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A. Appleby, E.A. Christman, and M. Jayko

April 1986

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RADIATION CHEMISTRY OF HIGH-ENERGY

CARBON, NEON AND ARGON IONS: HYDRATED ELECTRON YIELDS

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Radiation Chemistry of High Energy Carbon, Neon and Argon Ions:
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Abstract

Neutral aqueous solutions of sodium nitrate/ethanol have been irradiated with high energy heavy ions from the Berkeley Bevalac. Yields of nitrite have been used to estimate G-values for the hydrated electron as a function of the residual range of these ions. Values of $G(e_{aq}^{-})$ have been estimated as a function of ion energy by adjusting the measured values for the effects of heavy ion fragmentation.

Introduction

We have previously reported radiation chemical product yields as a function of residual range in several systems irradiated with high energy heavy ions; Fe^{3+} yields in aerated and deaerated acid ferrous solutions (1,2) and H_2O_2 yields in aerated neutral bromide and formate solutions (3). These products result from the ionization of water molecules by the energetic heavy ions directly, and by the energetic secondary electrons liberated by them. From these data it was possible to deduce G-values for the total reducing radicals produced at low pH, and of the hydroxyl radical yield in neutral solutions. These yields were compared with the primary product yields predicted from considerations of the expected pattern of energy deposition of these ions in water (4). The data were in all cases qualitatively consistent with these expectations. For example, the deduced OH radical yield decreased with increasing penetration depth (i.e. decreasing primary ion energy) and with increasing primary ion atomic number. In most cases, good quantitative agreement was also obtained, provided that fragmentation of the primary ion during its passage through the solution was taken into account. In continuation of this study we now report results from neutral solutions of sodium nitrate, from which we are able to determine the yields of the hydrated electron e_{aq}^-, as a function of the same variables.

Since 1963, free radical yields have been measurable by means of short pulses of radiation, enabling the time development of these yields to be studied. At the Bevalac, pulses are too long (0.5 sec) to permit this approach. Instead, product yields have

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been measured at long times after irradiation, when chemical equilibrium has been established. The radicals scavenged by a given concentration c of solute correspond approximately to the radical yield in pure water at a time of 1/kc, where k is the second-order rate constant for reaction of radical and solute.

Experimental

Irradiation, dosimetry and data analysis procedures have been described previously (2). Briefly, flat cylindrical quartz irradiation vessels containing solution to be irradiated were lined up on the axis of the heavy ion beam. Dosimetry was by a calibrated ion chamber positioned in front of the vessels Entrance doses were in the range 18.6 to 82.0, 18.0 to 140.4 and 28.2 to 184.2 Gy for C^{6+}, Ne^{10+} and Ar^{18+} ions respectively. The Bevalac provides 0.5 sec. pulses 15 times per minute. Entrance dose rates during the pulse were in the ranges 68 to 352, 80 to 800, and 19 to 205 Gy per minute, respectively, for carbon, neon and argon ions. G-values (molecules transformed per 100 eV) were obtained for each irradiated system from linear yield/dose plots of 4 to 10 points as a function of Q, the distance from the Bragg peak, for each ion using a general linear regression model in which Q appears as a classification variable. Only data from vessels upstream of the Bragg peak have been utilized in the present analysis. Solutions were prepared using analytical grade chemicals, and water was triply distilled. Nitrate solutions were deoxygenated by bubbling with nitrogen. Nitrite was determined colorimetrically (5) as soon as possible after irradiation,

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typically within 2-3 hr.

Results

Figure 1 shows nitrite yields expressed as G-values, the number of molecules measured at some distance from the ion Bragg peak per 100 eV absorbed at that depth, for solutions containing $2.5 \times 10^{-3}M$ $NaNO_3$ and $2.5 \times 10^{-2}M$ ethanol irradiated with carbon, neon or argon ions. The boxes cover ± 1 standard deviation of at least 24 data points. Yields were linear with dose at any given distance from the Bragg peak.
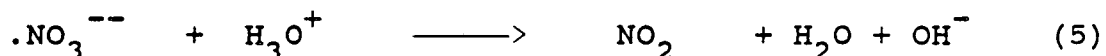
The radiation chemistry of solutions containing nitrate and an alcohol has been thoroughly studied with gamma rays (6,7,8). In the case of ethanol, the following reactions are expected to occur:

