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## The Thermal Stabilization and Sintering of Gold Smoke Deposits\*

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Gold smoke's made by evaporation in an inert gas atmosphere are initially in a thermodynamically unstable state. A theory based on diffusion of vacant sites to the surface of the crystallites has been developed to describe the process by which the deposit approaches equilibrium. Measurement at different temperatures of the change of resistance associated with the loss of vacant sites gives a value of 23.5 kcal./g atom for the activation energy of this process.

When heated above 100°C the deposits sinter rapidly and undergo pronounced changes in optical properties. However, a gold smoke deposit can be stabilized, by heat treatment at 70°C, so that sintering proceeds at an appreciably slower rate.

### INTRODUCTION

**G**OLD smoke deposits prepared under certain conditions are of particular interest because they are excellent absorbers of infra-red radiation with very low reflectance.<sup>1,2</sup> Electron microscopy studies reveal that a deposit consists of aggregates of individual spheroidal particles of varying size, the mean diameter in any given deposit being in the range of 40A to 200A, depending on the conditions of preparation.<sup>3</sup> Preliminary observations<sup>1</sup> on changes occurring in gold smoke deposits at elevated temperatures showed that the reflectance of the smokes increased markedly upon being heated to 120°C. A more detailed study of the effect of heating has now been made.

A slow decrease in the resistance of a deposit is observed at room temperature, and at higher temperatures pronounced changes in the optical characteristics occur which depend on the previous history of the specimen. It has been found necessary to treat the effects observed in the lower and higher temperature ranges as the results of two different processes. In the lower temperature (up to 80°C) process, the electrical resistance decreases with time, dropping to less than 0.3 of its original value, while the only change in the optical properties is a small decrease in the infra-red transmission. This process effects a stabilization of the system. The second process, which occurs at higher temperatures (greater than 100°C), produces not only an additional decrease in the electrical resistance but also pronounced changes in the optical characteristics. This process is to be associated with a sintering of the deposit.

### MECHANISM OF STABILIZATION

The stabilization of the system must be associated with internal changes in the individual particles observed with the electron microscope. Three types of

internal structure suggest themselves as probable ones in a freshly formed deposit.

1. Each particle consists of a number of crystallites surrounded by disordered regions. During stabilization the disordered region becomes ordered with a consequent increase in size of the crystallites. Such a model and mechanism have been used by Suhrmann and his co-workers<sup>4,5</sup> to describe the irreversible resistance changes of thin metallic deposits prepared in a high vacuum and condensed on surfaces cooled to as low as 20°K.

2. Each particle consists of a large number of smaller nuclei. During stabilization the nuclei grow to a single crystallite.

3. Each particle consists of a single crystallite having a non-equilibrium lattice. Energy considerations indicate that for such a model a lattice containing an excess of vacant sites over the number present in the equilibrium lattice is more probable than a distorted lattice with atoms in interstitial positions. Seitz and Huntington<sup>6,7</sup> have made calculations on self-diffusion in copper. Their results show that it would require about 9.5 ev to place a copper atom in an interstitial position in the lattice, while the creation of a vacant site requires only 1.23 ev. These results should also be applicable, qualitatively, to the gold lattice. Therefore it is to be expected that in such a non-equilibrium lattice, which is not too greatly disordered, the lattice will have an excess of vacant sites and should approach the equilibrium state as the excess vacant sites diffuse to the surface of the particle.

Model (1) can be excluded here since the rate of approach to equilibrium, as observed by Suhrmann and his co-workers,<sup>4,5</sup> for the deposits condensed at low temperatures is very much more rapid than the rate observed here for the smokes.

It is possible to decide between models (2) and (3) quite conclusively by x-ray diffraction patterns taken from a fresh deposit and from the same deposit after

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<sup>1</sup> Harris, McGinnies, and Siegel, *J. Opt. Soc. Am.* **38**, 582 (1948).

<sup>2</sup> E. K. Plyler and J. J. Ball, *J. Opt. Soc. Am.* **38**, 988 (1948).

<sup>3</sup> Harris, Jeffries, and Siegel, *J. App. Phys.* **19**, 791 (1948).

<sup>4</sup> R. Suhrmann and G. Barth, *Zeits. f. Physik* **103**, 133 (1936).

