CHEMICAL REACTIONS IN MOLTEN SALTS : IMPORTANCE OF ACIDITY

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Abstract : Chemical reactions in molten salts like molten chlorides, chloroaluminates, nitrates, hydrogenosulfates and disulfates, are described. Importance of acid-base equilibria on chemical reactions is outlined.

INTRODUCTION

Molten salts are more and more frequently employed as reaction media : they are available at higher temperatures than more usual solvents ; their liquid state and good thermal conductivity allow the realization of isothermal reactors ; an excellent dispersion of reactants may be obtained by dissolution in the melt (especially for catalysts) ; finally, if one or more reactants are in the gaseous state, a large exchange surface may be obtained by means of a convenient bubbling.

These advantages for use most generally put forward are based mainly on physical properties of molten salts (liquid state, thermal capacity, solvation of reaction intermediates or catalysts). Some chemical characteristics may intervene in a less evident way : some salts, in general defined compounds with congruent melting point, show autodissociation reaction. In that case, the activity of a compound of the ionized liquid may vary to a great extent, comparatively to the variation of composition ratio of salt components[1].

In the following, various possibilities for use of fused salts will be illustrated using some selected examples, in order to show the potential advantages of the so called acidity concept.

MOLTEN SALTS CONSIDERED AS SUPPORTING SOLVENTS FOR REACTIONS.

Molten salts - generally anhydrous - may be the only solvents for otherwise unstable chemical species : Sundermeyer[2] proposed a synthesis of tetra-hydrosilane SiH_4 , a compound of interest in the production of silicon. Starting material was tetrachlorosilane $SiCl_4$. The first process described to transform $SiCl_4$ into SiH_4 used lithium aluminum hydride $LiAlH_4$, alkaline and alkaline earth hydride having no convenient solvent   available at that time. However, lithium hydride was dissolved in fused LiCl : KCl eutectic (t = 400°C), allowing the reaction :

$$4 \ LiH + SiCl_4 \rightarrow SiH_4 + 4 \ LiCl \qquad (1)$$

Furthermore, Sundermeyer showed that the hydride could be restored (regenerated) by electrochemical reduction of hydrogen : an iron tube flushed by hydrogen during electrolysis acted as a cathode for the following reaction :

$$2Li^+ + H_2 + 2e \rightarrow 2LiH \qquad (2)$$

whereas chloride ions were oxidized on a graphite anode.

In this manner, the overall reaction was :

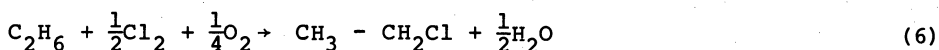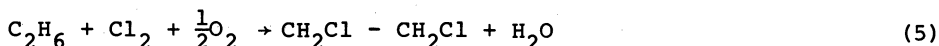$$2H_2 + SiCl_4 \rightarrow SiH_4 + Cl_2 \qquad (3)$$

with quantitative yield.

In this case, fused salt acts only as a solvent for the intermediate LiH. It
can also be used as a catalyst if one of its constituents is an active one.
Recently, two reviews have been devoted to this problem.

Jones and Osteryoung|3| reviewed reactions in melts containing $AlCl_3$. Aluminum
chloride promotes the formation of carbocations, giving condensation reactions
(Friedel Crafts reaction) or transposition reactions. Most of the reactions
studied are of this type. They are caused by the very acidic properties of
fused chloroaluminate. Thus the transformation reaction of phenylbutyric acid
into α-tetralone is performed as well in anhydrous fluorhydric acid as in the
mixture $AlCl_3$: NaCl (68 : 32 mol %) at t = 180 - 200°C. Jones and Osteryoung
indicated a lot of addition-condensation, dehydrogenation or isomerization
reactions but they noted that almost any work entailed the possibility of
changing the acidity of the melt by modifying its composition (cf. infra).

Kenney|4| examined the catalysis of gas reactions : condensation, cracking,
halogenation, oxidation, etc. Let us consider the Transcat process for vinyl
chloride production by oxidation and chloration of ethane and ethylene.
Oxidizing gas is either chlorine and air or chlorhydric acid and air. The
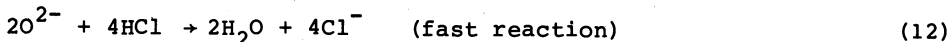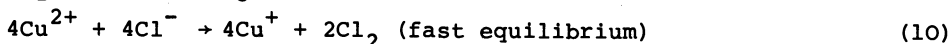melt is a fused $CuCl - CuCl_2 - KCl$ mixture. The presumed reactions include :

