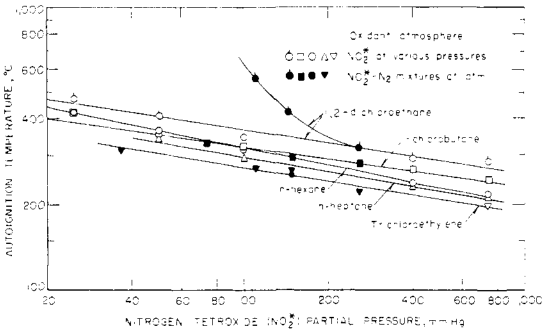

Figure 14. Logarithm autoignition temperature vs. logarithm nitrogen tetroxide (NO_2^*) partial pressure for five combustibles in NO_2^* and NO_2^*–nitrogen atmospheres at various mixture pressures (4900-cc. steel vessel)

Figure 13, the autoignition temperatures (° C.) are inversely proportional to $P_{O_2}^{0.3}$ for monomethylhydrazine and to $P_{O_2}^{<0.1}$ for the other combustibles; P_{O_2} is the oxygen partial pressure in millimeters of Hg.

A similar correlation of AIT with oxidant partial pressure was obtained for some of the present data in NO_2^* at various pressures and in NO_2^*-nitrogen mixtures at 1 atm. Figure 14 shows a plot of log AIT *vs.* log $P_{NO_2^*}$ for *n*-hexane, *n*-heptane, and three of the halogenated hydrocarbons. Here, most of the AIT data are inversely proportional to $P_{NO_2^*}^{0.15-0.2}$. However, those for 1,2-dichloroethane display a greater dependence upon NO_2^* percentage than upon mixture total pressure (without diluent) below 250 mm. of Hg. Nevertheless, the autoignition temperatures of these combustibles appear to correlate in this manner over at least a limited range of mixture pressures and oxidant concentrations.

CONCLUSIONS

The minimum autoignition temperatures of the combustibles examined in this study are lower in oxygen than in air, although the variation is not great for most of the combustibles at atmospheric pressure. Of the combustibles, the highest AIT's in these oxidants are found with hydrogen and methylene chloride and the lowest values with hydrazine and monomethylhydrazine. Halogenated hydrocarbons such as 1-chlorobutane, 1,2-dichloroethane, 1,1,1-trichloroethane, and trichloroethylene tend to ignite at lower temperatures than their parent hydrocarbons. In comparison, NO_2^* appears to be more effective than oxygen in promoting the ignition of all the combustibles except *n*-heptane and 1-chlorobutane; with this oxidant, the hydrazine fuels are hypergolic at room temperature.

The AIT's tend to increase abruptly when the pressure or oxidant concentration is decreased below some critical value, depending upon the fuel-oxidant system and the vessel size. Diluent type did not appear to be important. Some of the AIT data obtained at various test conditions correlate reasonably well with the oxidant partial pressure of the mixture.

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Calorimetric Study of Iron(III) Chloride

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Enthalpies of sublimation and vaporization, 30.6 ± 1 (550° K.) and 12.4 ± 0.5 (583° K.) kcal. mole^{-1} Fe_2Cl_6, respectively, have been determined calorimetrically. Preliminary calorimetric results are also reported for the formation of $Fe_2Cl_6(g)$ from the elements.

