Free Radical Statistics ⊘

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Free Radical Statistics*

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On the basis of a simplified statistical model, average concentrations of trapped free radicals condensed from a gaseous mixture are calculated. The trapped free radical concentration is obtained as a function of the free radical concentration in the gas and of the number of nearest neighbors in the solid. The mathematical problem presented by the model is solved rigorously in the one-dimensional case (two nearest neighbors) and approximately for arbitrary numbers of nearest neighbors. Typical calculated percentages of trapped free radicals range from 14% for a simple cubic lattice to 10% for a face-centered cubic lattice, when the solid is condensed from a completely dissociated gaseous mixture.

1. INTRODUCTION

WHEN gas molecules such as O_2, H_2, or N_2 are passed through a discharge they dissociate into free radicals of O, H, or N. These free radicals are extremely reactive. Upon collision they recombine with a liberation of energy which, per unit mass, dwarfs that usually encountered in chemical reactions. If these free radicals could be stabilized and then allowed to recombine in a controlled manner they might provide a useful source of energy.

Stabilization of small free radicals has been achieved on a laboratory scale by several groups[1-6] by condensing the free radicals on surfaces cooled to liquid helium temperatures. During the condensation process free radicals which land on a surface as neighbors combine but the recombination leaves a small number of free radicals completely surrounded by neighbors which have already formed molecules. These leftovers may remain trapped for a long time because of their low mobility at low temperatures.

The aim of this paper is to estimate the number of stabilized free radicals which might result from experiments of the type mentioned in the foregoing. It is of interest to determine this number as a function of the concentration of free radicals in the incident beam and as a function of the concentration of inert diluents which might also be in the beam.

Very little experimental information exists on the nature of the condensate and of the manner in which it

forms. In view of this ignorance we shall analyze an oversimplified model which might be revised as more experimental data accumulate. Data on stabilized free radical concentrations are still sparse and inconsistent, with percentages reported ranging from 0.1% to 15%.

We assume that the free radicals, molecules, and diluent atoms in a beam condense in a quasi-crystalline state and that the free radicals combine randomly. In particular we postulate:

(a) that each free radical combines at random with one of the free radicals (if any exist) among its nearest neighbors;

(b) that two nearest neighbor free radicals cannot remain in an uncombined state;

(c) that only diatomic molecules can form (no atom can be bound to more than one other).

We then consider all possible configurations of free radicals and combined atoms which are consistent with these assumptions and determine the number of free radicals present in each configuration. Finally for a given lattice type we find the expected fraction of atoms which exist as free radicals by averaging over all possible configurations.

We use these assumptions to calculate the average number of free radicals as a function of the lattice type of the condensate and of the concentration of free radicals in the incident beam. This is done exactly for a one-dimensional chain in Secs. 2 and 3. Section 2 is concerned with a pure beam of free radicals and Sec. 3 with a partially dissociated beam or one with diluents. The calculations of Sec. 4 for higher dimensional systems are only approximate. They are facilitated by the introduction of the hypothesis that the states of different nearest neighbors of a given free radical are independent of each other. This hypothesis leads to a number of free radicals on a linear chain which is three percent lower than that resulting from the exact calculation of Sec. 2.

Our assumptions probably lead to an overestimate of the average number of free radicals since we ignore all kinetic and energetic considerations which would

[1] F. O. Rice and M. Freamo, J. Am. Chem. Soc. **73**, 5529 (1951).
[2] H. P. Broida and J. R. Pellam, Phys. Rev. **95**, 845 (1954).
[3] I. L. Mador and M. C. Williams, J. Chem. Phys. **22**, 1627 (1954).
[4] A. M. Bass and H. P. Broida, Phys. Rev. **101**, 1740 (1956).
[5] Jen, Foner, Cochran, and Bowers, Phys. Rev. **104**, 846 (1956).
[6] A review has been prepared by H. P. Broida, Ann. N. Y. Acad. Sci. **67**, 530 (1957).

generally bring the number of free radicals closer to its almost vanishing equilibrium value.

Our results are then "average upper bounds" for the free radical concentration. Concentrations greater than those calculated would indicate the presence of mechanisms which retard recombination. Our main results are plotted in Fig. 6, where the free radical fraction is given as a function of the number of nearest neighbors in the lattice when one has a completely dissociated beam. Representative percentages are 13.7% for a simple cubic, 12.2% for a body-centered cubic, and 10% for a face-centered cubic lattice. If next nearest neighbor pairs also bind, the effective coordination number increases; for example, the sum of nearest and next nearest neighbors for a face-centered cubic lattice is 18, which corresponds to 8% free radical concentration. The variable f used in our curves is the fraction of atomic sites occupied by free radicals. In the absence of diluents it is the fraction of atoms that exist as free radicals. In the presence of diluents each diluent particle is assumed to occupy one lattice site.

It is frequently proposed that recombination of free radicals might be retarded by a strong magnetic field since for example the atoms in a hydrogen molecule are in the singlet state with antiparallel spins. If the triplet-singlet transition could be retarded or prevented by the field a new element would be introduced into our statistical analysis which would lead to higher free radical concentrations. It is not difficult to extend our work to include such effects; but in view of the small likelihood of experiments being performed in sufficiently strong magnetic fields in the forseeable future, we have not included a discussion of them.

An independent analysis of free radical statistics has recently been made by Professor S. Golden.[7] He calculates approximate nonequilibrium partition functions on the basis of a number of models. Those which involve statistical assumptions similar to ours lead to results of the same order of magnitude as ours. He also has investigated the influence of more detailed assumptions about the manner of condensation. We are indebted to Dr. Golden for several interesting discussions and for a preprint of his paper.