$$C_2H_4 + Cl_2 \rightarrow CH_2Cl - CH_2Cl \tag{4}$$

$$C_2H_6 + Cl_2 + \tfrac{1}{2}O_2 \rightarrow CH_2Cl - CH_2Cl + H_2O \tag{5}$$

$$C_2H_6 + \tfrac{1}{2}Cl_2 + \tfrac{1}{4}O_2 \rightarrow CH_3 - CH_2Cl + \tfrac{1}{2}H_2O \tag{6}$$

$$C_2H_6 + \tfrac{1}{2}Cl_2 \rightarrow C_2H_5Cl + HCl \tag{7}$$

together with the Deacon reaction :

$$2HCl + \tfrac{1}{2}O_2 \rightarrow Cl_2 + H_2O \tag{8}$$

and the cracking of 1 - 2 dichloroethane

$$CH_2Cl - CH_2Cl \rightarrow CH_2 CHCl + HCl \tag{9}$$

Patents protect the formation process but mechanisms and kinetics of many
of the reactions are unknown. The study of Deacon reaction in molten salt
is more developed. Ruthven and Kenney studied its kinetics in the mixture
$CuCl - CuCl_2 - KCl - LaCl_3$ and proposed the following mechanism :

$$4Cu^{2+} + 4Cl^- \rightarrow 4Cu^+ + 2Cl_2 \text{ (fast equilibrium)} \tag{10}$$

$$4Cu^+ + O_2 \rightarrow 4Cu^{2+} + O^{2-} \quad \text{(rate determining step)} \tag{11}$$

$$2O^{2-} + 4HCl \rightarrow 2H_2O + 4Cl^- \quad \text{(fast reaction)} \tag{12}$$

Although all of these reactions are oxidation or acid-base reactions their
analysis by means of acidity concept has not been systematically considered.
However, the Deacon reaction may be well explained by potential-acidity
diagrams (or Pourbaix diagrams|5|) the use of which might permit rational
choice and investigation for convenient catalysts.

Acidity must be defined and measured. In molten chlorides, acidity can be
defined using the exchange of oxide anion|6,7|: this choice is dictated by
the importance of oxide chemistry at high temperature. Moreover, this kind
of acidity (the oxo-acidity) is related to the Bronsted acidity if the
water, which frequently surrounds the melts, is involved. Thus :

$$O^{2-}(d) + 2HCl(g) \rightarrow H_2O(g) + 2Cl^-(d) \tag{13}$$

with : $K_D = a(O^{2-})P(HCl)^2 / P(H_2O)$ \hfill (14)
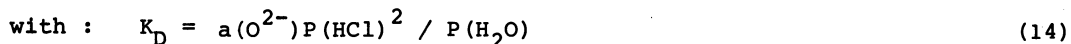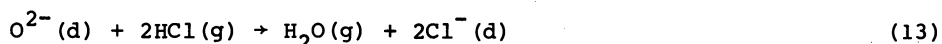
Acidity is determined by quantity $pO^{2-} = -\log a(O^{2-})$ or if activity coeffi-
cient is constant, by $pO^{2-} = -\log m(O^{2-})$.

In order to determine the quantity pO^{2-}, Combes and al.|8| showed that a
stabilized zirconia membrane electrode, schematized as follows :

| Reference electrode | melt | stabilized zirconia membrane | Inner reference electrode | (15) |
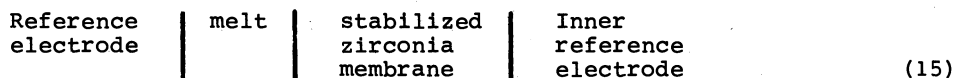
acts as a pO^{2-} indicator electrode in fused NaCl-KCl. By means of that
electrode the K_D constant was determined ($K_D = 10^{-15}$ at 1000K, O^{2-} concentra-
tion expressed in mol fraction) and also the diagram reported in Fig. 1.
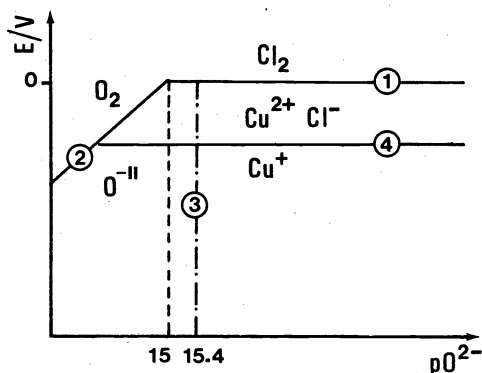
The diagram $E - pO^{2-}$ plotted in Fig.1
summarizes the noteworthy results.
Chloride ions are oxidized into chlo-
rine. The reaction is not dependent
on acidity and occurs at potential
represented by line 1. Oxidation of
$O^{(-II)}$ depends on acidity and oxygen
pressure. In the presence of air,
oxidation potential variation against
pO^{2-} is shown in the equation :

