EFFECTS OF GAMMA RADIATION ON AQUEOUS SOLUTIONS OF MOLYBDENUM (V) AND (VI)

by

FRANCIS JAMES LIBERATORI

B. S. (Chemistry), St. Josephs College, 1956

B. S. (Nuclear Engineering), Kansas
State University, 1964

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Department of Nuclear Engineering

KANSAS STATE UNIVERSITY
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Approved by:

Richard E. Faw
Major Professor

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Å	Angstrom unit (= 10^{-8} cm).
C_i	Initial solute concentration.
C_f	Final solute concentration.
ΔC	Solute concentration change due to both irradiation and auto-oxidation effects.
$\overline{\Delta C}_{ao}$	Solute concentration change due to auto-oxidation only.
$\overline{\Delta C}$	Solute concentration change due to irradiation of solution only.
D_A	Absorbed dose in air, rads.
D_M	Absorbed dose in material, rads.
D_v	Absorbed dose in solution, eV/ml.
eV	Electron volt.
G	G-value of a product, molecules per hundred eV.
M	Molarity, moles per liter.
N	Normality, equivalents per liter.
N_o	Avogadro's number.
R_A	Exposure dose in air, roentgens.
t_{ao}	Auto-oxidation time, hours.
V_i	Initial volume, ml.
V_f	Final volume, ml.
ΔV	$V_i - V_f$, ml.
w_i	Weight fraction of the i^{th} component of a mixture.
[X]	Concentration of material X, moles/liter.
Y	Yield of a specie, molecules/gram.
$(\overline{Z/A})$	Mean value of the ratio of atomic number to atomic weight for a medium containing more than one element.
ρ	Density, grams/ml.
σ_i^2	Variance of the i^{th} quantity.

σ_i	Standard deviation or uncertainty of the i^{th} quantity.
${}_e\sigma_a$	Compton electronic energy absorption coefficient, cm^2/electron.
(σ_a/ρ)	Compton mass energy coefficient, cm^2/gram.
$(\mu_a/\rho)_i$	Total mass energy coefficient for the i^{th} quantity, cm^2/gram.

1.0 INTRODUCTION

Much research effort has been expended in the past ten years upon elucidating the chemical effects of the absorption of ionizing radiation by various aqueous solutions. Spinks and Woods (82) and Allen (5) have published excellent treatises covering various aspects of the radiation chemistry of aqueous solutions. Many articles in media such as Annual Review of Physical Chemistry (8,27,77), Progress in Reaction Kinetics (17,26), Advances in Chemistry (1,2), and Physics in Medicine and Biology (14), to mention only a few, serve as excellent comprehensive reviews of world literature concerning current research work in this field. An excellent review of the history of the radiation chemistry of aqueous solutions is given by Hart (37).

This thesis reports a study of the cobalt-60 gamma radiation effects on the molybdenum (V)-molybdenum (VI) aqueous system. Specifically, the aqueous molybdenum system was investigated for its possible use as a chemical dosimeter, whereby the impingent radiation dose on the molybdenum solution could be determined by quantitative measurement of the chemical change produced in the system. Although a comprehensive knowledge of radiation chemistry is unnecessary for its practical use, an understanding of basic principles is helpful in applying this method of dosimetry. Books by Hine and Brownell (41), Attix (31) and Spinks and Woods (82) thoroughly cover the chemical dosimetry method. Reference (11) contains an excellent review of the literature from 1953 to 1965.

In the area of aqueous solutions of inorganic compounds, many systems have been found to undergo oxidation or reduction reactions when exposed to ionizing radiation. The classic system studied was the oxidation of iron (II) to iron (III) (in 0.8 N H_2SO_4) by X rays (30). For absorbed doses less than 50,000 rads*, this is the system most prevalently used in chemical dosimetry. Gamma rays reduce cerium (IV) to cerium(III) in 0.8 N H_2SO_4 (35). This is the basis of a chemical dosimeter widely used for measuring absorbed doses from 10^4 to 10^8 rads (87). Gold and silver salts are reduced to the metals by X rays in the presence of molecular hydrogen in solution (83). Mercury (III), from soluble mercuric chloride, is precipitated as mercurous chloride from solutions exposed to X rays (84). Permanganate ion is reduced to a mixture of manganese (II) and the insoluble MnO_2 by gamma rays (79). Arsenic (III) is oxidized to arsenic (V) (20); tellurium (IV) is oxidized to tellurium (VI) (34); tin (II) is oxidized to tin (IV) (15,39); and chromium (VI) is reduced to chromium (III) (7,23). These are but a few of the many aqueous systems of inorganic solutes which have been studied.

It has been found that several parameters affect the amount of oxidation or reduction which occurs when an aqueous inorganic system is subjected to ionizing radiation. Some of these parameters are the total absorbed dose, the dose rate, the concentration of other electrolytes present, concentration of the primary inorganic species undergoing oxidation or reduction, the pH of the solution, the type and intensity of the radiation, and the presence of dissolved gases in the solution. The most practical chemical dosimeter is one having a constant G-value over a broad range of these parameters since the dosimeter would have a linear dose response in this region. Also, spectrophotometric analysis of the dosimeter solutions should be possible in order to avoid the more cumbersome titrimetric method of analysis.

Two important theoretical models which have been developed to explain the observed chemical changes occurring when aqueous solutions are irradiated

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*One rad corresponds to the absorption of 100 ergs of energy per gram.

are the Samuel-Magee model (71), and the Lea-Gray-Platzman model (33,54,67). These models will be discussed in a subsequent section of this report.

Radiation chemistry is very much similar to photochemistry in many respects. The chief difference lies in the energy of the radiation initiating the reaction, the energy of the particles and photons in radiation chemistry being very much greater than that of the photons causing photochemical reactions. In photochemistry, each photon excites only one molecule and these excited species are distributed essentially uniformly in the photon beam. In radiation chemistry, each photon (via secondary electrons) or particle produces a variety of excited species, for example, electronically excited molecules, and ions in their ground or electronically excited states. Since the absorption phenomenon is a highly localized one, these species have a highly inhomogeneous spatial distribution. They are energetically unstable and undergo a sequence of transformations. The first set of transformations produces stable molecules, some of which differ from those initially present, and chemically unstable species, such as free radicals (atoms or molecules having one or more unpaired electrons available for the formation of chemical bonds). The next set of transformations consists of chemical reactions and diffusion involving the reactive species and produces, in the end, chemical equilibrium. In attempts to explain these transformations, the models mentioned in the previous paragraph involve the simultaneous chemical reaction and diffusion of all species taking active part in the reactions. Also, physical approximations concerning the amount, energies, and positions of the ions and electrons produced by the radiation are made.

2.0 OBJECT OF THE EXPERIMENT

The objective of this investigation was to study the effect of gamma rays on the aqueous molybdenum (V)-molybdenum (VI) system. A previous study of this type, using X rays, had been made in 1962 by Paddleford (66) who found that X rays oxidize molybdenum (V) to molybdenum (VI).

Because of the large uncertainties in Paddleford's experimental data, the decision was made to repeat the experiment using a large (4000 Ci) gamma-ray source and employing a different experimental technique. Also, an attempt was to be made to find and use a more sensitive analytical method for determining quantitatively the small change in the molybdenum ion concentrations occurring in the system upon irradiation.

The effect of radiation on many aqueous solutions of inorganic solutes has been found to depend on several parameters, such as concentration of solute, concentration of other electrolytes present, pH, total absorbed dose and the concentration of dissolved oxygen in the system. It has been found that in some of these systems, e.g. the aerated ferrous-ferric and the cerous-ceric systems, the number of ions in the solution that are oxidized or reduced is proportional only to the absorbed dose over a wide range of the abovementioned parameters. This proportionality can be expressed in terms of the G-value which is defined as:

$$G\text{ (Product)} = \frac{\text{molecules product formed}}{\text{100 eV energy absorbed}}$$

Once the G-value of the <u>particular</u> system is established, the system becomes a potential method for measuring the absorbed radiation dose which is easily related to the exposure dose*.

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*Exposure dose rate is an intrinsic property of the radiation field and is measured in terms of absorbed dose in air.

It was the purpose of this investigation to measure the G-value of the molybdenum system over various ranges of the abovementioned parameters. Since the oxidation or reduction induced by ionizing radiation are very slight (in these experiments on the order of $10^{-5}\ \frac{\text{moles}}{\text{liter-min}}$ for molybdenum); a sensitive method of analysis was needed. Several analytical procedures for determining the molybdenum ion concentration were investigated. If the G-value of the system was found to be proportional only to absorbed dose over a reasonable range of the aforementioned parameters investigated and if a rapid and accurate method for determining changes in molybdenum concentration could be found, the aqueous molybdenum solution could then be used as a radiation dosimeter. Oza (65) just recently published a paper on the use of ammonium molybdate (dissolved in the organic solvents alcohol or tetrahydrofuran) as a dosimeter for gamma radiations. In his system, the ammonium molybdate is reduced to most probably a mixture of the oxides MoO_3 and Mo_3O_8.

3.0 THEORY

3.1 Introduction

Radiation chemistry, the basis of chemical dosimetry, may be defined as the study of the chemical effects produced in a system by the absorption of ionizing radiation. This radiation includes high energy photons (X rays, gamma rays) and high speed material corpuscles (electrons or beta particles, protons, alpha particles, fission fragments, etc.). The following treatment of the theoretical basis of radiation chemistry has been freely drawn from the references (36,50,51,82).

The passage of radiation through matter can (via secondary electrons in the case of photons) ionize or excite a large number of molecules, which are distributed along its track. Excited states are produced when bound electrons in atoms and molecules of the stopping material gain energy and are raised to higher energy levels; ions are produced when the energy gained is sufficient, and the transient excited states so produced are such that electrons are expelled. Since the absorption phenomenon is a highly localized one, these excited and ionized species have a highly inhomogeneous spatial distribution.

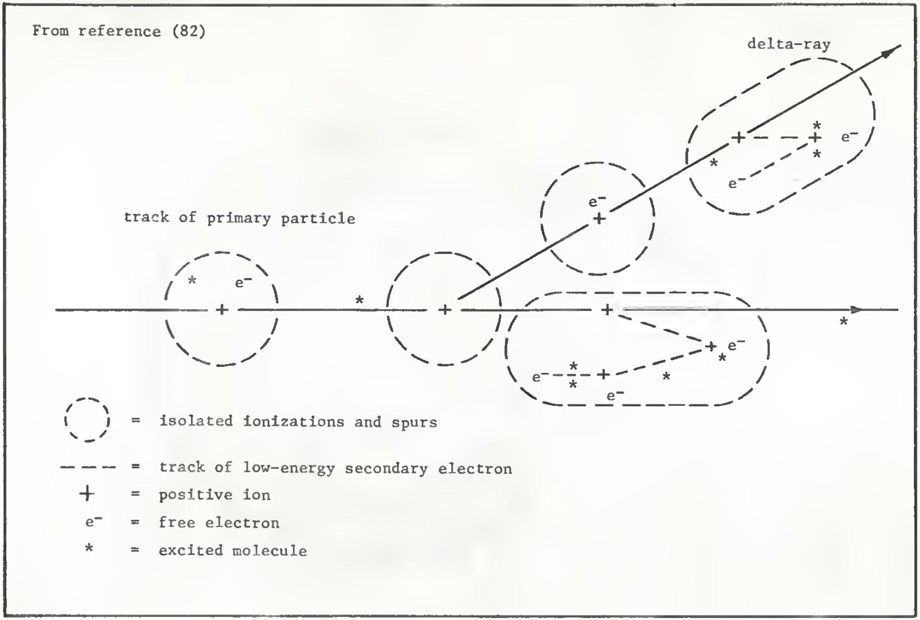
Electrons ejected as a consequence of the ionization produced by radiation may themselves produce further ionization and excitation. When the energy of these secondary electrons is less than about 100 eV, any secondary ionization they produce will be close to the original ionization; as a result a small cluster or spur of excited and ionized species is produced. Some of the secondary electrons will be sufficiently energetic to form tracks branching off and traveling further from the primary track. Such electrons are called delta rays (Fig. 1). These excited and ionized species are energetically unstable and undergo a sequence of transformations which terminate when thermodynamic equilibrium is re-established in the system. The first set of transformations lead to thermal equilibrium but not chemical equilibrium. The products of these transformations are stable molecules and chemically unstable species such as free radicals. The next set of transformations consists of chemical reactions and diffusion, occurring in individual spurs and in the overlap of the spurs, involving the reactive species and producing, in the end, chemical equilibrium.

3.2 Stages in Overall Radiation Process

We can divide the overall radiation process into three stages: (a) the physical stage, (b) the physicochemical stage, and (c) the chemical stage (50).

The physical stage consists of the dissipation of the radiant energy in the system. Its duration is of the order of less than 10^{-15} sec. The physicochemical stage consists of the processes which culminate in the establishment of thermal equilibrium in the system. Its duration is of the order of 10^{-12} sec. The chemical stage consists of diffusion and chemical reaction of the reactive species leading to the establishment of chemical equilibrium. Its duration ranges from 10^{-8} sec upwards, depending upon the rate constants and diffusion coefficients of the reactive species.

In looking at the physical stage, we shall briefly consider the phenomenon of energy transfer from the high-energy radiation to the system. Bethe and Ashkin (12) have analyzed in detail the rate at which the incident radiation loses its energy. The main mechanism of energy dissipation is by the electrostatic coulomb interaction between the charged particle and electrons



From reference (82)

Fig. 1. Distribution of ions and excited molecules in the track of a fast electron (not to scale).

of the medium. A small amount of energy is also dissipated by interaction with the nuclei of the medium. A fast electron can also lose energy in the medium by emitting "bremsstrahlung" as it passes close to the nuclei. This type of energy loss is usually very minor in radiation chemistry.

Kuppermann(50) lists some of the important conclusions regarding energy loss by incident radiation. (1) The rate of energy loss of a charged particle in a given medium is proportional to the electron density of that medium. (2) The loss rate increases as the particle slows down. (3) For two particles of equal energy but different mass, the heavier one will have a larger linear energy transfer or LET (i.e., loses energy at a higher rate). This means that the density of ionized and excited species along an alpha particle track is several thousand times larger than that along the track of an electron of the same energy. This fact is most important when interpreting the quantitative differences between the reactions induced by fast electrons and those induced by heavy particles.

The above discussion concerned the rate of energy loss by charged particles. When X rays and gamma rays pass through matter, they lose energy by the processes of photoelectric absorption (the incident photon transfers its entire energy to an electron in the medium), Compton scattering (the photon transfers part of its energy to an electron), and pair-production (the photon disappears and a high-energy electron and positron are formed). For photons in the range of 100 keV to 2 MeV, the main mechanism of energy loss in water is by Compton scattering (55). For 1 MeV photons, the energy of the Compton electrons varies from 0 to 0.8 MeV, having a mean value of 0.45 MeV.

We conclude from the above facts that the main effect of the absorption of high-energy photons by matter is the production of energetic electrons, which in turn dissipate their energy as described previously.

In the treatment above, we have considered only the incident radiation and its rate of energy loss. We shall now focus our attention on the medium and consider the nature and distribution of the initial species produced by the radiation.

The effect of transfer of energy from an energetic charged particle to the medium is to produce along its path a variety of excited species, such as electronically excited molecules and ions in their ground or electronically excited states, as well as free electrons. The production of ions also results in the production of secondary electrons with varying energies. The electronic transitions by which these species are formed occur in times on the order of 10^{-15} sec which are short compared to molecular vibration times (10^{-12} sec). These excited species are distributed nonhomogeneously along the particle track. They are formed in spherical clusters called spurs. The nature of the distribution of these spherically symmetric spurs along the track is primarily determined by the LET of the charged particle.

Spurs along the tracks of low LET charged particles are separated to the extent that they do not interact with each other. This is called spur ionization. High LET particles cause spherical spurs which are so close together that the track becomes, effectively, a cylinder of active species with no axial variation in concentration (53). This mode of ionization is termed columnar ionization.

Contained within the spurs located along the particle track are high concentrations of free radicals; hence there is a high probability that radical-radical reactions will occur in these zones. As the tracks or spurs expand by diffusion, the radicals, and the products of radical-radical reactions, have a chance to meet other species in the bulk of the solution. The yield from radical-radical reactions is called the molecular yield while that of radicals escaping into the bulk of the medium is called the free radical yield. Reference (5) describes the dependence of the values of the above yields on the LET of the radiation.

In the physicochemical stage, the excited species formed in the physical stage reach thermal equilibrium. It lasts about 10^{-12} sec, which is of the order of magnitude of molecular vibration times, during which internal molecular rearrangements can take place. During this stage, the excited ions and molecules dissipate their excess energy by bond rupture, luminescence, internal conversion, energy transfer to neighboring molecules, etc. Reference (82) gives a good description of the reactions of excited atoms, molecules and ions formed during this stage.

It is also important to consider here the fate of the low-energy secondary electrons produced (when the positive ions are formed) during the physical stage. Two divergent theoretical views exist on this matter.
The system most extensively studied is liquid water. In this system, positive ions other than H_2O^+ are ignored and the production of secondary electrons follows the reaction:

$$H_2O \rightarrow H_2O^+ + e^- \ . \qquad (1)$$

Samuel and Magee (71) assume that the secondary electrons formed lose kinetic energy because of the electric attraction by the parent ion and the inelastic collisions with other molecules in which they lose a fraction of their energy in each collision. They calculated that a 10 eV electron will travel a distance of about 20 Å from the parent ion before being reduced to thermal energy. At this distance, the electron will still be within the electrostatic field of the parent ion and it will be drawn back to the ion thereby neutralizing it. The parent ion is then transformed into a highly excited neutral molecule which can decompose into H and OH radicals lying close together:

$$H_2O^+ + e^- \rightarrow H_2O^{**} \rightarrow H\cdot + \cdot OH \ . \qquad (2)$$

Platzman (67) assumes the electron loses its energy by causing vibration of the bond dipoles and rotation of water molecules. He calculated that a 10 eV electron in water would travel an average distance of at least 50 Å from the positive ion before being reduced to thermal energy. At this distance it would be essentially free of the electrostatic attraction of the parent ion. In this model, the hydrogen radical is formed by the reaction:

$$e^-_{aq} + H_2O \rightarrow H\cdot + OH^-_{aq} \ . \qquad (3)$$

The parent ion dissociates according to:

$$H_2O^+ \rightarrow H^+ + \cdot OH \ . \qquad (4)$$

Consequently, according to the Platzman model, in agreement with Lea (54) and Gray (33), the H· and ·OH which result are far apart from each other whereas according to Samuel-Magee, they lie close together.

The difference between this initial distribution of the radicals is important for the chemical stage of the process.

During the chemical stage, the chemically reactive species undergo chemical reactions as they diffuse away from the site where they were originally produced. Two problems associated with this stage concern the relative importance of ionic versus free radical reactions and the spatial inhomogeneity of the initial distribution of reactive species.

It is believed that in condensed systems such as water, the main reactive species produced in the physicochemical stage, which react in the chemical stage, are free radicals. The excited primary molecules are generally ignored, the assumption being that they either return to the ground state directly by a non-radiative process or else dissociate into ·H and ·OH which have little extra energy and, confined by a "cage" of water molecules, recombine without producing any overall chemical change (82).

Because of the spatial inhomogeneity of reactive species concentration, conventional chemical kinetic analysis (time dependence only) cannot be made. The spatial and temporal dependence of species concentration is a function of the LET of the radiation (spur or columnar ionization), initial distribution of radicals (Samuel-Magee or Lea-Gray-Platzman model), the diffusion coefficients and rate constants of all reactive species present. The analysis of these processes is known as diffusion kinetics. A description of the various radical diffusion models proposed and their success in leading to calculations of product concentration in agreement with experiment has been extensively treated by Kuppermann(51) and Kuppermann and Belford (53) among others (29,61,72,75).

