MASTER

RESEARCH AND DEVELOPMENT STUDIES ON
WASTE STORAGE PROCESS

M. H. Ortner C. J. Anderson P. F. Campbell
(Vitro Laboratories)

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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M. H. Ortner C. J. Anderson P. F. Campbell

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PHILLIPS
PETROLEUM
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Atomic Energy Division

Contract AT(10-1)-205

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RESEARCH AND DEVELOPMENT STUDIES ON WASTE STORAGE PROCESS

M. H. Ortner, C. J. Anderson, P. F. Campbell

FOREWORD

This report summarizes the supplementary research on waste storage processes requested by Phillips Petroleum Company, Atomic Energy Division, in subcontract C-215 to Vitro Laboratories. The purpose of the study was to furnish process chemistry data on the thermal decomposition of fission product oxides and nitrates relative to waste calcination operations, and to determine the thermodynamic properties and measure the kinetics of decomposition of ruthenium tetroxide.

Most of the work that is reported is reasonably complete. However, it was impossible to complete all of the objectives of the original contract within the allotted time. In particular, the kinetic studies of ruthenium tetroxide decomposition were scarcely started, and hence are incomplete. The original contract was extended in order to complete the program. The work had been resumed only a short time when the contract was suddenly terminated at the convenience of the contractor. The incomplete results of the contract extension will not be published in report form, but will be abstracted in this foreword where they reflect on IDO-14504.

RuO₂ Decomposition

The thermal stability study of RuO₂ summarized on pages 6, 7 and 8 was extended to dissociation pressure measurements between 1000 and 1450°C. RuO₂ was prepared by several methods and its dissociation pressure measured in the presence and absence of excess ruthenium metal with a mercury manometer. The results were not sufficiently consistent over a series of six samples to give a satisfactory dissociation curve. All of the results were considerably lower than the presently accepted values reported by Remy in 1924. Since the heat and free energy of formation of RuO₂ in Table 3 are based upon Remy's data, they may prove to be in error. The heat of formation calculated from the new data is -75 Kcal/mol compared to -52.5 Kcal/mol in Table 3. Such a large discrepancy should be resolved by more precise measurements. An average of all of the data taken above 10 mm Hg pressure (under the extended contract) can be expressed by the equation

$$\ln P \text{ (mm)} = - \frac{37,900}{T \text{ (°K)}} + 27.5$$

The identification of the solid phase RuO₂ mentioned on page 78 was continued in the Spectrographic Laboratory at the ICPP by X-ray diffraction methods. A major crystalline component was observed but not identified.

Thermal Analysis of $\text{CsNO}_3\text{-Al}_2\text{O}_3$ Mixtures

A reaction between cesium oxide and alumina to give CsAlO_2 is suggested on page 68. Further studies on the compound failed to identify a crystalline form by X-ray diffraction. A number of medium and weak lines were unidentified. Platinum impurity and excess $\alpha\text{-Al}_2\text{O}_3$ were observed. A water soluble fraction indicated a Cs:Al mol ratio of 1 : 1 by chemical analysis.

Thermodynamic Functions of RuO_4

Investigation of the infra-red spectrum of RuO_4 gas in the CsBr region confirmed the existence of a fundamental absorption at $330 \pm 2 \text{ cm}^{-1}$. This frequency, together with the fundamental at 913 cm^{-1} as measured under the original contract, and a recent assignment for the class A, raman-active fundamental at 880 cm^{-1} , was used to calculate the frequency of the remaining class E raman-active fundamental. Thermodynamic functions reported on page 44 have been recalculated and reported in table i and table ii.

Thermal Decomposition of RuO_4

Although the gas phase decomposition of RuO_4 between $100\text{-}200^\circ\text{C}$ was the major objective of the extended contract, the program was terminated before any measurements could be made.

Strontium Volatility

On page 63 are described the TGA results on strontium oxide. The slight loss of weight was attributed to volatile SrO_2 , formed by the oxidation of SrO at temperatures up to 727°C . More recent studies at the Idaho Chemical Processing Plant have shown that upon heating strontium oxalate traced with strontium-85 and igniting the oxide at fixed temperatures between 500° and 1100°C for 1.5 to 3 hour periods under a stream of dry air, no strontium was found in any part of the equipment except the combustion boat within limits of 0.001 per cent.

C. M. Slansky

Technical Liaison Representative
Atomic Energy Division
Phillips Petroleum Company

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Table i

VIBRATIONAL THERMODYNAMIC FUNCTIONS OF RuO_4 (cal/g. mol $^\circ\text{K}$)

Adsorption Frequency $w_i(\text{cm}^{-1})$	Degeneracy (d_i)	$\frac{w_i}{298.16}$	$\frac{w_i}{400}$	$\frac{w_i}{500}$	$\frac{w_i}{600}$	$\frac{w_i}{700}$	$\frac{w_i}{800}$	$\frac{w_i}{900}$	$\frac{w_i}{1000}$
913	3	3.06	2.28	1.83	1.52	1.30	1.14	1.01	0.91
880	1	2.95	2.20	1.76	1.47	1.26	1.10	0.98	0.88
330	3	1.11	0.83	0.66	0.55	0.47	0.41	0.37	0.33
293	2	0.98	0.73	0.59	0.49	0.42	0.37	0.33	0.29
$(H-E_0/T)_{\text{vib}}$									
913	3	0.3261	0.7653	1.2159	1.6479	2.0313	2.3535	2.6445	2.8860
880	1	0.1230	0.2773	0.4348	0.5768	0.7027	0.8133	0.9051	0.9878
330	3	2.4180	3.0942	3.5724	3.9102	4.1712	4.3749	4.5144	4.6575
293	2	1.8102	2.2460	2.5232	2.7364	2.8936	3.0096	3.1050	3.2024
Total		4.6773	6.3828	7.7463	8.8713	9.7988	10.5513	11.1690	11.7337
C_{pvib}									
913	3	1.4490	2.6046	3.4479	4.0614	4.4898	4.7871	5.0142	5.1778
880	1	0.5280	0.9161	1.1952	1.3868	1.5217	1.6196	1.6882	1.7415
330	3	4.8411	5.3001	5.5323	5.6589	5.7384	5.7909	5.8218	5.8500
293	2	3.3764	3.6280	3.7436	3.8132	3.8550	3.8812	3.9000	3.9166
Total		10.1945	12.4488	13.9190	14.9203	15.6049	16.0788	16.4242	16.6859
$-(F-E_0/T)_{\text{vib}}$									
913	3	0.0720	0.2280	0.4452	0.7101	0.9978	1.2861	1.5882	1.8768
880	1	0.0285	0.0858	0.1647	0.2556	0.3542	0.4572	0.5563	0.6583
330	3	1.3497	2.1522	2.9166	3.6033	4.2351	4.8189	5.2752	5.7999
293	2	1.1126	1.7114	2.2198	2.7086	3.1426	3.5168	3.8666	4.2744
Total		3.2108	4.1774	5.7463	7.2746	8.7297	10.0790	11.2863	12.6094
$S_{\text{vib}} = (H-E_0/T) - (F-E_0/T)$									
Total		7.888	10.560	13.493	16.146	18.529	20.630	22.455	24.343

Table ii

TOTAL THERMODYNAMIC FUNCTIONS FOR $\text{RuO}_4(\text{g})$

	298.16°K	400°K	500°K	600°K	700°K	800°K	900°K	1000°K
<u>Heat Capacity (cal/g mol °K)</u>								
Translation	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97
Rotation	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98
Vibration	10.19	12.45	13.92	14.92	15.60	16.08	16.42	16.69
Total	18.14	20.40	21.87	22.87	23.55	24.03	24.37	24.64
<u>-Free Energy Function (Cal/g mol °K)</u>								
Translation	36.25	37.71	38.82	39.72	40.49	41.15	41.74	42.26
Rotation	17.46	18.34	19.01	19.55	20.01	20.41	20.76	21.07
Vibration	3.21	4.13	5.75	7.27	8.73	10.09	11.29	12.61
Total	56.92	60.23	63.58	66.54	69.23	71.64	73.79	75.94
<u>Enthalpy (cal/g mol)</u>								
Translation	1,481	1,587	2,483	2,980	3,476	3,973	4,470	4,966
Rotation	889	1,192	1,490	1,788	2,096	2,384	2,682	2,980
Vibration	1,395	2,553	3,873	5,323	6,859	8,441	10,052	11,734
Total	3,765	5,332	7,946	10,091	12,421	14,798	17,204	19,680
<u>Entropy (cal/g mol °K)</u>								
Translation	41.23	42.69	43.80	44.70	45.47	46.13	46.72	47.24
Rotation	20.48	21.36	22.03	22.57	23.03	23.43	23.78	24.09
Vibration	7.89	10.56	13.49	16.15	18.53	20.63	22.46	24.34
Total	69.60	74.61	79.32	83.42	87.03	90.19	92.96	95.67

RESEARCH AND DEVELOPMENT STUDIES ON
WASTE STORAGE PROCESS

Final Report
July 8, 1958 - June 30, 1959

by

M. H. Ortner, C. J. Anderson, F. F. Campbell

August 31, 1959

Research Subcontract C-215 Under Phillips Petroleum
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(Vitro Job 2138)

Approved:

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V I T R O L A B O R A T O R I E S

D I V I S I O N O F V I T R O C O R P O R A T I O N O F A M E R I C A

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Final Report
July 8, 1958 - June 30, 1959

Vitro Job 2138

RESEARCH AND DEVELOPMENT STUDIES ON WASTE STORAGE PROCESS

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Introduction

This is the final report on Research Subcontract C-215 under Phillips Petroleum Company Contract AT(10-1)-205, and covers work performed during the period July 8, 1958 through June 30, 1959.

The objective of the research under this program was to obtain fundamental information on:

- (1) The physical and chemical properties of the fission product oxides and nitrates of Ru, Cs, Ce, Sr, Nb, and Zr.
- (2) The thermal stability of selected fission product oxides and nitrates at temperatures up to 1500°C.
- (3) The gas phase decomposition of ruthenium tetroxide.

Previous quarterly progress reports in this series which were published by Vitro are numbered V-2138-3-0, V-2138-6-0, V-2138-9-0, and V-2138-12-0.

SUMMARY AND CONCLUSIONS

The basic objectives of this program were the determination of the thermal stability of various fission product oxides and nitrates, and an investigation of the gas phase decomposition of ruthenium tetroxide. To accomplish these objectives, a literature survey was first made of available physical and chemical data for the oxides and nitrates of Cs, Sr, Ru, Zr, Nb and Ce. This data was supplemented by a calculation of thermodynamic functions for RuO_4 vapor from the experimentally determined infrared spectrum and the theoretically calculated raman-active fundamentals.

The spectrum of RuO_4 vapor from 350-500 $\text{\AA}$, a solution of RuO_4 in CCl_4 from 4000-10,000 $\text{\AA}$, and liquid RuO_4 from 2-32 microns was determined. In the near ultraviolet and visible regions, absorptions were found at 385 and 600 $\text{\AA}$. One of the two infrared active fundamentals was identified at 913 cm^{-1} together with its first overtone at 1800 cm^{-1} . Although the low frequency end of the spectrum was masked by water bands, a tentative assignment for the second infrared fundamental was made at 333 cm^{-1} . The raman-active fundamentals, calculated by the orbital valency force field approximation, were at 689 cm^{-1} and 322 cm^{-1} .

Using the above values for the vibrational frequencies, the heat capacity, entropy, enthalpy, and free energy function for RuO_4 vapor were calculated at 100° intervals from 298.16°K to 1000°K . The following assumptions were made: chemical atomic weights, rigid rotor-harmonic oscillator approximation, an interatomic distance of 1.66 $\text{\AA}$ and symmetry number of 12, and nuclear spin and isotope mixing contributions were neglected. The calculated values of the thermodynamic functions at 298.16°K were:

Heat Capacity	18.45 cal/mol $^\circ\text{K}$
Entropy	68.76 cal/mol $^\circ\text{K}$
Free Energy Function	-56.13 cal/mol $^\circ\text{K}$
Enthalpy	3750 cal/mol

The thermodynamic and phase transition data were used to eliminate several stable compounds from the thermal stability studies and, in addition, as an aid in interpreting thermograms and weight loss vs. temperature curves obtained in differential thermal (DTA) and thermogravimetric (TGA) analysis.

Of the compounds considered for thermal analysis, only the oxides of Cs, Sr and Ru are susceptible to decomposition or volatilization at temperatures up to 1500°C. Literature data also indicated that no solid solutions or compounds are formed between Al_2O_3 and SrO, CeO_2 , or ZrO_2 below 1800°C, and that no reactions occur between Al_2O_3 and Nb or Zr metal up to 1600°C. The results of DTA and TGA of other non-stable fission product oxides and nitrates are summarized below.

Thermal Stability Studies

To determine the physical and chemical changes that might occur if the temperature of stored, calcined, fissioned product wastes should become uncontrolled and reach 1500°C, differential thermal (DTA) and thermogravimetric analyses were made of selected fission product oxides and nitrates both alone, and in the presence of alumina.

Equipment used for DTA and TGA was constructed and calibrated at WOL. The TGA apparatus was built around a conventional analytical balance which was modified by the addition of a linear variable differential transformer to one of the arms. Motion of the armature (attached to the balance beam) was converted to an AC signal, which was tapped off the transformer secondary, converted to DC, and fed to a strip chart recorder. The DTA apparatus was conventional. The design and operation of this equipment is described in the report.

Thermograms were obtained for strontium nitrate, strontium oxide, and mixtures of strontium oxide with alumina. For $\text{Sr}(\text{NO}_3)_2$, no crystalline transitions were noted up to the melting point (627°C). Decomposition was observed to begin at 650°C in DTA and at 610°C in TGA. The decomposition, accompanied by the evolution of nitrous fumes, was rapid and was complete at 750°C. No further thermal or chemical changes were noted up to 1400°C. The observed weight loss in TGA between 610° and 750°C was 99% of that calculated for the decomposition of $\text{Sr}(\text{NO}_3)_2$ to SrO.

Thermal analysis of SrO alone, and mixtures of $\text{SrO-Al}_2\text{O}_3$ indicated a small (~ 6%) weight loss in the 500°-700°C temperature range which may be due to the formation of volatile SrO_2 . In agreement with the literature, there was no evidence of compound formation up to 1510°C.

Several thermal changes were noted in DTA of cesium nitrate. At 200°C, a deep endotherm was obtained due to a hexagonal to cubic crystalline transition. Fusion was observed at 430°C. The temperature at which decomposition

begins was not evident in DTA but was easily determined by TGA. In TGA, the sample was stable to 710°C and then rapidly lost weight until, at 970°C, the sample was completely volatilized. As the relatively low temperature of volatilization might pose a problem in the operation of the ICPP Fluid Bed Calciner, an investigation of the effect of Al_2O_3 on the thermal stability of CsNO_3 was of interest.

Thermal analysis and chemical analysis of quenched samples of a 2 to 1 by weight mixture of calcined Al_2O_3 and CsNO_3 indicated that the compound CsAlO_2 is formed at 940°C which remains stable up to 1100°C. This process greatly reduces the volatility of the nitrates and oxides of cesium and is of significance in the storage of fission product wastes containing radioactive Cs^{134} or Cs^{137} .

The structure of the curves obtained in TGA and DTA of zirconyl nitrate dihydrate was very similar. Each curve showed a three stage endothermic volatilization process which occurred in the temperature ranges 60°-190°C, 190°-215°C, and 215°-300°C. The endothermic reactions were complete at 500°C and no other major thermal effects were noted up to 1520°C. Analysis of the curves indicates that zirconyl nitrate dehydrates and decomposes in a stepwise manner to ZrO_2 . The initial loss of two moles of water is complete at 190°C, the decomposition is complete at 450°C, and no further changes are observed up to 1500°C.

Cerous nitrate hexahydrate is quantitatively decomposed to CeO_2 , water, and nitrogen oxides between 100° and 400°C. Bound water is evolved between 100° and 270°C, and the anhydrous nitrate decomposes at a rapid rate to the oxide between 270° and 400°C. The product CeO_2 is stable up to 1500°C.

The only detectable phase transition, decomposition, or volatilization observed in DTA and TGA of mixtures of Al_2O_3 and Nb_2O_5 up to 1500°C was the melting of Nb_2O_5 at 1460°C. There was no evidence of compound formation.

TGA of ruthenium dioxide showed no significant weight loss below 1025°C. Above 1025°C, the sample began to lose weight, at a slow rate up to 1400°C, and then more rapidly up to 1515°C. The reaction was not complete at 1515°C. In DTA, only one endotherm was observed at elevated temperatures (1455°C) although the reported melting and boiling points are at 1228° and 1400°C. The weight loss observed between 1025°C and 1515°C was 130% of the theoretical loss, assuming that the only reaction which occurs is the decomposition of RuO_2 to the elements. Therefore, in this temperature range, volatilization of ruthenium as RuO_2 or RuO_4 is also an important process. When RuO_2 or

mixtures of RuO_2 and Al_2O_3 are rapidly quenched in air from 1200°C , the sample recovered is mainly ruthenium metal. Slow cooling from 1200°C yields RuO_2 .

Analytical data on the purity of purchased RuO_2 , and RuO_2 prepared at Vitro for use in the thermal stability and kinetics studies was conflicting. Spectrographic analysis and hydrogen reduction analysis indicated a purity greater than 99%. X-ray diffraction analyses, of the same material, however, showed the presence of a few percent ruthenium metal, and yielded a diffraction pattern which was not identical with the ASTM pattern. Work is now underway at ICPP to determine if an allotropic form of RuO_2 is present, which is not mentioned in the literature. An objective of the proposed future program at WOL is therefore the preparation of a well-characterized sample of RuO_2 for use in heat capacity measurements and kinetics studies.

Kinetics of the Vapor Phase Decomposition of RuO_4

A study of the kinetics of the vapor phase decomposition of RuO_4 was undertaken to assist in explaining the processes leading to ruthenium volatility in the ICPP calciner. In all runs, the decomposition was followed in a static system, wherein a weighed amount of RuO_4 and various additives were sealed into a Carius Tube. The sealed tubes were heated in a constant temperature bath for a measured time, and the reaction was then quenched in a dry-ice bath, the tubes opened and analyzed.

Although it was originally intended to study the reaction in a continuous system, early experiments in the static system gave non-reproducible results, and much effort was devoted thereafter to determining the cause of the variability and the effect of various additives on the rate of reaction. As a result of these studies, the precision of the data has been improved to the point that future studies will be conducted in a vacuum system, in which the concentration of RuO_4 may be continuously monitored and the effect of added gases on the rate of reaction determined.

