

## Dielectric Properties of Nitrobenzene in the Region of Anomalous Dispersion\*

GEORGE L. CLARK

*Department of Electrical Engineering, University of Illinois, Urbana, Illinois*

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The complex dielectric constant of highly purified nitrobenzene in the region of anomalous dispersion has been determined by measuring the input impedance of a variable length of a coaxial transmission line filled with the liquid. The measurements were carried out at frequencies from 0.65 kmcps to 3.00 kmcps in the temperature range between 15°C and 50°C. Good agreement was observed with an expression suggested by Cole and Cole, and the critical frequencies in this temperature region were found to be between 3 and 6 kmcps.

### INTRODUCTION

**I**N a general investigation of the possibility of building a light shutter capable of producing light pulses of a duration of only a few  $\mu\mu$ seconds, the applicability of Kerr cells<sup>1</sup> was examined. Because of the large electro-optic Kerr effect<sup>2</sup> exhibited by nitrobenzene, this liquid is commonly used in Kerr cell shutters for producing very short light pulses. The speed of an electro-optic shutter is limited by the time required for the polarization of the medium to reach equilibrium with the applied field, and since both the Kerr constant and the dielectric constant of nitrobenzene are strongly dependent upon dipole orientation, the time delay of the Kerr effect can be found from the frequency dependence of the complex dielectric constant. The work which is reported here was carried out to determine the highest frequency at which nitrobenzene can be used as a Kerr medium and to obtain data for the design of microwave Kerr cells.

### THEORETICAL BACKGROUND

No theory has as yet been advanced which gives satisfactory quantitative results for the dielectric behavior of concentrated polar liquids as a function of frequency and temperature. A number of semiempirical expressions have been developed which describe the observed variation of the dielectric constant with frequency. Possibly the best of these from the standpoint of agreement with observations is an expression proposed by Cole and Cole,<sup>3</sup>

$$\epsilon = \epsilon_{\infty}' + \frac{\epsilon_s' - \epsilon_{\infty}'}{1 + (j\omega\tau_0)^p}, \quad (1)$$

where  $\epsilon$  is the complex dielectric constant, defined by

$$\epsilon = \epsilon' - j\epsilon'' \quad (2)$$

with  $\epsilon'$  and  $\epsilon''$  the real dielectric constant and the loss factor, respectively,  $\epsilon_s'$  is the static field dielectric constant,  $\epsilon_{\infty}'$  is the optical or "infinite frequency"

dielectric constant,  $\omega$  is the radian frequency of the applied electric field, and  $\tau_0$  is the "observed relaxation time" of the liquid.

The exponent  $p$  in Eq. (1), which has a value between zero and unity, was introduced by Cole and Cole to account for a possible distribution of relaxation times about a most probable value, due to interaction between molecules. For  $p$  equal to 1, Eq. (1) describes the dielectric behavior of a liquid having only one relaxation time.

The complex dielectric constant is known to be not only a function of frequency but also of temperature. Hence, the four parameters  $\epsilon_s'$ ,  $\epsilon_{\infty}'$ ,  $\tau_0$ , and  $p$ , contained in Expression (1) for  $\epsilon$  can be considered to be functions of temperature, but are assumed to be constant if frequency only is varied. If for a particular temperature these four constants are given, the complex dielectric constant is determined for all frequencies.

### EXPERIMENTAL PROCEDURE

The technique applied to determine the real and imaginary part of the complex dielectric constant of nitrobenzene at a particular frequency and temperature consists essentially in measuring the input impedance of a variable length of transmission line filled with the dielectric to be investigated. These measurements yield two characteristic quantities of the liquid, *viz.*, the attenuation constant,  $\alpha$ , and the phase constant,  $\beta$ , which determine uniquely the two components of the complex dielectric constant, since

$$\epsilon' = n^2 \left( 1 - \frac{\alpha^2}{\beta^2} \right), \quad (3)$$

$$\epsilon'' = n^2 (2\alpha/\beta), \quad (4)$$

where  $n$  represents a generalized index of refraction and is defined by the ratio of the free space wavelength of the signal,  $\lambda_0$ , to the wavelength in the liquid  $\lambda$ :

$$n = \lambda_0/\lambda = \lambda_0\beta/2\pi. \quad (5)$$

The experimental setup is shown schematically in Fig. 1. Two stationary probes, equipped with crystal detectors, and spaced a quarter of a wavelength apart, are placed an integral number of quarter wavelengths

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<sup>1</sup> J. W. Beams, *Rev. Sci. Instr.* **1**, 780 (1930).

