C, C'' = constant
H = enthalpy of the solution; cal. per gram of solution
I = ionic strength = $\Sigma(m_i z_i^2)/2$
$\bar{L}_s$ = partial enthalpy of salts in solution; cal. per gram of salt
$\bar{L}_w$ = partial enthalpy of water in solution; cal. per gram of water
m_i = molality of ion i
m_+ = molality of positive ion
m_- = molality of negative ion
M_i = molecular weight of i
n = exponent in Equations 2, 3, and 4
R = gas constant
T = absolute temperature
W_s = mass of salt
x = mass fraction of salts in solution; (more exactly 0.001 times salinity in parts per thousand) the term '% salinity is 100 times x
Z_i = charge on ion i

$$\frac{\sigma I^{1/2}}{3} = \frac{1}{I^{3/2}}\left[1 + I^{1/2} - \frac{1}{1 + I^{1/2}} - 2 \ln (1 + I^{1/2})\right]$$

ϕL_s = apparent relative enthalpy of the salts in solution; cal. per gram of salt

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Heat Capacities of 90% Hydrogen Peroxide and Commercial Anhydrous Hydrazine

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Heat capacities of commercial 90% by weight hydrogen peroxide solution and commercial anhydrous hydrazine (97% by weight) were measured by means of heat balances on a small tube-in-tube exchanger at temperatures to 191° C. Data in the range from ambient to 200° C. are represented by a set of linear relations. The accuracy of these heat capacity data is estimated to be better than ±2%.

HIGH STRENGTH hydrogen peroxide and "anhydrous" hydrazine have become popular rocket propellants and have served both as an oxidizer and fuel, respectively, and as monopropellants. Both materials have become important items of commerce because of their high activity as an oxidizing and reducing agent, respectively. In both instances, applications require detailed knowledge of various physical and thermodynamic properties.

Both materials are thermodynamically unstable with respect to one or more decomposition reactions. The kinetics of decomposition lead to only modest rates at low temperatures. However, rates are finite and lead to measurable heat release with increasing temperatures. This research was undertaken in an effort to measure the heat capacities of 90% hydrogen peroxide and common "anhydrous" hydrazine (about 97% by weight).

The primary objective was to measure the properties of the fluids in a defined chemical state. Since equilibrium constants are very large, only such data are meaningful and offer any possibility of reproducibility. Conventional static experiments were erratic and involved large corrections owing to chemical reactions. Consequently, measurements were undertaken in a flow system involving accurate heat balances around a small tube-in-tube heat exchanger. Small corrections owing to homo- and heterogeneous decomposition were required. These corrections were substantially smaller, by as much as an order of magnitude, than corrections for a conventional calorimeter experiment. Finally, the choice of a particular concentration for hydrogen peroxide was dictated by the degree of interest in various high strength solutions offered by several commercial sources.

PROCEDURE

A flow bench was constructed of seamless Type 321 stainless steel tubing, thoroughly cleaned and passivated to assure compatibility with the test fluid. Water, heated electrically, was used to heat the test fluid in a simple tube-in-tube exchanger. This technique was used to limit the temperature of surfaces in contact with the test fluids. Temperature control was provided by regulating power to the water heater by means of a variable autotransformer. A pressure relief device on the water heater was set to operate at 600 p.s.i.g., corresponding to a water temperature of 252° C. Water flow to the test fluid heater would terminate if this condition were reached. Figure 1 is a schematic diagram of the apparatus.

Heat exchangers and flow paths were designed to reclaim as much heat from the exit streams as possible to minimize heater capacity and power consumption. Cold inlet water, at a pressure of about 500 p.s.i.g., was preheated by heat exchange with the test fluid after it had passed through

