

Kinetics of Positive-Charge and Electron Scavenging and the Kinetics of Charge Neutralization in the Radiolysis of Dielectric Liquids

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used. The assumption implicit here is that the experimentally determined rate parameters (at 1100°K) are also valid at room temperature. In the earlier study, thermal properties at 1100°K (reaction temperature) were used. This assumes that the value for $(k_{AA}k_{BB}/k_{AB}^2)^{1/2}$, which is determined near room temperature, has no temperature dependence. It should also be remembered that the tabulated thermal values at the lower temperatures are undoubtedly more reliable. In the previous report⁵ the confidence limits have been given as $10^{\pm 0.6}$ in the frequency factor and 3 kcal in the activation energy. These also hold for the present results.

The calculated rate parameters for 1-butene decomposition can be compared with the experimental values of Sehon and Szwarc⁷ and Kerr, Spencer, and Trotman-Dickenson.¹² It can be seen that the present activation energy and frequency factors are 10 kcal

and 2 orders of magnitude higher, respectively. The agreement in absolute rates is somewhat better. At 950°K (temperature at which flow experiments are carried out) the results of Sehon and Szwarc give $k=0.07 \text{ sec}^{-1}$, while those of Kerr and co-workers yield $k=0.12 \text{ sec}^{-1}$ (10 mm Hg pressure). The present calculations give a value of $k(950^\circ\text{K})=0.07 \text{ sec}^{-1}$. In making comparisons of this type, there is considerable room for error and a confidence limit of a factor of 3 is probably applicable. Nevertheless, inasmuch as the calculated rate is a unimolecular high-pressure value, the agreement found here indicates that the flow experiments have been carried out at or very close to the high-pressure limit. Thus, the large pressure effect (as observed by Kerr and co-workers) and the discrepancy in rate parameters might be due to some cause other than the hypothesis that the reaction is occurring well into the "falloff" region.

Kinetics of Positive-Charge and Electron Scavenging and the Kinetics of Charge Neutralization in the Radiolysis of Dielectric Liquids

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The kinetics of the scavenging of positive and negative species in spurs during the radiolysis of liquids is described. The motions of the positive ions, the solvated electrons, and the scavenger molecules are simultaneously taken into consideration. The kinetic equation contains two adjustable parameters, β and f , but in most instances f is taken as unity. The theory is tested, with moderate success, against previously published results of studies of positive-ion and electron scavenging in cyclohexane and *n*-hexane.

The recently observed complexity of the kinetics of ion-neutralization reactions in liquid cyclohexane, after a pulse of radiation, is explained in terms of the same model as that used in the scavenging kinetics.

It is concluded from the over-all success of the theory that solvated electrons form in suitable nonpolar molecular liquids, such as alkanes, during radiolysis.

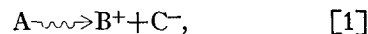
The terms "thermal electron" and "spur" are not used by all authors to mean the same things, so they are discussed in the Appendixes in the hope that the meanings of these terms will become more standardized. The quasifree, trapped, and solvated states of electrons are distinguished in Appendix A. A definition of the term "spur" is offered in Appendix B.

INTRODUCTION

IN this paper, a model that was presented earlier¹ to describe the scavenging of positive ions in the radiolysis of liquids is refined and generalized. It is then applied to the scavenging of positive ions and of solvated electrons and to the kinetics of charge neutralization in the radiolysis of saturated liquid hydrocarbons. The model makes use of nonhomogeneous kinetics.

The charged species generated during the radiolysis of a pure liquid compound form products in definite

yields. For example,



Suitable solutes in the liquid can react with the ions derived from the solvent before the neutralization reaction [2] occurs.



and/or



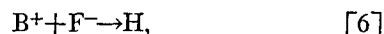
where S is a scavenger. The yield of product D is

¹ G. R. Freeman, J. Chem. Phys. **43**, 93 (1965).

thereby reduced and a new product is usually formed. For example,



or



and so on.

The competition of the ion-scavenging reactions [3] and [4] with the neutralization reaction [2] is studied by measuring the yield of D or of a new product, for example, G, as a function of the concentration of the scavenger.

An accurate description of the competition between Reactions [2], [3], and [4] would require accurate knowledge of (a) the initial relative spacial distribution of B^+ and C^- , (b) the motions of B^+ and C^- under the double influence of the random diffusion forces and the force of their mutual electric field,² (c) the effective encounter radii for Reactions [2], [3], and [4], and (d) the encounter efficiencies of Reactions [2], [3], and [4]. This accurate knowledge is not available, so a model will be presented in which reasonable estimates are used.

MODEL

Initial Relative Spacial Distribution of the Charges

The relative spacial distribution of the positive ions and the initially thermalized electrons (Appendix A) can be estimated from the shape of the spectrum of initial separation distances of the positive-ion-thermalized-electron pairs. The shape of the spectrum, not the absolute spectrum itself, is important in the present problem. A crude spectrum of initial separation distances has been constructed using an approximate distribution of initial energies of the electrons set in motion in the medium and the approximate penetration ranges of the electrons of different energies in the medium (Appendix B).

The $N(y)$ -vs- y spectra, where $N(y)$ is the relative number of positive-ion-thermalized-electron pairs that have an initial separation distance y , for water, cyclohexane, and n -hexane are given in Table I.

Motions of the Charged Species Under the Double Influence of the Random Diffusion Forces and the Force of Their Mutual Electric Field

It is necessary to have knowledge of the ion motions to be able to determine how many molecules each of the ions meet between their creation and neutralization. The electron thermalization process requires only 10^{-14} – 10^{-13} sec. The lifetime before neutralization, for the majority of the ions, is $\geq 10^{-11}$ sec, so the period during which the electrons are being thermalized is

² In polar solvents, ionic scavengers can be used, in which case the charge on S has to be considered.

TABLE I. Spectra of ion-pair separation distances in water, cyclohexane, and n -hexane at 20°.

