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Reaction in the silver zinc cell

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An adiabatic calorimeter was used to measure the thermodynamics of the silver zinc cell. The charge and discharge reactions were shown to take place in two stages involving the production of argentous oxide and argentic oxide respectively. No thermal evidence was found to suggest the existence of a higher oxide of silver. The cell reactions were

$$2Ag + ZnO \rightleftharpoons Ag_2O + Zn, \ \Delta H = 158{\cdot}7 \ kJF^{-1} \qquad (1)$$

$$Ag_2O + ZnO \rightleftharpoons Ag_2O_2 + Zn, \ \Delta H = 176{\cdot}1 \ kJF^{-1} \qquad (2)$$

If the cell was left on open circuit for a long period, or the positive electrodes heated, reaction (2) was suppressed and the discharge took place via reaction (1), without any reduction in capacity.

Introduction

Although batteries containing silver positive electrodes have been studied for many years, the mechanisms of their reactions are still not fully established. Luther and Pokorny [1] showed that three potential plateaux were formed when a silver electrode was charged anodically in potassium hydroxide solution. The potentials of these plateaux were 0·34 V, 0·57 V and 0·74 V measured against a hydrogen electrode in normal potassium hydroxide solution. They associated the first plateau at 0·34 V with the formation of argentous oxide, Ag_2O, the second plateau at 0·57 V with the conversion of argentous oxide to argentic oxide, Ag_2O_2, and the third plateau at 0·74 V was attributed to 'silver peroxide', Ag_2O_3, which then decomposed to form argentic oxide. Hickling and Taylor [2] extended this work to suggest that during the formation of the first argentous oxide plateau there may have been some absorption of oxygen or the possible formation of a silver sub-oxide. Jones, Thirsk and Wynne-Jones [3] did not agree that 'silver peroxide' was an intermediate in the production of argentic oxide, suggesting that the high potentials recorded by Luther and Pokorny were caused by the evolution of oxygen taking place simultaneously with the oxidation of argentous oxide to argentic oxide. They argued however, that 'silver peroxide' could possibly exist by considering the oxides of silver to be formed by the introduction of oxygen into the octants of a face centred cubic silver lattice. The compound Ag_2O_3 could then be regarded as an intermediate between AgO with half-filled octants and a hypothetical AgO_2 with completely filled octants.

Pleskov [4] has also suggested the formation of silver peroxide at high anodic potentials and the silver peroxide potential has been reported by Radlein [5] and Nagel, Ohse, and Lange [6]. Jones *et al* [3] however, examined the oxidation products of silver using X-ray diffraction techniques but found no evidence for oxides higher than argentic oxide and this work has been confirmed by Wales and Burbank [7, 8] again using X-ray diffraction methods.

All previous measurements on the silver oxide system have been carried out using either potential measurements or X-ray diffraction studies, but no thermal measurements have been reported. A new approach has been made to the subject in these laboratories by making thermal measurements, in an adiabatic calorimeter [9] where it was shown that the sum of the electrical energy and the heat absorbed by a working galvanic cell was constant, and equal to the change in enthalpy, at all charge and discharge currents. Preliminary experiments in this calorimeter showed that the charge reaction took place

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in two stages, the oxidation of elementary silver to argentous oxide, and its subsequent oxidation to argentic oxide. The accuracy of the calorimeter was insufficient, however, to diststinguish between the charge reactions which involved cell cooling, but it has now been modified to measure decreases in cell temperatures, allowing the charge and discharge reactions of the silver oxide zinc system to be studied in detail.

Experimental

The adiabatic calorimeter [9] was modified to follow decrease in temperature and is shown in Fig. 1. Air was circulated through a ducting (A) by a fan (B) which gave a complete change of air every five seconds. The ducting contained an electrical heater (C) and a cooling coil (D) which was connected to a heat exchanger (E) via a pump (F). The coolant liquid circulating through the heat exchanger was a mixture of ethyl alcohol and castor oil and the heat exchanger itself was immersed in a mixture of either ice and water or solid carbon dioxide and ethanol. A maximum cooling rate of 2°C per minute was obtained inside the calorimeter. The cooling circuit was operated continuously and heat was supplied to the system when required by the electrical heater (C) by comparing the output of two thermistors (G) as described previously [9]. The cell temperature was measured with a thermistor thermometer which covered a range of 15°C–45°C and was sensitive to 0·01°C, its response time being faster than the conventional mercury thermometer because of its much lower thermal capacity. The cell voltage was measured with a potentiometer accurate to 0·1%.