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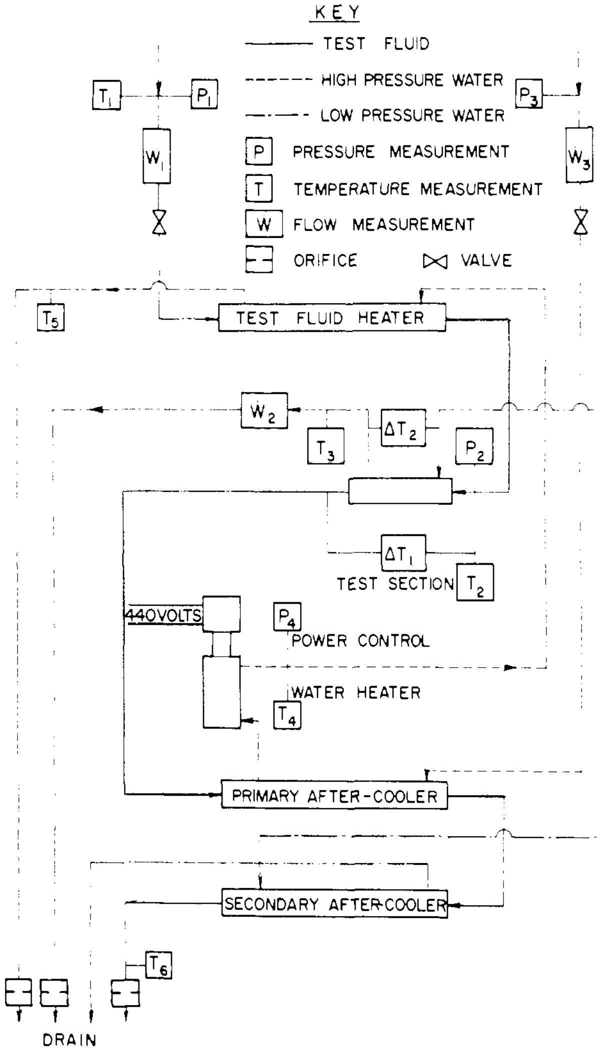

Figure 1. Heat capacity apparatus

the test section. This served the added purpose of cooling the test fluid before discharge from the apparatus. The water next passed through an electrical immersion heater and to the test fluid heat exchanger before being discharged. The test fluid from the high temperature heat exchanger flowed through the test section, then was cooled by the incoming water. A secondary cooler operating with cold, low-pressure water assured that the test fluid was cooled completely before it was discharged. A pressure of about 500 p.s.i.g. was maintained on both the heating water and the test fluid systems, at flow rates of about 1 gallon per minute, by orifices installed in the discharge lines.

The heat capacity test section consisted of a tube-in-tube heat exchanger approximately 12 inches long. Heated test fluid flowed through the central ½ inch O. D. × 0.035 inch wall stainless steel tube, and cold water passed through the annular section. Cold water was selected as the heat transfer medium for several reasons: The heat capacity of water is well known; radiant and corrective losses to the surroundings are minimized if the temperature of the outer test section wall is kept near ambient temperature; and the test section length required to maintain the desired temperature changes in the flow streams is minimized by having a large temperature difference between the two streams. A short test section had the dual advantage of minimized heat loss and minimized test fluid decomposition in the test section.

All flow measurements were made with turbine type flow meters; Potter Model ⅜-99 meters were used during hydrogen peroxide experiments, and Fischer-Porter ½-2 meters were used during hydrazine experiments. The output of these meters was recorded directly on a CEC oscillograph and, simultaneously, after conversion from A.C. to D.C., on a Leeds and Northrup Speedomax recorder. Temperature measurements used directly in the heat capacity determinations were made with sheathed platinum resistance thermometers. Outputs of the thermometers used for ΔT measurements on the two streams were recorded directly as differential measurements. Temperatures used only in operation of the apparatus were measured with sheathed iron-constantan thermocouples. These measurements were recorded on Leeds and Northrup Speedomax recorders. Pressure measurements were made with Statham strain gage pressure transducers and recorded on Foxboro Dynalog recorders. All instrumentation was calibrated before and after each test series to ensure maximum accuracy.

Data were obtained by bringing all flows to the desired level, turning on power to the water heater, and bringing the system to the desired temperature. After steady-state temperatures were attained, a series of data points were taken by activating the chart drives for 2 or 3 seconds at 1 minute intervals. Heater power was then increased to a new level or turned off and the system allowed to cool before flows were terminated. Calibration tests were made with water before the hydrogen peroxide tests and both before and after the hydrazine tests to provide corrections for heat losses and system errors. Calibrations followed the same procedures as test fluid experiments.