$N(y)$	y (10^{-8} cm)		
	H ₂ O	C ₆ H ₁₂	C ₆ H ₁₄
2150	14	17	20
1100	16	20	22
600	19	23	27
476	26	32	36
270	44	54	62
116	72	88	101
64	104	127	146
41	140	171	196
28	181	220	253
21	225	274	315
16	274	334	383
13	326	398	456
15	397	484	556
14	505	616	706
10	643	783	899
8	795	970	1110
6	960	1170	1340
8	1220	1490	1710
10	1650	2010	2310
34	>2200	>2700	>3100
Total	5000		

negligible. Therefore, only the postthermalization period is considered.

The ion pairs that undergo geminate recombination do so under the influence of their mutual electric field. The number of new molecules met by an ion before it undergoes geminate neutralization is equal to the number n of diffusive jumps made by the ion multiplied by the average number b of new neighbors that it meets per jump.

Williams³ improved the original theory¹ by calculating the number of diffusive jumps by using Eq. (1),

$$n = t_{gr}/t_1, \quad (1)$$

where t_{gr} is the time required for geminate recombination to occur and t_1 is the average time required for one diffusive jump. Now,⁴

$$t_{gr} = \epsilon(y^3 - r_0^3)/4.32 \times 10^{-7}(u_+ + u_-) \text{ sec}, \quad (2)$$

where ϵ is the static dielectric constant of the medium, r_0 is the encounter radius of Reaction [2], i.e., it is the center-to-center distance, in centimeters, of the positive and negative species at the instant the final electron jump occurs, and $(u_+ + u_-)$ is the sum of the mobilities, in square centimeters per volt-second, of the positive and negative species. The constant 4.32×10^{-7}

³ J. W. Buchanan and F. Williams, J. Chem. Phys. **44**, 4377 (1966).

⁴ G. R. Freeman and J. M. Fayadh, J. Chem. Phys. **43**, 86 (1965).

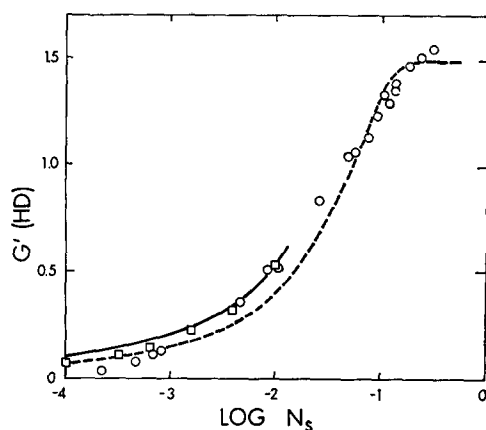


FIG. 1. Scavenging of positive ions in liquid cyclohexane. $G'(\text{HD})$ is the measured HD yield minus the amount of HD produced by the direct radiolysis of the scavenger. N_s is the mole fraction of scavenger S. \square , S is ND_3 (Ref. 6); \circ , S is $\text{C}_2\text{H}_5\text{OD}$ (Ref. 3).

has units of volt·centimeter. Furthermore,⁵

$$t_1 = d\lambda^2/6D \text{ sec}, \quad (3)$$

where d is a constant in the vicinity of unity and has the same value for all liquids, λ is the mean jump distance (or mean free path) in centimeters, and D is the diffusion coefficient of the species involved, in square centimeters per second.

The average number, b , of new molecules that an ion encounters per jump depends on the ion-molecule effective encounter radius, on the jump distance, on the packing of the molecules in the medium, and on the diffusion coefficients of the molecules in the medium. This, and the previous items (c) and (d), are considered in the following development of the kinetics of the charge-scavenging reactions.

KINETICS OF CHARGE SCAVENGING

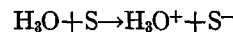
The equations that describe the fractions of the positive and negative charges that are scavenged at a given scavenger concentration must take into consideration the facts that all the species (positive, negative, and scavenger) move and that the encounter efficiencies of one or both of Reactions [3] and [4] can be less than unity. It is also possible that the encounter efficiency of Reaction [2] is less than unity, although the probability is small and is neglected.

The kinetics could be adjusted to include exceptional cases, if necessary. For example, if the H_2O formed by



has an appreciable lifetime, it is conceivable that the

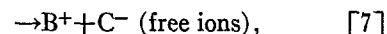
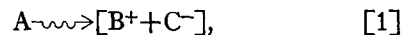
reaction



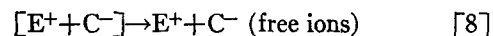
could occur. Such refinements as this are neglected in the present treatment.

The equation is derived for the scavenging of the positive ions. The equation for negative-charge scavenging can readily be shown to have exactly the same form.

The detailed mechanism for positive-ion scavenging is as follows. The square brackets around the reactants and products indicate that the entities are inside a spur.



The reaction



also occurs but does not affect the kinetics because it is followed by reaction [5fi] in the present mechanism.

The probability that B^+ will not encounter an S in one diffusive jump is given by the statistical expression $(1 - N_s)^{b_+}$, where N_s is the mole fraction of S in the solution and b_+ is the number of new neighbors that B^+ encounters per jump. Therefore, the probability that B^+ will encounter at least one S per diffusive jump is given by $[1 - (1 - N_s)^{b_+}]$. For the ions that undergo geminate recombination, the probability that B^+ encounters at least one S before encountering its counterion C^- is given by $[1 - (1 - N_s)^{b_+ n_+}]$, where n_+ is the number of diffusive jumps that B^+ takes before encountering its C^- . The probability that Reaction [3 sp] occurs before Reaction [2 sp] is given approximately by $[1 - (1 - f_+ N_s)^{b_+ n_+}]$, where $0 \leq f_+ \leq 1$ is the encounter efficiency of Reaction [3sp]. The last expression assumes that an encounter with x molecules of S at once is as effective as x encounters with a single S, and that the S molecules do not diffuse. If a different assumption were made; namely, that the scavenger and solvent molecules diffuse and the ion remains motionless during its lifetime, the probability that one of the diffusing molecules that encounters the ion during its lifetime is not a scavenger would be $(1 - N_s)^{b_+ n_+}$, where b_+ is the number of new neighbors that S encounters per diffusive jump and n_+ is the number of diffusive jumps that S makes in time t_{gr} . Actually, the ion, scavenger, and solvent molecules all move, so the total probability that the ion will not be scavenged during its lifetime is $(1 - f_+ N_s)^{(b_+ n_+ + b_s n_s)}$. Thus, the probability ϕ_+ that Reaction [3sp] occurs before Re-