A 15 Ah silver oxide zinc cell incorporating cellophane separators was filled with 33 ml of 7 N potassium hydroxide electrolyte and allowed to stand on open circuit for 72 hours. The thermal capacity of the cell was measured using cooling curves and found to be 221·8 J/°C. No significant change in thermal capacity was measured when the cell was in both a charged and discharged condition.

Charge and discharge cycles were carried out at various currents and the temperature and voltage of the cell was measured at regular intervals. Although the cell was initially at room temperature between 18°C and 21°C, it operated at between 25°C and 35°C depending on the experimental conditions for most of the time. Both the electrical and thermal energy which was either absorbed or evolved from the cell was calculated from this data. The change in enthalpy for the system, ΔH, was then found by adding these quantities. Similar measurements were carried out on a cell which had been stored in a dry charged condition for four years.

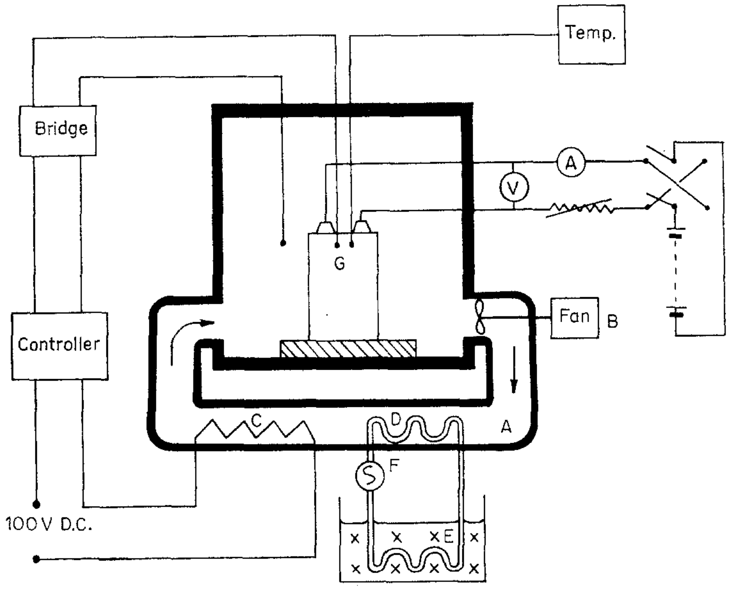

Fig. 1. Adiabatic calorimeter.

The effect of heat on the capacity of a silver electrode was measured by weighing an unformed silver electrode, forming it and re-weighing. It was then discharged at 1 A at 25°C and its capacity compared with the increase in weight during formation. After recharging, the electrode was again weighed and heated at 110°C for 15 minutes. It was then re-weighed and discharged again at 1 A.

Results

Charge reactions

The temperature and voltage characteristics of the cell when charged at 3 A are shown in Fig. 2 for the silver to argentous oxide reaction and in Fig. 3 for the argentous to argentic oxide reaction. Initially there was a linear decrease in temperature showing that the cell was evolving heat and this was accompanied by a potential plateau at 1·65 V corresponding to the formation of argentous oxide. After 90 minutes the potential suddenly rose to 1·95 V, the plateau corresponding to the formation of argentic oxide. This was accompanied by a rapid linear increase in temperature. Tables 1 and 2 show typical energy levels expressed in Joules per Faraday associated with each plateau. The rate of increase in temperature was measured by drawing tangents to the temperature time curves. The last column, ΔH, was obtained by adding the electrical energy absorbed and the heat absorbed by the system. The validity of this technique for deriving ΔH has been demonstrated previously [9]. Some error will be involved however, as the temperature varied over a range of some 10°C during the determinations. Hills [10] has shown that the temperature coefficients of the enthalpies of formation of argentous and argentic oxide are $-0{\cdot}000169$ and $+0{\cdot}0000570$ V°C^{-1} respectively. This represents a maximum error of some 2 mV in the cell potentials which produces an error of 0·01% in the value of ΔH which lies within experimental error. There was an open circuit period of 18 hours between the two stages of charge which accounts for the differences in working temperature together with the corresponding slight differences in potential between Fig. 2 and Fig. 3. These discrepancies have little effect on the results which are based solely on the rate of change of temperature.

