

FERROUS AND CERIC SULPHATE DOSIMETERS: INTERPRETATION OF THE EFFECT OF RADIATION QUALITY

DOSÍMETROS DO SULFATO FERROSO E SULFATO CÉRICO:
INTERPRETAÇÃO DO EFEITO DA QUALIDADE DA RADIAÇÃO

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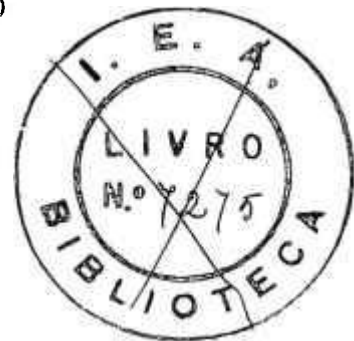
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INTERPRETATION OF THE EFFECT OF RADIATION QUALITY x

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INTRODUCTION

The ferrous and ceric sulphate dosimeters are widely used chemical dosimeters for measurements associated with radiation chemistry. The numbers $G_{\text{Fe}^{+3}}$ of ferric ions produced in the former and $G_{\text{Ce}^{+3}}$ of cerous ions in the latter, per 100 eV of absorbed energy, depend on the quality of the radiation used⁽¹⁻⁹⁾. It has been customary⁽¹⁰⁾ to interpret this effect assuming that for radiations of sufficiently low LET the tracks are formed by non-overlapping spherical spurs of free radicals, whereas for radiations of sufficiently high LET the spur overlap produces axially homogeneous cylindrical tracks. The radicals in the spurs or tracks can react among themselves or diffuse away from each other, reacting with the solutes present. On this basis, the molecular yields in the isolated spherical spur situation should be lower than in the cylindrical track one, since in the latter the radical concentration is on average higher, due to the spur overlap. This kind of model has been qualitatively successful⁽¹⁰⁾ in interpreting the variation of primary H_2 , H_2O_2 , H and OH yields with radiation quality, and hence in interpreting the variation of the $G_{\text{Fe}^{+3}}$ and $G_{\text{Ce}^{+3}}$ yields mentioned above.

In this kind of interpretation, three main facts are neglected. First, the fact that for a given radiation there exists a whole spectrum of local energy dissipation is not considered. This spectrum is due to the slowing down of incident charged particles as well as to the formation of secondary, tertiary, etc. electrons (δ rays) of varying energies. As pointed out by Burch⁽¹¹⁾, however, this spectrum is very important. For example, for Co^{60} gamma-rays 25% of the energy is dissipated by electrons of energy less than 800 eV, for which a cylindrical track model rather than an isolated spherical spur one should be used. A second fact neglected is the difference between the properties and possible initial distributions of H and OH . Finally, secondary reactions between radicals and molecular products of previous radical reactions are not considered.

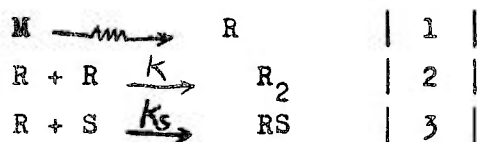
In a recent paper, Burch⁽¹²⁾ has done some calculations in which he attempted to take these three facts into account. His approach has been examined and criticized elsewhere⁽¹³⁾. The main objections to his calculation are

two-fold: he considers all tracks as being cylindrical one obeying Jeffe's⁽¹⁴⁾ prescribed diffusion law, and that the secondary reactions occur in separate stages which do not overlap in time with each other. Furthermore, he determines certain model parameters empirically, rather than from first principles, using radiations of widely different quality, and then calculates the yields for intermediate kinds of radiation. This gives the approach an interpolative rather than fundamental nature.

With the use of high-speed digital computers in diffusion kinetics^(13,15,16) it has become possible to solve the diffusion-kinetic equations for a one- or a two-radical model rigorously, including secondary reactions. In a detailed interpretation of the variation of yield with radiation quality, these solutions should be combined with a consideration of the spectrum of local energy dissipation. In the present paper this is done for a simple one-radical model, without secondary reactions, in order to understand how inclusion of this spectrum affects the calculated results. Obviously, detailed agreement with experiment could only be expected for a more realistic model. Nevertheless, a comparison of the results with experiment is given as a means to indicate the direction of future calculations.

