Table II. Solubilities and Activity Coefficients of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ at 25° C.

KCl, M	2,4-D, G./L.	$M \times 10^3$	μ	$f_\pm$	pk	$p\underline{K}$	$M_0 \times 10^3$
Calcium salt ($a = 2.5\ A$)							
0.000	4.00	9.0477	0.1646	0.712	5.53	5.97	6.44
0.001	4.05	9.1608	0.1688	0.707	5.51	5.96	6.48
0.005	4.20	9.5001	0.1830	0.689	5.46	5.95	6.55
0.010	4.30	9.7263	0.1979	0.671	5.43	5.95	6.53
0.050	4.90	11.083	0.2902	0.578	5.26	5.98	6.41
0.100	5.60	12.666	0.3712	0.513	5.09	5.96	6.50
					Av.	5.96	6.48
Magnesium Salt ($a = 3.5\ A$)							
0.000	11.1	25.107	0.2744	0.614	4.20	4.83	15.4
0.001	11.3	25.559	0.2787	0.610	4.18	4.82	15.6
0.005	11.7	26.465	0.2904	0.600	4.13	4.79	15.9
0.010	12.0	27.143	0.3023	0.596	4.10	4.78	16.2
0.050	12.7	28.726	0.3688	0.545	4.02	4.81	15.7
0.100	13.5	30.536	0.4380	0.505	3.94	4.83	15.4
					Av.	4.81	15.7

determined as 5.96 and 4.81, respectively, by Equations 4 and 9. The average M_o values at 25° C. for $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ were determined as 6.48×10^{-3} and 1.57×10^{-3}

The effect of temperature on solubility of these two salts was examined in distilled water. The solubilities increased from 3.26 grams/liter as 2,4-D at 4° C. to 5.21 grams/liter at 35° C. for $Ca(2,4\text{-}D)_2$ and from 8.4 grams/liter at 4° C. to 14.2 grams/liter at 35° C. for $Mg(2,4\text{-}D)_2$.

DISCUSSION

The calcium and magnesium salts of 2,4-D are quite soluble in distilled water at 25° C., 4000 mg./liter and 11,100 mg./liter, respectively. Therefore, the ordinary concentrations of calcium and magnesium ions in a surface water would not remove 2,4-D through precipitation reactions. Likewise, limestone products could not be used to remove 2,4-D at water treatment plants since formulations of this herbicide are applied to concentrations less than 3 mg./liter as the acid equivalent.

The assumption indicated in Equation 1, Table I, appears to be valid since the Debye-Hückel expression is followed up on ionic strengths of 0.138 for $Ca(2,4\text{-}D)_2$ and up to 0.192 for $Mg(2,4\text{-}D)_2$. This is substantiated by the close agreement of the $p\underline{K}$ value and of the M_o values.

NOMENCLATURE

A = activity coeficient
K = equilibrium constant
M = solubility, moles/liter
k = classical solubility product
$\underline{K}$ = activity solubility product
$f_\pm$ = mean activity coefficient of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$
Z = valence
μ = ionic strength
a = average effective diameter of the ions of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$, A.
M_o = solubility at zero ionic strength, moles/liter
v = total number of ions—*i.e.*, $v+$ + $v-$ produced from one molecule upon ionization
p = negative logarithm

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A Calorimetric Study of Nickel-Cadmium Cells

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NICKEL-CADMIUM batteries have been used as energy storage devices in many space power systems. They are usually employed in conjunction with solar cells. They are also utilized in many commercial and industrial applications where a rechargeable and portable power supply is required.

The thermal design of such a battery requires the availability of accurate and reliable thermal data. This article describes a calorimetric study of the heats generated during the discharge of some nickel-cadmium cells. This study has provided an experimental determination of the enthalpy of the cell reaction and thermal data for the

The amounts of heat evolved during the discharge of sealed nickel-cadmium cells were determined in a calorimeter. The heats liberated were a linear function of the per cent of discharge. The heat losses during discharge were 14 to 20% of the total energies obtained from the cells. The molar enthalpy of the cell reaction was determined to be 64 kcal. per gram-mole.

design of long-life, nickel-cadmium batteries.

EXPERIMENTAL METHODS

Samples of 20-AH rectangular sealed nickel-cadmium cells were obtained from the Sonotone Corp. These cells were typical samples of cells which were furnished for space power subsystems.

In a typical experiment, a nickel-cadmium cell was discharged outside of the calorimeter until the cell voltage decreased rapidly. The cell voltage decreased very rapidly when a cell was completely discharged. The cell was then charged at a current of 2 amp. for 14 hours. This charge of 28 amp.-hours represents 40% overcharge. The charged cell was then immersed in 1250 ml. of silicone fluid in the calorimeter and discharged at constant current for various periods of time. Discharge time, discharge current, closed circuit voltage, and temperature of the calorimeter were continuously monitored.

