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Molten Carbonate Fuel Cell Research at ORNL

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OAK RIDGE NATIONAL LABORATORY

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CHEMISTRY DIVISION

MOLTEN CARBONATE FUEL CELL RESEARCH AT ORNL

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†Part time on Fuel Cell Program.
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SUMMARY

This document summarizes the activities at ORNL during the period July 1976 to February 1977 on the molten carbonate fuel cell program, funded by the ERDA Division of Conservation Research and Technology. This period marks the initiation of molten carbonate fuel cell research at ORNL, making use of the extensive background of expertise and facilities in molten salt research. The activities described in this report include a literature survey on molten carbonates, design, acquisition and installation of apparatus for experimental studies of molten carbonates, initial experiments on materials compatibility with molten carbonates, electrolysis experiments for the determination of transference numbers, and theoretical studies of transport behavior and the coupling of mass flows in molten carbonate mixtures.

Significant accomplishments were: the theoretical prediction of a possibly appreciable change in the alkali ion ratio at molten carbonate fuel cell electrodes, operated at high current densities, as a result of mobility differences of the alkali ions; design, construction and assembly of an electrolysis cell, and initiation of measurements of composition profiles in mixed alkali carbonate electrolytes; initiation of differential scanning calorimetry of pure alkali carbonates for quantitative measurement of transition enthalpies, eventually leading to new, more reliable, values of the enthalpies and free energies of formation of the pure and mixed carbonates.

1. INTRODUCTION (J. Braunstein)

The projected growth of U. S. energy demand, the decreasing supplies and increasing costs of petroleum and natural gas, and the adverse environmental effects of increased combustion of hydrocarbon and carbonaceous fuels combine to emphasize the need for more efficient utilization of fuels in the generation of electricity¹. Direct electrochemical utilization of fuels by means of fuel cells, especially at elevated temperatures, offers one means of electrical energy generation that is potentially more efficient than combustion of the fuels. One of the promising candidates is the molten carbonate fuel cell with gaseous mixtures containing hydrogen and carbon monoxide, derived from hydrocarbon or carbonaceous fuels and water, as the active components of the fuel². The development of fuel cells of long life and high performance characteristics requires both a detailed knowledge of physicochemical properties of specified systems and a general understanding of the phenomena occurring in the molten salt electrolyte, at the electrodes, and in the auxiliary materials. Such understanding must be of sufficient depth to enable prediction of the effects of changes of design parameters such as electrolyte composition, fuel and oxidant gas composition, and supporting matrix on the life and performance characteristics of the fuel cells.

The program in the Chemistry Division of ORNL provides basic supportive research to the molten carbonate fuel cell program in the areas of experimental measurements and theoretical interpretation of the physicochemical behavior of molten carbonate electrolytes and their interactions with electrodes, gases and containment materials. Electrochemical and thermochemical methods are employed to determine properties such as electrical conductance, transference numbers, and other transport and thermodynamic properties relevant to melt stability and performance as a function of melt composition and gas composition. The experimental results and theoretical interpretation will be made available for the optimization of electrolyte composition and the provision of quantitative criteria needed in the development and demonstration of high-performance

high temperature fuel cells. The program at ORNL was initiated as a 1-1/2 man effort drawn from a broad background of expertise and facilities for experimental and theoretical molten salt and electrochemical research.

2. LITERATURE SURVEY (H. R. Bronstein)

One of the initial efforts of ORNL in the Molten Carbonate Fuel Cell Program was to provide input to a comprehensive survey of the recent literature on molten alkali carbonates covering not only their physical properties but all aspects relevant to fuel cell operation. The aim of the survey was to compile a critically evaluated data base and to identify information gaps and discrepancies for which reevaluation or new measurements are needed. Since much of the literature through 1970 has been summarized in reviews published up to that date, our search began with the years 1971 to the present. Using Chemical Abstracts, and the information retrieval services of S.D.C.'s "ORBIT" (International Search Service), Lockheed's "Dialog" and ERDA's "RECON", we have compiled a list of some 80 new references pertaining to alkali carbonate melts and carbonate fuel cells. These references have been incorporated in a review published as a quarterly status report of the Institute of Gas Technology².