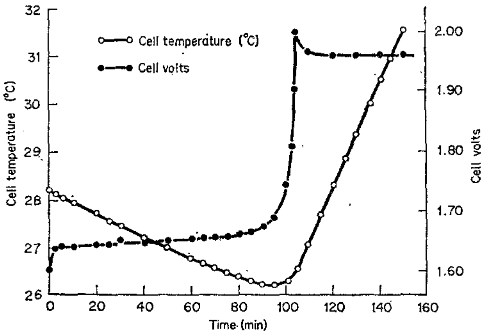

Fig. 2. Initial charge of silver zinc cell at 3A.

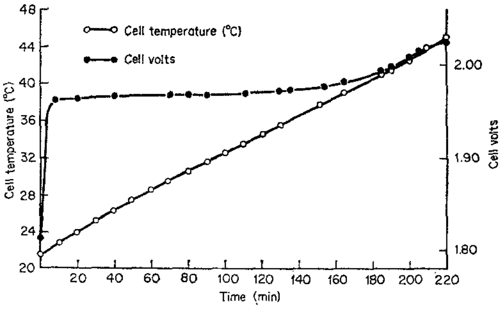

Fig. 3. Final charge of silver zinc cell at 3A.

Table 3 shows similar results when the battery was charged at 10 A. In this case heat was always evolved although the second part of the reaction was accompanied by a higher increase in temperature than the first.

Discharge Reactions

Fig. 4 and Table 4 show the results of a cell discharging at 5 A which had been dry charged and stored for a period of four years. After the initial polarization the voltage of the cell remained constant at 1·54 V during the discharge but the cell temperature increased linearly. The cell was then recharged at 5 A and allowed to stand on open circuit for two hours before discharging again. The results of this discharge are shown in Fig. 5 and Table 5 where the discharge was accompanied by the voltage plateaux, one at 1·78 V and the other at 1·53 V. The rate of increase in temperature increased at the transition point between the two voltage plateaux.

Table 1. Formation of argentous oxide

Time (min)	*Rate of increase in temp* (°Cs^{-1})	*Rate of heat absorbed* (*W*)	*Potential* (*V*)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
10	-4×10^{-4}	$8{\cdot}87\times10^{-2}$	1·640	157·5	2·85	160·4
25	-4×10^{-4}	$8{\cdot}87\times10^{-2}$	1·645	158·0	2·85	160·9
45	-4×10^{-4}	$8{\cdot}87\times10^{-2}$	1·650	158·4	2·85	161·3
135	$1{\cdot}89\times10^{-3}$	$-4{\cdot}18\times10^{-1}$	1·960	188·4	−13·48	174·9
150	$1{\cdot}89\times10^{-3}$	$-4{\cdot}18\times10^{-1}$	1·960	188·4	−13·48	174·9

Table 2. Formation of argentic oxide

Time (min)	*Rate of increase in temp* (°Cs^{-1})	*Rate of heat absorbed* (*W*)	*Potential* (*V*)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
20	$2{\cdot}2\times10^{-3}$	$-4{\cdot}88\times10^{-1}$	1·960	188·4	−15·70	172·7
60	$2{\cdot}1\times10^{-3}$	$-4{\cdot}66\times10^{-1}$	1·965	189·5	−14·97	174·5
100	$1{\cdot}66\times10^{-3}$	$-3{\cdot}69\times10^{-1}$	1·970	190·0	−11·85	178·2
160	$1{\cdot}66\times10^{-3}$	$-3{\cdot}68\times10^{-1}$	1·980	191·0	−11·85	179·2
210	$2{\cdot}16\times10^{-3}$	$-4{\cdot}79\times10^{-1}$	2·017	194·5	−15·40	179·1

