at room temperature, from which the quantity of gas removed in each pressure step is determined. When a pressure just above saturation is reached (point *e*), the entire cell contents are expanded, to give the density at that pressure. The densities at higher pressures (points *c,d*) are then obtained by adding the increments for each pressure step. This procedure is repeated for other mixtures (X_2, X_3), resulting in a network of P-ρ-X points in the compressed liquid region at temperature T_1. Temperatures have been measured by a platinum resistance thermometer calibrated by the National Bureau of Standards, and are accurate to within ±0.02° K. Pressures have been measured by a calibrated Heise bourdon gage, with an accuracy of ±0.5 atm. The unit of pressure is the international atmosphere.

RESULTS AND DISCUSSION

The experimental density measurements are shown in Table I with the equivalent molar volumes. Experimental density *vs.* pressure curves have been plotted in Figure 2 and extrapolated to the saturation pressure to give the saturation density for each mixture composition. Pure nitrogen density points in Figure 2 have been taken from reported data (*2*) and are estimated to be accurate to within ±0.1%. The expansion of each mixture in steps, as outlined above, reduces the accuracy of the mixture densities, as compared with those for pure liquid nitrogen, for which the entire cell contents were expanded from each P-T point. The mixture densities are estimated to be accurate to within ±1.0%.

A smooth curve has been drawn through the saturated liquid density points at each temperature. These curves for the 100.61° and 117.30° K. isotherms have an inflection point at pressures around 300 to 400 atm., but it is not clear whether this is a feature of the system or whether it is a result of scatter in the data. These curves might reasonably be expected to be complicated, since increasing pressure is accompanied by increasing helium content, and these two factors produce opposite effects on the density of the mixture. A plot of molar volume *vs.* composition for the saturated liquid is better behaved (Figure 3).

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Heat of Formation of Hydroxylammonium Perchlorate by Combustion Calorimetry

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The energy of combustion of solid hydroxylammonium perchlorate with diethyl oxalate as fuel was determined in a rotating bomb calorimeter. The standard heat of formation of hydroxylammonium perchlorate at 25° C. and 1 atm. is −66.16 ± 0.65 kcal. per mole (±0.65 is estimated standard deviation of the mean) and was calculated using a computer program which was developed for compounds containing carbon, hydrogen, nitrogen, oxygen, and chlorine.

COMBUSTION REACTION of hydroxylammonium perchlorate was carried out in an oxygen atmosphere using diethyl oxalate as the fuel. The idealized reaction equation from which the heat of formation is determined is:

$$H_4O_5N_1Cl_1(c) + C_6H_{10}O_4(l) + 4.75\ O_2(g) + 143.5\ H_2O(l) \rightarrow$$

$$6\ CO_2(g) + HCl \cdot 150\ H_2O(l) + 0.5\ N_2(g) \qquad (1)$$

The chlorine gas liberated in the reaction was converted to the chloride ion by adding arsenious acid solution to the bomb (*5*). The heats of formation of perchlorates or other highly oxygenated compounds are usually obtained from heat of solution experiments. For such reactions, however, the heats of formation of the other reactants and reaction products must be known. The reactants and products will vary for each different compound of the general formula $C_aH_bO_cN_dCl_e$ and so will their thermal data that must be obtained either from literature or experiments that subjects the final results to other possible sources of errors. The combustion of hydroxylammonium perchlorate with diethyl oxalate according to Equation 1 is equivalent to burning a compound of the general formula $C_aH_bO_cN_dCl_e$ in the presence of oxygen and water. The reaction products, CO_2, H_2O, HCl, and N_2 are always the same and no auxiliary data besides the heat of formation for diethyloxalate are necessary. Thus with a slight modification for chlorine compounds, the "Washburn corrections" used for $C_aH_bO_cN_d$ compounds can be applied. Since the final combustion products for all compounds are the same, a computer program has been set up for data reduction (*5*).