<sup>5</sup> R. Suhrmann and H. Schnackenberg, *Zeits. f. Physik* **119**, 287 (1942).

<sup>6</sup> H. B. Huntington and F. Seitz, *Phys. Rev.* **61**, 315 (1942).

<sup>7</sup> H. B. Huntington, *Phys. Rev.* **61**, 325 (1942).

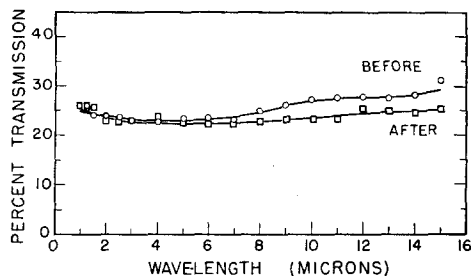


FIG. 1. Infra-red transmission before and after thermal stabilization.

stabilization. Particles made up of very small nuclei should give diffraction patterns with very broad diffuse rings which sharpen upon stabilization. In the case of non-equilibrium particles which are single crystallites with only an excess of lattice vacancies, the line breadth of the diffraction pattern from the fresh deposit should give a particle size correlating with the average diameter observed in the electron microscope, and this line breadth should not change with stabilization of the deposit. Line breadth measurements were made on the (111) diffraction line of gold using Cu radiation and a "Norelco" recording spectrometer. The natural line breadth for the setting of the slits used was  $0.27^\circ$  and a freshly prepared deposit gave a line breadth of  $1.07^\circ$ . Using the modification of the Debye-Scherrer formula given by Warren<sup>8</sup> the average particle size was found to be 120A which checks well within the range observed for such particles with the electron microscope. No sharpening of this line was observed after keeping the deposit at  $62^\circ\text{C}$  for a total of 27 hours during which time the resistance dropped to  $\sim 30$  percent of its original value.

The excess vacant site lattice arrangement in the non-equilibrium particle is further substantiated by the low temperature coefficient of resistivity observed in gold smoke deposits. The temperature coefficient of resistivity has been measured between  $70^\circ$  and  $25^\circ\text{C}$  and found to be about 0.1 percent per degree C, or one-third that of massive gold. The effect of the excess vacant sites on the resistivity of the deposit will be discussed in detail further on, but since these vacant sites must act as scatterers of the conduction electrons, they should lower the temperature coefficient of resistivity in the same manner as foreign atoms in the lattice.

#### DIFFUSION OF VACANT SITES

The stabilization process by the diffusion of excess vacant sites to the surface of the particles can be derived if we restrict the calculations to spherical particles of uniform size in which the surfaces of equal concentration are concentric. The diffusion equation in spherical coordinates is

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (1)$$

<sup>8</sup> B. E. Warren, *Zeits. f. Krist.* **99**, 448 (1938).

where  $C$  is the excess concentration of vacant sites above the equilibrium concentration;  $D$  is the diffusion coefficient for vacant sites and is given by

$$D = \frac{N}{N+N'} \frac{\nu_s \delta^2}{6} \exp(-\epsilon/kT), \quad (2)$$

where  $\delta$  is the lattice parameter and  $(\nu_s/6) \exp(-\epsilon/kT)$  is the probability that a vacant site will change places with an atom.  $\nu_s$  is the vibrational frequency of the lattice atoms and  $\epsilon$  is the activation energy required for the passage of an atom from one site to an adjacent vacant site. If the ratio of the number of vacant sites,  $N'$ , to the number of atoms,  $N$ , is small, as is generally the case,  $N/(N+N') \approx 1$ .

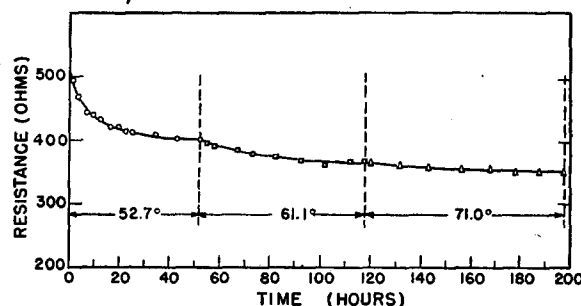


FIG. 2. Resistance change of a deposit at different temperatures.