In preliminary experiments involving RuO_4 vapor and air, it was determined that the decomposition exhibits an induction period, the duration of which was related to, but not entirely controlled by, the concentration of water vapor and the temperature. Upon addition of Anhydrone to the reaction vessel, the length of the induction period decreased but the time of initiation of the reaction remained uncontrolled, consequently plots of the percent decomposition versus time were extremely scattered. Pretreating the surface of the reaction vessel by coating with molten potassium pyrosulfate, heating to

elevated temperatures, cleaning with alkaline solutions, etching with HF, and the use of Vycor instead of Pyrex did not improve the reproducibility. In these early runs it was noted that the decomposition began at a small area of the glass surface where black RuO_2 was deposited, and the reaction then spread out from that point. It was therefore suspected that the reaction was autocatalytic, and the effect of the product RuO_2 on the rate was then investigated.

The addition of RuO_2 to the reaction vessel greatly decreased the duration of the induction period and the time of initiation of the reaction became better controlled. In the temperature range $110^\circ\text{--}140^\circ\text{C}$, with initial RuO_4 concentrations of the order of 0.3 atmospheres, and with the addition of 25-150 mg of RuO_2 , the apparent rate constant (taken as the slope of the straight line obtained by plotting the fraction of RuO_4 undecomposed vs. time) was given by

$$k(\text{min}^{-1}) = 7.119 \times 10^{14} e^{-30,500/RT},$$

and the entropy of activation at 140°C was equal to $13.4 \text{ cal/mol}^\circ\text{K}$. Under these conditions the rate was independent of the quantity of added RuO_2 . The duration of the induction period, however, could be decreased by increasing the temperature, the quantity of added RuO_2 , or by prolonged preheating of the RuO_2 ; and increased by increasing the initial concentration of RuO_4 . At this point, this study was suspended in favor of investigating the effect of ruthenium metal and silica gel on the rate of decomposition.

The experiments on the effect of ruthenium metal were conducted in Carius Tubes containing various amounts of RuO_4 , 1 gram of Anhydrone, and 100 mg of -80 mesh ruthenium powder. After heating for 3 hours at 110°C , 54% of the initial weight of RuO_4 had decomposed. After two hours at 140°C , the RuO_4 was completely decomposed. At least two modes of decomposition are thermodynamically possible in this system; decomposition of RuO_4 to RuO_2 and O_2 and/or reduction of RuO_4 to RuO_2 by ruthenium metal. Analysis of the ratio of the RuO_4 reacted to the RuO_2 produced in a series of such reactions indicated that the predominate mode of reaction is the direct decomposition. The rate of this reaction under the conditions used in the experiment was approximately 5 times as fast as the reduction.

The mechanism of decomposition of RuO_4 at a silica gel surface is apparently quite different than that which occurs in the presence of RuO_2 . In experiments in which silica gel was added to the reaction tubes containing RuO_4 , the

logarithm of the quantity of RuO_2 produced, rather than the fraction of the RuO_4 remaining, was found to be a linear function of time. The data, at 110°C and 125°C , are represented by

$$\ln (\text{Co}-\text{C}) = 0.0864t (\text{min}) - 1.192 \quad (110^\circ\text{C})$$

$$\ln (\text{Co}-\text{C}) = 0.2602t (\text{min}) - 1.082 \quad (125^\circ\text{C})$$

The slope in the above equations is the apparent rate constant, and the 95% confidence intervals about these values are 0.0495 to 0.123 and 0.197 to 0.323 at 110°C and 125°C , respectively. Substitution of the apparent rate constants in the Arrhenius Equation gave an energy of activation of 21.9 kcal/mol. Pre-drying the silica gel retarded the rate, the addition of ground glass to the reaction vessel did not significantly influence the rate, and the addition of RuO_2 to the silica gel increased the rate approximately 22%.

EXPERIMENTAL

I. Physical Properties of Fission Product Oxides and Metals

A. Miscellaneous Physical Data

To determine the changes in state and reactions which may occur when fission product oxides are heated to 1500°C, and to eliminate those materials which have already been studied from the present research, a thorough literature survey was made of transition temperatures, heats of transition, and thermodynamic functions for the metals Ru, Zr, Cs, Ce, Sr, Nb, and their oxides. Melting points, boiling points, heats of transition and other miscellaneous data are given in Table 1. In most cases, these data were obtained from standard sources (1, 2, 3, 4, 5, 6, 7) such as the thermodynamic compilations of the Bureau of Mines, Bureau of Standards, and American Chemical Society. These sources were supplemented by a survey of Chemical Abstracts, Nuclear Science Abstracts, and current journals. Small numbers in parentheses next to the tabulated data refer to the literature source, which may be found in the bibliography. If no reference is given, then the data were calculated by the methods discussed below.

B. Vapor Pressures and Heats of Vaporization

Vapor pressure data were available in several forms for many of the fission product oxides and metals (7, 8, 9, 10, 11, 12). All of the available data were reduced to the standard form:

$$\log P(\text{atm}) = \frac{-A}{T(^{\circ}\text{K})} + B \quad (A \text{ and } B \text{ are constants})$$

by plotting the logarithm of the vapor pressure in atmospheres against the reciprocal absolute temperature. The constants A and B were calculated from the slope and intercept of the straight-line plots and are listed in Table 2.

Comparison of the above vapor-pressure equation with the Clausius-Clapeyron equation:

$$\log P = \frac{-\Delta H_{\text{vap}}}{2.303RT} + B$$

TABLE 1
Miscellaneous Physical Data For
Fission Product Oxides and Metals

<u>Substance</u>	<u>Molecular Wt.</u>	<u>Melting Point °K</u>	<u>Heat of Transition kcal/mol</u>	<u>Boiling Point (°K)</u>	<u>Entropy of Transition (e. u.)</u>
Al	26.97	932	2.57	—	2.76
Al(l)	26.97	—	67.9	2600	26.0
Ce(s)	140.13	1048	2.1	—	2.0
Ce(l)	140.13	—	73.0	2800	26.0
Cs(s)	132.91	302	0.5	—	1.7
Cs(l)	132.91	—	16.32	963	17.0
Cs(g)	132.91	—	—	—	—
Nb(s)	92.91	2760	5.8	—	2.1
Ru α	101.70	—	0.034	—	0.026
Ru β	101.70	—	0.0	—	0
Ru γ	101.70	—	0.23	—	0.13
Ru δ	101.70	—	6.1	—	2.3
Sr(s)	87.63	1043	2.2	—	2.1
Sr(l)	87.63	—	33.61	1657	20.28
Sr(g)	87.63	—	—	—	—
Zr α	91.22	—	0.92	—	0.811
Zr β	91.22	—	4.9	—	2.3
Zr(l)	91.22	—	100.0	3900	26.0
Al ₂ O ₃ (s)	101.94	2300	26.0	—	11.0
Ce ₂ O ₃ (s)	328.26	1960	20.0	—	10.0
CeO ₂ (s)	172.13	3000	19.0	—	6.3
Cs ₂ O(s)	281.82	763	4.58	—	6.0
Cs ₂ O(l)	281.82	—	—	dec.	—

TABLE 1 (CONT'D)

Substance	Molecular Wt.	Melting Point °K	Heat of Transition kcal/mol	Boiling Point (°K)	Entropy of Transition(e. u.)
$\text{Cs}_2\text{O}_2(\text{s})$	297.82	867	5.5	—	6.3
$\text{Cs}_2\text{O}_2(\text{l})$	297.82	—	—	dec.	—
$\text{Cs}_2\text{O}_3(\text{s})$	313.82	775	7.75	—	10.0
$\text{Cs}_2\text{O}_3(\text{l})$	313.82	—	—	dec.	—
$\text{NbO}(\text{s})$	108.91	2650	16.0	—	6.0
$\text{NbO}_2(\text{s})$	124.91	2275	16.0	—	7.0
$\text{NbO}_2(\text{l})$	124.91	—	85.0	3800	22.0
$\text{Nb}_2\text{O}_5(\text{s})$	265.82	1733	28.0	—	16.0
$\text{Nb}_2\text{O}_5(\text{l})$	265.82	—	80.0	3200	25.0
$\text{RuO}_3(\text{s})$	133.70	1400 dec.	—	—	—
$\text{RuO}_4(\text{s})$	165.70	300	3.2	—	11.0
$\text{RuO}_4(\text{l})$	165.70	—	—	dec.	—
$\text{SrO}(\text{s})$	103.63	2703	16.7	—	6.2
$\text{SrO}_2(\text{s})$	119.63	488 dec.	—	—	—
ZrO_2^α	123.22	—	1.42	—	0.961
ZrO_2^β	123.22	—	20.8	—	7.0

indicates that the constant A is equal to the molar heat of vaporization, ΔH_{vap} , divided by $2.303 R$. In the case of RuO_4 , Nb_2O_4 , Al_2O_3 , and Nb , this relation was used to calculate ΔH_{vap} shown in Table 2. For the other oxides and metals, available data for ΔH_{vap} were used.

Table 2

Vapor Pressure and Heat of Vaporization of Various Metals and Oxides

$$\log P (\text{atm}) = \frac{-A}{T(^{\circ}\text{K})} + B$$

Material	A	B	Valid Temp. Range ($^{\circ}\text{K}$)	Reference	ΔH_{vap} (cal/mol)	Reference
Ru	33,700	7.579	2186-3219	8	135,700	2
$\text{RuO}_4(\text{s})$	3,190	8.932	273- 293	13	14,600	calc.
$\text{RuO}_4(\text{l})$	1,975	4.908	293- 343	13	9,230	calc.
Zr	26,200	6.672	1000-2730	11	139,000	2
ZrO_2	28,660	7.578	2014-2290	12	153,600	12
Sr	7,500	4.535	1040-1660	11	33,400	2
Nb_2O_4	40,800	9.643	2467-2812	8	186,500	calc.
Cs	3,630	3.725	280-1000	11	15,750	2
Al_2O_3	27,320	8.415	2633-2893	11	124,500	calc.
Nb	40,169	8.872	2304-2596	14	172,500	calc.
Ce	—	—	—	—	107,700	15

It will be noted that of the oxides listed in Tables 1 and 2, only ruthenium and cesium oxides have an appreciable vapor pressure at temperatures up to 1500°C . It was therefore concluded that volatilization can only be a significant process for these materials in differential thermal and thermogravimetric analysis studies.

C. Thermodynamic Functions at 298°K

Standard heats of formation, ΔH°_{298} , free energies of formation, ΔF°_{298} , and molar entropies, S°_{298} , for various oxides and metals are shown in Table 3. These data, when combined with values of the free energy function ($F_t - H^{\circ}_{298}/T$) may be used to estimate equilibrium constants for the decomposition of the oxides at temperatures other than the reference temperature. The use of the free energy function has been treated by Margrave (16) and others.

TABLE 3

Thermodynamic Functions for Oxides
and Metals at 298°K

<u>Material</u>	<u>$-\Delta H^\circ_{298}$ (kcal/mol)</u>	<u>$-\Delta F^\circ_{298}$ (kcal/mol)</u>	<u>S°_{298} (cal/mol °K)</u>
Al(s)	—	—	6.77
Ce(s)	—	—	13.8
Cs(s)	—	—	19.8
Nb(s)	—	—	8.3
Ru ^a	—	—	6.9
Sr(s)	—	—	13.0
Zr ^a	—	—	9.29
Al ₂ O ₃ (s)	400.2	378.0	12.19
Ce ₂ O ₃ (s)	435.0	415.0	33.5
CeO ₂ (s)	260.18	246.9	17.7
Cs ₂ O(s)	75.9	63.7	23.0
Cs ₂ O ₂ (s)	96.2	81.9	40.0
Cs ₂ O ₃ (s)	111.2	91.6	47.0
NbO(s)	97.0	91.0	12.0
NbO ₂ (s)	189.0	176.5	12.7
Nb ₂ O ₅ (s)	155.2	423.7	32.8
RuO ₂ (s)	52.5	39.7	12.5
RuO ₄ (s)	74.0	53.0	32.5
SrO(s)	141.0	133.7	13.0
SrO ₂ (s)	153.6	139.6	14.8
ZrO ₂ ^a	261.5	247.8	12.03

Several values of the entropy in Table 3 were calculated by the method of Latimer (17), Wenner (18), and Kelley (19), who showed that the molar entropy of a group of salts of the same stoichiometry, i.e. Fe_2O_3 , Al_2O_3 , Cr_2O_3 , etc., is given by:

$$S = A \log M + B \quad \text{where,}$$

S = molar entropy

M = molecular weight

A and B = constants

In other cases, the data were obtained from standard sources (9, 3, 20, 4, 6).

A semilog plot of these authors' data for oxides of the Type M_2O , M_2O_3 , and M_2O_4 is shown in Figure 1. This plot was used to estimate the entropy of Nb_2O_4 , Cs_2O , Cs_2O_3 , and Ce_2O_3 . Since there was not sufficient data available for the entropy of oxides of the type M_2O_2 , the entropy of Cs_2O_2 was calculated from the thermodynamic relation:

$$S^\circ_{\text{Cs}_2\text{O}_2} = \frac{\Delta H^\circ_{\text{Cs}_2\text{O}_2} - \Delta F^\circ_{\text{Cs}_2\text{O}_2}}{298} + 2S^\circ_{\text{Cs}} + S^\circ_{\text{O}_2}$$

D. Heat Capacities and Free Energy Functions For Oxides and Metals

The constants required for calculating free energy functions and heat capacities of various fission product oxides and metals at temperatures other than 298°K are given in Table 4. These data were taken from a recent compilation by Glassner (6). The relation between the constants a , b , c , A , and B , shown in Table 4 and the thermodynamic functions are summarized below.

$$C_p = a + (b \times 10^{-3})T + (c \times 10^5)T^{-2}$$

$$H_T - H_{298} = aT + \frac{1}{2}(b \times 10^{-3})T^2 - (c \times 10^5)T^{-1}$$

$$S_T = 2.303 \log T + (b \times 10^{-3})T - \frac{1}{2}(c \times 10^5)T^{-1} - B$$

FIG.1 MOLAR ENTROPY AT 25° FOR INORGANIC OXIDES

$$\frac{F_T - H_{298}}{T} = 2.303 \log T - \frac{1}{2}(b \times 10^3)T - \frac{1}{2}(c \times 10^5)T^{-2} - (B-a) + AT^{-1}$$

The reference state in Table 4 is the phase, at 298°K, indicated by the subscript next to chemical formula in the first column, i.e. s = solid, l = liquid, α = solid modification α , etc. In general, the enthalpy will be given by a sum of terms for each phase of the substance considered over its appropriate temperature range, plus terms representing the heats of transition, ΔH_{tr} . Values of ΔH_{tr} are given in Table 1.

With the aid of the material presented in Tables 1, 3, and 4, thermodynamic functions for the formation of compounds may be easily calculated. Thus, for the reaction

The free energy of formation is given by

$$\Delta F = - (2.303\Delta a)T \log T - \frac{1}{2} (\Delta b \times 10^{-3})T^2 - \frac{1}{2} (\Delta c \times 10^5)T^{-1} - T\Delta(B-a) - \Delta A + \Delta H^\circ_{298}$$

In this equation,

$$\Delta h = h(MX_{2n}) - h(M) - nh(X_2)$$

where the symbol h refers to any of the constants a , b , c , A , or B , and ΔH°_{298} is the heat of formation of the substance under consideration, from the elements at 298°K.

It should be noted that no data are available for $RuO_4(g)$, which is the most important oxide studied during this program. For this reason, thermodynamic functions for $RuO_4(g)$ were calculated by a theoretical method described in a later section of this report.

Table 4

Heat Capacities and Free Energy Functions For
Selected Fission Product Oxides and Metals

<u>Substance</u>	<u>Maximum Stable Temp. (°K)</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>Δ(kcal/g atom)</u>	<u>B(e. u.)</u>
Al(s)	932	4.94	2.96	—	1.604	22.26
Al(l)	2600	7.0	—	—	0.33	30.83
Ce(s)	1048	4.40	6.0	—	1.579	13.1
Ce(l)	2800	7.9	—	—	- 0.148	29.1
Cs(s)	302	7.42	—	—	2.212	22.5
Cs(l)	963	8.0	—	—	1.887	24.1
Cs(g)	—	4.97	—	—	- 17.35	- 13.6
Nb(s)	2760	5.66	0.96	—	1.73	24.24
Ru α	1308	5.25	1.50	—	1.632	23.5
Ru β	1473	7.20	—	—	2.867	35.5
Ru γ	1773	7.20	—	—	2.867	35.5
Ru δ	2700	7.50	—	—	3.169	37.6
Sr(s)	1043	5.60	1.37	—	1.731	19.3
Sr(l)	1657	7.7	—	—	0.976	30.4
Sr(g)	—	4.97	—	—	- 37.16	- 10.2
Zr α	1135	6.83	1.12	- 0.87	2.378	30.45
Zr β	2125	7.27	—	—	1.159	31.43
Zr(l)	3900	8.0	—	—	- 2.19	34.7
Al ₂ O ₃ (s)	2300	26.12	4.388	- 7.269	10.422	142.03
Ce ₂ O ₃ (s)	1960	23.0	9.0	—	7.258	100.2
CeO ₂ (s)	3000	15.0	2.5	—	4.579	68.5

Table 4 (cont'd)

Substance	Maximum Stable Temp. (°K)	a	b	c	A(kcal/g atom)	B(e.u.)
Cs ₂ O(s)	763	16.5	5.4	—	5.16	72.6
Cs ₂ O(l)	dec.	22	—	—	3.205	99.0
Cs ₂ O ₂ (s)	867	21.4	11.4	—	6.887	85.3
Cs ₂ O ₂ (l)	dec.	29.5	—	—	4.125	123.8
Cs ₂ O ₃ (s)	775	24.0	22.6	—	8.160	96.5
Cs ₂ O ₃ (l)	dec.	35	—	—	2.148	142.2
NbO(s)	2650	9.6	4.4	—	3.058	44
NbO ₂ (s)	2275	17.1	1.6	-2.8	6.109	84.6
NbO ₂ (l)	3800	24	—	—	1.033	127.2
Nb ₂ O ₅ (s)	1733	21.88	28.2	—	7.776	100.3
Nb ₂ O ₅ (l)	3200	44.2	—	—	-24.09	201.6
RuO ₂ (s)	1400 dec.	11.4	6.0	—	3.666	54.2
RuO ₄ (s)	300	20	—	—	5.963	81.5
RuO ₄ (l)	dec.	33	—	—	6.663	144.9
SrO(s)	2703	12.34	1.12	-1.806	4.335	58.7
SrO ₂ (s)	488 dec.	16.8	2.2	-3.0	6.113	83.3
ZrO ₂ α	1478	16.64	1.8	-3.36	6.168	85.21
ZrO ₂ β	2950	17.8	—	—	4.27	89.96

II. Thermodynamic Calculations Based On Tabulated Data

A. Decomposition Temperature of Fission Product Oxides

The free energy of formation, ΔF , of fission product oxides, when calculated as described in the previous section, may be used to calculate the decomposition temperature. The decomposition temperature, T_D , will be that temperature at which ΔF is zero. When ΔF is less than zero, formation of the oxide from the elements is favored, and when ΔF is positive, decomposition may occur. The decomposition temperature was calculated in this manner for the oxides RuO_2 , Cs_2O , Cs_2O_2 , Cs_2O_3 , CsO_2 , Ce_2O_3 , Ce_2O_3 , CeO_2 , Nb_2O_5 , SrO , SrO_2 , ZrO , Al_2O_3 , NbO , and NbO_2 . Of these oxides, only RuO_2 , Cs_2O_3 , CsO_2 and Cs_2O are subject to decomposition at temperatures up to 1500°C . The decomposition reactions and calculated decomposition temperatures are as follows:

<u>Reaction</u>	<u>T_D ($^\circ\text{K}$)</u>
$\text{RuO}_2(\text{s}) \rightarrow \text{Ru}(\text{s}) + \text{O}_2(\text{g})$	1419
$\text{Cs}_2\text{O}_3(\text{l}) \rightarrow 2\text{Cs}(\text{g}) + \frac{3}{2} \text{O}_2(\text{g})$	1400
$\text{CsO}_2(\text{l}) \rightarrow \text{Cs}(\text{g}) + \text{O}_2(\text{g})$	1625
$\text{Cs}_2\text{O}(\text{l}) \rightarrow 2\text{Cs}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g})$	1700

The other oxides are either thermodynamically stable to 1500°C , or the calculated decomposition temperatures are above the temperature range of validity of the data.

