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Thermodynamic Properties of the O_2—O_2^-—O_2^{2-}—O^{2-} System in Molten Alkali Carbonates

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The chemical equilibrium properties of the system $O_2-O_2^--O_2^{2-}-O^{2-}$ in molten alkali carbonates have been studied for various cation combinations (Li, Na, NaK, and LiNaK) in the temperature range 800 to 1200 K. The experimental method used was based on quenching of equilibrated melts followed by chemical analyses. The accuracy in some of the results is inferior because of the very severe corrosion in the "basic" carbonate melts. It was found that the stability of the peroxide and hyperoxide ions compared with that of the oxide ions increases with increasing cation "radius" and decreasing temperature.

It is well-known that the carbonate ions in molten alkali carbonates dissociate according to the reaction

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-}$$

In an oxygen atmosphere the oxide ions may be oxidized to peroxide and hyperoxide (superoxide) ions. Therefore, the following redox equilibria are assumed to exist in these melts.

$$O_2^{2-} \rightleftharpoons O^{2-} + \tfrac{1}{2}O_2(g) \qquad (R1)$$

$$2O_2^- \rightleftharpoons O_2^{2-} + O_2(g) \qquad (R2)$$

$$2O_2^- \rightleftharpoons O^{2-} + \tfrac{3}{2}O_2(g) \qquad (R3)$$

$$3O_2^{2-} \rightleftharpoons 2O^{2-} + 2O_2^- \qquad (R4)$$

Only two of these equilibria are independent (*e.g.*, R3 = R1 + R2; R4 = 2R1 − R2). The corresponding standard equilibrium constants may be written

$$K^\ominus_1 = [a(O^{2-})/a(O_2^{2-})][p(O_2)/p^\ominus]^{\frac{1}{2}} \qquad (1)$$

$$K^\ominus_2 = a(O_2^{2-})/[a(O_2^-)]^2[p(O_2)/p^\ominus] \qquad (2)$$

$$K^\ominus_3 = a(O^{2-})/[a(O_2^-)]^2[p(O_2)/p^\ominus]^{3/2} \qquad (3)$$

$$K^\ominus_4 = [a(O^{2-})]^2[a(O_2^-)]^2/[a(O_2^{2-})]^3 \qquad (4)$$

No systematic thermodynamic investigation of the redox system $O_2-O_2^--O_2^{2-}-O^{2-}$ in alkali carbonate melts has been carried out previously. However, some crude measurements which showed the importance of peroxide ions in "basic" alkali carbonate melts (see definitions and notations) were performed by the present author in the late sixties.[1,2] Information on the equilibrium properties of the mentioned reactions is important in applications of oxygen electrodes in alkali carbonate melts. For this reason it was decided to carry out more accurate measurements.

Recently Appleby and Nicholson [3,4] measured limiting oxygen reduction currents in "acid" $(Na,K)_2CO_3$- and Li_2CO_3-melts (see definitions and notations). No quantitative equilibrium data are given by these authors, but their results indicate the presence of both peroxide- and hyperoxide-ions in significant amounts in NaK-melts. They also conclude that hyperoxide-ions are not stable in Li-melts.

Studies of the system $O_2-O_2^--O_2^{2-}-O^{2-}$ in other oxy-anionic melts are of interest. Lux *et al.*[5] have investigated the formation of peroxides and hyperoxides by reactions between molten single cation alkali hydroxides and oxygen in the presence of water vapour at 683 and 733 K by means of an analytical method. In Li-melts neither O_2^{2-}-ions nor O_2^--ions could be detected, in Na-melts there is evidence that mainly O_2^{2-}-ions are formed, whereas in K-, Rb-, and Cs-melts O_2^--ions are the main reaction products. However, no quantitative equilibrium data were given.

Later Goret [6] and Goret and Trémillon [7] did voltammetric studies of the $O_2-O_2^- - O_2^{2-}-O^{2-}$-system in NaK-hydroxide melts at 500 K. This work also was of a qualitative nature only.