Fig.1. $E-pO^{2-}$ diagram in molten
        KCl-NaCl (T=1000K) |8|

$$E = -1.5 + (2.3RT/2F)pO^{2-} \quad (ref. \; Cl_2 \; 1atm/Cl^-) \tag{16}$$

and represented by line 2. When a gaseous mixture of HCl and H_2O is flushed
through the melt, acidity is fixed. For example if P(HCl) = 0.5 atm, P(H_2O) =
0.1 atm, then pO^{2-} = 15.4 (line 3). Then, oxygen is able to oxidize chloride
ions into chlorine. However the reaction needs some catalyst. The standard
potential of the redox pair Cu^{2+}/Cu^+ is equal to -0.2V (line 4) and copper
oxides appear only for acidity values of less than 15|9|. If Cu(II) is
added to the melt, it oxidizes Cl^- into Cl_2 until a state of equilibrium is
attained. At that time the Cu(I) concentration is not negligible and the
reoxidation reaction by oxygen occurs at a convenient rate. If the molten
salt composition is changed, the distance between lines 1 and 4 is presumably
changed as well as the rate of reaction(11) which is proportional to the Cu(I)
concentration in the stationary state.

        ACIDITY IN MOLTEN CHLOROALUMINATES.

In the preceeding case, acidity was "induced" either by chemical reactions
or by the surrounding gaseous phase. The anion and less frequently the cation
of some molten salts may undergo a dissociation that generate a solvent sys-
tem acidity|10|. It is the case for molten chloroaluminates nitrates, di-
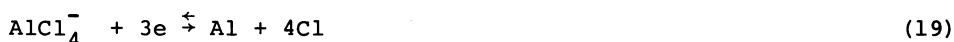sulfates and hydrogenosulfates.

In molten chloroaluminates, the autodissociation equilibrium is |11|:

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \tag{17}$$

with $K_1 = m(Al_2Cl_7^-).m(Cl^-)$ \hfill (18)

Acidity definition is based upon the Cl^- ion exchange and measured by

quantity $pCl = - \log m(Cl^-)$. An aluminum electrode is a pCl electrode indica-
tor. The electrode reaction is :

$$AlCl_4^- + 3e \rightleftharpoons Al + 4Cl \tag{19}$$

and the equilibrium potential is given by :

$$E = E° + (2.3RT/3F) \log a(AlCl_4^-)/m(Cl^-)^4 = E° + (4/3)(2.3RT/F) pCl^- \tag{20}$$

The Al electrode has been used for determining NaCl solubility and K_i value.
At 175°C, near values have been determined by various authors[11,12,13] :
$S = 5 \times 10^{-2}$ mol kg^{-1}, $K_i = 3.10^{-6}$ $mol^2 Kg^{-2}$. Thus, at that temperature, the
Cl^- activity (measured by its concentration) is multiplied by a factor equal
to 10^4 when the composition ratio $AlCl_3$: NaCl varies from 1.38 - 0.98
(in mol %).

As a consequence of that activity variation, important variations of the
nature of dissolved species may occur. Bermond[14] showed that Hg(I) and
Hg(II) species are depending on the acidity. More recently Trémillon and
Duchange[15] investigated the basic properties of fluoride anion F^- in
molten $NaAlCl_4$ and $NaAlBr_4$ (t = 210°C). A known amount of strong acid($Al_2Cl_7^{2-}$)
was introduced in the melt by coulometric oxidation of metallic aluminum
and neutralized by successive additions of NaF. It was shown that the F^- anion
has weak dibasic properties, the titration reaction being :

$$F^- + 2Al_2X_7^- \rightarrow Al_2X_6F^- + AlX_4^- \tag{21}$$

corresponding to the solvolysis equilibrium

$$F^- + 2AlX_4^- \rightleftharpoons Al_2X_6F^- + 2X^- \tag{22}$$

The basicity constant values are $10^{-3.5}$ and 10^{-4} in $NaAlCl_4$ and $NaAlBr_4$,
respectively. The authors assume a structure in which the F^- ion forms a
bridge between the two Al atoms, more stable than the bridge obtained with
anions Cl^- and Br^- but being broken by an excess of them.