2. FRACTION OF FREE RADICALS IN A LINEAR CHAIN

Let us now consider a linear chain of atoms. We assume that no atom can remain uncombined if it has an uncombined atom as a neighbor. The variation of the average number of free radicals with the length of the array is obtained below. We define

C_N = number of possible configurations of a chain of N atoms.

σ_N = total number free radicals in all possible configurations of chains of N atoms.

[7] S. Golden (to be published).

TABLE I. Possible configurations for short chains. Average fractions of points occupied by free radicals are given by f_N.

N	Possible configurations		C_N	a_N	n_N	f_N
1		●	1	1	1	1
2	(a)	●—●	1	0	0	0
3	(a)	●—● ●	2	2	1	0.333
	(b)	● ●—●				
4	(a)	●—● ●—●	2	2	1	0.25
	(b)	● ●—● ●				
5	(a)	●—● ● ●—●	3	3	1	0.20
	(b)	●—● ●—● ●				
	(c)	● ●—● ●—●				

$n_N = \sigma_N/C_N$ = average number of free radicals per chain of length N.

$f_N = \sigma_N/NC_N$ = fraction of atoms which remain uncombined in a chain of N atoms.

$f = \lim_{N\to\infty} f_N$ = fraction of uncombined atoms in very long chain.

We summarize the possible configurations of several short chains in Table I. If we start constructing chains (from left to right) of any length the first points of the chain are either in configuration (a) ●—● or (b) ● ●—●. The ensemble of chains of length N which start with (a) is in one to one correspondence with chains of the ensemble of all chains of $N-2$ points while the ensemble of all chains of length N which start from (b) is in one to one correspondence with the ensemble of all chains of $N-3$ points. Hence the total number of distinct possible chains of length N is

$$C_N = C_{N-2} + C_{N-3} \qquad (2.1)$$

while the total number of free radicals in the ensemble of all chains of length N, σ_N is

$$\sigma_N = \sigma_{N-2} + (C_{N-3} + \sigma_{N-3}) \qquad (2.2)$$

[since each chain which starts with (b) has one more free radical than the associated chain of $(N-3)$ points]. The numbers C_N, σ_N, n_N, and f_N for chains of length 1–24 are given in Table II.

A general expression for C_N is easily found by assuming that C_N is of the form αx^N. Then x is a root of

$$x^3 - x - 1 = 0. \qquad (2.3)$$

If the three roots of this cubic are x_1, x_2, and x_3 then

$$C_N = \sum_{j=1}^{3} \alpha_j x_j^N. \qquad (2.4)$$

The coefficients α_j are chosen so that the boundary conditions $C_1 = C_2 = 1$ and $C_3 = 2$ are fulfilled. One obtains

$$C_N = \sum_{j=1}^{3} \frac{(1+x_j)^2}{(2x_j+3)} x_j^{N-1}. \qquad (2.5)$$

The three roots (of which x_1 is of maximum modulus)

TABLE II. Statistical properties of linear chains of 1 to 24 lattice points. Here n_N is the average number of free radicals per chain of length N and n_N* is that calculated from Eq. (3.5) which is valid for large N. Also f_N is the mean fraction of free radicals on a chain of N lattice points.

N	C_N	σ_N	n_N	f_N	N	C_N	σ_N	n_N	n_N*	f_N
1	1	1	1	1.000	13	28	72	2.571	2.572	0.198
2	1	0	0	0	14	37	102	2.757	2.749	0.197
3	2	2	1	0.333	15	49	143	2.918	2.926	0.195
4	2	2	1	0.250	16	65	202	3.108	3.103	0.194
5	3	3	1	0.200	17	86	282	3.279	3.280	0.193
6	4	6	1.5	0.250	18	114	394	3.456	3.457	0.192
7	5	7	1.4	0.200	19	151	549	3.636	3.634	0.191
8	7	12	1.714	0.214	20	200	762	3.810	3.811	0.190
9	9	17	1.888	0.209	21	265	1057	3.988	3.988	0.190
10	12	24	2.000	0.200	22	351	1462	4.165	4.165	0.189
11	16	36	2.250	0.205	23	465	2019	4.342	4.342	0.189
12	21	50	2.381	0.198	24	616	2784	4.519	4.519	0.188

are

$$x_1 = 1.32471795$$

$$x_2 = -0.662359 + 0.562279i$$

$$x_3 = -0.662359 - 0.562279i. \quad (2.6)$$

As $N \to \infty$

$$C_N \sim \frac{(1+x_1)^2}{2x_1+3} x_1^{N-1} = 0.9566111 x_1^{N-1}. \quad (2.7)$$

The difference equation (2.2) can be solved for σ_N when the known expression (2.4) is used for C_N. Then

$$\sigma_N = N \sum_{j=1}^{3} x_j^{N-1} \left(\frac{1+x_j}{2x_j+3}\right)^2 + \frac{2}{23} \sum_{1}^{3} \frac{(8x_j-1)x_j^{N+1}}{(2x_j+3)} \quad (2.8)$$

so that as $N \to \infty$

$$\sigma_N \sim N \left\{\frac{1+x_1}{2x_1+3}\right\}^2 x_1^{N-1}.$$

The fraction of atoms in a long chain which remain free is then

$$f = \lim_{N\to\infty} \sigma_N / N C_N = (2x_1+3)^{-1} = 0.17700882 \quad (2.9)$$

or 17.70%.

