

DISSOCIATION AND SOLUBILITY VARIATION VERSUS pO^{2-} OF SCHEELITE $CaWO_4$ IN MOLTEN $NaCl-KCl$ (AT 1000 K)

R. COMBES* and B. TREMILLON

Laboratoire d'Electrochimie Analytique et Appliquée (associé au C.N.R.S.), Ecole Nationale Supérieure de Chimie de Paris, Université Pierre et Marie Curie, 11 rue P. et M. Curie, F-75231-Paris Cedex 05 (France)

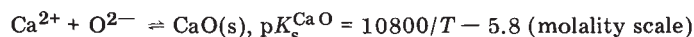
F. DE ANDRADE

Instituto da Quimica, Universidade Federal da Bahia, Salvador, Bahia (Brasil)

(Received 22nd June 1976; in revised form 25th October 1976)

ABSTRACT

The conditional solubility of scheelite $CaWO_4$ in molten $NaCl-KCl$ (1 : 1) has been studied either in oxobasic or oxoacidic media. In the former case it is increased by formation of sparingly soluble CaO according to:



In the latter case, WO_4^{2-} behaves as an oxobase according to the following equilibria:



The latter equilibrium favours an increase in the W^{VI} solubility when pO^{2-} is increased, for instance by injection of HCl . The whole set of results has been summarized by a conditional solubility diagram of scheelite versus pO^{2-} .

INTRODUCTION

The present study has been undertaken with the aim of determining the feasibility of an electrodeposition process for the industrial preparation of tungsten or ferro-tungsten alloys, starting from scheelite i.e. natural calcium tungstate. Though rather pure, this ore still contains some impurities such as aluminium, chromium, iron, magnesium and manganese oxides, which affect the quality of the alloy, which is obtained presently by aluminothermic reduction of scheelite.

In view of an electrochemical process, dissolution of the ore in a molten salt appears as one of the most convenient ways. In the same time, a separation of the impurities could probably be achieved, owing to a convenient control of some chemical conditions during the dissolution operation.

In order to determine these conditions, we have considered one of the simplest molten salts which might suit: the equimolar mixture of $NaCl$ and KCl . The mean temperature used was $727^\circ C$ (1000 K).

* To whom all correspondence should be addressed.

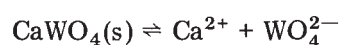
PRINCIPLE

CaWO_4 has appeared to be a sparingly soluble compound in the molten NaCl–KCl phase. Its low intrinsic solubility S_0 in the pure melt, only due to solvation effects on Ca^{2+} and WO_4^{2-} ions, is related to the solubility product:

$$K_s^{\text{CaWO}_4} = [\text{Ca}^{2+}][\text{WO}_4^{2-}] = S_0^2$$

if no other soluble species than these ions is implied.

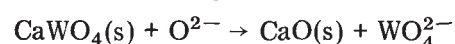
But an increase of the conditional solubility S of W(VI) is made possible by a chemical action, either on the calcium(II) ions or on the tungsten(VI) ions. Indeed, a shift of the equilibrium:



will occur in favor of dissolution, when Ca^{2+} ions are consumed, or WO_4^{2-} ions are transformed into some new soluble species by chemical reactions.

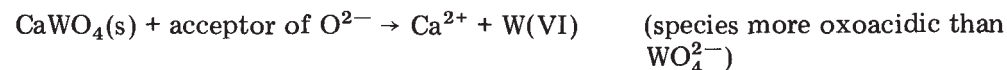
It is now well known that pO^{2-} acts in many molten salts as pH in aqueous solutions. Variations of the former produce changes in the chemical state of compounds belonging to oxoacid-oxobase systems, in a same way as variations of the latter produce changes in the chemical state of compounds belonging to acid-base systems. This is the action we have considered here. In this connection, let us remind that an electrochemical method for pO^{2-} measurements in fused NaCl–KCl has recently been described [1]; this method is grounded on the use of an ion-specific membrane electrode made of calcia-stabilized zirconia. Thanks to that means, a lot of oxoacid-oxobase equilibria in this melt have been studied. Particularly, relations were established between pO^{2-} , partial pressures of HCl and H_2O , and also between pO^{2-} , partial pressure of H_2O and concentration of OH^- , both systems ($\text{HCl}/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{OH}^-$) acting as pO^{2-} buffers.

