Two Phase System
CaCl₂ - NaCl

Fig. 1

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THERMOCOUPLE FOR THERMAL ANALYSIS OF SALT BATHS

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I Claim. (Cl. 136—4)

This invention relates to the thermal analysis of fused salt baths. More particularly, it relates to the rapid thermal analysis of salt baths of the type used to produce alkali and alkaline earth metals, especially sodium. In one aspect the invention is concerned with a process for analyzing baths used to produce sodium. In another aspect it is concerned with apparatus necessary for carrying out the process.

Background and objects of the invention

Alkali and alkaline earth metals, sodium in particular, are commonly obtained by electrolytic reduction from their respective compounds. Common salt, the most abundant and the cheapest compound of sodium, is usually chosen as the raw material for producing this element. The process is generally carried out in a Downs cell, U. S. P. 1,501,756, or a modification thereof, employing a fused mixture of sodium and calcium chlorides. A mixture of salts is necessary because sodium chloride melts at too high a temperature for satisfactory use alone. Under proper conditions, sodium is practically the only metal plated out from the mixtures.

While mixtures of sodium and calcium chlorides may melt at much lower temperatures than sodium chloride alone, control of the bath composition is difficult as the electrolysis proceeds. Additions of sodium chloride are made continuously or from time to time to replace that electrolyzed. Small amounts of calcium chloride are also consumed and must be replaced. A difficulty arises in determining the amount of calcium chloride to add. Conventional quantitative analyses are unsatisfactory because they cannot be made fast enough. Heretofore, visual inspection of the crust forming on the surface of the fused mixture has been relied on as a means of control. When there is too much crust the sodium chloride content of the bath is too high and an addition of calcium chloride is needed. Obviously, this method is crude at best since other factors such as cell temperature produce similar results. Much skill on the part of the operator is, therefore, required. The control problem is complicated by the fact that barium chloride is present as an impurity in the salts added and gradually increases in concentration in the bath. The rate of increase is, however, fairly constant and barium concentration can be estimated by an experienced operator from the age of the bath.

Attempts have been made to substitute thermal methods of control for the visual method outlined but until the present time they have been unsuccessful. In many cases the determination of cooling curves, the most convenient form of thermal analysis, cannot be made precisely or quickly enough to permit their use in control work. Usually the lack of precision has resulted from the apparatus and procedure employed. In typical known procedures a sample of the molten salt is taken in a metal container and a thermometer immersed therein. The sample is then allowed to cool and the temperature observed to obtain the arrest points or temperatures at which changes in phase occur.

Inaccuracies creep into such determinations from several sources. The bulk of the metal container and of the thermometer, for example, can seriously affect the results obtained. Variable placement of the thermometer and variable cooling conditions such as local drafts yield results even more erratic. Difficulties of these types are particularly noticeable in the large quantities of sample heretofore considered necessary for accurate results.

Use of a large sample also permits segregation of one phase from the liquid almost immediately adjacent to the walls of the container. This single phase continues to freeze out for a relatively long period as the molten salt approaches the composition of the eutectic mixture. When a cooling curve is plotted for such a sample, the arrest point denoting a change of phase is frequently not sharp enough to be of practical value. If the thermometer is located at the heat center of the mass, the eutectic temperature of the salt combination will be recorded and the earlier change in phase will not be detected. If the thermometer is not at the heat center, an arrest point will be noted as the freezing layer physically covers the thermometer and isolates it from the freezing mass. The temperature recorded will only accidentally correspond to any true arrest point caused by a change in phase within the sample.

Obtaining accurate information from the freezing of a bulky sample, in addition, requires time. Locating some individual points on Figure 1, for example, may have required as much as 100 hours. Such cooling periods obviously cannot be used commercially, particularly in electrolytic processes where many cells varying in composition are employed.

A primary object of this invention is, therefore, provision of a method for determining the composition of a fused salt mixture.

Another object is provision of a method for performing the thermal analysis of a fused salt bath of the type used for the electrolytic production of sodium.

Another object of the invention is provision of an apparatus for performing the thermal analysis of fused salt baths in an accurate, efficient and rapid manner.

