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CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

for Period Ending June 20 1954

E H Taylor Director
M A Bredig Associate Director

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CHEMISTRY DIVISION SEMIANNUAL PROGRESS REPORT

SUMMARY

INORGANIC AND PHYSICAL CHEMISTRY

The conclusions reported earlier that Zr(IV) exists in a predominantly monodisperse trimeric or tetrameric species in about 1 M HCl was confirmed and the same observation was made of Hf(IV) in 0 5 to 2 M HCl This species is stable over the temperature range of approximately 0 to 25°C for Hf(IV) in 1 M HCl In concentrations of 3 M HCl and higher and of 0 2 M HCl and lower Zr(IV) and Hf(IV) are distributed in polydisperse species and as expected a decrease of acidity increases polymerization Some polymerization of Hf(IV) is indicated even in 5 M HCl In 0 2 M HCl and lower concentrations zirconium is more polymerized than hafnium under corresponding conditions Polymerization increases with temperature in 0 08 M HCl in the range 0 to 25°C and is slowly reversible at these temperatures Boiling solutions of $ZrOCl_2$ for a short time results in changes that are less reversible

Contrary to conclusions from solvent extraction and anion exchange results Au(III) does not appear to be dimerized in 3 M HCl

Further study of Bi(III) in perchlorate solution confirmed the earlier report that a predominantly monodisperse species (pentamer or hexamer) exists at the same and at lower acidities than at those for which others postulated a continuous series of polymers of several times higher average molecular weight This species is stable over the temperature range of approximately 0 to 25°C

The study of the interaction of thiocyanato cations of tervalent cobalt and chromium with Ag(I) and Hg(II) cations in aqueous solution was continued The effects of ionic strength upon this interaction and of the interaction upon the rate of aquation of the complex ions were determined

The formation of hydrogen electrode sites on the silver chloride electrode is thought to be the cause of the discrepancy between experimental and theoretical potentials for this electrode system at temperatures above 150°C

In long continued observations on the inhibition of the corrosion of mild steel by the pertechnetate and tungstate ions no continuous increase was found in the amount of technetium precipitated on the specimens Osmium(VIII) oxide passivates mild steel by raising its potential above the value at which copper may be displaced This treatment gives a labile film and when the film is ruptured pitting attack follows Such a pitted specimen is inhibited when transferred to a technetium solution of adequate concentration The pertechnetate solution does not ennoble an iron specimen or otherwise induce passivity although its inhibitory properties are thoroughly established These observations permit a rational differentiation between passivity and inhibition

Measurements of the electrode potentials of oxidized stainless steel in dilute sulfuric acid disclosed the existence of several stages in the breakdown of the original film and the recovery of nobility These steps are marked by reproducible inflections in the potential time curve The corrosion rate is intimately associated with the electrode potential rising to extremely high values below −100 mv vs the saturated calomel electrode potential Devices which maintain specimens at more noble potentials also reduce greatly the dissolution of metal

In the study of alkali metal amalgams the decomposition rate in water appears to be controlled by the surface concentration of the alkali metal as calculated by the Gibbs adsorption equation This explains the observed indefinite fractional reaction order based on bulk concentration

The solubility of alkali halides M^+X^- in the corresponding liquid alkali metal M^+e^- was found to increase sharply with the atomic number or size of the M^+ cation that is from the lithium to the cesium systems This result and other details observed in such systems as a function of the nature of the components are readily correlated with cohesive energies or heats of vaporization and sizes and polarizabilities of the ions

The absence of a phase transition in solid cesium iodide and bromide at temperatures up to 5°C below the melting points was established by high temperature x ray diffraction measurements This observation suggests that the large volume increase on melting is the result of a structural change namely from an ionic coordination of 8 in the crystal to an average of probably 6 in the melt

[redacted]

Electrical conductivity and density measurements of molten salts were extended to cover the system potassium chloride–sodium chloride A minimum in the conductivity vs concentration plot is given the same interpretation as a similar minimum found previously in the potassium chloride–lithium chloride system This interpretation is based upon the effect of the size of the smaller one of the two cations on the anion semilattice spacing which controls the mobility of the larger more numerous K^+ cations Conductance was treated as a rate process and values were obtained for entropy and heat of activation for conduction which are useful in elucidating the behavior of these molten salts

A preliminary experimental value for the heat of combustion in the range of 650 kcal was obtained for boron carbide

NUCLEAR CHEMISTRY

Two samples of approximately 500 and 1000 curie intensity in Xe^{135} derived from the Homogeneous Reactor off gas were mounted for velocity selector absorption cross section studies for the Physics Division The mixed fission gases were rapidly separated purified and reduced to a 1 cc volume and sealed in a metal transmission chamber

Measurements have been completed on the 500 curie source and it has been opened to obtain the daughter Cs^{135} whose mass spectrographic analysis involving isotopic dilution was the principal method of assay The analysis gave a value of 481 curies in this sample The 1000 curie sample is now being assayed

The half lives of Kr^{85} and Co^{60} measured over a period of one year were found to be 10 53 ± 0 1 and 5 41 ± 0 05 years respectively

Measurements were carried out on three rhodium activities 21 hr Rh^{100} 5 9 day Rh^{101} and 243 day Rh^{102} and on four ruthenium activities ca 57 min Ru^{94} 1 63 hr Ru^{95} 2 93 day Ru^{97} and 39 5 day Ru^{103} incidental to continuing researches on the nuclear chemistry of technetium Sources were prepared either by means of cyclotron or pile bombardments and half lives and beta and gamma ray energies were determined by using a variety of techniques Several new gamma ray transitions were observed which previously had been found in the decay of the corresponding technetium isobars

ORGANIC CHEMISTRY

No isotope effect was found in the iodoform reaction of acetone 1 C^{14} A small isotope effect was found in the usual direction in the Schmidt reaction of acetone 1 C^{14} These results are contrary to those reported by earlier workers

A series of competitive reaction rate studies of the Diels Alder reaction by the use of dilution technique gave results in agreement with the accepted mechanism

A solution scintillation counter for C^{14} designed to measure ratios of activities and to correct for instrument drifts has been constructed and tested

Triphenylethylene glycol labeled in the 1 and 2 positions in the chain and in the phenyl groups both stereospecifically and nonstereospecifically was subjected to the pinacol rearrangement under a variety of conditions It was shown that an isotope effect attends the rearrangement and that three different reaction paths are followed during the rearrangement The contribution made by each of these paths under a given set of conditions was determined

CHEMICAL PHYSICS

Scattering reaction experiments with molecular beams of potassium and of HBr have been extended by varying the temperature of the HBr The increase of the apparent KBr with temperature confirmed the reality of the previous observations which indicated a definite but small amount of reaction

The presence of stably trapped atomic hydrogen was established in H_2SO_4 H_3PO_4 and $HClO_4$ irradiated at 77°K with gamma rays In a similar manner high concentrations of atomic hydrogen from adsorbed water were formed on glass surfaces

A microsynthesis for PD_3 is being developed for determining the nuclear moments of P^{32} by microwave spectroscopy The method is now being operated on a 10 μg level

Neutron diffraction from urea crystals shows that the molecule is planar with the following interatomic distances N H (*trans* to carbonyl) = 1 04 Å N H (*cis*) = 0 98 Å All nitrogen bond angles are close to 120 deg Strongly asymmetric thermal motion is indicated

A very small lambda like transition in the heat capacity of crystalline cadmium iodide at about 269°K was confirmed

A new precision high temperature adiabatic calorimeter has been built for making measurements of heat capacity of solid and liquid materials up to 1000°C This apparatus has several unique automatic controlling circuits and appears capable of maintaining at 950°C the temperature of the adiabatic shield to within better than 0 01°C of the calorimeter can temperature

RADIATION CHEMISTRY

The yield of H_2O_2 in gamma irradiated acidic KBr or KCl solutions containing oxygen is dependent upon the halide ion concentration This was interpreted to indicate that the halide ions can react with OH radicals in the tracks of the ionizing particles and thereby lower the primary H_2O_2 yield

It was also found that some solutes including O_2 and H_2O_2 lower the primary H_2 yield

The primary H_2O_2 yields in the decomposition of pure water and in 0 8 *N* H_2SO_4 solution were evaluated by extrapolating to zero halide ion concentration The same result was also obtained for pure water by measuring H_2O_2 formation in oxygen swept water

The primary yields of H OH H_2 and H_2O_2 were re evaluated to be 2 78 2 12 0 42 and 0 76 for the gamma ray decomposition of pure water and 3 70 2 92 0 39 and 0 78 for 0 8 *N* H_2SO_4 solution

Helium saturated water subjected to 1 5 Mev electrons in a flow system gave steady state H_2O_2 concentrations approximately proportional to the square root of radiation intensity Pulsed beam experiments indicated an average lifetime of 0 001 sec for the shortest lived radicals whose concentration affects the H_2O_2 steady state

The kinetics of the reactions of carbon monoxide in the presence and absence of xenon under alpha particle irradiation indicate that xenon does not alter the velocity constant Hence there is no charge transfer from CO to xenon which have ionization potentials of 14 1 ev and 12 1 ev respectively The velocity constant for a sphere 2 cm in diameter 11 4 for both reactions agrees with previous values of 11 4 for CO alone and 11 2 for CO and xenon – values calculated on the basis of partial pressure of CO only

REACTOR CHEMISTRY

The pH at 25 00 ± 0 04°C of uranium trioxide–sulfuric acid–water mixtures has been determined to a precision of ±0 004 pH unit from 0 024 to 10^{-4} *m* sulfuric acid and at UO_3/H_2SO_4 mole ratios from 0 70 to 1 20 The solubility of UO_3 in sulfuric acid at elevated temperature (150 to 300°C) has been determined by isolating a UO_3 saturated sample and comparing the pH of the isolated sample at 25°C with the pH data mentioned above By this method seven isotherms in the concentration range from 1 0 *m* down to 10^{-4} *m* have been obtained

Suitability of some of the more common acidic salt systems of thorium for use in a breeder blanket was investigated experimentally $Th(NO_3)_4$ + excess HNO_3 and $Th_3(PO_4)_4$ + H_3PO_4 with a PO_4 Th ratio of 10 have both the desired thermal stability and low viscosity The phosphate system attacks both titanium and zirconium but corrosion in the nitrate system might not be intolerable

INORGANIC AND PHYSICAL CHEMISTRY

ULTRACENTRIFUGAL STUDIES

R W Holmberg K A Kraus
J S Johnson

Zirconium and Hafnium Solutions

A more detailed analysis of results and some additional experiments confirm the conclusion reported in the last semiannual report[1] that Zr(IV) and Hf(IV) in aqueous chloride solutions at 1 M acidity exist essentially as monodisperse species probably trimeric but perhaps tetrameric The acid range of stability was investigated for hafnium and little if any change was found between 0 5 M HCl and 2 M HCl There was also no appreciable change in polymerization at 1 M acidity when the temperature was changed from 25° to 0°C

Studies of the effect of acidity and of temperature on polymerization of Zr(IV) and Hf(IV) have been extended outside of the range of monodispersity The experimental procedure and materials were the same as in the earlier work However the procedure[2] utilized to interpret the results for monodisperse charged species is not applicable to polydisperse charged systems Useful comparisons may be made however of the values of $N_{Z\,0}$ the degree of polymerization calculated as though the solute were not ionized since the studies at 1 M acidity indicate that z the charge per monomer unit is not large (0 5–1 0)

When as with the equipment used here the concentration variable is obtained from the observed refractive index gradients Lansing and Kraemer[3] showed that for a neutral polydisperse solute with constant species activity coefficients the observed molecular weight is a Z average molecular weight[4] (M_Z) defined as

$$(1) \qquad M_Z = \frac{\sum_i w\, M_i^2}{\sum_i w_i M_i}$$

where w_i is the weight concentration of species i for a given amount of solution and M_i is its molecular weight If the solution density ρ is assumed constant and the partial specific volumes $\bar{v}_i$ of all solute species are the same and constant the equation for equilibrium is

$$(2) \qquad \frac{d \log \dfrac{Z^*}{x}}{d\,(x^2)} = S_0 = \frac{M_Z(1 - \bar{v}\rho)\omega^2}{4\,606\, RT}$$

where x is the radius of rotation $\bar{v}$ the partial specific volume of the solute ω the angular velocity R the gas constant T the absolute temperature and Z^* the difference in the values of Z (an observed number proportional to the refractive index gradient dn/dx) for centrifugations of solutions identical except for the presence of the polymeric solute Z^* is proportional to the refractive index gradient attributable to the presence of the polymeric solute While for a monodisperse system S_0 is expected to be constant a polydisperse system is indicated by an increase in S_0 with x i e an upward curvature of a plot of $\log Z^*/x$ vs x^2

The quantity to be used for comparison of the degrees of aggregation $N_{Z\,0}$ is equal to $M_{Z\,0}/M$ where M is the molecular weight of the assumed monomeric species here assumed to be $ZrOCl_2$ and $HfOCl_2$ It is again emphasized that $N_{Z\,0}$ does not have an exact physical significance since the effects of charge are neglected and also since the monomeric unit may change in the range of acidities covered here In chloride systems however a change in degree of hydrolysis of the assumed monomer (e g $Zr(OH)Cl_3$ instead of $ZrOCl_2$) does not affect the computed $N_{Z\,0}$ greatly since changes in M are largely compensated by changes in the partial molar volumes

The results are summarized in Table 1 Polydisperse systems are indicated in this table by two values of $N_{Z\,0}$ which were computed at $x = 6\,3$ and $x = 6\,9$ points approximately 3 mm from the extremes of the cell

Hafnium was found to be somewhat polymerized even in 5 M HCl Some doubt is introduced at this acidity by the fact that sedimentation of HCl at this concentration is accompanied by sizeable changes in the activity coefficients $\gamma_{\pm HCl}$ across

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[1] J S Johnson R W Holmberg and K A Kraus *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 6

[2] J S Johnson K A Kraus and G Scratchard *J Phys Chem* (in press)

[3] W D Lans ng nd E O Kraemer *J Am Chem Soc* 57 1369 (1935)

[4] For polydispe se systems the Z aver ge molecular weight emphas zes the high molecular we ght species more than either the weight or number averages

TABLE 1 POLYMERIZATION OF Zr(IV) AND Hf(IV)

Element	Con (M)	Med m		Speed of Rotat o (rpm)	Temp (0°C)	$N_{Z\ 0}$
		M HCl	M LiCl o NaCl( )			
Hf	049	5		27 690	33	1 2 – 1 8
Hf	049	3		23 150	29	1 9 – 2 3
Z	043	3		27 670	29	2 1 – 2 7
Hf	050	2		23 120	26	2 8
Hf[a]	048	1	1	27 675	32	2 9
Z	049	1	1	27 690	33	3 0
Hf	050	0 5	1 5	23 115	26	3 0
Hf[a]	048	0 2	1 9	20 390	30	3 0
Zr[a]	043	0 2	1 9	27 675	30	4 1 – 5 4
Hf	050	08	1 9	17 980	27	5 6 – 6 9[b]
Hf	050	08	1 9	17 980	10	4 2 – 5 1[b]
Zr	051	08	1 9	23 120	26	6 8 – 11 4[b]
Zr	051	08	1 9	23 120	1	5 2 – 7 0[b]

[a]Solute ntroduced as MCl_4 In other cases sol te i trodu ed as $MOCl_2\ 8H_2O$
[b]Equil b um not atta ned

the cell If the effect on the activity coefficients of the polymer are in the same direction the observed values of $N_{Z\ 0}$ should be lower than the actual degree of aggregation In 3 M HCl hafnium is still clearly polydisperse Hf(IV) is essentially monodisperse in the region 0 2 to 2 M HCl although there is slight indication (not shown in Table 1) of polydispersity in 0 2 M HCl This acidity is computed as an excess over the stoichiometric formula $HfOCl_2$ although prepared by dissolving $HfCl_4$ in 0 1 M HCl

In centrifugation of 0 05 M $HfOCl_2$ in 08 M HCl–1 9 M LiCl equilibrium distribution was not approached in a normal manner After elapse of a period of time considerably longer than usually required to reach centrifugation equilibrium the refractive index gradients showed almost constant change from day to day rather than the usual roughly exponential approach to constancy Further polymerization was apparently taking place in addition to sedimentation The values of $N_{Z\ 0}$ listed in Table 1 were those obtained at the termination of the room temperature portion of the experiment (after ca 10 days) they have only relative significance but demonstrate that polymerization increases with decrease in acidity

The results for Zr(IV) are very similar to those for Hf(IV) Definite polydispersity is observed in 3 M HCl the highest acidity studied In 1 M HCl the solute is monodisperse In 0 2 M HCl–1 9 M NaCl (prepared by dissolving $ZrCl_4$ in 0 1 M HCl–1 9 M NaCl) Zr(IV) is clearly polydisperse and more polymerized than in 1 M HCl In a centrifugation of a 05 M $ZrOCl_2$– 08 M HCl–1 9 M LiCl solution equilibrium was not attained in 8 days similar to the analogous experiment with Hf(IV)

Comparison of the experiments on the Zr(IV) and Hf(IV) reveal definite though minor differences between these elements although the indicated differences (Table 1) in 3 M HCl may not be significant The difference between the two elements shows up clearly for the 0 2 M HCl solutions where Hf(IV) is definitely less polymerized than Zr(IV) While equilibrium was not attained for the oxychlorides in 08 M HCl it seems significant that Zr(IV) indicated higher values of

$N_{Z\ 0}$ at the termination of the experiment than Hf(IV) and these values were increasing faster for zirconium than for hafnium If the degree of hydrolysis can be directly related to the degree of polymerization this observation is in agreement with the earlier suggestion[5] that zirconium hydrolyzes more extensively than hafnium

In contrast to the finding[1] that polymerization of Hf(IV) (and presumably also Zr(IV)) in the monodisperse system (ca 1 M HCl) is insensitive to temperature in the range 0 to 25°C the polydisperse systems of both elements in 0 08 M HCl showed a sharp decrease in polymerization with decreasing temperature For Hf(IV) the refrigeration was started at the termination of the room temperature centrifugation previously discussed while the refractive index gradients were still rising The gradients then began to fall and were still going down when the experiment was terminated after five days The $N_{Z\ 0}$ values given in Table 1 were obtained at the termination of the experiment For Zr(IV) the solution was prepared at room temperature but was centrifuged at the lower temperature from the beginning After the usual initial rise in Z a decrease set in which presumably indicated reversal of the polymerization that had taken place at room temperature The experiment was terminated (after 11 days) before equilibrium was attained The values of $N_{Z\ 0}$ reported for all experiments in 0 08 M HCl have only relative significance since they were not obtained at equilibrium However the direction of the changes taking place at the termination of the experiments make clear that the apparent heat of polymerization is positive in this temperature range Further polymerization is slowly reversible under these conditions

Ruer[6] observed a markedly different chemistry for boiled and unboiled $ZrOCl_2$ solutions In order to correlate his findings with possible changes in polymerization a 0 25 M $ZrOCl_2$ solution was boiled for 1 hr and from this a solution of 0 05 M $ZrOCl_2$–2 M LiCl was prepared Equilibrium in the centrifugal field (at ca 9200 rpm) was obtained without difficulty at room temperature and values $N_{Z\ 0}$ = 30 to 40 were computed for x = 6 3–6 9 cm Apparently rather drastic and comparatively irreversible changes had taken place on boiling

To summarize the major qualitative conclusions which can be drawn from this work are as follows

1 The monodisperse species existing in 1 M acid has considerable acid stability range although in general as expected polymerization increases with decreasing acidity

2 Polydispersity becomes apparent at acidities greater than 3 M and less than 0 2 M

3 Hf(IV) is less polymerized than Zr(IV) at the lower acidities

4 Polymerization increases with temperature in the lower acid range

Au(III) in 3 M HCl

Irvine[7] has postulated on the basis of concentration effects in solvent extraction and anion exchange that Au(III) dimerizes at high HCl concentrations This hypothesis was checked by centrifugation of 0 05 M Au(III) in 3 M HCl under which conditions his results indicated a preponderance of dimer Combined with our measured value of 92 cc for the molar volume ($\bar{V}$) of $HAuCl_4$ in 3 M HCl the centrifugation results gave a molecular weight of 330 which compares with the (theoretical) formula weight of $HAuCl_4$ of 340 0 There is some uncertainty in this value since Traube[8] found the sharply different value $\bar{V}$ = 126 cc for the molar volume of $HAuCl_4$ in water This value would give a molecular weight of 388 In either case the centrifuge results conflict with the dimerization hypothesis

Bismuth(III) Perchlorate Solutions

Previously [1] ultracentrifugation of Bi(III) perchlorate solutions had been carried out under conditions similar to those of Graner and Sillen[9] in their investigation of Bi(III) hydrolysis (i e acidities that were equal to or greater than that corresponding to an $HClO_4/\frac{1}{2}Bi_2O_3$ ratio of three) These investigations have now been extended to considerably lower acidities and the previous results have been improved by determinations of the partial specific volume $\bar{v}$ of $BiOClO_4$ in $NaClO_4$ solutions The results are summarized in Table 2 These results are based on an average

[5] See e g E M Larsen and A M Gammill *J Am Chem Soc* **72** 3615 (1950)

[6] R Ruer *Z anorg u allgem Chem* 43 282 (1905)

[7] J W Irvine private communication

[8] J Traube *Z anorg u allgem Chem* 8 12 (1895)

[9] F Graner and L G Sillen *Acta Chem Scand* 1 631 (1947)

TABLE 2 POLYMERIZATION OF Bi(III)

Exp No	Bi(III) (M)	$NaClO_4$ (M)	Excess Molar ty of H^+	N		
				z = 0 0	z = 0 5	z = 1 0
1	0 05	3	+0 080	4 0 – 4 5	4 3 – 4 8	4 7 – 5 3
2	0 05	3	+0 007	3 1 – 4 5	3 4 – 4 9	3 7 – 5 4
3	0 05	3	–0 013	4 8	5 1	5 7
4	0 05	3	–0 090	4 8	5 2	5 7
5	0 05	1	0 00	4 9	5 4	6 6
6	0 05	1	0 00	4 8	5 3	6 4
7	0 025	3	0 00	3 9 – 5 3	4 2 – 5 7	4 5 – 6 1
8	0 006	3	ca –0 090	~5 4	~5 7	~6 1

Excess molarity of $HClO_4$ beyond $HClO_4/\frac{1}{2} B_2O_3$ ratio of 3
At T = 1°C II others at T = ca 27°C
A double val e for N indicates polydispersity the values are the approx mate range of N calculated from S_0 as though the solution were monodisperse

value of $\bar{v}$ = ca 0 16 cc/g Although some trend in $\bar{v}$ was noted with both acidity and $NaClO_4$ concentration it is felt that the precision of the data particularly in 3 M $NaClO_4$ is insufficient to justify the use of more than an average value It should be noted that because of the insensitivity of the $(1 - \bar{v}\rho)$ term in the centrifuge equation (Eq 2) an error of 10% in $\bar{v}$ will cause an error of only about 2 5% in the degree of aggregation N under the most extreme conditions investigated The calculation of N was made by a method de scribed earlier [2] assuming the monomeric com ponent to be $BiOClO_4$ Results based on charges for the monomeric unit of z = 0 0 5 and 1 0 are included in the table The potentiometric results of Graner and Sillen (i e determination of hy droxyl numbers) essentially rule out the possibility of higher values of z

In contradiction to the hypothesis of continuous polymerization of Graner and Sillen both the general linearity of the log Z^*/x vs x^2 plots and the consistency of the N values indicate that a more or less discrete hydrolytic species predomi nates over a considerable acidity range Further evidence for the monodispersity of the system is shown by the observation that N is independent of temperature (compare experiments 5 and 6 in which the same solutions are centrifuged to equi librium at 27° and 1°C) If a mixture of species existed at room temperature it is improbable that essentially the same distribution would be found at both temperatures A comparison of the values of N for the different charges reveals a greater consistency with assumed charges z = 0 0 and z = 0 5 than for z = 1 0 This would indicate that the polymeric species is somewhat complexed by perchlorate ions Such a result is not implausible for a highly charged species

THE HYDROGEN ELECTRODE–SILVER CHLORIDE ELECTRODE SYSTEM AT HIGH TEMPERATURES AND PRESSURES

M H Lietzke

A knowledge of the behavior of the hydrogen electrode at high temperatures and pressures will ultimately afford a means of measuring the pH of aqueous solutions above 100°C Theoretical curves have been plotted which predict the be havior of the hydrogen electrode–silver chloride electrode system at temperatures up to 250°C and pressures up to 40 atm The agreement be tween calculated potentials which are based on extrapolation of data obtained at lower tempera tures and experimental data obtained directly at the higher temperatures has been shown and dis cussed in ORNL 1741 [10]

[10] M H Lietzke *The Hydrogen Electrode–Silver Chloride Electrode System at High Temperatu es and Pressures* ORNL 1741 (in press)

At temperatures up to 150°C and pressures up to 18 atm the experimental potentials obtained by Choudhury and Bonilla[11] agree with the calculated potentials to within experimental error At higher temperatures and pressures the experimental potentials are lower than the calculated values A possible explanation of this discrepancy might be a lowering of the silver chloride electrode potential by the hydrogen The fact that this effect can be very appreciable was experimentally demonstrated by Choudhury and Bonilla The mechanism of the potential lowering probably involves the establishment of hydrogen electrode sites on the silver chloride electrode This effect would be most pronounced at higher temperatures at constant pressure and at higher hydrogen pressures at constant temperature The deviations between the experimental and calculated values are in these directions

THE INTERACTION OF THIOCYANATO CATIONS WITH METAL CATIONS IN AQUEOUS SOLUTION

W C Waggener

The interaction of thiocyanato cations of tervalent cobalt and chromium with silver(I) and mercury(II) cations in aqueous solution has been described previously[12] Most of the quantitative experiments were conducted with cobalt complexes because of their greater solution stabilities though it was emphasized that the analogous thiocyanato chromium(III) ions exhibit no qualitative difference with respect to interaction with silver(I) or mercury(II) ions Two developments during the present period have made further studies feasible particularly with regard to the behavior of the chromium(III) complexes and systems involving interaction with silver(I) ion

The first development was the recognition that solutions of the thiocyanatoamminechromium(III) cations are photosensitive A brief study for example of thiocyanatopentaamminechromium(III) nitrate in dilute acid revealed that the instability observed for this solution was due largely to photochemical decomposition through exposure to the fluorescent laboratory lighting Figure 1 illustrates the effect of the light upon the absorption spectrum of thiocyanatopentaamminechromium(III) nitrate The shifts in its absorption curve are due not simply to partial decoordination of thiocyanate from the pentaammine cation but also to the decoordination of ammonia from the chromium The latter effect was measured by an increase in the pH of the solution occurring during irradiation The end result of irradiation of thiocyanatopentaamminechromium(III) ion was the complete decomposition of the complex and appearance of flocculent green chromium(III) hydroxide The comparative stability of thiocyanatopentaammine cobalt(III) ion under the same conditions is indicated also in Fig 1

A second development has been the use of a nitrobenzene emulsion to sequester traces of colloidal silver thiocyanate from solutions immediately prior to spectrophotometric measurements By protecting the solutions from unnecessary light and by eliminating the interference to precise spectrophotometric measurements of traces of colloidal silver thiocyanate the interaction of thiocyanatopentaamminechromium(III) ion with Ag(I) and Hg(II) ions respectively now has been treated as satisfactorily as the cobalt analog

The aquation of thiocyanatopentaamminechromium(III) ion proceeds slowly at room temperature and has been found to follow a first order rate law[13] at 25°C The half life $t_{0.5}$ is calculated to be 1830 hr

Interaction of the thiocyanatopentaamminechromium(III) cation with Ag(I) or Hg(II) ions would be expected to increase the rate of aquation and this is found to be the case Figures 2 and 3 give the absorption curves of the thiocyanatopentaamminechromium cation alone and in equimolar mixture with Ag(I) and Hg(II) respectively as a function of time Under the conditions specified in Figs 2 and 3 the aquation of the interaction cation follows a first order rate plot with $t_{0.5}$ = 370 hr with silver(I) ion and $t_{0.5}$ = 1 3 hr with mercury(II) ion

The effect of ionic strength upon these cation cation interactions has been studied in some detail by the method of continuous variations

[11] R N Choudhury and C F Bonilla thesis submitted by R N Choudhury n partial fulfillment of the requirements for the degree of Master of Science Columbia University May 1 1952

[12] W C Waggener *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 7

[13] A W Adamson and R G W lkins *Exchange and Aquation Studies With Thiocyanate Complexes* Technical Report Office of Naval Research Contract N6onr 23809 Department of Chemistry University of Southern California Nov 1953

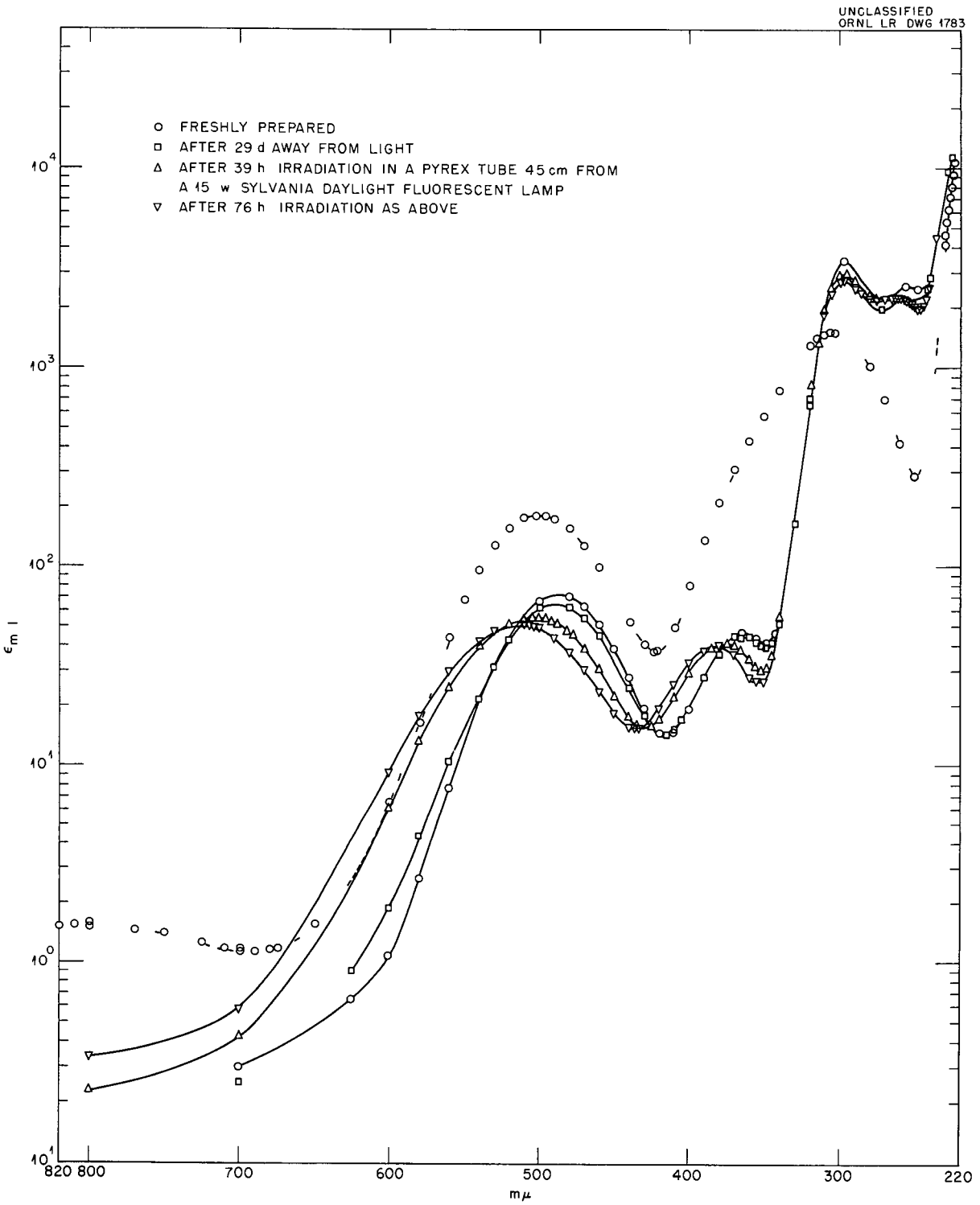

Fig 1 The Effect of Light and Time upon the Absorption of – – – 0 001 M $[Co(NH_3)_5NCS](NO_3)_2$ (no significant effect observed) ——— 0 001 M $[Cr(NH_3)_5NCS](NO_3)_2$ in aqueous 10^{-2} to 10^{-3} M $HClO_4$ as solvent at 24°C

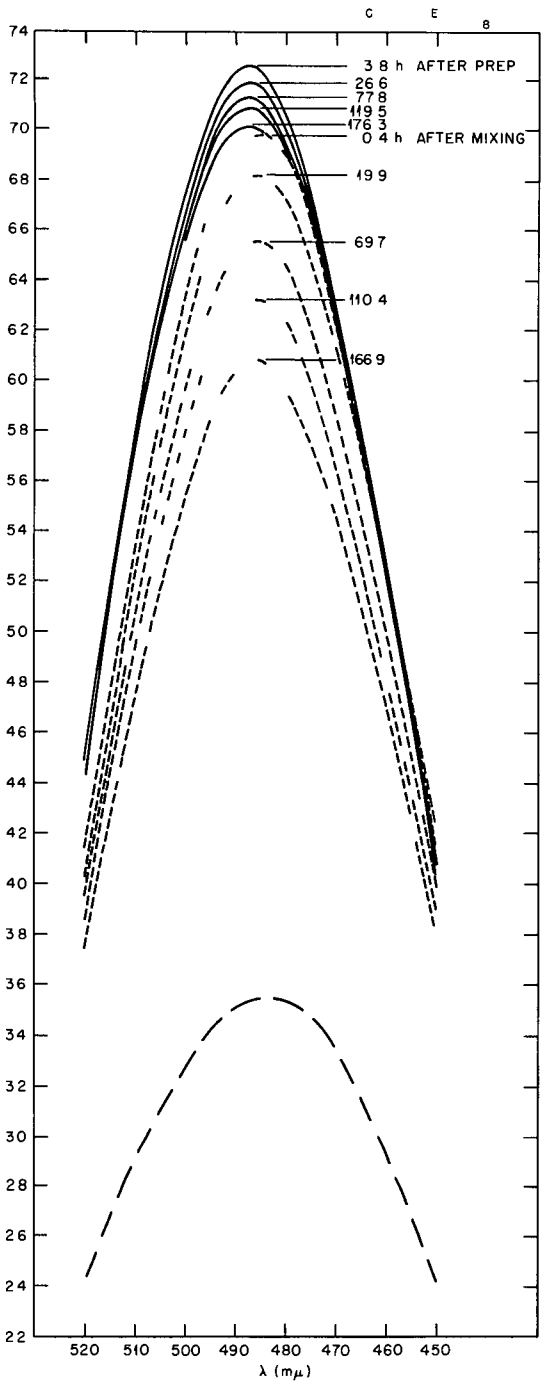

Fig 2 The Effect of $AgNO_3$ upon the Absorption (520 to 450 mμ) of $[Cr(NH_3)_5NCS](NO_3)_2$ as a Function of Time at 24°C ——— 0 001 M $[Cr(NH_3)_5NCS](NO_3)_2$ in 10^{-4} M $HClO_4$ – – – equimolar (0 001 M) mixture of $[Cr(NH_3)_5NCS](NO_3)_2$ and $AgNO_3$ in 10^{-4} M $HClO_4$ — — 0 001 M $[Cr(NH_3)_5H_2O](NO_3)_3$ in 10^{-4} M $HClO_4$