⁵ Equation (3) is at least a useful approximation and d is usually taken as unity. (a) S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943); (b) S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley & Sons, Inc., New York, 1958), pp. 81-83 (1 on p. 82 refers to the number of collisions in time t , not to the total path length as stated); (c) W. Jost, *Diffusion in Solids, Liquids, Gases* (Academic Press Inc., New York, 1960), pp. 25-30.

action [2sp] is

$$\phi_+ = 1 - (1 - f_+ N_s)^{(b_+ n_+ + b_s n_s)}. \quad (4)$$

With the aid of Eqs. (1)–(3), Eq. (4) can be rewritten as

$$\phi_+ = 1 - (1 - f_+ N_s)^{\beta_+ \nu}, \quad (5)$$

where

$$\beta_+ = [1/(u_+ + u_-)] [(b_+ D_+ / \lambda_+^2) + (b_s D_s / \lambda_s^2)] V / \text{cm}^2, \quad (6)$$

$$\nu = 6\epsilon(\gamma^3 - r_0^3) / 4.32 \times 10^{-7} d \text{ cm}^2 / V, \quad (7)$$

D_+ and λ_+ are the diffusion coefficient and average jump distance of the positive ions, and so on.

A certain fraction ϕ_{fi} of the ions escape geminate recombination and become free ions (Reaction [7]). This fraction is given by⁴

$$\phi_{fi} = e^{-r/\nu}, \quad (8)$$

where $r = \xi^2 / \epsilon k T$, ξ is the charge on an electron (esu), k is Boltzmann's constant (ergs per degree), and T is the temperature (degrees Kelvin).

It should be noted that ϕ_{fi} does not depend directly on N_s , whereas ϕ_+ does. However, ϕ_{fi} does change if ϵ changes with N_s .

At scavenger concentrations where scavenging of B^+ ions in the spurs becomes appreciable, all the B^+ free ions are scavenged, because the lifetimes of the free ions at dose rates obtainable with ^{60}Co γ sources ($< 10^{23}$ eV/g·h) are several orders of magnitude longer than the lifetimes of the ions that undergo geminate recombination. Thus, under these conditions the total probability Φ_+ that a B^+ ion with an initial B^+ - C^- separation distance y is scavenged, is given by

$$\Phi_+ = \phi_{fi} + \phi_+(1 - \phi_{fi}). \quad (9)$$

It should be noted that

$$\Phi_+ = f n(N_s, f_+, y, r_0, u_+, u_-, b_+, \lambda_+, b_s, D_s, \lambda_s, \epsilon, T),$$

but that the only separately adjustable parameters in the kinetic analysis are β_+ and f_+ .

Furthermore, under these conditions,

$$G(E^+) = [\sum N(y) \Phi_+ / \sum N(y)] G(B^+)_0, \quad (10)$$

where $G(B^+)_0$ is the yield of B^+ initially formed by Reaction [1].

Equation (10) is solved numerically, with the aid of the $N(y)$ -vs- y spectrum.

Similarly, it can be shown that the probability ϕ_- that Reaction [4sp] occurs before Reaction [2sp] is given by Eq. (11).



$$\phi_- = 1 - (1 - f_- N_s)^{\beta_- \nu}, \quad (11)$$

where $0 \leq f_- \leq 1$ is the encounter efficiency of Reaction [4sp], N_s and ν are the same as before, and

$$\beta_- = [1/(u_+ + u_-)] [(b_- D_- / \lambda_-^2) + (b_s D_s / \lambda_s^2)], \quad (12)$$

where b_- , D_- , and λ_- are, respectively, the average number of new neighbors encountered per jump, the diffusion coefficient, and average jump distance of C^- . Furthermore,

$$\Phi_- = \phi_{fi} + \phi_-(1 - \phi_{fi}), \quad (13)$$

where ϕ_{fi} is the same as before. Thus,

$$G(F^-) = [\sum N(y) \Phi_- / \sum N(y)] G(C^-)_0, \quad (14)$$

where $G(C^-)_0$ is the yield of C^- initially formed by Reaction [1].

Equation (14) is also solved numerically, with the aid of the $N(y)$ -vs- y spectrum.

For the radiolysis of a given liquid A in the presence of a given concentration of scavenger S, $G(E^+)$ and $G(F^-)$ can differ because of differences in the values of f_+ and f_- , of u_+ and u_- (hence of D_+ and D_-), of b_+ and b_- and of λ_+ and λ_- .

Application of Eqs. (10) and (14)

Positive ions in liquid cyclohexane have been scavenged with ND_3 ⁶ and $\text{C}_2\text{H}_5\text{OD}$,³ and those in *n*-hexane have been scavenged by D_2S .⁷ Electrons in liquid cyclohexane have been scavenged by N_2O .⁸ These results provide a test of the theory presented in the previous section.⁹

It is assumed for all these systems that: $r_0 = 1.0 \times 10^{-7}$ cm; $d = 1$; $G(\text{total ionization}) = 3.0$.¹ Furthermore, at 25°C : $D_e = 0.026 u_e \text{ cm}^2/\text{sec}$; $r = 5.60 \times 10^{-6}/\epsilon \text{ cm}$. The pertinent equations are (5) to (14).