Mathematical formulation of the one-radical model^(13,15)

It is assumed that passage of the radiation through the dosimeter produces a single kind of radical R (whose properties are intermediate between those of H and OH). These can react with themselves or diffuse away and react with scavenger S. The overall mechanism is thus



where M represents the major component of the system (i.e., water). Equation | 1 | is not intended to be stoichiometric, but only to indicate that radicals R are formed by passage of high energy radiation through the system under consideration. The problem is to determine what fraction of the radicals R formed by reaction | 1 | undergoes reaction | 2 | and what fraction undergoes reaction | 3 |.

Let c represent the concentration of radicals R at any point P of coordinates x, y, z , and at any time t . Let c_s be the concentration of scavenger S, which is assumed constant. Let us assume that the dose-rate is sufficiently low so that radicals originating in tracks formed by different incident particles or quanta do not overlap. Under these conditions, the equation obeyed by c is (13,17).

$$\frac{\partial c}{\partial t} = D \nabla^2 c - kc^2 - k_s c_s c \quad (1)$$

Here, D represents the diffusion coefficient of radicals R, and ∇^2 is the usual Laplacian operator $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. If the initial and boundary conditions are known, then Eq. (1) can be integrated by numerical (although not in general by analytical) methods. The number of R_2 and RS molecules formed at infinite time are then given respectively by

$$N_{R_2} = \frac{1}{2} \int_0^\infty dt \int_V kc^2 dV \quad (2)$$

$$N_{RS} = \int_0^\infty dt \int_V k_s c_s c dV \quad (3)$$

where the index V indicates integration over entire volume of the system. If N_0 is the initial number of radicals, then the fractions of radicals which undergo reactions (2) and (3) are given respectively by

$$I_{R_2} = \frac{N_{R_2}}{N_0} = \frac{1}{N_0} \int_0^\infty dt \int_V kc^2 dV \quad (4)$$

$$I_S = \frac{N_{RS}}{N_0} = \frac{1}{N_0} \int_0^\infty dt \int_V k_s c_s c dV \quad (5)$$

Let us now consider the extreme cases mentioned in the introduction: isolated spherical spurs and axially homogeneous cylindrical tracks. Let r be the distance to the center of the spur in the first one and to the axis of the track in the second one. We assume the initial condition to be Gaussian, i.e.,

$$c(r, 0) = \frac{N_0}{8} \frac{e^{-r^2/2r_0^2}}{r_0^3} \quad (6)$$

4.

$$c(r,0) = \frac{N_0 e}{2 \pi L r_0^2} \frac{r^2}{2r_0^2} \quad (7)$$

respectively for spherical and cylindrical cases. The quantity r_0 is called the spur or track radius. L is the length of the cylindrical track, for which end effects are neglected. Under these conditions one may introduce the dimensionless variable.

$$r' = \frac{r}{r_0} \quad t' = \frac{D_2}{r_0} t \quad c' = \frac{c}{c(0,0)} \quad (8)$$

In terms of these new variables Eq (1) becomes

$$\frac{\partial c'}{\partial t'} = \frac{\partial^2 c'}{\partial r'^2} + \frac{E}{r'} \frac{\partial c'}{\partial r'} - k' c'^2 - K' c' \quad (9)$$

where $E=2$ for the spherical case and $E=1$ for the cylindrical one. The quantity k' is a dimensionless rate constant given for these two cases respectively by

$$k' = \frac{k N_0}{S^{1/2} \pi^{3/2} r_0 D} \quad \text{spherical} \quad (10)$$

$$k' = \frac{k N_0}{2 \pi L D} \quad \text{cylindrical} \quad (11)$$

and K' is given in both cases by

$$K' = k_S c_S \frac{r_0^2}{D} \quad (12)$$

For these dimensionless variables the initial condition becomes, in both cases,

$$c'(r',0) = e^{-\frac{r'^2}{2}} \quad (13)$$

Since the spur or track are considered to be in a container large compared to their size, the boundary conditions are given by

$$\lim_{r' \rightarrow \infty} c'(r', t') = 0 \quad (14)$$

Under these conditions it is possible to integrate numerically Eq (9) and obtain $c'(r', t')$ for any chosen values of the two dimensionless parameters k' and K' . In terms of these and c' , I_R and I_S defined by Eqs (4) and (5) are given by the following formulae:

a) spherical spurs

$$I_R = \left(\frac{2}{\pi}\right)^{1/2} k' \int_0^{\infty} dt' \int_0^{\infty} c'^2(r', t') r'^2 dr' \quad (15)$$

$$I_S = \left(\frac{2}{\pi}\right)^{1/2} K' \int_0^{\infty} dt' \int_0^{\infty} c'(r', t') r'^2 dr' \quad (16)$$

a) axially homogeneous cylindrical tracks

$$I_R = k' \int_0^{\infty} dt' \int_0^{\infty} c'^2(r', t') r'^2 dr' \quad (17)$$

$$I_S = K' \int_0^{\infty} dt' \int_0^{\infty} c'(r', t') r' dr' \quad (18)$$

We thus see that the fraction I_R and I_S of radicals which recombine and react with scavenger respectively are entirely determined by the two dimensionless parameters k' and K' only. They have been tabulated as a function of two other parameters related to these by Flanders and Fricke⁽¹⁵⁾ for spherical spurs and axially homogeneous cylindrical tracks. Since these are extreme cases, the value of I_R and I_S for intermediate tracks formed by partially overlapping spurs can be obtained with sufficient accuracy by interpolating between the values given in these tables. Thus, I_R and I_S can be obtained as a function of k' and K' for any track consisting of equidistant identical spherical spurs, whether these are very far apart, very close together or at intermediate distance. Inclusion of the spectrum of local energy dissipation will be considered in Section 8.1.

6.

Calculation of $G_{Fe^{+3}}$ and $G_{Ce^{+3}}$

From the accepted mechanisms for the ferrous and ceric sulphate dosimeters (19), the $G_{Fe^{+3}}$ and $G_{Ce^{+3}}$ yields are related to the primary radical and molecular yields by

$$G_{Fe^{+3}} = 3 G_H + G_{OH} + 2 G_{H_2O_2} = 3 G_H + G_{-H_2O} \quad (19)$$

$$G_{Ce^{+3}} = 2 G_{H_2O_2} + G_H - G_{OH} = 4 G_{H_2O_2} - G_{H_2} \quad (20)$$

In a one-radical model it is implicitly assumed that

$$G_H = G_{OH} \quad (21)$$

$$G_{H_2} = G_{H_2O_2} \quad (22)$$

and that the yield G_{H_2O} of the chemically undetectable water formed by $H + OH$ recombination is given by

$$G_{H_2O} = G_{H_2} + G_{H_2O_2} \quad (23)$$

The total radical and molecular yields in the one-radical model are thus respectively given by

$$G_R = G_H + G_{OH} \quad (24)$$

$$G_{R_2} = 2(G_{H_2} + G_{H_2O_2}) \quad (25)$$

In terms of these, the ferric and cerous ion yields are given by

$$G_{Fe^{+3}} = 2 G_R + 0.5 G_{R_2} \quad (26)$$

$$G_{Ce^{+3}} = 0.5 G_{R_2} \quad (27)$$

Thus, the calculation of $G_{Fe^{+3}}$ and $G_{Ce^{+3}}$ in a one-radical model is reduced to the calculation of G_R and G_{R_2} .

3.1 General Method

Let $w = (w) \cdot 100$ eV be the energy necessary to form a radical. The radical and molecular yields can be expressed in terms of I_R , I_S and (w) by the expressions

$$G_R = \frac{I_S}{(w)} \frac{\text{radicals}}{100 \text{ eV}} \tag{28}$$

$$G_{R_2} = \frac{I_R}{2(w)} \frac{\text{molecules}}{100 \text{ eV}} \tag{29}$$

On the other hand, since the only possible fates of radicals R are either to react with themselves or with the scavenger S, one may write

$$I_R + I_S = 1 \tag{30}$$

From Eqs (26) through (30) it follows that:

$$G_{Fe^{+3}} = \frac{1}{(w)} (1.75 I_S + 0.25) \frac{\text{ions}}{100 \text{ eV}} \tag{31}$$

$$G_{Ce^{+3}} = \frac{0.25}{(w)} (1 - I_S) \frac{\text{ions}}{100 \text{ eV}} \tag{32}$$

The problem is now to determine I_S taking into account the spectrum of local energy dissipation of the radiation under consideration. Let T_{max} be the maximum energy of the incident high energy charged particles or photons. As a result of the passage of these particles or photons, electrons will be produced in the medium with energies from zero up to not more than T_{max} . In addition, the incident charged particles will have their energies varying from their initial value down to zero as they are stopped by the medium. Let the term "local energy dissipation" denote kinetic energy losses of the particles in the medium dissipated through collisional energy transfers up to 100 eV. Let us divide up the total energy range 0 to T_{max} into n intervals.

