponding molybdenum derivatives, are stable to the action of atmospheric oxygen[78]. The composition of the chloride complexes of quinquevalent tungsten has not been adequately studied[79-81].

In contrast to W^V, the chloride complexes of Mo^V exist in two forms — monomeric (> 7 *N* HCl) and dimeric (< < 2.5 *N* HCl) — which coexist in equilibrium in the intermediate range (2.5–7 *N* HCl).[46,78,82-87] However, as Babko points out[82], the composition of the chloride complexes of Mo^V and their equilibrium conditions have not been established at concentrations of hydrochloric acid of 3–6 *N*. The compounds $M_2[MoOCl_5]$, where M is an alkali metal, have been isolated from solutions of concentrated hydrochloric acid. According to this author[82], quinquevalent molybdenum does not form stable chloride complexes in solutions of dilute hydrochloric acid, but is most probably present as the cation MoO_2^+. As the concentration of hydrochloric acid increases, the cation MoO^{3+} is formed:

$$MoO_2^+ + 2H^+ \rightleftarrows MoO^{3+} + H_2O.$$

Further increase in the concentration of the acid results in the formation of the complexes $MoOCl^{2+}$, $MoOCl_2^+$, and $MoOCl_3$.

Many investigations have been made of the conditions of formation and the composition of the thiocyanate complexes of molybdenum and tungsten[88-127]. Several workers assume that the thiocyanate complex of tungsten is represented by the formula $W(CNS)_5$, while other results indicate that the tungsten is tervalent[121], the formula of the complex being WOCNS. Maximum light absorption occurs at 400 nm. Contradictory views are held on the valency of molybdenum in the thiocyanate complex: Maas[90] and Krauskopf[91] state that molybdenum is tervalent in such compounds, Markle[93] regards it as quadrivalent, and finally Sand[92] considers it to be quinquevalent. Babko's investigations[94,95], together with those of other workers[99], indicate that molybdenum is quinquevalent in this compound, whose composition corresponds to the formula $Mo(CNS)_5$ (λ_{max} = 420 nm).

There are indications of the existence of halide complexes of quadrivalent tungsten and molybdenum[128] having the formulae MCl_4, $MBrCl_3$, etc., which are unstable in aqueous solution.

The halide complexes of tervalent tungsten[129] and molybdenum[130-133] have been studied the most thoroughly. Various authors state that tervalent molybdenum exists in two forms — green and red — in hydrochloric-acid solution. The green form is produced in dilute hydrochloric acid. Some workers have therefore assumed that it corresponds to the cation Mo^{3+} or MoO^+, and that the red form, which is present in concentrated solutions of hydrochloric acid, represents the anion $MoCl_6^{3-}$. Other workers[131] regard the occurrence of two forms of tervalent molybdenum as due to *cis–trans* isomerism of a complex having the same composition $MoOCl.4H_2O$ or $[MoCl_2(H_2O)_4]^+$.

The green form is unstable, being converted into the red form by increasing the acidity or raising the temperature. A characteristic property of tervalent molybdenum is its comparatively ready oxidation by hydrogen ions to yield quinquevalent molybdenum. As a consequence, aqueous solutions of tervalent molybdenum are unstable. Spectrophotometry of the solutions confirms the presence of two forms: the D–λ curves exhibit two absorption maxima, at 420 and 520 nm (7 *N* HCl).[132,133]. Dilution of the solution results in a shift in the maximum to shorter wavelengths, which corresponds to a change in composition of the complexes, with the ultimate formation of tervalent molybdenum hydroxide.

The chloride complexes of tervalent tungsten also exist as two forms — $H_5W_3Cl_{14}$ and $H_3W_2Cl_9$ — with absorption maxima in the region of 515 and 462 nm (red and yellow respectively). According to other workers[129], however, the occurrence of two forms of tervalent tungsten is due, as in the case of molybdenum, to *cis–trans* isomerism.

Tungsten and molybdenum blues constitute a peculiar group of compounds[134-139], whose exact composition has not been established.

3. ELECTROLYSIS OF SOLUTIONS

The first work on the electrolytic reduction of sexivalent molybdenum was done by Gahn[140]. This work was qualitative in character, as were investigations by other workers[141-145]. In particular Grotthus[141], who reduced sexivalent molybdenum in sulphuric-acid solution, noted the appearance of blue oxides of molybdenum on the cathode, metallic molybdenum not being isolated. The first attempt to isolate metallic molybdenum by electrolysis with a mercury cathode was made by Férée[146], who used a current density of 5 A cm^{-2} in the cold. The reduced molybdenum dissolved in the mercury to form an amalgam. Later Meyer[147,148] obtained molybdenum amalgam by the electrolysis of sulphuric-acid solutions. This work was repeated by Russell[149] and by Bock[150], who found the optimum conditions

(1–1.5 N H_2SO_4, cathodic c.d. 0.6 A cm^{-2}) for the quantitative deposition of molybdenum. Electrolysis with a mercury cathode was used for the quantitative separation of molybdenum from several elements which do not form amalgams. Electrolysis with solid cathodes, on the other hand, proved useful for the quantitative isolation of molybdenum as the oxide Mo_2O_3 [151,152] with subsequent quantitative determination.

Detailed investigations of the electrolytic reduction of sexivalent molybdenum were made by Chilesotti[5,130,153] and by Foerster[4,154], who studied the effect of several factors — the material of the electrode, the nature and concentration of the electrolyte, the current density, etc.

Chilesotti's results showed that the current efficiency is close to 100% at not very high current densities (0.047 A cm^{-2}), but it falls considerably with increase in current density. The variation in current efficiency with the concentration of hydrochloric acid is irregular: the efficiency decreases on passing from 9N to 6N HCl, and then increases again on passing to more dilute solutions of the acid. The time variation in the current efficiency shows considerable irregular fluctuations. The initial decrease in efficiency is most probably associated with the formation of insoluble products on the mercury surface, which lower the hydrogen overpotential. Chilesotti explained the subsequent rise in the curve by the formation of molybdenum amalgam. The process was accelerated by raising the temperature, the current efficiency being increased. The maximum current efficiency was observed on a lead electrode; values of the same order were obtained on mercury and platinum electrodes.

Chilesotti regarded the high current efficiency on lead as possibly due to the discharge of lead ions which had passed into solution under the influence of an oxidant (molybdenum). During electrolysis with platinum, mercury, and iridium cathodes, the cathode potential became more negative, reaching 0.40 V. No change in potential was observed on tin and lead cathodes.

It follows from the above survey that metallic molybdenum was not deposited when solutions were electrolysed with solid electrodes. However, a series of papers have shown that metallic molybdenum can be deposited in the presence of added iron, nickel, or cobalt salts[155–161]. The additives are usually regarded as depolarising the discharge of Mo^{VI} by forming an alloy on the cathode. Furthermore, the hydrogen overpotential on the alloy is greater than that on pure molybdenum, which also favours the process. According to Ernest and Holt[161], the mechanism of the electrode reaction is

$$M^{2+} + 2e \rightarrow M^{\circ},$$
$$MoO_4^{2-} + 4H_2O + ne \rightarrow Mo(OH)_{6-n} + (2+n)\,OH^-,$$
$$Mo(OH)_{6-n} + (6-n)\,H + M \rightarrow MMo + (6-n)\,H_2O,$$

where n = 1–3. This scheme is seen to involve the participation of atomic hydrogen in the reduction of Mo^{VI}.

Many workers have investigated the electrolytic reduction of W^{VI}. One of the first papers on the electrolysis of tungsten[162] contains a brief mention of the possibility of obtaining an amalgam by electrolysing acid solutions of tungstates containing hydrofluoric acid. This possibility has been confirmed in later work[163]. Leiser[163] made a systematic investigation of the electrolytic reduction of W^{VI} with platinum and lead cathodes, nickel being used as anode. In all cases sparingly soluble blue products were formed, whose composition could not be established. The current efficiency was low, not exceeding 3%.