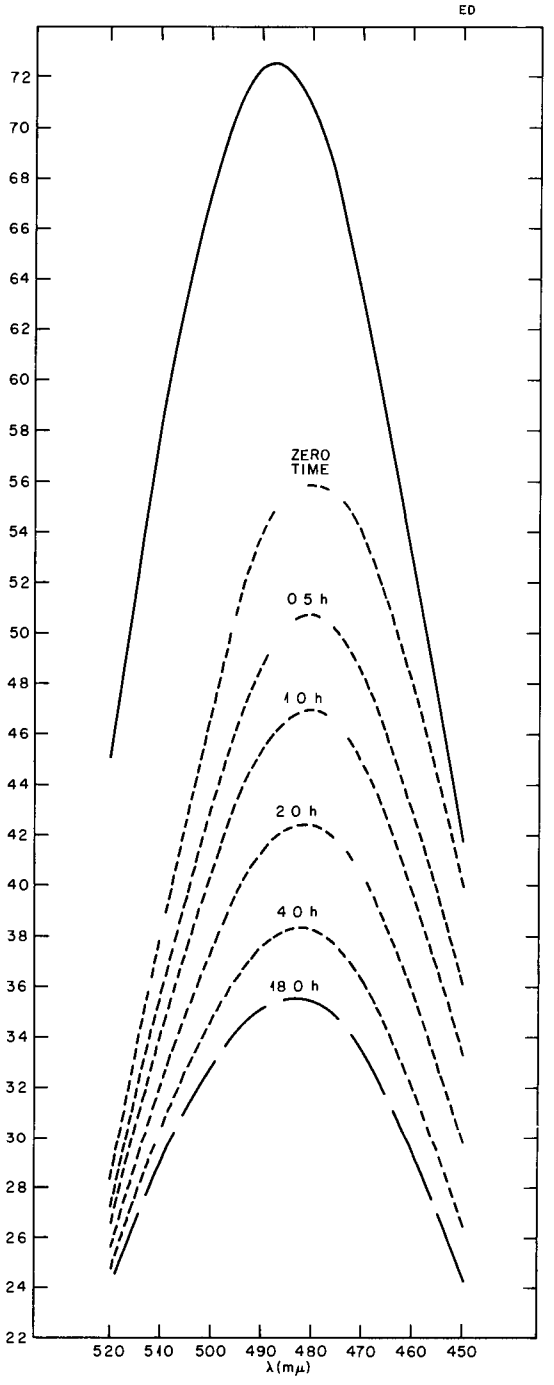

Fig 3 The Effect of $Hg(NO_3)_2$ upon the Absorption of $[Cr(NH_3)_5NCS](NO_3)_2$ as a Function of Time at 24°C ——— 0 001 M $[Cr(NH_3)_5NCS](NO_3)_2$ in 10^{-4} M $HClO_4$ – – – equimolar (0 001 M) mixture of $[Cr(NH_3)_5NCS](NO_3)_2$ and $Hg(NO_3)_2$ in $HClO_4$ pH = 1 62 —— —— 0 001 M $[Cr(NH_3)_5H_2O](NO_3)_3$ in 10^{-4} M $HClO_4$

using spectrophotometric measurements Results from analysis of these data agree with predictions based upon the Debye Huckel equation At ionic strengths of 0 1–0 2 and less the cation cation interaction increases with increasing μ Likewise the hydrolysis of the Hg(II) cation should be repressed

In the previous report it was pointed out that the interaction of thiocyanatopentaamminecobalt(III) ion and Hg(II) is acid dependent the interaction ratio Co Hg varying from 1 1 to 2 0 in 0 001 to 0 1 M $HClO_4$ Figure 4 illustrates the ionic strength dependence of this system at a constant pH as measured with a glass electrode The analogous thiocyanatopentaamminechromium(III)–mercury(II) system also was found to show a similar acid and ionic strength behavior though less pronounced because of the weaker cation cation interaction

The thiocyanatopentaamminecobalt(III)–silver(I) system has been studied at several ionic strengths and concentrations The predominant interaction species appears to have a mol ratio of 1 1 (NCS Ag) though there is good evidence for the

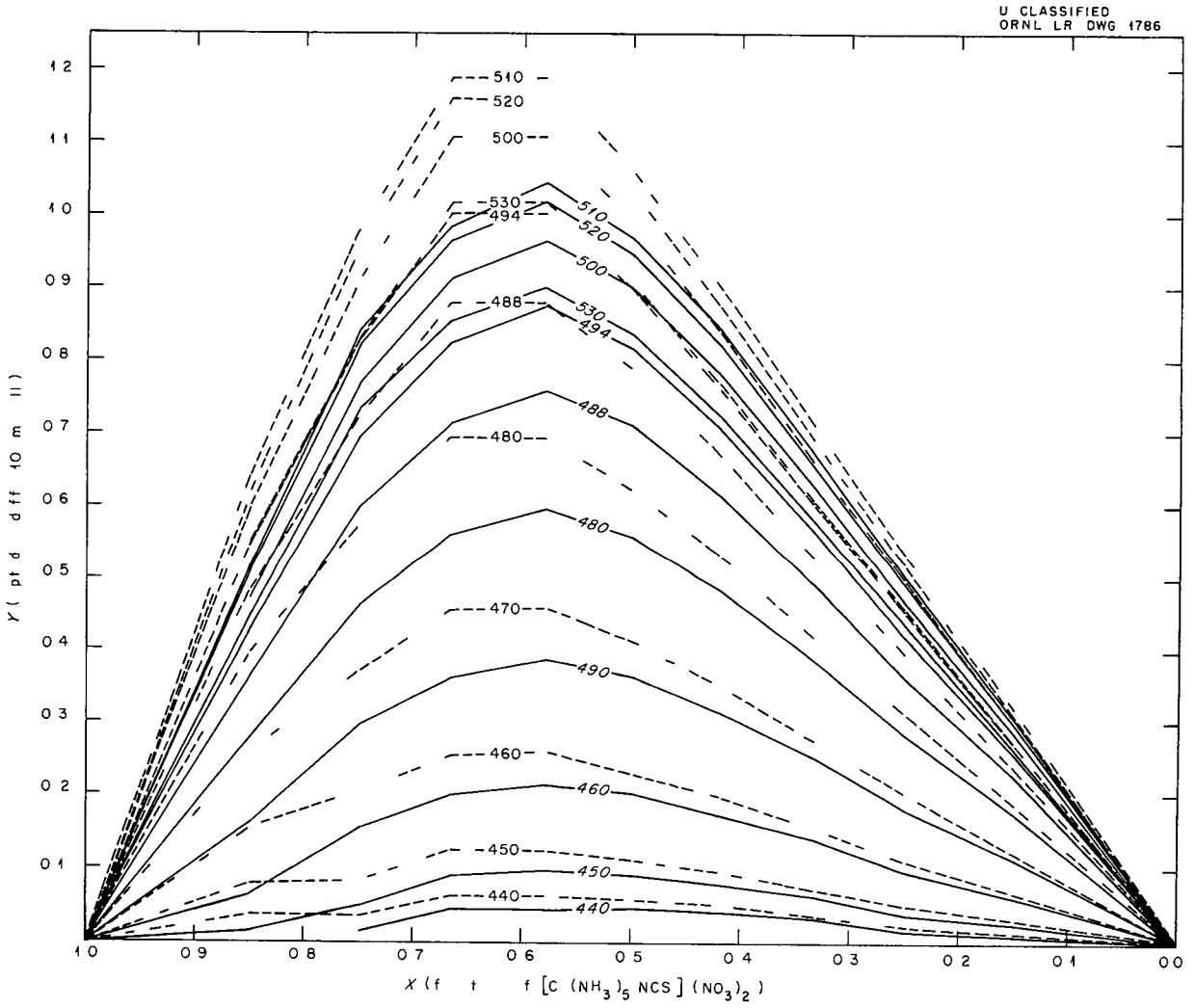

Fig 4 Ionic Strength Effect in Continuous Variations Experiments with the 0 002 M System $[Co(NH_3)_5NCS](NO_3)_2$–$Hg(NO_3)_2$ in Aqueous $HClO_4$ pH = 2 10 at 24°C ——— μ = 0 014 – – – μ = 0 104 Points are from data at ten wavelengths between 440 and 530 mμ

existence in addition of a 2 1 complex This system is independent of pH in the acid range as would be expected The effect of ionic strength is pronounced however and an increase in μ from 0 007 to 0 1 increases the interaction by a factor of 1 7

CHEMISTRY OF CORROSION

Studies on Inhibitor Action

G H Cartledge

During the past half year work on the studies on inhibitor action has involved three phases (1) continued observation of certain specimens that have been under surveillance for extended periods (2) further work on osmium(VIII) oxide and (3) a comparative study of technetium and osmium in the development of a rational distinction between passivity and inhibition

Phase 1 The carbon steel (SAE 1010) specimens referred to in the last report[14] have remained in tubes at room temperature with access to air since January 1953 There is still no evidence of corrosion and the beta activities have remained nearly constant These samples were inhibited initially by 50 ppm of technetium in distilled water one solution containing 10 ppm of chloride ion as potassium chloride Likewise the inhibition by 0 01 *f* sodium tungstate has been maintained for a total of 13 months This test included 708 hr at 100°C during the first 15 weeks and has continued at room temperature subsequently All the experiments with both pertechnetate and tungstate indicated that rusting of the specimens at 100°C will be apparent within 1 hr if failure is to occur

Tests to locate the minimum concentration of the pertechnetate ion required for inhibition under the conditions of these experiments have now extended over a period of eight months In one test of four weeks a specimen exposed to 5 ppm of technetium showed no measurable change in weight or other evidence of attack whereas a similar specimen exposed to 3 ppm lost 8 1 mg from an initial weight of 0 5650 g The corroded specimen gave a beta count indicating the precipitation of $4\ 5 \times 10^{-3}$ mg of technetium (presumably TcO_2) on the metal the inhibited specimen showed the precipitation of only $2\ 6 \times 10^{-4}$ mg In another test a 5 ppm solution has now completely inhibited corrosion for a total of eight months part of the test being at 100°C and part at room temperature

Phase 2 The behavior of osmium(VIII) oxide OsO_4 in corrosion has been further studied at room temperature It has been found that under these conditions a visible film presumably of mixed Fe_2O_3 and OsO_2 formed after several days but no continuing corrosion was detectable The experiments were conducted at various concentrations of OsO_4 in test tubes exposed to the atmosphere through the short condensers previously described Protection was afforded down to 4×10^{-3} *f* OsO_4 but corrosion resulted at 2×10^{-3} *f* As previously reported the osmium treatment gives a labile film which is easily disturbed at 100°C and therefore pitting attack follows This attack is very rapid when electrolytes are present in the solution It was observed that the osmium film functions well as a conducting cathode for corrosion by local currents So long as the film remained intact at room temperature the electrode potential was ennobled so that no copper deposited upon addition of cupric sulfate If the film ruptured however and pits were allowed to develop the potential diminished and then insertion of the specimen into a suitably adjusted cupric sulfate solution caused the osmium film to become plated with copper while the pits remained bright When a sample that had been pitted in an osmium solution was transferred to a pertechnetate solution corrosion was stopped and autoradiograms showed that technetium had deposited in the pits that is in the previously anodic areas Such pitted specimens have been inhibited in the technetium solution for months without further attack

The osmium work may be summarized as follows Aqueous osmium(VIII) oxide passivates and ennobles carbon steel upon immersion for a few seconds Visible film formation results after a period of days at 23°C and after a period of hours at 100°C The film is labile at the high temperature and when ruptured permits pitting corrosion The volatility of OsO_4 from the solution causes ultimate failure in systems open to the air at 100°C

Phase 3 Additional studies of the behavior of the pertechnetate ion have shown that a limiting minimum concentration is necessary for inhibition

[14] G H Cartledge *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 14

even when the specimen has been inhibited for a time by a high concentration It was found for example that dilution of the solution in stages from the 30 to 60 ppm range led to corrosion when a concentration of 3 to 4 ppm of technetium was reached This observation demonstrated that the inhibition results from a dynamic reversible condition in the system which requires a certain concentration of dissolved pertechnetate ion for its maintenance The previous history such as film formation at the higher initial concentration was ineffectual in maintaining protection in the diluted solution

Some experiments were made for determining whether the corrosion of cast iron may also be inhibited by the pertechnetate ion It was found that emeried specimens could be protected but that higher concentrations were required than were necessary for carbon steel Thus corrosion resulted when the specimen was kept in 25 ppm of technetium in distilled water at 100°C during the daytime and at 23°C during the night At 50 ppm much technetium dioxide was precipitated on the surface but rusting did not occur Pretreatment of a specimen in 10^{-3} *f* potassium chromate decreased by a considerable factor the amount of technetium deposited

An important distinction between the respective actions of osmium(VIII) oxide and the pertechnetate ion has been observed which it is believed may be developed to give a basis for a rational differentiation between passivation and inhibition by inorganic ions or molecules As previously reported it is possible to obtain inhibition with the pertechnetate ion under conditions such that only an extremely small amount of technetium is reduced and precipitated on the metal It was found to be impossible however to produce passivity as ordinarily defined in that copper always precipitated when a specimen previously inhibited in a pertechnetate solution was transferred to a cupric sulfate solution It was found that inhibiting concentrations of potassium pertechnetate did not greatly ennoble the potential of a specimen of either carbon steel or stainless steel

On the contrary a 1% solution of osmium(VIII) oxide in water was found to passivate iron or steel as readily as concentrated nitric acid does While no visible film resulted in the few seconds during which the specimen was exposed to the osmium solution such a film did form but slowly It was also observed that the electrode potential was ennobled by the osmium solution hence no copper precipitated It is therefore not an unlikely assumption that the ennobling and passivity arise from a film of reaction products containing iron osmium and oxygen and that the unique character of the film which makes it passivating is that it contains an electron deficient configuration of atoms The lability of the passive state would then arise from the fact that a geometrically possible array of interfacial atoms initially results from the adsorption which must be disturbed however before a thermodynamically stable film substance can result It may be significant to consider that reaction between an iron atom and an adsorbed TcO_4^- would lead to Fe(III) and Tc(IV) by a three electron transfer thus producing stable valence states for both elements In an osmium solution on the contrary the corresponding result would be Fe(III) and Os(V) which is electron deficient in the sense that Os(IV) rather than Os(V) is the stable reduced form in this case The breakdown of such a labile configuration would involve the moving around of both atoms and electrons in accordance with the well known transmission of activity on passive surfaces

Studies on Electrode Potentials

G H Cartledge

In order to gain a clearer understanding of the nature and fate of the films on stainless steel when they are placed in hot dilute sulfuric acid electrode potential measurements have been made on specimens that had been oxidized in air at various temperatures The experiments are a continuation of work previously reported [15] and the measurements have been made in the manner there indicated The general procedure has been to prepare specimens of type 347 stainless steel having areas between 0 5 and 12 sq cm with integral connecting leads and having either a mill finish or an emeried (2/0) or electropolished surface The electrodes were heated in a muffle furnace at various temperatures between 300 and 450°C and for times ranging from 15 min to 2 days These oxidations produced films of pure golden color on the electropolished specimens rust brown and dull on the mill finish and blue and brass

[15] G H Cartledge a d R P Yaffe *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 11

colored on the emeried surfaces After oxidation the leads to the electrodes were lacquered with G E Glyptal clear varnish No 1202 and left in an oven at 110°C overnight or until used

The electrolytes used have been sulfuric acid between 0 01 and 0 5 *N* or sulfuric acid–sodium sulfate mixtures of 0 05 total sulfate formality and having pH s between 1 25 and 2 05 Experiments have been made from 40 to 90°C In all cases the solution has been stirred in contact with air With the established conditions the 600 rpm glass stirrer just failed to carry bubbles into the solution

For comparative purposes a smooth platinum electrode was usually measured simultaneously with the stainless steel Both were measured against a silver–silver sulfate half cell which was connected through a bridge containing 0 1 *N* sulfuric acid The silver half cell was compared with a saturated calomel half cell momentarily dipped into the flask solution at the end of an experiment Since the silver reference electrode was always at 23°C the measurements included an unknown potential due to the temperature gradient in the bridge There is reason to believe that this potential is not large and that it is approximately compensated for by the calibration procedure employed It certainly is unimportant in view of the large changes of potential involved in the experiments

At the beginning of an experiment the platinum wire alone was inserted the temperature adjusted (±0 5°C) and the observations continued until the platinum potential stabilized in the neighborhood of 550 to 600 mv positive to the S C E This pseudooxygen potential changed over to a rapidly reversible ferrous ferric potential later on after significant amounts of steel had gone into solution

After the platinum potential was stabilized the prepared stainless steel electrode was inserted and measurements of both electrodes were made alternately by use of a Flexopulse switch set to record the platinum potential for 0 5 min and the steel potential for 1 5 min At critical times manual switching replaced the Flexopulse as desired When the general features of the experiment had become clear determinations were made on the total iron in solution at various times Ten milliliter aliquots were withdrawn and 10 ml of preheated electrolyte was immediately added to maintain an essentially constant volume of 150 ml The aliquots were analyzed spectrophotometrically with thioglycolic acid[16] in a 10 cm Beckman cell In calculating the results allowance was made for the iron content of all aliquots previously withdrawn The solution resulting from one typical experiment was analyzed for Fe Cr and Ni (made by J H Edgerton s Analytical Group) The Fe Cr ratio found was 4 5 corresponding to about 3 9 for the original metal Considering the very small amounts of material involved (Cr = 1 3 ppm) the results probably indicate no selective dissolution of the different components under the conditions of the experiments

Although the different surface treatments and other variables mentioned affect the results in detail the general behavior of the potentials may be described for a particular set of conditions by reference to Fig 5 The experiment illustrated here was done in a 0 05 *f* sulfate mixture at pH 1 46 at 85°C and the steel electrode was an emery polished coil of 11 2 sq cm total area It had been heated for 2 0 hr at 445°C and was yellow brass in color In general the potential time curves are made up of several distinct sections as follows

1 One was a noble section with a maximum potential in the neighborhood of the platinum potential This potential more or less rapidly debases while the platinum potential remains nearly constant

2 There was a sudden drop to a potential of approximately –400 mv vs the S C E Usually this drop has a brief halt or an actual inflection in the vicinity of –25 mv During this extremely rapid debasing the last of the brown film may be seen to disappear Simultaneously the platinum potential drops abruptly

3 The steel potential reaches a minimum of –400 mv usually and within a few minutes ennobles to about –325 mv at which point it may become constant or nearly so depending upon the particular conditions During these few minutes metal passes into solution very rapidly the potential being so base that the iron and chromium occur as Fe^{++} and Cr^{+++} and hydrogen is also formed The metal first appearing more or less like the unoxidized original specimen darkens to a sooty black as this dissolution occurs

[16] H W Swank and M G Mellon *Ind Eng Chem Anal Ed* 10 7 (1938)

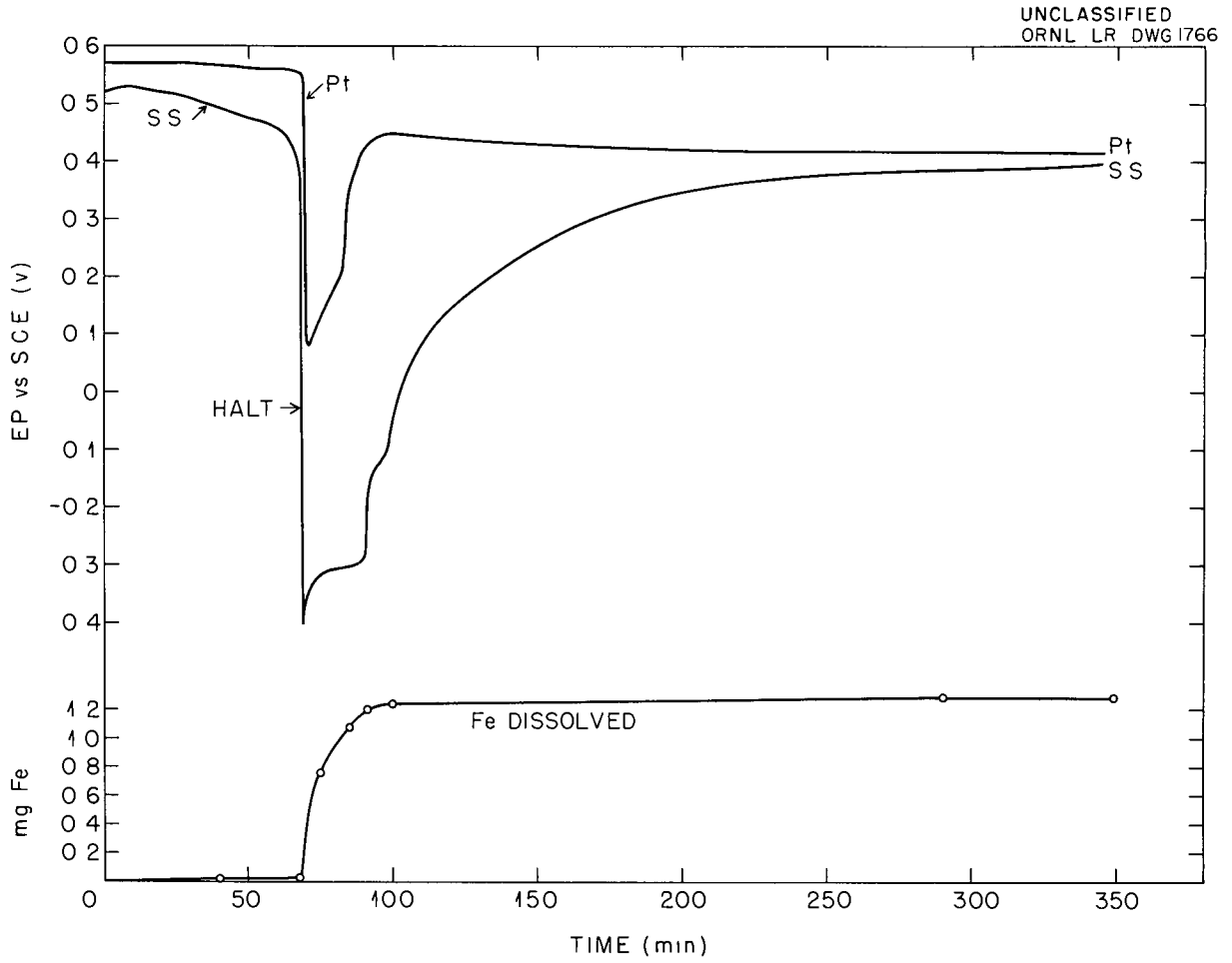

Fig 5 Electrode Potential–Time Curves for Platinum and Oxidized Stainless Steel Electrodes in a Sulfate Mixture pH 1 46 at 85°C

4 If conditions are such that the potential slowly ennobles after reaching –325 mv then another sudden change occurs beginning at about –300 mv and leading to another inflection point at about –125 to –150 mv

5 Continued ennobling follows often with a clearly noticeable minor inflection corresponding to the one observed during the debasing stage at approximately –25 mv Beyond this point the potential ennobles slowly until it again approaches the platinum potential at a value which depends upon the Fe^{+++} Fe^{++} ratio

The general character of the potential time curve is strikingly similar to the oscillograms reported by Bonhoeffer and Vetter[17] for the passivation and activation of mild steel in concentrated nitric acid Whereas their cycle of changes was completed in 0 5 sec however the present experiments extend over a period of hours so it is possible to follow and analyze the changes more readily

The experiment demonstrates that the oxide coating that is stable in air is not stable in the acid and gradually transforms to a different surface state which is subject to extremely slow corrosion in the acid environment Between these extreme conditions however the curve discloses the existence of intermediate states and processes characterized by rather definite potentials Figure 5

[17] K F Bo hoeffer and K J Vetter *Z phys k Chem* 196 127 (1950)

clearly shows that dissolution of the metal is very slow so long as the potential is more noble than −100 mv vs the S C E whether the specimen is on the debasing or the ennobling portion of the curve This result confirms and elaborates the observation recently reported by Edeleanu[18] that the dissolution of an 18 8 stainless steel at 25°C in 20% sulfuric acid decreases to extremely low rates when the metal is maintained at potentials between +900 and −100 mv vs the S C E At the nobler potentials dissolution leads to anodic formation of Cr^{6+} rather than to Cr^{+++} which forms at the lower potentials

In the present work it has been observed that a carefully electropolished and oxidized specimen may pass from the air stable state to the acid stable state without going into the region of base potentials It has also been found possible to maintain the steel potential above the corroding level by shorting it to a platinum electrode throughout the experiment In both cases the total dissolution was far less than in those cases in which a base potential was reached Further details concerning the different stages in the potential time diagram are being currently investigated

Chemistry of Amalgams

W E Clark

In the last report[19] it was pointed out that the half order kinetics commonly reported for the decomposition of alkali amalgams is at best an approximation and that in the case of stirred amalgams the reaction rate appears to be essentially independent of the amalgam concentration Evaluation of data obtained since the last report plus data from other sources [20–22] indicates that the decomposition rate is probably controlled by the activity of the alkali metal in the surface phase of the amalgam

Since the potential of the amalgam is the thermodynamic equilibrium value within the accuracy of measurement the evolution of hydrogen can hardly be the sole rate determining step If such were the case an appreciable polarization of the amalgam electrode should be observed Furthermore the concentration of alkali in the aqueous phase has been found to have no measurable effect on the decomposition rate [20 21] in contradiction of the requirements for hydrogen evolution control [23]

From the data on the interfacial tension of amalgams vs water it is possible to calculate the surface activity of the alkali metal by means of the Gibbs adsorption equation

$$\Gamma = -\frac{a}{RT}\frac{d\sigma}{da}$$

in which Γ is the excess of alkali metal in the surface phase over that in the bulk of the amalgam a is the activity of alkali in the bulk of the amalgam and σ is the interfacial tension of the amalgam vs water

Available data on the interfacial tension of amalgam vs water systems are insufficient for a quantitative test of the theory but preliminary calculations based on the data of Googin[20] indicate the probability of the reaction being first order with respect to the surface concentration of the alkali metal In Fig 6 Googin s data are compared with those of Thomason and Chilton[24] for the system lithium amalgam vs LiCl in propylene diamine As can be seen the data are very scant and considerably more data must be obtained before a definitive test of the theory can be made

Qualitatively the theory explains the effects observed Since the concentration of aqueous alkali has a negligible effect on the surface tension of the amalgam phase [25] the decomposition rate would be expected to be independent of aqueous concentration Over a fairly wide concentration range the surface phase is doubtlessly saturated with alkali metal resulting in a constant decomposition rate which would decrease somewhat at low concentrations as the surface phase became unsaturated A more detailed discussion of the theory has been given elsewhere

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[18] C Edeleanu *Nature* 173 739 (1954)

[19] W E Clark *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 17

[20] J M Googin private communication

[21] N A Krohn private communication

[22] S I Sklyarenko and B A Sakaharov *Zhur Obshchei Khim* 17 1385 (1947) (Engl sh translat on available in ORNL library)

[23] O L Kaptsan and Z A Iofa *Zhur Fiz Khim* 26 201 (1952) *ibid* 26 193 (1952) (English translation available in ORNL library)

[24] Reported by A C Jealous *Unit Operations Status Report for Week Ending Jan 23 1954* ORNL CF 54 1 153 pp 7 9 10 (Jan 26 1954)

[25] R J Johnsto and A R Ubbelohde *Proc Roy Soc (London)* A206 275 (1951)

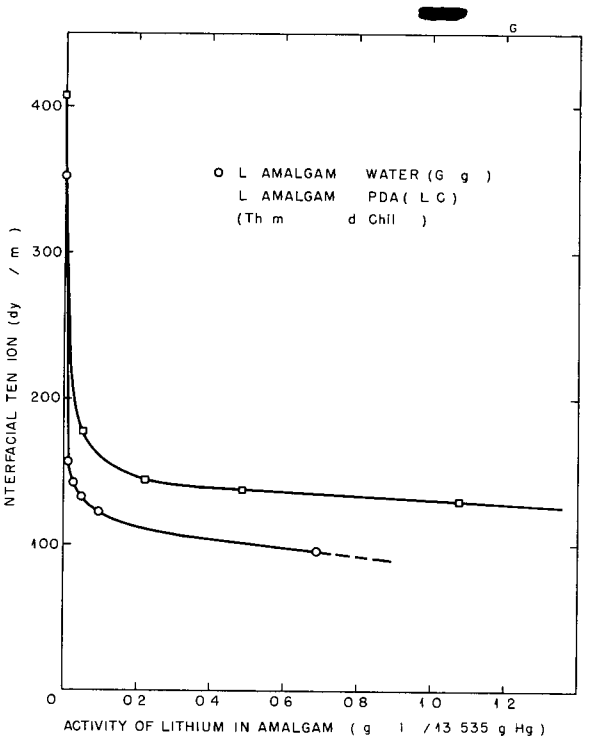

Fig 6 Interfacial Tension of Lithium Amalgam

More data on the lithium system are now being obtained and investigations have been begun on the potassium and barium systems

CHEMISTRY OF FUSED SALTS

A S Dworkin I S Yaffe
F J Miller[26] E R Van Artsdalen

Electrical Conductivity and Density

Determination of conductance and density has been completed for the molten system potassium chloride–sodium chloride The experimental tech niques were identical with those described in the last semiannual report [27] The density of either pure salt or of any mixture can be expressed as a linear function of temperature but the specific conductance follows a quadratic function of temper ature Conductance and density relationships for this system are shown in Table 3 The molar volume isotherms vs composition show very slight positive deviations from strict additivity with the maximum deviation of about 0 5% at 50 mole %

[26] A alyt cal Chemistry D vision

[27] A S Dwork n *et al* *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 21

TABLE 3 DENSITY AND CONDUCTANCE OF THE MOLTEN SYSTEM KCl NaCl

KCl (mole %)	Applicable Tempe ature Range (°C)	Density $\rho = a - bt$ (g/cc)		Spec fic Conductance $\kappa = a + bt + ct^2$ (mho cm^{-1})			Equivalent Conductance $\log \Lambda = A - B(1000/T) + C \log (1000/T)$ (mho sq cm equiv^{-1})		
		a	$b(\times 10^3)$	a	$b(\times 10^3)$	$c(\times 10^6)$	A	B	C
100 0_0	800 to 940	1 9767	0 5831	−1 749	7 383	−3 000	3 3420	1 3530	1 2434
79 6_0	740 to 940	1 9794 (est mated)	0 5818	−2 058	8 429	−3 665	3 5204	1 5307	1 6956
59 0_0	700 to 920	1 9774	0 5750	−2 854	10 75_0	−5 018	3 9746	1 9721	2 6732
48 7_7	680 to 920	1 9764	0 5680	−1 291	7 179	−2 828	2 9497	0 9361	0 5304
34 8_5	700 to 960	1 9815	0 5574	−1 611	8 194	−3 267	3 0836	1 0565	0 7625
27 0_6	720 to 940	1 9851	0 5595	−2 549	10 770	−4 825	3 6187	1 5828	1 9082
15 2_3	780 to 960	1 9891	0 5542	−1 373	8 458	−3 383	2 9911	0 9317	0 6002
0 00	800 to 1040	1 9911	0 5430	−0 169_7	6 259	−1 953	2 4252	0 3369	−0 5911

t = degrees Cels us T = degrees Kelv n

KCl Representative isotherms are given in Fig 7 The reliability and reproducibility of measurements of specific conductance κ for molten NaCl are shown by the data plotted in Fig 8 Literature values[28–32] are shown in this figure for comparison It is observed that the more recent work is in good agreement with ORNL data

It was found that the equivalent conductance Λ of this system can be expressed in the form

$$(1) \quad \log \Lambda = A + B \frac{1000}{T} + C \log \frac{1000}{T}$$

[28] J D Edwards C S Taylor A S Russell and L F Maranville *J Electrochem Soc* 99 530 (1952)

[29] E K Lee and E P Pearson *Trans Electrochem Soc* 88 171 (1945)

[30] R W Huber E V Potter and H W St Clair *U S Bur Mines Rept Invest* 4858 (March 1952)

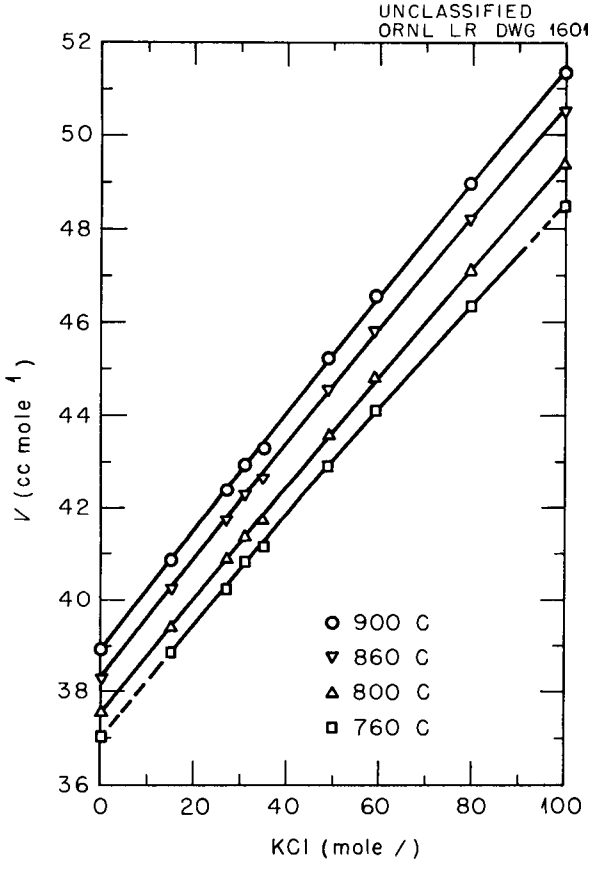

Fig 7 Molar Volume of the Molten System KCl NaCl

in which T is expressed in degrees absolute A is a constant of integration B is the intercept and C is 2302 6 times the slope of the straight line resulting from graphical differentiation of log Λ vs $1000/T$ Data are presented in Table 3 and equivalent conductance isotherms vs composition are plotted in Fig 9 It appears likely that the form of Eq 1 is general in nature and applicable to many molten salt systems This point is being investigated with other systems However this equation cannot be applied to temperatures lower than approximately 10 or 20 deg above the freezing point of the system because conductivity drops very rapidly close to the melting point

The general conclusions concerning the reasons for a minimum in the equivalent conductance isotherms described in the last semiannual report appear to be applicable to the KCl NaCl molten system In this case the minimum is less pronounced than that observed with the system KCl LiCl because of the smaller difference in equivalent conductance of the pure salts This in turn is closely correlated with the fact that the ionic radius of the Na^+ ion is appreciably greater than that of the Li^+ ion

If electrolytic conduction is treated as a rate process equivalent conductance may be expressed in the Arrhenius form

$$(2) \qquad \Lambda = Ae^{-\Delta H^{\ddagger}/RT}$$

[31] W Biltz and W Klemm *Z anorg u allgem Chem* 152 267 (1926)

[32] E Ryschkewitsch *Z Electrochem* 39 531 (1933)

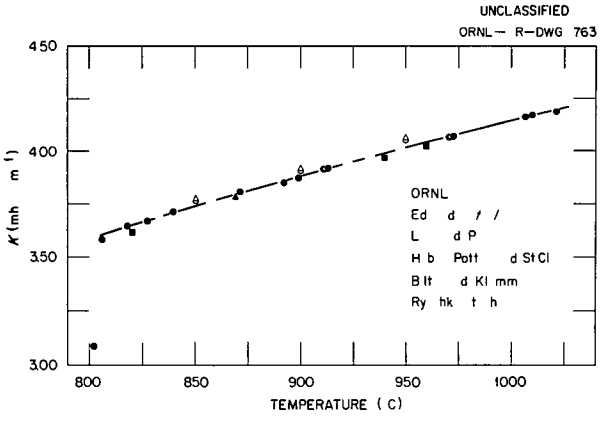

Fig 8 Specific Conductance of Molten NaCl

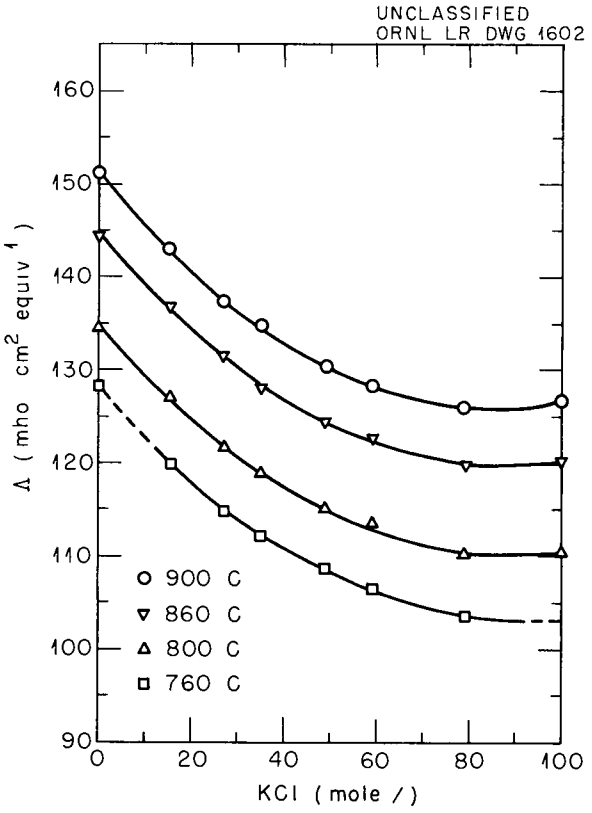

Fig 9 Equivalent Conductance Isotherms for the Molten System KCl NaCl

where A is a constant T is expressed in degrees Kelvin R is the gas constant and $\Delta H^{\ddagger}$ the heat of activation for conduction can be evaluated from a plot of log Λ vs $1/T$ The heats of activation for conduction by the pure salts KCl and LiCl as well as their mixtures have been calculated over a range of temperatures The heat of activation does not remain constant with changing temperature but in general shows a small approximately linear decrease with rising temperature The rate of this change is dependent upon composition The decrease of heat of activation with rising temperature can be explained qualitatively as resulting from expansion of the liquid Thus as the temperature rises the ions acquire greater kinetic energy and move somewhat farther apart thereby making migration easier However the heat of activation for conduction by pure sodium chloride appears to be anomolous for it actually rises with increasing temperature In general the heat of activation tends to be a maximum in those compositions which show minimum equivalent conductance