3.3 Radiation Chemistry of Water and Aqueous Solutions (5,82)

The radiation chemistry of water and aqueous solutions has been the subject of a great deal of theoretical and experimental study. In aqueous systems, as in any other medium, ionizing radiation produces excited and ionized species. The distance between successive ionizations in the path of a primary recoil electron produced by cobalt-60 gamma rays in water is of the order of 1000 Å (36). At each point of ionization, recoil electrons promote further ionization of the water forming a group of ion pairs. The original diameter of this spur of ionization is on the order of 10 to 20 Å (36). The result of this ionization process is a net dissociation of the water molecule into hydrogen atoms, hydroxyl radicals and hydrated electrons according to reaction (5):

$$H_2O \rightarrow \cdot OH + [H\cdot \text{ or } e^-_{aq}]. \tag{5}$$

Hart (38) studied the properties of the hydrated electron e^-_{aq}. In many of its chemical properties it behaves like a hydrogen atom. Both species are reducing agents differing only in chemical reactivity. e^-_{aq} is important only in solutions of pH greater than about 1.0. At lower pH, e^-_{aq} is rapidly converted to ·H by reaction (6):

$$e^-_{aq} + H_3O^+ \rightarrow H\cdot + H_2O \ . \tag{6}$$

Below pH 1.0, this reaction takes place so rapidly that e^-_{aq} reactions with solutes of moderate concentrations are unimportant. In this thesis, the reactions of e^-_{aq} are ignored because solution pH was kept below 1.0.

After conversion into free radicals but before appreciable diffusion has occurred, the ionization spurs will contain several pairs of hydrogen and hydroxyl free radicals. Hydrogen and hydrogen peroxide are postulated to be formed by the following reactions:

$$H\cdot + \cdot H \rightarrow H_2 \ , \tag{7}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \ . \tag{8}$$

On the basis of this theory, approximately one half of the free radicals recombine according to the reaction:

$$H\cdot + \cdot OH \rightarrow H_2O \ . \tag{9}$$

If the solute species are present in concentrations above 10^{-6} M, the hydrogen and hydroxyl radicals escaping reactions (7), (8), and (9) may react with the solute. These reactions would occur in the volume of liquid appreciably outside the original spur. The hydrogen and hydrogen peroxide formed as a result of reactions (7) and (8) are called molecular products. The free radicals which diffuse away from the original ionization zones to react with other species constitute the radical yield.

The basic radiation induced water decomposition equation may now be written as:

$$H_2O \rightarrow a\ H_2 + b\ H_2O_2 + c(\cdot H) + d(\cdot OH) \ . \tag{10}$$

Equation (10) is important in explaining chemical phenomena associated with the irradiation of aqueous solutions. Most of the observed chemical changes can be explained by invoking only the four intermediates shown in reaction (10). One of the tasks of the radiation chemist is to measure the yields of the molecular and radical species formed by reaction (10).

3.4 Chemical Dosimetry (5,82)

Dosimetry of the ionizing radiations is a prerequisite for quantitative studies in irradiated systems. Since the ionization density is a function of the radiation LET, the energy absorption in the system rather than radiation flux is normally determined. To simplify quantitative comparison of effects, reaction yields are expressed in units of molecules converted per 100 eV of ionizing energy absorbed. Yields thus defined are called G-values (82). In the following discussion, G(X) refers to the number of molecules of a product, X, formed on irradiation per 100 eV of energy absorbed. G(-Y)* refers to the loss of material, Y, that is destroyed per 100 eV of absorbed energy. These values can be determined experimentally. G_Z is used to denote the earliest detectable yield of Z, as it emerges from the spurs. G-values are now the common means of expressing radiation-chemical yields.

In chemical dosimetry, the radiation dose absorbed in a system is determined from the observed chemical change produced in the system. It is necessary to invoke the yields of the four intermediates of water radiolysis (reaction 10) given by G_{H_2}, $G_{H_2O_2}$, G_H, and G_{OH} in order to explain these chemical changes. These primary radiation yields are useful in determining the ability of a given radiation to form products in a given system and in deducing mechanisms of reaction.

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*G(-Y) in the molybdenum system refers to $G(-Mo^{5+})$. However, in this report $G(Mo^{5+})$ will be used to signify $G(-Mo^{5+})$. Also, the terms G-value and $G(Mo^{5+})$-value will be used interchangeably.

One of the most widely used chemical dosimeters is the Fricke (30)*, or ferrous sulfate, dosimeter. The reaction mechanism has been established for an air equilibrated solution of ferrous sulfate subjected to radiation (82):

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \ , \qquad (11)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \cdot OH + OH^- \ , \qquad (12)$$

$$H\cdot + O_2 \rightarrow HO_2\cdot \ , \qquad (13)$$

$$HO_2\cdot + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \ , \qquad (14)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \ . \qquad (15)$$

From the above mechanism, it is noted that each peroxide molecule oxidizes two ferrous ions, each hydroxyl radical oxidizes one ferrous ion, and each hydrogen atom oxidizes three ferrous ions. Consequently, we may write:

$$G(Fe^{3+}) = 2\ G_{H_2O_2} + 3\ G_H + G_{OH} \ , \qquad (16)$$

and

$$G_{H_2} = G(H_2) \ . \qquad (17)$$

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*Originally Fricke developed this dosimeter for applications in X-ray therapy. He estimated that the ferrous sulfate solution and a standard air ionization chamber would have identical relative responses to X rays of different wavelengths if the aqueous medium was 0.8 N in sulfuric acid. No particular advantage is gained by the use of 0.8 N sulfuric acid medium in purely chemical studies, but custom dictates its continued usage.

We further assume that hydrogen atoms and hydroxyl radicals are formed in equimolar amounts via reaction (5) and disappear via reactions (7) and (8) to form hydrogen and hydrogen peroxide. The equations of material balance are:

$$G_{-H_2O} = G_{OH} + 2\ G_{H_2O_2}\ , \tag{18}$$

$$G_{-H_2O} = G_H + 2\ G_{H_2}\ . \tag{19}$$

From (18) and (19) we have:

$$G_{OH} + 2\ G_{H_2O_2} = G_H + 2\ G_{H_2}\ . \tag{20}$$

Equations (16), (17), and (20) provide three equations for evaluating three unknown quantites since $G(Fe^{3+})$ can be measured experimentally.

A frequently employed reaction used to provide the necessary information for computing the primary radiation yields for aqueous solutions involves the use of the ceric sulfate dosimeter (35,87). The established mechanism is:

$$H\cdot + O_2 \rightarrow HO_2\cdot\ , \tag{13}$$

$$HO_2\cdot + Ce^{4+} \rightarrow Ce^{3+} + H^+ + O_2\ , \tag{21}$$

$$H_2O_2 + Ce^{4+} \rightarrow Ce^{3+} + HO_2\cdot + H^+\ , \tag{22}$$

$$\cdot OH + Ce^{3+} \rightarrow Ce^{4+} + OH^-\ . \tag{23}$$

For this mechanism we may write:

$$G(Ce^{3+}) = G_H + 2\ G_{H_2O_2} - G_{OH}\ . \tag{24}$$

Combining (20) and (24), $G(Ce^{3+})$ may be expressed as:

$$G(Ce^{3+}) = 4\ G_{H_2O_2} - 2\ G_{H_2}\ . \tag{25}$$

From (17) and (25), $G_{H_2O_2}$ is obtained:

$$G_{H_2O_2} = \frac{G(Ce^{3+}) + 2\ G(H_2)}{4}\ . \tag{26}$$

From (16) and (20) we get:

$$G_H = \frac{G(Fe^{3+})}{4} - \frac{G(H_2)}{2}\ . \tag{27}$$

Similarly using (24):

$$G_{OH} = \frac{G(Fe^{3+})}{4} + \frac{G(H_2)}{2} - \frac{G(Ce^{3+})}{2}\ . \tag{28}$$

Recalling that G (Product) quantities are measurable by experiment, G_{H_2}, $G_{H_2O_2}$, G_H, and G_{OH} may be calculated from equations (17), (26), (27), and (28). As reported by Allen (3), the following are representative values for irradiation of an 0.8 N sulfuric acid solution with cobalt-60 gamma rays:

$G_{H_2} = 0.39$ $\quad$ $G_{H_2O_2} = 0.78$ $\quad$ $G_H = 3.70$

$G_{OH} = 2.92$ $\quad$ $G_{-H_2O} = 4.5$ $\quad$ $G_{e^-_{aq}} = 0.00$

These values are independent of solute concentration when dilute aqueous solutions are irradiated. This is so because practically all of the absorbed energy is deposited in the water molecules and the observed chemical changes are brought about indirectly via the primary radiation products. At higher solute concentrations direct action may be significant (57) and there is some evidence that excited water molecules may transfer energy directly to the solute (69).

3.5 Analysis of Some Parameters Affecting Dosimetric Yields (5,31,82)

Any solution or irradiation parameter which affects the primary radiation yields or the structure of the solute (which will alter its reactivity) may also affect the G-value of the system. In this section, the effect of varying solution pH, solute concentration, dose, temperature and solution oxygen concentration will be outlined briefly. Other parameters which affect the G-value are the LET of the radiation and dose rate. Since LET and dose rate were not varied in this experiment, only brief mention will be made of their effects. In the following discussion, repeated reference will be made to the much-studied ferrous sulfate dosimeter which is the standard aqueous inorganic system.

3.5.1 Response Versus Dose

As the radiolytic reaction proceeds, the composition of the solution changes. Products that generally are reactive accumulate, and the initial resctive constituents become depleted. Consequently, the radiation product yield generally lessens with increasing dose. A linear response may result when (1) the yield is independent of the concentration of initial constituents and (2) all products formed are relatively insensitive to radiation. In the Fricke dosimeter, the $G(Fe^{3+})$ has a constant value of 15.5 (5) over the dose range 4×10^3 to 5×10^4 rads. The lower limit is set by the sensitivity of analytical methods available for accurately determining the concentration of Fe^{3+} snd the upper limit by the depletion of dissolved oxygen in the system. The linear response with absorbed dose of the Fricke dosimeter is illustrated in Figure 2.

3.5.2 Dose Rate

At dose rates up to kilorads/sec for steady irradiation and up to about 10^8 rads/sec in microsecond pulses, most dosimetric reactions are independent of dose rate. At higher dose rates the yields and reactions change because reactions involving the hydrated electron become more important (31). The Fricke dosimeter has been found to be independent of gamma-ray dose rate in the range 0.1 to 4000 rads/sec (62).

3.5.3 Solute Concentration

The yield obtained in an irradiated solution is determined by the number of active species escaping from the tracks and is independent of solute concentration, at low concentration (generally 10^{-5} to 10^{-3} M) and in the absence of competitive reactions. A change in yield is found at higher concentrations because of solute interfering with the spur and track reactions forming the molecular products (i.e., reactions (7) and (8)). The yield may increase or decrease depending on the reaction mechanism.

Careful examination of the concentration effect has revealed that, even at low concentration, solutes which react with hydroxyl radicals (e.g., Br^-, Cl^-) gradually lower the molecular yield of hydrogen peroxide as their concentration is increased (86):

$$\cdot OH + Cl^- + H^+ \rightarrow Cl\cdot + H_2O \ . \qquad (29)$$

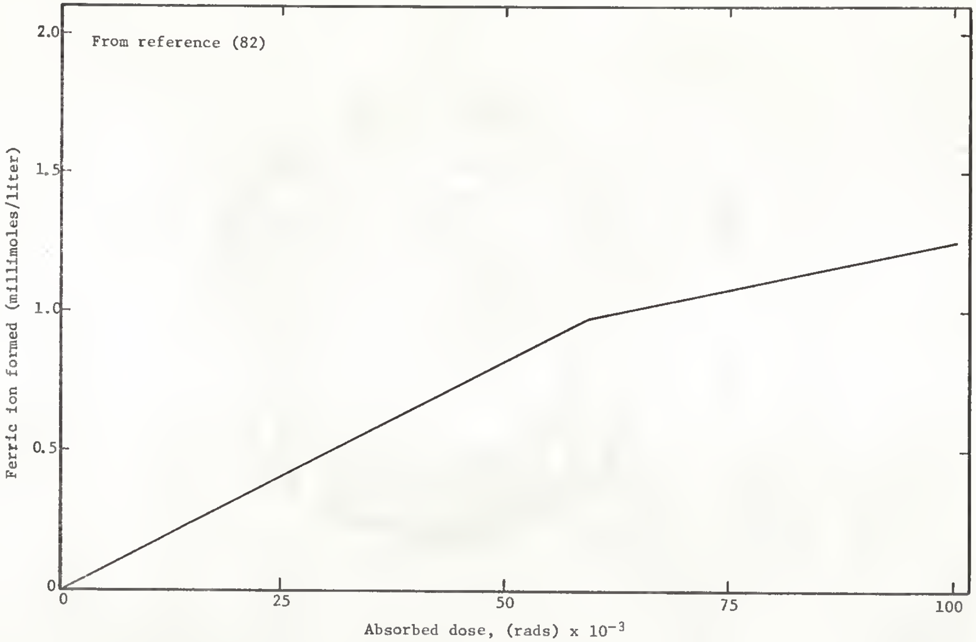

Fig. 2. Radiation induced oxidation of air-saturated ferrous sulfate solution.

Solutes which react with hydrogen atoms or solvated electrons (e.g., O_2, H_2O_2, KNO_2, $CuSO_4$, etc) reduce the molecular yield of hydrogen (22):

$$H\cdot + H_2O_2 \rightarrow \cdot OH + H_2O \ . \qquad (30)$$

Another important point to consider is that if the solute structure undergoes changes such as ionization or dimerization, its reactivity may also depend upon concentration. The G-value for the Fricke dosimeter has been found to be independent of Fe^{2+} concentration in the range 0.1 mM to 10.0 mM. Above this concentration range in air-saturated solutions, $G(Fe^{3+})$ has been found to decrease.

3.5.4 Concentration of Oxygen in the Solution

Dissolved O_2 in an aerated dosimeter solution will affect the reaction mechanism since it reacts with e^-_{aq} and $\cdot H$. If the reaction of O_2 with these species is much faster than their reaction with added solute, the yield would be essentially independent of O_2 concentration.

In the Fricke dosimeter, the O_2 is a very efficient scavenger* for hydrogen atoms, combining with them to give perhydroxyl radicals according to the reaction:

$$H\cdot + O_2 \rightarrow HO_2\cdot . \qquad (13)$$

The $HO_2\cdot$ is not as reactive as $H\cdot$; however, it is a strong oxidizing agent and oxidizes three ferrous ions as shown in reactions (11), (12), (14), and (15).

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*A scavenger is a substance having a great affinity for a particular radical.

In the absence of oxygen, the reaction mechanism for the Fricke dosimeter is altered in the following manner: Reaction (13) is replaced (reference 52) by reaction (31):

$$H\cdot + H^{+} + Fe^{2+} \rightarrow Fe^{3+} + H_2 \qquad (31)$$

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \qquad (11)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \cdot OH + OH^{-} \qquad (12)$$

Weiss (88) suggests the H· can act as an oxidizing agent by first forming the radical ion H_2^{+}, which can accept electrons to form molecular hydrogen, i.e.,

$$H\cdot + H^{+} \rightarrow H_2^{+} \ , \qquad (32)$$

$$H_2^{+} + Fe^{2+} \rightarrow Fe^{3+} + H_2 \ . \qquad (33)$$

$G(Fe^{3+})$ in the absence of oxygen (e.g., in evacuated samples) is given by:

$$G(Fe^{3+})_{deaerated} = 2\ G_{H_2O_2} + G_H + G_{OH}\ , \qquad (34)$$

$$\begin{aligned} G(Fe^{3+})_{deaerated} &= 2(.8) + 3.70 + 2.90, \\ &= 8.20. \end{aligned}$$

In Figure 2, the break in the yield curve above 50,000 rads is due to the depletion of dissolved O_2 in the system. At this point, the $G(Fe^{3+})$ drops from 15.5 to 8.2. Curves of this general shape are typical of many other radiation-induced reactions in aqueous solution where the yield of products is dependent on the presence of oxygen.

3.5.5 Temperature

Since the primary reactive species yields depend only slightly on temperature, radiolytic yields generally exhibit only small temperature coefficients. A temperature dependence will also be exhibited if there results solute molecular structural changes or changes in rate constants for individual reactions.

Conflicting experimental data exist regarding the temperature dependence of G(Fe^{3+}) for the Fricke dosimeter. Hochanadel and Ghormley (43) reported a change of 0.09%/°C in the range 2 to 65°C, Schwarz (73) found 0.04 ± 0.03%/°C between 0 and 70°C, whereas Shalek, Sinclair and Calkins (78) observed no temperature dependence in the range 20 to 45°C.

3.5.6 pH

The yield may be affected by pH because of competition for e^-_{aq} between H^+ and solute. In some solutions pH will determine the structure of the solute; in all solutions changes in pH may alter the nature and reactivity of the primary radicals. The following pH dependent reactions of the primary radicals serve as an illustration of this:

(1) conversion of a solvated electron to a hydrogen atom in acid solution:

$$e^-_{aq} + H^+ \rightleftarrows H\cdot \tag{35}$$

(2) association of a hydrogen atom and a hydrogen ion in acid solution:

$$H_2^+ \rightleftarrows H\cdot + H^+ \tag{36}$$

(3) dissociation of the hydroxyl radical in alkaline solution:

$$\cdot OH \rightleftarrows H^+ + O^- \tag{37}$$

(4) dissociation of the perhydroxyl radical in neutral or alkaline solution:

$$HO_2\cdot \rightleftarrows H^+ + O_2^- \tag{38}$$

(5) conversion of a hydrogen atom to a solvated electron in alkaline solution:

$$H\cdot + OH^- \rightleftarrows e^-_{aq} \tag{39}$$

(6) At pH below about 3 and above about 11, the yields of reducing and hydroxyl radicals increase without any corresponding decrease in the yields of molecular hydrogen and hydrogen peroxide. It is believed (5) that this increase in radical yield in highly acid solution ($pH<3.0$) is due to attack upon the acid by an intermediate that would otherwise revert to water. The intermediate is believed to be either an excited water molecule or an isolated radical pair ($H\cdot + \cdot OH$) trapped in a solvent "cage". The possible reactions are:

$$H_2O^* + H^+ \rightarrow H_2^+ + \cdot OH\ , \tag{40}$$

or

$$(H\cdot + \cdot OH) + H^+ \rightarrow H_2^+ + \cdot OH\ . \tag{41}$$

Solutes may also react with the intermediate, competing with reactions (40) or (41) above.

The sulfuric acid concentration can be lowered from 0.8 to 0.1 N in Fricke dosimeter with only a 2% decrease in $G(Fe^{3+})$ according to Allen, Hogan and Rothschild (4). In more dilute acid the curve of Fe^{2+} oxidized versus dose, instead of being linear, shows a decrease in rate as the reaction proceeds. This decrease in rate involves two separate effects: a competition between ferric ions and oxygen for H radicals, and then a competition between ferric and ferrous ions for $HO_2\cdot$ (5). This is illustrated by the reactions:

$$H\cdot + FeOH^{2+} \rightarrow Fe^{2+} + H_2O \ , \qquad (42)$$

$$H\cdot + O_2 \rightarrow HO_2\cdot , \qquad (13)$$

$$Fe^{2+} + HO_2\cdot + H_2O \rightarrow FeOH^{2+} + H_2O_2 \ , \qquad (43)$$

$$FeOH^{2+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H_2O \ . \qquad (44)$$

The reason for the pH dependence probably lies in the formation of $FeOH^{2+}$ at higher pH, which reacts much more rapidly with reducing radicals than $FeSO_4^+$ the main species present at lower pH.