It is instructive to obtain this result by an alternate method. Consider a site in the middle of a long chain of $(2N+1)$ points and consider the probability of having a free radical there. It is just the probability that the atom at the Nth site is bound to the left and that the atom at the $(N+2)$nd site is bound to the right. The former is $\frac{1}{2}(1-f)$ while the probability of the latter when the former is known to be true is (since in this case the chain of N atoms to the right of the $(N+1)$st is a new independent chain) the ratio of the number of configurations of an N chain which start with a bond, C_{N-2}, to the total number of configurations of an $N+1$ chain C_{N+1}. Hence, since this middle point in the chain becomes a typical point as $N \to \infty$,

$$f = \frac{1}{2}(1-f) \lim C_{N-2}/C_{N+1} = \frac{1}{2}(1-f) \lim_{N\to\infty} \frac{C_{N-2}}{C_{N-2}+C_{N-1}}$$

$$= \frac{1}{2}(1-f)/(1+x_1)$$

which is equivalent to (2.9).

A further discussion of free radicals in a linear chain is given in the appendix.

3. FRACTION OF FREE RADICALS IN A LINEAR CHAIN WITH DILUENT

Let us now consider the effect of adding inactive diluents to a gas composed of free radicals. Upon condensation on a surface the inactive diluents, keeping active atoms apart, prevent some free radicals from combining. Since this is done at the expense of wasting valuable space which might otherwise be available for free radicals, it is not immediately obvious whether a net gain is achieved in the total number of free radicals per unit length of chain. The calculation required for this judgment is given below.

A set of γ inactive diluent particles in a chain of N points breaks the chain into $(\gamma+1)$ shorter subchains. In order to determine the average number of free radicals in the long chain we must know the average number of subchains with a given number of points. The statistics of subchains has already been obtained in the theory of depolymerization of linear polymers. Depolymerization is a process of cutting bonds in polymer chains. We first exhibit a correspondence between subchains flanked by diluents and subchains resulting from bond cutting in a depolymerization.

Suppose the chain of N points exhibited in Fig. 1(A) contains diluent particles at points indicated by arrows. A chain of $(N+1)$ points is "depolymerized" in the bottom of the Fig. 1(B) in that a cut is made at all bonds which lie to the right of the lattice points which contain diluents in A. Note that the sequence of chains between diluents in Fig. 1(A) is 3, 0, 1, 3, 4, 0 while that of chain between broken bonds is 4, 1, 2, 4, 5, 1. It is clear that in general, if diluent atoms appear at points $x_1, x_2 \cdots x_\gamma$ on an N chain one can cut an $(N+1)$ chain at bonds $x_1, x_2, \cdots x_\gamma$ so that a one to one corre-
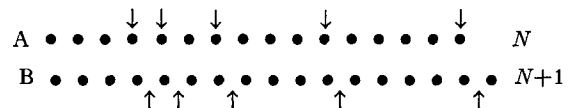

FIG. 1.

spondence exists between each t chain in the diluent problem and a $(t+1)$ chain in the depolymerization problem. Hence the average number of t chains which results from the insertion of γ diluents in an N chain is the same as the number of $(t+1)$ chains which results from making γ cuts in an $(N+1)$ chain. This number is known from the theory of depolymerization to be[8]

$$(N+1)\binom{N-t-1}{\gamma-1} \Big/ \binom{N+1}{\gamma+1}. \qquad (3.1)$$

If $N\to\infty$ and $\gamma\to\infty$ so that $\gamma/N=\alpha$ this number approaches

$$N\alpha^2(1-\alpha)^t \qquad (3.2)$$

for all fixed t. This could have been deduced by noting that if one starts at a diluent atom the probability of t successive nondiluents is $(1-\alpha)^t$ and α is the probability that the $(t+1)$st point is a diluent. This multiplied by the number of diluent starting points $N\alpha=\gamma$ gives exactly (3.2).

The mean total number of free radicals in a very long chain with a fraction α of diluent atoms is then

$$n_F = N\alpha^2 \sum_{t=1}^{\infty} n_t(1-\alpha)^t. \qquad (3.3)$$

When the chain is almost filled with diluent so that $\alpha\simeq 1$ most subchains are very short and we find the fraction of sites occupied by free radicals to be

$$f = \lim n_F/N$$
$$= \alpha^2(1-\alpha)\{1+(1-\alpha)^2+(1-\alpha)^3+(1-\alpha)^4$$
$$+\tfrac{3}{2}(1-\alpha)^5+\cdots\}. \qquad (3.4)$$

In order to obtain an expansion which is appropriate for small values of α we find from Eqs. (2.7) and (2.8) that as $t\to\infty$

$$n_t = \sigma_t/C_t \sim \frac{t}{3+2x_1} + \frac{2}{23}\frac{(8x_1-1)x_1^2}{(1+x_1)^2} + 0([x_2/x_1]^t). \qquad (3.5)$$

We can write f as

$$f = \alpha^2\{(1-\alpha)+(1-\alpha)^3+\cdots$$
$$+n_{s-1}(1-\alpha)^{s-1}+R_s\} \qquad (3.6)$$

where for all s

$$R_s = \sum_{t=s}^{\infty} n_t(1-\alpha)^t$$

and for large s

$$R_s \sim \frac{1}{2x_1+3}\sum_{t=s}^{\infty}t(1-\alpha)^t + \frac{2}{23}\frac{(8x_1-1)x_1^2}{(1+x_1)^2}\sum_{t=s}^{\infty}(1-\alpha)^t$$
$$= \frac{(1-\alpha)^{s+1}}{\alpha^2(3+2x_1)} + \frac{1}{\alpha}(1-\alpha)^s\left\{\frac{s}{3+2x_1} + \frac{2}{23}\frac{x_1^2(8x_1-1)}{(1+x_1)^2}\right\}. \qquad (3.7)$$

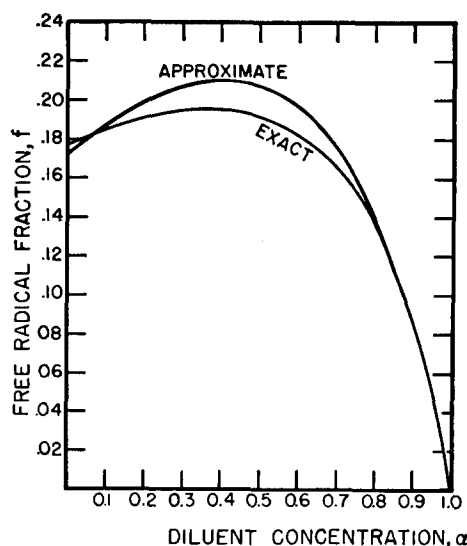[8] E. Montroll and R. Simha, J. Chem. Phys. **8**, 721 (1940).