Absolute reaction rate theory has been applied to electrolytic conduction in aqueous solution by Glasstone Laidler and Eyring [33] and similar methods have been employed here to derive an expression for conduction by fused salts It is found that equivalent conductance may be expressed by the equation

(3)

$$\Lambda = 5\ 19 \times 10^{18}(D + 2)\, d^2 e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H^{\ddagger}/RT}$$

where D is the dielectric constant of the fused salt d is half the distance the conducting ion must migrate in going from one equilibrium position to the next nearest one and $\Delta S^{\ddagger}$ is the entropy of activation The relationship between Eqs 2 and 3 is obvious By using the experimentally determined $\Delta H^{\ddagger}$ values $\Delta S^{\ddagger}$ has been calculated for the KCl NaCl system at 850°C d was estimated for the pure salts from crystallographic data and known expansion up to 850°C and it was assumed that there was no change in coordination number The value of d for mixtures was assumed to be a linear function of composition between the pure salts since molar volumes for the mixture are practically additive No measurements of the dielectric constant for these fused salts are available so D has been assumed to be 3 which is at least a reasonable value in view of the high conductivity of these salts Absolute values of $\Delta S^{\ddagger}$ calculated in this way may have appreciable uncertainty but trends should be discernible The values for the system KCl NaCl are plotted in Fig 10 A smooth progression of values is noted with a maximum negative entropy of activation in the region of minimum equivalent conductance Thus both heat of activation and entropy of activation are working in the same direction for this system

It is regretted that an error was made in the calculation of $\Delta S^{\ddagger}$ for the system KCl LiCl given in the last report The data have been recalculated and corrected values of $\Delta S^{\ddagger}$ for this system are shown in Fig 11 No explanation is offered for quantitative differences between the two systems at present but it is hoped that data to be obtained with other systems will be useful in such interpretations

[33] S Glasstone K J Laidler and H Eyring *The Theory of Rate Processes* p 552 ff McGraw Hill New York 1941

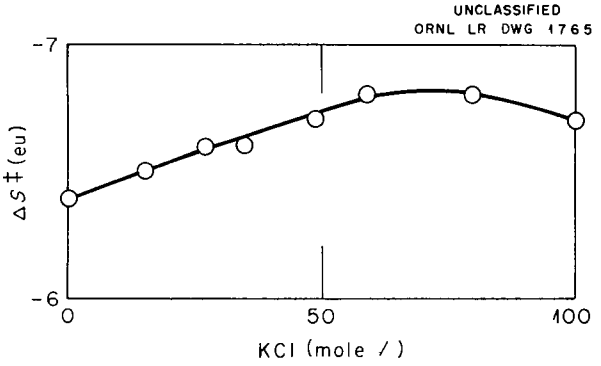

Fig 10 Entropy of Activation for Electrical Conductance in the Molten System KCl NaCl

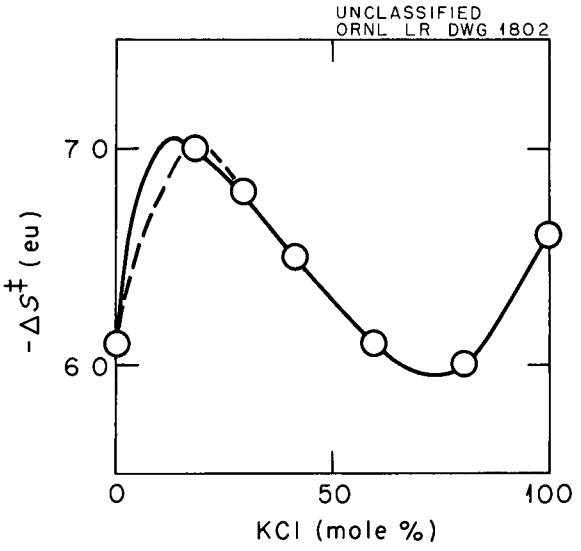

Fig 11 Entropy of Activation for Electrical Conductance in the Molten System KCl LiCl

Emf Measurements in Fused Salts

Transport numbers for the system $AgNO_3$ $NaNO_3$ have been measured by Aziz and Wetmore [34] who used the Hittorf method The emf of a concentration cell with transference for this system in which silver electrodes are used can be expressed by the equation

$$(4) \quad E = t_{Ag} \frac{RT}{\mathfrak{F}} \ln \frac{{}^{3}X_{N\ NO_3}\ {}^{2}X_{AgNO_3}}{{}^{2}X_{N\ NO_3}\ {}^{3}X_{AgNO_3}}$$

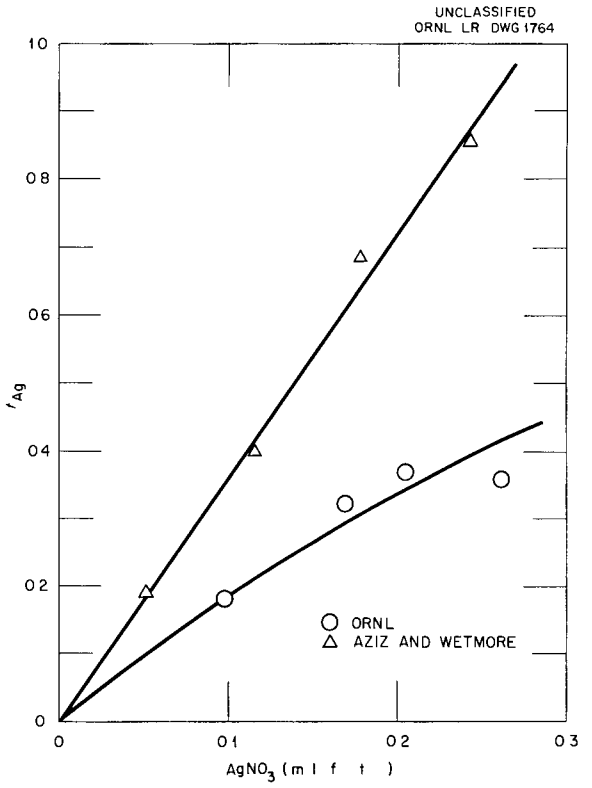

Fig 12 Apparent Transport Number of Ag^+ in Molten $AgNO_3$ $NaNO_3$

as described previously [35] with the assumption that the activity coefficients are unity and that the cations are the sole conducting species Transport numbers have been computed for Ag^+ ion from measured emf values by use of Eq 4 and the results are plotted in Fig 12 and may be compared with the values of Aziz and Wetmore which are also shown in this figure It is evident that both sets of data substantiate the concept that Ag^+ is a better conductor than Na^+ in these melts The quantitative difference between the two results may be indicative of deviations from ideal behavior and/or some conduction by anions Further studies to elucidate these questions are planned

[34] P M Aziz and F E W Wetmore *Can J Chem* 30 779 (1952)

[35] A S Dworkin *et al* *Chem Semiann Prog Rep* Dec 20 1953 ORNL 1674 p 25

HEAT OF COMBUSTION OF BORON CARBIDE

A S Dworkin E R Van Artsdalen

The heat of combustion calorimeter described previously [36] has been recalibrated and several preliminary combustions of boron carbide B_4C have been run Boron carbide burns incompletely according to the equation

$$B_4C + 4O_2 = 2B_2O_3 + CO_2 \quad (5)$$

The amount of B_4C burned must be determined by analysis of the products of combustion of each experiment The determination of B_2O_3 is by titration as described previously [36] and CO_2 is measured by absorption in Ascarite A further check of the material balance is obtained from the weight of unburned residue Preliminary results indicate that it is possible to carry out this combustion satisfactorily in the absence of any promoter and that the heat of combustion of boron carbide is in the range of 680 kcal/mole The heat of formation of B_4C will be calculated from final combustion data

MISCIBILITY OF LIQUID METALS AND SALTS

M A Bredig H R Bronstein
J W Johnson W T Smith Jr [37]

Solubility studies were extended to the following five systems NaF Na KCl K CsF Cs CsCl Cs and CsI Cs Although the data are incomplete the results obtained confirm relationships between the solubility and properties of the components discussed in the last report [38] especially the absolute and relative sizes and the polarizabilities of the cations and anions The present data are concerned almost exclusively with the solubility of salts especially the solid salts in the liquid metals rather than with the solubility of the metals in the fused salts

Figures 13 and 14 give a summary of the data Figure 13 which refers to the fluoride systems of Na K and Cs demonstrates that the greater the atomic number or size of the M^+ cation common to the salt M^+X^- and the metal M^+e^- in each system the greater the solubility of the salt in the liquid metal This relationship is in marked contrast to the similarity of all sodium systems illustrated by a previously published diagram [39] It was previously pointed out[40] that the cation effect newly demonstrated by adding the CsF Cs system must be due to the decrease in the fluoride systems of the cohesive energies as reflected in the heats of vaporization and boiling points of both the metals and the salts (Table 4)

From the slopes of the straight lines in Fig 14 which is a plot of the logarithm of the solubility vs the reciprocal of the absolute temperature for all of the nine systems on which work has been in progress partial heats of solution at saturation of the solid salt in the liquid metal were calculated An examination of Table 4 in which some of these values are summarized will show the effect of the variation of the salt on salt solubility and its temperature dependence for each metal The difference between the heat of solution e g of the fluoride and the chloride in the liquid metal becomes more negative in going from the sodium to the cesium systems as does the difference in the heats of vaporization of the salts This behavior may be attributed to the larger polarizability of the cesium and potassium cations compared with that of the sodium Polarization of the cation by the comparatively small fluoride ion is larger than that by the chloride ion and energetically favors the formation not only of the gas molecules of the salts [41] but also of the liquid state and of a solution in a solvent such as the metal in which the salt may be thought of as being present as associated ion pairs or molecules

The increase in the heat of solution from the sodium–sodium chloride to the sodium–sodium iodide system which does not occur in the corresponding cesium systems may be connected with the increasing difficulty of substituting an anion of increasing size ($Cl^- < Br^- < I^-$) for an electron e^- in sodium metal Na^+e^- where the intercationic spaces are small In cesium metal these

[36] A S Dworkin D J Sasmor and E R Van Artsdalen *Chem Semiann Prog Rep June 20 1953* ORNL 1587 p 23

[37] Consultant from the University of Tennessee

[38] M A Bred g *et al Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 27 Part of the data i e those conce n ng the sod um–sod um hal de systems have been subm tted to the *J Am Chem Soc* opie of the manus r pt are a ilable to anyone interested

[39] M A Bredig *et al Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 Fig 21 p 28

[40] *Ibid* p 31

[41] Cf e g K Fajans *Chemical Forces and Optical Properties of Substances* Cornell Univers ty Press 1931 and *J Chem Phys* 9 378 (1941)

TABLE 4 SOLUBILITY AND HEAT OF SOLUTION OF SALT IN METAL AS A FUNCTION OF PROPERTIES OF COMPONENTS

Sy t m		P p t f				ΔH_v		ΔH	S l b l ty f	
		C t M^+		A X^-		H t f V p t (k l)		H t f S l t f S l d S lt M t l t S t t	S lt M t l (m l %)	
S lt	M t l	C y t l P l R d A b l ty		C y t l P l g R d A P w		S lt	M t l	k l	550°C	600 C
N F	N	0 98	1	1 33	2 7	53 3	23 1	+26 ± 2	(0 06)	(0 15)
KF	K	1 33	4	1 33	2 7	41 3	18 9	+19 5 ± 0 5	(1 8)	(3 7)
C F	C	1 65	14	1 33	2 7	34 3	16 3	+10 0 ± 0 5	26 5	37 0
N F	N	0 98	1	1 33	2 7	53 3	23 1	+26 ± 2	(0 06)	(0 15)
D ff	(N F N Cl)					+12 5		+ 6		
N Cl	N	0 98	1	1 81	1 4	40 8	23 1	+20 ± 3	0 15	0 33
N B	N	0 98	1	1 96	1 2	37 9	23 1	+24 ± 1	0 18	0 43
N I	N	0 98	1	2 20	1 0	38 2	23 1	+28 ± 2	0 18	0 46
KF	K	1 33	4	1 33	2 7	41 3	18 9	+19 5 ± 0 5	(1 8)	(3 7)
D ff	(KF KCl)					+ 2 5		− 1 5		
KCl	K	1 33	4	1 81	1 4	38 8	18 9	+21 0 ± 1	1 4	3 1
C F	C	1 65	14	1 33	2 7	34 3	16 3	+10 0 ± 0 5	26 5	38 0
D ff	(C F C Cl)					− 1 4		− 7 0		
C Cl	C	1 65	14	1 81	1 4	35 7	16 3	+17 0 ± 0 5	16 0	32 0
C I	C	1 65	14	2 20	1 0	35 9	16 3	+16 0 ± 0 5	19 0	35 0

V l p th by t p l t f m m m t th gh t mp t

spaces are larger and substitution for an electron is therefore less dependent on the size of the substituting anion

The data of Figs 13 and 14 are indicative though as yet too incomplete for final confirmation of the possibility mentioned in the previous report that equilibria between two liquid phases may not exist in the cesium fluoride–cesium system

One experiment with the lithium iodide–lithium metal system indicates very low solubility 0 7 mole % LiI at 760°C in lithium metal This is much lower than the solubility for the corre sponding sodium system and is in good agreement with predictions [40] On the other side of the equilibrium diagram the solubility of lithium in the molten salt at this same temperature was 30 mole %

[42] M A Bred g J W Johnson and W T Smith *Chem Quar Prog Rep Dec 31 1952* ORNL 1482 p 32 F g 9 p 33

STRUCTURE OF SOLID AND FUSED ALKALI HALIDES

M A Bredig P A Agron

In a previous report[42] it had been pointed out that unusually large volume increases on melting occur in several of the alkali halides and that at least some if not all of these cases may be interpreted as being connected with a structural change i e a decrease to a lower ionic coordi nation in the melt The cases of cesium bromide and cesium iodide seem to be of special interest because a third cesium salt cesium chloride does not show the large volume increase on melting probably because this salt before reaching its melting point of 642°C undergoes a solid phase change at 450°C from a cubic to a face centered cubic structure with an accompanying large volume increase and a decrease in coordination from 8 to 6 Melting in this case then represents largely the loss of long range order without any material

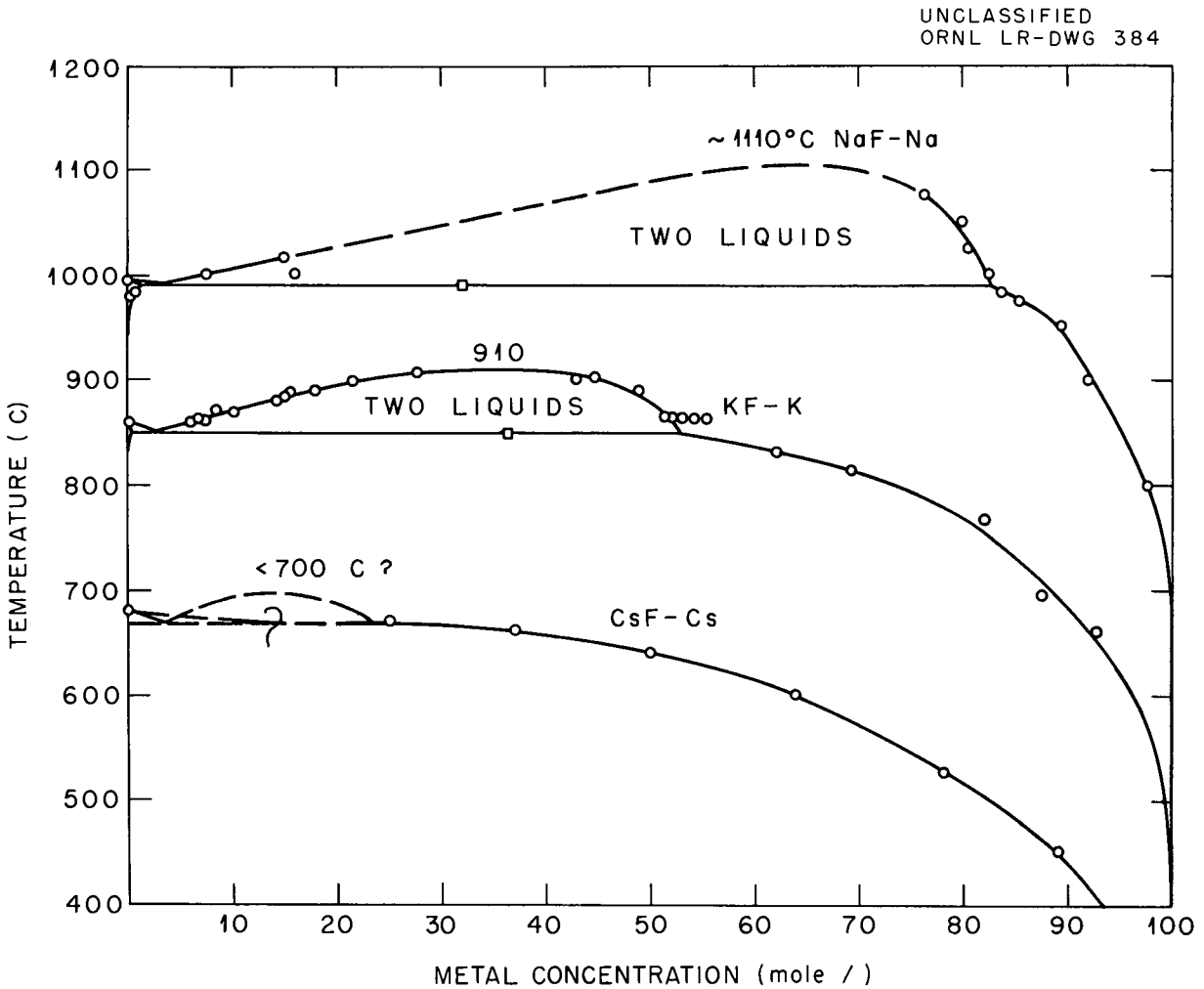

Fig 13 Phase Diagrams of the Systems NaF Na KF K and CsF Cs

change in the number of ions of the first sphere of coordination X ray diffraction measurements on cesium bromide and iodide had not in the past been carried out above a temperature of 50 deg below the melting points [43] possibly because of difficulties connected with accurate temperature control or with the comparatively high vapor pressures of the salts Both difficulties were overcome in a new design of a sample holder for the high temperature x ray diffractometer in which a stainless steel support for the powder sample was combined with a gas tight beryllium metal cover thin enough to permit unrestricted passage of x rays

With this assembly it was possible to make x ray measurements at temperatures up to 5°C below the melting points of cesium iodide and bromide and no transformation was observed in either salt Unless one occurs in the very small temperature range still unexplored it can be concluded that the structural change i e the lowering in the number of nearest ion neighbors in the first sphere of coordination occurs on melting rather than in the solid phase and that this number changes from a value of 8 in the crystal to an average of

[43] G Wagner and L Lippert *Z physik Chem* B31 263 (1936)

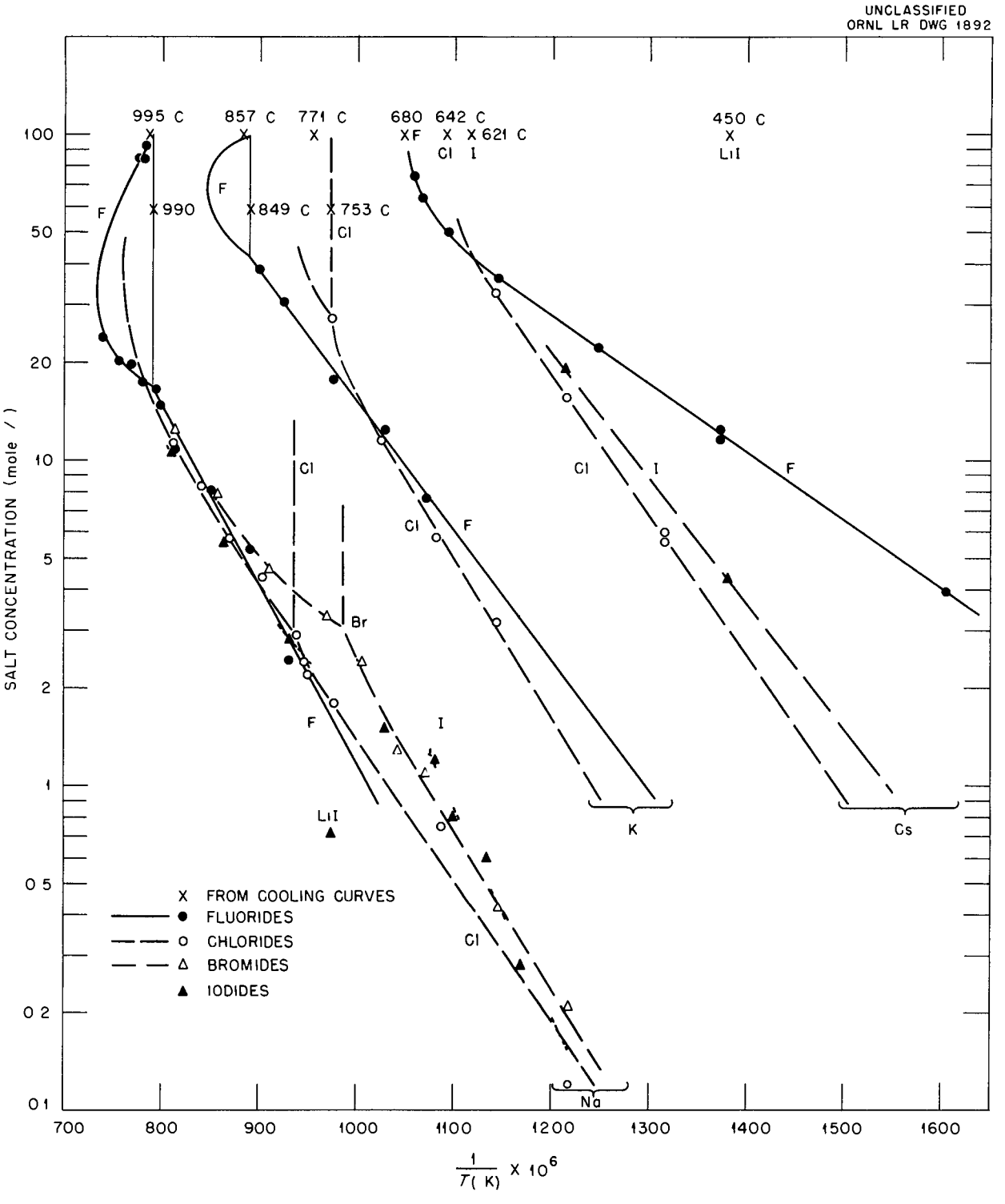

Fig 14 Solubility of Alkali Halides in Liquid Alkali Metals

probably 6 in the melt The large volume increases on melting for the iodide and bromide on which the assumption of this structural change is based are approximately 28 and 26% respectively They are calculated from the densities of the molten salts[44] and from the lattice constants a_0 = 4 72 Å for the iodide and 4 45 Å for the bromide at 625°C measured with nickel powder admixed to the salts as an internal standard whose thermal expansion is known [45]

[44] E W Washb rn (editor in chief) *International C itical Tables of Numerical Data Physics Chemistry and Technology* Vol 3 p 24 McGraw Hill New York 1930

[45] L Jordan and W H Swange *J Research Nat Bur Standards* 5 1291 (1930)

NUCLEAR CHEMISTRY

PREPARATION AND ASSAY OF KILOCURIE SAMPLES OF Xe^{135}

G E Creek P M Lantz
W J Martin G W Parker

The value of the xenon resonance cross section obtained by Bernstein *et al* [1] has been reliable however only a very limited range in neutron energy (0 03 to 0 20 ev) has been measured Therefore with the available higher beam intensity from the LITR and the simultaneous operation of an 84 channel time of flight spectrometer it be came of interest to expand measurements along the energy range both downward and upward in a cooperative program between the chemists and the physicists [2] For this purpose it was fortunate that the HRE was in operation at the same time because it was capable of producing up to 40 000 curies of 9 2 hr Xe^{135} per day Other less at tractive methods of xenon production including the destructive heating of an MTR type of fuel unit were investigated[3 4] as alternate sources

In its terminal operation four runs were specially scheduled at the HRE for the collection of kilocurie amounts of the 9 2 hr xenon The first two runs were required for developing the rapid processing techniques and for providing the usual amount of equipment adjustment The two latter runs were successfully processed and used for physical measurements and were initially evaluated at 500 and 1000 curies respectively on the basis of transmission values alone In order to assign absolute values to the cross section data considerable attention has been directed toward a precision assay of the intensity of each sample

Coincident with the mass analyses of the xenon samples some opportunity was afforded to de termine that no significant portion of the xenon had remained in the reactor for a sufficiently long period to result in a measurable amount of burnup

[1] S Bernstein *et al* *Phys Prog Rep for Dec Jan Feb 1948 1949* ORNL 325 p 6

[2] G S Pawlicki E C Smith and P E F Thurlow *Phys Semiann Prog Rep Sept 10 1953* ORNL 1630 p 39

[3] J W Culvahouse *et al* *Production of Xe^{135} for Laboratory Purposes* HW 28732 (July 15 1953)

[4] G W Parker to C B Ellis *High Level Sources of 9 2 hr Xenon* ORNL CF 50 12 45 (Dec 15 1950)

HRE Gas System

The HRE off gas as produced was essentially a low pressure oxygen stream from which large amounts of recombined hydrogen and oxygen had been stripped The blanket oxygen flowed through a ½ in pipe into a 600 ft continuous charcoal bed and a vacuum pump the rate of flow was usually about ½ to 1 liter/min In order to divert gas into a trap system it was necessary to provide only an additional pressure drop over that existing in the off gas line Normally the off gas was dry but contained in leakage air as well as the fission products Rb Cs and Sr resulting from decay of Xe and Kr however it contained no halogens

Gas Collection at the HRE

In Fig 15 some consideration is taken of the production of relative amounts of the noble gas fission products Since some 20 to 30% of the total fission products originate as a gaseous pre cursor or pass through such a stage it is im

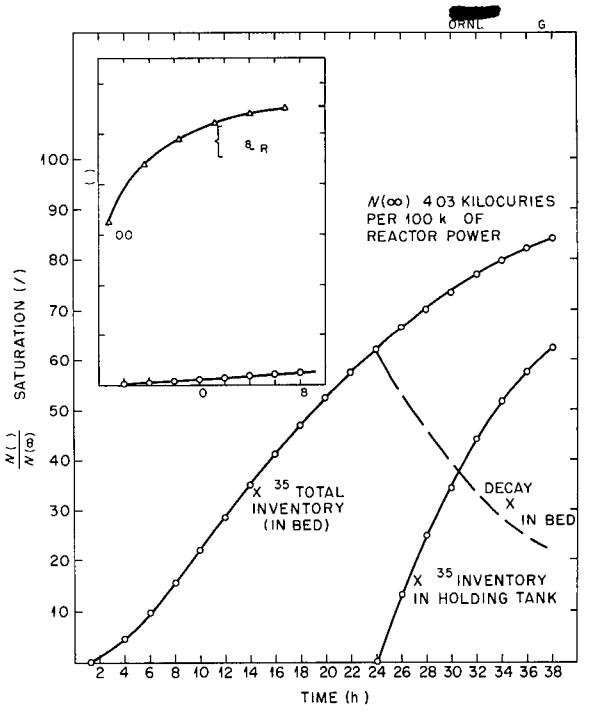

Fig 15 Relative Intensities of Fission Gas Activities

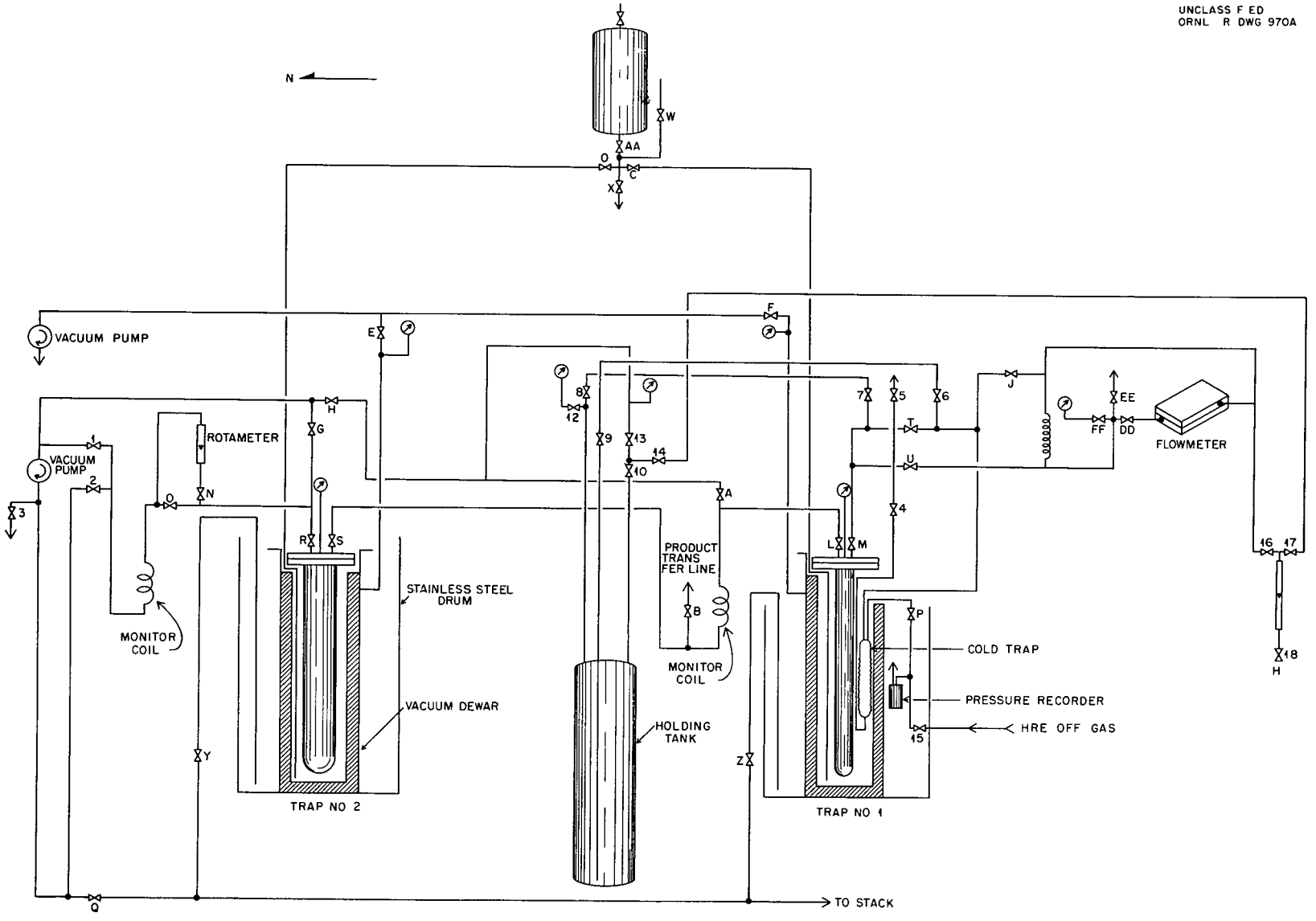

Fig 16 Schematic Flow Diagram of Off Gas Collection Equipment

mediately evident that in order to collect a predetermined 5 to 10 kilocurie xenon fraction 10 or 20 times as much krypton and rubidium (the rubidium isotopes are short lived) must be taken Disregarding the Xe^{135} handling of the other activities represented a formidable task

Since every reasonable precaution had to be observed to prevent out leakage of even trace amounts of the gas into the working area and very slightly larger amounts into the fan stack a procedure was devised which permitted collection over a long period of a measured flow of gas into a previously evacuated holdup tank (see Fig 16) In this manner much of the intense radiation was already spent during the collecting time Then by outgassing the holding tank with a lamellar flow of helium a further cooling period was obtained for the fresher portion of the gas in the tank

In making a collection the off gas was cooled in a cold trap to liquid oxygen temperature to remove condensables such as water vapor and then was passed through a flowmeter into the holding tank at such a rate that the tank was filled in 4 to 5 hr The collected gas was allowed a 2 hr decay time to reduce the intense irradiation due to 78 min Kr^{87} and 2 7 hr Kr^{88} After cooling the xenon and krypton were displaced with helium and adsorbed on a 2 in dia by 36 in long silica gel bed (trap No 1) maintained at liquid oxygen temperature The gas stream passed through a backup silica gel bed (trap No 2) and then through a controlled vacuum pump to the HRE stack

Separation of the krypton fraction was made on trap No 1 by removing the liquid oxygen coolant from the Dewar and raising the trap temperature to −60°C The krypton was eluted from the silica gel by means of helium flow at 1000 cc/min and adsorbed on the backup silica gel bed (trap No 2) A typical Kr Xe elution curve is shown in Fig 17

After removal of the contaminant krypton the silica gel bed was heated to 100°C and the xenon fraction was eluted with helium and adsorbed on a movable shielded adsorber bed which could be used for transporting the xenon to the hot laboratory building

Xenon Purification and Mounting

Transfer of the xenon from the movable shield to a 100 ml volume liquid oxygen cooled silica gel bed (Fig 18) was made by heating the adsorbent bed with steam and eluting with a hydrogen flow of 50 cc/min After the transfer was completed helium and hydrogen were removed from the cooled silica gel bed by means of a pump Pumping was discontinued when the xenon showed an appreciable break through

The liquid oxygen coolant was removed and the trap was heated to 100°C allowing the xenon to expand into an evacuated purification system consisting of a heated barium getter furnace which removed oxygen nitrogen water vapors etc From the barium furnace the gas stream was passed through a hot palladium valve which effectively removed hydrogen The stream was then circulated through the barium furnace–palladium valve system by means of a Toepler pump until sufficiently purified (as indicated by the residual pressure)