RESULTS AND DISCUSSION

Three tests comprising seven or eight replications, at three temperatures, were made with hydrogen peroxide; four tests, comprising 10 to 14 replications at each of six temperatures, were made with hydrazine. Both hydrogen peroxide and hydrazine were analyzed prior to tests. The hydrogen peroxide was 90.1% by weight, the remainder water, by standard potassium permanganate titration. Hydrazine composition was 97.0 weight % N_2H_4, 0.5 weight % NH_3, and 2.5 weight % H_2O with traces of aniline and heptane. Hydrazine concentration was obtained by iodate titration; water and ammonia were determined by gas chromatography. In addition, the concentrations of effluent hydrogen peroxide and hydrazine were determined on samples collected during operation at highest temperatures. The decrease in hydrogen peroxide concentration after passage through the apparatus was less than 0.5%. Consequently, the test concentration was assumed to be 90% in all cases. No change in hydrazine concentration could be detected.

Two corrections were applied to raw data: a correction for system constants obtained from the water calibration tests and a correction for decomposition of the test fluid in the test section.

The first correction was applied as a simple proportionality factor to raw data. This is a consequence of using relatively constant, ambient temperature water in the annulus of the heat exchanger. Both the correction factor (in calories per second) and total heat transfer to the water were proportional to the test fluid temperature, since flow rates were essentially constant for all sets of tests. The correction was treated as a percentage of the raw heat capacity. The correction for hydrazine measurements determined from the post-test calibrations was slightly lower than that derived from the pretest calibration. An arithmetic average of these values was used in the final analysis.

These corrections were negative. This is contrary to the results that would be expected if corrections were due primarily to heat losses from the test section. Apparently, the primary source of the correction was heat transfer to the water through the flow system structure. A larger correction in the hydrazine tests was caused by differences in insulation of the system and the different flow rates used in this latter set of tests.

Decomposition corrections were calculated from experimental kinetic data, for both homogeneous and heterogeneous decomposition, available in the literature for hydrogen peroxide (*1*, *4*) and for hydrazine (*5*). These references report rate data for reactions in tubular, stainless steel reactors of varying length-to-diameter with high flux heat transfer. The close similarity of experimental techniques and conditions suggested the validity of extrapolation for use in this study. Actual changes in concentration were small, as predicted by the extrapolation, and were at the limits of significance for available analytical schemes.

Calculations were based on average test conditions at each temperature. Corrections were applied by subtracting enthalpy due to decomposition from the total heat transferred to the water.

$$|\dot{W}C_p(\Delta T)|_t = (1 + F/100)|\dot{W}C_p(\Delta T)|_w - rV(\Delta H) \qquad (1)$$

where $\dot{W}$ = flow rate, grams per second; C_p = heat capacity, calories per gram per ° C.; (ΔT) = temperature change through test section, ° C.; F = system correction, per cent; r = reaction rate, gram-moles per cubic centimeter per second; V = test section volume, cubic centimeters; (ΔH) = heat of reaction, calories per gram-mole; and the subscripts t and w refer to the test fluid and water, respectively. These corrections were reduced to percentages for presentation in the data tables.

Heat capacity data for hydrogen peroxide are summarized in Table I and Figure 2. Giguere *et al.* (*2*) measured an average heat capacity over the range 0° to 27° C. for hydrogen peroxide–water solutions as a function of concentration. Interpolation of these data gave a value of heat capacity for 90% by weight hydrogen peroxide of 0.660 calorie per gram per ° C. over this temperature range. This point, which is the only previous determination reported in the literature, and the points from the current investigation were subjected to a straight-line, least-squares curve fit. The accuracy of data did not justify a fit to a higher order polynomial. The resulting equation is:

$$C_p = 0.657 + 2.11 \times 10^{-4}T \qquad (2)$$

where T is temperature, ° C.

Heat capacity data for hydrazine are also given in Table I and in Figure 3. A linear least-squares curve fit of these data gives the equation:

$$C_p = 0.734 + 5.33 \times 10^{-4}T \qquad (3)$$

for the heat capacity of commercial (97%) hydrazine. Data of Scott *et al.* (*6*) for essentially pure hydrazine, over the temperature range 0° to 67° C. and Hough, Mason, and Sage (*3*) for pure hydrazine and for 97% hydrazine–3% water from 40° to 90° C. are included in Figure 3 for comparison.