Table 3. High rate charge of silver zinc cell

Time (min)	*Rate of increase in temp* (°Cs^{-1})	*Rate of heat absorbed* (*W*)	*Potential* (*V*)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
5	$1{\cdot}23\times10^{-3}$	$-2{\cdot}73\times10^{-1}$	1·695	163·5	−2·64	160·9
12·5	$1{\cdot}33\times10^{-3}$	$-2{\cdot}95\times10^{-1}$	1·707	164·5	−2·85	161·7
15	$1{\cdot}58\times10^{-3}$	$-3{\cdot}47\times10^{-1}$	1·715	165·5	−3·35	162·2
35	$8{\cdot}66\times10^{-3}$	−1·92	1·982	191·2	−18·55	172·7
50	$8{\cdot}66\times10^{-3}$	−1·92	1·999	192·8	−18·55	174·3

Table 4. Discharge of silver zinc cell after 4 years dry shelf life

Time (min)	*Rate of increase in temp* (°Cs^{-1})	*Rate of heat absorbed* (*W*)	*Potential* (*V*)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
15	$3{\cdot}90\times10^{-3}$	$-8{\cdot}66\times10^{-3}$	1·540	−148·0	−16·70	−164·7
35	$3{\cdot}05\times10^{-3}$	$-6{\cdot}75\times10^{-1}$	1·540	−148·0	−13·03	−161·0
60	$2{\cdot}90\times10^{-3}$	$-6{\cdot}43\times10^{-1}$	1·540	−148·0	−12·40	−160·4
85	$2{\cdot}50\times10^{-3}$	$-5{\cdot}52\times10^{-1}$	1·540	−148·0	−10·64	−158·6
100	$2{\cdot}40\times10^{-3}$	$-5{\cdot}32\times10^{-1}$	1·540	−148·0	−10·26	−158·3

Table 5. Discharge of silver zinc cell after two hours open circuit.

Time (min)	*Rate of increase in temp* ($^{\circ}Cs^{-1}$)	*Rate of heat absorbed* (W)	*Potential* (V)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
10	$1{\cdot}616\times10^{-3}$	$-3{\cdot}58\times10^{-1}$	1·779	−171·8	−6·91	−178·7
25	$2{\cdot}05\times10^{-3}$	$-4{\cdot}55\times10^{-1}$	1·760	−169·5	−8·79	−178·3
30	$2{\cdot}06\times10^{-3}$	$-4{\cdot}56\times10^{-1}$	1·742	−168·0	−8·84	−176·8
40	$3{\cdot}91\times10^{-3}$	$-8{\cdot}67\times10^{-1}$	1·645	−158·8	−16·70	−175·5
55	$3{\cdot}90\times10^{-3}$	$-8{\cdot}65\times10^{-1}$	1·525	−147·0	−16·65	−163·7

Table 6. Discharge of silver zinc cell to 1·6 *V*

Time (min)	*Rate of increase in temp* ($^{\circ}Cs^{-1}$)	*Rate of heat absorbed* (W)	*Potential* (V)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
20	$5{\cdot}83\times10^{-4}$	$-12{\cdot}93\times10^{-2}$	1·796	−173·3	−4·17	−177·5
35	$7{\cdot}33\times10^{-4}$	$-16{\cdot}23\times10^{-2}$	1·777	−171·5	−5·23	−176·7
50	$1{\cdot}041\times10^{-3}$	$-2{\cdot}306\times10^{-1}$	1·744	−168·3	−7·42	−175·7
65	$1{\cdot}31\times10^{-3}$	$-2{\cdot}90\times10^{-1}$	1·704	−164·3	−9·33	−173·6
80	$1{\cdot}93\times10^{-3}$	$-4{\cdot}28\times10^{-1}$	1·656	−159·7	−13·74	−172·6
95	$2{\cdot}5\times10^{-3}$	$-5{\cdot}50\times10^{-1}$	1·605	−154·8	−17·80	−172·6