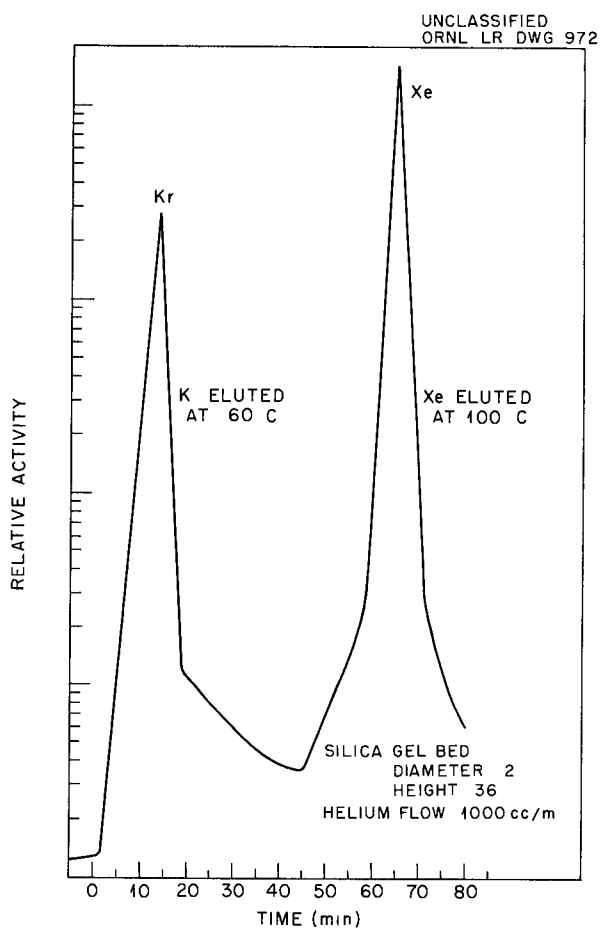

Fig 17 Elution of Krypton and Xenon from Silica Gel

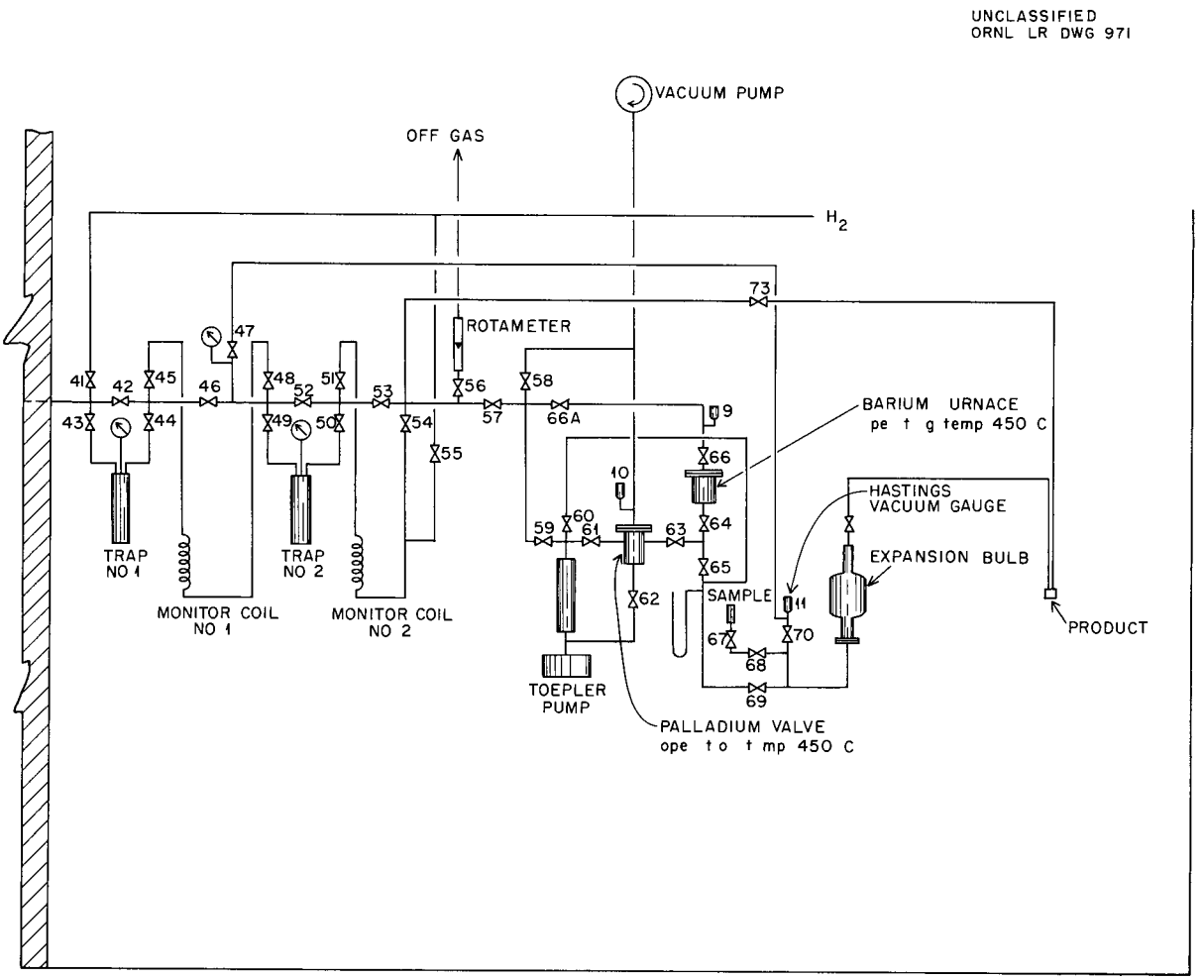

Fig 18 Schematic Flow Diagram of Xenon Equipment

and was then expanded into a 1 liter evacuated glass bulb

The xenon sample bomb holding a 1 ml gas volume (Fig 19) was fabricated from a copper or steel block having an inside opening measuring 0 900 × 1 125 × 0 060 in and matching the general beam dimensions The xenon was pushed into the evacuated holder through 0 023 in ID stainless steel tubing by means of a mercury leveling bulb and was condensed at liquid nitrogen temperature Any uncondensed gas was released back into the barium furnace–palladium valve system for re cycling

After loading the sample holder was raised from the coolant and the inlet and outlet tubes were crimped sheared and soldered by remote manipu lation The sealed sample was allowed to warm up and was checked for leakage by pulling air over the holder and onto a monitored charcoal bed

Absolute Assay of Xe^{135}

In order to establish the absolute number of xenon atoms present in the bomb at the time trans mission measurements are made a number of methods of assay were considered These methods can be divided into two classes physical measure ments and radiochemical methods and include absolute gas counting radiation calorimetry gamma coincidence counting xenon and cesium mass spectrometry and cesium absolute beta counting For this work three somewhat inde pendent measurements were selected and have been applied to the 500 curie sample

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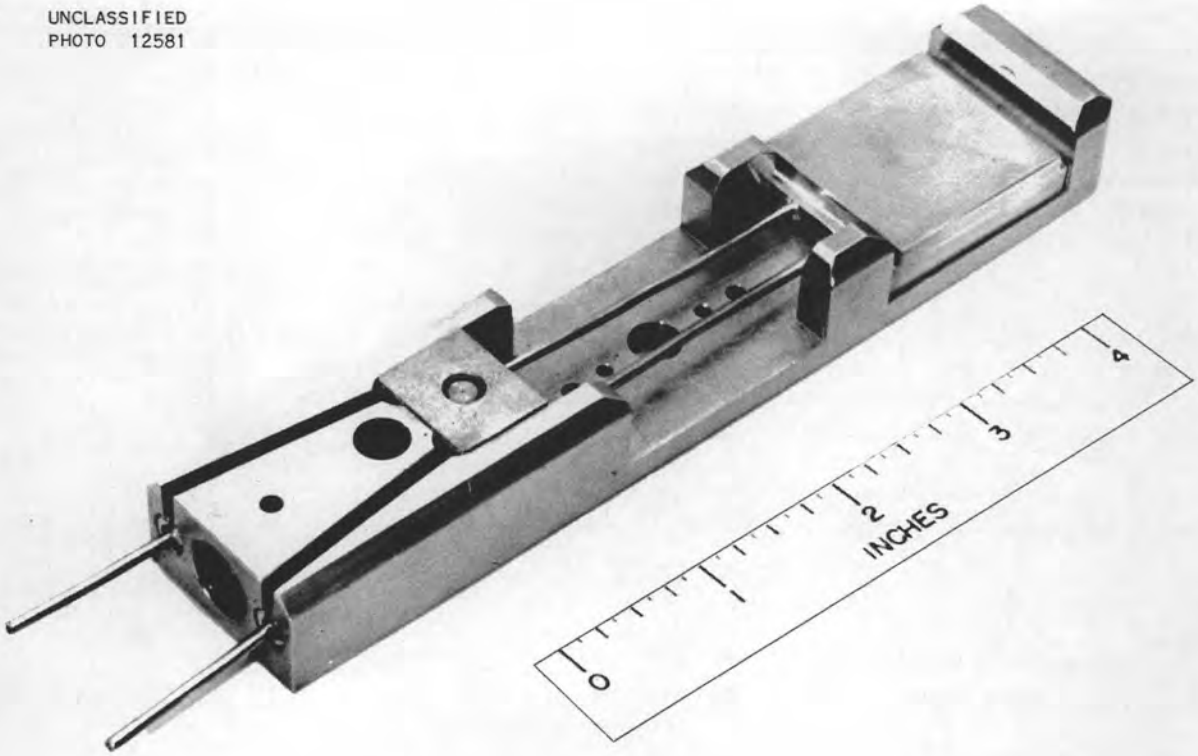


Fig. 19. Xenon Transmission Bomb and Holder.

Absolute Gas Counting. It was felt that by no reasonable method could a representative aliquot be made of the gas actually contained in the bomb at the time of closure; therefore an indirect method involving an arbitrary sample taken at the sealing time was used to establish only the ratio between 9.2-hr Xe^{135} and 5.2-day Xe^{133}. For this purpose and for the remainder of the gas counting, a proportional, internal gas counter was used which had a volume of about 300 ml, contained argon-methane, and operated at about 2000 v (see Fig. 20). The sensitive volume as determined by Macklin and Banta was 85%, and the energy dependence was negligible. The procedure required that the gas contained in the bomb after a reasonable period of decay should be accurately diluted in a calibrated system and that the disintegration rate obtained should then be extrapolated on the 5.2-day decay curve to sealing time.

In practice, some difficulty was experienced with this method because the samples were not available for opening and counting within a reasonable number of half-lives of the 5.2-day activity (more than 100 days elapsed), and this resulted in counting a predominance of 12-day Xe^{131m}, whose x rays have a high counting efficiency. The gamma spectra in Fig. 21 indicate a more nearly correct proportion of the two activities.

Absolute Beta Counting of Radiogenic Cs^{135}. The second method of assay was based on the pure beta activity of the cesium daughter of Xe^{135}. A strict requirement with this method is an accurate value for the half life of the cesium, which, unfortunately, was not available. The values reported by Sugarman ($2.1 \pm 0.7 \times 10^6$ years) and by Zeldes *et al.* ($2.95 \pm 0.3 \times 10^6$ years) were obtained under somewhat unfavorable conditions, and because of their uncertainty the assay would have been of little value. However, in this case, by comparing these values with those acquired by other methods of assay, it was possible to obtain an improved half-life value for cesium.

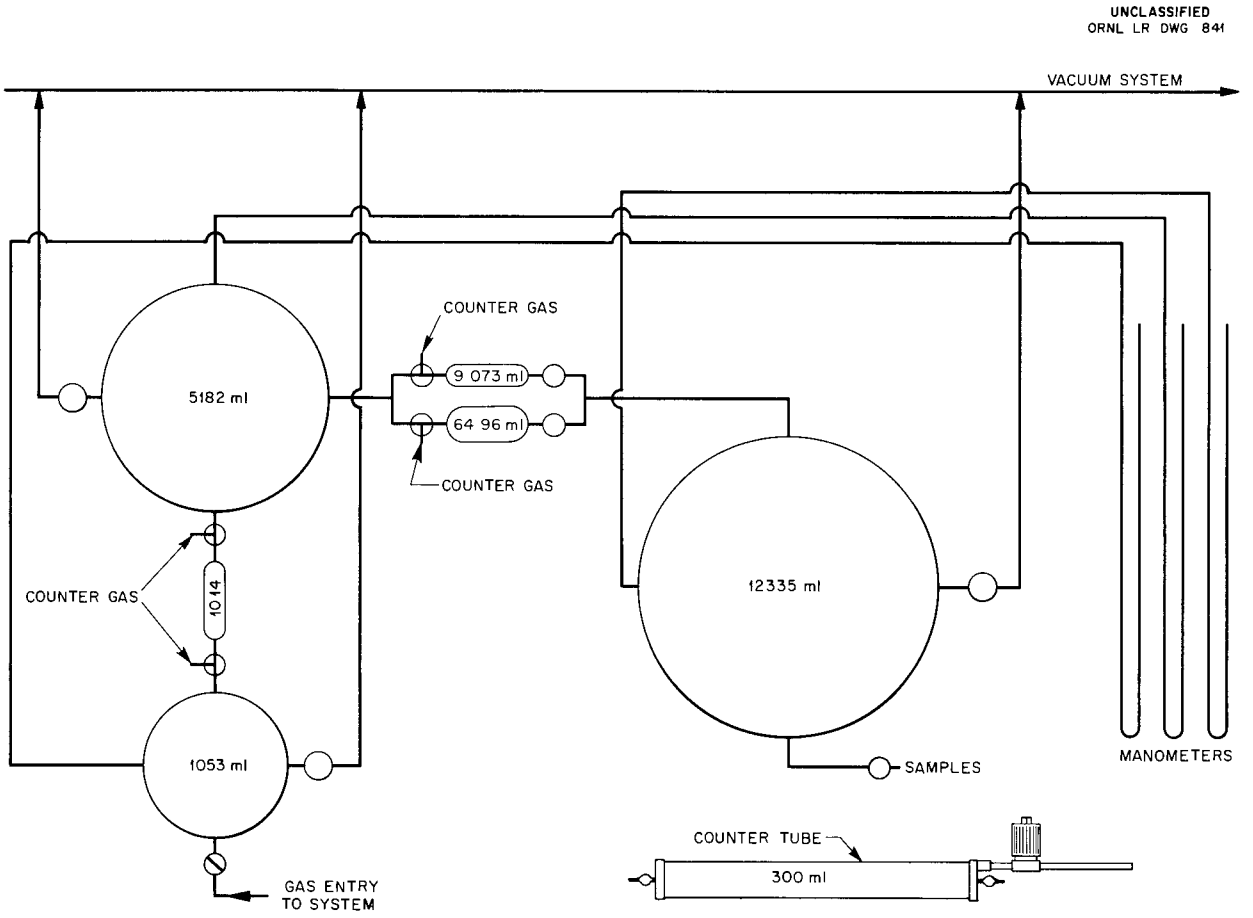


Fig 20 Gas Dilution System and Proportional Gas Counter

The procedure for quantitatively recovering cesium from the gas bomb was as follows Before the xenon was released into the aliquoting system Tygon capillary tubes were sealed over the 0 035 in stainless steel tubes a glass wool plug was inserted and with the gas container cooled to liquid nitrogen temperature the outlet tube was flexed until it was work hardened and broken The bomb was then warmed to room temperature and the inlet tube was also broken so that counter gas could be passed through the bomb to sweep out all the xenon The bomb was then detached along with the glass filter and both were washed with water until the rate of the beta activity being removed had decreased to zero Finally a dilute acid wash was used to make sure that no trace of cesium had been left This material was all made up to exactly 10 ml from which many aliquots were counted The mass of the mounted samples was determined by direct weighing and correction was applied for self absorption For 100 λ (1% of the total sample) the observed average counting rate was 2650 counts/min By correcting for the mass of the sample (60 μg on an area of 0 3 sq cm) by a plot (Fig 22) of successively decreasing sample sizes (from 400 to 20 λ) and normalizing each to the equivalent of the 100 λ count an extrapolation to zero sample thickness gave a corrected count of 3100 counts/min Samples were mounted on 75 μg/sq cm Zapon film and counted in a flow type of proportional counter at 50% geometry The slide chamber was provided with a 50 cc gas pocket below the sample to reduce backscatter Based on the use of the number 279 000 (310 000 minus 10% for backscattering) for the total disintegration rate at 50% geometry and the value 190 μg for the weight of the cesium (given in the paragraph below) a value

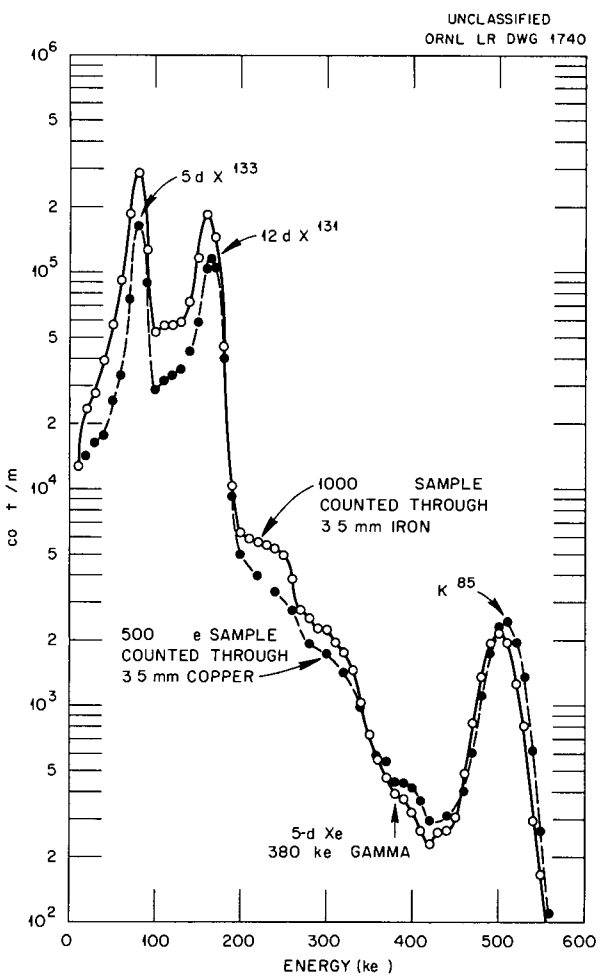


Fig 21 Gamma Spectrograms of Xenon Bomb Samples

of 2 0 × 10^6 years ± 10% is proposed for the half life of Cs^{135}

Cesium Assay by Isotopic Dilution One of the most unique properties of cesium is its high thermal ionization efficiency Therefore an un usual opportunity was presented through the co operation of R Baldock and J R Sites and the Mass Spectrometer Group for the isotopic dilution analysis of the extracted cesium (Table 5)

By using the average value of 19 μg/ml or a total of 190 μg of Cs^{135} and by calculating the equivalent in 9 2 hr activity (Xe^{135}) a value of 480 curies is indicated This agrees well with the approximate 500 curies estimated by the physi cists from the transmission data

At present the 1000 curie sample is being as sayed A new cesium standard and additional samples spiked at different ratios are being used to detect possible systematic errors and to pursue the method to its limit of accuracy

HALF LIFE MEASUREMENTS

A R Brosi B H Ketelle

The decay of Kr^{85} has been followed for a period of one year by the method described previously [5] A statistical analysis of the data gives a half life of 10 53 ± 0 1 years Decay data taken on a Co^{60} sample over the same period give a half life of 5 41 ± 0 05 years The errors quoted are for the 95% confidence level

[5] A R Brosi and B H Ketelle *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 36

TABLE 5 ISOTOPIC DILUTION ANALYSIS OF EXTRACTED CESIUM

Material	Relative Abundance		Ratio	Co ent at o of C 135 (μg/ml)	Xenon (es)
	Xe^{133}	Xe^{135}			
Sp ke (nat al)	100	0			
Unknown (hot)	84 12	15 88 ± 0 06			
1*s* + 2*x*	87 49	12 51 ± 0 12	6 99	19 6	495
2*s* + 1*x*	92 58	7 42 ± 0 13	12 48	18 5	467
Average				19 0 ± 1 0	481

s = spike (normal cesium 660 μg/ml) aliquoted in 100 λ portions
x = unknown (aliquoted in 100 λ portions)

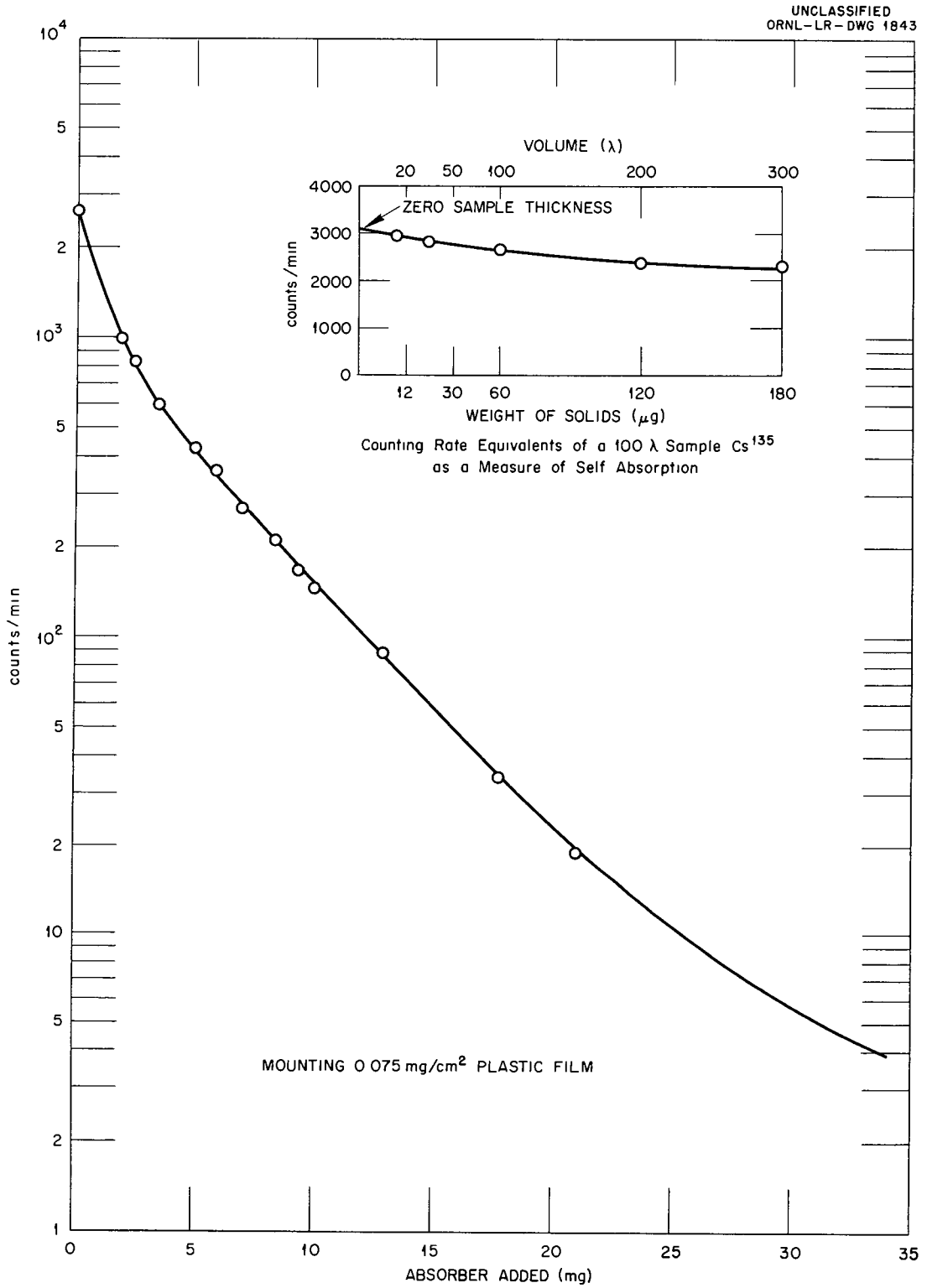


Fig 22 Cesium 135 Beta Absorption Curve

OBSERVATIONS ON THE NUCLEAR CHEMISTRY OF RUTHENIUM AND RHODIUM

G E Boyd Q V Larson

In connection with continuing studies on the nuclear chemistry of technetium isotopes of other elements in the same region of the periodic table have been prepared and studied In particular observations were made on certain of the ruthenium radioisotopes and on a few of the rhodium radio isotopes These findings which are of a survey nature are reported in this progress report in the hope that they may be of possible use to others desiring to conduct further investigations

Chemistry of the Rhodium Source Preparations

The rhodium activities examined were separated from purified ruthenium dioxide irradiated for 1 hr with an average beam of 100 μa of 20 Mev protons from the ORNL 86 in cyclotron [6] A purified rhodium fraction was isolated by adding a small amount of the inactive element to the target and then distilling off the irradiated ruthenium after it was oxidized to the volatile tetraoxide with perchloric acid This distillation was repeated twice after additions of inactive ruthenium The residue in the distilling flask was made alkaline with sodium hydroxide and ethyl alcohol was added to precipitate the rhodium This precipitate was dissolved in hydrochloric acid the solution again made alkaline and the rhodium reprecipi tated After the precipitate was dissolved in hydrochloric acid metallic rhodium was formed by adding magnesium metal Aliquots of this final rhodium were then mounted in order to prepare sources for measurement By the time measure ments were begun all 9 min Rh^{98} 31 min Ru^{97} and 4 5 hr Ru^{99} activities had decayed to negli gibly low intensity Measurements of the decay of the total radiations with the use of an end window G M counter were begun 15 days after the end of bombardment and were continued for more than 800 days The curve could be resolved into 6 0 day about 46 day and 243 day periods

Measurements on 21 hr Rh^{100}

Gamma ray spectra (Fig 23) were measured with a scintillation spectrometer after 47 71 and 199 hr of decay Transitions associated with the 21 hr Rh^{100} could be identified and in the main their energies agreed quite well with those derived from conversion electron measurements reported recently [7] The reported level at 301 kev was not observed because of interferences nor were the weak transitions at 372 and 742 kev evident It is of interest to note that the strongest gamma ray (534 kev) in 21 hr Rh^{100} has also been seen[8 9] in the decay of 15 8 sec Tc^{100} Presumably this transition is from the first excited level in the even even nucleus Ru^{100}

Measurements on 5 9 day Rh^{101}

The gamma ray spectrum (Fig 23) also showed a line at 309 kev which decayed with a 5 to 6 day half life Subsequent measurements (not shown) further indicated a much weaker gamma ray at about 560 kev There was however no indication of unconverted gamma rays originating from a level recently reported at 148 ± 5 kev [10] The 309 kev level in Ru^{101} is also excited in the decay[11] of 13 5 min Tc^{101} Measurements of the absorption of the total radiations in aluminum showed the presence of conversion electrons and of ruthenium x rays in considerable abundance in the decay of the 5 9 day Rh^{101} There was no indication of positrons associated with this period in rhodium

Measurements on 243 day Rh^{102}

A somewhat greater half life for Rh^{102} than the reported value of 215 days was found Measure ments of the absorption of the total radiations in aluminum gave beta ray energies in good agreement with those derived from similar measurements re ported previously [12] Gamma rays were found in high relative abundance and there was evidence for ruthenium x rays The presence of the latter was confirmed by measurements with a krypton filled x ray spectrometer Unfortunately the source was too weak to determine whether a gamma ray of about 0 50 Mev was present in the

[6] R S Livingston *Nature* 170 221 (1952)

[7] L Ma q e *Phys Rev* 92 1511 (1953)

[8] G E Boyd and E C Campbell unp blished studies (1952)

[9] G E Boyd Q V Larson and G W Pa ker *Phys Rev* 86 1051 (1952)

[10] C L Scoville S C Fultz and M L Pool *Phys Rev* 85 1046 (1952)

[11] G E Boyd and B H Ketelle *Phys Rev* 83 216A (1951)

[12] W H Sullivan N R Sleight nd E M Glodrow Paper 331 in *Radiochemical Studies The Fission Products* NNES Vol 9 Book 3 McGraw Hill New York 1951

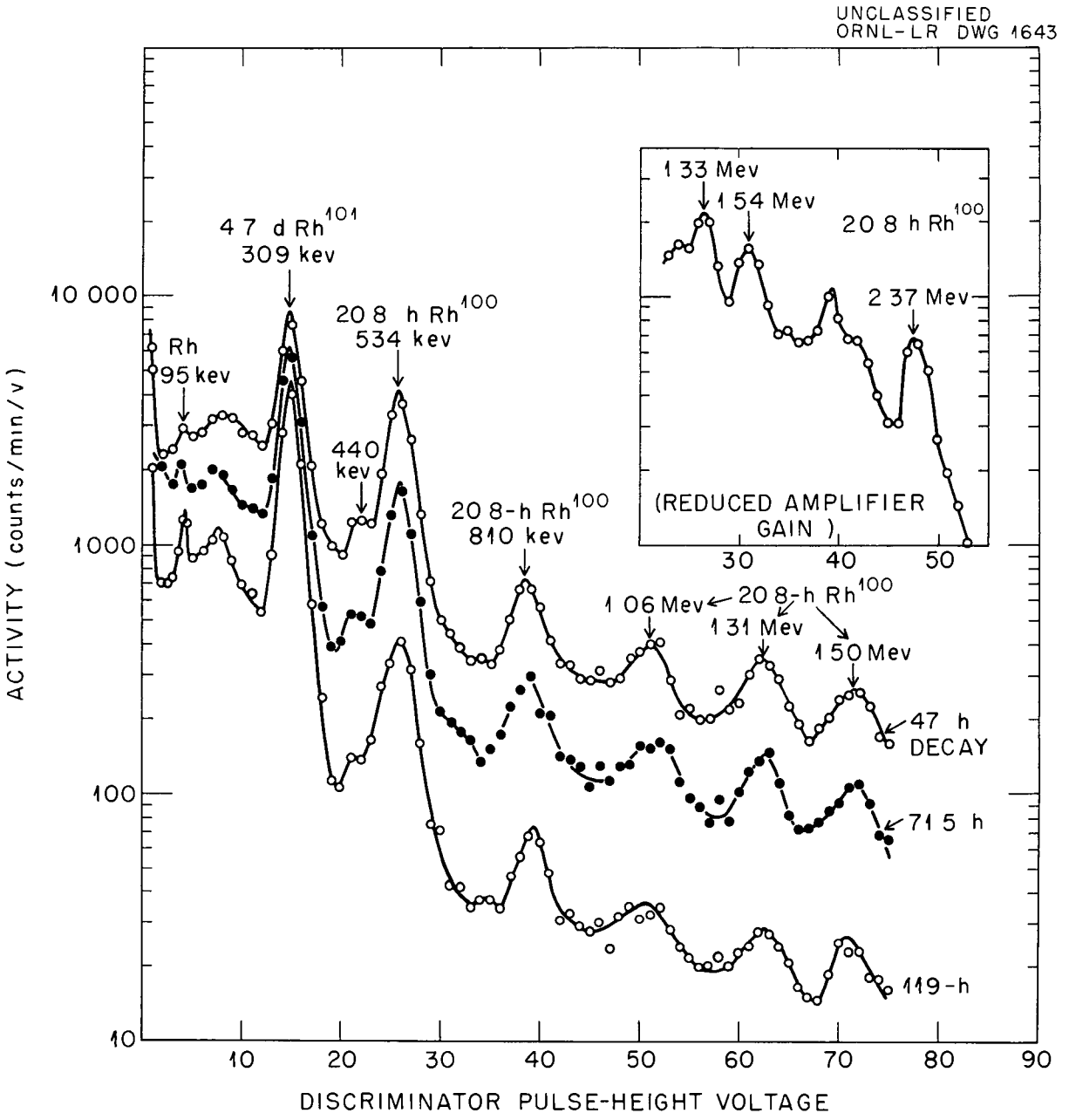


Fig 23 Gamma Ray Spectrum of Rhodium Fraction from Ruthenium Plus 20 Mev Protons

decay On the basis of the nuclear systematics of even even isotopes [13 14] a level of about this energy would be expected in Ru^{102} However no gamma rays have been detected in the decay of the isobaric Tc^{102} activity [15]

Measurements on 57 min Ru^{94} and 1 63 hr Ru^{95}

The preparation of Ru^{94} was undertaken in the hope that it might prove to be long lived and hence

[13] G Scharff Goldhaber *Phys Rev* 90 587 (1953)

[14] D B Kochendorfe and D J Farme *Bull Am Phys Soc* 29 No 6 20 (1954)

[15] G E Boyd a d Q V La son npubl shed es Its (1952)

suitable for the extraction of its daughter (52 min Tc^{94}) activity some uncertainties concerning the gamma radiations of this activity still exist A long lived ruthenium parent might be expected because (1) Ru^{94} is a 50 neutron nuclide and by reason of its enhanced stability the energy available for its decay to Tc^{94} should be reduced to about 0 5 Mev (2) the spin change in the Ru^{94} Tc^{94} decay is expected to be large so that the transition will be forbidden (The spin of Ru^{94} an even even nuclide should be 0^+ while a spin of 3^+ has been assigned[16] to 52 min Tc^{94})

A target of enriched molybdenum (92 1% Mo^{92}) was bombarded for 2 hr with a 36 μa beam of nominal 28 Mev alpha particles from the 60 in cyclotron at the Department of Terrestrial Mag netism Carnegie Institution of Washington Wash ington D C The irradiated molybdenum together with about 5 mg of inactive ruthenium was placed in a distilling flask containing a mixture of per chloric and phosphoric acids and the desired ruthenium and technetium activities were distilled into 6 *N* NaOH The separation of these two elements was then accomplished by adding ethyl alcohol to precipitate RuO_2 from the alkaline so lution The precipitate was redissolved in per chloric acid and the ruthenium was distilled from added inactive molybdenum and again reprecipi tated Finally a solution of known volume con taining the purified ruthenium was made up and from it aliquots were taken for the preparation of sources of ruthenium activity for measurement and for periodic Ru Tc separations (i e milkings) The latter were performed after the ruthenium was separated as RuO_2 from the 6 *N* sodium hydroxide by neutralizing the supernatant base adding 1 to 2 mg of rhenium and coprecipitating the tech netium activity with tetraphenyl arsonium per rhenate at 0°C

Technetium milkings at approximately 1½ hr and at 4½ hr after bombardment gave both the 52 min Tc^{94} and the 20 hr Tc^{95g} activities The fifth and last milking at 21 hr gave only 20 hr Tc^{95g} activity It was therefore concluded that Ru^{94} almost certainly possesses a half life of the order of 1 hr or less thereby precluding its use as a convenient parent of Tc^{94} Neither positrons nor gamma rays were found which could be associated with Ru^{94} presumably this nuclide emits only x rays and possibly low energy gamma rays The foregoing observations appear to be in agreement with other preliminary findings recently reported [17]

The absorption was measured of the radiations in aluminum and in lead emitted by a ruthenium fraction purified 9 2 hr after the end of the bom bardment By this time Ru^{94} should have decayed to negligible levels Also the growth of 20 hr Tc^{95g} into this source could be neglected for measurements were completed within 1 hr Reso lution of the aluminum absorption curve (Fig 24) showed the presence of beta particles technetium x rays and gamma rays The maximum positron energy was estimated as 1 3 ± 0 1 Mev from the range value of 590 mg of aluminum per sq cm derived by applying Feather s comparison method Lead absorption measurements (Fig 25) gave a gamma ray half thickness $\tau_{1/2}$ of 13 2 g of lead per sq cm from which an energy E_γ of 1 1 ± 0 1 Mev was obtained by using a ($\tau_{1/2}$ E_γ) curve determined in the same low scattering geometry arrangement with sources emitting gamma rays of

[16] H Med cus P Preiswerk and P Scherrer *Helv Phys Acta* 23 299 (1950)

[17] A van der Wiel and A H W Aten Jr *Physica* 18 356 (1952)

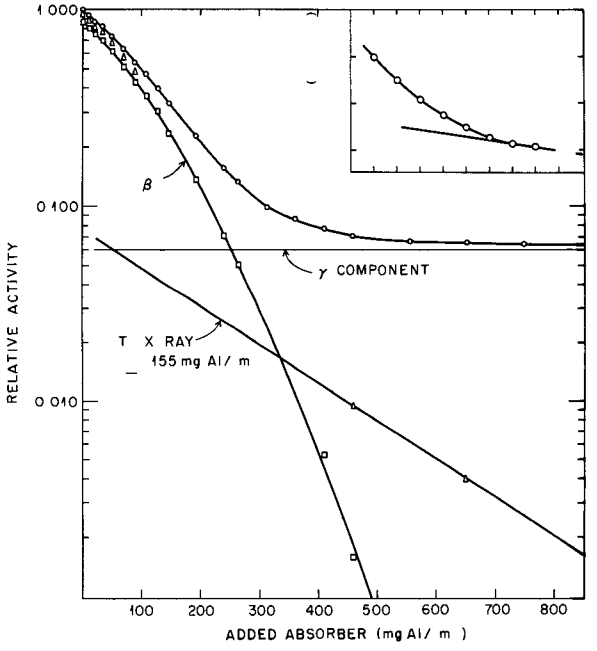


Fig 24 Absorption of Radiation from 1 63 hr Ru^{95} in Aluminum Measurements were extended to 1436 mg of aluminum per sq cm