B. Disproportionation and Oxidation of Fission Product Oxides

When more than one oxide of a metal exists, there is a possibility of converting one oxide to another through disproportionation or oxidation. An example of the latter process is the oxidation of Ce_2O_3 by O_2 to yield CeO_2 . The free energy of this reaction may be calculated by addition of the free energy of formation equations for the individual oxides. The data below and in Table 5 were taken from the tabulation of Coughlin (3).

Thus, the oxidation of Ce_2O_3 to CeO_2 by O_2 is spontaneous up to 1048°K (the upper limit of the valid temperature range).

Similar calculations were made for several fission product oxide reactions. The results are presented in Table 5 where the free energies of reaction and the valid temperature ranges are given. The data indicate that all the reactions are spontaneous as written within the valid temperature range with the exception of the formation of SrO_2 from SrO . This reaction reverses at about 735°K .

TABLE 5

Fission Product Oxide Reactions

<u>Reaction</u>	<u>Free Energy of Reaction (cal/mol)</u>	<u>Valid Temperature Range ($^\circ\text{K}$)</u>
$\text{Ce}_2\text{O}_3(\text{c}) + 1/2 \text{O}_2(\text{g}) \longrightarrow 2\text{CeO}_2(\text{c})$	$- 55,260 + 22.50\text{T}$	298-1048
$\text{SrO}(\text{c}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{SrO}_2(\text{g})$	$- 12,000 + 16.30\text{T}$	298-1000
$\text{Cs}_2\text{O}(\text{c}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{Cs}_2\text{O}_2$	$- 19,850 + 17.74\text{T}$	298-763
$\text{Cs}_2\text{O}(\text{c}) + \text{O}_2(\text{g}) \longrightarrow \text{Cs}_2\text{O}_3(\text{c})$	$- 34,240 + 36.98\text{T}$	301-763
$\text{Cs}(\text{l}) + \text{CsO}_2(\text{c}) \longrightarrow \text{Cs}_2\text{O}(\text{c}) + 1/2 \text{O}_2(\text{g})$	$- 15,220 + 2.17\text{T}$	298-763
$\text{Cs}_2\text{O}(\text{c}) + 3/2 \text{O}_2(\text{g}) \longrightarrow 2\text{CsO}_2(\text{c})$	$- 46,460 + 35.58\text{T}$	298-705
$\text{CeO}_2(\text{c}) + \text{Ce}(\text{c}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{Ce}_2\text{O}_3(\text{c})$	$- 185,090 + 27.72\text{T}$	298-1048
$\text{Nb}_2\text{O}_4(\text{c}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{Nb}_2\text{O}_5(\text{c})$	$- 72,350 + 17.53\text{T}$	700-1785

C. Interaction Between Fission Product Oxides and Alumina

Consideration was given to a study of the interactions between the fission products and Al_2O_3 by means of differential thermal analysis or thermogravimetric analysis, since such processes may have a bearing on the mechanism of the calcination process. The interactions which may occur include reduction of Al_2O_3 by a fission product metal, formation of solid or liquid mixed oxide solutions, or compound formation.

Reduction of Al_2O_3 is extremely unlikely due to the large negative free energy of formation of Al_2O_3 (-262.2 kcal/mol at 1800°K). This conclusion is supported, in part, by the work of Economos and Kingery (21) who show little reaction, if any, occurring between Nb or Zr and Al_2O_3 at temperatures to 1600°C. No phase equilibria or thermodynamic data were found for reactions between Al_2O_3 and the oxides of Ru, Cs and Nb. Levin's data (22), however, indicate that no solid solutions or intermediate compounds are formed between Al_2O_3 and SrO , CeO_2 , or ZrO_2 below a temperature of 1800°C.

III. Absorption Spectrum of RuO₄

The absorption spectrum of RuO₄ was of interest in this study in calculating the thermodynamic properties of the molecule and as a possible analytical tool for following the rate of the RuO₄ decomposition. The spectrum of a solution of RuO₄ in CCl₄, liquid RuO₄, and RuO₄ vapor was determined in the regions 400-1000 mμ, 2-15μ, and 350-500 mμ, respectively. The results are summarized below.

A. Near Ultraviolet and Visible Spectrum

Krasikov (23) and Qviller (24) determined the near ultra-violet spectrum of RuO₄ vapor and liquid. Absorption peaks were noted at 2990, 3064, 3100, 3138, 3212, and 3850 Å.

At West Orange, a portion of the near ultra-violet vapor spectrum was obtained using a sealed Carius Tube as a cell and a Beckman Model DU spectrophotometer. The results, in the 3500-5000 Å region, are shown in Figure 2. The peak absorption occurred at 3850 Å, in agreement with the literature value.

Absorption measurements were also made in the visible region, using a solution of 0.16g RuO₄ per liter of CCl₄. The results are shown in Figure 3. Curve A is the spectrum of a fresh solution and curve B is the spectrum of an hour-old solution. The absorption, at 6000 Å, decreased with time due to the slow decomposition of RuO₄.

B. Infrared Absorption Spectrum

Several attempts were made to determine the IR spectrum of RuO₄ with a Beckman Model IR-4 Spectrophotometer. Sample techniques tested included pressing a KBr-RuO₄ pellet, mulling RuO₄ in Nujol, using a liquid cell, and spreading a film of liquid RuO₄ between salt plates. The pellet and Nujol mull procedure caused rapid decomposition of the RuO₄. Although difficulty was experienced in keeping liquid RuO₄ between the KBr plates, an absorption curve was finally obtained by this method. The spectrum between 2 and 15 microns is shown in Figure 4.

One fundamental is evident at 11 microns (913 cm⁻¹), together with its first overtone at 5.6 microns (1800 cm⁻¹). By analogy with OsO₄ (25, 26) another absorption band should be present at approximately 300 cm⁻¹. Examination of this region of the spectrum, however, required CsBr or KRS-5 optics

FIGURE 2 VAPOR SPECTRUM RuO₄ VAPOR

FIGURE 3 VISIBLE SPECTRUM RuO₄ (0.16gm RuO₄/Liter CCl₄)

which were not available at Vitro. Accordingly, arrangements were made to run the spectrum to 31 microns on a Perkin Elmer Model 112 instrument which was available at the Polytechnic Institute of Brooklyn. Although there was some evidence of an absorption band at 30 microns, the results were not clear-cut since many water bands masked the low frequency region. To complete the calculation of the thermodynamic functions of RuO_4 , however, an absorption band at 30 microns was assumed.

The simplicity of the infra-red spectrum between 1 and 15 microns lends support to the hypothesis that RuO_4 is a tetrahedral molecule similar to OsO_4 . Tetrahedral symmetry in a 5-atom structure leads to the occurrence of two triply degenerate infra-red fundamentals, and one doubly degenerate, and one non-degenerate raman-active vibration. Any less symmetrical structure would have a much more complex infra-red spectrum than was observed for RuO_4 . Accordingly, for the purposes of calculation, the infra-red active fundamentals were assigned as follows:

$$\nu_2 (F_2) = 913 \text{ cm}^{-1} \text{ (observed)}$$

$$\nu_3 (F_2) = 333 \text{ cm}^{-1} \text{ (estimated)}$$

The problem still remained, however, of determining the frequencies of the two raman-active fundamentals. It is not likely that these frequencies can be determined experimentally, since the intense radiation from the mercury arc used in raman spectroscopy, and the long exposure times would probably cause decomposition of the RuO_4 . A theoretical calculation of the raman-active fundamentals was therefore carried out.

C. Calculation of the Raman-Active Fundamental Frequencies of RuO_4

The most successful theoretical treatment of the calculation of force constants and absorption frequencies for tetrahedral molecules is due to Heath and Linnett (27) and is known as the orbital valency force field (OVFF) approximation. In this method one sets up a potential function for the molecule involving forces which tend to restore the valence bonds and angles to the equilibrium values, and for forces due to repulsions between non-bonded atoms. The vibrational frequencies arising from this force field are then calculated by the methods of classical mechanics (28). The equations for the frequencies based on the OVFF method are

Class A

$$v_1 = \frac{1}{m_2} (k_1 + 8A) \quad (1)$$

Class F₂

$$v_2 + v_3 = \left[\frac{1}{m_2} + \frac{4}{3m_1} \right] \left[k_1 + \frac{8}{3A} - \frac{4}{3} \frac{B}{R} \right] + \left[\frac{1}{m_2} + \frac{8}{3m_1} \right] \left[k^1 + \frac{4A}{3} + \frac{10B}{3R} \right] \\ - \frac{8}{3m_1} \left[\frac{8A}{3} - \frac{4B}{3R} \right] \quad (2)$$

$$v_2 v_3 = \left[\frac{1}{m_2^2} + \frac{4}{m_1 m_2} \right] \left[\left(k_1 + \frac{8A}{3} - \frac{4B}{3R} \right) \left(k^1 + \frac{4A}{3} + \frac{10B}{3R} \right) - \frac{1}{2} \left(\frac{8A}{3} + \frac{4A}{3R} \right)^2 \right] \quad (3)$$

Class E

$$v_4 = \frac{1}{m_2} \left[k^1 + 2A + \frac{B}{R} \right] \quad (4)$$

where:

$v_1 = 4\pi^2 c^2 w_1^2$, where w_1 is the frequency of the i_{th} vibration in wave numbers

m_1 = mass of metal atom = 16.89×10^{-23} g. Ru/atom

m_2 = mass of oxygenation/atom = 2.66×10^{-23} g. oxygen/atom

k_1 = bond stretching force constant of Ru-O bond

k^1 = angle bending force constant of O-Ru-O bond

Class F₂ refers to triply degenerate infrared active vibrations

Class E refers to doubly degenerate raman-active vibrations

Class A refers to non-degenerate raman-active vibrations

-B, A/2 = first and second derivatives, respectively, of the potential function

By substituting experimental values of v_1 for a series of homologous compounds and calculating the force constants, Heath and Linnett showed that the following relation holds between the constants

$$B/R = 2A/13$$

The angle bending force constant, k^1 , depends upon the non-metal atom which is contained in the tetrahedral compound. We have used the value

$$k^1 = 3A$$

since this gave the best agreement between the measured and calculated frequencies for OsO_4 (29).

Substituting for m_1 , $m_2 \frac{B}{R}$, and k^1 in the F_2 vibration equations (2) and (3), we obtain

$$\begin{aligned} \nu_2 + \nu_3 &= [0.45 \times 10^{23} (k_1 + 2.45A)] + [0.53 \times 10^{23} \times 7.85A] \\ &- [0.39 \times 10^{23} A] \end{aligned} \quad (5)$$

$$\nu_2 \nu_3 = 2.27 \times 10^{45} [(k_1 + 2.46A) (7.85A) - 3.03A^2] \quad (6)$$

Now, taking the observed infrared frequency $\nu_2 = 913 \text{ cm}^{-1}$ and the estimated frequency $\nu_3 = 333 \text{ cm}^{-1}$, ν_2 and ν_3 may be calculated and substituted in (5) and (6). The following equation is obtained from (6) after this substitution.

$$k_1 = \frac{5.13 \times 10^{10} - 16.28A^2}{7.85A} \quad (7)$$

Substituting equation (7) in (5) yields a quadratic in A, from which

$$A = 1.9 \times 10^4 \text{ dyne cm}^{-1}$$

Finally substituting for A in equation (7), we obtain

$$k_1 = 3.04 \times 10^5 \text{ dyne cm}^{-1}$$

These values of k_1 and A may now be substituted in the Class E and Class A equations, (1) and (4), to calculate the raman-active vibration frequencies.

The results are:

$$\begin{aligned} \nu_2 (F_2) &= 913 \text{ cm}^{-1} \text{ observed} \\ \nu_3 (F_2) &= 333 \text{ cm}^{-1} \text{ estimated} \\ \nu_1 (A_1) &= 689 \text{ cm}^{-1} \text{ calculated} \\ \nu_4 (E) &= 322 \text{ cm}^{-1} \text{ calculated} \end{aligned}$$

These frequencies are utilized in the following section to calculate the vibrational contributions to the thermodynamic functions of RuO_4 .

IV. Calculation of Thermodynamic Functions For RuO₄(g) From Spectroscopic Data

As mentioned in the section on the Physical Properties of Fission Product Oxides, practically no thermodynamic data is available in the literature for RuO₄, with the exception of the free energy and enthalpy of formation and the entropy at 298.16°K. Since RuO₄ was one of the most important compounds studied during the course of this program, work was undertaken to calculate thermodynamic functions from the infra-red spectrum and molecular structure of this material. The theory of the calculation is summarized briefly below and the results of the calculation are tabulated. Further details of the theory and calculations will be found in V-2138-6-0 and V-2138-9-0, or may be obtained from standard references (30, 31, 32).

A. Theory of the Calculation and Compilation of General Formulae

The total energy of a collection of identical, non-interacting, gaseous molecules is made up of contributions due to internal energy (vibrational, rotational, electronic degrees of freedom), and a term due to the translational or external energy.

The conventional thermodynamic functions are related to the possible internal and external energy states through the partition function, Q , which is defined as follows:

$$Q = p_0 e^{-E_0/kT} + p_1 e^{-E_1/kT} + \dots = \sum_j p_j e^{-E_j/kT} \quad (1)$$

This equation gives the fraction of molecules in any state, possessing the energy E_j above the ground state at temperature T . The symbol k is the Boltzmann Constant and p_j is the degeneracy of the j^{th} energy level.

If A is the number of molecules per mole in the ground state, then N_j , the number of molecules in energy state E_j is given by:

$$N_j = A \sum_j p_j e^{-E_j/kT} = AQ \quad (2)$$

Since the j^{th} energy state contributes $E_j A p_j e^{-E_j/kT}$ ergs of energy to the total molar internal energy, the total internal energy, E_j in excess of the zero point energy E_0 at temperature T is:

$$(E_i - E_0) = AE_0 e^{-E_0/kT} + AE_1 e^{-E_1/kT} + \dots = A \sum_j p_j E_j e^{-E_j/kT} \quad (3)$$

Substituting for A from equation (2), differentiating (1) with respect to temperature, and combining the resulting equations, we arrive at:

$$(E_i - E_0) = RT^2 \frac{d \ln Q}{dT} \quad (4)$$

Equation (4) is an expression for the thermodynamic internal energy in terms of the partition function. Expressions for the internal heat capacity at constant volume C_i , the internal entropy S_i , and the internal free energy, F_i , are derived from (4) in the usual manner and are listed below.

$$C_i = \frac{d E_i}{dT} = \frac{R}{T^2} \frac{d^2 \ln Q}{d(\frac{1}{T})^2} \quad (5)$$

$$S_i = \int C_i d \ln T = R (\ln Q + T \frac{d \ln Q}{dT}) \quad (6)$$

$$F_i = E_i + PV - TS_i = E_0 + RT - RT \ln Q \quad (7)$$

Equations (4) - (7) give only the contribution of the internal energy states to the thermodynamic functions. To these, we must add the contribution from the translational (external) energy, in order to obtain the total thermodynamic internal energy E, entropy S, and free energy, F. The pertinent equations follow.

$$E = E_0 + RT^2 \frac{d \ln Q}{dT} + 3/2 RT \quad (8)$$

$$S = R \ln Q + RT \frac{d \ln Q}{dT} + 3/2 R \ln M + 5/2 R \ln T - R \ln P + 5/2 R - 7.267 \quad (9)$$

(In equation (9), M is the molecular weight, and P is the pressure in atmospheres)

$$F = E_0 + RT (\ln P - \ln Q - 3/2 \ln M - 5/2 \ln T + 7.267T) \quad (10)$$

Equation (8) - (10) are perfectly general, and can be used to calculate thermodynamic functions for an assembly of ideal gas molecules at any temperature if the partition function Q can be evaluated.

For diatomic or polyatomic molecules at ordinary temperatures, however, a great number of vibrational and rotational energy states are occupied, thus making the calculation of the partition function at various temperatures very tedious. Approximate methods have therefore been developed to simplify the calculation, and these are described below.

B. Evaluation of the Rotational and Vibrational Partition Functions - Working Formulae For RuO_4

The following are the major approximations used in deriving working formulae for evaluating the partition function of a polyatomic molecule.

- a) The energy levels of the translational, vibrational, and rotational states are independent of one another (Born-Oppenheimer Approximation).
- b) The molecule behaves as a rigid rotator (no centrifugal stretching), and possesses one harmonic oscillator for each vibrational degree of freedom.
- c) For molecules such as RuO_4 which do not contain unpaired electrons, the electronic energy levels lie about 100 kcal above the ground state, do not contribute significantly to the thermodynamic functions at ordinary temperatures, and are therefore disregarded in the calculation.
- d) The assembly of molecules is considered an ideal gas.

With these assumptions, the problem of calculating the partition function reduces to one of evaluating the allowed energies and degeneracies of the rigid rotator and the harmonic oscillator, and substituting these expressions into the definition of the partition function. This treatment is outlined below.

1. The Rotational Partition Function

The allowed rotational energy levels for a rigid rotator are given by the solution of the appropriate Schrodinger Equation for the system and are of the form

$$E_j = \frac{h^2}{8\pi^2 I} J(J+1) \quad (11)$$

where h is Planck's Constant, I is the moment of inertia, and J is the total angular momentum quantum number which may assume a zero or positive integral value.