A broad investigation was made by Rosenheim[164], who used phosphoric, arsenic, and organic acids ($H_2C_2O_4$, $H_2C_4H_4O_6$) as complexing agents. Lead, platinum, mercury, and zinc were examined as cathodes. Reduction took place in stages. From the colour changes occurring in the solution (blue, brown, cerise), this worker concluded that quinquevalent, quadrivalent, and tervalent tungsten was formed. Neither changing the current density nor varying the temperature resulted in further reduction. Collenberg[165,166] showed that, when a mercury cathode was used, the current efficiency did not exceed 24%, and fell sharply with time. It increased slightly with decrease in the current density. Reduction took place at negative values of the cathode potential. Thus at a current density of 0.016 A cm^{-2} the initial potential was -0.70 V, and at 0.004 A cm^{-2} it was close to zero.

Tervalent tungsten was obtained as the final product of reduction on mercury, lead, and tin cathodes. The current efficiency was far smaller on a mercury cathode than on lead.

Rosenheim suggested the following mechanism of reduction

$$\left.\begin{aligned} W^{VI} + e &\rightarrow W^{V} \\ W^{V} + 2e &\rightarrow W^{III} \\ W^{V} + e &\rightarrow W^{IV} \end{aligned}\right\}.$$

On a platinum cathode the final reduction product is merely quinquevalent tungsten.

It must be noted that molybdenum and tungsten redox systems, although reversible in the equilibrium state, are appreciably polarised during electrolytic reduction[154,169]. This is presumably due to the formation of insoluble films on the electrode surface.

Neumann and Richter[167] investigated cyanide solutions of tungsten, and attempted to deposit the metal on a mercury cathode, but were unsuccessful. However, Jackson et al.[168] confirmed Feree's preparation[162] of tungsten amalgam, and pointed out that no acid other than hydrofluoric should be present in the solution. The optimum acid concentration was 4.6 N HF, and the current density 0.60–1 A cm^{-2}.

As with molybdenum, metallic tungsten is not deposited from aqueous solution on solid cathodes. However, it has been deposited from solutions in organic solvents[170,171].

The need for tungsten coatings of high corrosion resistance led to comprehensive investigations of the conditions for the deposition of metallic tungsten from aqueous solution. The problem was first solved by Fink[172]. The tungsten deposits obtained were dense, bright, and stable to the action not only of hydrochloric and sulphuric acids but even of nitric acid. Holt[173] proposed an alkaline electrolyte for this purpose. In the cold a deposit of tungsten oxides was obtained from an alkaline solution. At 85° the cathode became covered with a silver-white film of metallic tungsten. The current efficiency was ~ 1%, which diminished with increase in current density, the optimum value of which was 0.1 A cm^{-2}. Phosphate solutions also were useful for the deposition of metallic tungsten, but the weight of the deposit did not exceed 0.0077 g.

Holt showed[174-176] that metallic tungsten can be deposited from aqueous solution only if the solution contains traces of iron (0.001 g per 75 ml of solution). The cathode deposit contains up to 35% of iron. The quality of the cathode deposit is equally affected by raising or lowering the concentration of iron in the solution: in both cases oxides of varying composition, not metallic tungsten, are deposited.

Nickel, cobalt, and copper have also been proposed[177-179] as impurities promoting the deposition of metallic tungsten. The tungsten content of the cathode deposit did not exceed 50%. In later work Holt[180] has examined aluminium, beryllium, zinc, manganese, tin, cadmium, etc. as additives, and other workers[181-185] have also investigated this problem.

The mechanism by which the additives exert their effect has not yet been elucidated. Various views have been expressed[180,186-188].

1. The discharge of W^{VI} involves two alternating processes at the cathode:

$$(a)\ M^{n+} + 2e \rightarrow M^{\circ},$$
$$(b)\ WO_4^{2-} + 8H^+ + 6e \rightarrow W^{\circ} + H_2O.$$

Reaction (*a*) continues until the surface is completely covered with a thin layer of the impurity metal, which then catalyses the discharge of W^{VI} ions, reaction (*a*) giving way to reaction (*b*). Thus the processes alternate. The hydrogen overpotential is lower on the pure metals (iron, cobalt, nickel) than on their alloys with tungsten.[180,186,188,189].

2. An alloy is formed by the discharge of mixed complexes of tungsten with the impurity metal. Holt[186] used a polarographic method to test this hypothesis. He found that the half-wave potential of the second reduction wave of nickel (-2.02 V) is displaced to more positive values (-1.67 V) in the presence of tungsten. In his opinion this indicates the discharge of a mixed complex of nickel and tungsten.

3. A layer of impurity metal deposited on the cathode promotes formation of an active form of hydrogen, which reduces the W^{VI}. The theory that several compounds are hydrogenated by atomic hydrogen formed on the cathode surface is supported by Kobozev[190-193]. It has been shown[194] that tungsten trioxide placed a short distance from the cathode surface acquires a blue colour as a result of its reduction by atomic hydrogen emitted from the mercury surface. However, Bagotskii and Iofa state[195] that the trioxide is not reduced when not in immediate contact with the cathode, which they explain by the direct reduction of WO_3 to W_2O_5:

$$2WO_3 + 2H^+ + 2e \rightarrow W_2O_5 + H_2O.$$

4. Depolarisation of the discharge of W^{VI} is due to the formation of an alloy of tungsten with the impurity metal, a view supported by Solov'eva and Vagramyan[187], who reject the theory that the metals are deposited layer by layer. If this did occur, fluctuations should be observed in the cathode potential, but these are not in fact observed.

The electrolytic oxidation of tungsten passes through the stage of formation WO_2, W_2O_5, and WO_3.[196,197]

Several papers have appeared[198-200] on the electrolysis of non-aqueous solutions and of melts of tungsten salts, but these fall outside the scope of the present review.

4. REDUCTION WITH METALS AND AMALGAMS

Reducing agents of various strengths have been used for the non-electrolytic reduction of sexivalent molybdenum[201-223] and tungsten[224-253]. Such electronegative metals as lead, cadmium, and zinc were used as reducing agents in the early work. Reduction with zinc was first employed by Pisani[201] and by Pfordten[224]. This method has subsequently been tried by a number of investigators[202,203,211,225-231].

Tervalent molybdenum and tungsten were obtained as the final products. Reduction involved the successive formation of quadrivalent and quinquevalent molybdenum and tungsten. Some workers did not achieve a definite degree of reduction[203-205].

More recently[206,207] metallic aluminium has been used as reductant. According to Riegel and Schwartz[206] reduction in 2 *N* HCl or 1.25 M H_2SO_4 solution first yields orange quinquevalent molybdenum and then green tervalent molybdenum. When this work was checked[207], it was actually found that reduction extended only to the quinquevalent state. However, further reduction is achieved by adding a tin(II) salt. The mechanism of the process was assumed[207] to be

$$Mo^{VI} + Sn^{II} \rightarrow Mo^{IV} + Sn^{IV}, \quad (1)$$

$$Mo^{IV} \rightarrow Mo^{V} + Mo^{III}, \quad (2)$$

$$Mo^{V} + Sn^{II} \rightarrow \begin{matrix} Mo^{III} + Sn^{IV} \\ Mo^{IV} \end{matrix}. \quad (3)$$

Reaction (3) takes place after Mo^{VI} has been completely converted into Mo^{V}.

Electropositive metals such as silver and mercury have also been studied[208-212] as reducing agents, reductors filled with the freshly deposited metals being used. Furman[212] observed the quantitative conversion of sexivalent into tervalent molybdenum in solutions in concentrated hydrochloric acid. In more dilute (1.5–3.5 *N*) acid only quinquevalent molybdenum was formed. Silver had a similar effect. Holtje and Geyer[205] found results for the reduction of molybdenum(VI) by mercury and silver to be reproducible and reliable. Reduction of W^{VI} with silver and mercury in concentrated hydrochloric acid[248-250] yields W^{V}. A method based on preliminary reduction of Mo^{VI} and W^{VI} with silver has been used for the quantitative determination of molybdenum and tungsten in iron–molybdenum, iron–tungsten, and iron–molybdenum–tungsten alloys[253].