The effect of changing from sulfuric acid to hydrochloric acid media for the ferrous-ferric dosimeter was investigated by Schwarz (75). He found that reactions of the type 42-44 were even more prominent in the ferrous chloride-hydrochloric acid media, making it more pH dependent than the Fricke dosimeter.

3.5.7 Energy of Radiation

As mentioned previously, chemical yields depend on the energy of radiation because of the fact that the spatial distribution of the primary radiation species is a function of the LET of the radiation in the particular solution. High LET radiation gives rise to higher molecular yields, whereas low LET radiation favors higher free radical yields. Depending upon the particular reaction mechanism, the relative proportions of molecular and free radical yields will either increase or decrease the final quantitative chemical yield. In this study, the effect of radiation LET was not studied. The reader is referred to references 5 and 8 for a complete discussion of LET effects on particular dosimeter solutions.

3.6 Dosimetric Calculations (G-value and Absorbed Dose)

The experimental determination of G-values involves determination of the change in concentration of the substance for a given amount of absorbed radiation dose in the solution. The concentration change of the substance can be determined by any available sensitive analytical method, i.e., spectrophotometric, polarographic, volumetric, etc. The absorbed dose can be evaluated by the application of the principles of radiation dosimetry. The following discussion is based on reference (82). Some common definitions are included to insure continuity.

The exposure dose of X or gamma radiation at a given location is an intrinsic property of the radiation field at that location. The definition of the exposure dose, and the basis for its measurement, rest on the ability of X and gamma rays to produce ionization. The unit of exposure dose for X or gamma radiation is the roentgen (symbol r). One roentgen is an exposure dose of gamma radiation such that the associated corpuscular emission per 0.001293 g of air produces, in air, ions carrying one electrostatic unit of charge of either sign.

The absorbed dose of any ionizing radiation is the energy imparted to matter[*] by ionizing particles per unit mass of irradiated material at the place of interest. The unit of absorbed dose is the rad-equivalent to an energy absorption of 100 ergs per gram. The absorbed dose can also be given in units of eV/ml. One rad is equal to $6.24 \times 10^{13} \times \rho$ eV/ml, where ρ(g/ml) is the density of the material. The absorbed dose is determined by the composition of the absorbing material as well as by the radiation field.

The relationship between the exposure dose and the absorbed dose in air exposed to gamma radiation may be calculated on the basis of the definition of the roentgen:

$$\frac{1}{0.001293}\,\frac{(\text{e.s.u.})}{(\text{g})(\text{r})} \times 2.082 \times 10^{9}\,\frac{(\text{electrons})}{(\text{e.s.u.})}$$

$$\times\ 34\,\frac{(\text{eV})}{(\text{electron})} \times 1.602 \times 10^{-12}\,\frac{(\text{erg})}{(\text{eV})}$$

$$\times\ \frac{1}{100}\,\frac{(\text{rad})}{(\text{ergs/g})}$$

$$= 0.877 \text{ rad (in air)/roentgen} \qquad (45)$$

Ionization measurements can be used to determine the absorbed dose in media other than air by measuring the exposure dose in air at a given point

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[*] The International Commission on Radiological Units distinguishes between energy released to secondary charged particles (kerma) and energy imparted to matter locally. The two differ primarily with respect to bremsstrahlung emission during slowing down of the charged particles. The difference is significant only if there is a large gradient in the flux of ionizing radiation and is of negligible importance in this work. [See NBS Handbook 84 (1962)]

(e.g. by means of a calibrated chemical dosimeter) and then substituting the material to be irradiated at the same position, so that it is exposed to the same beam of radiation.

If certain conditions are met*, the energy absorbed by the sample and by air are proportional to their mass energy absorption coefficients (μ_a/ρ) and,

$$D_M = D_A \times \frac{(\mu_a/\rho)_M}{(\mu_a/\rho)_A} \text{ (rads) },\tag{46}$$

where D_M and D_A are the absorbed doses in the medium and air respectively and $(\mu_a/\rho)_M$ and $(\mu_a/\rho)_A$ are the corresponding mass energy absorption coefficients. From equation (45),

$$D_A = 0.877 \; R_A \text{ (rads) },\tag{47}$$

where R_A is the exposure dose in roentgens; therefore,

$$D_M = 0.877 \; R_A \times \frac{(\mu_a/\rho)_M}{(\mu_a/\rho)_A} \text{ (rads) }.\tag{48}$$

For a given material, the value of $(\mu_a/\rho)_M/(\mu_a/\rho)_A$ is constant in the range of photon energies where only Compton interactions occur (i.e., the condition met in this research).

In the Compton absorption region the total μ_a/ρ is equal to the Compton mass energy absorption coefficient (σ_a/ρ) and this is related to the Compton

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*See page 86 of reference (82) for a listing of these conditions. The appropriate conditions were met in this research.

electronic energy absorption coefficient (${}_e\sigma_a$) by,

$$\sigma_a/\rho = {}_e\sigma_a(Z/A)N_o \ , \tag{49}$$

where (Z/A) is the ratio of atomic number to atomic weight and N_o is Avogadro's number. For radiation of a given energy, (${}_e\sigma_a$) is the same for all materials and therefore,

$$\sigma_a/\rho \propto (Z/A)N_o \ , \tag{50}$$

or

$$\sigma_a/\rho \propto Z/A \ . \tag{51}$$

Thus, when the Compton process predominates, Z/A can replace μ_a/ρ in equation (48), e.g.,

$$D_M = 0.877 \ R_A \frac{(Z/A)_M}{(Z/A)_A} \ . \tag{52}$$

For compounds and mixtures, a mean value of Z/A must be used:

$$(\overline{Z/A}) = \Sigma \ w_i \ (Z/A)_i \ , \tag{53}$$

w_i being the fraction by weight of the i^{th} element in the medium. Table 4.4 of reference (82) lists the values of $(\overline{Z/A})$ for air and 0.8 N sulfuric acid (Fricke Dosimeter):

$$(\overline{Z/A})_{air} = 0.499 \ ,$$

$$(\overline{Z/A})_{0.8 \ N \ H_2SO_4} = 0.553 \ .$$

For any chemical system, the G-value is given by:

$$G\ (\text{Product}) = \frac{\text{molecules product formed}}{\text{100 eV energy absorbed}} \tag{54}$$

$$1\ \text{rad} = \text{an energy absorption of 100 ergs/g} \tag{55}$$

Combining these equations, we obtain a relationship between the measured yield, Y (molecules/gram), the G-value (molecules/100 eV) and the absorbed dose D, in rads:

$$\begin{gathered} D = \frac{100\ Y}{G} \times \frac{1.602 \times 10^{-12}(\text{erg/eV})}{100\ \text{ergs/g rad}} \\ D(\text{rad}) = 1.602 \times 10^{-12}\ Y/G \end{gathered} \tag{56}$$

Equation (56) may be applied to any chemical system. Using a Fricke dosimeter ($G(Fe^{3+}) = 15.5$), Kumar* used a modification of this equation to determine absorbed dose and, in conjunction with equation (52), determined the exposure dose rate in the gamma-cell (same cell as used in this research) to be equal to 2.676×10^5 roentgens/hr as of 7 February 1966.

For the molybdenum system studied, equation (56) is modified to take into account the fact that the change in molybdenum (V) concentration was measured, even though molybdenum (VI) is the product of the reaction. Also, the absorbed dose in units of eV/ml was used. For this system, equation (54) becomes,

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*Kumar, S. S., Fast-Neutron Radiolysis of Heavy Water, Masters Thesis, Kansas State University, Manhattan, Kansas (1967).

$$G(Mo^{5+})^{*} = \frac{100 \text{ x molecules } Mo^{5+} \text{ depleted/ml}}{\text{energy absorbed (eV/ml)}} \; . \qquad (57)$$

The depletion of Mo^{5+} was measured by means of volumetric analysis, hence,

$$\frac{\text{molecules } Mo^{5+} \text{ depleted}}{\text{ml}} = \text{change in } Mo^{5+} \text{ concentration } \frac{\text{(m moles)}}{\text{(ml)}}$$

$$\text{x } 6.023 \text{ x } 10^{20} \frac{\text{(molecules)}}{\text{(m moles)}} \; . \qquad (58)$$

Substituting (58) into (57), we get,

$$G(Mo^{5+}) = \frac{6.023 \text{ x } 10^{22} \frac{\text{(molecules)}}{\text{(m moles)}} \text{ x } \overline{\Delta C} \frac{\text{(m moles)}}{\text{(ml)}}}{D_v \text{(eV/ml)}} \; , \qquad (59)$$

where $\overline{\Delta C}$ is the change in Mo^{5+} concentration and D_v is the absorbed dose in units of eV/ml.

The absorbed dose (in rads) in the Mo^{5+} solution can be computed from equation (52). The absorbed dose in units of eV/ml can be obtained by use of the conversion factor for rads to eV/ml (1 rad = $6.24 \text{ x } 10^{13} \text{ x } \rho$ eV/ml).

Equation (59) was used in computing the $G(Mo^{5+})$ values arrived at in this research.

Since the gamma radiation does not reduce the Mo^{6+} in the aqueous solutions investigated, the oxidation of one Mo^{5+} ion results in the formation of one Mo^{6+} ion. We can therefore say

$$G(Mo^{5+}) = G(Mo^{6+}). \qquad (60)$$

$G(Mo^{5+})$ and $G(Mo^{6+})$ will be used interchangeably throughout this report.

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[*] Ibid, p. 16.

4.0 Procedure

The samples were irradiated in a cobalt-60 gamma-cell. The exposure dose rate in this cell, averaged over the size of specimens irradiated, was 2.843×10^5 roentgens/hr.

For air equilibrated samples, 55 ml of Mo^{5+} solution was added to the reaction vessel which was then placed into the gamma-cell. The vessels remained in the gamma-cell for residence times from 1 to 720 minutes.

For deaerated samples, the molybdenum solution was evacuated by means of a high vacuum apparatus before the reaction vessel was placed into the gamma-cell.

The initial (before irradiation) and final (after irradiation) Mo^{5+} concentrations were determined by titration with ceric sulfate. The $G(Mo^{5+})$, or $G(Mo^{6+})$ value was calculated from the decrease in Mo^{5+} concentration; however, a correction had to be made for the air oxidation (auto-oxidation) of Mo^{5+}.

4.1 Description of Apparatus

The gammacell-220 irradiator (4000 Ci) of Kansas State University was supplied by the Atomic Energy of Canada, Ltd., and is shown in Fig. 3. In this instrument, the cobalt forms a hollow cylindrical assembly into and out of which a reaction vessel can be moved. The inside dimensions of the cylindrical sample chamber of the gamma-cell were 3" radius by 8 1/8" height. A platform was placed inside this chamber so that the reaction vessel would be centered in the radiation field and the position of the vessel would not vary from run to run. The period of irradiation was set exactly by a timer which raised the sample chamber at the end of the pre-set time.

Fig. 3. A view of the gammacell showing the sample holder in place.

The reaction vessels, shown in Fig. 4, were specially constructed from pyrex. The vessels were made by closing off one end of a 40 mm O.D. glass tube, tapering the other end and attaching it to a 10 mm O.D. O-ring joint.

A special fitting, also shown in Fig. 4, was constructed from 10 mm O.D. tubing to which was fitted two O-ring joints and a high vacuum stopcock. The outside dimensions of the vessel were 1 1/2" diameter by 2 3/4" high (to the taper point). The special fitting was 3 1/2" long.

The vacuum fitting was attached to the reaction vessel by means of a clamp and the stopcock closed after the Mo^{5+} solution was added to the vessel and before the sample was irradiated. When samples were to be deaerated, the vessel-vacuum fitting assembly was attached to a high vacuum system and the sample evacuated.

The volume of the reaction vessel was approximately 56 ml and 55 ml of solution were added to it for all runs.

The high vacuum apparatus is shown in Fig. 5. It had O-ring joints to which the reaction vessel-vacuum fitting assembly could be attached for sample evacuation. A vacuum of 1×10^{-6} mm Hg (with reaction vessel attached) was attainable with this system. According to Schmidt (72), this would mean an O_2 concentration of approximately 10^{-6} M existed in the deaerated sample.

The water distillation apparatus (Fig. 6) was used to produce the highly purified water which must be used in radiation chemistry. It consisted of a 1000 ml pyrex boiling flask. A vapor bulb assembly was attached to the flask and a condenser to the vapor bulb assembly. The collecting vessel was a 1000 ml pyrex flask. Appropriate fittings were attached to the flasks

Fig. 4. Reaction vessel with teflon O-ring, high-vacuum fitting and clamp.

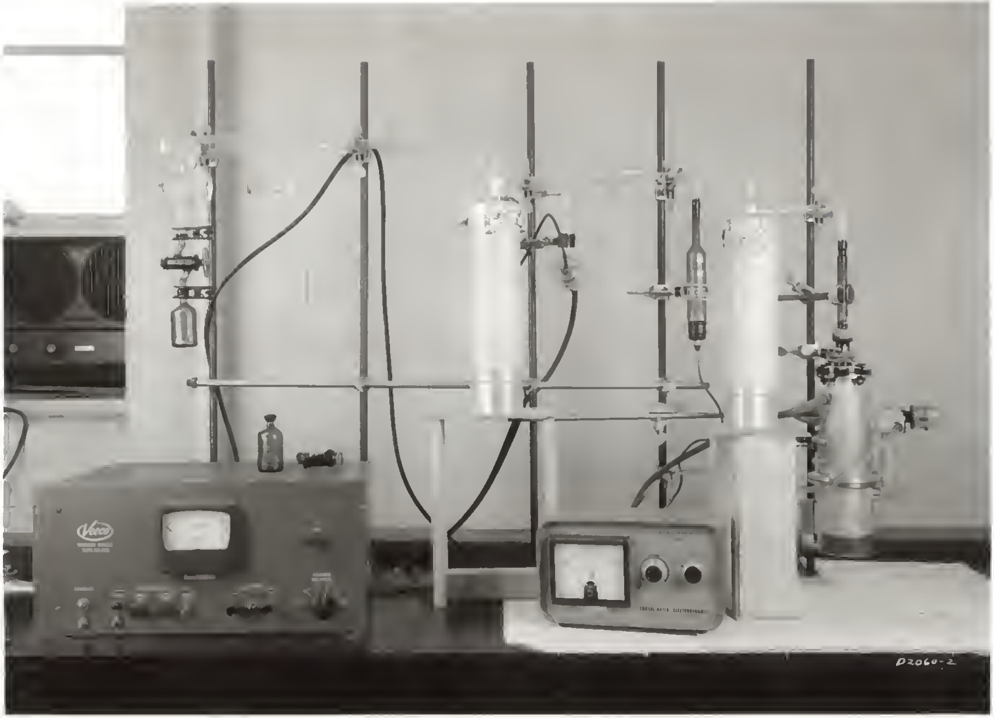

Fig. 5. A view of the high vacuum system showing the reaction vessel-high vacuum fitting assembly in place.

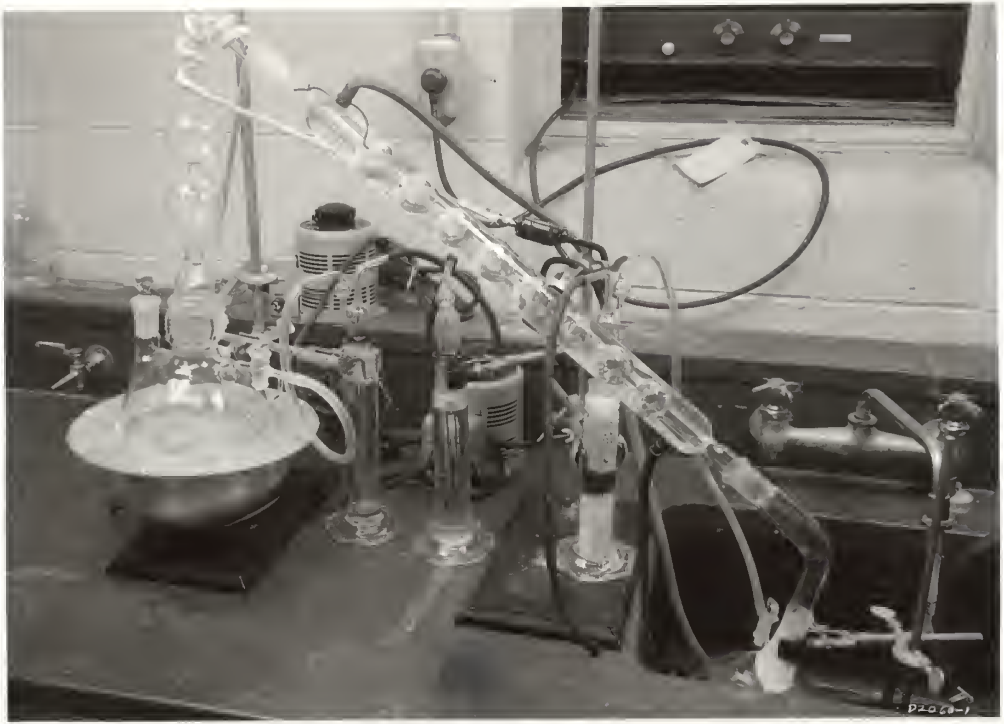

Fig. 6. A view of the water purification apparatus.

so that air purification trains could be connected to the distillation apparatus. A short section at the top of the vapor bulb assembly was heated via a heating tape in order to break the film of water on the inside of the column so as to prevent impurities from creeping over by capillarity. The height of the vapor bulb assembly was 13 1/4".

4.2 Reagents

Triply distilled water was used in preparing all molybdenum solutions to be irradiated.

All solutions were prepared from reagent grade compounds without further purification. Haybittle, Saunders and Swallow (40) showed that the use of reagent grade compounds will not affect the G-value of an irradiated system.

Redistilled mercury was used in reducing the molybdenum solutions.

The arsenious oxide used in standardizing the ceric sulfate solution was supplied by the U. S. Bureau of Standards.

4.3 Experimental Procedure

All accurate work in the radiation chemistry of aqueous solutions requires unusually high standards of water purity and cleanliness of reaction vessels. The reason is that any impurity present in the water will compete for reaction with the free radicals formed in water radiolysis (see Section 3). Organic impurities are the most important of these offenders. Even water of very low conductivity may still contain organic impurities and be unsuitable for radiation chemical research. Dewhurst (24) has described in detail the effect of organic impurities on $G(Fe^{3+})$ determinations.

Pure water (free of both inorganic and organic impurities) was obtained by the process described below which is a modification of that used by Allen (5).

Ordinary distilled water from a Barnstead still was redistilled (using the apparatus pictured in Fig. 6) first from an acid dichromate solution, then from an alkaline permanganate solution and finally with no added reagent into a pyrex container. The water was not allowed to come into contact with rubber or plastic. The still was protected from dust and vapors by a purification train containing activated charcoal, "Drierite", and sulfuric acid. This triply distilled water was stored in a well stoppered flask.

Even the most careful water purification is of no avail unless the reaction vessels are cleaned with equal care.

All glassware were thoroughly cleaned with the aid of a mixture of warm sulfuric acid and potassium dichromate. They were then washed with tap water, which was followed by washing and rinsing with distilled water. After drying, the openings of the glassware were wrapped with paper. Reaction vessels were subjected to further purification. Cleaned vessels were rinsed with triply distilled water. They were then subjected to a current of steam obtained by boiling the triply distilled water. The vessels were then filled with the purified water and were irradiated in the gamma-cell for about eight hours (a dose of approximately 2.5×10^6 rads). After irradiation, they were emptied, washed with the purified water, dried, then refilled with purified water and closed, using the vacuum fitting. They were kept this way until they were used.