EXPERIMENTAL

Material. Hydroxylammonium perchlorate was synthesized at this laboratory. After synthesis, the material was dissolved in ethyl ether, filtered, and precipitated by the rapid addition of benzene, yielding fine needles. The very fine needles were desirable to provide the most intimate contact between the oxidizer and fuel to obtain good combustion. The precipitate was filtered and dried at 50° C.

Table I. Values of Density, Heat Capacity, and $(\partial E/\partial P)_T$ of Hydroxylammonium Perchlorate (HAP) and Auxiliary Materials

	Density, Gram/Ml.	C_p, Cal./Deg. Gram	$(\partial E/\partial P)_T$ Atm-Gram
HAP	1.96	0.21[a]	−0.0028[a]
Benzoic acid (*3*)	1.2659	0.29	−0.0028
Diethyl oxalate	1.079	0.43	−0.006[a]
Polypropylene	0.9	0.31	−0.008[a]
Thread (*3*)	1.5	0.4	−0.007
Bomb solution initial (*2*)	...	...	−0.00186
Bomb solution final (*2*)	...	...	−0.00199

[a] Estimated.

under a vacuum of less than 10^{-3} mm. of Hg for 8 hours. All operations were conducted under dry nitrogen. The final melting point was 88° to 89° C. An analysis of the hydroxylamine content (Raschig method) showed a purity of 99.92%.

A commercial grade of diethyl oxalate was distilled several times before combusting it with the hydroxylammonium perchlorate. The energies of combustion and formation, determined at this laboratory were: $\Delta E_c^\circ/M = -4875.81 \pm 0.55$ cal. per gram and $\Delta H_f^\circ = -193.05 \pm 0.48$ kcal. per mole, respectively.

The sample holders were made from polypropylene obtained from Kordite Corp., Macedon, N. Y. The energies of combustion and formation of this polypropylene material, determined at this laboratory, were $\Delta E_c^\circ/M = -11070.99$

Table II. Summary of Calorimetric Data of Comparison Experiments for Hydroxylammonium Perchlorate

Run No.	1	2	3
m' (benzoic acid), gram	0.487443	0.486958	0.487221
m'' (polypropylene), gram	0.380990	0.383674	0.386746
m'''' (thread), gram	0.009397	0.009442	0.009487
n^i (H_2O), moles	1.0917	1.1067	1.1096
n^i (As_2O_3), moles	0.00131	0.00131	0.00135
n' (As_2O_5), moles	0.000318	0.000318	0.000302
Δt_c, deg. ($t_f - t_i - \Delta t_{corr}$)	1.765023	1.77126	1.78071
Δt_{corr}, deg.	0.023234	0.02334	0.02391
$-\Delta E$, corr to st. states, cal.	−11.35	−11.52	−11.61
$-\Delta E^f_{dec}$ (HNO_3), cal.	−2.25	−0.89	−0.03
$-\Delta E_{ign}$, cal	−0.87	−1.07	−0.99
$-\Delta E^i$(cont.)($t_i - t_h$), cal.	+39.51	+39.98	+40.30
$-\Delta E^f$(cont.)($t_h - t_f - \Delta t_{corr}$)	−0.71	−0.55	−0.56
$n'\Delta Ec$(benzoic acid), cal.	−3077.21	−3074.14	−3075.80
$n''\Delta Ec$(polypropylene), cal.	−4217.96	−4247.66	−4281.66
$n'''\Delta Ec$(thread), cal.	−38.06	−38.24	−38.42
E_{app} (Calor.)(Δtc), cal.	−7308.90	−7334.08	−7368.77
E_{app} (Calor.), cal./deg.	4140.97	4140.60	4138.11
E_{app} (Calor.), cal./deg. average =	4139.89 ± 1.55		