For a tetrahedral molecule such as RuO_4 there are $(2J + 1)^2$ states of nearly equal energy for each value of J . The rotational degeneracy is therefore $(2J + 1)^2$. Setting $b = h^2/8\pi^2IkT$ and substituting (11) in (1), we obtain the rotational partition function Q_r .

$$Q_r = \sum_{j=0}^{\infty} (2J + 1)^2 e^{-bJ(J+1)} \quad (12)$$

Since b is small, except at very low temperatures, the summation may be replaced by an integral. Integrating (12) and disregarding exponential terms in b , we obtain:

$$Q_r = \pi^{1/2} b^{-3/2} = \pi^{1/2} \left(\frac{8\pi^2IkT}{h^2} \right)^{3/2} \quad (13)$$

In (13), the only unknown term is I , the product of the principal moments of inertia, and this may be calculated as described below from the geometry of the molecule. One other factor, the symmetry number, must be added to (13) in order to obtain a complete description of the energy levels. In RuO_4 , these are three-fold rotational axes through each of the four vertices which give rise to 12 indistinguishable orientations of the molecule. Q_r must be reduced by this factor, therefore the complete equation for the rotational partition function of RuO_4 is

$$Q_r = \frac{\pi^{1/2}}{12} \left(\frac{8\pi^2IkT}{h^2} \right)^{3/2} \quad (14)$$

2. Principal Moments of Inertia For RuO_4

To evaluate (14), the product of the principal moments of inertia of RuO_4 must be determined. To determine this quantity, a coordinate system is first established with respect to the molecule so that the center of gravity (ruthenium atom) is at the origin.

To do this we will first orient the molecule so that three of the oxygen atoms are in the same plane. A sketch of the molecule in this configuration is

shown in Figure 5. It is assumed here that the RuO_4 molecule has the structure of a regular tetrahedron. Justification of this assumption is given in the discussion which follows.

In Figure 5 the tetrahedron is oriented so that oxygen atoms O_1 , O_2 , and O_4 are in the x-y plane; "a" is the O-O distance and "d" is the Ru-O bond length. From the geometry of the figure the coordinates of the atoms are:

$$\begin{aligned} \text{Ru} &= \left(\frac{a}{2}, \frac{a}{2\sqrt{3}}, \frac{\sqrt{3}a}{6\sqrt{2}} \right) & \text{O}_3 &= \left(\frac{a}{2}, \frac{a}{2\sqrt{3}}, \frac{\sqrt{2}a}{\sqrt{3}} \right) \\ \text{O}_1 &= \left(\frac{a}{2}, \frac{a\sqrt{3}}{2}, 0 \right) & \text{O}_4 &= (0, 0, 0) \\ \text{O}_2 &= (a, 0, 0) \end{aligned} \quad (15)$$

The following transformation will bring the Ru atom to the origin:

$$\begin{aligned} x^1 &= x - \frac{a}{2} \\ y^1 &= y - \frac{a}{2\sqrt{3}} \\ z^1 &= z - \frac{\sqrt{3}a}{6\sqrt{2}} \end{aligned} \quad (16)$$

Carrying out this transformation gives the new coordinates

$$\begin{aligned} \text{Ru} &= (0, 0, 0) \\ \text{O}_1 &= \left(0, \frac{a}{\sqrt{3}}, \frac{-\sqrt{3}a}{6\sqrt{2}} \right) \\ \text{O}_2 &= \left(\frac{a}{2}, \frac{-a}{2\sqrt{3}}, \frac{-\sqrt{3}a}{6\sqrt{2}} \right) \\ \text{O}_3 &= \left(0, 0, \frac{3a}{2\sqrt{6}} \right) \\ \text{O}_4 &= \left(-\frac{a}{2}, \frac{-a}{2\sqrt{3}}, \frac{-\sqrt{3}a}{6\sqrt{2}} \right) \end{aligned} \quad (17)$$

FIGURE 5 STRUCTURE OF RuO_4 MOLECULE

In this coordinate system the bond length, d , is equal to the distance from the origin to any one of the oxygen atoms. For example, considering the distance Ru-O₂

$$d = \sqrt{x^2 + y^2 + z^2} = \sqrt{\frac{a^2}{4} + \frac{a^2}{12} + \frac{a^2}{24}} = \frac{3a}{2\sqrt{6}} \quad (18)$$

Rewriting the coordinates in equation (17) in terms of d

$$\begin{aligned} \text{Ru} &= (0, 0, 0) \\ \text{O}_1 &= \left(0, \frac{2\sqrt{2}d}{3}, \frac{-d}{3}\right) \\ \text{O}_2 &= \left(\frac{\sqrt{6}d}{3}, \frac{-\sqrt{2}d}{3}, \frac{-d}{3}\right) \\ \text{O}_3 &= (0, 0, d) \\ \text{O}_4 &= \left(\frac{-\sqrt{6}d}{3}, \frac{-2d}{3\sqrt{2}}, \frac{-d}{3}\right) \end{aligned} \quad (19)$$

Knowledge of the bond distance, d , is now sufficient to calculate the principal moments of inertia.

There is little information in the literature regarding the structure of RuO₄. We have assumed a tetrahedral structure since this geometry has been proved for OsO₄ (26), CrO₄²⁻, MoO₄²⁻, PO₄³⁻ and other similar ions (31). Silverman and Levy (33) studied the related molecule KRuO₄ by x-ray diffraction and found the ruthenate anion to be tetragonal and the Ru-O bond distance to be 1.79 Å. Braune and Stute (34) studied RuO₄ and OsO₄ and state that the four Ru-O and Os-O bond distances are unequal and occur in pairs with $d = 1.66$ Å for two of the Ru-O and Os-O bonds, and $d = 1.01$ Å for the other two bonds in RuO₄ and OsO₄. Their results, however, are in conflict with the x-ray measurements of Brockway (35) on OsO₄, who found the four bond lengths to be equal to 1.66 ± 0.05 Å. Additional evidence that Braune and Stute's data are in error, at least for OsO₄, is found in the infrared and raman spectra for this molecule (36). The spectra definitely support a regular tetrahedral structure since only four fundamentals are observed. A structure such as that proposed by Braune and Stute, on the other hand, would belong to the C_{2v} point group and would give rise to 9 fundamental vibrations, 8 of which would be active in the infrared. Accordingly, we have assumed that the four Ru-O bonds are equivalent and that $d = 1.66 \pm 0.1$ Å.

Calculation of the products of the principal moments of inertia from the set of Cartesian coordinates in equation 19 is most easily accomplished by the method of Hirschfelder (37). Hirschfelder has shown that if x_i , y_i , z_i , and m_i are the coordinates and mass respectively of the i^{th} atom in a molecule of mass M , then the product of the principal moments of inertia is given by a determinant

$$I = \begin{vmatrix} A & -D & -E \\ -D & B & -F \\ -E & -F & C \end{vmatrix} = ABC - AF^2 - CD^2 - 2DEF - BE^2, \text{ where}$$

$$A = \sum_i m_i (y_i^2 + z_i^2) - \frac{1}{M} \left(\sum_i m_i y_i \right)^2 - \frac{1}{M} \left(\sum_i m_i z_i \right)^2$$

$$B = \sum_i m_i (x_i^2 + z_i^2) - \frac{1}{M} \left(\sum_i m_i x_i \right)^2 - \frac{1}{M} \left(\sum_i m_i z_i \right)^2$$

$$C = \sum_i m_i (x_i^2 + y_i^2) - \frac{1}{M} \left(\sum_i m_i x_i \right)^2 - \frac{1}{M} \left(\sum_i m_i y_i \right)^2 \quad (20)$$

$$D = \sum_i m_i x_i y_i - \frac{1}{M} \sum_i m_i x_i \sum_i m_i y_i$$

$$E = \sum_i m_i x_i z_i - \frac{1}{M} \sum_i m_i x_i \sum_i m_i z_i$$

$$F = \sum_i m_i y_i z_i - \frac{1}{M} \sum_i m_i y_i \sum_i m_i z_i$$

Substituting the coordinates from equation (19) and setting

$$m_i = \text{mass oxygen atom} = 2.66 \times 10^{-23} \text{ g./atom}$$

$$M = \text{mass RuO}_4 \text{ molecule} = 27.43 \times 10^{-23} \text{ g./molecule}$$

$$d = 1.66 \times 10^{-8} \text{ cm.} = \text{Ru-O bond distance, we obtain,}$$

$$A = B = C = \frac{8d^2 m_i}{3M} (M - m_i) = 1.768 \times 10^{-38} \text{ g} - \text{cm}^2$$

$$D = E = 0 \quad (21)$$

$$F^2 = \left[\frac{2\sqrt{2} d^2 m_i}{9M} (M - m_i) \right]^2 = 4.325 \times 10^{-78} \text{ g}^2 \text{ cm}^4$$

$$I = ABC - AF^2 = 54.28 \times 10^{-115} \text{ g}^3 \text{ cm}^6 / \text{molecule} \quad (22)$$

3. The Vibrational Partition Function

A non-linear polyatomic molecule consisting of n atoms has $3n - 6$ vibrational degrees of freedom. The partition function Q_{vib} will therefore contain $3n - 6$ terms. Under the assumption that each of the vibrational degrees of freedom is equivalent to an harmonic oscillator, the energy levels of each oscillator are given by

$$E_v = (v + \frac{1}{2}) hW \quad (23)$$

where v is the vibrational quantum number, 0, 1, 2 -----, and W is the fundamental vibration frequency in units of sec^{-1} . Depending upon the magnitude of W and the temperature, the molecules are distributed over different energy levels of the oscillator for which $v = 0, 1, 2$, etc. Hence the partition function for the harmonic oscillator corresponding to one of the $3n - 6$ vibrations degrees of freedom is given by:

$$Q_{\text{vib}} = e^{-(0 + \frac{1}{2}) hW/kT} + e^{-(1 + \frac{1}{2}) hW/kT} + e^{-(2 + \frac{1}{2}) hW/kT} + \dots$$

or,
$$Q_{\text{vib}} = e^{-hW/kT} (1 + e^{-hW/kT} + e^{-2hW/kT} + \dots) \quad (24)$$

The partition function for the vibrational energy in excess of the zero point energy (for which $v = 0$) is then

$$Q_{\text{vib}} = 1 + e^{-hW/kT} + e^{-2hW/kT} + \dots = (1 - e^{-hW/kT})^{-1} \quad (25)$$

If there are i vibrational degrees of freedom in the molecule, then there will be W_i fundamental vibrations and the total partition function for the $3n - 6$ vibrations will be given by

$$Q_{\text{vib}} = \prod_i (1 - e^{-W_i h/kT})^{-1} \quad (26)$$

Finally, if $d_1, d_2, d_3 \dots$ are the degrees of degeneracy of the vibrations $W_1, W_2, W_3 \dots$ respectively, then the partition function will be of the form:

$$Q_{\text{vib}} = (1 - e^{-W_1 h/kT})^{-d_1} (1 - e^{-W_2 h/kT})^{-d_2} (1 - e^{-W_3 h/kT})^{-d_3} \dots \quad (27)$$

The vibrational partition function can therefore be calculated if the fundamental vibrational frequencies and their degeneracies are known. This information is obtained by a study of the infrared absorption spectrum of the molecule under consideration.

C. Calculation of Thermodynamic Functions for RuO₄ From The Working Formulae

1. Translational Contributions To The Thermodynamic Functions of RuO₄

Equations (8) to (10) contain implicitly, terms involving the contribution of translational energy to the internal energy, E, entropy, S, and free energy, F. The translational contributions to these functions, to the heat capacity at constant pressure, C_p, and to the enthalpy, H, are given explicitly below.

$$-F_t = RT [3/2 \ln M + 5/2 \ln T - \ln P - 3.664] \quad (28)$$

$$C_{pt} = 5/2 R \quad (29)$$

$$E_t = 3/2 RT \quad (30)$$

$$H_t = 5/2 RT \quad (31)$$

$$S_t = R (3/2 \ln M + 5/2 \ln T - \ln P) - 2.298 \quad (32)$$

where M is the gram molecular weight, P is the pressure in atmospheres, and the subscript t indicates a translational contribution.

At one atmosphere pressure, equations (28) and (32) reduce to:

$$-F_t = 11.44 T \log T + 7.94T \quad (33)$$

$$S_t = 11.44 \log T + 12.92 \quad (34)$$

2. Rotational Contributions to the Thermodynamic Functions of RuO₄

Equations (14) and (22) give the rotational partition function and the product of the principal moments of inertia (I^3) for RuO₄.

Substituting the following constants in (14),

$$k = 1.3805 \times 10^{-16} \text{ erg/molecule } ^\circ\text{K}$$

$$h = 6.624 \times 10^{-27} \text{ erg-sec}$$

$$I^3 = 54.28 \times 10^{-115} \text{ g}^3\text{cm}^6/\text{molecule},$$

Taking the natural log and differentiating twice with respect to $\ln T$, the following relations are obtained.

$$\ln Q_r = \frac{3}{2} \ln T + 0.26 \quad (35)$$

$$\frac{d \ln Q_r}{d \ln T} = \frac{3}{2} \quad \frac{d^2 \ln Q_r}{d (\ln T)^2} = 0 \quad (36)$$

Finally, utilizing equation (4) through (7), the following expressions are obtained for the rotational contribution to the thermodynamic functions of RuO_4 (subscript r indicates a rotational contribution).

$$C_{p_r} = 3/2 R \quad (37)$$

$$(E-E_0)_r = (H-H_0)_r = 3/2 RT \quad (38)$$

$$S_r = 3/2 R \ln T + 1.76 R \quad (39)$$

$$\frac{F_r - E_0}{T} = -R (3/2 \ln T + 0.26) \quad (40)$$

3. Vibrational Contributions to the Thermodynamic Functions of RuO_4

Equation (27) gives the vibrational partition function for a molecule having the normal vibrational frequencies W_i of degeneracy d_i . If the frequencies are expressed in wave numbers, and the values of the Planck and Boltzmann Constant's are substituted in this equation, we obtain

$$Q_{\text{vib}} = \prod_i (1 - e^{-1.4384 W_i/T})^{-d_i} = \prod_i (1 - e^{-x_i})^{-d_i} \quad (41)$$

where,

$$x_i = 1.4384 W_i/T$$

$$W_i = \text{wave number of } i^{\text{th}} \text{ fundamental vibration}$$

taking the logarithm,

$$\ln Q_{\text{vib}} = - \sum_i d_i \ln (1 - e^{-x_i}) \quad (42)$$

The vibrational contribution to the thermodynamic function of RuO_4 may now be obtained by substituting (42) into equations (4) through (7) to yield:

$$C_{p\text{vib}} = R \sum_i d_i x_i^2 e^{x_i} / (e^{x_i} - 1)^2 \quad (43)$$

$$(H-E_0)_{\text{vib}} = RT \sum_i e^{x_i} / (e^{x_i} - 1) \quad (44)$$

$$S_{\text{vib}} = R \sum_i \{ [x_i d_i / (e^{x_i} - 1)] - [d_i \ln (1 - e^{-x_i})] \} \quad (45)$$

$$(F-E_0/T)_{\text{vib}} = R \sum_i d_i \ln (1 - e^{-x_i}) \quad (46)$$

To facilitate computation, tables are available (38) which give the vibrational contributions to the free energy, heat capacity, and enthalpy as a function of x_i . Vibrational contributions to the entropy are obtained from these tables through the relation:

$$S_{\text{vib}} = \left(\frac{H-E_0}{T} \right)_{\text{vib}} - \left(\frac{F-E_0}{T} \right)_{\text{vib}} \quad (47)$$

It should be noted that the entries in these tables refer to non-degenerate vibrational frequencies. For frequencies of degeneracy d , each value taken from the table should be multiplied by the factor d .

To calculate the vibrational contributions to the thermodynamic functions of RuO_4 , values of W and d given in the section of this report on the infra-red spectrum of RuO_4 were used to calculate x_i over the temperature range $298.16^\circ - 1000^\circ\text{K}$, and these values of x_i and d were used with the Schumann Tables to obtain solutions of equations (43) - (47). The results of these calculations are summarized below.

4. Total Thermodynamic Functions For RuO_4

The total heat capacity, enthalpy, entropy, and free energy of RuO_4 , based upon a reference state of the ideal gas at 0°K , is obtained by adding the translational, rotational, and vibrational contributions to each thermodynamic function.

For example, from equations (29), (37), and (43), the total heat capacity of RuO_4 is given by:

$$C_p = 5/2R + 3/2R + R \sum_i \frac{d_i x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} = 7.948 + 1.987 C_{p_{\text{vib}}} \quad (48)$$

The calculated results for all of the thermodynamic functions are summarized in Table 6. The major source of error in these calculations is in the vibrational contributions due to the calculated absorptions at 322 cm^{-1} and 689 cm^{-1} . The overall error in the thermodynamic functions, however, is not expected to exceed $\pm 15\%$. A more accurate calculation can be made when the low frequency infra-red absorption is determined with precision.

TABLE 6
TOTAL THERMODYNAMIC FUNCTIONS FOR RuO_4 (g)

	Heat Capacity(cal/g-mol °K)							
	298.16 °K	400°	500°	600°	700°	800°	900°	1000°
Translation	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97
Rotation	2.98	2.93	2.98	2.98	2.98	2.98	2.98	2.98
Vibration	10.50	12.68	14.12	15.08	15.74	16.20	16.52	16.76
Total	18.45	20.63	22.07	23.03	23.69	24.15	24.47	24.71
- Free Energy Function (cal/g-mol °K)								
Translation	36.25	37.71	38.82	39.72	40.49	41.15	41.74	42.26
Rotation	17.46	18.34	19.01	19.55	20.01	20.41	20.76	21.07
Vibration	2.42	4.04	5.62	7.11	8.59	9.97	11.26	12.56
Total	56.13	60.09	63.45	66.38	69.09	71.53	73.76	75.89
Enthalpy (cal/g-mol)								
Translation	1,481	1,987	2,483	2,930	3,476	3,973	4,470	4,966
Rotation	889	1,192	1,490	1,738	2,086	2,384	2,682	2,980
Vibration	1,380	2,564	3,904	5,359	6,914	8,511	10,150	11,834
Total	3,750	5,743	7,877	10,127	12,476	14,868	17,302	19,780
Entropy(cal/g-mol °K)								
Translation	41.23	42.65	43.80	44.70	45.47	46.13	46.72	47.24
Rotation	20.48	21.36	22.03	22.57	23.03	23.43	23.78	24.09
Vibration	7.05	10.45	13.43	16.04	18.46	20.60	22.54	24.39
Total	68.76	74.50	79.26	83.31	86.96	90.16	93.04	95.72

V. Thermal Stability of Fission Product Oxides and Nitrates

In the ICPP waste storage process, spent fuel elements are dissolved in nitric acid, calcined in a fluidized bed of Al_2O_3 , and stored as a solid product. The effluent is a solid mixture of unreacted fission product nitrates, fission product oxides, and Al_2O_3 . To determine the physical and chemical changes that may occur if the temperature of the solid product should become uncontrolled and reach 1500°C , differential thermal and thermogravimetric analysis were made of the fission product oxides and nitrates, both alone and in the presence of alumina. This work is described below.