Another example of the influence of acidity on properties of solutes in
chloroalumina e is the electrochemical oxidation of N.N.Dimethylaniline,
as reported by Jones and Osteryoung[16], using linear sweep voltammetry
technique. The curves obtained for various values of pCl are reported on
fig. 2. The first action on the system is an oxidation (fig. 2a, curve 1).
On B, the potential variation is reversed and the products formed during
the oxidizing step are reduced. Two peaks are observed, the first one increa-
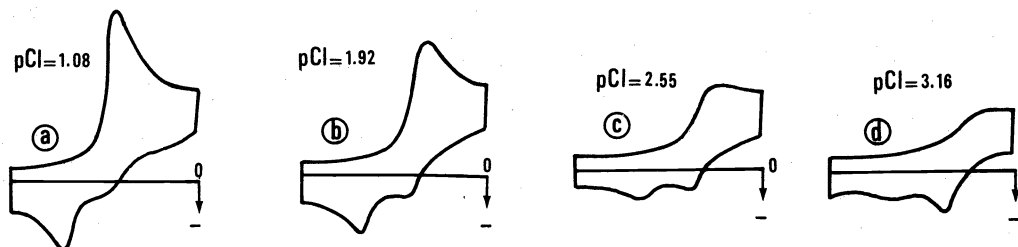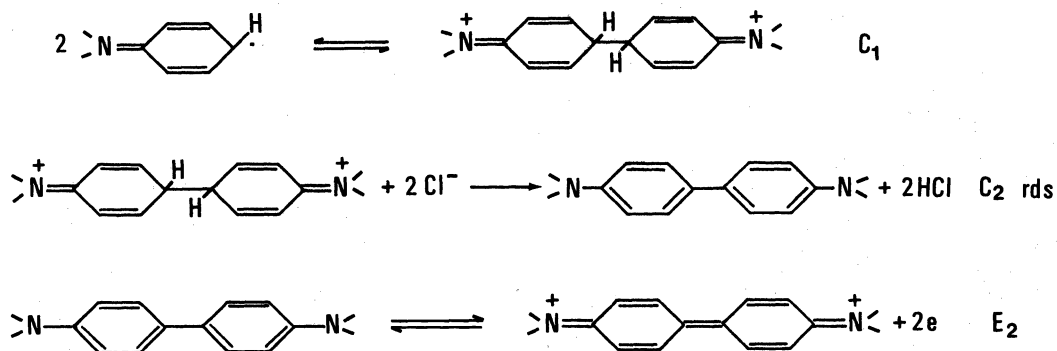sing and the second one decreasing for increasing acidity. (increasing pCl).

Fig. 2. Cyclic voltammograms for N-N dimethylaniline in NaCl-AlCl_3 melt
        (t = 175°C, scan rate 0.5 V s^{-1})[16].

The authors propose the following ECE mechanism :

$$2 \; {>}N{=} \cdots \cdots \overset{H}{\underset{\cdot}{\rule{0pt}{0pt}}} \rightleftharpoons \; {>}\overset{+}{N}{=} \cdots \overset{H}{\underset{H}{\rule{0pt}{0pt}}} \cdots {=}\overset{+}{N}{<} \qquad C_1$$

$$ {>}\overset{+}{N}{=} \cdots \overset{H}{\underset{H}{\rule{0pt}{0pt}}} \cdots {=}\overset{+}{N}{<} + 2\,Cl^- \longrightarrow {>}N{-} \cdots \cdots {-}N{<} + 2HCl \quad C_2 \; rds$$

$$ {>}N{-} \cdots \cdots {-}N{<} \rightleftharpoons {>}\overset{+}{N}{=} \cdots \cdots {=}\overset{+}{N}{<} + 2e \qquad E_2$$

The radical cation formed during the stage of oxidation (E_1) dimerizes (step C_1) giving a strong acid which is neutralized by the base Cl^- (step C_2). Then, the base is oxidized (step E_2). For increasing acidity, more and more cation radical is available for reduction. Thus, step C_2 is the rate determining step and step C_1 is a fast one.

In aprotic solvents, such as acetonitrile, formation of radical cation has never been observed with N-N-dimethylaniline. Jones and Osteryoung suggest that aprotic solvents, always containing at least 10^{-3} mol l^{-1} of water are sufficiently basic for step C_2 is always fast. The hypothesis has been also postulated by Fung, Chambers and Mamantov|17| and it would be interesting to link it with the catalysis reactions.

ACIDITY IN MOLTEN NITRATES.