3. MATERIALS COMPATIBILITY IN MOLTEN CARBONATES

3.1 Sodium Beta Alumina (H. R. Bronstein)

In order to determine thermodynamic properties of molten salt mixtures relevant to melt stability, vaporization equilibria and transport behavior, emf measurements of formation cells such as A/AX/X are desirable³. However, in the case of the alkali carbonates, reaction BX would occur with the pure alkali metals. Two alternatives are the use of alloys of low activity and the use of selective ion conductive membranes. Sodium beta alumina⁴ is a sodium ion solid ionic conductor, and an investigation of its feasibility for achieving a separation of the metal from the salt was initiated.

Initial results of contacting single crystal sodium beta alumina with the molten ternary carbonate eutectic for two hours at 725°C in a gold boat showed no reaction with the melt, as determined by microscopic and ion probe studies. Continued long term, ten day tests showed no visible signs of attack by the ternary eutectic melt; however, a small weight gain indicated the possibility of some replacement of sodium ions by potassium, known to occur in nitrate melts⁵. Chemical analysis showed a negligible amount of lithium ion in the beta alumina, but approximately one-third of the sodium ions had been replaced by potassium ions. The results suggest that sodium beta alumina may be applicable as a sodium conductive membrane to separate molten sodium from melts for unambiguous electrochemical measurements in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$, and possibly also in $\text{K}_2\text{CO}_3\text{-Na}_2\text{CO}_3$, if the mobility of the sodium ion is sufficiently greater than that of the potassium ion in solid sodium beta alumina.

Highly purified and well characterized sodium beta alumina powder has been obtained from Dr. P. E. D. Morgan of The Franklin Institute. Tubes to be prepared from this material will be evaluated as to their usefulness in electrochemical measurements of thermodynamic and transport properties.

3.2 Boron Nitride (H. R. Bronstein and J. Braunstein)

In electrochemical measurements in molten alkali-carbonates, refractory insulators stable to the carbonate melts are needed. High density alumina or lithium aluminate are the recommended container materials, but for studies of the chemical interaction of alumina or of lithium aluminate with melts, as well as for versatility of experimental design, alternative insulators would be desirable. Both thermodynamic calculations and experimental tests indicated that pyrolytic boron nitride might have limited applicability. Thermodynamic estimates were based on an assumed corrosion reaction of BN in carbonates given by

From data in the JANAF Tables, the standard free energy change for this reaction is -25 kcal at 1000K (-12 kcal/mol BN), and -10 kcal at 700K (-5 kcal/mol BN) indicating instability of the BN, unless there is a

kinetic barrier to its decomposition.

The effect of varying reducing or oxidizing conditions can be evaluated by writing the free energy as

$$\Delta G = \Delta G^\circ + RT \ln \frac{p_{N_2} a_{B_2O_3} p_{CO}^3}{a_{BN} p_{CO_2}^3}$$

The activity of solid BN is unity. If an acceptable activity of the corrosion product B_2O_3 is arbitrarily set at 10^{-3} , the expression, at 1000K, becomes

$$\Delta G/\text{kcal} = \Delta G^\circ_{1000K} + 4.600 \log \left[p_{N_2} \left(\frac{p_{CO}}{p_{CO_2}} \right)^3 10^{-3} \right]$$

$$\Delta G_{1000K} = -33.6 + 4.6 \log p_{N_2} \left(\frac{p_{CO}}{p_{CO_2}} \right)^3$$