A. Differential Thermal Analysis (DTA) Apparatus and Procedure

Differential thermal analysis involves a measurement of the temperature at which thermal changes occur in a material when it is heated continuously to an elevated temperature. Several excellent reviews of the subject are available (39, 40). This technique may be used to detect any phase changes or chemical reactions which occur in a heated sample at elevated temperatures. Rough quantitative measurements may also be made by determining the area under the exothermic or endothermic peaks which are found in the time-temperature plot.

The apparatus consists of three major components: a sample holder, a controlled source of heat, and a temperature measuring device. In practice, the difference in temperature is measured between the sample and a stable reference material (e. g. , Al_2O_3) by means of a differential thermocouple. The apparatus used in this study was conventional; i. e. , a Silicon Carbide furnace with associated programmer, controller, and recorder; an alumina sample holder, 2-1/2 inches in diameter by 1-1/16 inches thick, containing four equally spaced holes 1/2 inch in diameter by 9/16 inch deep; and a Pt/Pt-13% Rh differential thermocouple. The design of the assembled furnace and support is shown in Figure 6. A detail of the cast Alundum sample holder is given in Figure 7, and a close-up view of the furnace is shown in Figure 8.

During the preliminary runs to establish operating techniques for obtaining a uniform heating rate and the best possible base line curves, the heating rate was controlled by a manually adjusted Powerstat. After the heating characteristics were determined, it became possible to control the heating rate from 400°C to 1500°C with the automatic Wheelco programmer-controller and minimum manipulation of the manual Powerstat. Because of the non-linear relationship between the resistance and temperature of the Hot Rod

FIGURE 6 DIFFERENTIAL THERMAL ANALYSIS, FURNACE AND SUPPORTS

Plan View

Side View

Cast From Alundum
33 HD Cement

FIGURE 7 DTA SAMPLE HOLDER

FIGURE 8 CLOSE-UP OF DTA FURNACE

heating elements, a uniform heating rate for the lower temperature (0° - 400°C) was more difficult to maintain.

Since the resistance of the silicon carbide heating elements increases with age, the base line curve was checked periodically. It was also necessary to control the maximum furnace temperature very closely since the heating elements rapidly deteriorated at temperatures above 1500°C .

The sample holder consisted of an Alundum cylindrical block containing four symmetrically positioned crucibles. Two of the crucibles contained the reference material. In all runs, Type A-2, low iron, -325 mesh, calcined Al_2O_3 was used as the reference material for recording the furnace temperature and for activating the Wheelco programmer-controller. Two programmed heating rates, i. e., $6.3^{\circ}\text{C}/\text{min}$ (4-hour cycle) and $10^{\circ}\text{C}/\text{min}$. (2-1/2 hour cycle) were used effectively in operating from 0 to 1500°C . Most of the work was carried out at the $10^{\circ}\text{C}/\text{min}$. heating rate.

Initially, the differential thermocouple output voltages were measured with a Type K Leeds and Northrup potentiometer and Rubicon galvanometer. Manual operation required constant attention to the equipment during the run and was very time consuming. The galvanometer also required frequent standardization. A Kintel Model 111BF dc amplifier was obtained on loan initially from RMC Associates, Englewood, N. J. for a trial. Since this instrument performed well and permitted continuous recording of the amplified differential EMF on a Brown recorder, it was decided to purchase a similar unit. The range of the recorder was modified so that by using an amplifier gain of 20, a direct reading in $^{\circ}\text{C}$ of the differential temperature was obtained. As the recorder had a constant resistance, designed for a 13.7 microvolt/ $^{\circ}\text{C}$ output, it was necessary to correct for the resistance vs. temperature variation of the Pt-Pt-13% Rh thermocouple over the 0° - 1500°C temperature range. Chart speed on this recorder and the Brown recorder for the furnace temperature were the same.

During this program it was necessary to obtain base line curves (Al_2O_3 vs Al_2O_3) for correcting DTA curves at comparable heating rates. The base lines were obtained periodically, usually after modifications to the heating system such as replacement and rearrangement of heating elements, and after improvements were made to eliminate stray ac pickup in the thermocouple leads at high temperatures. Improvements in the equipment which effected a more uniform base line included the following:

- (a) Ground loops were eliminated by grounding the thermocouple lead wire, recorder, and d. c. amplifier to a common point.
- (b) A Sola transformer was used to supply constant voltage to the Kintel amplifier.
- (c) The thermocouples were shielded with a grounded platinum foil.

A further refinement for the elimination of stray AC in the DTA apparatus was effected by the addition of a 15-mil thick platinum liner to the inside of the furnace. The platinum liner and electronic and controlling equipment were grounded at a common point. The platinum liner also improved the heat distribution in the furnace and thus smoothed out the heating rate in the lower temperature range. Careful manual control of the heating rate is also helpful in the 0-400°C range. Minor temperature fluctuations above 400°C are attributed to variations in the position of the thermocouples, size of the thermocouple beads, particle size, and packing of the samples. The effect of the improvements made during the course of the work is illustrated in comparing one of the first base line thermograms (Figure 9) with one of the more recent base lines (Figure 10).

In order to check the sensitivity of the apparatus in detecting known transition and decomposition temperatures, a DTA curve of Ag_2SO_4 , corrected for the base line, was run with the results shown in Figure 11.

The data obtained in this run were compared with the transition and decomposition temperatures reported by Barshad (41). Three endotherms were observed, the peak values occurring at 420°, 665° and 1075°C. These correspond to a crystalline transition reported at 410°-417°C, and the melting point, reported at 654°-676°C. The large endotherm which begins at 980°C and reaches a peak at 1075°C is caused by the decomposition of Ag_2SO_4 to Ag, O_2 , and SO_2 , and the melting of Ag. The literature reports that the decomposition begins at 961°C. The cause of the small endotherm at 1445°C is not known.

Since the results of this run proved satisfactory in reproducing the data reported in the literature, the study of the various fission products was then undertaken.

B. Thermogravimetric Analysis (TGA) Apparatus and Procedure

Thermogravimetric analysis involves the measurement of the gain or loss in weight of a heated sample as a function of the temperature and of the time. The essential elements of a thermogravimetric system are a furnace in which the rate of temperature increase is held constant, and an automatic recording

FIGURE 9
DTA BASE LINE Al_2O_3 VS. Al_2O_3

FIGURE 10 DTA BASE LINE Al_2O_3 VS Al_2O_3

Average Heating Rate 6.5°C/Minute

DTA OF Ag_2SO_4 VS. Al_2O_3 CORRECTED FOR BASE LINE

balance which carries a sample extending from the beam upward into a furnace. For automatically recording weight changes, various investigators have used such detectors as photoelectric cells, strain gages, solenoids, and variable capacitors which operate at the pointer or beam of an analytical balance. The recording system proposed for use in this program was recently described by Campbell and Gordon (42).

In this system, a conventional analytical balance is modified by the addition of an Atcotran linear variable differential transformer to one of the arms. A differential transformer consists of a moveable magnetic armature which is centered within a transformer core. Motion of the armature (attached to the balance beam) is converted to an A-C signal which is tapped off the secondary of the transformer, demodulated, and fed to a strip chart recorder. The weight of the balance is varied by suspending a rod beneath the magnetic armature which dips into liquids of various densities.

The other arm of the balance carries a yoke from which a refractory rod extends upward, through the balance case into the furnace. The rate of temperature rise of the furnace is controlled by a Wheelco "Chronotrol" and the temperature is recorded. A schematic of the thermogravimetric apparatus is shown in Figure 12.

A detailed sketch of the furnace used for this part of the program is shown in Figure 13 while Figure 14 shows the complete TGA apparatus with accessory equipment as it was used during the experimental work.

After modifications to the analytical balance were completed, the balance and associated controlling and recording equipment were set up under the furnace in preparation for thermogravimetric analysis of the fission product oxides and nitrates.

The weight range of the balance is determined by the diameter of a metal rod, suspended beneath the linear differential transformer core, which dips into a liquid of known density. Under these conditions the weight range is given by:

$$\begin{aligned} W &= \pi r^2 d h, \text{ where} \\ r &= \text{radius of rod} \\ d &= \text{density of liquid} \\ h &= \text{vertical deflection of rod} \end{aligned}$$

FIGURE 12 THERMOGRAVIMETRIC ANALYSIS APPARATUS

FIGURE 13 THERMOGRAVIMETRIC ANALYSIS FURNACE

FIGURE 14 APPARATUS FOR TGA

The maximum vertical deflection of the rod is fixed by the linear range of the transformer which is ± 0.5 cm. from the null position. Therefore, using mineral oil as a liquid ($d = 0.85$ g/cm³), the following weight ranges can be obtained for rods of various diameters:

Rod Diameter (cm.)	Weight Range For 0.5 cm. Deflection ($\pm$ grams)
0.95	0.300
1.27	0.538
2.22	1.645
2.54	2.153

For the calibration tests, the sample holder and sample-holder support rod consisted of a small platinum crucible held on the end of a 1/8-in. diameter length of the Alundum thermocouple shielding. Temperatures were measured with a small Pt-13% Rh vs. Pt thermocouple located very close to the platinum crucible. The output voltage of the linear variable differential transformer was recorded on a Brown Recorder which was modified to a zero center instrument to permit recording both gains and losses of weight of the sample. The sensitivity of the system was maximized by varying the input voltage to the transformer so as to obtain full scale deflection of the Brown Recorder for a ± 0.5 cm. motion of the armature. A typical calibration curve, obtained by adding and removing weights from one of the balance pans, is shown in Figure 15. The linearity of the differential transformer for motion of the armature about the null point is evident from the curve. The error of the system is determined by the minimum detectable deflection of the Brown Recorder (approximately 1/2 division).

The temperature and weight-recording portions of the TGA system were checked further by runs with zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). The TGA curves for these materials were obtained from the literature (43) and compared with the experimental results. In the run with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, a 1.194-gram sample was heated in an alundum crucible at $6.25^\circ\text{C}/\text{min.}$ to 1300°C. The input voltage to the transformer was 9.2 volts and one division on the Brown Recorder chart corresponded to a weight change of 0.0167 grams. The experimental curve is shown in Figure 16. According to Duval, the decomposition occurs in two steps in the range of temperatures indicated below:

FIGURE 15 CALIBRATION OF TGA BALANCE
(TRANSFORMER INPUT-6 VOLTS)

FIGURE 16 TGA OF ZINC SULFATE

The final reaction is reported to be quantitative.

The shape of the curve in Figure 16 is in agreement with Duval's mechanism, except that the observed decomposition temperatures are about 100°C too high and the loss of SO_3 is incomplete (100 mg. observed vs. 369.6 mg. calculated). These results suggest that the sample temperature lagged the furnace temperature by $100^\circ - 150^\circ\text{C}$. For this reason, in the next run with $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, the sample size was reduced to 0.3603 grams, the Alundum sample holder was replaced by a small, thin-walled platinum crucible, and the thermocouple bead was carefully positioned with respect to the sample. The results are shown in Figure 17.

Calcium oxalate monohydrate, according to Duval's measurements, decomposes in a series of steps as follows:

Our observed decomposition temperatures were within $5^\circ - 10^\circ\text{C}$ of Duval's values and the observed weight losses in each step agree with the theoretical values to within 2 - 5%. The total weight loss was 99.3% of theory. Changing the sample size and sample holder greatly improved the accuracy of the system.

Before proceeding with TGA of fission product oxides and nitrates, the zero center recorder was replaced by a 4-point Brown Recorder to increase the sensitivity of the system. With the 4-point recorder, a full-scale deflection was obtained for a ± 0.5 cm. movement of the armature. The error, using this recorder, was reduced to approximately ± 0.5 to 1.0% .

C. Thermal Stability Studies

1. Strontium Nitrate

Thermograms of L. T. Baker, C. P. grade $\text{Sr}(\text{NO}_3)_2$ were run at a heating rate of $6.3^\circ\text{C}/\text{min}$. The data obtained were compared with the results of

FIGURE 17 TGA OF CALCIUM OXALATE

Campbell and Gordon (44) who ran thermal analyses of 17 different nitrates including CsNO_3 . The alkaline earth nitrates all show the same behavior upon heating. No crystalline transitions are observed up to the boiling point. At temperatures slightly above the melting point, bubbling of the melt occurs, and at about 50°C above the melting point nitrous fumes are evolved as the nitrate decomposes to the oxide. The thermogram shown in Figure 18 is indicative of this behavior, and is similar to the curve obtained by Campbell and Gordon. The deep endotherm at 627°C occurs at the melting point, followed by an exotherm, which reaches a peak value at 652°C . This exotherm is probably due to an increased heat transfer rate caused by bubbling. Above 652°C a wide endotherm occurs as the $\text{Sr}(\text{NO}_3)_2$ decomposes. Decomposition is essentially complete at 750°C and no further changes occur up to 1400°C . The results indicate that $\text{Sr}(\text{NO}_3)_2$ will remain undecomposed if the calciner is operated below 650°C .

The TGA curve for $\text{Sr}(\text{NO}_3)_2$ is shown in Figure 19. For this test the initial sample weight was 0.3687 gms.

From 0° - 470°C a weight loss of 45 mg. occurred which is attributed to residual moisture. The TGA curve is then flat up to 610°C , at which temperature an abrupt loss of weight occurs due to decomposition. This reaction is complete at 745°C . The observed weight loss (neglecting the 45 mg. due to water) is 0.1865 g. as compared to a calculated weight loss for the complete decomposition of 0.3617 g. of $\text{Sr}(\text{NO}_3)_2$ to SrO of 0.1846 g. The transition temperatures observed in this experiment coincide closely with those obtained in the differential thermal analysis of the same material. It is concluded, therefore, that $\text{Sr}(\text{NO}_3)_2$ decomposes quantitatively to SrO at temperatures above 600°C , and that SrO is stable from 750° - 1400°C .

2. Strontium Oxide and Strontium Oxide-Alumina Mixtures

A TGA was run on a 316.3 mg. sample of anhydrous, C.P. strontium oxide purchased from the A. D. Mackay Co. The average heating rate in this run was 7.7°C/hr . The results are shown in Figure 20. No weight loss was observed up to 500°C . Between 500°C and 630°C there was a 13 mg. loss and the sample was then stable from 630°C to 1070°C . Seven mg. were lost between 1070°C and 1165°C , and a slight increase in weight (2.5 mg.) took place between 1165°C and 1510°C .

Similar behavior was shown in a TGA of a 2 to 1 by weight mixture of SrO and Al_2O_3 (Figure 21). A slow loss in weight began at 460°C and continued to 1280°C . The total weight loss was 7.5 mg., equivalent to 6.1% of the

FIGURE 18
DTA OF $\text{Sr}(\text{NO}_3)_2$ VS Al_2O_3 (CORRECTED FOR BASE LINE)

FIGURE 19 TGA OF STRONTIUM NITRATE

Average Heating Rate = 7.7 °C/min.

Weight Of Sample, 316.3 mg
Anhydrous C. P. Strontium Oxide

FIGURE 20 TGA OF STRONTIUM OXIDE

Average Heating Rate=6.6 $^{\circ}\text{C}/\text{min}$.

Weight Of Sample, 370.1 mg

FIGURE 21 TGA OF Al_2O_3 -SrO MIXTURE
(2:1 WEIGHT RATIO)

SrO present in the sample. Minor fluctuations in weight were observed between 1280°C and 1510°C.

These results are in agreement with the literature on SrO. Thermodynamic data indicate that volatile SrO_2 may be formed by oxidation of SrO at temperatures up to 727°C, and the data of Levin (22) indicate that no solid solutions or intermediate compounds are formed between SrO and Al_2O_3 below a temperature of 1800°C.

3. Cesium Nitrate and Cesium Nitrate-Alumina Mixtures

The data obtained in a thermal analysis of A. D. Mackay, C. P. grade CsNO_3 is shown in Figure 22. Cesium nitrate is typical of the alkali metal nitrates in that it undergoes a crystalline transition at low temperatures and decomposes very slowly at about 200°C above the melting point. The deep endotherm with a minimum at 200°C is due to a hexagonal to cubic solid transition. The International Critical Tables list this transition as occurring at 153.5°C with a heat of transition of 120 k cal/mole. The next endotherm, due to melting, is observed at 430°C. Campbell and Gordon (44) report the melting point to be 404°C. The temperature at which decomposition begins is not apparent in Figure 22, but can be seen quite clearly in the results of the TGA of the same material shown in Figure 23. The sample was stable up to 710°C, and then rapidly lost weight until, at 970°C, the sample was completely volatilized. This result is in good agreement with Campbell and Gordon, who found that decomposition was still occurring at 900°C, the highest temperature reached in their experiments. The complete loss of sample at 970°C is not surprising since cesium metal and its various oxides all decompose or volatilize at about 700°C. Since the relatively low temperature volatilization of cesium nitrate and cesium oxide might pose problems in the operation of the fluid bed calciner, it was of interest to determine the effect of Al_2O_3 on the thermal stability of CsNO_3 .

A 2 to 1 by weight mixture of calcined Al_2O_3 and C. P. CsNO_3 (191.4 mg) was used for TGA at a heating rate of 6.9°C. The results are shown in Figure 24. As in the previous run with CsNO_3 alone, no significant change in weight occurred up to a temperature of 725°C. Between 725°C and 940°C a weight loss of 96.5 mg. was observed. From 940°C to 1100°C the curve was flat, and then a slow loss of an additional 64.5 mg. occurred between 1100° and 1525°C. These results suggested the formation of an intermediate compound at 940°C which is more stable than CsNO_3 or the various cesium oxides. The increase in stability of CsNO_3 or cesium oxide in the presence of alumina is of significance in the fluid bed calcination process since the volatilization of radioactive Cs^{134} or Cs^{137} may be reduced by as much as 20%.

Average Heating Rate - 9.6°C/Minute

FIGURE 22
DTA OF C₅NO₃ VS. Al₂O₃ (CORRECTED FOR BASE LINE)

FIGURE 23 TGA OF CESIUM NITRATE

FIGURE 24 TGA OF $\text{Al}_2\text{O}_3 - \text{C}_5\text{NO}_3$ MIXTURE (2:1 WEIGHT RATIO)

To further investigate the possibility of compound formation between 940°C and 1100°C , a stoichiometric mixture of CsNO_3 and Al_2O_3 was heated to 1025°C and quenched in air. Qualitative tests indicated that some of the aluminum was water soluble. This test was repeated, and the quenched sample was leached with dilute acid and the extract analyzed for soluble cesium and aluminum. The molar ratio of soluble Cs to Al was 1:1.1, thus proving the formation of CsAlO_2 . Not all of the initially added Cs, however, was recovered in the quenched sample, since approximately 60% volatilized below 940°C .