During the last decade Zambonin and coworkers have studied the redox chemistry and mechanisms of the same system in molten alkali nitrates. Zambonin [8] calculated the following "equilibrium constants" for the reactions R1 and R2 at 503 K

$$K_1' = [O^{2-}][O_2]^{\frac{1}{2}}/[O_2^{2-}] \simeq 10^{-8} \text{ (mol kg}^{-1})^{\frac{1}{2}}$$

and

$$K_2' = [O_2^{2-}][O_2]/[O_2^-]^2 \simeq 5 \times 10^{-7}$$

where the brackets denote molality concentrations. The data given are those for the (Na,K)-NO_3-system with 50 mol % Na. Desimoni *et al.*[9] have determined Henry's law constants for oxygen solubility in the same system by means of rotating disk electrode voltammetry. They obtained the Henry's law constants 4.6×10^{-6} and 5.3×10^{-6} mol kg^{-1} atm^{-1} at 511 and 533 K, respectively. From the data given above the following "equilibrium constants" on a mol fraction/pressure basis are deduced (standard states are given later in this section): $K_1 \simeq 5 \times 10^{-6}$, $K_2 \simeq 1.3$, $K_3 \simeq 6 \times 10^{-6}$, $K_4 \simeq 2 \times 10^{-12}$. All data refer to a temperature of about 500 K. These data show clearly that when $p(O_2) \approx 101$ kPa and $x(O_2^-) < 0.03$ it follows that $x(O^{2-}) \ll x(O_2^{2-}) < x(O_2^-)$.

Because of the different solvent anions and especially because of the relatively low temperatures used in the works of Zambonin and coworkers it is difficult to estimate data for the corresponding equilibria in alkali carbonate melts from the information above. However, an attempt to do this will be discussed later.

In the present investigation an experimental method based on quenching followed by chemical analyses was adapted in order to study the $O_2-O_2^- - O_2^{2-}-O^{2-}$-system in molten alkali carbonates.

Definitions and notations. The following definitions and notations are used:

a. Standard states are "pure" substances – M_2O(l), M_2O_2(l), MO_2(l), and O_2(g) – at the pressure 101.325 kPa.

b. All thermodynamic data refer to the stoichiometry used in the reactions R1 – R4.

c. Data in parentheses refer to temperatures below the melting points of the respective alkali carbonates.

d. The general term "oxide" is used for oxide, peroxide, as well as for hyperoxide.

e. Anionic fractions of the "oxide" species, $x(\text{i})$ are defined as $x(\text{i}) = n(\text{i})/n$ where $n(\text{i})$ is number of mol of ion i and $n = n(CO_3^{2-}) + n(O^{2-}) + n(O_2^{2-}) + \frac{1}{2}n(O_2^-)$.

f. Mol fraction of "oxide" $= x_{\text{ox}}$

$$x_{\text{ox}} = x(O^{2-}) + x(O_2^{2-}) + \tfrac{1}{2}x(O_2^-) \qquad (5)$$

g. Apparent mol fraction of peroxide =

$$x^*(O_2^{2-}) = x(O_2^{2-}) + \tfrac{1}{2}x(O_2^-) \qquad (6)$$

h. Relative amount of oxide, peroxide or hyperoxide = mol % oxide, peroxide or hyperoxide of total amount of "oxide"

$$Y(O^{2-}) = [x(O^{2-})/x_{\text{ox}}] \times 100 \text{ (mol \%)} \qquad (7)$$

$$Y(O_2^{2-}) = [x(O_2^{2-})/x_{\text{ox}}] \times 100 \text{ (mol \%)} \qquad (8)$$

$$\tfrac{1}{2}Y(O_2^-) = [\tfrac{1}{2}x(O_2^-)/x_{\text{ox}}] \times 100 \text{ (mol \%)} \qquad (9)$$

i. Apparent equilibrium constants of reactions R1 and R3

$$K^*_1 = [x(O^{2-})/x^*(O_2^{2-})][p(O_2)/p^\ominus]^{\frac{1}{2}} \qquad (10)$$

$$K^*_3 = x(O^{2-})/[2x^*(O_2^{2-})]^2[p(O_2)/p^\ominus]^{3/2} \qquad (11)$$

j. Carbonate melts are denoted "acid" when they are under a relatively high CO_2 pressure (of the order 100 kPa) and "basic" when relatively large quantities of "oxide" have been added to the melts (typically 1 – 3 mol %) and the CO_2 pressure above the melts is negligible.

k. The symbol f is used for activity coefficient on mol fraction basis.

EXPERIMENTAL

Chemicals. The chemicals used in the present investigation were: Li_2CO_3 (Riedel-de Haën, Hannover, Chem. Pure), Na_2CO_3, K_2CO_3, Na_2O_2 (Riedel-de Haën, Hannover, P.A.), Li_2O and Na_2O (K & K Laboratories Inc., Plainview, N.Y. and Hollywood, California).

