ENERGY TRANSFER IN THE GAMMA RADIOLYSIS OF ISOLATED NITRATE AND NITRITE IONS

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I. INTRODUCTION

The application of some types of energy transfer phenomena, such as the use of the luminescence of phosphors, has far outstripped the knowledge of what happens when energy is transferred. Important uses of energy transfer occur in the operation of cathode ray tubes and fluorescent lights, in scintillation counting of radiation, and in the use of transistors. Much emphasis is presently being placed on finding workable mechanisms to describe energy migration in living systems, in catalysts, and in phosphors.

An inorganic phosphor contains metallic impurity ions which absorb and/or emit radiation under excitation. Many investigations have shown the effects of energy transfer from the matrix to the acceptor ions, or activators, and between the activators. The study of a crystalline system in which energy transfer results in permanent chemical change instead of a radiative process should be a new approach to the problem of finding mechanisms of energy transfer in solids.

Nitrate and nitrite ions have been shown to decompose when energy is transferred to them from an alkali halide matrix, and they both show a very simple infrared spectrum which can be used for quantitative analysis. For these reasons nitrate and nitrite ions were chosen as the chemical indicators of energy transfer to be studied in this investigation.

Although the alkali halide compressed disk method of infrared sampling has been used in quantitative analysis, various aspects of the technique must be standardized in order to obtain reproducible results from the analysis of a radiation-induced reaction. Information on the radiolysis of isolated nitrate and nitrite ions might also be applied to the radiolysis of the pure salts.

The purpose of this investigation is to determine the effects of and possible mechanisms for transfer of energy to anion impurities in compressed pellets of potassium bromide.

II. LITERATURE REVIEW

The gamma radiolysis of nitrate and nitrite ions in alkali halide matrices and the energy transfer process accompanying the decomposition will be discussed in the following sections using available material from the literature. The discussion will cover properties of gamma radiation, general effects of ionizing radiation on solids, radiation-induced chemical reactions in solids, decomposition of solid nitrates by radiation, radiation effects in alkali halides, luminescence and energy transfer in solids, infrared spectroscopy, the alkali halide pressed disk method of infrared sampling, dosimetry and colorimetric analysis, and purification of potassium nitrite.

Properties of Gamma Radiation

Properties of gamma rays, the radiation used in this investigation, are discussed in the following paragraphs.

Ionization of Matter by Gamma Rays. Gamma rays are ionizing radiation, so called because they cause ionization when they impinge on matter. Gamma radiation, which is important to this investigation, interacts with matter in three ways(25): (1) the photoelectric effect, in which a photon knocks an orbital electron out of an atom and vanishes; (2) the Compton process, in which a photon loses some of its energy upon being scattered by a free electron; and (3) pair production, in which the photon vanishes and an electron-hole pair is produced.

Cascade Ionization. In the photoelectric effect the orbital electrons knocked out of the atoms by gamma rays are called primary electrons. These primary electrons possess enough energy to knock out other electrons called secondary electrons from surrounding atoms. The secondary electrons knock out other electrons, and so forth, in a cascade effect. Effects of gamma radiation are therefore caused by the three types of interaction listed in the preceding paragraph and also by the cascade electrons. According to Taylor(71), the cascade electrons account for almost all of the ionizing effects of radiation on matter.

General Effects of Ionizing Radiation on Solids

Reviews of radiation effects on solids have been presented by Seitz(67), Neal(27,28), and others(71,10). A short, basic summary of these reviews appears in the following paragraphs.

Point Defects and Dislocations. The properties of crystalline solids not applicable to a perfect crystal can be explained(67) by the assumption of certain imperfections in the crystal structure. One type of imperfection is the point defect. Point defects are caused by misplaced elements of the crystal or by atoms of an impurity. A vacancy, or Schottky defect, is a lattice site at which the normal occupant is absent. An interstitial atom or ion is in an abnormal position in the lattice. The combination of these two is called a Frenkel defect. These point defects distort the electron distribution of the lattice and in so doing may trap electrons at points of high positive charge called negative ion vacancies, which are the vacancies left when negative ions are displaced from their normal lattice positions. Electrons and holes trapped in the vacancies absorb characteristic wavelengths of light and are called color centers.

The other type of imperfection involves dislocation of planes of atoms displaced to different degrees from their ideal positions. These dislocations include in their makeup local strains, and these local strains attract point defects to themselves during irradiation of the solid.

Stored Energy. The most basic change occurring during irradiation of a crystal is the increase of energy in the lattice. This increase of energy is referred to as stored energy(10). Stored energy is the energy of the defects caused by irradiation. Annealing is the process whereby the stored energy is released and this usually involves heating the irradiated solid. Chemical decomposition of one or more of the constituents of the lattice is another way to release the stored energy.

The Cage Effect. The cage effect must have a large effect on the ease of chemical reactions in solids. This effect, as stated by Heal(27), is the hindrance by the surrounding lattice of the escape of radicals or atoms from the decomposition site. Large radicals will usually not escape and will recombine with each other. A large molecule will either break off small radicals and single atoms or decompose by rearrangement into large product molecules.

Another possible result of the cage effect is that dissociations impossible at a normal lattice site may be possible at a defect site since there the cage will be more or less open on one side.

Radiation-Induced Reactions in Solids

Radiation-induced chemical reactions in solids are discussed in the following paragraphs. This material is included in reviews by Taylor(71) and Heal(28).

Breaking of Covalent Bonds. Covalent bonds in solids may be broken by excitation or ionization. This effect is shown by metal nitrates, chlorates, perchlorates, bromates, and to a small extent by sulfates. Nitrates are typical of this group; the end products of radiation-induced decomposition of alkali metal nitrates are the corresponding nitrites and molecular oxygen. Alpha particles decompose ferric chloride to form ferrous chloride and chlorine, and the irradiation of ice results in the breaking of oxygen-hydrogen bonds as does the radiolysis of liquid water.

Dependence of Yields on the Type of Bond. The yield of breakage of a single type of bond should depend on the strength of the bond and on its frequency of appearance. This rule should also apply to liquids and gases, and this has been shown to be true in the case of trichloro-bromo-methane in which there is no change in the rate of bromine production under gamma radiation whether the sample is at the melting point or at a phase transition point. Frerichs(21) has reported that some of the photochemical reactions employing ionizing radiation, for example the formation of color centers, are up to ten per cent efficient, based on the amount of energy absorbed in the sample.

Decomposition of Solid Nitrates by Radiation

The decomposition of solid nitrates by radiation has been studied by a number of investigators. Doigan and Davis(14), Hochanadel and Davis(33), and Pringsheim(61) used ultraviolet light; Hennig, Lees, and Matheson(29) used pile radiation; and Cunningham and Heal(8) used X-rays as the incident radiation. The results of these and other workers concerned with the decomposition of nitrates by radiation are discussed in the following paragraphs.

Decomposition of the Nitrate Ion. According to Cunningham and Heal(8), the overall equation for the decomposition of nitrate ions can be written in the following manner:

$$2NO_3^- = 2NO_2^- + O_2 \qquad (1)$$

The oxygen gas formed can be released by heating the irradiated solid, and it is released without heating after the nitrate has been decomposed to some extent. Magnetic susceptibility measurements made by Hennig, Lees, and Matheson(29) have shown that the oxygen is trapped inside the crystals as oxygen gas and not as atomic oxygen.

This, however, in no way precludes the possibility that oxygen atoms are split off the nitrate ions and migrate through the solid until they react with other oxygen atoms to form molecular oxygen.

Stoichiometry. The amount of oxygen release from the irradiated solid has been shown(8,29,14) to be stoichiometric with the number of nitrite ions found in accordance with Equation (1) above. The amount of nitrite ion was measured in water solutions of the irradiated solid. Doigan and Davis(14) have reported, from mass spectroscopy measurements, only oxygen in the gas above the irradiated solid; Cunningham and Heal(8) found 99.5 per cent oxygen and no nitrogen or oxides of nitrogen; and Hennig, Lees, and Matheson(29) found about 98.5 per cent oxygen and a small amount of an inert gas which was believed to be nitrogen.

Effect of Nitrite Buildup. Cunningham and Heal(8) have reported that pure potassium nitrite is not much decomposed by ionizing radiation. Since the decomposition rate of the nitrate ions is nearly proportional to the amount of nitrate present and not to the nitrate plus the nitrite, energy transfer from the nitrite to the nitrate probably does not enter into the process.

Possible Reactions of Oxygen Atoms. Possible reactions of oxygen atoms probably released from the nitrate ions are:

$$NO_3^- + O = NO_2^- + O_2 \qquad (2)$$

$$NO_2^- + O = NO_3^- \qquad (3)$$

The absence of any considerable temperature effect on the decomposition has led Doigan and Davis(14) to conclude that Equations (2) and (3) are negligible or have equal activation energies. The possibility of an equilibrium has nevertheless been suggested by some researchers(7,33).

Dependence of the Rate on Free Space. Cunningham and Heal(7) have shown that the decomposition rates of nitrates depend strongly on the free space in the lattice. Potassium nitrate, for instance, shows the highest decomposition rate of the monovalent nitrates, and it also has the most free space in the lattice. This indicates that the oxygen and the nitrite ion formed in the decomposition of a nitrate ion may tend to recombine unless there is enough space available for the oxygen to be expelled from the decomposition site.

Hydrated Nitrates. Hydrated nitrates show a higher rate of decomposition than do the corresponding anhydrous nitrates, according to Baberkin(3) and Hochanadel and Davis(33). Potassium nitrate does not form a hydrate so it does not show this effect.

Decomposition Rate of Potassium Nitrate. The decomposition rate of potassium nitrate shows some deviation with temperature(8), and a log-log plot of nitrite ions formed versus energy absorbed in the sample of potassium nitrate shows a change of slope at about two per cent decomposition. Reported decomposition rates, or "G" values, for nitrite formation from pure, solid potassium nitrate at temperatures near 25 degrees, Centigrade, are 0.8(63), 1.96(7), and 1.57(33) nitrite ions formed per hundred electron volts absorbed in the sample.

The number of nitrite ions was determined in these experiments from the concentration of nitrite ions in a water solution of the sample.

Infrared Absorption of Irradiated Nitrates. Cunningham and Heal(8) found, upon irradiation of potassium nitrate, that two new absorption maxima appeared in the infrared region at 1250 and 1270 wave numbers. The maximum at 1250 wave numbers appeared first, and the maximum at 1270 wave numbers appeared after about four per cent of the nitrate had been decomposed. The second maximum increased more rapidly than the first one. Cunningham and Heal attribute the absorption maximum at 1250 wave numbers to single nitrite ions in the potassium nitrate lattice and the peak at 1270 to regions of nitrite lattice in the sample.

Ultraviolet Absorption of Irradiated Nitrates. Pringsheim(61) studied the ultraviolet absorption of solid, irradiated sodium nitrate. One absorption band, which was continuous and showed a maximum near 3550 Angstroms, was easily bleached by ultraviolet light even at low temperatures and was partially bleached by ionizing radiation at room temperature. This band was attributed to color centers formed in the sodium nitrate crystal. Another band, attributed to nitrite ions, appeared at about 3450 Angstroms. This band was stable, and it was the stronger of the two bands when the sample was irradiated at temperatures above 25 degrees, Centigrade. According to Pringsheim, the closeness of the two bands indicates that the color centers are somehow connected with the presence of the nitrite ions; perhaps they are caused by nitrite ions strongly perturbed by trapped electrons nearby.

Radiation Effects in Nitrites. Cunningham and Heal(8) have reported that decomposition of solid nitrites under irradiation is very slight. Boyle(4) irradiated fused sodium nitrite and found only nitrogen and nitrous oxide in the gaseous products. Mollwo(55) irradiated crystals of potassium bromide containing both nitrate and nitrite ions and found some evidence for the formation of potassium-oxygen bonds during the irradiation. Zeldes(72) has reported evidence, from electron spin resonance studies on irradiated nitrites, for the presence of nitrogen dioxide formed by radiolysis at liquid nitrogen temperature (-196 degrees, Centigrade).

Effects of Ionizing Radiation on Alkali Halides

The formation of color centers in single crystals of alkali halides and in polycrystalline compressed pellets of alkali halides is discussed in the following paragraphs.

Formation of F Centers. Seitz(67) has presented an extensive review of studies of color centers formed in crystals of alkali halides. Schottky defects, which are ion vacancies in the lattice, appear to predominate in irradiated alkali halides at elevated temperatures. Both positive ion vacancies and negative ion vacancies are produced during irradiation. These defects can move, and the positive ion vacancies are much more mobile than the negative ion vacancies.

Alkali halides are colored in what is called the F band(67) by ionizing radiation and by the presence of excess alkali metal.

The color centers in this band, called F centers, are probably electrons trapped at negative ion vacancies. The F centers absorb light in the visible spectrum, the wavelength of the F band depending on the alkali halide chosen. The color in irradiated alkali halides is quickly bleached by sunlight even at temperatures near 30 degrees, Centigrade, but the F centers become more stable as the temperature is lowered. The F band in potassium bromide is seen around 6100 Angstroms.

Formation of V Centers. According to the review presented by Seitz(67), color centers which absorb in the ultraviolet region of the spectrum are also formed upon irradiation of alkali halides. These color centers, called V centers, have also been detected in alkali halides colored by an excess of halogen. The V centers probably involve positive ion vacancies at which holes are trapped. There are two major V bands formed in potassium bromide; the absorption band around 2300 Angstroms is called the V_3 band, and the maximum around 2650 Angstroms is called the V_2 band. Other, minor bands in the ultraviolet region are observed upon the bleaching of F centers. The V bands are very slowly bleached by sunlight or heat and are stable at low temperatures.

Density of F Centers in Potassium Bromide. Jordan and Alger(41) propose that excitation energy is transferred to absorption centers in alkali halides by excitons, free electrons, and holes, and that the absorbed energy goes to chemical reactions, annihilation of holes by electrons, and formation of color centers. In pure potassium bromide crystals the concentration of F centers formed by X-rays was found(41) to level off at about 1 x 10^{16} F centers per cubic centimeter after a dose of about 5 x 10^{17} electron volts had been absorbed per cubic centimeter.

Color Centers in Polycrystalline Alkali Halide Disks. Hersh(30) observed V bands in polycrystalline alkali halide compressed disks colored with excess halogen and also in disks irradiated with X-rays. The irradiated disks also were colored in the F band, and the color center bands for both the F and V centers occurred at the same wavelengths as the centers in irradiated single crystals of alkali halide. Hersh also observed that the polycrystalline disks gave much greater intensities of absorption for both types of centers.

The F centers produced by irradiation of the pressed disks were more easily bleached than those formed in single crystals. The ratio of peak absorption of the F and V bands is not constant but varies with irradiation and bleaching.

When the irradiated disks were dissolved in water halogen gas was liberated, but nothing is known of the fate of the alkali metal ions. The reduction of the halide is attributed to reaction of the halide ions with trapped holes in the solid.

Color Centers in Potassium Iodide Doped with Thallium Ions. According to Hersh(31), at concentrations around 0.01 mol per cent of thallium iodide in potassium iodide matrices, thallium metal is formed instead of F centers upon coloration of the samples by electrolysis or by the addition of excess potassium metal. The thallium impurity appears to affect both the nature and the production rate of V centers in potassium iodide; the production rate is enhanced by the presence of the thallium ions. No iodine was found in solutions of these samples.

Color Centers in Alkali Halides Doped with Nitrite Ions. The presence of nitrite ions, even in concentrations as low as 0.01 mol per cent, was found by Hutchinson and Pringsheim(35) to greatly suppress F center formation in alkali halide crystals under X-irradiation, except for sodium chloride in which the F center formation is enhanced by the presence of nitrite ions. Another band, called the C band, was observed to reach saturation after which time the F center concentration increased rapidly. The C band is a continuous band which is also observed during the irradiation of pure nitrites.

Luminescence and Energy Transfer in Solids

The recent theories and applications of luminescence and energy transfer in solids will be discussed in the following paragraphs.

Application and Causes of Luminescence. Luminescent systems, or phosphors, are widely used in scintillation counters for radiation (22,46,58), in the study of energy transfer in solids(30,31,19), and in such familiar devices as fluorescent lights and cathode ray tubes. The glowing, or luminescence, of materials which have been irradiated is a byproduct of annealing out the effects of irradiation and getting rid of the stored energy(10). The energy expended in this expulsion of photons may be thought of as the difference between the excited state of an atom or molecule and a more stable state to which it converts(46).

Luminescent Systems. Most inorganic luminescent systems consist of a host material or matrix into which small amounts of foreign atoms or ions, called activators(46), are incorporated. Some luminescent systems also contain small amounts of sensitizers(12) which improve the efficiency or some other property of the luminescence. One example of a simple phosphor which is widely used(30,31,65) is potassium chloride doped with small amounts of thallium chloride. The symbol for this system is KCl:Tl. Other systems involve organic materials. According to Taylor(71), direct evidence for energy transfer is shown by napthacene-anthracene mixtures. Irradiated solid solutions of 0.0001 mol fraction of napthacene in anthracene show the green fluorescence of the napthacene rather than the violet of the anthracene. In this system the energy is transferred rapidly and efficiently.

Energy Transfer in Alkali Halide Pressed Disks. Jones(39) has found that, if nitrate ions are incorporated into an alkali halide matrix in the form of a polycrystalline pressed disk, energy transfer from the matrix to the nitrate ions occurs when the disk is irradiated with gamma rays. Assuming that the energy absorbed in a material from gamma radiation is proportional to the number of electrons that the material contains, the G value for decomposition of the isolated nitrate ions should be of the order 10^{-4} instead of the G value observed of about 0.5 nitrate ions decomposed per hundred electron volts of energy absorbed in the disk for a potassium nitrate concentration of 0.05 mol per cent.

Preparation of Phosphors. Inorganic phosphors(58) have cationic impurities incorporated into the host lattice. The concentration range of an activator sufficient to cause luminescence varies from one part per billion for copper ions in zinc sulfide sensitized by lead to several mol per cent for other phosphors(58,59). Because of the low concentrations required for a large difference in luminescent properties, the making of phosphors is a very exact procedure and involves the utmost cleanliness. The purification of the host material is very important. The phosphors are single crystals grown from a melt to which the activator material has been added. Information concerning the preparation of specific phosphors is available from many sources(58,17,65,38,22,46), and the properties of these systems are usually discussed also. It is interesting to note that attempts(35,55) to incorporate nitrate ions into a host lattice by growing crystals from a melt has always resulted in a mixture of nitrate and nitrite ions because of the thermal decomposition of the nitrate ions.

Methods of Energy Transfer. Luminescent systems may be divided into three categories with regard to methods for energy transfer(46): (1) systems in which absorption and emission of energy takes place in the same center, (2) systems in which absorption occurs in one center and luminescence in another, the energy transfer taking place with no movement of charge carriers, and (3) systems in which energy transfer by means of charge carriers is the dominant feature.

In systems in which the absorption center and the emission center are different but there is no transfer of energy by charge carriers, energy may be transferred by a cascade mechanism involving a radiative transfer of energy through the emission and reabsorption by the activator of photons, or by a nonradiative transfer associated with resonance between the absorbing center and the emitting center. If the cascade mechanism is to be important, the activator, which is the emitter, must also be an efficient absorber of the primary luminescence. In general, both primary and secondary luminescence will be observed in such a system. The size and shape of the sample also affect the efficiency of the cascade mechanism.

In systems in which charge carriers are involved in energy transfer, the mechanism should involve mostly electron and hole migration. Luminescence in this case appears to depend more on the host lattice than on the activator.

Recent Interpretation of Energy Transfer. In a recent lecture Förster(19) stated that the mechanism of transfer of electronic excitation energy is a very specific mechanism but a very general one. The case of emission and reabsorption of the excitation energy by the acceptor molecules, or activators, was regarded as trivial. Förster suggested that the large transfer distances observed in crystalline systems may indicate migration transfer in which the energy travels from one molecule to another by some kind of Brownian movement until it reaches the neighborhood of an acceptor molecule. During this lecture Förster also pointed out that, in a case where spontaneous deactivation of the acceptor sites results from the transfer, a formal treatment gives an equation of the Stern-Volmer type for the quantum efficiency of the luminescence process:

$$\frac{\eta_A}{\eta_A^{max}} = \frac{c}{k + c} \qquad (1)$$

where:

η_A^{max} = maximum quantum yield of fluorescence

η_A = observed quantum yield of fluorescence

c = acceptor concentration

k = parameter dependent on the type of phosphor.

The parameter k in Equation (1) can be defined so as to include the effects of energy traps other than activators.

Absence of Luminescence in Pure Crystals. Dexter and Schulman(9) have studied energy transfer processes in "concentration quenching", in which large concentrations of activator tend to destroy the luminescence of a phosphor. It was proposed from this work that the absence of luminescence in irradiated pure crystals is the result of resonant transfer of energy to imperfections and impurities. According to Klick and Schulman(46), this mechanism probably applies to the pure alkali halides, the transfer rates of which are very high. In this concept the energy is transferred from ion to ion in the alkali halide lattice until it reaches a quenching site in the crystal. At the quenching site the energy is used up in lattice vibrations, annealing of defects, chemical reactions, and similar processes.

Properties of Luminescence of Inorganic Phosphors. Luminescence is temperature dependent. Some phosphors do not emit light until they are heated to a certain temperature; this "thermo-luminescence"(59) also depends on the rate of heating and can be promoted by infrared light or other exciting radiation. Other phosphors, such as the thallium activated potassium chloride, emit radiation at room temperature. The glow curves of the luminescence decay exponentially(16) upon cessation of excitation for phosphors like KCl:Tl; the decay curves for some of these phosphors show half-lives as low as 10^{-7} seconds.

Photons from the phosphors are picked up by photomultiplier circuits(46), and a measured output voltage signal is the result. The measured signal is proportional to the quantum yield of luminescence; the quantum efficiency of the luminescence is defined(62) as the photons put into the phosphor divided by the photons emitted by the activator. Many phosphors emit light of more than one wavelength, and the calculation of the total quantum yield is based on the entire emission spectrum of the phosphor.

Dependence of Quantum Efficiency on Activator Concentration: I. The Analysis of Schulman, et al.(65) The concentrations of activator sites necessary to produce appreciable concentration quenching are such that most activator ions would have other activators as nearest neighbors if quenching is to result from modification of the thermal activation energy for radiationless transitions due to interaction of the activators. In this case quenching could occur at the same site at which absorption takes place, and no energy transfer mechanism need be involved.

Dexter and Schulman(9) have argued that this mechanism of quenching is unlikely since activator ions up to 4000 lattice sites apart would have to be considered near neighbors. They have proposed that the energy is transferred from activator to activator by means of an overlap in the absorption and emission spectra until it reaches a quenching site in the crystal. In view of the poor overlap in the case of the KCl:Tl phosphor, Schulman, et al (65) have proposed that there should be very little concentration quenching in this phosphor; the quantum efficiency of the KCl:Tl phosphor should therefore remain constant over a wide range of activator concentration.

Experiments by Schulman and his co-workers have shown that the effect of concentration quenching is only slightly greater than their experimental error for the KCl:Tl phosphor. The results obtained by Johnson and Williams(38) are therefore reported to be in question because the concentration quenching observed in this phosphor may be merely a loss of brightness rather than a true decrease in quantum efficiency. The values of quantum efficiency reported by Johnson and Williams are also questioned because they are calculated on the basis of quanta emitted per incident quanta rather than quanta emitted per absorbed quanta. Schulman, et al used ultraviolet light at 2470 Angstroms and 2537 Angstroms as the exciting radiation, and the quantum efficiencies reported were measured at the 3050 Angstrom emission of KCl:Tl.

Dependence of Quantum Efficiency on Activator Concentration; II. The Analysis of Johnson and Williams.(38) The theory presented by Johnson and Williams is applied to a wide variety of inorganic phosphors under various types of excitation. Included in the formulation are the direct excitation of the activator, the creation of conduction electrons and excitons, and the transfer of energy from these to luminescent and non-luminescent activator ions and to other impurities and lattice defects.

The quantum efficiency of the luminescence can be expressed as:

$$\eta = \frac{\sigma' x'}{\sum_{\nu} \sigma^{\nu} x^{\nu}} \qquad (1)$$

where:

σ = capture cross section of an absorption site for energy from conduction electrons, excitons, and exciting light, sq cm

x = mol fraction of sites available for energy absorption

superscript ' refers to luminescent activators

superscript ν refers to all types of energy absorption sites including the luminescent activators.

From consideration of the three types of exciting mechanisms, which are conduction electrons, excitons, and exciting light:

$$\eta = \frac{\sigma_m' x'}{\Sigma_\nu \sigma_m^\nu x^\nu} \tag{2}$$

where:

σ_m = weighed mean cross section for energy absorption, sq cm.

Letting the parameter Z be defined in general as the number of lattice positions surrounding an activator ion such that if one of these sites is occupied by another activator, luminescence is quenched, and assuming that:

$$x^\nu = (1 - c), \text{ for non-activators,} \tag{3}$$

then:

$$\eta = \frac{c(1 - c)^Z}{c + \frac{\sigma}{\sigma'}(1 - c)} \tag{4}$$

where:

c = total mol fraction of activator

σ = total cross section for non-activators, sq cm.

In general, Z and $\frac{\sigma}{\sigma'}$ are adjustable parameters although $\frac{\sigma}{\sigma'}$ can be determined experimentally for some phosphors under exciting light. The above equation agrees well with experimental data.

Dependence of Quantum Efficiency on Activator Concentration; III. The Analysis of Ewles and Lee(17). For the case of luminescence resulting from exciting light, Ewles and Lee have applied a modified concept of large centers to the data of Johnson and Williams(38). One very important point made in the work of Ewles and Lee is that crystal defects can act as centers for both luminescence and quenching.

Heat treatment of the matrix of a phosphor will result in lattice defects such as vacancies, interstitial atoms, and regions of strain. Purified calcium oxide exhibits luminescence if it is cooled suddenly, but slowly cooled calcium oxide does not luminesce. These observations indicate that lattice defects can act both as luminescent centers and as quenching centers.

Using the concept that a luminescent center consists of an impurity atom linked with a number of host atoms and assuming random distribution of the luminescent centers, Ewles(15) showed that the fraction, F, of such centers for an atomic concentration, c, of activator ions, would be:

$$F = \frac{c}{(1 + c)^{-n}} \qquad (1)$$

where:

n = number of host atoms per center.

If c is small this fraction is:

$$F = c \exp(-nc). \qquad (2)$$

Ewles and Lee(17) assumed:

(1) activator centers and structure centers are both large

(2) exciting radiation is absorbed appreciably by both kinds of centers but to different extents, in accordance with Johnson and Williams(38)

(3) absorption of the ideal lattice and nonradiative activators is negligible for both exciting and emitted radiation

(4) the activator will not function as a luminescent center if perturbed by the overlap of another center

(5) the concentration of the structure centers is approximately the same in phosphors with the same host and prepared in the same manner.

If these restrictions are applied to Equation (2) it follows that:

$$E = k\,\eta = k/\left[1 + \alpha c^{-1} \exp (nc)\right] \qquad (3)$$

where:

E = measured light pulse

k = normalizing constant

η = quantum efficiency

n = number of lattice ions associated with a radiative center

c = mol fraction of activator

$\alpha = \dfrac{f_2 c'}{f_1 B}$ = parameter dependent on the centers present

f_2 = absorption coefficient of a structure center

c' = mol fraction of structure centers

f_1 = absorption coefficient of an activator center

B = constant = $\exp (nc')$.

Equation (3) fits the data of Johnson and Williams(38) except at high concentrations of activator.

Limitations of Luminescence Theory. The theoretical considerations made by Ewles and Lee(17) were greatly simplified. The limitations of the theory presented in the above section are:

(1) no account was taken of the fact that one type of excitation may excite more than one type of emission

(2) absorption and emission by nonradiative activators may become significant at large activator concentrations and wherever the absorption and emission spectra overlap

(3) there will be a number of different, competitive structure centers even in the most carefully prepared phosphor crystals.

These limitations must be taken into account in any detailed theoretical work on phosphors and similar materials.

Infrared Spectroscopy

The use of infrared spectroscopy for qualitative and quantitative analysis is discussed in the following paragraphs. Sawyer(64) has prepared a very complete, basic review of infrared spectroscopy from the theoretical viewpoint. The material in the first two sections has been taken from this review.

Units Used in Infrared Spectroscopy. Two units are used to characterize infrared radiation. A wavelength (λ) unit, the micron ($\mu = 10^4$ Angstroms $= 10^{-4}$ centimeters), is used throughout the spectrum; and a frequency (ν) unit, the wave number or reciprocal centimeter (cm^{-1}), is used in the infrared region of the spectrum.

Molecular Spectra. Molecular spectra may be divided into rotational spectra, vibrational spectra, and electronic spectra. Rotational spectra are caused by the absorption of photons and conversion of the light energy into rotational energy. Similarly, vibrational spectra are caused when the absorption of radiant energy produces changes in the energy of molecular vibrations. Each molecule has only certain discrete energy levels, and the absorption of light corresponds to a transition between two of these energy levels. Vibrational spectra are thus discrete instead of continuous. The rotational energy changes of a molecule are much smaller than the vibrational changes, and the rotational spectra have the effect of widening the vibrational absorption line into a band. The number of absorption bands is not necessarily equal to the number of fundamental vibrational frequencies of a molecule; the number may be changed by combination tones, overtones, and difference tones.

Qualitative Analysis by Infrared Methods. Spectroscopists have used the infrared absorption method for determination of the structure of molecules(6,18,20) and for analysis of their rotations and vibrations(8,18,43). Infrared spectrophotometry is widely used(64,50,32) in the identification of organic compounds and for qualitative analysis of organic liquids. Herzberg(32) has presented an excellent coverage of the use of infrared spectroscopy in qualitative analysis and structural studies.

Infrared Absorption of Nitrate and Nitrite Ions. Both nitrate ions and nitrite ions show(54) a single, intense absorption peak. The wavelength of these peaks change with the anions of the lattice, but the general shapes of the spectra remain very simple. Potassium nitrate shows a large absorption peak at 1393 wave numbers and a minor peak at about 827 wave numbers. Reagent grade potassium nitrite absorbs intensely at about 1280 wave numbers and shows a medium sized peak at about 1390 which may be caused by the presence of a small nitrate impurity(42). Because they have very simple infrared absorption spectra potassium nitrate and nitrite can be accurately determined quantitatively on any good infrared spectrophotometer.

Errors in Infrared Analysis. The most important errors in infrared intensity measurements are(49): (1) uncertainty of radiation measurement; (2) stray light; and (3) non-linearity of the measuring system. For best results the transmission should be between 20 and 60 per cent transmission, which corresponds to optical densities between 0.5 and 0.1.

According to the instruction manual(36) supplied by the Perkin-Elmer Corporation for the Model 21 spectrophotometer, the reproducibility of the instrument is within one-half per cent in transmission and 0.005 microns in wavelength. The instruction manual advised that quantitative analysis should not be done at optical densities of 0.9 or more (15 per cent transmission or less). Noise level, zero error, 100 per cent transmission error, slit width, and sampling techniques can introduce errors to exceed these specifications.

The Alkali Halide Pressed Disk Method of Infrared Sampling

The method of infrared analysis by means of placing a small sample of the material to be analyzed into powdered alkali halide and pressing the mixture is well known and widely used for qualitative analysis of solid organic materials(36,20,24). The use of this method of sampling in radiation research is new(39), except in the case of studies on luminescent materials(30). The techniques and limitations of the alkali halide pressed disk method will be discussed in the following paragraphs.

Optical Properties of the Pressed Disks. Polycrystalline(30,24) pressed disks of alkali halides, like pure crystals of alkali halides, do not absorb infrared light, visible light, or ultraviolet light to any extent(67,44). Alkali halides and pressed disks do not absorb infrared light upon being irradiated with ionizing radiation(67,30). When powdered alkali halide is doped with solid material and pressed into a clear disk the infrared spectrum of the disk is that of the trace impurity(44). The doping process gives sharper resolution of absorption peaks for solids than does the mull method(6,18); the pressed disk method is therefore much better for quantitative analysis of solids.

Materials Used in the Pressed Disks. Potassium bromide is the most widely used(43,44,53) disk material, but other alkali halides have special uses as disk carrier material. Hersh(30,31) used potassium iodide and potassium chloride to make the phosphors KI:Tl and KCl:Tl for color center studies. French, et al(20) report that potassium iodide disks are more reproducible than potassium bromide disks when the pressing has to be done at lower pressures. Hales and Kynaston(24) have found that potassium chloride is less reactive and more stable to heat than potassium bromide, but that the chloride is harder to dry.