The Mo^{6+} solutions were prepared by dissolving ammonium molybdate in the triply distilled water. The solution was adjusted to approximately 0.2 N in H_2SO_4 to insure stability of the molybdenum.

Mo^{5+} solutions were prepared by shaking Mo^{6+} solutions 3 N in HCl in a mercury reductor as suggested by Furman and Murray (32). The reduced molybdenum solution was then stored in a volumetric flask from which aliquots were taken for each of the irradiation runs. Solutions of various concentration and pH were prepared by appropriate dilution with purified water and reagent grade HCl or H_2SO_4. The concentration of the Mo^{5+} was determined (see Section 4.4) at this point, along with the time which was needed in correcting for air oxidation of the solution over the irradiation period.

Fifty-five ml of the Mo^{5+} solution were added to the reaction vessel which was then coupled to the vacuum fitting to insure air tightness.

This assembly was placed in the gamma-cell for times ranging from 1 to 720 minutes.

Samples which were to be deaerated before irradiation were attached to the high vacuum apparatus and evacuated. Freeze (liquid N_2)-pump-thaw-freeze cycles were used until the vacuum system pressure stabilized at approximately 10^{-6} mm Hg.

After irradiation, the concentration of the Mo^{5+} was again determined and recorded along with the time of the determination.

The $G(Mo^{5+})$ of the system was determined by the change in Mo^{5+} concentration ($\overline{\Delta C}$) due to the radiation. The change in Mo^{5+} concentration due to auto-oxidation had to be taken into account. The absorbed dose by the system was determined from the exposure dose in the gamma-cell. A more complete discussion of $G(Mo^{5+})$ and auto-oxidation calculations is given in the appendices.

4.4 Analytical Method

The standard solutions of ceric sulfate (approximately 0.01 N) were prepared by dissolving ceric sulfate in 0.06 M H_2SO_4 and titrating against an accurately weighed amount of arsenious oxide using osmium tetroxide catalyst. This is the procedure given on page 245 of reference (89).

The concentration of the Mo^{5+} solutions was determined by colorimetric titrations with standard solutions of ceric sulfate using ferroin as indicator and syrupy phosphoric acid as catalyst as suggested by Rao and Suryanarayana (70). This method was used in analyzing Mo^{5+} solutions before and after irradiation. It was found that good end points could be obtained even with ceric solutions of 0.008 N.

Titration blanks were prepared containing everything (including Mo^{6+}) but the Mo^{5+}. The blank correction was applied in determining C_i and C_f of the Mo^{5+}.

The analysis of the irradiated solutions required that Mo^{5+} or Mo^{6+} be determined in the presence of the other. A method of analysis, preferably of a rapid spectrophotometric nature, specific for 10^{-4} M amounts of Mo^{6+} in the presence of from 10^{-2}-10^{-4} M Mo^{5+} was needed. This was so because the $G(Mo^{6+})$ could have then been determined directly from the Mo^{6+} formed rather than from the more inaccurate difference method used to get the change in Mo^{5+} concentration. No specific method of analysis of this type was found in the literature. Several methods of analyzing for molybdenum were presented in the literature, none of which made mention of the influence of Mo^{5+} in the presence of Mo^{6+} or vice-versa. It was decided to investigate several of these analytical methods for possible use in this research. A short discussion of the results of this investigation follows.

Stevens (85) had separated the hexa and pentavalent molybdenum by the use of paper chromatography. This was a qualitative method, however, and appeared to be too time consuming and complex to use for obtaining quantitative results.

Busev and Fan (18) reported a direct complexometric titration method for hexavalent molybdenum. They used ethylene diamine tetraacetic acid (EDTA) as the complexing agent and a 0.1% aqueous solution of pyrocathechol, (containing 0.1% indigocarmine), as a colorimetric indicator. The titration was performed at a solution pH of 4-5. It was reported that pentavalent molybdenum also formed a complex with EDTA. In this work it was found that the Mo^{5+} forms the same bright green colored complex with the indicator that Mo^{6+} does, therefore this method was abandoned.

Majumdar and Savariar (59) reported a sensitive method for the spectrophotometric determination of micro quantities of Mo^{6+} based on the formation of a rose red complex with 9-methyl-2,3,7-trihydroxy-6-flourone-(methyl flourone). In this procedure, the solution to be determined containing 10 p.p.m. of Mo^{6+} was transferred to a 25 ml volumetric flask; one ml of 0.4% gelatin solution, 2 ml of methyl flourone solution, 3 ml methyl alcohol, and 3 ml buffer solution (pH 2.0) were added and dilution to volume made using distilled water. It was found that Mo^{5+} (same concentration as Mo^{6+}) also forms a colored complex with the methyl flourone when the solution described above is prepared. A Beckman DU spectrophotometer was used to investigate the Mo^{5+} and Mo^{6+} complexes formed. A blank solution containing everything but the molybdenum was also prepared. The absorbances of these solutions were determined by comparing the amount of light transmitted by each solution with that transmitted by the blank solution. The results of this spectrophotometric study are given in Table 1.

Table 1. Absorbance vs. Wavelength Data for Mo^{5+} and Mo^{6+} Complexes with Methyl Flourone.

wavelength λ(mμ)	absorbance Mo^{5+}	absorbance Mo^{6+}
460	0.082	0.020
470	0.232	0.068
480	0.305	0.094
490	0.383	0.118
500	0.406	0.127
510	0.378	0.121
520	0.318	0.104
530	0.264	0.092
540	0.208	0.078
550	0.152	0.058
560	0.093	0.036
580	0.013	0.000

From the above data, it was decided this method of analysis could not be used since the absorption spectra of the Mo^{5+} and Mo^{6+} complexes with methyl flourone were too similar.

The following colorimetric methods of analysis attempted were obtained from Snell and Snell (80).

The method of spectrophotometric analysis for Mo^{6+} based on the reduction of Mo^{6+} to Mo^{5+} with stannous chloride and measurement of the absorbance of the Mo^{5+} thiocyanate complex was tried without the addition of stannous chloride in hopes that Mo^{5+} could be determined in a mixture of both. This method was found to be unreliable, even when the precautions mentioned by Hurd and Allen (45) to insure solution stability were taken.

Hexavalent molybdenum may be determined colorimetrically by treating a solution of sample with pyrogallol. Unfortunately, it was found that the Mo^{5+} and Mo^{6+} complexes with pyrogallol had overlapping absorption spectra. The same overlapping of absorption spectra occurred when the spectrophotometric methods involving complexes of molybdenum with potassium ethyl xanthate, phenyl hydrazine, hydrogen peroxide, pyrocathechol, hematoxyline, toluene-3, 4-dithiol, and tannic acid were tried.

The analytical method involving the formation of the yellow silico-12-molybdate complex between molybdenum and silica was also tried. This is the procedure outlined in Vol. II, pages 161-173, of reference (48). The procedure was found to be very time comsuming and difficult and was abandoned when it was discovered that the Mo^{5+} and Mo^{6+} complexes with silica had very similar absorption spectra.

Moss, Mellon and Frederick (64) reported a sensitive test involving the complexing of molybdenum with 1, 10-phenanthroline. However, the reddish purple color was obtained with both the Mo^{5+} and the Mo^{6+} complexes.

The last spectrophotometric method tried involved the analysis of Mo^{5+} in HCl solutions making use of the natural Mo^{5+} absorbance (42). This method was found to be unreliable because of the drift in absorbance readings which occurred with the instrument used. Since this method also involved determining the concentration change of molybdenum by before and after absorbance readings on the Mo^{5+} solutions, and since Paddleford (66) reported that this led to greater errors than the titrimetric method, the decision was made to use the titrimetric method involving ceric sulfate mentioned previously.

5.0 Results and Discussion

Experimental data and calculations are presented in the appendices. The G-value for the aqueous molybdenum system was determined for initial Mo^{5+} concentrations ranging from 0.49 to 18.42 mM, for absorbed doses ranging from 0.27×10^{18} to 213×10^{18} eV/ml, for acid (HCl or H_2SO_4) concentration varying from 0.8 to 2.4 N, and for both air equilibrated and deaerated solutions. The results of these determinations are listed in Tables 2, 3 and A-1 and are illustrated in Figures 7-17.

5.1 Stability of Molybdenum (V)

Aqueous solutions of Mo^{5+} are known to be unstable (32), undergoing an auto-oxidation reaction to Mo^{6+} on standing in an air atmosphere. Since the effect of the gamma radiation was also to oxidize the molybdenum, this decrease in Mo^{5+} due to auto-oxidation had to be accounted for in calculating G-values. The data concerning auto-oxidation rate may be found in Appendix B and the use of this data in calculating the G-value is shown in Appendix C.

5.2 Effect of Gamma Rays on Molybdenum Ions

Table 2 shows a typical set of data (from run 15) illustrating the oxidizing effect of gamma rays on Mo^{5+}. It is seen that less oxidizing agent, ceric sulfate, was required for determination of Mo^{5+} after the solution was irradiated than before the irradiation. This is in agreement with Paddleford's (66) work with X rays. The change in Mo^{5+} concentration due to auto-oxidation is also shown.

Table 2. Mo^{5+} Inventory by Titration for a Typical Irradiation Run.*

Initial Mo^{5+} Concentration	$Ce(SO_4)_2$ before	$Ce(SO_4)_2$ after	Time irradiated	Change in $[Mo^{5+}]$ due to radiation	Change in $[Mo^{5+}]$ due to auto-oxidation	G-value calculated
m moles/ml	ml	ml	minutes	m moles/ml	m moles/ml	$\frac{\text{ions oxidized}}{100\text{ eV}}$
$19.94\text{x}10^{-4}$	4.68 ±0.05	3.55 ±0.05	10	$4.80\text{x}10^{-4}$	$0.01\text{x}10^{-4}$	9.76±1.01

*See Table A-1 for complete data.

A sample of Mo^{6+} was also irradiated and analyzed by titration. No reduction in Mo^{6+} was found (run 61). This fact is in agreement with Paddleford (66) who found no reduction of Mo^{6+} when aqueous solutions of the ion were subjected to X radiation.

Since it has been determined (66) that radiation does not cause reduction of Mo^{5+} to a lower oxidation state, the overall effect of gamma rays on Mo^{5+} samples can be expressed as,

$$Mo^{5+} \xrightarrow{\text{gamma rays}} Mo^{6+} \; . \tag{61}$$

Since the molybdenum (V) solutions were very dilute, it can be assumed that this oxidation process occurred by the diffusion controlled chemical reactions between the solute and radiation decomposition products of water (see sections 3.3 and 3.4).

It was not the purpose of this thesis to arrive at a reaction mechanism for the system. Any such attempt at postulating a reaction mechanism for this system (i.e. similar to the mechanism shown for the ferrous sulfate dosimeter in section 3.4) would have to take into account the nature of the molybdenum ion species present in aqueous acid media.

Much useful information (but by no means a complete listing) concerning the nature and chemistry of molybdenum species present in aqueous media can be found in references (9), (25), (47), (63), and (81). Babko and Nabivanets (9) postulate that in strongly acid solution monomeric forms of molybdenyl ions are present, i.e., $[MoO_2]^{2+}$ or $[MoO(OH)_2]^{2+}$. In concentrated HCl solution, the cations are formed in the narrow concentration range (~0.2-2N HCl). With a further increase in the concentration of HCl, complex chloride anions are formed. In H_2SO_4 solution, complex anions predominate for acid concentration >0.2 N. Diamond (25) postulates that $H\,Mo_2O_6{}^+$ exists in dilute acid and $(MoO_2Cl_2)_2$ in more concentrated HCl for the concentration range 10^{-4}-10^{-3} M (Mo^{6+}). In the review article by Mitchell (63), it is mentioned that, in solutions 1-12 N in HCl, MoO_2Cl_2 is present as the major species. Below 4 N HCl, dimers are thought to form. The nature of the species in <2 N HCl is uncertain. The excellent and comprehensive review article on the electrochemical properties of molybdenum by Sperenskaya, Mertsalova and Kulev (81) reveals that Mo^{6+} forms the species $H_2Mo_4O_{13}$ in dilute HCl whereas, in more concentrated solutions, the $H\,Mo_2O_6{}^+$ cation is formed. In 5-6 N HCl solutions, MoO_2Cl_2 forms according to:

$$H\,Mo_2O_6{}^+ + 3\,H^+ + 4\,Cl^- \rightarrow 2\,MoO_2Cl_2 + 2\,H_2O. \qquad (62)$$

The chloride complexes of Mo^{5+} exist in two forms, monomeric (>7 N HCl) and dimeric (<2.5 N HCl), which coexist in equilibrium in the intermediate range (2.5-7 N HCl). The composition of these chloride complexes and the equilibrium conditions have not yet been established in this intermediate range.

Molybdenum (V) does not form stable chloride complexes in dilute HCl, but exists as the cation MoO_2^+. As the HCl concentration is increased, MoO^{3+} is formed according to:

$$MoO_2^+ + 2\ H^+ \rightleftarrows MoO^{3+} + H_2O. \tag{63}$$

Further increase in HCl concentration results in the formation of $MoOCl^{2+}$, $MoOCl_2^+$ and $MoOCl_3$.

The preceding discussion on the composition of molybdenum complexes in aqueous solution is presented to demonstrate the complexity of this solution chemistry as well as the lack of complete agreement by the various authors as to the exact molybdenum species which do exist. The radical diffusion model of radiation chemistry (Section 3) involves the diffusion coefficients and reaction rate constants of ALL reactive species present in solution. It is immediately apparent that the particular acid used, acid concentration, and concentration of solute will determine the particular molybdenum species present. This in turn determines the diffusion coefficients and reaction rate constants applicable in any kinetic or reaction mechanism study.

5.3 Dependence of G-value on Absorbed Dose

Molybdenum (V) samples were irradiated for various lengths of time at a constant dose rate ($\sim 3\text{x}10^{17}$ eV/ml-min). The G-values for the Mo^{5+} to Mo^{6+} reaction were calculated from the change in Mo^{5+} concentration (see Appendix C) and are tabulated in Table A-1

The response of the molybdenum system to absorbed dose for aerated solutions of various initial Mo^{5+} concentrations is shown in Figures 7-11. The object of these runs was to determine the relationship of the G-value to absorbed dose for this system. It was hoped that the G-value would be constant over the dose range studied so that the Mo^{5+} system could be used as an accurate radiation dosimeter (see Section 2.0).

Figure 7 is taken from runs 9, 10, 11, and 14. The initial concentration of Mo^{5+} was 8.12 mM and the dose range covered was 2.91×10^{18} to 29.13×10^{18} eV/ml.

The results of runs 15-18, 20-22, and 24 are illustrated in Fig. 8. Runs 19 and 23 were not plotted because the very short irradiation time (1 minute) used in these runs caused only a small change in Mo^{5+} concentration and therefore led to very large errors in G-values. The initial concentration of Mo^{5+} was 1.99 mM, the HCl concentration was 2.41 N and the dose was varied from 1.48×10^{18} to 47.40×10^{18} eV/ml.

The results of runs 30-34 are illustrated in Fig. 9. The abscissa is an absorbed dose (D_v) scale, greatly expanded in order to illustrate the large uncertainty in G at low doses. The G-value for run 29 was not plotted as it was a 1-minute irradiation. The solutions were very dilute in Mo^{5+}, having an initial concentration of only 0.49 mM. The HCl concentration was 2.41 N and the dose varied from 0.59×10^{18} to 3.56×10^{18} eV/ml. A dose much larger than this resulted in complete depletion of the Mo^{5+}.

Figure 10 is a plot of the results of runs 41-45. Runs 46 and 47 (very large dose) were not included as no important information would be shown by plotting these points and the abscissa scale would have been so compressed that the dependence of G on D_v at low dose would have been obscured. Fig. 11 includes data points obtained for the largest absorbed doses. The initial Mo^{5+} concentration for these runs was 4.22 mM, the HCl concentration was again 2.41 N and the dose varied from 1.48×10^{18} to 53.25×10^{18} eV/ml.

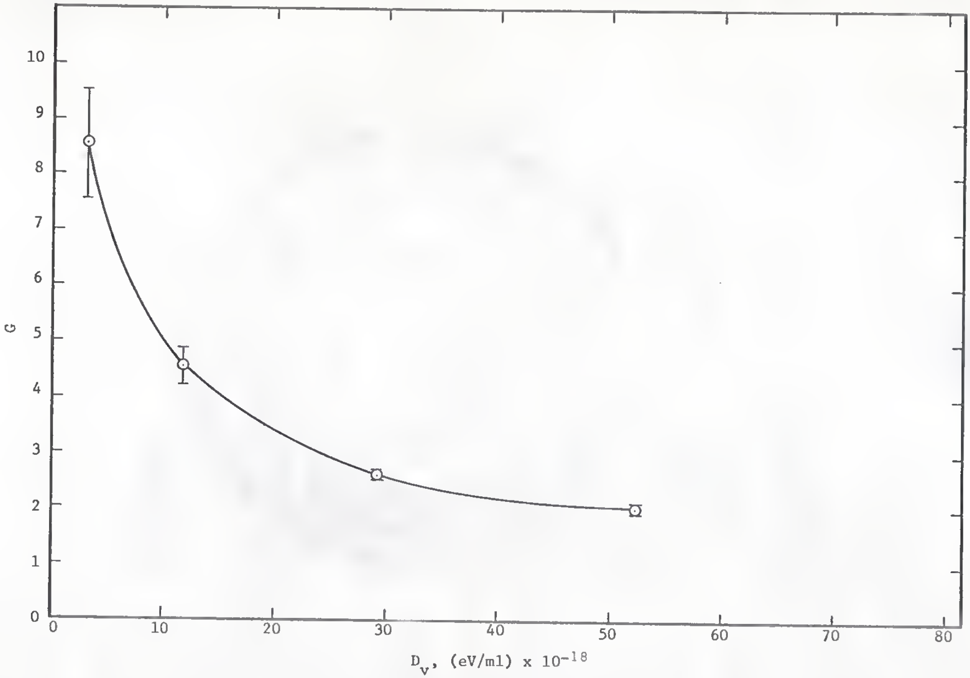

Fig. 7. Dependence of G(Mo^{5+}) value on absorbed dose. Initial concentration Mo^{5+} 8.12 mM, 1.32 N HCl, aerated solution.

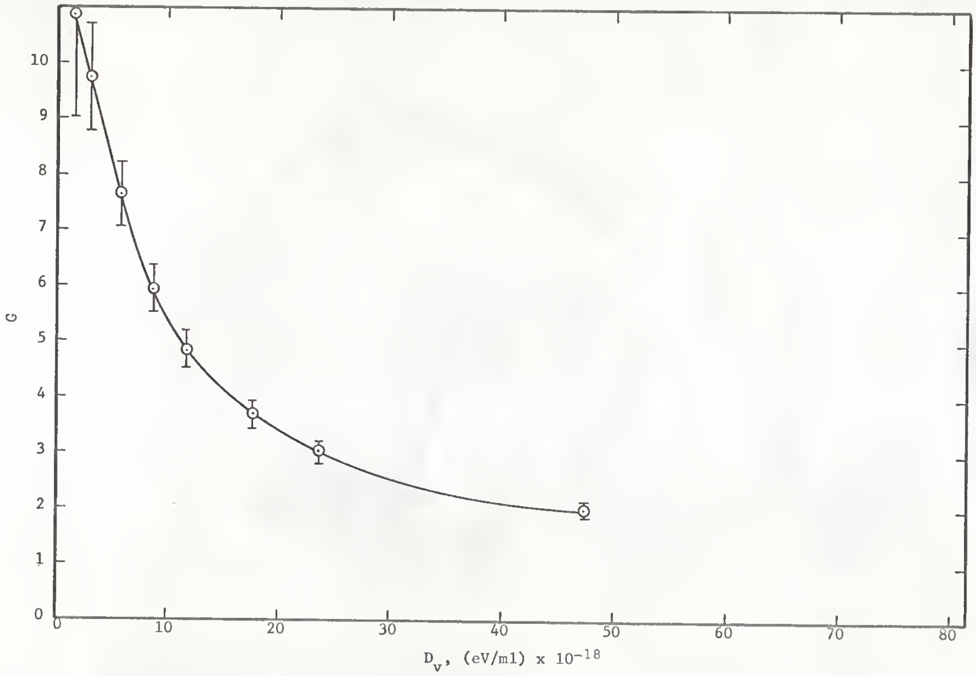

Fig. 8. Dependence of $G(Mo^{5+})$ value on absorbed dose. Initial concentration Mo^{5+} 1.99 mM, 2.41 N HCl, aerated solution.