The second term on the right can be increased by increasing N_2 pressure or the CO/CO_2 ratio, the latter having the greater effect. At one atmosphere pressure of N_2 a ratio $p_{CO}/p_{CO_2} \sim 1000$ would change the sign of the free energy, indicating stability unless some other corrosion reaction occurs. The calculation suggests that under sufficiently reducing conditions, BN might be stable to carbonates even in the absence of a kinetic barrier. In experimental tests at 500°C , under a CO_2 pressure slightly greater than atmospheric, pyrolytic boron nitride specimens contacted with the molten ternary eutectic $(\text{Li-Na-K})_2CO_3$ in a gold boat for a period of 5 hours exhibited no visible signs of attack or weight change. However, specimens held at $600\text{--}700^\circ\text{C}$ for 3 hours showed a weight loss of 5%. The experimental tests indicate the possible limited compatibility of pyrolytic boron nitride with carbonate melts at temperatures below 550°C . The calculations show that evaluation of the possible usefulness of BN would require a more detailed study of possible stabilization in controlled reducing and nitrogenous atmospheres.

4. TRANSPORT BEHAVIOR

4.1 Theoretical and Model Studies* (J. Braunstein, C. E. Vallet, D. Heatherly)

In the development of more efficient batteries and fuel cells for energy storage and conversion, high temperature devices offer the possibility of lower losses from ohmic, activation and mass transport polarization, and from degradation of the thermal energy available from the primary source. Molten salts offer the capability of high temperature operation, and their mixtures provide a wide range of choices for physical and electrochemical properties of electrolytes⁶. Mass transport polarization in electrolytic devices such as batteries and fuel cells may arise from two kinds of concentration gradients. The first, commonly recognized kind, is that of electroactive species which may be present at low concentrations in the melt, e.g., H_2 , CO_2 , O_2 , H_2O and CO in molten carbonates. A second, frequently overlooked, contribution may arise from concentration gradients of the major constituents as a result of migrational separation or migrational polarization of, e.g., Li^+ and K^+ in a mixture of Li_2CO_3 and K_2CO_3 in a carbonate fuel cell^{7,8,9}. Although the primary effect of such concentration gradients of Li^+ and K^+ on cell voltage is probably small, the secondary effects of changes in composition at the electrode surfaces may be significant, and need to be considered in cell design and modeling.

In a fuel cell analog with a (binary) Li_2CO_3 - K_2CO_3 electrolyte, a CO anode and CO_2 , O_2 cathode the electrodes behave as membranes permeable to carbonate ion constituent and, relative to an electrode, the transference number of carbonate ion is $t_C^V = -1$. In terms of the Hittorf transference number of Li^+ relative to carbonate ion ($t_L^C = 1 - t_K^C$; $t_C^C = 0$), the flux equation, derived from the thermodynamics of irreversible processes, for the flow of lithium ions relative to the electrode surface is⁷

* The theoretical basis of the model studies applied to molten carbonate fuel cell electrolytes is part of a program "Physical Chemistry of Molten Salts in Energy Utilization," supported by the Materials Science Branch of ERDA's Division of Physical Research.

$$-J_L^V = D \frac{\partial C_L}{\partial \xi} - (t_L^C - X_L) I/F \quad (2)$$

The boundary conditions at the electrode-electrolyte interfaces ($\xi=0$; $\xi=\Xi$) become, since alkali ions do not cross the boundaries,

$$\left[J_L^V = 0; \quad I = F \frac{D}{t_L^C - X_L} \frac{\partial C_L}{\partial \xi} \right]_{\xi=0, \xi=\Xi}$$

The diffusion-migration equation becomes

$$\frac{\partial C_L}{\partial t} = \frac{\partial}{\partial \xi} \left[D \frac{\partial C_L}{\partial \xi} - (t_L^C - X_L) I/F \right] \quad (3)$$