In alkali chloride melts, Ca^{2+} behaves as an acceptor of O^{2-} (oxoacid), CaO being a sparingly soluble compound. Thus, it can be predicted that a first way for dissociating CaWO_4 will be to decrease the pO^{2-} , leading to insoluble CaO and soluble WO_4^{2-} according to the reaction:



A quantitative prediction of this reaction requires, in addition to the $K_s^{\text{CaWO}_4}$ value, the knowledge of the solubility product K_s^{CaO} .

On the other hand, WO_4^{2-} behaves as a donor of O^{2-} (oxobase) and can be transformed into more oxoacidic species by increasing the pO^{2-} . Then, a second way for destroying CaWO_4 can result from this oxoacidity action concerning the tungstate system:



Thus, the study is made up of three successive steps: the first one is devoted to the experimental determination of the solubility product of CaO, the second one to the determination of the oxobasicity equilibrium constants of WO_4^{2-} , and the last one is an estimation of the solubility product of CaWO_4 with the help of a few thermochemical data. Then we will be able to predict the variations of the conditional solubility S versus pO^{2-} .

EXPERIMENTAL PART AND RESULTS

(1) Solubility product of calcium oxide

The values of K_s^{CaO} were obtained by measuring the concentration of dissolved Ca^{2+} ions in equilibrium with a melt saturated with solid CaO, at imposed pO^{2-} and at various temperatures between 710 and 820°C. The variation of this concentration versus pO^{2-} verifies the validity of the solubility product law in this case, i.e.:

$$\log K_s^{\text{CaO}} = \log[\text{Ca}^{2+}] - \text{pO}^{2-}$$

Concentrated enough hydroxide ions and an imposed partial pressure of H_2O , were used as a pO^{2-} buffer. The corresponding system:



has already been studied [1] and it has been shown that pO^{2-} is given by:

$$\text{pO}^{2-} = \text{p}K + \log(P_{\text{H}_2\text{O}}/[\text{OH}^-]^2)$$

with (between 710 and 820°C):

$$\text{p}K = 8.15 \times 10^3 T^{-1} - 5.55$$

(pressures being expressed in atm, concentration in mol kg^{-1} and T in K).

Experimental. The various pO^{2-} values imposed have been checked by means of the previously described oxide ion indicator electrode [2,3], which is made of a calcia-stabilized zirconia tube dipping in the solution and filled with a mixture of nickel and nickel oxide powders. The corresponding potentials were measured with respect to a silver-silver chloride reference electrode of the well known type [4].

The pressure of water, $P_{\text{H}_2\text{O}}$, has been imposed by bubbling in the melt nitrogen which was pre-saturated by passing through aqueous solutions of calcium chloride. The corresponding values of $P_{\text{H}_2\text{O}}$ were found in the literature [5].

The crucible and various tubes for bubbling or sampling were of pure alumina (Degussa).

Temperature was maintained constant within one degree, in the range of 710–820°C, by means of a furnace and a regulation device already described [2].

The samples of CaO-saturated melt have been taken by suction through a porous alumina tube, in the cold upper part of which a quick solidification occurred.

After cooling down under dry nitrogen, these samples were weighed and dissolved in water. Then, Ca^{2+} was determined either by EDTA titration or by atomic absorption photometry, the results of both methods being in good agreement.

Sodium and potassium chlorides were from Carlo Erba; soda, calcium chloride and tungsten trioxide (for the second part of this work) from Merck.

Results. The solubility of Ca^{2+} ions in equilibrium with the buffered melt, for various pO^{2-} values and different temperatures, as well as the corresponding

TABLE 1

Solubility of Ca^{2+} and $\text{p}K_s^{\text{CaO}}$ in NaCl–KCl at different temperatures and values of imposed pO^{2-} (expressed in the molality scale)