Some years ago, Zambonin and Jordan|18| following Goret's work with hydroxides |19| demonstrated the existence of peroxide ion O_2^{2-} and superoxide ion O_2^- in molten nitrates, provided that the melt is basic. De Haan and Vander Poorten |20| gathered all the data concerned with and proposed a potential pO^{2-} diagram, which resumes the work accomplished.
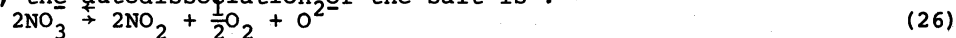
Acidity is defined by O^{2-} ion exchange : nitrate anion is a base in the reaction :

$$NO_3^- \rightarrow NO_2^- + O^{2-} \tag{23}$$
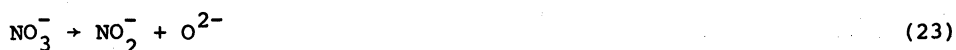
But the acidic cation NO_2^+ reacts on the nitrate ion in excess, giving the following sequence of reactions :

$$NO_2^+ + NO_3^- \rightarrow N_2O_5 \tag{24}$$

$$N_2O_5 \rightarrow N_2O_4 + \tfrac{1}{2}O_2 \rightarrow 2NO_2 + \tfrac{1}{2}O_2 \tag{25}$$

Finally, the autodissociation of the salt is :

$$2NO_3^- \rightarrow 2NO_2 + \tfrac{1}{2}O_2 + O^{2-} \tag{26}$$

in which both an acid base and a redox reaction intervene. De Haan and Van der Poorten calculated the equilibrium constant of reaction|26|. They found $K = 1.6 \; 10^{-28}$ mol kg^{-1} atm $^{5/2}$ at $t = 229°C$. The E. pO^{2-} diagram shows the behaviour of the NO_3^- anions when they are either oxidized or reduced. Oxidation is in fact oxidation of oxygen $O^{(-II)}$ they contain. If the oxidation goes directly to gaseous oxygen ($O°$) the reactions are, successively :

$$NO_3^- - 2e \rightarrow NO_2^+ + \tfrac{1}{2}O_2 \; (g) \tag{27}$$

$$NO_3^- + NO_2^+ \rightarrow 2NO_2 + \tfrac{1}{2}O_2 \; (g) \tag{28}$$

and the overall reaction is :

$$NO_3^- - e \rightarrow NO_2 + \tfrac{1}{2}O_2 \; (g) \tag{29}$$

Autodissociation equilibrium (26) is always assumed to be completed and
reaction (29) is equivalent to :

$$O^{2-} - 2e \rightarrow \tfrac{1}{2} O_2 (g) \tag{30}$$

Oxydation of nitrate ions is achieved at a potential given by :
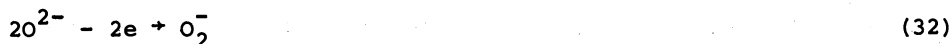
$$E = E°(O_2) + (2.3RT/4F) \log P(O_2) + (1/2)(2.3RT/F) \, O^{2-}$$

The authors calculated, from Zambonin's experimental values the quantity $E°(O_2)$
They found :

$$E = 0.250 + (\alpha/4) \log P(O_2) + (\alpha/2) \, pO^{2-} \tag{31}$$

$$(\alpha = 2.3 \; RT/F) \quad (\text{ref. electrode : } NO_3^-/NO_2^-, \, O^{2-})$$

Similarly, oxidations into peroxide and superoxide are defined by :

$$2O^{2-} - 2e \rightarrow O_2^- \tag{32}$$

$$E = -0.043 + (1/2) \log m(O_2^{2-}) + \alpha pO^{2-} \tag{33}$$

and

$$2O^{2-} - 3e \rightarrow O_2^- \tag{34}$$

$$E = 0.181 + (\alpha/3) \log m(O_2^-) + (2/3)\alpha \; pO^{2-} \tag{35}$$

Reduction of nitrate ions gives either nitrites (N(III)) or nitrogen
dioxide (N(IV)) :

$$NO_3^- + 2e \rightarrow NO_2^- + O^{2-} \tag{36}$$

$$E = 0 - (\alpha/2) \log m(NO_2^-) + (\alpha/2) pO^{2-} \tag{37}$$

and $$NO_3^- + e \rightarrow NO_2 + O^{2-} \tag{38}$$

$$E = -1.625 - \alpha \log P(NO_2) + \alpha \; pO^{2-} \tag{39}$$

All the straight lines $E = f(pO^{2-})$ in the $E - pO^{2-}$ axis delimit the
stability range of nitrates. Fig. 3 has been drawn supposing $m(O_2^-) = m(O_2^{2-}) =$
10^{-3} mol kg^{-1} and P(gas) = 1 atm. Prevailing species are indicated in their
stability area. Species O_2^- and O_2^{2-} are out of the stability area of the

Fig. 3. $E.pO^{2-}$ diagram in molten
        nitrates (t=229°C) |19|.

salt. However they are observed by
voltamperometric technique for ex.,
owing to important overvoltages in
the electrochemical oxidation of the
melt.