The curve for a 97% hydrazine–3% water solution was obtained by interpolating Hough's data given as a function of concentration. The slope of the present data agrees well with that of Scott; however, it is 1.5% higher in the range of overlapping temperatures. This can be attributed, in part, to the presence of impurities in the hydrazine used in this investigation. The data of Hough indicate that addition of 3% water by weight increases the heat capacity of hydrazine about 1%. This correction brings present data into good agreement with Scott.

The maximum coefficient of variation for heat capacities of hydrogen peroxide, over the temperature range 0° to 200° C., as calculated from Equation 2 using conventional maximum likelihood theory, is 0.11%. Similarly, using Equation 3 for hydrazine over the temperature range 40° to 200° C., the maximum coefficient of variation is 0.16%. Random error was estimated from the variance of replications relative to the group means. A value of 0.9% characterizes the over-all program; values calculated separately for the two test fluids did not differ significantly.

Measurement errors were minimized by complete instrument calibration prior to each test series. There were no significant changes in calibration factors during the program. This confirmed a high degree of reproducibility for the measurement systems. As noted above, the entire system was calibrated by operation with water as the test fluid. A correction for spurious heat flows was calculated and

Table I. Heat Capacity Data

Set	Av. Temp., ° C.	Measured C_p, Cal./G., ° C.	Decomposition Correction, %	System Correction, %	Corrected C_p, Cal./G., ° C.
		Hydrogen Peroxide, 90%			
1	113	0.698	0	-2.4	0.681
2	152	0.705	-0.31	-2.4	0.686
3	188	0.727	-1.67	-2.4	0.698
		Hydrazine, ~ 97%			
1	58	0.786	0	-3.6	0.759
2	83	0.811	0	-3.6	0.783
3	111	0.822	0	-3.6	0.793
4	136	0.839	0	-3.6	0.810
5	168	0.858	0	-3.6	0.828
6	191	0.863	-0.25	-3.6	0.831

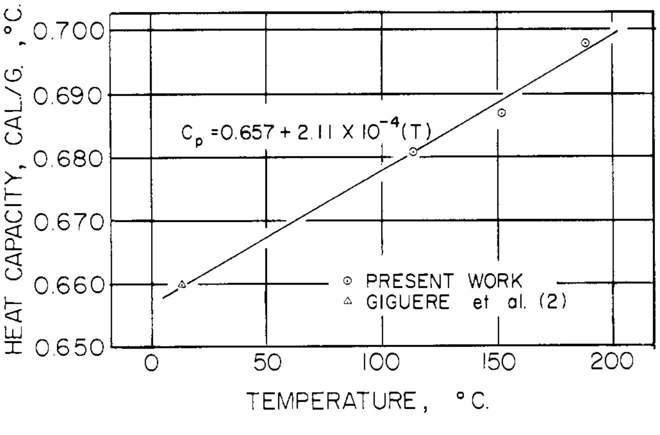

Figure 2. Heat capacity of 90% hydrogen peroxide

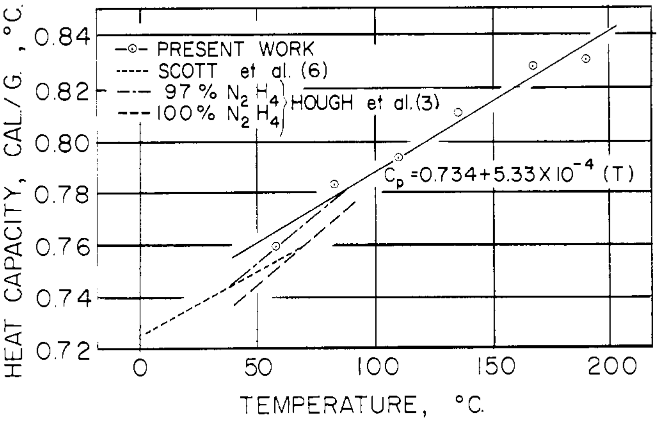

Figure 3. Heat capacity of commercial anydrous hydrazine

applied to all test fluid data. Temperature and volume flow rate measurements were accurate to within 0.3° C. and 0.25%, respectively. The accuracy of density data, necessary to conversion of turbine flowmeter output to mass flows, was better than 0.1%. Finally, data were corrected for heat release due to propellant decomposition within the apparatus. The over-all error assignable to values of heat capacity reported herein is less than 2%. This conclusion is consistent with the comparisons of present data with prior measurements cited in the literature.