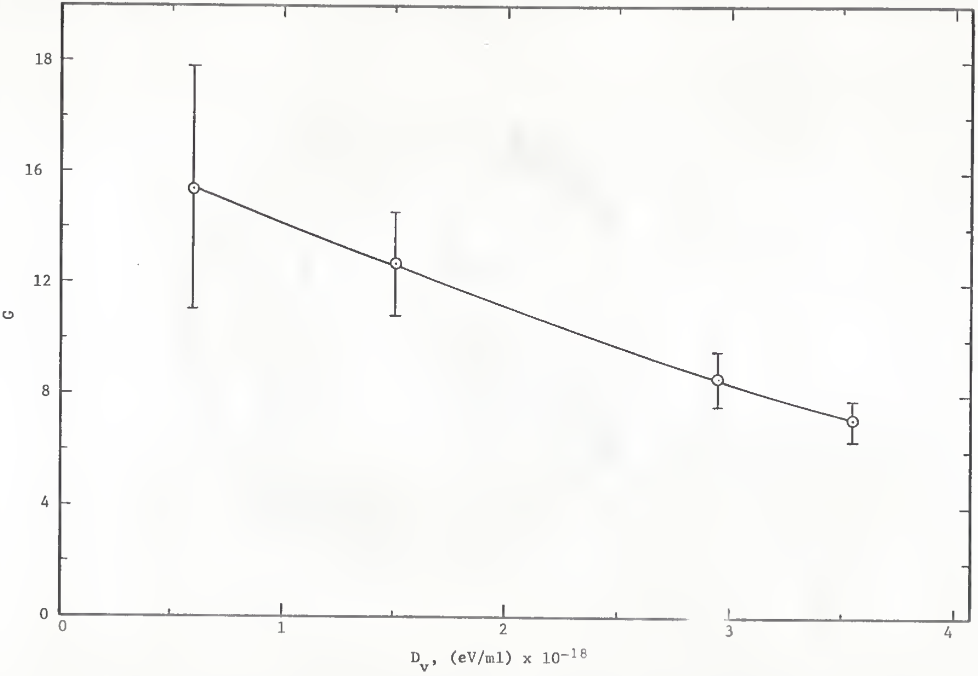

Fig. 9. Dependence of $G(Mo^{5+})$ value on absorbed dose. Initial concentration Mo^{5+} 0.49 mM, 2.41 N HCl, aerated solution.

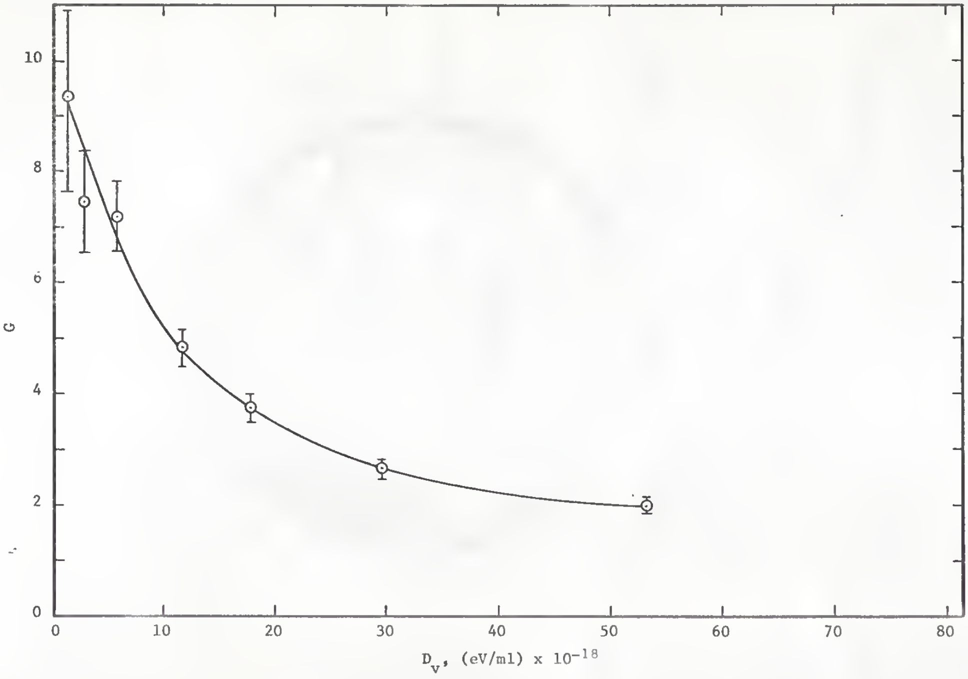

Fig. 10. Dependence of G(Mo^{5+}) value on absorbed dose. Initial concentration of Mo^{5+} 4.22 mM, 2.43 N HCl, aerated solution.

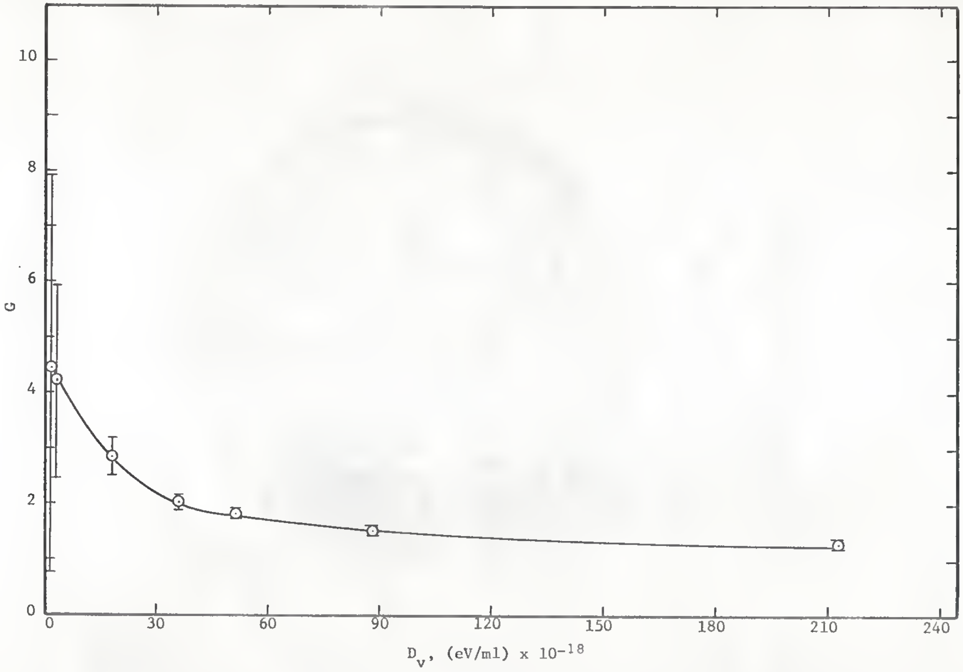

Fig. 11. Dependence of G(Mo^{5+}) value on absorbed dose. Initial concentration of Mo^{5+} 18.42 mM, 2.43 N HCl, aerated solution.

The inclusion of run 46 (G = 1.51) and run 47 (G = 1.31) in Fig. 10 would have shown the G-value curve to be still descending even at these higher doses.

Results of runs 41-47 are plotted in Fig. 11. These represent the most concentrated Mo^{5+} solution studied, 18.42 mM. Also, the dependence of G on dose over the very broad dose range (1.48×10^{18} to 212.99×10^{18} eV/ml) is illustrated. The HCl concentration was 2.43 N.

Figure 12 is a plot of the results of runs 15-24. It shows the yield of Mo^{6+} as a function of absorbed dose. Dosage curves of this type are typical of the many radiation-induced reactions in aqueous solution where the yield of products is dependent on the presence of oxygen (Fig. 2). Had this curve been linear, the G-value would have been constant over the range of linearity. If O_2 enters into the reaction mechanism, which apparently it does (see Section 5.6), the break in the curve at about 10×10^{18} eV/ml might be due to the depletion of absorbed oxygen in the system. The change in the curve may also be associated with a change in the kinetics of the reaction as the dose is increased, i.e., change from a second or third order to a zero, first or second order reaction as intermediates and product (Mo^{6+}) build up.

It is obvious from Figures 7-11 that the G-value is not constant with dose over the dose range investigated. It is seen that G stabilizes at higher doses ($> 90 \times 10^{18}$ eV/ml), particularly for the more concentrated Mo^{5+} solutions (Fig. 11).

The variability of G with D_v appears to rule out the use of this aqueous molybdenum system as a radiation dosimeter in its present form. However, perhaps an additive for the system can be found which would cause the G-value

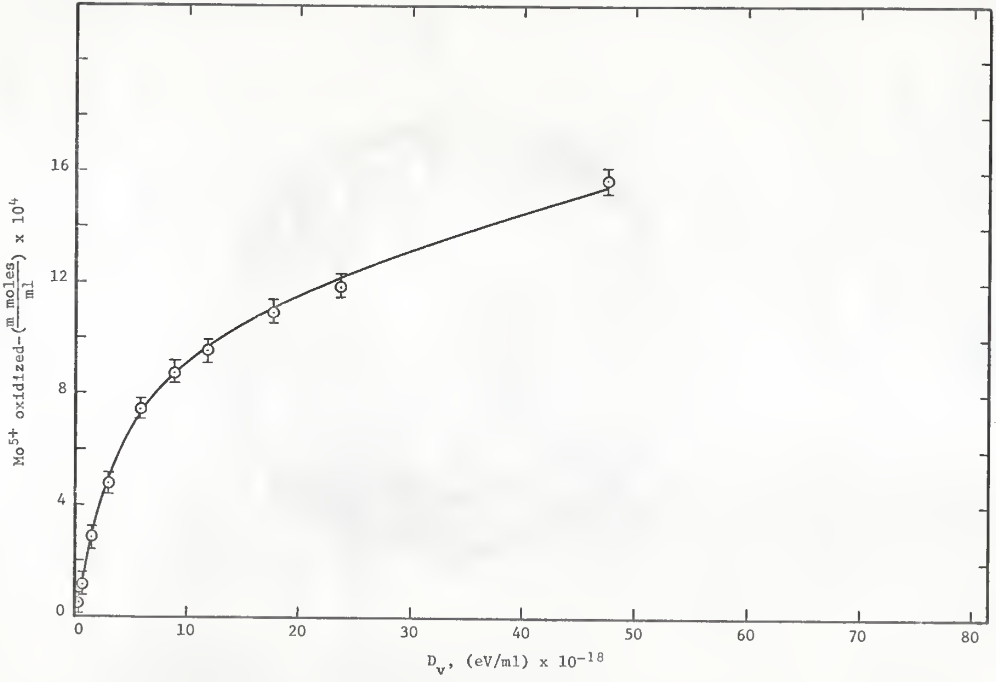

Fig. 12. Plot showing dependence of amount Mo^{5+} oxidizedonabsorbed dose for a typical run: Initial concentration Mo^{5+} 1.99 mM, 2.41 N HCl, aerated solution.

to remain constant with dose similar to the NaCl additive in the aqueous ferrous system which is used to stabilize the G-value (24).

In Section 3.5.1 it was noted that a constant G-value (or linear dosage curve, i.e., for this system: yield of Mo^{6+}* versus dose) may result only when (1) the yield is independent of the concentration of initial constituents and (2) all products are relatively insensitive to radiation. Section 5.4 demonstrates that condition (1) is not met since the G-value is dependent on initial Mo^{5+} concentration. The complex solution chemistry of molybdenum makes it possible that condition (2) also might not be met in this system.

The irradiation of iodide and ferrocyanide solutions both exhibit the same effect of starting with an initially high value of G which falls off rapidly as the product concentration builds up (5). In fact, in the case of the ferrocyanide system, the value of G drops from 5.4 to 0.95. It was postulated for this system that an unstable intermediate was formed which reacted with the primary reaction products of the water radiolysis.

Wojtczak and Lassocinska (91) found that when an aqueous solution of sodium permolybdate was irradiated with X rays, the yield of product was also a non-linear function of dose exhibiting a relationship between product yield and absorbed dose very similar to that of Fig. 12. They did not explain their results as they were still working on the problem.

Haissinsky and Ghosh-Mazumdar (34) found that in the gamma radiolysis of acid solutions of tellurium, the yields decreased with an increase in irradiation time. This element is a member of the same group of the periodic table (VI) as molybdenum and also has a very complex solution chemistry.

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*The yield of Mo^{6+} (m moles/ml) is equal to the depletion of Mo^{5+} (m moles/ml) in this system. (See section 3.5.8.)

Imai (46) reported that the rate of decomposition of aqueous ammonium molybdate solutions by ultraviolet radiation was reduced as the exposure was continued. No definitive explanation was given.

The results obtained in this work are not in agreement with those obtained by Paddleford (66) for the X-ray irradiation of molybdenum solutions. On the basis of his data he assumed that the G-value was approximately constant with dose over the dose range 4×10^{18} to 29×10^{18} eV/ml; however, he listed insufficient raw experimental data and no sample calculations to demonstrate his methods of data analysis. Furthermore, Paddleford presented an incomplete statistical analysis of the uncertainties in G-values. The G-values he tabulated (66) span a range from 10.3 to 6.8 for the irradiation time range 40 to 210 minutes. A reworking of some data presented in Table 18 of reference (66), G-value versus acid concentration, made it appear to this author that the G-values (by titration) which appear in the table are in error by a large factor. The entry in the table for 1.0 N HCl, 60 minute irradiation time lists a G-value of 8.02. Reworking the data given using equation (29) of reference (66) gave a $G(Mo^{6+})$ value of 3.92. Due to apparent discrepancies of this nature, the lack of sufficient raw data, and the lack of a more complete statistical analysis, the assumption of Paddleford that G versus dose is constant is questionable.

It is interesting to note that recomputing the entry in his Table 18 for a 2.5 N HCl solution (he lists a $G(Mo^{6+})$ value of 7.62) gave a value of $G(Mo^{6+}) = 3.50$. This recomputed G is in very good agreement with the average G-value of 3.73 ± 0.25 obtained in this investigation (runs 22 and 34) for the 60-minute irradiation of a 2.4 N HCl solution.

Figures 13 and 14 are illustrations of the results of runs 54-60 and 65-69 respectively. Here, the effect of changing from an HCl to an H_2SO_4 medium was investigated. Again, it is seen that the G-value is not constant with dose and that the curves have the same general shape as those for the HCl solution. Figure 15 includes G versus D_v dats for both HCl and H_2SO_4 and is based on runs 15-17, 20, 22, 55-58, 60 and 66-69. Here, we see more clearly that the shape of the G curves are independent of the acid medium within the limits of experimental accuracy. A further discussion of the effect of acid type and concentration on G is presented in section 5.5.

5.4 Dependence of G(Mo^{5+}) on Initial Concentration of Molybdenum (V)

Molybdenum (V) samples of various concentrations were irradiated for a given length of time. Figure 16 shows the dependence of the G-value on the initial Mo^{5+} concentration for irradiations of three different lengths of time. This figure is taken from runs 15, 16, 22, 32, 34, 37, 40, 42, 43, snd one point which was interpolated from Fig. 11. A straight line dependence is shown since further detail could only be revealed by determining the kinetics and mechanism of the reaction which was beyond the scope of this investigation. Suggestions on further studies which could be made to assist in the determination of the reaction mechanism are presented in section 5.8. In Fig. 16 we see that G decreases with increasing Mo^{5+} concentration for all doses shown but the rate of decrease in G with Mo^{5+} concentration is smaller at the higher doses.

The above results are again not in agreement with Paddleford (66) who assumed that G versus Mo^{5+} concentration is approximately constant. However, examinstion of Table 17 of reference (66) shows that G actually varied from

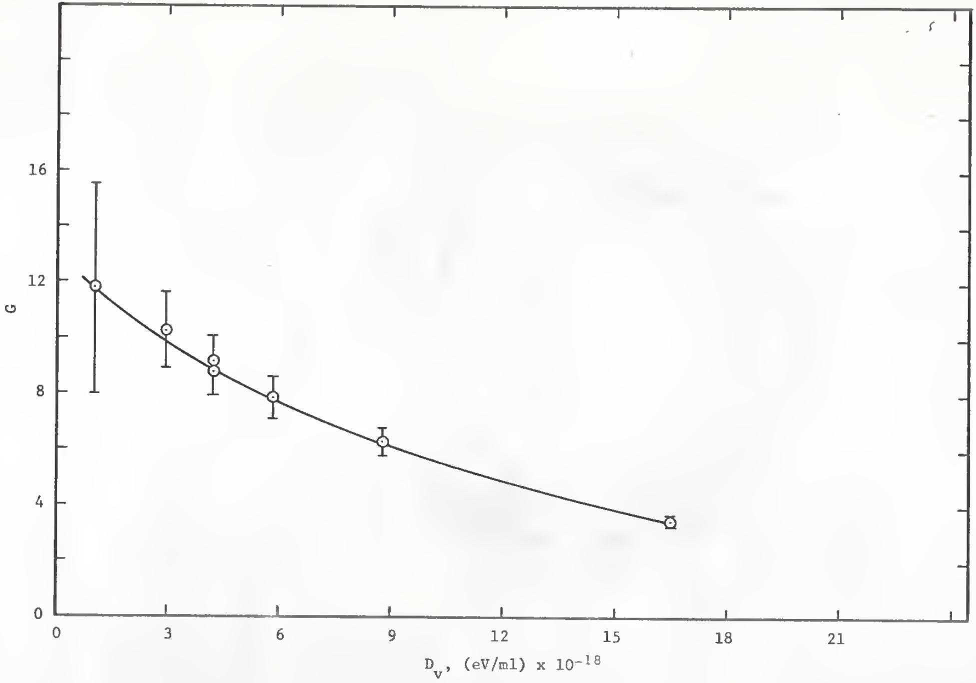

Fig. 13. Dependence of $G(Mo^{5+})$ value on absorbed dose. Initial concentration of Mo^{5+} 1.52 mM, 0.77 N H_2SO_4-0.04 N HCl, aerated solution.