Table III. Summary of Calorimetric Data for Hydroxylammonium Perchlorate

Run No.	93042	94041	94044	94053	94056
m' (cpd.), grams	1.056814	1.021680	1.004309	1.115446	1.067880
m'' (diethyl oxalate), grams	1.038790	1.130522	1.155054	1.124153	1.116679
m''' (propylene film), gram	0.053987	0.062339	0.058762	0.082384	0.085505
m'''' (fuse), gram	0.009462	0.008521	0.008506	0.007761	0.008231
n^i (H_2O), moles	1.077400	1.117530	1.085840	1.050600	1.057800
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg.	1.532360	1.651356	1.669959	1.712635	1.706123
$\Delta t_{corr'}$, deg.	0.023129	0.022654	0.023590	0.023165	0.023032
E_{app}(calor.)($-\Delta tc$), cal.	−6343.80	−6836.43	−6913.44	−7090.12	−7063.16
ΔE_{ign}, cal.	1.27	1.03	1.11	1.07	0.87
ΔE, corr. st. states, cal.	11.66	12.94	12.79	12.64	12.61
ΔE_{dec} (HNO_3), cal.	11.60	10.58	14.41	12.53	15.34
ΔE_{dec} (As_2O_5), cal.	33.00	26.58	23.88	34.44	25.70
$n''\Delta Ec$(diethyloxalate), cal.	−5064.95	−5512.21	−5631.83	−5481.16	−5444.72
$n'''\Delta Ec$(prop. film), cal.	−597.69	−690.16	−650.55	−912.07	−946.62
$n''''\Delta Ec$(fuse), cal.	−38.32	−34.51	−34.46	−31.43	−33.33
E^i(cont)($t_i - t_h$)	−34.34	−38.71	−38.22	−38.08	−38.13
E^f(cont)($t_h - t_f + \Delta t_{corr}$)	+0.48	+0.52	+0.54	+0.48	+0.48
ΔEc, kcal./mole (energy of reaction between one mole of HAP + one mole of diethyl oxalate in presence of oxygen and water as given above in equation, and at constant volume)	−790.817	−789.196	−789.922	−789.427	−790.259
ΔHc, kcal./mole (same as Ec but at constant pressure)	−789.780	−788.160	−788.886	−788.390	−789.222
ΔH_f°, kcal./mole	−65.26	−66.89	−66.16	−66.66	−65.82
Average					
ΔEc, kcal./mole	−789.92 ± 0.65				
ΔHc, kcal./mole	−788.88 ± 0.65				
ΔH_f°, kcal./mole	−66.16 ± 0.65				
ΔH_f°, kcal./100 gram	−49.86 ± 0.49				

$\pm$ 4.1 cal. per gram and $\Delta H_f^\circ = -20.34 \pm 0.17$ kcal. per mole, respectively. The fuse was an unmercerized cotton thread ($\Delta E_c^\circ/M = -4050$ cal. per gram).

The benzoic acid used for comparison experiments was a standard sample 39h of the National Bureau of Standards, $\Delta E_c^\circ/M = -6312.96$ cal. per gram.

Apparatus. The combustion experiments were carried out in a rotating bomb calorimeter built after a design of the Bureau of Mines, Bartlesville, Okla. (*3*). The modifications to the original instrumentation were that the ignition circuit was modified to provide a constant current ignition pulse, a precision timer was installed to program the ignition current, and the jacket heater circuit was modified and obtained a constant jacket temperature of $\pm 0.002°$ C.

The bomb (fabricated from stainless steel) has a platinum lining. The internal fittings, including the gas inlet tube, electrodes, crucible, and gimbal were made of platinum. The sealing gaskets are of fine gold and Teflon.

The average deviation from the mean in these measurements was 0.035%, and the maximum deviation was 0.059%. The temperature increments were measured with a Pt resistance thermometer and a Mueller bridge for precision resistance measurements accurate to 0.001° C.