4. Zirconyl Nitrate Dihydrate

The material used for these studies was C.P. grade zirconyl nitrate, purchased from the Amend Drug and Chemical Co., Inc. The thermogram shown in Figure 25, corrected for the base line, was obtained at a heating rate of $10.0^{\circ}\text{C}/\text{min}$.

A deep endotherm was observed in the range 60°C - 450°C with a minimum at 300°C . The decreasing branch of the endotherm shows three regions; a gradual drop between 60°C and 190°C , a flat portion from 190°C to 215°C and a rapid decrease between 215°C and 300°C . These temperature regions correspond closely to the structure of the TGA curve of the same material (see below). The endothermic reactions are essentially complete at 450°C - 500°C and no other major thermal effects are noted from 500°C to 1520°C ; the highest temperature reached in the experiment. The interpretation of this curve based upon the stepwise dehydration and subsequent decomposition of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to ZrO_2 is given below.

A TGA curve for a 272.6 mg. sample of C.P. grade zirconyl nitrate is shown in Figure 26. This curve was obtained at a heating rate of $6.1^{\circ}\text{C}/\text{min}$.

It is interesting to compare the structure of the TGA and DTA curves for this compound. Three major temperature regions are evident in the TGA curve, within which, weight losses occur at different rates. The temperature at the three transition points agree closely with those shown in the DTA curve. Assuming the overall reaction to be:

FIGURE 25 DTA OF ZIRCONYL NITRATE

Weight Of Sample = 272.6 mg

Average Heating Rate = 6.1°C/min

FIGURE 26 TGA OF ZIRCONYL NITRATE

5. Cerous Nitrate Hexahydrate

Differential thermal analysis was conducted at a heating rate of $10^\circ\text{C}/\text{min}$ on a sample of C. P. grade $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ which was purchased from the A. D. Mackay Co., and predried over Drierite for 60 hours. The results are shown in Figure 27. A broad endotherm is evident in the $75^\circ\text{--}420^\circ\text{C}$ temperature range, with successive minima at 140°C , 270°C , and 350°C . No further thermal changes are noted up to 1510°C . These minima correspond to the dehydration and the subsequent decomposition of $\text{Ce}(\text{NO}_3)_3$ to CeO_2 , which is complete at 450°C . Quantitative data are available from the TGA curve of the same material shown in Figure 28, which was run at a heating rate of $6^\circ\text{C}/\text{min}$. For the TGA run, the sample was dried at 130°C for one hour and then weighed. The dried sample was somewhat fused and weighed 373.2 mg. The experimental curve indicates a four stage decomposition in the temperature ranges $100^\circ\text{--}180^\circ$, $180^\circ\text{--}270^\circ$, $270^\circ\text{--}315^\circ$, and $315^\circ\text{--}500^\circ\text{C}$. The use of a lower heating rate would probably pinpoint the temperatures at which the stepwise dehydration occurs.

If it is assumed that the overall reaction is represented by

then the observed total weight loss of 213.4 mg. is 94.7% of the theoretical weight loss. The portion of the curve from 270°C to about 400°C corresponds very closely to the weight loss expected for the decomposition of $\text{Ce}(\text{NO}_3)_3$ to CeO_2 . Therefore, the initial portion of the curve from $100^\circ\text{--}270^\circ\text{C}$ must correspond to the loss of the water of hydration remaining in the sample after drying. Since only 74 mg. were lost up to 270°C as compared to the calculated value of 92.8 mg., it is apparent that some of the water of hydration was lost in the drying operation.

FIGURE 27 DTA OF CEROUS NITRATE (CORRECTED FOR BASE LINE)

Weight Of Sample = 373.2 mg
Average Heating Rate = 6.0°C/min

FIGURE 28 TGA OF CEROUS NITRATE

6. Niobium Pentoxide-Alumina

DTA and TGA curves were run on a 2 to 1 by weight mixture of Al_2O_3 and Nb_2O_5 . No thermal changes or weight loss was observed up to 1500°C .

7. Ruthenium Dioxide and Ruthenium Dioxide-Alumina Mixtures

a) Preparation and Analysis of Starting Materials

Because of the emphasis on ruthenium chemistry in this program, considerable effort was devoted to studies of the thermal stability of RuO_2 and mixtures of RuO_2 with Al_2O_3 . Three different RuO_2 starting materials were used during the course of this program. In the following discussion these will be identified as:

Type a) Purchased material, used as received from A. D. Mackay

Type b) Vitro-prepared RuO_2 , used for thermal stability studies

Type c) Vitro-prepared RuO_2 , used for kinetics studies

The RuO_2 used initially in the thermal studies was prepared from the RuO_4 and RuO_2 used in the kinetics studies (See Section VI). The KOH-ruthenate solution from the RuO_4 analysis, and the RuO_2 which formed during the Carius Tube tests were collected in a beaker, and after sufficient material was recovered, the RuO_2 slurry was filtered, washed with acid, and dried.

The RuO_2 used in the kinetics studies and in some of the DTA and TGA experiments was prepared by fusing the A. D. Mackay material with a mixture of KOH and KNO_3 to form the ruthenate and perruthenate salts. The cooled melt was dissolved in water, and insolubles were removed by filtration. Acetone was added to the clear liquor to reduce the ruthenium to the insoluble hydrated oxide. Paper pulp was then added to the slurry, the slurry was filtered, and the cake was washed with water and ignited to form the oxide. A sample of this material was analyzed by hydrogen reduction. The weight loss corresponded to 100.7% RuO_2 and the produced water calculated to 99.8% purity. This material was used exclusively towards the end of the program.

The results of spectrographic analysis of the three types of RuO_2 are shown in Table 6. Type (a) RuO_2 contained only traces of impurity while type (b) contained potassium as a minor impurity and type (c) contained potassium, nickel, and silver as major contaminants along with small quantities of other impurities. X-ray analysis of powdered specimens indicated the

TABLE 6

Qualitative Spectrographic Analysis of RuO₂

<u>Element</u>	<u>RuO₂ Prepared for Kinetics Study</u>	<u>A. D. MacKay RuO₂</u>	<u>RuO₂ Prepared for Thermal Study</u>
Ruthenium	Major	Major	Major
Potassium	Minor (low)	Not found	Major (low)
Calcium	0.0X	0.0X	0. X
Copper	0.0X (low)	0.00X	0. X (low)
Silver	0.00X (low)	0.00X (low)	Minor
Lead	0.00X (low)	0.00X (low)	0. X (low)
Tin	Not found	0.00X (low)	0.00X
Silicon	Not found	0.00X (low)	0.0X
Nickel	Not found	Not found	Major (low)
Magnesium	Not found	Not found	0. X
Barium	Not found	Not found	0. X
Iron	Not found	Not found	0.0X
Strontium	Not found	Not found	0.0X
Sodium	Not found	Not found	0.0X
Platinum	Not found	Not found	0.0X (low)
Gold	Not found	Not found	0.00X
Aluminum	Not found	Not found	0.00X

Elements checked but not found: Palladium, Rhodium, Titanium, Chromium, Cobalt, Molybdenum Vanadium, Tungsten, Zinc, Cadmium, Indium, Bismuth, Arsenic, Iridium.

presence of small amounts of ruthenium metal together with a major component which did not match the standard diffraction pattern for RuO_2 . In view of the results of spectrographic and hydrogen reduction analysis, however, it is believed that the unknown material found in x-ray diffraction is an allotropic form of RuO_2 . This hypothesis is now under investigation at ICPP.

Significant differences in the behavior of these RuO_2 samples were also noted in TGA. This information is summarized below.

b) Summary of TGA Results on RuO_2 Samples

In Table 7, the weight loss observed in TGA of the various types of RuO_2 in different temperature regions is compared with the calculated weight loss, assuming the decomposition reaction to be

RuO_2 has been reported (4) to melt and decompose at 1228°K and 1400°K , respectively.

It will be noted from the data in Table 7 that the A. D. Mackay material contained an impurity which was volatile below 1025°C , while types (b) and (c) RuO_2 lost no weight up to 1025°C . For each sample, the observed weight loss above 1025°C is greater than the calculated weight loss. It follows, therefore that some other reaction must occur at high temperature, which removes Ru as well as O_2 . Possible reactions are a) Air oxidation of RuO_2 to RuO_4 b) Sublimation or volatilization of RuO_2 . Although the significance of the correlation is not clear, the differences between the observed and calculated weight losses for the three types of RuO_2 follow the same order as the order of purities observed in spectrographic analysis.

In the following sections the thermal analysis curves for the three types of RuO_2 are presented and discussed.

c) Thermal Analysis of RuO_2 Purchased From A. D. Mackay

A thermogram of A. D. Mackay RuO_2 run at a heating rate of $9.75^\circ\text{C}/\text{min}$, is shown in Figure 29. The curve exhibits a deep endotherm in the $150^\circ\text{--}350^\circ\text{C}$ temperature range, probably caused by the vaporization of a volatile impurity. The curve then gradually rises, crossing the zero line to the exothermic

TABLE 7

Results of Thermogravimetric Analysis of RuO₂ Samples

	RuO ₂ Type (a)	RuO ₂ Type (b)	RuO ₂ Type (c)
Observed Total Weight Loss to 1500°C (%)	37.1	41.1	30.2
Observed Weight Loss to 1025°C (%)	14.8	0	0
Observed Weight Loss 1025°-1500°C (%)	22.3	41.1	30.2
Calculated Weight Loss 1025°-1500°C (%)	20.4*	23.9	23.9

*For the purpose of this calculation the weight of low temperature volatile material was subtracted from the initial sample weight.

FIGURE 29 DTA OF A.D. MACKAY RuO_2 VS Al_2O_3 (CORRECTED FOR BASELINE)

region at 800-850°C. A second endotherm begins at 1355°C and continues to 1500°C, at which temperature the run was terminated.

A TGA curve of the same material is shown in Figure 30. The sample weight was 264.1 mg. and a heating rate of 6.25°C/min was used. 14.8% of the sample was volatile up to 1125°C although the largest fraction of the weight loss occurred between room temperature and 350°C. The overall weight loss was 37.1% of the original sample weight.

d) Thermal Analysis of Types (b) and (c) RuO₂

The results of TGA of this material are shown in curve B of Figure 30. In this run, the initial sample weight was 0.3458g. and the heating rate was 6.25°C/min. In contrast to the A. D. Mackay material, no weight loss was observed up to 1025°C although there were some minor fluctuations at lower temperatures. The overall weight loss was 41.1% of the initial sample weight as compared to a theoretical loss of 23.9%.

The TGA curve of the RuO₂ prepared at Vitro for kinetics studies (type c), is also shown in Figure 30. The initial sample weight was 212.2 mg. and a heating rate of 6.3°C/min was used. This sample was predried at 130°C for one hour, which probably explains the absence of fluctuation in the TGA curve up to 1025°C. No weight loss took place in this range. The sample then lost 64 mg. between 1025°C and 1500°C as compared to a theoretical loss of 50.7 mg.

e) Ruthenium Dioxide-Alumina Mixtures

Several DTA and TGA curves were run on mixtures of the various types of RuO₂ with Al₂O₃. A typical DTA curve is shown in Figure 31. The low temperature endotherm in the 65°-300°C temperature range corresponds to a similar endotherm for DTA of this type of RuO₂ alone (see Figure 29), and to the weight loss curve for A. D. Mackay RuO₂ shown in Figure 30. Undoubtedly, therefore, this endotherm is due to the removal of volatile impurities.

A new feature in Figure 31 is the exotherm which begins at 1235°C and continues to 1500°C. It was originally thought that this endotherm was due to reaction between RuO₂ and Al₂O₃, however, x-ray diffraction analysis of an air-quenched specimen indicated the presence of ruthenium metal rather than a new compound. It is now believed, due to the discrepancy between the observed and calculated weight losses observed at high temperatures in

FIGURE 3D TGA OF TYPES (a),(b) AND (c) RuO₂

FIGURE 31 DTA OF Al₂O₃-A.D. MACKAY RuO₂ MIXTURE

TGA, that this exotherm is due to air oxidation of RuO_2 to RuO_4 . Further experimentation is required to settle this point.

TGA curves for $\text{RuO}_2\text{-Al}_2\text{O}_3$ mixtures were similar to those observed for RuO_2 alone and are not reproduced here. It should be noted, however, that in TGA of $\text{RuO}_2\text{-Al}_2\text{O}_3$ mixtures it was again observed that the weight loss occurring above 1025°C was greater than could be accounted for by the reaction

VI. Kinetics of the Ruthenium Tetroxide Decomposition

A. Physical Properties of Ruthenium Tetroxide

An analysis of the phenomena prevailing in the ICPP calciner indicates that the most logical approach to elucidating the processes leading to volatilization of ruthenium is a basic study of ruthenium tetroxide.

RuO_4 is a volatile form of ruthenium. The vapor is yellow, with an odor similar to that of concentrated ozone and it is poisonous. The solid exists in two crystalline forms; a labile form crystallizing as yellow needles when the vapor is condensed, and an orange-brown form solidifying in a granular-crystalline state when the liquid is cooled below the melting point. The yellow form melts at 25.5°C to a brown liquid, from which the brown form, m.p. 27°C , solidifies. The fused oxide has been obtained in distinct crystals only by sublimation, which readily occurs with a slight change of temperature at a pressure of 3 or 4 mm. RuO_4 begins to volatilize at 7°C . No boiling point has been determined. At 100.8°C , the vapor pressure is 183 mm. At about 108°C , the distillation is so rapid, that with a large quantity of liquid, a violent explosion occurs with production of dense black fumes. The physical properties of RuO_4 that are reported in the more recent literature (46) are given below:

Solid State (0° to 20°C)

$$\log p = 3190/T + 11.8130 \text{ (probable error } 0.09 \text{ mm)}$$

$$\Delta H_{\text{vap.}} = 14.59 \text{ kcal/mol}$$

$$\text{Melting point} = 23.6^\circ\text{C} \text{ (may be in transitional region and not a true m.p.)}$$

Liquid State

$$\log p = 1975/T + 7.7189 \text{ (probable error } 0.18 \text{ mm)}$$

$$\Delta H_{\text{vap.}} = 9.04 \text{ kcal/mol}$$

$$\Delta H_{\text{fus.}} = 5.04 \text{ kcal/mol}$$

$$\Delta S_{\text{fus.}} = 18.7 \text{ cal/}^\circ\text{C mol}$$

$$\text{estimated boiling point} = 135^\circ\text{C}$$

Where p is in mm of Hg and T is $^\circ\text{K}$.

Mellor (47) states that vapors of RuO_4 are very stable up to 500°C , but decompose above this temperature to RuO_2 and O_2 . Although RuO_4 is metastable

at room temperature, it undergoes no change if it is kept in the dark and complete absence of moisture. In water, it begins to decompose after a few hours. In a chlorine stabilized solution, the solubility is 22.1 g/l at 25° and 22.8 g/l at 75°C. RuO₄ is best handled or stored in CCl₄. Vapor pressure and distribution measurements show that solutions of RuO₄ in H₂O and CCl₄ are ideal below 0.2 molar. RuO₄ is reduced by hydrogen halides and hydrogen peroxide, and it dissolves in alkalis to give ruthenates and/or perruthenates. The best available survey of the literature on ruthenium chemistry up to 1938 was written by Deford (48).

B. Kinetics of RuO₄ Decomposition

A primary objective of this program was an investigation of the kinetics of the vapor phase decomposition of RuO₄:

After considering the relative merits of several experimental approaches, it was decided to conduct a series of static tests to determine the order of magnitude of the decomposition rate and the effect of various parameters on the rate. These tests were conducted in sealed 15 x 20 x 250 mm Carius tubes which were generally cleaned by a series of soap and water, cleaning solution, and distilled water rinses, and then dried at 115°C.

The RuO₄ was prepared along the lines of the procedures described by Shecter (54) and Marshall (55). Either RuO₂ or Ru metal was roasted in air at about 700°C to drive off any volatiles. The ruthenium was then transferred to a nickel crucible and slurried in molten KOH. Potassium nitrate was added slowly and the mixture heated to a dull red heat. The melt was then cooled, dissolved in water and acidified with H₂SO₄. The acid solution was added to a distilling flask and the ruthenium oxidized to the volatile octavalent state using K₂S₂O₈ and a silver catalyst. The pot temperature was held at 70-80° and a stream of gas (N₂ or O₂) was used to carry the RuO₄ from the still. The vapors were condensed in a dry ice-acetone bath.

The condensate contained RuO₄ and some H₂O. To remove the latter, 1-2 ml of concentrated H₂SO₄ are added to the condensate and the receiver is warmed to about 30° to 40°C to melt the RuO₄. The mixture of RuO₄ and H₂SO₄ is cooled to 10°C to freeze the RuO₄ and the H₂SO₄ is decanted. This treatment is repeated two or three times to remove the bulk of the H₂O. Some of the RuO₄ is lost in this step but the amount is inconsequential. The crude RuO₄ is then redistilled with the stream of gas passing through a short drying tube

of Anhydrone prior to freezing. The RuO_4 was generally redistilled just prior to use. The RuO_4 which condenses from the vapor forms very long needle-like structures, but on melting and refreezing it forms an orange-brown mass.

A sample of the liquid RuO_4 was then added to the clean tube using a small weighing pipette, and the tube was immersed in a dry ice-acetone bath to freeze the RuO_4 . The tube was quickly sealed and allowed to come to room temperature. The Carius tube was then placed in a constant temperature bath. After a measured time, the reaction was quenched in a dry ice-acetone bath, the tube opened, and the unreacted RuO_4 determined.

This procedure was used to investigate the decomposition of RuO_4 when the following materials were added with the RuO_4 to the tubes:

- a) Anhydrone
- b) Anhydrone and RuO_2
- c) Anhydrone and Ruthenium Metal
- d) Silica Gel
- e) Silica Gel and RuO_2

The results of some preliminary tests using RuO_4 alone and Anhydrone plus RuO_4 are described below.

1. Preliminary Tests

The detailed data on the preliminary tests are tabulated in the Second Quarterly Progress Report (V-2138-6-0).

The first group of these tests (Series 15, 16, and 17) were conducted at 98°C . The time at the test temperature ranged from 30 min. to 6 hr., with initial RuO_4 additions of 22 to 83 mg. Although the results were not reproducible, the appearance of the reaction tubes suggested a surface reaction.

