Solubility and Solvation of Carbon Dioxide in the Molten $Li_2CO_3/Na_2CO_3/K_2CO_3$ (43.5:31.5:25.0 mol-%) Eutectic Mixture at 973 K

I. Experimental Part

Paul Claes,*[a] Dominique Moyaux,[a] and Daniel Peeters[b]

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The solubility of CO_2 in the molten ternary eutectic mixture Li_2CO_3–Na_2CO_3–K_2CO_3 (43.5, 31.5, 25.0 mol.%) at 973 K has been determined by a titration technique. From the obtained titration curve, the solubility has been found to amount to $9.5 \cdot 10^{-2}$ mol·L^{-1} ($\sigma = 1.0$) under a pressure of CO_2 of 1 atm and the pK_d value of the carbonate melt has been evaluated to 5.37 ($\sigma_5 = 0.24$) if the concentrations of the solutes are expressed in mol·L^{-1}. This pK_d value is in good agreement with literature data but the solubility value reported in this work is much higher than most of those reported in the literature. A chemical dissolution of CO_2 as $C_2O_5^{2-}$ is proposed and the consequences of the occurrence of this species on the acidobasic properties of molten carbonates are discussed. It appears from the experimental results that the $CO_2/C_2O_5^{2-}$ equilibrium in the carbonate melt is a slow process.

1. Introduction

The use of molten carbonates as reaction media for chemical or electrochemical applications needs a deep understanding of their chemical properties and particularly of their acidobasic and redox behaviour. Carbonate melts are amphoteric oxoacidobasic liquids whose autodissociation equilibrium is generally written as follows:[1]

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-}_{solv} \tag{1}$$

where O^{2-}_{solv} represents a solvated oxide ion.

The corresponding autodissociation constant (K_d) is then written:

$$K_d = a(O^{2-}_{solv}) \cdot P(CO_2) \tag{2}$$

where $a(O^{2-}_{solv})$ and $P(CO_2)$ are the activity of solvated oxide ions in the melt and the partial pressure of carbon dioxide in the gas phase in equilibrium with the liquid phase. According to this, the solvated oxide ion is the strongest base available in the melt, while CO_2 is the strongest acid.

Acidity scales may be based on pO^{2-} values [pO^{2-} = $-\log a(O^{2-}_{solv})$] or on $-\log P(CO_2)$ values. The two scales are, of course, related:

$$pK_d = pO^{2-} - \log P(CO_2) \tag{3}$$

These scales extend from $pO^{2-} = pK_d$ or $-\log P(CO_2) = 0$ for the most acidic media to $pO^{2-} = 0$ or $-\log P(CO_2) = pK_d$ for the most basic media.

The scales described in this way are quite satisfactory from a thermodynamic point of view but fail to give a sound and complete explanation of chemical or electrochemical behaviours. The concentration of CO_2 physically dissolved in a melt is indeed related to its partial pressure according to Henry's law:

$$C(CO_2) = k_H \cdot P(CO_2) \tag{4}$$

where k_H is the Henry's constant. For a given partial pressure of carbon dioxide, depending on the value of Henry's constant, significant differences might occur in the kinetics of chemical and electrochemical reactions whose rates are limited by the diffusion of CO_2.

Surprisingly, solubility data for CO_2 in carbonate melts are scarce and scattered as shown in Table 1 which presents some literature data for Henry's constant in three carbonate melts. Nevertheless, the knowledge of the correct value of the solubility of carbon dioxide is essential to a complete understanding of phenomena occurring in molten carbonates.

Table 1. Henry's constant for CO_2 in carbonate melts

Melt	T [K]	k_H [mol·L^{-1}·atm^{-1}]	Ref.
Na_2CO_3	1153	$9.6 \cdot 10^{-3}$	[2]
$(NaK)_2CO_3$	1073	$1.83 \cdot 10^{-1}$	[3]
$(LiNaK)_2CO_3$	973	$3.6 \cdot 10^{-3}$	[4]
	973	$1.19 \cdot 10^{-2}$	[5]
	833	10^{-1}	[6]