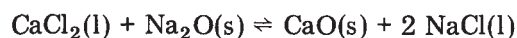
$T/^\circ\text{C}$	pO^{2-} (± 0.1)	$10^{-3} [\text{Ca}^{2+}]$ mol kg^{-1}	$\text{p}K_s^{\text{CaO}}$
710	3.0 ₅	4.5 ± 1.7	5.4 ± 0.3
720	2.5 ₅	2.8 ± 0.9	$5.1 \pm 0.2_5$
	2.7	6.3 ± 1.4	4.9 ± 0.2
	3.0 ₅	7.1 ± 2.0	5.2 ± 0.3
727	2.5	4.0 ± 0.9	4.9 ± 0.2
	3.0 ₅	14.1 ± 1.5	$4.9 \pm 0.1_5$
	3.3 ₅	15.5 ± 1.4	$5.1_5 \pm 0.1_5$
	3.6 ₅	28.2 ± 3.2	$5.2 \pm 0.1_5$
760	2.3	6.3 ± 1.4	4.5 ± 0.2
765	2.2	4.0 ± 0.9	4.6 ± 0.2
800	2.0	4.0 ± 0.9	4.4 ± 0.2
	2.4	7.9 ± 2.5	$4.5 \pm 0.2_5$
820	1.8 ₅	11.2 ± 3.5	$3.8 \pm 0.2_5$
	2.3	10.0 ± 2.3	$4.3 \pm 0.2_5$

$\text{p}K_s^{\text{CaO}}$, are collected (with their experimental uncertainty) in Table 1.

By plotting $\text{p}K_s^{\text{CaO}}$ against the reciprocal of the absolute temperature, one obtains a straight line whose equation has been determined by the least squares method:

$$\text{p}K_s^{\text{CaO}} = 10.8 \times 10^3 T^{-1} - 5.8$$

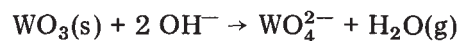
This equation allows $\text{p}K_s^{\text{CaO}}$ to be calculated at any temperature in the range considered, with an uncertainty of 0.3 unit (for a confidence level of 95%). For example, at 1000 K (727°C), one obtains $\text{p}K_s^{\text{CaO}} = 5.0$. This value is not very far from $\text{p}K_s^* = 7.6$ which can be calculated from Kubaschewski and Evans' thermodynamic data [6] for the reaction:



at the same temperature. The difference is certainly ascribable to the activity coefficient of calcium chloride in the molten mixture.

(2) Oxobasicity of tungstate ion WO_4^{2-}

The oxobasic properties of WO_4^{2-} have been determined by potentiometric titrations with the pO^{2-} indicator electrode mentioned above. Solid tungsten trioxide was added progressively to a melt originally containing a known amount of OH^- ions, under an imposed pressure of water vapor. At the beginning of the process, the oxoacid-oxobasic reaction occurring is:



The equivalence point for this reaction is obtained at $\alpha = 0.5$ (α is the mole number ratio of WO_3 added to original OH^-). Beyond this point, a supplementary addition of WO_3 brings this oxoacid and the oxobase WO_4^{2-} together, which can either constitute a single oxoacid-oxobase couple or react by forming amphoteric polytungstic compounds, according to the general scheme:



The equivalence point for such a reaction would correspond to $\alpha' = n - 1$ (α' = mole number ratio of supplementary WO_3 to WO_4^{2-}) or, in the continuation of the previous titration, to $\alpha = 0.5 + 0.5 (n - 1) = 0.5 n$.

The curve obtained by plotting the indicator electrode potential measured after each addition of WO_3 will allow to clarify the nature of the reaction involved, thanks to the equivalence point position, and permit the determination of the corresponding equilibrium constant, by application of theoretical equations to the potential variations.

These equations are easily obtained by making the assumption, which was verified experimentally, that the considered reactions are nearly quantitative. Thus, for the reaction of WO_3 with OH^- ($\alpha < 0.5$), the electrode potential must obey:

$$E = A - a \log(1 - 2\alpha) \quad (2)$$

with

$$A = E^0 + (2.3 RT/2 F) \text{p}K + (2.3 RT/2 F) \log(P_{\text{H}_2\text{O}}/c_0^2)$$

$$a = 2.3 RT/F$$

$\text{p}K$ is the dissociation constant of $\text{OH}^-/\text{H}_2\text{O}$ system; c_0 is the starting concentration of OH^- . After this first reaction, for $\alpha > 0.5$, if a reaction of type (1) occurs, the following expression may be written:

$$E = B + b \log\{(\alpha - 0.5)/(n/2 - \alpha)^n\} \quad (3)$$

with

$$B = E^0 + \frac{2.3 RT}{2 F(n - 1)} \text{p}K_n - \frac{2.3 RT}{2 F} \log \frac{c_0}{n - 1}$$

$$b = 2.3 RT/2 F(n - 1)$$

and

$$K_n = [\text{O}^{2-}]^{n-1} [\text{W}_n \text{O}_{3n+1}^{2-}] / [\text{WO}_4^{2-}]^n$$