<sup>2</sup> F. Gabler and P. Sokob, *Z. Physik* **6**, 198 (1936).

<sup>3</sup> K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

TABLE I. Results of measurements of the dielectric properties of nitrobenzene as a function of frequency with the temperature constant at 25°C.

Frequency <i>f</i> /mcps	Attenuation constant $\alpha$ /neper·cm <sup>-1</sup>	Index of refraction <i>n</i>	Dielectric constant	
			Real part $\epsilon'$	Imaginary part $\epsilon''$
650	0.052	5.72	32.5	4.5
800	0.083	5.69	32.1	5.6
1000	0.14	5.68	31.8	7.44
1100	0.18	5.62	30.7	9.0
2100	0.47	5.18	25.7	11.1
3000	0.84	4.73	20.6	12.65

away from the surface of the liquid. A source of UHF power is connected to the upper end of a transmission line shorted on the lower end and the two crystal currents,  $I_1$  and  $I_2$ , coming from the probes are observed as the depth of immersion,  $s$ , of the line is varied. If a coaxial transmission line is used, the ratio of these two currents as a function of the immersion depth is theoretically given by the following equation:

$$I_1/I_2 = K \frac{\cosh 2\alpha s - \cos 2\beta s}{\cosh 2\alpha s + \cos 2\beta s}, \quad (6)$$

where  $K$  is an apparatus constant.

The quantities  $\alpha$ ,  $\beta$ , and  $n$  are evaluated from these measurements in the following way: first, the ratio of the crystal readings is plotted against the immersion depth,  $s$ , giving a curve which, according to Eq. (6), oscillates with exponentially decreasing amplitude as  $s$  increases. Second, a horizontal line is drawn which is cut by the curve into equal segments. As can be shown, the length of each of these segments is equal to one quarter of the wavelength in the liquid, hence the values of  $n$  or  $\beta$  are established at once with Eq. (5). The position of this line furthermore evaluates the constant  $K$ , since its ordinate represents the magnitude of this constant.

Halfway between the points of intersection of the function  $I_1/I_2(s)$  with the horizontal line mentioned above, the oscillating curve is tangent to one of its

TABLE II. Results of measurement of the dielectric properties of nitrobenzene as a function of temperature with the frequency constant at 3.0 kmcps.

Temperature <i>T</i> /°C	Attenuation constant $\alpha$ /neper·cm <sup>-1</sup>	Index of refraction <i>n</i>	Dielectric constant	
			Real part $\epsilon'$	Imaginary part $\epsilon''$
15	0.94	4.69	19.8	14.05
20	0.84	4.81	21.35	12.9
25	0.84	4.73	20.6	12.65
30	0.77	4.91	22.6	12.0
40	0.76	4.78	21.4	11.6
50	0.70	5.01	23.9	11.15

two bounding curves:

$$\text{Upper bound: } I_1/I_2 = K \coth^2 \alpha s \quad (7a)$$

$$\text{Lower bound: } I_1/I_2 = K \tanh^2 \alpha s. \quad (7b)$$

Each of the points of tangency  $[(I_1/I_2)_i, s_i]$  yields a value of the attenuation constant,  $\alpha$ , through substitution of  $(I_1/I_2)_i, s_i$  and  $K$  in one of the above equations. Having thus determined  $\alpha$ ,  $\beta$ , and  $n$ , for a particular frequency and temperature, the real and imaginary component of the complex dielectric constant may be computed through Eqs. (3) and (4).