$$CH_3CH_2OH + \cdot OH \longrightarrow CH_3\dot{C}HOH + H_2O \qquad (1)$$

$$CH_3CH_2OH + \cdot H \longrightarrow CH_3\dot{C}HOH + H_2 \qquad (2)$$

$$\cdot NO_3^- + e^-_{aq} \longrightarrow \cdot NO_3^{--} \qquad (3)$$

The $\cdot NO_3^{--}$ species produces NO_2^- either by reacting directly with the alcohol radical:

$$\cdot NO_3^{--} + CH_3\dot{C}HOH \longrightarrow NO_2^- + OH^- + CH_3CHO \qquad (4)$$

or via NO_2:

$$\cdot NO_3^{--} + H_3O^+ \longrightarrow NO_2 + H_2O + OH^- \qquad (5)$$

$$NO_2 + CH_3\dot{C}HOH \longrightarrow NO_2^- + H^+ + CH_3CHO \qquad (6)$$

On this basis we expect $G(NO_2^-) = G(e^-_{aq})$. Baquey, Roux and Sutton (7) have shown that below about 10^{-3} M nitrate the nitrite yield is lower than this because of products competing with reaction 3, but that above this concentration this effect is negligible, and between 10^{-3} M and $5 \times 10^{-3}M$ the nitrite yield accurately reflects the yield of available electrons. It is for

this reason that we have chosen to use a nitrate concentration of 2.5×10^{-3} M. The alcohol concentration was chosen to be sufficient to prevent formation of significant additional nitrite through reaction 7:

$$NO_3^- + H \longrightarrow HNO_3^- \tag{7}$$

in competition with

$$CH_3CH_2OH + H \longrightarrow CH_3\dot{C}HOH + H_2 \tag{8}$$

The ratio k7/k8 is about 0.2 (8) so under our conditions the extent of reaction 7 is only about 2% of reaction 8. From previous studies with lighter ions (9) we expect $G_H < G(e_{aq}^-)$, so the additional NO_2^- from rection (7) will be less than 2% of reaction (3).
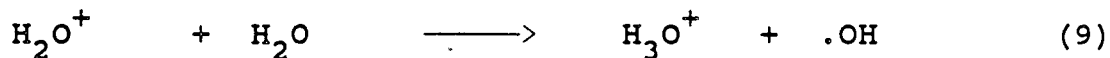
Discussion

Since the development of pulse radiolysis in the early 1960's the yields of free radicals in radiation chemistry have been most conveniently determined by this technique. A major advantage of pulse radiolysis is the ability to investigate the time dependence of these yields. This has been done with ions of lower mass and energy (10,11) but the long pulse length of the Bevalac at present precludes investigations of this kind with these high energy heavy ions. We must therefore rely on observations made after the systems have come essentially to equilibrium to test theoretical models of radiolysis at early times with these radiations.

We have previously reported values of G_{OH} from neutral solutions for high energy heavy ions (3). The present data on $G(e_{aq}^-)$ consistently parallels these values (Fig. 4). Like

G_{OH}, $G(e_{aq}^-)$ decreases with decreasing distance from the Bragg peak and with increasing atomic number of the incident ion (Fig.1) . This behavior of course conforms to the prediction of diffusion theory and reflects the greater probability with more densely ionizing radiations that radicals will encounter and react with other radicals before reacting with a scavenger solute, such as nitrate.

The nitrite yield also depends on the alcohol concentration, as shown in Figure 2. This has been seen before with gamma rays (6) where $G(NO_2^-)$ from deaerated methanol/nitrate solutions increased by about 2-4% while the methanol concentration was increased from $10^{-2}M$ to $10^{-1}M$, the nitrate concentration being kept constant. A possible reason for this effect is similar to an explanation offered by Baquey, Roux & Sutton (7) for enhanced aldehyde yields from gamma irradiated 1M ethanol solutions. An electron in the vicinity of the parent positive ion can be promptly recaptured by it, or a little later by the .OH formed by reaction (9):

$$H_2O^+ \quad + \quad H_2O \quad \longrightarrow \quad H_3O^+ \quad + \quad .OH \qquad (9)$$

$$e^- \quad + \quad .OH \quad \longrightarrow \quad OH^- \qquad (10)$$

(The pre-solvated electron does not react rapidly with H_3O^+ (11)). In high concentrations of an alcohol many of these .OH radicals would be rapidly replaced by an alcohol radical (reaction (1)) which may be much less likely then .OH to react with the electron. Consequently, reaction (10) will be depressed and solvation and escape of the electron promoted. This process would presumably be especially important for isolated ion pairs. With gamma rays the increased $G(NO_2^-)$ amounts to about 0.05-0.10