Someya's work[217,232,236] was based on the use of liquid amalgams as reducing agents, and during subsequent years many workers have studied the reduction of Mo^{VI} and W^{VI} with amalgams[213-223,233-235,237-252].

Bismuth amalgam reduces Mo^{VI} to the tervalent or the quinquevalent state depending on the acidity of the solution[217]. Sexivalent tungsten is reduced to W^{V} only in concentrated hydrochloric acid.

The amalgams of lead, tin, cadmium, and zinc reduce molybdenum and tungsten quantitatively to the tervalent state[223,234]. According to other workers, however, quadrivalent tungsten is formed on reduction with cadmium amalgam[235] and with metallic cadmium[17]. The reduction of tungsten is prevented by the presence of phosphates and fluorides[237]. Different authors have divergent opinions on the degree of reduction of W^{VI} by lead amalgam. Thus

Someya[236], Holt[237], Babko[238], and Vlasak[239] state that at 60° lead amalgam converts W^{VI} into W^{III}. According to Polotebnova[240], however, lead reduces W^{VI} to W^{IV}. The lack of agreement among the results may be due to differences in the temperature conditions.

Most authors tend to regard the method based on preliminary reduction of tungsten followed by oxidimetric titration as unsuitable for quantitative purposes. Nevertheless, the method has recently been applied to the analysis of steel[245].

Work has been done on the reduction of W^{VI} by lead, zinc, and sodium amalgams in non-aqueous solution[247]. Zinc amalgam effects complete reduction to W^{III}, lead amalgam to W^{IV}, and sodium amalgam reduces W^{VI} incompletely to W^{IV}.

5. POLAROGRAPHY

Several papers have been published on the polarographic reduction of molybdenum[254-291] and tungsten[292-312] at a dropping mercury cathode. The first work in this field was done by Uhl[254], who effected reduction in nitric-acid solutions, using lactic and oxalic acids as complexing agents. The Mo^{VI} polarograms comprised two waves having half-wave potentials of -0.35 and -0.50 V (relative to the saturated calomel electrode, s.c.e.). The proportionality of the height of the first wave to the concentration of molybdenum formed the basis of a method for the quantitative determination of molybdenum and phosphorus. Stern[255] applied Uhl's method to the analysis of biological materials, and obtained two waves with half-wave potentials of -0.40 and -1.20 V. A well defined pH dependence of the wave heights was observed. The wave height is strictly proportional to the molybdenum concentration only within a narrow range of the latter[256], and hence the polarographic determination of molybdenum with nitric acid as supporting electrolyte is not very promising. According to Gokhshtein[257] the reduction of molybdenum in nitric-acid solution is complicated by polymerisation phenomena. He suggested phosphoric acid as supporting electrolyte for the polarographic determination of molybdenum.

Stackelberg et al.[258] found that sharp molybdenum waves are obtained in sulphuric acid, whose concentration should be a least 18 *N*. Molybdenum gives one wave with a potential of -0.26 V. The wave height is proportional to the molybdenum concentration, which also permits the method to be used for quantitative analysis[259]. A detailed investigation of the process occurring in aqueous sulphuric acid has been made by Kolthoff[260].

As Stackelberg points out[258], the molybdenum reduction wave appears also in aqueous hydrochloric acid. According to him, however, it corresponds to the reduction not of molybdenum but of mercuric chloride resulting from the oxidation of metallic mercury by molybdic acid.

Kanevskii and Shvartsburd[261] obtained cathodic waves of Mo^{VI} in 88–90 vol.% phosphoric acid. A method was worked out for determining molybdenum in ores containing 0.005–50%.

Molybdophosphoric heteropolyacid undergoes reduction in phosphoric acid solution. The polarography of heteropolyacids of molybdenum — molybdosilicic, molybdogermanic, etc. acids — has formed the subject of several recent papers. Grasshoff and Hahn[262-265] state that, when these acids are reduced at a dropping mercury cathode, tervalent and quinquevalent molybdenum is formed. They find that the wave heights depend on the acid concentration.

A few papers have been published on the polarography of the lower states of oxidation of molybdenum. In particular, Deshmukh[266] has studied the reduction of quinquevalent molybdenum, a solution of which he obtained by reduction with hydrazine. The polarogram obtained with sulphuric acid as supporting electrolyte consisted of two waves, which he regarded as due to stepwise reduction to quadrivalent and tervalent molybdenum. The half-wave potentials are greatly dependent on the acidity of the solution, becoming more positive with increasing acidity.

Meits[267] obtained polarograms in a citrate buffer solution. Sexivalent molybdenum gives a single wave with a half-wave potential of -0.927 V. Tungsten is not reduced under these conditions, so that the method can be used for the quantitative determination of molybdenum in the presence of tungsten. This worker assumes that reduction involves the formation of quadrivalent molybdenum. Parry and Yakubik[268] consider that polarographic reduction in tartrate solutions yields tervalent and quinquevalent molybdenum. A similar opinion is held by Pecsok and Parkhurst[269]. Pantani[270] has made a polarographic investigation of the citrate, oxalate, and tartrate complexes.

Complexone III has also been proposed as complexing agent[271-273], and it masks the interfering effect of tungsten. Ammonium fluoride has been proposed for a similar purpose[274].

Sinyakova and Glinkina[275] obtained two Mo^{VI} reduction waves (with half-wave potentials of -0.27 V and -0.73 V) using acetic acid as supporting electrolyte. With increasing concentration of the acid, the second wave disappears, while the half-wave potential of the first wave becomes more positive. Two sharp waves are obtained also in a solution containing Complexone III. The half-wave potentials depend on the pH. The reduction of molybdenum takes place also in neutral medium (ammonium oxalate), but the shape of the wave depends on the concentration of the supporting electrolyte[276].

With mixed supporting electrolytes ($HCl + HClO_4$, $HCl + H_2O_2$) catalytic polarographic currents have been observed. Thus Jones[277], while reducing Mo^{VI} with a supporting electrolyte comprising 0.75 M H_2SO_4 + 1 M $HClO_4$, observed a catalytic wave due to reoxidation of tervalent to quadrivalent molybdenum by the perchloric acid, the half-wave potential being -0.21 V.

Holten[278] used this supporting electrolyte for the quantitative determination of molybdenum in minerals and ores. The method proved convenient in the analysis of titanium alloys[279]. Tungsten does not interfere with the determination.

The catalytic reaction in perchloric-acid solutions has been studied by Rechnitz and Laitinen[280], who found that the rate of the process depends on several factors, in particular on the concentrations of molybdenum and perchloric acid.

Sinyakova and Glinkina[281] explained the appearance of a catalytic current in solutions of perchloric acid containing Mo^{VI} by the reoxidation of quadrivalent to quinquevalent molybdenum by the perchloric acid. To confirm this hypothesis they recorded polarograms of molybdenum which had been prepared by reducing sexivalent molybdenum by iron(II) sulphate, with perchloric acid as supporiing electrolyte. The polarogram comprised one wave having a

half-wave potential corresponding to the second Mo^{VI} wave in the same supporting electrolyte. Tervalent molybdenum gave a small wave having a more negative half-wave potential†.

Haight[282-284] also believes that quadrivalent molybdenum catalyses the reduction of perchloric acid. Catalytic currents representing the reduction of perchlorates and nitrates are used for the polarographic determination of molybdenum[285,286].