In strongly basic media NO_3^- ions dis-
sociate into nitrite and peroxide O_2^{2-}.
If pO^{2-} is less than about 10, oxygen
oxidizes NO_3^- ions into peroxide and/
or superoxide. Formation of O_2^- and
O_2^{2-} occurs only in basic media as
claimed by Zambonin and water or any
other acids such as metasilicate or
Li^+ ions prevent that formation:

Water behaves as an acid :

$$H_2O + O^{2-} = 2OH^- \tag{40}$$
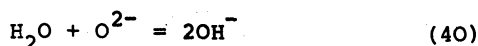
$$(K = m(O^{2-})m(H_2O)/m(OH^-)^2 = 10^{-14.4}) \tag{41}$$

and reacts on the NO_3^- base following :

$$H_2O + 2NO_3^- \rightleftharpoons 2NO_2 + \frac{1}{2}O_2 + 2OH^- \tag{42}$$

$$(K = 10^{-12.2})$$

Water in the melts causes hydroxide formation, the concentration of which depends on oxygen and nitrogen dioxide pressures. If $P(O_2) = 1$ atm and $P(NO_2) = 10^{-5}$ (oxygen electrode), the pO^{2-} value is found equal to 16.6, at which value neither O_2^- nor O_2^{2-} exist. In order to observe them, one has to neutralize the excess of water with a strong base like Na_2O.

In acidic (or hydrated) medium, the indication of an oxygen electrode has a Nernst slope vs pO^{2-} equal to $(1/2)(2.3RT/F)$, as observed by Kust and Duke[21] and some others reported by Schlegel[22]. However, owing to the complication of the concerned mechanisms and reactions involved, it is possible that the thermodynamic equilibrium is never attained.

ACIDITY IN MOLTEN POTASSIUM DISULFATE.

For several years, our group has been studying molten disulfate and hydrogeno-sulfate. These salts show autodissociation reactions and solvoacidity may be defined. Despite their narrow range of variation, it was shown that the acidity range allowed modifications in the nature of dissolved species.

In molten potassium disulfate ($F=414°C$), $S_2O_7^{2-}$ anion undergoes an autodissociation as follows :

$$S_2O_7^{2-} (l) \rightleftharpoons SO_4^{2-} (d) + SO_3 (g) \tag{43}$$

and acidity may be based either by SO_4^{2-} or by SO_3 exchange. The addition of the former species in known quantity being easier, it was chosen to represent acidity using the quantity $pSO_4 = -\log a(SO_4^{2-})$. $a(SO_4^{2-})$, represents the activity of dissolved sulfate anion, related to the concentration by :

$$a(SO_4^{2-}) = \gamma(SO_4^{2-}).m(SO_4^{2-}) \tag{44}$$

$$m(SO_4^{2-})/mol \ kg^{-1}, \ \gamma^\infty(SO_4^{2-} = 1$$

Acidity was measured potentiometrically, using a sulphur dioxide electrode as indicator electrode. The metal of the electrode was gold : preliminary results, obtained by voltammetry on rotating gold electrode showed that the electrochemical reaction corresponding to solvent reduction could be :

$$2S_2O_7^{2-} + 2e = SO_2 (g) + 3 SO_4^{2-} \tag{45}$$

for which the equilibrium potential variation vs $P(SO_2)$ and $a(SO_4^{2-})$ is :

$$E = E° -(2.3 \ RT/2F)\log P(SO_2).a(SO_4^{2-})^3 \tag{46}$$

The validity of equation has been verified by plotting the equilibrium potential of SO_2 electrode ($P(SO_2) = 1$ atm) against the log. of added sulfate concentration (Δm). However, the melt initially contains some quantity of excess sulphate, arising from a partial decomposition of the salt during melting, or initially present in the starting material. If m_i is that initial concentration (to which corresponds a value γ_i of the coefficient γ), equation (46) may be stated as follows :

$$10^{(2/3)(F/2.3RT)(E_i-E)} = \frac{\gamma}{\gamma_i} (1 + \Delta m/mi) \tag{46}$$

In fig. 4 the variation of the exponential term against Δm is plotted for

two series of determinations. These are two straight lines whose point of intersection with the vertical axis is equal to the unit. Thus the activity coefficient is constant and equal to $\gamma\infty$ ($\gamma\infty$ = 1) in the considered variation range. The reciprocal of the slopes give the m_i values and the solution is saturated when $m > m_s$, for which the potential value remains constant. The solubility values are respectively 0.25 and 0.26 mol kg^{-1}.