In the reaction under study, gaseous RuO_4 decomposed to form black, solid RuO_2 and gaseous O_2 . The appearance of the black deposit was used as an indication of the start of reaction. Usually the black deposit appeared first on a small area of the tube and then progressed along the surface. The deposit was fairly uniform except at the ends of the tube which were often clear with a sharp ring marking the end of the RuO_2 deposit.

Since the lack of reproducibility in the first experiments was suspected to be due either to the presence of traces of water or to variations in the condition of the tube surface, Series 19, 20 and 22 were run to test various methods of pretreating the reaction vessel, and also to determine the effect of adding a dehydrating agent to absorb any traces of moisture. Surface treatment of the tubes included coating part of the tube with potassium pyrosulfate, heating all or part of the tube to about 500°C prior to use, cleaning the tubes with KOH solution, and using Vycor instead of Pyrex tubes. Both Anhydron $[\text{Mg}(\text{ClO}_4)_2]$ and Drierite (CaSO_4) were used in 1/2-1 gram quantities as additives to adsorb water. Although the surface pretreatment procedures and the Drierite seemed to have little effect on the stability of RuO_4 , the Anhydron apparently stabilized the reaction for a short period of time. For example, at 98°C, a black deposit did not appear for 6.7 and 10 hr in two of the tubes containing Anhydron and in Series 22 there was no sign of decomposition in one of the tubes after heating for 6 hours.

The remainder of the preliminary tests were made at higher temperatures (120° and 142° for Series 23, 155° for Series 27, and 154° for Series 30 and 32). The tubes contained, initially, 35-55 mg. of RuO_4 and one gram of Anhydron (except for a few from Series 23 in which only one-half gram of Anhydron was used). The time at test temperatures ranged from 15-45 minutes.

In all of these tests, RuO_4 remained stable for a time and then decomposed onto the tube surface. The length of the induction period was a function of temperature. Figure 32 shows a plot of the longest induction time obtained for each of the four test temperatures. These are single value points, not averages. At about 125°C, there is a very sharp reduction in the induction period. The reason for this is not known but it may be related to the properties of the Anhydron. The vapor pressure of the lowest hydrate formed by Anhydron ($\text{MgClO}_4 \cdot 2\text{H}_2\text{O}$) is virtually zero up to a temperature of 135°C (49). At this temperature, Anhydron begins to lose its perfect dehydration efficiency.

The results obtained at 154-155°C (Series 27, 30 and 32) are shown in Figure 33. Here the induction period and decomposition time were considerably shorter than that at lower temperatures. Although the data were still too scattered to bear analysis, they indicated qualitatively, that after a 15-minute induction period the RuO_4 is completely decomposed in an additional 15-20 minutes.

In view of the scatter of the above results all of the tubes that were prepared in this way were not tested. Several were kept in the dark for over a month

FIGURE 32 APPARENT REACTION INDUCTION PERIOD VS. TEMPERATURE

FIGURE 33 RuO_4 CONCENTRATION VS. TIME AT 154° - 155°

without any sign of decomposition. When these were exposed to daylight they slowly darkened. The center third of one tube was wrapped with black tape and then exposed to daylight. After a period of time the tube wall at both ends became completely black while the middle remained clear, thus illustrating the importance of possible photochemical reactions. The RuO_2 on the wall was reddish brown while the loose RuO_2 was black.

To summarize the results of these preliminary tests, it was established that the RuO_4 decomposition exhibits an induction period which is quite sensitive to the presence of water vapor and to temperature, and less sensitive to exposure to light. Although the addition of Anhydrone to the RuO_4 lengthened the induction period, the initiation of reaction was uncontrolled. Consequently, plots of percent decomposition vs. time were extremely scattered. Various treatments of the surface of the reaction vessel did not improve the reproducibility. In all of these runs it was noted that the decomposition began at a small area of the glass surface, where RuO_2 was deposited, and spread out from that point. For this reason, it was suspected that the reaction was autocatalytic. The effect of the product (RuO_2) on the induction period and rate of reaction was therefore studied.

2. Decomposition of RuO_4 In the Presence of Anhydrone and RuO_2

(The results in this section are presented in graphical form. Detailed tabulations will be found in Quarterly Progress Report V-2138-9-0)

The first set of runs (Series 35) was designed to eliminate any effects due to the glass surface by precoating the walls with RuO_2 and then using the same vessel to study the decomposition of a sample of RuO_4 . To obtain the RuO_2 coating, the following procedure was used. Eight-inch long glass extensions were connected to Carius tubes; RuO_4 and 1g. of Anhydrone were added and the tubes sealed; the tubes were then placed in a 115°C oven for about 4 days to insure the complete decomposition of RuO_4 . The RuO_2 deposited more or less uniformly on the surface of the tubes except near the bottom. After coating, the tubes were opened, weighed amounts of RuO_4 ranging from 36.2 to 70.7 mg. were added, and the tubes resealed. They were then tested at 154°C for 5, 10, 15, and 20 minutes. The results are shown in Figure 34. In previous tests at this temperature, the reaction generally proceeded with an induction period of about 20 minutes followed by decomposition in an additional 20 minutes. Although agreement between duplicates was only fair in this series of runs, the RuO_2 coating apparently eliminated the induction period.

FIGURE 34 SERIES 35-RuO₄ DECOMPOSITION AT 154°C
(TUBE WALLS COATED WITH RuO₂)

Since the reaction proceeded without an induction period when the walls were precoated with RuO_2 , an attempt was made to determine the nature of the reaction by adding RuO_2 powder directly to the RuO_4 sample without coating the walls. The RuO_2 used in these runs (Series 37), was purchased from A. D. MacKay Inc. and ignited at dull red heat for 1/2 hour to remove volatile impurities. Three tubes were prepared, each containing 0.2g of the ignited RuO_2 , 60-72 mg RuO_4 , and 1g. of Anhydrone. The sealed tubes were heated at 154° for 2, 5, and 15 minutes. This quantity of RuO_2 was considerably higher than that used to coat the walls in the previous runs. In this series 84% of the RuO_4 was decomposed after 2 minutes and no RuO_4 was found in the 5 and 15 minute samples. The reaction proceeded without an induction period and the product did not deposit on the walls of the tube. The increase in rate over the preceding runs was due to either the increased weight of RuO_2 or to the fact that both RuO_2 and the glass surface were present in the present experiments.

In the next set of runs (Series 40), reaction tubes were prepared containing 31.5 to 69 mg. of RuO_4 , 1g. of Anhydrone, and 0, 25, 50, and 150 mg. additions of RuO_2 . The tubes were heated at 125°C for various periods of time and then quenched. The results are shown in Figure 35. The fraction of RuO_4 not decomposed was a linear function of time, thus indicating a zero-order reaction. The rates for the 25, 50, and 150 mg. additions of RuO_2 , derived from the least squares lines in Figure 35 were 0.0103, 0.0103, and 0.0124 fraction RuO_4 remaining per minute, respectively. The apparent induction period was determined by extrapolating the lines in Figure 35 to the ordinate $f = \text{fraction } \text{RuO}_4 \text{ remaining} = 1$. The corresponding times at $f = 1$ are plotted in Figure 36. The data indicate that the apparent induction period is linearly related to the quantity of added RuO_2 .

In this analysis, the rate constant k , is defined by the equation of a zero-order reaction

$$-\frac{dc}{dt} = k', \quad (1)$$

where C = concentration of RuO_4 at time t .

Integrating between the limits $C = C_0$ at $t = 0$ and $C = C$ at $t = t$:

$$-k't = C - C_0 \quad (2)$$

FIGURE 35 SERIES 40 RuO_4 DECOMPOSITION AT 125°C

FIGURE 36 EFFECT OF QUANTITY OF RuO_2 ON
INDUCTION PERIOD OF RuO_4 DECOMPOSITION

Dividing through by C_0 and rearranging to get this expression in terms of f ,

$$f = \frac{C}{C_0} = 1 - kt \quad (\text{where } k = \frac{k^1}{C_0}) \quad (3)$$

Equation (3) represents the data of Series 40, however, the intercept of the equation may be some constant other than 1 due to the induction period. For any run, the linear portion of the curve of f vs. t , may be brought into correspondence with equation (3) by translating the line along the time axis so that $f = 1$ when $t = 0$.

Zero order kinetics for a gaseous reaction on the surface of a solid is typical of a system wherein the active sites of the surface are completely covered by adsorbed molecules and the rate is controlled by the diffusion of these molecules into the solid. This behavior has been observed for the decomposition of ammonia on osmium and hydrogen iodide on gold (50, 51). It is typical of these systems, that as the initial concentration of the gaseous reactant is reduced a point is reached where the surface is no longer fully covered. The rate then becomes dependent upon the initial concentration of the reactant and a transition to first-order kinetics is observed. Observation of this transition from zero-order to first order kinetics would be an interesting verification of the role of the surface in the $\text{RuO}_2 - \text{RuO}_4$ system, however a vacuum system would be required to control the initial concentration of RuO_4 at very low partial pressures.

The most significant result of Series 35 and 37, is that the addition of RuO_2 to RuO_4 shortened the induction period, thereby improving the reproducibility of the data. In these runs there was no reaction on the walls during times up to 30 minutes (30-50% decomposition). This observation was encouraging, since it may be possible to continuously monitor the reaction by optical methods when RuO_2 or some other catalyst is initially present.

To determine the variation in reaction rate with temperature at a fixed concentration of added RuO_2 , a group of experiments (Series 47) was run at 110° , 125° , and 140°C , using 1 g. of Anhydrone, 200 mg. RuO_2 , and various initial concentrations of RuO_4 . The data obtained are shown in Figure 37, where the initial weight of RuO_4 is indicated next to each experimental point. The results were analyzed statistically by a quadratic polynomial regression technique with time, temperature, and initial amount of RuO_4 as independent variables, and the fraction of RuO_4 unreacted as the dependent variable. The analysis indicated a linear relation between the fraction unreacted and time,

FIGURE 37 SERIES 47 DECOMPOSITION OF RuO₄
(VARIOUS TEMPERATURES - 0.2g RuO₂)

with the slope of the line (reaction rate) independent of the initial RuO_4 concentration. The following equations gave the best fit to the experimental data:

$$f_{110^\circ\text{C}} = -1.518 - 0.00224t + 0.07553C_0 - 0.0005803C_0^2 \quad (4)$$

$$f_{125^\circ\text{C}} = 0.5993 - 0.01967t + 0.01665C_0 - 0.0000609C_0^2 \quad (5)$$

$$f_{140^\circ\text{C}} = 1.204 - 0.04110t - 0.004026C_0 + 0.00006075C_0^2 \quad (6)$$

where

$f_{T^\circ\text{C}}$ = The fraction of RuO_4 unreacted at $T^\circ\text{C}$

t = time in minutes

C_0 = initial weight of RuO_4 in milligrams

The quadratic dependence of C_0 was arbitrary since the data could be fitted equally well to an equation linear in C_0 . The lines in Figure 37 were drawn from these equations by substituting the average value of C_0 (57 mg.). The weighted estimate of the standard deviation of the experimental values of f from the least squares line is 0.103. The rate constants derived from the slopes of the least squares lines at 110° , 125° , and 140°C were 0.00222, 0.01967, and 0.0411 per minute, respectively. The standard deviations of the reaction rates were 0.00104, 0.00315, and 0.00345 respectively.

The rate constants are related to the temperature by the Arrhenius equation

$$\text{Log } k = \text{log } P - \frac{\Delta H_a}{2.303RT} \quad (7)$$

where,

k = the rate constant

T = Temperature ($^\circ\text{K}$)

ΔH_a = heat of activation

P = frequency factor

A least squares fit of the experimental rate constants to the Arrhenius equation gave:

$$\log k = \log (7.119 \times 10^{14}) - \frac{30,500}{2.303RT} \quad (8)$$

The frequency factor, P, is related to the entropy of activation, ΔS_a , by the equation

$$P = \frac{RT}{Nh} e^{\Delta S_a/R} \quad (9)$$

Substituting values for Avogadro's number, N, and Planck's Constant, h, gives

$$\Delta S_a = 2.303R \log 3.41 \times 10^4/T \quad (10)$$

At 140°C, the calculated ΔS_a is 13.4 cal/mol°K, which is a reasonable value for a unimolecular decomposition (52).

Since the decomposition of RuO_4 in the preceeding experiments was a surface reaction, it was expected that variation in the properties of the RuO_2 would affect the rate of reaction and induction period. To determine the magnitude of this effect, four batches of RuO_2 (Series 44) were prepared by different procedures and these were then used to catalyze the decomposition of RuO_4 . The RuO_2 samples were prepared as follows:

Type 1 - RuO_4 was added to a water-acetone mixture and digested overnight. The solution was filtered, the residue washed well with water and ignited at 850°-900°C for 2 hours.

Type 2 - RuO_2 , purchased from A. D. Mackay, was fused with a mixture of KOH and KNO_3 to form the potassium salt. The melt was dissolved in water and the insolubles removed by filtration. Acetone was added to the filtrate, and the resulting slurry of RuO_2 was digested overnight and then filtered. The coke was washed and ignited at low temperatures to remove the filter paper. The residue was then slurried in boiling water, filtered, washed, and ignited at 850°-900°C for 2 hours.

Type 3 - RuO₂, purchased from A. D. Mackay was ignited as received for 2 hours at 850°-900°C.

Type 4 - The RuO₂ used in Series 39 and 40 was slurried in water, filtered, washed, and ignited for 2 hours at 850°-900°C.

Reaction tubes were prepared containing 1g. of Anhydrone, 100 mg. of the various types of RuO₂, and 44.3-76.0 mg. of RuO₄. These were heated at 125°C for various periods of time and then quenched. Plots of the fraction RuO₄ remaining versus time for the various types of RuO₂ again gave a straight line, indicating a zero-order reaction. The slopes (reaction rates) of all the lines were approximately the same, and it was noted that prolonged ignition of the RuO₂ (20 hours at 850°-900°C) increased the induction period but did not change the rate.

To test the rate equation derived from the results of Series 44, the four sets of data were composited and plotted as shown in Figure 38. The reaction rate (slope of the line) was 0.0142 min⁻¹ which was within 12% of the value calculated at 125°C, using rate equation (8).

To summarize the results of the decomposition of RuO₄ at an RuO₂ surface, the reaction follows zero-order kinetics from 110°-140°C at initial concentrations of RuO₄ of the order of 0.3 atmosphere. The apparent rate constant (taken as the slope of the f vs t curve) over this temperature range is given by

$$k \text{ (min}^{-1}\text{)} = 7.119 \times 10^{14} e^{-30,500/RT}$$

The rate constant is independent of the quantity of RuO₂ added, when the additions range between 25 and 150 mg. The observed zero-order kinetics are typical of a catalyzed reaction wherein the active sites of the catalytic surface are fully covered by adsorbed molecules so that the rate of reaction is independent of the concentration of reactant in the gas phase.

The decomposition exhibits an induction period, the duration of which is decreased by increasing either the temperature, or the initial weight of RuO₂, and increased by increasing the initial concentration of RuO₄. The latter observation suggests that some material is present in the RuO₄ which poisons the RuO₂ catalyst for a short period of time. The induction period is also reduced by prolonged heating of the RuO₂ before using it as a catalyst.

FIGURE 38 DECOMPOSITION OF RuO₄ AT 125°C - DATA FROM SERIES 44

The present experimental set-up was not elaborate enough to permit study of the mechanism of the reaction. Accordingly, work in the Anhydrone RuO_4 - RuO_2 system was suspended in favor of an investigation of the decomposition of RuO_4 on silica gel and ruthenium metal surfaces. A proposal was submitted to Phillips Petroleum Company for continuing the experimental work in a vacuum system wherein the initial concentration of RuO_4 may be closely controlled, foreign gases may be excluded, and the reaction may be followed continuously by spectrophotometric methods.

3. Decomposition of RuO_4 in the Presence of Anhydrone and Ruthenium Metal

The Ru used in these experiments was a -80 mesh powder, purchased from A. D. Mackay Inc. The reaction was carried out in Carius tubes containing various amounts of RuO_4 , 1 gram of Anhydrone, and 100 mg of ruthenium metal. At 110°C , (during a three hour period) no visual change was observed in the RuO_4 or on the walls of the reaction vessel. After three hours the reaction was quenched and the remaining RuO_4 determined. 47.2% of the initial weight of RuO_4 was found. The product did not appear to coat the ruthenium metal since the metallic luster remained. When the experiment was repeated at 140°C , all the RuO_4 decomposed in 2 hours and there was a slight deposition of RuO_2 on the walls.

At least two modes of decomposition are thermodynamically possible in this system. These are:

To determine which reaction predominates, both the RuO_4 reacted and the RuO_2 produced was determined. The ratio of $\text{RuO}_2/\text{RuO}_4$ should be equal to 1:1, 2:1, or some intermediate value depending upon the relative rates of the two reactions.

In Series 57, four tubes were prepared and heated at 125°C for about 5 hours to completely decompose the RuO_4 , thereby simplifying the analysis for RuO_2 . The tubes were analyzed as follows: The tubes were opened and the contents transferred to a centrifuge tube, using water to wash out the tube and to dissolve the Anhydrone. The residue in the tube after centrifuging was washed well with water and then dried at 120°C for about 2 hours. The residue was

transferred to a small boat and dried to constant weight. The boat and contents were further heated to 800°C in a nitrogen atmosphere. At this temperature, the nitrogen was turned off and the hydrogen turned on to reduce the RuO_2 to Ru metal and produce H_2O . The H_2O was swept from the tube furnace and trapped in a Nesbit bulb, the loss in weight during reduction and the quantity of H_2O produced was determined and calculated to RuO_2 .

The results obtained in the 57 Series are given in Table 8, where they are reported in terms of the % of theoretical weight of the reaction products assuming first Reaction (1) as a basis, and then Reaction (2). An examination of Table 8 indicates that the predominate RuO_4 Reaction is (1). If any of the decomposition proceeds via Reaction (2), it is probably less than 20% of the total under test conditions. In view of these results a further investigation of the reaction may be desirable in the future. The method of study used in the program gave an approximate overall rate. A knowledge of the individual reaction rates is also important. One way of determining the rate for Reaction (2) is to measure the pressure decrease in the system as a function of time. The change in pressure can be correlated with the reaction rate since the gaseous RuO_4 is converted to the solid RuO_2 with no gas products as in Reaction (1).