Consider first ND_3 and $\text{C}_2\text{H}_5\text{OD}$ in cyclohexane. For these two scavengers, the values of ϕ_+ [Eq. (5)] at a given value of N_s can differ because of differences in the values of f_+ and β_+ . The values of β_+ [Eq. (6)] can differ because of differences in the values of the term $(b_s D_s / \lambda_s^2)$ and because the scavengers might also interact with the negative species and alter u_- . Thus f_+ and β_+ will be treated as adjustable parameters. The value of ν [Eq. (7)] will change at high values of N_s because of the change in dielectric constant of the solution, but it is assumed that the microscopic dielectric constant is equal to that of the bulk solution, so ν is not considered to be adjustable. The dielectric constant of the bulk solution is taken as

$$\epsilon = \epsilon_A(1 - N_s) + \epsilon_s N_s, \quad (15)$$

where ϵ_A and ϵ_s are the static dielectric constants of pure liquid A and pure liquid scavenger, respectively.

⁶ F. Williams, J. Am. Chem. Soc. **86**, 3954 (1964).

⁷ G. Meissner and A. Henglein, Ber. Bunsenges. Physik. Chem. **69**, 264 (1965).

⁸ G. Scholes and M. Simic, Nature **202**, 895 (1964).

⁹ The equation applied by Williams³ to the scavenging of positive ions by $\text{C}_2\text{H}_5\text{OD}$ in cyclohexane was $\Phi_+ = 1 - (1 - zN_s)^n$, where z is the number of nearest neighbors surrounding the ion. For the model he used, this equation should have been $\Phi_+ = 1 - (1 - N_s)^n$ and, furthermore, z is the number of new neighbors encountered per diffusive jump of the ion. However, the present Equation (10) is based on a more complete model than either of those published earlier.^{1,5}

TABLE II. Fundamental quantities.

	C ₆ H ₁₂ -ND ₃	C ₆ H ₁₂ -C ₂ H ₅ OD	C ₆ H ₁₂ -N ₂ O	C ₆ H ₁₄ -D ₂ S	Ref.
ϵ	2.02(1- N_s) + 15 N_s	2.02(1- N_s) + 24 N_s	2.02	1.89(1- N_s) + 5.8 N_s	
f_+	0.60	1.0		1.0	
f_-			1.0		
u_+ (10 ⁻⁴ cm ² /V·sec)	5.4	5.4	5.4	14	a
u_- (10 ⁻³ cm ² /V·sec)	2.5	2.5	2.5	3.2	b
b_+	4	4		4	
b_-			6		
λ_+ (10 ⁻⁸ cm)	2.7	2.7		3.0	c
λ_- (10 ⁻⁸ cm)			1		
b_s	4	4	4	4	
λ_s (10 ⁻⁸ cm)	2.7	2.7	2.7	3.0	c
D_s (10 ⁻⁶ cm ² /sec)	3.6	2.0	2.8	7.4	a

^a Calculated as in Ref. 16.

^b The mobility of a solvated electron in water at room temperature [1.8×10^{-4} cm²/V·sec, calculated from $D(e_{aq}^-) = 4.7 \times 10^{-5}$ cm²/sec, E. J. Hart, quoted by M. Anbar, *Advan. Chem. Ser.* **50**, 59 (1965)] is 3.5 times that of a solvated sodium ion in water (5.2×10^{-4} cm²/V·sec). The corresponding ratio of mobilities in liquid ammonia at -33° is $9.1 \times 10^{-3} / 1.5 \times 10^{-3} = 6.1$ [calculated from data of

D. S. Berns, *Advan. Chem. Ser.* **50**, 82 (1965)]. It is therefore assumed as a first approximation, that $u_-/u_+ \approx 5$ in cyclohexane.

^c The mean free paths, determined from viscosity measurements, of molecules in liquid ether, benzene, and chloroform, are approximately half of the molecular diameters, at room temperature [R. D. Kleeman, *A Kinetic Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1920), p. 132].

Calculations on the cyclohexane-ND₃ system were done as follows. It was assumed that there was no isotope effect in Reaction [9],



so 3.0 units of ND₃H⁺ would result in the formation of 2.25 units of HD by Reaction [10].

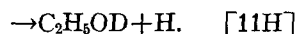
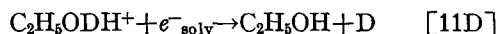


Therefore,

$$G(\text{HD}) = \left[\sum N(y) \Phi_+ / \sum N(y) \right] 2.25. \quad (16)$$

The data required to calculate Φ_+ are given in Table II. The $N(y)$ -vs- y spectrum is in Table I. An example calculation is given in Table III and the calculated curve is shown along with Williams's results⁶ in Fig. 1. At these low concentrations of ND₃ ($N_{\text{ND}_3} \leq 0.010$), the same curve would be obtained by using $f_+ = 1.0$ and $\beta_+ = 5.4 \times 10^{13}$ V/cm², and this set of parameters is just as reasonable as the set shown in Table III, so far as is known at present. The values of the "fundamental quantities" in Table II are not known accurately, so the lower value of β_+ could be obtained by altering the values of these quantities.

Calculations on the other systems were done similarly. In the cyclohexane-C₂H₅OD system it was assumed that there was no isotope effect in Reaction [11].



Thus,

$$G(\text{HD}) = \left[\sum N(y) \Phi_+ / \sum N(y) \right] 1.5. \quad (17)$$

With the aid of the information in Tables I and II, the dashed curve in Fig. 1 was calculated. The experimental points are those of Williams, corrected for HD production from the direct radiolysis of the C₂H₅OD.³

For the cyclohexane-N₂O system, most of the values of the fundamental quantities in Table II are essentially those that would be expected for ordinary ions or molecules in cyclohexane, but the values of b_- and λ_- are abnormal. The solvated electron has a relatively diffuse structure, i.e., the electron is not completely confined to a single cavity, so the electron might diffuse by small deformations of the local structure of the liquid. In this case λ_- would be small, e.g., 1 Å. However, since the electron is not confined to a single cavity, it has a relatively large reaction radius.¹⁰ Thus the electron meets more new neighbors per diffusive jump than would a normal ion with the same λ . Hence the value $b_- = 6$ does not seem unreasonable. The theoretical curve is shown in Fig. 2. The experimental points were calculated from results of Scholes and Simic.⁸ For a measure of the yield of scavenged electrons, $\Delta G(\text{H}_2)$ was used instead of $G(\text{N}_2)$ because of the uncertainty of the origin of the large yields of nitrogen. If $G(\text{N}_2)/2$ were used as a measure of the yield of scavenged electrons, it would be necessary to decrease β_- (e.g., by decreasing b_-/λ_-^2) by a factor of 3 to obtain agreement between theory and experiment. This would indicate that the solvated electron was even more localized than was assumed above.