The alkali carbonates were dried in the following way: They were kept for a period of 24 h or more at about 470 K. Then the salts were slowly heated and melted in dry CO_2 atmosphere and CO_2 gas was bubbled through the melts for at least 12 h.

The gases used were supplied by A/S Dansk Ilt- & Brintfabrik, Copenhagen (O_2 and N_2) and Nordisk Kulsyrefabrik A/S, Copenhagen (CO_2). The gases were dried by passing through tubes with silica gel, "Anhydrone" ($MgCl_2$), and/or P_2O_5. The gases O_2 and N_2 also passed tubes with "Carbosorb" (soda lime).

The aluminia used for crucibles and tubes was the quality DEGUSSIT AL 23 (>99.5 % Al_2O_3) supplied by Degussa, Frankfurt a.M.

Apparatus and procedure. A standard type resistance furnace as described by Motzfeldt[10] was used in the experiments. This furnace made it possible to work in a controlled atmosphere at a rather constant temperature (within ± 0.2 K in the melt, when an appropriate temperature controlling system was applied).

Alkali oxide or alkali peroxide was added (usually 3.0 mol %) to the alkali carbonate melt (about 50 g) and the mixture was kept in an atmosphere of dry oxygen at constant pressure (about 101 kPa) until equilibrium was attained.[*] Stirring was achieved by bubbling oxygen through the melts.

Samples (about 5 g) were taken out by means of an alumina pipette and quenched to room temperature within a few seconds. This process was carried out as fast as possible under protection of an inert gas (nitrogen). Different quenching conditions, *e.g.*, change in the cooling rate, did not have any influence on the results, and, therefore, the "oxide"-equilibria could be considered as sufficiently "frozen". The contents of "oxide" and apparent amount of peroxide in the samples were determined by means of volumetric analyses.[**],[***] Special precautions had to be taken to prevent loss of active oxygen.

The following alkali carbonate systems were investigated: Li_2CO_3, Na_2CO_3, $(Na,K)_2CO_3$ (56.0 mol % Na), and $(Li,Na,K)_2CO_3$ (the ternary eutectic melt – 43.5 mol % Li and 31.5 mol % Na). The melting points of these carbonates are 999, 1131, 983, and 670 K, respectively.

The container and the thermocouple protection tube were made of high purity alumina.

Two hours or less was sufficient time to attain equilibrium in the melts when Na_2O and Na_2O_2 were added. It was observed that addition of Na_2O and Na_2O_2 gave the same results, thus indicating the "oxide"-reactions to be reversible. When Li_2O was added to $(Li,Na,K)_2CO_3(l)$ the time to reach equilibrium was longer, probably because of the smaller solubility of Li_2O in carbonate melts.

RESULTS

In Fig. 1 the experimentally determined apparent equilibrium constants *versus* $1/T$ are shown for the Na-, NaK-, and LiNaK-systems. The total "oxide" concentration in the melts was about 3.0 mol %. Application of higher "oxide" concentrations was restricted because of the very severe corrosion taking place.[11] In the Li-containing melts the "oxide" concentrations had to be chosen equal to or less than the solubilities of Li_2O. When hyperoxide is present in significant amounts it should be remembered that $Y(O^{2-})$ is a function of x_{ox}.

In the cases where Li-melts were investigated the peroxide contents at equilibrium were found to be less than that which could be determined by the analytical method used, that is, $Y(O_2^{2-}) < 0.2$ mol %.

The results in Fig. 1 were fitted to straight lines ($\log K^*_1 = b/T + a$) by least squares treat-

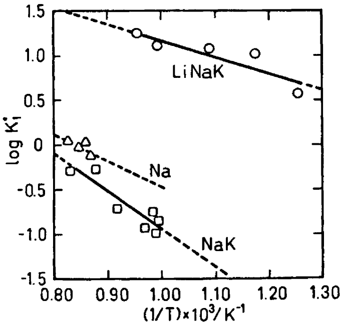

Fig. 1. Plots of log K^*_1 *versus* $1/T$ for reaction R1 $[O_2^{2-} = O^{2-} + \frac{1}{2}O_2(g)]$ in molten alkali carbonates. $x_{ox} \approx 0.03$, $p(O_2) \approx 101$ kPa.

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[*] Equilibrium in the total system was not attained since CO_2 formed by the dissociation of CO_3^{2-}-ions did escape. This process, however, is very slow and the influence on the $O_2 - O_2^- - O_2^{2-} - O^{2-}$ equilibrium was neglected.