The technique outlined above is a modification of a method recently described by Little.<sup>4</sup> The use of coaxial transmission line rather than wave guide as used by Little makes it possible to use the same equipment

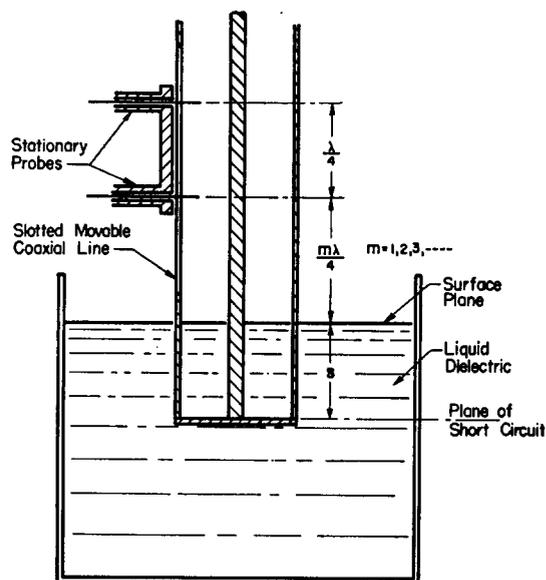


FIG. 1. Schematic drawing of the apparatus for measuring the dielectric properties of liquid dielectrics at microwave frequencies.

over a wider range of frequency and also simplifies the calculation of results, since no "guide" wavelengths are involved. Furthermore, the present equipment requires only a single adjustment between readings instead of the two needed by Little's.

The measurements which were carried out with this setup can be divided into two groups; one, where the temperature is maintained at a constant value of 25°C and the frequency is varied from 650 mcps to 3000 mcps; and the other, where at a constant frequency of 3000 mcps, the temperature is varied from 15°C to 50°C.

The frequency range between 650 mcps and 2100 mcps was covered by a square-wave modulated, coaxial line oscillator employing a 2C40 lighthouse triode. 3000 mcps power was obtained from a QK-61 magne-

<sup>4</sup> V. I. Little, Proc. Phys. Soc. (London) **B66**, 175 (1953).

tron, operated with one microsecond pulses at a repetition rate of 1000 pps. Frequencies were checked with a TS-175 Signal Corps Frequency Meter.

Low power levels were maintained throughout the measurements to avoid local heating caused by absorption. The temperature of the sample was controlled by a Cenco Serological Bath. The output of the crystal detectors was amplified and displayed by a Browning TAA-16 standing wave amplifier. Deviations from square law response were determined over the whole frequency range and the correction was applied to all probe readings.

Since the distance from the liquid surface to one of the probes is very critical, the principal source of experi-

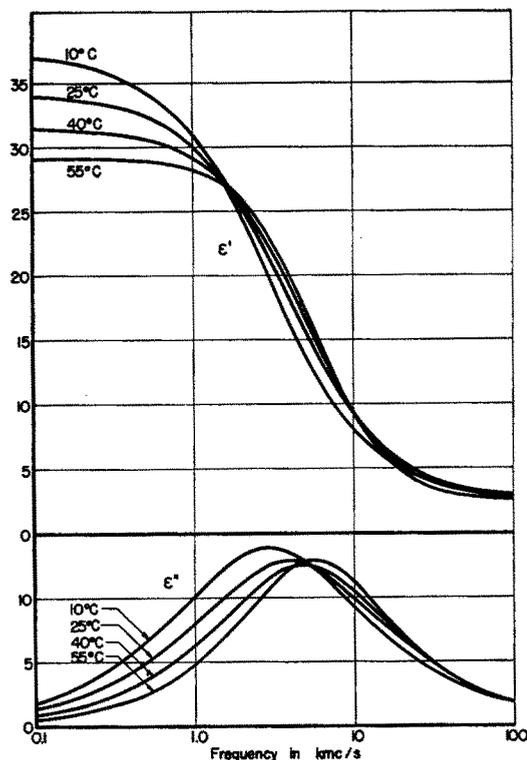


FIG. 2. The dielectric constant,  $\epsilon'$ , and loss factor,  $\epsilon''$ , of nitrobenzene computed as functions of frequency at selected temperatures from Eq. (1), using the values of the parameters given in Table IV.