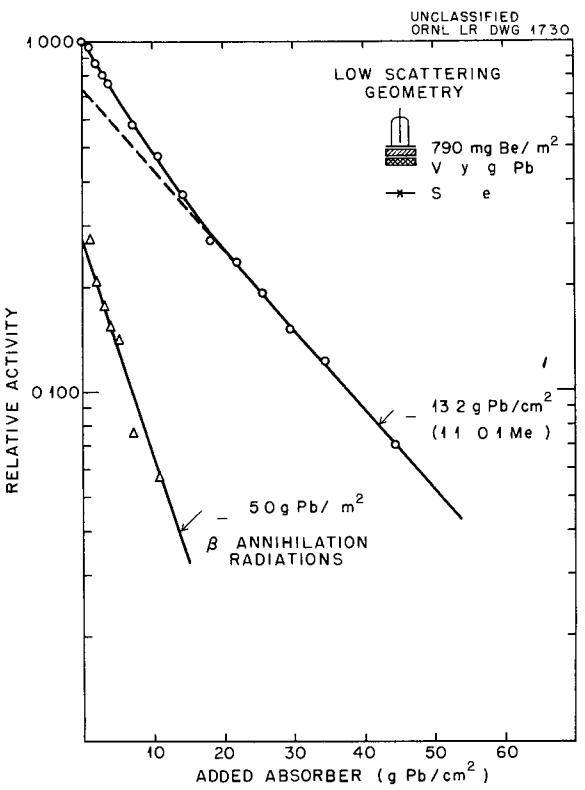


Fig 25 Absorption of Gamma Radiation from 1 63 hr Ru^{95} in Lead

accurately known energies Decay measurements on both the total radiations and on the gamma rays gave a half life for Ru^{95} of 1 63 ± 0 05 hr In terestingly this activity appeared to decay almost exclusively to form the 20 hr ground state of Tc^{95} The half life and gamma energy here found are in good agreement with those previously reported by Eggen and Pool [18] However the positron maximum energy in the experiments here is higher by about 0 2 Mev Positron to x ray and x ray to gamma ray counting rate ratios estimated for zero absorber after being corrected for detection efficiency and for fluorescent yield indicated that positrons were emitted in about 20% of the 1 63 hr Ru^{95} disinte grations and that they were followed by 1 1 Mev gamma rays

[18] D T Eggen and M L Pool *Phys Rev* 74 57 (1948)

[19] W H Sullivan N R Sleight and E M Gladrow *Phys Rev* 70 778 (1946)

[20] J Y Mei C M Huddleson and A C G Mitchell *Phys Rev* 79 429 (1950)

Measurements on 2 9 day Ru^{97}

There is various evidence that in addition to the 90 day Tc^{97m} activity amounts of the ap proximately 10^4 year Tc^{97g} are also produced by the decay of 2 9 day Ru^{97} If the percentage branching to form Tc^{97g} were known a better half life for this long lived technetium might be obtained Considerations based on energetics and on shell theory make it seem highly improbable that either Tc^{97m} or Tc^{97g} is formed directly by orbital electron capture in 2 9 day Ru^{97} Such direct transitions should be highly forbidden and a half life much longer than three days would have been observed Accordingly gamma transitions must occur in the decay The occurrence of a low energy gamma ray has in fact been reported and its energy has been estimated by absorption techniques [19] With the use of a magnetic beta ray spectrometer [20] a value of 217 kev was estimated from the K photoelectron line from a lead radiator Owing however to the presence of much larger quantities of Ru^{103} in the source examined neither the L line nor any other lines from the 2 9 day Ru^{97} were seen

The sources of Ru^{97} used here were prepared by irradiating molybdenum metal with an 8 3 μa beam of 40 Mev alpha particles from the 60 in cyclotron at the Radiation Laboratory of the Uni versity of California Upon receipt of the cy clotron target the molybdenum was dissolved in sulfuric acid to which a small amount of phos phoric acid had been added Approximately 5 mg of ruthenium carrier was added and the sulfuric acid was distilled to near dryness This operation served to remove all technetium formed either directly in the bombardment or by decay of shorter lived ruthenium isotopes Next 25 ml of per chloric acid was added to the distilling flask and the ruthenium was codistilled and was col lected in 6 N sodium hydroxide Subsequently the ruthenium was precipitated as RuO_2 with ethyl alcohol redissolved in perchloric acid redistilled from added inactive molybdenum reprecipitated from alkaline solution and then dissolved in hydrochloric acid and reduced to its metallic state by treatment with magnesium metal Aliquots of this metallic ruthenium were used for making up the sources

A half life of 2 93 ± 0 05 days was derived from accurate measurements of the decay of the gamma

radiations with a 4π geometry ionization chamber filled with 40 atm of argon gas

The gamma ray spectrum (Fig 26) was measured with a NaI scintillation spectrometer Lines at 220 ± 5 325 ± 5 and 565 ± 10 kev were observed The lowest energy gamma ray was approximately 14 times more intense than the 325 kev ray and over 450 times that of the 565 kev ray There was no indication of a photoelectron peak arising from the annihilation of positrons possibly emitted in the decay In addition the x ray spectrum measured with a krypton filled proportional counter showed only technetium x rays Presumably therefore 2 9 day Ru^{97} decays almost entirely by orbital electron capture accompanied by several low energy gamma rays

The conversion electron spectrum was examined in collaboration with B H Ketelle by using a thin lens magnetic beta ray spectrometer (Fig 27) and the occurrence of 220 and 325 kev gamma rays was confirmed The K/L ratio for the lower energy gamma ray was 7 1 which value is consistent with a low multipole order ($E1$ or $M2$) for this transition The ratio of 4 1 for the 320 kev gamma ray suggested a much higher multipole order The conversion electron spectrum was also measured with an anthracene crystal and a photomultiplier Conversion lines at 200 and at 307 kev were seen confirming both the scintillation and the magnetic beta ray spectrometer findings

Coincidence rate measurements were made with the use of a sodium iodide gamma ray detector and a mica end window proportional counter as a beta ray detector Technetium x ray gamma ray coincidences were observed in amounts sufficient to suggest that a large fraction of the disintegrations of 2 9 day Ru^{97} goes through the 220 kev level in Tc^{97} An attempt was made to estimate the branching ratio by comparisons with coincidence rate measurements on Cr^{51} whose branching ratio α in K capture decay to a 320 kev excited state in V^{51} has been reported[21] as 8% On the assumption that there is no direct formation of

[21] W S Lyon *Phys Rev* **87** 1126 (1952)

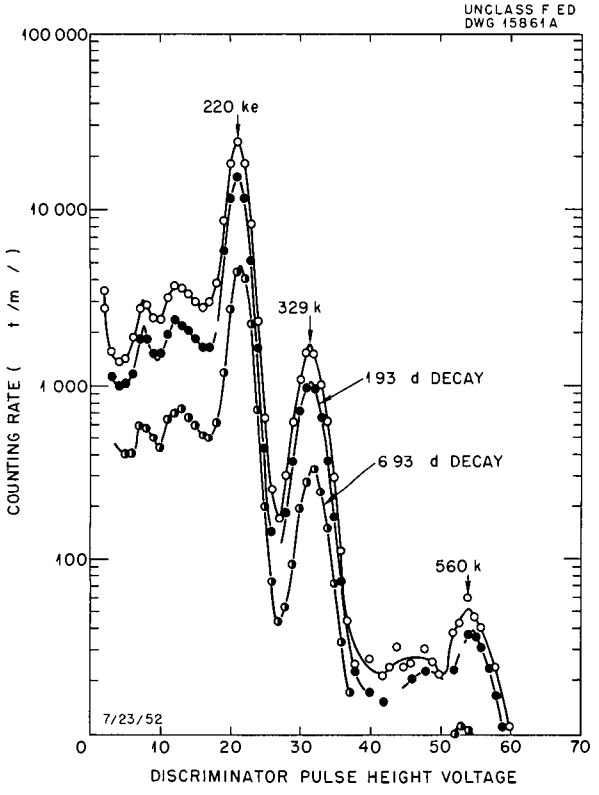


Fig 26 Gamma Ray Spectrum of 2 9 day Ru^{97} Taken at Varying Times with a NaI(Tl) Scintillation Counter Spectrometer

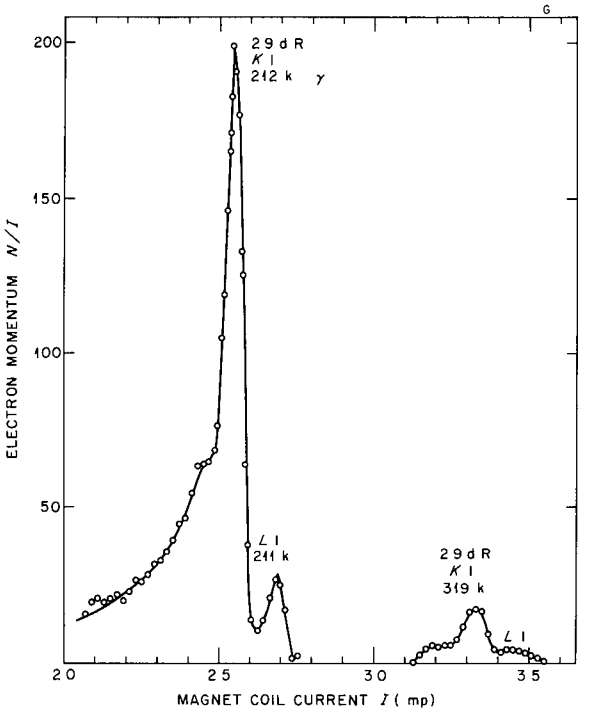


Fig 27 Conversion Electron Momentum Distribution for 2 9_3 day Ru^{97}

either the metastable or the ground state of Tc^{97} in the decay of 2 9 day Ru^{97} the branching to the 220 kev level was estimated to be 44% This value seems to be too low in view of the 14 fold greater intensity of the 220 kev compared with the 325 kev gamma ray However if the value of 21% reported[22] for the branching in Cr^{51} is used the branching in 2 9 day Ru^{97} to the 220 kev level is close to 100% which is probably too high Other types of measurements evidently will be necessary to settle this uncertainty

Measurements on 39 5 day Ru^{103}

A recent report[23] has indicated that the decay scheme for Ru^{103} may be somewhat more complex than was previously supposed by a relatively large number of investigators This recent report has been confirmed by the present study which there fore may be of interest

Fractional gram quantities of purified RuO_2 were irradiated for approximately 12 hr in the ORNL Graphite Reactor Radiochemical purifications were performed with the use of alternate perchloric acid distillations and reductions of ruthenium with magnesium metal in hydrochloric acid solution Sources for gamma ray decay measurements and for scintillation spectrometry were then made up from the purified ruthenium

An accurate half life was determined by using a stable wide range 4π geometry ionization chamber filled with 40 atm of argon [24] Ionization currents were measured by a null point method wherein voltage drops produced across fixed high valued resistors (e g 10^8 to 10^{11} ohms) were amplified by a dynamic condenser electrometer and then balanced in a recording Brown potenti ometer to give an instantaneous value of the radio active intensity at any time The potentiometer readings were corrected for background for non linearity in scale response owing to ion recombi nations and for resistance ratios between scales Measurements taken over a period of 600 days showed an exponential decay with a half life of 39 5 ± 0 2 days for more than eight half lives The agreement with the half life of 39 8 ± 0 4 days reported by Kondaiah[25] is noteworthy

The gamma ray spectrum (Fig 28) taken by use of a scintillation counter spectrometer (1½ in dia × 2 in cylindrical thallium activated sodium iodide crystal) showed photoelectric peaks from the well known line at 498 kev as well as from a more energetic line at 610 kev present in lower intensity The apparent line at 192 kev was caused by Compton backscatter from the lead shielding about the crystal as shown by changes in its relative intensity with varying source to detector geometries and by its persistence even when thicknesses of lead sufficient to absorb low energy gamma rays completely were placed between the crystal and the source Because of its large internal conversion coefficient no photo peak was seen from the 39 6 kev line emitted by 57 min Rh^{103m} in equilibrium with the 39 5 day Ru^{103} There was no indication of a gamma ray from a level in Rh^{108} reported[23] at 52 9 kev probably owing to its low yield and/or to its appreciable internal conversion All parts of the

[22] D Maeder P Preiswerk and A Stainemann *Helv Phys Acta* 25 461 (1952)

[23] J M Cork J M LeBla c F B Stumpf and W H Nester *Phys Rev* 86 575 (1952)

[24] C J Borkowski *Anal Chem* 21 348 (1949)

[25] E Kondaiah *Arkiv Fysik* 4 81 (1952)

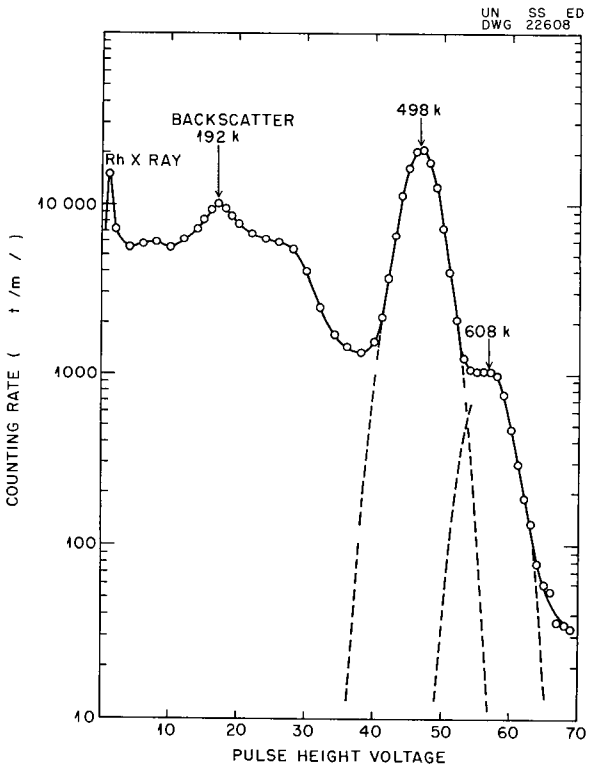


Fig 28 Gamma Ray Spectrum of 39 5 day Ru^{103}

spectrum decayed with the proper half life for Ru^{103}

The intensity of the 610 kev relative to the 498 kev gamma ray was estimated by fitting Gaussian curves to each photopeak and then determining the ratio of the areas under these curves An average value of 0 053 ± 0 001 1 0 was estimated from four spectra which after correction was made for the detection efficiency ratio 0 71 1 0 gave the relative abundance of the higher to the lower energy gamma ray as 0 075 1 0

A beta particle group of about 140 kev maximum energy seems to be required if the 610 kev quantum radiations result from a transition to the ground state of Rh^{103} The occurrence of such a beta ray branch in approximately 7% of the disintegrations leads to a log ft value of 6 1 suggesting either an allowed or possibly a first forbidden (i e $\Delta I = 0$ 1 Yes) transition This relatively low log ft value however cannot be easily reconciled with a probable $d^{+}_{5/2}$ ground state for Ru^{103} and a multipole order of $E4$ for the 610 kev gamma ray as has been proposed[23] from its measured K/L ratio of 4 0 ± 1 5

ORGANIC CHEMISTRY

EXAMINATION OF THE IODOFORM AND SCHMIDT REACTIONS OF ACETONE 1 C^{14} FOR ISOTOPE EFFECTS

G A Ropp M T Clark
W A Bonner V F Raaen

The reverse isotope effect reported[1] for the iodoform reaction of acetone 1 C^{14} has appeared to be an exception to the general rule that C^{12} C^{14} bonds break less rapidly than C^{12} C^{12} bonds Partly on the basis of this exceptional result a new theory has been stated [2 3] Because of the extreme importance of these developments to the field of isotope effect studies attempts have now been made to repeat the original experimental work The present authors have carefully carried out the iodoform reaction with acetone 1 C^{14} but have observed no measurable isotope effect of any kind Four different runs at room temperature were performed at three levels of radioactivity by different chemists working independently at differ ent seasons of the year In addition alternative modes of mixing the reactants were employed The only item common to all four runs was an ioni zation chamber with a vibrating reed electrometer for radioactivity assay Two different samples of acetone 1 C^{14} which were used in these reactions were prepared by different synthetic methods Both samples were carefully fractionated One sample was subsequently distilled from calcium oxide to eliminate the possibility that it might contain acetic acid

Table 6 presents the results of the four inde pendent experiments All samples were assayed for radioactivity and Van Slyke solution was used in the usual wet combustion procedure (for wet combustion of derivatives containing nitrogen a lead dioxide trap at 180°C was included in the line) [4 5] The resultant carbon dioxide was counted in a stainless steel ion chamber For all assays

[1] A Roe and E L Albenesius *J Am Chem Soc* 74 2402 (1952)

[2] Abstracts of Papers 124th Meeting of the Ame ican Chem cal Society Ch cago Ill Sept 6 11 1953 pp 65-0–67 0

[3] *Chem Eng News* 31 3980 (1953)

[4] O K Neville *J Am Chem Soc* 70 3499 (1948)

[5] V F Raaen nd G A Ropp *Anal Chem* 25 174 (1953)

TABLE 6 SPECIFIC ACTIVITIES OF REACTANTS AND PRODUCTS (μc/mmole) IN THE IODOFORM REACTION

React on	Acetone Used (x 0 5)	Der vat ve	Iodoform	Acetic Acid	Derivat ve	Proced re
1	0 741 ± 0 004	2 4 Dinitrophenyl hydrazone	0 738 ± 0 006			A
2	2 898 ± 0 002	2 4 D n trophenyl hydrazone	2 881 ± 0 007	2 863 ± 0 003	*S* 1 Naphthylmethyl th uronium salt	B
3	5 60 ± 0 03	Semicarbazo e	5 57 ± 0 08	5 63 ± 0 08	*p* Nit oben yl este	C
4	5 60 ± 0 03		5 55 ± 0 06			D

A Acetone (0 200 ml) in aq eous base was treated with excess iodine in potassium iodide solution as originally described [1] The yield of odoform was 80% Acetic acid was not recovered

B Acetone (2 00 ml) was added to water (200 cc) containing iodine (14 4 g 10% excess) and sodium iodide (20 g) 10% sod um hydroxide solut on was added dropwise until the iod ne colo disappeared The iodoform was f ltered the filtrate was ac dified and sod um hydroxide was added until the solution became colorless The odditional iodoform which separated was filtered and the process was repeated until no more iodoform sepa rated The total yield of iodoform was 90% Res dual iodine was destroyed with sodium bisulf te The slightly bas c filtrate was evaporated to dryness and sodium iodide was removed by acetone extraction The acidified solution of the remaining salts was steom distilled to recover acetic ac d

C To 2 00 ml of acetone in 400 ml of 2 *N* sodium hydroxide solution 600 ml of iodine solution (contain ng 15 g of od ne and 22 g of sodium odide enough fo eact on of 70% of the acetone) was added The odoform yield was 95% based on iodine The acet c acid was isolated n a manner similar to that described under B except that sod um acetate was ext ted f om the o etone nsoluble salts w th hot ethanol A 55% recove y of sodium acetate resulted

D Reaction was run with just enough reagent to react with only 5% of the acetone present

from a given reaction the same ion chamber was used

The data of Table 6 indicate that no measurable *intramolecular* or *intermolecular* isotope effect accompanies the iodoform reaction of acetone 1 C^{14} Several sets of reaction conditions were employed including the reaction conditions originally reported [1]

Since the Schmidt reaction of acetone 1 C^{14} has also been reported to involve a reverse *intramolecular* isotope effect [2 3] three runs have been made in an attempt to repeat this work As Table 7 reveals the data fail to confirm the reverse effect previously reported instead small *intramolecular* and *intermolecular* isotope effects in the usual direction are indicated Experimental conditions used were those described by Wolff [6] The reactions were carried out in benzene solution at 0 to 5°C and the per cent reaction was in each case controlled by the amount of hydrazoic acid solution used Acetic acid product was converted to the *p* nitrobenzyl ester methylamine was converted to the phenylthiourea derivative and acetone was converted to the 2 4 dinitrophenylhydrazone These derivatives were carefully purified and radioassayed in the same manner[4] as were the iodoform reaction products

Further studies of these reactions of labeled acetone and related ketones are in progress in an attempt to correlate any observed isotope fractionation factors with reaction mechanisms

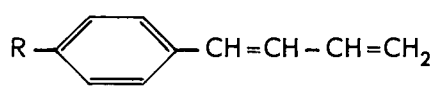
[6] H Wolff *Organic Reactions* Vol 3 pp 327 9 John Wiley and Son New York 1946

[7] ORINS research participant summer 1953

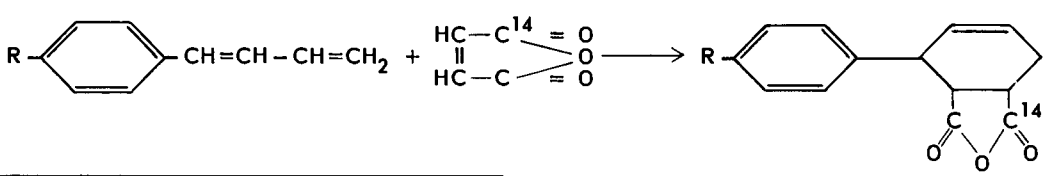
A COMPETITIVE RATE STUDY OF THE REACTIONS OF MALEIC 1 C^{14} ACID ANHYDRIDE WITH *PARA* SUBSTITUTED PHENYLBUTADIENES

C T Lester[7] G A Ropp

Some reaction rate studies of the Diels Alder reaction have been reported [8 9 10] but few quantitative data related to the effect of diene structure on reaction rate are available The paucity of such data is doubtless due in part to the experimental difficulties involved in analyzing for the Diels Alder reaction product in the presence of unreacted diene and dienophile Because of these experimental difficulties a special method of analysis has been applied here Use was made of the isotope dilution principle in determining the relative reaction rates of several dienes which were mixed and allowed to compete for a very small quantity of the dienophile maleic 1 C^{14} acid anhydride The dienes used were of the following type



in which R = *p* OCH_3 *p* CH_3 H *p* Cl and *p* NO_2 Since these dienes differ only in the type of *para* substituent their relative reaction rates have been treated in terms of the Hammett equation [11]



[8] R A Fairclough and C N Hinshelwood *J Chem Soc* 1938 236

[9] A Wassermann *Nature* 138 369 (1936) *J Chem Soc* 1942 618

[10] W E Bachman and L B Scott *J Am Chem Soc* 70 1462 (1948)

[11] L P Hammett *Physical Organic Chemistry* Chap VII McGraw-Hill New York 1940

TABLE 7 SPECIFIC ACTIVITIES OF REACTANTS AND PRODUCTS (μc/mmole) IN THE SCHMIDT REACTION

Reaction	Acetone Used (x 0 5)	Unreacted Acetone Recovered (x 0 5)	Methylamine	Acetic Acid	Acetone Reacted (%)
1	1 034 ± 0 007		1 015 ± 0 010	1 021 ± 0 006	85 to 100
2	1 496 ± 0 020		1 443 ± 0 010	1 483 ± 0 015	50
3	1 464 ± 0 009	1 495 ± 0 002	1 423 ± 0 005	1 472 ± 0 002	30

The reaction proceeds quantitatively at 25°C in benzene solution In separate experiments 1 phenyl 1 3 butadiene (R = H) was dissolved with an equimolar amount of each of the other dienes in benzene To each separate reaction mixture of diene pairs enough maleic 1 C^{14} acid anhydride (60 μc/mmole) was added to accommodate only 5 mole % of the total dienes present

After the solution was kept at 25°C in a thermo stat until reaction was complete in each case solution aliquots were taken and were added to measured amounts of pure unlabeled adducts pre pared separately by reaction of the corresponding dienes with unlabeled maleic anhydride From each aliquot thus diluted a sample of labeled product was isolated and was crystallized to constant specific activity By taking into account the dilution factors used with the two aliquots from the same reaction mixture and by considering the initial specific activity of the maleic 1 C^{14} acid anhydride and the final specific activities of the diluted adducts it was possible to calculate one ratio of rate constants k_R/k_H for each reaction mixture These ratios and the corresponding Hammett plot are shown in Fig 29 With the ex ception of the point for the *para* methyl group the points for the various substituents form a reason ably straight line The value of ρ −2 1 calculated

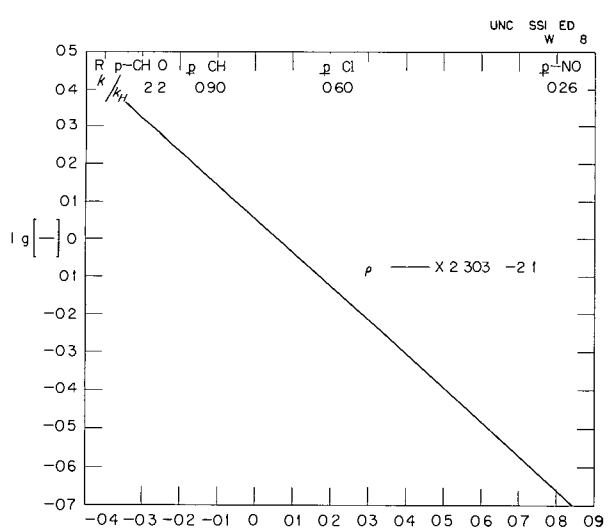


Fig 29 Hammett Plot for Diels Alder Reactions of Maleic Anhydride and R – ⟨⟩ –C(H)=C(H)–C(H)=CH_2

from the slope is close to that reported[12] for the reaction of *para*-substituted dimethylanilines with trinitrophenol methyl ether in acetone solution at 35°C The negative value of ρ signifies that electron releasing groups in the *para* position on the phenyl ring cause an increase in reaction velocity This is in accord with the accepted ionic mechanism for the reaction It is surprising that the Hammett plot is as nearly linear as these experiments indicate because the Hammett re lationship

$$\ln\left(\frac{k_R}{k_H}\right) = \rho\sigma$$

considers only the effect of the substitutent on the permanent polarization of a molecule and the corre sponding effect on a reaction rate or equilibrium It ignores the induced polarization of one reactant due to the field of an approaching second reactant Since dienes have high refractive indices and are known to be easily polarized because of their system of conjugated bonds the induced polari zation of the diene may be of considerable im portance among factors which determine the rates of Diels Alder reactions The fact that the present data nevertheless form a reasonable Hammett plot may mean that the induced polarization enters into all the reaction rates of this series in such a way that the logarithmic Hammett relationship still holds

A LIQUID SCINTILLATION COUNTER FOR C^{14} EMPLOYING AUTOMATIC SAMPLE ALTERNATION

J B Davidson A J Weinberger
G A Ropp

The vibrating reed electrometer when used with a Borkowski type ionization chamber is a standard instrument for the measurement of C^{14} The organic compound is burned to form $C^{14}O_2$ which when introduced into the ionization chamber produces a current that is measured by the electrometer [4]

A different approach one that does not require combustion of the organic material was suggested by earlier work on scintillation counting of C^{14} labeled compounds [13 14]

[12] E Hertel and J Dressel *Z physik Chem* **B29** 178 (1935)

[13] E C Farme a d J A Berstein *Science* **115** 460 (1952)

[14] F N H yes R D Hiebert and R L Sch h *Science* 116 140 (1952)

The use of refrigerated systems employing two photomultipliers two amplifiers and a coincidence circuit to reduce background has been described by several writers [15 16] and a commercially available unit has been recently introduced [17] These dual channel systems are characterized by high efficiencies for C^{14} (values as high as 75% have been reported) and by low backgrounds (100 to 200 counts/min) However the systems are bulky because refrigerators and rack mounting are required and the electronic circuiting is fairly complex These systems also require that the counting cell and contents be refrigerated to 0°C or below which generally decreases the solubility of the scintillator and the sample in the solvent Also they are expensive

Description of Equipment

In the instrument described below high accuracy preferably comparable to that obtained with the vibrating reed electrometer was of major consideration Since it seemed that a counter with one refrigerated phototube and one amplifier would be more stable easier to maintain and incidentally less expensive than one with two such units and a coincidence circuit plus a large refrigerator the first scheme was chosen The amplifier and scaling unit used in the counter to be described are those of a commonly used proportional counter thus a counter of this type may appeal to those who already possess such equipment In an attempt to reduce the effects of instrument drift and changes in background an automatic sample changer was incorporated so that three samples could be counted alternately for short intervals with the integrated counts stored on a separate register for each sample

Detector The detector is a 1P21 photomultiplier which is operated at liquid nitrogen temperature The tube rests with its base up on the bottom of a 500 ml Dewar flask and with its cathode facing a $1\frac{1}{4} \times 2$ in unsilvered window in the side of the flask The base of the phototube is partially removed by chucking the base end in a lathe and cutting away the upper part of the base until there is no mechanical connection with the glass envelope except that of the wire leads This is done in order to eliminate the strains on the envelope and on the soldered connections to the prongs of the base which are caused by the drastic cooling that occurs when liquid nitrogen is poured over the phototube

Although part of the base of the tube is removed the tube remains rigid and is easily plugged into a standard socket around which are wired the voltage divider resistors During operation these resistors are also at liquid nitrogen temperature The high voltage and signal leads to the phototube are No 10 solid wire and serve to keep the phototube in place in the Dewar flask These leads are brought out to connectors mounted on the side of the sheet brass housing The phototube output is developed across a 15 k resistor and is fed directly to the input of the amplifier through an 8 in coaxial cable

Sample Changer Since the measurements desired in many tracer studies are ratios of activity level above background of pairs of samples an alternating sample changer was included which would count in short cycles the cell series sample background and standard Figure 30 is a schematic diagram of the system It consists of a carriage operated by a yoke driven by a 10 rpm Bodine motor Inside the carriage housing are located three dpdt microswitches which stop the motion of the carriage position the cell being counted in front of the window switch in the appropriate register and start the timer At the end of the timing period which may be from 1 to 20 min the carriage moves the next sample in place and the timing cycle is repeated In order to position the cells accurately and to prevent the carriage from coasting through a position without counting a d c braking current is applied to the windings of the motor driving the carriage The positioning of each sample in front of the window is reproducible to within approximately ±0 5 mm By means of a switch either two or three samples may be included in the counting cycle

The cells used are standard rectangular spectrophotometer cells of approximately 19 ml capacity They are contained in removable holders which are held in position on the carriage by dowel pins On the back of the holder is an aluminum reflector The cell is held in the cell holder by means of a spring loaded yoke which also keeps the lid firmly on the cell and makes it lighttight except for the opening for the phototube Plate glass lids were used The dimensions of the window in the cell holder are several millimeters larger than those of

[15] R D Hiebert and R J Watts *Nucleonics* 11 No 12 38 (1953)

[16] J Arnold *Science* 119 155 (1954)

[17] Tracerlab Inc *Tracerlog* No 59 2 (April 1954)

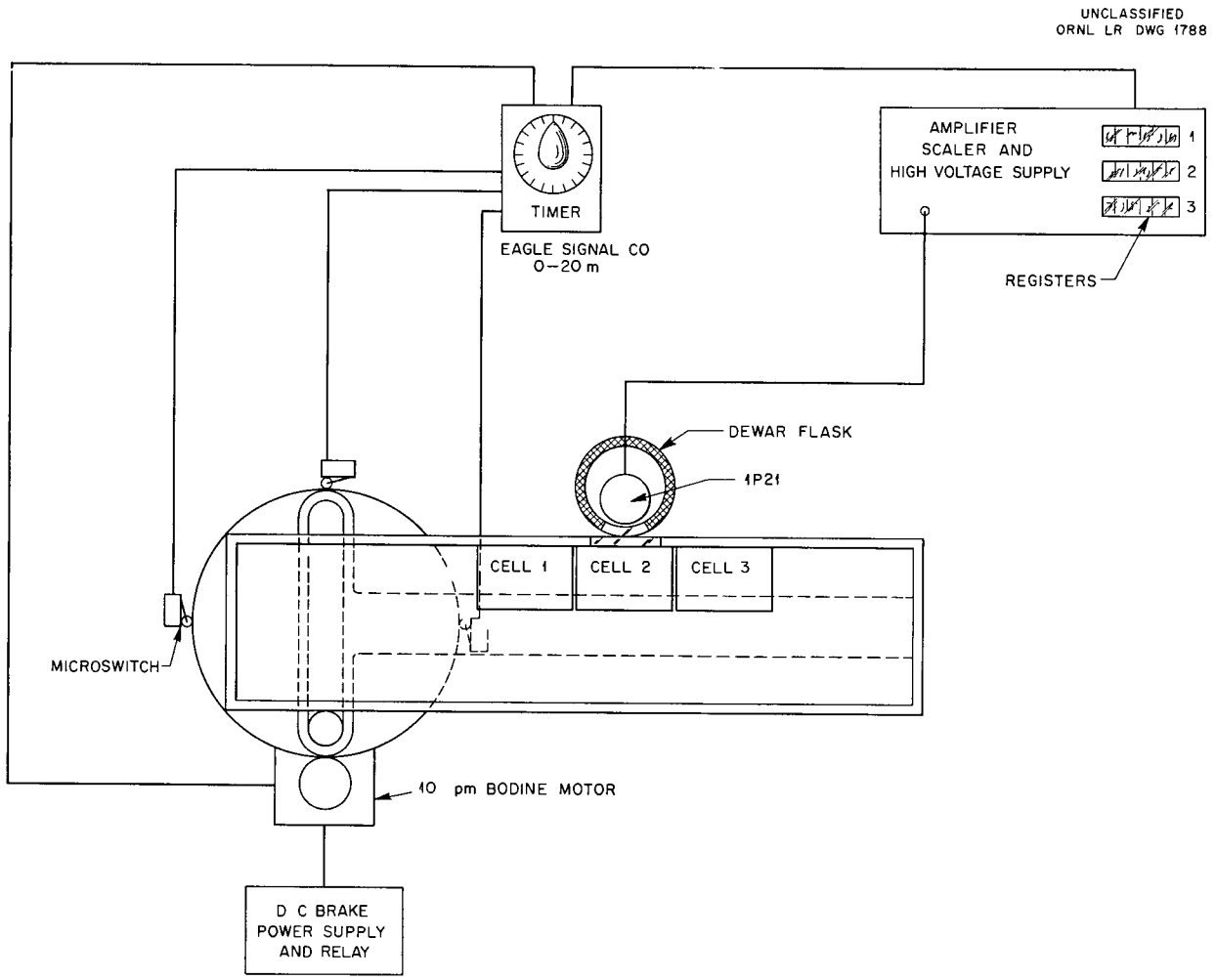


Fig 30 Schematic Diagram of Automatic Solution Scintillation Counter

the opening for the phototube and so the geometry is essentially constant The changer may be manually operated by setting the timer for a short interval say 5 sec and bringing the desired sample into position The timer is then turned off

Amplifier and Scaler The counter proper is a Nuclear Instrument and Chemical Co model 162 proportional counter which had been previously modified by the Chemistry Division Instrument Group for improved signal to-noise ratio and dynamic range when used as a proportional counter The modified circuit was retained except for the diode load at the input that was replaced by a 15 k resistor The high voltage supply was rebuilt according to ORNL Drawing Q 1144 1 The circuit was changed slightly to give 700 to 1400 v and was connected as a positive supply It possesses excellent regulation and is free from the tube selection which was necessary in the original model 162 supply The 0 to 1 ma meter in the counter was replaced with a 0 to 200 μa meter and provision was made for monitoring the phototube voltage with a potentiometer A switch operated by means of the sliding door of the cell housing removes the voltage from the phototube when the door is opened The scaler section of the counter was unchanged except for the mounting of the three registers on the front panel and the inclusion of a scaling factor switch The scaling factor switch allows the selection of the factor which stores the maximum number of counts on the registers without exceeding their speed limitations

Experimental Procedure

Preparation of Solutions for Test Runs A stock solution (I) of 8 5 g of recrystallized terphenyl in 2 liters of cp xylene was prepared Each cell used for counting background contained 15 ml of this solution Stock solution II was obtained by dis solving 20 mg (20 μc) of benzoic α-C^{14} acid in 1 liter of stock solution I Stock solution III was obtained by mixing equal volumes of solution I and solution II Thus all three stock solutions contained the same concentration of terphenyl but different concentrations of labeled benzoic acid Fifteen milliliters of solution II (0 30 μc) was pipetted into a clean cell and 15 ml of solution III (0 15 μc) was pipetted into a second clean cell in order to obtain a pair of cells with a 2 1 ratio of activities After each run the solutions were dis carded and the cells and their plate glass tops were washed thoroughly with xylene and then with acetone They were then dried No difference within experimental error was found when the cells holders and sample position were interchanged

Results Figures 31 and 32 show the curves of counting rate vs phototube voltage for background and a sample containing benzoic C^{14} acid Tables 8 and 9 show the precision obtained when the ratio of the activity above background of two benzoic acid samples was determined The shorter counting intervals as compared with the larger intervals give ratios which deviate somewhat less from the calculated value and from the mean The counting efficiency for C^{14} for the results in the tables was approximately 3%

Conclusions

A scintillation counter for C^{14} which uses so lution phosphors has been described This instru ment has been used to measure the activity ratio