Equipment for Pressing the Disks. The best results(44,53) from the pressed disk method have been obtained by using evacuable, stainless steel dies and anvils which have mirror-polished pressing surfaces. Kirkland(44) and French, et al(20) have described evacuable dies for pressing alkali halide disks. Pressures used have varied from 10,000 to 200,000 pounds per square inch. Kirkland(44) has also outlined a pressing procedure in which the alkali halide is powdered, dried, mixed with the additive, dried again if possible, apportioned in a dry box, and then placed in the die, evacuated, and pressed for at least five minutes. Jones(39) has found that the disks are reproducible if they are evacuated until the vacuum pump sounds "hard" and pressed for at least three minutes.

Effects of Grinding and Drying. Meeks and his co-workers(50) have stated that the study of the trace water concentrations in infrared samples is merely a study of handling methods and atmospheric conditions. Milkey(53) has described the effects of grinding on the water content and general background of the pressed disks. Absorption of water in the infrared region, in bands at 2.9 and 6.1 microns, is less in coarser powders. Disks completely free of water cannot be made from fine powders. Hard grinding of the potassium bromide causes absorption bands at 7.0 and 9.0 microns besides the water bands; the general background absorption of the disks is less when coarser powder is used. Anfang(2) has reported that the infrared grade potassium bromide sold by Harshaw Chemical Company is dried for 48 hours at 150 degrees, Centigrade, in a dry room. This infrared grade potassium bromide shows no appreciable absorption at 2.9 and 6.1 microns.

Determination of Water in the Disks. Since even very small amounts of water present in the pressed disks may change the properties greatly it will be necessary to know approximately how much water is present and what its effects are.

There have been no quantitative measurements of trace water in infrared samples although studies have been made on the effects of trace water in nonpolar solutions(50,18) and in solid samples(6,18,20). Hydrogen bonds were shown by Folman and Yates(18) to strongly affect the absorption of infrared radiation by the hydroxyl group so that the extinction coefficient of the hydroxyl group changes when hydrogen bonds are present. Coblentz(6) has found that compounds containing water of crystallization show the absorption bands of water and that those containing water of composition do not.

Crystalline solids which are soluble in certain organic solvents have been quantitatively analyzed for water content by the Karl Fischer method(1). This method involves titration of the sample (sulfur dioxide, hydrocarbons, alcohols, or acetone can be used as the sample or as the solvent for a solid sample) with a methanol or glycol solution of iodine, pyridine, and sulfur dioxide until free iodine is evident. This procedure has been adapted to electrometric analysis by Almy, Griffin, and Wilcox(1). According to Smith, et al(69), the reaction involving water is expressed by the following equation:

$$I_2 + SO_2 + 3C_5H_5N + H_2O = 2(C_5H_5N \cdot HI) + C_5H_5NOSO_2. \qquad (1)$$

In the electrometric method of the Fischer analysis the iodine is regenerated electrolytically within the electrometric cell, and the current necessary for this is the measured quantity.

Solid Solutions. Potassium nitrate and nitrite appear to form solid solutions with potassium bromide in the pressed disks. Ketelaar, Schutte, and Schram(43) have determined that the solubility of potassium nitrite in potassium bromide is about 0.1 mol per cent. The method used in this determination involved infrared analysis of pressed potassium bromide disks doped with small amounts of sodium nitrite. Up to 0.1 mol per cent sodium nitrite only the infrared absorption of potassium nitrite was seen; above 0.1 mol per cent, there were absorption peaks for both sodium and potassium nitrite. These absorption peaks are about 30 wave numbers apart and are clearly separated. It was suggested(42) that the same method could be applied to the nitrate and other potassium salts to find solubilities in potassium bromide.

Analytical Methods and Dosimetry

The analytical methods other than infrared spectrophotometry, the reagents used, and the dosimetry of the gamma source are discussed in the following paragraphs.

Colorimetric Analysis of Nitrite Ions in Aqueous Solution. Nitrite ions formed from nitrates by irradiation have been quantitatively determined by the formation of an azo dye in dissolved samples of irradiated solid nitrates(14,29). From Snell and Snell(70), the diazo compound formed by the reduction of sulfanilic acid by nitrite ions forms an intensely colored azo dye upon reaction with dimethyl-N, N-naphthylamine. The optical density is read at 5350 Angstroms and is either calibrated with standard samples of nitrite or used to calculate nitrite concentration by the relationship(47):

$$\text{micromoles of nitrite ion per liter} = 23.2 \times \Delta\text{O.D.} \times \text{dilution} \qquad (1)$$

where:

ΔO.D. = observed optical density less the blank

dilution = total volume of sample, ml, divided by the volume of the sample less reagents, ml.

The Cobalt-60 Gamma Source. Cobalt-60, with a long half-life of 5.1 years and energetic gamma rays of 1.17 and 1.34 million electron volts (mev), makes an excellent source for radiation for studies of radiation effects on materials. Hochanadel and Ghormley(23) have described a gamma source of 300 curies of cobalt-60 which was located at the Oak Ridge National Laboratory. A similar gamma source of the same design but containing 1100 curies of cobalt-60 was located in Room 206, Building 4501, at the Oak Ridge National Laboratory. For the larger source there was always 14 inches of lead shielding surrounding the cobalt.

The source itself was in the shape of a circular annulus with rings of cobalt-60 arranged so that there was only a few per cent variation in intensity over the whole inner cylinder. Samples could be precisely positioned in the center of the source to give reproducible results. Tubes leading into the source allowed piping, vacuum lines, and electrical wiring to be used inside the cavity.

Gamma Source Dosimetry. The ferrous dosimeter proposed by Hochanadel and Ghormley(34) is well suited for use in a gamma source such as that described above. The calculation of dose rate by the ferrous dosimeter was based on 15.6 ± 0.3 ferrous ions oxidized per hundred electron volts absorbed in an air-saturated, 0.4 molar sulfuric acid solution of ferrous sulfate. The concentration of ferrous sulfate was 2×10^{-3} molar. The optical density of the irradiated dosimeter solution was read at 3050 Angstroms; the extinction coefficient for ferric ions at 3050 Angstroms in this solution was 453 (micromols per liter) per (change in optical density per minute). Dosimetry was then based on the assumption that the ratio of true mass absorption coefficients for gamma radiation of two materials is equal to the ratio of the energy absorbed per unit weight of the materials.

Infrared Quality Potassium Bromide. Infrared quality potassium bromide is a particular grade of material which shows no appreciable impurities under infrared analysis. The specifications(26) of the Harshaw Chemical Company for infrared quality potassium bromide are the following. The potassium bromide powder must be prepared from pure single crystals of the highest infrared quality. Each batch must be tested at the factory and found free of measurable amounts of organic impurities prior to bottling. Particular care should be exercised in opening the bottle to exclude any organic vapors, and all equipment used in handling the powder must be clean and dry. A pellet of this material one millimeter thick shows less than four per cent at 2.9 microns due to moisture. If opened and stored in an atmosphere of less than 40 per cent relative humidity, this potassium bromide powder will not normally pick up additional moisture.

Purity of the Potassium Nitrate. Several investigators(8,29) have reported that, in the irradiation of reagent grade potassium nitrate crystals, further purification is not necessary. There may be a small amount of adsorbed moisture on the nitrate which can easily be removed by drying under an infrared lamp.

Purification of Potassium Nitrite

Methods for the purification of potassium nitrite are discussed in the following paragraphs.

Purity of Available Potassium Nitrite. According to the Merck Index(52) commercial potassium nitrite contains impurities in the amount of about 15 per cent by weight. These impurities are mostly potassium nitrate and water. Reagent grade potassium nitrite contains at least 97 per cent nitrite by weight. The other three per cent probably consists of nitrate, since potassium nitrite is produced commercially from the nitrate(51), and some adsorbed water.

Methods of Purification. According to Mellor(51), potassium nitrate is easily reduced to the nitrite by powdered lead or zinc at temperatures approaching 400 degrees, Centigrade.

Schwarz and Allen(66) recrystallized reagent grade potassium nitrite from water six times and succeeded in reducing the amount of potassium nitrate to about 0.6 mol per cent, or about 0.7 per cent by weight. That this is a difficult process is evident from the relative solubilities of potassium nitrite and potassium nitrate in water. Published values for the solubility of potassium nitrite in water at zero and 100 degrees, Centigrade, are 281 and 413 grams per 100 grams of water, respectively; for potassium nitrate the values are 13.3 and 247 grams per 100 grams of water, respectively.

Pure potassium nitrite has also been prepared from the reaction of organic nitrites with potassium hydroxide. Petru and Pokorny(57) reacted ethyl nitrite with potassium hydroxide in ethyl alcohol for two days and reportedly obtained pure potassium nitrite.

It has also been found(56) that amyl nitrite and potassium hydroxide react upon standing in amyl alcohol to form potassium nitrite.

Other Possible Means of Separation. Another possible method for the physical separation of potassium nitrite and potassium nitrate is suggested by the published values(5) of the solubilities of these compounds in absolute alcohol. Potassium nitrite is slightly soluble in absolute alcohol, and potassium nitrate is insoluble in absolute alcohol. The nitrate should crystallize out of an alcohol solution along with some nitrite as the alcohol is boiled off, most of the nitrite being left in solution.

Another possible chemical method of accomplishing the separation is suggested(40) by the fact that the ratio of the solubilities of silver nitrate and silver nitrite is about 800 to one in water.

III. EXPERIMENTAL

The experimental work done on the investigation of "Energy Transfer in the Gamma Radiolysis of Isolated Nitrate and Nitrite Ions" is presented in the following sections.

Purpose of Investigation

The purpose of this investigation was to determine the effects of and possible mechanisms for transfer of energy to anion impurities in compressed pellets of potassium bromide.

Plan of Experimentation

The plan of experimentation of this investigation was as follows:

1. A study of the available literature was made
2. The alkali halide pressed disk method of infrared sampling was adapted for use in the investigation
3. Data were obtained from the irradiation of potassium bromide disks containing varying amounts of potassium nitrate and potassium nitrite
4. The results obtained from the irradiations were interpreted in order to show effects of and possible mechanisms for energy transfer in the samples.

Materials

The materials used in the course of this investigation are described in the following paragraphs.

Acetic Acid, Glacial. Reagent grade, code 1019, lot no M285M280, min CH_3COOH 99.7 per cent. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the colorimetric determination of nitrite ion concentration.

Acetone. Reagent grade, lot no P337P328. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used to clean the die and in the dry ice-acetone bath.

Alcohol, Ethyl. USP, 190 proof. Obtained from Publicker Industries, Philadelphia, Pa. Used to extract excess KOH in the purification of potassium nitrite.

Alcohol, Iso-Amyl. Reagent grade, lot no K295. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the purification of potassium nitrite.

Alcohol, Methyl. Absolute, 99.9 per cent CH_3CH, lot no 20748. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used in the purification of potassium nitrite and in the colorimetric determination of nitrite concentration.

Calcium Chloride. Anhydrous grains, 12 mesh, no 4136. Obtained from Mallinckrodt Chemical Works, St. Louis, Mo. Used as a desiccant to keep the pellets dry.

Calcium Chloride. Anhydrous 1/2-in chunks, lot no L098. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used as a desiccant to keep the pellets dry.

Dimethyl-1-Naphthylamine, N,N-. For sulfanilamide test, 5 per cent or more aryl amine, no 1060. Obtained from Eastman Organic

Chemicals, Rochester, N. Y. Used in the colorimetric determination of nitrite concentration.

Drierite. Anhydrous $CaSO_4$ desiccant, 10-20 and 20-30 mesh. Manufactured by W. A. Hammond Drierite Co., Xenia, O. Used to dry the helium and nitrogen gases.

Dry Ice. Obtained from the dry ice locker, Bldg. 4500, Oak Ridge National Laboratory, Oak Ridge, Tenn. Used in the dry ice-acetone bath.

Ferrous Sulfate. Reagent grade crystals of $FeSO_4 \cdot 7H_2O$, lot no M338. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the preparation of the dosimeter solution.

Helium. Cylinder size 1; 1500 psi. Obtained from Chemical Stores, Oak Ridge National Laboratory, Oak Ridge, Tenn. Supplied by Southern Chemical Co., Nashville, Tenn. Used to keep the pellets dry and cool during irradiation.

Lead. Analytical reagent grade grains, lot no 4668. Obtained from Mallinckrodt Chemical Works, St. Louis, Mo. Used in the purification of potassium nitrite.

Nitric Oxide. Liquid, in lecture bottle, no AM-3501. Obtained from the Matheson Co., Inc., East Rutherford, N. J. Used to obtain its infrared spectrum.

Nitrite, Iso-Amyl. Boiling point 96-99 °C, no 436. Obtained from Eastman Organic Chemicals, Rochester, N. Y. Used in the purification of potassium nitrite.

Nitrogen. Liquid, cylinder size 1; 2000 psi. Obtained from Chemical Stores, Oak Ridge National Laboratory, Oak Ridge, Tenn. Supplied by Southern Chemical Co., Nashville, Tenn. Used as a dry atmosphere in the Cary and as a coolant in the purification of potassium nitrite.

Nitrogen Dioxide. Liquid, in lecture bottle, no AB-5196. Obtained from the Matheson Co., Inc., East Rutherford, N. J. Used to obtain its infrared absorption spectrum.

Nitrous Oxide. Liquid, in lecture bottle, no 14385. Obtained from the Matheson Co., Inc., East Rutherford, N. J. Used to obtain its infrared spectrum.

Petroleum Jelly. "Vaseline", white. Manufactured by Cheesebrough-Pond's, Inc., New York, N. Y. Used to seal samples for Karl Fischer analysis and as a preservative for the die apparatus.

Potassium Bromide. Powdered, infrared quality, lot no 5120, I-R spectrum no 5744. Obtained from Harshaw Chemical Co., Cleveland, O. Used for the carrier or matrix in the samples.

Potassium Hydroxide. Reagent grade pellets, min KOH 85 per cent, max K_2CO_3 two per cent, lot no M275. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used to obtain its infrared absorption spectrum and in the purification of potassium nitrite.

Potassium Nitrate. Reagent grade crystals, lot no 2186. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used in the preparation of samples.

Potassium Nitrite. Reagent grade crystals, min KNO_2 94 per cent, no 7044. Obtained from Mallinckrodt Chemical Works, St. Louis, Mo. Used in the preparation of samples.

Sodium Peroxide. Reagent grade grains, 35 mesh or finer, min Na_2O_2 95 per cent, lot no M158. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used to obtain the infrared absorption spectrum of K_2O_2.

Sulfanilic Acid. Reagent grade crystals, no CB786, lot no 363063. Obtained from Matheson, Coleman, and Bell Division of the Matheson Co., Inc., East Rutherford, N. J. Used in the colorimetric determination of nitrite concentration.

Sulfuric Acid. CP grade, sp gr 1.84, 95.5-96.5 per cent H_2SO_4, lot no E511020. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the preparation of the dosimeter solution.

Water, Triple-Distilled. The distilled water used throughout this investigation was obtained from the still in Rm. 206, Bldg. 4501, Oak Ridge National Laboratory, Oak Ridge, Tenn. The purification involved distillation from an acid dichromate solution, distillation from a basic permanganate solution, distillation from an all-silica system, and storage in silica containers.

Apparatus

The apparatus used in the course of this investigation is described in the following paragraphs.

Balance, Analytical. Type DLB, no 16918, lab no X-27257. Manufactured by Wm. Ainsworth and Sons, Denver, Colo. Obtained from Eimer and Amend, New York, N. Y. Used to weigh samples and reagents.

Bulbs, Sample. Three required, 50 cc Pyrex bulbs fitted with two 8-in Pyrex tubes with 24/40 male fittings, one with a break seal. Fabricated in the Glassblowing Shop, Bldg. 4500, Oak Ridge National Laboratory, Oak Ridge, Tenn. Used to contain samples for mass spec analysis.

Cary Recording Spectrophotometer. Model 11 MS, ser no 156, model N power supply. Obtained from Applied Physics Corp., Pasadena, Calif. Used in colorimetric and scattered light analyses.

Die, Evacuable. Designed to press 15-mm diameter pellets. Fabricated in the Chemistry Division Experimental Shop, Bldg. 4500, Oak Ridge National Laboratory, Oak Ridge, Tenn. Used to compress the samples.

Disk Holder. Brass cylinder, 7/8-in diameter, sealed at one end and with a threaded brass cap on the other end. Copper fittings at both ends for gas flow. Capable of placing six disks in the region of constant source intensity. Fabricated in the Chemistry Division Experimental Shop, Bldg. 4500, Oak Ridge National Laboratory, Oak Ridge, Tenn. Used to position the samples in the source.

Gamma Ray Source. Lead pig containing 1100 curies of cobalt-60 around a cylindrical cavity 1.375 inches in diameter by 11 inches deep. Source surrounded at all times by 14 inches of lead. Fabricated in the shops of Oak Ridge National Laboratory, Oak Ridge, Tenn. Used as the source of gamma radiation.

Hot Plate. Ser no R-92. Manufactured by Edwin L. Weigand Co., Pittsburgh, Pa. Used to heat solutions in the purification of potassium nitrite.

Infrared Lamp. Lamp on stand, General Electric 375 watt bulb. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to dry the powders before pressing.

Infrared Recording Spectrophotometer. P-E Model 21, double-beam type, ser no 377, lab no X-57968. Obtained from The Perkin-Elmer Corp., Norwalk, Conn. Used in analysis of the samples.

Infrared Recording Spectrophotometer. P-E Model 221, double-beam type, ser no 218. Obtained from The Perkin-Elmer Corp., Norwalk, Conn. Used in analysis of the samples.

Laboratory Equipment. Small laboratory equipment, such as glassware, mortars, tubing, etc. were obtained from the Chemistry Division Stockroom, Bldg. 4500, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Load Indicator. "Baldwin-Tate-Emery", no 60-TE-1274, 0-60,000 lb. Built by the A. H. Emery Co., New Canaan, Conn. Used to measure pressure during the pressing operation.

Oven, Vacuum. Constant temperature 115°C, lab no USCL-B-50381. Used to dry the samples.

Oven, Vacuum. Variable temperature 25-200°C; 115/230 v, 550 watts. Model 5830, ser no 1K59, lab no X-75599. Obtained from National Appliance Co., Portland, Ore. Used to dry the samples.

Press. "Baldwin-Tate-Emery", 60,000 lb capacity, ser no 522635, lab no X-52800. Obtained from Baldwin-Lima-Hamilton Corp., Philadelphia, Pa. Used to apply pressure to the powdered samples.

Races, Ball Bearing. Steel inner races, 15-mm ID, no E-15-B. Obtained from Norma-Hoffmann Bearings Corp., Stamford, Conn. Used to contain the pressed samples.

Races, Ball Bearing. Steel inner races, 15-mm ID, no ND-15. Obtained from New Departure Division of General Motors Corp., Bristol, Conn. Used to contain the pressed samples.

Timer, Electric. Type S-60, no 19872, 115 v ac, 60 cy, 1 rpm. Scaled in fifths of a second. Manufactured by the Standard Electric Time Co., Springfield, Mass. Used to measure irradiation time by means of a switch connected to the gamma source.

Vacuum Pump. Welch Duo-Seal, ser no 8603-0, lab no X-40397; single stage, 115 v ac, 60 cy motor. Manufactured by W. M. Welch Mfg. Co., Chicago, Ill. Used to evacuate the vacuum ovens.

Vacuum Pump. Welch Duo-Seal, ser no 468, lab no X-30415; single stage, 115 v ac, 60 cy motor. Manufactured by W. M. Welch Mfg. Co., Chicago, Ill. Used to evacuate the die assembly before removal to the press.

Vacuum Pump. Welch Duo-Seal, ser no 14496-0, lab no X-52026; single stage, 115 v ac, 60 cy motor. Manufactured by W. M. Welch Mfg. Co., Chicago, Ill. Used to evacuate the die assembly during pressing.

Vacuum Rack, Glass. Capable of maintaining pressure of 0.05 microns of mercury. Equipped with mercury diffusion pump, Welch "Duo-Seal" vacuum pump, Cenco electric heater, liquid nitrogen trap, and Hastings and Philips pressure gages. Located in Rm. 208, Bldg. 4501, Oak Ridge National Laboratory, Oak Ridge, Tenn. Fabricated in the ORNL shops. Used to evacuate samples for mass spec analysis.

Valve. Helium regulator, 0-50 psig. Manufactured by Bastian and Blessing Co., New York, N. Y. Used to regulate the flow of helium over the samples during irradiation.

Valve. Nitrogen regulator, 0-100 psig. Manufactured by Bastian and Blessing Co., New York, N. Y. Used to regulate flow of nitrogen into the Cary and over the lead-nitrite mixture in the purification of potassium nitrite.

Method of Procedure

The method of procedure followed in this investigation is presented in the following paragraphs. All of the operations involving the disks, except the actual pressing and the irradiations, took place in a dry room in which the relative humidity was kept below 40 per cent.

Preparation of Potassium Nitrate and Nitrite Solutions. The desired amount of chemically pure or purified potassium nitrite or chemically pure potassium nitrate was weighed with an analytical balance. The weighed samples were poured into volumetric flasks, and the flasks were filled to the mark with triple-distilled water. The concentrations of the solutions varied according to the desired concentration of the pressed disks. Solutions were prepared a short time before the disks were made to prevent loss of nitrate or nitrite from decomposition by light or heat.

Addition of Solutions to Potassium Bromide. The desired quantity of infrared quality, powdered potassium bromide was weighed with an analytical balance and poured into an alumina mortar. Nitrite or nitrate solution was added with a pipet. The volume of solution added was such that about half of the potassium bromide was dissolved. For 6.000 grams of potassium bromide a solution would be prepared so that the desired amount of nitrite or nitrate could be added with a one or two milliliter pipet. The solution was sprayed about over the powdered potassium bromide so that all of the material in the mortar would be wetted, and in such a way that no drops of solution were left on the sides of the mortar.

Drying the Powder by Infrared Lamp. The mortar was usually heated with an infrared lamp prior to the mixing operation described above. The lamp was also left on during the addition of potassium bromide and the solution. At this point the mixture was a water slurry. The slurry was allowed to dry without attention until there was no obvious liquid phase, after which time precipitated potassium bromide was repeatedly scraped off the mortar and mixed about with a spatula. When most of the water had been removed the mixture was ground with a pestle into a thin layer which was allowed to dry further. When this layer had set up into a thin, hard cake, it was scraped off with a spatula, crushed, and placed in a weighing bottle which had been cleaned and labeled.

Drying the Powder by Vacuum Oven. The weighing bottle containing the moist powder was placed in a vacuum oven kept between 115 and 120 degrees, Centigrade. The powder for the dry disks was dried in the oven for at least 48 hours, but other powders which were to be used in investigations of effects of water content were dried for different lengths of time. If the water content of the disks was not critical the powders were stored in a desiccator containing calcium chloride desiccant until used; if the water content was important the dried powders were stored in the oven until used.

The Pressing Apparatus. The pressing apparatus, or die, used in pressing the potassium bromide was similar to the evacuable die described by Kirkland(44) and pressed a pellet 15 millimeters in diameter. The evacuable die used was designed by A. R. Jones of Oak Ridge National Laboratory and was fabricated according to Oak Ridge National Laboratory Drawing D-25695 (not classified). The apparatus consisted of plunger, rubber spacer, evacuation fittings, anvil, and sealable base for the anvil. The pressing surfaces of the plunger and the anvil were optically flat surfaces. When evacuated, the entire apparatus was sealed tightly enough to be carried around by the plunger. The pressing surfaces were cleaned periodically with distilled water and acetone, and petroleum jelly was periodically wiped on and off the entire plunger and die to inhibit rusting. When not in use the dies were stored in a desiccator.

A pressed disk, in proper relation to the race which holds it, is shown on Figure 1, page 49. The plunger and the anvil of the die were designed so as to fit snugly inside the races.

Pressing the Disks. A steel ball bearing race was fitted onto the anvil of the die. The desired amount of powder was weighed to ± 0.0005 gram with an analytical balance. The sample was poured into the race and tamped with a stainless steel rod slightly hollowed out on the tamping end. The die was then assembled and attached to a vacuum pump. The remaining powder was then returned to the desiccator or to the vacuum oven. After the vacuum pump was disconnected the sealed die was transported to the room in which the press was located. The die was attached to a vacuum pump and was evacuated for three or four minutes before the pressing operation. The disk was then compressed under 40,000 pounds for about ten minutes. This weight corresponds to about 143,000 pounds per square inch if all the weight is borne by the disk.

Removal from the Die and Storage. The die assembly was sealed, the pressure was released, and the vacuum pump was disconnected. The die was transported back to the dry room and disassembled. The race and disk usually had to be separated from the anvil with sharpened

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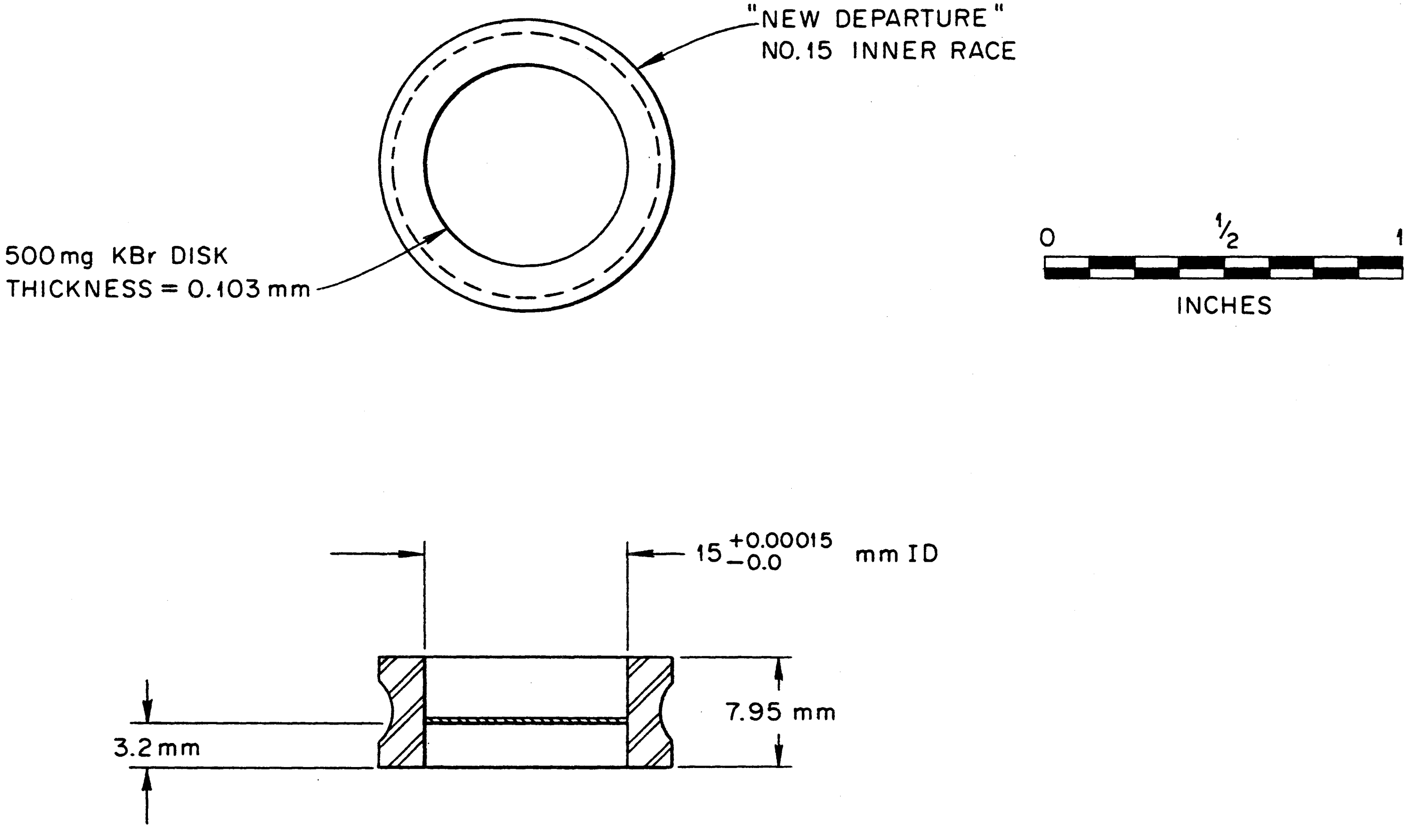

Fig. 1. Inner Race with Disk in Position.

shears. The disk, held by the race, was then placed in a marked envelope, and the envelope was placed in a desiccator until the disk was used. Care was taken in all subsequent operations to insure that the disks were returned to their proper envelopes.

Operation of the Infrared Spectrophotometers. The Model 21 and the Model 221 Perkin-Elmer infrared spectrophotometers were operated according to instruction manuals(36,37) furnished by the Perkin-Elmer Corporation. The disks were mounted on a holder which correctly positioned the disk in the infrared beam.

Infrared Analysis for Water. Whenever the relative water content of the disks had to be known, the infrared spectrum of each newly-pressed sample was taken in the region from 4000 to 2900 wave numbers before the disk was placed in its envelope. It was assumed that, with proper precautions being taken, any enhancement of water optical density would be caused by water adsorbed on the surface of the disk.

The reported optical densities of water in the samples were measured at the maximum near 3440 wave numbers (2.9 microns) relative to some flat portion of the spectrum between 3000 and 2900 wave numbers and checked by the flat portion between 4000 and 3750 wave numbers.

Infrared Analysis for Nitrate and Nitrite Ions. The optical densities of the pressed disks were calibrated with respect to the known concentrations of nitrate and nitrite ions in the unirradiated disks. The disks were allowed to remain overnight in a desiccator before the initial optical densities of the nitrate or nitrite absorption peaks were measured. The heights (optical densities) of the nitrate absorption peak at 1391 wave numbers and of the nitrite absorption peak at 1276 wave numbers were measured relative to the flat portion of the spectrum between 1340 and 1290 wave numbers. After some irradiation both peaks were present, and the optical densities of each were measured relative to the highest part of the spectrum between the two peaks. The analysis for nitrate and nitrite ion optical densities was usually made immediately after the conclusion of irradiation, but no changes in optical densities were ever detected after the disks had been stored for long periods of time.

Purification of Potassium Nitrite. Various methods of procedure were followed in trying to obtain potassium nitrite free enough of nitrate ion to permit infrared analyses of nitrite decomposition with no interference from nitrate. All of the attempts to purify potassium nitrite made during the course of this investigation are described in the following paragraphs. The infrared quantitative analyses of the amount of nitrate in samples of potassium nitrite were made using the pressed disk technique described above, the amounts of nitrate present being taken from the calibration curve for potassium nitrate in potassium bromide. From this method of analysis chemically pure potassium nitrite contains about 3.7 mol per cent nitrate.

Recrystallization from Water. About 400 milliliters of distilled water was saturated with chemically pure potassium nitrite at room temperature. The solution was decanted and saved. Water was then evaporated until about half of the nitrite had precipitated out, at which time the hot solution was filtered with vacuum over a fritted glass filter and the solids were saved. After a number of these cycles had been completed the product was dried under an infrared lamp, and potassium bromide disks containing the product were made and analyzed in the usual manner.

Chemical Methods of Purification. Chemically pure potassium nitrite was placed with finely divided lead in a glass tube. The tube was heated to 300 degrees, Centigrade, for two hours in a furnace; and dry nitrogen was passed through the tube during the heating. The reacted mixture was dissolved in water and filtered. The water was evaporated from the product, and the product was analyzed by the pressed disk technique.

Re-distilled amyl nitrite was allowed to stand with excess potassium hydroxide for two days. The reacted mixture was heated under vacuum to remove the organic material, and the product was washed with ethyl alcohol to remove excess hydroxide. The product was then dried and analyzed by the usual method.

Silver nitrite was formed by the addition of silver nitrate to a solution of potassium nitrite. The resulting precipitate was filtered and washed with water, and was then placed in a water solution of potassium bromide. After the mixture had stood overnight the silver bromide was filtered off. The remaining solution was evaporated, and the resulting product was dried and analyzed for nitrate content.

Separation with Absolute Methanol. Acetone-free methanol of 99.9 per cent purity obtained from the stockroom was saturated with the chemically pure potassium nitrite. Four hundred milliliters of methanol dissolved about five grams of nitrite at room temperature. The saturated solution was then placed in a dry ice-acetone bath at about 197 degrees, Kelvin, contained in a large beaker, and an insulated cover was placed over the mouth of the beaker. After ten or fifteen minutes the cold methanol solution was removed from the bath and filtered through filter paper, and the liquid was saved. The remaining solution was boiled on a hot plate until some nitrite had begun to crystallize out. Then the solution was again placed in the dry ice-acetone bath for ten or fifteen minutes before the solids were filtered off again. When the desired number of cycles had been completed the solution was gently boiled to near dryness, and the crystals of potassium nitrite which had precipitated were dried under an infrared lamp, weighed, and tested for nitrate ion concentration.

