THE SOLUBILITY OF CHLORIDE SALTS
IN METALLIC SODIUM AND LITHIUM AT 350-600°C

C. H. Lemke and L. B. Dworsky
E. I. du Pont de Nemours & Company, Incorporated,
Industrial Chemicals Department, Experimental Station,
Wilmington, Delaware 19898

ABSTRACT

The solubility of chloride salts, derived from typical electrowinning electrolytes, is presented for sodium and lithium metals in the temperature range 350-600°C. The determinations were made by analysis of metal phase samples removed from the equilibrated systems at various temperatures. The pipet sampling system was designed for elevated temperature applications. Data for the chloride salt-sodium system agree well with an extrapolation of literature values for the sodium chloride-sodium system at higher temperatures.

Commercial production of metallic sodium and lithium involves molten electrolytes usually containing two or more chloride salts. Electrolyte for sodium manufacture contains at least sodium and calcium chlorides and may contain strontium chloride or potassium chloride. The usual electrolyte for lithium production is a mixture of potassium and lithium chlorides. These metals at cell operating conditions contain dissolved chloride derived from the respective electrolytes. These solubilities were studied at 350-600°C to aid in evaluation of process modifications. Information on the sodium-sodium chloride system at higher temperatures has been developed by Bredig and co-workers, but no previous work on the more complex systems under consideration is known.

In the course of this work it was found that with respect to sodium metal the solubility of chloride salt appears to be the same if the salt is derived from sodium chloride or either of two mixed chloride melts studied.
EXPERIMENTAL PROCEDURE

The expected solubilities of chloride salt in sodium and lithium at the temperatures of interest suggested that thermal analysis would not give meaningful data. A simple approach was tried which proved to be satisfactory between about 350-600°C.

Equilibration and sampling of the salts and metals were done in a dry argon-filled glove box. Open-top vessels made of 1-1/2 inch schedule 40 steel pipe with welded steel plate bottoms were used to contain the alkali metal-salt systems. These vessels were secured in a larger steel vessel containing molten sodium as a heat transfer medium. The outer vessel was electrically heated and the temperature was controlled with an Electronic Control Systems Model 690 controller. System temperatures were measured with calibrated chromel-alumel thermocouples and a Leeds and Northrup potentiometer (Figure 1).

For each of the three systems studied, the desired salt mixture (about 200 g) was melted in one of the steel vessels and a sample taken by dipping a cold steel rod briefly into the melt. The appropriate metal (150-200 g) was added, the system stirred vigorously with a steel rod, equilibrated, and allowed to settle for the periods of time shown in Tables I and II.

Metal phase samples were taken by pipet after equilibration. Tubes of Pyrex glass and steel were used as pipets for sodium and lithium respectively. In all cases the pipets were preheated to the system temperature before use.

Each filled pipet was cooled, carefully cleaned on the outside to remove adhering alkali metal and cut to short lengths to facilitate dissolving the sample. Samples were dissolved in methanol-water mixture and the chloride content determined as silver chloride by measurement of turbidity. Results were erratic below about 50 ppm chloride (as Cl⁻) and data below this limit were not used in deriving the solubility equations.

EXPERIMENTAL DATA

Solubility vs. temperature data are shown in Tables I and II along with equilibration times and chloride source information. The data of Bredig, Johnson and Smith(5), recalculated to mole fraction basis, are also tabulated.
Derived equations for chloride salt solubility as a function of temperature are:

Chloride salt* in sodium:

\[ L_{Na} = 2.799 - \frac{4666}{\theta_K} \] (350-960°C) (Figure 2)

Standard deviation = 0.076
Maximum deviation = 0.146

Chloride salt** in lithium:

\[ L_{Li} = 0.1767 - \frac{3808}{\theta_K} \] (400-650°C) (Figure 3)

Standard deviation = 0.117
Maximum deviation = 0.151

where \( L_{Na} \) and \( L_{Li} \) = Log\(_10\) mole fraction chloride salt dissolved in sodium and lithium metal respectively.

DISCUSSION

The low temperature solubilities of chloride salt in sodium measured in this study fit an extrapolation of the higher temperature data of reference 5. This result was not expected since the chloride sources used in this work were mixtures of alkali and alkaline earth chlorides containing less than 30 wt. % NaCl in contrast to the pure sodium chloride used by Bredig and co-workers. This may be related to the fact that the metal phase in equilibrium with the mixed salts is nearly pure sodium containing only a percent or two of calcium and parts per million of barium and potassium.

* Chloride salt derived from sodium chloride (reference 5 data) and from the two mixtures of Table I.

** Chloride salt derived from the KCl-LiCl mixture of Table II.
REFERENCES

1. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 18, p. 444.