The calorimeter consisted of a well-insulated Dewar flask which contained silicone fluid (GE-SF96-200 cs.). The calorimeter was calibrated by passing a known amount of electrical current through a nichrome wire (total resistance of 2.019 ohms) in the silicone fluid for a given period of time. The electrical energy put into the calorimeter could be readily calculated. The temperature of the silicone fluid was continuously monitored during the experiment. The specific heat capacity of the silicone fluid was determined to be 0.368 cal. per ° C. These experiments were carried out without a nickel-cadmium cell in the calorimeter.

Another series of similar experiments with a "dummy" nickel-cadmium cell in the silicone fluid was carried out. From the results of these experiments, the heat capacity of a typical 20-AH nickel-cadmium cell was 234 cal. per ° C. Each cell weighed about 1000 grams and the specific heat capacity was about 0.234 cal. per ° C.

The specific heat capcity of a nickel-cadmium cell was calculated on the basis of the amounts of various materials in the cell and their heat capacities. The following heat capacities were used: stainless steel-0.107, Ni-0.11, NiOOH-0.11, $Cd(OH)_3$-0.55, KOH(30%)-0.85. The cellulose and polyethylene were neglected since they were present in relatively small amounts in the cell. The result gave a specific heat capacity of 0.251 cal. per ° C.

RESULTS AND DISCUSSION

The results obtained for single cells discharged in steps at various current densities are given in Table I. In these experiments, the quantity of heat generated during each step was determined.

Some of the properties of these data are more adequately demonstrated in Figure 1. The quantities of heat liberated are directly proportional to the extent of discharge. In addition, they are independent of the discharge current.

Both the least squares line and the line through origin are shown in Figure 1. The correlation coefficients of these two lines are 0.981 and 0.975, respectively. The probabilities of linear correlations are greater than 99% in both cases. All of the data points in Figure 1 are within the 90% confidence range for any single estimated value. The confidence range was calculated from the variances of the least squares line.

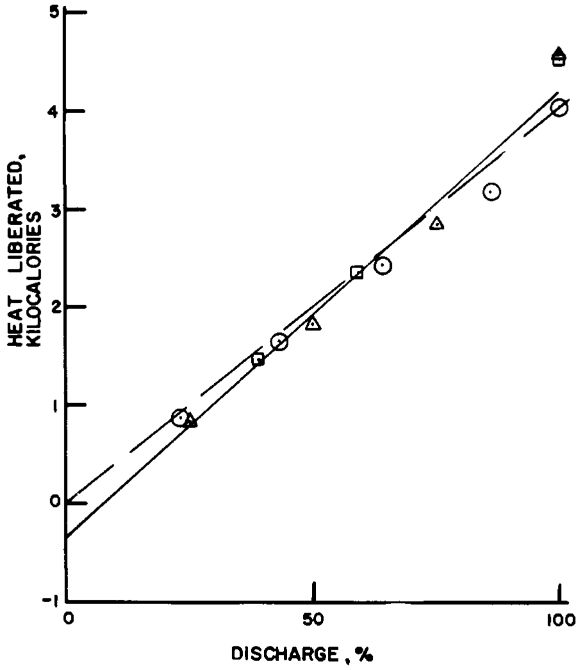

Figure 1. Heat liberated during discharge

——— least squares line

--------- line-through-origin with minimum squared deviations

● Experiment 1

▲ Experiment 2

■ Experiment 3

The discharge voltages in experiments, 1, 2, and 3 were approximately 1.2 volts. They remained constant except near the conclusions of the experiments when they decreased rapidly. Assuming an average discharge voltage of 1.2 volts, the energies delivered to the loads in experiments 1, 2, and 3 were 24.2, 20.3, and 26.3 kcal., respectively. The heat losses during discharge were 14, 20, and 16%, respectively, of the total energies obtained from the cells.