Calibration of the Gamma Source. The ferrous dosimeter solution, made according to Hochanadel and Ghormley(34), was used to calibrate the 1100 curie cobalt-60 gamma source. The brass holder used to hold the disks in place in the source was filled with steel races, a wire screen spacer on top of the third race from the bottom, and a test tube containing dosimeter solution was placed through the races until it rested on the spacer. The test tube stood up above the top race, but the dosimeter solution was all positioned in the region of constant intensity. The position of the brass holder was not changed during the calibration.

After each five minutes of exposure the dosimeter solution was placed in a quartz cell, and its optical density was measured at 3050 Angstroms on the Cary spectrophotometer. Three different samples of dosimeter solution were used in the calibration.

Irradiation of Samples. The brass holder can place six disks in the region of uniform intensity. The races containing disks, hereafter referred to as "disks", were separated from each other and from the empty races at the top and bottom of the vertical holder with spacers made of coarse screen. The purpose of the spacers was to permit good flow of dry helium over each disk. The brass holder, filled and sealed in the dry room, was placed in the cavity; and fittings on the holder were attached to inlet and outlet lines for the helium. The helium, dried by passage through a Drierite bottle, was brought into the cavity with copper tubing. After it had passed through the sample holder the helium was exhausted through an oil-filled bubbler. The helium was flushed through the holder for about three minutes before the cobalt was lowered into the cavity. At the end of the desired irradiation time the holder was removed from the source to the dry room, and the disks were removed, returned to their envelopes, and stored in desiccators until they could be analyzed. The temperature of all the irradiations was 25 ± 2 degrees, Centigrade.

Colorimetric Calibration and Analysis. The reagents for colorimetric analysis of nitrite ions were prepared according to Snell and Snell(70). In the colorimetric analysis of the samples the disk was knocked out with a spatula into a mortar and was ground to powder with a pestle. The powder was then added to distilled water, the reagents were added, the sample was allowed to set for 30 minutes, and the optical density of the sample in a one centimeter quartz cell was read at 5350 Angstroms on the Cary spectrophotometer. Conversion of optical density to nitrite concentration was corrected for zero nitrite.

Preparation of Disks for Water Analysis. Disks used in the attempts to determine the amount of water present in the potassium bromide by Karl Fischer reagent contained no nitrate or nitrite impurities. The potassium bromide was pressed directly from the bottle for the driest disks. Samples containing varying amounts of moisture were prepared by different amounts of grinding or by the addition of small amounts of water to the dry potassium bromide. After being pressed the disks were analyzed on the infrared spectrophotometer for relative water optical density and were then knocked out of the races and ground to powder. The powdered samples were then sealed in ten milliliter weighing bottles having ground glass caps which were sealed on with petroleum jelly. The sealed bottles were marked and were then delivered to the Analytical Chemistry Group which operated the coulometric titration equipment.

Determination of Water Effects. The disks used in the determination of water effects were doped with nitrate or nitrite ions as described above, and the water concentrations of the disks were varied by varying the time of drying the powders in the vacuum oven.

Inspection of the Disks. The pressed disks were thrown out if there were any visible flaws or cloudiness. Disks which did not meet water or weight specifications and those which did not follow the calibration curve of optical density versus concentration were also discarded. After the method of pressing had been set the original weight specification set at ± 0.5 per cent of the desired disk weight was no longer important, and the disks were thereafter checked only by their optical densities at the peaks.

Dilution Method of Analysis. Disks containing so much nitrite ion than their concentrations could not be analyzed by the usual method were ground up after irradiation and diluted with a weighed amount of potassium bromide. The diluted powder was mixed by light grinding, and disks were made from the diluted material and analyzed on the infrared machine. The nitrite ion concentration of the diluted disks times the dilution factor gave the concentration of nitrite in the irradiated disk. Since the original disks were destroyed during analysis extreme care was taken so that they would all be uniform.

Analysis of Concentrated Disks Containing Nitrate Ions. Irradiated disks too concentrated in nitrate ion to be analyzed with the infrared machine by the standard procedure were analyzed by three different methods based on the premise that one nitrite ion is formed for each nitrate ion decomposed by radiolysis. In the first method the nitrate peak was compensated for by an unirradiated sample containing nitrate ions placed in the reference beam of the infrared spectrophotometer and the optical density of the nitrite peak was measured without interference from the nitrate peak. In the second method, the nitrite peak formed was measured off the shoulder of the large nitrate peak without any compensation. The third method consisted of dissolving the irradiated disk in water and colorimetrically determining the nitrite concentration as described above except that a quartz cell five centimeters long was used to hold the samples.

Determination of the Solubility of Potassium Nitrate in Potassium Bromide. Disks containing various amounts of potassium nitrate were analyzed for optical density at 4000 Angstroms on the Cary Spectrophotometer. The optical density measurement was a measure of the amount of light scattered by each disk. During the analysis the chamber wherein the sample was held was flooded with gaseous nitrogen which had been passed over a desiccant.

Product Analysis. The infrared absorption bands of products from the radiolysis of isolated nitrate and nitrite ions were determined with disks which had been exposed to large doses of gamma radiation. The optical density scale of the Model 221 infrared spectrophotometer was expanded twenty times to expose product peaks.

Spectra of various possible products such as the oxides of potassium and nitrogen were determined by the pressed disk method. The solid materials were added directly to the potassium bromide and mixed; the gases were allowed to flow into the evacuated die so that the disks were pressed in an atmosphere of the desired gas. The spectra of the prepared disks were compared with the absorption bands attributed to products of the radiolysis.

Preparation of Samples for Mass Spectrometric Analysis. Mass spectrometric analyses were made to determine the volatile products formed during the irradiation of potassium bromide disks containing nitrate ions. Identical samples of five grams of potassium bromide doped to 0.2 mol per cent with potassium nitrate were placed in a glass bulb equipped with a break-seal and were dried for 72 hours in a vacuum oven. The bulb was then attached to a vacuum line and was evacuated to 0.06 microns of mercury, pressure, for 24 hours. The bulb was then sealed under vacuum.

The samples were labeled, and one of them was placed in the gamma source for five weeks. The irradiated sample was removed, both samples were heated to 150 degrees, Centigrade, in an oven for 48 hours, and both samples were then sent to the Mass Spectrometry Group of the Oak Ridge National Laboratory for analysis of the gas in the bulbs.

Data and Results

The data and results from this investigation are presented in the following section. The individual measurements made on the disks, such as optical densities and weights, were omitted unless they were directly involved in the results shown on the table.

Reproducibility of Disks. The reproducibility of the nitrate-doped potassium bromide pressed disks made from the same powder is shown on Table I, page 60. The disks were compared by weights and by nitrate optical densities before and after irradiation.

Effects of Treatment. The effects of various treatments on the optical densities of nitrate ion and water are shown on Table II, page 61. The treatments specified in the table were successive from left to right.

Stability of Nitrate-Doped Disks. The stability of the optical density of the nitrate ion in potassium bromide disks stored over a desiccant is shown on Table III, page 62.

Effects of Water Concentration. The effects of water concentration on the gamma radiolysis of isolated nitrate ions in potassium bromide disks are shown on Table IV, page 63, and on Table V, page 64. Similarly, the effects of water concentration on the gamma radiolysis of nitrite ions in potassium bromide disks are shown on Table VI, page 65. The data on these tables are presented in graphical form on Figures 2, 3, and 4, pages 66, 67, and 68, respectively. The results of the Karl Fischer analysis for water in the disks are presented on Table VII, page 69.

Mass Spectrometric Analysis. The mass spectrometric analysis of the gas phase above irradiated and unirradiated samples of potassium bromide doped with potassium nitrate is presented on Table VIII, page 70.

TABLE I

Reproducibility of NO_3^--Doped KBr Disks Made From the Same Powder

Disk No	Weight gm	NO_3^- Optical Density at 1391 cm^{-1} After Irradiation Time = t hours in Co^{60} Gamma Source				NO_2^- Optical Density at 1276 cm^{-1} After Irradiation Time = t hours in Co^{60} Gamma Source			
		t = 0	t = 1	t = 2	t = 4	t = 0	t = 1	t = 2	t = 4
A-14-1	0.4004	0.308	0.267	0.236	0.185	0	0.005	0.012	0.017
A-14-2	0.4003	0.312	0.266	0.237	0.185	0	0.006	0.013	0.018
A-14-3	0.4008	0.311	0.267	0.237	0.186	0	0.005	0.011	0.018
A-14-4	0.3986	0.309	0.267	0.237	0.186	0	0.006	0.012	0.017
A-14-5	0.3999	0.311	0.267	0.238	0.186	0	0.005	0.012	0.018

Note: The water optical densities of these disks at 3440 cm^{-1} were all about 0.050. The optical densities were measured on a Perkin-Elmer Model 21, NaCl prism, slit program 927, from base line standard.

TABLE II

Effects of Treatment on Nitrate Ion and Water Optical Densities in KBr Disks

Disk No	Weight gm	Drying Times In Vacuum Oven at 115°C for Powder Before Pressing hr	Initial Optical Densities		Disks Exposed 48 hr at 30% Relative Humidity		Disks Dried 24 hr in Vacuum Oven at 115°C		Disks Repressed at 40,000 lb
			H_2O	NO_3^-	H_2O O.D.	NO_3^- O.D.	H_2O O.D.	NO_3^- O.D.	NO_3^- O.D.
A-13-1	0.3987	0	0.231	0.477	0.092	0.486	0.054	0.500	-
A-13-2	0.4001	0	0.214	0.462	0.093	0.488	0.051	0.500	-
A-13-3	0.4009	1	0.091	0.375	0.091	0.464	0.050	0.481	0.480
A-13-4	0.3985	1	0.090	0.370	0.084	0.467	0.049	0.488	0.489
A-13-5	0.3992	2	0.076	0.371	0.092	0.444	0.048	0.486	0.489
A-13-6	0.4012	2	0.074	0.372	0.099	0.432	0.047	0.515	0.505
A-13-7	0.4003	20	0.044	0.375	0.132	0.393	-	-	-
A-13-8	0.3997	20	0.045	0.383	0.131	0.412	-	-	-
A-13-9	0.3959	70	0.041	0.370	-	-	-	-	-
A-13-10	0.4000	70	0.040	0.376	-	-	-	-	-

Note: The optical densities were measured on Perkin-Elmer Model 21, NaCl prism, slit program 927, from base line standard. The optical density of NO_3^- was measured at 1391 cm^{-1} and that of water at 3440 cm^{-1}.

TABLE III

Stability of Nitrate Optical Density in KBr Disks Stored Over $CaCl_2$ Desiccant at Room Temperature

Disk No	NO_3^- Optical Density[a] After Storage over $CaCl_2$ for t hours					
	t = 0	t = 20	t = 30	t = 50	t = 60	Average
A-14-1	0.307	0.310	0.307	0.309	0.307	0.308
A-14-2	0.313	0.310	0.312	0.312	0.312	0.312
A-14-3	0.312	0.309	0.312	0.311	0.311	0.311
A-14-4	0.307	0.308	0.310	0.311	0.311	0.309
A-14-5	0.309	0.312	0.310	0.313	0.312	0.311

[a] Optical densities measured on Perkin-Elmer Model 21, slit program 927, from base line standard, NaCl prism.

Note: Powder used for these disks was dried 48 hours in a vacuum oven at 115°C. The initial optical densities for water at 3440 cm^{-1} were approximately 0.050 for all the disks and did not change on storage.

TABLE IV

Effect of Water Concentration on the Gamma Radiolysis of Nitrate Ions in 300 mg KBr Disks with Average Initial NO_3^- Optical Density of 0.241

Disk No	Initial Water Optical Density at 3440 cm^{-1}	Fraction of NO_3^- Optical Density at 1391 cm^{-1} Removed by Irradiation; t = Irradiation Time, hr			
		t = 0.5	t = 1.0	t = 2.0	t = 3.0
A-15-6	0.018	0.079	0.141	0.237	0.312
A-15-5	0.023	0.079	0.138	0.238	0.313
A-15-7	0.025	0.078	0.140	0.236	0.312
A-15-1	0.027	0.079	0.137	0.236	0.322
A-15-2	0.033	0.078	0.136	0.243	0.314
A-15-10	0.038	0.079	0.145	0.244	0.325
A-15-3	0.040	0.079	0.153	0.282	0.346
A-15-4	0.044	0.078	0.156	0.281	0.386
A-15-9	0.050	0.076	0.151	0.271	0.385
A-15-8	0.063	0.075	0.149	0.256	0.364

Note: Optical densities measured on Perkin-Elmer Model 21, NaCl prism, slit program 927, from base line standard.

TABLE V

Effect of Water Concentration on the Gamma Radiolysis of Nitrate Ions in 300 mg KBr Disks with Average Initial NO_3^- Optical Density of 0.097

Disk No	Initial Water Optical Density at 3440 cm^{-1}	Fraction of NO_3^- Optical Density at 1391 cm^{-1} Removed by Irradiation; t = Irradiation Time, hr			
		t = 0.25	t = 0.50	t = 1.0	t = 1.5
A-16-3	0.017	0.082	0.124	0.185	0.222
A-16-4	0.026	0.080	0.120	0.185	0.225
A-16-2	0.036	0.082	0.124	0.186	0.222
A-16-1	0.043	0.080	0.125	0.205	0.262
A-16-6	0.047	0.083	0.131	0.234	0.327
A-16-5	0.060	0.074	0.124	0.249	0.330

Note: Optical densities measured on Perkin-Elmer Model 21, NaCl prism, slit program 927, from base line standard.

TABLE VI

Effect of Water Concentration on the Gamma Radiolysis of Nitrite Ions in 300 mg KBr Disks with Average Initial NO_2^- Optical Density of 0.326

Disk No	Initial Water Optical Density at 3440 cm^{-1}	Fraction of NO_2^- Optical Density at 1276 cm^{-1} Removed by Irradiation; t = Irradiation Time, hr			
		t = 1.0	t = 3.0	t = 12	t = 32
C-1-10	0.010	0.025	0.057	0.136	0.226
C-1-9	0.012	0.022	0.057	0.138	0.227
C-1-3	0.014	0.022	0.056	0.129	0.224
C-1-4	0.017	0.022	0.063	0.138	0.226
C-1-11	0.023	0.021	0.052	0.132	0.259
C-1-6	0.031	0.024	0.066	0.160	0.286
C-1-5	0.043	0.024	0.073	0.201	0.335
C-1-8	0.051	0.021	0.077	0.255	0.381
C-1-7	0.052	0.026	0.082	0.261	0.383

Note: Optical densities measured on Perkin-Elmer Model 21, NaCl prism, slit program 927, from base line standard.

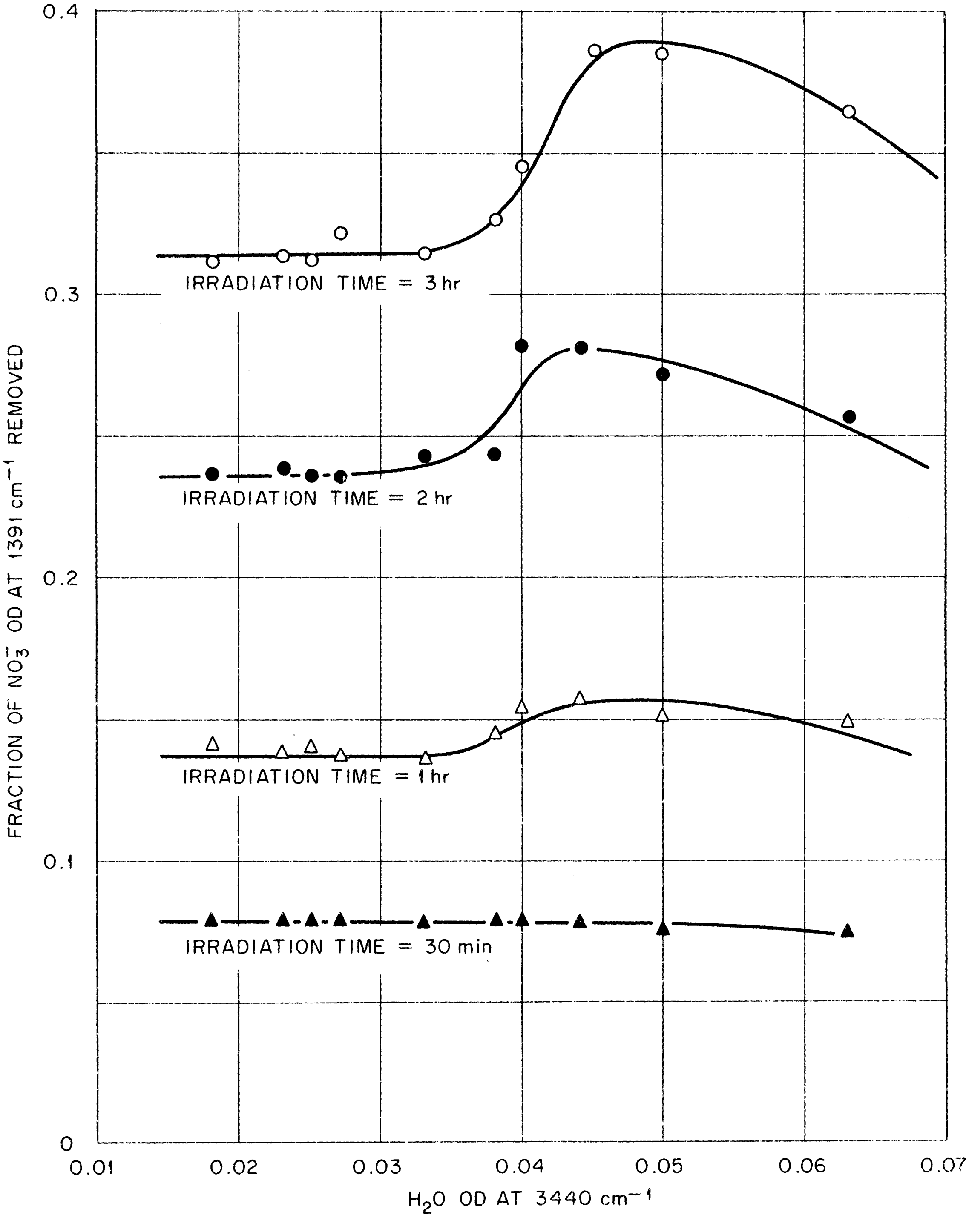

Fig. 2. Effect of Water on Nitrate Ion Decomposition for Series A-15.

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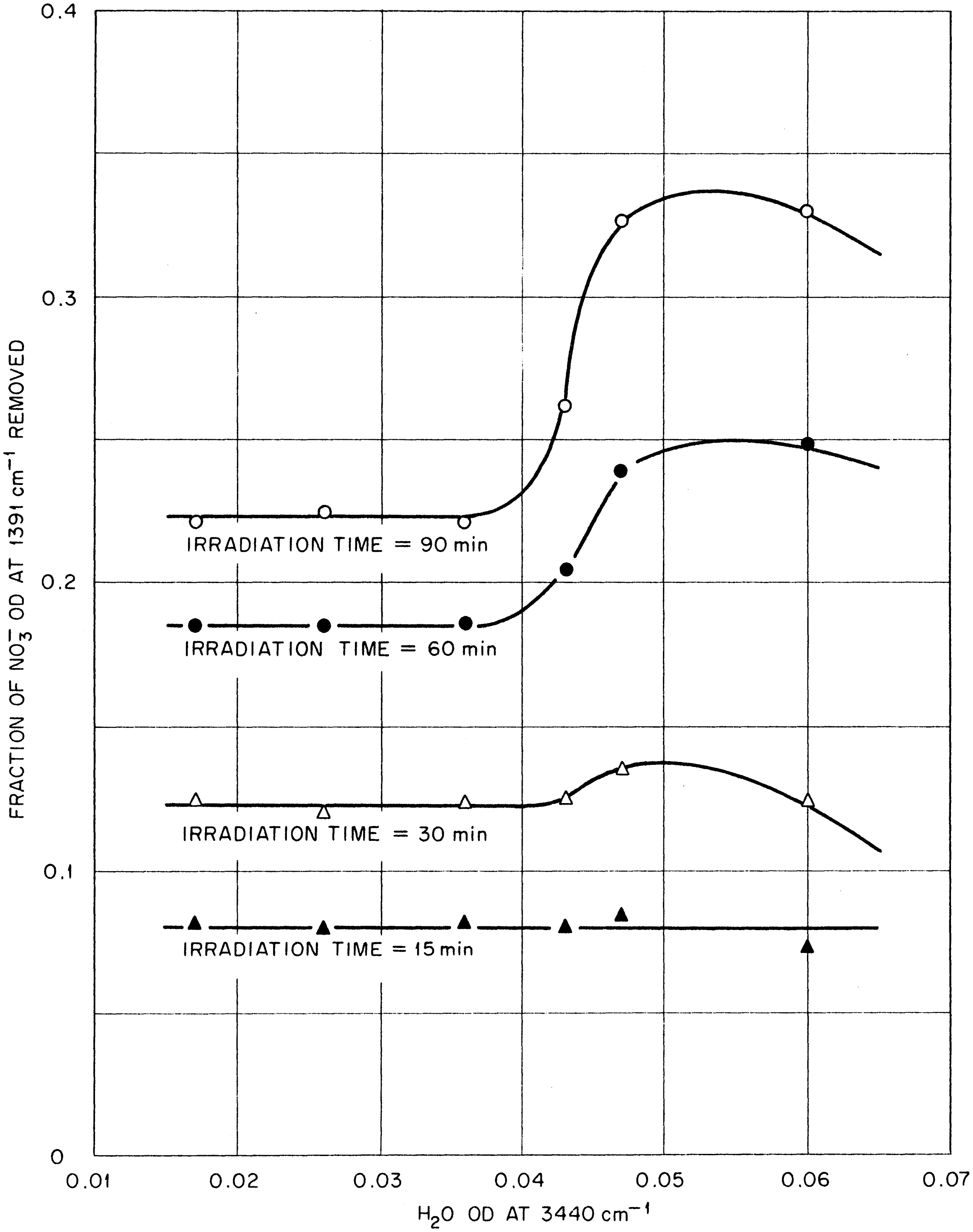

Fig. 3. Effect of Water on Nitrate Ion Decomposition for Series A-16.

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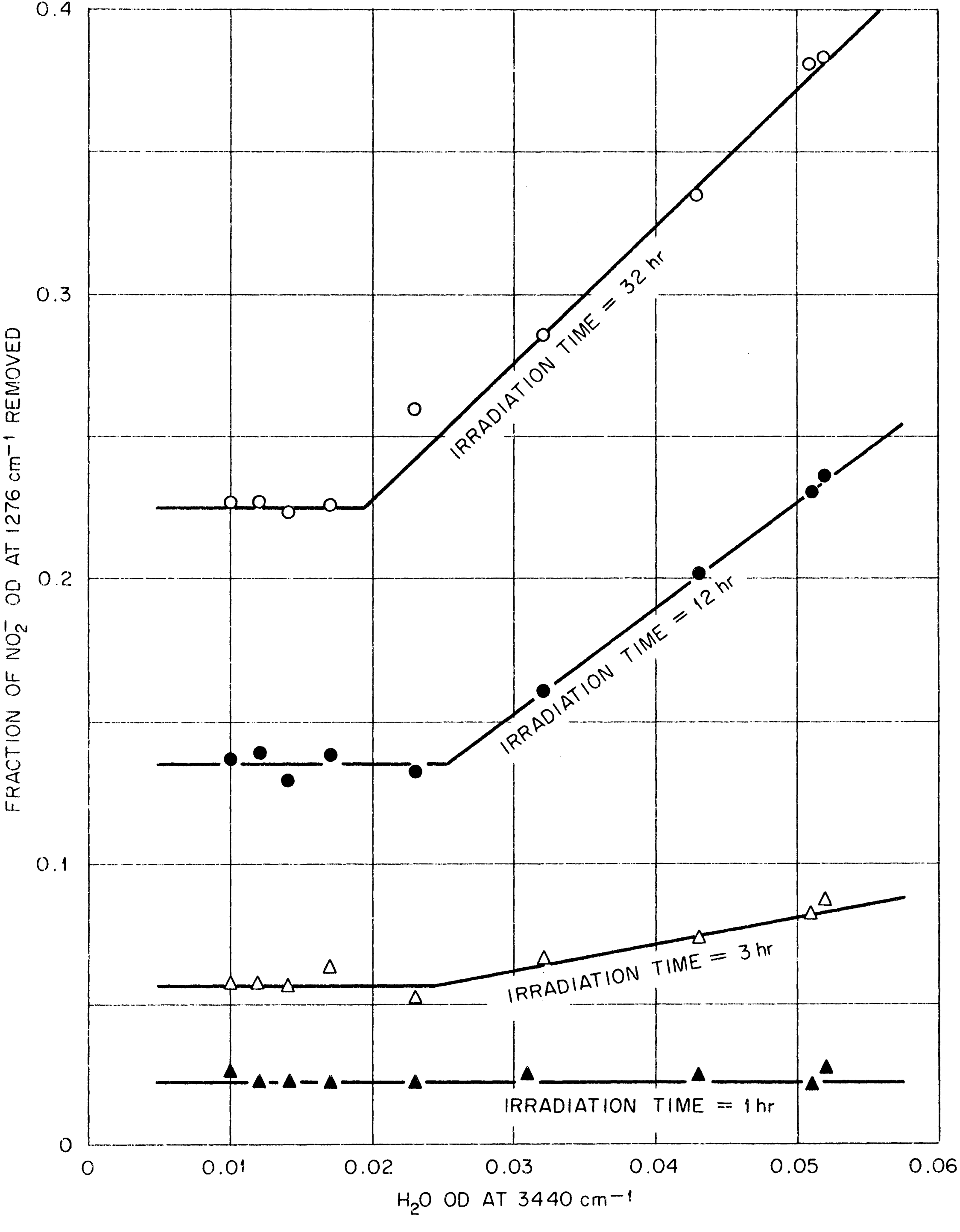

Fig. 4. Effect of Water on Nitrite Ion Decomposition for Series C-1.

TABLE VII

Results of Karl Fischer Analysis for Water Content in 400 mg KBr Disks

Disk No	Water Optical Density at 3440 cm^{-1}	Water Content from Fischer Reagent mg/disk
WB-3	0.084	< 0.5
WB-5	0.114	< 0.5
WB-1	0.128	< 0.5
WB-4	0.268	< 0.5
WB-2	0.285	< 0.5

Note: Optical densities from Perkin-Elmer Model 21, NaCl prism, 927 slit program, from base line standard.

TABLE VIII

Mass Spectrometric Analysis of Volatile Products from Gamma Radiolysis of Nitrate Ions in Powdered Potassium Bromide

Mass No	Probable Compound	mol per cent in Gas over 5 gm. Heated Samples		
		Sample MS-1 Irradiated	Sample MS-2 Non-irradiated (Low Pressure)	Sample MS-3 Irradiated (Very Low Pressure)
2	H_2	0	0	0
16	CH_4	0	0	3
18	H_2O	17.1	33.1	19
28	N_2, CO	28.4	15.7	48
30	NO	1.9	26.1	0
31	(?)	1.1	0.9	0
32	O_2	1.2	0.2	0
44	N_2O, CO_2	48.2	22.8	30
46	NO_2	0	0	0
69	(?)	1.1	0.7	0
80	Br	<0.5	<0.5	0
81	HBr	<0.5	<0.5	0
110	$NOBr$	0	0	0
160	Br_2	0	0	0

Calibration Curves for Nitrate and Nitrite Ion Content of Pressed Disks. Data for the calibration of nitrate and nitrite content of the pressed disks by infrared quantitative analysis are presented on Table IX, page 72, Table X, page 73, Table XI, page 74, and Table XII, page 75. The calibration plots are presented on Figures 5, 6, 7, and 8, pages 76, 77, 78, and 79, respectively.

Calibration of the Gamma Source. The data obtained from the calibration of the cobalt-60 gamma source by use of the ferrous dosimeter are presented on Table XIII, page 80.

Effects of Disk Thickness. The data obtained from the irradiation of nitrate-doped disks of different thicknesses are presented on Table XIV, page 81. These results are presented in graphical form on Figure 9, page 82.

Properties of Diluted Disks. The properties of samples made from doped powders which had been diluted with fresh potassium bromide are shown on Table XV, page 83. Results from the irradiation of these diluted disks are presented on Table XVI, page 84.

Purification of Potassium Nitrite. The results from the various methods used to obtain pure potassium nitrite for use in this investigation are shown on Table XVII, page 85.

Colorimetric Calibration of Nitrite Concentration. Data from the sulfanilic acid method for the determination of nitrite concentration in water are presented on Table XVIII, page 86. The calibration curve is shown on Figure 10, page 87.

TABLE IX

Calibration of Nitrate Ion Optical Density at 1391 cm^{-1} for Perkin-Elmer Model 21 Spectrophotometer[a]

Series	NO_3^- Ions per 300 mg Disk, X 10^{-17}	Average NO_3^- Optical Density
F-1	0.05	0.013
F-2	0.10	0.023
F-3	0.20	0.052
F-4	0.40	0.084
F-5	0.80	0.180

[a] NaCl prism, slit program 927, optical density from base line standard.

TABLE X

Calibration of Nitrite Ion Optical Density at 1276 cm^{-1} for Perkin-Elmer Model 21 Spectrophotometer[a]

Series	Number of NO_2^- Ions per Disk, X 10^{-17}	Average NO_2^- Optical Density
D-8	0.27	0.019
D-7	0.40	0.028
D-6	0.80	0.057
D-5	1.60	0.113
D-4	2.62	0.176
14-C-1	3.62	0.247
D-3	3.96	0.265
14-C-2	4.83	0.326
D-2	7.96	0.495
D-16	8.85	0.578
14-C-3	12.01	0.790

[a] NaCl prism, slit program 927, optical density from base line standard.

TABLE XI

Calibration of the Nitrate Ion Per Cent Absorbance at 1391 cm^{-1} for Perkin-Elmer Model 221 Spectrophotometer[a]

Series	Number of NO_3^- Ions per 300 mg Disk, X 10^{-17}	Ave. % Absorbance at 1391 cm^{-1}, of NO_3^-
F-1	0.05	2.9
F-3	0.20	9.8
F-4	0.40	15.8
F-5	0.80	28.8
F-6	1.0	35.8
F-7	2.0	51.7
F-8	3.0	62.7
F-9	5.0	73.5
F-10	10.0	79.9

[a] NaCl prism, slit program 927, per cent absorbance = 100 - per cent transmittance measured from base line standard.

TABLE XII

Calibration of Nitrite Ion Optical Density at 1276 cm^{-1} for Perkin-Elmer Model 221 Spectrophotometer[a]

Series	Number of NO_2^- Ions per 300 mg Disk, X 10^{-17}	Average NO_2^- Optical Density
D-3	3.98	0.258
D-4	2.60	0.164
D-5	1.61	0.106
D-6	0.81	0.055
D-7	0.40	0.027

[a] NaCl prism, slit program 927, optical density from base line standard.

