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RADIATION INDUCED NITRITE FORMATION
FROM CONCENTRATED NITRATE SOLUTIONS

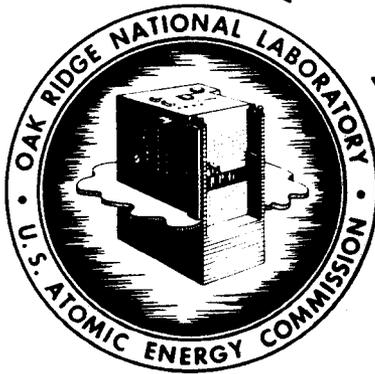
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CONCENTRATED NITRATE SOLUTIONS

Harvey A. Mahlman

Date Issued
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CHAPTER I

INTRODUCTION

A. Radiation Chemistry

Radiation chemistry is usually defined as the study of the chemical effects produced by the interaction of ionizing emissions with matter.¹ Included among these emissions are particles (such as electrons, positrons, protons, neutrons, alpha particles, beta particles, and nuclei) as well as radiations (such as x-rays, gamma rays, and light quanta). When emissions pass through matter, they lose energy by transfer to any one or a combination of the following: electrons, nuclei, ions, atoms, or molecules. These processes may result in any one or combination of free electrons, ions, atoms, or molecules, which, in most cases, then go on to produce detectable chemical effects.¹

B. Proposed Investigation

In recent years, interest has grown in the emission-induced decomposition of aqueous solutions as evidenced by the increasing number of literature publications. Included among the investigations has been some work on solutions of metal nitrates.²⁻¹⁷ Information on nitrate decomposition is becoming valuable since nitrate solutions are being used in the processing of highly radioactive metals, and nitrate solu-

tions are being extensively considered for use in certain types of nuclear reactors. In most of the previous work on nitrate solutions, nitrite has been reported as the major product.²⁻¹⁷ However, it has been observed that irradiations of thorium nitrate solutions produce inordinately small amounts of nitrite as compared to solutions of sodium nitrate.¹⁸ This observation gave rise to the suspicion that the cation accompanying the nitrate ion in concentrated aqueous solutions might have an effect upon the production of nitrite. It was the aim of this research to investigate that suspicion by the irradiation of the nitrate salt solutions of various metal ions with the gamma rays from cobalt-60.

C. History

Upon referring to the literature, one finds that the decomposition of the nitrate ion in aqueous solutions is not a new problem. In 1907, various chemical effects were observed when solutions of several solutes were exposed to the emissions of a quartz-mercury arc lamp.² Among these solutes was potassium nitrate. The production of both nitrite and hydrogen peroxide was noted. Since that first experiment in 1907, many investigators have irradiated nitrate solutions, using light,²⁻¹⁴ x-rays,¹⁵⁻¹⁷ gamma rays,¹⁸ neutrons,¹⁸ and fission fragments.¹⁸ Most of them agree that nitrite and oxygen are produced, and some have reported that the decomposition proceeds more rapidly in basic than in acidic solution. Most of the previous work on the decom-

position of aqueous nitrate has been carried out on dilute solutions.
Little, if any, work has been reported for the concentrated region,
where cation effects should evidence themselves if they are present.

CHAPTER II

THEORETICAL TREATMENT

A. Aqueous Reactions

1. Measurement of Yields

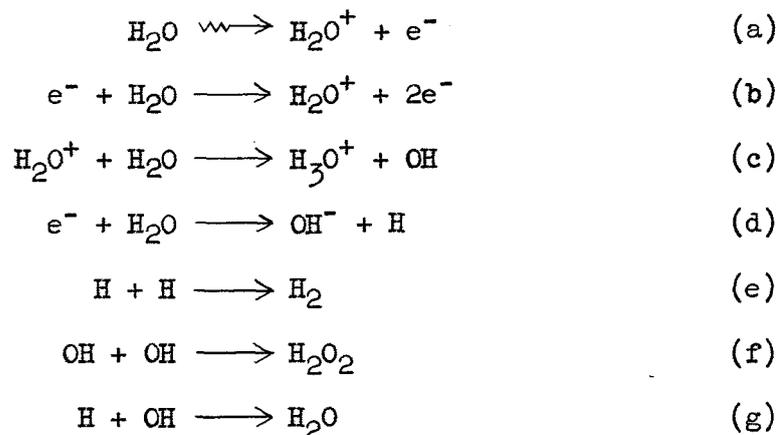
Several methods have been used for reporting the yields of the various products obtained when aqueous solutions are irradiated.¹⁹⁻²¹ In general, two measured quantities are necessary in order to calculate a yield: (1) the amount of energy absorbed in the solution, and (2) the amount of product produced. The energy input may be measured directly by calorimetry or indirectly by the use of a calorimetrically-standardized chemical dosimeter. The amounts of products may be measured by conventional analytical techniques. The usual mode of expressing the yield of a given product is molecules produced per 100 ev of absorbed energy²¹ denoted by G.

2. Aqueous Reaction Products

The major absorption process by which the gamma rays of cobalt-60 interact with water results in the ejection of an electron having an average energy of about 0.60 Mev.²² The electron so produced has sufficient energy to ionize and excite numerous molecules near the site of the parent ion, giving rise to "hot spots" of reaction fragments.²³ These fragments then react with one another at that site, or they may diffuse into the bulk of the solvent where they then undergo reaction.²³

If a solute is present, reaction with it is also possible.

Although several sets of reactions have been postulated in order to explain the chemical effects produced when water is irradiated,^{24,25} one of the most widely accepted is as follows:^{26,27}



Thus it may be seen that the most important primary effect of the irradiation of water is the production of hydrogen atoms and hydroxyl radicals. Some of these primary products react in the hot spot to give molecular hydrogen and hydrogen peroxide.

The yields of the products of water decomposition by cobalt-60 gamma rays have been reported.²⁸ They are as follows, the yield in 0.8-N sulfuric acid being listed first, and that in 0.01-N sulfuric acid second: radical hydrogen (3.70, 2.78), molecular hydrogen (0.39, 0.42), radical hydroxyl (2.92, 2.12), and hydrogen peroxide (0.78, 0.75).