8.

$\Delta T_i = T_i - T_{i-1}$, ($i=1, 2, \dots, n$) with $T_0 = 0$ and $T_n = T_{\max}$. Let $Q(T_i)\Delta T_i$ represent the total local energy loss of particles whose energy lies in the interval ΔT_i . Let $I_S(T_i)$ represent the fraction of the radicals produced by such particles which react with the solute. If the intervals ΔT_i are adequately chosen then the quantity I_S is, to a good approximation, given by

$$I_S = \frac{\sum_{i=1}^n I_S(T_i) Q(T_i) \Delta T_i}{\sum_{i=1}^n Q(T_i) \Delta T_i} \quad (33)$$

Tables of $Q(T_i)\Delta T_i$ as a function of T_i and ΔT_i are available for several different radiations ^(11,20). Thus, to calculate I_S , and hence $G_{Fe^{+3}}$ and $G_{Ce^{+3}}$, it is sufficient to determine $I_S(T_i)$, i.e., the fraction of local radicals produced by particles in the energy range T_{i-1} to T_i which react with the scavenger. If this range is not too large, the portion of the corresponding tracks can be considered axially homogeneous in the sense that the average distance between neighboring spurs does not vary appreciably along the track axis. On this basis, $I_S(T_i)$ can be obtained from the digital computer calculations described in Section 2. For this purpose, a choice is made of the rate constants k and k' , the spur radii r_0 , the radical diffusion coefficient D , the scavenger concentration c_s and the number N_0 of radicals formed per spur. This determines K' and the values of k' for the spherical case according to Eqs (10) and (12). For values of T_i such that $\frac{dT}{dx}$, the linear rate of local energy transfer, is sufficiently small for the spurs not to interact, $I_S(T_i)$ can be obtained with those values of K' and k' from published tables ⁽¹⁵⁾. For values of T_i such that the tracks are cylindrical, the value of k' will now be a function of N_0/L , the number of radicals formed per unit track length, according to Eq (11) This quantity is related to $\frac{dT}{dx}$ by

$$\frac{N_0}{L} = \frac{1}{w} \frac{dT}{dx} \quad (34)$$

so that, for cylindrical tracks, Eqs. (11) and (34) furnish:

$$K'(T_i) = \frac{k}{2\pi Dw} \frac{dT}{dx} \quad (35)$$

Values of $\frac{dT}{dx}$ as a function T_i are also available⁽²⁰⁾ for electrons, protons and alpha particles. Thus, from Eq (35), $k'(T_i)$ and hence $I_S(T_i)$ can be obtained for portions of the tracks which can be considered to be axially homogeneous cylinders. Finally, $I_S(T_i)$ for intermediate kinds of track portions can be obtained by plotting $I_S(T_i)$ against $\frac{dT}{dx}$, using the spherical formula for small $\frac{dT}{dx}$ and the cylindrical one for large $\frac{dT}{dx}$ and joining smoothly the two curves thus obtained. Once $I_S(T_i)$ is obtained, Eqs (31) through (33) furnish $G_{Fe^{+3}}$ and $G_{Ce^{+3}}$.

3.2 Choice of parameters

Since the purpose of the present calculations was more to develop a feeling for the importance of including the spectrum of local energy dissipation rather than to obtain agreement with experiment, no attempt was made to choose parameters which fitted the experimental data. Instead, "reasonable" parameters were chosen which furnished the correct value of $G_{Fe^{+3}}$ for Co^{60} gamma-rays, before taking the spectrum of energy dissipation into account. These parameters were used throughout all the calculation and are:

$$\begin{aligned} r_0 &= 12 \text{ \AA} \\ N_0 &= 10 \text{ radicals} \\ D &= 4.5 \times 10^{-5} \text{ cm}^2/\text{sec.} \\ k &= k_S = 10^{-11} \text{ cm}^2/\text{sec.} \times \text{radic} \\ c_S &= 10^{-3} \text{ mole/l} \\ W &= 10 \text{ ev/radical} \end{aligned}$$

The track formed by independent spherical spurs were taken to be those for which $\frac{dT}{dx} < 0.5 \frac{\text{KeV}}{\mu}$, corresponding to an interspur distance of 2000 \AA. The axially homogeneous cylindrical portions were taken to be those for which $\frac{dT}{dx} > 25 \frac{\text{KeV}}{\mu}$ corresponding to an interspur distance of 400 \AA. The transition region corresponded to

$$0.5 \frac{\text{KeV}}{\mu} < \frac{dT}{dx} < 25 \frac{\text{KeV}}{\mu}$$

10.