Computer simulation of composition profiles by means of a finite difference algorithm⁸ has been carried out for a molten carbonate fuel cell analog using plausible estimates of the physical parameters for an order of magnitude estimate of the effect^{7,10}. The transference number was written $t_L^C = \frac{C_L U_L}{C_L U_L + C_K U_K}$ with constant but unequal alkali ion

mobilities relative to carbonate. The mobility ratio of the alkali cations was taken as 2 ($U_L/U_K \sim 2$). A constant current density of 0.15 A/cm^2 was employed in the initial calculations, with an electrode separation of 0.2 cm. Although some computations with variable diffusion coefficient have been carried out, the essential features are indicated with a constant $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Figure 1 shows the depletion with time of Li^+ at one electrode. A nearly symmetrical accumulation occurs at the other electrode. A significant concentration gradient develops in a short time, and a steady state is attained in about thirty to forty minutes. Since the direction of positive current flow through the cell is from the (negative) anode to the (positive) cathode, the more mobile cation (Li^+) is depleted at the anode and accumulated at the cathode. (If the cell were subjected to electrolysis, the more mobile Li^+ would accumulate at the negative electrode and be depleted at the positive electrode.)

Fig. 1. Migrational contribution to concentration change at positive electrode vs. square root of time.

Fig. 2. Migrational contribution to steady state composition profile.

With an initial composition of about 0.4 mole fraction Li_2CO_3 , as indicated in Fig. 2, the Li steady state concentration at the anode is nearly 20% below the initial, indicating a composition gradient of nearly 40% across the electrodes. Actual composition gradients would undoubtedly be modified by convection (which is reduced however, by the porous matrix containing the electrolyte), current variations, coupling to the flows of additional constituents and of thermal energy, effects of pore size and shape in the matrix and in the electrodes, edge effects, and (conceivably) the generation of dissipative structures. Nevertheless, these computations indicate the magnitude of the driving force towards a separation of the electrolyte components, which can have important consequences for the choice of electrolyte compositions and operating conditions, and emphasize the need for reliable transport property data. Wetting behavior, physical and chemical gas solubility, and phase stability in the electrolyte can be expected to differ at the two electrodes, affecting electrolyte losses in different regions of the cell, corrosion, and the possible precipitation of unwanted solid phases.

The effect of changed operating conditions (e.g., current density) or changed physical properties such as t , D , etc. (resulting from changes of the initial composition or changes effected by the pore structure) can be estimated from the initial slope of the plot in Fig. 1, which is proportional to $(t_L^C - x_L) I/\sqrt{D}$. (We have also derived analytical expressions for the steady state composition profile, and the results will be summarized in a forthcoming report.) The effect of decreasing electrode separation is to decrease the difference between the steady state compositions at the two electrodes, since the migrational composition change at one electrode will cause the other electrode to see a steeper diffusional gradient which tends to counteract further migrational separation.

Since the extent of migrational separation depends on the difference of cation mobilities, the effect might be expected to be smallest in mixtures of Na_2CO_3 and K_2CO_3 . In order to lower the freezing temperature and increase the electrical conductivity of fuel cell electrolytes, however, Li_2CO_3 - K_2CO_3 , Li_2CO_3 - Na_2CO_3 or ternary alkali carbonate mixtures

are more likely candidates so that migrational polarization may be a phenomenon that needs to be lived with and better understood.

Experimental tests of the above concepts and equations have been initiated. Apparatus for the measurement of composition profiles under the influence of current flow in alkali carbonate-lithium aluminate tiles are described in 4.2 below. Experimental tests of the validity of the migrational polarization equations are being carried out also in a simpler model system for which the transport coefficients (diffusion coefficients and transference numbers) are known, $\text{KNO}_3\text{-AgNO}_3$. Silica cells with silver electrodes have been constructed for electrolysis experiments with free electrolyte and with electrolyte confined in a porous matrix consisting of silica frits of differing porosity. Concentrations at the electrode surface are determined as a function of time by monitoring the emf, and the porous frits are sectioned and analyzed following electrolysis to determine the composition profile. Preliminary experiments with the free electrolyte cells show initial time dependence of the concentration at the electrode surface consistent with our computations and the known diffusion coefficient and transference number. The long time behavior and the effects of porous matrix and of electrode separation are being investigated.