Table 7. Further discharge of above cell after six days rest

Time (min)	*Rate of increase in temp* ($^{\circ}Cs^{-1}$)	*Rate of heat absorbed* (W)	*Potential* (V)	*Energy input* (kJF^{-1})	*Heat absorbed* (kJF^{-1})	ΔH (kJF^{-1})
30	$1{\cdot}708\times10^{-3}$	$-3{\cdot}78\times10^{-1}$	1·543	−149·0	−12·17	−161·2
60	$1{\cdot}66\times10^{-3}$	$-3{\cdot}68\times10^{-1}$	1·543	−149·0	−11·85	−160·9
100	$1{\cdot}25\times10^{-3}$	$-2{\cdot}78\times10^{-1}$	1·543	−149·0	−8·90	−157·9
120	$1{\cdot}183\times10^{-3}$	$-2{\cdot}62\times10^{-1}$	1·543	−149·0	−8·45	−157·5
140	$1{\cdot}025\times10^{-3}$	$-4{\cdot}28\times10^{-1}$	1·542	−148·8	−7·30	−156·1

Table 8. Effect of heating an argentic oxide electrode

Cycle	*Wt. of unformed plate (g)*	*Wt. of formed plate (g)*	*Wt. after heating (g)*	*Discharge capacity A. min*	*Discharge potential*	
					10 *min* (*V*)	50 *min* (*V*)
1	8·686	9·366	–	97·5	1·745	1·499
2	8·686	9·424	9·424	113·5	1·530	1·498

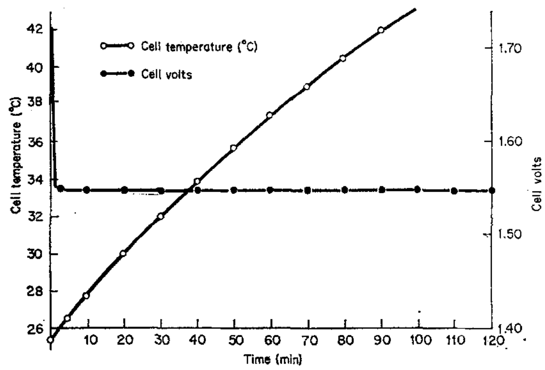

Fig. 4. Discharge of silver zinc cell at 5A after 4 years dry shelf life.

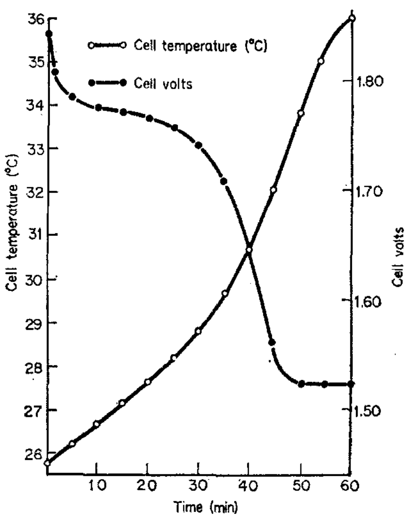

Fig. 5. Discharge of freshly charged silver zinc cell at 5A after 2 hours open circuit.

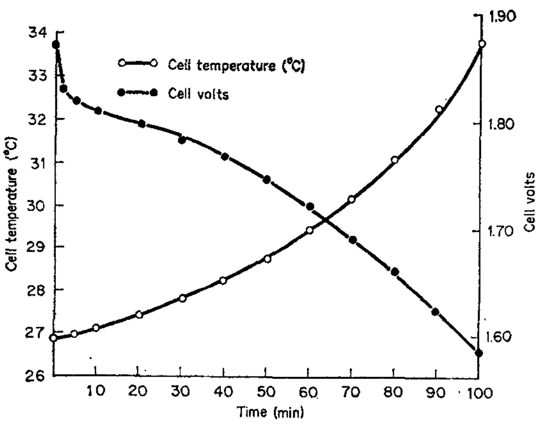

Fig. 6. Discharge of silver zinc cell at 3A after 45 min O/C. Argentic oxide stage.

The cell was then recharged to a potential of 2·10 V and was allowed to stand on open circuit for 45 minutes and was discharged to the end of the first potential plateau. The results are shown in Fig. 6 and Table 6. The cell was then allowed to stand on open circuit for six days and the discharge was continued, when a second potential plateau was obtained. Typical results are shown in Fig. 7 and Table 7.

Charges at 1·5 A and 5 A and discharges at 7·5 A were also carried out. The results were similar to those shown above and are included in the energy balance diagram in the discussion section.