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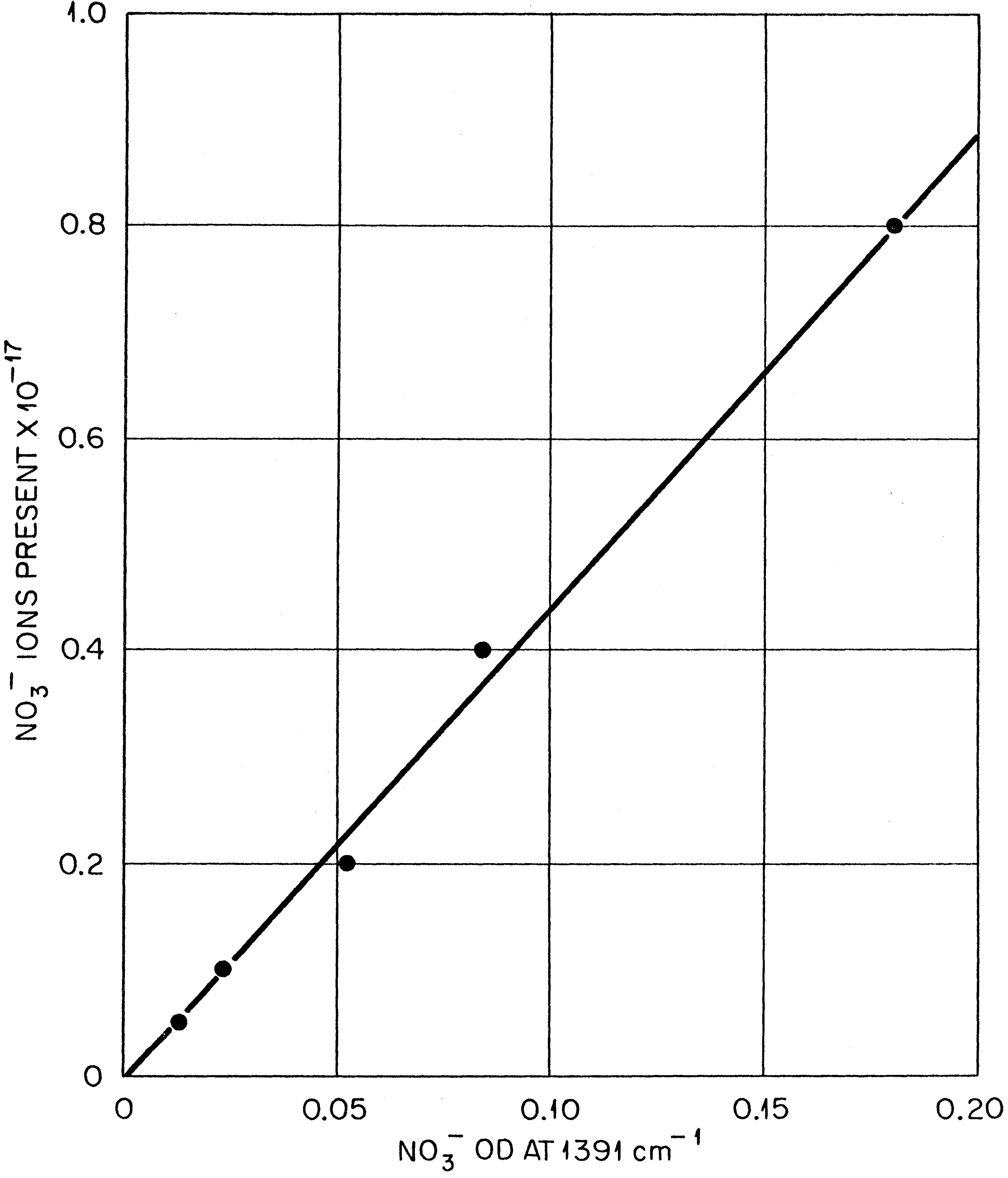

Fig. 5. Calibration of NO_3^- Optical Density at 1391 cm^{-1} on Perkin-Elmer Model 21.

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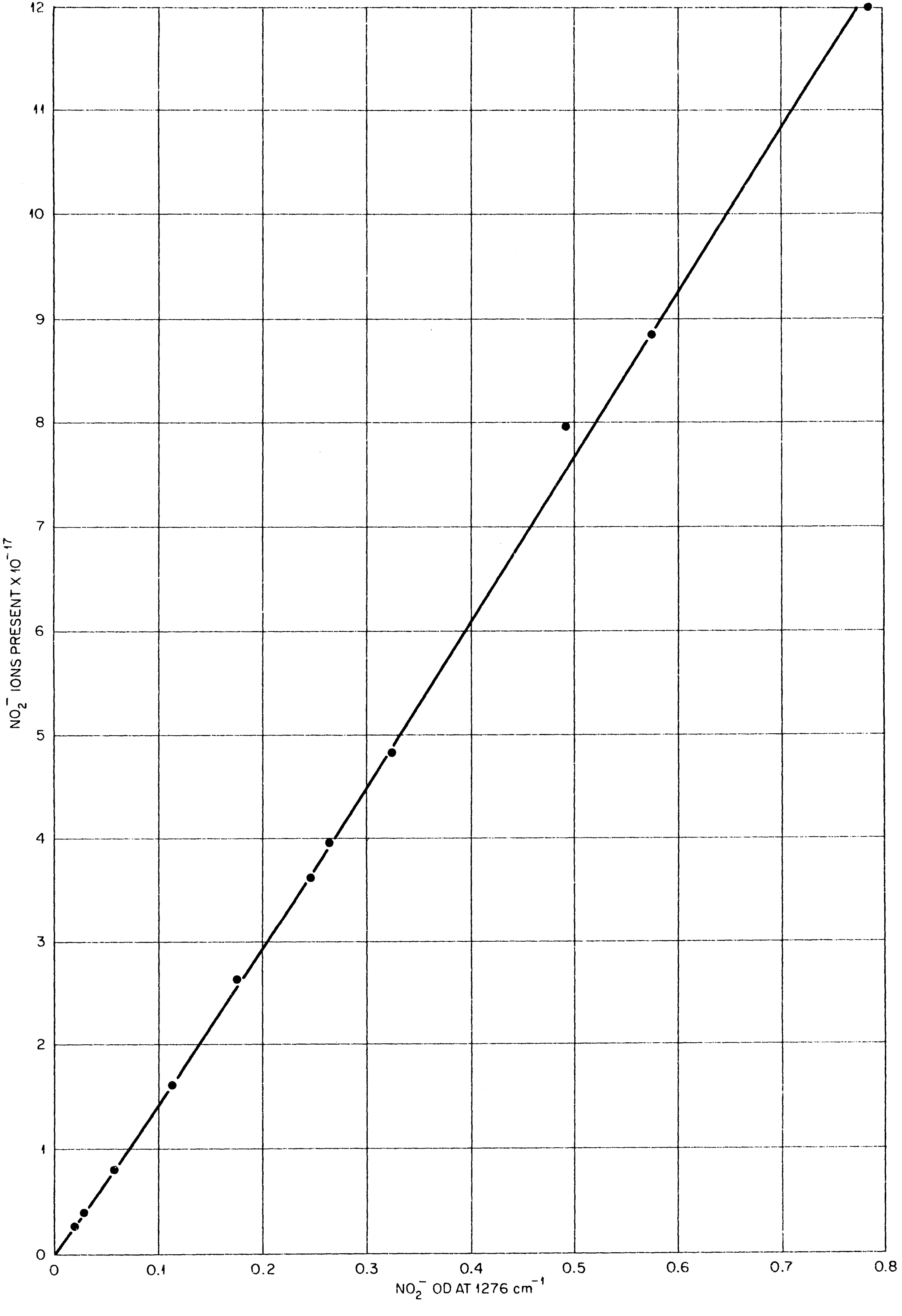

Fig. 6. Calibration of Nitrite Optical Density at 1276 cm^{-1} on Perkin – Elmer Model 21.

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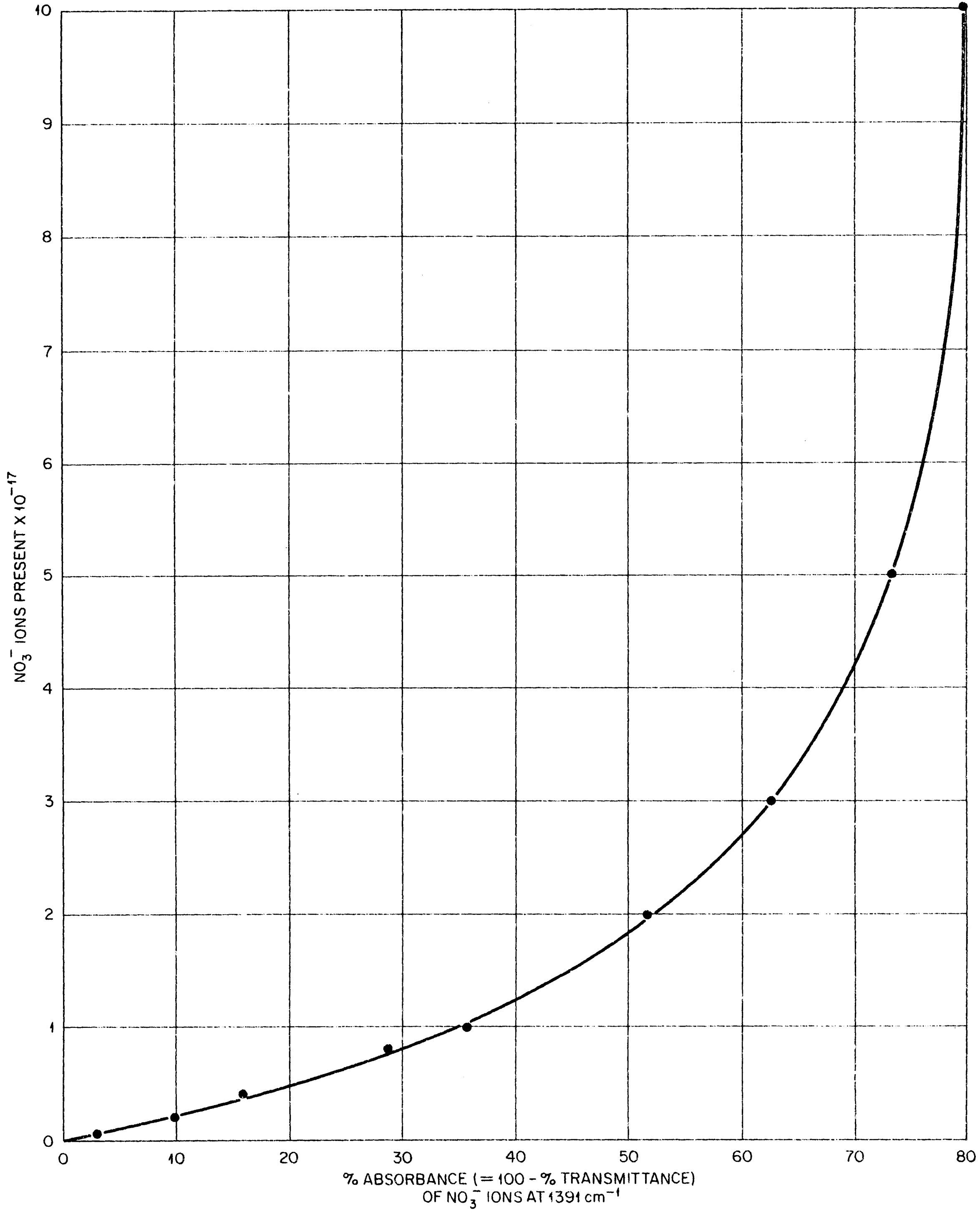

Fig. 7. Calibration of Nitrate Absorbance at 1391 cm^{-1} on Perkin-Elmer Model 221.

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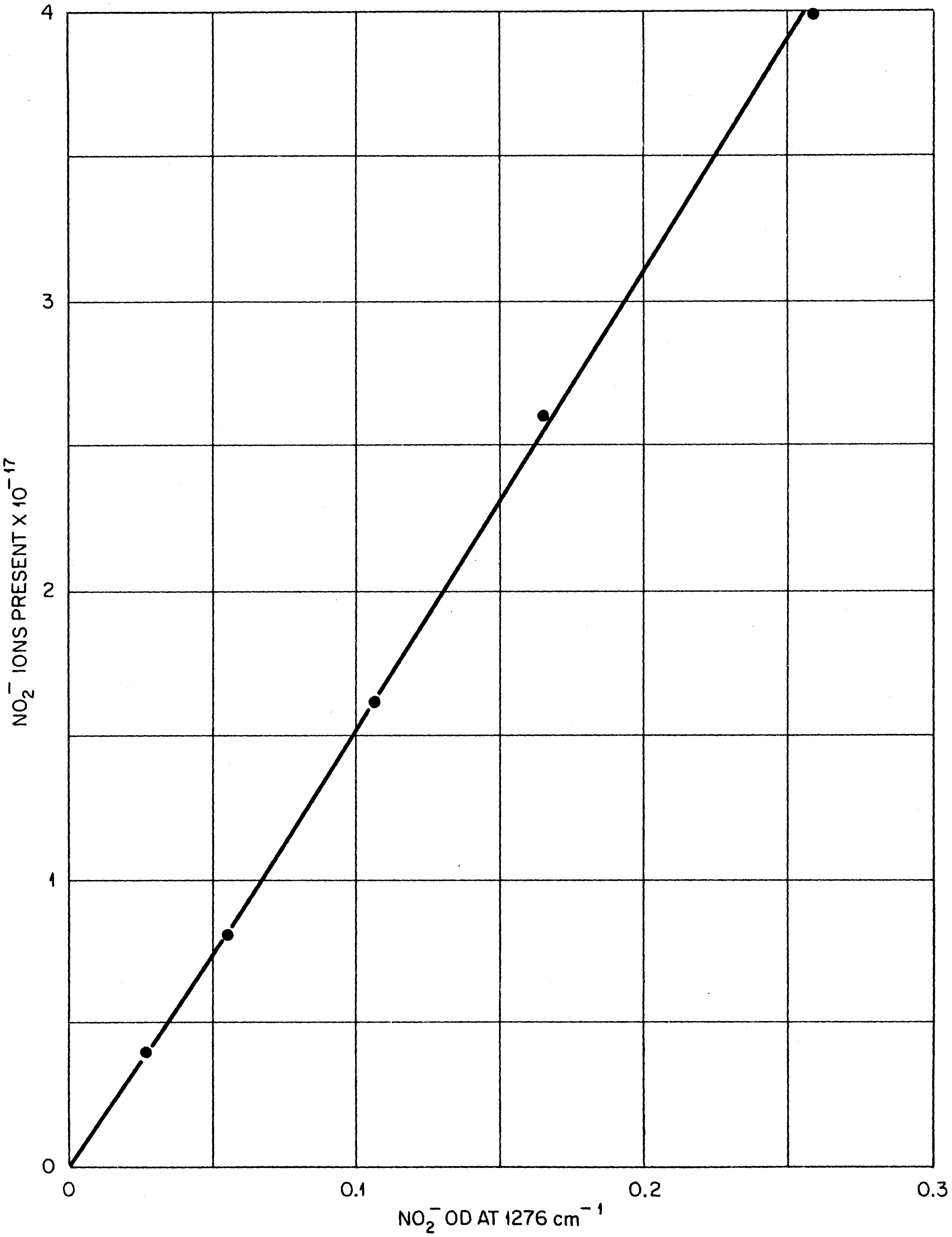

Fig. 8. Calibration of Nitrite Optical Density at 1276 cm^{-1} on Perkin-Elmer Model 221.

TABLE XIII

Calibration of the 1100 Curie Cobalt-60 Gamma Source with the Ferrous Dosimeter[a]

Dosimeter Solution No	Irradiation Time = 0	Irradiation Time = 5 min		Irradiation Time = 10 min	
	Optical Density[b]	O.D.	ΔO.D./min	O.D.	ΔO.D./min
I	0.432	1.604	0.0234	2.757	0.0231
II	0.431	1.633	0.0240	2.678	0.0209
III	0.363	1.568	0.0241	2.792	0.0246
	Average ΔO.D./min = 0.0234[c]				

[a] The dosimeter solution was made according to Hochanadel and Ghormley(34).

[b] The optical densities were read on the Cary Model 11 Spectrophotometer at 3050 Angstroms using a one-centimeter quartz call.

[c] The calibration was made May 23, 1960. Dose rate at that time = 3.25 X 10^{17} ev/gm KBr-min.

TABLE XIV

Effect of Disk Thickness on the Decomposition of Nitrate Ions in 15mm-Diameter KBr Disks under Co^{60} Gamma Irradiation[a]

Disk No	Weight[b] gm	NO_3^- Ions Present X 10^{-17} at Irradiation Time = t hr					NO_3^- Ions Decomposed X 10^{-17} per 300 mg of Sample at Irradiation Time = t hr				
		t=0	t=0.25	t=0.50	t=0.75	t=1.0	t=0	t=0.25	t=0.50	t=0.75	t=1.0
14-1-C	0.2996	1.287	1.102	1.023	0.991	0.943	0	0.185	0.264	0.296	0.344
14-2-C	0.3997	1.757	1.532	1.439	1.392	1.323	0	0.169	0.239	0.274	0.326
14-3-C	0.5000	2.244	1.931	1.808	1.748	1.695	0	0.188	0.262	0.298	0.330

[a] Dose rate = 3.25 ev/gm-min.

[b] Thickness of pressed disk = 0.205 mm/gm KBr.

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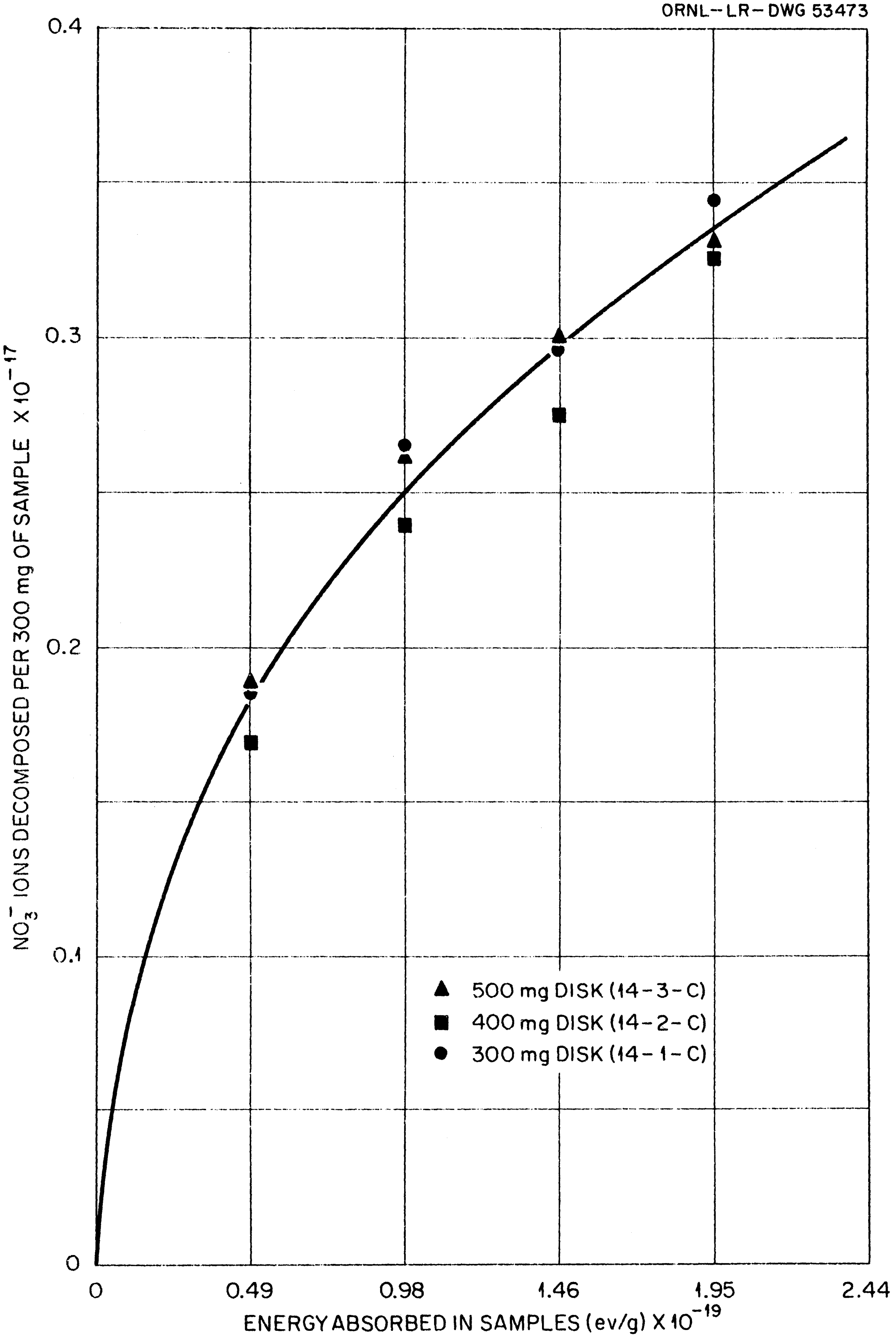

Fig. 9. Effect of Disk Thickness on the Decomposition of Nitrate Ions.

TABLE XV

Properties of Nitrate- and Nitrite-Doped KBr Disks Made by Dilution of Doped Powder with Fresh KBr

Disk No	Original KNO_3 Content mol %	Final KNO_3 Content mol %	Weight gm	Initial Water O.D. at 3440 cm^{-1}	Initial Nitrate O.D. at 1391 cm^{-1}
F-24-1	0.0065	0.0065	0.2973	0.009	0.198
F-24-2	0.0065	0.0065	0.2991	0.009	0.199
F-25-1	0.0130	0.0065	0.2994	0.008	0.205
F-25-2	0.0130	0.0065	0.2987	0.008	0.198
F-26-1	0.0196	0.0065	0.2989	0.010	0.203
F-26-2	0.0196	0.0065	0.2984	0.009	0.203

Disk No	Original KNO_2 Content mol %	Final KNO_2 Content mol %	Weight gm	Initial Water O.D. at 3440 cm^{-1}	Initial Nitrite O.D. at 1391 cm^{-1}
D-24-1	0.011	0.011	0.2995	0.018	0.108
D-24-2	0.011	0.011	0.2994	0.019	0.108
D-25-1	0.017	0.011	0.2981	0.024	0.101
D-25-2	0.017	0.011	0.2989	0.021	0.101
D-26-1	0.026	0.011	0.2978	0.023	0.106
D-26-2	0.026	0.011	0.3000	0.023	0.105

Note: Optical densities measured from base line standard on Perkin-Elmer Model 21, slit program 927, NaCl prism.

TABLE XVI

Decomposition of Nitrate and Nitrite Ions from Co^{60} Gamma Irradiation of KBr Disks Made from Doped Powders Diluted with Fresh KBr

Series No	Volume of Solution Added to Make the Original Powder	Original KNO_3 Content	Average Nitrate Optical Density Change at 1391 cm^{-1} for Irradiation Time = t hr		
	ml/4.0gm KBr	mol %	t = 0.25	t = 0.50	t = 2.0
F-24	0.30	0.0065	0.011	0.018	0.041
F-25	0.60	0.0130	0.011	0.018	0.042
F-26	0.90	0.0196	0.010	0.018	0.042

Series No	Volume of Solution Added to Make the Original Powder	Original KNO_2 Content	Average Nitrite Optical Density Change at 1276 cm^{-1} for Irradiation Time = t hr		
	ml/4.0gm KBr	mol %	t = 1.5	t = 7.0	t = 22
D-24	0.15	0.011	0.008	0.017	0.37
D-25	0.25	0.017	0.008	0.016	0.36
D-26	0.375	0.026	0.008	0.017	0.36

Note: Optical densities measured from base line standard on Perkin-Elmer Model 21, NaCl prism, slit program 927.

TABLE XVII

Purification of Potassium Nitrite

Method	Nitrate Content[a] mol %	Comments
Recrystallization from Water Four Cycles	1.3	Noticeable NO_3^- Peak on I-R; 2 % recovery of KNO_2
Recrystallization from Water Six Cycles	0.6	Noticeable NO_3^- Peak on I-R; 1 % recovery of KNO_2
Reduction of NO_3^- with Lead at 300°C	2	K_2O Formed; Purification Difficult
From Organic Nitrite + KOH	-	Nitrite and KOH Impure; Removal of Excess KOH and K_2CO_3 Very Difficult
Extraction with Absolute MeOH Two Cycles	0.5	Noticeable NO_3^- Peak on I-R; 50 % Recovery of KNO_2; Removal of MeOH by Drying - No MeOH Peak on I-R
Extraction with Absolute MeOH Five Cycles	0.08	No Noticeable NO_3^- or MeOH Peaks on I-R; 25 % Recovery of KNO_2
Purification of $AgNO_2$, Reaction with KBr	10	Difficult to Remove AgBr and to React all $AgNO_3$; I-R Peak Looked Like $AgNO_3$

[a] Nitrate content by I-R analysis at 1391 cm^{-1} on Perkin-Elmer Model 21, NaCl prism, 927 slit program. Initial nitrate content = 3.7 mol per cent.

TABLE XVIII

Colorimetric Calibration of Nitrite Ion Concentration in Water Solutions of 400mg KBr Disks

Disk No	Nitrite Ion Content ions X 10^{-17}	Optical Density at 5350 Å[a]
X-1	0	0.045
11-1(1)	3.36	0.80
11-3(1)	5.65	1.20

[a] Analysis by Cary Model 11 using 1-cm cell.

(1) Minges, M. L. and R. G. Edwards, Radiation Induced Decomposition of Nitrate Ion in a Potassium-Bromide Matrix, M.I.T. Engineering Practice School Memo EPS-X-421, pg. 21, Oct. 1, 1959.

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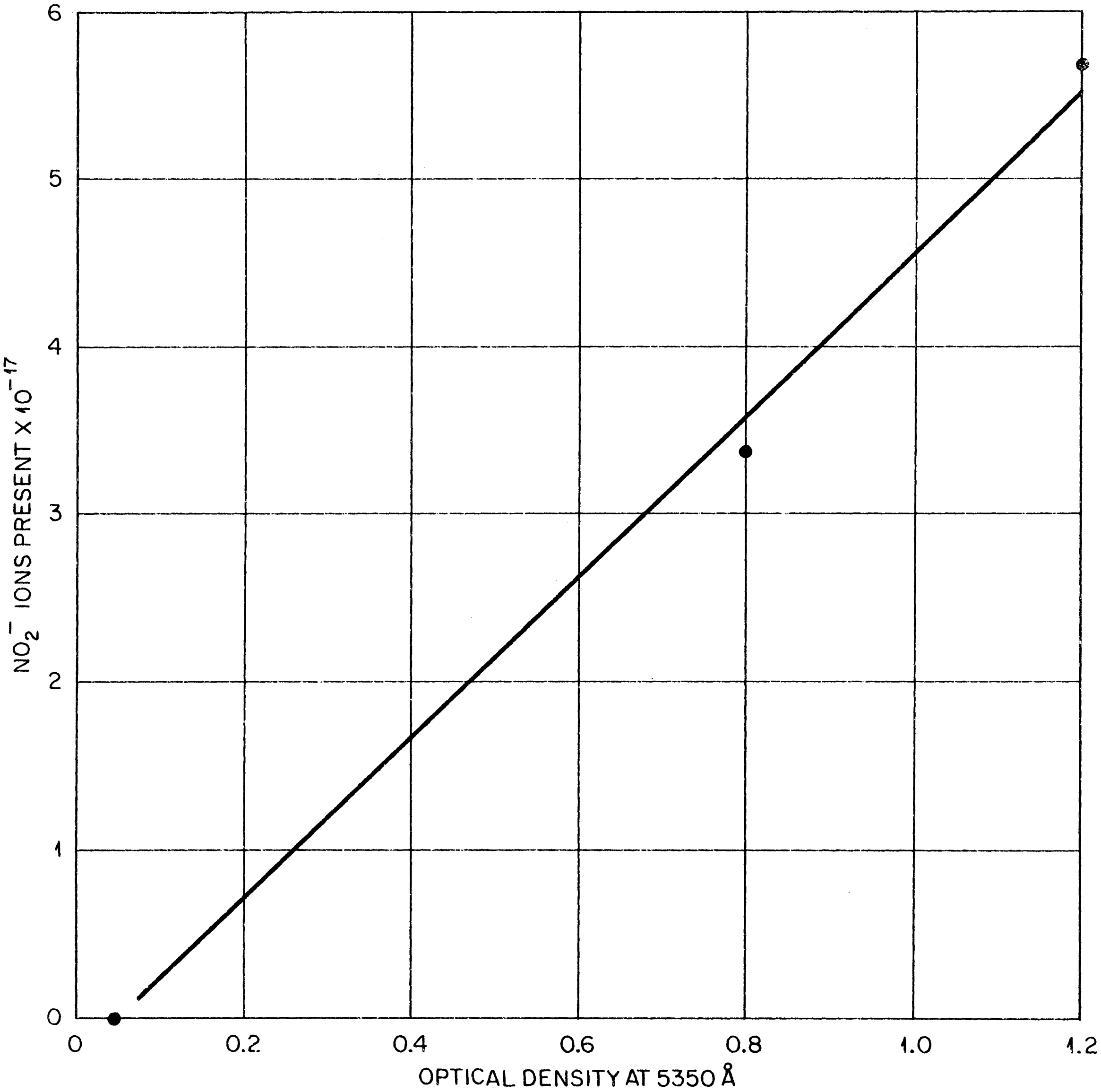

Fig. 10. Calibration of Colorimetric Determination of Nitrite Ion Content by Sulfanilic Acid Method.

Results of Gamma Radiolysis of Nitrate Ions in Series 15-2 Disks. The results of the gamma irradiation of series 15-2 disks are shown on Table XIX, page 89. The number of nitrite ions formed during irradiation was measured by both infrared and colorimetric analyses. The agreement of the colorimetric analysis with the infrared analysis is shown on Figure 11, page 90.

Gamma Radiolysis of Nitrate Ions in Dilute Disks of Series 14-2 and 10-2. The results of the gamma radiolysis of nitrate ions in disks dilute in nitrate content are presented on Table XX, page 91, for series 14-2, and on Table XXI, page 92, for series 10-2. These results are presented in graphical form on Figure 12, page 93, for series 14-2, and on Figure 13, page 94, for series 10-2.

Results of Gamma Radiolysis of Nitrite Ions in Disks of Various Initial Nitrite Contents. The results of gamma radiolysis of nitrite ions in disks containing various initial concentrations of nitrite are shown on Table XXII, page 95. The formation of nitrate ions in the nitrite-doped disks is shown on Table XXIII, page 96. A typical plot of the nitrite ions decomposed and nitrate ions formed versus dose is presented on Figure 14, page 97, and typical plots used in the determination of G_o for nitrite-doped disks are shown on Figure 15, page 98.

Dependence of G_o on Initial Acceptor Concentration for Nitrite-Doped Disks. The dependence of G_o on initial acceptor concentration for nitrite-doped disks is shown on Table XXIV, page 99, and this dependence is shown graphically on Figure 16, page 100.

TABLE XIX

Infrared and Colorimetric Analysis of Nitrite Ions Formed From Nitrate-Doped, 400mg KBr Disks under Co^{60} Gamma Irradiation

Sample[1] Code No	Energy[1] Absorbed per Sample ev X 10^{-19}	Nitrite Ions Formed X 10^{-17}		
		From[1] Infrared Analysis	From[2] Colorimetric Calibration	From Corrected[3] Colorimetric Calibration
15-2	2.36	0.299	0.51	0.31
15-2	7.08	0.875	1.00	0.85
15-2	11.79	1.364	1.54	1.30
15-2	18.85	1.995	2.03	1.93
15-2	28.30	2.65	2.59	2.57
15-2	40.10	3.41	3.68	3.41

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(1)Hinges, M. L. and R. G. Edwards, Radiation Induced Decomposition of Nitrate Ion in a Potassium-Bromide Matrix, M.I.T. Engineering Practice School Memo EPS-X-421, pg. 5, Oct. 1, 1959.

(2)Ibid, pg. 7.

(3)Corrected for zero nitrite.

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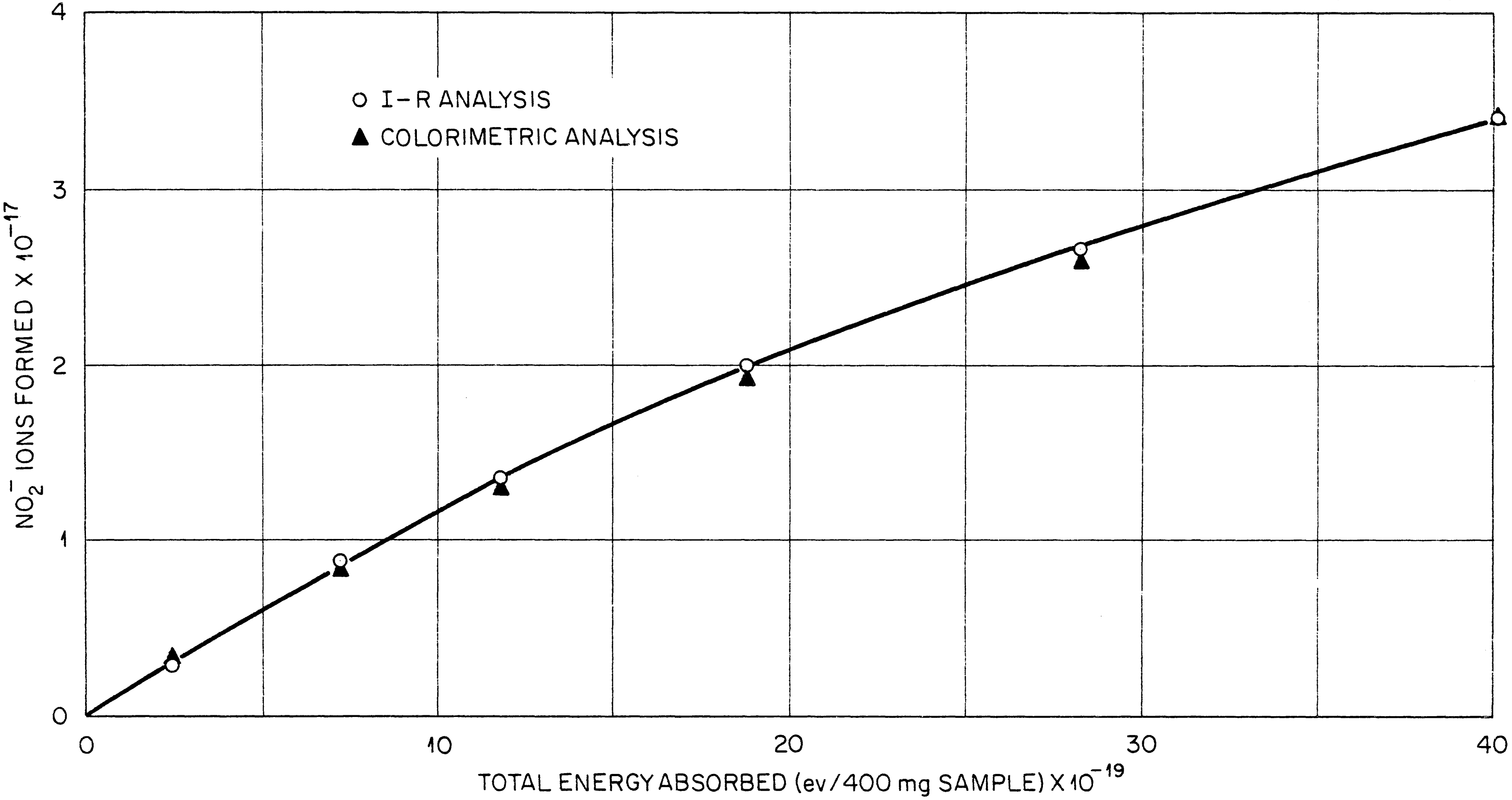

Fig. 11. Analyses of Nitrite Content in Irradiated KBr Disks Doped with Nitrate.