The aim of this work is to determine the Henry's constant of CO_2 in a carbonate melt (its solubility under a partial pressure of carbon dioxide of 1 atmosphere) by carrying out a potentiometric titration of a saturated carbonate melt at high temperature. This kind of experiment is probably

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[a] Laboratory of Inorganic and Analytical Chemistry,
[b] Laboratory of Quantum Chemistry,
Catholic University of Louvain, Department of Chemistry,
Pl. Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium
Fax: (internat.) +32-10/472330
E-mail: claes@inan.ucl.ac.be

the most direct way to the determination of the solubility of carbon dioxide; it does not need any assumption nor any calibration nor any change of temperature or physical state of the system and gives thus, in our opinion, the best confidence about the accuracy of the results.

2. Titration Procedure

The principle of the method is very simple. An accurately known amount of carbonate melt previously saturated with carbon dioxide under a pressure of 1 atmosphere is neutralized by adding to the liquid weighed portions of sodium oxide. The potential of an oxygen electrode dipped into the molten salt is measured after the complete dissolution and reaction of the added sodium oxide. The titration curve is obtained by plotting the measured potentials as a function of the amount of added sodium oxide. The end point of the titration allows to calculate the solubility of carbon dioxide and the pK_d value may be computed from the experimental solubility and from the amplitude of the titration curve.

The melt contained in an alumina crucible was saturated with carbon dioxide by flowing pure CO_2 through the cell for 24 hours. The time needed to reach equilibrium conditions after the addition of a given amount of Na_2O was about 6 hours. On the other hand, the potential difference underwent a slight potential shift which precluded to carry out a complete titration in one continuous experiment by adding successive amounts of Na_2O to one carbonate sample and by measuring the potential difference after each addition. An example of the evolution of the potential difference after addition of a given amount of sodium oxide to a CO_2 saturated melt is shown in Figure 1. The first part of the graph shows the effect of the neutralization reaction which is followed by a regular shift of the potential.

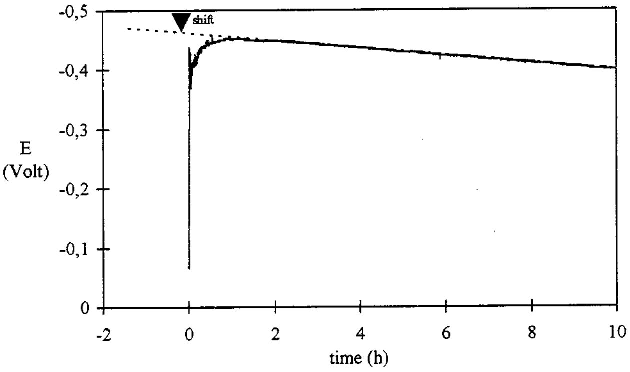

Figure 1. Evolution of the potential difference between the working and the reference electrodes as a function of the time elapsed from the addition of Na_2O to an acidic melt (1.1739 g of Na_2O added to 170.4 ml of melt)

In order to prevent too long observation times, each point of the titration curve was the result of one experiment where a given amount of sodium oxide was added to a freshly saturated sample. By increasing the amount of added Na_2O from one experiment to another, it was possible to construct the complete titration curve.

The neutralization reaction consumed not only the carbon dioxide dissolved in the melt but also the carbon dioxide contained in the free volume of the cell. Each titration point must thus be corrected for this extra consumption. Therefore, the amount of carbon dioxide contained in the cell was accurately measured in the following way. The cell containing an empty crucible was filled with carbon dioxide under a pressure of 1 atmosphere. The gas was then flushed out of the cell by a stream of pure nitrogen and allowed to bubble through a given volume of a standard solution of sodium hydroxide. The amount of absorbed carbon dioxide was determined by titration of the excess sodium hydroxide with a standard solution of hydrogen chloride. Three independent determinations have been carried out. The number of moles of CO_2 contained under a pressure of 1 atmosphere in the cell containing an empty crucible was found to be 0.0290 mol with a standard deviation of $2.9 \cdot 10^{-4}$ mol.