[**] *Determination of "oxide" content in alkali carbonates.* The samples were dissolved in hot water. Excess of $BaCl_2$-solution was added and the precipitated $BaCO_3$ filtered off. The OH^--content was determined by pH-metric titration in an inert atmosphere. 2 mol of OH^--ions correspond to 1 mol of "oxide"-ions. When the concentrations of OH^--ions were small the concentrations of CO_3^{2-}- and HCO_3^--ions in the filtered solutions had to be taken into account.

[***] *Determination of apparent peroxide content in alkali carbonates.* About 1 g of the pulverized sample was transferred very slowly to a vigorously stirred mixture prepared from 50 ml crushed ice and water, 20 ml 1:10 sulfuric acid, and 1 g pure boric acid. This mixture was titrated with standard 0.02 N $KMnO_4$-solution. Since O_2^--ions react with water to form O_2^{2-}-ions, only the apparent contents of peroxide in the samples could be determined. Blind experiments confirmed the usefulness of this method.

Table 1. Apparent equilibrium constants for the reaction R1 in molten alkali carbonates.

System (M)	log K^*_1	S.D.	Temperature range/K
Li	>2.7	–	$1000-1100$
LiNaK	$(-1800/T)+2.98$	0.14	$800-1050$
Na	$(-3000/T)+2.52$	0.064	$1150-1210$
NaK	$(-4250/T)+3.31$	0.13	$1000-1200$

ments. The functions and standard deviations are tabulated in Table 1.

From the results of the chemical analyses only the oxide concentrations, $x(O^{2-})$, and the apparent peroxide concentrations, $x^*(O_2^{2-})$, are obtained. The following question now arises: What are the relative amounts of peroxide and hyperoxide ions in various melts under specified experimental conditions? If this question could be answered "real" thermodynamic data could be calculated for the reactions R1 – R4. The following experimental method was used: The total "oxide" concentration and oxygen pressure $[x_{ox}, p(O_2)]$ were changed from (0.03, 101 kPa) to (0.01, 101 kPa) or (0.03, 10.1 kPa) and the changes in the apparent equilibrium constants, K^*_1, were studied.

These measurements, which were of a semiquantitative nature, showed that under the experimental conditions $x_{ox}\approx 0.03$ and $p(O_2)\approx$ 101 kPa the ratio $x(O_2^{2-})/[\frac{1}{2}x(O_2^-)]$ is about 4/1 for the Na-system near 1150 K and about 1/1 for the NaK-system near 1100 K. Furthermore, calculations show that the ratio $x(O_2^{2-})/[\frac{1}{2}x(O_2^-)]$ probably does not change very much in the temperature range 1000 – 1200 K. For the LiNaK-system no measurable amounts of O_2^--ions could be detected by the present method.

Table 2. Standard equilibrium constants for the reaction R1 in molten alkali carbonates. Assumption: $f(O^{2-})\approx f(O_2^{2-})$.

System (M)	log $K^\ominus_1$ 800 K	900 K	1000 K	1100 K	1200 K
Li	–	–	–	>2.7	–
LiNaK	0.73	0.98	1.18	1.34	1.48
Na	–	–	(–0.39)	(–0.11)	0.12
NaK	–	–	–0.65	–0.25	0.07

Table 3. Standard equilibrium constants for the reaction R3 in molten alkali carbonates. Assumption: $f(i)=1$.

System (M)	log $K^\ominus_3$ 1000 K	1100 K	1200 K
Na	(1.96)	(2.32)	2.65
NaK	0.63	1.07	1.49

Using this information combined with the experimentally determined data for the apparent equilibrium constants (Table 1) the "true" standard equilibrium constants were calculated for the reactions R1 and R3 for the Na- and NaK-systems (Tables 2 and 3).

DISCUSSION

General. Tables 2 and 3 show clearly that the stability of the peroxide/hyperoxide ions increases with increasing cation "radius" (or decreasing cation ionic potential). The strength of the M – O bonding weakens when the distance between the centres of the atomic cores increases, and, therefore, the relative strength of the O – O bonding increases.

According to the literature[12] pure LiO_2 cannot be isolated and the only evidence for its existence is the similarity in the absorption spectra of the pale yellow solutions of Li, Na, and K on rapid oxidation of the metals in liquid ammonia at 195 K by oxygen.

Using (a) the statements above, (b) the experimental result that the hyperoxide concentration is small or negligible compared with the peroxide concentration in the LiNaK-system, (c) the qualitative results of Appleby and Nicholson[4] and of Lux *et al.*,[5] it seems to be well justified to assume that hyperoxide ions are not present in measurable amounts in "basic" alkali carbonate melts rich in Li^+-ions.