3. Alteration of Yields

Evidence has been presented which shows that the yields of the molecular products of the decomposition of water by gamma irradiation

can be altered by the addition of certain solutes.²⁸⁻³⁵ If a solute is capable of oxidation or reduction, it may serve as an effective getter for radicals. For example, halide ions may react with hydroxyl radicals:³⁶



and the atomic halogen may then react with hydrogen radicals:



The over-all reaction thus turns out to be:



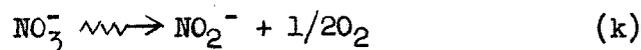
The hydrogen peroxide yield in aqueous solution has been shown to be lowered as a function of the halide ion concentration.²⁸⁻³¹ This is what would be expected from an examination of equations (f) and (h). Solutes capable of being reduced by hydrogen radicals are effective in lowering the yield of molecular hydrogen. Examples of such solutes are the copper(II) ion,³¹ the nitrite ion,³³ cerium(IV) ion,³⁴ oxygen,³⁵ and hydrogen peroxide.³⁴

B. Nitrate Decomposition

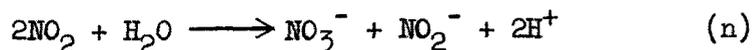
1. Aqueous Nitrate Reactions

By analogy with similar reactions and from previous results, it is believed that in acid solutions nitrite is produced from nitrate by gamma rays through two types of reaction. The first of these involves the direct interaction of radiation with the nitrate ion.³⁷ This may occur by the interaction of an incident gamma ray, a scattered gamma

ray, or an ejected electron with the nitrate ion. The net reaction may be represented as follows, but this representation is by no means meant to indicate the mechanism:^{14,16}



The second type involves the production of free radicals by the interaction of radiation with water, then the attack by the radicals upon the nitrate ion:³⁸

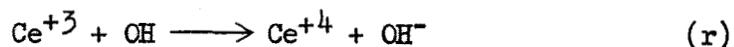
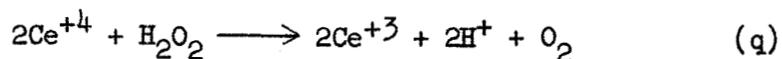
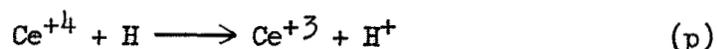


As equations (l), (m), and (n) show, every two hydrogen radicals that participate in this series of reactions produce one nitrite. Also, it will be recognized that as long as there is a high concentration of nitrate as compared to nitrite, the back reaction of nitrite with the hydrogen radical will not be too important. A third important observation is that as long as the nitrate is relatively dilute, the process described by equation (k) will be negligible as compared to the process described by equations (l), (m), and (n). However, as the concentration of the nitrate increases, the reaction shown in equation (k) becomes more and more important.

2. Aqueous Cerium(IV) Reactions

In acid solutions containing cerium(IV) ions, the following processes are important:³⁹

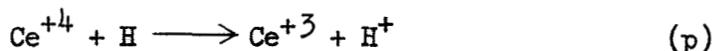
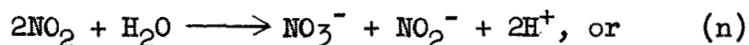
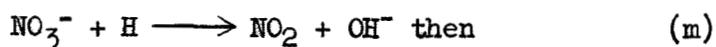




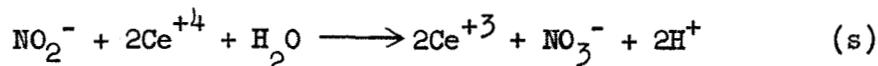
The molecular hydrogen produced does not react. Thus the radiolysis products of water are rapidly removed from solution and interaction among these products is negligible.

3. The Combined System

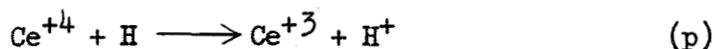
When both nitrate and cerium(IV) ions are present in acid solutions, the hydrogen radical may react by either of the following routes:



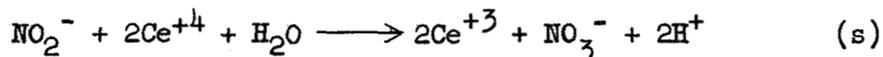
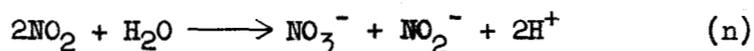
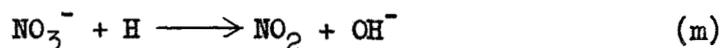
The nitrite produced by the sequence of equations (m) and (n) or by the direct action process of equation (k) will then react with cerium(IV) according to this equation:⁴⁰



Thus, as soon as nitrite is formed, and regardless of its manner of formation, it will react to produce cerium(III). Also, it should be noted that the same number of cerium(III) ions are produced by a given number of hydrogen radicals regardless of the exact reaction route that the hydrogen radicals take, whether it be direct:

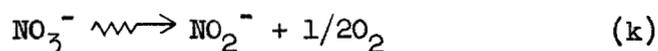


or indirect:



4. Direct Action

Production of nitrite by direct action is symbolized in this equation:



This same reaction has been proposed for the photolysis and x-ray irradiation of aqueous nitrate solutions.^{14,16} It is this reaction that was of particular interest in the present investigation. As has been pointed out, such a process should be negligible in dilute solutions, but as the nitrate becomes more concentrated, it should assume increasing importance. It was proposed to find out if this prediction could be verified. Also, it was of interest to try to determine if the cation accompanying the nitrate had an influence upon the production of nitrite by the direct action process.

As was shown in the previous section, acid solutions containing cerium(IV) and small concentrations of, or no nitrate should give the same yield of cerium(III). This is because of the equivalence of the reaction sequence (m), (n), and (s) with reaction (p), and because the process of reaction (k) can be considered negligible. However, as the concentration of nitrate is raised, reaction (k) cannot be neglected. Any increase in the yield value of cerium(III) therefore can be assigned to the direct action process. Thus measurements of cerium(III) yields

in acid solutions containing cerium(IV) plus nitrate, should provide the data which will allow the calculation of the nitrite produced by direct action in the latter solutions. The yield of nitrite by direct action will be equal to one-half the difference between the yield of cerium(III) in the latter solutions and the yield in the former ones. The figure of one-half may be realized by reference to equations (k) and (s).

CHAPTER III

EXPERIMENTAL WORK

A. Materials and Equipment

1. Reagents

Reagent grade nitrate salts of lithium, sodium, potassium, magnesium, aluminum, ammonium and zinc, cerium(IV) hydrogen sulfate, nitric acid, sulfuric acid, acetic acid, sodium hydroxide, ethyl alcohol, iron(II) diammonium sulfate, potassium thiocyanate, and technical grade sulfanilic acid and dimethyl alpha-naphthylamine were employed. Purified Code 104 thorium nitrate was obtained from the Lindsay Light and Chemical Company. Cesium nitrate was supplied by the Fisher Scientific Company, and was recrystallized from water twice before use. Rubidium hydroxide of undetermined quality was obtained from A. D. Mackay, Inc. This material was neutralized with nitric acid and the resulting salt was recrystallized twice from water. All water was distilled four times.