When the experimental results were plotted in order to construct the titration curve, the amounts of sodium oxide added to the melt were corrected for the number of moles of CO_2 contained in the gas phase at equilibrium $n(\mathrm{CO_2})_{\mathrm{gas}}$ calculated according to:

$$n(\mathrm{CO_2})_{\mathrm{gas}} = 0.0290 - \frac{PV_{\mathrm{melt}}}{\mathrm{R}T} \tag{5}$$

where P and V_{melt} are the pressure at equilibrium (1 atm) and the volume of the carbonate melt. Due to this procedure, the number of moles of Na_2O is plotted on a scale where it remains negative as long as the total amount of Na_2O added to the system is lower than the quantity required to neutralize the CO_2 contained in the free volume of the cell. The number of moles of sodium oxide calculated in this way was further divided by V_{melt} expressed in liters in order to normalize all the data to 1 liter of carbonate melt. This number $n_{\mathrm{norm}}(\mathrm{Na_2O})$ was finally plotted as abscissa.

With the experimental set-up used in this investigation, the number of moles of CO_2 dissolved in the melt amounted to about 20% of the total number of moles introduced into the cell for each experiment.

Another procedure, less accurate than the preceding one, was also used. In this case, when the melt was saturated with CO_2, the cell was connected to the vacuum device for a short time (10 sec) in order to remove the carbon dioxide contained in the free volume. After that time, the residual pressure in the cell was about 1 cm Hg. It is of course impossible to state whether the extraction time was correctly choosen or not. It seems however highly probable that some positive (incomplete exhaustion of the CO_2 from the free volume) or negative (degassing of the melt) occurred in this procedure.

3. Results

Figures 2 and 3 show respectively a titration curve obtained by the first and by the second procedure. From the first graph, the solubility of carbon dioxide at 700°C in the ternary eutectic under a pressure of 1 atmosphere is found to be $9.5\ 10^{-2} \pm 1.0 \times 10^{-2}$ mol·L^{-1}atm^{-1} (this value was obtained by fifth-order polynomial fit with a correlation factor of 0.95). The equivalent point of the titration curve of the second graph corresponds to a solubility of $5.5 \cdot 10^{-2}$ mol·L^{-1}atm^{-1}. The agreement between these two values is reasonable if the difference between the two experimental procedures is taken into account. The observed difference may be attributed to a partial degassing of the melt during the emptying of the free volume.

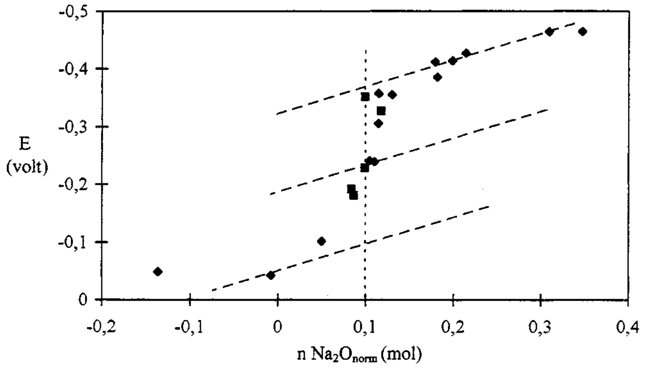

Figure 2. Titration curve obtained after correction for the neutralization of the amount of CO_2 contained in the free volume of the cell

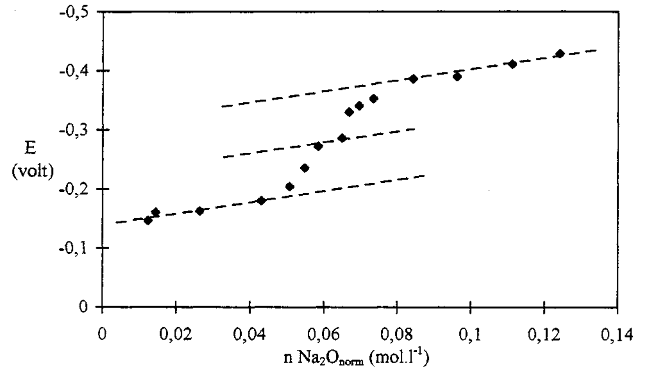

Figure 3. Titration curve obtained after the possibly incomplete removal of the CO_2 contained in the free volume of the cell

The pK_d value of the ternary eutectic at 700°C can be calculated from the value of the potential of the working electrode characteristic of the melt saturated with CO_2 under a pressure of 1 atm on the one hand and from the potential obtained for equilibrium conditions when an excess of sodium oxide has been added to the liquid on the other hand. The excess concentration of sodium oxide must of course be lower than the solubility of sodium oxide in the ternary eutectic at 700°C. According to White and Twardoch, this concentration limit amounts to 0.054 mol·L^{-1} [7].