But, if no reaction occurs between WO_4^{2-} and WO_3 , two other expressions for the electrode potential are possible according to the fact that tungsten trioxide may either be insoluble or soluble in the melt; in the former case:

$$E = B' = E^0 + (2.3 RT/2 F) \text{p}K_0 + (2.3 RT/2 F) \log \frac{1}{2} c_0 \quad (4)$$

with

$$K_0 = [\text{O}^{2-}] / [\text{WO}_4^{2-}]$$

Or, in the latter case:

$$E = E^0 + (2.3 RT/2 F) pK_1 + (2.3 RT/2 F) \log(2\alpha - 1) \quad (5)$$

with

$$K_1 = [O^{2-}][WO_3]/[WO_4^{2-}]$$

Results. All the experimental values of potential measured versus α are collected in Table 2.

Two different types of curves were obtained, according to the time left between each addition of WO_3 and the potential measurement.

When the experiment was quickly performed, curves showing only one reaction ($2 OH^- + WO_3 \rightarrow WO_4^{2-} + H_2O$) were observed. One of them is presented in Fig. 1 (curve 1).

On the contrary, curves showing two reactions (formation of a polytungstate ion after that of WO_4^{2-}) were observed. Curve 2 of Fig. 1 is one of them.

Other successive reactions might take place here, but were not studied because of the too long time needed to perform the measurements. The experimental titration curves could not be extended far beyond the second equivalence point.

The position of the second equivalence point, on this type of curves, shows that the polytungstate ion formed is tritungstate $W_3O_{10}^{2-}$. The formula is confirmed by a mathematical analysis of the curve $E = f(\alpha)$, whose results are collected in Table 3.

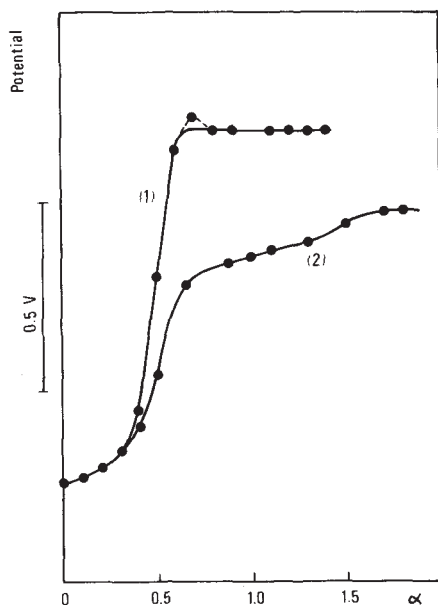


Fig. 1. Titration curves obtained by addition of WO_3 to a melt containing OH^- ions. (1) Electrode potential measured immediately after each addition. (2) Electrode potential measured several hours (6–20 h) after each addition.

TABLE 3

Analysis of the titration curves showing the formation of tritungstate $W_3O_{10}^{2-}$
 Experimental values of A and a of eqn. (2) verified before the first equivalence point; experimental values of B and b of eqn. (3) verified between the two equivalence points (values determined by the least squares method, uncertainty for a confidence level of 95%)

$10^{-2} c_0 / \text{mol kg}^{-1}$	$0 < \alpha < 0.5$		$0.5 < \alpha < 1.5$	
	A/mV	a/mV^a	B/mV	b/mV^b
3.8	-659 ± 8	191 ± 10	-143 ± 10	42 ± 9
7.9	-758 ± 2	204 ± 9	-194 ± 4	49 ± 3

^a Theoretical value at 1000 K: 198.2. ^b Theoretical value at 1000 K: 49.5.

The value of the dissociation constant K_3 :

$$K_3 = [O^{2-}]^2 [W_3O_{10}^{2-}] / [WO_4^{2-}]$$

is deduced from A and B according to the relation:

$$pK_3 = (4 F / 2.3 RT)(B - A) + 2 pK + 2 \log(P_{H_2O} / 2 c_0)$$

Taking into account the value 2.6 for pK , we obtain, respectively for $c_0 = 3.8 \times 10^{-2} \text{ mol kg}^{-1}$ and $c_0 = 7.9 \times 10^{-2} \text{ mol kg}^{-1}$, two values of pK_3 :

$$pK_3 = 12.5 \pm 0.4 \quad \text{or} \quad 13.0 \pm 0.2 \quad (\text{molality scale})$$

which are in a rather good agreement.