Kolthoff and Parry[287] obtained catalytic currents with $HCl-H_2O_2$ supporting electrolytes. The current was proportional to the concentration of Mo^{VI} and hydrogen peroxide. According to these workers, the MoO_4^{2-} ion forms a peroxo-compound MoO_5^{2-}, which is then reduced at the dropping mercury cathode to MoO_4^{2-}:

$$MoO_5^{2-} + 2H^+ + 2e \rightarrow MoO_4^{2-} + H_2O.$$

Vlček[288] assumes that the Mo^{VI} polarographic currents in concentrated sulphuric-acid solution are also catalytic in character, being due to reoxidation of Mo^{V} to Mo^{VI} by the sulphuric acid.

In addition to the acid and neutral supporting electrolytes mentioned above, those of basic character have also been suggested[289] for the reduction of molybdenum.

Polarography has been used to study the composition of the citrate, tartrate, and phosphate complexes of molybdenum, with perchloric and nitric acids as supporting electrolytes[290]. Thus various supporting electrolytes have been used in studying the polarographic reduction of Mo^{VI} in order to find conditions which are of practical convenience for its quantitative determination.

In several of these papers suggestions have been made concerning the mechanism of the process. However, different authors hold contradictory views on this topic, which suggests that insufficient study has been made of the polarographic reduction of molybdenum[291]. This applies equally to catalytic processes.

Little study has been made of the mechanism of the electrolytic reduction of molybdenum with a large mercury cathode and its reduction by amalgams.

Relatively little work has been done on the polarographic reduction of tungsten. Stackelberg[292] found that W^{VI} is not reduced at a dropping mercury cathode in neutral and alkaline solutions, whereas in concentrated hydrochloric-acid solutions it gives a wave having a half-wave potential of -0.42 V. A sharp wave appears also in the presence of phosphoric acid. This workers does not indicate the degree of reduction of the tungsten to which this process corresponds.

Lingane and Small[293] made a detailed investigation of the polarographic reduction of W^{VI} in concentrated hydrochloric acid. The degree of reduction of the tungsten was determined coulometrically or by titration with potassium iodate solution. They also used electrolysis with a mercury cathode at a controlled potential to elucidate the mechanism of the process. The individual forms of reduced tungsten were identified spectrophotometrically. These workers found that in 12 N HCl the tungsten(VI) gives two waves, the first beginning at zero applied e.m.f., and the second wave having a half-wave potential of -0.56 V (s.c.e.). In less concentrated solutions the potential of the second wave becomes more negative. From the ratio of the constants for the diffusion currents of first and second waves it was concluded[293] that reduction extends to the quinquevalent and tervalent states respectively. The coulometric measurements at the corresponding potentials (-0.40 and -0.67 V) and titration with iodate support this view.

Laitinen et al.[294] studied the polarographic behaviour of W^{VI} in hydrochloric-acid solutions containing perchloric acid and lithium chloride. The half-wave potential and the number of electrons involved in the reaction were determined from the slope of the linear plot of $\log [i/(id - i)]$ against the electrode potential. These workers consider[294] that quinquevalent and tervalent tungsten is formed during the polarographic process. However, they do not exclude the possibility of the formation of quadrivalent tungsten, since the reverse process passes through this stage. A catalytic current due to reduction of the perchlorate ion was observed on a portion of the first wave in these solutions. Laitinen and Ziegler[295] explained the appearance of the catalytic current by reoxidation of the quinquevalent tungsten ion, formed during polarography, by perchloric acid. The catalytic current is large, and depends not only on the concentration of W^{VI} but also on the concentrations of hydrochloric and perchloric acids. A catalytic current has been observed also in the polarography of solutions containing hydrogen peroxide. Kolthoff and Parry[287] established that the magnitude of the catalytic current depends on the concentrations of tungsten(VI), hydrogen peroxide, and acid. The maximum catalytic current was observed in sulphuric-acid solution. These workers tend to think that the variation in the catalytic current with change in acid concentration is due to different degrees of polymerisation of the tungsten(VI).

The catalytic current is suppressed by the presence of complexing agents in the solution, and this effect has been used to determine the composition of the oxalate complexes[296].

Souchay[297,298] studied the polarographic reduction of sexivalent tungsten in solutions of various inorganic complexing agents (PO_4^{3-}, AsO_4^{3-}, GeO_3^{2-}, SeO_3^{2-}, BO_3^{3-}, etc.). Other authors have discussed the mechanism of this process[299,300].

Souchay[301] has recently studied the polarographic reduction of metatungstates in aqueous hydrochloric and sulphuric acids. Electrolysis using a mercury cathode, combined with spectrophotometry, suggests a stepwise reduction of W^{VI} to W^{V} and W^{III} in concentrated acid solutions. In dilute solutions of the acids three or more waves appear. The half-wave potentials and the wave heights depend on the acid concentration. Souchay attributes this to different degrees of polymerisation of the metatungstate and hence to variation in the number of electrons taken up by each molecule, which he regards as fluctuating between 21 and 36.

A polarographic method has been used in several investigations to determine the composition of complexes[302,303]. According to Pantani and Desideri[304] W^{VI} gives a well defined wave in solutions of phosphoric acid ($> 4\,N$). In dilute solutions the polarograms consist of three or more waves. These workers assume that reduction extends to

‡ The method employed by these workers is incorrect: (1) they do not exclude the effect if iron and cadmium on the polarograms; and (2) mixing Mo^{III} with perchloric acid before polarography should result in the instantaneous oxidation of the former by the ClO_4^- ions. An intermediate reduction product of perchloric acid, chlorine, will then appear in the solution.

the quinquevalent state. The occurrence of more than one wave, however, they attribute to variation in the diffusion coefficient of large complex molecules with increase in the acid concentration.

Two waves are present in the reduction of sexivalent tungsten from hydrochloric-acid solutions containing ammonium thiocyanate, their appearance being explained by successive reduction of the chloride and the thiocyanate complexes[305].

In the presence of organic complexing agents (oxalic, tartaric, citric acids, etc.), too, W^{VI} is reduced at a dropping mercury electrode in acid solutions[306-310]. The wave heights vary with the acid concentration. The optimum pH depends on the nature of the complexing agent.

A method based on the use of concentrated hydrochloric acid as supporting electrolyte has been recommended for the analysis of steels, alloys, etc.[292,311,312].

The published information shows that the mechanism of the polarographic reduction of sexivalent molybdenum and tungsten has not yet been thoroughly elucidated. Therefore no indication is given in reference works as to the degree of reduction of tungsten. The point is reflected in the treatise by Krykova et al.[291]