Taking the boundary conditions as

1.  $C=0$ , at  $r=a$ , for all values of  $t$  ( $a$  represents the particle radius)
2.  $C$  = finite, at  $r=0$ , for all values of  $t$
3. Uniform distribution of sites,  $C_0$ , at  $t=0$ ,

the solution of Eq. (2) is

$$C = C_0 \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\frac{2a}{n\pi} \sin\left(\frac{n\pi}{a}r\right)}{r} \exp(-n^2\lambda t), \quad (3)$$

where

$$\lambda = (\nu_s/6)(\pi^2/a^2)\delta^2 \exp(-\epsilon/kT). \quad (3a)$$

The ratio of the total number of vacant sites to the total number of atoms as a function of time is obtained by integrating  $C$  in Eq. (3) over the volume of the sphere.

$$\frac{N' - N'_e}{N} = 4\pi \int_0^a Cr^2 dr = 4\pi C_0 \int_0^a \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2a}{n\pi} \sin\left(\frac{n\pi}{a}r\right) \exp(-n^2\lambda t) dr. \quad (4)$$

If  $N'_0$  is the total number of vacant sites in the volume at  $t=0$ , and  $N'_e$  is the number at equilibrium, then the integration over the volume gives

$$\frac{N' - N'_e}{N'_0 - N'_e} = A \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\lambda t), \quad (4a)$$

where

$$A = \frac{1}{\sum_{n=1}^{\infty} (1/n^2)} = \frac{6}{\pi^2}.$$

At large  $t$ , only the first term in the series is significant and the relation reduces to

$$\ln \frac{N' - N_e'}{N_0' - N_e'} = -\lambda t + \ln A. \quad (4b)$$

#### MEASUREMENT OF RATE OF STABILIZATION

The stabilization process is characterized by a decrease in the electrical resistance of a deposit and this change in resistance is to be correlated with the change in the number of vacant sites. A vacant site will disrupt the periodicity of the lattice and will act as a scatterer of conducting electrons. If  $Q_v$  is the cross section of scattering by a vacant site, then in a particle of volume  $V$  with  $N'$  vacant sites, the mean-free path,  $L_v$ , for scattering by vacant sites is given by<sup>9</sup>

$$1/L_v = (N'Q_v/V). \quad (5)$$

Since electrical resistance is inversely proportional to the mean-free path of the conducting electrons there will be a resistance,  $R'$ , associated with the presence of vacant sites, which is directly proportional to the number of vacant sites, and if  $R_0'$  is this resistance at  $t=0$

$$R'/R_0' = N'/N_0' \quad (6)$$

or, in terms of the differences from the equilibrium resistance,  $R_e'$ , associated with the number of vacant sites at equilibrium,

$$\frac{R' - R_e'}{R_0' - R_e'} = \frac{N' - N_e'}{N_0' - N_e'}. \quad (7)$$

It can be shown that the total resistance of a deposit at time  $t$  is given by

$$R_t = R' + R_c, \quad (8)$$

where  $R_c$  is the normal resistance due to the thermal motion of the atoms and is thus time-independent. After stabilization the resistance of a smoke deposit will be

$$R_{\infty} = R_c + R_e', \quad (9)$$

and the change in the number of vacant sites can thus be related to the measured resistance by

$$\frac{N' - N_e'}{N_0' - N_e'} = \frac{R' - R_e'}{R_0' - R_e'} = \frac{R_t - R_{\infty}}{R_0 - R_{\infty}}. \quad (10)$$

From Eq. (4a)

$$\frac{R_t - R_{\infty}}{R_0 - R_{\infty}} = A \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \lambda t) \quad (11)$$

<sup>9</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 541.

and at large  $t$

$$\ln \frac{R_t - R_{\infty}}{R_0 - R_{\infty}} = -\lambda t + \ln A. \quad (12)$$

#### EXPERIMENTS ON STABILIZATION OF DEPOSITS

Deposits weighing 50 to  $100 \times 10^{-6}$  grams/cm<sup>2</sup>, with mean particle diameter between 200 and 300Å, were prepared. These deposits showed a decrease in resistance to as low as twenty percent of their original value when heated to less than 80°C and showed only a small decrease in transmission for wave-lengths greater than  $5\mu$  and no measurable change in reflectivity. The infrared transmission before and after heating a deposit of gold-black on rock salt at 67.5°C for 18 hours is shown in Fig. 1. The resistance of this deposit decreased to 27 percent of its original value after the heat treatment.