The following table shows the increase in weight due to oxidation, the capacity and mean working voltage of a silver electrode which was charged and discharged at 1 A and 20°C before and after heating the dry plate at 110°C for 15 minutes.

It can be seen that no change in weight occurred when the electrode was heated, but Fig. 8 shows that the initial discharge potential of 1·75 V associated with argentic oxide was suppressed after the plate had been heated. No significant change in capacity occurred, the higher capacity of the second discharge being normal for this type of electrode. This is reflected in the increase in formed weight in the second cycle in Table 8.

Discussion

The changes in heat content associated with the charging of the cell at 10 A, some of which appear in Table 3, are tabulated in Table 9 together with the cell potentials and charge times.

It can be seen that ΔH started at 159·5 kJF^{-1} and then increased to 174·3 kJF^{-1} during the course of the discharge. This was compatible with the reaction being initially the oxidation of silver to argentous oxide followed by an increase in the proportion of the current being carried by the oxidation of argentous oxide to argentic oxide until this finally became the bulk of the reaction. However, ΔH never exceeded 176·1 kJF^{-1}, the energy associated with the reaction between argentic oxide and zinc. There was, therefore, no thermal evidence for the formation of a higher oxide than argentic oxide even though the above

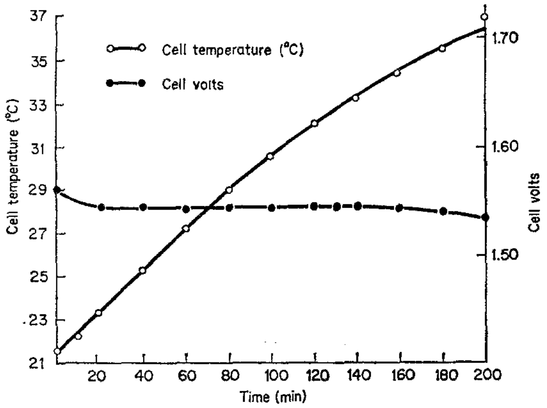

Fig. 7. Discharge of silver zinc cell at 3A after 6 days O/C. Argentous oxide stage.

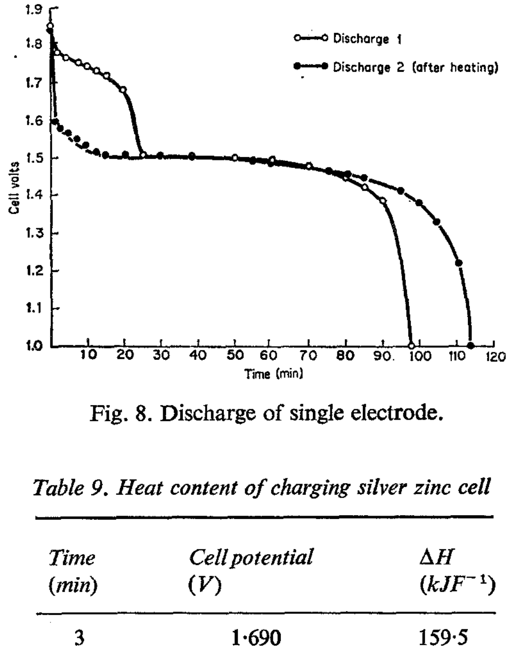

Fig. 8. Discharge of single electrode.

Table 9. Heat content of charging silver zinc cell

Time (min)	*Cell potential (V)*	ΔH (kJF^{-1})
3	1·690	159·5
5	1·695	160·9
12·5	1·707	161·7
15	1·715	162·2
35	1·982	172·7
41	1·985	172·8
45	1·992	173·0
47	1·995	173·3
50	2·000	174·3

table shows that the potential of the cell was greater than the argentic oxide potential. This agreed with the X-ray diffraction work of Wales and Burbank [7, 8] and the potential studies of Wynne-Jones *et al* [3].