1. B.V.Nekrasov, "Kurs Obshchei Khimii" (Course of General Chemistry). Goskhimizdat, Moscow, 1962, p.324.
2. W.M.Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions" (Translated into Russian), Inostr.Lit., Moscow, 1954.
3. I.M.Kolthoff and V.A.Stenger, "Volumetric Analysis" (Translated into Russian), Goskhimizdat, Moscow, 1950, Vol. 1, pp.357, 365.
4. F.Foerster, E.Fricke, and R.Hausswald, Z.phys.Chem., A 146, 81, 177 (1930).
5. A.Chilesotti, Z.Elektrochem., 12, 173 (1906).
6. A.R.Tourky and H.K.El-Shamy, J.Chem.Soc., 140 (1949).
7. H.K.El-Shamy, and A.M.El-Aggan, J.Amer.Chem.Soc., 75, 1187 (1953).
8. V.S.Syrokomskii and V.B.Avilov, Zavod.Lab., 14, 1279 (1948).
9. V.S.Syrokomskii and V.B.Avilov, Zavod.Lab., 16, 11 (1950).
10. V.M.Tarayan and M.G.Ekimyan, Zavod.Lab., 19, 639 (1953).
11. O.Collenberg and A.Guthe, Z.anorg.Chem., 136, 252 (1924).
12. Yu.A.Chernikhov and V.G.Goryushina, Zavod.Lab., 11, 137 (1945).
13. Yu.A.Chernikhov and V.G.Goryushina, Zavod.Lab., 12, 397 (1946).
14. A.R.Tourky, I.M.Issa, and A.M.Amin, Analyt.Chim.Acta, 10, 168 (1954).
15. R.Geyer and G.Henze, Z.analyt.Chem., 172, 409 (1960).
16. R.Geyer and G.Henze, Z.analyt.Chem., 177, 185 (1960).
17. V.V.Stepin and E.V.Silaeva, Zavod.Lab., 19, 409 (1953).
18. K.N.Mikhalevich and V.M.Litvinchuk, Zhur.Neorg.Khim., 3, 1846 (1958).
19. O.Tomiček, Rec.Trav.chim., 43, 784 (1924).
20. H.Brintzinger and F.Oschatz, Z.anorg.Chem., 165, 221 (1927).
21. H.Brintzinger and W.Schieferdecker, Z.analyt.Chem., 78, 110 (1929).
22. H.Brintzinger and B.Rost, Z.analyt.Chem., 115, 241 (1939).
23. H.Brintzinger and B.Rost, Z.analyt.Chem., 115, 250 (1939).
24. R.Flatt and F.Sommer, Helv.Chim.Acta, 27, 1522 (1944).
25. V.G.Goryushina and T.V.Cherkashina, Zavod.Lab., 14, 255 (1948).
26. A.I.Busev and Li Kêng, Zhur.Anal.Khim., 13, 519 (1958).
27. G.G.Rao and S.R.Sagi, Talanta, 10, 169 (1963).
28. G.V.Klark and G.V.Akimov, "Trudy 2-oi Vsesoyuznoi Konferentsii po Korrozii Metallov" (Proceedings of the Second All-Union Conference on the Corrosion of Metals), 1943, Vol. 2, p.33.
29. A.Ya.Shatalov and I.A.Marshakov, Zhur.Fiz.Khim., 28, 42 (1954).
30. A.C.Kruger and L.Kahlenberg, Trans.Amer.Electrochem.Soc., 58, 107 (1930).
31. W.E.Korner, Trans.Amer.Electrochem.Soc., 31, 221 (1917).
32. S.E.S.Elwakkad, T.M.Saleut, and I.A.Elsayed, J.Chem.Soc., 3770 (1957).
33. B.N.Kabanov and L.Ya.Polyak, Zhur.Anal.Khim., 11, 678 (1956).
34. A.L.Holven, Ind.Eng.Chem., Analyt., 21, 935 (1929).
35. I.R.Baylis, Ind.Eng.Chem., 15, 852 (1923).
36. F.Chauveau, Compt.rend., 243, 2455 (1956).
37. J.F.Keggin, Proc.Roy.Soc., A 144, 75 (1934).
38. G.Jander, Z.phys.Chem., 187, 149 (1940).
39. E.A.Nikitina, "Geteropolisoedineniya" (Heteropolycompounds), Goskhimizdat, Moscow, 1962.
40. S.H.Allen and M.B.Hamilton, Analyt.Chim.Acta, 7, 483 (1952).
41. A.I.Busev, "Analiticheskaya Khimiya Molibdena" (Analytical Chemistry of Molybdenum), Izd.Akad.Nauk SSSR, Moscow, 1962.
42. A.I.Busev and Chang Fan, Zhur.Anal.Khim., 16, 695 (1961).
43. A.I.Busev and Chang Fan, Zhur.Anal.Khim., 16, 578 (1961).
44. E.H.Havermans, F.Verbeck, and J.Hoste, Analyt.Chim.Acta, 26, 326 (1962).
45. B.Sarma, J.Sci.Ind.Res., India, 16B, 478 (1957).
46. A.K.Majumdar and C.P.Saveriar, Analyt.Chim.Acta, 22, 158 (1960).
47. T.W.Gilbert and E.B.Sandell, J.Amer.Chem.Soc., 82, 1087 (1960).
48. M.L.Moss and M.G.Mellon, Ind.Eng.Chem., Analyt., 14, 931 (1942).
49. V.I.Spitsin and K.G.Koneva, Zhur.Neorg.Khim., 1, 2488 (1956).
50. C.Scheibler, Ber., 5, 801 (1872).
51. J.Lefort, Chem.News, 45, 57 (1882).
52. M.Jean, Compt.rend., 210, 2237 (1955).
53. N.K.Babko and A.G.Pilipenko, "Kolorimetricheskii Analiz" (Colorimetric Analysis), Goskhimizdat, Moscow–Leningrad, 1951.
54. A.P.Dumanski and S.I.Djatshkowski, Kolloid Z., 48, 49 (1929).
55. M.Sprenger, J.prakt.Chem., 22, 421 (1880).
56. F.Kehrmann, Ber., 20, 1813 (1887).
57. G.von Knorre, Z.analyt.Chem., 47, 37 (1908).
58. G.von Knorre, Ber., 38, 783 (1905).
59. E.Kafka, Z.analyt.Chem., 52, 501 (1913).
60. E.Eegriwe, Z.analyt.Chem., 70, 403 (1927).
61. W.R.Schoeller and C.Jahn, Analyst, 52, 504 (1927).
62. G.Heyhe, Z.angew.Chem., 44, 237 (1931).
63. S.Halberstadt, Z.analyt.Chem., 92, 86 (1933).
64. S.G.Simpson, W.C.Shub, and M.A.Siminsky, Ind.Eng.Chem., Analyt., 10, 243 (1938).
65. J.H.Yol and A.Z.Jones, Ind.Eng.Chem., Analyt., 16, 45 (1944).
66. P.Fischer, R.Spers, and P.Lisan, Ind.Eng.Chem., Analyt., 16, 607 (1944).
67. D.A.Lambie, Analyst, 70, 124 (1945).
68. C.E.Bricker and G.R.Waterbury, Analyt.Chem., 29, 1093 (1957).
69. K.E.Kleiner and A.Kh.Klibus, Zhur.Obshch.Khim., 28, 2013 (1958).
70. C.C.Miller, Analyst, 69, 109 (1944).