Figure 2 shows the change of total resistance at three temperatures for a gold smoke deposited at a moderate rate, in an atmosphere of nitrogen (pressure 3 mm of mercury) on a glass slide  $\sim 0.2$  mm thick. The slide was placed inside a massive metal block maintained to within  $\pm 0.2^\circ\text{C}$  during the experiment. The resistances were recorded continuously.

In Fig. 3 are shown, as encircled points, values of  $(R_t - R_{\infty})/(R_0 - R_{\infty})$  at different values of  $t$ , as calculated from the data of Fig. 2, and using the  $R_{\infty}$  value corrected for temperature.  $R_{\infty}$  was taken as the resistance of a deposit that had been maintained at 72°C for at least 100 hours. (Heating at 80°C produced no further change in resistance.)  $\lambda$  and  $A$  were determined by successive approximations so that Eq. (11) gave a curve which best fitted the experimental points. The calculated curves are shown by the solid lines in Fig. 3; the dashed lines represent the limiting Eq. (12). The initial time for the 61.1°C calculated curve was obtained from the relation  $(\lambda t)_{52.7^\circ\text{C}} = (\lambda t)_{61.1^\circ\text{C}}$ , so that 52 hours at 52.7° is equivalent to 19.3 hours at 61.1°.

The average of the observed values for  $A$  is 0.38; according to Eq. (4a),  $A = 6/\pi^2 = 0.61$ . The observed

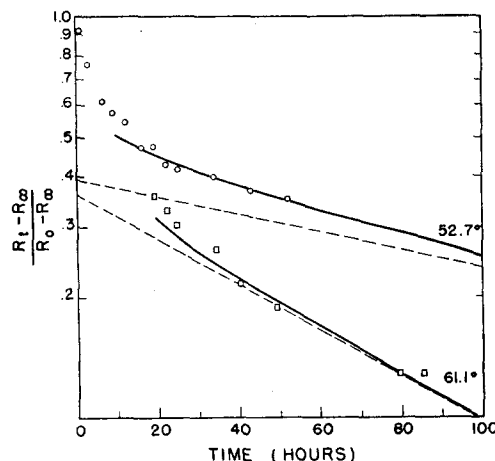


FIG. 3.  $(R_t - R_{\infty})/(R_0 - R_{\infty})$  versus time.

TABLE I. Values of  $\lambda$ , sec.<sup>-1</sup>, and  $\epsilon$ , kcal./g atom, at different temperatures for three different smoke deposits.

Deposit	Atmosphere	$\lambda$ 's sec. <sup>-1</sup>		$\epsilon$ kcal./g atom
#11 B	3 mm Nitrogen	$\lambda_{52.7^\circ\text{C}} = .180 \times 10^{-5}$	$\lambda_{61.1^\circ\text{C}} = .450 \times 10^{-5}$	23.8
12 A	3 mm Nitrogen	$\lambda_{52.7^\circ\text{C}} = .170 \times 10^{-5}$	$\lambda_{61.1^\circ\text{C}} = .400 \times 10^{-5}$	22.2
10 C	4 mm Helium	$\lambda_{50.4^\circ\text{C}} = .133 \times 10^{-5}$	$\lambda_{60.1^\circ\text{C}} = .396 \times 10^{-5}$	24.2
10 C	4 mm Helium	$\lambda_{60.1^\circ\text{C}} = .396 \times 10^{-5}$	$\lambda_{70.8^\circ\text{C}} = 1.24 \times 10^{-5}$	24.3
10 C	4 mm Helium	$\lambda_{60.4^\circ\text{C}} = .133 \times 10^{-5}$	$\lambda_{70.8^\circ\text{C}} = 1.24 \times 10^{-5}$	23.5
Mean				23.5 kcal./g atom.

discrepancy may be due to non-uniform concentration of vacant sites at  $t_0$ .

The calculated values of  $(R_t - R_\infty)/(R_0 - R_\infty)$  for small values of  $t$  were, in most cases, less than the observed values. This discrepancy may be attributed to a non-uniform initial distribution of vacant sites or to a particle size distribution which has been neglected in the derivation of Eq. (3).