2. Gamma Source

The gamma radiation employed in the investigation was obtained from a cobalt-60 source located at the Oak Ridge National Laboratory, Oak Ridge, Tennessee. This source consists of about 150 curies of cobalt-60 situated in a large shield provided with arrangements for the placement of samples in the radiation field.⁴¹ The cobalt-60 emits two gamma rays with energies of 1.17 and 1.33 Mev and a 0.31 Mev beta par-

ticle. The cobalt-60 has a half-life of 5.3 years.⁴²

3. Other Apparatus

All spectrophotometric measurements were made on a Cary Model 11 Ms Recording Spectrophotometer. All measurements of pH values were made with a Beckman Model M pH Meter. The irradiation cells were supplied by Pyrocell Manufacturing Company, New York, New York. These quartz cells had special fused quartz windows that were not colored by gamma radiation. Thus the irradiations and the spectrophotometric determinations were made using the same cells.

B. Analytical Methods

1. The Iron(III) Ion

a. Direct determination. The iron(III) ion produced by irradiation of solutions containing the iron(II) ion was measured spectrophotometrically on the Cary Spectrophotometer. Each 3-ml. sample before irradiation was 0.001 M in iron(II) diammonium sulfate and 0.4 M in sulfuric acid. After irradiation, the sample was placed in the Cary Spectrophotometer and the absorption of the iron(III) ion was determined directly at 3050 A.³⁵ This absorption value allowed the concentration of iron(III) to be calculated. The molar extinction coefficient for iron(III) ion in 0.4 M sulfuric acid at 3050 A has been found to be 2240 at 25° C.³⁵

b. Thiocyanate method.⁴³ Iron(III) concentrations were also ascertained by determining the absorption of iron(III) thiocyanate at

4820A. This absorption value allowed the concentration of iron(III) to be calculated. The molar extinction coefficient of iron(III) thiocyanate was found to be 9033. This value was determined by analyses of standards. Checks were provided by the direct iron(III) method and the gamma radiation-induced oxidation rate of iron(II).

2. The Cerium(III) Ion

a. Direct determination. The concentrations of cerium(III) produced by irradiation of solutions containing cerium(IV) were determined by an indirect spectrophotometric procedure. Each 3-ml. sample before irradiation was 0.0002 M in cerium(IV), 0.4 M in sulfuric acid, and in most cases contained a known amount of nitrate. After irradiation, the sample was placed in the Cary Spectrophotometer, and the absorption of the cerium(IV) was determined at 3300A.¹⁰ This value allowed the concentration of cerium(III) ions to be calculated by difference. The molar extinction coefficient for cerium(IV) ions in 0.4 M sulfuric acid at 3300A was determined by measuring the absorption of standard cerium(IV) solutions. These solutions were prepared to contain 0.0002 moles per liter cerium(IV) ions, 0.4 M sulfuric acid, and various amounts of nitrate ion. From the data obtained, the molar extinction coefficient was found to be 5359. The cerium(IV) concentration was also checked spectrophotometrically by determining the absorption at 3200A.³⁵

b. Indirect determination. The direct determination of cerium(IV) ions could not be applied to solutions containing concentrated thorium.

The thorium interferes with the formation of the absorbing cerium(IV) species. An alternative method was devised which utilized the iron(III) thiocyanate method. After irradiation of the thorium nitrate solutions, 0.5 milliliter of 0.02 M iron(II) diammonium sulfate was added. The cerium(IV) not reduced during the irradiation was reduced by the iron(II). The oxidation product, iron(III), was then determined by the thiocyanate method. Since the iron(III) concentration is equivalent to the cerium(IV) concentration, the cerium(III) formation rate could be calculated.

3. Dosimetry

a. Standard. The cobalt-60 gamma source was calibrated with the iron(II) dosimeter. Air-saturated solutions 0.001 M in iron(II) diammonium sulfate and 0.4 M in sulfuric acid were irradiated for given time intervals. After irradiation, the iron(III) produced in the solution was determined spectrophotometrically. Previous experiments have shown that in such solutions, 15.6 ± 0.3 iron(II) ions are oxidized to iron(III) ions for every 100 ev of energy absorbed in the solution.³⁵ Using this value, it was found that 1.370×10^{17} ev/min/ml were being absorbed by the iron(II) dosimeter on March 20, 1956. The radioactive cobalt-60 decays with a half-life of 5.3 years.⁴² This amounts to a decay of about one percent per month and necessitates frequent energy calibrations.

b. Energy absorbed by the solvent. Since the solvent of the standard dosimeter and that employed in the experiments was the same (0.4 M sulfuric acid), the absorbed energy was the same, amounting to

1.338×10^{17} ev/min/g(solvent), E(gs). This value arises by use of the density of a 0.4 M solution of sulfuric acid which is 1.024 g/ml.

As the concentration of solute increased in the various samples employed, the amount of solvent per unit volume decreased. The grams of solvent present in each milliliter of solution was calculated by subtracting the grams of solute per milliliter of solution from density of the solution. The grams of solvent per milliliter of solution multiplied by the ev/min/g (solvent) then gave the energy absorbed by the solvent as ev/min/ml of solution, which will be symbolized E(s).

c. Energy absorbed by the solute. It was assumed that the absorption of energy per gram by the solvent and the solute was proportional to their respective gamma-ray mass absorption coefficients. This coefficient, g(T), is actually the sum of three individual mass absorption coefficients which describe the efficiencies of the three major processes by which gamma rays lose energy.⁴⁴ These processes are known as the photoelectric effect, Compton scattering, and pair production, and their respective mass absorption coefficients will be symbolized by g(P), g(C), and g(PP). Thus one may write:

$$g(T) = g(P) + g(C) + g(PP) \quad (t)$$

The individual mass absorption coefficients may be calculated for various atoms by using the following empirical equations:^{45,46,47}

$$g(P) = aW^3 - bW^4 \quad (u)$$

$$g(C) = cA/Z \quad (v)$$

$$g(PP) = dZ(Z + 1) (E - 1.02)/AE \quad (w)$$

where a, b, c, and d are constants, W is the wave length of the gamma ray in angstroms, A is the atomic weight, Z is the atomic number, and E is the energy of the incident gamma ray in Mev. The values of g(P) and g(PP) for cobalt-60 gamma rays turn out to be very small as compared to that of g(C) except where Z is large.