mental error in these measurements is believed to be the variation of the liquid meniscus inside the coaxial line. In order to keep the experimental error as low as possible, between 25 and 60 different readings of the crystal currents as a function of the immersion depth were taken for each frequency and temperature, allowing four independent determinations of both  $\alpha$  and  $\beta$ , whose mean values, having a probable error of about 7%, are used in the computation of  $\epsilon'$  and  $\epsilon''$ .

Particular care was taken to obtain high purity of the nitrobenzene ( $4 \times 10^{-11}$  mho/cm  $< \sigma < 3 \times 10^{-10}$  mho/cm) and maintain this purity during the measurements. After neutralization, and double distillation in vacuum

TABLE III. Values of the parameters  $\rho$  and  $\tau_0$  at constant temperature computed from the measured data given in Table I.

$f/\text{mcps}$	$\rho$	$\tau_0/\mu\text{sec}$
650	0.85	28.7
800	0.87	31.6
1000	0.95	38.4
1100	0.95	44.6
2100	0.86	37.5
3000	0.86	43.6

the sample was constantly handled in an atmosphere of pure, dry nitrogen, to prevent oxidation and absorption of water vapor. All of the metallic parts of the apparatus coming into contact with the liquid were gold-plated to avoid chemical action and contamination.

## RESULTS

The results of the two sets of measurements as mentioned above are listed in Tables I and II. These results may be used to determine the dielectric behavior of nitrobenzene for all radio frequencies if Eq. (1) is considered to be an adequate description of the polarization processes in this frequency range.

If the four parameters  $\epsilon_s'$ ,  $\epsilon_\infty'$ ,  $\tau_0$ ,  $\rho$ , which are independent of frequency, are determined as a function of temperature, the complex dielectric constant  $\epsilon$  is completely defined for all frequencies and those temperatures for which these parameters are known. Since the values of both the static and the optical dielectric constant,  $\epsilon_s'$  and  $\epsilon_\infty'$ , are experimentally well established for a wide temperature range, it suffices to determine the values for just two of these parameters, *viz.*,  $\tau_0$  and  $\rho$ .

Separating the real and imaginary parts in Eq. (1), one can solve explicitly for both unknowns  $\tau_0$  and  $\rho$  in terms of  $\epsilon_s'$ ,  $\epsilon_\infty'$ ,  $\epsilon'$ , and  $\epsilon''$ :

$$\rho = -\frac{2}{\pi} \tan^{-1} \left( \frac{A}{B} \right) \quad (8)$$

$$\tau_0 = 1/\omega \left( \frac{A^2 + B^2}{C^2} \right)^{1/2\rho} \quad (9)$$

TABLE IV. Smoothed and extrapolated values of the dielectric constant,  $\epsilon_s'$ , and loss factor,  $\epsilon_s''$ , of nitrobenzene as a function of temperature at 3.0 kmcps taken from Table II, and corresponding values of  $\rho$ ,  $\tau_0$ , and the critical frequency  $f_c$  computed from these values.

$T/^\circ\text{C}$	$\epsilon_s'$	$\epsilon_s''$	$\rho$	$\tau_0/\mu\text{sec}$	$f_c/\text{kmcps}$
10	19.7	13.9	0.854	54.2	2.94
15	20.3	13.6	0.854	49.4	3.22
20	20.8	12.9	0.854	44.9	3.54
25	21.3	12.6	0.859	40.9	3.90
30	21.7	12.2	0.869	37.5	4.25
35	21.9	11.8	0.883	35.0	4.55
40	22.2	11.6	0.903	32.9	4.84
45	22.5	11.4	0.929	31.1	5.12
50	22.8	11.2	0.953	29.4	5.42
55	23.0	10.9	0.978	27.9	5.70