2. U.S. Patent 2,850,442, W. S. Cathcart et al, 9/2/58.

3. U.S. Patent 3,020,221, W. H. Loftus, 2/6/62.

4. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 12, p. 535.

5. Bredig, M. A., Johnson, J. W. and Smith, Wm. T., Jr., J.A.C.S., 77, 307-12 (1955).

6. Bredig, M. A. and Bronstein, H. R., J. Phys. Chem., 64, 64 (1960).
### TABLE I

Chloride Salt Solubility in Sodium Metal

| Salt | Temp, °C | Equilibration Time, hrs | Mole Fraction Chloride (Cl) |
|------|----------|--------------------------|-----------------------------|
| Melt A | 142      | 72                       | 1.362 X 10^{-5}             |
|       | 204      | 24                       | 1.427 X 10^{-5}             |
|       | 204      | 24                       | 1.427 X 10^{-5}             |
|       | 290      | 24                       | 1.427 X 10^{-5}             |
|       | 368      | 62                       | 4.02 X 10^{-5}              |
|       | 368      | 62                       | 2.98 X 10^{-5}              |
|       | 494      | 48                       | 5.28 X 10^{-4}              |
|       | 606      | 48                       | 2.94 X 10^{-3}              |
|       |          | 23                       | 2.39 X 10^{-3}              |
| Melt B | 142      | 72                       | 1.362 X 10^{-5}             |
|       | 204      | 24                       | 1.427 X 10^{-5}             |
|       | 204      | 24                       | 1.03 X 10^{-5}              |
|       | 290      | 24                       | 1.56 X 10^{-5}              |
|       | 368      | 62                       | 4.15 X 10^{-5}              |
|       | 368      | 62                       | 3.76 X 10^{-5}              |
|       | 494      | 48                       | 4.21 X 10^{-4}              |
|       | 606      | 48                       | 2.79 X 10^{-3}              |
|       | 606      | 23                       | 1.63 X 10^{-3}              |
|       | 606      | 23                       | 2.20 X 10^{-3}              |
| NaCl* | 550      | -                        | 1.2 X 10^{-3}               |
|       | 649      | -                        | 7.5 X 10^{-3}               |
|       | 750      | -                        | 1.8 X 10^{-2}               |
|       | 781      | -                        | 2.2 X 10^{-2}               |
|       | 784      | -                        | 2.4 X 10^{-2}               |
|       | 790      | -                        | 2.9 X 10^{-2}               |
|       | 832      | -                        | 4.2 X 10^{-2}               |
|       | 874      | -                        | 5.8 X 10^{-2}               |
|       | 913      | -                        | 8.3 X 10^{-2}               |
|       | 957      | -                        | 1.11 X 10^{-1}              |

| Melt A | Melt B |
|--------|--------|
| NaCl, wt. % | 28.5   | 23.2   |
| CaCl₂, wt. % | 23.3   | 17.0   |
| BaCl₂, wt. % | 48.2   | 49.3   |
| KCl, wt. %   | 1.2    | 9.0    |

*Data for chloride derived from NaCl are from Bredig, Johnson and Smith, ref. 1.*

541
### TABLE II

**Chloride Salt* Solubility in Lithium Metal**

| Temp, °C | Equilibration Time, hrs | Mole Fraction Chloride (Cl) |
|---------|--------------------------|-----------------------------|
| 200     | 24                       | $6.26 \times 10^{-6}$       |
| 250     | 48                       | $3.91 \times 10^{-6}$       |
| 250     | 48                       | $4.69 \times 10^{-6}$       |
| 250     | 48                       | $3.91 \times 10^{-6}$       |
| 295     | 48                       | $1.95 \times 10^{-6}$       |
| 295     | 48                       | $4.11 \times 10^{-6}$       |
| 349     | 72                       | $2.54 \times 10^{-6}$       |
| 349     | 72                       | $4.11 \times 10^{-6}$       |
| 399     | 48                       | $2.54 \times 10^{-6}$       |
| 399     | 48                       | $4.50 \times 10^{-6}$       |
| 450     | 48                       | $7.04 \times 10^{-6}$       |
| 450     | 48                       | $6.06 \times 10^{-6}$       |
| 454     | 96                       | $8.61 \times 10^{-6}$       |
| 428     | 48                       | $7.24 \times 10^{-6}$       |
| 630     | 48                       | $1.06 \times 10^{-4}$       |
| 533     | 48                       | $2.49 \times 10^{-5}$       |
| 323     | 96                       | $1.95 \times 10^{-6}$       |
| 228     | 96                       | $2.54 \times 10^{-6}$       |

*Chloride derived from a mixture of 50 wt. % LiCl, 50 wt. % KCl. Metal phase in equilibrium is substantially pure lithium.
Figure 1. Apparatus

Figure 2. Solubility of Chloride in Sodium

Figure 3. Solubility of Chloride in Lithium