Equations (6) and (7) describe the electrode reactions of the oxygen redox system respectively in basic and in acidic conditions:

$$O_2 + 4\,e^- \rightleftharpoons 2\,O^{2-} \tag{6}$$
$$O_2 + 2\,CO_2 + 4\,e^- \rightleftharpoons 2\,CO_3^{2-} \tag{7}$$

The corresponding Nernst equations are written:

$$E = E^\circ_{O2/O^{2-}} + (RT/4F)\ \ln P(O_2) - (RT/4F)\ \ln a(O^{2-}) \tag{8}$$
$$E = E^\circ_{O2/O^{2-}} + (RT/4F)\ \ln P(O_2) - (RT/4F)\ \ln K_d + (RT/4F)\ \ln P(CO_2) \tag{9}$$

If the partial pressure of oxygen, which is the residual pressure of oxygen, is considered as a constant, Equations (7) and (8) may be rewritten:

$$E = A - (RT/4F)\ \ln a(O^{2-}) \tag{10}$$
$$E = A - (RT/4F)\ \ln K_d + (RT/4F)\ \ln P(CO_2) \tag{11}$$

The potential value for the excess Na_2O concentration was corrected for the potential shift which occurred in basic media. Therefore, the electrodes were allowed to rest in the melt after the neutralization of the carbon dioxide by the introduced sodium oxide and the potential difference was measured as a function of the time. Using this shift per unit time measured experimentally for each neutralization experiment, the value of the potential obtained for the basic melt was corrected considering the time elapsed between the introduction of sodium oxide and the end of the experiment. Taking into account Equations (10) and (11) as well as the correction for the potential drift [$(\Delta E)_{drift}$] and assuming that the activity of oxide ions in Equation (10) may be replaced by the excess concentration of sodium oxide [$C(Na_20)_{exc}$] (the concentration corresponding to the amount of Na_2O introduced in the saturated melt less the solubility of carbon dioxide), one finds for the difference between the initial and the final potentials (ΔE):

$$\Delta E = -(RT/4F)\ \ln K_d - (RT/4F)\ \ln C(Na_2O)_{exc} - (\Delta E)_{drift} \tag{12}$$

The pK_d values were determined from five independent experiments whose results are shown in Table 2. This table gives successively the normalized amount of sodium oxide introduced into the saturated melt [$n_{norm}(Na_2O)$], the excess concentration of sodium oxide [$C(Na_2O)_{exc}$], the potential of the gold electrode measured at the beginning of the experiment ($E_{t\,=\,0}$) and 8 hours later ($E_{t\,=\,8}$), the experimental drift correction [$(\Delta E)_{drift}$], the potential difference (ΔE) and the calculated pK_d value.

The mean value is pK_d = 5.37 with a standard deviation of $\sigma_5 = 0.24$

4. Discussion

4.1. Comparison with the Literature

The Henry's constant determined in this work is one order of magnitude higher than those measured by Appleby[4] and by Broers[5] but it agrees with the value given by Dubois.[6] This disagreement might be due to differences between experimental techniques used in these investigations. Appleby deduced his solubility data using a melt-chilling method based on the measurement of the quantity of dissolved gas released on freezing of the melt. This technique is certainly suitable for the determination of physical solu-