Using the relations given above, g(T) values were calculated for the various atoms involved in the study. Table I presents the values of g(T) which were used. The energy absorbed by the cation, E(c), expressed in ev/min/ml of solution was calculated by use of the following equation:

$$E(c) = \frac{E(gs) \times g(Tc) \times W(c)}{g(Ts)} \quad (x)$$

where g(Tc) is the gamma-ray mass absorption coefficient for the cation, g(Ts) is the gamma-ray mass absorption coefficient for the solvent, and W(c) is the grams of cation per milliliter of solution. The energy absorbed by the anion, E(a), expressed in ev/min/ml of solution was calculated by use of the following equation:

$$E(a) = \frac{E(gs) \times g(Ta) \times W(a)}{g(Ts)} \quad (y)$$

where g(Ta) is the gamma-ray mass absorption coefficient for the anion and W(a) is the grams of anion per milliliter of solution. The calculations of the mass absorption coefficients of the anion and the solvent from the mass absorption coefficients of the constituent atoms were performed as follows. The mass absorption coefficient of a compound or complex ion is the weighted sum of the mass absorption coefficients of

TABLE I

CALCULATED GAMMA-RAY MASS ABSORPTION COEFFICIENTS
(cm^2/g)

Atom	$g(\text{P})$	$g(\text{c})$	$g(\text{PP})$	$g(\text{T})$
H	0.00000	0.05288	0.00000	0.05288
Li	0.00000	0.02304	0.00000	0.02304
N	0.00000	0.02663	0.00001	0.02664
O	0.00000	0.02665	0.00001	0.02666
Na	0.00000	0.02549	0.00002	0.02551
Mg	0.00001	0.02630	0.00002	0.02633
Al	0.00002	0.02569	0.00001	0.02572
S	0.00003	0.02660	0.00003	0.02666
K	0.00004	0.02590	0.00003	0.02597
Zn	0.00019	0.02445	0.00004	0.02468
Rb	0.00034	0.02308	0.00005	0.02347
Cs	0.00117	0.02207	0.00007	0.02331
Th	0.00550	0.02066	0.00011	0.02627

its constituent parts.⁴⁸ The weighting is proportional to their percentage weights in the compound or ion. This type of calculation yielded a value of 0.02666 for $g(\text{Ta})$ and of 0.03022 for $g(\text{Ts})$.

d. Total energy absorbed. The total energy absorbed, E , expressed as $\text{ev}/\text{min}/\text{ml}$ was obtained by summing the energies absorbed in the solvent, the cation, and the anion, that is:

$$E = E(s) + E(c) + E(a) \quad (z)$$

This value of E was then used to calculate G values for cerium(III) in the various experiments.

C. Preliminary Experiments

1. Calibration

As has been indicated in the previous section, calibration of the source with the iron(II) dosimeter indicated that 1.370×10^{17} $\text{ev}/\text{min}/\text{ml}$ were being absorbed in a solution 0.001 M in iron(II) diammonium sulfate and 0.4 M in sulfuric acid on March 20, 1956.

2. Aqueous Cerium(IV) Experiments

A solution 0.0002 M in cerium(IV) hydrogen sulfate and 0.4 M in sulfuric acid was irradiated. Figure 1 shows a plot of the cerium(III) concentration as a function of time of irradiation. From these data, the yield of cerium(III) was shown to be 2.40 ions of cerium(III) produced per 100 ev of energy absorbed in the solution.

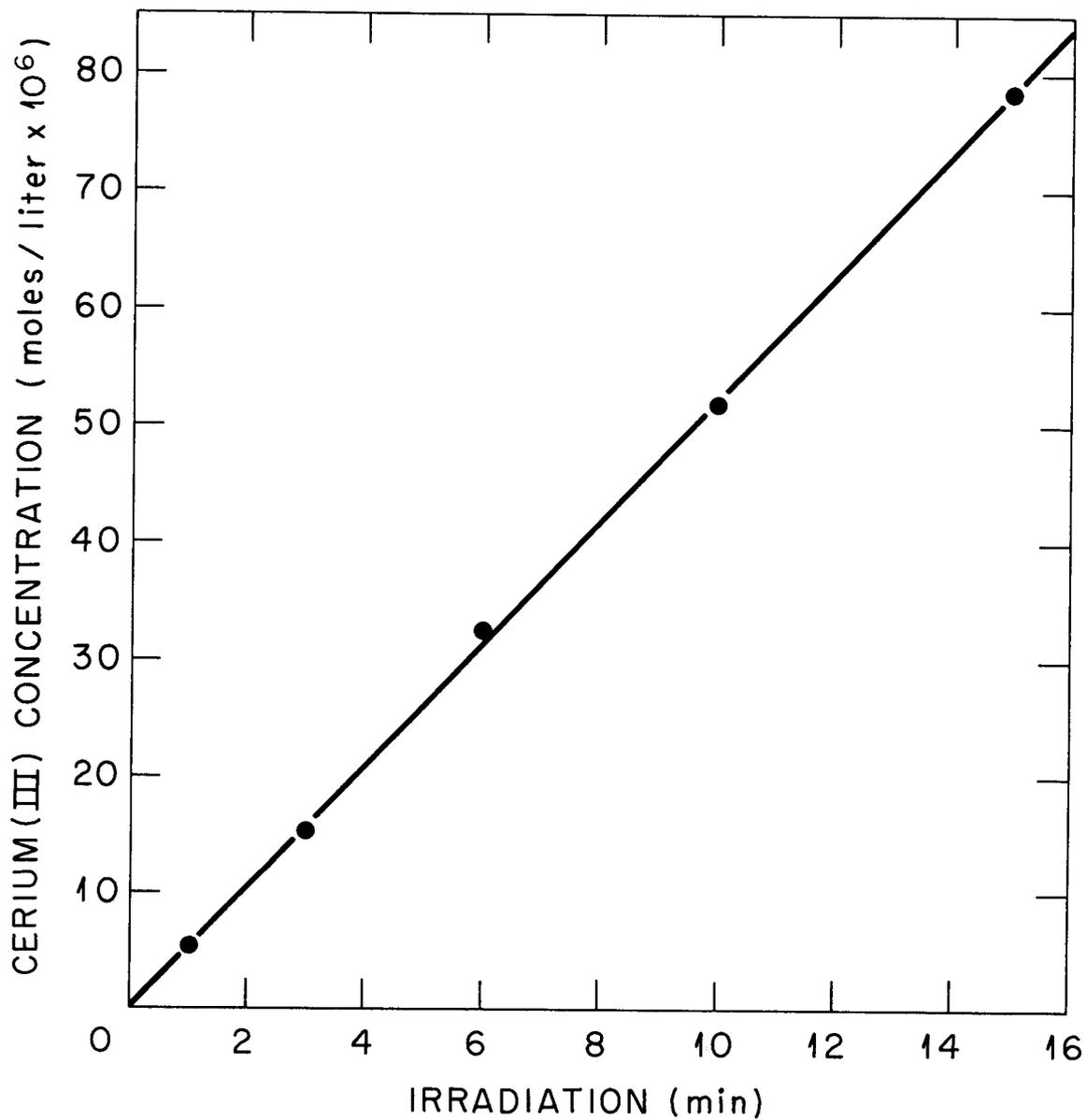
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Figure 1

CERIUM(IV) REDUCTION IN 0.4 M SULFURIC ACID

This observed yield of cerium(III) in 0.4 M sulfuric acid compared very well with the reported yield of cerium(III), 2.39.⁴⁹ Other values have been reported varying from this 2.34 to 2.52.^{35,49,50} Since this cerium(III) yield contains experimental error, it was decided that the theoretical value of 2.34 would be used to correct the enhanced cerium(III) yield so that a value could be determined for direct action nitrite.