FIG. 2. Effect of inert diluents on number of free radicals in stabilized matrix (one-dimensional case).

As $\alpha\to 0$ the coefficient of α^2 causes all terms in (3.6) to vanish except R_s. Since the first term in R_s is proportional to α^{-2} in this limit, $f\to(2x_1+3)^{-1}$ which, being exactly (2.9) shows that (3.4) is consistent with (2.9).

As $\alpha\to 0$

$$f \sim (2x_1+3)^{-1} - \alpha\left\{(2x_1+3)^{-1} - \frac{2}{23}\frac{(8x_1-1)x_1^2}{(1+x_1)^2}\right\} + 0(\alpha^2)$$
$$= 0.177009 + 0.09399\alpha + 0(\alpha^2). \qquad (3.8)$$

We have plotted f as a function of α for the entire range $0\leq\alpha\leq 1$ in Fig. 2. It is to be noted in Table II that the asymptotic formula (3.5) for n_t is in error by no more than 0.3% when $t>15$. Hence our calculations for the figure were made by choosing $s=15$ in Eq. (3.6).

If the incident beam is not completely dissociated the undissociated molecules can be treated as diluents which occupy two adjacent lattice sites. The calculation of the fraction of sites occupied by free radicals is essentially the same as the derivation of (3.4). Let b be the number of molecules and $N-2b$ the number of free atoms. The molecules separate the atoms on a linear chain into independent sets. A typical configuration is given in Fig. 3.

Since molecules cannot overlap in our linear model, a molecule on the chain is always followed by a space (see Fig. 3). We identify such a complex by Y and a space between points which does not have a molecule to the left of it by an X. Then every configuration can
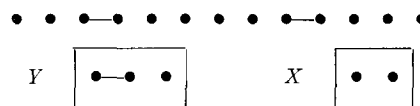

FIG. 3.

be represented by a sequence of X's and Y's. The configuration shown in Fig. 3 is $XXYXXXXYXX$. The total number of bonds and the total number of Y's is b. Since there are N points on our chain there are $(N-1)$ (which we approximate by N as $N \rightarrow \infty$) spaces between points and since each Y occupies two spaces, the number of X's and Y's in a typical sequence is $(N-b)$. The probability that an element in the sequence is a Y is

$$b/(N-b) = \beta/(2-\beta) \qquad (3.9)$$

while that of an element being an X is

$$1 - [b/(N-b)] = (N-2b)/(N-b)$$
$$= 2(1-\beta)/(2-\beta), \qquad (3.10)$$

where we define β to be the probability that an atom is bound:

$$\beta = 2b/N. \qquad (3.11)$$

The probability that t atoms lie between two molecules in a configuration of atoms and molecules is the same as that of a sequence of t X's being bounded on each end by a Y. The expected number of subchains of t consecutive atoms is

(number of bonds) (probability of t X's followed by a Y)

$$= b[1-\beta(2-\beta)^{-1}]^t [\beta(2-\beta)^{-1}]$$
$$= \tfrac{1}{2}N^2\beta^2(2-\beta)^{-1}[1-\beta(2-\beta)^{-1}]. \qquad (3.12)$$

The mean fraction of free radicals is then [following the derivation of (3.3) and (3.4)]

$$f = \tfrac{1}{2}[\beta^2/(2-\beta)]\sum_{1}^{\infty} n_t \left(1 - \frac{\beta}{2-\beta}\right)^t. \qquad (3.13)$$
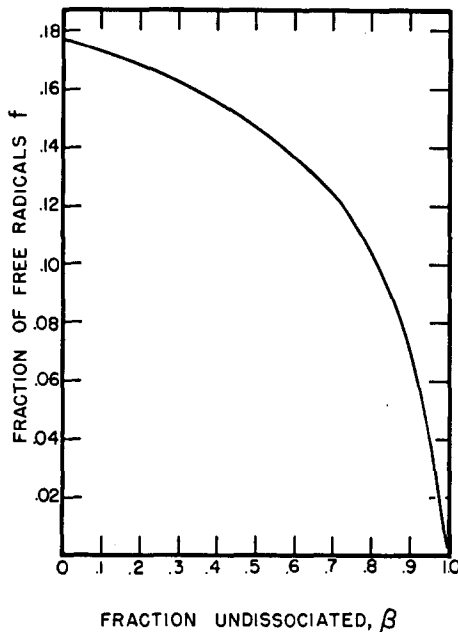

FRACTION UNDISSOCIATED, β

FIG. 4. Free radical concentration in matrix stabilized from a partially dissociated beam (one-dimensional).

The largest possible value of β is 1. This corresponds to $b = N/2$, no free radicals in the incident beam. Then $f = 0$ as is to be expected. As $\beta \rightarrow 0$ one formula becomes identical with (3.6) if $\tfrac{1}{2}\beta$ is replaced by α. Then (3.8) applies. We have plotted f as a function of β in Fig. 4.