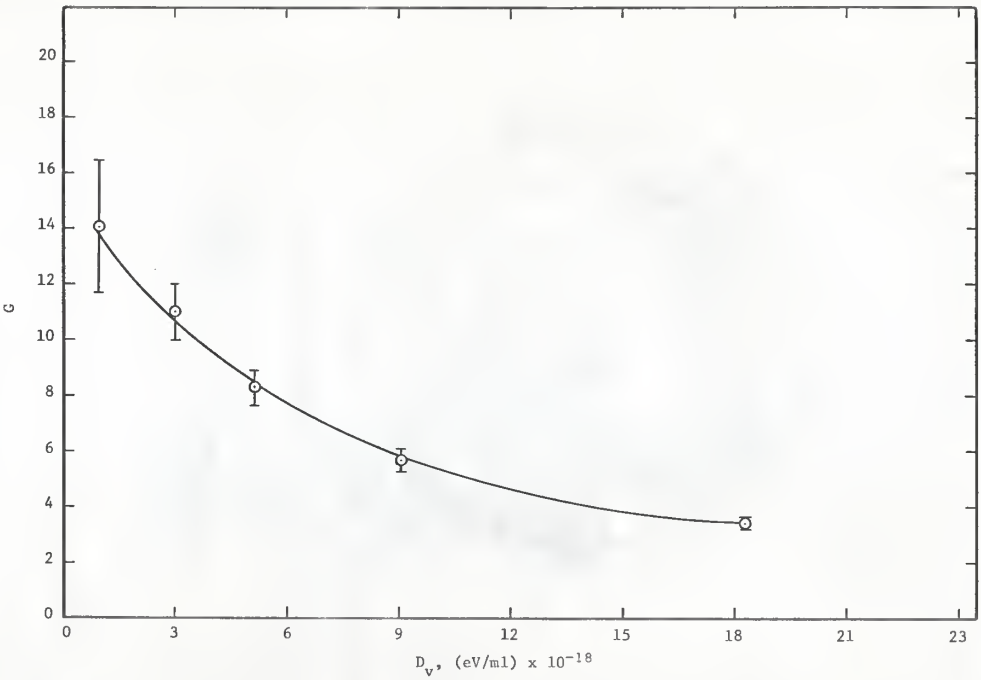

Fig. 14. Dependence of G(MO^{5+}) value on absorbed dose. Initial concentration of Mo^{5+} 1.90 mM, 2.34 N H_2SO_4-0.07 N HCl, aerated solution.

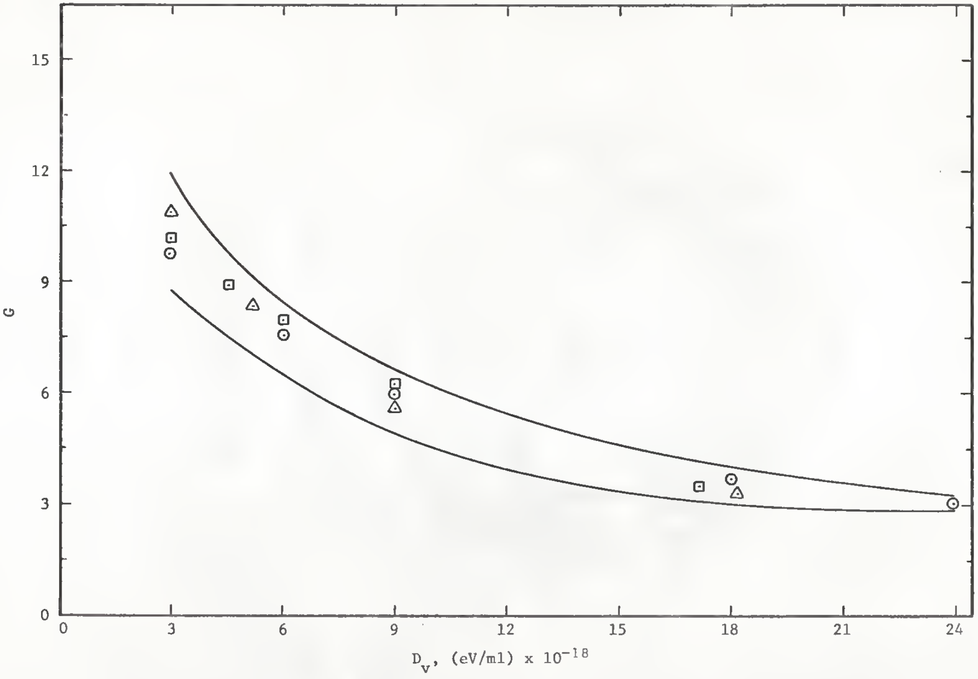

Fig. 15. Dependence of G(Mo^{5+}) on absorbed dose for solutions of HCl and H_2SO_4. ⊙, 2.41 N HCl 1.99 mM Mo^{5+}; △, 2.34 N H_2SO_4-.07 N HCl, 1.90 mM Mo^{5+}; ⊡, 0.77 N H_2SO_4-0.04 N HCl, 1.52 mM Mo^{5+}. All solutions aerated. Limits of error indicated by solid curves.

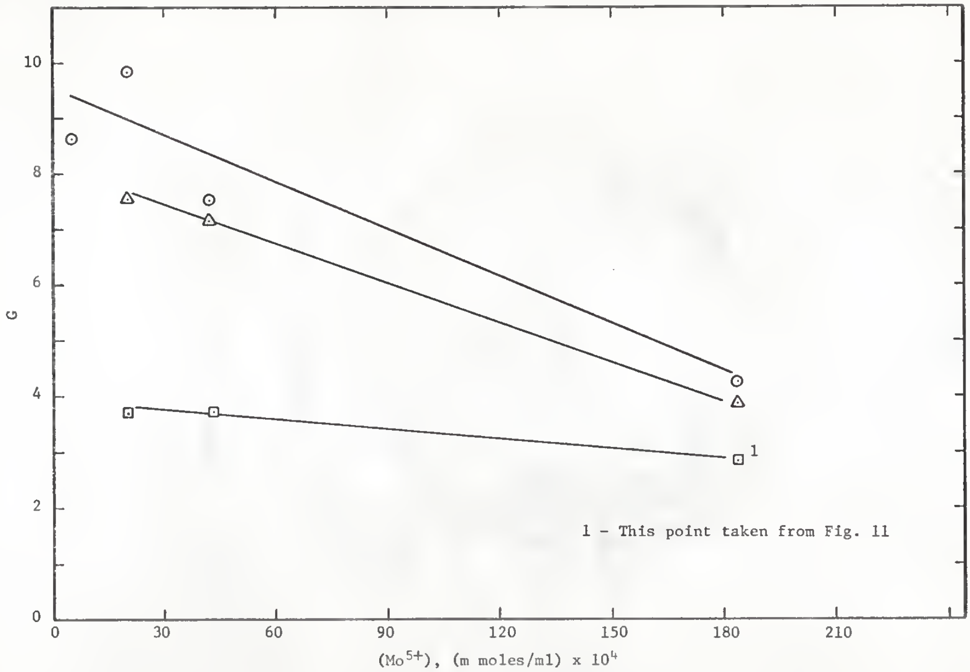

Fig. 16. Dependence of G(Mo^{5+}) on initial concentration of Mo^{5+}. ⊙, D_v = 2.96 x 10^{18} eV/ml; △, D_v = 5.92 x 10^{18}eV/ml; ⊡, D_v = 17.76 x 10^{18} eV/ml. All solutions 2.4 N HCl and aerated. Error bars omitted for clarity.

5.72 to 12.4 in the runs made. No raw data, sample calculations or statistical data on individual G-values were given for this table. The assumption of the constancy of G is therefore questionable.

Bhatacharya, Kar and Sur (13) found that in a photochemical study of molybdenum solution (using UV light), the velocity of the reaction which occurred was inversely proportional to the initial concentration of molybdenum ion. This is in qualitative agreement with the findings of this thesis.

5.5 Dependence of G on Type and Concentration of Acid

The G-value was determined for aqueous solutions of molybdenum (V) varying from 0.8 to 4.0 N in HCl and for 0.8 and 2.4 N H_2SO_4. The data and G-values obtained are tabulated in Table A-1 and illustrated in Fig. 17, which is a plot of the results of runs 16, 48-52, 58, and two points which were extrapolated from other figures as indicated. It should be noted that the runs made using H_2SO_4 still contained some HCl since the process used in preparing molybdenum (V) involved the reduction of molybdenum (VI) in 3 N HCl.

In Fig. 17 it is seen that the G-value decreases with increasing acid concentration and the decrease is most abrupt when going from a 3 to a 4 N acid solution.

As explained in section 3.5.6, the yield may be affected by acid concentration because of ionization or complex formation of the reactive species or solute. In section 5.2, the complex chemistry of molybdenum in aqueous solution is seen to be highly dependent on pH. The yield would therefore be expected to change with pH since the diffusion coefficients and rate constants of the molybdenum species would depend on the pH.

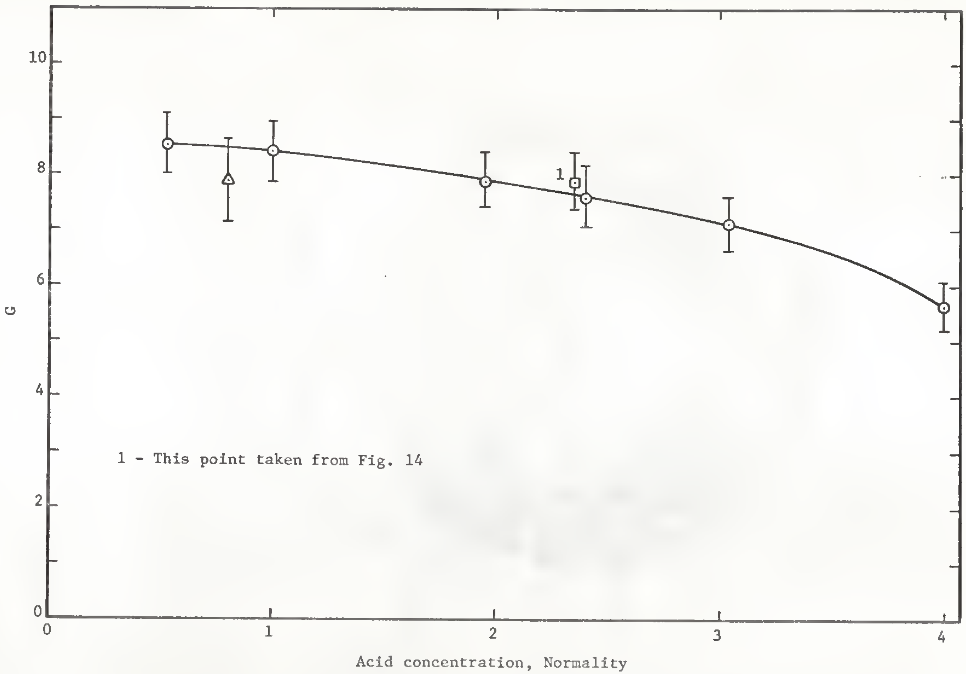

Fig. 17. Dependence of $G(Mo^{5+})$ on acid concentration. ⊙, HCl, concentration Mo^{5+} = 2.14 mM; △, H_2SO_4, concentration Mo^{5+} = 1.52 mM; ⊡, H_2SO_4, concentration Mo^{5+} = 1.90 mM; $D_v \cong 5.85 \times 10^{18}$ eV/ml; all solutions aerated.

It is interesting to note that Asai and Ikeguchi (7) found this same decrease of G with acid concentration for the $K_2Cr_2O_7$ dosimeter in the acid concentration range 0.8 to 4 N. Cr is also a member of group VI b of the periodic table.

Bagaenko and Moralev (16) studied the effect of X rays on aqueous solutions of HCl from 1-6 N. They found that there is a direct radiation action effect on the chloride ion which they postulated led to the formation of chlorine atoms and hydrated electrons which are converted into chlorine molecules and hydrogen atoms which subsequently take part in reactions with the solute. Extending their work to the aqueous ferrous chloride system, they found that in HCl medium the dosage curves for yield Fe^{3+} produced versus dose departed from linearity showing a decrease in oxidation rate as the dose was increased. They attributed this decrease in oxidation rate to the accumulation of Fe^{3+} in the system which formed an ionic complex with the chloride ion, which ionic complex was much more easily reduced by atomic hydrogen than the uncomplexed Fe^{3+}. Their results are in agreement with Schwarz and Hritz (76) who also found a non-linear response of Fe^{3+} yield with absorbed dose in HCl solutions. They also attributed the non-linearity of the dosage curve to the formation of iron (III)-chloride complexes.

Since Kraus and Nelson (49) found that, in anion exchange studies, Mo^{6+} does form strong complexes (pH dependent) with chloride ions, it is possible that the formation of these complexes leads to the reduction in G-value as the acid concentration is increased. A similar phenomenon occurs in ferrous chloride solutions.

It is interesting to note that Daniellson (21), in some anion exchange studies, found that molybdenum also forms strong complexes with the sulfate ion, the nature of which are pH dependent. Within the limits of experimetal accuracy no differences in the G-value for HCl or H_2SO_4 solutions were found in the overlapping range of acid concentrations studied (see Fig. 17).

5.6 Effect of Degassing on the G-Value

As described in section 4, samples of molybdenum (V) were deaerated before irradiation. The G-values of the deaerated samples were compared with the G-values of identical samples which were irradiated without degassing. The G-values of the degassed samples were consistently lower. The ratios of the G-values are listed in Table 3, which is based on runs 70-77.

Table 3. Ratios of G-values for Aerated and Deaerated Molybdenum (V) Samples.

Run	Time Irradiation	$G_{aerated}$	$G_{deaerated}$	$G_{deaerated}/G_{aerated}$
70 & 72	2 minutes	13.99	3.90	0.28
71 & 73	10 minutes	10.44	2.05	0.20
74 & 76	1 minute	11.12	2.18	0.20
75 & 77	5 minutes	11.23	2.80	0.25

The results in Table 3 indicate that the deficiency of oxygen in the deaerated solutions depressed the Mo^{6+} yield. It would appear therefore that any mechansim of reaction for the irradiated molybdenum system must include an oxygen effect. Section 3.5.4 describes in detail the manner in which oxygen enters into the reactions of the ferrous sulfate dosimeters For that dosimeter, the G-value is also found to decrease when the solution is deaerated.

Paddleford (66) also found a depressing of the G-value for the deaerated molybdenum samples in his studies using X rays.

5.7 Summary and Conclusions

1. The overall effect of the gamma irradiation of molybdenum (V) solutions is the oxidation of Mo^{5+} to Mo^{6+}.

2. Molybdenum (V) solutions will auto-oxidize to Mo^{6+} on standing in an air atmosphere.

3. The G-value is a function of absorbed dose in the range studied (0.3×10^{18} to 213×10^{18} eV/ml).

4. The G-value is a function of initial Mo^{5+} concentration over the concentration range 0.49 to 18.42 mM.

5. The G-value decreases with increasing acid concentration with the sharpest decrease occurring in HCl solutions in the range 3 N to 4 N.

6. The G-value decreases as oxygen is removed from the system, thus suggesting that oxygen enters into the mechanism of reaction for this system.

7. As a consequence of items 2-5 above, the aqueous molybdenum (V) system is not suitable for chemical dosimetry.

5.8 Suggestions for Further Work

The greatest single difficulty in the investigation of the effects of gamma radiation on aqueous molybdenum (V) solutions was the lack of a highly sensitive method of analysis for the irradiation yields. Recently, Wittick and Rechnitz (90) reported on the polarographic behavior of molybdenum (VI) in acidic chloride media. They investigated Mo^{6+} solutions in the concentration range 1×10^{-3} to 5×10^{-6} M and for acid solutions varying from 0.1 to 5.0 N

HCl. It would be of interest to test the applicability of their method for the direct quantitative determination of the yield of Mo^{6+}, thus avoiding measurement of small changes in Mo^{5+} concentration.

It was not the object of this investigation to study the kinetics and mechanism of the reaction occurring. However, it would be necessary to determine the mechanism and kinetics of the reaction if the results obtained in this study were to be fully exploited. One method of determining the overall reaction rate constant for the system would be to use the flow reactor system of Faw, McCabe and Isbin (28). The determination of G_{H_2} and $G_{H_2O_2}$ by means of gas chromatography would aid in the determination of the reaction mechanism since the $G(Mo^{6+})$ could then be related to the G-values for the products of water decomposition (see Section 3.4).

6.0 ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to Dr. R. E. Faw for his extensive advice, guidance, and encouragement throughout this study. Appreciation is expressed to Dr. S. Z. Mikhail for suggesting the problem. Thanks are also extended to Dr. W. R. Kimel for his extremely helpful and encouraging attitude and to Miss Shirley Wilson for typing the thesis under extremely difficult circumstances. Finally, the author expresses his gratitude to Mr. Robert Iotti for his particular contribution.

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8.0 APPENDICES

8.1 APPENDIX A

Experimental and Calculated Data

TABLE A-1

Experimental Data and Calculated* G-Values for Various Aqueous Molybdenum (V) Solutions Subjected To Cobalt-60 Gamma-Radiation.

Run	t_{irrad} (min.)	t_{ao} (hours) 1	V_i ml 2	V_f ml 3	C_i * $(\frac{mm}{ml})x10^4$ 4	C_f $(\frac{mm}{ml})x10^4$ 5	$\overline{\Delta C}_{ao}$ $(\frac{mm}{ml})x10^4$ 6	$\overline{\Delta C}$ $(\frac{mm}{ml})x10^4$ 7	$\sigma_{\overline{\Delta C}}$ $(\frac{mm}{ml})x10^5$ 8	D_v $(\frac{eV}{ml})x10^{-18}$ 9	Acid Type & Normality 10	$G(Mo^{5+})$ 11	σ_G	Temp ^oC 12
1	5	0.08	0.825	0.396	2.62	0.80	0.01	1.81	2.57	1.486	2.48-A	7.35	1.11	27
3	5	0.50	1.120	0.498	3.88	1.23	0.03	2.62	2.59	1.486	2.48-A	10.62	1.18	27
4	10	0.50	1.120	0.258	3.88	0.21	0.03	3.64	2.63	2.973	2.48-A	7.38	0.65	27
5	2	0.50	0.854	0.574	2.74	1.55	0.03	1.16	2.57	0.594	2.48-A	11.79	2.67	27
6	2	0.25	0.770	0.541	2.39	1.41	0.01	0.96	2.56	0.594	2.48-A	9.74	2.64	27
7	4	0.50	0.770	0.340	2.39	0.55	0.03	1.80	2.57	1.188	2.48-A	9.13	1.38	27
8	3	2.50	0.770	0.428	2.39	0.93	0.15	1.30	2.59	0.891	2.48-A	8.82	1.80	27
9	10	0.75	19.27	18.30	81.15	76.90	0.05	4.20	4.47	2.964	1.32-A	8.54	1.00	27
10	40	1.50	19.27	17.16	81.15	72.21	0.09	8.85	4.51	11.652	1.32-A	4.58	0.33	28
11	180	7.00	19.27	14.99	81.15	62.92	0.42	17.81	5.29	52.440	1.32-A	2.01	0.12	31
12	630	11.00	19.79	9.55	83.37	39.74	0.67	42.95	8.47	183.54	1.32-A	1.41	0.08	36
13	300	16.00	19.79	13.84	83.37	58.02	0.97	24.38	6.33	87.400	1.32-A	1.68	0.10	33
14	100	18.25	19.79	16.57	83.37	69.65	1.11	12.61	5.41	29.133	1.32-A	2.61	0.17	30
15	10	0.17	5.04	3.91	19.94	15.12	0.01	4.80	4.33	2.964	2.41-A	9.76	1.01	27
16	20	0.67	5.04	3.27	19.94	12.40	0.04	7.50	4.44	5.928	2.41-A	7.62	0.59	27
17	80	3.00	5.04	2.21	19.94	7.88	0.18	11.87	4.72	23.712	2.41-A	3.02	0.19	27

TABLE A-1 (continued)