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in the methanol concentration range of 10^{-2}M to 10^{-1}M. If the above explanation is correct, ethanol should show an equal effect between about 5×10^{-3} and 5×10^{-2}M, based upon its greater reactivity with .OH (13). Figure (3) shows that for argon the increase in $G(NO_2^-)$ is about this magnitude at the highest argon energy, but diminishes as the Bragg peak is approached. Such behavior would be expected if this effect of ethanol involved scavenging predominantly from isolated pairs of ions, since the probability of an ion or radical pair being close to other radicals will obviously increase near the Bragg peak.

Figure 4 shows values of $G(e_{aq}^-)$ alongside G_{OH}, as a function of Z^2/β^2, where Z is the ion atomic number and β is the ratio of its velocity to that of light. With high energy heavy ions the observed yields in a thick target include a contribution from lighter ions produced as a result of fragmentation upstream. We have previously (3) estimated the extent of this effect on G_{OH} measured in aerated formate and bromide solutions using a model which makes use of fragmentation parameters derived from experiment and theory (14). Figure 4 includes the present data for $G(e_{aq}^-)$, showing the effects of an adjustment for fragmentation made in this way.

It should be noted that free radical yields can be compared legitimately only if they are measured in solutions that are equivalent in radical scavenging properties. In high nitrate concentrations, for example, scavenging of the electron recombination reactions would be expected to increase the measured $G(NO_2^-)$, an effect that is well established in gamma

radiolysis (17). For each of the radicals in Figure 4 the data refer to consistent radical scavenging conditions. The G_{OH} values in Figure 4 have all been normalized to a value of kc of about 4 x 10^6 sec^{-1} for electron and OH scavenging. On the basis of available rate constant data (13,15) this value is obtained at the concentrations listed below for the solutes used in these studies.

O_2	air-saturated
Br^-	5 x 10^{-3}M
Formate	1.9 x 10^{-2}M

$G(H_2O_2)$ from formate is essentially independent of formate concentration in the relevant range (16). G_{OH} in Figure 4 is the difference between $G(H_2O_2)$ from 5 x 10^{-2}M formate and from 5 x 10^{-3}M bromide solutions (3) - this latter value obtained by interpolation. In the ethanol/nitrate system, kc of 4 x 10^6 corresponds to 2.5 x 10^{-3}M ethanol and 3.5 x 10^{-4}M nitrate. The actual solute concentrations used to generate the e^-_{aq} data in Figure 4 were about on order of magnitude higher than this; 2.5 x 10^{-2}M ethanol and 2.5x10^{-3}M nitrate. Hence kc(OH) is 4x10^7 and kc(e^-_{aq}) is 3 x 10^7. Figure 3 shows that $G(e^-_{aq})$ is not affected significantly by varying ethanol concentration below about 2.5 x 10^{-2}M. We have not studied the effects of nitrate concentration on $G(e^-_{aq})$ with high energy heavy ions.

In Figure 4, G-values are plotted against Z^2/β^2. It can be seen that, for both e^-_{aq} and OH, the parameter Z^2/β^2 is unifying only if fragmentation is ignored. This apparent unification must therefore be regarded as coincidental, and not fundamental.

Conclusions

Solvated electron yields, like .OH radical yields, vary quantitatively with the physical parameters of the heavy ions producing them, in a manner predicted by diffusion theory. The solvated electron yield measured in the presence of an .OH-scavenger, ethanol, is enhanced at high ethanol concentrations because of the liberation of electrons that would otherwise have back reacted with .OH, principally in isolated radical pairs. The data are consistent with a diminished proportion of such isolated pairs as the incident heavy ion slow down. The parameter z^2/β^2 appears to unify the data, but only if fragmentation is ignored.