4.2 Electrolysis of $\text{LiAlO}_2\text{-(Li,K)CO}_3$ Tiles (H. R. Bronstein and J. Braunstein)

Among the needed transport coefficients in potential molten carbonate fuel cell electrolytes are the cation transference numbers relative to the carbonate ion. The classical methods for the measurement of transference numbers are: emf measurements of cells with and without transference; moving boundary; and the Hittorf (electrolysis) method. The first method requires electrodes reversible to a cation and an anion of the electrolyte and is not yet feasible for molten carbonate mixtures. The second requires boundary-sensing devices, which would be difficult to apply in molten carbonates. The Hittorf method is based on measurement by analysis of the net change in the quantity of an ion constituent in the vicinity of an electrode as a result of the faradaic process at that electrode and the migration of that ion constituent

towards (or away from) the electrode. In the application of the Hittorf method to a dilute constituent, the solution in the regions near the electrodes, where all of the composition changes take place, and in a central region undergoing no composition change are analyzed to determine the transference number in a small composition interval, and the electrode spacing is large enough to prevent diffusive mixing during the time of the electrolysis. Special consideration is needed in applying the method to the transference numbers of major constituents in a molten salt mixture. The basic equations of the Hittorf experiment are those of section 3.1, and Figs. 1 and 2 indicate several constraints in the application of a Hittorf-type method to binary molten salt mixtures:

- 1) The number of coulombs in the electrolysis must be large enough to permit accuracy in the small differences of composition to be measured.
- 2) The composition change between the electrode surface and the central region of unchanged composition must be small enough that the calculated (average) transference number is meaningful for the average concentration.
- 3) The electrode separation, current density, and electrolysis time must be such as to permit a central region of unchanged composition between the regions of changed composition at the electrodes. Electrolysis experiments have been initiated, both to evaluate the feasibility of the Hittorf method for transference numbers and, perhaps more important, to obtain direct measurements of composition profiles across an electrolyzed tile.

An apparatus constructed for evaluation of a Hittorf-type measurement of transference numbers and for determination of composition profiles produced by current flow in alkali carbonate-lithium aluminate tiles is illustrated in Fig. 3. The carbonate tile^{*}, E, is a disk 74 mils thick by 1 inch in diameter with a composition of 50 weight percent of equimolar Li_2CO_3 - K_2CO_3 and 50 weight percent lithium aluminate. The tile is compressed between the sintered nickel disk^{*} electrodes, D, by means of the insulating ("Lucalox") telescoping cylinders, B, when the two stainless steel sections are bolted together. Contacting the

^{*} Supplied by Dr. John Ackerman, Argonne National Laboratory.

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Fig. 3. Hittorf cell.

nickel electrodes are the perforated stainless steel disks, C, of the current leads. The perforations permit gas contact with the sintered nickel electrodes. The closed end support tubes, A, welded to the steel disks serve two purposes: 1) as a current lead out through the gland fittings at either end of the apparatus; 2) for positioning thermocouples to measure the temperature at each electrode. Also shown is the exposed end of the insulated gold wire, F, which makes contact with the carbonate tile and is intended to serve as the reference electrode $\text{Au}, \text{CO}_2, \text{O}_2, \text{CO}_3^{2-}$. The nickel electrodes were preconditioned at 565°C with a 50-50 volume percent mixture of CO_2 and O_2 to convert them to Ni-NiO electrodes for the electrolysis reaction

A PAR Model 173 Potentiostat/Galvanostat and a Model 179 Digital Coulometer are used for the constant current electrolysis. In the initial experiment, the electrolysis time was five hours at a current density of 40 mA/cm^2 . A section of the electrolyzed carbonate tile perpendicular to the faces has been cut and polished, and the composition profile will be determined using x-ray fluorescence and ion probe scanning techniques for analysis of Li, K and Al. A similar analysis, in addition to chemical analysis of tile sections, is being carried out on tile samples prior to electrolysis in order to provide a blank determination and to evaluate the inhomogeneity in the distribution of the equimolar Li_2CO_3 - K_2CO_3 within the tile.