After that it was demonstrated that acidity could be determined using the displacement of voltammetric curves corresponding to solvent reduction, allowing the determination of the autodissociation constant of the melt :
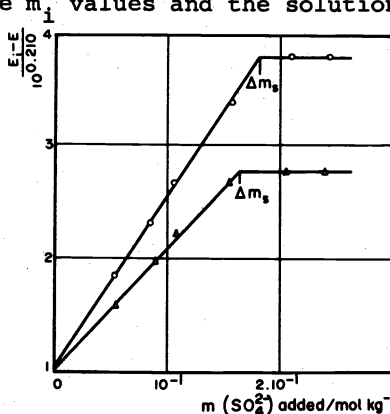
$$K_i = m(SO_4^{2-}) \cdot P(SO_3) \qquad (47)$$

Fig. 4. Verification of the reversibility of the S(VI)/S(IV) system.

The melt was equilibrated with gaseous SO_3 ($P(SO_3)$ initial = 1 atm) and titration curves pSO_4 = f(added K_2SO_4) were obtained (fig. 5, curve 1). The equivalent point was obtained by applying Gran's method |24| , taking into account the SO_3 in the gaseous phase surrounding the melt. (Fig. 5, curve 2). Sulphur trioxide solubility and K_i value were found equal to $10^{-1.05}$ and $10^{-3.25}$, resp., the later being in good agreement with the value extrapolated from Flood and Boye results ($10^{-3.2}$) |25| .
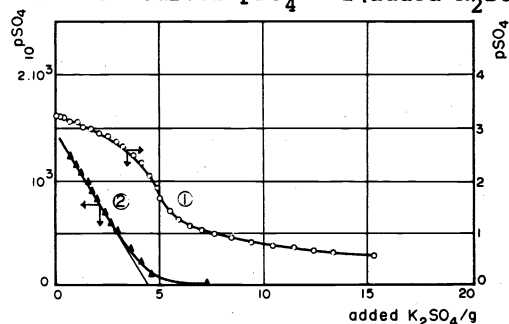
Fig. 5. Titration of SO_3 by K_2SO_4

    1 : pSO_4 variation ;

    2 : Gran's plot.

Another application of acidity measurement was the determination of acidic properties of dissolved phosphorous pentoxide |26| where P_2O_5 behaves as a weak acid, dissolving K_2SO_4 in excess. Metaphosphate anion is a weak base and pyrophosphate anion a strong one, which precipitates potassium sulphate from neutral solution. Analysis of titration curves allowed to show that the acid-base equilibrium is, in fact :

$$PO_3^- + S_2O_7^{2-} \rightleftharpoons PO_3SO_3^- + SO_4^- \qquad (48)$$

ACIDITY IN MOLTEN HYDROGENOSULFATE.

The case of molten hydrogenosulfate is more complex |27|. Anion HSO_4^- is a Brønsted acid :

$$HSO_4^- \rightarrow H^+ + SO_4^{2-} \qquad (49)$$

but under thermal influence, it dehydrates as follows :

$$2HSO_4^- \rightleftharpoons H_2O(g) + S_2O_7^{2-} \qquad (50)$$

$$K_{H_2O} = \frac{P(H_2O) \times (S_2O_7^{2-})}{x(HSO_4^-)^2} \qquad (51)$$

Thus, three bases, HSO_4^-, H_2O and $S_2O_7^{2-}$, could fix the proton H^+ given by the

HSO_4^- ion. Furthermore, equilibrium (5) indicates that the melt composition (that is the ratio $x(HSO_4^-)/x(S_2O_7^{2-})$) depends on the water pressure $P(H_2O)$ in equilibrium with the molten salt.

Three autoprotolysis equilibria have to be considered :

$$2HSO_4^- \;\rightleftharpoons\; H_2SO_4 + SO_4^{2-} \qquad\qquad (52\text{-}a)$$

$$HSO_4^- + H_2O \ (g) \;\rightleftharpoons\; H_3O^+ + SO_4^{2-} \qquad\qquad (52\text{-}b)$$

$$HSO_4^- + S_2O_7^{2-} \;\rightleftharpoons\; HS_2O_7^- + SO_4^{2-} \qquad\qquad (52\text{-}c)$$
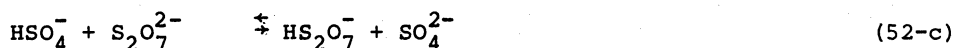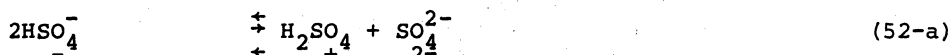
to which correspond three autoprotolysis constants :

$$K_a = m(H_2SO_4)m(SO_4^{2-})/x(HSO_4^-)^2$$

$$K_b = m(H_3O^+)m(SO_4^{2-})/P(H_2O)x(HSO_4^-)$$

$$K_c = m(HS_2O_7^-)m(SO_4^{2-})/x(S_2O_7^{2-})\,x(HSO_4^-)$$

(In expressing the mass action constants, concentrations of diluted species are expressed in mol kg^{-1} and those of melt constituents in molar fractions). The $x(HSO_4^-)$ and $x(S_2O_7^{2-})$ values are fixed when the water vapour pressure is fixed and calculated after determination of the dehydration constant value K_{H_2O}. For constant values of $P(H_2O)$, equation (52-a), (52-b) and (52-c) may be expressed :