The ranges of test conditions were well removed from the critical points of the test fluids. Estimates of the effect of pressure on heat capacity were made on the basis of density data. In both cases, this effect was less than 0.1% of the values reported. Thus, these data well represent a standard state at 1 atm. or the saturation condition.

SAFETY

Hydrazine is a highly toxic material. It can be absorbed through the skin and can cause blindness on very short contact with the eye. Every effort should be made to avoid oral ingestion, breathing, or skin contact. Good ventilation, safety glasses, and rubber gloves are mandatory.

Compounds of the hydrazine family can undergo violent autodecomposition at high temperatures. They decompose readily in the presence of inorganic catalysts and common residues. Clean glassware and/or stainless steel equipment are necessary safety precautions. Excessive heating—i.e., above 150° C.—is to be avoided. Prolonged confinement under pressure and/or in metal containers is not good practice.

Hydrogen peroxide is nontoxic, but a powerful oxidizing agent. Contact with organic materials should be rigidly avoided. Safety glasses and loose protective garments are recommended for handling quantities beyond laboratory scale.

High strength hydrogen peroxide decomposes readily in the presence of foreign materials and at high temperatures. The procedures recommended above for hydrazine should be adhered to.

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Enthalpy of Formation of Cerium Sesquioxide

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Oxygen bomb calorimetry was used to determine the energy of combustion of Ce_2O_3. The enthalpy change for the reaction Ce_2O_3-hexagonal + $\frac{1}{2}O_2 = 2CeO_2$ was $\Delta H^\circ_{298.15^\circ K.} = -91.05 \pm 0.16$ kcal., which leads to a value for the enthalpy of formation of Ce_2O_3 of $\Delta H^\circ_{f\,298.15\ K.} = -429.31 \pm 0.68$ kcal. per mole.

THE enthalpy of combustion in oxygen of Ce_2O_3 has been measured by Kuznetsov, Rezukhina, and Golubenko (*9*), who found $\Delta H^\circ_{298.15\ K.} = -85.43 \pm 0.26$ cal. per mole, and by Mah (*10*) who found $\Delta H^\circ_{298.15\ K.} = -93.35 \pm 0.10$ kcal. per mole. The difference is 7.92 kcal. per mole, many times the combined estimated uncertainties of the measurements.

In addition, the reaction $CeO_{2-x} + (x/2)O_2 = CeO_2$ has been studied by measurements of oxygen partial pressures by Kuznetsov *et al.* (*8*), Brauer, Gingerich, and Holtschmidt (*2*), and Bevan and Kordis (*1*) and by electromotive force measurements on cells with solid electrolytes by Kuznetsov *et al.* (*8*) and by Markin and Rand (*11*). These various equilibrium measurements are in reasonable agreement among themselves. Those of Bevan and Kordis (*1*) are perhaps the most complete, and they find, for the oxidation of Ce_2O_3-hexagonal to CeO_2, the value $\Delta H^\circ_{1353\ K.} = -93.2 \pm 1.0$ kcal. per mole, which, on conversion to room temperature (*4*) becomes $\Delta H^\circ_{298\ K.} = -90.3 \pm 1.0$ kcal. per mole, a value lying intermediate between the two combustion values.

In view of this discrepancy, the enthalpy of combustion of Ce_2O_3-hexagonal was remeasured to obtain a more reliable value for its enthalpy of formation.

EXPERIMENTAL

Cerium nitrate (American Potash and Chemical Corp.) was converted to the oxalate, which was then ignited to CeO_2. The CeO_2 was reduced in a graphite boat under purified H_2 at about 1300° C. for 12 hours. Hydrogen was purified using a model Ch-A Milton Roy Serfoss hydrogen purifier. The preparations with the higher oxygen content were made with less pure hydrogen. Spectrochemical analysis showed the presence of faint traces of silicon and copper. Other impurities were less than the limits of detection. X-ray analysis of preparation 1 showed the presence of the hexagonal form of Ce_2O_3 with lattice parameters $a = 3.892 \pm 0.001$ A. and $c = 6.059 \pm 0.001$A. and small amounts of another phase, presumably a higher oxide. Combustion analysis of each preparation showed H_2 ranging from 0.003 to 0.012% and carbon from 0.005 to 0.010%.