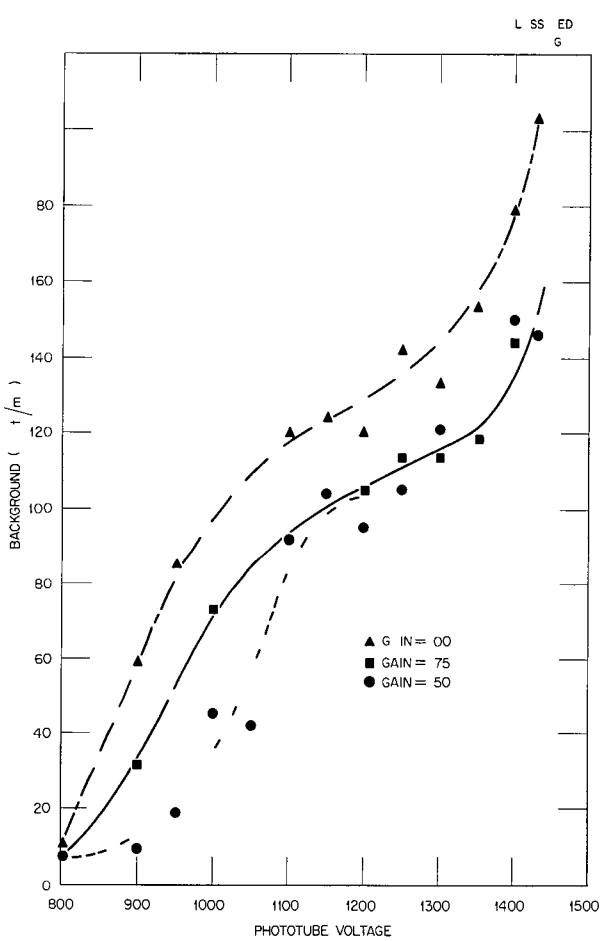


Fig 31 Background of Terphenyl Xylene Blank Cell

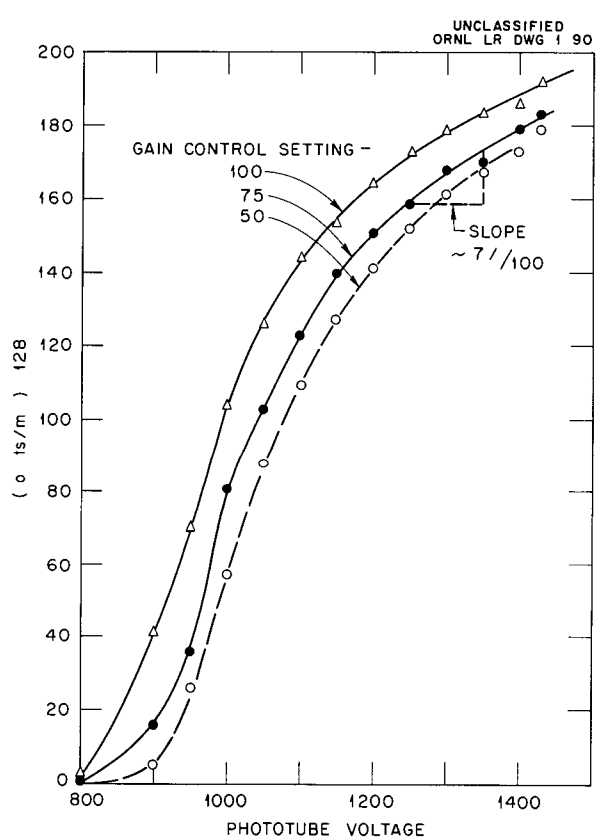


Fig 32 Carbon 14 Sample Counting Rate vs Phototube Voltage

TABLE 8 RATIOS OF SUCCESSIVE DAILY PAIRS OF SAMPLES HAVING A CALCULATED RATIO OF 2 000

Samples counted alternately for the nterval shown total counting time for a g ven nterval 4 hr

Interval Time (m n)	Sample Pair Numbe						Average for the Interval	Deviat on from the Calculated Rat o (%)
	1	2	3	4	5	6		
1	1 993						1 993	–0 4
5	1 981	1 973					1 977	–1 1
10		1 980	1 975				1 978	–1 0
20			1 970				1 970	–1 5
60				2 002	1 952	1 970	1 975	–1 3
120					1 934	1 996	1 965	–1 8

The dev at ons have negat ve val es because the countrate for each sample dec eased w th t me and because each run was started w th the lower act v ty sample

TABLE 9 RESULTS OBTAINED FROM COUNTING THE SAME PAIR OF SAMPLES OVER A PERIOD OF 32 hr FOR 1 min 1 h AND 2 hr INTERVALS

Calculated ratio = 2 000

4 hr Pe od from Which Ratio Was Taken	Rat o of Co nts from Ten 1 m n Inte vals	Ratio of Co nts from Two 1 hr Intervals	Rat o of Counts from Two 2 hr Inte vals
1	1 983	1 970	1 947
2	1 989	1 997	1 996
3	1 990	1 989	1 996
4	2 015	1 995	1 998
5	1 996	1 989	1 980
6	2 001	1 966	1 962
7	2 003		
Mean	1 997	1 984	1 980
Ave ge dev t o of mea	±0 008	±0 011	±0 017
Dev ation of mean from calculated value %	–0 15	–0 8	–1 0

of a pair of C^{14} containing solutions with an aver age deviation of approximately 0 5% from the mean and from the calculated value It employs automatic alternate counting of three cells one of which is usually a standard and one a background The alternating feature was designed to reduce possible effects of instrument drift and changing background on the results from long counting periods A series of experiments to test this feature are reported

The counter is simple electronically The me chanical parts are not difficult or expensive to build when adequate shop facilities are available

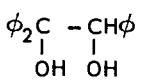
THE PINACOL REARRANGEMENT OF TRIPHENYLETHYLENE GLYCOL

C J Collins

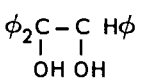
Introduction and Presentation of Results

Triphenylethylene glycol (I) has been labeled in four different positions with C^{14} as shown (Ia

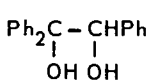
Ib $\alpha\beta$ *dl* Ic α-*dl* Ic) and each of these labeled species has been subjected to the pinacol rearrangement with the following separate catalysts concentrated sulfuric acid dilute sulfuric acid oxalic acid dihydrate and formic acid In addition Ia and $\alpha\beta$ *dl* Ic were rearranged in the presence of 100% sulfuric acid



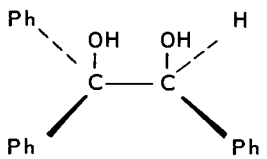
Ia



Ib



$\alpha\beta$ *dl* Ic



α *dl* Ic

The radiochemical structure of each labeled species was demonstrated by oxidation of the glycol with permanganate to benzoic acid and benzophenone followed by radioactivity assay of the 2 4-dinitrophenylhydrazone of the benzophenone fractions [18] The product from the pinacol rearrangement of the chain labeled glycols was chain labeled phenyl benzhydryl ketone (IIab) while the product from the pinacol rearrangement of the ring labeled glycol was ring labeled phenyl benzhydryl ketone (IIcd)

IIab IIcd

The radiochemical structures of the IIab and IIcd samples obtained were determined in the same way[18] as the radiochemical structures of the starting glycols In Table 10 are given the results of this study

In Chart 1 are shown four reaction paths which may be taken by triphenylethylene glycol (I) Shown in Table 11 is the per cent C^{14} rearrangement which would be expected in the product obtained through each path by which phenyl benzhydryl ketone may be formed when Ia and Ic are subjected

[18] W A Bonner and C J Collins *J Am Chem Soc* 75 5372 (1952)

TABLE 10 RADIOCHEMICAL RESULTS OF PINACOL REARRANGEMENT OF CHAIN AND RING LABELED GLYCOLS

Catalyst	P oduct	Radiochemical Rearrangement (%) for Starting Compounds			
		Ia	Ib	$\alpha\beta$ *dl* Ic	α-*dl* Ic
Concentrated H_2SO_4 cold	IIab	7 5 ± 0 4	3 6 ± 0 1		
	IIcd			30 7 ± 0 2	29 7 ± 0 2
100% H_2SO_4	IIab	6 9 ± 0 3			
	IIcd			30 3 ± 0 1	
D lute H_2SO_4 reflux	IIab	8 3 ± 0 5	4 5 ± 0 1		
	IIcd			7 2 ± 0 5	7 7 ± 0 3
$(COOH)_2$ $2H_2O$ reflux	IIab	7 6 ± 0 2	3 8 ± 0 1		
	IIcd			20 9 ± 0 1	18 3 ± 0 1
HCOOH reflux	IIab	9 0 ± 0 3	4 7 ± 0 5		
	IIcd			21 8 ± 0 1	20 3 ± 0 1

CHART 1

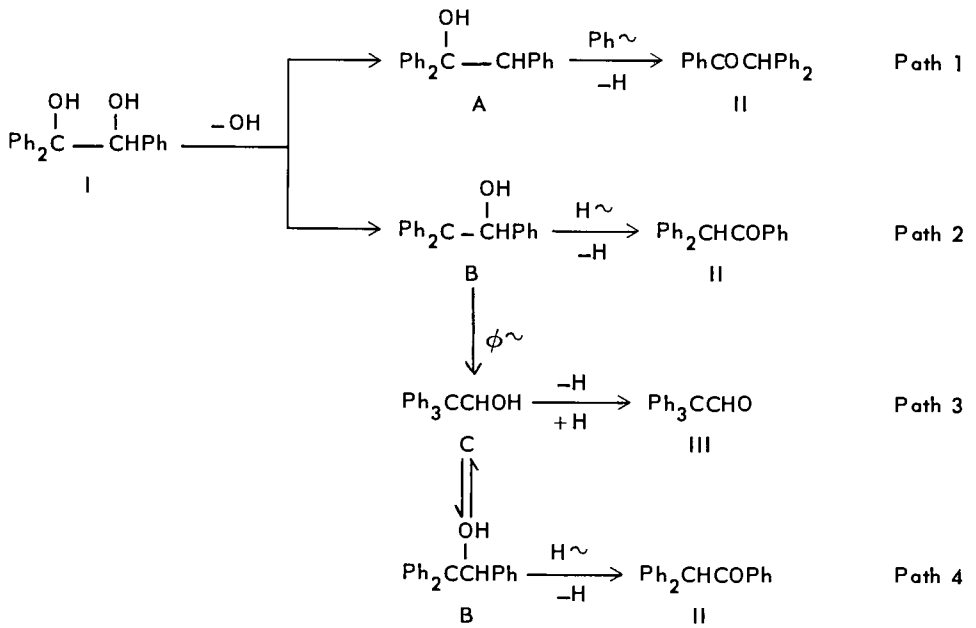


TABLE 11 RELATION OF REACTION PATH TO C^{14} DISTRIBUTION IN THE PINACOL REARRANGEMENT OF CHAIN AND RING LABELED TRIPHENYLETHYLENE GLYCOL

Rea t nt	Path Thro gh Wh ch Prod ct Is Formed	Product	C^{14} Rearrangeme t (%)
OH OH Ph2C - CHPh Ia	Path 1	PhC OCHPh2 IIb	100
	Path 2	Ph2C HCOPh IIa	0
	Path 4	Ph2C HCOPh IIa	0
OH OH Ph2C - CHPh Ic	Path 1	Ph COCHPh2 IIcd	50
	Path 2	Ph2CHCOPh IIc	0
	Path 4	Ph2CHCOPh IIcd	33 3

to the pinacol rearrangement In Table 12 is given the contribution of each of these paths under each of the five reaction conditions employed with the data for Ia and $\alpha\beta$ *dl* Ic being used for the calculations

TABLE 12 CONTRIBUTIONS OF REACTION PATHS 1 2 AND 4 UNDER VARIOUS REACTION CONDITIONS DURING THE TRANSFORMATION I ⟶ II

Reaction Cond tions	Contribution of Paths (%)		
	1	2	4
Dilute H_2SO_4 reflux	8	82	10
Concentrated H_2SO_4 cold	7	12	81
100% H_2SO_4 cold	7	12	81
Oxalic acid dihydrate refl x	8	41	51
Formic acid reflux	9	39	52

Expressed as the nearest whole number

Discussion

From Table 10 the following conclusions may be drawn

1 An isotope effect attends the pinacol rearrangement of either Ia Ib or both or an isotope effect must attend the permanganate oxidation of IIab since the apparent per cent rearrangement when Ib is subjected to any of the four reaction conditions employed is always less than the apparent per cent rearrangement when Ia is subjected to the same conditions The reaction which exhibits this isotope effect is now being sought

2 The increase in importance of Path 4 as the catalyst is changed from dilute to concentrated sulfuric acid must mean that the ions of Chart 1 are allowed a longer half life in the more strongly ionizing medium

3 That identical results were obtained for Ia in concentrated sulfuric acid and in 100% sulfuric acid and for $\alpha\beta$ *dl* Ic in these same media is taken to mean that the intrinsic migratory aptitudes of phenyl and hydrogen stand in the approximate ratio of 81 12

4 A comparison of the data for $\alpha\beta$ *dl* Ic and for α-*dl* Ic fails to reveal whether or not Path 1 proceeds in a concerted fashion under any of the conditions employed

CHEMICAL PHYSICS

EXPERIMENTS IN CHEMICAL KINETICS WITH MOLECULAR BEAMS

S Datz E H Taylor

Scattering-reaction experiments with molecular beams of potassium and of HBr have been extended by varying the temperature of the HBr The small amount of KBr previously reported was found to vary in the expected manner that is to increase with increase in HBr temperature

Because of the non Maxwellian distribution of velocities in a beam and because all collisions are at right angles the Arrhenius equation is not the appropriate one to use in relating the reaction probability to the energy of activation The proper expression for the fraction of all collisions having a relative velocity at least equal to v is

$$G = \frac{\alpha_1^2\alpha_2^2}{(\alpha_1 - \alpha_2)^2}\left\{\frac{e^{-\alpha_1 v^2}}{\alpha_1}\left[\frac{3\alpha_1 - \alpha_2}{\alpha_1(\alpha_1 - \alpha_2)} + v^2\right] - \frac{e^{-\alpha_2 v^2}}{\alpha_2}\left[\frac{3\alpha_2 - \alpha_1}{\alpha_2(\alpha_1 - \alpha_2)} - v^2\right]\right\}$$

where $\alpha_1 = m_1/2kT_1$ and $\alpha_2 = m_2/2kT_2$ in which the m s are the masses and the T s are the temperatures of the two beams For the conditions of the present experiments the fraction G varies with HBr temperature almost entirely because of terms not containing v so no very good value for the activation energy is obtainable from these first experiments with temperature variation A new potassium oven has been built which will allow the pressure and temperature of the potassium to be controlled independently of each other and experiments are under way to measure the activation energy by its use

Considerable difficulty has been experienced with reflection of the primary potassium beam from parts of the apparatus moving with the detector even when such parts are near 77°K Such reflections striking the two detector wires unequally may give rise to apparent positive or negative KBr at certain angles Although the distribution of real KBr within the region of these anomalies is not precisely known it is almost certain that the spurious effects vanish before the region of maximum KBr is reached (from about 25 deg outward from the line of the potassium beam) The observation of a temperature coefficient in reasonable agreement with that expected from the distribution function lends further support to the reality of the KBr being observed

RADIO FREQUENCY SPECTROSCOPY

Paramagnetic Resonance

R Livingston H Zeldes
E H Taylor

The paramagnetic resonance equipment previously described[1] has been rebuilt and the nature of the measurements has been considerably extended The basic equipment change has been the completion of a new magnet with a greatly improved field homogeneity (approximately 0 1 gauss over the usual sample size) and low leakage flux Work has been started on an improved current regulated power supply for the magnet

Final measurements have been made on atomic hydrogen formed in H_2SO_4 H_3PO_4 and $HClO_4$ irradiated at 77°K with Co^{60} gamma rays these measurements have been published[2] The hydrogen hyperfine separation was very close to the atomic beam value clearly indicating the presence of atomic hydrogen

The considerable effort that has been made to observe atomic hydrogen in ice irradiated at 77°K was not successful In the course of the work it was found that atomic hydrogen could be stably formed at 77°K in high concentrations on glass surfaces as a product of adsorbed water In typical experiments glass beads containing uniform pores of 71 Å and also 36 Å and previously exposed to atmospheric moisture were irradiated Very strong atomic hydrogen lines were seen after a few days of irradiation at 77°K in a 1000 curie Co^{60} source Covering similar beads with D_2O for 30 hr then freezing and cooling to 77°K and irradiating for a

[1] R Liv g ton H Zelde and E H Taylo *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 58

[2] R L v ng ton H Zeldes and E H Taylor *Phys Rev* 94 725 (1954)

few days gave both atomic hydrogen and deuterium lines The concentration of atomic hydrogen was higher than that of deuterium in the beads with a pore size of 36 Å while the reverse was true for the 71 Å pore size these differences in concentration seemed to be an indication of the diffusion and exchange of D_2O for H_2O inside the glass beads

In order to further understand an inability to find atomic hydrogen in gamma irradiated ice at 77°K a number of additional experiments have been started One has been the study of the strength of the atomic hydrogen lines in various dilutions of sulfuric acid In one preliminary experiment in which a one day irradiation at 77°K in a 1000 curie Co^{60} source was used the hydrogen lines were seen with signal to noise ratios of approximately 20 1 in 10 1 (mole ratio H_2O H_2SO_4) acid 3 1 in 100 1 acid and roughly 1 1 in 500 1 acid The line was just detectable in 2000 1 acid and not detectable in 10 000 1 acid There seemed to be no gross change in the width of the lines or in the hyperfine separation

The Phosphorus Problem

B Benjamin R Livingston

Cooperative experiments have been resumed with Duke University on determining the nuclear moments of P^{32} The present plans are to examine the $J = 0 \rightarrow 1$ rotational transition of PD_3 which appears at about 139 000 Mc A microwave spectrometer to be used as an analytical tool has been constructed by the Duke group and assembled at ORNL The main problem is to devise a method of synthesizing PD_3 on a 1 μg level The general method being tried has been to fuse the microgram quantities of starting phosphorus as a phosphate with calcium metal The cooled melt containing calcium phosphide that is reacted with D_2O yields PD_3 D_2 and excess D_2O as gaseous products The PD_3 is separated from these products and analyzed in the microwave spectrometer It was necessary to use a fluorinated stopcock grease to eliminate hydrogen exchange with the PD_3

In several initial experiments the calcium fusion was carried out in a tantalum crucible with a silica liner An inert atmosphere of argon was used and the crucible was heated with an induction heater Very weak microwave absorption signals were seen with as little as 10 μg of starting phosphorus as Na_2HPO_4 however the results were not consistent and usually large amounts of foreign gases were also formed

A more satisfactory crucible liner has been needed and tests have been made with stainless steel platinum calcium fluoride pressed powder beryllium oxide pressed powder magnesium oxide crystal sintered aluminum oxide and others Lithium metal and sodium metal fusions have also been tried The best results so far have been obtained with a calcium metal fusion in a calcium fluoride crystal crucible A DCl solution reacts with the melt much better than D_2O but gives the added problem of more purification of the gaseous product With the use of 10 μg of phosphorus good microwave signals have now been seen and an effort will soon be made to further reduce the scale

NEUTRON DIFFRACTION STUDIES

H A Levy S W Peterson
J E Worsham Jr

Positions of Hydrogen Atoms in Urea Crystals

Recent interest[3-6] in the structure of the amide group in organic compounds along with attacks on the problem of protein structure indicates the desirability of a precise determination of the positions of hydrogen atoms in this group by diffraction measurements Several amides have already been studied in this fashion by means of xrays[7 8 9] However x ray diffraction methods failed to give precise information regarding hydrogen atom positions because of the weak scattering of hydrogen compared with that of the other heavier atoms present It seemed that neutron diffraction techniques could contribute important information in this case

Principally two considerations led to the choice of urea as the crystal for study Urea is a simple tetragonal crystal space group $P\bar{4}\,2_1m$ with only

[3] W W Bates and M E Hobbs *J Am Chem Soc* 73 2151 (1951)

[4] L Pauling R B Corey and H R Branson *Proc Nat Acad Sci U S* 37 205 (1951)

[5] G R Leader and J F Gormley *J Am Chem Soc* 73 5731 (1951)

[6] J E Worsham Jr and M E Hobbs *J Am Chem Soc* 76 206 (1954)

[7] P Vaughn and J Donohue *Acta Cryst* 5 530 (1952)

[8] F Senti and D Harker *J Am Chem Soc* 62 2008 (1940)

[9] G B Carpenter and J Donohe *J Am Chem Soc* 72 2315 (1950)

two molecules per unit cell making it possible to obtain a two dimensional Fourier projection with all the atoms nearly completely resolved and a recent complete analysis of x ray data was available for this crystal Two disadvantages to this choice are the large temperature motion in the crystal and the objection that urea might not be a typical amide

Previous x ray studies[7] indicated that a Fourier projection in the $h0l$ zone would show the hydrogen atoms to be reasonably well resolved

All data were taken at room temperature The spectrometer used is very similar to one described by Wollan and Shull [10] Integral peak intensities were measured for all $h0l$ zone reflections accessible to the instrument that is $\sin \theta/\lambda \leq 0\ 77$ Experimental structure factors were put on an absolute basis by calibrating the instrument with the 400 reflection of a NaCl crystal

The specimen used for study was a cylinder 3 17 mm in diameter weighing 41 6 mg a basal axis ($h0l$ zone axis) being the cylinder axis This cylinder was cut from a cube $1 \times 1 \times 1\frac{1}{2}$ cm grown by evaporation at 43°C from a solution containing urea ammonium bromide and water in the proportions 4 2 2 2 1 0 respectively [11] Before the cylinder was mounted for measurement it was chilled several times by dipping it in liquid nitrogen to decrease extinction effects

[10] E O Wollan ond C G Shull *Phys Rev* 73 830 (1948)

[11] C W B nn *P oc Roy Soc (London)* A141 567 (1933)

TABLE 13 TEMPERATURE FACTORS OF ATOMS IN UREA

	C	O	N	H(1)	H(2)
α	3 0	3 2	5 5	6 0	6 5
β	1 0	1 2	1 3	3 5	2 0

In order to assign phases to the observed reflections a set of structure factors was calculated on the basis of the x ray data of Vaughn and Donohue and on the assumption that the N H bond lengths were 1 00 Å and the H N H and C N H angles were 120 deg The signs of these structure factors were tentatively assigned to the experimental structure factors and a Fourier map was calculated By repeated comparisons of calculated and experimental maps and back shifting of parameters the calculated structure factors were brought into agreement with the observed ones The average discrepancy

$$\frac{\Sigma(|F_{ob}| - |F_{c\ lc}|)}{\Sigma|F_{ob}|}$$

is 6 9% omitting those reflections which measured zero

That there is a large temperature motion of the urea molecules at room temperature is shown by the large values of α and β in the temperature factor expression

$$\exp - \left(\frac{\alpha b^2}{4a^2} + \frac{\beta l^2}{4c^2}\right)$$

(see Table 13) The especially large α values indicate this to be an anisotropic temperature motion with the greatest amplitude parallel to the $a\ b$ plane The increase of α with the perpendicular distance from the C O axis suggests a libration about this axis in addition to the other thermal vibrations that give more nearly isotropic average displacements

The atom parameters of this work are given in Table 14 and are compared with the most recent x ray data [7] When the uncertainties introduced by the large temperature motion are considered the parameters of the heavy atoms seem to be in reasonable agreement

The bond angles and interatomic distances determined by this work are given in Table 15 and

TABLE 14 ATOMIC PARAMETERS IN UREA

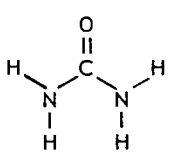
	z_C	z_O	x_N	z_N	$x_{H(1)}$	$z_{H(1)}$	$x_{H(2)}$	$z_{H(2)}$
Data of Va ghn and Donohue	0 3308	0 5987	0 1429	0 1848				
ORNL data	0 334	0 595	0 144	0 183	0 259	0 284	0 141	0 975

TABLE 15 INTERATOMIC DISTANCES AND BOND ANGLES IN UREA

	C N	C O	N H(1)	N H(2)	N O	N O	H(1) O	H(2) O
D stance (Å)								
Data of Vaugh and Donoh e	1 34	1 24			3 04	2 99		
ORNL d ta	1 36	1 23	1 04	0 98	3 04	3 00	2 01	2 12

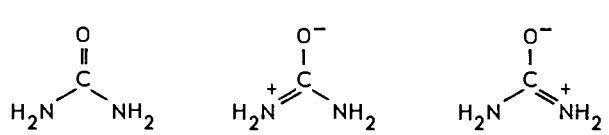
	N C O	H(1) N C	H(2) N C	H N H	N H(1) O	N H(2) O
Angle (deg)						
Dat of Vaughn and Donohue	121					
ORNL data	122	121	120	119	169	149

are compared with the most recent x ray data The values definitely indicate the symmetrical planar configuration of urea shown in the following diagram



There are two kinds of hydrogen atoms in the urea crystal the hydrogen *trans* to the carbonyl oxygen is designated as H(2) and the other as H(1) That these hydrogen atoms participate in hydrogen bonding to quite different extents is apparent from the respective N H distances N H(1) = 1 04 Å N H(2) = 0 98 Å The differing extent of partici pation is also indicated by the fact that H(1) is more nearly on the line connecting hydrogen bonded atoms than is H(2) thus the angle N H(1) O is 169 deg and N H(2) O is 149 deg

The C N bond shortening of 0 12 Å as compared with the normal C N length[12] of 1 48 Å and the C O bond lengthening of 0 03 Å as compared with the normal C=O length of 1 20 Å adopted by Vaughn and Donohue[7] have been explained by the latter authors on the basis of resonance between forms A B and C



A B C

[12] V Schomaker and D P Stevenson *J Am Chem Soc* 63 37 (1941)

having contributions of 40 30 and 30% respec tively This explanation also accounts for the coplanarity of the hydrogen atoms observed in this work

On the basis of N H bond stretching force con stants determined by infrared absorption spectra Richards[13] has suggested sp^2 hybridization of the N H bonds The C N H and H N H bond angles of about 120 deg agree with the geometry of this type of hybridization The short N H(2) bond distance of 0 98 Å found in this investigation compared with 1 01 Å in ammonia is in accord with the increased overlap from sp^2 hybridization as com pared with the hybridization of less *s* character of the N H bonds in ammonia[14] This is analogous to the shorter C H bond length found in ethylene as compared with that found in methane The length ening of the N H(1) bond to 1 04 Å is consistent with its greater participation in hydrogen bonding Calculated and observed structure factors are listed in Table 16

LOW TEMPERATURE CALORIMETRY

Heat Capacity of Cadmium Iodide

A S Dworkin D J Sasmor
E R Van Artsdalen

The heat capacity of a second sample of crystal line cadmium iodide CdI_2 has been measured in the temperature range between about 240 and 290°K

[13] R E Richards *Trans Faraday Soc* 44 40 (1948)

[14] C A Coulson *Valence* p 198 Clarendon Press Oxford 1952

TABLE 16 CALCULATED AND OBSERVED STRUCTURE FACTORS FOR *h0l* ZONE OF UREA OBTAINED BY NEUTRON DIFFRACTION

h0l	F_c	$\|F\|_o$	*h0l*	F_c	$\|F\|_o$
001	−1 25	1 23	400	−0 09	0 17
002	−2 71	2 74	401	−1 02	1 07
003	−3 44	3 26	402	1 99	1 96
004	−3 08	2 90	403	2 53	2 71
005	2 46	2 44	404	−0 60	0 53
006	1 77	1 64	405	−0 31	0 34
007	−0 89	0 82	406	0 42	0 43
101	2 66	2 55	501	0 12	0 00
102	1 73	1 84	502	−0 29	0 48
103	−1 24	1 31	503	−0 55	0 59
104	0 19	0 28	504	1 04	1 10
105	−1 39	1 28	505	−0 50	0 49
106	0 80	0 79	506	−0 30	0 00
107	2 47	2 63	600	−1 71	1 92
200	−3 00	2 72	601	0 64	0 55
201	1 76	1 74	602	0 77	0 87
202	0 49	0 64	603	−0 17	0 33
203	−2 61	2 67	604	0 55	0 64
204	0 48	0 61	605	−0 29	0 20
205	0 45	0 42	701	−0 57	0 81
206	0 30	0 30	702	−0 32	0 28
301	1 91	1 86	703	0 35	0 30
302	1 93	2 06	704	−0 16	0 20
303	0 43	0 50	800	0 56	0 55
304	2 72	2 71	801	−0 31	0 28
305	0 35	0 39	802	−0 12	0 00
306	1 30	1 34			

to check the opparent anomaly reported previously [15] This sample of CdI_2 was heated at about 150°C under high vacuum for several days and was occasionally purged with helium A different calorimeter can was used in this set of measurements A peak was found in these measurements which corresponded quite exactly in magnitude and temperature with that reported previously The shape of the peak is similar to that associated with lambda transitions However the heat and entropy involved are extremely small about 2 cal/mole and 0 01 eu respectively These results indicate no changes in the thermodynamic constants of CdI_2 reported earlier

[15] A S Dwo k D J Sasmo a d E R Van Artsdalen *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 60

HIGH TEMPERATURE CALORIMETRY

D J Sasmor J E Sutherland
E R Van Artsdalen

An adiabatic heat capacity calorimeter has been built for use in the temperature range from room temperature to 1000°C Certain unique features have been incorporated into the design and construction of the calorimeter and its associated control and measuring equipment It is intended to use this calorimeter to determine the heat capacities of materials in the high temperature range with sufficient accuracy and precision to detect and measure temperatures and heats of transition and change of state It is expected that information will be obtained which will be useful in elucidating solid state structure as well as structure and chemical properties of fused salts High temperature heat capacity data when combined with known low temperature thermodynamic properties will enable the reliable determination of high temperature thermodynamic quantities Thus it is anticipated that more exact determinations of free energies of formation of pure compounds can be obtained than were heretofore available in the high temperature range Heat capacity measurements on mixtures of molten salts should enable the determination of accurate values for heats of mixing from which in turn relevant information about activity coefficients can be derived

The main features of the calorimeter are shown schematically in Fig 33 The calorimeter can the adiabatic shield and the furnace are constructed of pure nickel The radiation shields are fabricated from stainless steel while the outer can which is water cooled is made of brass Furnace and adiabatic shield windings are of nichrome V threaded through Stupakoff interlocking beads and wound in grooves machined into the calorimeter parts The calorimeter heater is made of nichrome V B&S gage No 26 wound on a machined lavite form The resistance of the heater is 1 94 ohms at 25°C The entire assembly operates in a deep vacuum

Temperature control of the adiabatic shield and furnace is maintained by means of platinum platinum–13% rhodium differential thermocouples (located as shown in Fig 34) which operate through the elaborate automatic controllers shown in Fig 35 The potentials of the differential thermocouples for control of the adiabatic shield are

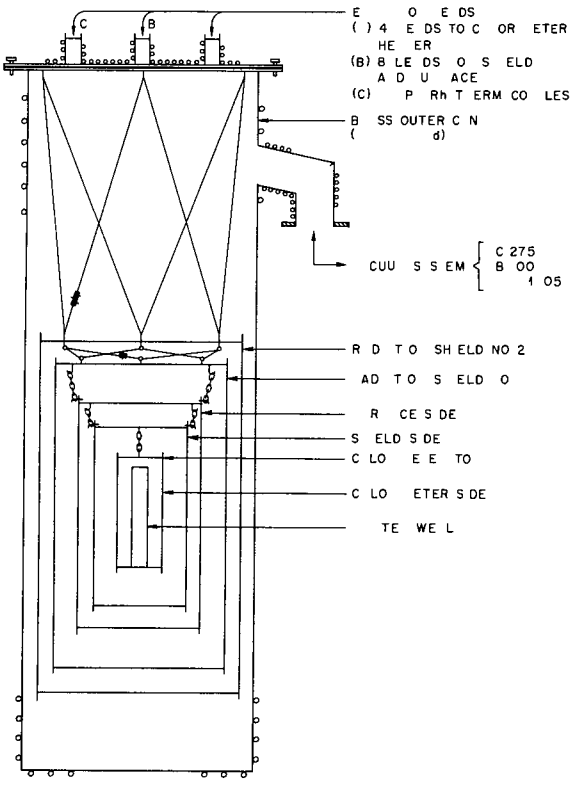


Fig 33 High Temperature Adiabatic Calorimeter Assembly

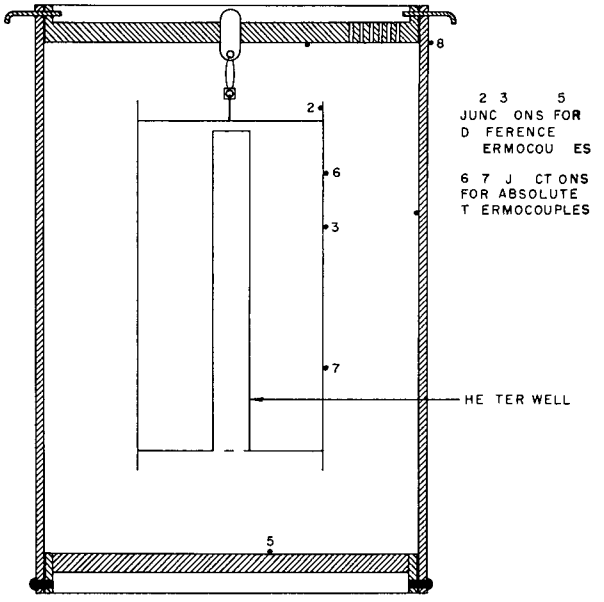


Fig 34 High Temperature Adiabatic Calorimeter Detail Showing Thermocouple Locations

amplified by Liston Becker model 14 microvolt amplifiers and fed into Speedomax PAT recorder controllers which drive autotransformers for control of heater voltage in the manner shown in Fig 35 A unique feature of this control circuit is the interaction between side and top can and shield controls A simpler system also shown in Fig 35 is used for control of the furnace temperature when less precise temperature regulation is required

Absolute temperature of the calorimeter is measured by platinum platinum–13% rhodium thermocouples which were calibrated by the National Bureau of Standards Potentials of the couples are measured with a Rubicon type B potentiometer Bureau of Standards calibration points for the thermocouples were fitted to an eighth power polynomial by the Mathematics Panel by use of the ORACLE and potentials were tabulated at 1 deg intervals

The addition and measurement of heat supplied to the calorimeter can by means of the calorimeter heater are indicated in Fig 36 The calorimeter has been designed to operate as a constant current device rather than as the usual constant voltage mechanism Timing is accomplished by an electric clock operating from a fixed frequency (60 000 ± 0 0005 cps) high precision oscillator manufactured by Riverbank Laboratories The constant current supply for the calorimeter heater during experiments operates on a dummy circuit for stability purposes when not actually passing through the heater

Preliminary tests of the entire apparatus have been successful It appears that the adiabatic shield can be controlled automatically to within 0 01°C of the temperature of the calorimeter can The furnace is lagged 5 or 10 deg behind the adiabatic shield in order to maintain positive control over the shield A few minor difficulties have been experienced and as soon as corrections have been made to eliminate them a final electrical calibration will be made After electrical cali

bration it is planned to make a second check of the calibration and accuracy of the calorimeter by using a standard sapphire sample which has been calibrated by the National Bureau of Standards

J F Potts of the Instrument Department has been responsible for the development and building of control and heater circuits Detailed specification and performance reports will be issued later