Table I. Heat Losses of Nickel-Cadmium Cells

Experiment	Discharge Current, Amp.	Level of Charge, %		Heat Liberated, Kcal.		Discharge Time, Min.
		From	To	Differential	Total	
1	10	100	77	0.87	0.87	30.0
		77	57	0.79	1.66	30.2
		57	36	0.78	2.44	30.0
		36	14	0.74	3.18	30.0
		14	0	0.87	4.05	21.0
2	15	99	75	0.84	0.84	20.0
		75	50	1.00	1.84	20.2
		50	25	1.01	2.85	20.4
		25	0	1.73	4.58	18.1
3	20	100	61	1.46	1.46	30.0
		61	41	0.89	2.35	15.4
		41	0	2.19	4.54	31.3

The enthalpy of the over-all discharge reaction of the cell is equal to the sum of the heat liberated and the energy delivered to the load during discharge. The electrochemical equivalent is 1.61 × 10^3 amp.-min. per gram-equivalent. Thus the enthalpies obtained from experiments 1, 2, and 3 are 32.2, 33.9, and 32.4 kcal. per gram-equivalent, respectively. The molar enthalpy for the discharge reaction is about 64 kcal. per gram-mole based on these results.

The above results are in excellent agreement with the enthalpies obtained by other methods. Salkind and Bruins (*2*) determined the voltage of nickel-cadmium cells as a function of temperature. From these data, they calculated the enthalpy of the cell reaction from the Gibbs-Helmholtz equation to be 64 kcal. per gram-mole. Salkind and Bruins also calculated the enthalpy of the cell reaction by means of the vapor reference plot originally developed by Othmer and Gilmont (*1*). The application of this method to the data resulted in a value of 62 kcal. per gram-mole for this reaction.

Salkind and Bruins (*2*) have proposed the following simplified reaction for the nickel-cadmium cell:

$$2\,NiOOH + Cd + 2H_2O = 2Ni(OH)_3 + Cd(OH)_2$$

They have shown that an enthalpy of 64 kcal. per gram-mole for this reaction is in agreement with the known thermochemical data for the individual components in this reaction.

The results of this calorimetric study have shown that the quantities of heat liberated during discharge of nickel-cadmium cells are directly proportional to the extent of discharge. The heat losses during discharge of a typical cell are about 15% of the total energy obtained from the cell. The enthalpy of the cell reaction calculated from the calorimetric data is in excellent agreement with those obtained by other methods.

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Heat Content and Entropy of Strontium Chloride from 298° to 1200° K.

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The heat content and entropy of $SrCl_2$ from 298° to 1200° K. have been measured by means of a copper block drop calorimeter. The following equations for the heat content (cal. mole^{-1}) were obtained: $H_T - H_{298.15} = -4875 + 15.28T + 4.045 \times 10^{-3}T^2$ (298° to 940° K.); $H_T - H_{298.15} = -12{,}430 + 28.53T$ (1040° to 1146° K.); $\Delta H_{(fusion)} = 3850$ (1146° K.); and $H_T - H_{298.15} = -7070 + 27.22T$ (1146° to 1205° K.). A second order transition was found between the temperatures of about 940° and 1040° K.

STRONTIUM CHLORIDE, which has the calcium fluoride type of structure, was recently found to have an unusually low entropy of fusion of 3.4 e.u. (*3*). This suggested the existence of a transition in $SrCl_2$ similar to that known for CaF_2 which also has an unusually low entropy of fusion (*5*). The heat content measurements reported here show such a second order transition occurring in $SrCl_2$ about 140° below its melting point.

EXPERIMENTAL

Materials. Strontium chloride hydrate (containing less than 0.01% nonvolatile anions), which was pretreated in a vacuum desiccator over P_2O_5 for several days, was further dehydrated by slowly heating under vacuum for a period of several days to 100° below its melting point. The salt was melted in a stream of dry HCl gas, purged with argon, and filtered in situ through sintered quartz. The anhydrous $SrCl_2$ was free of foreign metals as determined spectrographically and showed no alkalinity from pyrohydrolysis.

Heat Content. The copper block calorimeter used for the measurements and the experimental procedure were previously described in detail (*2*). Measurements were made with two samples of $SrCl_2$ designated as Series I and II in Table I. The "run number" indicates the order in which the measurements were made. The defined calorie is equal to 4.184 absolute joules, and the molecular weight of $SrCl_2$ is 158.54 grams.

RESULTS

The measured heat contents of $SrCl_2$ are given in Table I. The following equations were obtained by the method of least squares for $H_T - H_{298.15}$ (cal. mole^{-1}).

$$H_T - H_{298.15} = -4{,}875 + 15.28T + 4.045 \times 10^{-3}T^2 \text{ (298-940° K.)} \quad (1)$$

$$H_T - H_{298.15} = -12{,}430 + 28.53T \text{ (1040-1146° K.)} \quad (2)$$

$$\Delta H\text{(fusion)} = 3{,}850 \text{ (1146° K.)} \quad (3)$$

$$H_T - H_{298.15} = -7{,}070 + 27.22T \text{ (1146-1205° K.)} \quad (4)$$