The curve calculated for the *n*-hexane-D₂S system is also shown in Fig. 2. None of the values of the fundamental quantities for the *n*-hexane-D₂S system (Table II) are unusual except perhaps that assumed for u_- , which is only 2.3 times that of u_+ . Solvated electrons have been reported to react with D₂S in water.¹¹ Although they apparently do not react with D₂S in *n*-hexane,⁷ perhaps the interaction is strong enough that

¹⁰ The value of r_0 in Eqs. (2) and (7) was taken as 10 Å because it was assumed that the radius of a cyclohexane ion was about 3 Å and the effective reaction radius of a solvated electron in cyclohexane or *n*-hexane was roughly 7 Å.

¹¹ G. Meissner and A. Henglein, *Ber. Bunsenges. Physik. Chem.* **69**, 3 (1965).

the electron becomes associated with a D_2S molecule if it meets one, thereby decreasing the value of u_- . It is evident from the cyclohexane solutions considered above that the electrons are more readily scavenged than are the positive ions. Thus, if an electron becomes associated with a D_2S molecule and u_- decreases, the probability that the parent ion will be scavenged increases. This type of behavior has been observed in the scavenging of positive ions in liquid alkanes by cyclopropane- d_6 , in the presence and absence of carbon tetrachloride.¹²

The agreement between experiment and theory is not excellent, but it is good enough to encourage one to seek refinements in both theory and experiment. At very low values of N_s , the theoretical curves lie above the experimental points. This has several possible explanations, two of which are that the secondary electron-energy distribution probably decreases more rapidly than E^{-2} at $E > 150$ eV,¹³ and that traces of impurities might enter the reaction mechanism when the added scavenger is present at very low concentrations, thereby preventing the formation of some of the expected product.

In the cyclohexane- C_2H_5OD system, the agreement between theory and experiment might be improved by considering that the alcohol associates to some extent at higher concentrations, thereby decreasing the effective scavenger concentration. This would decrease the curvature of the intermediate portion of the curve in Fig. 1. Association of the alcohol might also alter the microscopic dielectric constant significantly from the average dielectric constant of the bulk liquid.

Removal of other crude approximations from the theory, e.g., by including a distribution of spur populations, might also improve the agreement with experiment.

TABLE III. Calculation of $G(HD)$ for cyclohexane radiolysis when $N_{ND_2} = 1.0 \times 10^{-2}$.^a

y (10^{-8} cm)	$N(y)$	ϕ_{fi}^b	$\beta_+ \nu^c$	ϕ_+^d	$N(y) \Phi_+$
17	2150	10^{-7}	11	0.064	138
20	1100	10^{-6}	19	0.108	119
23	600	10^{-5}	30	0.164	98
31	476	10^{-4}	86	0.40	191
54	270	0.0081	423	0.92	248
88	116	0.052	1840	1.00	116
>100	288	>0.08	>2700	1.00	288
Total	5000				1198

^a $G(HD) = (2.25)(1198)/5000 = 0.54$.

^b $\phi_{fi} = \exp(-2.60 \times 10^{-6}/y)$.

^c $\beta_+ = 9.0 \times 10^{13} \text{ V/cm}^2$, $\nu = 3.0 \times 10^7 (y^3 - 1.0 \times 10^{-21}) \text{ cm}^2/\text{V}$.

^d $(1 - f_+ N_s) = 0.9940$.

¹² P. Ausloos, A. A. Scala, and S. G. Lias, J. Am. Chem. Soc. **88**, 1583 (1966).

¹³ Expression (20), Appendix B, is not exact because E has a maximum value equal to half of the primary electron energy. Hence, for a monoenergetic primary electron beam, $P_E \approx AE^{-2} - BE^j$, where $j > -2$. The over-all initial energy distribution of the electrons set in motion in a radiolysis system is then $N(E) \approx \sum_i (A_i E^{-2} - B_i E^j) \propto E^{-k}$, where $k > 2$, for $E > 100$ or 200 eV.

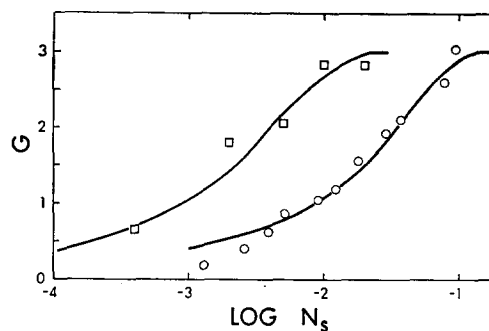


FIG. 2. Scavenging of electrons in cyclohexane, and of positive ions in n -hexane. N_s is mole fraction of scavenger. \square , $\Delta G(H_2)$ for N_2O in cyclohexane (Ref. 8), $\Delta G(H_2) = 5.6 - G(H_2)_{\text{observed}}$; \circ , $G(D_2)$ for D_2S in n -hexane (Ref. 7).

KINETICS OF CHARGE NEUTRALIZATION

In recent pulse-radiolysis experiments it has been observed that the ion-neutralization reaction in liquid cyclohexane does not follow a simple order.¹⁴ The yield of positive and negative ions of aromatic solutes was measured spectroscopically. Furthermore, it was observed that the ion yield was 10%–20% greater at a few tenths of a microsecond than it was at 2–3 μsec .

The decrease of the concentration of ions in a liquid, as a function of time after an instantaneous pulse of radiation, can be estimated with the aid of the present model.