TABLE XX

Decomposition of Nitrate Ions in Series 14-2[a] KBr Disks under Co^{60} Gamma Irradiation

Irradiation Time[b] hr	NO_3^- Ions Present X 10^{-17} (I-R Analysis)[c]	NO_3^- Ions Decomposed X 10^{-17} (I-R Analysis)	NO_2^- Ions Formed X 10^{-17} (Colorimetric Analysis)[d]	Nitrite Ions Formed X 10^{-17} (I-R Analysis)[e]
0	1.83	0.0		0.0
1	1.70	0.13		0.12
2	1.56	0.27		0.21
3	1.44	0.39		0.28
4	1.31	0.52	0.22	0.35
6	1.11	0.72		0.46
8	0.94	0.89		0.55
10	0.81	0.92	0.55	0.62
15	0.62	1.21		0.66
20	0.48	1.35		0.66
30	0.39	1.44	0.54	0.59
47	0.35	1.48	0.51	0.52

[a] Series 14-2 consisted of four disks weighing 400 ± 3mg with an initial nitrate content of 0.012 mol per cent. Water optical densities at 3440 cm^{-1} were below 0.040.

[b] Dose rate was 3.25 X 10^{17} ev/gm-min.

[c] Analysis at 1391 cm^{-1} using base line standard.

[d] Analysis on Model 11 Cary spectrophotometer at 5350 A by sulfanilic acid method.

[e] Analysis at 1276 cm^{-1} using base line standard.

Note: I-R analyses were made on the Perkin-Elmer Model 21, NaCl prism, 927 slit program.

TABLE XXI

Decomposition of Nitrate Ions in Series 10-2[a] KBr Disks under Co^{60} Gamma Irradiation at 25°C

Irradiation Time[b] hr	Nitrate Ions Decomposed[c] X 10^{-17}	Nitrite Ions Formed[d] X 10^{-17}
0	0	0
1	0.147	0.13
2	0.233	0.21
3	0.289	0.22

[a] Series 10-2 consisted of four disks weighing 400 ± 1mg with an initial nitrate content of 0.003 mol per cent. Water optical densities at 3440 cm^{-1} were less than 0.04.

[b] Dose rate = 3.25 X 10^{17} ev/gm-min.

[c] Analysis at 1391 cm^{-1} using base line standard.

[d] Analysis at 1276 cm^{-1} using base line standard.

Note: Infrared analyses were on Perkin-Elmer Model 21, NaCl prism, 927 slit program.

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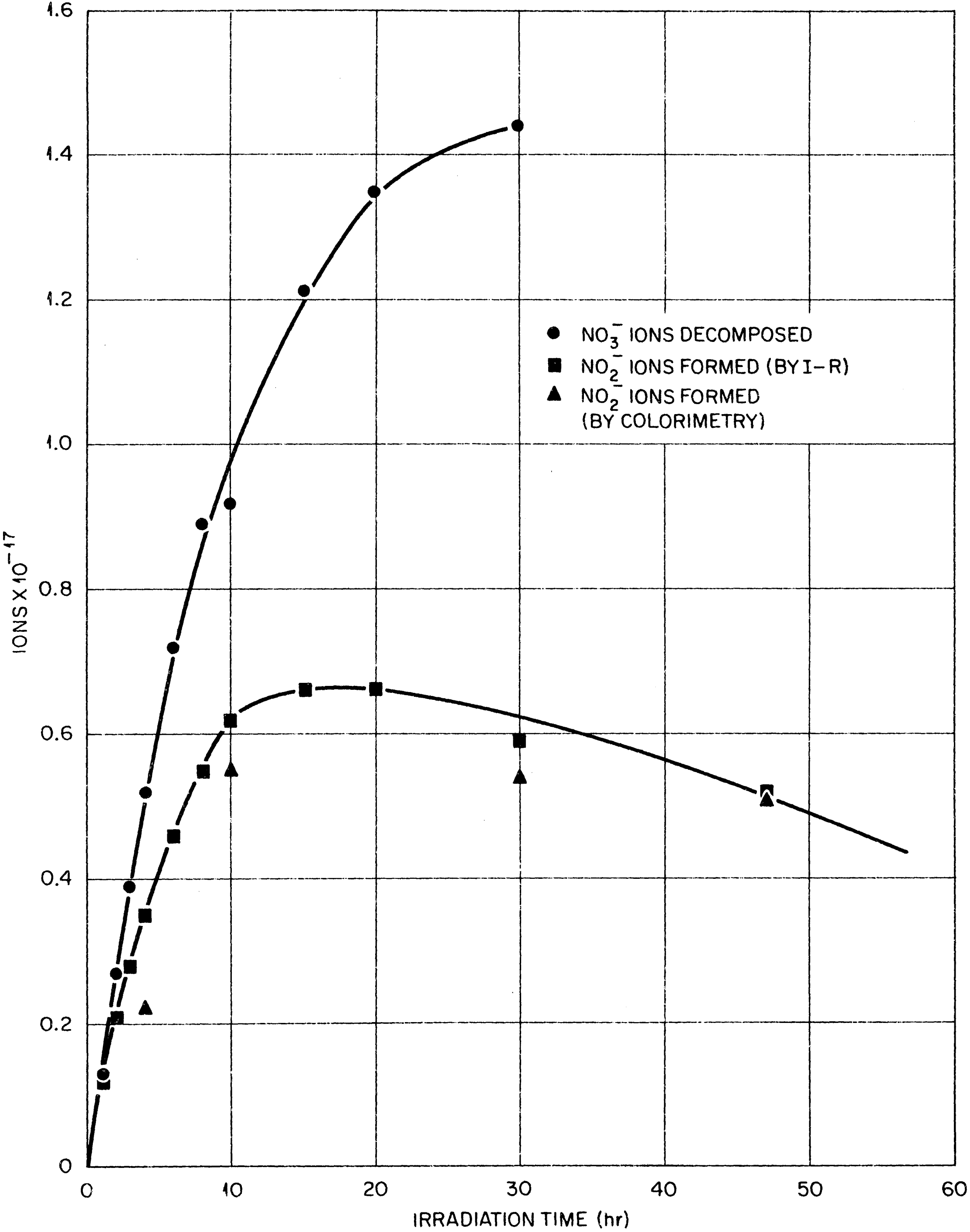

Fig. 12. Gamma Radiolysis of Nitrate Ions in Series 14-2 KBr Disks.

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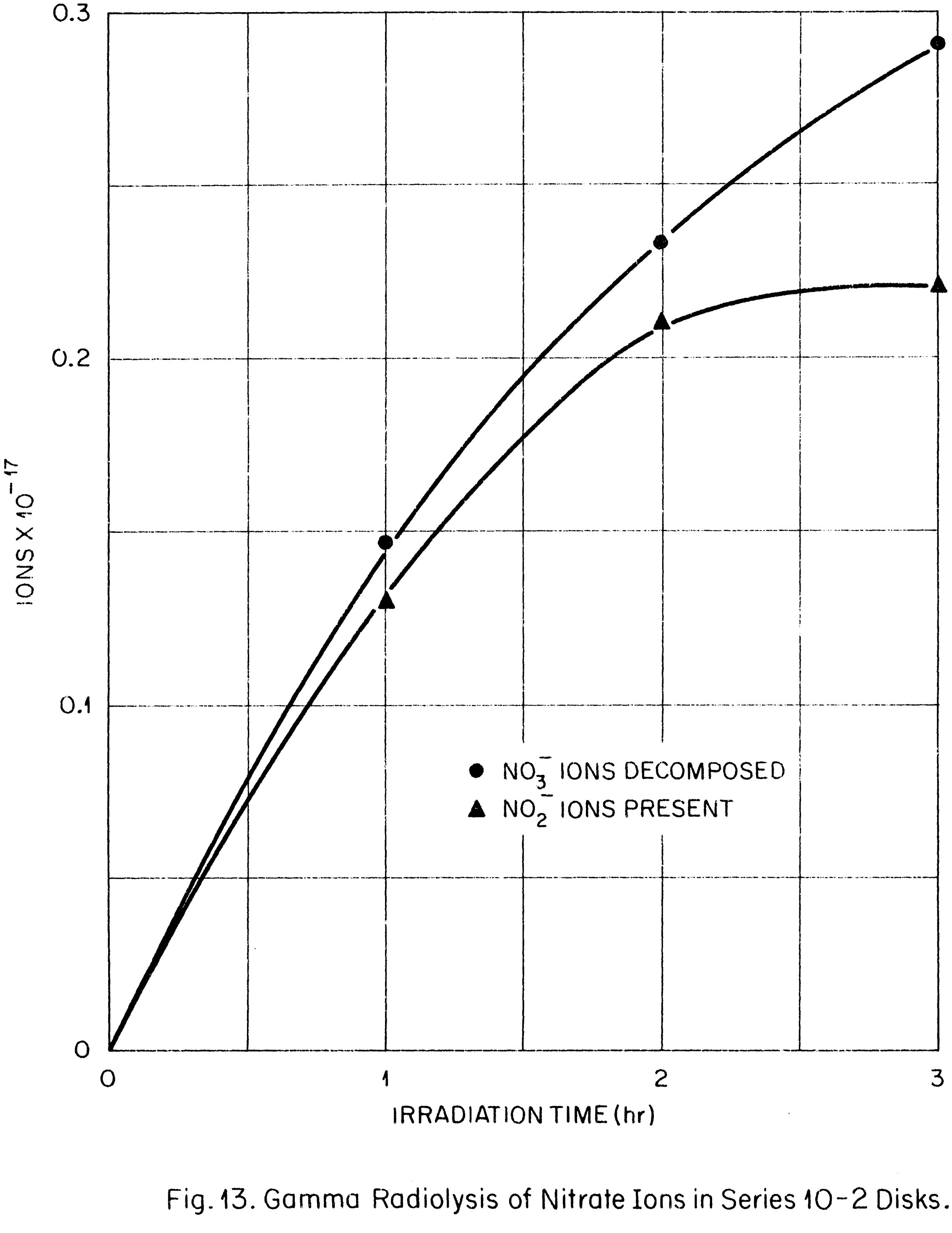

Fig. 13. Gamma Radiolysis of Nitrate Ions in Series 10-2 Disks.

TABLE XXIV

Decomposition of Nitrite Ions in KBr Disks by Co^{60} Gamma Radiation at 25°C

Average Number of Nitrite Ions Decomposed X 10^{-17} per 300mg KBr Disk of Series D-X, Initial KNO_2 Content = c mol per cent																	
Dose[a]	D-2	D-3	Dose	D-4	D-5	Dose	D-6	D-7	Dose	D-8	D-9	Dose	D-16	D-17[b]		D-18	D-19
ev X 10^{-19}	c = 0.052	c = 0.026	ev X 10^{-19}	c = 0.017	c = 0.011	ev X 10^{-19}	c = 0.0052	c = 0.0026	ev X 10^{-19}	c = 0.0021	c = 0.0018	ev X 10^{-19}	c = 0.069	c = 0.105		c = 0.140	c = 0.28
0.146	0.12	0.09	0.292	0.12	0.08	0.292	0.07	0.05	0.585	0.04	0.02	0.585	0.32	1.02		-	-
0.292	0.18	0.15	0.585	0.22	0.14	0.876	0.13	0.11	1.76	0.07	0.05	1.17	0.52	1.62	1.08	0.24	0.30
0.439	0.28	0.20	0.877	0.25	0.20	2.05	0.22	0.17	2.92	0.09	0.09	1.76	0.71	1.23		-	-
0.730	0.39	0.28	1.17	0.30	0.21	3.22	0.33	0.19	4.10	0.11	0.14	2.34	0.89		1.80	0.45	0.51
1.022	0.54	0.37	2.34	0.57	0.39	4.97	0.37	0.21	5.85	0.16	0.16						
2.195	0.71	0.57	3.51	0.67	0.47	8.19	0.49	0.25	7.61	0.17	0.17						
3.66	1.16	0.83	5.26	0.81	0.61	13.20	0.58	0.29									
4.73	1.34	0.94	7.30	0.98	0.71												
6.29	1.56	1.13	9.62	1.15	0.81												
7.45	1.73	1.29	11.7	1.24	0.90												
9.35	1.98	1.36	15.8	1.43	1.04												
11.11	2.21	1.51	19.9	1.60	1.15												
13.17	2.44	1.73															
15.8	2.69	1.93															
21.9	3.04	2.27															
31.6	3.71	2.59															

[a] Dose rate = 3.25 X 10^{17} ev/gm-min.

[b] Series 17 was made in two sets for a check.

Note: Analyses of Series D-2 through D-16 by Perkin-Elmer Model 21, NaCl prism, 927 slit program, at 1276 cm^{-1} using base line standard. Analyses of Series D-17, 18, 19 by same method, after dilution of irradiated disks with fresh KBr. The water optical densities at 3440 cm^{-1} of these disks were below 0.018.

TABLE XXIII

Formation of Nitrate Ions from Decomposition of Nitrite Ions in KBr Disks under Co^{60} Gamma Irradiation

Average Number of Nitrate Ions Formed X 10^{-17} per 300 mg KBr Disk of Series D-X, Initial KNO_2 Content = c mol per cent								
Dose[a]	D-2	D-3	Dose	D-4	D-5	Dose	D-6	D-7
ev X 10^{-19}	c = 0.052	c = 0.026	ev X 10^{-19}	c = 0.017	c = 0.011	ev X 10^{-19}	c = 0.0052	c = 0.0026
0.439	0.012	0.011	0.877	0.014	0.012	0.877	0.024	-
0.730	0.020	0.018	1.17	0.025	0.018	2.05	0.032	0.014
1.022	0.025	0.021	2.34	0.073	0.054	3.22	0.061	0.026
2.195	0.105	0.069	3.51	0.088	0.061	4.97	0.069	0.042
3.66	0.138	0.092	5.26	0.109	0.079	8.19	0.064	0.037
4.73	0.181	0.108	7.30	0.144	0.105	13.20	0.069	0.036
6.29	0.205	0.133	9.62	0.126	0.099			
7.45	0.277	0.184	11.7	0.124	0.100			
9.35	0.279	0.198	15.8	0.128	0.096			
11.11	0.346	0.217	19.9	0.124	0.097			
13.17	0.392	0.236						
15.8	0.390	0.203						
21.9	0.430	0.196						
31.6	0.460	0.204						

[a] Dose rate = 3.25 X 10^{17} ev/gm-min.

Note: Analyses were made on the Perkin-Elmer Model 21, NaCl prism, 927 slit program, at 1276 cm^{-1} using a base line standard.

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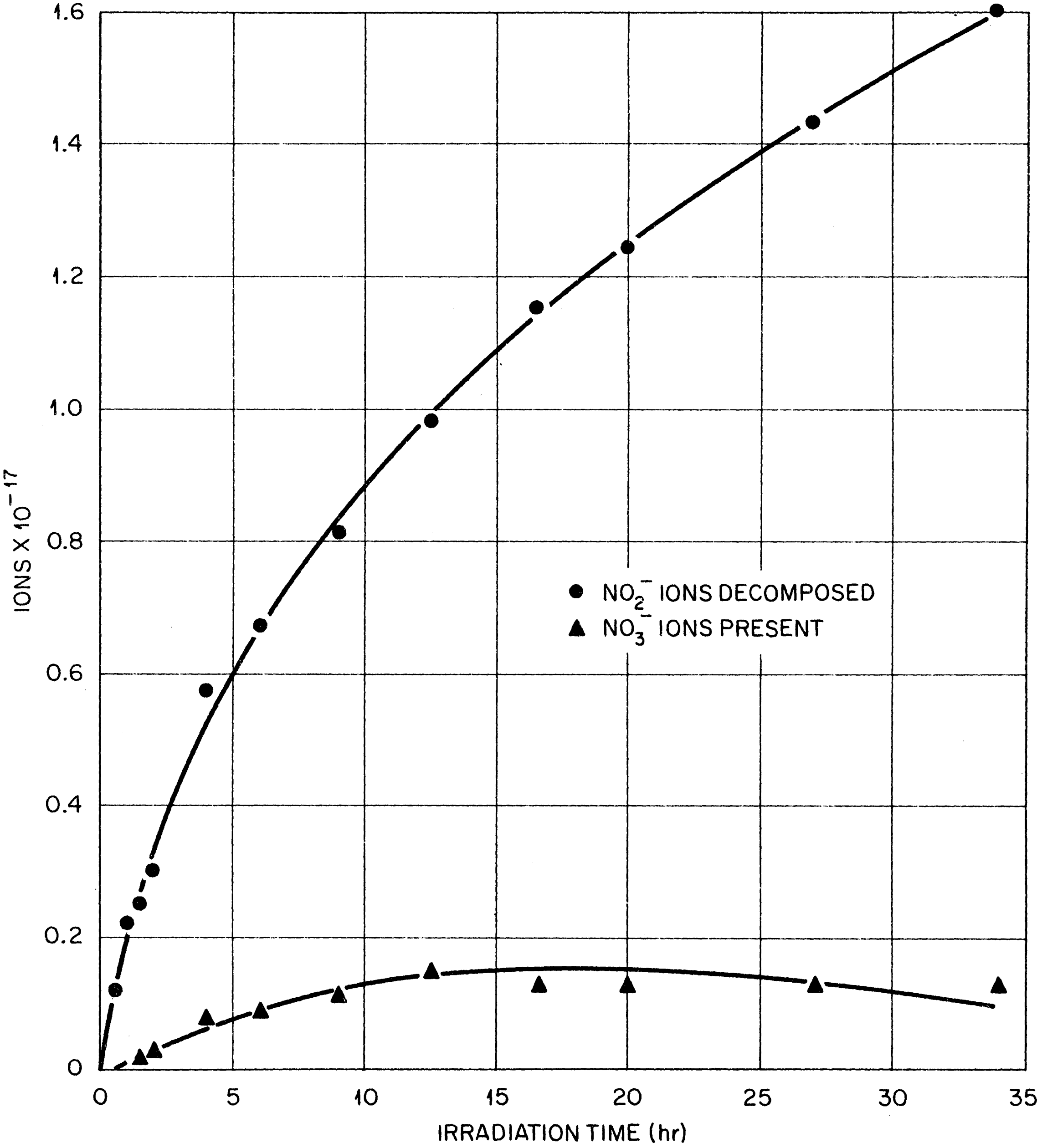

Fig. 14. Typical Plot of Gamma Radiolysis of Nitrite Ions in KBr Disks, Series D-4.

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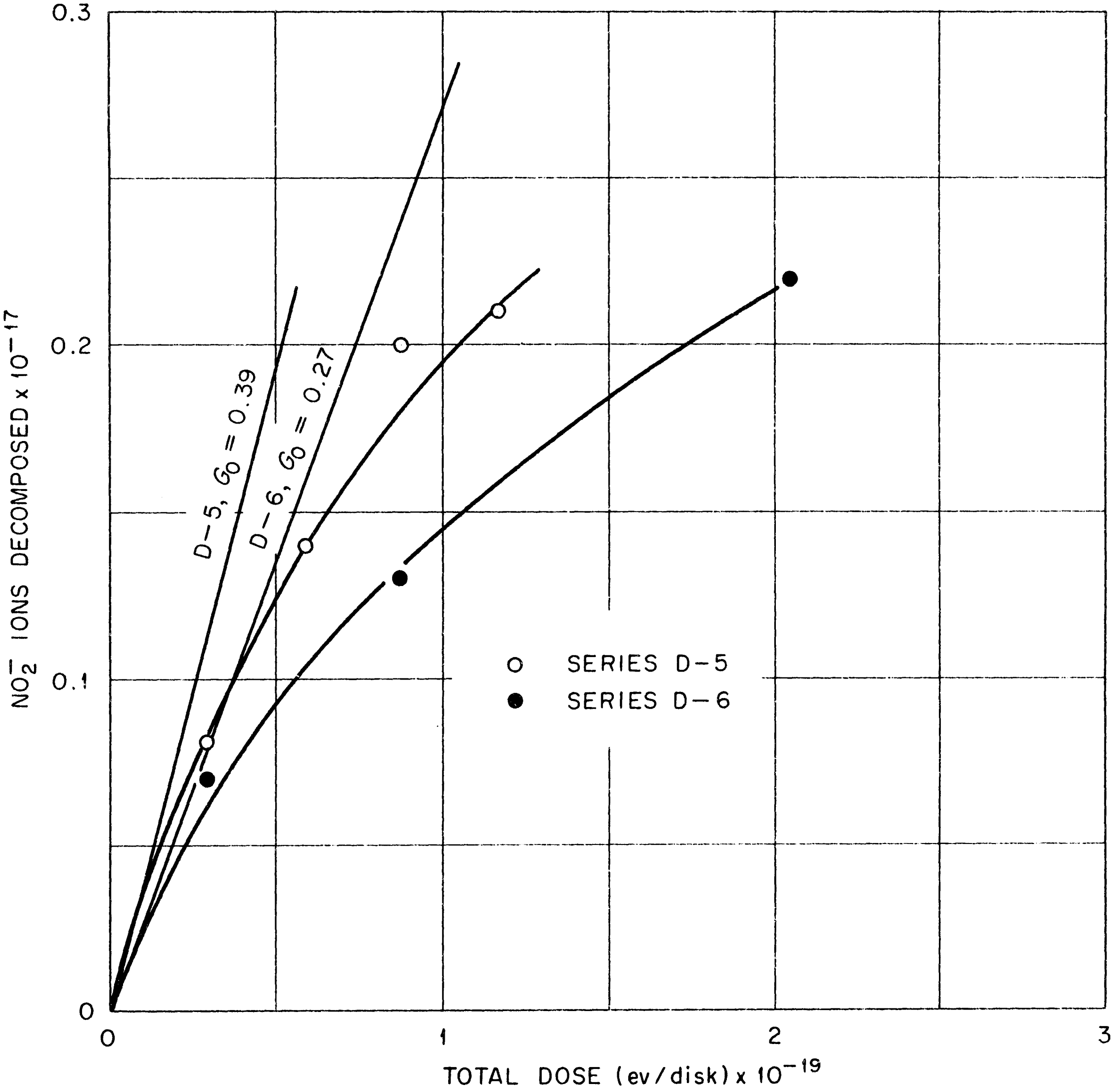

Fig. 15. Typical Plot for Determination of G_0 for Nitrite Ion Radiolysis.

TABLE XXIV

Concentration Dependence of Initial Decomposition Rate for Nitrite Ions in KBr Disks under Co^{60} Gamma Irradiation

Series	Initial Nitrite Content	Go for NO_2^- Decomposition
No	mol per cent	Ions/100ev absorbed in the disk
D-9	0.0018	0.07
D-8	0.0021	0.10
D-7	0.0026	0.16
D-6	0.0052	0.27
D-5	0.011	0.39
D-4	0.017	0.51
D-3	0.026	0.56
D-2	0.052	0.64
D-16	0.069	0.65
D-17	0.105	1.07[a]
D-18	0.140	0.28
D-19	0.280	0.36

[a] Lower value from two sets of D-17 disks.

Note: Dose rate was 3.25×10^{17} ev/gm-min. The values of Go-NO_2^- were the initial slopes of the plots of NO_2^- ions decomposed versus dose. Temperature was 25°C.

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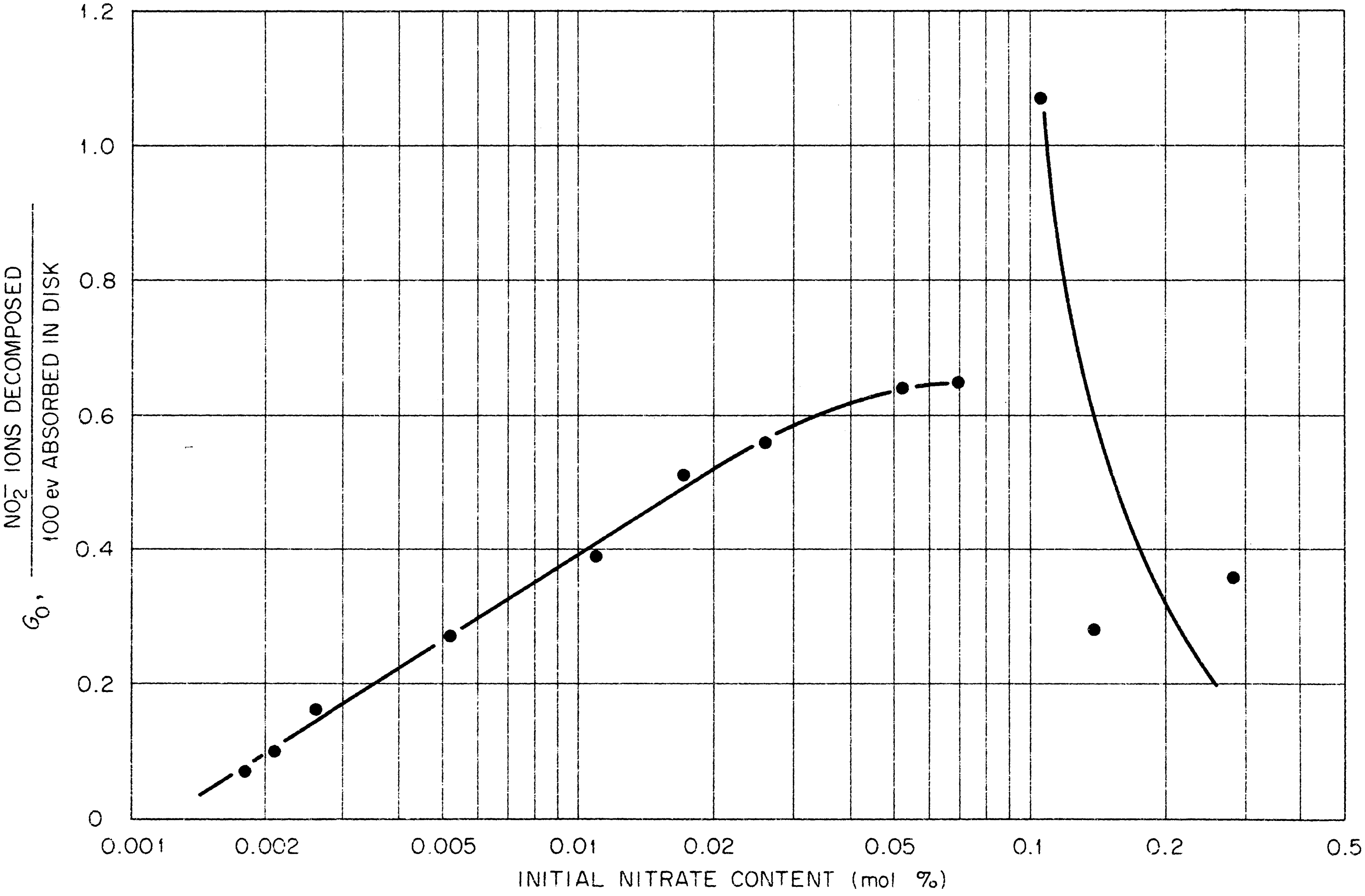

Fig. 16. Dependence of G_0 for Nitrite Radiolysis on Initial Concentration.

Results of Gamma Radiolysis of Nitrate Ions in Disks of Various Initial Nitrate Contents. The results of gamma radiolysis of nitrate ions in disks containing various initial concentrations of nitrate ions are presented on Table XXV, page 102, and Table XXVI, page 103. Typical plots used in the determination of G_o for the nitrate-doped disks are presented on Figure 17, page 104.

Dependence of G_o on Initial Acceptor Concentration for Nitrate-Doped Disks. The dependence of G_o on initial acceptor concentration for the nitrate-doped disks is shown on Table XXVII, page 105, and the dependence is shown graphically on Figure 18, page 106.

Agreement of Stern-Volmer Relationship with Experimental Data. The agreement of the derived Stern-Volmer type relationship between G_o and initial acceptor concentration is shown on Figure 19, page 107, for nitrite ion acceptors, and on Figure 20, page 108, for nitrate ion acceptors.

Dependence of Optical Density at 4000 Angstroms on Acceptor Concentration. The optical densities at 4000 Angstroms were measured for disks containing various amounts of nitrate and nitrite ions. The results of these measurements are presented on Table XXVIII, page 109, and the results are presented graphically on Figure 21, page 110.

Infrared Absorption Bands of Products and Possible Products. Infrared absorption bands attributed to products of nitrite ion decomposition because of their presence in the infrared absorption spectrum of irradiated disks containing nitrite ions are listed on

TABLE XXV

Decomposition of Nitrate Ions in Dilute[a] KBr Disks under Co^{60} Gamma Irradiation at 25°C

Series No	Nitrate Content	Average NO_3^- Ions Decomposed X 10^{-17} per 300 mg KBr Disk for a Total Energy Absorption = E X 10^{19} ev/sample[b]						
	mol %	E = 0.292	E = 0.439	E = 0.585	E = 0.877	E = 1.17	E = 1.32	E = 1.46
F-3	0.0013	0.042	-	0.055	0.078	0.093	-	0.100
F-4	0.0026	0.057	-	0.117	0.144	0.189	-	0.200
F-5	0.0052	0.059	-	0.107	0.164	0.180	-	0.207
F-6	0.0065	0.063	-	0.124	0.152	0.204	-	0.221
F-7	0.0130	0.17	-	0.26	0.35	0.41	-	0.46
F-8	0.0196	-	0.27	-	0.46	-	0.59	-
F-9	0.0326	-	0.39	-	0.67	-	0.80	-
F-10	0.0652	-	0.84	-	1.40	-	1.78	-

[a] Initial nitrate content less than 0.1 mol per cent.

[b] Dose rate = 3.25 X 10^{17} ev/gm-min.

Note: Analyses by Perkin-Elmer Model 221 at 1391 cm^{-1}, NaCl prism, 927 slit program, optical densities from base line standard. Initial O.D. for H_2O was less than 0.020 for these disks.

TABLE XXVI

Formation of Nitrite Ions in Concentrated[a] KBr Disks under Co^{60} Gamma Irradiation at 25°C

Series F-11; Initial Nitrate Content = 0.131 mol per cent			
I. Blanking Method[b]		II. Shoulder Method[c]	
Dose ev/sample X 10^{-19}	NO_2^- Ions Formed X 10^{-17} per 300mg Sample	Dose ev/sample X 10^{-19}	NO_2^- Ions Formed X 10^{-17} per 300mg Sample
0.585	0.27	0.292	0.18
1.17	0.40	0.585	0.27
		1.46	0.45
		2.34	0.66

Series No	Initial Nitrate Content	Nitrite Ions Formed[d] X 10^{-17} per 300 mg KBr Disk for Total Energy Absorption per sample = E X 10^{19} ev.			
	mol %	E = 0.585	E = 1.17	E = 1.76	E = 2.54
F-12	0.26	0.204	0.270	0.318	0.396
F-13	0.52	0.160	0.271	0.325	0.444
F-14	1.05	0.126	0.199	0.242	0.299

[a] Initial nitrate content greater than 0.1 mol per cent.
[b] Nitrate peak compensated for by a blank; NO_3^- read at 1276 cm^{-1}.
[c] Nitrite peak read at 1276 cm^{-1} off the shoulder of the large NO_3^- peak.
[d] Nitrite content by colorimetric analysis.

Note: Peak height analyses by Perkin-Elmer Model 221, NaCl prism, 927 slit program, from base line standard. Colorimetric analyses by Cary Model 11 using sulfanilic acid method read at 5350 Å.