Acknowledgements

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List of Figures and Tables

Figure 1

Nitrite yields from (a) carbon, (b) neon and (c) argon ion irradiation of 2.5×10^{-3} M sodium nitrate / 2.5×10^{-2} M ethanol solutions as a function of residual range (cm.) of the primary ion.

Figure 2

Nitrite yields from argon ion irradiation of 2.5×10^{-3} M sodium nitrate solutions containing (a) 2.5×10^{-3} M (b) 2.5×10^{-2} M (c) 0.3 M (d) 1.0 M ethanol, as a function of residual range of the primary ion.

Figure 3

Nitrite yields from argon irradiation of 2.5×10^{-3} M sodium nitrate / ethanol solutions as a function of ethanol concentration. Data at three locations upstream of the Bragg peak.

Figure 4

G_{OH} and $G(e^-_{aq})$ as a function of z^2/β^2 of the primary ion for heavy ion radiolysis of aqueous solutions. See text for values of kc. Dashed lines show estimated G-values for the primary ions after adjustment for fragmentation.
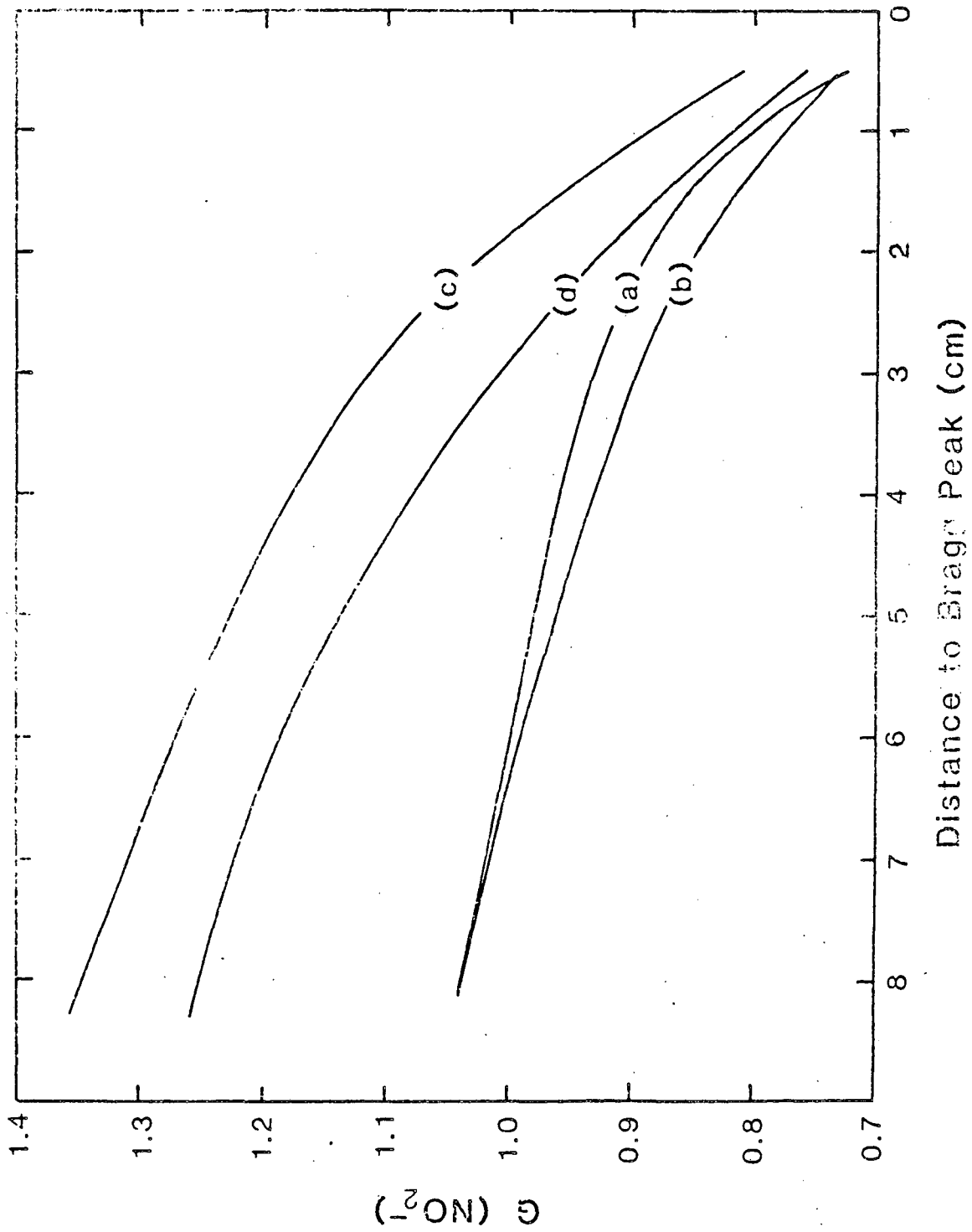
Distance to Bragg Peak (cm)
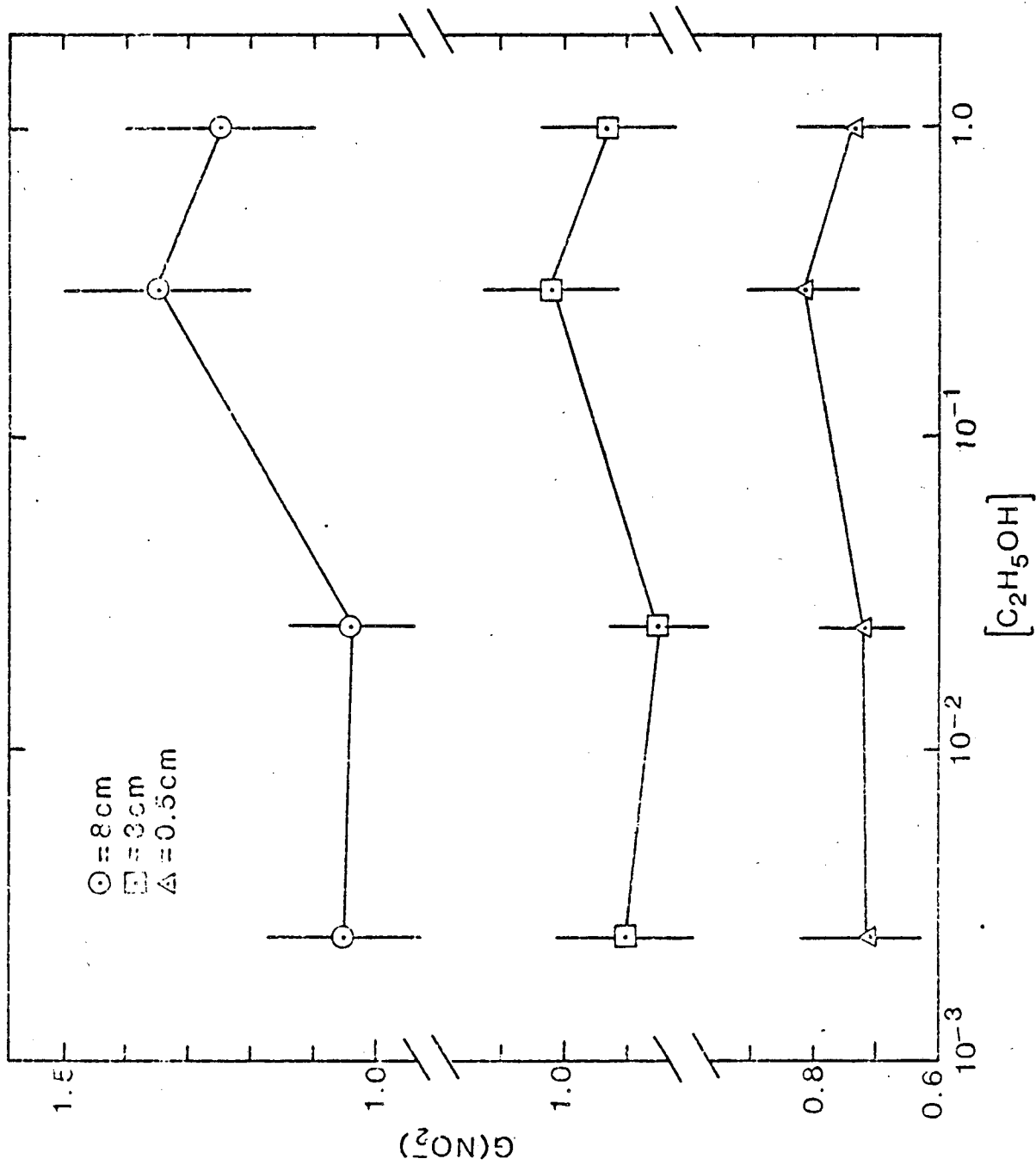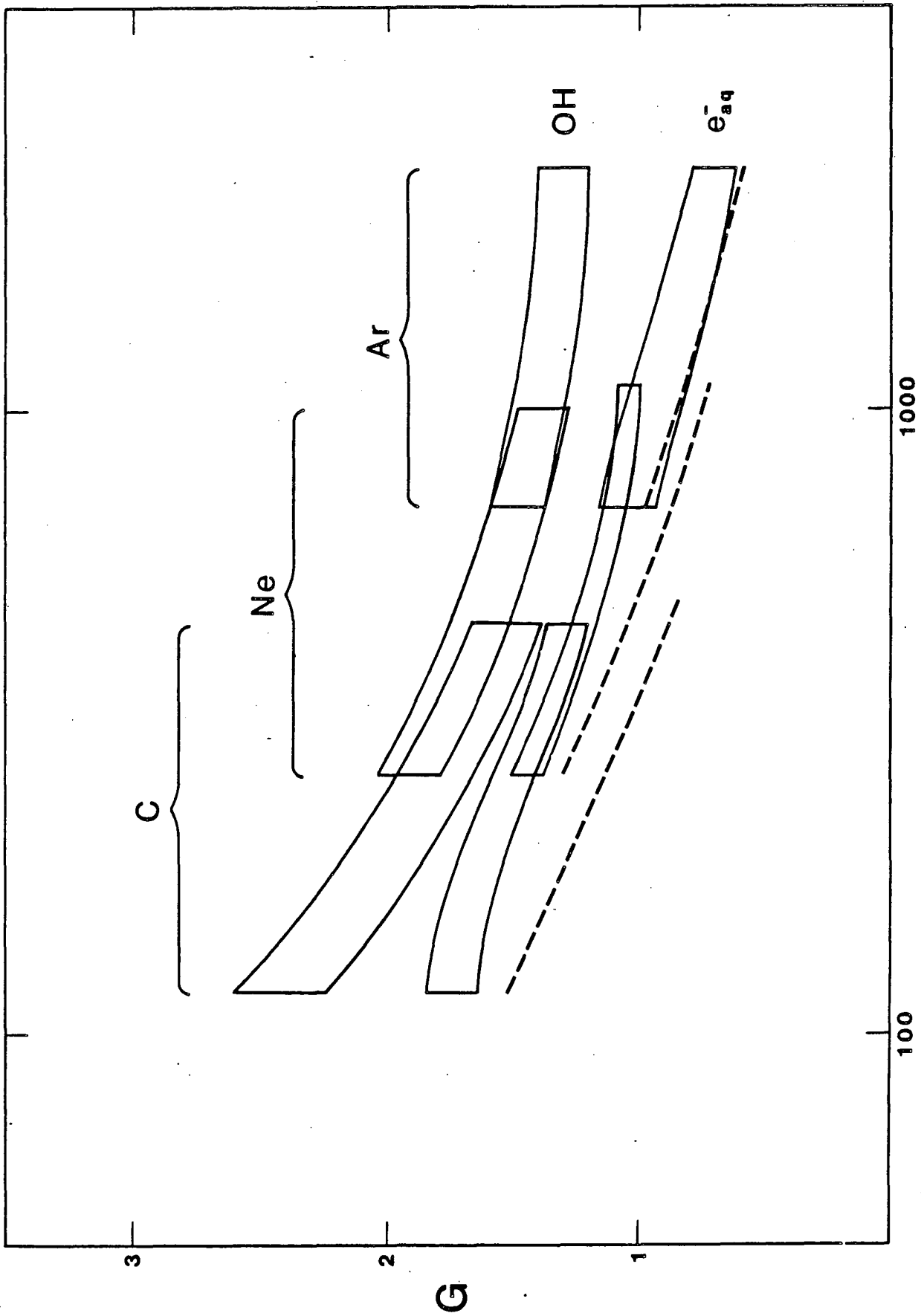
Fig. 1

$G(NO_2^-)$

Fig. 2

G (NO$_2^-$)

Distance to Bragg Peak (cm)

Fig. 3

Fig. 4

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