5. THERMODYNAMIC PROPERTIES

5.1 Thermochemical Properties of Alkali Carbonates (S. Cantor and D. E. Heatherly)

Accurate thermochemical properties are vital for predicting the many equilibria that occur in the preparation and in the operation of fuel cells. We have begun a critical review, starting with the electrolyte components.

The thermochemical functions of Li_2CO_3 , Na_2CO_3 and K_2CO_3 are compiled in the JANAF tables¹¹, the last review of the data having been completed in March 1966. The tables for the three carbonates were examined and some errors and omissions were found:

Li_2CO_3 : There is an error in the listing of a solid transition at 623°K with an estimated enthalpy of transition of 0.134 kcal/mol⁻¹. This transition was attributed to Reisman¹² who obtained the data, via DTA, in the absence of a CO_2 atmosphere over the salt sample; in fact, Reisman assigned the result to either a solid transition in Li_2O or, more likely, to a eutectic at high carbonate concentration in the system, $\text{Li}_2\text{O-Li}_2\text{CO}_3$. Thus, there is no experimental basis for assigning a solid transition to Li_2CO_3 at 623°K.

In the JANAF listing, the other solid transition, at 683°K, is estimated to have a transition enthalpy of 0.535 kcal mol⁻¹, exactly one twentieth of the listed enthalpy of fusion. This value was obtained from the relative DTA areas given in Reisman's paper. Given the qualitative nature of the original data, the value of 0.535 kcal mol⁻¹ must be considered very uncertain.

Na_2CO_3 : The listed temperature of solid transition (723.15°K) and its associated enthalpy (0.165 kcal mole⁻¹) are very questionable. In fact, it is now known from crystallographic and DTA evidence¹³ that Na_2CO_3 has two solid transitions, at ~ 634°K and at ~ 762°K.

Since the last JANAF update for Na_2CO_3 , new, more reliable heat capacities have been measured¹⁴ in the range, 15-300°K. When the new value for S_{298}° (=32.26 cal mol⁻¹ deg⁻¹) is applied, the standard entropy of formation and free energy of formation at 298.15°K, now change to -67.19 cal mol⁻¹ deg⁻¹ and -250.23 kcal/mol⁻¹.

K_2CO_3 : As for the other two alkaline carbonates, there is question about solid transitions. JANAF does not note a solid transition, even though Reisman had reported one at 695°K.

It seems clear that some JANAF-listed properties (especially enthalpy of transition and heat capacities) of the crystalline alkali carbonates are incorrect. These errors increase the uncertainties in the formation thermochemistry of these compounds. Apparently, B. K. Anderson¹⁵,

Technical University of Denmark, has also noted uncertainties in the JANAF data.

Finally, the formation thermochemistry given in the JANAF tables are shown as Table I. This is noted here because a similar table given by Maru et al., p. 86, contains some rather large errors.

Table I. STANDARD ENTROPY, ENTHALPY AND FREE ENERGY OF FORMATION AT 298.15K BASED ON JANAF TABLES

	ΔS_{298}°		ΔH_{298}°		ΔG_{298}°	
	cal mol ⁻¹ deg ⁻¹	J mol ⁻¹ deg ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹	kcal mol ⁻¹	kJ mol ⁻¹
Li ₂ CO ₃	-67.216	-281	-290.64	-1216	-270.6	-1132
Na ₂ CO ₃	-66.281	-277	-270.26	-1131	-250.5	-1048
K ₂ CO ₃	-68.603	-287	-274.9	-1150	-254.4	-1064

DSC Measurements: The foregoing indicated a real need for improvement in the thermochemical data of the alkali carbonates. Accordingly, we have initiated a calorimetric study of Li₂CO₃, Na₂CO₃, and K₂CO₃, using a Perkin-Elmer (DSC-2) Differential Scanning Calorimeter. This instrument is ideally suited for determining enthalpies of transition and changes of heat-capacity that occur in the range, -65° to 727°C.