Table 2. Determination of the pK_d value

$n_{norm}(Na_2O)$ [mol·L^{-1}]	$C(Na_2O)_{exc}$ [mol·L^{-1}]	$E_{t=0}$ [Volt]	$E_{t=8h}$ [Volt]	$(\Delta E)_{drift}$ [Volt]	ΔE [Volt]	pK_d
0.179	0.084	0.043	0.412	0.033	0.402	5.24
0.115	0.020	0.043	0.357	0.056	0.370	5.53
0.114	0.019	0.043	0.306	0.096	0.359	5.44
0.130	0.035	0.043	0.355	0.031	0.343	5.01
0.118	0.023	0.069	0.327	0.130	0.388	5.65

bilities but might lead to underestimations in the case of chemical solubilities if the chemical reactions which take place in the dissolution process are slow. Broers used a procedure based on impedance determinations at a stationary CO,CO_2/CO_3^{2-}/Au electrode over a range of $P(CO)/P(CO_2)$ ratios which allows the CO_2/CO solubility ratio to be calculated. The CO_2 solubility is then deduced from the solubility of CO measured by an amperometric titration method. The interpretation of impedance spectroscopy determinations is much more complex than our measurements and needs that dissolved CO_2 and CO both occur in the melt as definite species reacting at the electrode at a well defined potential.

The pK_d value obtained in this work (pK_d = 5.37 ± 0.24) is in reasonable agreement with the result obtained by Andersen (pK_d = 5.8)[8]. A small lack of accuracy might occur in our determinations due to the fact that the residual partial pressures of oxygen in the carbon dioxide and in the nitrogen used to generate the gaseous atmosphere in equilibrium respectively with the acidic and basic melts are not exactly the same. The accuracy might probably be improved by adding a small constant partial pressure of oxygen to the gaseous atmospheres successively imposed above the melt during the determinations in place of using “pure” carbon dioxide and “pure” nitrogen.

4.2. Comparison with the Electrochemical Behaviour of Carbon Dioxide

Earlier results have shown that CO_2 is electroactive in molten carbonates and that the corresponding CO_2/CO redox system exhibits a reversible behaviour[3,9−11]. The proposed electrochemical reaction is:

$$2\ CO_2 + 2\ e^- \rightleftharpoons CO + CO_3^{2-} \qquad (13)$$

This was indeed confirmed in this work since a cathodic peak occurs at about −0.8 V versus the reference electrode in the linear sweep voltammograms of CO_2 saturated melts. Such a voltammogram is shown in Figure 4. The current density of this signal was allways very small, of the order of magnitude of 1 mA·cm^{-2}.

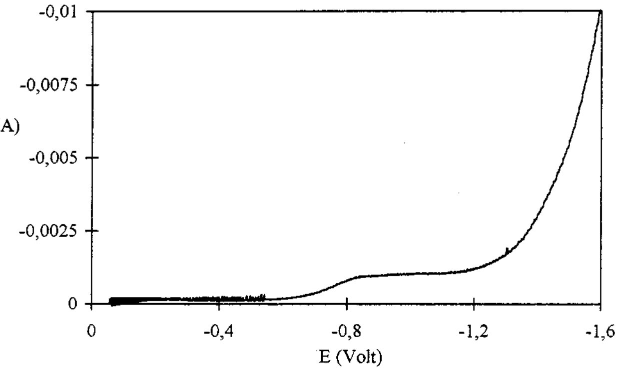

Figure 4. Voltammogram of a CO_2 saturated carbonate melt. (ν = 1 V·s^{-1})

$$i_p = 0.4463(\nu D/RT)^{1/2}(nF)^{3/2}SC \qquad (14)$$

From the Randles−Sevcikc Equation (14) in which $i_p = 10^{-3}$ A, $n = 1$, $S = 1$ cm^2, $T = 973$ K, $\nu = 1$ Vs^{-1} and $D = 10^{-5}$ cm^{2}s^{-1}, which is the order of magnitude of diffusion coefficients in molten carbonates in the temperature range 873−973 K[3,7,11−13], a concentration value of $2\cdot10^{-3}$ mol·L^{-1} is calculated. This calculation is in agreement with the results of Peelen[11] who reports a value of $0.95\cdot10^{-8}$ mol·cm^{-2}s$^{-1/2}$ for the product $s \times D^{1/2}$ (where s is the solubility) relative to CO_2 in a molten Li/K carbonate mixture at 848 K. From this, with the same diffusion coefficient, the value of the solubility s is found to be $3\cdot10^{-3}$ mol·L^{-1}. These solubilities are lower by about two orders of magnitude than the Henry's constant measured by the titration technique.

