On the Solubility of Carbon Dioxide in Molten Alkali Nitrates and Alkali Fluorides

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Some years ago an investigation of carbon dioxide solubilities in molten salts was initiated at our institute. Values obtained for the carbon dioxide solubility in certain molten alkali halides [1] and in cryolite melts containing alumina [2,3] already have been reported. Our work recently has been extended to comprise even molten alkali nitrates and alkali fluorides.

Experimental. The experimental method employed in the present work is the so-called "chilling method", described in detail elsewhere.[2,3] The melt is saturated with gas in a furnace, and thereafter transferred to a chilling chamber where the dissolved gas is expelled as the salt freezes. The following systems have been studied: $NaNO_3$, NaF and KF.

Chemicals. NaF: *pro analysi* and *suprapur*, E. Merck A.G., Darmstadt, Germany. KF: analytical grade, Baker & Adamson, N.Y., USA.

$NaNO_3$: *pro analysi*, E. Merck AG., Darmstadt, and Riedel de Haën A.G., Seelze-Hannover, Germany.

CO_2: Oslo Kulsyrefabrik A/S, Oslo, Norway, 99.85 vol. % CO_2. All salts were dried *in vacuo* at 450°C for 12 h.

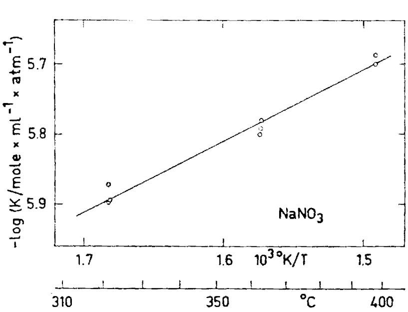

Fig. 1. Solubility of CO_2 in molten $NaNO_3$ (on a logarithmic scale) *versus* reciprocal absolute temperature.

In Fig. 1 the results obtained for the molten $NaNO_3$ are given.[1] The solubility is cited as moles ml^{-1} atm^{-1}. In all systems studied the CO_2 solubility is of the order of 10^{-6} moles ml^{-1} atm^{-1}.

According to Uhlig [4] the solubility of a gas in a liquid is given by the relation:

$$\ln K_c = \ln \frac{C_d}{C_g} = \frac{-4\pi r^2 \sigma + E}{kT} \qquad (1)$$

Here C_d and C_g denote the concentration of gas in the liquid and gaseous phase, respectively, r is the radius of the gas molecule and σ is the surface tension of the liquid. The term E is an "interaction energy" between solvent and solute. The interaction energy, as calculated from our CO_2 solubility measurements in molten alkali chlorides and bromides in the temperature range from 800 to 1000°C, turns out to be approximately -2 kcal $mole^{-1}$. This suggests repulsive forces between gas and solvent in these systems.

Application of the same eqn. (1) on the experimental results of Fig. 1 gives an interaction energy of 1.4 kcal $mole^{-1}$, which indicates attractive forces between dissolved gas and the surrounding medium. This is in accordance with what is generally found for the dissolution of gas in liquids at moderate temperatures. It was demonstrated by Uhlig,[4] from his measurements of the solubility of different gases in organic solvents, that the solubility increases with increasing energy of vaporization of the gas at its boiling point. A high energy of vaporization is a result of strong forces between gas molecules in the pure, liquid state. If this also implies relatively strong forces between gas molecules and solvent molecules in the solution, then these forces would be expected to decrease with increasing temperature, just as the energy of vaporization decreases with increasing temperature. This may, therefore, explain why the interaction energy E, which takes account of just the solute-solvent interaction, decreases when passing from the low-temperature (320–400°C) region of the molten nitrates to the high temperature (800–1000°C) region of the molten chlorides and bromides.[1]

Fig. 2 gives the results obtained for the molten fluorides. If the interaction energy E were the same in the fluorides as in the remaining halides, the CO_2 solubility in the fluorides should be the lower, due to the higher surface tension of the fluorides

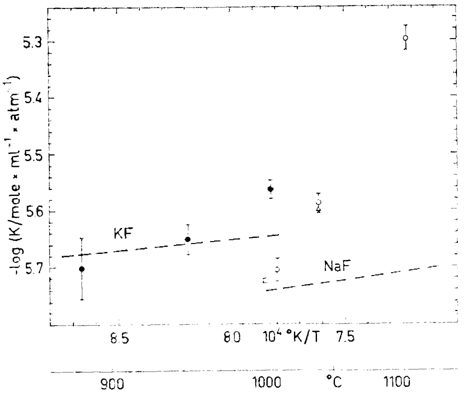

Fig. 2. Solubility of CO_2 in molten NaF and KF (on a logarithmic scale) *versus* reciprocal absolute temperature. Open circles: NaF, analytical grade; open triangle: NaF, Suprapur grade; open square: NaF, analytical grade, thermogravimetric method.[1]

Filled circles: KF, analytical grade
Dotted lines: Predicted slope.

compared to the other halides. The solubility in the fluorides, as found in the present investigation, is, however, higher than for the chlorides and bromides.[1]

A tentative explanation may be that the interaction energy is larger in the fluorides. It is not unreasonable to assume a certain degree of chemical interaction between the relatively highly polarizing fluoride ion and the carbon dioxide molecule, giving a kind of ion-induced dipole bond. The possibility of a definite ion species, *e.g.* the CO_2F^- ion, being formed under these conditions, has been considered. The CO_2F^- ion should be more stable than the corresponding CO_2Cl^- ion, just as COF_2 is far more stable than $COCl_2$.[5] It should be possible to draw some conclusions with regard to this question from spectroscopic studies of molten fluorides or carbonate-fluoride mixtures saturated with carbon dioxide.

A serious source of error connected with the measurements in molten fluorides is the oxide impurities in the salts. In fact, the observed solubility is of the same order of magnitude as the concentration of basic impurities in the salts, as stated by the manufacturer. The possibility, therefore, of CO_2 reacting to form CO_3^{2-}, which subsequently decomposes during cooling in an inert atmosphere, cannot be dismissed without consideration. In order to find out whether carbonate, if formed, would decompose under the actual experimental conditions, small amounts of sodium carbonate were added to the fluoride. Experiments proved that carbonate addition drastically increased the observed solubility of CO_2 at temperatures above 1000°C. Below this temperature the observed solubility seemed unaffected by the carbonate addition. This phenomenon is connected with the experimental method, as the observed solubility is represented by the amount of CO_2 expelled from the melt after the CO_2 pressure has been removed. It is reasonable to assume that the decomposition of carbonate is an activated reaction, the rate of which being almost negligible at sufficiently low temperatures, *e.g.* 1000°C. Therefore the observed solubility of CO_2 in the molten fluorides probably is too high at the higher temperatures. This also agrees with a qualitative estimate of the enthalpy of solution. Since the interaction energy E seems higher for the fluorides, the numerator in eqn. (1) is less negative, which means that the temperature coefficient of the solubility K_c is smaller, compared to that of the chlorides and bromides.[1] This is indicated by the dotted lines of Fig. 2.

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