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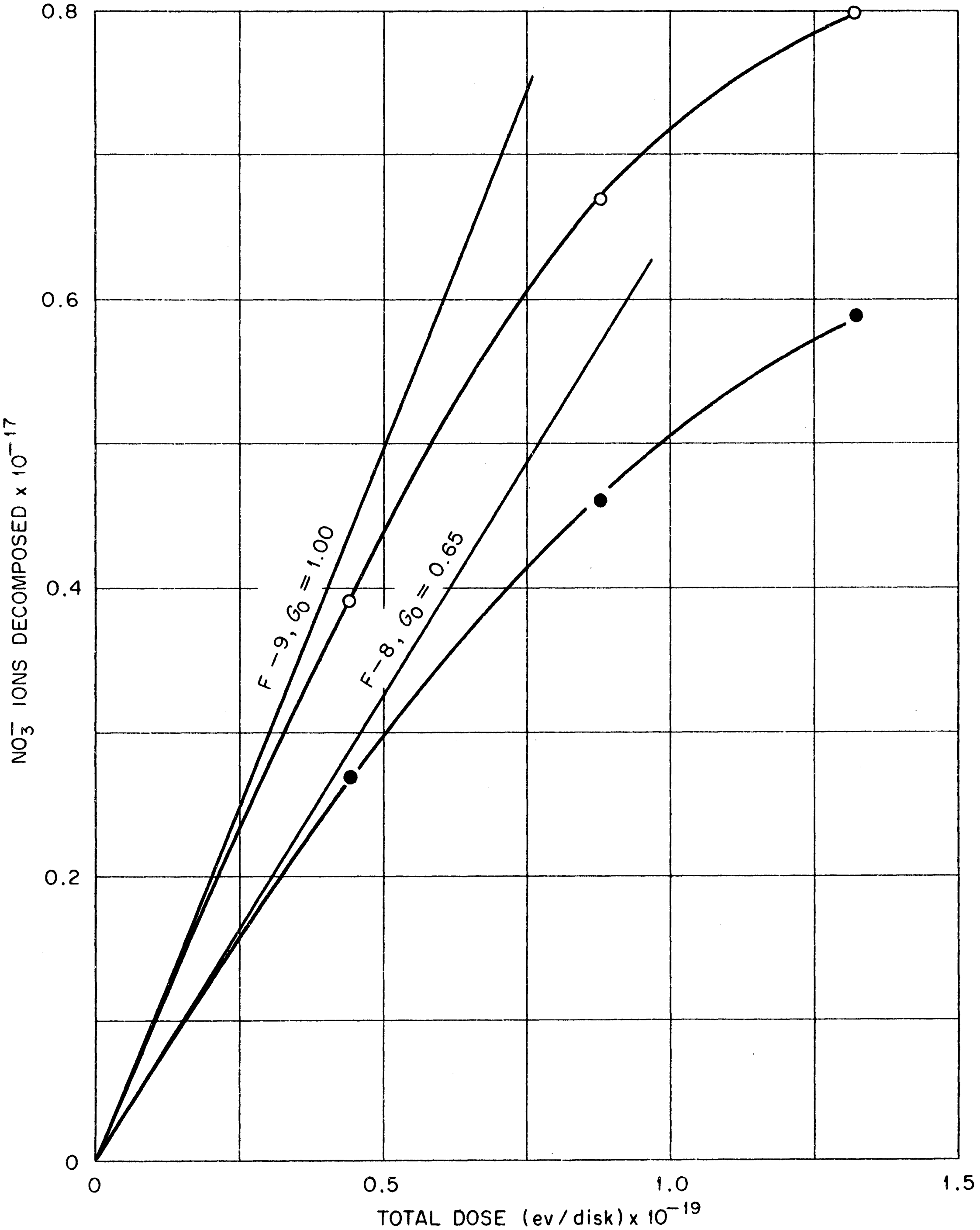

Fig. 17. Typical G_0 Determination for Nitrate Ion Radiolysis.

TABLE XXVII

Concentration Dependence of Initial Decomposition Rate for Nitrate Ions in KBr Disks under Co^{60} Gamma Irradiation

Series	Initial Nitrate Content	Go for NO_3^- Decomposition
No	mol per cent	Ions/100ev absorbed in the disk
F-3	0.0013	0.12
F-4	0.0026	0.20
F-5	0.0052	0.22
F-6	0.0065	0.30
F-7	0.013	0.58
F-8	0.0196	0.71
F-9	0.0326	1.00
F-10	0.065	1.30
F-11	0.13	1.44[a]
F-12	0.26	0.78
F-13	0.52	0.53
F-14	1.05	0.37

[a] For F-11, 12, 13, 14; Go for NO_2^- formation = Go for NO_3^- decomposition.

Note: Dose rate = 3.25×10^{17} ev/gm-min. The values of Go were the initial slopes of the decomposition curves. Temperature was 25°C.

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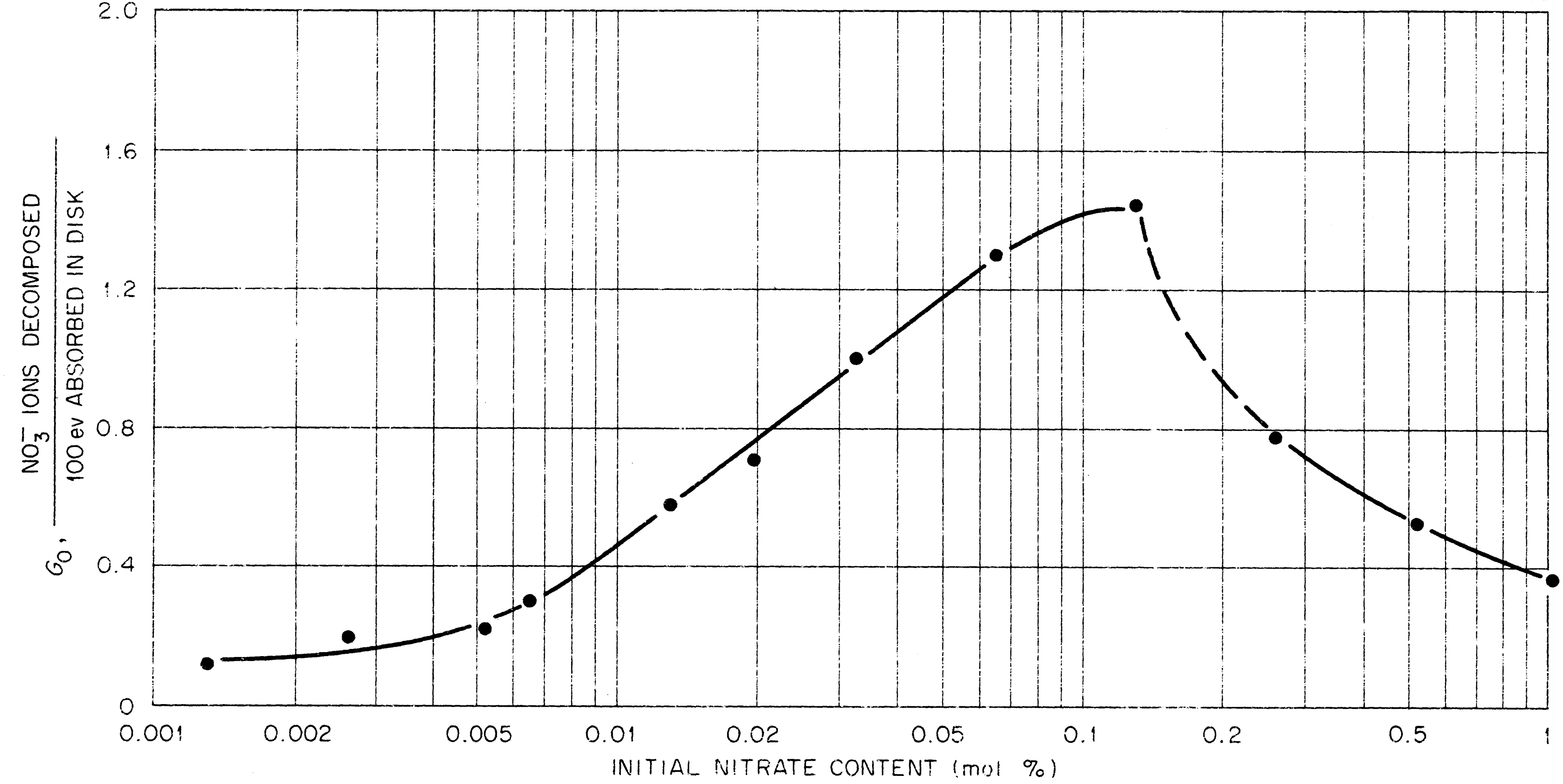

Fig. 18. Dependence of G_0 for Nitrate Radiolysis on Initial Concentration.

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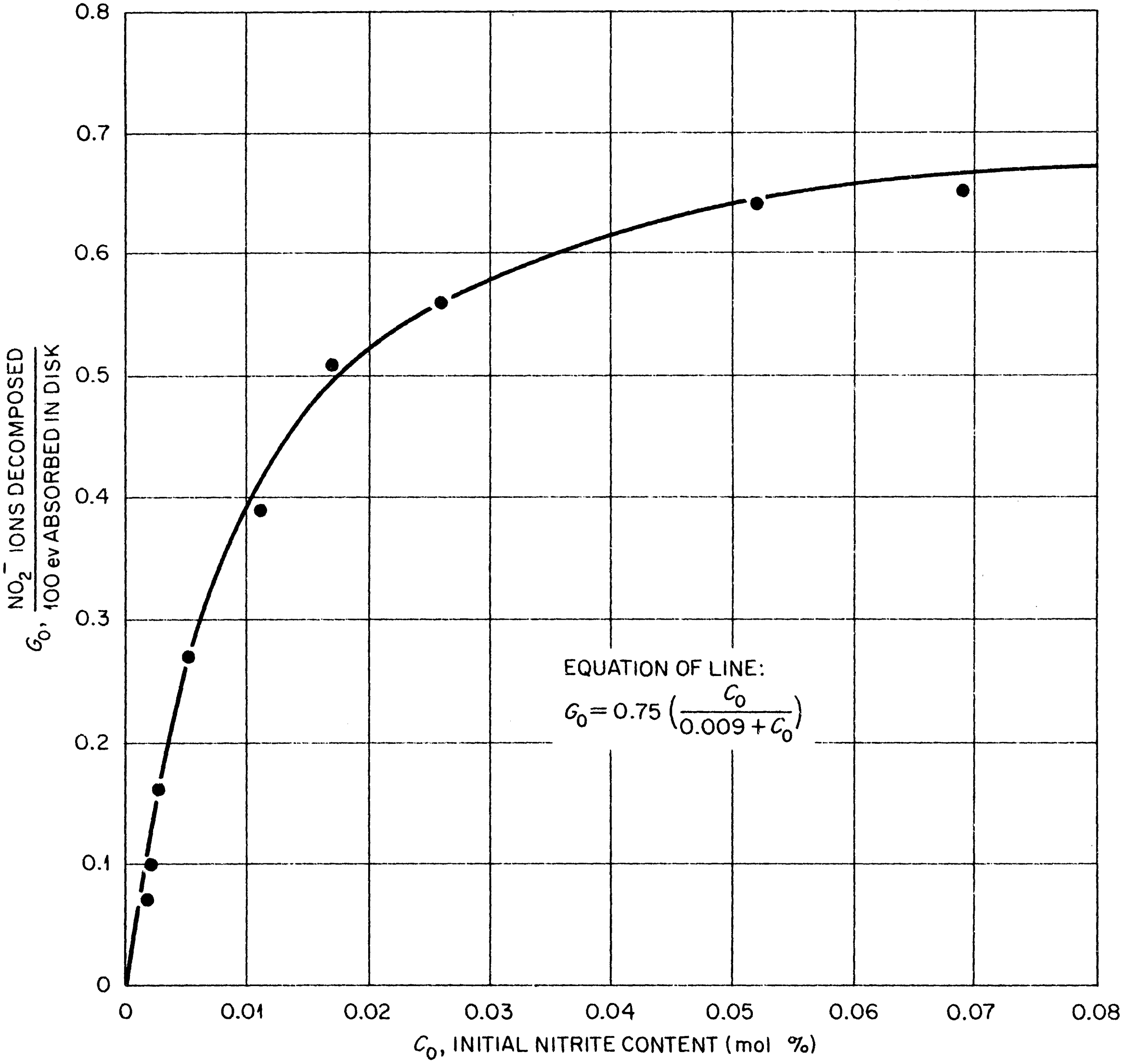

Fig. 19. Agreement of Stern-Volmer Type Equation with Results of Nitrite Radiolysis.

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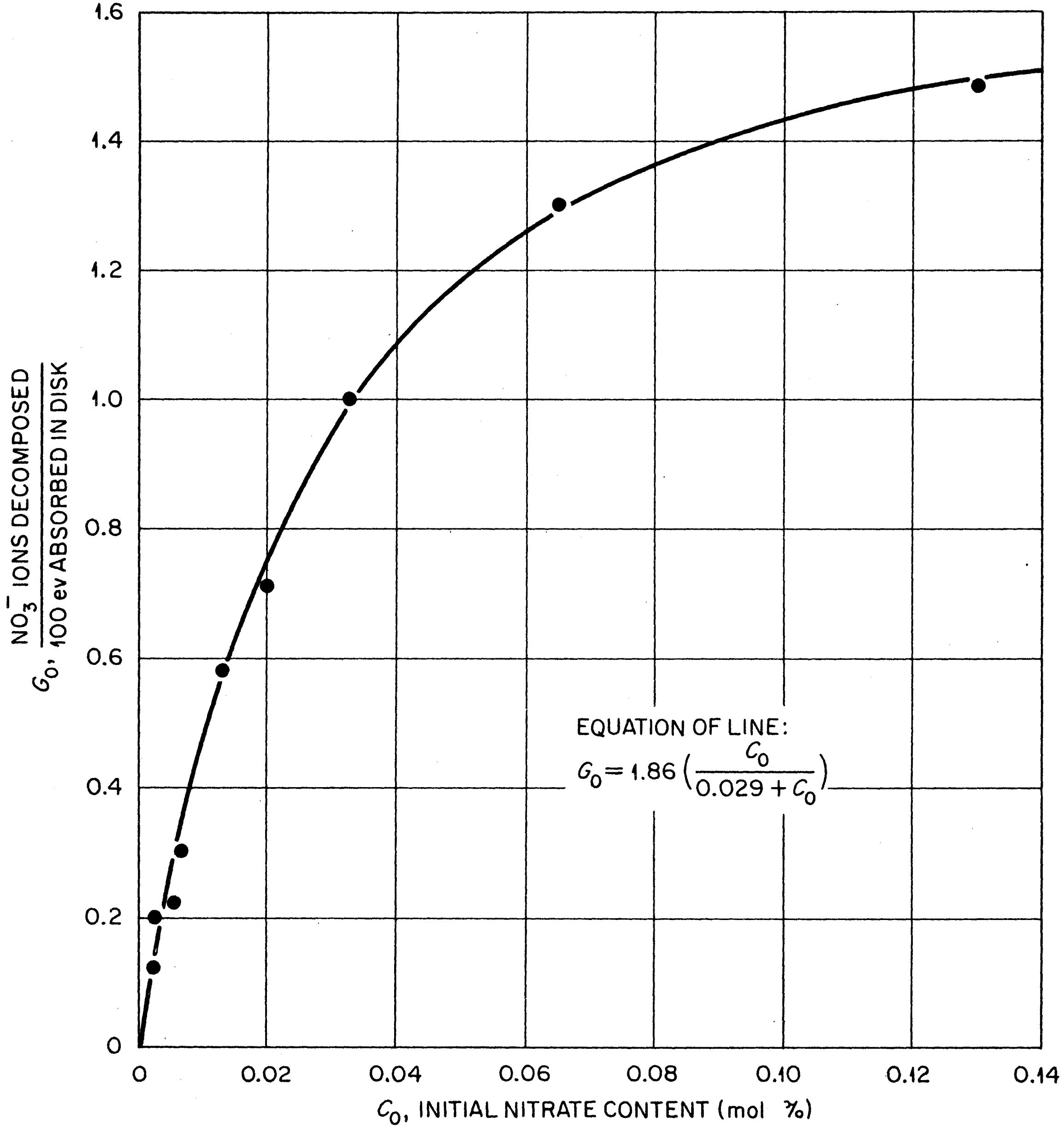

Fig. 20. Agreement of Stern–Volmer Type Equation with Results of Nitrate Radiolysis.

TABLE XXVIII

Variation of Optical Density at 4000 Å with Nitrate or Nitrite Concentration for 300mg KBr Pressed Disks

Series No	Initial Nitrite Content mol %	Optical Density at 4000 Å
D-4	0.017	0.48
D-3	0.026	0.54
D-2	0.052	0.44
D-16	0.069	0.49
D-17	0.105	0.87
D-18	0.140	1.35
D-19	0.280	1.25

Series No	Initial Nitrate Content mol %	Optical Density at 4000 Å
F-8	0.0196	0.50
F-9	0.0326	0.47
F-11	0.13	0.48
F-12	0.26	0.62
F-13	0.52	0.92
F-14	1.04	1.35

Note: Optical densities measured on Cary Model 11.

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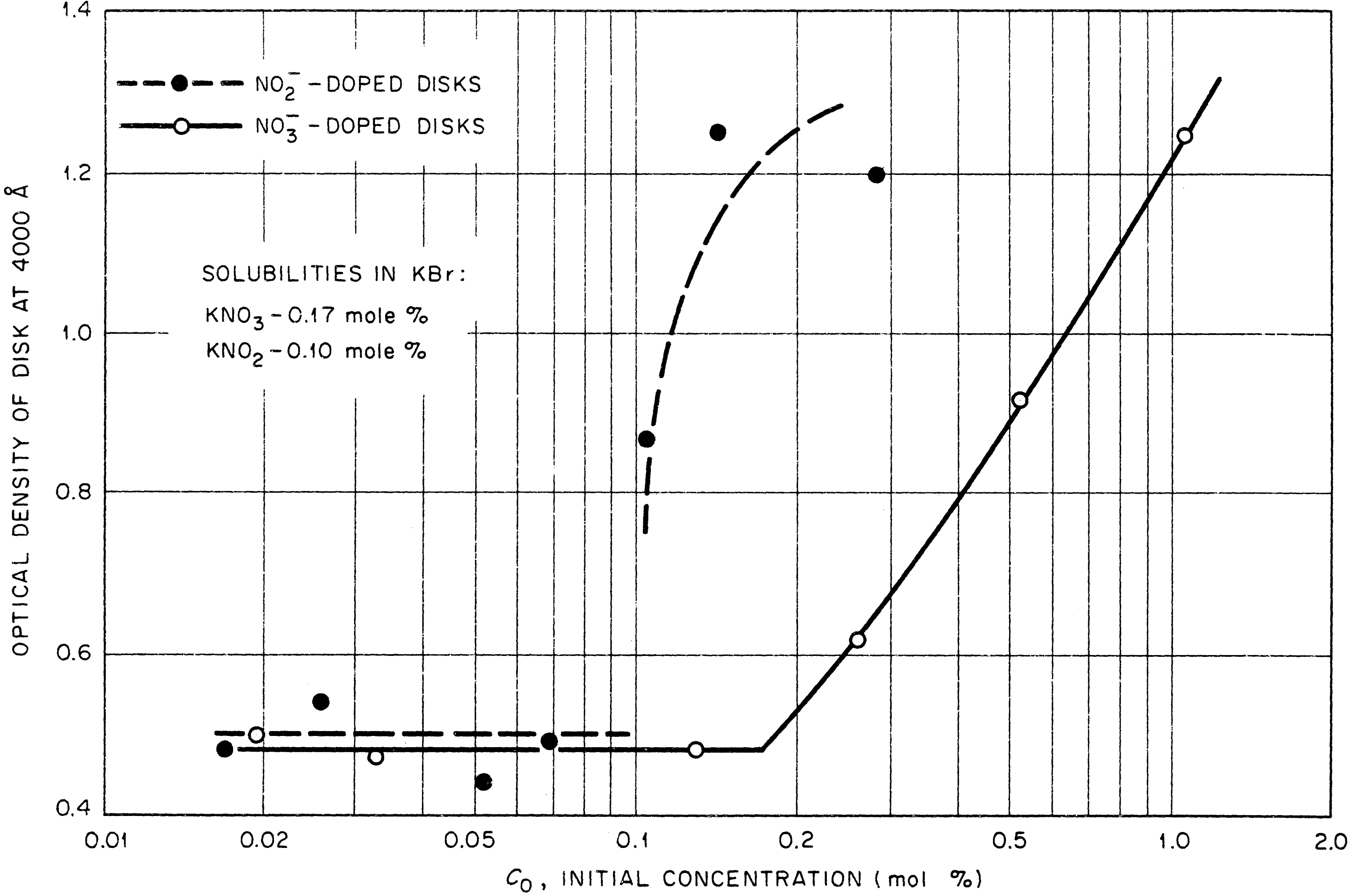

Fig. 21. Determination of Solubilities of KNO$_3$ and KNO$_2$ in KBr Pressed Disks.

Table XXIX, page 112. Infrared absorption bands of possible products from the decomposition of nitrate or nitrite ions in potassium bromide disks are listed on Table XXX, page 113.

Typical Calculations for the Derived Rate Expression. Calculations of the derived rate expression:

$$\beta \ln \frac{C_0}{C} + (C_0 - C) = kt \qquad (1)$$

for series 14-2, D-2, and D-5 are presented on Table XXXI, page 114. The plots of the calculated values versus time are presented on Figure 22, page 115, for series 14-2, and on Figure 23, page 116, for series D-2 and D-5.

Values of Rate Constant for Various Initial Acceptor Contents. Values of the rate constant, k, obtained from plots such as those on Figure 22, page 115, and Figure 23, page 116, for series of various initial nitrate and nitrite ion contents, are presented on Table XXXII, page 117.

Sample Calculations

The calculations necessary to find the dose rate of the cobalt-60 gamma source for samples of potassium bromide are shown in the following paragraphs.

Calibration of the Cobalt-60 Gamma Source with the Ferrous Dosimeter Solution. The calibration of the cobalt-60 source was

TABLE XXIX

Infrared Absorption Bands of Products from Decomposition of Isolated Nitrite Ions

Peak Wavelength	Description	Possible Products
cm^{-1}		
800	Very Intense Fairly Broad Sharp Peak	-
878	Fairly Intense Very Sharp Peak	K_2O_2
1570	Low Intensity Broad Band Multiple	From Water (?)
3530	Fairly Intense Broad Band	From Water (?)

Note: Disks of KBr containing nitrate or nitrite ions were irradiated with Co^{60} gamma rays at 25°C. Analysis was by Perkin-Elmer Model 221, scale expansion 20X, NaCl prism, slit program 980 X 2.

TABLE XXX

Major Infrared Absorption Peaks of Possible Products of Radiolysis of Nitrate and Nitrite Ions

Compound	Major Peaks[a]	Description
	cm^{-1}	
NO	2180	Multiple peak Low intensity
NO_2	1750 2400	Very sharp, intense peak Multiple peaks
N_2O	2230	Fairly intense, multiple peak
KOH	1430 760 700	Very broad, intense peak Intense, sharp peaks
K_2O_2[b]	878	Sharp, intense peak
NOBr	1825 2400	Very intense peak Sharp peak

[a] The infrared spectra of these compounds were taken with a Perkin-Elmer Model 221, NaCl prism, slit program 927, by means of the alkali halide pressed disk technique.

[b] The potassium bromide was doped with Na_2O_2.

TABLE XXXI

Typical Calculations of $\left[\beta \ln \frac{Co}{C} + (Co - C)\right]$, Series 14-2, D-2, and D-5

Series 14-2 Co = 0.012 mol % Nitrate Doped				Series D-2 Co = 0.052 mol % Nitrite Doped				Series D-5 Co = 0.011 mol % Nitrite Doped			
Irrad. Time hr	C ions X 10^{-17}	Co - C ions X 10^{-17}	R[a] hr^{-1} X 10^{-17}	Irrad. Time hr	C ions X 10^{-17}	Co - C ions X 10^{-17}	R[a] hr^{-1} X 10^{-17}	Irrad. Time hr	C ions X 10^{-17}	Co - C ions X 10^{-17}	R[a] hr^{-1} X 10^{-17}
0	1.83	0	0	0	7.95	0	0	0	1.61	0	0
1	1.70	0.13	0.48	0.25	7.83	0.12	0.14	0.5	1.53	0.08	0.15
2	1.56	0.27	0.98	0.50	7.77	0.18	0.21	1.0	1.47	0.14	0.27
3	1.44	0.39	1.45	0.75	7.69	0.28	0.32	1.5	1.41	0.20	0.38
4	1.31	0.52	1.99	1.25	7.56	0.39	0.46	2.0	1.40	0.21	0.40
6	1.11	0.72	2.92	1.75	7.41	0.54	0.64	4.0	1.22	0.39	0.77
8	0.94	0.89	3.82	3.75	7.24	0.71	0.84	6.0	1.14	0.47	0.94
10	0.81	0.92	4.51	6.25	6.79	1.16	1.38	9.0	1.00	0.61	1.26
15	0.62	1.21	5.98	8.25	6.61	1.34	1.59	12.5	0.90	0.71	1.51
20	0.48	1.35	7.26	10.75	6.39	1.56	1.86	16.5	0.80	0.81	1.77
30	0.39	1.44	8.26	12.75	6.22	1.73	2.07	20	0.71	0.90	2.02
47	0.35	1.48	8.77	16.0	5.97	1.98	2.37	27	0.57	1.04	2.47
				19.0	5.74	2.21	2.66	34	0.46	1.15	2.87
				22.5	5.51	2.44	2.94				
				27.0	5.26	2.69	3.26				

[a] $R = \beta \ln \frac{Co}{C} + (Co - C)$; β for $NO_3^- = 4.4 \times 10^{17}$; β for $NO_2^- = 1.37 \times 10^{17}$, ions

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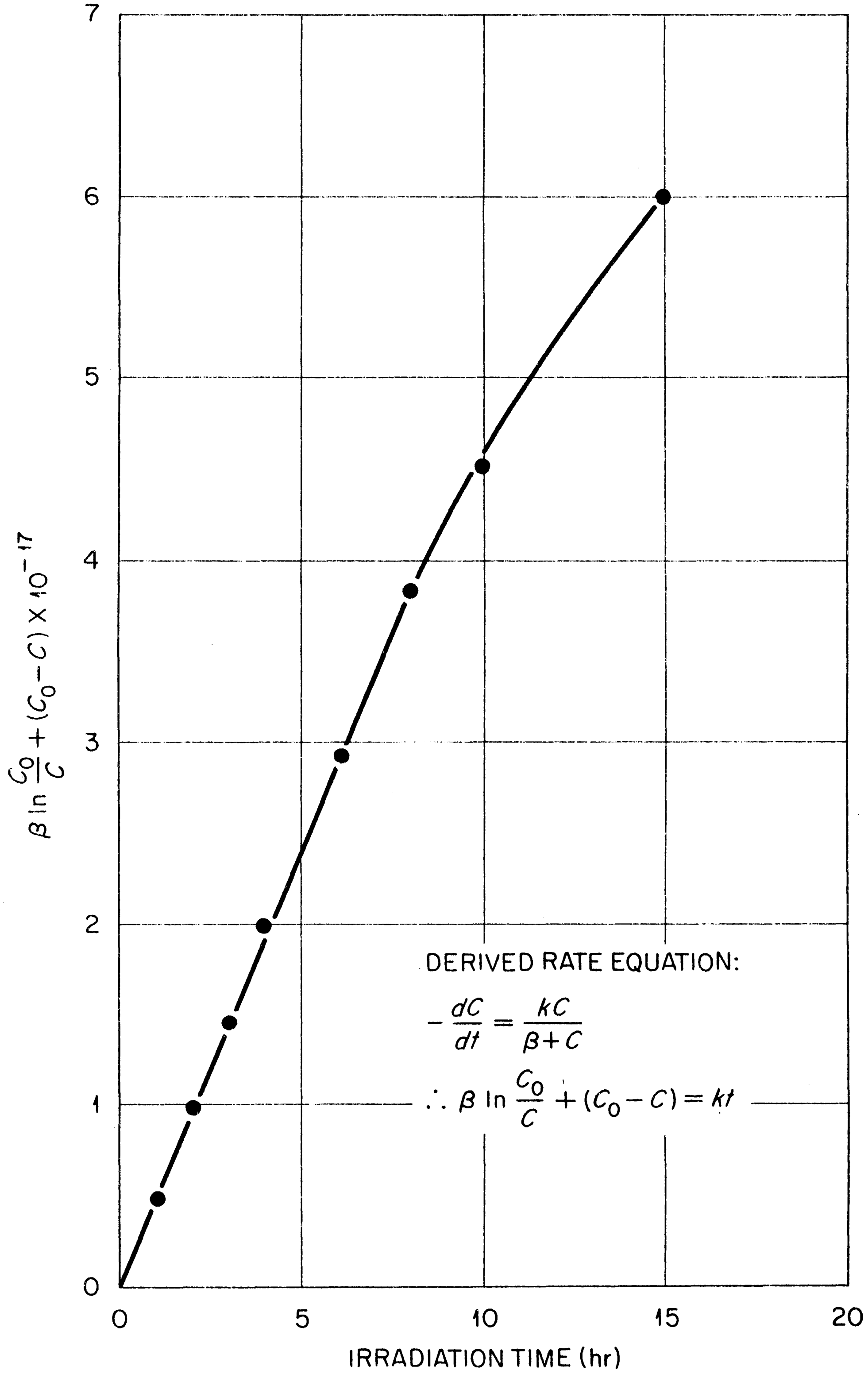

Fig. 22. Typical Plot of Derived Rate Function for Nitrate Radiolysis vs Irradiation Time.

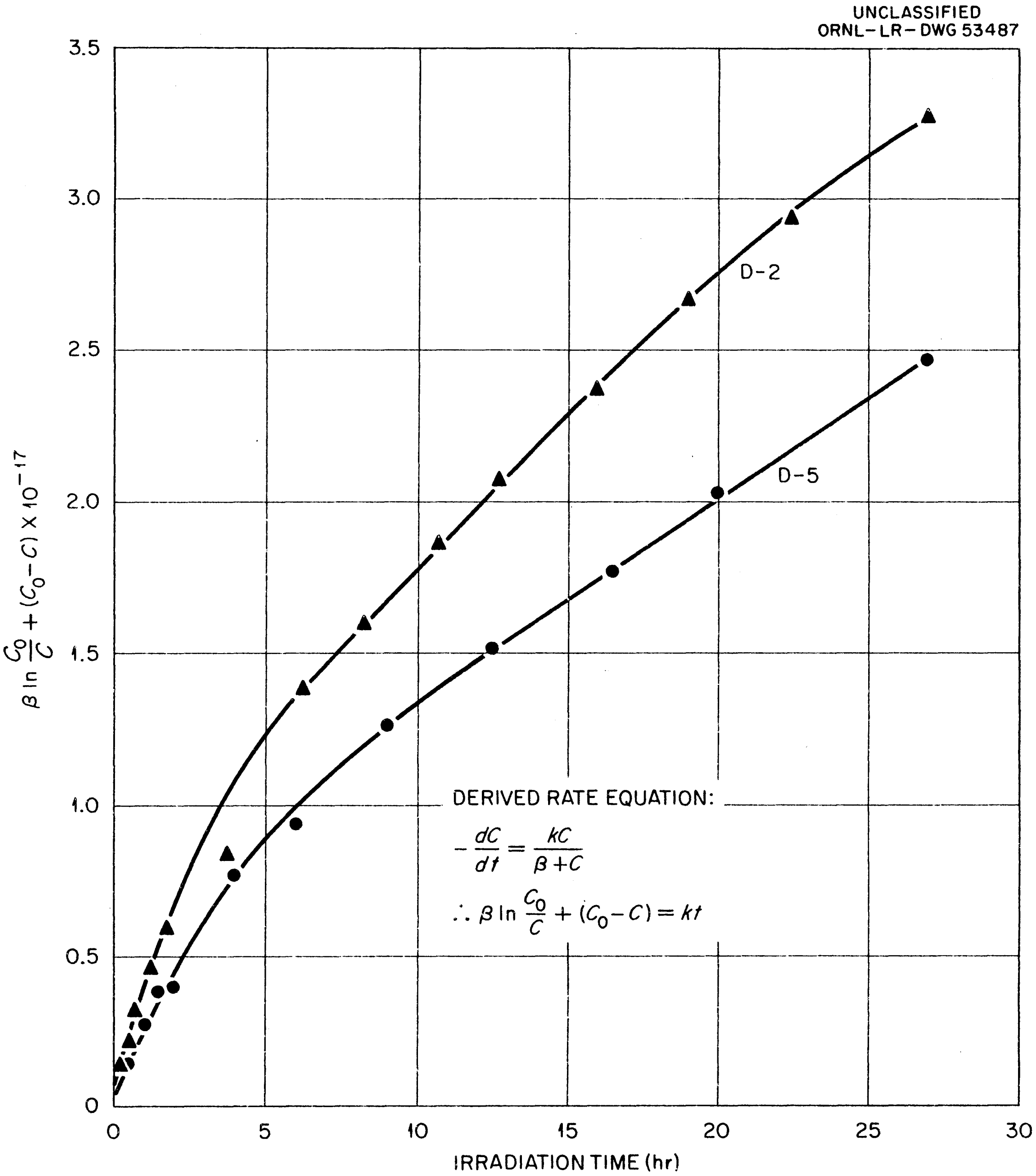

Fig. 23. Typical Plots of Derived Rate Function for Nitrite Radiolysis vs Irradiation Time.