Procedure. The weight of hydroxylammonium perchlorate to diethyl oxalate was 1 to 1. The amounts of reactants sealed in the polypropylene bag were chosen to give a temperature rise of approximately 1.6° to 1.7° C. The bag was placed in the platinum crucible of the bomb with 20 ml. of 0.0850*M* arsenious acid solution added to the bottom of the bomb. The same procedure as described in (7) was used.

ANALYTICAL

Evidence for the complete combustion of the hydroxylammonium perchlorate was obtained by infrared analysis of the gaseous reaction products and by determination of carbon dioxide by absorption on Ascarite. The results were within 1% of the calculated value. For the detection of chlorine the gaseous reaction products were vented into a vacuum system and passed through a starch KI solution. Chloride concentration in the final bomb solution was determined by the Volhard method. The NO_3^- and any NO_2^- were reduced to ammonia by Devarda's alloy, and the ammonia was distilled into excess standardized HCl. The total acidity of the bomb washings was determined by titration with NaOH after CO_2 has been removed by boiling and using phenolphthalein as indicator. The As^{+3} ions (in the solution after combustion) were analyzed by titration with standardized $KMnO_4$. The analysis showed that 13 to 17% of the chlorine in hydroxylammonium perchlorate burned to Cl_2, which was then converted to HCl by H_3AsO_3. No reaction of the HCl with the platinum lining was observed. Analysis of HCl in the bomb solution showed a recovery of 99.9% of the theoretical value.

COMPARISON EXPERIMENTS

The solubility and heat of solution of carbon dioxide in solutions of arsenious oxide, arsenic oxide, and hydrochloric acid are necessary for data reduction to standard states, but cannot be obtained by the standard calibration procedures. Therefore, the energy equivalent of the calorimeter was determined by a series of comparison experiments in which polypropylene film and benzoic acid were used (*3*). The amounts were adjusted to evolve nearly the same energy and quantity of carbon dioxide as in the combustion experiments. All data pertinent to the comparison experiments are listed in Table II.

RESULTS

The heats of formation were calculated from the combustion experiments by applying a computer program and are summarized with other calorimetric data in Table III. The energy of reaction at constant pressure and 25° C. is -788.88 ± 0.64 kcal. per mole (estimated standard deviation of the mean). The heats of formation for carbon dioxide, water, and $HCl \cdot 150H_2O$ are −94,051.8 cal. per mole (*6*), −68,317.5 cal. per mole (*6*), and −39,722 cal. per mole (*4*), respectively, and were used to calculate the heat of formation of hydroxylammonium perchlorate.

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NOMENCLATURE

m = mass of compound, gram
n = number of moles of compound
n^i = initial number of moles
t_f = final temperature of calorimeter, ° C.
t_i = initial temperature of calorimeter
t_h = reference temperature to which combustion reaction is referred
Δt_{corr} = rise in temperature of calorimeter due to thermal leakage from the outer jacket
Δtc = $t_f - t_i - \Delta t_{corr}$
E^i(cont.) = thermal changes in the bomb due to initial conditions of the bomb before ignition
E^f(cont.) = thermal changes in the bomb due to final conditions of the bomb
ΔE, corr. st. states = Washburn corrections
Σ(cont.) = $E_i(\text{cont.})(t_i - t_h) + E_f(\text{cont.})\ (t_f - t_i - \Delta t_{corr})$
$\Delta E_{dec\cdot}$ (HNO_3) = energy released from formation of nitric acid, cal.
ΔE_{dec} (As_2O_5) = energy released from formation of As_2O_5, cal.
ΔE_{ign} = energy released due to ignition, cal.
ΔEc = energy of combustion of a compound at constant volume, kcal. per mole
ΔHc = enthalpy of combustion of a compound at constant pressure, kcal. per mole
ΔH_f° = heat of formation of compound, kcal. per mole
E_{app} (calor.) = calibration of the calorimeter with thermal changes for the solubility of the gases in the bomb in As_2O_3–As_2O_5–HCl solutions that are not considered in Washburn corrections, cal. per degree.

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