71. K. B. Yatsimirskii and K. E. Prik, Zhur. Neorg. Khim., 7, 1589 (1962) [Russ. J. Inorg. Chem., 821 (1962)].
72. P. Pascal, "Traité de Chimie minérale", 1932, Vol. II, p. 160.
73. M. J. Bailie and D. H. Brown, J. Chem. Soc., 3611 (1961).
74. A. A. Vorontsova and I. V. Tananaev, Zhur. Neorg. Khim., 5, 964 (1960) [Russ. J. Inorg. Chem., 462 (1960)].
75. G. S. Savchenko, Khimiya Redkikh Elementov, No. 2, 68 (1955).
76. O. Vartapétian and P. Sakellaridis, Compt. rend., 234, 1621 (1952).
77. W. Reiders and J. A. M. van Liempt, Rec. Trav. chim., 50, 1050 (1931).
78. A. R. Tourky, M. J. Faran, and H. K. El-Shamy, Analyst, 73, 258 (1948).
79. A. R. Tourky, J. M. Issa, and A. M. Daess, Rec. Trav. chim., 75, 22 (1956).
80. I. M. Issa and A. M. Daess, Chem. Analyst, 44, 89 (1955).
81. A. R. Tourky, I. M. Issa, and A. M. Daess, Analyt. Chim. Acta, 16, 81 (1957).
82. A. K. Babko and T. I. Get'man, Zhur. Neorg. Khim., 4, 585 (1959) [Russ. J. Inorg. Chem., 266 (1959)].
83. S. R. Carter and F. U. Clews, J. Chem. Soc., 125, 1880 (1924).
84. L. Sacconi and R. Cini, J. Amer. Chem. Soc., 76, 4239 (1954).
85. C. F. Hiskey and V. W. Meloche, J. Amer. Chem. Soc., 63, 964 (1941).
86. C. F. Hiskey and V. W. Meloche, J. Amer. Chem. Soc., 62, 1565 (1940).
87. C. F. Hiskey and V. W. Meloche, J. Amer. Chem. Soc., 61, 3125 (1939).
88. L. Braun, Z. analyt. Chem., 6, 86 (1867).
89. W. King, Ind. Eng. Chem., Analyt., 15, 350 (1923).
90. J. Maas and J. Sand, Ber., 41, 1861 (1908).
91. F. S. Krauskopf and C. E. Swartz, J. Amer. Chem. Soc., 48, 302 (1926).
92. J. Sand and O. Burger, Ber., 38, 3384 (1905).
93. G. E. Markle and D. F. Boltz, Analyt. Chem., 25, 1261 (1953).
94. A. K. Babko and A. T. Pilipenko, "Kolorimetricheskii Analiz" (Colorimetric Analysis), Goskhimizdat, Moscow–Leningrad, 1951).
95. A. K. Babko, Zhur. Obshch. Khim., 17, 642 (1947).
96. A. K. Babko and O. F. Drako, Zhur. Anal. Khim., 12, 342 (1957).
97. A. K. Babko, Zavod. Lab., 16, 527 (1950).
98. I. A. Tananaev and A. P. Lokhvitskaya, Zavod. Lab., 11, 6 (1945).
99. A. L. Davydov and V. F. Mal'tsev, Zavod. Lab., 8, 264 (1939).
100. C. E. Crouthamel and C. E. Johnson, Analyt. Chem., 26, 1284 (1954).
101. H. Freund, M. L. Wright, and R. K. Brookshier, Analyt. Chem., 23, 784 (1951).
102. C. H. R. Gentry and L. G. Sherrington, Analyst, 73, 57 (1948).
103. H. Buss, H. W. Kohlschütter, and S. Miedtank, Z. analyt. Chem., 178, 1 (1960).
104. A. K. Babko, "Fiziko-khimicheskii Analiz Kompleksnykh Soedinenii v Rastvorakh" (Physicochemical Analysis of Complex Compounds in Solution), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1955, p. 169.
105. F. Feigl and P. Krumholz, Z. angew. Chem., 45, 674 (1932).
106. F. A. Fer'yanchich, Zavod. Lab., 3, 301 (1934).
107. S. Ferjančič, Z. analyt. Chem., 97, 332 (1934).
108. F. A. Fer'yanchich, Zavod. Lab., 6, 289 (1937).
109. A. T. Voznesenskii, Zavod. Lab., 9, 25 (1940).
110. N. S. Poluektov, Zavod. Lab., 10, 92 (1940).
111. K. M. Popov and M. N. Dorokhova, Zavod. Lab., 9, 1315 (1940).
112. F. S. Grimaldi and V. North, Ind. Eng. Chem., Analyt., 15, 652 (1943).
113. A. S. Shakhov, Zavod. Lab., 10, 470 (1941).
114. Ya. D. Fridman and O. A. Songina, Trudy Khim. Inst. Kirgiz. Fil. Akad. Nauk SSSR, No. 1 (1946).
115. O. A. Songina, Izv. Akad. Nauk Kazakh. SSR, Ser. Metallurg., No. 1 (1946).
116. O. A. Songina and P. A. Karpova, Zavod. Lab., 13, 38 (1947).
117. O. A. Songina and M. T. Kozlovskii, Zavod. Lab., 13, 677 (1947).
118. F. A. Fer'yanchich, Zavod. Lab., 13, 668 (1947).
119. W. Westwood and A. Mayer, Analyst, 72, 464 (1947).
120. M. A. Popov, Zavod. Lab., 14, 34 (1948).
121. C. H. R. Gentry and L. G. Sherrington, Analyst, 73, 57 (1948).
122. A. G. Bogdanchenko and A. D. Sapir, Zavod. Lab., 15, 11 (1949).
123. Yu. A. Chernikhov and R. S. Tramm, Zavod. Lab., 15, 15 (1949).
124. H. Freund, M. L. Wright, and R. K. Brookshier, Analyt. Chem., 23, 781 (1951).
125. C. E. Crouthamel and C. E. Johnson, Analyt. Chem., 26, 1288 (1954).
126. D. N. Finkel'shtein, Zavod. Lab., 22, 911 (1956).
127. G. S. Smith, Ind. Chemist, 21, 250 (1945).
128. R. C. Young and R. A. Laudise, J. Amer. Chem. Soc., 78, 4861 (1956).
129. R. A. Laudise and R. C. Young, J. Amer. Chem. Soc., 77, 5288 (1955).
130. A. Chilesotti, Z. Elektrochem., 12, 146 (1906).
131. W. Wardlaw and R. L. Wormell, J. Chem. Soc., 130 (1927).
132. L. Guibe and P. Souchay, Compt. rend., 244, 780 (1957).
133. L. Guibe and P. Souchay, J. Chim. phys., 54, 684 (1957).
134. Z. F. Shakhova and R. K. Motorkina, Zhur. Obshch. Khim , 26, 2663 (1956); Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 8, 100 (1958).
135. G. Marchetti, Z. anorg. Chem., 19, 391 (1899).
136. Z. M. Vaisberg and B. Ya. Dain, Izv. Sektora Platiny Drug. Blagorod. Metal., Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, No. 26, 154 (1951).
137. L. T. Kurtz, Ind. Eng. Chem., Analyt., 14, 855 (1942).
138. M. L. Tsai, Zavod. Lab., 21, 251 (1955).
139. R. M. Veitsman, Zavod. Lab., 23, 153 (1957).
140. J. G. Gahn, Ann. Physik, 14, 242 (1803).
141. C. I. T. DeGrotthus, Ann. Chim. (France), 57–58, 54 (1806).
142. H. Buff, Ann. Chem. Pharm., 110, 275 (1859).
143. W. Hampe, Chem.-Ztg., 12, 4 (1888).
144. O. von der Pfordten, Ber., 15, 1925 (1882).
145. F. Peters, Angew. Elektrochem., 2, 111 (1898).
146. J. Férée, Compt. rend., 122, 733 (1896).
147. R. E. Meyer, J. Amer. Chem. Soc., 26, 1124 (1904).
148. R. E. Meyer, Z. Elektrochem., 11, 112 (1905).
149. J. L. Merrill and A. S. Russell, J. Chem. Soc., 2389 (1929).
150. R. Bock and K. G. Hackstein, Z. analyt. Chem., 138, 339 (1953).
151. L. G. Kollock and E. F. Smith, J. Amer. Chem. Soc., 23, 669 (1901).
152. L. G. Kollock and E. F. Smith, Z. Elektrochem., 7, 957 (1901).
153. A. Chilesotti, Z. Elektrochem., 12, 198 (1906).
154. F. Foerster, E. Fricke, and R. Hauswald, Z. phys. Chem., 146, 177 (1929).
155. I. N. Frantsevich, T. F. Frantsevich-Zabludovskaya, and E. F. Zhel'vis, Zhur. Prikl. Khim., 25, 350 (1952).
156. T. F. Frantsevich-Zabludovskaya, I. N. Frantsevich, and D. K. Modylevich, Zhur. Prikl. Khim., 27, 413 (1954).
157. T. F. Frantsevich-Zabludovskaya, Zhur. Prikl. Khim., 28, 700 (1955).
158. T. F. Frantsevich-Zabludovskaya, and A. I. Zayats, "Trudy 4-go Soveshchaniya po Elektrokhimii" (Proceedings of the