Equation (2) demonstrates that for a given pair of ions in a spur in a given liquid, each value of the initial separation distance y has a corresponding value of the geminate recombination time t_{gr} .¹⁵ Thus an $N(y)$ -vs- y spectrum (Table I) can be transformed into an $N(t_{gr})$ -vs- t_{gr} spectrum. $N(t_{gr})$ is a step function and it is too coarse for present purposes, so it is transformed into a continuous function as follows. The total number of ions $N(t)$ that survive at time $t < 10^{-6}$ sec after an instantaneous pulse of radiation is given by

$$N(t) = \sum_{t_{gr} \leq t} N(t_{gr}) \cdot (1 - \phi_{fi}) + \sum N(y) \phi_{fi}. \quad (18)$$

Equation (18) takes into account the formation of free ions (Reaction [7]), which have relatively long lifetimes. However, Eq. (18) neglects the mutual neutralization of the free ions in the bulk solution (Reaction

¹⁴ J. P. Keene, E. J. Land, and A. J. Swallow, J. Am. Chem. Soc. **87**, 5284 (1965).

¹⁵ In the application of Eq. (2) to polar liquids at values of y smaller than about 15 Å, the complex dielectric constant would have to be used because the recombination times would be similar to the dielectric relaxation time of the liquid. However, if very small values of y were included, $G(\text{total ionization}) > 3.0$ would have to be used because $W < 33$ eV for organic compounds. The ion pairs with very small values of y , and hence recombination times of 10^{-12} sec or less, can be considered in the present context to be excited molecules and are neglected in this paper.

The present work deals only with saturated hydrocarbons, whose complex dielectric constants are very nearly the same as their static dielectric constants. Furthermore, the experiments of the next few years will probably be limited to a time resolution of 10^{-9} sec, so the application of the theory has not been extended below 10^{-10} sec (see Fig. 3).

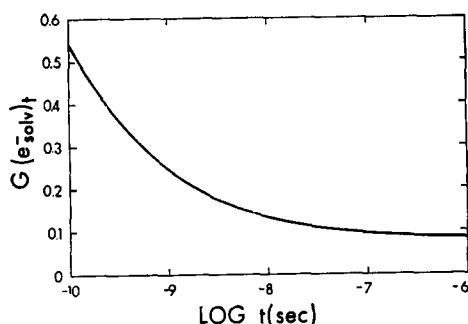


FIG. 3. The yield of solvated electrons that would be observed at time t in liquid cyclohexane.

[2fi]). In the pulsed electron radiolyses of cyclohexane¹⁴ the free-ion concentrations must have approached 10^{-7} M at the doses and dose rates used, so Reaction [2fi] must have become significant at $t > 10^{-8}$ sec. Thus Eq. (18) applies only to $t < 10^{-8}$ sec in this case.

By drawing a smooth curve through a plot of $N(t)$ vs t , a continuous function $n(t)$ is obtained.

The yield of C^- ions $G(C^-)_t$ that would be observed spectroscopically at time t can be calculated from $n(t)$ according to Eq. (19).

$$G(C^-)_t = [n(t)/n(0)] G(\text{total ionization}), \quad (19)$$

where $n(0)$ is the number of C^- ions at $t=0$.

It is demonstrated in a later section of the paper that C^- is a solvated electron in liquid saturated hydrocarbons. Figure 3 shows a plot of $G(e^-_{\text{solv}})_t$ vs t for $t = 10^{-10}$ to 10^{-6} sec in pure cyclohexane at 25° . This curve was calculated by using $r_0 = 1.0 \times 10^{-7}$ cm, $(u_+ + u_-) = 3.0 \times 10^{-3}$ cm²/V·sec, and $G(\text{total ionization}) = 3.0$, as in the previous section.

For the present purpose, the absolute values of $G(e^-_{\text{solv}})_t$ are less important than is the shape of the curve. In nonhomogeneous kinetics, the concept of the order of a reaction cannot be properly used, but the concept is so well known that it is useful to use it in the present context. The "order" of the charge neutralization decreases from 1.4 at 10^{-10} sec to 1.1 at 10^{-7} sec. The order continues to decrease toward unity until the time when the second-order recombination of the free ions in the bulk solution becomes significant, at which time the order increases toward 2.0.

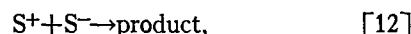
The above considerations apply to the positive ions as well as to the solvated electrons in the system.

When sufficient scavenger is present that the charged species that are observed are scavenger ions, the same treatment and conclusions apply to the neutralization of the scavenger ions. The appropriate values of r_0 , u_+ , and u_- must be used.

The observation that the neutralization of the aromatic ions in cyclohexane did not follow a simple order¹⁴ is thus explained.

Biphenyl and anthracene were the solutes used in the experiments in which the ion yield was observed to be

10%–20% greater at a few tenths of a microsecond than it was at $2\text{--}3 \mu\text{sec}$. Each of these solutes captures both positive and negative charges, so in each case the observed neutralization reaction was



where S represents the solute. Thus, $(u_+ + u_-) \approx 7 \times 10^{-4}$ cm²/V·sec.¹⁶ The results are not very sensitive to the value of r_0 , so $r_0 = 1.0 \times 10^{-7}$ cm was used. The calculated value of $G(S^+ + S^-)$ at 2×10^{-7} sec was 20% higher than that at 2×10^{-6} sec, in agreement with experiment.

The apparent value of the rate constant for charge neutralization in the cyclohexane–styrene solution (1.7×10^{12} liters/mole·sec)¹⁴ is only about three times larger than would be expected¹⁶ for the neutralization of two styrene ions, not 200 times greater as suggested by Keene *et al.*¹⁴ Since the quantity actually measured was the ratio of the rate constant to the extinction coefficient, if the extinction coefficient of the species is about 8000 liters/mole·cm at 4100 \AA , rather than 23 000 liters/mole·cm as suggested, the transient could be identified as a styrene ion.