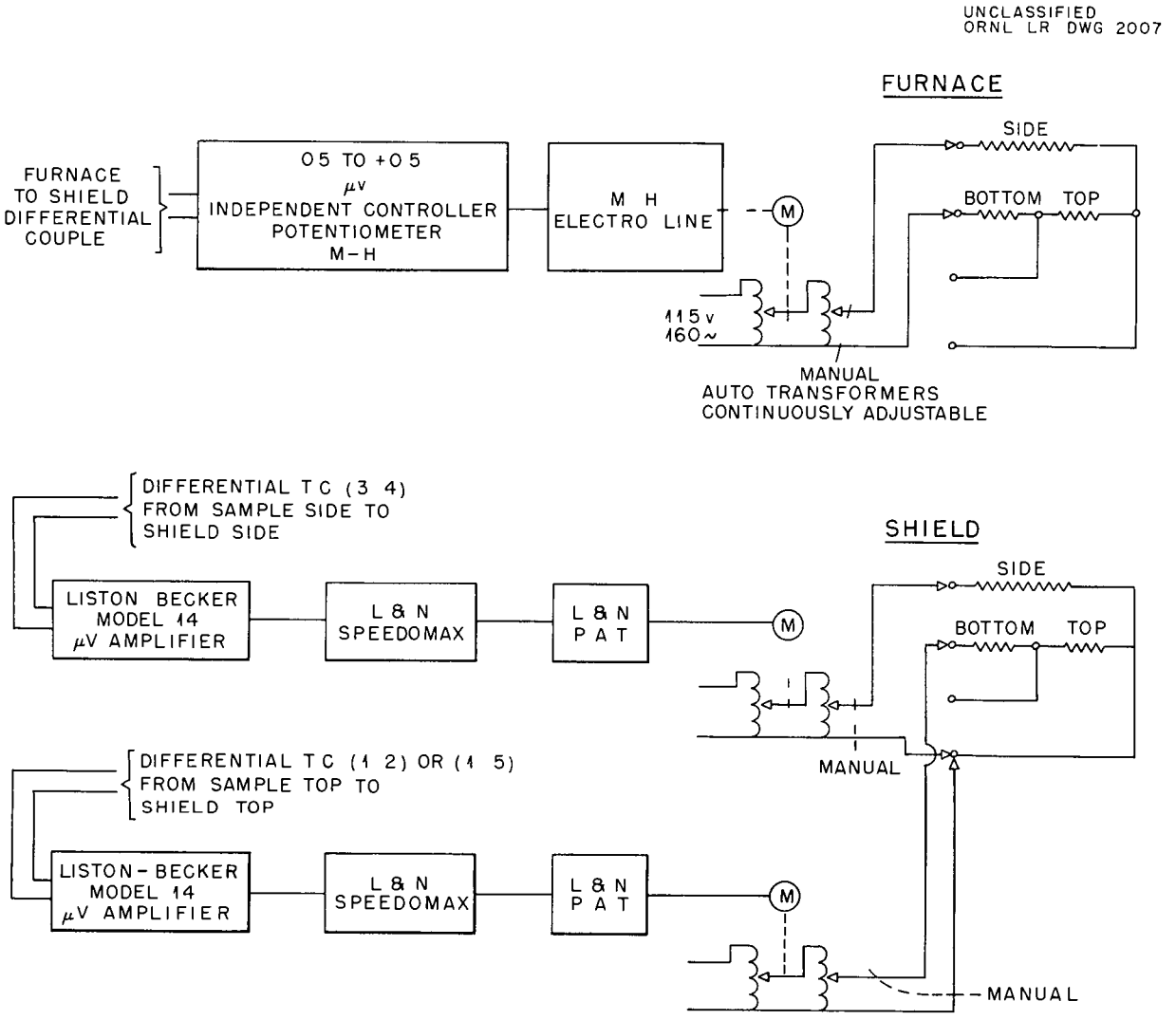


Fig 35 Block Diagram of Furnace and Shield Control Circuits

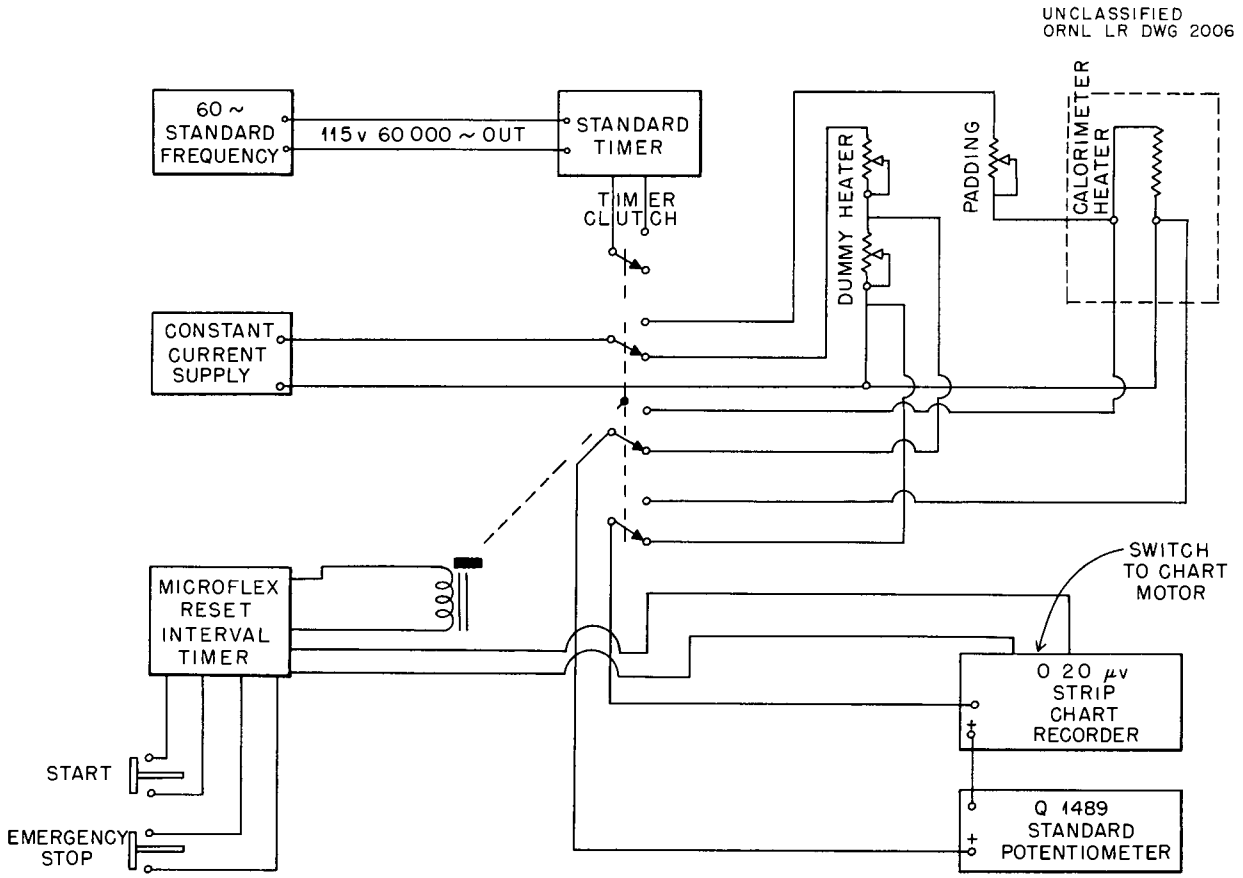


Fig 36 Block Diagram of Heater and Timer Circuits

RADIATION CHEMISTRY

HYDROGEN PEROXIDE FORMATION BY COBALT GAMMA RADIATION

T J Sworski

The chemical effects of ionizing radiation on water and aqueous solutions have been interpreted as resulting from the formation of the radicals[1] H and OH and the product molecules[2] H_2 and H_2O_2. It has become useful to express the formation of these products in the decomposition of water by the following equations [3]

$$(F) \qquad 2H_2O \longrightarrow H_2 + H_2O_2$$

$$(E) \qquad 2H_2O \longrightarrow 2H + H_2O_2$$

$$(R) \qquad H_2O \longrightarrow H + OH$$

The yields of the four reaction products (H_2 H_2O_2 H and OH) in molecules per 100 ev are denoted by G_{H_2} $G_{H_2O_2}$ G_H and G_{OH} F R and E represent the yields of the corresponding reactions in molecules per 100 ev In this notation[3] $F = G_{H_2}$ $E = G_{H_2O_2}$ G_{H_2} $R = G_{OH}$

Bromide ion is a radical scavenger in water subjected to ionizing radiation [2] The initial yield of H_2O_2 in oxygen free acidic KBr solutions equal to G_{H_2} is independent of KBr concentration over a wide range [4] The initial yield of H_2O_2 in KBr solutions containing O_2 is dependent upon the KBr concentration[5] (see Figs 37 and 38) It is proposed[5] that the initial yield of H_2O_2 in KBr solutions containing O_2 is equal to $F + 2E$ when KBr is present in concentrations equal to or greater than 10^{-5} M The dependence of the H_2O_2 yield upon the KBr concentration in KBr solutions containing O_2 is interpreted as an indication that KBr (even at concentrations as low as 10^{-5} M) decreases $G_{H_2O_2}$ by reaction of bromide ion with OH radical in regions of high ionization density according to reaction 1 before the OH radicals combine according to reaction 2

$$(1) \qquad Br^- + OH \longrightarrow Br + OH^-$$

$$(2) \qquad OH + OH \longrightarrow H_2O_2$$

Chloride ion known to react with the OH radical in acidic aqueous solutions [6] is also a radical

[1] J Weiss *Nature* 153 748 (1944)
[2] A O Allen *et al* *J Phys Chem* 56 575 (1952)
[3] A. O Allen *Radiation Research* 1 85 (1954)
[4] H Fr cke and E J Hart *J Chem Phys* 3 596 (1935)
[5] T J Sworski *J Am Chem Soc* 76 (in press)
[6] H Ta be and W C B ay *J Am Chem Soc* 62 3357 (1940)

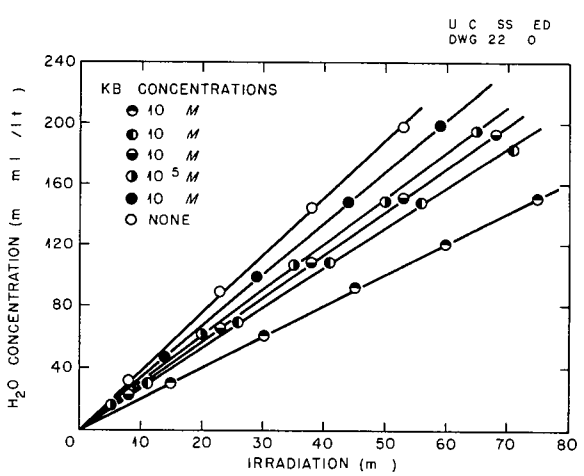


Fig 37 Effect of Bromide Ion Concentration on the Yield of H_2O_2 by Cobalt Gamma Irradiation of Air saturated Sulfuric Acid Solutions at a pH of 2 Dose rate 1 76 × 10^{20} ev/liter/min

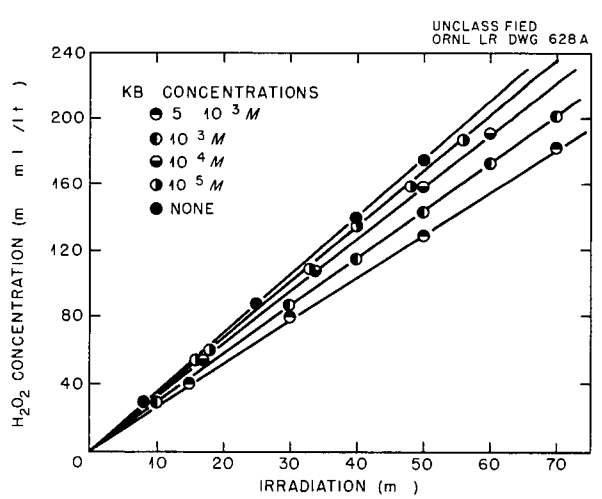


Fig 38 Effect of Bromide Ion Concentration on the Yield of H_2O_2 by Cobalt Gamma Irradiation of Air saturated 0 8 *N* Sulfuric Acid Solutions Dose rate 1 80 × 10^{20} ev/liter/min

scavenger in acidic aqueous solutions [2] When air saturated KCl solutions are subjected to cobalt gamma radiation the initial yield of H_2O_2 is also dependent upon the concentration of KCl (see Figs 39 and 40) The effect of KCl concentration is interpreted as being identical to that of KBr At any particular KCl concentration the chloride ion more effectively decreases $G_{H_2O_2}$ in 0 8 *N* sulfuric acid than in sulfuric acid solutions at a pH of 2 (see Fig 41) This pH sensitivity of the chloride ion effect is interpreted as additional experimental evidence supporting the suggestion[5] that halide ion decreases $G_{H_2O_2}$ by its reaction with the OH radical in regions of high ionization density While KBr is a radical scavenger independent of pH KCl is a radical scavenger only in solutions with pH less than 4 (Refs 2 and 4)

This study of aqueous halide solutions has resulted in a new determination[5] of the initial yields of primary products in the decomposition of water These yields are listed in Table 17 The initial yield of H_2O_2 in 10^{-3} *M* KBr solutions was used in previous determinations[7] of the yields of the primary products

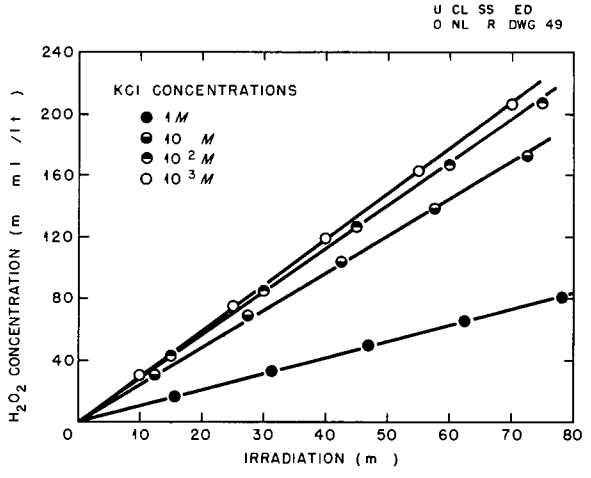


Fig 39 Effect of Chloride Ion Concentration on the Yield of H_2O_2 by Cobalt Gamma Irradiation of Air saturated Sulfuric Acid Solutions at a pH of 2 Dose rate 1 74 × 10^{20} ev/liter/min

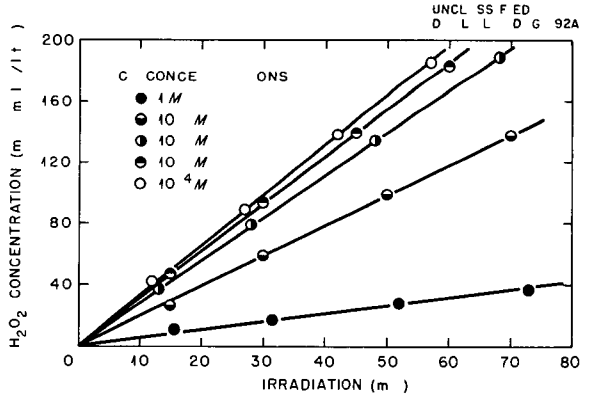


Fig 40 Effect of Chloride Ion Concentration on the Yield of H_2O_2 by Cobalt Gamma Irradiation of Air saturated 0 8 *N* Sulfuric Acid Dose rate 1 76 × 10^{20} ev/liter/min

[7] T J Sworski *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 74

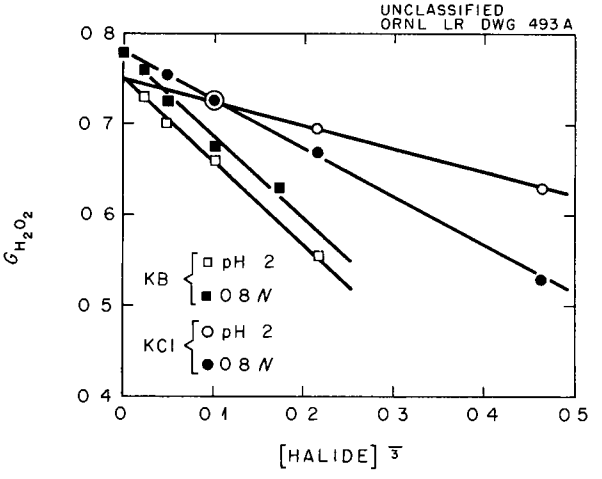


Fig 41 $G_{H_2O_2}$ as a Function of Halide Ion Concentration

TABLE 17 EFFECT OF H_2SO_4 CONCENTRATION UPON THE YIELDS OF PRIMARY PRODUCTS IN THE DECOMPOSITION OF WATER

	Sulfuric Acid	
	0 8 *N*	pH = 2 0
G_{H_2}	0 39	0 42
$G_{H_2O_2}$	0 78	0 75
G_H	3 70	2 78
G_{OH}	2 92	2 12

YIELDS OF HYDROGEN AND HYDROGEN PEROXIDE IN THE IRRADIATION OF OXYGEN SATURATED WATER WITH COBALT GAMMA RAYS

J A Ghormley C J Hochanadel

In the radiation chemistry of water and aqueous solutions many observations have been interpreted on the basis of the intermediate formation of H OH H_2 and H_2O_2 by decomposition of the water The initial yield of H_2 from oxygen saturated water irradiated with x rays has been reported[8] to be the same as that from solutions in which the solute prevented secondary reaction of H_2 with OH This observation was an important consideration in a mechanism proposed[9] to interpret H_2O_2 formation in oxygen saturated water Studies of H_2O_2 formation in potassium bromide solutions[10] have indicated that this mechanism is not adequate Previous studies[11] have indicated that the secondary reaction of H_2 with OH occurs readily and should lead to a low H_2 yield in oxygen saturated water The H_2 consumed in this secondary reaction should result in the formation of an equivalent amount of H_2O_2 Therefore H_2 and H_2O_2 yields from oxygen saturated water in ampoules having no gas space have been measured also measured were H_2O_2 yields from water through which oxygen was continuously swept during irradiation in order to remove the H_2 produced

A Co^{60} gamma ray source giving a dose rate of about $1\ 7 \times 10^{20}$ ev/liter min was used for these irradiations All yields are based upon a yield of 15 6 ferrous ions oxidized per 100 ev for the ferrous sulfate dosimeter

Buildup of H_2 and H_2O_2 with radiation dosage is shown in Figs 42 and 43 The initial yield of H_2 from oxygen saturated water containing KBr which prohibits removal of H_2 through secondary reaction with OH was 0 41 ± 0 01 The observed initial yield of H_2 from oxygen saturated water

[8] E R John on and A. O Allen *J Am Chem Soc* 74 4147 (1952)

[9] A O Allen *Radiation Research* 1 85 (1954)

[10] T J Sworsk *J Am Chem Soc* 76 (in press)

[11] C J Hochanadel *J Phys Chem* 56 587 (1952)

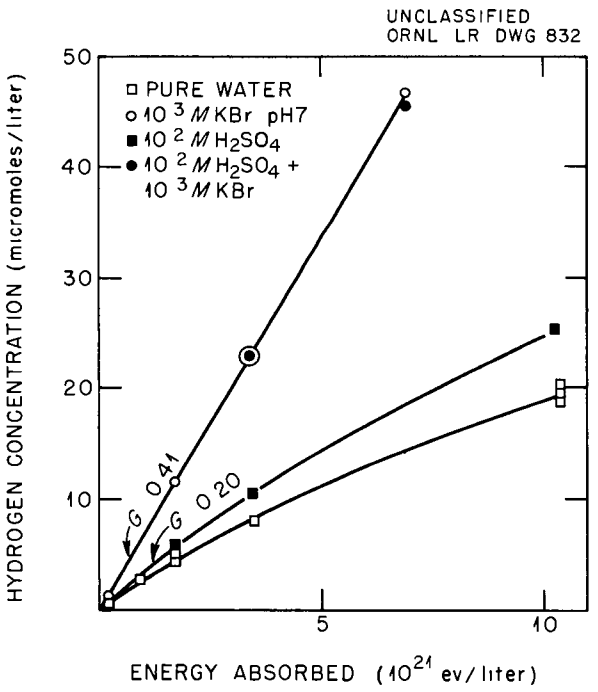


Fig 42 Hydrogen Production in Oxygen saturated Solutions in Closed Vessels Subjected to Co^{60} Gamma Rays

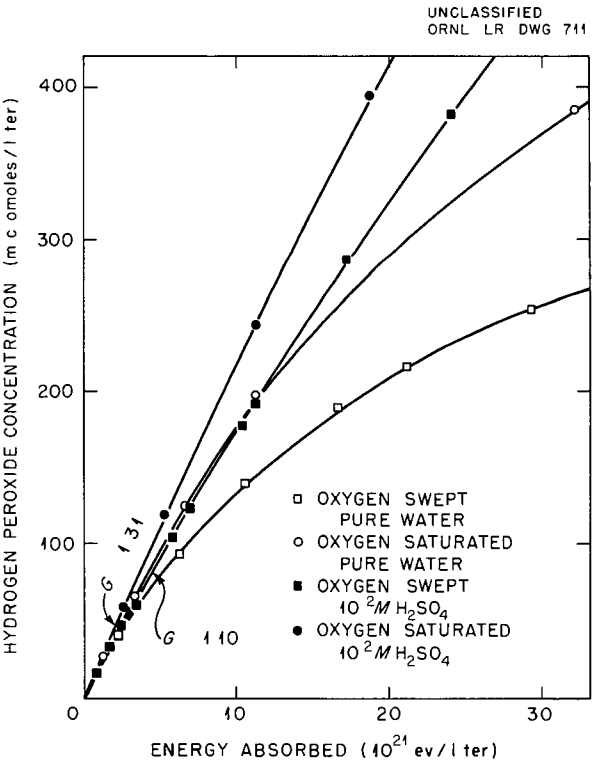


Fig 43 Hydrogen Peroxide Production in Solutions Subjected to Co^{60} Gamma Rays

was 0 20 ± 0 02 Thus the H_2 yield was lowered by 0 21 through the secondary reaction of H_2 with OH With oxygen sweeping through the solution during irradiation to remove the H_2 produced the initial yield of H_2O_2 was 1 10 The initial yield of H_2O_2 in oxygen saturated water in closed vessels was 1 31 Thus the H_2O_2 formed through the secondary reaction of the H_2 was equivalent to the H_2 used up 0 21

The initial yields were the same at pH 7 and at pH 2 (H_2SO_4) but the steady state concentrations were higher at the lower pH The steady state concentrations of H_2 and H_2O_2 in oxygen saturated solutions were approximately 40 and 500 μM respectively at pH 7 and approximately 220 and 2300 μM at pH 2 The steady state concentrations of H_2O_2 in oxygen swept solutions were about 300 μM at pH 7 and about 1500 μM at pH 2 In general the steady state concentrations were less reproducible than were the initial yields and are presumably more sensitive to the presence of small amounts of impurities

These results combined with results from studies by Sworski[10] of potassium bromide solutions indicate that the mechanism proposed by Allen[9] can be applied to oxygen swept solutions The value obtained here of 1 10 for the initial H_2O_2 yield corresponds to $F + 2E$ in the Allen terminology and agrees with the value 1 08 obtained by Sworski by extrapolation to zero potassium bromide concentration With 3 2 taken as the initial H_2O_2 yield in solutions of hydrogen plus oxygen in which every radical is converted to H_2O_2[11] the yields of H OH H_2 and H_2O_2 from the decomposition of oxygen saturated water by cobalt gamma rays are 2 8 2 1 0 41 and 0 76 respectively

HYDROGEN YIELDS IN THE GAMMA RAY DECOMPOSITION OF SOME DILUTE AQUEOUS SOLUTIONS

J A Ghormley C J Hochanadel

Identical hydrogen yields were reported[8] for the x ray decomposition of dilute solutions of several oxidizing and reducing agents at various concentrations and it was suggested that the primary hydrogen is formed in a molecular reaction rather than by combination of randomly diffusing hydrogen atoms Others[12 13] have found that the hydrogen yield varies from solution to solution and have suggested that the primary hydrogen yield depends upon the oxidizing power and concentration of the solute It was also found[14] that the hydrogen yield decreased with increased concentration of uranyl sulfate Considerable discrepancy exists among the absolute yields reported by various authors It has also been observed[10] that the primary H_2O_2 yield was lowered by the presence of Br^- or Cl^- even at low concentrations (10^{-5} M) presumably by reaction of halide ions with OH radicals in the tracks of the ionizing particles It seemed likely that the primary hydrogen yield might also be affected by some solutes either by reacting with free radicals or with excited water molecules in the particle tracks Hydrogen yields in the gamma ray decomposition of a number of solutions were measured in order to determine the effect of various solutes on the yield and also to establish more accurate values for these yields Solutions were irradiated with cobalt gamma rays at a dose rate of 1 7 × 10^{20} ev/liter min Gases were analyzed by the usual McLeod gage micro method Yields are given as molecules per 100 ev based on the ferrous sulfate dosimeter with a yield of 15 6 Fe^{+++} per 100 ev The rate of H_2 formation was usually constant in the dose range studied (10^{21} to 10^{22} ev/liter) and each yield is the average of three or four measurements

KBr Solutions

The yield of H_2 from oxygen saturated solutions was the same 0 41 ± 0 01 at bromide concentrations from 10^{-6} to 10^{-1} M Sworski[10] on the other hand has shown that the primary H_2O_2 yield is appreciably lowered by bromide in this concentration range The H_2 yield increased to 0 46 ± 0 01 in 1 M KBr solution

The data in Table 18 show the effects of O_2 and H_2O_2 on the H_2 yield in 10^{-3} M KBr In the absence of O_2 or H_2O_2 either at pH 7 or pH 2 (H_2SO_4) the H_2 yield 0 47 ± 0 01 was appreciably higher than that in the oxygen saturated solution Addition of H_2O_2 caused a continuous decrease in H_2 yield with increasing H_2O_2

[12] J We ss and T Rigg *Discuss ons Fa aday Soc* No 12 119 (1952)

[13] M Lefort and M Ha ssinky *Discussions Faraday Soc* No 12 122 (1952)

[14] J W Boyle *et al* *Reactor Sci Technol* 3 No 1 32 (1953) TID 2008

TABLE 18 EFFECT OF ADDED O_2 AND H_2O_2 ON HYDROGEN YIELDS IN THE GAMMA RAY DECOMPOSITION OF 10^{-3} *M* KBr SOLUTIONS

H_2O_2 (*M*)	pH	Gas	G_{H_2}
0	7	O_2	0 41 ± 0 01
0	2	O_2	0 41
0	7	He	0 48
0	2	Vacuum	0 46
$7\ 0 \times 10^{-5}$	7	He	0 46
$8\ 0 \times 10^{-4}$	7	Vacuum	0 43
$1\ 6 \times 10^{-3}$	7	He	0 41
$6\ 8 \times 10^{-3}$	7	He	0 37
$1\ 0 \times 10^{-1}$	7	He	0 30
$7\ 0 \times 10^{-1}$	7	He	0 21
1 4	7	He	0 17

Solutions in 0 8 *N* H_2SO_4

Hydrogen yields for several solutions in 0 8 *N* H_2SO_4 are listed in Table 19 The yields are nearly the same for the various dilute solutions However the acid at this high concentration (0 8 *N*) lowers the H_2 yield by 15% as was reported previously Also dissolved oxygen (10^{-3} *M*) lowered the yield slightly and at the higher concentration (0 1 *M*) $Ce(SO_4)_2$ lowered the yield and $FeSO_4$ increased the yield

It is evident that the primary hydrogen yield is in some cases affected by the solute The data at present do not allow a choice among the possible mechanisms by which the solute may alter the hydrogen yield These mechanisms may include electron capture charge transfer with H_2O^+ energy transfer from excited water molecules to the solute or reaction with free radicals along the tracks of the ionizing particles

TABLE 19 H_2 YIELDS IN THE RADIOLYSIS OF 0 8 *N* H_2SO_4 SOLUTIONS

Solute	Gas	G_{H_2}
None	Va u m	0 41 ± 0 01
None	O_2	0 35 ± 0 01
10^{-3} *M* H_2O_2	O_2	0 35 ± 0 01
10^{-3} *M* KBr[a]	Vacuum	0 39 ± 0 02
10^{-3} *M* KBr[a]	O_2	0 38 ± 0 02
2×10^{-3} *M* $FeSO_4$	O_2	0 35 ± 0 01
2×10^{-2} *M* $FeSO_4$[a]	O_2	0 49 ± 0 04
1×10^{-1} *M* $FeSO_4$	O_2	0 68 ± 0 03
4×10^{-4} *M* $Ce(SO_4)_2$	O_2	0 35 ± 0 01
3×10^{-3} *M* $Ce(SO_4)_2$[a]	Vacuum	0 40 ± 0 02
1×10^{-1} *M* $Ce(SO_4)_2$	O_2	0 30 ± 0 01

[a]Measurements by analytical ampoule method cf J A Ghormley and C J Hochanadel *Chem Semiann P og Rep Dec 20 1953* ORNL 1674 p 71

LIFETIME OF INTERMEDIATES IN WATER SUBJECTED TO 1 5 Mev ELECTRONS

J A Ghormley

In previous work[15] on the decomposition of pure water by 1 Mev electrons the steady state concentration of gaseous products was found to increase approximately as the square root of the electron beam current This dependence of product concentration on energy density is assumed to be related to the concentration of free radical intermediates which can react with each other to form the stable products or can induce reaction between the stable products to form water Intermittent irradiation of varying frequency permits determination of the lifetime of the intermediates from the relationship between the concentration of products produced and the frequency of the radiation pulses

Some pulsed beam experiments have been initiated in which helium saturated water in a flow system was subjected to 1 5-Mev electrons from a Van de Graaff generator Figure 44 shows observed H_2O_2 concentrations plotted against square root of electron beam current The irradiated volume was about 0 5 ml and the flow rate was 0 1 ml/sec Under these conditions the observed H_2O_2 changed very little with change in flow rate and was assumed to be the steady state concentration Figure 45 shows results obtained when the beam was interrupted with a rotating sector disk having 50 sector openings of approximately the same width as the cross section of the beam and a dark to light ratio of 10 1

As seen in Fig 45 frequencies of about 1000 pulses/sec or greater give H_2O_2 concentrations the same as those given by steady currents equal to the average currents in the pulsed beam experiments This indicates that the average lifetime of the shortest lived intermediates whose concentration affects the steady state H_2O_2 concentration is of the order of 0 001 sec under the conditions

[15]A O Allen *Chemical Effects of Ionizing Radiation on Simple Inorganic Compounds and Aqueous Solut ons* MDDC 363 (Sept 12 1946)

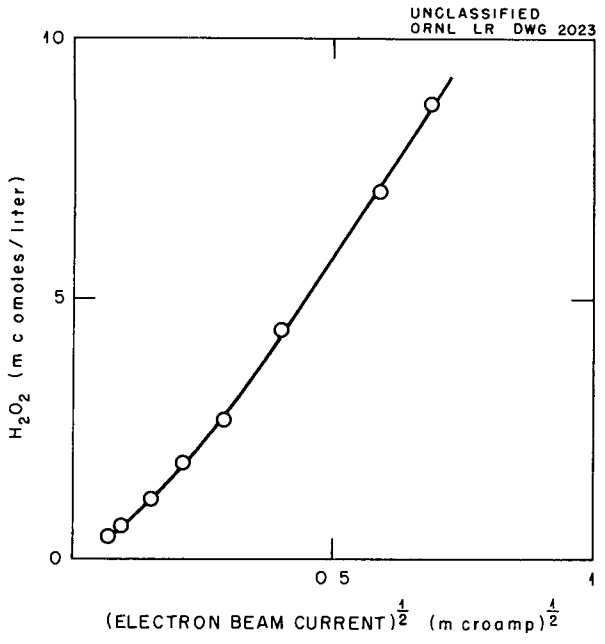


Fig 44 Hydrogen Peroxide Produced in Helium saturated Water by 1 5 Mev Electrons

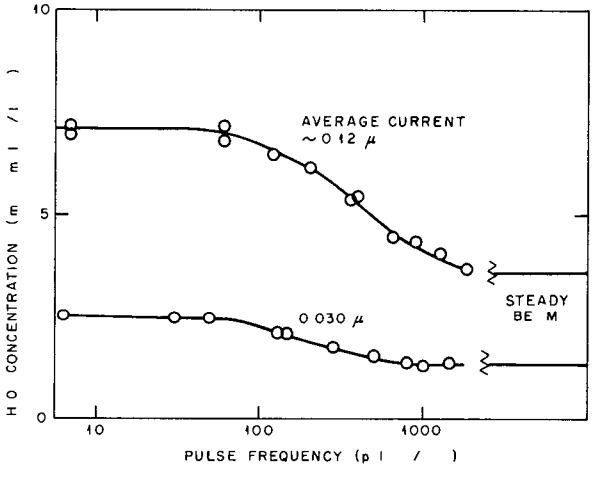


Fig 45 Hydrogen Peroxide Produced in Helium saturated Water by 1 5 Mev Electrons with Beam Pulsed at Various Frequencies

of these experiments At frequencies between 100 and 10 pulses/sec the H_2O_2 is approximately constant and it is assumed that during each pulse a steady state concentration of these same intermediates is approached The data in Fig 45 suggest a decrease in intermediate lifetime with increase in beam current as would be expected

Previous results[15] indicated the existence of an intermediate having a lifetime of a few tenths of a second which is significantly greater than that observed here and a modification of the apparatus will permit extension of the measurement to lower pulse frequencies

GAS PHASE IRRADIATION

S C Lind P S Rudolph

A third experiment on the alpha particle induced recombination of H_2 and O_2 in the presence of CO_2 completely corroborates the findings previously reported[16] The values of the velocity constant ($k\ \mu/\lambda$) corrected[17] to a common diameter of 2 cm are 32 0 31 4 and 31 2 for the three experiments

A mixture of approximately two parts of $H_2O(g)$ to one of CO_2 was irradiated with alpha particles at about 100°C There was no reaction between these gases

Carbon monoxide with and without xenon is being irradiated with alpha particles from radon The two reactions run simultaneously in small spherical reaction vessels of essentially the same volume and with essentially the same quantity of radon The kinetics show that the xenon has no effect on the velocity of the reaction The velocity constants for both reactions agree when calculated on the basis of the partial pressure of the CO and a plot of the log P_{CO} vs $e^{-\lambda t}$ gives a straight line The step wise velocity constant based on P_{CO} shows no trend whereas this same constant based[18] on $P_{CO} + P_{eq\ vX}$ shows a slightly but definitely decreasing value The results of the present experiments and previous work are shown in Table 20 where columns 2 and 3 give the reactions with xenon and column 4 the experiments with CO alone The velocity constant in column 2 is based on the partial pressure of CO and the equivalent pressure[18] of xenon $[(\iota_{Xe}/\iota_{CO})P_{Xe}]$ whereas the constants in columns 3 and 4 are based on the partial pressure of the CO only

Since the presence of xenon does not influence the reaction rate there is no indication of charge

[16] S C L nd and P S Rudolph *Chem Semiann Prog Rep Dec 20 1953* ORNL 1674 p 70

[17] S C L nd *The Chemical Effects of Alpha Particles and Electrons* 2d ed p 119 ff Chemical Catalogue Co Inc New York 1928

[18] *Ibid* p 186

TABLE 20 COMPARISON OF $(k\,\mu/\lambda)$ CORRECTED TO A 2 cm SPHERE

Reference	CO + Xe		CO	Volume of Sphere	E_0 (mc)	$P_{0_{CO}}$ (mm Hg)	P_X (mm Hg)
	$(k\,\mu/\lambda)_{P_{CO} + P_{eq\ X}}$	$(k\,\mu/\lambda)_{P_{CO}}$	$(k\,\mu/\lambda)_{P_{CO}}$				
L nd and Rudolph[a]	8 7	11 4		8 4	79 7	685 0	54 2
Lind and Rudolph[a]			11 4	8 4	79 3	747 9	0
Lind and Vanpee[b]	4 5	11 2		11 0	85 9	325 2	149 6
L nd and Bardwell			11 4	4 1	102	689 6	0

[a]S C L nd and P S Rudolph current work
[b]S. C Lind and M Vanpee *J Phys & Colloid Chem* 53 899 (1949)
S. C L nd and D C Bardwell *J Am Chem Soc* 47 2684 (1925)

transfer from CO to xenon although their ionization potentials are 14 1 and 12 1 ev respectively Lind has previously shown[19] that excitation is not *the* answer to the effect of inert gases on gas phase radiation chemical reactions The CO + Xe reaction is the first instance known in which trans fer of ionization does not occur although it is energetically possible This may be due to an inability of a polyatomic ion (CO^+) to capture an electron from an inert atom Other similar cases must be examined before a generalization is justi fied

An attempt to further elucidate the mechanism of the inert gas effect will be the basis of future work In addition it is planned to complete the series of reactions initiated by the $H_2 + O_2 + CO_2$ reaction in order that the effect of CO_2 may be better understood

[19]S C Lind *J Phys Chem* 56 920 (1952)

REACTOR CHEMISTRY

THE pH OF UO_3 H_2SO_4 H_2O MIXTURES AT 25°C AND ITS APPLICATION TO THE DETERMINATION OF THE SOLUBILITY OF UO_3 IN SULFURIC ACID AT ELEVATED TEMPERATURE

W L Marshall C H Secoy

The pH at 25 00 ± 0 04°C of uranium trioxide–sulfuric acid–water mixtures has been determined to a precision of ±0 004 pH unit from 0 024 to 10^{-4} *m* sulfuric acid and at UO_3/H_2SO_4 mole ratios from 0 70 to 1 20 The solubility of UO_3 in sulfuric acid at elevated temperature (150 to 300°C) has been determined by isolating a UO_3 saturated sample and comparing the pH of the isolated sample at 25°C with the pH data mentioned above By this method seven isotherms in the concentration range from 1 0 *m* down to 10^{-4} *m* have been obtained