3.3 Results

If the spectrum of local energy dissipation for Co^{60} gamma-rays is neglected, and the tracks are considered to be formed by independent spherical spurs, the value of I_S for the parameters chosen is 0,745, for which $G_{\text{Fe}^{+3}} = 15.6$ ions/100 eV (according to Eq (31), which agrees with the experimental value. (9).

Calculations were performed for Co^{60} gamma-rays, Po^{210} alpha-particles and tritium beta-particles, using the spectra of energy dissipation mentioned in section 3.1 (11,20). The results obtained, together with the experimental ones, are given in Table I, together with the values of I_S .

TABLE I
Theoretical and experimental
yields

Radiation	Calculated yields (ions/100 eV)		Experimental yields (ions/100 eV)		I_S
	$G_{\text{Fe}^{+3}}$	$G_{\text{Ce}^{+3}}$	$G_{\text{Fe}^{+3}}$	$G_{\text{Ce}^{+3}}$	
Co^{60} γ -rays	14.0	0.85	15.5 ⁽¹⁾	2.45 ^x	0.658
Tritium β -particles	13.3	0.95	12.9 ^(3,8)	4.61 ^{xx}	0.619
Po^{210} α -particles	9.2	1.54	5.6 ⁽⁹⁾	3.23 ^x	0.384

xx Obtained from the ratio $G_{\text{Fe}^{+3}}/G_{\text{Ce}^{+3}} = 2.8$ (21)

x Cited in reference 12.

The large disagreement between theory and experiment should not be surprising, since, as mentioned above, no attempt to obtain such agreement was made.

4. Discussion

Several interesting observations arise from the results of Table I. As mentioned in Section 2., the calculated value for $G_{Fe^{+3}}$, neglecting the effect of the spectrum of local energy dissipation, is 15.6 ions/100 eV. The value of 14.0 ions/100 eV, obtained after that effect was included, indicates that it is indeed a relatively important one. The fraction of radicals which react with solute falls from 0.745 to 0.658 as a result of this inclusion. This is a consequence of the cylindrical tracks of the secondary low energy electrons (with less than 800 eV).

Although the trend of the variation of $G_{Fe^{+3}}$ with radiation quality is the same as the experimental one, the variation in the calculated values is much smaller than in the experimental ones. This is very probably due to the assumptions of the one-radical model represented by Eqs (21) and (22), - which are known to be quite wrong. Thus, for a better agreement with experiment to be obtained, it would probably be necessary to use a two-radical model. This is probably also the cause of the different trends of the calculated and experimental values of $G_{Ce^{+3}}$ with radiation quality. However, both the theoretical - and experimental $G_{Ce^{+3}}$ values are much smaller than the $G_{Fe^{+3}}$ ones indicating that the basis model is probably correct.

One may conclude that a useful calculation to perform is one in which the digital computer results for a two-radical model is coupled with a consideration of the spectrum of local energy dissipation. The one-radical model considered in this paper does not seem capable of proving good agreement - between theoretical and experimental yields, even when the model parameters are varied.

5. Summary

Calculations have been performed of $G_{Fe^{+3}}$ and $G_{Ce^{+3}}$ in the ferrous

12.

and ceric sulphate dosimeters respectively. The method of calculation involved the use of digital computer solutions for the equation describing a one-radical model, coupled with a consideration of the spectrum of local energy dissipation.

The radiation considered were Co^{60} γ -rays, Po^{210} α -particles and tritium β -particles. The conclusions of these calculations were:

- a) The spectrum of local energy dissipation is an important factor.
- b) The calculated Fe^{+3} yields show the correct trend with radiation quality but the Ce^{+3} ones do not.
- c) An improvement of the agreement between theory and experiment requires the consideration of a two-radical model.

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