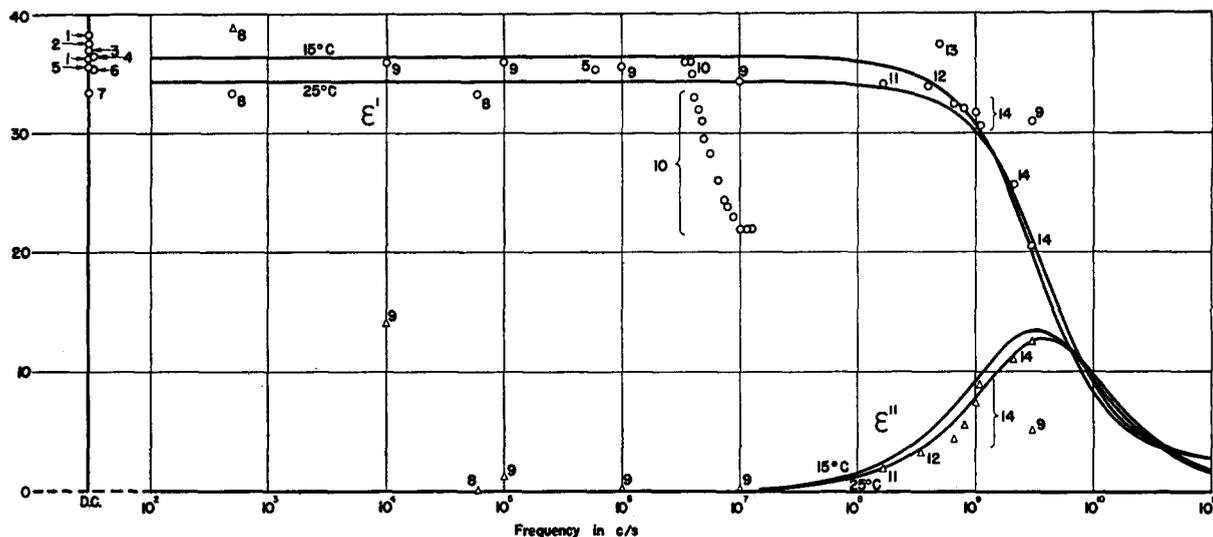


FIG. 3. The dielectric constant,  $\epsilon'$ , and loss factor,  $\epsilon''$ , of nitrobenzene computed as functions of frequency at 15°C and 25°C from Eq. 1, using the values of the parameters given in Table IV; and collected results of measurements reported by various authors: [1] Hehlhans,<sup>8</sup> 18°C; [2] Löwe,<sup>9</sup> 17°C; [3] Abegg and Seitz,<sup>10</sup> 19°C; [4] Turner,<sup>11</sup> 18°C; [5] Jezewsky,<sup>6</sup> 18.6°C; [6] Walden,<sup>12</sup> 20.5°C; [7] Walden,<sup>13</sup> 25°C; [8] Smyth and Hitchcock,<sup>14</sup> 20°C; [9] Von Hippel,<sup>15</sup> 25°C; [10] Hilke,<sup>16</sup> 25°C (?); [11] Szymanowski,<sup>17</sup> 20°C; [12] Drude,<sup>18</sup> 17°C; [13] Dobroserdov,<sup>19</sup> 20°C; [14] Data reported herein, 25°C.

with

$$A = \epsilon''(\epsilon_s' - \epsilon_\infty')$$

$$B = (\epsilon_s' - \epsilon')(\epsilon' - \epsilon_\infty') - (\epsilon'')^2$$

$$C = (\epsilon' - \epsilon_\infty')^2 + (\epsilon'')^2.$$

For each frequency and temperature,  $p$  and  $\tau_0$  have been computed from Eqs. (8) and (9) using the values of  $\epsilon'$  and  $\epsilon''$  given in Tables I and II, and taking for  $\epsilon_s'$  and  $\epsilon_\infty'$ , the expressions given by Gabler and Sokob,<sup>5</sup> who represented Jezewsky's<sup>6</sup> and Falk's<sup>7</sup> measurements by the following very accurate empirical equations:

$$\epsilon_s' = -3.5179 + 5.2682 \times 10^3/T + 1.7938 \times 10^6/T^2 \quad (10)$$

$$(\epsilon_\infty')^{1/2} = n = 1.6974 - 4.74 \times 10^{-4}T. \quad (11)$$

The results of this computation are given in Tables III and IV.