A VACUUM heat-leak calorimeter (*1*), suitable for measurement of heats of formation and vaporization of many substances volatile in the range between room temperature and 700° K., has been used for a thermochemical study of iron(III) chloride. A ca. 100-ml. round-bottomed borosilicate glass bulb was used as a reaction cell. After inserting a small capsule, containing either $FeCl_3$ or Fe, and a magnetically controlled drop weight system which served to break the capsule at the appropriate time, the flask was evacuated and baked out. Prior to final seal-off, it was filled with chlorine at a pressure sufficient either for the reaction of the iron and/or for the prevention of decomposition of the iron(III) chloride. The prepared cell was surrounded by a radiation shield and placed inside an isothermal iron cylinder, held within ± 0.01° C.; the whole assembly was covered with a steel bell jar and evacuated. The cell temperature was monitored with a calibrated Chromel-Alumel thermocouple, used in conjunction with a Leeds and Northrup K-3 potentiometer, Fluke Electronic Galvanometer, and a Leeds and Northrup recorder. Immediately following each study of a vaporization reaction the energy equivalent of the observed temperature change was determined by applying power to a nichrome heater (encased in borosilicate glass inside the cell) at a rate such that the temperature-time curve produced by the reaction was duplicated as closely as possible. For endothermic processes, the authors assumed, since the temperature changes were only of the order of a few tenths of a degree, that a calibration which produced a mirror image of the curve represented an equivalent amount of energy. Generally, six to 10 suitable calibration runs were made, and the calibration constants (watt-seconds per microvolt rise) for these were averaged. The over-all uncertainty was of the order of 5% for measured heats as small as 2 calories, dropping to about 2% for heats larger than 10 calories.

The heat of vaporization of mercury (Table I) was measured to check the over-all performance of the apparatus. Corrections for the quantity of mercury already vaporized within the capsule prior to its rupture and for gas imperfection were negligible. The average of 14.7 kcal. mole^{-1} is about 3% larger than the value 14.3 based on vapor pressure data (*2*). The difference appears well within the combined experimental uncertainties of the calorimetric and vapor pressure work.

B and A reagent grade (for standardization) iron wire, assayed as 99.90% Fe, was used. Samples of $FeCl_3$ were prepared by reaction of iron wire with an excess of purified chlorine in an all borosilicate glass vacuum system at about 400° C. Crystals of iron(III) chloride were transferred into capsules without opening the system. The quantity of $FeCl_3$ was determined after the calorimetric measurements by spectrophotometric analysis as the 1,10-phenanthroline complex of Fe(II).

Chlorine was obtained by thermal decomposition of vacuum dried (120° C.) cupric chloride. The gas evolved around 450° C. contained small amounts of water and HCl. The chlorine was isolated by vacuum distillation several times from −80° to −196° C. and several times from −52° to −80° C., each time removing the first and last (ca. 5%) fractions.

The vaporized product in the calorimeter cell was always observed to condense in the form of jet black easily-sublimed crystals. No trace of the colored oxide or of oxyhalide derivatives of iron, which may be expected to leave a nonvolatile residue on gentle flaming in vacuum, was observed.

RESULTS AND DISCUSSION

Density measurements at temperatures between 760° and 1070° K. give evidence that at pressures in the vicinity of 1 atm., the vapor of iron(III) chloride is a mixture of $FeCl_3(g)$ and $Fe_2Cl_6(g)$ (*3-5*). Although not in close quantitative agreement, all the independent studies indicate that, in the temperature and pressure range of the present work, the dimer is the dominant species (> 95%). Equation 1, derived by Wilson and Gregory (*6*) from the data of Kangro and Bernstorff (*4*), was used to calculate

$$\log_{10}(P^2_{FeCl_3}/P_{Fe_2Cl_6})_{torr} = -6907\ T^{-1} + 9.391 \qquad (1)$$

the composition of the vapor products. Chlorine pressures expected for equilibrium between $FeCl_2(s)$ and $Fe_2Cl_6(g)$ were based on Equation 2 (*6*).

$$\log_{10}(P_{Cl_2}/P_{Fe_2Cl_6}) = 1408\ T^{-1} - 3.710 \qquad (2)$$

A sufficient excess of chlorine was used to exceed these values by a large margin. The partial pressure of $FeCl_2(g)$ expected at the temperatures of these studies is not sufficient to influence the calorimetric results (*7*).

Table I. Calorimetric Measurement of the Heat of Vaporization of Mercury

Temperature, ° K.	552	553	583
Moles of Hg × 10^4	3.67	3.90	2.38
Final pressure, Hg(g)(torr)	134.4	143.0	84.7
Satd. vapor pressure, Hg(torr)	152.9	156.6	305.6
Pressure of argon in cell(torr)	142	102	102
Calories measured	4.93	5.33	3.23
$\Delta H°$ [Hg, (liq) → Hg, (g)], 550° K., kcal. mole^{-1} (2)[a]	14.5	14.8	14.8

[a] Relative enthalpy data (2) were used to convert enthalpies to a common temperature of 550° K., the temperature mean for $FeCl_3$ sublimation studies.