4. FRACTION OF FREE RADICALS IN THREE-DIMENSIONAL CONDENSATES

Unfortunately it is difficult to extend the calculations made in the last two sections to three-dimensional systems. Difference equations (in several variables) similar to (2.1) can be derived but the characteristic equations involve large determinants. In view of the primitive character of our model we shall limit ourselves here to the derivation of an approximate formula for the free radical concentration f which seems to give a fairly accurate dependence of f on the number of nearest neighbors to a given lattice point.

Consider a lattice of coordination number z. The probability of the occupation of a given lattice point, say A, by a free radical is the same as that of the occupation of all its nearest neighbors by atoms bound in a molecule (whose other atom is not located at A). The fraction of sites occupied by free radicals, f, is our

$$
\begin{array}{ccc}
x & x_D & x_C \\
 & & | \\
x & \bullet_A & x_B \\
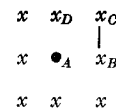x & x & x \\
\end{array}
$$

FIG. 5.

required probability. Generally an atom in a molecule can be bound to any one of z neighboring atoms. Hence the probability of it being bonded to a particular one is $(1-f)/z$. If our special lattice point A is to be a free radical each of its bound nearest neighbors can be bonded to one of only $(z-1)$ of its nearest neighbors (its bonding with A being excluded). The probability that a given nearest neighbor is bound is then

$$(z-1)(1-f)/z. \qquad (4.1)$$

For simplicity let us assume that the bonding of various neighbors of A are independent events. Then the probability of all neighbors of A being bound is

$$f = \{(z-1)(1-f)/z\}^z. \qquad (4.2)$$

This independence hypothesis is clearly incorrect as can be seen from Fig. 5. Suppose B is bound to C. Then only two rather than three bound states are available for D.

We can consider Eq. (4.2) as a first approximation to a more exact one. In order to appreciate its validity we examine the case $z = 2$. Then it is easily seen that

$$f = 3 - 2\sqrt{2} = 0.1716$$

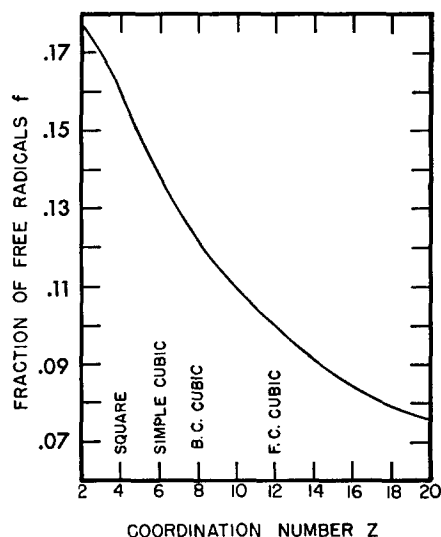which compares favorably with the exact value 0.1770 derived in Sec. 2.

FIG. 6. Variation of free radical concentration with coordination number, z, of stabilized matrix.

Let

$$g_1(f)=f \quad \text{and} \quad g_2(f)=\left[\frac{(z-1)}{z}(1-f)\right]^z.$$

If $g_1(f)$ and $g_2(f)$ are plotted together as functions of f the intersection of the two curves determine the solution of (4.2). It has been found that when $z=6$, 8, and 12 (simple, body-centered, and face-centered cubic lattices) the values of f are respectively 0.138, 0.121, and 0.100. We have plotted f as a function of z in Fig. 6. Since free radicals condense in lattices with many defects and irregularities the average coordination number may not be an integer. Since second neighbors are almost as close to a given site in a face-centered cubic lattice as nearest neighbors one should perhaps choose the effective number of neighbors z to be between 15 and 18 rather than 12 in this case. In a more exact calculation the topology of the lattice as well as the coordination number is important.

The above analysis can be generalized to include the effect inert diluents. As in Sec. 3, we let α be the probability that a site is occupied by an inert diluent. Then the probability of an atom being bound to another is $(1-\alpha-f)$ and that of its being bound to a particular one of its neighbors is $(1-\alpha-f)/z$. Now the probability that a site A is occupied by a free radical f is the product of the probability that it is not occupied by a diluent $(1-\alpha)$ and the probability that all its nearest neighbor sites are occupied by a bound atom or a diluent. As in the nondiluent case only $(z-1)$ of the nearest neighbor sites to a nearest neighbor of A are available for bonding. Hence the probability of a nearest neighbor being bound when A is unbound is

$$(z-1)(1-\alpha-f)/z. \tag{4.3}$$

Since the probability that a given nearest neighbor

site of A is occupied by a diluent is α, our independence hypothesis yields

$$f=(1-\alpha)[\alpha+(z-1)(1-\alpha-f)/z]^z. \tag{4.4}$$

We have solved this equation for free radical concentration f, as a function of diluent concentration α, in the case $z=2$. The results are plotted in Fig. 2 where they are compared with the exact curve which was obtained in Sec. 3. The peak occurs at about the same diluent concentration as it does in the exact analysis but is overestimated by about 10% in the approximate curve. This error is greatest at the peak and is considerably diminished in the high and low diluent concentration range.

Figure 7 shows the variation of f with α in the cubic lattices. Note that the concentration of free radicals is insensitive to diluent concentration until α increases beyond 0.5. Similar but not quite so striking results can be expected when the diluent is an undissociated molecule from the incident beam. If it is difficult to form a completely dissociated beam one can relax his efforts at the expense of losing a relatively small fraction of free radicals in the condensate.