THE IDENTITY OF C^-

The negative species initially generated in Reaction [1] is an electron. In liquid compounds such as those in the present work, that do not capture electrons to form negative molecular ions, C^- must be a quasifree, trapped, or solvated electron. If C^- were a quasifree electron, a value of $u_-/u_+ \approx 10^{\pm 1}$ would be expected. The mobilities of positive ions in liquid cyclohexane are $10^{-4}\text{--}10^{-3}$ cm²/V·sec, whereas that of a quasifree electron would be $10\text{--}10^2$ cm²/V·sec.¹⁷ If C^- were a trapped or a solvated electron, a value of $u_-/u_+ \lesssim 10$ would be expected.¹⁸ Agreement was obtained between experiment and theory using $u_-/u_+ < 10$ for both charge scavenging and charge neutralization. The fact that this low value of the ratio applies to the charge-scavenging experiments, where large concentrations of scavengers caused C^- to be scavenged in less than 10^{-10} sec, means that the low value cannot be explained by saying that trace impurities scavenged the electrons, thereby lowering their mobilities. Thus C^- in a liquid saturated hydrocarbon is a trapped or a solvated electron. The distinction between the trapped and solvated states of electrons is made on the basis of lifetime, a solvated electron being one that lives for a period longer than the dielectric relaxation time of the liquid before being neutralized or scavenged (Appendix A).

GENERAL CONCLUSION

The same over-all theory explains values of $G(\text{free ions})$ in different liquids,⁴ positive-ion and electron-

¹⁶ Calculated as in G. R. Freeman, J. Chem. Phys. **39**, 988 (1963); **41**, 901 (1964).

¹⁷ The mobility of quasifree electrons in liquid argon at 85°K is $440 \text{ cm}^2/\text{V}\cdot\text{sec}$; H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. Letters **15**, 187 (1965).

¹⁸ Footnote b, Table II.

scavenging and charge-neutralization kinetics. It is therefore concluded that solvated electrons form in suitable nonpolar molecular liquids, such as alkanes, during radiolysis.

ACKNOWLEDGMENT

I would like to express appreciation to Dr. Ffrancon Williams for sending me a preprint of Ref. 3.

APPENDIX A: STATES OF THERMALIZED ELECTRONS IN LIQUIDS

A thermal electron is one that has only thermal energy available for diffusion or translation through the medium. Thus, in the term "thermalized electron," the word "thermalized" does not include the internal kinetic energy, i.e., the zero-point energy, of a trapped or solvated electron.

The term "thermalized electrons" encompasses trapped and solvated electrons and also includes quasifree electrons of thermal energy. There is lack of clarity in the literature about the differences between these states of electrons. Some of the differences are illustrated in the following paragraphs.

An extra electron in a molecular medium can be attached to a single molecule, forming a negative ion, or it can be bound more or less equally by several molecules at the same time, forming a trapped or a solvated electron, or it can be relatively uninfluenced by the medium, in which case it is a quasifree (nearly free) electron. The mobilities of trapped and solvated electrons in the liquid phase are of the same order of magnitude as that of a negative ion, whereas that of a quasifree electron is several orders of magnitude higher.

When an energetic electron is slowed down and "trapped" in a medium, the trapped state of the electron is only transient and it changes into the "solvated" state as the dielectric medium relaxes about the region of localized charge. The structure of the solvent around a solvated electron is in thermal equilibrium with the rest of the medium, whereas that around a trapped electron is not.

As a trapped electron is transformed into a solvated electron by the relaxation of the medium around it, it is bound more tightly to the medium.

It has recently been suggested that the dielectric relaxation of the medium facilitates the escape of secondary electrons from their parent ions only if the electrons move slowly enough.¹⁹ It was also suggested that secondary electrons have a much greater probability of escape from a cylindrical spur (e.g., created by an α particle) than from a spherical spur (e.g., created by a high-energy electron).¹⁹ The Schiller model¹⁹ implicitly assumed that the electrons remain as quasifree particles for a significant period after

thermalization in water. The model used in the present work, and in Refs. 1 and 4, assumes that an electron is not quasifree after thermalization in a liquid such as water or an alkane. The present model leads to suggestions opposite to those of Schiller mentioned above.

APPENDIX B: SPECTRUM OF INITIAL SEPARATION DISTANCES OF THE POSITIVE-ION-THERMALIZED-ELECTRON PAIRS

The over-all distribution of initial energies of all the electrons set in motion in the medium is given by the sum of the energy distributions of the primary, secondary, tertiary, and so on, electrons. Most of the primary electrons each cause tens of thousands of other electrons to be set in motion, so the contribution of the primary electrons to the over-all energy distribution is negligible. The number-vs-energy distribution of all generations of electrons except the primaries peak at zero energy and have similar shapes. Therefore, the over-all distribution has a shape at least qualitatively similar to that of the secondary electron distribution that would be generated by monoenergetic primary electrons that have an energy somewhat less than the mean primary initial energy (i.e., somewhat less than 0.59 MeV in ⁶⁰Co γ radiolysis).

The secondary electron energy distribution of 0.38 MeV primaries was used in the present problem.^{20a} It is of the form

$$P_E \propto E^{-2}, \quad (20)$$

where P_E is the probability that a secondary electron obtains an energy E , and

$$E = W + I, \quad (21)$$

where W is the initial kinetic energy of the secondary electron and I is the binding energy of the electrons of the medium.^{20b} Expression (20) applies to knock-on collisions²¹ and is not valid for E below about 100 eV. In the present work, the electron energy distribution was extrapolated from about 100 eV to I (i.e., to $W=0$, so $E=I \approx 10$ eV) with the aid of "relative frequency of ion clusters containing various numbers of ionizations" data,²² assuming that 30 eV were expended per ionization event. The cluster frequency data indicate that 80% of ionization events have $W < 100$ eV, so the distribution above $W=100$ eV accounted for only 20% of the events. The $N(>E)$ -vs- E curve for the region

²⁰ (a) D. E. Lea, *Actions of Radiations on Living Cells* (Cambridge University Press, New York, 1955), 2nd ed., p. 29. (b) Lea neglected I .