On the other hand, it can be observed on the curves of the other type (curve 1, Fig. 1) that a constant potential is reached soon after the equivalence point $\alpha = 0.5$. This corresponds to a melt saturation by WO_3 , the potential being imposed by the system $WO_3(s) + WO_4^{2-}$ at constant concentration.

The insolubility of WO_3 was confirmed by the observation of a yellow precipitate in the crucible after each experiment of this type.

The value of the constant potential $E = B'$ allows the determination of the constant pK_0 according to eqn. (4) above. The corresponding results, for three different values of c_0 , are collected in Table 4.

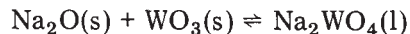
The mean value $pK_0 = 10.0$ can be compared to the constant calculated from

TABLE 4

Analysis of the titration curves without formation of polytungstate ion
 Experimental values of A , a , B' and pK_0

$10^{-2} c_0 / \text{mol kg}^{-1}$	$0 < \alpha < 0.5$		$\alpha > 0.5$	
	A/mV	a/mV	B'/mV	pK_0
3.96	-701 ± 6	214 ± 12	194 ± 4	10.1 ± 0.1
6.34	-739 ± 2	194 ± 8	188 ± 4	10.2 ± 0.1
6.65	-660 ± 5	204 ± 10	220 ± 4	9.8 ± 0.1

the thermochemical data [6] for the reaction:



that is $\text{p}K_0^* = 14.3$, allowing us to say that the activity coefficient of WO_4^{2-} in NaCl–KCl at 1000 K is close to 0.1, considering the previously determined value for the oxide ion [3].

DISCUSSION

The reaction of WO_3 with WO_4^{2-} is undoubtedly very slow, despite the high temperature, as was confirmed experimentally by the potential decay observed when leaving WO_3 saturated melt evolve with time. This phenomenon could be explained by the structural reorganisation needed to form a polytungstate ion from the highly polymeric WO_3 .

It is interesting to note that Delimarskii et al. [7], in a study on the electrochemical reduction of WO_4^{2-} in NaCl–KCl, have concluded that the reaction:



is slow in direction 1, which could be understood at the light of the dissociation equilibrium (1) found to be very slow too, in this work.

More surprising is the fact that no $\text{W}_2\text{O}_7^{2-}$ was formed in either case, contrary to the numerous mentions to this ion either in pure tungstates [8–10] or in other molten salts [11–14], or to the comparable one, $\text{Mo}_2\text{O}_7^{2-}$, whose electrochemical reduction has been recently studied by Popov and Laitinen [15]. On the contrary, we are in agreement with Gelsing et al. [16] who, according to infrared studies in molten alkali tungstates, made the assumption that $\text{W}_2\text{O}_7^{2-}$ would undergo the following dissociation:

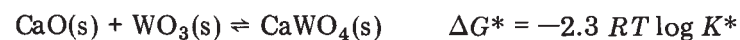


This hypothesis was confirmed by density and surface tension measurements made recently by Gossing and Stevels [17] on the molten mixtures M_2WO_4 – WO_3 ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and by Hassamein and Kordes [18–20] at the end of a comparative study on alkali chromates, molybdates and tungstates.

The greater stability of this tritungstate might be understood because of the weakness of a two-tetrahedron structure at elevated temperatures, but it is interesting to note that such a compound was mentioned also in aqueous solutions [21].

(3) Solubility product of calcium tungstate CaWO_4

The solubility product of CaWO_4 can be calculated, if the Gibbs energy, ΔG^* , of the following reaction between pure substances is known:



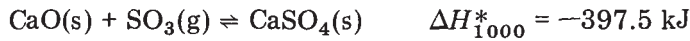
The relation is indeed:

$$K_s^{\text{CaWO}_4} = [\text{Ca}^{2+}][\text{WO}_4^{2-}] = K_s^{\text{CaO}}/K_0K^*$$

As, to our knowledge, ΔG^* has not been experimentally determined, its value at 1000 K was calculated thanks to the relation:

$$\Delta G_{1000}^* = \Delta H_{1000}^* - 1000 \Delta S_{1000}^*$$

ΔS_{1000}^* was estimated according to Kelley's [22] and Latimer's [23] rules and ΔH_{1000}^* extrapolated from the enthalpy at the same temperature for the reaction:



This is justified by the works of Navrotsky and Kleppa [24] who compared the enthalpies of formation, at 970 K, of MWO_4 , MCO_3 , MAl_2O_4 and MSO_4 (with $M = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd}$). A great analogy between MWO_4 and MSO_4 can be seen, the ΔH^* values being shifted by the mean value 192 kJ. Thus, one obtains $\Delta G_{1000}^* = -163.8 \text{ kJ}$.