The variation of f with α as $\alpha\to0$ can be obtained by finding $(df/d\alpha)$ as $\alpha\to0$ from (4.4). Then

$$f=f_0[1+\alpha/(z-1)+\cdots]$$

where f_0 is the fraction of free radicals in the absence of diluent. As $\alpha\to1$ most free radicals are surrounded by diluent. Hence

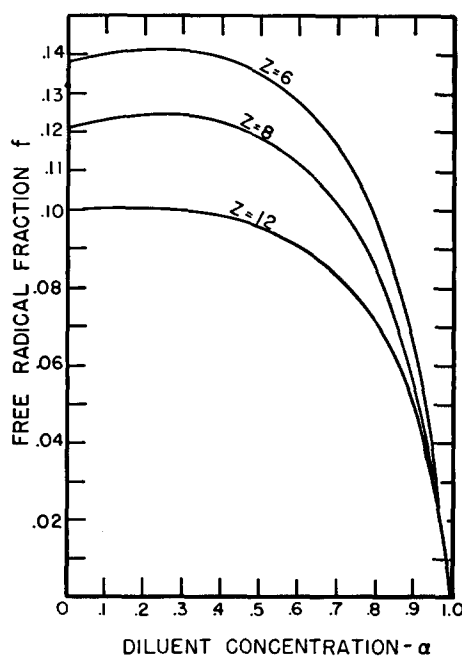$$f=(1-\alpha)\alpha^z\sim(1-\alpha)[1-z(1-\alpha)].$$

FIG. 7. Effect of inert diluents in beam on free radical concentration on stabilized matrix. $z=$coordination number.

The next approximation is obtained by allowing for the possibility of the nearest neighbor to a free radical being part of a molecule. Then

$$f \sim (1-\alpha)[1-z(1-\alpha)+z(z-1)(1-\alpha)^2+\cdots].$$

APPENDIX. FURTHER REMARKS ON FREE RADICALS IN A LINEAR CHAIN

This is an expansion of Sec. 2.

An array of free radicals and molecules can be characterized by a sequence of "B"s and "U"s, where a "B" corresponds to a pair of adjacent atoms connected by a bond and U an unbonded pair. A certain number of free radicals is associated with any sequence of U's and B's. We call this number n_F. An example of a possible sequence is $BUUBUBUUBU$. Possible sequences for a chain of N atoms are those which do not contain runs of two or more B's or three or more U's. Furthermore, if n_B and n_u are respectively the number of B's and U's in a sequence, the number of free radicals is

$$n_F = 1 + n_u - n_B. \tag{A.1}$$

An alternative method of characterizing possible sequences is through the possible configuration of triples of atoms, which we enumerate by

$$\begin{array}{ccc} 1 & \bullet\!\!-\!\!\bullet \ \ \bullet & \text{or} \ \ BU \\ 0 & \bullet \ \ \bullet \ \ \bullet & \text{or} \ \ UU \\ -1 & \bullet \ \ \bullet\!\!-\!\!\bullet & \text{or} \ \ UB. \end{array} \tag{A.2}$$

Then the above sequence is equivalent to

$$1, -1, -1, 0, 1. \tag{A.3}$$

We represent the ith triple by a parameter σ_i.

The mean number of free radicals as well as the distribution function of the number can be obtained from the characteristic function

$$z(\theta) = \sum_{\sigma_1,\sigma_2\cdots=0,\pm1} f(\sigma_1\sigma_2\cdots\sigma_N)$$
$$\exp i\theta[1+n_u(\sigma_1\cdots\sigma_N)-n_B(\sigma_1\cdots\sigma_N)] \tag{A.4}$$

where $f(\sigma_1\cdots\sigma_N)$ is the weight associated with the sequence. The probability density $G(x)$ of n_F is then the Fourier transform of

$$E(\exp i\theta x) = z(\theta)/z(0) \tag{A.5}$$

or

$$G(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}[z(\theta)/z(0)]e^{i\theta x}d\theta. \tag{A.6}$$

Also

$$\langle N_F\rangle_{\text{Av}} = -i\partial \log z(\theta)/\partial\theta]_{\theta=0}. \tag{A.7}$$

When the number of lattice points N is even it is necessary to introduce a σ_0 which refers to the state of the first bond,

$$\sigma_0 = \begin{cases} 1 & \text{if} \ \ \bullet\!\!-\!\!\bullet \ \ \text{or} \ \ B \\ -1 & \text{if} \ \ \bullet \ \ \bullet \ \ \text{or} \ \ U. \end{cases} \tag{A.8}$$

Then

$$z(\theta) = \sum_{\sigma_0=\pm1;\sigma_1,\sigma_2\cdots=0,\pm1,} f(\sigma_0,\sigma_1\cdots) \ \exp i\theta[n_F(\sigma_0\cdots\sigma_N)]. \tag{A.9}$$

Since we shall be interested in the distribution function of free radicals in long chains, we expect the end conditions of the chains to be unimportant. Hence, for convenience we shall discuss rings of an even number $2N$ of atoms. In this case

$$n_F = n_U - n_B.$$

Stipulations of the introduction tell us that the possible configurations of a pair of adjacent bonds (say σ_j) depend only on neighboring pairs of bond configurations (σ_{j-1} and σ_{j+1}). Hence, the weight function $g(\sigma_1, \cdots\sigma_N)$ can be factored into functions of successive pairs of σ's.

$$g(\sigma_1\cdots\sigma_N) = f(\sigma_2\sigma_1)f(\sigma_3\sigma_2)\cdots f(\sigma_1\sigma_N). \tag{A.1}$$

The value of n_u-n_B associated with a given value of σ is $2(1-\sigma^2)$. Hence, we can finally write the characteristic function $z(\theta)$ of our ring as

$$z(\theta) = e^{2Ni\theta}\sum_{\sigma=0,\pm1}\prod_{i=1}^{N}\{f(\sigma_{i+1}\sigma_i) \ \exp[-i\theta(\sigma_i{}^2+\sigma_{i+1}{}^2)]\}. \tag{A.11}$$