Statement of the invention

The above-mentioned and further objects may be achieved in accordance with this invention by determining the cooling curve of the fused sample. It is desired to analyze in a specially designed apparatus. This apparatus consists basically of a thermocouple developed especially for this particular usage connected to a potentiometric circuit terminating in a continuous recorder. An optional but useful piece of equipment is a furnace to receive the sample chosen and to provide a known ambient temperature therefor. Details of this invention will be evident from the remainder of the specification and from the attached drawings in which:

Figure 1 shows the freezing point curve of mixtures of calcium chloride and sodium chloride with compositions varying continuously from 100% calcium chloride to 100% sodium chloride. The curve is taken from Menge, Z. Anorg. Allgern. Chem., 72, 200 (1911);

Figure 2 shows cooling curves for three mixtures of calcium chloride-sodium chloride as determined by the method and apparatus of this invention;

Figure 3 is a view of the preferred embodiment of the thermocouple of this invention in perspective with part cut away to show detail;

Figure 4 is a perspective of a second embodiment of the thermocouple with part cut away; and

Figure 5 is a schematic view of the complete apparatus necessary to determine freezing points in accordance with this invention.

Figure 1 graphically illustrates the reciprocal effects of
3. Sodium and calcium chlorides on each other. Point A is the melting point of calcium chloride, 777 °C., while point C is the melting point of sodium chloride, 808 °C. A eutectic mixture of the two contains about 32% sodium chloride and melts at 500 °C. represented by point B. At point D, around 605 °C., a transition occurs between solid phases. The four points mentioned are connected by liquidus curve ABCD. The broken solid lines within the solid field on the right of the diagram represent transitions between solid phases.

The lowest possible operating temperature is desirable both to conserve energy and to minimize the vapor pressure of CaCl₂. At temperature F and 4NaCl-CaCl₂ a eutectic begins to form. As the double salt is deposited, the melt is depleted in NaCl and the composition of the liquid moves to the lower left along line BC. Complete solidification, of course, takes place at B, the eutectic.

Point E is arbitrarily chosen to facilitate the control of cell constants. Any shift from E to a lower position, as to G, increases cell efficiency because of the lowered operating temperature (560 °C.) but demands better cell analysis and control since the branches of the liquidus curves are closer together below E. Any points between E and G, i.e., between 38 and 36% NaCl, would also give satisfactory operation. H is the point at which the double salt begins to form from an initial mixture corresponding to that at G. Compositions varying down to that of the eutectic can, of course, also be used but will greatly increase the problems of control.

Figure 2 illustrates the application of cooling curves to salt analysis in the manner of the present invention. Curves for three CaCl₂-NaCl mixtures are shown, each with two transition points. Points F and G in curve 2 are lettered in accordance with Figure 1. Thus, the initial temperature-composition points are lettered E₁, E₂, and E₃ respectively, and represent the point E of Figure 1 as applied to samples 1, 2, and 3. The upper arrest points, point F in Figure 1, are lettered F₁, F₂, and F₃. In similar fashion the eutectics, differing only slightly in impurities, are labelled B₁, B₂, B₃ and B₄. The rapidity with which the curves can be determined is apparent from Figure 2 where each horizontal division represents 1.6 seconds.

The eutectic temperature for the pure CaCl₂-NaCl mixture is shown to be 500 °C. on Figure 1. The difference between the observed eutectic temperatures of Figure 2 and the theoretical is normally due to the barium chloride present and is constant for all points on the cooling curve. Consequently the lowering of the temperature at the eutectic, say 2 °C. as in the case of the curve of sample 3, can be read from the eutectic and added to all other points on the curve to obtain correct temperatures. Applying the 2 °C. correction to the upper arrest point F₂ of sample 3, Figure 2, the theoretical arrest point is found to be 542 °C. Referring again to Figure 1, a point at which the first change in phase occurs is 542 °C. as is seen to correspond to a NaCl content in the mixture of 34% and a CaCl₂ content of 66% in the eutectic mixture. Since the phases of these elements represent a salt mixture within the satisfactory range for cell operation, no adjustments in composition need be made.