Hence:

$$pK_s^{\text{CaWO}_4} = 3.5 \quad (\text{molality scale})$$

As expected, CaWO_4 appears intrinsically more soluble than CaO , on account of the larger dimension of WO_4^{2-} compared to O^{2-} .

CONCLUSION

Thanks to the various equilibrium constants determined in this study, the conditional solubility variation versus $p\text{O}^{2-}$ of CaWO_4 has been calculated. It is represented by the diagram on Fig. 2.

The intrinsic solubility S_0 , obtained by equilibrating CaWO_4 with a pure melt, is low and close to $2 \times 10^{-2} \text{ mol kg}^{-1}$ ($K_s^{\text{CaWO}_4} 1/2$).

The intrinsic solubility S is high ($\sim 1 \text{ mol kg}^{-1}$) in strongly oxobasic media, $p\text{O}^{2-} < 1.5$, because of the insolubility of CaO greater than that of CaWO_4 .

An acidification also leads to a destruction of CaWO_4 , here by dissociation of WO_4^{2-} . A fast acidification will give rise to the direct formation of insoluble WO_3 . Curve 2 of Fig. 2 represents the variation of S in this case: S decreases,

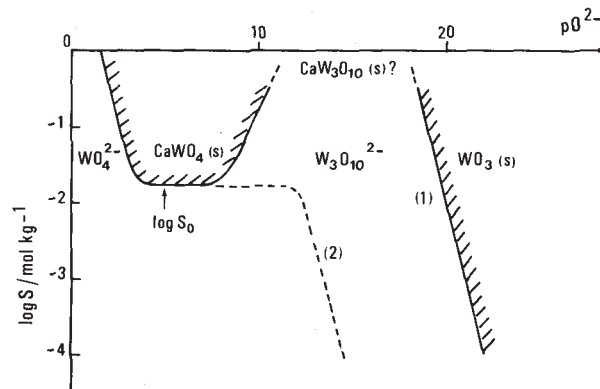


Fig. 2. Diagram representing the variation versus $p\text{O}^{2-}$ of the conditional solubility S of scheelite CaWO_4 in NaCl-KCl melt at 1000 K. (1) Equilibrium solubility (slow formation of $\text{W}_3\text{O}_{10}^{2-}$); (2) non-equilibrium solubility (quick acidification).

from S_0 , for $pO^{2-} > 12$. A minimal value of S , not represented here, could correspond to the intrinsic solubility of WO_3 (e.g. under the form of WO_3Cl^-), which is very low.

The slow acidification, or the evolution of the melt after a fast one, will allow the formation of the $W_3O_{10}^{2-}$ ion. The calcium tritungstate CaW_3O_{10} is probably much more soluble than $CaWO_4$, considering the anion size; then this formation leads to an increase in the conditional solubility S of W^{VI} (maximal value: CaW_3O_{10} intrinsic solubility if little soluble) for $pO^{2-} > 8$. In more acidic media, $W_3O_{10}^{2-}$ will then be destroyed, with precipitation of WO_3 , for $pO^{2-} > 18$ (if other soluble polytungstates do not appear before).

Taking everything into account, two ways can be considered to solubilize $CaWO_4$ in molten $NaCl-KCl$:

(a) In oxobasic medium, by formation of soluble sodium *orthotungstate*, the insoluble residue being CaO . To obtain the necessary pO^{2-} (< 1.5), addition of $NaOH$ under a low water vapor pressure can be used (at 1000 K, $pO^{2-} < 1.5$ is obtained for $[OH^-] > 1 \text{ mol kg}^{-1}$ and $P_{H_2O} < 0.1 \text{ atm}$).