$$K_i^* = m(H^+).m(SO_4^{2-}) \qquad\qquad (53)$$

K_i^* is a conditional constant, depending on $P(H_2O)$ and H^+ represents the solvated proton (either H_2SO_4, $HS_2O_7^-$ or H_3O^+) K_i^* values for various $P(H_2O)$ were determined by potentiometric titration of sulfate solution by sulphuric acid. Indicator electrode was a convenient glass electrode. Then the quantities K_a, K_b and K_c were calculated and plotted against $P(H_2O)$. Only the K_a quantity remains constant, so that autoprotolysis equilibrium of the solvent is equilibrium (52-a), involving H_2SO_4.

The solubility of potassium sulfate in the melt is low and the acidity range of fused $KHSO_4$ is narrow (2.2 pH units at 210°C and $P(H_2O)$ = 0.03 atm. However, a change in the solvation of dissolved species was observed, in the case of mercury compounds|28| and vanadium compounds|29|

Let us consider the case of vanadium species. Solubility of vanadium(IV) sulphate ($VOSO_4$) in molten ammonium hydrogenosulfate (t = 200°C, $P(H_2O)$= 0.03 atm)was first determined for various acidity values. Vanadyl sulphate, slightly soluble in neutral media redissolves in both acidic and basic media (fig. 6). The limiting slope values indicate that the species soluble are respectively VO^{2+} and $VO(SO_4)_2^{2-}$. The corresponding acid-base equilibria are :
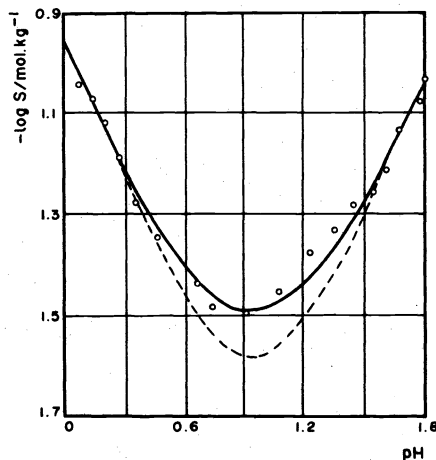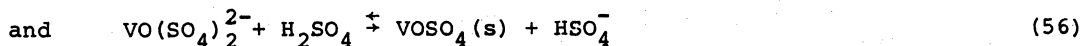

Fig. 6. Variation of V(IV) solubility in molten NH_4HSO_4

$$VOSO_4(s) + H_2SO_4 \rightleftharpoons VO^{2+} + HSO_4^- \tag{54}$$

with $K_1 = m(H_2SO_4)/m(VO^{2+})$ $\hspace{6cm}$ (55)

and $\hspace{1cm} VO(SO_4)_2^{2-} + H_2SO_4 \rightleftharpoons VOSO_4(s) + HSO_4^-$ $\hspace{4cm}$ (56)

with $\hspace{1cm} K_2 = m(VO(SO_4)_2^{2-})/m(H_2SO_4)$ $\hspace{5cm}$ (57)

The overall solubility, S_t, is thus :

$$S_t = m(H_2SO_4)/K_1 + S + K_2/m(H_2SO_4) \tag{58}$$

where S is the solubility of $VOSO_4$. The values of K_1 S and K_2 have been deter-
mined by fitting equation (58) with experimental points by the least squares
method using the pit-mapping technique proposed by Sillen|30|. The calculated
curve (fig. 6, full line) fits experimental points well (open line curve has
been obtained using the same adjusment technique but assuming S = O). Similar-
ly, it was shown that vanadium V species are VO_2^+ in acidic media and $VO_2SO_4^-$
in basic media.

       CONCLUSION.

Despite a small acidity variation in molten ammonium hydrogenosulphate,
three vanadium(IV) complexes and two vanadium(V) complexes were observed.
The acidity variation corresponds to a composition variation $H_2SO_4 : (NH_4)_2SO_4$
ranging from (55 : 45) to (45 : 55) (molar fraction scale). In molten
chloroaluminates, similar composition variations give largest acidity varia-
tion. Furthermore, even in simple molten salts, like fused alkali chloride
that have no possibility of autodissociation equilibria, acid base reaction
may appear; either because induced by surrounding atmosphere or caused by
chemical reactions.

Thus, it is essential to take into account, the possible acidity variations
in forecasting and investigation of chemical reactions in fused salt, in
order to favour some reactions and inhibit others.

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