In order to make the experimental solubility compatible with the electrochemical observations, it may be assumed that most of the carbon dioxide dissolved in the carbonate melt is so strongly solvated that it should react at the cathode at a potential at which the reduction of carbonate ions still occurs. The formation of dicarbonate ions may be proposed:

$$CO_2 + CO_3^{2-} \rightleftharpoons C_2O_5^{2-} \qquad (15)$$

with an equilibrium constant:

$$K = \frac{a(C_2O_5{}^{2-})}{P(CO_2)} \quad (16)$$

According to this assumption, a small proportion of CO_2 dissolves physically in the melt, yielding "free" CO_2 responsible for the observed electrochemical reduction. As calculated above, this physical dissolution accounts for only about 2% of the dissolved CO_2. The largest part of the dissolution occurs chemically yielding dicarbonate ions. Furthermore, these dicarbonate ions have to be inactive in the electrochemical window. The "complexation" of CO_2 by $CO_3{}^{2-}$ or the overpotential for the reduction of $C_2O_5{}^{2-}$ must therefore be strong enough to shift that reaction to potential values where the reduction of $CO_3{}^{2-}$ still occurs. In order to explain the weakness of the cathodic signal due to the reduction of CO_2, it must also be assumed that the production of CO_2 through equilibrium (15) is slow enough that the consumption of CO_2 in the electrochemical reduction is not compensated by the equilibrium. The sluggishness of the formation−dissociation kinetics of pyrocarbonate ions applies to all phenomena consuming carbon dioxide and the unexpected high solubility of CO_2 contributes little, for instance, to enhance CO_2 mass transfer in MCFC cathodes. The occurrence of a physical and a chemical solubility might also explain, at least partly, the discrepancies between solubility determinations by different techniques.

Unfortunately, we are unable at the moment to propose any experimental evidence for the occurrence of dicarbonate ions in acidic carbonate melts. However, the quantum chemical approach proposed in the second part of this work provides good arguments for the formation of that species.

4.3. Acidobasic Properties of Carbonate Melts

The occurrence of a chemical solubility of carbon dioxide besides its physical solubility leads to a second autodissociation reaction of carbonates, which would be written as Equation (17) and which would occur in the melt besides equilibrium (1).

$$2\ CO_3{}^{2-} \rightleftharpoons C_2O_5{}^{2-} + O^{2-} \quad (17)$$

The corresponding autodissociation constant is:

$$K_d' = a(C_2O_5{}^{2-}) \cdot a(O^{2-}) \quad (18)$$

For practical purposes, this is written:

$$K_d' = [C_2O_5{}^{2-}]\cdot[O^{2-}] \quad (19)$$

Taking into account equilibrium (16), one finds:

$$K_d' = KP(CO_2)[O^{2-}] = K_dK \quad (20)$$

The neutrality condition for autodissociation, which is a relationship between the concentrations of basic and acidic species in a pure carbonate melt should then be written:

$$[O^{2-}] = [CO_2] + [C_2O_5{}^{2-}] \quad (21)$$

The titration carried out in this work does not allow the direct measurement of Henry's constant, which accounts only for the physical solubility. The measured constant is in fact ($k_H + K$) since both chemically and physically dissolved carbon dioxide react with Na_2O:

$$[CO_2] + [C_2O_5{}^{2-}] = (K + k_H)\cdot P(CO_2) = 9.5\cdot10^{-2} \pm 1.0\cdot10^{-2}\ \mathrm{mol\cdot L^{-1}} \quad (22)$$

The ratio of the concentration of physically and chemically dissolved carbon dioxide depends only on the temperature of the melt:

$$\frac{[CO_2]}{[C_2O_5{}^{2-}]} = \frac{k_H}{K} \quad (23)$$

An approximative value of this ratio may be proposed from the results obtained in this work: $[CO_2]$ has been evaluated to be $2\cdot10^{-3}\ \mathrm{mol\cdot L^{-1}}$ from the peak current density for the electrochemical reduction of carbon dioxide in a saturated melt and $[C_2O_5{}^{2-}]$ may be considered as the experimental solubility since, taking into account the level of approximation, the physical solubility may be neglected in comparison with the chemical solubility. The value of $2\cdot10^{-2}$ is thus a good approximation of the ratio of the physical to the chemical solubility.