Iron(III) chloride saturation vapor pressures have been reported by a number of investigators (*5-13*). The equations

$$[\text{above } FeCl_3(s)]\ (6)\ \log_{10}P_{Fe_2Cl_6}(\text{torr}) = -7142\ T^{-1} + 15.111 \qquad (3)$$

$$[\text{above } FeCl_3(\text{liq})]\ \log_{10}P_{Fe_2Cl_6}(\text{torr}) = -2662\ T^{-1} + 7.351 \qquad (4)$$

are representative of the more consistent sets of results. Equation 4 was estimated in the present work from the data of Stirnemann (*9*), as corrected for the presence of $FeCl_3(g)$ and Cl_2 by Kangro and Petersen (*14*). The melting point of $FeCl_3(s)$ is reported as 577° K. (*15*).

For the present system $Q_v = \Delta E = \Delta H - \Delta(PV)$. Correction for gas imperfection (estimated) (*16*) appeared never to exceed, and in general to be much less than, 1% of the measured heat. Hence, the calculated enthalpy changes have been represented as standard state values. For comparison, enthalpies were converted to a common temperature (Tables II and III) with relative enthalpy data from (*2*).

The table entries labelled "capsule correction" indicate the number of moles of Fe_2Cl_6 already vaporized in the small capsule before its rupture. These numbers were subtracted from the total number of moles present. The entries "correction for $FeCl_3(g)$—" indicate the number of calories necessary to dissociate $Fe_2Cl_6(g)$ to form the equilibrium amount of $FeCl_3(g)$ in the final mixture as predicted by Equation 1. These values were subtracted from the total number of calories measured in the vaporization studies to get the heats equivalent to vaporization of a number of moles of Fe_2Cl_6 equal to half the number of moles of iron (less the capsule correction) in the system. These corrections are small.

The heat of sublimation determined calorimetrically, if the vapor is assumed to be Fe_2Cl_6, is only slightly below the result based on vapor pressure studies (31.8 kcal. at 550° K.) (*2*). The fact that the calorimetric value agrees reasonably well only on the basis of dimer gives additional evidence that this species is the dominant one.

The calorimetric value for the heat of vaporization is also in reasonably good agreement with values based on vapor pressure studies. Both Stirnemann (*9*) and Cook (*17*) have measured pressures above liquid $FeCl_2$ and $FeCl_3$ solutions; the interpretation of their data is made difficult by problems relating to liquid state activities and knowledge of the composition of the vapor phase. Kangro and Peterson (*14*) have corrected Stirnemann's data to allow for the decomposition pressure of chlorine and derive a value of 12.2 kcal. for the enthalpy of vaporization of a mole of Fe_2Cl_6; Cook (*17*) obtains 14.6 kcal.; the present direct value is 12.4 kcal. Cook has also determined the heat of fusion by drop calorimetry as 9.0 kcal. mole^{-1} $FeCl_3(s)$; when this value is combined with this heat of vaporization, the result is in excellent agreement with the calorimetric value for the enthalpy of sublimation. The authors were unable to detect any systematic variation of the heats

Table II. Calorimetrically Determined Heat and Enthalpy of Sublimation of $FeCl_3$(s)