Let $F(\theta)$ be a 3×3 matrix with elements

$$f(\sigma,\sigma') \ \exp[-i\theta(\sigma^2+\sigma'^2)]. \tag{A.12}$$

Then our sum over σ's is exactly the trace of the Nth power of the matrix $F(\theta)$:

$$z(\theta) = e^{2Ni\theta} \ \text{Trace}[F(\theta)]^N$$
$$= e^{2Ni\theta}\{\lambda_1{}^N(\theta)+\lambda_2{}^N(\theta)+\lambda_3{}^N(\theta)\} \tag{A.13}$$
$$\sim e^{2Ni\theta}\lambda_m{}^N(\theta)$$

where $\lambda_m(\theta) = \max\{\lambda_j(\theta)\}$ is the characteristic value of $F(\theta)$ with the largest absolute value.

The character of $G(x)$ as $N\to\infty$ follows from the expansion

$$\{\lambda_m(\theta)\}^N = \exp N[\log\lambda_m(\theta)]$$
$$= [\lambda(0)]^N \exp N\bigg\{\{\theta\lambda'(0)/\lambda(0)$$
$$+\tfrac{1}{2}\theta^2\bigg[\frac{\lambda''(0)}{\lambda(0)}-\bigg(\frac{\lambda'(0)}{\lambda(0)}\bigg)^2\bigg]+0(\theta^3)\bigg\}.$$

Then

$$G(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\theta\{x-2N+iN[\log\lambda(\theta)]'_{\theta=0}\})$$
$$\exp\tfrac{1}{2}N\{\theta^2[\log\lambda(\theta)]''_{\theta=0}+0(\theta^3)\}d\theta.$$

If we let

$$y^2 = -N\theta^2[\log\lambda(\theta)]''_{\theta=0}$$

and take the limit as $N \to \infty$ we find after taking Fourier transforms

$$G(x) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}} \exp\left\{ -\frac{(x-\bar{n}_F)}{2\sigma^2} \right\} \qquad \text{(A.14)}$$

with

$$\bar{n}_F = N\{2 - i[\log\lambda(\theta)]'_{\theta=0}\} \qquad \text{(A.15)}$$

and

$$\sigma^2 = \langle (n_F - \bar{n}_F)^2 \rangle_{Av} = -N[\log\lambda(\theta)]''_{\theta=0}. \qquad \text{(A.16)}$$

Hence n_F has a Gaussian distribution with mean value (A.15) and dispersion (A.16) in the limit as $N \to \infty$.

We find numerical estimates of $\bar{n}_F$ and σ^2 by introducing a more detailed model for the explicit construction of $f(\sigma_{j+1}, \sigma_j)$ and the calculations of $\lambda_m(\theta)$. We

TABLE III.

		Diagram		Weight
σ_{j+2}	σ_j	σ_j	σ_{j+2}	
1	1	•—• •—• •	$\alpha(p^2q^2)$
1	0	• • •—• •	$\beta(pq^3)$
1	−1	• •—•—• •	0
0	1	•—• • • •	0
0	0	• • • • •	0
0	−1	• •—• • •	$\beta(pq^3)$
−1	1	•—• • •—•	$\gamma(p^2q^2)$
−1	0	• • • •—•	0
−1	−1	• •—• •—•	$\alpha(p^2q^2)$

assign the following weights to the various possible configurations of (σ_{j+1}, σ_j) in Table III. All impossible configurations are given a weight zero. If an a priori weight of p is given to every B and q to every U, our weights α, β, and γ are, respectively, p^2q^2, pq^3, and p^2q^2.

The matrix $F(\theta)$ with elements (A.12) is then

$$F(\theta) = e^{-2i\theta} \begin{bmatrix} \alpha & \beta e^{i\theta} & 0 \\ 0 & 0 & \beta e^{i\theta} \\ \gamma & 0 & \alpha \end{bmatrix}. \qquad \text{(A.17)}$$

The characteristic values λ are roots of the cubic equation

$$\lambda(\alpha - \lambda e^{2i\theta})^2 = \gamma\beta^2. \qquad \text{(A.18)}$$

If we set

$$\tau^2 = \gamma\beta^2/\alpha^2 (= q^2/p^2) \quad \text{and} \quad \lambda(\theta) = \alpha\mu(\theta) \exp(-2i\theta) \qquad \text{(A.19)}$$
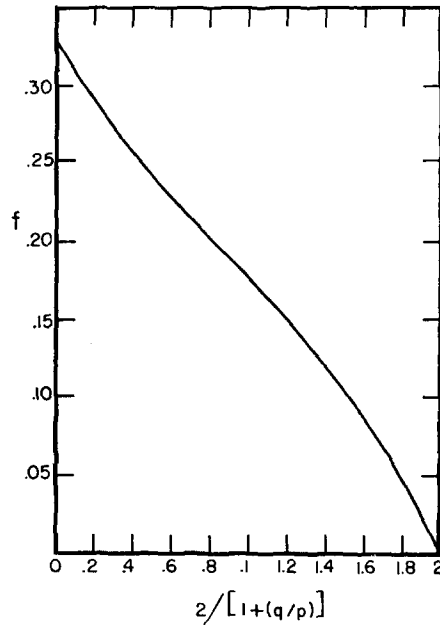

FIG. 8. Free radical concentration when the a priori probability of a bond is not random, one-dimensional case. Here $\tau = q/p$ with q being a priori weight of no bond and p that of a bond.