As a basis for the calculation of the temperature dependence of  $\tau_0$  and  $p$ , smoothed values of  $\epsilon'$  and  $\epsilon''$  from Table II have been used and are denoted by  $\epsilon_*'$  and  $\epsilon_*''$ . As seen in Table III, the parameters  $\tau_0$  and  $p$  show only fluctuations in the very large frequency range from 0.6 kmcps to 3.0 kmcps, while Table IV shows a definite trend for these parameters for the relatively small change in absolute temperature ( $\sim 15\%$ ). This fact seems to justify the use of Eq. (1) as a possible representation of the data.

Since all four parameters of Eq. (1) are now known, the complex dielectric constant has been plotted as a function of frequency in Fig. 2 for four selected tem-

peratures, using for the 10- and 55-degree curves the extrapolated, smoothed values  $\epsilon_*'$  and  $\epsilon_*''$  from Table IV.

As a resumé of the work of different investigators on the dielectric behavior of nitrobenzene,<sup>8-19</sup> Fig. 3 shows the findings as reported by these authors together with the complex dielectric constant at 15° and 25°C, as computed from Eq. (1), and the corresponding values from Table I. The wide scatter of reported values is probably due to the difficulty of obtaining and maintaining high purity of the nitrobenzene.

## CONCLUSION

Measurements of the complex dielectric constant of nitrobenzene have been carried to a high enough frequency and over a large enough temperature range that its dielectric behavior can be approximated for the entire radio-frequency spectrum. At low frequencies, the effect of increasing temperatures is to decrease the real part of the dielectric constant due to the shift in the statistical equilibrium between the aligning force of the field and the randomizing effect of thermal motion. In the region of anomalous dispersion, however,

<sup>8</sup> F. Hehlhans, *Physik. Z.* **32**, 718 (1931).

<sup>9</sup> K. F. Löwe, *Ann. Physik* **66**, 390 (1898).

<sup>10</sup> R. Abegg and W. Seitz, *Z. physik. Chem.* **29**, 242 (1899).

<sup>11</sup> B. B. Turner, *Z. physik. Chem.* **35**, 385 (1900).

<sup>12</sup> P. Walden, *Z. physik. Chem.* **70**, 569 (1910).

<sup>13</sup> P. Walden, *Z. physik. Chem.* **54**, 129 (1906).

<sup>14</sup> C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **54**, 4631 (1932).

<sup>15</sup> A. Von Hippel, editor, *Dielectric Materials and Applications* (The Technology Press of Massachusetts Institute of Technology and John Wiley and Sons, Inc., New York, 1954), p. 364.

<sup>16</sup> O. Hilke, *Z. Physik* **103**, 350 (1936).

<sup>17</sup> W. T. Szymanowski, *J. Chem. Phys.* **1**, 809 (1933).

<sup>18</sup> P. Drude, *Z. physik. Chem.* **23**, 267 (1897).

<sup>19</sup> Dobroserdov, *J. Russ. Chem. Soc.* **43**, 73, 225, 454 (1911).

<sup>5</sup> See reference 2, p. 200.

<sup>6</sup> M. Jezewsky, *J. phys. radium* **3**, 293 (1922).

<sup>7</sup> K. G. Falk, *J. Am. Chem. Soc.* **31**, 806 (1909).

the dielectric constant may rise with increasing temperature because of the effect of temperature on the relaxation time. There is a frequency region in which the two effects tend to cancel, making the dielectric constant insensitive to changes in temperature. This unique property of polar liquids suggests uses in matched terminations or in calorimetric measurement of power where dielectrics are desired whose properties do not change with temperature.