$C_2O_5{}^{2-}$ is a weak acid relative to CO_2, which is the strongest acid available in carbonate melts. The respective strengths of these acids are measured by the equilibrium constants (K_1 and K_2) of the reactions of these acids with oxide ions:

$$C_2O_5{}^{2-} + O^{2-} \rightleftharpoons 2\ CO_3{}^{2-} \quad (24)$$

$$CO_2 + O^{2-} \rightleftharpoons CO_3{}^{2-} \quad (25)$$

$$\frac{K_1}{K_2} = \frac{[CO_2]}{[C_2O_5{}^{2-}]} \quad (26)$$

$C_2O_5{}^{2-}$ is thus a weaker acid than CO_2 by a factor of about $2\cdot10^{-2}$.

5. Conclusions

The experimental value of the solubility of carbon dioxide in carbonate melts depends on the technique used for the determination. The solubility measured in this work by a titration technique is much higher than those reported in the literature for the same melt at the same temperature. These differences may be explained by the occurrence of a physical and a chemical solubility due to the formation of dicarbonate ions. This chemical solubility is about 50 times more important than the physical solubility. The simultaneous occurrence of CO_2 and $C_2O_5{}^{2-}$ in carbonate melts means that the autodissociation of carbonate ions occurs in two different ways producing two different conjugated acids of the solvent. The comparison of these two acids from a thermodynamic point of view shows that the strength of the dicarbonate ion is about 50 times lower than that of carbon dioxide, which is the strongest acid available in molten carbonates. Our results do not allow the deduction of any information about the kinetic properties of these two species, but the occurrence of $C_2O_5^{2-}$ offers a convenient explanation for the slowness of the neutralization reaction of oxide ions in acidic carbonate melts as demonstrated by Lu and Selman[15]. This is a rather speculative consideration but it seems important to pay some attention to this point in the future.

Experimental Section

Chemicals: Lithium-, sodium-, and potassium carbonates were analytical grade reagents from Merck. The lithium salt was dried at 200°C for 24 hours under vacuum before use.

200 g of a dry homogeneous mixture of salts with the composition of the ternary eutectic $Li_2CO_3-Na_2CO_3-K_2CO_3$ (43.5%, 31.5% and 25.0% mol. respectively) was used for each experiment. The sample was progressively heated up to 400°C under a nitrogen pressure of 1 atmosphere in order to remove residual water. After melting, nitrogen was replaced by carbon dioxide and the temperature of the liquid was raised to 700°C.

The gases were supplied by Air Liquide; their purities are certified to be at least 99.999% for nitrogen, 99.99% for O_2, and 99.995% for CO_2. The water content of all these gases is lower than 5 ppm.

When mixtures of gases were needed (reference electrode), the expected proportions were obtained by adjusting the streams of the components with precision valves and flowmeters to a buffer vessel, where the gases were allowed to mix together.

Experimental Set-up: The carbonate melt was contained in an alumina (Al23 Degussa) crucible setted in an alumina (Al23 Degussa) cell located in a vertical furnace whose temperature was regulated to ±2°C. The cell was provided with an airtight cover which allowed to introduce into the melt a working and a reference electrode and with alumina tubings intended to introduce sodium oxide, carbon dioxide and nitrogen into the cell.

Addition of Na_2O was carried out without changing the composition of the gaseous atmosphere in the cell by means of a lock chamber.

During the titration procedure, nitrogen was progressively introduced to compensate for the consumption of carbon dioxide in order to keep constant the total pressure in the cell.

Electrochemical Device: The working electrode used in potentiometric determinations is a 0.5 mm diameter gold wire which acts as an oxygen electrode. The reference electrode is an oxygen electrode in an acidic melt contained in a pythagoras tubing dipped into the investigated melt. The electrochemical arrangement is thus:

Au / CO_2 (0.66 atm), O_2 (0.33 atm) / CO_3^{2-} / pythagoras / CO_3^{2-} sample / CO_2 or O^{2-}, O_2 (res.) / Au

The electrochemical determination have been carried out with a Princeton Applied Research potentiostat/galvanostat model 273.

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