Experimental temperature, ° K.	546	547	549	552	553
Quantity as moles $Fe_2Cl_6 \times 10^4$	0.964	1.430	1.694	1.916	3.018
Final pressure Fe_2Cl_6(torr)	38.6	52.0	68.0	77.0	110.8
Satd. vapor pressure Fe_2Cl_6, Equation 3	107.1	113.2	126.5	148.9	157.0
Partial pressure $FeCl_3$(g), Equation 1	0.15	0.17	0.21	0.24	0.30
Partial pressure Cl_2(torr)	33.4	33.5	33.6	33.7	33.8
Pressure Cl_2(torr) needed to prevent formation of $FeCl_2$(s), Equation 2	2.9	3.8	5.0	5.4	7.7
Calories measured	2.71	4.04	5.16	5.88	8.82
Correction (cal.) for $FeCl_3$(g), Equation 1	0.006	0.008	0.009	0.010	0.013
Capsule correction:[a] moles $Fe_2Cl_6 \times 10^6$	0.97	1.21	1.13	1.28	1.39
$\Delta H°$ (corrected to 550° K.) kcal. mole^{-1} for $2FeCl_3(s) \rightarrow Fe_2Cl_6(g)$[a]	29.4	29.5	31.7	31.9	30.5

[a] The average value of $\Delta H°_{550° K.}$ (sublimation) is 30.6 kcal. mole^{-1} with a standard deviation of 1 kcal. The standard deviation $[\delta^2/n]^{1/2}$ is of the order expected from the experimental uncertainties in calibration and analysis.

Table III. Calorimetrically Determined Heat and Enthalpy of Vaporization of $FeCl_3$(liq)

Experimental temperature, ° K.	583	584	617
Quantity as moles of $Fe_2Cl_6 \times 10^3$	1.050	1.069	0.219
Final pressure Fe_2Cl_6(torr)	406.6	478.0	98.0
Satd. vapor pressure Fe_2Cl_6, Equation 4	608	619	1085
Partial pressure $FeCl_3$, Equation 1	1.2	1.3	1.2
Partial pressure of Cl_2(torr)	113	113	702
Pressure of Cl_2(torr) needed to prevent formation of $FeCl_2$(s), Equation 2	21	25	36
Calories measured	11.93	12.30	2.196
Correction (cal.) for $FeCl_3$(g), Equation 1	0.05	0.05	0.04
Capsule correction; moles $Fe_2Cl_6 \times 10^6$	4	4	3
$\Delta H°$ (corrected to 583° K.) kcal. mole^{-1} for $2FeCl_3(liq) \rightarrow Fe_2Cl_6(g)$[a]	12.5	12.7	11.9

[a] The average value of $\Delta H°_{550° K.}$ (vaporization) is 12.4 kcal. mole^{-1}; the standard deviation for the three measurements was 0.3 kcal.; however the over-all uncertainty of the value is estimated as 0.5 kcal.

with change in the quantity—i.e., partial pressures in the final state—of iron(III) chloride.

A series of calorimetric measurements of the heat of reaction of elemental iron with chlorine (in excess) was also completed. Seven independent experiments between 587° and 654° K. gave an average standard enthalpy of formation of Fe_2Cl_6(g) of -180 ± 5 kcal. per mole. This result is unexpectedly large, however, when taken with heat capacity and heat of vaporization data to derive a standard enthalpy of formation of $FeCl_3$(s) at 298° K., a value of -107 ± 3 kcal. mole^{-1} is obtained. The latter is ca. 11 kcal. more negative than the currently accepted result (2) based on heat of solution measurements (*18*). Although the heat of solution studies involve a complicated series of solution and solution reaction processes, the result seems generally consistent with enthalpy values deduced from independent equilibrium studies—e.g., $\Delta H°$ from Equation 2 and a heat of solution based heat of formation of $FeCl_2$(s) (*2*). In the present authors' work, the assumed vapor composition does not appear to be critical; this effectively cancels when the formation and vaporization results are combined. No dependence of the molar heats of formation on the amount of iron used (final pressure of the vapor varied between 5 and 80 torr) or the relative excess of chlorine (varied by a factor of 2) could be detected. The authors have no reasonable explanation to propose for the discrepancy; it appears considerably larger than the estimated uncertainty; yet in view of the limited amount of experience with calorimetric study of formation reactions of this type, the authors' result is reported as tentative. It must be confirmed by further calorimetric work before the validity of the currently accepted enthalpy of formation of Fe_2Cl_6(g) is seriously questioned.

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