The curve of sample 2 of Figure 2 is merely that of another sample similar to that of sample 3 and can be analyzed in the same manner. Obviously a larger correction will be needed for sample 2 than for sample 3. The curve of sample 1 reveals a eutectic temperature higher than 500 °C. The mixture, therefore, contains materials other than CaCl₂, NaCl and a small amount of BaCl₂. The method of calculation suggested is inapplicable until chemical analysis is used to orient the curve position.

The thermocouple 10 of Figure 3 overcomes the difficulties encountered with conventional thermocouples. Two wires 11 and 12 of dissimilar metals are shown connected at junction 13. Wire 12 spirals around wire 11 for several turns but may terminate in a few turns of constant diameter. This wire forms in effect an open cup or basket 14. The spiral at the bottom of the cup is almost essential to retain a liquid sample therein.

Junction 13 is preferably located at a point slightly below the geometrical center of the cup. Insulator 15, made of firecrete or other heat-resistant material, may optionally be employed to space the wires or leads properly. Insulator 16 is desirable to protect the hands of an operator. Sliding tube 17 (Figure 5) may be utilized to protect the contents of the basket from drafts if it is so desired.

The particular dissimilar metals from which the thermocouple can be made are not critical, i.e., any of the commonly used thermocouple pairs are suitable. Chromel-Alumel, iron-constantan and platinum-platinum alloy 10% rodium are alike satisfactory.

The size of the basket and the gauge of the wires employed is, however, of great importance. For best results the weight of the sample removed by the basket should weigh between about one and two times as much as the basket itself and their combined weights should total no more than about 0.4 g.

A satisfactory sample basket can be made from chromel-Alumel 24 A. W. G. wire having the Chromel wire bent downward from the junction 3½ inch. From this point below the junction the Chromel wire is bent in an Archimedean spiral having two turns of wire forming the frustum of a cone with the base upwards. Above the cone are an additional five turns of wire in the form of an open cylinder with an internal diameter of 3½ inch. The cylinder can be replaced by a continuation of the spiral but the replacement is unnecessary. All turns forming this basket should preferably be spaced apart by the diameter of one wire. The Chromel wire is displaced, at its termination within the basket, at a right angle to the circumference thereof and is extended parallel to the Alumel wire. The basket described will weigh about 0.2 g. and 0.2 g. of molten salt from a sodium chloride-calcium chloride bath.

The 24 A. W. G. wire is sufficiently rugged for plant service and gives cooling curves with fairly sharp arrest points. Finer wire, however, gives slightly more accurate results. A preferred basket is made from 30 A. W. G. Chromel-Alumel and has the same physical configuration as that shown above with one or two additional turns of Chromel wire. Such a basket weighs about 0.1 g. and will lift out about 0.2 g. of molten salt. This basket can also be used in plant operation but requires somewhat more care than does the less preferred basket.

Figure 4 shows an alternative embodiment of the thermocouple in which basket 14 is solid, i.e., contains no interstices. Basket 18 is of the same metal as wire 12 and preferably integral with it. Junction 13 is the connection between basket 14 and wire 11.

Figure 5 shows thermocouple 10 connected with other equipment, represented essentially in block diagram, necessary for carrying out the process of the invention. Wires 11 and 12 make connection at a cold junction 20 with leads 21 and 22. These leads are connected to a conventional source of back electromotive force 23 used to minimize the current drawn from the junction 20. This source 23 is connected through leads 24 and 25 to recorder 26 provided with its own power supply. Stylus 27 is actuated by the potential generated by the thermo-
couple 10 and records the cooling curve of the sample. In practice, the thermocouple is dipped into the salt mixture it is desired to analyze and removed to entrap a sample of appropriate size. It may be inserted into a furnace (not shown) if desired to maintain a constant temperature. The sample is then allowed to cool in the thermocouple and the cooling curve automatically plotted on the recorder. The correction made necessary by the presence of barium chloride is determined from the eutectic temperature, added to the temperature at the upper arrest point and the composition of the baths read from the curve of Figure 1. Additions of CaCl₂ are then made, if necessary, to bring the bath composition within the preferred range.

I claim:

A thermocouple for determining cooling curves comprising two wires of dissimilar thermoelectric metals joined together at an electrical junction, one of said wires spiralling around said junction to form an open cup adapted to hold a molten sample the cooling curve of which is to be determined.

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