Fourth Conference on Electrochemistry), Izd. Akad. Nauk SSSR, Moscow, 1959, p.524.
159. T. F. Frantsevich-Zabludovskaya, and K. B. Kladnitskaya, Zhur. Prikl. Khim., 30, 400 (1957).
160. T. F. Frantsevich-Zabludovskaya, and N. A. Fominskaya, Zhur. Prikl. Khim., 36, 578 (1963).
161. D. W. Ernst and M. L. Holt, J. Electrochem. Soc., 105, 686 (1958).
162. J. Férée, Bull. Soc. chim. France, 19, 213 (1898).
163. H. Leiser, Z. Elektrochem., 13, 690 (1907).
164. R. Rosenheim, Z. angew. Chem., 22, 1153 (1909).
165. O. Collenberg and J. Backer, Z. Elektrochem., 30, 230 (1924).
166. O. Collenberg and K. Nillson, Z. Elektrochem., 31, 555 (1925).
167. B. Neumann and H. Richter, Z. Elektrochem., 30, 474 (1924).
168. K. S. Jackson, A. S. Russell, and J. L. Merrill, J. Chem. Soc., 2394 (1929).
169. S. Glasstone, "Introduction to Electrochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1951, p.659.
170. A. Fischer, Z. anorg. Chem., 81, 102, 170 (1913).
171. J. A. M. van Liempt, Z. Elektrochem., 31, 249 (1925).
172. C. G. Fink and F. L. Jones, Trans. Electrochem. Soc., 59, 461 (1931).
173. M. L. Holt and L. Kahlenberg, Metal Ind. (New York), 31, 94 (1933).
174. M. L. Holt, Trans. Electrochem. Soc., 66, 453 (1934).
175. M. L. Holt and D. Smalheim, Ind. Eng. Chem., Analyt., 11, 254 (1939).
176. M. L. Holt, Trans. Electrochem. Soc., 71, 301 (1937).
177. W. E. Clark and M. L. Holt, Trans. Electrochem. Soc., 94, 244 (1948).
178. M. H. Lietzke and M. L. Holt, Trans. Electrochem. Soc., 94, 252 (1948).
179. L. E. Vaaler and M. L. Holt, Trans. Electrochem. Soc., 90, 43 (1946).
180. D. R. Markwell and M. L. Holt, J. Electrochem. Soc., 104, 489 (1957).
181. C. Lebrun, Galvano, No. 77, 24 (1938).
182. L. E. Yntema, J. Amer. Chem. Soc., 54, 3775 (1932).
183. L. N. Gol'ts and V. N. Kharlamov, Zhur. Prikl. Khim., 9, 631, 640 (1936).
184. S. I. Sklyarenko and O. S. Druzhinina, Zhur. Prikl. Khim., 13, 1326 (1940).
185. W. D. Treadwell and R. Nieriker, Helv. Chim. Acta, 24, 1067 (1941).
186. M. L. Holt and E. Vaaler, J. Electrochem. Soc., 94, 50 (1948).
187. Z. A. Solov'eva and A. T. Vagramyan, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 230 (1954).
188. T. P. Hoar and I. A. Bucklow, Chem. and Ind., 1061 (1955).
189. A. G. Pecherskaya and V. V. Stender, Dokl. Akad. Nauk SSSR, 75, 831 (1950).
190. N. I. Kobozev, Zhur. Fiz. Khim., 25, 1111 (1951).
191. N. I. Kobozev, Zhur. Fiz. Khim., 26, 438 (1952).
192. N. I. Kobozev, Zhur. Fiz. Khim., 26, 113 (1952).
193. N. I. Kobozev and V. V. Monblanova, Zhur. Fiz. Khim., 22, 1511 (1948).
194. O. M. Poltarak, Zhur. Fiz. Khim., 27, 599 (1953).
195. V. S. Bagotskii and Z. A. Iofa, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 53, 439 (1946).
196. S. E. S. El Wakkad, H. A. Rizk, and I. G. Ebaid, J. Phys. Chem., 59, 1004 (1955).
197. V. A. Lavrenko, Zhur. Fiz. Khim., 35, 1095 (1961) [Russ. J. Phys. Chem., 537 (1961)].
198. Shoo-Tze Leo, Tsing-Nang Shen, Trans. Electrochem. Soc., 66, 461 (1934).
199. L. Weiss, Z. anorg. Chem., 65, 279 (1910).
200. D. B. Keyes and S. Swamyr, Metal Ind., 37, 87 (1930).
201. F. Pisani, Compt. rend., 59, 289 (1864).
202. E. Müller, P. Brun, and G. Unger, Z. Elektrochem., 33, 182 (1927).
203. J. Kassler, Z. analyt. Chem., 75, 457 (1928).
204. W. D. Treadwell, M. Lutew, and A. Rheiner, Helv. Chim. Acta, 4, 562 (1921).
205. R. Holtje and R. Geyer, Z. anorg. Chem., 246, 243 (1941).
206. E. R. Riegel and R. D. Schwartz, Analyt. Chem., 26, 410 (1954).
207. R. G. De Carvalho, Analyt. Chim. Acta, 14, 28 (1956).
208. G. H. Walden, L. P. Hammett, and S. M. Edmonds, J. Amer. Chem. Soc., 56, 350 (1934).
209. N. Birnbaum and G. H. Walden, J. Amer. Chem. Soc., 60, 64 (1938).
210. G. G. Rao and M. Suryanarayona, Analyst, 88, 590 (1963).
211. B. Stehlik, Coll. Czech. Chem. Comm., 4, 418 (1932).
212. N. H. Furman and W. M. Murray, J. Amer. Chem. Soc., 58, 1689 (1936).
213. N. Kano, J. Chem. Soc. Japan, 43, 333 (1922).
214. N. Kano, J. Chem. Soc. Japan, 43, 550 (1922).
215. T. Nakazono, J. Chem. Soc. Japan, 42, 526 (1921).
216. T. Nakazono, J. Chem. Soc. Japan, 48, 17 (1927).
217. K. Someya, Z. anorg. Chem., 152, 368 (1926).
218. T. Tashiro, J. Chem. Soc. Japan, 53, 13 (1932).
219. G. A. Panchenko, Zhur. Prikl. Khim., 8, 361 (1935).
220. A. F. Andreev, Zavod. Lab., 6, 793 (1937).
221. E. I. Fogel'son and N. V. Kalmykova, Zavod. Lab., 11, 31 (1945).
222. J. Doležal, B. Moldán, and J. Zýka, Coll. Czech. Chem. Comm., 24, 3769 (1959).
223. E. F. Speranskaya and V. E. Mertsalova, "Khimiya i Khimicheskaya Tekhnologiya, Tom II, Sbornik Statei Aspirantov i Soiskatelei" (Chemistry and Chemical Technology, Vol. 2, Collected Papers by Postgraduate Students and Candidates), MV i SSO Kazakh. SSR, Alma-Ata, 1964.
224. O. von der Pfordten, Ber., 16, 508 (1883).
225. O. Herting, Z. angew. Chem., 14, 165 (1901).
226. G. Dotreppe, Chimie et Industrie, 25, 173 (1931).
227. M. L. Holt, Ind. Eng. Chem., Analyt., 6, 476 (1934).
228. E. Kuklin, Stahl und Eisen, 24, 27 (1904).
229. E. Knecht and E. Hibbert, Analyst, 36, 96 (1911).
230. E. Knecht and E. Hibbert, Z. analyt. Chem., 62, 23 (1923).
231. R. Casares López and L. Villanúa Fungairiño, Anales real Soc. espan. Fis. Quim., 42, 69 (1946).
232. K. Someya, Z. anorg. Chem., 163, 206 (1927).
233. M. Kibiku, Bunseki Kagaku, 6, 356 (1957).
234. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1931, Vol. 11, p.673.
235. C. Yosimura, J. Chem. Soc. Japan, 73, 701 (1952).
236. K. Someya, Z. anorg. Chem., 145, 168 (1925).
237. M. L. Holt and A. G. Gray, Ind. Eng. Chem., Analyt., 12, 144 (1940).
238. A. K. Babko, Nauk. Zap. Kiivs'k. Derzh. Univ., Khim. Zbirnik, 1, 147 (1935).
239. F. Vlasak, Coll. Czech. Chem. Comm., 10, 278 (1938).
240. N. A. Polotebnova and L. M. Vranover, Uch. Zap. Kishinev. Univ., 14, 119 (1954).
241. C. Yoshimura, J. Chem. Soc. Japan, 74, 116, 118 (1953).
242. N. A. Tananaev and E. Davitashvili, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 397 (1937).
243. W. S. Stephen, Ind. Chemist, 29, 79 (1953).
244. W. S. Stephen, Ind. Chemist, 29, 169 (1953).
245. C. L. Luke, Analyt. Chem., 33, 1965 (1961).
246. N. A. Tananaev, "Ob'emnyi Analiz" (Volumetric Analysis), GONTI, Sverdlovsk–Moscow, 1939, p.351.
247. H. M. Stevens, Analyt. Chim. Acta, 19, 334 (1958).
248. T. Yoshimura, J. Chem. Soc. Japan, 73, 362 (1952).
249. C. Yoshimura, J. Chem. Soc. Japan, 76, 409 (1955).