Run	t_{irrad} (min.)	t_{ao} (hours)	V_i ml	V_f ml	C_i $(\frac{mm}{ml})\times10^4$	C_f $(\frac{mm}{ml})\times10^4$	$\overline{\Delta C}_{ao}$ $(\frac{mm}{ml})\times10^4$	$\overline{\Delta C}$ $(\frac{mm}{ml})\times10^4$	$\sigma_{\overline{\Delta C}}$ $(\frac{mm}{ml})\times10^5$	D_v $(\frac{eV}{ml})\times10^{-18}$	Acid Type & Normality	$G(Mo^{5+})$	σ_G	Temp °C
18	40	4.00	5.04	2.75	19.94	10.18	0.24	9.51	4.58	11.856	2.41-A	4.83	0.34	27
19	2	4.25	5.04	4.71	19.94	18.53	0.26	1.15	4.30	0.593	2.41-A	9.95	4.41	27
20	30	4.75	5.04	2.91	19.94	10.86	0.29	8.78	4.56	8.891	2.41-A	5.95	0.43	27
21	5	5.00	5.04	4.29	19.94	16.74	0.30	2.89	4.35	1.482	2.41-A	10.90	1.86	27
22	60	6.25	5.04	2.38	19.94	8.60	0.38	10.95	4.72	17.784	2.41-A	3.71	0.25	27
23	1	6.25	5.04	4.84	19.94	19.08	0.38	0.47	4.34	0.296	2.41-A	9.61	8.83	27
24	160	8.75	5.04	1.22	19.94	3.66	0.53	15.74	5.17	47.400	2.41-A	2.00	0.14	31
25	2	0.08	4.79	4.47	18.87	17.51	0.00	1.36	4.27	0.593	2.41-A	13.79	4.39	27
26	10	0.33	4.79	3.64	18.87	13.97	0.02	4.88	4.34	2.964	2.41-A	9.91	1.01	27
27	40	1.00	4.79	2.39	18.87	8.65	0.06	10.16	4.58	11.854	2.41-A	5.16	0.35	27
28	80	3.00	4.79	1.79	18.87	6.09	0.18	12.60	4.77	23.712	2.41-A	3.20	0.20	29
29	1	0.17	1.34	1.20	4.86	4.26	0.01	0.59	4.26	0.296	2.41-A	11.91	8.68	27
30	2	0.25	1.34	0.98	4.86	3.32	0.01	1.52	4.27	0.593	2.41-A	15.41	4.40	27
31	5	2.25	1.34	0.57	4.86	1.58	0.14	3.13	4.27	1.482	2.41-A	12.73	1.86	27
32	10	2.25	1.34	0.31	4.86	0.48	0.14	4.24	4.33	2.964	2.41-A	8.62	1.01	27
33	12	3.75	1.34	0.28	4.86	0.36	0.23	4.27	4.35	3.556	2.41-A	7.22	0.82	27
34	60	0.25	10.26	7.66	42.17	31.10	0.01	11.26	4.63	17.749	2.41-A	3.75	0.25	28

TABLE A-1 (continued)

Run	t_{irrad} (min.)	t_{ao} (hours)	V_i ml	V_f ml	C_i $(\frac{mm}{ml})\times10^4$	C_f $(\frac{mm}{ml})\times10^4$	$\overline{\Delta C}_{ao}$ $(\frac{mm}{ml})\times10^4$	$\overline{\Delta C}$ $(\frac{mm}{ml})\times10^4$	$\sigma_{\overline{\Delta C}}$ $(\frac{mm}{ml})\times10^5$	D_v $(\frac{eV}{ml})\times10^{-18}$	Acid Type & Normality	$G(Mo^{5+})$	σ_G	Temp °C
35	5	1.50	10.26	9.70	42.17	39.79	0.09	2.29	4.28	1.479	2.41-A	9.34	1.80	28
36	40	2.25	10.26	8.00	42.17	32.55	0.14	9.49	4.55	11.833	2.41-A	4.83	0.35	28
37	10	2.50	10.26	9.36	42.17	38.34	0.15	3.68	4.32	2.958	2.41-A	7.49	0.92	28
38	180	5.50	10.26	6.01	42.17	24.07	0.33	17.77	5.25	53.248	2.41-A	2.01	0.12	32
39	100	7.10	10.26	7.08	42.17	28.63	0.43	13.12	4.91	29.583	2.41-A	2.67	0.17	32
40	20	8.00	10.26	8.48	42.17	34.59	0.48	7.70	4.54	5.916	2.41-A	7.22	0.63	27
41	5	0.25	22.16	22.03	184.15	183.05	0.01	1.09	8.55	1.479	2.43-A	4.44	3.49	27
42	10	0.50	22.16	21.91	184.15	182.03	0.03	2.10	8.55	2.958	2.43-A	4.27	1.75	27
43	60	1.50	22.16	21.15	184.15	175.56	0.09	8.50	8.57	17.748	2.43-A	2.88	0.32	27
44	120	4.00	22.16	20.70	184.15	171.73	0.24	12.18	8.57	35.496	2.43-A	2.07	0.18	30
45	175	7.00	22.16	20.28	184.15	168.16	0.42	15.57	8.61	51.769	2.43-A	1.81	0.13	32
46	300	12.00	22.16	19.45	184.15	161.09	0.73	22.33	8.73	88.749	2.43-A	1.51	0.10	33
47	720	24.00	21.58	16.56	184.15	136.50	1.45	46.20	9.24	212.99	2.43-A	1.31	0.07	38
48	20	0.42	6.77	4.39	21.37	13.23	0.02	8.11	3.43	5.758	0.52-A	8.52	0.56	27
49	20	0.42	6.77	4.40	21.37	13.27	0.02	8.08	3.43	5.798	1.00-A	8.42	0.55	27
50	20	0.42	6.77	4.51	21.37	13.65	0.02	7.70	3.43	5.876	1.96-A	7.90	0.52	27
51	20	0.42	6.77	4.70	21.37	14.23	0.02	7.05	3.43	5.967	3.04-A	7.11	0.50	27

TABLE A-1 (continued)

Run	t_{irrad} (min.)	t_{ao} (hours)	V_i ml	V_f ml	C_i $(\frac{mm}{ml})x10^4$	C_f $(\frac{mm}{ml})x10^4$	$\overline{\Delta C}_{ao}$ $(\frac{mm}{ml})x10^4$	$\overline{\Delta C}$ $(\frac{mm}{ml})x10^4$	$\sigma_{\overline{\Delta C}}$ $(\frac{mm}{ml})x10^5$	D_v $(\frac{eV}{ml})x10^{18}$	Acid Type & Normality	$G(Mo^{5+})$	σ_G	Temp ^oC
52	20	0.42	6.77	5.10	21.37	15.66	0.02	5.69	3.43	6.044	4.00-A	5.66	0.44	27
53	1	0.05	4.67	4.83	15.16	14.74	0.02	0.40	5.48	0.292	0.77-B	8.30	6.31	27
54	3	0.10	4.67	4.44	15.16	13.41	0.03	1.72	5.48	0.875	0.77-B	11.82	3.82	27
55	30	0.67	4.67	2.24	15.16	5.88	0.23	9.05	5.49	8.748	0.77-B	6.23	0.49	27
56	60	3.00	4.67	1.69	15.16	3.97	1.03	10.16	5.94	16.496	0.77-B	3.50	0.27	28
57	10	3.50	4.67	3.16	15.16	8.99	1.21	4.96	6.09	2.916	0.77-B	10.21	1.36	27
58	20	4.00	4.67	2.32	15.16	6.12	1.38	7.66	6.27	5.832	0.77-B	7.92	0.76	27
59	15	4.33	4.67	2.62	15.16	7.15	1.49	6.52	6.40	4.374	0.77-B	8.96	0.99	27
60	15	6.00	4.67	2.39	15.16	6.36	2.07	6.73	7.14	4.374	0.77-B	9.24	1.09	27
†61	15		0.54	0.54							2.41-A			
64	1	0.50	6.07	5.78	18.95	17.95	0.08	0.92	3.43	0.304	2.34-C	18.13	6.84	27
65	3	0.67	6.07	5.42	18.95	16.72	0.10	2.12	3.45	0.909	2.34-C	14.06	2.37	27
66	30	1.67	6.07	3.49	18.95	10.12	0.25	8.57	3.47	9.089	2.34-C	5.66	0.36	27
67	60	3.17	6.07	2.90	18.95	8.10	0.48	10.36	3.58	18.257	2.34-C	3.42	0.22	27
68	10	3.50	6.07	4.29	18.95	12.86	0.53	5.56	3.60	3.043	2.34-C	11.00	1.00	27
69	17	4.50	6.07	3.77	18.95	11.08	0.68	7.19	3.71	5.173	2.34-C	8.37	0.60	27
70	2	0.08	5.91	5.81	21.11	20.72	0.00	0.08	4.06	0.591	2.41-A	3.90	3.04	27

TABLE A-1 (continued)

Run	t_{irrad} (min.)	t_{ao} (hours)	V_i ml	V_f ml	C_i $(\frac{mm}{ml})x10^4$	C_f $(\frac{mm}{ml})x10^4$	$\overline{\Delta C}_{ao}$ $(\frac{mm}{ml})x10^4$	$\overline{\Delta C}$ $(\frac{mm}{ml})x10^4$	$\sigma_{\overline{\Delta C}}$ $(\frac{mm}{ml})x10^5$	D_v $(\frac{eV}{ml})x10^{-18}$	Acid Type & Normality	$G(Mo^{5+})$	σ_G	Temp ^oC
71	10	0.67	5.91	5.64	21.11	20.06	0.04	1.01	4.07	2.954	2.41-A	2.05	0.83	27
72	2	1.00	5.91	5.54	21.11	19.67	0.06	1.37	3.88	0.591	2.41-A	13.99	4.01	27
73	10	1.25	5.91	4.58	21.11	15.91	0.08	5.12	3.91	2.954	2.41-A	10.44	0.95	27
74	1	4.00	5.91	5.82	21.11	20.76	0.24	0.11	4.10	0.295	2.41-A	2.18	2.10	27
75	5	4.00	5.91	5.64	21.11	20.18	0.24	0.69	4.10	1.477	2.41-A	2.80	1.69	27
76	1	7.00	5.91	5.66	21.11	20.14	0.42	0.55	3.99	0.295	2.41-A	11.12	8.15	27
77	5	7.00	5.91	5.09	21.11	17.93	0.42	2.76	4.01	1.477	2.41-A	11.23	1.72	27
78	30	8.00	5.91	8.43	21.11	11.48	0.48	9.14	4.15	8.863	2.41-A	6.20	0.42	28

*See Appendix C for sample calculations.

1. Auto-oxidation time of Mo^{5+} to Mo^{6+} by atmospheric oxygen; this is the time from when Mo^{5+} first titrated (V_i) to final titration time (V_f) after sample was irradiated. For deaerated samples, it is the time from when V_i taken to time sample evacuated.

2. Volume of $Ce(SO_4)_2$ required to oxidize Mo^{5+} to Mo^{6+} before sample was irradiated.
   Runs 1-8; Micro-pipette was used accurate to ± 0.001 ml.
   Runs 9-78; Burettes were used accurate to ± 0.01 ml.
   Runs 41-47; Aliquot titrated = 10 ml.
   All Other Runs; Aliquot titrated = 25 ml.
   All Runs; Volume of solution irradiated = 55 ml.

3. Volume $Ce(SO_4)_2$ required to oxidize Mo^{5+} to Mo^{6+} after sample was irradiated. Comments in 2 above apply.

4. Concentration of Mo^{5+} $[Mo^{5+}]$, calculated from V_i, before sample was irradiated.
    Runs 1-40; Normality of $Ce(SO_4)_2 = 0.01065$
    Runs 41-69; Normality of $Ce(SO_4)_2 = 0.00855$
    Runs 70-79; Normality of $Ce(SO_4)_2 = 0.00970$
    Runs 1-14 and 29-33; Titration blank = 0.22 ml.
    Runs 15-28 and 34-40; Titration blank = 0.36 ml.
    Runs 41-69; Titration blank = 0.53 ml.
    Runs 70-78; Titration blank = 0.47 ml.

5. $[Mo^{5+}]$, calculated from V_f, after sample was irradiated.

6. Change in $[Mo^{5+}]$ because of auto-oxidation only. See Appendix B for data on auto-oxidation rates of the various solutions.

7. Change in $[Mo^{5+}]$ because of radiation only; correction being made for change due to auto-oxidation.

8. Standard deviation of $\overline{\Delta C}$.
    Runs 1-8 (micro-pippette); deviation in volume difference $(V_i - V_f)$ assumed to $= \pm 0.06$ ml.
    All other runs; deviation volume difference $(V_i - V_f)$ assumed to $= \pm 0.10$ ml.

9. Dose absorbed by molybdenum solution. Experiment performed during the time period 18 August to 5 September, 1965. The exposure dose rate in the Cobalt-60 gamma cell decreased from 2.848×10^5 to 2.828×10^5 roentgens/hr during this period.

10. A signifies an HCl solution.
    B signifies a solution composed of 0.77 N H_2SO_4 and 0.04 N HCl.
    C signifies a solution composed of 2.34 N H_2SO_4 and 0.07 N HCl.

11. $G(Mo^{5+}) = \frac{\text{Number of } Mo^{5+} \text{ ions oxidized to } Mo^{6+}}{\text{100 eV absorbed Cobalt-60 radiation}}$

12. Temperature of solution (± 0.5°C) upon completion of irradiation.

** $(\frac{mm}{ml})$ means $(\frac{\text{m moles}}{\text{milliliter}})$.

† This run was made using Mo^{6+} to see if the radiation reduced Mo^{6+}.

TABLE A-2

Levels of Parameters Investigated*.

Irradiation time	Absorbed Dose	Initial Concentration Mo^{5+}	Acid Concentration
minutes	(eV/ml)x10^{-18}	(m moles/ml)x10^{4}	normality
1	0.29	2.39	0.52 (HCl)
2	0.59	3.88	1.00 (HCl)
5	1.48	4.86	1.96 (HCl)
10	2.95	15.16	2.4 (HCl)
15	4.37	18.87	3.04 (HCl)
20	5.93	18.95	4.00 (HCl)
30	8.89	19.94	0.77 (H_2SO_4)
40	11.86	21.11	2.34 (H_2SO_4)
60	17.78	21.37	
80	23.71	42.17	
100	29.13	81.15	
120	35.50	83.37	
160	47.40	184.15	
180	52.44		
300	87.40		
630	183.54		
720	212.99		

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*Taken from Table A-1.

APPENDIX B

8.2 Auto-oxidation Data for Molybdenum (V) Solutions

TABLE B-1

Raw Data and Calculated Auto-oxidation Rates for Molybdenum (V) Solutions (air-equilibrated).

ΔV ceric sulfate required	Temp.	Normality ceric sulfate	t_{ao} Auto-oxidation time	Aliquot Mo^{5+} titrated	Change Mo^{5+} concentration	Acid concentration	Auto-oxidation rate Mo^{5+}
ml	°C		hr	ml	m moles/ml	normality	$(\frac{\text{m moles}}{\text{ml-hr}})\times 10^6$
0.381	28	0.01065	20	25	1.63×10^{-4}	2.4 N HCl	8.12
0.25	28	0.01065	24	25	1.07×10^{-4}	2.4 N HCl	4.44
0.58	28	0.00855	36	25	1.97×10^{-3}	2.4 N HCl	5.46
0.13	28	0.00970	8	25	5.00×10^{-5}	2.4 N HCl	6.23
0.17	35	0.01065	10	25	7.26×10^{-5}	2.4 N HCl	7.26
0.61	28	0.00855	6	25	2.07×10^{-4}	0.8 N H_2SO_4	34.5
0.21	28	0.00855	5	25	7.20×10^{-5}	2.3 N H_2SO_4	14.4

The auto-oxidation time for deaerated samples was taken as the time from the determination of V_i to the time sample was evacuated.

The auto-oxidation rate was calculated from the expression:

$$\text{Auto-oxidation rate} = \frac{V(\text{ml}) \times \text{Norm } Ce(SO_4)_2 \ (\frac{\text{meq}}{\text{ml}})^*}{\text{aliquot (ml)} \times t_{ao} \text{ (hr)}} \ (\frac{\text{m moles}}{\text{ml-hr}}) \qquad \text{(B-1)}$$

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*For the reaction of Ce^{4+} with Mo^{5+}, $\frac{\text{meq}}{\text{ml}} = \frac{\text{m moles}}{\text{ml}}$.

APPENDIX C

8.3 Sample Calculations

The following listing is of the original experimental data from run 15 (Table A-1):

Date run		25 August 1965
Sample irradiation time		10 minutes
Type acid and normality		2.41 N HCl
Vol. $Ce(SO_4)_2$ required before sample irrad. (V_i)		5.02 ml
		5.06 ml
	avg.	5.04 ml
Vol. $Ce(SO_4)_2$ required after sample irrad. (V_f)		3.93 ml
		3.89 ml
	avg.	3.91 ml
Normality of $Ce(SO_4)_2$		0.01065
Volume solution irradiated		55 ml
Aliquot titrated		25 ml
Titration blank		0.36 ml
Time run started (V_i taken)		1030
Time run stopped (V_f taken)		1035
$\therefore$ t_{ao} (auto-oxidation time)		15 min.
Final temperature irradiated sample		27 ± 1°C
Room temperature		27 ± 1°C

8.3.1 Exposure Dose

The exposure dose rate for the gamma-cell was determined by Kumar*. He used the same type irradiation vessel and the same position in the cell as used in this thesis. He found the exposure dose rate to be 2.676 x 10^5 roentgens/hour on 7 February 1966.

The exposure dose rate of the gamma-cell decreases exponentially with time; the decay constant of cobalt-60 being 0.01096 month^{-1}.

Correcting the exposure dose rate to the starting date of this run, (25 August 1965), we get:

$$R_A(r/hr) = R_{AO}\, e^{-\lambda t} , \tag{C-1}$$

$$R_{AO} = \frac{R_A}{e^{-\lambda t}} ,$$

$$R_{AO}(r/hr) = \frac{2.676 \times 10^5}{e^{-(0.01096 \text{ mos}^{-1})(5.66 \text{ mos})}} ,$$

$$R_{AO}(\text{roentgens/hr}) = 2.843 \times 10^5 \text{ as of 25 August 1965.}$$

8.3.2 Absorbed Dose**

8.3.2.1 Calculation of $\overline{(Z/A)}_M$

The density of 2.41 N HCl was taken from page 2008 of reference (44),

$$\rho = 1.038 \text{ g/ml.}$$

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*Kumar, S. S., Fsst Neutron Radiolysis of Heavy Water, Masters Thesis, Kansas State University, Manhattan, Kansas, pp. 77-78 (1967).