It is now possible to calculate approximate thermodynamic data also for systems which have not been investigated experimentally (the Li-, LiNa(53.3 mol % Li)-, LiK(50.0 mol % Li)-, and K-systems). The calculations are based on the data in Tables 2 and 3 and the assump-

Table 4. Standard thermodynamic data for the reaction R1, $M_2O_2(l) = M_2O(l) + \frac{1}{2}O_2(g)$, in $M_2CO_3(l)$. Assumption: $f(O^{2-}) \approx f(O_2^{2-})$.

System (M)	$\Delta G^\ominus_1$/kJ mol^{-1} 1000 K	1100 K	1200 K	$\Delta S^\ominus_1$ J K^{-1} mol^{-1}	log $K^\ominus_1$ (1000 K)
Li	–	< -57	–	–	–
Li[a]	-68.2	-71.9	-76.2	≈ 40	3.56
LiNa[a]	-32.9	-37.2	-41.9	≈ 45	1.72
LiK[a]	-24.7	-31.4	-38.0	≈ 67	1.29
LiNaK	-22.6	-28.3	-34.0	57	1.18
Na	(7.5)	(2.3)	-2.8	≈ 52	$(-0.39$
NaK	12.4	5.3	-1.6	70	-0.65
K[a]	(18.8)	(9.0)	0.1	≈ 93	(-0.98)

[a] Calculated values (see Discussion).

tion that the O_2^--concentration is negligible in Li-containing systems. In these calculations deviations from ideal mixtures were to be neglected (or the differences between the excess functions of reactants and products are assumed to be small). Furthermore, extrapolations have to be made outside the experimentally investigated temperature and in some cases also below the normal melting points.

Tables 4 and 5 show increases in standard Gibbs free energy and entropy as well as standard equilibrium constants at 1000 K of the reactions R1 and R3 for all seven possible cation combinations. Except for the LiNaK- and NaK-systems the uncertainties in the entropy functions are large; the orders of magnitude, however, seem to be reasonable.

Table 6 shows the relative amounts of oxide-, peroxide-, and hyperoxide-ions in alkali carbonate melts with a total "oxide" concentration of 3.0 mol % and under an oxygen pressure of 101 kPa. The values for the systems not studied experimentally are calculated from the data in Tables 2 and 3.

Table 6 as well as Tables 4 and 5 shows again clearly how the stability of O^{2-}-ions compared with that of the O_2^{2-}- and/or O_2^--ions decreases with increasing cation "radius". The stability of the O^{2-}-ions is slightly larger in the LiK-system than in the LiNaK-system at the same temperature. This may be due to the higher Li-content in the LiK-system. Except for the Li-system it is observed that the stability of the O^{2-}-ions increases with increasing temperature. The apparent anomality observed in the case of the Li-system probably is due to uncertainties in the experimental data and the approximations used in the calculations. It is also noticed that the calculated relative amounts of O_2^{2-}-ions in the Li-system (0.03 mol % $< Y(O_2^{2-}) < 0.05$ mol % in the temperature range 1000 – 1200 K) is consistent with the experimental statement that $Y(O_2^{2-}) < 0.2$ mol %.

This paper deals only with the thermodynamic aspects of the reactions R1 – R4 and no attempts has been made to study the kinetics or the mechanisms of the mentioned pro-

Table 5. Standard thermodynamic data for the reaction R3, $2MO_2(l) = M_2O(l) + \frac{3}{2}O_2(g)$, in $M_2CO_3(l)$. Approximation: $f(i) \approx 1$.

System (M)	$\Delta G^\ominus_3$/kJ mol^{-1} 1000 K	1100 K	1200 K	$\Delta S^\ominus_3$/ J K^{-1} mol^{-1}	log $K^\ominus_3$ (1000 K)
Na	(-38)	(-49)	61	≈ 117	(1.96)
NaK	-12	-23	-34	≈ 111	0.63
K[a]	(20)	(11)	0	≈ 103	(-1.06)

[a] Calculated values (see Discussion).

Table 6. Relative amounts of oxide, peroxide, and hyperoxide ions in molten alkali carbonates containing 3.0 mol % "oxide".
$p(O_2) \approx 101$ kPa.