TABLE XXXII

Values of Rate Constant, k, for Co^{60} Gamma Radiolysis of Nitrate and Nitrite Ions in KBr Pressed Disks at 25°C

NO_3^--Doped Disks $\beta = 4.4 \times 10^{17}$			NO_2^--Doped Disks $\beta = 1.37 \times 10^{17}$		
Series No	Co	k^a	Series No	Co	k^a
	ions $\times 10^{-17}$	$hr^{-1} \times 10^{-17}$		ions $\times 10^{-17}$	$hr^{-1} \times 10^{-17}$
F-3	0.20	1.16	D-9	0.26	0.21
F-4	0.40	1.26	D-8	0.29	0.24
F-5	0.80	0.73	D-7	0.39	0.30
F-6	1.0	0.61	D-6	0.81	0.20
14-2[b]	1.83	0.65	D-5	1.61	0.23
F-7	2.0	0.63	D-4	2.60	0.22
F-8	3.0	0.60	D-3	3.98	0.27
F-9	5.0	0.75	D-2	7.95	0.30
F-10	10.0	0.88			

[a] k taken as the slope of the plot of the derived rate function, $\left[\beta \ln \frac{Co}{C} + (Co - C)\right]$, versus irradiation time.

[b] Series 14-2 disks weighed 400mg; the other series all were 300mg disks.

Note: Dose rate = 3.25×10^{17} ev/gm-hr.

based on a constant rate of 15.6 ferrous ions oxidized to ferric ions per 100 electron volts absorbed in the ferrous dosimeter solution. The calibration of the source for water samples was as follows$^{(34)}$:

$$I = \frac{(\Delta O.D.)(E.C.)(N)}{(G_{Fe^{+3}})(\rho)(k)}$$

where:

I = source intensity, ev/gm-min

ΔO.D. = change in optical density of the ferrous dosimeter solution at 3050 Å per minute = 0.234 (from Table XIII, page 80)

E.C. = extinction coefficient = 453 μ mol/lit - ΔO.D.

N = Avogadro's number = 6.02×10^{23} ions/mol

$G_{Fe^{+3}}$ = rate of formation of ferric ions = 15.6 ions/100 ev

ρ = density of the dosimeter solution = 1.024 gm/ml

k = conversion factor = $(10^{3}$ ml/lit$)(10^{6}$ μ mol/mol$)$.

Therefore:

$$I = \frac{(0.234\ \Delta O.D./\text{min})(453\ \mu\ \text{mol/lit} - \Delta O.D.)(6.02 \times 10^{23}\ \text{ions/mol})}{(15.6\ Fe^{+3}/100\ \text{ev})(1.024\ \text{gm/ml})(10^{3}\ \text{ml/lit})(10^{6}\ \mu\ \text{mol/mol})}$$

$$I = 4.00 \times 10^{17}\ \text{ev/min-gm.}$$

<u>Calculation of Dose Rate for Potassium Bromide Samples</u>. The calculation of the dose rate of the cobalt-60 gamma source for

potassium bromide samples was based on the absolute mass absorption coefficients measured by Snyder and Powell(70a) for various substances under cobalt-60 gamma irradiation:

absolute mass absorption coefficient for KBr = $0.0238 \text{ cm}^2/\text{gm}$

absolute mass absorption coefficient for water = $0.0293 \text{ cm}^2/\text{gm}$.

Therefore:

$$I = (4.00 \times 10^{17}) \left(\frac{0.0238}{0.0293}\right)$$

$$I = 3.25 \times 10^{17} \text{ ev/min - gm KBr.}$$

The dose rate for the potassium bromide samples was therefore 3.25×10^{17} electron volts absorbed per minute of irradiation time per gram of potassium bromide in the disk.

IV. DISCUSSION

The following section contains a discussion of the work done in this investigation. The section includes a discussion of results, recommendations for future investigation, and the limitations imposed on this investigation.

Discussion of Results

The results obtained in this investigation are discussed in the following paragraphs.

Stability and Reproducibility of Disks Doped with Nitrate and Nitrite Ions. The optical density data presented on Table I, page 60, and Table III, page 62, show that the nitrate ion is stable and that the optical densities are constant when the disks are carefully made and stored. Disks can be made from the same powder to within ± 0.4 per cent in weight and to ± 1.0 per cent in optical density. In the course of this investigation it was found that nitrite ions in potassium bromide are also stable and that the optical densities of nitrite-doped disks are constant when the disks are carefully handled. The changes in nitrate ion and nitrite ion content for nitrate-doped disks under irradiation are shown by Table I, page 60, to be reproducible in duplicate disks.

Effects of Treatment on Nitrate-Doped Disks. The initial optical densities of water and nitrate shown on Table II, page 61, indicate that the amount of water present in a disk affects the optical density of the nitrate ion. When the disks were exposed to air of 30 per cent relative humidity they came to equilibrium with the air; some lost water and some gained water. The apparent optical densities of the nitrate ions increased on exposure of the disks to air for two days, and they continued to increase when the disks were dried in the vacuum oven. After the dried disks had been repressed they were stored over calcium chloride in a desiccator; neither the water optical density nor the nitrate optical density changed upon extended storage of the disks in this manner.

Cloudiness was observed in the disks after exposure to air of 30 per cent relative humidity, and the cloudiness was not removed by drying the disks in the vacuum oven. Tiny cracks were also observed in the dried disks. Since cloudiness of the disks was accompanied by an increase in the apparent optical density of the nitrate ions it was concluded that disks which appeared cloudy should not be used for the irradiation tests.

No explanation is presented for the increase of nitrate optical density from the adsorption of water or from drying. Both of these processes could possibly decrease the pressure in the disks, but to apply this possibility to the observed changes in nitrate optical density is beyond the scope of this investigation.

<u>Maximum Allowable Concentrations of Water</u>. Based on the data presented on Figure 2, page 66, and Figure 3, page 67, the maximum allowable optical density at 3440 wave numbers for water in potassium bromide disks doped with nitrate ions was set at 0.037. No difference

in allowable water optical density was detected between series A-15 (Figure 2, page 66) and series A-16 (Figure 3, page 67) although a disk of series A-15 contained four times as many nitrate ions as a disk of series A-16. Based on the data presented on Figure 4, page 68, the maximum allowable water optical density for disks doped with nitrite ions was set at 0.023.

Most of the disks of the D and F series which contained less than 0.1 mol per cent nitrate or nitrite showed water optical densities between 0.008 and 0.014, and all were below 0.020. Powders containing more than 0.1 mol per cent nitrate or nitrite produced disks with optical densities of water between 0.020 and 0.030 even after the concentrated powders had undergone the same treatment as the powders containing less than 0.1 mol per cent nitrate or nitrite. The concentrated disks were considered usable for determinations of the initial rate of decomposition of the nitrate or nitrite ions because, from Figures 2, 3, and 4, no effects of water content were evident until the irradiations had progressed for some time.

According to Figures 2, 3, and 4, pages 66, 67, and 68, respectively, the presence of water above a certain concentration increased the decomposition rate of nitrate and nitrite ions in potassium bromide. If, at the higher water concentrations, some of the nitrate or nitrite ions had one or more water molecules as nearest neighbors, then these ions would essentially be hydrated. Hydrated nitrates have been shown(3,33) to decompose more readily than the corresponding anhydrous nitrates. If this were also true for nitrites the hydration described above would be an explanation of the increase in decomposition rate for isolated nitrate and nitrite ions in potassium bromide with increased water content. No explanation is offered for the downward direction of the curves for nitrate ions (Figures 2 and 3, pages 66 and 67, respectively) as the water content continued to increase.

Results of Karl Fischer Analysis. From Table VII, page 69, it is clear that the water concentration in a disk with a water optical density of about 0.020 is very small because a water optical density of 0.285 corresponded to less than 0.5 milligrams of water per 400 milligram disk. If it is assumed that a water optical density of 0.300 corresponds to a water concentration of 0.5 milligrams per 400 milligram disk and that the optical density is linear with concentration (Beer's Law applies), then a water optical density of 0.020 corresponds to a water concentration of approximately 0.0015 mol per cent. This is lower than any concentration of nitrate or nitrite used in this investigation.

Effects of Air in the Disks. Disks pressed without prior evacuation were cloudy, probably because of air bubbles trapped between the crystals. When the die was evacuated for thirty seconds or longer before pressing, all of the disks came out clear. Because of the small free volume inside the die (about one cubic centimeter), it was assumed that three minutes of evacuation would remove enough air so that there would be essentially none present in the pressed disks. If the pump reached 0.1 millimeter of mercury, pressure, and all the air was retained in the disk the air concentration would be approximately 1 X 10^{-5} mol per cent, based on one cubic centimeter of free space in the die before pressing and none during pressing. This concentration is small compared to the molar concentrations of nitrate and nitrite ions in the disks.

Results of Mass Spectrometric Analysis. The components of the gas phase of irradiated and unirradiated samples of potassium nitrate in potassium bromide are listed, along with their volume per cents, on Table VIII, page 70. Oxygen is a major product(8,14,29) of the radiolysis of nitrate ions, and the amount of oxygen produced is a measure of the extent of the decomposition. The percentage of oxygen for the irradiated sample MS-1 was six times the percentage of oxygen for the unirradiated sample MS-2, and the pressure was much greater in sample MS-1. It is likely that much of the oxygen formed during irradiation reacted with organic impurities in the sample to form carbon dioxide and carbon monoxide. The organic impurities could have been introduced during drying of the samples in an oven evacuated with an oil-filled vacuum pump.

From the statements in the above paragraph it is concluded that a large fraction of the nitrate in sample MS-1 was decomposed by radiation. If the potassium bromide matrix entered into the decomposition compounds such as nitrosyl bromide and gaseous bromine would be two possible products. The absence of nitrosyl bromide, bromine gas, or any other volatile combination product of nitrogen and bromine in the gas phase of MS-1 (Table VIII, page 70) indicates that there was no chemical reaction with the matrix in the radiolysis of nitrate ions in potassium bromide.

The small amount of hydrogen bromide present in both MS-1 and MS-2 probably came from the reaction of moisture on the surface of the sample with potassium bromide.

Calibration in Per Cent Absorbance. The use of per cent absorbance, calculated as 100 less the per cent transmittance, as a measure of infrared absorption (Table XII, page 75, and Figure 7, page 78) gave very reproducible results when the base line was carefully set at the same point for each reading. Although the calibration curve was logarithmic instead of linear the precision of the per cent absorbance readings was within ± 1.0 per cent.

Effect of Disk Thickness. It is seen from Figure 9, page 82, that nitrate-doped potassium bromide disks of different thicknesses showed the same decomposition rate per unit weight. This means that the size and shape of the disks had no effect on the transfer of energy in the disks, and that transfer of energy to or from the steel race may be neglected. It follows from this analysis that the transfer of energy from the matrix to the ions which decomposed was not a radiative process since energy transfer by radiation depends on the size and shape of the sample(15).

Effects of Diluting the Doped Powders with Potassium Bromide. According to the data presented on Table XV, page 83, disks pressed from doped powders which had been diluted with potassium bromide to the same nitrate or nitrite content absorbed an amount of infrared radiation corresponding to the original nitrate or nitrite content divided by the dilution factor. Dilution of an irradiated disk too concentrated in nitrite for direct infrared analysis was therefore a valid method of determining the number of nitrite ions in the original disk by infrared analysis. The original doped powder was obviously well mixed with the fresh potassium bromide because the optical densities of the diluted disks were very close, as shown by Table XV, page 83.

Results from Varying the Volume of Solution Added in Making the Original Powder. Any deviation in decomposition rates between the disks containing nitrate or between disks containing nitrite, described on Table XV, page 83, was caused by varying the volume of solution added since there were no other variables. The possibility of a decomposition rate dependence on the volume of solution added was based on the following reasoning: the greater the volume of solution added, the more potassium bromide dissolved and the greater the chance for a nitrate or nitrite ion to be inside the potassium bromide lattice. It is evident from Table XVI, page 84, that the decomposition rates did not depend on the volume of solution added. It was concluded from this result that the solution and the potassium bromide quickly came to equilibrium, the nitrate or nitrite ions being distributed between the solid and liquid phases.

Purification of Potassium Nitrite. According to Table XVII, page 85, the most effective of the methods tried in obtaining pure potassium nitrite was the extraction of the nitrite with absolute methanol at dry ice temperature. From all indications this is a new and a very efficient method of separating potassium nitrite from potassium nitrate. The infrared method of analysis of the nitrate impurity in potassium nitrite requires special equipment for pressing the disks, but the method is extremely sensitive. As little as 0.05 mol per cent nitrate in nitrite can be measured with the potassium bromide pellets.

Agreement of Colorimetric and Infrared Methods of Analysis for Nitrite Concentration. In investigations(14,29) of the radiolysis of crystalline nitrates the amount of nitrite formed was measured by colorimetry. It is seen from Figure 11, page 90, and from Figure 12, page 93, that the agreement between the colorimetric and the infrared methods of analysis of nitrite concentration was excellent. Values from infrared quantitative analysis were actually more reproducible than those from colorimetry at lower concentrations of nitrite, and the infrared method was more useful in this investigation because the samples were not destroyed during analysis.

Results of Pressing Series D-17, D-18, and D-19. The disks of series D-17, D-18, and D-19 (Table XXII, page 95) were clear when taken from the press. However, after five or ten minutes in a desiccator, the disks became dotted with white spots. The disks of series D-17 showed only a few white spots near the center, but disks of the other two series appeared to be filled with white rosettes to such an extent that the surfaces were rough and slightly disrupted.

All of the disks of each series appeared identical to the eye, and series D-18 appeared slightly whiter than series D-19.

Dilution Method of Analysis. The opacity of the disks of series D-17, D-18, and D-19 did not affect their analysis because the irradiated disks were diluted with potassium bromide, and the disks pressed from the diluted material did not become white on standing. The greatest error in the dilution method of analysis should arise from the loss of irradiated material between weighing and mixing. This error would increase the apparent number of nitrite ions decomposed by radiation. Although this error was likely to occur because the disks sometimes shattered on being crushed, the dilution method was the most accurate method available for measuring small differences between relatively large amounts of nitrite.

Determination of "G_o". The initial rates of decomposition of irradiated substances, crystalline nitrates for example(8), are often used to express radiation effects because the system usually becomes extremely complicated after a short time. The determinations of "G_o" in this investigation, as typified by Figure 15, page 98, and Figure 17, page 104, were made by visually placing a straightedge tangent to the plot of ions decomposed versus dose at zero dose.

The values of "G_o" reported were the initial rates of decomposition of the specified ions expressed as ions decomposed per 100 electron volts of energy absorbed in the potassium bromide pellet.

Check Points for Series D-17. The extremely high value obtained for the initial decomposition rate of nitrite ions for series D-17 (see Figure 16, page 100) was checked with a duplicate series (Table XXII, page 95). Values of "G_o" for these series were 1.07 and 1.35, and the smaller was reported as correct (Table XXIV, page 99) because the errors in the dilution method of analysis would tend to raise the value of "G_o".

The validity of the high value of "G_o" for series D-17 was also checked in the following way. A chunk of disk D-19-5 was knocked out and pressed with 300 milligrams of D-4 powder. The whitish area of D-19 material was clearly visible in the center of the pressed disk, but the boundaries were not distinct. The D-19 area was wholly within the infrared beam during analysis. The apparent nitrite concentration of the disk was 3.96×10^{17} ions, and the value of "G_o" was expected to fall between the values of "G_o" for series D-4 and series D-19 of 0.51 and 0.36, respectively, from Table XXVI, page 103. The observed value of "G_o" of 0.84 for the combination disk showed that the presence of a few of the white spots in the center of a disk caused the value of "G_o" to be greatly increased and therefore validated a high value of "G_o" for series D-17.

Methods of Analysis for Disks of High Nitrate Content. The nitrite concentration in series F-11 (Table XXVI, page 103) was measured both by blanking out the nitrate peak and by reading the nitrite optical density off the shoulder of the nitrate peak. The agreement between the two methods was very good. For series F-12, F-13, and F-14 (Table XXVI, page 103) the only usable method of nitrite determination was colorimetry. The reason for this was that, for disks containing more than about 0.2 mol per cent nitrate, the nitrate ions absorbed essentially all of the incident infrared radiation and left none for the nitrite ions.

Determination of G_o'' for Nitrate Decomposition in Disks of High Nitrate Content. The values reported for the initial decomposition rates of nitrate ions in series F-11, F-12, F-13, and F-14 (Table XXVII, page 105) were based on the premise that the initial rate of decomposition of nitrate ions was equal to the initial rate of formation of the nitrite ions. This premise is shown to be correct by the curves on Figure 12, page 93, and Figure 13, page 94.

Designation of Nitrate and Nitrite Ions as Anion Acceptors. The nitrate or nitrite ions in the disks will henceforth be referred to as "anion acceptors" or as "acceptor ions". The term "activators", used to describe those impurities in luminescent systems which luminesce or promote luminescence$^{(17,38)}$, would be misleading in the present case; the potassium bromide matrix is assumed to be doing the activating.

Derivation of Dependence of G_o'' on Acceptor Concentration. The initial decomposition rates for the acceptor ions should be some function of the initial concentrations of the acceptors. If this function could be determined it should help to propose a mechanism for the transfer of energy to the anion acceptors. The following is the derivation of the theoretical dependence of initial decomposition rate on acceptor concentration.

It is first assumed that all of the acceptor ions occupy anion (bromide) sites in the potassium bromide lattice, that the acceptor ions are isolated from each other, and that each disk is homogeneous with respect to acceptor concentration. It is also assumed that all of the acceptor ions are equally subject to activation by transfer of energy from the matrix. The direct action of gamma rays on the acceptor ions is neglected because of the small electron fractions of the acceptor ions in all of the cases studied.

The observed rate of decomposition, "G", for the case of anion acceptors in a matrix and based on the total energy absorbed in the sample is expressed as:

$$G = \frac{n}{E_T} \qquad (1)$$

where:

G = measured initial rate of decomposition of the acceptor ions, ions/100 ev

n = number of ions decomposed

E_T = total energy absorbed in the sample, 100 ev.

All of the anion acceptors excited by energy transfer from the matrix may not decompose. If this possibility is taken into account, the rate of decomposition can also be expressed as:

$$G = fG_A \qquad (2)$$

where:

f = fraction of excited acceptor ions which decompose

G_A = rate of activation of acceptor ions, ions/100 ev.

It follows from Equation (2) that:

$$E_D = fE_A \qquad (3)$$

where:

E_D = energy used in decomposing acceptor ions, 100 ev

E_A = energy used in activating acceptor ions, 100 ev.

If α is defined as the energy in hundreds of electron volts required to decompose one acceptor ion, then:

$$E_D = \alpha n \qquad (4)$$

and, combining (3) and (4):

$$n = \frac{f}{\alpha} E_A. \qquad (5)$$

Therefore, combining (5) and (1) gives:

$$G = \frac{f}{\alpha} \frac{E_A}{E_T} = \frac{f}{\alpha} \phi \qquad (6)$$

where:

ϕ = fraction of total absorbed energy which is used to activate the acceptor ions.

Let:

C = number of acceptor sites in the sample

$\sum X_i$ = number of energy absorption sites other than acceptor sites in the sample

P_C = probability that an acceptor site will be activated

$\sum P_{X_i}$ = probability that an X site will be activated

A_C = energy absorbed per activated acceptor site, ev

$\sum A_{X_i}$ = energy absorbed per X site activated, ev.

The total energy absorbed in the sample, E_T, can therefore be expressed as:

$$E_T = \sum(A_{X_i} \; P_{X_i} \; X_i) + A_C \; P_C \; C \tag{7}$$

and the energy used to activate acceptor ions, E_A, can be expressed as:

$$E_A = A_C \; P_C \; C. \tag{8}$$

Therefore:

$$\phi = \frac{E_A}{E_T} = \frac{A_C \; P_C \; C}{\sum(A_{X_i} \; P_{X_i} \; X_i) + A_C \; P_C \; C} \tag{9}$$

or:

$$\phi = \frac{C}{\beta + C} \tag{10}$$

where:

$$\beta = \frac{\sum(A_{X_i} \; P_{X_i} \; X_i)}{A_C \; P_C}. \qquad (11)$$

Combining (6) and (10):

$$G = \frac{f}{\alpha} \frac{C}{\beta + C} \; . \qquad (12)$$

At zero dose, Equation (12) is expressed as:

$$G_o = k \frac{C_o}{\beta + C_o} \qquad (13)$$

where

G_o = initial decomposition rate for acceptor ions, ions/100 ev

C_o = initial concentration of acceptor ions, mol per cent

k = dimensional parameter depending on f and α, $(100 \text{ ev})^{-1}$.

Interpretation of the Derived Equation. Equation (13) above states that the initial decomposition rate of anion acceptors isolated in a crystalline matrix and subject only to energy transferred from the matrix should be proportional to the fraction of the absorbed energy which is transferred to the acceptors. The parameter "k" should depend mostly on the anion acceptor chosen, and the parameter β should depend on both the acceptor and the matrix.

The parameter β expresses the competition of energy traps with the acceptors for the available energy in the disk. These energy traps could include any lattice defects and strains present in the disk before irradiation. Energy traps formed in the disk during irradiation would cause β to change, but the number and types of traps present is assumed to be constant in unirradiated disks made of the same material under the same conditions.

Alternative Interpretation of the Derived Equation. Equation (13) above can also be expressed as:

$$G_o = G_\infty \phi \tag{14}$$

where:

G_o = initial decomposition rate of acceptors, ions/100 ev

G_∞ = decomposition rate at a hypothetical infinite acceptor concentration, ions/100 ev

ϕ = fraction of absorbed energy used to activate acceptor ions.

Form of the Derived Dependence of G_o on Acceptor Concentration. The Stern-Volmer type equation shown on page 18,

$$\frac{\eta_A}{\eta_A^{max}} = \frac{C}{k + C} \tag{15}$$

was proposed by Förster(19) to show the dependence of luminescence efficiency on activator concentration for the case in which spontaneous deactivation of activator sites results from the energy transfer. It follows from this that the efficiency of decomposition of anion acceptors which decompose as soon as energy is transferred to them should also follow a Stern-Volmer type relationship. Equation (13) on page 134, which is the theoretical dependence of the initial decomposition rate on acceptor concentration, is indeed a Stern-Volmer type equation.

Agreement of the Stern-Volmer Type Equation with Experimental Data for Luminescent Systems. Johnson and Williams(38) derived a Stern-Volmer type relationship between quantum efficiency of various phosphors and activator concentration. This equation, Equation (4), page 22, agreed closely with experimental data and was analogous to Equation (13), page 134, except that it contained a term, $(1 - C)^Z$, which took into account the observed concentration quenching in the luminescent systems.

Agreement of Stern-Volmer Type Equation with Experimental Data. Equation (13), page 134, was fitted to the data presented on Tables XXIV and XXVII, pages 99 and 105, respectively, by a trial and error process. The equation for the dependence of "G_o" on acceptor concentration (C_o) for nitrite acceptors in potassium bromide was:

$$G_o = 0.75 \frac{C_o}{0.009 + C_o} . \tag{16}$$

The equation for the dependence of "G_o" on acceptor concentration (C_o) for nitrate ion acceptors in potassium bromide was:

$$G_o = 1.86 \frac{C_o}{0.029 + C_o} . \tag{17}$$

From the excellent agreement of Equations (16) and (17) with experimental data, as shown on Figure 19, page 107, and Figure 20, page 108, respectively, it was concluded that Equations (16) and (17) described the initial decomposition of isolated nitrite and nitrate ions, respectively, in potassium bromide pressed disks for acceptor concentrations below 0.1 mol per cent.

Dependence of G_o on Acceptor Solubility: I. Potassium Nitrite-Doped Disks. It is obvious from Figure 16, page 100, that the values of initial decomposition rate obtained for series D-17, D-18, and D-19 (Table XXIV, page 99) do not fit the Stern-Volmer type Equation (16), page 136. The disks of these series became white on standing for a few minutes, and the cause of the whiteness was assumed to have been the cause of the poor agreement of the values of G_o with Equation (16) for the concentrated series.

Disks of series D-17, containing 0.105 mol per cent nitrite, showed a few white spots near the center. Since the solubility of potassium nitrite in potassium bromide was reported(43) to be approximately 0.1 mol per cent, it was concluded that the solubility limit of nitrite in potassium bromide had been exceeded in series D-17, D-18, and D-19, and that the white spots were voids and regions of nitrite lattice caused when the potassium nitrite came out of a supersaturated solid solution. If this were correct the solubility of potassium nitrite in potassium bromide would be about 0.1 mol per cent, which would agree with the published figure.

The scattering of light at 4000 Angstroms by disks of various nitrite contents is shown on Figure 21, page 110. The plot of optical density of the disks versus nitrite content shows a discontinuity at 0.1 mol per cent nitrite. Since the optical densities of disks with nitrite contents below 0.1 mol per cent were approximately the same, this was taken to be more evidence that the values of G_o for nitrite ion decomposition depended on the solubility of potassium nitrite in potassium bromide.

It follows from these results that the initial decomposition rate of nitrite ions in irradiated potassium bromide disks is a Stern-Volmer type function of the nitrite concentration, according to Equation (16), page 136, up to the solubility limit of potassium nitrite in potassium bromide.

Dependence of G_o on Acceptor Solubility: II. Potassium Nitrate. It is obvious from Figure 18, page 106, that the values of the initial decomposition rate for nitrate ions in disks of series F-12, F-13, and F-14 (Table XXVII, page 105) do not fit the Stern-Volmer type Equation (17), page 136. The dependence of "G_o" on acceptor concentration for nitrate ions should be analogous to that for nitrite ions, so the possibility of a solubility limit of potassium nitrate in potassium bromide was investigated.

The disks of series F-12, F-13, and F-14 did not become white on standing, but they did appear more opaque than the less concentrated disks. Based on the data presented on Figure 21, page 110, the optical densities at 4000 Angstroms for the nitrate-doped disks were constant until a nitrate concentration of 0.17 mol per cent had been reached. Since none of the disks containing nitrate became disrupted on standing the increase in optical density must have been due to regions of potassium nitrate lattice which did not go into the potassium bromide lattice. This analysis led to the conclusion that the solubility limit of potassium nitrate in potassium bromide was approximately 0.17 mol per cent nitrate.

It follows from this conclusion that the initial decomposition rate of nitrate ions in irradiated potassium bromide disks was a Stern-Volmer type function of the nitrate concentration according to Equation (17), page 136, up to the solubility limit of potassium nitrate in potassium bromide.

Relation of Sizes of Nitrite and Nitrate Ions to the Solubility Limits in Potassium Bromide. For solid solutions the size of the solute molecules is very important. A molecule of radius more than 15 per cent larger than the radius of the solvent will not go into solution to any great extent(71c). Assuming the ions to be closely packed cubes, the volumes of the nitrate ion and the nitrite ion calculated from the densities of the potassium salts are 26.4 and 44.0 cubic Angstroms, respectively. This difference in the relative sizes of the nitrate and nitrite ions accounts in part for the difference in their solubility limits in potassium bromide of 0.17 and 0.1 mol per cent, respectively. An interesting result of these calculations is that the ratio of the relative sizes of the nitrite ion to the nitrate ion was 1.67, which is very close to the value of 1.7 for the ratio of the solubilities of nitrate ion to nitrite ion.

Dependence of Nitrite Solubility on Pressure. When potassium nitrite in concentrations more than 0.1 mol per cent was pressed into potassium bromide at a pressure near 144,000 pounds per square inch the pressed material was optically clear. After five or ten minutes at atmospheric pressure the disks turned white, presumably from voids and nitrite crystallites formed when the nitrite came out of the solid solution. Based on the fact that potassium nitrite is so soft and compressible that crystals of it may be compressed with the fingers, two possible explanations for the pressure dependence of nitrite solubility in potassium bromide are:

(1). Under high pressure the small areas of nitrite lattice in the doped powder were smeared out in very thin layers over the surfaces of the small potassium bromide crystals in the disk. After the disk was removed from the die, the pressure inside slowly decreased. When the pressure had decreased to a certain extent, the thin layers of nitrite tended to reform regions of nitrite lattice. The formation of small regions of nitrite lattice caused separation of the potassium bromide crystals and produced cracks and voids in the disk.

(2). Under high pressure the potassium nitrite molecules were distorted to such an extent that more of them fitted into the potassium bromide lattice. When the pressure in the disk decreased the nitrite molecules which had been distorted reverted to their original size and came out of the potassium bromide lattice to cause voids and regions of nitrite lattice in the disk.

Evidence For and Against the Second Explanation. Evidence supporting the second explanation in the preceding paragraph includes the results of Weir, et al(71a), which showed that bond distances in compressible materials such as calcite ($CaCO_3$) can be distorted by pressures near 30,000 atmospheres, and the results of Parsons and Drickamer(55a), which showed that bond distances in transition metal complexes such as $[Ni(H_2O)_6]SO_4$ are altered by high pressures. This evidence notwithstanding, the first explanation above appears more reasonable at the pressures around 10,000 atmospheres used in this investigation because no splitting of the infrared absorption peaks of the nitrite ion due to altering the bond distances was ever noticed.

Dependence of Energy Transfer on Acceptor Solubility: I. Potassium Nitrite-Doped Disks. The shape of the plot of "G_o" versus nitrite concentration presented on Figure 16, page 100, can be explained by separating the plot into the following three regions:

Region I. Region I covers nitrite concentrations up to 0.1 mol per cent, the solubility limit of nitrite in potassium bromide. In Region I, "G_o" depended on nitrite concentration in a Stern-Volmer relationship featuring competition for the absorbed energy between the nitrite ions and energy traps in the disks.

Region II. Region II covers a short range of nitrite concentrations beginning at 0.1 and ending between 0.105 and 0.14 mol per cent nitrite. In Region II the presence of a small number of voids and cracks in the disks lessened the cage effect described on page 5 while energy transfer to the nitrite ions still in the disk remained efficient. The effect of the voids and cracks was to provide space for the products from the decomposition to move away from the decomposition site. This served to decrease the possibility of back reaction and caused the decomposition rate to increase.

Region III. Region III covers the remainder of the concentration range up to pure nitrite. In Region III disks, many nitrite crystallites, voids, and cracks are present. The presence of large numbers of regions of strain, which would be energy traps, served to decrease the fraction of the energy which went to the nitrite ions and therefore decreased the decomposition rate of the nitrite ions. Energy transfer to the nitrite crystallites was probably inefficient because the crystallites were surrounded by regions of strain.

<u>Dependence of Energy Transfer on Acceptor Solubility: II. Potassium Nitrate-Doped Disks</u>. Potassium nitrate did not form

supersaturated solid solutions in potassium bromide at high pressure, probably because potassium nitrate is not compressible. Under high pressure the potassium bromide probably flowed around the insoluble regions of nitrate lattice so that, in the pressed disks, there were no voids or cracks but only regions of strain around the areas of nitrate lattice when the nitrate concentration was above 0.17 mol per cent. From this analysis the shape of the curve on Figure 18, page 106, can be explained by separating the plot into two regions:

Region I. Region I covers the nitrate concentration range up to 0.17 mol per cent, the solubility of nitrate in potassium bromide. In Region I, "G_o" depended on nitrate concentration in a Stern-Volmer relationship featuring competition for the absorbed energy between the nitrate ions and energy traps in the disks.

Region II. Region II covers the nitrate concentration range from 0.17 mol per cent nitrate upwards. In Region II, the strains in the neighborhood of areas of nitrate lattice served as energy traps and competed with the original traps and the nitrate ions for the available energy. This added competition caused the value of "G_o" to decrease with an increase of the amount of nitrate lattice in the disks.

Dependence of "G_o" on Optical Density for Concentrated Samples. When the values of "G_o" (Table XXIV, page 99, for nitrite; Table XXVII, page 105, for nitrate) for series in which the solubility limits of the acceptor ions are exceeded are compared with the optical densities of these series at 4000 Angstroms (Table XXVIII, page 109), it is clearly seen that the value of "G_o" decreased as the optical density increased. This relationship held even when the optical density did not increase with increased concentration, as shown by series D-18 and D-19. These results indicate that the "quenching", or decrease in "G_o", observed as the concentration of acceptors increased past the solubility limit was not strictly a function of the acceptor concentration but depended to a large extent on the amount of strain and disruption in the potassium bromide lattice.