TABLE 8
 RuO_4 Decomposition in the Presence of Anhydrone and Ru Metal

Reaction	No.	% of Theoretical		
		Wgt. of Residue ($\text{RuO}_2 + \text{Ru}$)	Wgt. of RuO_2 (Calculated from Wgt. Loss Dur- ing H_2 Reduction)	Wgt. of RuO_2 (Calculated from H_2O Produced During H_2 Reduc- tion)
(1) $\text{RuO}_4 \longrightarrow \text{RuO}_2 + \text{O}_2$	174-57-1	101.9	113.2	—
	174-57-2	99.8	116.1	117.6
	174-57-4	100.5	120.1	—
	174-57-5	100.4	115.6	118.7
(2) $\text{RuO}_4 + \text{Ru} \longrightarrow 2\text{RuO}_2$	174-57-1	96.2	56.6	—
	174-57-2	90.8	58.0	58.8
	174-57-4	92.8	60.1	—
	174-57-5	91.0	57.8	59.5

4. Decomposition of RuO₄ on Silica Gel

(The data in this section is presented in graphical form. Detailed tabulations will be found in Quarterly Progress Report V-2138-12-0).

The decomposition of RuO₄ on silica gel is of interest, since silica gel is used to adsorb RuO₄ from the fluid bed calciner off-gas stream at NRTS. Pilot Plant experience indicates that the capacity of the silica gel may improve after use, and this was believed to be related to the catalytic effect of RuO₂ which initially forms on the gel surface.

In Series 53 tubes were prepared containing 1 g of Davison's Grade A, Type 3, 6-16 mesh silica gel and RuO₄. Several plots of the data were tried but none were completely satisfactory since the scatter was high. The lack of reproducibility was traced to differences in the activity of the particles of silica gel as indicated by the color of the particles in the tubes where the RuO₄ was partially decomposed. When the reaction was quenched some of the particles were completely black while others were clear yellow.

To overcome this difficulty, a smaller particle size (28-200 mesh) silica gel was used in Series 55. This tended to minimize the tube to tube variation in silica gel since the number of particles per gram was considerably increased.

This Series was run at 110° and 125°C. The fraction RuO₄ remaining and the amount of RuO₄ decomposed were plotted in several forms, and the appearance of the data on semilog paper (Figures 39 and 40) indicated that the log of the amount of RuO₄ decomposed was linear with time, or,

$$\ln (C_0 - C) = kt + A \quad (A = \text{Constant})$$

To determine if the initial or final amounts of RuO₄ had any effect on the reaction, additional terms for these quantities were included in the above equation. A multiple regression analysis was carried out on the data at both temperatures and it was concluded that neither quantity had a significant effect. Therefore, the data can be represented by:

$$\ln (C_0 - C) = 0.0864t - 1.192 \text{ (at } 110^\circ\text{C)}$$

$$\ln (C_0 - C) = 0.2602t - 1.082 \text{ (at } 125^\circ\text{C)}$$

FIGURE 39 SERIES 55 DECOMPOSITION OF RuO₄ ON SILICA GEL AT 125° C

FIGURE 40 SERIES 55 DECOMPOSITION OF RuO_4 ON SILICA GEL AT 110°C

The slope in the above equations is defined as the reaction rate constant, and the 95% confidence intervals for the true values are 0.0495 to 0.123 and 0.197 to 0.323 at 110°C and 125°C, respectively. Substitution of the estimated rate constants in the Arrhenius equation gave an energy of activation of 21.9 kcal per mole.

In view of the apparent relationship between the amount of RuO_4 decomposed (e.g. RuO_2 produced) and time, Series 60 was run to determine the effect of added RuO_2 . Two sets of tubes were prepared, each containing 1 g of silica gel and RuO_4 with 25 mg. RuO_2 in the first set and 50 mg. added to the second. These were tested at 110°C.

Since the log of the amount of RuO_4 decomposed was found to be linear with time in Series 55, the data from Series 60 was fitted to

$$\ln (\text{Co}-\text{C}) = a_0 + a_1 t + a_2 \text{Co} + a_3 \text{Co}^2 + a_4 \text{Co} t$$

where the a's were constants to be determined.

Regression analysis of the 25 and 50 mg. sets of data indicated that the effects of the Co and Co^2 terms were significant for both sets of data. The interaction term, $\text{Co} t$, was insignificant for the 25 mg. data but was significant for the 50 mg. RuO_2 data. The equations derived from these data were as follows:

25 mg. RuO_2

$$\ln (\text{Co}-\text{C}) = -.5915 + 0.1114t - 0.04214 \text{Co} + 0.0007955 \text{Co}^2$$

50 mg. RuO_2

$$\ln (\text{Co}-\text{C}) = -5.080 + 0.2654t + 0.08195 \text{Co} + 0.0003686 \text{Co}^2 - 0.003229 \text{Co} t$$

Figures 41 and 42 show plots of these data. Since the initial RuO_4 concentrations entered into these equations, the plotted lines were calculated for the average initial RuO_4 weight. Under these conditions, the equations for the lines representing the 50 and 25 mg. sets of data, respectively, reduced to:

FIGURE 41 SERIES 60
RuO₄ DECOMPOSITION ON SILICA GEL AT 110° C
(25 mg RuO₂ ADDED)

FIGURE 42 SERIES 60- DECOMPOSITION OF RuO₂ ON SILICA GEL AT 110°C
(50 mg RuO₂ ADDED)

$$\ln (Co-C) = -0.35 + 0.111 t$$

$$\ln (Co-C) = -0.79 + 0.111 t$$

The equivalent equation for Series 55 (no added RuO_2) is:

$$\ln (Co-C) = -1.19 + 0.0864 t$$

A comparison of the three equations indicates that the slopes (e. g. reaction rates) of the 25 and 50 mg. data lines are the same, but with no added RuO_2 the rate was about 22% lower. The apparent lowering of rate may not be significant since this is a comparison of the results from two series of tests and may be within the series to series variation. The intercepts are different and appear to indicate a trend e. g. the greater the quantity of the added RuO_2 the less negative the intercept.

The silica gel used in the above tests underwent a 1.2% decrease in weight upon being heated at $130^\circ C$ for 19 hours. This weight loss can be attributed to adsorbed gases or water. Series 67 was conducted to determine if the adsorbed material had a significant effect on the kinetics. In addition, a second objective of Series 67 was to determine the effect of added glass surface area on the reaction. To realize these objectives, Series 67 was divided into 4 groups as follows:

Group 1 - 1 g as received silica gel, 50 mg. RuO_2 , RuO_4 .

Group 2 - 1 g dried silica gel, 50 mg. RuO_2 , RuO_4 .

Group 3 - 1 g dried silica gel, 50 mg. RuO_2 , 1 g ground glass, RuO_4 .

Group 4 - 1 g dried silica gel, 50 mg. RuO_2 , 2 g ground glass, RuO_4 .

The silica gel used in Group 2 to 4 was dried at $130^\circ C$ for about 4 days. The glass in Group 3 and 4 was one of the Pyrex tubes used in these tests ground to -40 mesh, soaked in cleaning solution, washed with water, soaked in water and dried overnight at $130^\circ C$. The reaction tubes were cleaned in a similar manner. The RuO_2 and dried silica gel were weighed into the tubes and placed in a $130^\circ C$ oven overnight and then RuO_4 was added and the tubes sealed. These were tested at $110^\circ C$.

The results of these tests were plotted, and it was found that the rate using the dried silica gel was approximately half that of the as received material. The primary cause of the retardation could have been (1) the removal of adsorbed water, (2) the removal of adsorbed gases and/or, (3) deactivation of the silica gel. The data from Group 1 was not compared mathematically with Series 60 but visually they appeared to compare reasonably well.

The data from Groups 2, 3, and 4 are plotted in Figure VC₂d-7 as the mg. of RuO₄ decomposed vs. time. Curves were drawn to approximate the data. The data from Groups 3 and 4 showed that the addition of glass did not significantly affect the reaction. In spite of the addition of a glass surface, most of the reaction still took place on the glass walls.

To summarize the results of the silica gel experiments, the logarithm of the amount of RuO₄ decomposed was a linear function of time, and the rate was independent of the initial concentration of RuO₄. At 110°C and 125°C, the 95% confidence intervals for the reaction rates were 0.049 to 0.123 and 0.197 to 0.323 reciprocal minutes, respectively. Substitution of these rate constants in the Arrhenius Equation gave an energy of activation of 21.9 kcal.

Predrying the silica gel had a retarding effect on the reaction and the addition of ground glass did not significantly influence the rate. The addition of 25-50 mg. of RuO₂ to the reaction vessel increased the rate approximately 22%.

C. Suggested Future Work

When the study of the kinetics of the gas phase decomposition of RuO₄ was begun, it was anticipated that the major portion of the work would be conducted in a system where the concentration of RuO₄ was monitored continuously. Initial experiments designed to determine the order of magnitude of the rate under static conditions, however, led to many difficulties in obtaining reproducible data. These difficulties have only recently been resolved, and it is now feasible to consider continuing this work in a high vacuum system where the variables involved in the reaction may be closely controlled.

Since the present data was obtained in sealed bulbs in the presence of air, the effect of added gases on the rate of reaction was not determined.

One of the chief difficulties in the present experimental method was the problem of exactly reproducing experimental conditions such as the initial concentration of RuO_4 and the condition of the catalyst (RuO_2) surface. These difficulties can be eliminated if future work is carried out in a vacuum system where the catalyst surface may be thoroughly degassed before each run, and where the initial concentration of RuO_4 may be fixed by introducing the reactant to the reaction vessel until a predetermined pressure is reached. It is expected that the reaction may be followed continuously by optical methods, thereby facilitating the rapid accumulation of data.

The basic requirements for a vacuum system for studying the kinetics of the RuO_4 decomposition are storage bulbs for the RuO_4 and any gases to be added to the RuO_4 , a heated reaction vessel and pressure measuring device, and a detection system for following the concentration of RuO_4 as a function of time. Since RuO_4 will oxidize stopcock lubricants or mercury, special stopcocks and manometers such as float valves, and glass diaphragm pressure gages are required in the system.

Two methods are proposed for following the rate of reaction. An optical technique may be used in which light from a mercury lamp is collimated, filtered to pick out the radiation in the absorption band of RuO_4 ($3850 \text{ \AA}$), passed through the reaction vessel which is positioned along the axis of a tube furnace, and impinged upon a photomultiplier tube. This type of system has been used by Schuler and Murphy (53) to follow the rearrangement of vinyl allyl ether to allylacetaldehyde at 250°C . The optics for this system could probably be taken from a Beckman DU Spectrophotometer, although a new mercury lamp source might be required to provide the intensity necessary for the long path through the furnace. A second technique which could be used in lieu of the optical method is based upon a colorimetric method for RuO_4 which was developed by Deford (48), and is sensitive to 0.25γ of Ru. In this system, a small calibrated leak would be withdrawn from the reaction bulb at measured time intervals and analyzed by the colorimetric method. The sample volume and reaction bulb volume would be such that the change in concentration of RuO_4 due to the withdrawal of the samples would be negligible.

A sketch of a proposed system, based upon the optical method of analysis is shown in Figure 43. RuO_4 is sublimed several times and finally stored as a solid in an evacuated bulb. After heating, degassing, and evacuating the lines and reaction vessel, the RuO_4 is warmed and transferred to the reaction bulb to a known pressure as indicated by the glass diaphragm gage. The

FIGURE 43 APPARATUS FOR KINETICS STUDY

rate of reaction is determined by comparing the output of the photomultiplier tube with a previously determined calibration curve. The effect of added gases such as O_2 , nitrogen oxide, and water vapor is determined by adding these materials to the reaction vessel from an auxiliary system shown at the top of Figure 43.

VII. Analytical Methods

A. Determination of RuO₄ In CCl₄

Several methods were considered for analysing RuO₄. The characteristics of these methods and a literature reference for each method are shown in Table 9. The ruthenate procedure was selected for this study since it was applicable to the concentration range of the static rate experiments and was particularly suited for carbon tetrachloride solutions of RuO₄. To check out the procedure, two samples of ruthenium, one metal (J. A. Samuel and Co.) and the other an oxide (A. D. MacKay) were ignited in air at 800°C to constant weight. Part of the resultant oxides were fused with a KOH-KNO₃ mixture, dissolved in acid, and the Ru determined gravimetrically as the metal. A second portion of the oxides was then analyzed using the ruthenate spectrophotometric method. The results of these experiments are given in Table 10. In view of the good agreement between the two results for the oxide sample, the study was extended to carbon tetrachloride solutions of RuO₄, since this was the type of sample obtained from the sealed tube kinetic experiments. A portion of RuO₄ was dissolved in CCl₄ and an aliquot of the solution was added to a nickel crucible. Acetone was added to reduce the RuO₄. After evaporation, the sample was fused and analyzed. This gave a calculated purity of 89.5% RuO₄. It was noticed that the color of the sample was not stable; therefore, a study of the effect of KOH concentration, temperature and time of extraction was undertaken. A solution of RuO₄ in CCl₄ was prepared, extracted at room temperature with KOH solutions of different concentrations, and the absorbance of the aqueous phase measured as a function of time. The results are shown in Figure 44. It is readily apparent that the absorbance is a function of time as well as KOH concentration. The shape of the maximum in the curves for 3N and 4N KOH may be explained by the occurrence of a set of consecutive reactions such as:

Assuming that RuO₄⁻ is the only one of the compounds which absorbs at 465 mμ and that the rate $k_2 > k_3$, it is characteristic of this scheme that absorbance will reach a maximum and then decrease. It can also be seen from Figure 44 that the rate k_2 is sensibly independent of OH⁻ concentration while the decomposition of RuO₄⁻ increases with increasing OH⁻ concentration. It follows from

TABLE 9

Analytical Methods for Ruthenium

<u>Type of Analysis</u>	<u>Mg. Ru Used</u>	<u>Source</u>
Gravimetric	50-100	Analytical Chemistry of the Manhattan Project - C. J. Rodden, Vol. VIII - 1 of National Nuclear Energy Series.
Spectrophotometric (Potassium Ruthenate Absorption)	8	Anal. Chem., <u>22</u> , 795 (1950)
Spectrophotometric (Thiourea)	0.7	Sandell, E. B., "Colorimetric Determination of Traces of Metals"
Tracer (Ru ¹⁰⁶)	large range	Standard tracer practice

TABLE 10

Analysis of Ruthenium Metal and Oxide

<u>Item</u>	<u>J. A. Samuel</u> <u>Ru Metal</u>	<u>A. D. Mackay</u> <u>Ru Oxide</u>
Changes in weight on ignition	17.5%	-23.0%
Ru as RuO ₂ in ignited sample:		
Gravimetric	105 %	99.3%
Colorimetric	102 %	99.3%

FIGURE 44 EFFECT OF KOH CONCENTRATION ON EXTRACTION OF RuO_4 FROM CCl_4

the curves that the optimum OH^- concentration for extracting ruthenate from a CCl_4 solution of RuO_4 is approximately 2N.

To determine the effect of temperature on the extraction a second series of experiments was performed in which the extracting agents were hot 2N KOH, room temperature 2N KOH, and water, followed by the addition of sufficient KOH to make a 2N solution. The absorbance-time curves are shown in Figure 45. The absorbance of the room temperature KOH extract increased slowly with time and gradually approached that of the warm KOH and solid KOH extracts. Addition of solid KOH to the water extract probably raised the temperature above that of the warm KOH solution used in the comparison run, thus causing the small amount of decomposition of RuO_4^- indicated in Figure 45.

These data explain the low result (89.5%) obtained in the original analysis of the RuO_4 prepared from pure (99.3%) ruthenium metal and RuO_2 . Since room temperature KOH was used to extract the fusions, it is probable that the RuO_4^- decomposition was not complete at the time the absorption measurements were made.

To determine the effect of RuO_4 concentration on the analytical method, as well as to obtain a calibration curve, a series of samples containing 9-50 mg. RuO_4 per liter were analyzed. A plot of the absorbance vs. concentration resulted in a straight line, thus indicating conformance to the Beer-Lambert Law. The calculated molar extinction coefficient in a 1 cm. cell at 465 m μ is 1806.

These results provided a basis for the spectrophotometric analysis of RuO_4 in the static rate experiments.

Most of the samples analyzed during the program were recovered in sealed Carius Tubes and were in one of two major categories, namely, samples containing Anhydron-RuO₂-RuO₄ and samples containing silica gel-RuO₂-RuO₄. The RuO_4 in these samples was determined using the ruthenate method as described below.

B. Determination of RuO_4 In The Presence Of Anhydron And RuO_2

One end of the sealed Carius tube was placed in a dry ice-acetone bath and the other was warmed with a hair dryer so that the RuO_4 condensed in the cold end of the tube. The top of the tube was cracked using a hot wire and opened. After the addition of 15 ml of CCl_4 , the tube was allowed to come to room temperature. The CCl_4 and the tube contents were transferred with

FIGURE 45 EFFECT OF TEMPERATURE ON EXTRACTION OF RuO_4 FROM CCl_4

CCl_4 washing to a centrifuge tube and centrifuged. The centrifugate was added to a beaker containing 50 ml of 2N KOH. The residue in the tube was crushed with a glass rod and re-extracted with CCl_4 . The organic extract was added to the original centrifugate. The mixture of CCl_4 and alkali was warmed at about 65 to 70°C until the CCl_4 layer was clear (about 1/2 hour). The mixture was transferred to a separatory funnel, the two layers separated, and the CCl_4 discarded. The aqueous layer was transferred to the original beaker and reheated to about 80 or 90°C for about 15 minutes. The KOH solution was transferred to a 250 ml volumetric flask, cooled, and made up to volume with 2N KOH. The absorbance was then measured at 465 m μ on the Beckman DU spectrophotometer. In some instances, the color did not develop fully, therefore the absorbance was remeasured the following day to insure a maximum reading. Solutions prepared in this manner have exhibited exceptional stability. For example, the optical density of a freshly made sample was 0.527, after 1 day 0.528, and after 5 days, 0.530. Initially, the stability was very poor, but repeated use of the same glassware apparently had a beneficial conditioning action. As a result, all new glassware was soaked in KOH-ruthenate solution prior to use.

C. Determination of RuO_4 In The Presence Of RuO_2 And Silica Gel

The procedure described in the previous section for determining RuO_4 had to be modified for the silica gel tests. Extraction of the RuO_4 from the silica gel with CCl_4 is very slow and several extractions are required for complete removal of RuO_4 . After a short investigation it was shown that the RuO_4 adsorbed on the silica gel can be removed by completely dissolving the silica gel in 2N KOH along with the RuO_4 , thus eliminating the extraction.

The Carius tube is opened as before, and the contents are transferred to a beaker containing about 50 ml of 2N KOH to dissolve the silica gel. The tube is then washed with three-10 ml portions of CCl_4 to remove any residual RuO_4 that might be on the tube walls.

When the silica gel is added to the KOH there is some gassing, but at no time is there an odor of RuO_4 . The beaker is placed on a hot plate and the CCl_4 is boiled off (about 20 minutes). The KOH solution is then centrifuged to remove any RuO_2 which was carried along with the silica gel. The KOH solution and washings are returned to the original beaker and heated for about 20 minutes, cooled, made up to a volume with 2N KOH, and the absorbance measured at 465 m μ .

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