System (M)	$Y(O^{2-})-Y(O_2^{2-})-\frac{1}{2}Y(O_2^-)$/mol % 1000 K			1100 K			1200 K		
Li[a,b]	99.97	0.03	0.00	99.96	0.04	0.00	99.95	0.05	0.00
LiNa[a]	98.1	1.9	0.0	98.3	1.7	0.0	98.5	1.5	0.0
LiK[a]	95.1	4.9	0.0	96.9	3.1	0.0	97.8	2.2	0.0
LiNaK	94.0	6.0	0.0	95.7	4.3	0.0	96.8	3.2	0.0
Na	(25	60	15)	(38	49	12)	51	39	10
NaK	10	45	45	22	39	39	37	32	32
K[a]	(0.9	8.5	91)	(2.9	7.9	89)	8.6	8.7	83

[a] Calculated. [b] Experimentally determined: $Y(O_2^{2-})<0.2$ mol %.

cesses in molten carbonates. One possibility is, though it is not likely to be significant in "basic" carbonate melts, that the CO_3^{2-}-ions take part in the redox processes, *e.g.*, $CO_3^{2-}+\frac{1}{2}O_2=CO_2+O_2^{2-}$.

Comparison with literature data. Thermodynamic data for the alkali oxides, peroxides, and hyperoxides are scarce – even at room temperature – and it is not possible to calculate or estimate data for the equilibrium properties of the reactions R1–R4 with any reasonable accuracy.

The results obtained in this investigation agree with the qualitative results given by Appleby and Nicholson [3,4] for $(Na,K)_2CO_3$- and Li_2CO_3-melts and also with the information given by Lux *et al.*[5] for single cation alkali hydroxides.

Using the equilibrium constants for the reactions R1 and R3 in NaK-melts at about 500 K calculated from experimental data published by Zambonin [8] and by Desimoni *et al.*[9] (see Introduction) together with estimated increases in standard entropy it is possible to calculate thermodynamic data for the reactions R1 and R3 at higher temperatures (see Table 7). Comparing these results with the corresponding data obtained in this investigation (Tables 2–5) a rather good consistency is observed. The different oxy-anions in the two systems and an extrapolation over a temperature range of 500 to 700 K indicates, however, that this consistency may be fortuitous.

Ionic species in molten alkali carbonates. Most authors agree that molten alkali carbonates are almost completely ionized and that the predominant species are the planar CO_3^{2-}-ions and the M^+-ions. Janz *et al.*[14–16] also believe that "contact ion pairs" [like $(M^+CO_3^{2-})^-$] may be of some importance. They suggest that these ions contribute to the mechanism of electrical transport.

In the presence of an O_2 atmosphere it seems likely, as assumed in this work, that O^{2-}-ions are oxidized to O_2^{2-} and O_2^--ions. The presence of O_2^{2-}-ions is demonstrated by the quenching experiments and analyses, but no definite proof has been given of the existence of O_2^--ions. The observed change in the apparent equilibrium constant, K^*_1, by decreasing x_{ox} or $p(O_2)$,

Table 7. Standard thermodynamic data for the reactions R1 and R3 in NaK-melts (50 mol % Na) calculated from experimental results of Zambonin [8] and Desimoni *et al.*,[9] and estimated standard entropy changes.

Reaction	$\Delta G^\ominus$/kJ mol^{-1} 500 K	1000 K	1200 K	log $K^\ominus$ 500 K	1000 K	1200 K
R1	51.0	13.8	−0.4	−5.3	−0.7	0.0
R3	49.8	−14.6	−37.2	−5.2	0.8	1.6

however, indicates the presence of O_2^--ions in some of the systems, and from an energetic point of view it seems likely that O_2^--ions are stable in melts with negligible amounts of Li^+-ions. The electro-analytical studies of Appleby and Nicholson described previously also strongly indicate the presence of O_2^--ions in NaK-carbonate melts. Furthermore, Zambonin[17] has used the paramagnetic property of hyperoxide ions to detect O_2^--ions in molten NaK-nitrates by means of ESR spectroscopy in the corresponding quenched matrices.

O^--ions may be present as intermediate species, but it is unlikely that these ions are stable. It is also assumed that other "oxide"-species such as O_3^- and O_3^{2-} do not play an important part as stable ions.

Various carbonate-oxygen or carbonate-"oxide" species such as CO_4^{2-} and CO_4^{4-} also seem possible. However, one should here remember the controversy in defining complexes in molten salts. From a thermodynamic point of view this author considers it to be well justified to assume that the stable species in "basic" alkali carbonate melts are limited to the following ones: Cations Li^+, Na^+, K^+; Anions CO_3^{2-}, O^{2-}, O_2^{2-}, O_2^-; Molecules O_2, CO_2.

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