our equation for μ becomes

$$\mu(\theta)[1 - \mu(\theta)]^2 = \tau^2 e^{2i\theta}. \qquad \text{(A.20)}$$

It is easy to show that if $\mu(0)$ satisfies

$$\mu(0)[1 - \mu(0)]^2 = \tau^2 \qquad \text{(A.21)}$$

then

$$[\log\lambda(\theta)]'_{\theta=0} = 4i\mu(0)/[1 - 3\mu(0)]$$

$$[\log\lambda(\theta)]''_{\theta=0} = -\frac{8\mu(0)[\mu(0) - 1]}{[3\mu(0) - 1]^3}.$$
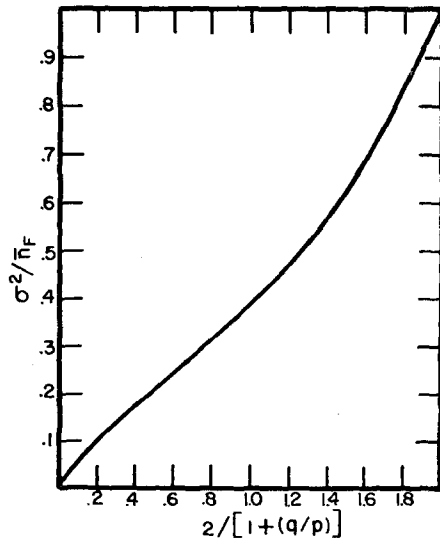

FIG. 9. Square of dispersion of number of free radicals from mean value in one-dimensional case [see Eq. (A.23)].

Hence

$$\bar{n}_F = \frac{2N[\mu(0)-1]}{[3\mu(0)-1]} \tag{A.22}$$

$$\sigma^2 = \frac{8N\mu(0)[\mu(0)-1]}{[3\mu(0)-1]^3}. \tag{A.23}$$

We have plotted the fraction of atoms which are free radicals, $f = \bar{n}_F/2N$, in Fig. 8 as a function of τ; and $\sigma^2/\bar{n}_F$ in Fig. 9. Notice that in the completely random case, $\tau = 1$, $f = 0.1770$, and $\sigma^2/n_F = 0.385$. It is actually not necessary to solve the cubic equation (A.21) in order to plot these graphs if one chooses μ as the independent variable and τ as the dependent one.

Determination of the Electronic Conductivity in Silver Halides by Means of Polarization Measurements

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The current passing through a cell, silver/silver halide/graphite, has been measured as a function of applied potential in the temperature range between 200 and 370°C, for potentials less than 0.5 volt. Under these conditions, the current for steady-state conditions is mainly electronic. Definite results were obtained for AgBr and AgI, but not for AgCl because of sluggish approach to steady-state conditions. From an analysis of the current-potential curves it is concluded that excess electron conduction prevails in AgBr, but hole conduction in AgI.

INTRODUCTION

DIRECT-current polarization measurements as a means for investigating the electronic conduction in substances with prevalent ionic conductivity have been suggested by Hebb[1] and Wagner.[2,3] The method has been applied to cuprous halides by Wagner and Wagner,[4] to PbCl$_2$ and PbBr$_2$ by the same authors,[5] to AgBr and AgI by Kiukkola and Wagner.[6] In what follows, further results for AgBr, AgI, and AgCl in the temperature range from about 200 to 360°C are reported.

APPARATUS

The apparatus used for these measurements was essentially the same as the one described earlier by Kiukkola and Wagner.[7] Essentially, the disk-shaped silver halide sample was mounted sandwich-wise between a silver cathode and a graphite anode. Platinum as an anode material was discarded because attack

on this metal by iodine was observed. This cell was supported by long Pyrex rods and surrounded by a protective atmosphere of purified nitrogen within the furnace, the temperature of which was maintained constant within ±0.5 deg during a run. The applied potential could be read with an accuracy of ±0.2 mv. Because of increasing contributions of anodic decomposition of the silver halides, no potentials higher than 0.5 volt could be applied. With samples of about 6-mm diam and 2-mm thickness, currents between 10^{-9} and 10^{-6} amp were measured, still smaller currents being excluded because of increasing scatter. Because of these two limitations, there was with all three materials a certain range of temperatures within which the electronic currents assumed values larger than 10^{-9} amp and less than the decomposition currents which could be estimated in a similar way as described in reference 4.

According to Wagner,[2,3] in a setup such as that described in the foregoing the current density $i_\ominus$ for the contribution of conduction electrons to the total current is given by

$$i_\ominus = (RT/LF)\cdot\kappa_\ominus^0[1-\exp(-EF/RT)], \tag{1}$$

and that of the electron holes by

$$i_\oplus = (RT/LF)\cdot\kappa_\oplus^0[\exp(+EF/RT)-1], \tag{2}$$

where L is the thickness of the sample and F is Faraday's constant. Thus, with increasing potential E the electronic part of the current tends to assume a saturation value $(RT/LF)\kappa_\ominus^0$, while on the other hand the con-

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[1] M. Hebb, J. Chem. Phys. 20, 185 (1952).
[2] C. Wagner, *International Committee of Electrochemical Thermodynamics and Kinetics, Proceedings of the 7th Meeting Lindau, 1955* (Butterworth Publications, Ltd., London, 1957).
[3] C. Wagner, Z. Elektrochem. 60, 4 (1956).
[4] J. B. Wagner and C. Wagner, J. Chem. Phys. 26, 1597 (1957).
[5] J. B. Wagner and C. Wagner, J. Electrochem. Soc. 104, 509 (1957).
[6] K. V. Kiukkola and C. Wagner (private communication) [quoted in (3)].
[7] K. V. Kiukkola and C. Wagner, J. Electrochem. Soc. 104, 379 (1957).