**See section 3.6 for development of equations used.

Basis: 1 ml solution

$$N_{HCl}\left(\frac{\text{molecules}}{\text{ml}}\right) = \frac{\left(\frac{\text{g HCl}}{\text{g solution}}\right)\left(\rho_{\text{solution}}\frac{\text{g}}{\text{ml}}\right)\left(N_o\frac{\text{molecules}}{\text{mole}}\right)}{\left(M_{HCl}\frac{\text{g HCl}}{\text{mole}}\right)}\ , \tag{C-2}$$

$$\left(\frac{\text{g HCl}}{\text{g solution}}\right) = \frac{\left(N\frac{\text{meq}}{\text{ml}}\right)\left(\frac{\text{g}}{\text{meq}}\right)}{\left(\rho_{\text{solution}}\frac{\text{g}}{\text{ml}}\right)}\ , \tag{C-3}$$

$$N_{HCl} = \frac{(2.41\text{ N})(.0365\ \frac{\text{meq}}{\text{ml}})(6.023 \times 10^{23}\ \frac{\text{molecules}}{\text{mole}})}{(36.5\text{ g/mole})}$$

$$N_{HCl} = 1.493 \times 10^{21}\text{ molecules/ml}\ ,$$

$$N_{H_2O} = \frac{\left(\frac{\text{g H}_2\text{O}}{\text{g solution}}\right)(\rho_{\text{solution}})(N_o)}{(M_{H_2O})} \tag{C-4}$$

$$\frac{\text{g H O}}{\text{g solution}} = 1 - \frac{\text{g HCl}}{\text{g solution}} = 1 - 0.0871 = 0.9129,$$

$$N_{H_2O} = \frac{(0.9129)(1.039)(6.023 \times 10^{23})}{(18)}\ ,$$

$$N_{H_2O} = 3.174 \times 10^{22}\text{ molecules/ml},$$

$$N_H\text{ (from HCl)} = 0.149 \times 10^{22}\text{ atoms/ml},$$

$$N_H\text{ (from H}_2\text{O)} = 2 \times N_{H_2O} = 6.348 \times 10^{22}\text{ atoms/ml},$$

$$N_H\text{ (in solution)} = 6.497 \times 10^{22}\text{ atoms/ml},$$

$$N_O\text{ (from H}_2\text{O)} = 3.174 \times 10^{22}\text{ atoms/ml},$$

N_{Cl} (from HCl) $= 0.149 \times 10^{22}$ atoms/ml.

$$(N \cdot A)_{Cl} \text{ (g)} = 0.149 \times 10^{22} \times \frac{35.46}{6.02 \times 10^{23}} = \frac{5.294 \times 10^{22}}{6.02 \times 10^{23}}$$

$$(N \cdot A)_{H} \text{ (g)} = 6.497 \times 10^{22} \times \frac{1.008}{6.02 \times 10^{23}} = \frac{6.549 \times 10^{22}}{6.02 \times 10^{23}}$$

$$(N \cdot A)_{O} \text{ (g)} = 3.174 \times 10^{22} \times \frac{16.00}{6.02 \times 10^{23}} = \frac{50.784 \times 10^{22}}{6.02 \times 10^{23}}$$

$$\frac{\text{Total wt}}{\text{1 ml solution}} \text{ (g)} = \frac{62.627 \times 10^{22}}{6.02 \times 10^{23}}$$

$$W_{Cl} \text{ (weight fraction Cl)} = \frac{\dfrac{5.294 \times 10^{22}}{6.02 \times 10^{23}}}{\dfrac{62.627 \times 10^{22}}{6.02 \times 10^{23}}}$$

$w_{Cl} = 0.0845$

$w_{H} = 0.1046$

$w_{O} = 0.8109$

$$(\overline{Z/A})_M = w_{Cl} (Z/A)_{Cl} + w_H (Z/A)_H + w_O (Z/A)_O \,, \tag{C-5}$$

$(Z/A)_{Cl} = 17/35.46 = 0.4795$,

$(Z/A)_{H} = 1/1.008 = 0.9921$,

$(Z/A)_{O} = 8/16 = 0.5000$.

$(\overline{Z/A})_M = (0.0845)(0.4795) + (0.1046)(0.9921) + (0.8109)(0.5000)$

$(\overline{Z/A})_M = 0.550$ for 2.41 N HCl at 27°C.

The concentration of molybdenum in this solution is too low to contribute to $\overline{(Z/A)}_M$ as explained in aection 3.6.

8.3.2.2 Calculation of Absorbed Dose

Using equation (52) for D_M,

$$D_M = 0.877\ R_{AO} \frac{\overline{(Z/A)}_M}{\overline{(Z/A)}_{air}}\ (\text{rada/hr}) \ , \tag{52}$$

$$D_M = (0.877)(2.843 \times 10^5) \frac{(0.550)}{(0.499)^*} \ ,$$

$$D_M = 2.750 \times 10^5 \text{ rads/hr} \ ,$$

$$D_M = 4.574 \times 10^4 \text{ rads/10 min} \ ,$$

$$D_v = (4.574 \times 10^4 \text{ rads/ 10 min}) \frac{(6.242 \times 1.038 \times 10^{13} \text{ eV/ml})}{(1 \text{ rad})} \ ,$$

$$D_v = 2.964 \times 10^{18} \text{ eV/ml-10 min.}$$

8.3.3 Calculation of $\overline{\Delta C}$

$$C_i = (V_i\text{-blank})(\text{ml}) \frac{N \cdot Ce(SO_4)_2\ (\text{meq/ml})}{\text{aliquot titrated (ml)}}\ (\text{meq/ml}) \tag{C-6}$$

meq/ml = m moles/ml aince the oxidation reaction occurring in the titrimetric analyaia ia,

$$Mo^{5+} + Ce^{4+} \rightarrow Mo^{6+} + Ce^{3+} \ .$$

---

*From page 88 of reference (82).

$$C_i = \frac{(5.04\ \text{ml} - 0.36\ \text{ml}) \times (.01065\ \text{meq/ml})}{25\ \text{ml}}\ ,$$

$$C_i = 19.94 \times 10^{-4}\ \text{m moles/ml}\ .$$

$$C_f = (V_f\text{-blank})\ (\frac{N\ Ce(SO_4)_2}{\text{aliquot}})\ , \qquad \text{(C-7)}$$

$$C_f = (3.91 - 0.36)\ (\frac{.01065}{25})\ ,$$

$$C_f = 15.12 \times 10^{-4}\ \text{m moles/ml}\ .$$

$\overline{\Delta C}_{ao}$ = auto-oxidation rate* for 2.41 N HCl at 27°C x t_{ao}

$$\overline{\Delta C}_{ao} = 6.06 \times 10^{-6}\ \frac{\text{m moles}}{\text{ml-hr}}\ (\Delta C_{ao}) \times 0.25\ \text{hr} \qquad \text{(C-8)}$$

$$\overline{\Delta C}_{ao} = 1.5 \times 10^{-6}\ \text{m moles/ml}$$

$$\overline{\Delta C} = C_i - (C_f + \overline{\Delta C}_{ao}) \qquad \text{(C-9)}$$

$$\overline{\Delta C} = 19.94 \times 10^{-4} - (15.12 \times 10^{-4} + 0.02 \times 10^{-4})\ (\frac{\text{m moles}}{\text{mole}})$$

$$\overline{\Delta C} = 4.80 \times 10^{-4}\ \text{m moles/ml}\ .$$

8.3.4 Calculation of G-Value

$$G(Mo^{5+}) = \frac{(\overline{\Delta C}\ \text{m moles/ml})(N_o\ \text{molecules/m moles})\ (100)}{D_v(\text{eV/ml})} \qquad (59)$$

---

[*] See Appendix B (Section 8.2) for these rates.

For an irradiation time of 10 minutes,

$$G(\mathrm{Mo}^{5+}) = \frac{(4.80 \times 10^{-4})(6.023 \times 10^{20})(100)}{(2.764 \times 10^{18})} ,$$

$$G(\mathrm{Mo}^{5+}) = 9.76 \left(\frac{\text{ions } \mathrm{Mo}^{5+} \text{ oxidized}}{\text{100 eV absorbed energy}}\right) .$$

8.3.5 Statistics[*][†][**]

8.3.5.1 Calculation of $\sigma_{\overline{\Delta C}}$

$$\overline{\Delta C} = (C_i - C_f) - \overline{\Delta C}_{ao} = \Delta C - \overline{\Delta C}_{ao} , \tag{C-9}$$

$$\sigma_{\overline{\Delta C}}^2 = \left(\frac{\partial \overline{\Delta C}}{\partial \Delta C}\right)^2_{\overline{\Delta C}_{ao}} \sigma^2_{\Delta C} + \left(\frac{\partial \overline{\Delta C}}{\partial \overline{\Delta C}_{ao}}\right)^2_{\Delta C} \sigma^2_{\overline{\Delta C}_{ao}} , \tag{C-10}$$

---

[*] The statistical method is that given in Mickley, Sherwood and Reed (60).

[†] N in this subsection refers to normality NOT number of molecules or atoms/ml.

[**] The standard deviation of the yield ($\sigma_{\overline{\Delta C}}$), as calculated in this subsection and incorporated in Table A-1 and Figures 7-17, reflects only the maximum possible titration errors involved in obtaining $\overline{\Delta C}$.

A more realistic estimate of the standard deviation of the yield (Y in equation 56 or $\overline{\Delta C}$ in equation 59 of Section 3.6) can be obtained from the limited amount of replicate data available. Using replicate data analysis would account for differences in the experiments run under identical conditions (systematic errors) as well as titration errors. This replicate data analysis has been performed in Section 8.3.6.

$$\sigma^2_{\overline{\Delta C}} = \sigma^2_{\Delta C} + \sigma^2_{\overline{\Delta C}_{ao}} \qquad \text{(C-11)}$$

$$\Delta C = \frac{(V_i - V_f)(\mathrm{ml}) \times N(Ce(SO_4)_2)\ (\mathrm{meq/ml})}{\text{aliquot (ml)}} = \frac{\Delta V \times N}{25\ \mathrm{ml}}\ , \qquad \text{(C-12)}$$

$$\sigma^2_{\Delta C} = \left(\frac{\partial \Delta C}{\partial \Delta V}\right)^2_N \sigma^2_{\Delta V} + \left(\frac{\partial \Delta C}{\partial N}\right)^2_{\Delta V} \sigma^2_N\ , \qquad \text{(C-13)}$$

$$\sigma^2_{\Delta C} = \left(\frac{N}{25}\right)^2 \sigma^2_{\Delta V} + \left(\frac{\Delta V}{25}\right)^2 \sigma^2_N\ . \qquad \text{(C-14)}$$

$$\overline{\Delta C}_{ao} = \text{auto-oxidation rate } (\Delta C_{ao})_o \times t_{ao}\ ,$$

$$\sigma^2_{\overline{\Delta C}_{ao}} = {t_{ao}}^2\, \sigma^2_{\Delta C_{ao}} + \Delta C^2_{ao}\, \sigma^2_{t_{ao}}\ , \qquad \text{(C-15)}$$

It was assumed that the accuracy in reading the burette and reproducing the end point in the titration was ± 0.05 ml for both V_1 and V_f. The uncertainty in ΔV is then ± 0.10 ml, i.e.,

$$\sigma_{\Delta V} = 0.10\ \mathrm{ml}.$$

The following values for the normality of $Ce(SO_4)_2$ were obtained for three samples:

$0.01072\ N_1$

$0.01082\ N_2$

$0.01041\ N_3$

Average normality = 0.01065 N.

$$\sigma_N^2 = \frac{\sum^n (N_i - N)^2}{n} , \tag{C-16}$$

$$\sigma_N^2 = \frac{(0.49 \times 10^{-8}) + (2.89 \times 10^{-8}) + (5.76 \times 10^{-8})}{3} ,$$

$$\sigma_N^2 = 3.05 \times 10^{-8} \text{ (meq/ml)}^2 ,$$

$$\sigma_N = 1.75 \times 10^{-4} \text{ meq/ml}^* .$$

The following values of auto-oxidation rates (ΔC_{ao_i}) were obtained for four determinations, (Appendix B),

8.12×10^{-6} m mole/ml-hr

4.44×10^{-6} m mole/ml-hr

5.46×10^{-6} m mole/ml-hr

6.23×10^{-6} m mole/ml-hr

Avg. auto-oxidation rate (ΔC_{ao}) = 6.06×10^{-6} m moles/ml-hr.

$$\sigma_{\Delta C_{ao}}^2 = \frac{\sum^n (\Delta C_{ao_i} - \Delta C_{ao})}{n} , \tag{C-17}$$

$$\sigma_{\Delta C_{ao}}^2 = 1.79 \times 10^{-12} \text{ (m moles/ml-hr)}^2 ,$$

---

[*] Using original experimental data, the following values of σ_N for the other solutions are obtained:

σ_N for 0.00855 N $Ce(SO_4)_2$ = 2.44×10^{-5} (meq/ml) ,

σ_N for 0.00970 N $Ce(SO_4)_2$ = 1.01×10^{-4} (meq/ml) .

$$\sigma_{\Delta C_{ao}} = 1.34 \times 10^{-6} \text{ m moles/ml-hr.}^{*}$$

$$\sigma^2_{\Delta C} = \left(\frac{N}{25}\right)^2 \sigma^2_{\Delta V} + \left(\frac{\Delta V}{25}\right)^2 \sigma^2_{N} , \qquad \text{(C-18)}$$

$$\sigma^2_{\Delta C} = \left(\frac{0.01065}{25}\right)^2 (0.10)^2 + \left(\frac{1.13}{25}\right) (1.75 \times 10^{-4})^2 ,$$

$$\sigma^2_{\Delta C} = 18.78 \times 10^{-10} \text{ (meq/ml)}^2 .$$

$$\sigma^2_{\overline{\Delta C}_{ao}} = t_{ao}{}^2 \, \sigma^2_{\Delta C_{ao}} = (0.25)^2 (1.34 \times 10^{-6})^2 , \qquad \text{(C-19)}$$

$$\sigma^2_{\overline{\Delta C}_{ao}} = (0.0005 \times 10^{-10}) \text{ (meq/ml)}^2 .$$

$$\sigma^2_{\overline{\Delta C}} = \sigma^2_{\Delta C} + \sigma^2_{\overline{\Delta C}_{ao}} , \qquad \text{(C-11)}$$

$$\sigma^2_{\overline{\Delta C}} = 18.78 \times 10^{-10} + 0.0005 \times 10^{-10} ,$$

$$\sigma^2_{\overline{\Delta C}} = 18.78 \times 10^{-10} \text{ (m moles/ml)}^2 ,$$

$$\sigma_{\Delta C} = 4.34 \times 10^{-5} \text{ (m moles/ml)} .$$

8.3.5.2 Calculation of σ_G

$$G = \frac{(\overline{\Delta C})(N_o)(100)}{(D_v)} . \qquad \text{(59)}$$

---

[*] Using the data from Appendix B, the following values of $\sigma_{\Delta C_{ao}}$ for the other solutions are obtained:

$\sigma_{\Delta C_{ao}}$ for solution B = 0.76×10^{-5} meq/ml ,

$\sigma_{\Delta C_{ao}}$ for solution C = 0.32×10^{-5} meq/ml .

$$\sigma_G^2 = \left(\frac{100\ N_o\ \overline{\Delta C}}{D_v^{\,2}}\right)^2 \sigma_{D_v}^2 + \left(\frac{100\ N_o}{D_v}\right)^2 \sigma_{\overline{\Delta C}}^2 \quad , \tag{C-20}$$

The accuracy of the Fricke dosimeter is ± 5 per cent (31), i.e., we get for the uncertainty on D_v,

$$\sigma_{D_v} = (0.05) \times 2.964 \times 10^{18} \text{ eV/ml-10 min} \ ,$$

$$\sigma_{D_v} = 0.148 \times 10^{18} \text{ eV/ml-10 min} \ .$$

Using equation (C-20), we get

$$\sigma_G^2 = \left[\frac{(100 \times 6.023 \times 10^{20} \times 4.80 \times 10^{-4})}{(2.964 \times 10^{18})^2}\right]^2 (0.148 \times 10^{18})^2$$

$$+ \left[\frac{(100 \times 6.023 \times 10^{20})}{(2.964 \times 10^{18})}\right]^2 (18.78 \times 10^{-10}) \ ,$$

$$\sigma_G^2 = 0.238 + 0.774 \ ,$$

$$\sigma_G^2 = 1.01 \ ,$$

$$\sigma_G = 1.01 \left(\frac{\text{ions Mo}^{5+} \text{ oxidized}}{\text{100 eV energy absorbed}}\right) .$$

8.3.6 Calculation of Uncertainties Using Replicate Data Analysis

The $\sigma^2_{\overline{\Delta C}}$ (equation C-20) computed in Section 8.3.5 reflect only the maximum possible titration errors involved in obtaining $\overline{\Delta C}$. A more realistic estimate of the uncertainty in the yield $(\overline{\Delta C})$ can be made by analysis of the limited amount of replicate data available. This analysis is presented below.

TABLE C-1

Replicate Data Used in Estimating the Uncertainty* of the Yield ($\overline{\Delta C}$)

Run	Irradiation Time minutes	Initial [Mo^{5+}] ($\frac{\text{m moles}}{\text{ml}}$)x$10^4$	[HCl] normality	$\overline{\Delta C}$ ($\frac{\text{m moles}}{\text{ml}}$)x$10^4$	G-Value
19	2	19.9	2.41	1.15	9.95
25	2	18.9	2.41	1.36	13.79
15	10	19.9	2.41	4.80	9.76
26	10	18.9	2.41	4.88	9.91
18	40	19.9	2.41	9.51	4.83
27	40	18.9	2.41	10.16	5.16
17	80	19.9	2.41	11.87	3.02
28	80	18.9	2.41	12.60	3.20

TABLE C-2

Uncertainties* of the Yields and G-Values as Computed from the Replicate Data in Table C-1

Run	Uncertainty* of $\overline{\Delta C}$	Uncertainty* of G
19 25	1.48x10^{-5}	2.72
15 26	0.56x10^{-5}	0.11
18 27	4.60x10^{-5}	0.23
17 28	5.16x10^{-5}	0.13

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[*] 50 percent confidence limits for an individual measurement.

TABLE C-3

Comparison of Uncertainties as Calculated Using Methods of Sections 8.3.5 and 8.3.6

Run	Uncertainty of $\overline{\Delta C}$ (%) (From § 8.3.5)	Uncertainty of $\overline{\Delta C}$ (%) (From § 8.3.6)	Uncertainty of G (%) (From § 8.3.5)	Uncertainty of G (%) (From § 8.3.6)
19	± 34.1%	± 8.7%	± 44.3%	± 27.3%
15	± 8.9%	± 1.2%	± 10.3%	± 1.1%
18	± 4.7%	± 4.5%	± 7.0%	± 4.8%
17	± 3.9%	± 4.3%	± 6.3%	± 4.3%

It appears by analysis of Table C-3 that the method of computing $\sigma_{\overline{\Delta C}}$ and σ_G used in Section 8.3.5 gives a conservative estimate of the standard deviation for both the G-value and $\overline{\Delta C}$.

EFFECTS OF GAMMA RADIATION ON AQUEOUS SOLUTIONS OF MOLYBDENUM (V) AND (VI)

by

FRANCIS JAMES LIBERATORI

B. S. (Chemistry), St. Josephs College, 1956

B. S. (Nuclear Engineering), Kansas State University, 1964

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ABSTRACT

The main purpose of this investigation was to study the effects of gamma rays on the aqueous molybdenum (V)-molybdenum (VI) system and to evaluate the suitability of this system for chemical dosimetry. In particular, the dependence of the G-value for oxidation of molybdenum (V) was investigated for the following variables: absorbed dose, initial molybdenum (V) concentration, pH, and concentration of dissolved oxygen.

Molybdenum (V) solutions of different composition and acidity were irradiated in a cobalt-60 gamma irradiation and the yield of molybdenum (VI) was determined by titrimetric analysis. Both air equilibrated and deaerated samples were analyzed.

The following results were obtained:

1. Gamma rays oxidize Mo^{5+} to Mo^{6+} in acidic aqueous media.

2. Mo^{5+} oxidizes to Mo^{6+} in the presence of oxygen therefore G-values for air-equilibrated solutions must be corrected for auto-oxidation.

3. The G-value is a function of absorbed dose in the range studied (0.3×10^{18} to 213×10^{18} eV/ml).

4. The G-value is a function of initial Mo^{5+} concentration in the concentration range studied (0.49 to 18.42 mM).

5. The G-value decreases with increasing acid concentration with a particularly large decrease occurring in HCl solutions in the range 3 N to 4 N.

6. The G-value decreases when oxygen is removed from the solution thus suggesting that oxygen enters into the mechanism of chemical reaction.

It was concluded that as a consequence of items 2-5 above, the aqueous molybdenum (V) system is not suitable for chemical dosimetry.

Suggestions for further investigation of this system have been made with respect to a more accurate method of determining the Mo^{6+} yield and to methods for elucidating the chemical reaction mechanisms governing the radiolysis of the molybdenum (V)-molybdenum (VI) aqueous system.