250. R. Weiner and P. Boriss, Z. analyt. Chem., 168, 195 (1959).
251. E. F. Speranskaya, Metallurg. Khim. Prom. Kazakhstana, 6, 68 (1961).
252. E. F. Speranskaya, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 6, 195 (1963).
253. J. B. Headridge and M. S. Taylor, Analyst, 88, 590 (1963).
254. F. A. Uhl, Z. analyt. Chem., 110, 102 (1937).
255. A. Stern, Ind. Eng. Chem., Analyt., 14, 74 (1942).
256. V. I. Gorokhovskaya, Trudy Kazansk. Khim.-tekhnol. Inst., No. 21, 113 (1956).
257. Ya. P. Gokhshtein, Zhur. Obshch. Khim., 10, 1725 (1942).
258. M. von Stackelberg, P. Klinger, W. Koch, and E. Krath, Arch. Eisenhüttenw., 13, 259 (1939).
259. M. L. Nichols and L. H. Rogers, Ind. Eng. Chem., Analyt., 16, 137 (1944).
260. I. M. Kolthoff and I. Hodara, J. Electroanalyt. Chem., 4, 369 (1962).
261. E. A. Kanevskii and L. E. Shvartsburd, Zavod. Lab., 9, 283 (1940).
262. K. Grasshoff and H. Hahn, Z. analyt. Chem., 168, 247 (1959).
263. H. Hahn and K. Grasshoff, Z. analyt. Chem., 173, 29 (1960).
264. K. Grasshoff and H. Hahn, Z. analyt. Chem., 173, 190 (1960).
265. K. Grasshoff and H. Hahn, Z. analyt. Chem., 180, 18 (1961).
266. G. S. Deshmukh and J. P. Srivastava, Z. analyt. Chem., 176, 28 (1960).
267. L. Meits, Analyt. Chem., 25, 1752 (1953).
268. E. P. Parry and M. G. Yakubik, Analyt. Chem., 26, 1294 (1954).
269. R. Pecsok and R. Parkhur, Analyt. Chem., 27, 1920 (1955).
270. F. Pantani, Ricerca sci., A 3, [2], 641 (1963).
271. R. Klement, Z. analyt. Chem., 136, 17 (1952).
272. R. Přibil and A. Blazek, Coll. Czech. Chem. Comm., 16, 561 (1953).
273. R. Přibil, "Komplexony v chemické Analyse" (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 225.
274. E. F. Speranskaya and M. T. Kozlovskii, Zavod. Lab., 30, 403 (1964).
275. S. I. Sinyakova and M. I. Glinkina, Zhur. Anal. Khim., 13, 186 (1958).
276. I. A. Korshunov and K. M. Shennikova, Zhur. Anal. Khim., 4, 5 (1949).
277. C. B. Jones, Analyt. Chim. Acta, 10, 584 (1954).
278. C. H. Holten, Acta Chem. Scand., 15, 943 (1961).
279. M. Codell, J. J. Micula, and G. Narwitz, Analyt. Chem., 25, 1441 (1953).
280. G. A. Rechnitz and H. A. Laitinen, Analyt. Chem., 33, 1473 (1961).
281. S. I. Sinyakova and M. I. Glinkina, Zhur. Anal. Khim., 11, 544 (1956).
282. G. P. Haight, Analyt. Chem., 23, 1505 (1951).
283. G. P. Haight and W. F. Sager, J. Amer. Chem. Soc., 74, 6056 (1952).
284. G. P. Haight, Acta Chem. Scand., 15, 2012 (1961).
285. M. G. Johnson and R. J. Robinson, Analyt. Chem., 24, 366 (1952).
286. R. U. Bikbulatova and S. I. Sinyakova, Zhur. Anal. Khim., 19, 1434 (1964).
287. I. M. Kolthoff and E. P. Parry, J. Amer. Chem. Soc., 73, 5315 (1951).
288. A. Vlček, Chem. Listy, 47, 1162 (1953).
289. H. Wolfson, Nature, 153, 375 (1944).
290. E. W. Zahnow and R. J. Robinson, J. Electroanalyt. Chem., 3, 263 (1962).
291. T. A. Kryukova, S. I. Sinyakova, and T. V. Aref'eva, "Polyarograficheskii Analiz" (Polarographic Analysis), Goskhimizdat, Moscow, 1959, p. 340.
292. M. von Stackelberg, P. Klinger, W. Koch, and E. Krath, Arch. Eisenhüttenw., 13, 249 (1939).
293. J. J. Lingane and L. A. Small, J. Amer. Chem. Soc., 71, 973 (1949).
294. H. A. Laitinen, K. B. Oldham, and W. A. Ziegler, J. Amer. Chem. Soc., 75, 3048 (1953).
295. H. A. Laitinen and W. A. Ziegler, J. Amer. Chem. Soc., 75, 3045 (1953).
296. K. B. Yatsimirskii and L. I. Budarin, Zhur. Neorg. Khim., 7, 1824 (1962) [Russ. J. Inorg. Chem., 942 (1962)].
297. P. Souchay, Ann. Chim. (France), 18, 73, 169 (1943); 19, 102 (1944); 20, 73, 96 (1945).
298. A. Tchakirian and F. Souchay, Ann. Chim. (France), 1, 232 (1946).
299. B. Breyer and S. Havobian, Analyt. Chim. Acta, 16, 497 (1957).
300. E. F. Speranskaya, Zhur. Anal. Khim., 18, 9 (1963).
301. P. Souchay and C. Tourne, Compt. rend., 254, 4176 (1962).
302. W. E. Clark and M. H. Lietzke, J. Electrochem. Soc., 99, 245 (1952).
303. R. Ripan, A. Duca, and N. Calu, Studii si Cercetari Sti. Chim. (Fil. Cluj), 11, 7 (1960).
304. F. Pantani and P. Desideri, Ricerca sci., [2], 1A, 249 (1961).
305. A. S. Tikhonov and Z. G. Goman, Zavod. Lab., 17, 916 (1951).
306. L. E. Reichen, Analyt. Chem., 20, 1302 (1954).
307. P. Beran, J. Čihalík, J. Doležal, V. Simon, and J. Zýka, Chem. Listy, 47, 1315 (1953).
308. Z. S. Mikhina and A. A. Tikhonova, Zavod. Lab., 22, 1154 (1956).
309. G. S. Deshmukh and J. P. Srivastava, Zhur. Anal. Khim., 15, 601 (1960).
310. F. Pantani, Ricerca sci., [2], A3, 873 (1963).
311. B. Ya. Kaplan and I. Ya. Sorokovskaya, Zavod. Lab., 29, 391 (1963).
312. I. A. Bucklow and T. P. Hoar, Metallurgia, 48, 317 (1953).

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APPLICATION OF SYNTHETIC ZEOLITES (MOLECULAR SIEVES) TO CATALYSIS

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