The reactions for the charge of the silver oxide zinc cell are confirmed as

$$2Ag+ZnO \rightleftharpoons Zn+Ag_2O,\ \Delta H=158{\cdot}7\ kJF^{-1}\ (1)$$
$$Ag_2O+ZnO \rightleftharpoons Ag_2O_2+Zn,\ \Delta H=176{\cdot}1\ kJF^{-1}(2)$$

The above enthalpies were calculated from the standard enthalpy of formation of argentous oxide, determined as $-30{\cdot}6$ kJ mole^{-1} by Pitzer and Smith [11] who used a calorimetric technique, and argentic oxide by Jirsa [12] as $-26{\cdot}35$ kJ mole^{-1}, from the reduction of argentic oxide with hydrazine. The enthalpy of formation for zinc oxide of -348 kJ mole^{-1} was taken as the mean of values stated in the published works of Maier [13] who used an electrically heated calorimeter, Maier, Parks and Anderson [14], who used an electrolytic cell to reduce zinc oxide, and Maier and Ralston [15], who reduced zinc oxide with carbon monoxide.

It can be seen in Table 9 that the first half of the reaction corresponded to equation 1 and the second part of the reaction corresponded to equation 2, although the measured values of ΔH were somewhat higher than expected for the first reaction and lower for the second reaction. It is significant, however, that the extreme ends of the table approached the calculated values. This would suggest that both reactions were occurring simultaneously, reaction 1 being dominant during the first stages of the charge and reaction 2 being dominant during the second stage. The active material in the positive electrode must therefore have been present in the form of silver, argentous oxide, and argentic oxide at the same time. This was in fact observed by Wales and Burbank [8].

Fig. 9 shows an energy balance diagram for both the charge and discharge of the cell. The heat evolved and the electrical energy either taken from or put into the system are plotted against both the charge and discharge currents. The line *AB* is the electrical energy associated with the argentous oxide reaction calculated from the mean voltage of the potential plateau. The line *CD* is the corresponding heat either absorbed or evolved from the system. The line *EF* is the sum of these two energy terms and it can be seen to be constant, intersecting the ordinate at 158·7 kJF^{-1}. As the current was zero at the ordinate, the system could be considered to be working reversibly in the thermodynamic

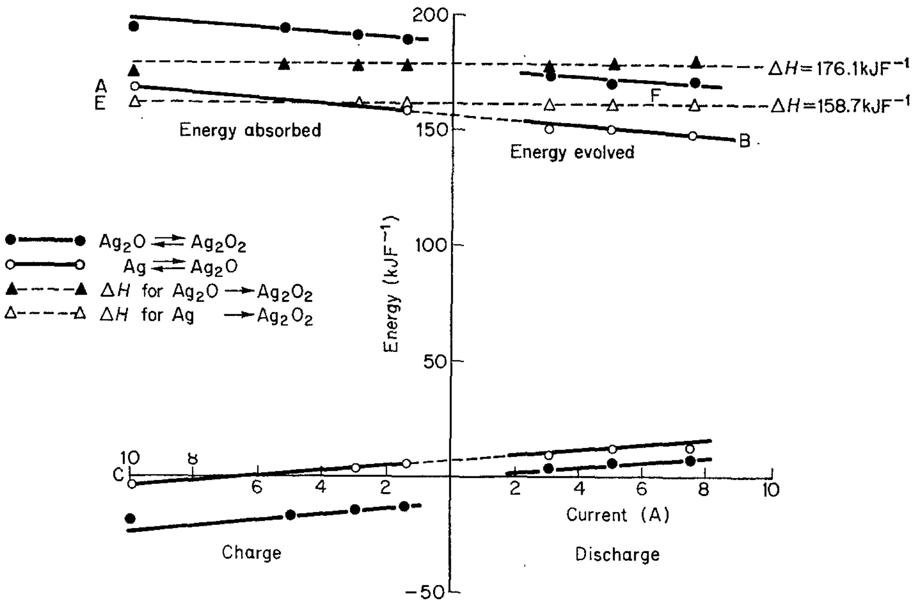

Fig. 9. Energy balance of silver zinc cell.

sense. The intercept of *EF* with the ordinate, 158·7 kJF^{-1} was therefore ΔH, the change in heat content of the reaction. Similarly the change in heat content of the argentic oxide reaction was 176 kJF^{-1}. Hence it is possible to measure the change in enthaply of the reaction by adding the electrical energy absorbed by the system to the heat absorbed when the cell is working under conditions which deviate considerably from those of thermodynamic reversibility. It is interesting to note that no matter how great the deviation from reversibility the summation is constant and is independent of the specific nature of the polarization in the cell. The method can therefore be used under conditions where it is not possible to measure individual electrode potentials or to distinguish between the various types of overpotential. As these figures were identical with the calculated heat contents of equations 1 and 2, the reactions were identified as the reactions occurring in the silver zinc system, confirming the results of earlier workers [1, 2]. It is again significant that there was no evidence of any heat contents higher than 176 kJF^{-1} and it would appear that no oxides higher than argentic oxide were formed.