²¹ (a) H. A. Bethe and J. Ashkin, in *Experimental Nuclear Physics*, E. Segre, Ed. (John Wiley & Sons, Inc., New York, 1953), Vol. 1, p. 276. (b) U. Fano, in *Symposium on Radiobiology*, J. J. Nickson, Ed. (John Wiley & Sons, Inc., New York, 1952), p. 13.

²² Reference 20, p. 27. These data refer to the gas phase but, for the lack of anything better, may serve as a guide for the liquid phase.

¹⁹ R. Schiller, *J. Chem. Phys.* **43**, 2760 (1965).

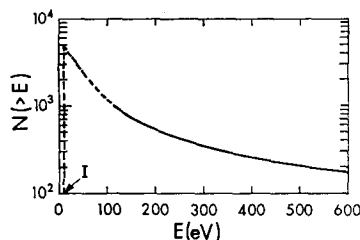


FIG. 4. Initial energy distribution of electrons in a system irradiated with γ rays.

$E=10-600$ eV is shown in Fig. 4, where

$$N(>E) = a \int_E^\infty P_E dE, \quad (22)$$

and a is a proportionality constant.

Ranges of electrons in water, for $W > 100$ eV, are given by Lea.²³ The range-energy plot was semiarbitrarily extrapolated from 100 to 15 eV, using the parabolic function

$$\text{range } (\text{\AA}) = 20 + 1.0 \times 10^{-3} W^2, \quad (23)$$

which was obtained with Lea's values in the region 100 to 300 eV. These ranges refer to distances along the bent path of the electrons and it was estimated²³ that they were 40% greater than the "penetration ranges." The latter ranges are required in the present work, so the values from the plot were divided by 1.4. The penetration range thereby obtained for a 15-eV electron was 14 \AA , which is consistent with the calculations of Samuel and Magee.²⁴

The present treatment neglects the fact that the penetration ranges of electrons of a given energy have a Gaussian distribution about the mean range and that this probably has a significant effect on the low-energy end of the range spectrum.

From the preceding information a spectrum of $N(y)$ vs y , where $N(y)$ is the relative number of positive-ion-thermalized-electron pairs that have an initial separation distance y , was constructed for water (see Table I). In this simple model, $N(y)$ is a step function of y .

$N(y)$ -vs- y spectra for other liquids were calculated from the water spectrum, with the aid of the Bethe equation.²⁵ The secondary electron energy spectra will be nearly the same in all the liquids under consideration (water, ammonia, alcohols, hydrocarbons, etc.) so the $N(y)$ values remain unchanged while adjustments are made to y . The most important part of the y spectrum for the present kinetic analysis is the part for electron energies below 1 keV. The excitation potentials of the inner-shell electrons of carbon and oxygen are about 280 and 520 eV, respectively, so the B rn approximation is not valid for secondary electrons with energies much below 1 keV. However, the B rn

approximation, and hence the Bethe equation, is valid if only the valence electrons are considered in the calculations. Thus the valence-electron densities and the first ionization potentials (gas phase) of the media were used in the Bethe equation to calculate values of $(-dT/dx)$ in the various liquids relative to the value in water. The relative ranges of 100-eV electrons in water, cyclohexane, and n -hexane were calculated to be 1.00, 1.22, and 1.40, respectively (see Table I).

The ranges of electrons that have only a few electron volts of energy are not known with any degree of certainty. The uncertainty is as large as several tens of angstroms in water.²⁶ Furthermore, the ion cluster frequency data used here were those of Wilson²² and if the more recent data of Beekman²⁷ had been used, the $N(>E)$ -vs- E curve would have had a steeper slope at $E < 160$ eV. Several different distributions can be constructed, depending upon the way in which the ion cluster data are grafted on to the $P_E \propto E^{-2}$ data. The distribution most different from the one used in the present work was obtained by joining Beekman's "320-keV electrons in air data" to Lea's " $P_E \propto E^{-2}$ data" at $E = 160$ eV (assuming that 30 eV are expended per ion pair and that $I = 10$ eV). If this distribution had been used, it would have been necessary to use larger values (by 40–50 \AA) for the electron ranges to fit the radiolysis experimental results. Since neither the electron energy distribution at $E < 100$ or 200 eV nor the electron range (within a few tens of angstroms) are accurately known, the $N(y)$ -vs- y spectrum contains a large degree of arbitrariness. The spectrum used in the present calculations was obtained by a self-consistent usage of data from Lea's book^{20,22,23} and it will serve to show that the kinetic model described herein is worthy of further consideration.

An accurate kinetic treatment of charge-scavenging reactions in liquids would also require knowledge of spur population densities. A spur can be defined as the location of one or more excitation or ionization events in a condensed medium that is under radiolysis. More precisely, a spur is a grouping of reactive intermediates that are close enough together that there is a significant probability that the intermediates in it will react with each other. There is a wide distribution of spur populations and sizes. The largest dimension of a spur that contains a single ion-electron pair is the ion-electron separation distance at the moment the electron becomes thermalized. The relative spacings of the positive ions and thermalized electrons in a spur that contains two or more ion pairs would have to be included in an accurate treatment of the reaction kinetics. To simplify the present analysis, the gross assumption has been made that there is only one ion pair per spur.

²³ Reference 20, p. 24. Lea refers to water as "tissue of density 1 g/cm³."

²⁴ A. H. Samuel and J. L. Magee, J. Chem. Phys. **21**, 1080 (1953).

²⁵ G. J. Hine and G. L. Brownell, *Radiation Dosimetry* (Academic Press Inc., New York, 1956), p. 98.

²⁶ (a) J. L. Magee, Natl. Acad. Sci.—Natl. Res. Council Publ. No. 305, 51 (1953); (b) R. L. Platzman, *ibid.* No. 305, 22 (1953).

²⁷ (a) W. J. Beekman, Physica **15**, 327 (1949); (b) A. Ore and A. Larson, Radiation Res. **21**, 331 (1964).