Preliminary measurements have been carried out on 5-10 mg samples of the carbonates sealed in standard DSC gold containers. The samples had been dried by passing CO₂ for 18 hours at 425°C over analytical-or reagent-grade materials contained in a shallow gold vessel; this treatment presumably converted trace oxide and hydroxide into carbonate. To prevent contamination by moisture, all sample transfer and sealing operations were carried out in a helium-filled glovebox.

The results obtained thus far are presented in the following table:

DSC MEASUREMENTS IN CRYSTALLINE Li_2CO_3 , Na_2CO_3 , K_2CO_3

	Transition Temp.	Type of Transition	Interpretation of DSC Thermograms
Li_2CO_3	410°C	First-order	$\Delta H = 200 \pm 20 \text{ cal mol}^{-1}$
Na_2CO_3	357-360°C	Second-order	Slight upsweep in C_p with temp., then C_p decreases $\sim 6 \text{ cal mol}^{-1} \text{ deg}^{-1}$
	484-488°C	Second-order	Roughly the same, except C_p decreases $\sim 9 \text{ cal mol}^{-1} \text{ deg}^{-1}$
K_2CO_3	420-422°C	Second-order	Same features as for Na_2CO_3 ; C_p decreases $\sim 13 \text{ cal mol}^{-1} \text{ deg}^{-1}$

All samples were studied in the full temperature range, -65° - 727°C . Only Li_2CO_3 showed first order transitions: at 410°C and at $\sim 725^\circ\text{C}$, the melting point. (The instrument is presently being used to obtain the heat of fusion of Li_2CO_3 .) The transition temperature observed for Na_2CO_3 and for K_2CO_3 has been previously noted¹³ but the type of transition has not been clear. It is expected that better resolution of transition energetics in Na_2CO_3 and K_2CO_3 will be obtained when we measure heat capacities.

In the near future, DSC measurement of carbonates and other fuel cell materials will continue. We plan to study the following:

- enthalpy of fusion of Li_2CO_3 and of LiKCO_3
- enthalpy of transition of LiAlO_2
- heat capacities of crystalline Li_2CO_3 , Na_2CO_3 , and K_2CO_3 .

5.2 Free Energies of Molten Carbonate Mixtures

5.2.1 Electrochemical Measurements (H. R. Bronstein)

With the demonstrated compatibility of sodium beta alumina to alkali carbonate melts, thermodynamic measurements can now be made on Na_2CO_3 containing melts by emf measurements of the formation cell:

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{Na}_2\text{CO}_3}}{P_{\text{CO}_2} P_{\text{O}_2}^{1/2}}$$

The cell can be employed to obtain the composition dependence of activity coefficients in Na_2CO_3 -containing melts. Furthermore, the free energy of formation of Na_2CO_3 in the precipitating solid phase (pure Na_2CO_3 or solid solution) can be obtained at various temperatures by slightly exceeding the solubility limit in the various carbonate melts.

An apparatus is now being fabricated for performing the above emf experiment. A Hasting Gas Blending System has been obtained for accurately controlling the CO_2 - O_2 ratios and both the incoming and outgoing gas stream from the carbonate electrode will be analyzed with a Carle Analytical Gas Chromatograph Model 111H.