It is of interest to note that discontinuities occurred at zero current in the energy diagram in Fig. 9 for the plots of both electrical energy and heat energy associated with the argentic oxide reaction, although the sum of the heat energy and electrical energy was constant at all currents. The reaction was therefore not reversible and it is possible that the mechanism for the oxidation of argentous oxide to argentic oxide differed from that of its reduction back to argentous oxide. This is the only evidence which can be found to support Hickling and Taylor's suggestion that argentic oxide would be formed by the reduction of silver peroxide and its consequent decomposition.

Tables 4 and 5 show that the time elapsed between charging and discharging the cell had a profound effect on the working voltage. When the cell was discharged after a short open circuit period, as in Fig. 5, the plateau associated with the discharge of argentic oxide appeared at 1·78 V, and was followed by a plateau at 1·53 V corresponding to the discharge of argentous oxide. In the case of a discharge after the cell had been stored for four years, the voltage of the cell fell immediately to 1·54 V, the argentous oxide potential. No plateau corresponding to the discharge of argentic oxide was observed. This phenomenon was confirmed by Fig. 6 and Fig. 7. Fig. 6 shows the discharge of a freshly charged silver zinc cell over its argentic oxide stage, the discharge finishing just before the end of the argentic oxide plateau. The cell was allowed to rest on open circuit for 6 days and the discharge continued. The plateau at 1·54 V shown in Fig. 7 was obtained, no traces of the argentic oxide reaction remaining. The heat evolved during these reactions (see Tables 4–7) was consistent with the cell potential in all cases, considerably less heat being associated with the argentic oxide reaction than with the argentous oxide.

Thus it may be concluded that when a silver oxide zinc cell was charged to its argentic oxide stage and allowed to stand on open circuit for a considerable period, most of the argentic oxide changed to argentous oxide. As this process was not accompanied by a loss in capacity the decomposition of argentic oxide to argentous oxide and oxygen could not have occurred. The argentic oxide must therefore have reacted with free silver in the active material to form argentous oxide by the following equation:

$$Ag_2O_2+2Ag \rightleftarrows 2\ Ag_2O$$

The only alternative explanation would be that after long periods of rest instead of progressing via reactions 1 and 2 the cell operated by the reaction

$$Ag_2O_2+2Zn \rightleftarrows 2Ag+2ZnO,\ \Delta H=167{\cdot}4\ kJK^{-1} \quad (3)$$

There is little evidence for this reaction although in Table 4 a change in enthalpy of 164·7 kJF^{-1} was recorded after fifteen minutes discharge. No plateau occurred at this point and as ΔH quickly fell to the order of 159 kJF^{-1} it is unlikely that this reaction can have made any significant contribution to the overall process.

The reaction between argentic oxide and silver was confirmed by heating a silver electrode which had previously been formed to the argentic oxide state at 110°C for 15 minutes. The results in Table 8 and Fig. 8 show that as no change in weight occurred, no thermal decomposition resulting in the loss of oxygen had taken place. The argentic oxide plateau had, however, completely disappeared, the whole of the discharge occurring at the potential of 1·54 V associated with the discharge of argentous oxide. Heating the plate must therefore have promoted a reaction between the argentic oxide and free silver to form argentous oxide.

It can be concluded that no calorimetric evidence has been obtained for reactions involving oxides of silver other than argentous oxide and argentic oxide. The argentous oxide reaction was shown to be reversible but the argentic oxide reaction was not reversible. The latter reaction could be suppressed by allowing the cell to stand on open circuit for some time, or by heating the positive plates. The discharge then took place solely via the reduction of argentous oxides to silver but there was no change in capacity.

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