Absence of "Concentration Quenching". Because of the simple, Stern-Volmer type dependence of "G_o" on acceptor concentration in the solid solution regions of acceptor concentration, it can be concluded that there was no "concentration quenching" effect, whether by a radiative process(65) or by modification of thermal activation energies(38), observed at acceptor concentrations below the solubility limits in potassium bromide. From the preceding paragraph it is clear that the quenching observed at concentrations of acceptors above the solubility limits probably was caused by the action of acceptors on the matrix instead of interaction of acceptor ions. These results indicate that there was no effect of "concentration quenching" by interaction of acceptor ions over the concentration ranges studied.

Distance of Energy Transfer in Potassium Bromide Disks. By means of an experiment in which a pressed disk of potassium bromide containing nitrate ions was irradiated with alpha particles, Jones(40a) was able to show that energy transfer in the pressed disk under alpha irradiation did not take place over a distance of the order 0.1 millimeters. The alpha particles lost their energy in a thin layer of the disk, and no radiolysis of nitrate ions was observed from infrared analysis of the disk from which the bombarded layer had been scraped away. This indicated that the energy was transferred from the potassium bromide matrix to the acceptors and energy traps near the site of the primary absorption process.

Formation of Repulsive States. The absence of "concentration quenching" in the radiolysis of nitrate and nitrite ions isolated in potassium bromide indicates that the states to which the acceptors were excited by energy transfer were not affected by the closeness of another acceptor in a lower state. From this, it is proposed that the activated states of the acceptors which decomposed were "repulsive states", or that the only course an activated acceptor containing an amount of energy above a certain minimum could take was to decompose. This would mean that activated acceptors containing an amount of energy below the minimum required for a repulsive state would not be counted as a decomposition on analysis of the irradiated sample.

The proposal of the formation of repulsive states was also based on the assumption that any products of the decomposition of nitrate or nitrite ions, oxygen atoms for example, would be extremely reactive and that one of the products would have to be expelled from the decomposition site if the decomposition is to be counted.

Primary Processes in Absorption of Energy from Ionizing Radiation. Since direct action of the incident gamma rays and the primary electrons on the acceptor ions can be neglected because of the small electron fractions of acceptors at the concentrations studied, the basic competition for the absorbed energy was between transfer to acceptors, transfer to energy traps, and heating of the lattice. It is reasonable to assume that the thermal energy released to the lattice would not excite acceptor ions to repulsive states, and it is also reasonable that the nitrate and nitrite ions would not trap electrons and thus become excited. It is therefore proposed that the creation of repulsive states of the anion acceptors involved energy transfer by packets of excitation energy, called "excitons"(67), and recombination of free electrons and holes near the acceptor sites. Competition for the available energy between acceptor ions and energy traps would occur for both these processes.

Proposed Mechanism of Energy Transfer. From consideration of the distance of energy transfer to anion acceptors in potassium bromide disks, the formation of repulsive states of the acceptors, the primary processes in the absorption of energy from ionizing radiation, and the Stern-Volmer type dependence of "G_0" on acceptor concentration up to the solubility limits, the proposed mechanism for the energy transfer from the potassium bromide matrix to nitrate and nitrite acceptor ions is as follows:

1. The gamma ray caused primary ionization in the potassium bromide matrix.
2. Primary electrons excited the potassium bromide along tracks, forming excited bromide ions with energies ranging from the ground state to energetic electrons separated from the bromine atoms.
3. The free electrons and holes, along with the packets of excitation energy associated with the excited bromide ions, moved or were scattered randomly through the potassium bromide lattice. The electron-hole combination in either case can be pictured as moving from bromide ion to bromide ion by a resonance transfer of energy; from this picture it can be said that the excitons, or packets of excitation energy, are scattered by bromide ions as they move through the potassium bromide lattice.
4. The excitons moved through the lattice until they reached sites which could use all of their energy. These sites included the anion acceptors and energy traps such as vacancies or strains in the lattice.
5. The energy traps used the energy released from the excitons to anneal themselves; the acceptor ions used the energy released from the excitons to form repulsive states which decomposed.

Agreement of Proposed Mechanism with the Results of Kallmann and Dresner(41a). The electron-hole combinations, whether free or bound, were referred to in the preceding paragraph as excitons because they all served to transfer packets of excitation energy to the acceptors and energy traps. The possibility of trapping holes at anionic impurities cannot be ignored, and the recombination of these trapped holes with free electrons would release energy to the acceptors. This is in agreement with the results of Kallmann and Dresner which showed that both bimolecular recombination of electrons and holes and energy transfer from excited anions are necessary to explain high initial quantum efficiencies in the luminescence of crystalline phosphors such as zinc oxide under ionizing radiation. Such luminescence occurs at metallic ion sites at which free electrons can be trapped.

Critical Transfer Distance of Excitation Energy Transfer. Förster(19a) has defined a critical transfer distance, "R_o", for which excitation transfer and deactivation in fluorescent systems are of equal probability. The critical transfer distance corresponds to a critical acceptor concentration, "C_c", at which one acceptor ion on the average is contained in a sphere of radius "R_o". The critical transfer distance should be a standard measure of the distance that energy is transferred in the present system if the value of "C_c" is taken to be the concentration at which "G_o" is half the limiting value, "G_∞", at a hypothetical infinite acceptor concentration.

Calculation of "R_o" for Nitrate and Nitrite Ions in Potassium Bromide Disks. One-half of "G_∞" for nitrite ion acceptors is 0.375 [from Equation (16), page 136]; for nitrate ion acceptors, $G_\infty/2$ is 0.93 [from Equation (17), page 136]. From Figure 19, page 107, a value of G_o of 0.375 corresponds to an initial nitrite concentration of approximately 0.01 mol per cent; from Figure 20, page 108, a G_o of 0.93 corresponds to an initial nitrate concentration of approximately 0.03 mol per cent.

Since there are about 1.5 X 10^{21} molecules of potassium bromide per 300 milligram disk and the dimensions of a 300 milligram disk are 1.5 centimeters diameter by 0.062 centimeters thick, the volume per acceptor for nitrite ion acceptors, $V_{NO_2^-}$, is:

$$V_{NO_2^-} = \frac{0.062 \times \frac{\pi}{4} (1.5)^2}{(1 \times 10^{-4})\ (1.5 \times 10^{21})} = 7.5 \times 10^{-19} \text{cc} \qquad (18)$$

and the volume per acceptor for nitrate ion acceptors, $V_{NO_3^-}$, is:

$$V_{NO_3^-} = \frac{0.062 \times \frac{\pi}{4} (1.5)^2}{(3 \times 10^{-4})\ (1.5 \times 10^{21})} = 2.5 \times 10^{-19} \text{cc.} \qquad (19)$$

Since the critical transfer distance is the radius of the sphere surrounding one acceptor, on the average, then:

$$R_o = \left(\frac{3}{4\pi} V\right)^{1/3} \qquad (20)$$

where:

R_o = critical transfer distance, cm

V = volume of sphere surrounding one acceptor, cc.

Therefore, for nitrite ion acceptors:

$$R_o = \left(\frac{3}{4\pi} \times 7.5 \times 10^{-19}\right)^{1/3} = 5.5 \times 10^{-7} \text{ cm} \qquad (21)$$

and, for nitrate ion acceptors:

$$R_o = \left(\frac{3}{4\pi} \times 2.5 \times 10^{-19}\right)^{1/3} = 4.0 \times 10^{-7} \text{ cm.} \qquad (22)$$

Distance of Energy Transfer in Various Materials. The values of the critical transfer distance of nitrate and nitrite ions in potassium bromide disks of 40 and 55 Angstroms, respectively, agree closely with energy transfer distances in organic fluorescent materials, such as 20 Angstroms for transfer between amino acids and groups on the acids(19a), 20 Angstroms for a solid solution of terphenyl in polystyrene(21b), and up to 400 Angstroms for a solid solution of terphenyl in anthracene(21b). Although the transfer distances agree closely for these different systems and transfer by the exciton mechanism may be applicable to all of them, a critical comparison of the possible mechanisms of energy transfer in organic systems with those in inorganic systems is beyond the scope of this investigation.

Distance of Energy Transfer in Single Crystals of Alkali Halides. The critical transfer distances calculated for the nitrite and nitrate ions in polycrystalline disks of potassium bromide do not agree with estimated(67) values of from 10^3 to 10^4 Angstroms for the distance an exciton can travel in a single crystal of alkali halide. It has been reported(30) that color centers are much more numerous in polycrystalline pressed disks of an alkali halide than in a single crystal of the alkali halide, and that the color centers also are more rapidly bleached in the polycrystalline material. These results indicate that there would be increased competition for the energy of the excitons in polycrystalline disks, and that their lifetimes (and also the distance that they travel) would be less in the polycrystalline material. This could account in part for the difference between estimated energy transfer distances in single crystals of alkali halides and observed distances of energy transfer in the polycrystalline disks.

Comparison of "R_o" for Anion Acceptors with the Data of Johnson and Williams(38). If the limiting value of the relative quantum efficiency for the phosphors studied by Johnson and Williams is taken to be 120 per cent, the critical concentration corresponding to "R_o" would be the concentration at which the relative quantum efficiency was 60 per cent. For the phosphor ZnF_2:Mn, the critical concentration would be approximately 1.0 mol per cent, which would correspond to a value of the critical transfer distance of about 10 Angstroms. For the phosphor KCl:Tl, the critical concentration would be approximately 0.2 mol per cent, and "R_o" would be about 20 Angstroms. For the phosphor ZnS:Cu, the critical concentration would be approximately 0.003 mol per cent, and "R_o" would be about 85 Angstroms. From comparison of these values of "R_o" with the values of 55 and 40 Angstroms for nitrite and nitrate ions, respectively, in pressed disks of potassium bromide, it is clear that the energy is transferred in the potassium bromide disks over distances comparable to transfer in the phosphors.

Factors in the Decomposition of Isolated Nitrate Ions. Factors considered in proposing a mechanism for the decomposition of isolated nitrate ions in a pressed disk of potassium bromide were:

1. The disks became cloudy upon long irradiation, presumably from the collection of oxygen gas in visible pockets.
2. The initial decomposition rate of the nitrate ions was equal to the initial production rate of the nitrite ions, from Figure 12, page 93, and Figure 13, page 94. The curves representing the production of nitrite ions on Figures 12 and 13 bent downward because of decomposition of the nitrite ions formed.
3. It was proposed on page 145 that the excited states of the nitrate ions which decomposed were repulsive states.
4. There was neither nitrosyl bromide nor nitrogen dioxide present in the gas phase of irradiated samples of nitrate-doped potassium bromide powder (Table VIII, page 70).

5. There is evidence(21a, 71b) that an atom can move through a crystal lattice but that a molecule such as O_2 or NO diffuses very slowly through the lattice. This has been observed(30) in the case of polycrystalline disks of potassium chloride and potassium iodide exposed to chlorine and iodine gas, respectively.

Proposed Mechanism for the Decomposition of Isolated Nitrate Ions. The proposal of the mechanism for the decomposition of isolated nitrate ions in potassium bromide disks, based on the factors listed in the preceding paragraph, is as follows:

1. A repulsive state of the nitrate ion was formed from transfer of excitation energy from the matrix by:

$$NO_3^- \rightsquigarrow NO_3^{-*}. \tag{23}$$

2. The repulsive state decomposed into a nitrite ion and an oxygen atom by:

$$NO_3^{-*} = NO_2^- + O. \tag{24}$$

3. The oxygen atom was expelled from the decomposition site, and the excess energy of the repulsive state was released as thermal energy to the potassium bromide lattice.
4. The oxygen atom migrated to a grain boundary in the disk where it combined with another oxygen atom to form an oxygen molecule by:

$$O + O = O_2. \qquad (25)$$

5. Pockets of oxygen gas at the grain boundaries of the disk were enlarged by the energy released from the combination of the oxygen atoms.

<u>Extraction of Oxygen from Nitrate Ions by Oxygen Atoms</u>. The oxygen gas formed during the radiolysis of isolated nitrate ions collected in pockets large enough to be seen. This oxygen gas arose either from the combination of oxygen atoms by Equation (25) or from the following reaction:

$$NO_3^- + O = NO_2^- + O_2. \qquad (26)$$

For this method of formation of nitrite, by the extraction of oxygen from the nitrate ions, to be important the oxygen gas formed would have to diffuse through the potassium bromide lattice in order to form large pockets of gas. Since there is evidence(21a, 71b) against a measurable amount of diffusion of molecules through such a lattice, it is concluded that the mechanism proposed in the preceding paragraph was the major route of decomposition of isolated nitrate ions in potassium disks. However, nitrate ions located on or near grain boundaries may have decomposed according to Equation (26).

Comparison of G_∞ for Isolated Nitrate Ions with Decomposition Rates of Pure Potassium Nitrate. From comparison of Equation (13), page 134, with Equation (14), page 135, it is seen that the value of "k," or "G_∞," should approximate the decomposition rate of pure potassium nitrate or nitrite. From Equation (17), page 136, the value of "k" for isolated nitrate ions was found to be 1.86 ions per 100 electron volts absorbed, and this value compares well with the reported decomposition rates of potassium nitrate of 1.96, from Cunningham and Heal(7), and 1.6, from Hochanadel and Davis(33). Whether or not this agreement was merely fortuitous has not been established, but it follows from these results that the mechanism of decomposition of the pure nitrate may be similar to the mechanism for isolated nitrate ions.

Factors in the Decomposition of Isolated Nitrite Ions. Factors considered in the proposal of a mechanism for the decomposition of isolated nitrite ions in potassium bromide were:

1. No gas collected in visible pockets in disks irradiated for long periods of time.
2. From Table XXIII, page 96, nitrate ions were produced during the radiolysis of nitrite ions in potassium bromide. From comparison of the values for nitrite ions decomposed, on Table XXII, page 95, with the values for nitrate ions formed, on Table XXIII, page 96, it was estimated that one nitrate ion was formed for every five nitrite ions decomposed.

3. It was proposed, as in the case of the nitrate ions, that the excited states of the nitrite ions which decomposed were repulsive states.
4. It was assumed that atoms could move through the potassium bromide lattice but that molecules could not.
5. From Table XXIX, page 112, and Table XXX, page 113, no products of nitrite ion radiolysis except nitrate ions and potassium peroxide have been identified, and the existence of the peroxide in the disks has not been firmly established.

Postulated Mechanism for the Decomposition of Isolated Nitrite Ions. From consideration of the factors listed in the preceding paragraph, it is obvious that not all of the products of the nitrite ion radiolysis have been identified. Because of this it is not possible to postulate a complete mechanism for the decomposition of the nitrite ions. The postulated mechanism, although incomplete, is as follows:

1. The nitrite ion was excited to a repulsive state by the transfer of excitation energy from the matrix according to:

$$NO_2^- \rightsquigarrow NO_2^{-*}. \qquad (27)$$

2. Since nitrate ions were formed during the radiolysis of nitrite ions, oxygen atoms must have been present in the system, possibly from the reaction:

$$NO_2^{-*} = NO^- + O. \qquad (28)$$

According to Bellamy[3a] the infrared absorption peak for the fundamental stretching vibration of the nitrogen-oxygen bond occurs around 800 wave numbers. It is possible that the hypothetical compound KNO formed from Equation (28) was stable in the potassium bromide matrix and was the product which absorbed around 800 wave numbers as shown on Table XXIX, page 112.

3. The oxygen atom formed from Equation (28) migrated through the lattice until it was scavenged by a nitrite ion by:

$$NO_2^- + O = NO_3^-. \qquad (29)$$

This would account for the formation of nitrate ions during the irradiation.

4. Since the irradiated disks were clear upon prolonged irradiation it may be assumed that all of the oxygen produced was scavenged by nitrite ions to form nitrate ions. It was observed that one nitrate ion was formed for about five nitrite ions decomposed. If all the oxygen atoms were scavenged by nitrite ions, Equations (28) and (29) account for only two-fifths of the number of nitrite ions decomposed. There must therefore have been at least one other method

of decomposition of nitrite ions involved in the overall reaction.

5. One other method of nitrite ion decomposition should account for the suspected presence of peroxide in the samples, from Table XXIX, page 112. Perhaps this method of decomposition was:

$$NO_2^{-*} = NO + O^{-}. \tag{30}$$

The singly charged oxygen ion formed in Equation (30) could have been, or could have moved, close enough to another decomposition site for the peroxide bond to have been formed. The nitric oxide would have to be stable and immovable in the potassium bromide matrix, and its infrared absorption peak may have been too weak to show up on the spectrum of an irradiated sample (Table XXX, page 113).

Dependence of the Rate Equation on Products and Energy Traps Caused by Irradiation. According to Equation (12), page 134, the decomposition of nitrate and nitrite ions in potassium bromide should follow the following rate equation:

$$-\frac{dC}{dt} = \frac{kC}{\beta + C} \tag{31}$$

This equation expresses the competition for energy between acceptors and energy traps already present in the disk. The parameter,

β, which depends on the number of energy traps in the sample, may be expected to change as the number of vacancies, color centers, and other defects caused by ionizing radiation changes with dose. If the value of β increases with dose (or irradiation time), then the decomposition rate may be expected to decrease from the value predicted by Equation (31). Similarly, any buildup of products of the decomposition which compete for the available energy would also serve to decrease the decomposition rate.

Derivation of Rate Expression for Small Total Doses. If the study of the decomposition of the acceptors is limited to such short irradiation times that both radiation effects on the matrix and the amount of products formed are negligible, Equation (31) may be integrated as follows:

$$\frac{\beta + C}{C}\, dC = -\, k\, dt \tag{32}$$

or:

$$\frac{\beta}{C}\, dC + dC = -k\, dt. \tag{33}$$

Integrating between t = 0 and t = t:

$$\beta \left[\ln C\right]_{C_o}^{C} + \left[C\right]_{C_o}^{C} = -k \left[t\right]_{0}^{t} \tag{34}$$

or:

$$\beta \ln \frac{C_o}{C} + (C_o - C) = kt. \tag{35}$$

It is seen from Equation (35) that a plot of the derived rate expression, $\left[\beta \ln \frac{C_o}{C} + (C_o - C)\right]$, versus time should produce a straight line at low values of irradiation time.

Plots of Derived Rate Expression Versus Time. Typical plots of the derived rate expression versus time are shown on Figure 22, page 115, for nitrate-doped disks, and on Figure 23, page 116, for nitrite-doped disks. It is obvious from these figures that the plots initially follow a straight line, but all the plots for the nitrite-doped series and most of the plots for the nitrate-doped series showed a positive intercept on the ordinate.

Agreement of Rate Constants. The values of the rate constant, "k," for various series of disks doped with nitrite or nitrate ions, presented on Table XXXII, page 117, agree very well with each other, except for the two series of lowest nitrate content. This agreement shows that the effects of radiation on the matrix and the effects of products were not important at small total doses, and this validates the use of the initial decomposition rate to describe the decompositions of isolated nitrite and nitrate ions in potassium bromide disks by gamma irradiation for all the series except F-3 and F-4.

Agreement of Rate Constants with "G_∞". The value of "G_∞", from Equation (14), page 135, expresses the theoretical value of the rate constant, k, at zero dose. For nitrate-doped series, "G_∞" was found to be 1.1 X 10^{17} $(\text{hour})^{-1}$, and for nitrite-doped series, "G_∞" was found to be 0.44 X 10^{17} $(\text{hour})^{-1}$. The deviation of the calculated values of the rate constant, "k," shown on Table XXXII, page 117, from the values of "G_∞" was almost certainly due to the presence of the positive intercepts on the plots of the derived rate expression versus irradiation time (Figure 23, page 116, for example). These positive intercepts could have been caused by the presence of an impurity or by acceptor ions which were extremely sensitive to small amounts of irradiation.

Dosimetry with Doped Disks. Since the energy which decomposed the nitrate or nitrite acceptor ions was transferred from the matrix and was not due to direct action of radiation on the acceptors, there should be no dependence of decomposition rate on source intensity. Irradiation of the doped disks could therefore serve as a method of dosimetry. Nitrate- or nitrite-doped potassium bromide disks would be a dosimeter which would fit into a very small space and which could be analyzed long after irradiation. The disks could be used in a completely enclosed system or in a moving system.

The data on Table XXII, page 95, could serve as calibrations for dosimeter disks containing the concentrations of nitrite acceptors listed. Disks containing 0.052 or 0.026 mol per cent nitrite probably would give the most reproducible results because the peak heights for disks in this range of concentrations can be read accurately and the decomposition rates are comparatively large.

Recommendations

The following recommendations for future investigation were made from observations arising from the study of energy transfer to anion acceptors in pressed disks of potassium bromide.

Effects of Water on Nitrate and Nitrite Ion Decompositions. It is recommended that the causes of the dependence of the decomposition rates of isolated nitrate and nitrite ions on water concentration be determined. These causes should help to determine the mechanisms of decomposition of the isolated nitrate and nitrite ions.

Effects of Water on the Nitrate Ion Optical Density. It is recommended that the enhancement of nitrate ion optical density by the presence of water and by drying be investigated in order to determine the causes of the enhancement and to more clearly define the positions of the anion acceptors in the matrix.

Nitrite Purification. It is recommended that possible uses of nitrate-free potassium nitrite be determined and that the feasibility of an industrial process for the purification of potassium nitrite by extraction by methanol at dry ice temperature be investigated.

Infrared Quantitative Analysis. Investigation is recommended of possible applications of the alkali halide pressed disk method to quantitative analysis of impurities in solid, inorganic materials which are difficult to analyze by chemical methods. Potassium nitrite containing a small nitrate impurity is a typical example of such a material.

Energy Transfer in Different Matrices. It is recommended that the transfer of energy to anion acceptors in different matrices be studied in order to more clearly define mechanisms of energy transfer and to determine any effects of varying the "free space" in the matrix. Almost all of the alkali halides could be used for disks which could be analyzed by infrared methods. Possible matrices could also include single crystals of alkali halide containing nitrite ions.

Value of "G_∞" for Pure Materials. It is recommended that values of "G_∞" be determined for other nitrates and for other anion acceptors to ascertain the value of "G_∞" as a measure of the decomposition rate of the pure material under irradiation.

Products of Nitrite Ion Decomposition. It is recommended that the products of the decomposition of isolated nitrite ions be determined. This determination should serve to clarify the mechanism of decomposition of the nitrite ions and the mechanism of energy transfer from the matrix to the nitrite ions.

Dosimetry with Doped Disks. It is recommended that the use of potassium bromide disks doped with nitrite or nitrate ions in radiation dosimetry be investigated. This type of dosimeter should be useful in closed systems, moving systems, or where there is limited space.

Limitations

The limitations of the investigation of energy transfer to anion acceptors in pressed disks of alkali halide are given in the following paragraphs.

Acceptors and Matrix. The anion acceptors used were nitrate and nitrite ions, and the matrix used was potassium bromide.

Temperature. The temperature of the irradiations and of the analyses of the samples was 25 ± 2 degrees, Centigrade.

Humidity. The relative humidity of the dry room wherein the samples were prepared was kept below 40 per cent.

Cobalt-60 Gamma Source. The intensity of the cobalt-60 gamma source was 3.25×10^{17} electron volts absorbed per minute of irradiation time per gram of potassium bromide. The intensity of the source was measured in the region of constant intensity by means of the ferrous dosimeter.

Pressure during Pressing. The disks were pressed under 40,000 pounds, which would correspond to 143,000 pounds per square inch if all the weight was borne by the sample.

Measurement of Optical Density. The infrared quantitative analyses were made on the Perkin-Elmer Model 21 or Model 221 spectrophotometer. The optical densities were measured from a base line standard using the 927 slit program and a sodium chloride prism.

Nitrate and Nitrite Concentrations. Concentrations of nitrate in the nitrate-doped disks ranged from 0.000326 to 1.044 mol per cent.

Concentrations of nitrite in the nitrite-doped disks ranged from 0.0018 to 0.280 mol per cent.

Disk Size. Pressed disks were made weighing 300, 400, or 500 milligrams. The diameter of the disks was 1.5 centimeters; the thickness of the disks corresponded to 0.205 centimeters per gram of disk material.

V. CONCLUSIONS

The investigation of energy transfer in the gamma radiolysis of anion acceptors in potassium bromide disks led to the following conclusions:

1. From powdered potassium bromide doped with potassium nitrate or nitrite, pressed disks can be made for which the optical densities of the doped material agree within ± 1.0 per cent even after long storage in a desiccator or after irradiation.

2. The maximum allowable optical density of water at 3440 wave numbers was 0.027 for nitrate-doped potassium bromide disks and 0.023 for nitrite-doped disks. Water concentrations above those corresponding to these limits affected the decomposition rate of the nitrate or nitrite ions under gamma irradiation.

3. Extraction with absolute methanol at dry ice temperature is a very efficient method of obtaining potassium nitrite which is essentially free of nitrate.

4. The solubility of potassium nitrite in potassium bromide is approximately 0.1 mol per cent, as is reported in the literature.

5. The solubility of potassium nitrate in potassium bromide is approximately 0.17 mol per cent.

6. The initial decomposition rate, "G_o", of nitrate and nitrite ions in the disks showed a Stern-Volmer type dependence on initial acceptor concentration, "C_o", up to the solubility limits of the

acceptor ions in potassium bromide. The Stern-Volmer type relationship for nitrite acceptors was:

$$G_o = 0.75 \frac{C_o}{0.009 + C_o}$$

and, for nitrate acceptors:

$$G_o = 1.86 \frac{C_o}{0.029 + C_o} .$$

7. The energy transfer mechanism involved competition between acceptors and energy traps for electronic excitation energy which migrated through the potassium bromide lattice.

8. The critical transfer distance for nitrite acceptors in potassium bromide disks was 55 Angstroms; for nitrate acceptors, the critical transfer distance was 40 Angstroms.

9. The major route of decomposition of the excited nitrate ions was by:

$$NO_3^{-*} = NO_2^- + O.$$

The oxygen atoms formed diffused to grain boundaries and combined to form pockets of gaseous oxygen.

10. The decomposition of the excited nitrite ions involved more than one mode of decomposition. One possible mechanism was:

$$NO_2^{-*} = NO^- + O.$$

The oxygen atoms formed were scavenged by nitrite ions by:

$$NO_2^- + O = NO_3^-.$$

This mechanism could account for about 40 per cent of the nitrite ions which decomposed.

11. For small total doses, the decomposition of nitrite or nitrate ions in potassium bromide disks follow the relationship:

$$\beta \ln \frac{C_o}{C} + (C_o - C) = kt$$

where:

β = parameter dependent on the matrix and the acceptors
C_o = initial concentration of acceptors, ions per disk
C = concentration of acceptors, ions per disk
k = rate constant, $(hr)^{-1}$
t = irradiation time, hr.

This relationship was predicted by the Stern-Volmer dependence of the initial decomposition rate on acceptor concentration.

VI. SUMMARY

The gamma radiolysis of nitrate or nitrite acceptor ions in a potassium bromide matrix was studied by means of the alkali halide pressed disk technique of infrared sampling. Standards for the samples were set so that disks could be duplicated and so that neither air nor water in the disks would affect the decomposition of the nitrate or nitrite ions.

The theoretical dependence of the initial decomposition rate of the acceptors on acceptor concentration was shown to be a Stern-Volmer type function, based on a competition for the available energy between acceptor ions and energy traps such as defects and strains in the potassium bromide lattice. The dependence of the initial decomposition rate on acceptor concentration was found to agree with the theoretical relationship up to the solubility limits of the acceptor ions in potassium bromide, which were 0.1 mol per cent for nitrite ions and 0.17 mol per cent for nitrate ions.

The proposed mechanism of energy transfer from the potassium bromide matrix to the acceptor ions involved migration transfer of electronic excitation energy through the potassium bromide lattice until it reached an acceptor or an energy trap. The proposed excited states of the acceptors were repulsive states. The critical transfer distances, which can be interpreted as the mean distances of energy transfer, were found to be 40 Angstroms for nitrate-doped samples and 55 Angstroms for nitrite-doped samples. These distances were shown to be comparable to values of critical transfer distances in organic and inorganic phosphors.

The major route of decomposition of the excited nitrate ions was shown to be the splitting off of an oxygen atom to form a nitrite ion, the oxygen atom migrating to a grain boundary and combining with another oxygen atom to form oxygen gas.

A complete mechanism for the decomposition of the excited nitrite ions was not proposed, but one route of decomposition appeared to be the splitting off of an oxygen atom to form a hyponitrite ion, the oxygen atom being scavenged by another nitrite ion to form a nitrate ion.

The decomposition of the nitrate or nitrite ions was found to follow the Stern-Volmer type rate equation for values of total dose small enough so that effects of energy traps formed by irradiation and products of the decomposition were negligible.

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ABSTRACT

"Energy Transfer in the Gamma Radiolysis of Isolated Nitrate and Nitrite Ions"

by Robert L. Durfee

Pressed pellets of infrared quality potassium bromide doped with from about 0.002 to about 1.0 mol per cent nitrate or nitrite ions were irradiated at 25 degrees, Centigrade, with cobalt-60 gamma rays at a dose rate of 3.25×10^{17} electron volts per minute per gram of sample. The samples were prepared by pressing powdered potassium bromide, to which had been added reagent grade potassium nitrate or purified potassium nitrite in water solution with subsequent drying in a vacuum oven, into a 15-millimeter diameter disk at 40,000 pounds in an evacuated die. Purified potassium nitrite containing 0.08 mol per cent nitrate was obtained by extraction of the nitrite from reagent grade material with absolute methanol cooled to dry ice temperature, the cycle being repeated five times.

The analysis of the irradiated samples, except those extremely concentrated in nitrate, was by infrared quantitative analysis, on the Perkin-Elmer Model 21 or Model 221 infrared spectrophotometer, using peak heights at 1391 wave numbers for nitrate and at 1276 wave numbers for nitrite measured from a base line standard. Irradiated samples too concentrated in nitrate for infrared analysis

were analyzed for nitrite using the sulfanilic acid method of colorimetry for aqueous solutions of the disks.

The dependence of the initial decomposition rate of the isolated nitrate or nitrite ions on acceptor concentration was found to follow a theoretical Stern-Volmer type function which was based on competition for available energy between acceptors and energy traps such as defects or strains in the lattice. The dependence of "G_o" on "C_o" for nitrite ions was:

$$G_o = 0.75 \frac{C_o}{0.009 + C_o}$$

and, for nitrate ions:

$$G_o = 1.86 \frac{C_o}{0.029 + C_o}$$

where:

C_o = initial acceptor concentration, mol per cent

G_o = initial decomposition rate, ions decomposed per 100 electron volts absorbed in the disk.

These equations were followed only up to the solubility limits of the acceptor ions in potassium bromide, which were determined by the measurement of 4000 Angstrom light scattered by disks of various concentrations to be 0.1 mol per cent for nitrite and 0.17 mol per cent for nitrate. Values of "G_o" above the solubility limits appeared to depend on the amount of strain and disruption caused by regions of nitrate or nitrite lattice in the disk, and they were generally lower than values predicted by the above equations.

No "concentration quenching" by alteration of the thermal activation energies was evident for the concentrations studied. This led to the proposal of the decomposition of repulsive states of the acceptor ions.

The proposed mechanism of energy transfer from the potassium bromide matrix to the acceptors involved migration transfer of electronic excitation energy through the lattice until it reached an acceptor or an energy trap. The acceptor then absorbed the energy, forming a repulsive state which decomposed; or the energy trap used the energy to relax the lattice or to anneal itself.

The values of "R_o", the mean (or critical) transfer distance, were 40 Angstroms for nitrate-doped disks and 55 Angstroms for nitrite-doped disks. The values of "R_o" corresponded to the radius of the sphere containing one acceptor, on the average, at the acceptor concentration at which the probability for decomposition was equal to the probability of loss of the energy to a trap. The values of "R_o" for the anion acceptors were found to be comparable to mean transfer distances in organic and inorganic phosphors.

The major route of decomposition of the excited nitrate ions was shown to be the splitting off of an oxygen atom to form a nitrite ion, the oxygen atom migrating to a grain boundary and combining with another oxygen atom to form oxygen gas.

A complete mechanism for the decomposition of the excited nitrite ions was not proposed, but one route of decomposition appeared to be the splitting off of an oxygen atom to form a hyponitrite ion, the oxygen atom being scavenged by another nitrite ion to form a nitrate ion.

The decomposition of the nitrate or nitrite ions was shown to follow the predicted Stern-Volmer rate equation for values of total dose small enough so that the effects of energy traps formed by irradiation and products of the decomposition were negligible.