3. Aqueous Cerium(IV) Plus Dilute Nitrate Experiments

Solutions 0.0002 M in cerium(IV) hydrogen sulfate, 0.4 M in sulfuric acid, and 0.01 M in lithium, sodium, or potassium nitrate were irradiated. Table II presents the values of energy absorbed, cerium(III) formed, and the nitrite ion yield for these experiments. It will be observed that the yield of cerium(III) is almost the same as that obtained in solutions which do not contain small amounts of nitrate. The indication is as was predicted, namely that the direct action process as described by equation (k) is not too important in dilute nitrate solutions.

4. Purification Experiments

Some experiments to test the propriety of using Reagent Grade chemicals as received were carried out. A sizable quantity of sodium nitrate was run through 4 recrystallizations from water. Sufficient material was removed from each step to prepare a 1.00 M solution. Then the five solutions 1.00 M of sodium nitrate, 0.4 M in sulfuric acid, and 0.0002 M in cerium(IV) hydrogen sulfate were prepared from the five

TABLE II

NITRITE YIELDS FROM DILUTE NITRATE SOLUTIONS

Salt	Concn. (moles/L)	Energy Absorbed per Milliliter (ev/ml/min x 10 ¹⁷)				Formation Rate (Ce ⁺³) (moles/ml/min x 10 ⁹)	G (Ce ⁺³) _t *	G (Ce ⁺³) _s **	G (NO ₂ ⁻)-da
		Cation	Anion	Solvent	Total				
LiNO ₃	0.01	.00007	.00074	1.351	1.3518	5.63	2.51	2.34	0.08
NaNO ₃	0.01	.00026	.00074	1.357	1.3580	5.70	2.53	2.34	0.09
KNO ₃	0.01	.00046	.00074	1.358	1.3592	5.90	2.61	2.34	0.13

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

batches of material, representing the various times of recrystallization. The data obtained from irradiation of these are presented in Table III and Figure 2.

From a plot of the type shown in Figure 2, many conclusions may be reached. If an easily oxidizable contaminant is present, the initial irradiation will show a greater rate of cerium(III) formation than the remaining irradiations. A straight line drawn through the experimental points will represent the rate of cerium(III) formation, and the cerium(III) intercept at zero irradiation time will represent the amount of oxidizable contaminant present. If the intercept is a constant for various nitrate salt concentrations, the contaminant is present in the water. If the intercept is proportional to the nitrate salt concentration, the contaminant is present in the salt. This may be generally eliminated by aging the solution before irradiation. An intercept on the irradiation time scale represents the presence of a contaminant more easily reducible than cerium(IV). The intercept is an indication of the amount and type of contaminant present.

Purification by recrystallization of the sodium nitrate from water was accomplished as illustrated by the diminishing extrapolated zero irradiation cerium(III) intercept value. However, since the zero irradiation time intercept can be determined and used to correct the experimentally determined values, accurate G values can be obtained in the presence of reasonably small amounts of contaminants.

TABLE III

CERIUM(IV) REDUCTION FROM RECRYSTALLIZED SODIUM NITRATE
 Moles of Cerium(III) formed ($\times 10^6$)

Irradiation Time (Min)	A*	B**	C**	D**	E**	F***	G***
0	-	-	-	-	-	-	-
1	15.49	14.93	15.49	14.55	14.55	16.61	16.79
3	42.92	42.54	42.92	41.80	40.68	44.60	43.85
6	80.61	84.53	85.84	82.10	81.92	85.28	81.54
10	134.54	136.03	134.17	134.91	141.62	136.96	134.35
G Ce(III)	5.63	5.74	5.64	5.71	5.72	5.72	5.63

* Salt as received.