#### EVALUATION OF THE ACTIVATION ENERGY, $\epsilon$

The energy  $\epsilon$  necessary to permit an atom to move from a lattice site to an adjacent vacant site can be evaluated from the  $\lambda$ -values at two temperatures since from Eq. (3a) we have the relation

$$\epsilon = \frac{T_1 T_2}{T_2 - T_1} R \ln(\lambda_1 / \lambda_2). \quad (13)$$

Measurements on many deposits showed considerable variation in the value of  $\lambda$  from deposit to deposit in spite of all attempts to prepare them under the same conditions. Therefore to obtain values of  $\epsilon$  from Eq. (12),  $\lambda_1$  and  $\lambda_2$  must be obtained on the same deposit measured at different temperatures. An example of such a measurement has already been shown in Figs. 2 and 3. In Table I are listed some pairs of  $\lambda$ 's which have been obtained on typical deposits. The mean value of the activation energy  $\epsilon$  was found to be 23.5 kcal./g atom.

#### THE SINTERING OF GOLD SMOKE DEPOSITS

The electron microscope observations show the particles of gold smoke in contact with each other,

forming loose aggregates which make up a spongy structure. When a deposit is heated sufficiently above the temperature at which only the stabilization of individual particles occurs, there is a continued decrease in the resistance of the deposit and at the same time a pronounced change in its optical characteristics. We attribute this change to sintering due to the coalescence of the particles. It has been found that the minimum temperature and time required to sinter a given deposit depend first on the particle size in the deposit (determined by the conditions of preparation), and second, on the thermal history of the specimen.

Fresh deposits of gold smoke, prepared at low pressures and low rates of evaporation, have a very small particle size (mean diameter 15–40Å),<sup>3</sup> and such deposits sinter at temperatures as low as 40–50°C. A typical example is a specimen prepared in 0.4 mm of nitrogen at a slow rate. The infra-red reflectance increased from 19 percent to 52 percent during a 40-hour treatment at 50°C.

Deposits prepared under conditions producing large particles (mean diameter 100–200Å) show negligible sintering below 80°C (the stabilization process which occurs has already been described). At temperatures above ~100°C, however, behavior of these deposits depends to a great extent on the degree of previous stabilization. Figure 4 shows the change of infra-red reflectance at 150° for two similarly prepared deposits: A was freshly made whereas B was thoroughly stabilized.

Above 175° stabilized deposits show appreciable sintering within a few hours. Figure 5 shows the change of infra-red reflectance *versus* time at three temperatures for similarly prepared and stabilized deposits.

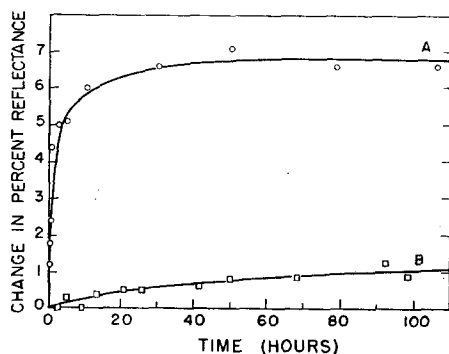


FIG. 4. Reflectance change at 150°C for a stabilized (B) and an unstabilized (A) deposit.

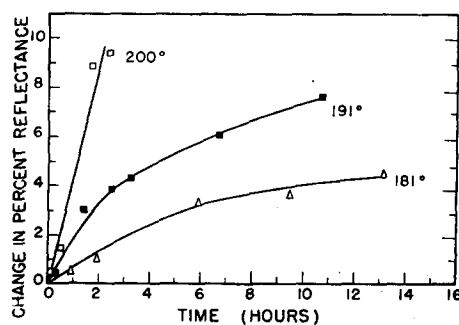


FIG. 5. Reflectance change at high temperature for stabilized deposits.