5.2.2 Activity Coefficients from Phase Diagrams (S. Cantor)

A review of the phase diagrams of the alkaline carbonates is being carried out: a) to provide estimates for comparison with activity coefficients to be derived from upcoming emf measurements (by H. R. Bronstein), b) to determine whether or not the activity coefficients fit simple models of solution, and c) to uncover uncertainties in the phase diagrams themselves or in the thermodynamic data (heats of fusion and heat capacities) through which activity coefficients are computed from liquidus temperatures.

Activity coefficients obtained from the phase diagrams of the systems, Li_2CO_3 - Na_2CO_3 and Li_2CO_3 - K_2CO_3 , are listed in Table II. Deviations from ideality are greater in Li_2CO_3 - K_2CO_3 than in Li_2CO_3 - Na_2CO_3 . Excess partial molar free energies of mixing, calculated from

these activity coefficients, tend to be roughly 0.5 kcal/mol more negative than the corresponding partial molar heats of mixing, the latter obtained from Andersen and Kleppa¹⁶. Thus, these binary molten mixtures are definitely not regular solutions. In fact, for Li_2CO_3 - Na_2CO_3 the magnitude of the $T\Delta\bar{S}^{\text{XS}}$ term is greater (i.e., more negative) than the corresponding partial molar heat of mixing.

Finally, it should be remembered that in calculating the activity coefficients (and excess free energies), we assumed that, at the liquidus temperature, a pure alkaline carbonate, not a solid solution, precipitates from the melt. For the Li_2CO_3 -rich side of the phase diagrams, this is, in all probability, a valid assumption. However, for the Na_2CO_3 -rich side (of the Li_2CO_3 - Na_2CO_3 system), it is not difficult to imagine the smaller Li^+ ion fitting into a cation lattice site. Although there is presently no evidence for solid solubility of Li_2CO_3 in Na_2CO_3 , the activity coefficients of Na_2CO_3 presented in Table II should, nevertheless, be used with some caution.

Table II

ACTIVITY COEFFICIENTS^a IN Li_2CO_3 - Na_2CO_3 AND
 Li_2CO_3 - K_2CO_3 DERIVED FROM LIQUIDUS TEMPERATURES^b

$\text{Li}_2 - \text{Na}_2\text{CO}_3$			$\text{Li}_2\text{CO}_3 - \text{K}_2\text{CO}_3$		
Mol Frn Li_2CO_3	$\gamma_{\text{Li}_2\text{CO}_3}$	$\gamma_{\text{Na}_2\text{CO}_3}$	Mol Frn Li_2CO_3	$\gamma_{\text{Li}_2\text{CO}_3}$	$\gamma_{\text{K}_2\text{CO}_3}$
0.9	0.903	----	0.9	0.871	----
0.8	0.780	----	0.8	0.680	----
0.7	0.561	----	0.72	0.462	----
0.6	0.500	----	0.62	0.301	----
0.55 ^c	0.414	----	0.427	----	0.441
0.54 ^c	0.399	----	0.42	----	0.457
0.533 ^c	0.389	----	0.4	----	0.494
0.503 ^c	----	0.409	0.3	----	0.663
0.50 ^c	----	0.413	0.2	----	0.811
0.48	----	0.463	0.1	----	0.930
0.45	----	0.509			
0.4	----	0.579			
0.3	----	0.726			
0.2	----	0.843			
0.1	----	0.935			

^aCalculated from the eq., $\ln \gamma_N = \int_{T_M}^T (\Delta H_f / RT^2) dT$; N is mole fraction, T_M is the melting temp. (K) of the pure component, ΔH_f is the heat of fusion; heat of fusion and heat capacity taken from G. J. Janz et al., Trans. Farad. Soc. 59, 841 (1963).

^bMost liquidus temp. taken from G. J. Janz and M. R. Lorenz, J. Chem. Eng. Data 6, 321 (1961).

^cLiquidus temp. from E. J. Cairns and D. I. MacDonald, Nature 194, 441, May 5, 1962.

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