(b) In oxoacidic medium, by slow formation of tritungstate (calcium salt probably soluble), after the fast formation of trioxide WO_3 , sparingly soluble. The latter formation enables to consider a separation of pure WO_3 .

The solubility under the form of tritungstate is maximal in a pO^{2-} range 12–17. This range corresponds to the buffer system HCl/H_2O , since, at 1000 K (according to ref. 3):

$$pO^{2-} = 14 + \log(P_{HCl}^2/P_{H_2O})$$

Thus, a prolonged treatment by a gaseous stream of wet HCl will provoke the progressive dissolution of the $CaWO_4$ suspension in the melt.

Of these two possibilities, the former appears more advantageous for some reasons: the strongly oxobasic medium would maintain under the form of insoluble oxides most of the metallic impurities of scheelite, included the calcium; the W^{VI} solubility is probably higher in these conditions; the dissolution is faster; the atmosphere is not as corrosive as with HCl ; lastly, the electrochemical reduction of W^{VI} will not be impeded by the one of hydrogen ions as in the case of HCl , and could be realized continually by simple reloading of the melt in $CaWO_4 + NaOH$ (if oxide ions are consumed at the anode). These conditions would be close to those recommended in a British patent [25] or by Baraboshkin and Perevoskin [26] for the preparation of tungsten from its oxides in molten calcium chloride.

REFERENCES

- 1 R. Combes, J. Vedel and B. Tremillon, C.R. Acad. Sci., 273 (1971) 1740.
- 2 R. Combes, Thesis, Paris, 1973.
- 3 R. Combes, J. Vedel and B. Tremillon, Electrochim. Acta, 20 (1975) 191.
- 4 S.N. Flengas and R. Ingraham, J. Electrochem. Soc., 106 (1959) 714.
- 5 International Critical Tables, Vapor Pressure Lowering, p. 292.
- 6 O. Kubaschewski and E.L. Evans, La Thermochimie en Métallurgie, Gauthier-Villars, Paris, 1964.
- 7 Y. Delimarskii, V. Shapoval, V. Grishcharko and L. Zambitskaya, Dokl. Akad. Nauk SSSR, 205 (1972) 879.
- 8 J. Vallier, J. Chim. Phys., 63 (1966) 1530.
- 9 E. Kordes and G. Nolte, Z. Anorg. Allgem. Chem., 371 (1969) 149.
- 10 E. Kordes and G. Nolte, Z. Anorg. Allgem. Chem., 371 (1969) 156.

- 11 J. Harrison, G. Petit and R. Plancel, *C.R. Acad. Sci.*, **241** (1965) 402.
- 12 A. Baraboshkim, V. Perevozkin, Z. Bnomareva and A. Filosofova, *Tr. Inst. Elektrokhim., Akad. Nauk SSSR, Ural Filial*, **15** (1970) 60.
- 13 Y. Rybkin and A. Serederiko, *Ukr. Khim. Zh.*, **40** (1974) 137.
- 14 R. Kust, *Inorg. Chem.*, **6** (1967) 157.
- 15 B. Popov and H.A. Laitinen, *J. Electrochem. Soc.*, **120** (1973) 1346.
- 16 R. Gelsing, H. Stein and J. Stevels, *Phys. Chem. Glasses*, **7** (1966) 185.
- 17 R. Gossing and J. Stevels, *Z. Anorg. Allgem. Chem.*, **388** (1972) 282.
- 18 M. Hassanein and E. Kordes, *Z. Anorg. Allgem. Chem.*, **381** (1970) 241.
- 19 M. Hassanein and E. Kordes, *Z. Anorg. Allgem. Chem.*, **387** (1972) 1.
- 20 E. Kordes, *Z. Anorg. Allgem. Chem.*, **388** (1972) 291.
- 21 E. Bettinger and R. Tyree, *J. Amer. Chem. Soc.*, **79** (1957) 3355.
- 22 K. Kelley, *U.S. Bur. Mines Bull.*, no. 371, 1934.
- 23 W. Latimer, *J. Amer. Chem. Soc.*, **73** (1951) 1480.
- 24 A. Navrotsky and O. Kleppa, *Inorg. Chem.*, **4** (1969) 756.
- 25 H. Slatin, *British Patent*, 918 (1963) 167.
- 26 A. Baraboshkim and V. Perevoskin, *Elektrokimiya*, **2** (1966) 966.