## DISCUSSION

It would be of considerable interest to obtain a value of the energy involved in the sintering process. This process in which the spheroidal particles coalesce undoubtedly proceeds by a process of self-diffusion.<sup>10</sup>  $\epsilon''$ , the energy required for self-diffusion by the vacancy mechanism in a crystalline lattice, is equal to the sum of  $\epsilon'$  and  $\epsilon$ , where  $\epsilon'$  is the energy required to move an atom from an interior lattice site to the surface, and  $\epsilon$  is the activation energy required for an atom to move from one site in the lattice to an adjacent vacant site.  $\epsilon'$  would thus be given by the difference in  $\epsilon''$  and  $\epsilon$ . Also since the equilibrium ratio of the number of vacant sites to the total number of atoms is

$$N_v'/N \approx \exp(-\epsilon'/kT) \quad (14)$$

a knowledge of the magnitude of  $\epsilon'$  would permit calculation of the equilibrium number of vacant sites.

Unfortunately, it has not been possible to relate satisfactorily the change in resistance or reflectance observed during the sintering process to any mechanism involving the coalescence of the particles.

If  $\epsilon$  has the same value for massive gold as for gold smoke, then  $\epsilon'$  for massive gold would be 27.5 kcal./g

atom, since  $\epsilon''$  for massive gold is 51 kcal./g atom.<sup>11</sup> This value of  $\epsilon'$  is to be compared with the value of 28 kcal./g atom, calculated by Huntington<sup>6</sup> for the energy required to move a copper atom from an interior site to the surface. The energies for the copper lattice should be somewhat higher than for gold since the measured value of self-diffusion in copper is 57 kcal./g atom.<sup>12</sup> For gold smoke, however,  $\epsilon'$  must be considerably smaller than 27.5 kcal./g atom in order to account for the rapid changes observed at temperatures below 200°C. When a smoke deposit is stabilized by heating below 80°C, the number of vacant sites is decreased and  $\epsilon'$  is increased correspondingly. The difference in behavior above 100°C, shown in Fig. 4 at 150°C, between an untreated and a stabilized deposit indicates that the increase in energy required for the process after stabilization is probably of the order of magnitude of 5 to 10 kcal./g atom.

## ACKNOWLEDGMENTS

We are indebted to Mr. John K. Beasley for many helpful discussions during the course of this investigation, and to Professor John T. Norton for the x-ray studies.

<sup>11</sup> H. McKay, *Trans. Faraday Soc.* **34**, 845 (1938).

<sup>12</sup> Steigman, Shockley, and Nix, *Phys. Rev.* **56**, 13 (1939).

<sup>10</sup> J. Frenkel, *J. Phys. U.S.S.R.* **9**, 385 (1945).

## Some Studies in Molecular Orbital Theory

## I. Resonance Structures and Molecular Orbitals in Unsaturated Hydrocarbons\*

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The predictions of qualitative resonance theory, as to the electronic structures of unsaturated hydrocarbons, are analyzed in terms of LCAO molecular orbital theory. The following results are proved for "alternant" hydrocarbons, that is, hydrocarbons containing no odd-membered unsaturated rings:

- (1) The number of unpaired electrons present in the ground state is at least as great as the number of carbon atoms having a deficiency of valence bonds in any principal resonance structure.
- (2) With a few special exceptions, these odd electrons are distributed over just those atoms which have a deficiency of valence bonds in one or more of the principal resonance structures.
- (3) In singly charged hydrocarbon anions or cations the ionic charge is located on just those atoms which bear charges in the various principal resonance structures.

It follows that enumeration of the principal resonance structures of a hydrocarbon molecule or ion gives much valuable information as to its electronic structure; and in particular, an alternant hydrocarbon possessing no normal Kekulé-type structure must have a paramagnetic ground state, and behave as a radical or multiradical.

These results do not depend on the neglect of overlap, or the assumption of a constant carbon-carbon resonance integral.

## 1. NOTATION

THE following is a summary of the notation used in this paper:

$\phi_t$ ,  $\phi_u$  are  $2p$  atomic orbitals (AO) on the carbon atoms  $t$ ,  $u$ .  
 $N$  is the number of such AO.

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† Now at the Department of Chemistry, Manchester University, Manchester, England.

$T$  is the maximum number of double bonds (a triple bond being counted as two double bonds) occurring in any resonance structure.

$\psi$  is a molecular orbital (MO) of form  $\sum_t c_t \phi_t$ ; its binding energy is  $\epsilon$ .

$r$  is any "starred" carbon atom in an alternant hydrocarbon.

$s$  is any "unstarred" carbon atom.

$\mu$  is any "active" carbon atom.

$\nu$  is any "normal" carbon atom.

$R$  is the total number of starred atoms.