As for the frequency limitation on nitrobenzene as a

Kerr medium, the behavior of the dielectric constant indicates that dipole polarization above 1000 mcps falls away rapidly with increasing frequency.

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## Theory of Radiation Chemistry. III. Radical Reaction Mechanism in the Tracks of Ionizing Radiations\*

A. K. GANGULY AND J. L. MAGEE

*Department of Chemistry, University of Notre Dame, Notre Dame, Indiana*

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This paper develops a model for the dissipation of the tracks of high-energy particles. It is assumed that all chemical effects are due to one kind of radical and that there are no effects of overlapping of neighboring tracks, i.e., that there is a sufficiently high concentration of scavenger to prevent such overlapping. The model of Samuel and Magee is used and extended to take into account the interaction of randomly distributed spurs along the track. Calculated values of the extent of scavenger reactions and radical reactions are presented in graphical form. General trends of experimental results to be expected according to the model are indicated. Quantitative correlation with experiments was not attempted because of the uncertainty in the values of various parameters used and because of the serious limitations of the one-radical model of tracks.

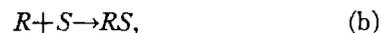
#### INTRODUCTION

RECENT papers<sup>1-5</sup> have developed the theory of diffusion and reaction of radicals in the tracks of ionizing particles in liquids. These treatments generally follow the lines set forth by Jaffe<sup>6</sup> in his pioneering study of the ionization density in columnar tracks. Lea<sup>7</sup> pointed out that high-energy electrons do not form columns, but more or less isolated "spurs,"† and this fact has been recognized in most subsequent work.

In this paper the authors have studied a model for a particle track which consists of a series of spurs randomly spaced along the linear trajectory of the particle. A Gaussian distribution for the position of the radicals in a spur is assumed, and all spurs are assumed to have the same number of radicals. The treatment used here only applies to the "low background" case, i.e., the

case in which sufficient "scavenger" is present to react with the radicals of a track before they intermingle with radicals from adjacent tracks. The intermingling of radicals from adjacent spurs of the same track is, however, taken into account and the concentration of the scavenger is also varied.

A chemical reaction mechanism for the one-radical track can be given as



where  $R$  and  $S$  stand for radical and scavenger, respectively.

The emphasis in this paper is upon a study of the method for treatment of the competition of reactions (a) and (b) in a track which is expanding by diffusion. Although this is a one-radical model, it may be possible that the radiation chemistry of water can be understood essentially on the basis of this model.<sup>2-5</sup> We have used only "average" spurs of six radicals each and a study has not been made of the effect of actual spur-size distribution. Recently Gray<sup>8</sup> has made a study along different lines in which there was a significant effect attributed to the highly ionizing delta rays.

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<sup>1</sup> J. L. Magee, *J. Am. Chem. Soc.* **73**, 3270 (1951).

<sup>2</sup> A. H. Samuel and J. L. Magee, *J. Chem. Phys.* **21**, 1080 (1953).

<sup>3</sup> J. L. Magee, 5<sup>e</sup> Réunion, Société de Chimie Physique, Paris, 1955; *J. chim. phys.* **52**, 528 (1955).

<sup>4</sup> H. A. Schwarz, *J. Am. Chem. Soc.* **77**, 4960 (1955).

<sup>5</sup> H. Fricke, *Ann. N. Y. Acad. Sci.* **59**, 567 (1955).

<sup>6</sup> G. Jaffe, *Ann. Phys. Lpz.* **42**, 303 (1913).

<sup>7</sup> D. E. Lea, *Proc. Cambridge Phil. Soc.* **30**, 80 (1933-34).

† Lea used the expression "cluster." We use "spur" to denote the group of radicals formed in all processes following one primary event.

<sup>8</sup> L. H. Gray, 5<sup>e</sup> Réunion, Société de Chimie Physique, Paris, 1955.