** Successive recrystallizations.

*** Different batches of salt.

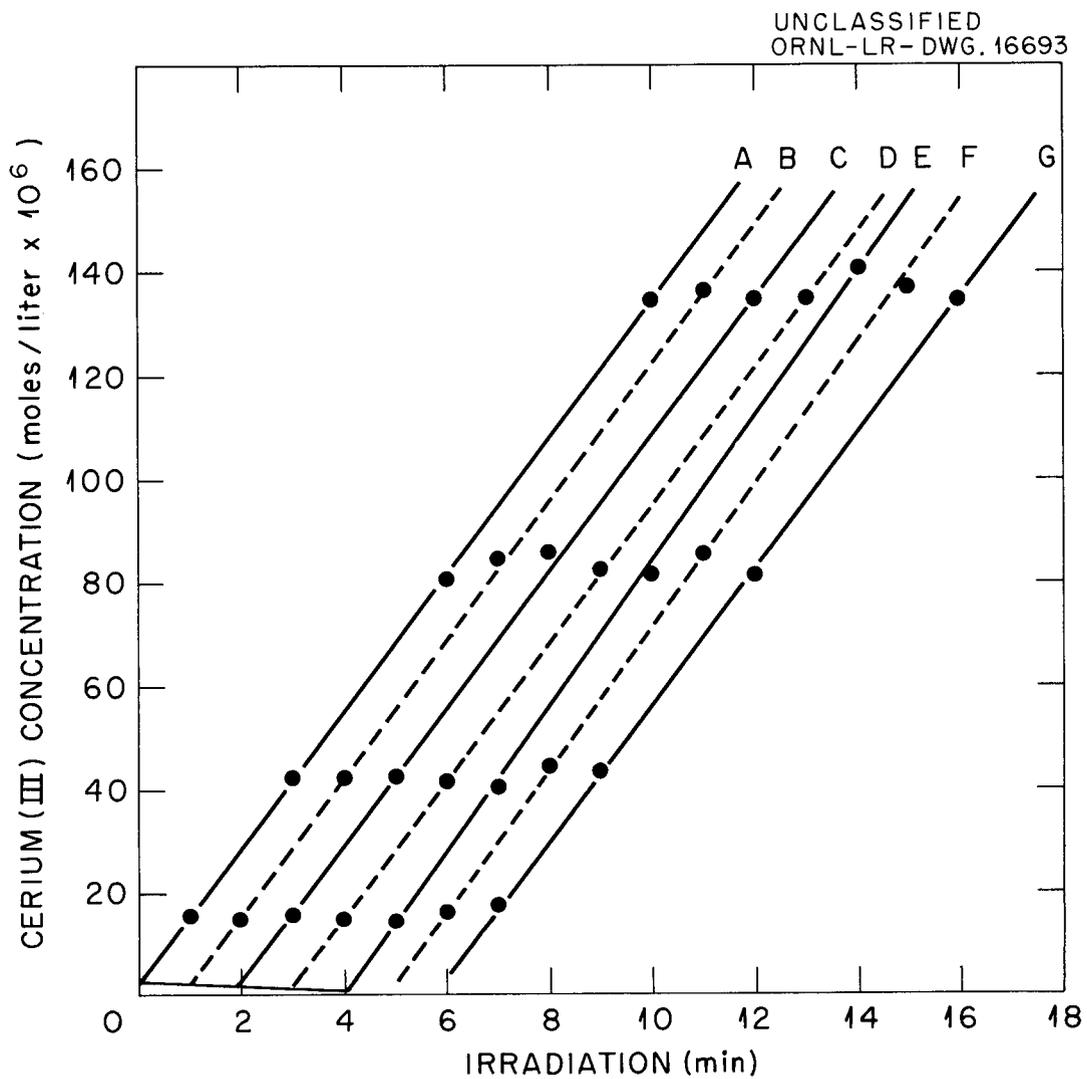


Figure 2
CERIUM (IV) REDUCTION FROM RECRYSTALLIZED SODIUM NITRATE
(Each Curve Successively Displaced One Unit)

5. Accuracy of Method

The precision of the cerium(IV) method for determining the direct action on nitrates is good. From the data tabulated in Table III, it was found that the average yield of cerium(III) was 5.68 molecules per 100 ev of absorbed energy. The standard deviation and probable error were determined to be 0.05 and 0.03 molecules respectively.

D. Detailed Experiments

1. Alkali Metal Nitrate Experiments

A large number of solutions which were 0.0002 M in cerium(IV) hydrogen sulfate and 0.4 M in sulfuric acid were prepared. In addition these solutions were of differing molarities in various alkali metal nitrates. These solutions were irradiated for varying times and the cerium(III) yields were determined. Then the amount of cerium(III) produced by radical action in each case was calculated.

The amount of cerium(III) formed by interaction of cerium(IV) with radicals (equations (p), (q), and (r)) will be proportional to the amount of solvent present per milliliter of solution. In very dilute solution, one milliliter of solution contains very nearly one milliliter of solvent, however, in more concentrated solutions, the amount of solvent per milliliter of solution decreases as the solute concentration increases. Thus, if the theoretical yield of cerium(III) in dilute solutions 0.4 M in sulfuric acid is 2.34, the yield of cerium(III) in concentrated solutions 0.4 M in sulfuric acid will be lowered propor-

tionally to the amount of solvent present. The corrected yield of cerium(III) produced by radical and molecular action in each case was then subtracted from the total yield of cerium(III) to obtain the cerium(III) produced by nitrite which had been formed by direct action. Then the yield of nitrite produced by direct action was obtained by halving the yield of cerium(III) produced by direct action. These data are presented in Tables IV, V, VI, and VII.

2. Experiments on Other Nitrates

Experiments identical with those in the previous section with the exception that other nitrates were substituted for the alkali metal nitrates were carried out. The nitrates used were those of ammonium, magnesium, zinc, aluminum, and thorium. The results of these experiments are reported in Tables VIII, IX, X, and XI.

E. Conclusions

In the nitrate salts studied, it was found that the yield of nitrite produced by direct action in solutions 0.4 M in sulfuric acid and 0.0002 M in cerium(IV) hydrogen sulfate is dependent upon the nitrate concentration. A semi-log arithmetic plot presented all the data in a consistent manner. The enhanced yield of cerium(III) expressed as nitrite and determined by a least squares analysis of all the data may be represented by:

$$G(\text{NO}_2^-) = 1.22 \log [\text{NO}_3^-] + 1.70 \quad (\text{aa})$$

TABLE IV

NITRITE YIELDS FROM LITHIUM NITRATE SOLUTIONS

Concn. (moles/L)	Energy Absorbed per Milliliter (ev/ml/min x 10 ⁻¹⁷)				Formation Rate (Ce ⁺³) (moles/ml/min x 10 ⁹)	G (Ce ⁺³)-t*	G (Ce ⁺³)-s**	G (NO ₂ ⁻)-da
	Cation	Anion	Solvent	Total				
0.10	--	0.007	1.357	1.364	7.74	3.42	2.33	0.54
0.20	0.001	0.014	1.350	1.365	8.99	3.96	2.32	0.82
0.30	0.002	0.021	1.345	1.368	10.08	4.44	2.31	1.07
0.50	0.003	0.036	1.334	1.373	11.42	5.01	2.29	1.36
1.00	0.007	0.073	1.318	1.398	13.77	5.93	2.27	1.83
2.00	0.014	0.145	1.257	1.416	14.99	6.37	2.16	2.10

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE V

NITRITE YIELDS FROM SODIUM NITRATE SOLUTIONS

Concn. (moles/L)	Energy Absorbed per Milliliter (ev/ml/min x 10 ¹⁷)				Formation Rate (Ce ⁺³) (moles/ml/min x 10 ⁹)	G (Ce ⁺³)-t *	G (Ce ⁺³)-s **	G (NO ₂ ⁻)-da
	Cation	Anion	Solvent	Total				
0.1	0.002	0.007	1.346	1.355	7.49	3.33	2.33	0.50
0.2	0.005	0.014	1.340	1.359	9.18	4.07	2.32	0.88
0.3	0.008	0.022	1.343	1.373	9.92	4.35	2.31	1.02
0.5	0.013	0.036	1.334	0.383	11.39	4.96	2.30	1.33
1.0	0.026	0.072	1.308	1.406	12.88	5.51	2.27	1.62
3.0	0.075	0.210	1.202	1.487	16.33	6.61	2.14	2.24
5.0	0.126	0.351	1.116	1.593	18.96	7.16	1.98	2.59