Experimental

The pH s at 25 00 ± 0 04°C were measured by use of a vibrating reed electrometer coupled with a Leeds & Northrup K 2 potentiometer and Brown recorder for making a record of the final potential obtained by means of the apparatus of Kraus Holmberg and Borkowski [1 2] Thermostatted water was circulated around both the calomel electrode and the test tube containing the sample solution the salt bridge tip and the glass electrode A schematic drawing is shown in Fig 46 The fluctuation of potential on the Brown recorder was of the order of ±0 04 mv

Mallinckrodt UO_3 hydrate which had been washed thoroughly with hot water to remove as much nitrate impurity as possible (NO_3^- after washing <24 ppm) was analyzed weighed and dissolved in 0 02441 *m* H_2SO_4 solutions to produce the desired mole ratios UO_3/H_2SO_4 Calibrated volumetric pipets and flasks were used in this operation and the final concentrations were checked by weighing the solutions These UO_3 H_2SO_4 H_2O solutions were also diluted successively by the use of calibrated volumetric apparatus Three control buffer solutions were used for relating the measured potentials to pH These controls were 0 009928 0 003157 and 0 001005 *M* HCl solutions to which sufficient cp KCl was added to obtain a total chloride concentration of 0 100 *M* in each solution The pH value[3] used for the 0 009928 *M* HCl solution was 2 079 and the values for the other two solutions were related accordingly The pH s of the buffers were checked before and after all series of measurements and the sample potentials were related to these values The Nernst slope was found to lie between 59 00 and 59 50 mv per pH unit but the precision was ±0 10 mv per pH unit for any series of measurements The pH s of the control solutions were measured under the above conditions and are believed to be reproducible to approximately ±0 004 pH unit

A schematic diagram of the bomb and assembly for measuring solubilities at elevated temperature is shown in Fig 47 One of the two unique features of this bomb assembly is the use of pure Teflon gasketing fitted into a circular groove in the bomb head This groove prevents the Teflon from extruding upon being subjected to high temperature and pressure There is no need for auxiliary screws to tighten on a pressure plate since upon heating the bomb to temperatures above 100°C the Teflon expands and effects a leakproof seal It has been found that manual tightening of the bomb prevents any leakage Upon cooling back to room temperature the Teflon contracts thus allowing in most cases the bomb to also be opened manually However a wrench is usually used for tightening and loosening the bomb head The bomb assembly is cooled within several minutes by removing it from the thermostat and placing it directly in an ice bath

The Teflon gasket can be used repeatedly under these conditions to approximately 325°C at which temperature a physical change occurs within the Teflon [4] Experiments have been performed on aqueous systems at 4500 psi and no failure occurred until 325°C was reached These observations indicate that it is not the water vapor pressure (the pressure of saturated steam at 325°C

[1] K A Kraus R W Holmbe g and C J Borkowski *Anal Chem* **22** 341 (1950)

[2] R W Holmberg and K A Kraus made valuable sug gest ons concer ing the use of a vibrating reed elec trometer for determining the pH

[3] R G Bates *Chem Rev* 42 1 (1948)

[4] E I du Pont de Nemours & Co In publ shed reports on prope t es of Teflon (T ansit o tempe a tu e = 327°C)

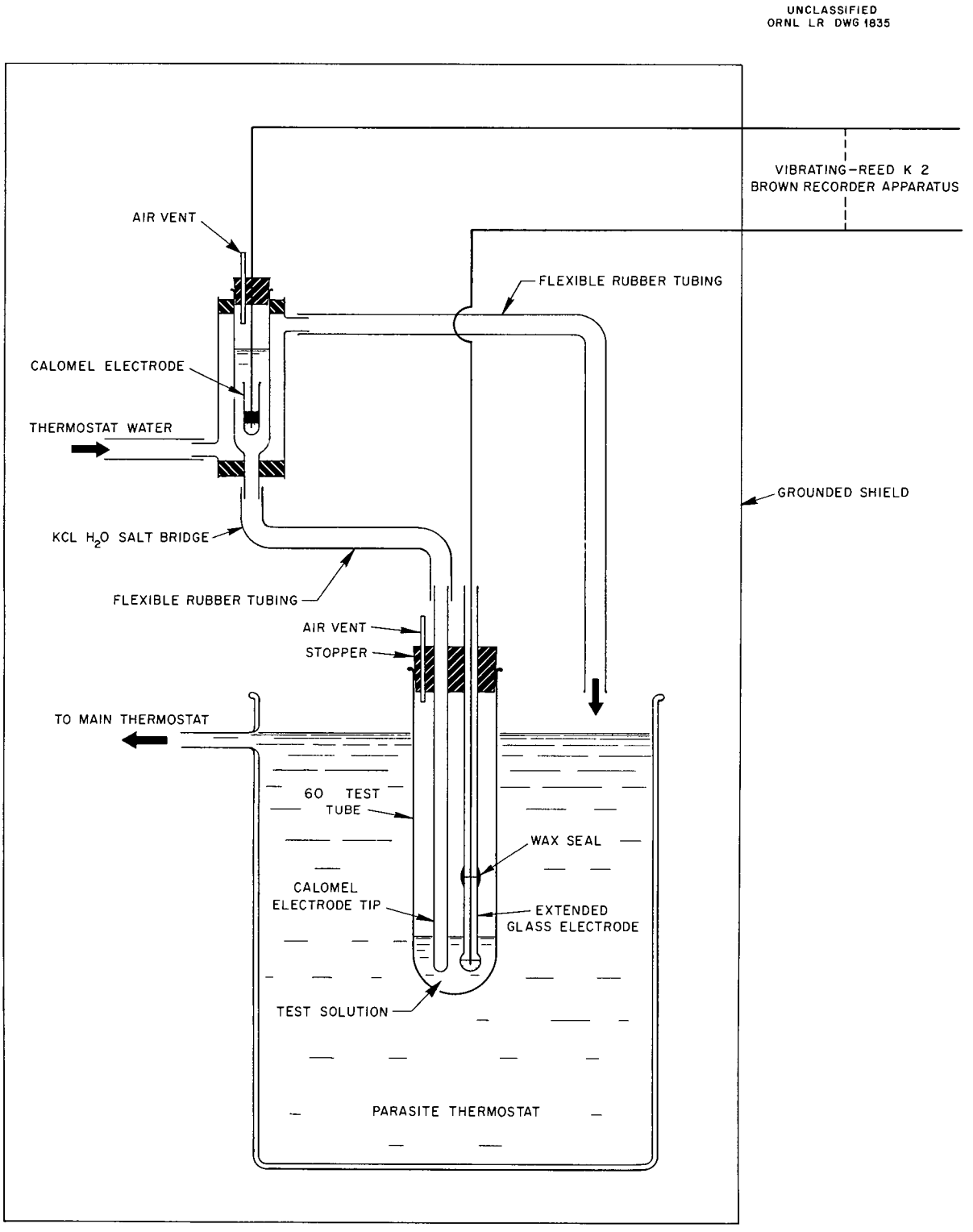


Fig 46 Schematic Drawing of Thermostatted Electrodes

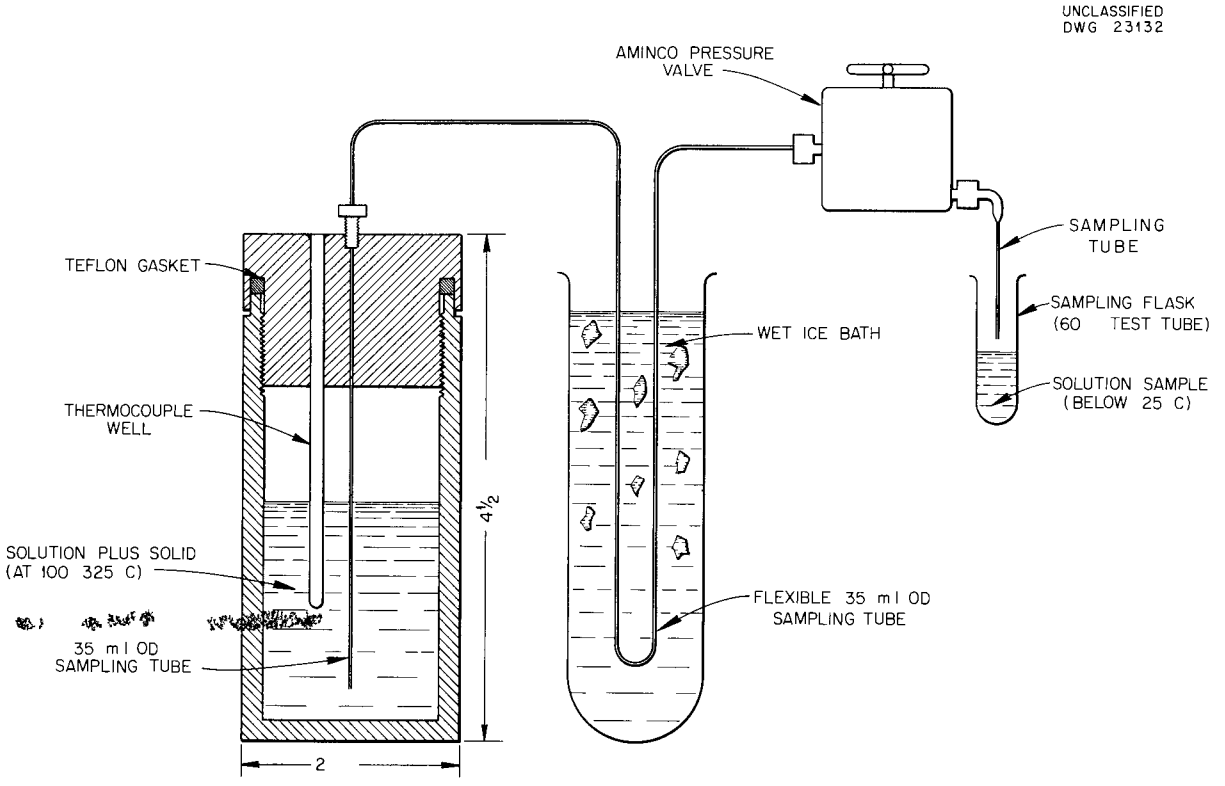


Fig 47 Schematic Diagram of Aqueous Solution Sampling Assembly

is 1750 psi) which causes the leakage at 325°C but rather the physical change of the Teflon

The other unique feature is the use of 30 mil OD 20 mil ID stainless steel capillary tubing for sampling solutions By virtue of the small size of the capillary tubing the solution regardless of temperatures below 325°C is cooled rapidly as it passes through that portion of capillary inserted in the ice bath The internal pressure of the system affords the necessary pressure for pushing the solution through the capillary A conventional Aminco valve is opened slowly and the solution comes out either dropwise or in a stream to deliver as much as 15 to 20 cc/min

Procedure for Determining Solubilities

A 60 00 cc volume of standard H_2SO_4 solution was added to a weighed quantity of UO_3 hydrate The mole ratio of total UO_3 to total H_2SO_4 was kept at about 3 1 A 4 00 cc volume of cp 30% H_2O_2 was added upon decomposition at elevated temperature the H_2O_2 formed oxygen and prevented reduction of uranyl ion to U^{4+} Uranium peroxide which was formed at the lower temperature by reaction with H_2O_2 decomposed to UO_3 hydrate at the elevated temperature and thus the final system did not involve the peroxide A volume dilution correction was made for the hydrogen peroxide addition

The bomb loaded with excess solid and solution was inserted into an insulated heated aluminum cylinder The temperature was controlled through a Brown Pyr O Vane controller to ±1°C The whole assembly including bomb thermostat capil lary tubing and sampling valve was placed on a large shaker The shaker was run at a rate of 100 cpm thereby affording ample mixing of the solution and solid

Solution and solid were equilibrated at a particu lar temperature a 3 cc holdup sample was removed and a 5 cc sample of the equilibrated solution was delivered to a standard 60 cc test tube This sample solution was thermostatted at 25°C and the pH determined in the manner described above The

mole ratio UO_3/H_2SO_4 was determined from curves of pH vs ratio (Fig 48) for the particular concentration of H_2SO_4 The pH data of Orban[5] were used for concentrations greater than 0 024 *m* It was found that after the initial hydrogen peroxide and uranium peroxide had decomposed the system came to equilibrium within 15 to 20 min between 150 and 290°C Samples obtained within this time limit agreed with samples obtained several hours later For the most part the system was equilibrated 1 to 1½ hr and in some cases overnight The equilibration temperature was approached from higher and lower temperatures and the solubilities thus obtained indicated complete reversibility

[5]E Orban *The pH Measurement of U anyl Sulfate Solutions from 25° to 60°C* MLM 729 (Aug 1 1952) *The pH of U anyl Sulfate–Uranium T ioxide Solutions* MLM 738 (Aug 14 1952)

pH Data at 25°C

The pH data at 25 00 ± 0 04°C are given in Table 21 and are shown in Figs 48 and 49 There is a satisfactory overlap of data for stoichiometric UO_2SO_4 obtained by previous investigators [5–8] However the previous data lacked the precision of the data obtained by use of the present apparatus These more precise data were necessary to derive the greatest benefit from using the data for analytical means An attempt will be made to

[6]L Helmholz and G Friedlande *Physical Properties of Uranyl Sulfate Solutions* LAMS 30R (Dec 15 1943)

[7]D A Ma Innes and L G Longsworth *The Measurement and Interpretation of pH and Conductance Values of Aqueous Solutions of U anyl Salts* A 380 (Nov 24 1942)

[8]M H L et ke H W W ight ond W L Ma shall *HRP Quar P og Rep Aug 15 1951* ORNL 1121 p 124

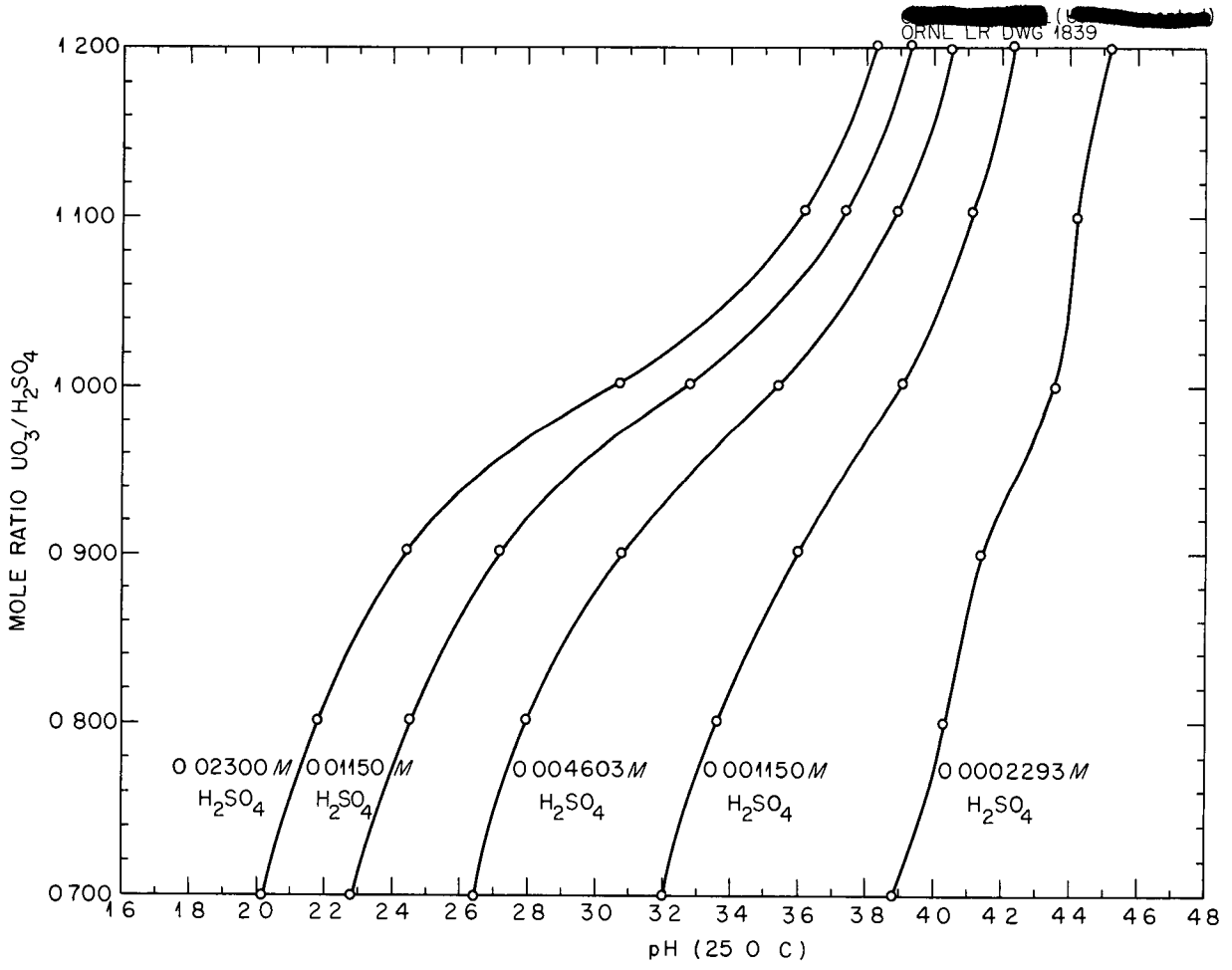


Fig 48 Mole Ratio vs pH of UO_3 H_2SO_4 H_2O Mixtures

TABLE 21. THE pH OF UO_3-H_2SO_4-H_2O SOLUTIONS AT 25.00 ± 0.04°C

H_2SO_4 (M)	pH Values*					
	Molar Ratios UO_3/SO_4					
	0.7006	0.8017	0.9024	1.0029	1.1042	1.2020
0.02432	1.995	2.151	2.425	3.043	3.612	3.823
0.01214	2.259	2.422	2.692	3.267	3.731	3.922
0.004866	2.619	2.784	3.046	3.526	3.874	4.038
0.003656	2.730	2.900	3.155	3.604	3.913	4.074
0.002437	2.905	3.065	3.321	3.708	3.977	4.124
0.001216	3.174	3.348	3.592	3.906	4.093	4.214
0.0004850	3.587	3.715	3.903	4.130	4.250	4.354
0.0003646	3.671	3.822	3.996	4.201	4.304	4.395
0.0002424	3.851	4.004	4.127	4.326	4.411	4.500

*These values are based on a determined pH of 2.075 for 0.01000 M HCl, 0.0900 M KCl (see Ref. 3). For pH's relative to the analytical concentration of HCl, subtract 0.075 pH unit from each of the above values.

[redacted]

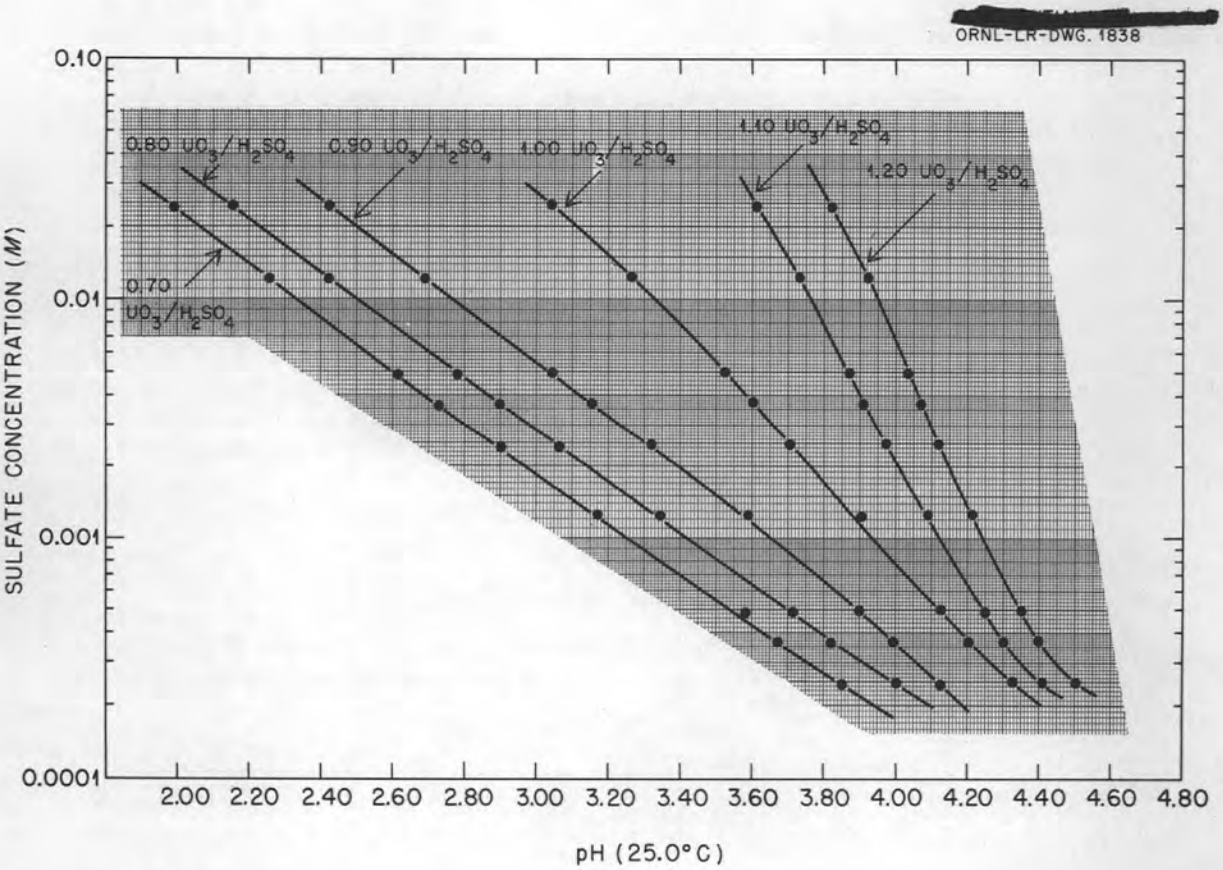


Fig. 49. Sulfuric Acid Concentration vs pH of UO_3-H_2SO_4-H_2O Mixtures.

interpret the pH data to give hydrolysis constants for UO_2^{++} and equilibria involving sulfate.

Solubility Data

The solubility data are given in Table 22 and in Figs. 50 and 51. There appears to be a direct correlation between the hydrogen ion activity at a particular temperature and the mole ratio as a function of H_2SO_4 concentration, as evidenced by the linear relationships shown on the log $[H_2SO_4]$ vs $[UO_3]/[H_2SO_4]$ plot (Fig. 50). The straight line portions of Fig. 50 can be represented by the equation

$$\log [H_2SO_4] = k \frac{[UO_3]}{[H_2SO_4]} + C \quad .$$

If the slopes, k, are plotted against $1/T$, where T = °A, a break in the resultant curve occurs at 205°C. The break presumably represents a transition from α-$UO_3 \cdot H_2O$ to β-$UO_3 \cdot H_2O$. This break also appears at 205°C on plots of C vs $1/T$. Approximate linear relationships are observed above and below 205°C for both k and C plots. Two empirical equations have been derived to express the solubility data and are believed to be accurate to ±1% in mole ratio in the respective temperature and concentration ranges. They are given as follows and are applicable from approximately 0.05 to 10^{-4} m H_2SO_4 (UO_3 and H_2SO_4 are expressed in molalities).

Equation 1 (for use between 150 and 205°C) in which t = °C is as follows:

$$\log [H_2SO_4] = \left(\frac{4150}{t} - 14.42\right)\frac{[UO_3]}{[H_2SO_4]} - \frac{5230}{t} + 17.74 \quad ,$$

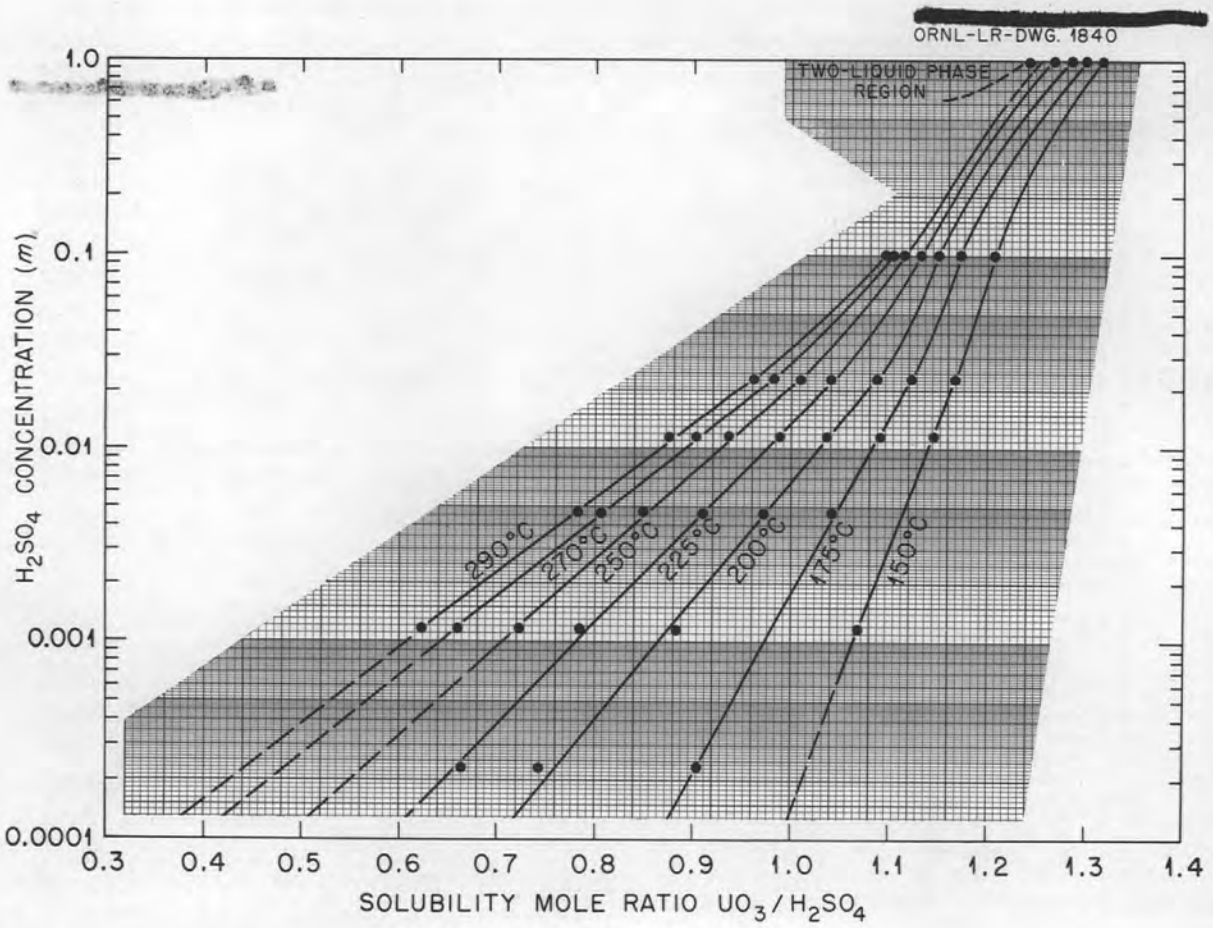


Fig. 50. Sulfuric Acid Concentration vs Mole Ratio of UO_3 in H_2SO_4-H_2O Mixtures.

TABLE 22 SOLUBILITY OF UO_3 IN H_2SO_4 H_2O SOLUTIONS

Temperature (°C)	Concentration (M)		UO_3/H_2SO_4 Mol r Rat o	pH at 25 0°C	Concentration (m)	
	H_2SO_4	UO_3			H_2SO_4	UO_3
150	1 000	1 318	1 318	3 111		
	0 1000	0 1205	1 205	3 627	0 1008	0 1215
	0 02300	0 02686	1 168	3 784	0 02309	0 02697
	0 01150	0 01318	1 146	3 843	0 01154	0 01322
	0 001150	0 001230	1 070	4 053	0 001154	0 001235
175	1 000	1 300	1 300	3 081		
	0 1000	0 1174	1 174	3 565	0 1008	0 1183
	0 02300	0 02578	1 121	3 676	0 02309	0 02588
	0 01150	0 01255	1 091	3 699	0 01154	0 01259
	0 004603	0 004792	1 041	3 700	0 004618	0 004807
	0 0002293	0 0002080	0 907	4 153	0 0002301	0 0002087
200	1 000	1 285	1 285	3 053		
	0 1000	0 1151	1 151	3 503	0 1008	0 1160
	0 02300	0 02498	1 086	3 543	0 02309	0 02507
	0 01150	0 01194	1 038	3 484	0 01154	0 01198
	0 004603	0 004465	0 970	3 368	0 004618	0 004479
	0 001150	0 001015	0 883	3 560	0 001154	0 001019
	0 0002293	0 0001704	0 743	3 953	0 0002301	0 0001710
225	1 000	1 268	1 268	3 019		
	0 1000	0 1132	1 132	3 443	0 1008	0 1141
	0 02300	0 02392	1 040	3 302	0 02309	0 02401
	0 01150	0 01138	0 990	3 191	0 01154	0 01142
	0 004603	0 004193	0 911	3 103	0 004618	0 004207
	0 001150	0 0009016	0 784	3 331	0 001154	0 0009047
	0 0002293	0 0001497	0 653	3 793	0 0002301	0 0001502
250	1 000	1 243	1 243	2 967		
	0 1000	0 1114	1 114	3 372	0 1008	0 1123
	0 02300	0 02318	1 008	3 095	0 02309	0 02327
	0 01150	0 01080	0 939	2 868	0 01154	0 01084
	0 004603	0 003903	0 848	2 908	0 004618	0 003916
	0 001150	0 0008314	0 723	3 224	0 001154	0 0008343
270	0 1000	0 1105	1 105	3 330	0 1008	0 1114
	0 02300	0 02256	0 981	2 895	0 02309	0 02265
	0 01150	0 01037	0 902	2 709	0 01154	0 01041
	0 004603	0 003710	0 806	2 813	0 004618	0 003722
	0 001150	0 0007590	0 660	3 137	0 001154	0 0007616
290	0 1000	0 1098	1 098	3 293	0 1008	0 1107
	0 02300	0 02213	0 962	2 762	0 02309	0 02212
	0 01150	0 01008	0 877	2 622	0 01154	0 01012
	0 004603	0 003599	0 782	2 765	0 004618	0 003611
	0 001150	0 0007164	0 623	3 088	0 001154	0 0007189

Mol rities e on a 25°C bas s

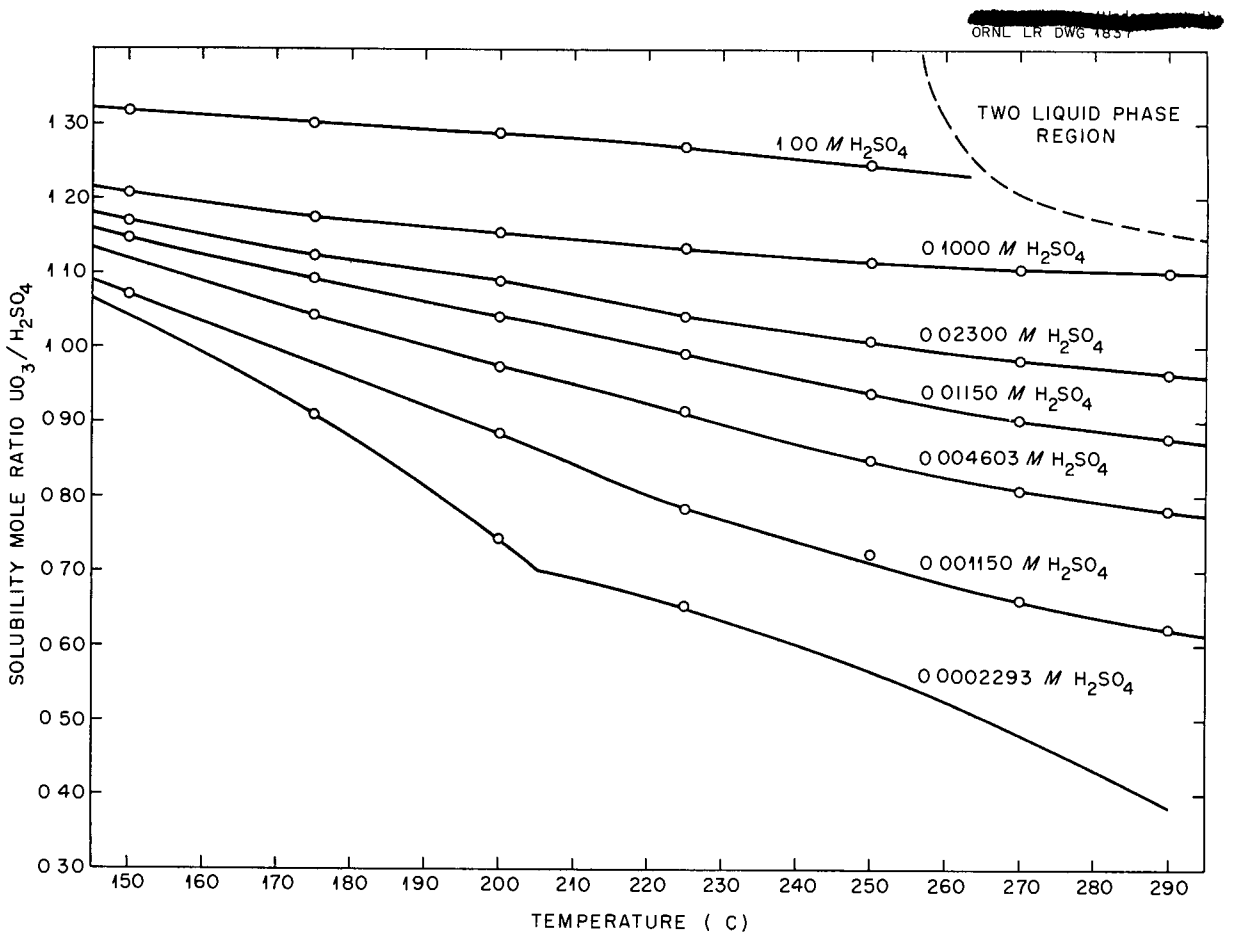


Fig 51 Mole Ratio vs Temperature for the Solubility of UO_3 in H_2SO_4 H_2O Mixtures

and Eq 2 (for use between 205 and 290°C) is

$$\log [H_2SO_4] = \left(\frac{1400}{t} - 1\ 096\right) \frac{[UO_3]}{[H_2SO_4]} - \frac{1880}{t} + 1\ 324$$

PRESENT STATUS OF THE INVESTIGATION OF AQUEOUS SOLUTIONS SUITABLE FOR USE IN A THORIUM BREEDER BLANKET

M H Lietzke W L Marshall

Experiments involving the investigation of some of the more common acidic salt systems of thorium suitable for use in a thorium breeder blanket have been concluded The most recent experimental work as well as work previously reported in HRP and Chemistry Division quarterly reports has been summarized elsewhere [9] Of the systems investigated only two – the $Th(NO_3)_4$ + excess HNO_3 and the $Th_3(PO_4)_4$ + H_3PO_4 with a PO_4/Th ratio of 10 – have both the necessary thermal stability and desirably low viscosity

From the standpoint of neutron capture cross section the $Th_3(PO_4)_4$ H_3PO_4 system is probably satisfactory In the case of the $Th(NO_3)_4$ system a separated N^{15} isotope would have to be used

There is no present evidence that corrosion in the nitrate system would be intolerable However the phosphate system attacks both titanium and

[9] M H Lietzke and W L Marshall *Present Status on the Invest gat on of Aqueous Solut ons Suitable fo Use in a Thorium Breeder Blanket* ORNL 1711 (J ne 7 1954)

zirconium at relatively low temperatures and no satisfactory container is yet known for this system A more thorough study of the corrosion properties of the solutions should be made

The radiation decomposition of nitrate (including the products formed under varying conditions) appears to be the most important unknown concerning the nitrate system A preliminary experiment by Bidwell of Los Alamos who used a uranyl phosphate–H_3PO_4 solution containing enriched U^{235} in the LITR showed no gross decomposition of phosphate ion

On the basis of the rather extensive survey that has been made it seems unlikely that any thorium systems other than the two mentioned will be formed that satisfy the requirements for thermal stability and low neutron capture cross section However this statement cannot be made with certainty until a thorough phase study is made of some of the systems investigated