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE VI

NITRITE YIELDS FROM POTASSIUM NITRATE SOLUTIONS

Concn. (moles/L)	Energy Absorbed per Milliliter (ev/ml/min x 10 ¹⁷)				Formation Rate (Ce ⁺³) (moles/ml/min x 10 ⁹)	G ^{Ce⁺³} _{-t} *	G ^{Ce⁺³} _{-s} **	G ^{NO₂⁻} _{-da}
	Cation	Anion	Solvent	Total				
0.14	0.006	0.010	1.352	1.368	8.36	3.68	2.32	0.68
0.20	0.009	0.014	1.349	1.372	9.21	4.04	2.32	0.86
0.34	0.015	0.025	1.338	1.378	10.39	4.54	2.30	1.12
0.50	0.022	0.036	1.322	1.380	11.59	5.06	2.28	1.39
1.0	0.044	0.072	1.290	1.406	13.26	5.68	2.23	1.73
1.36	0.061	0.099	1.275	1.435	14.48	6.07	2.19	1.94
1.75	0.076	0.123	1.208	1.407	14.44	6.18	2.15	2.02

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE VII

NITRITE YIELDS FROM RUBIDIUM NITRATE AND CESIUM NITRATE SOLUTIONS

Concn. (moles/L)	Energy Absorbed per Milliliter (ev/ml/min x 10 ⁻¹⁷)				Formation Rate (Ce ⁺³) (moles/ml min x 10 ⁹)	G (Ce ⁺³)-t*	G (Ce ⁺³)-s**	G (NO ₂ ⁻)-da
	Cation	Anion	Solvent	Total				
<u>Rubidium</u>								
0.1	0.009	0.007	1.355	1.351	7.37	3.28	2.33	0.48
0.3	0.026	0.022	1.328	1.376	9.32	4.08	2.31	0.89
0.4	0.035	0.029	1.290	1.354	10.67	4.74	2.30	1.22
0.5	0.042	0.035	1.265	1.342	11.68	5.03	2.30	1.37
<u>Cesium</u>								
0.1	0.014	0.007	1.332	1.353	7.53	3.35	2.32	0.52
0.3	0.041	0.022	1.315	1.378	10.45	4.57	2.29	1.14
0.5	0.068	0.036	1.284	1.388	11.52	5.00	2.24	1.38
1.0	0.134	0.071	1.255	1.460	13.81	5.72	2.19	1.76

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE VIII

NITRITE YIELDS FROM AMMONIUM NITRATE SOLUTIONS

Concn. (moles/L)	Energy Absorbed per Milliliter (ev/ml/min x 10 ¹⁷)				Formation Rate (Ce ⁺³) (moles/ml min x 10 ⁹)	G (Ce ⁺³)-t*	G (Ce ⁺³)-s**	G (NO ₂)-da
	Cation	Anion	Solvent	Total				
0.10	0.002	0.006	1.329	1.337	7.63	3.44	2.33	0.55
0.20	0.004	0.012	1.323	1.339	8.85	3.98	2.32	0.83
0.30	0.005	0.018	1.319	1.342	9.77	4.38	2.31	1.04
0.50	0.013	0.036	1.299	1.348	11.25	5.02	2.28	1.37
1.0	0.025	1.071	1.268	1.364	12.82	5.66	2.22	1.72
2.0	0.055	0.135	1.180	1.370	14.39	6.32	2.10	2.11
3.0	0.076	0.214	1.165	1.455	17.05	7.05	1.99	2.53
5.0	0.124	0.350	1.007	1.481	17.63	7.17	1.76	2.71

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE IX

NITRITE YIELDS FROM ZINC NITRATE AND MAGNESIUM NITRATE SOLUTIONS

Concentration (moles NO_3^-/L)	Energy Absorbed per Milliliter (ev/ml/min $\times 10^{-17}$)				Formation Rate (Ce^{+3}) (moles/ml min $\times 10^9$)	$G_{(\text{Ce}^{+3})-t}^*$	$G_{(\text{Ce}^{+3})-s}^{**}$	$G_{(\text{NO}_2)-da}$
	Cation	Anion	Solvent	Total				
<u>Zinc</u>								
0.10	0.003	0.007	1.329	1.339	7.37	3.31	2.33	0.49
0.20	0.007	0.014	1.326	1.347	9.04	4.04	2.32	0.86
0.40	0.014	0.029	1.365	1.365	10.55	4.65	2.31	1.17
0.60	0.021	0.043	1.316	1.380	11.11	4.85	2.31	1.27
1.00	0.034	0.069	1.310	1.413	13.06	5.56	2.29	1.63
<u>Magnesium</u>								
0.10	0.002	0.007	1.342	1.351	7.59	3.38	2.33	0.53
0.20	0.003	0.015	1.339	1.359	8.74	3.88	2.33	0.78
0.40	0.006	0.029	1.334	1.369	10.68	4.70	2.32	1.19
0.60	0.008	0.043	1.328	1.379	11.12	4.85	2.31	1.27
1.00	0.014	0.072	1.320	1.406	12.54	5.37	2.29	1.54
2.00	0.027	0.144	1.297	1.468	14.25	5.84	2.26	1.79
4.00	0.056	0.248	1.241	1.585	18.40	6.99	2.16	2.42

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE X

NITRITE YIELDS FROM ALUMINUM NITRATE SOLUTIONS

Concentration (moles NO_2^-/L)	Energy Absorbed per Milliliter ($\text{ev/ml/min} \times 10^{17}$)				Formation Rate (Ce^{+3}) (moles/ml min $\times 10^9$)	$G_{(\text{Ce}^{+3})-t}^*$	$G_{(\text{Ce}^{+3})-s}^{**}$	$G_{(\text{NO}_2^-)-da}$
	Cation	Anion	Solvent	Total				
0.15	0.001	0.011	1.340	1.352	8.34	3.71	2.33	0.69
0.30	0.002	0.022	1.334	1.358	9.20	4.08	2.32	0.88
	0.002	0.022	1.304	1.328	9.13	4.14	2.32	0.91
0.60	0.007	0.043	1.327	1.377	10.98	4.80	2.31	1.25
0.90	0.009	0.065	1.318	1.392	11.72	5.07	2.29	1.39
1.50	0.016	0.108	1.303	1.427	13.68	5.77	2.27	1.75
3.00	0.030	0.215	1.267	1.512	15.73	6.26	2.21	2.03

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

TABLE XI

NITRITE YIELDS FROM THORIUM NITRATE SOLUTIONS

Concentration (moles NO_3^-/L)	Energy Absorbed per Milliliter (ev/ml/min $\times 10^{17}$)				Formation Rate (Ce^{+3}) (moles/ml min $\times 10^9$)	$G_{(\text{Ce}^{+3})-t}^*$	$G_{(\text{Ce}^{+3})-s}^{**}$	$G_{(\text{NO}_2^-)-da}$
	Cation	Anion	Solvent	Total				
0.10	0.006	0.007	1.302	1.315	7.30	3.34	2.34	0.50
0.20	0.013	0.014	1.293	1.320	8.48	3.87	2.32	0.78
0.30	0.019	0.021	1.290	1.330	10.37	4.70	2.32	1.19
0.50	0.032	0.036	1.283	1.351	11.38	5.07	2.31	1.38
1.00	0.065	0.071	1.269	1.405	13.45	5.76	2.28	1.74
2.00	0.128	0.141	1.242	1.511	16.60	6.61	2.23	2.19
3.00	0.193	0.212	1.214	1.619	19.52	7.26	2.18	2.54

* Total Ce(III) formed.

** Ce(III) formed by solvent radiolysis.

where $[\text{NO}_3^-]$ represents the molar concentration of the nitrate. Figure 3 is a plot of the line described by equation (aa), which illustrates the formation of nitrite from solutions 0.1 to 5.0 M in nitrate. If extrapolated, it indicates that direct action ceases below a nitrate concentration of 0.04 M, since this is the point at which $G(\text{NO}_2^-)$ becomes zero.

The total energy absorbed by the solution was used to calculate the cerium(III) yields. The consistency of this method of calculation as evidenced in the experimental data, indicates that the energy absorbed by all the constituent parts of the solution is probably effective in decomposing nitrate to nitrite. The physical properties of the nitrate salt and the cation it contained appeared to have no influence upon the rate of nitrite formation. The only criterion determining the rate of nitrite formation appeared to be the nitrate concentration.

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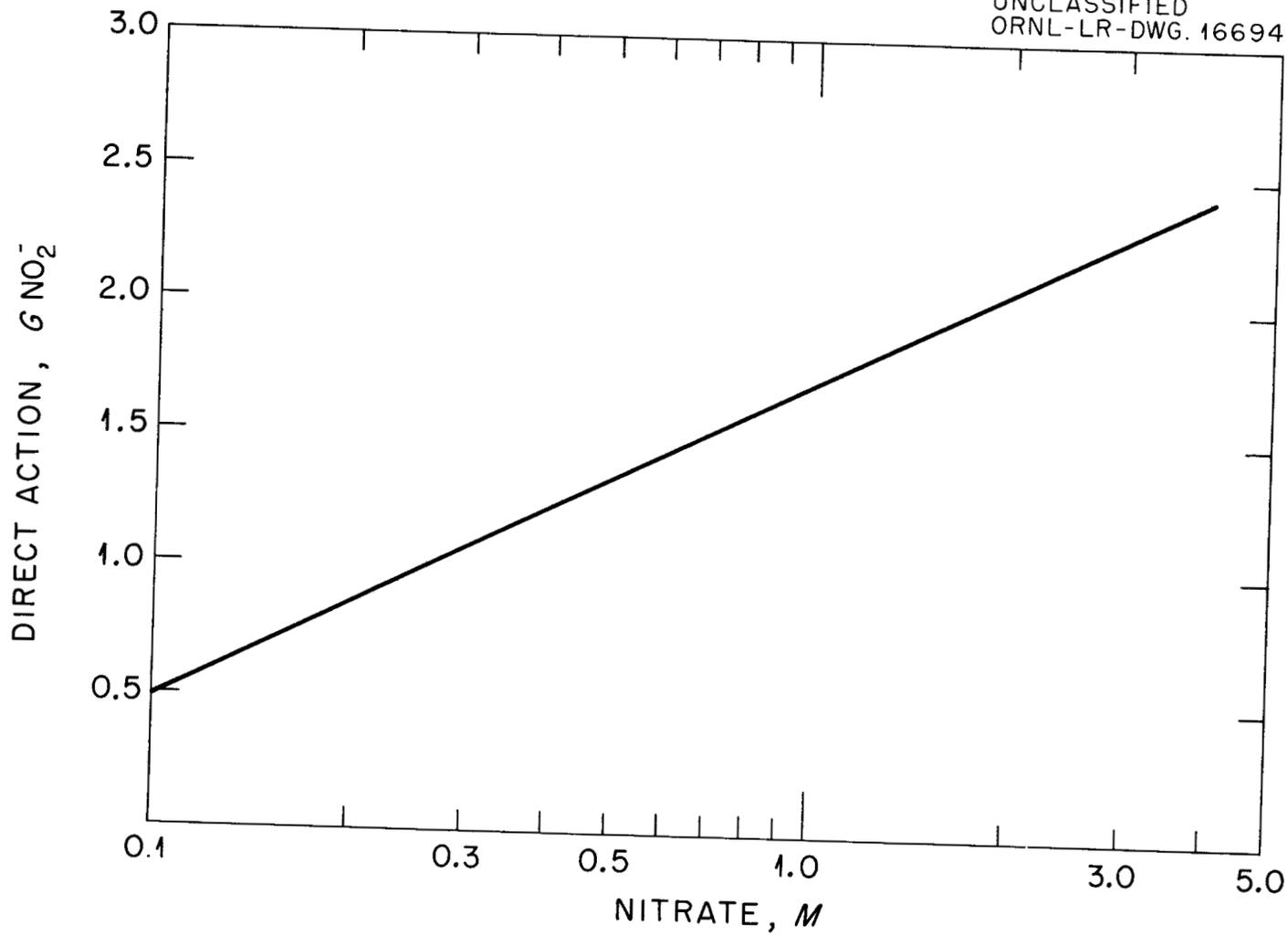


Figure 3
THE DIRECT ACTION NITRITE YIELD FROM NITRATE SOLUTIONS

CHAPTER IV

SUMMARY

This investigation consisted of experiments designed to measure the rate of nitrite production when solutions of metal nitrates were irradiated with gamma rays. Of particular interest were (1) the effect of the cation and (2) the effect of concentration. Solutions of various metal nitrates in the concentration range 0.01 to 5.0 M were employed. Elimination of back reaction which destroyed nitrite was effected by the use of cerium(IV) ion, which removed reducing radicals and molecular products. Any enhancement of the cerium(III) yield over that obtained in the absence of nitrate was interpreted to be due to the direct formation of nitrite.

An analysis of all the data showed that the yield of nitrite produced by direct action was (1) independent of the cation, (2) dependent only upon the nitrate concentration, and (3) dependent upon the total absorbed energy regardless of the particular constituents of the solution. This yield could be represented by $G(\text{NO}_2^-)_{\text{da}} = 1.22 \log [\text{NO}_3^-] + 1.70$, where $G(\text{NO}_2^-)_{\text{da}}$ is the yield of nitrite produced by direct action and $[\text{NO}_3^-]$ symbolizes the molar concentration of nitrate. From this equation, one may realize that the direct action production of nitrite becomes practically zero at a molar concentration of about 0.04. It is felt that this work is significant in that it represents one of the few excursions into the region of concentrated solutions. It is

interesting that no unexpected phenomena occurred in these concentrated solutions, that is, phenomena which could not be predicted by an extrapolation of experience in dilute solutions.

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