but this example illustrates the uncertainty associated with assigning spurious bands on the basis of position alone.

The new infrared data, Fig. 3, are in full accord with Joyner and Glockler's assignment. The band at 458 cm^{-1} is infrared active and has the C type structure expected for the CCl_2 wagging mode, whereas the 375-cm^{-1} band has the A type structure expected for the CCl_2 rocking mode. The remaining low-lying mode at 299 cm^{-1}, the CCl_2 bending mode, was beyond the range of the infrared instrument. The qualitative depolarization-ratio value for this Raman band obtained by Joyner and Glockler was confirmed—the band although of symmetry species A_1 is only very slightly polarized. The measured value was 0.86 ± 0.02.

Now that Joyner and Glockler's assignment of the

fundamental modes has been shown to be unassailable the reason for the discrepancy between measured and calculated entropies must be looked for elsewhere. It was found that the recently published microwave structural data for vinylidene chloride by Sekino and Nishikawa[6] were sufficiently different from the early electron diffraction data to change the rotational entropy contribution so that the total calculated entropy fell within the experimental uncertainty range of the measured entropy. The new moments of inertia were 113, 249, and 362×10^{-40} g cm^2. Calculated and measured entropy values are compared in the preceding paper.

[6] S. Sekino and T. Nishikawa, J. Phys. Soc. Japan **12**, 43 (1957).

Conjugation and Polar Effects in Butadiene

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Various valence bond structure functions are projected onto approximate ground-state wave functions of butadiene. The most important structure, $C=C—C=C$, contributes approximately 70% of the total. The next most important structure corresponds to two attractive dipoles and contributes over 40% to the ground state, while structures with double bonds between the central carbons contribute relatively little. It appears that ionic contributions may be important to the central carbon-carbon bond length, with the dipole-dipole interaction behaving like an effective repulsion because of the variation of the electronic wave function. The problem of the nonorthogonal valence bond representation is examined: it is found that conjugation is strongly inherent even in a "nonconjugated" structure $C=C—C=C$, and that conjugation and dipolar interaction are nearly separable.

OF LATE, there has been a revival of interest in the problem of conjugation effects in butadiene and other unsaturated hydrocarbons. Cook,[1] Dewar,[2] and Stoicheff[2] have all focused attention on the length of carbon-carbon single bonds, and its dependence on hybridization. Dewar[2] has gone further, raising the question of whether conjugation is an important effect, and even whether we have any unequivocal evidence at all for its existence, in the ground states of olefinic hydrocarbons. In view of this interest, it seemed that it might be enlightening to examine various approximate wave functions representing the π electrons of butadiene in terms of some of the valence bond structures which are endowed with relatively clear physical significance. In addition to whatever light this examination might shed on the conjugation problem, it

also makes apparent some of the difficulties inherent in the physical interpretation suggested by a valence bond representation, or any nonorthogonal representation for that matter.
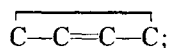
Specifically, this investigation involves an examination of the projections of various wave functions onto each other. The functions $\Psi_I—\Psi_{VI}$, corresponding to several valence bond (VB) structures, are projected onto a number of approximate ground state wave functions of the four-electron system; we have considered the four functions derived by self-consistent field (SCF) and configuration interaction (CI) methods, within the framework of both antisymmetrized molecular orbital (ASMO) and atoms-in-molecules (AIM) approaches. It also has proved informative to project the VB functions onto each other, and to construct from the various "excited" VB functions new functions orthogonal to the "normal" structure Ψ_I, and examine their projections onto the molecular orbital and CI functions. The square of each projection is exactly the

[1] D. Cook, J. Chem. Phys. **28**, 1001 (1958).
[2] M. J. S. Dewar, Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June, 1958; B. Stoicheff, *ibid*.
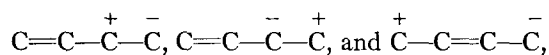
fraction of one of the projected functions in the other, exactly like the square of the scalar product of two vectors. The four molecular orbital and CI functions used were those derived by the author,[3] except in the case of the ionic structure projections onto the ASMO CI function. Here, for convenience, values were taken from the work of Fain and Matsen.[4] Their treatment is exactly equivalent to a complete study of the ASMO CI function in terms of VB structures. However, their choice of basis, the choice of nonionic structures specifically, made it desirable to take the projections of the two unionized structure functions onto the ASMO CI function of reference 3.

The valence bond functions we have considered include Ψ_I, corresponding to the normal C=C—C=C structure; Ψ_{II}, representing the "long bond" structure,

$$\overline{C—C=C—C};$$

Ψ_{III}, Ψ_{IV}, and Ψ_V,

representing the three structures

$$\overset{+}{C}=C—\overset{-}{C}—C,\ \overset{-}{C}=C—\overset{+}{C}—C,\ \text{and}\ \overset{+}{C}—C=C—\overset{-}{C},$$

respectively, and Ψ_{VI}, representing two ion pairs in their attractive

$$\overset{+}{C}\overset{-}{C}\overset{+}{C}\overset{-}{C}$$

order. The related functions Ψ_{II}'—Ψ_{VI}' are derived by removing from each Ψ_J that part parallel to or included in Ψ_I. If S_{IJ} is the overlap integral between Ψ_I and Ψ_J, and N_J is a normalizing factor, $\Psi_J'=N_J(\Psi_J-S_{IJ}\Psi_I)$, so Ψ_J is orthogonal to Ψ_I. The primed functions have been studied because the VB functions representing structures are not orthogonal to each other, and therefore do not correspond to mutually exclusive conditions of the π electrons. Thus, for example, when one represents the π electrons of butadiene approximately with Ψ_I, one is automatically including some "long bond" character in one's representation. This nonorthogonality can be rather large, as can be seen from Table I, a table of S_{JK}^2 for pairs of VB structures. It is particularly important for Ψ_I and Ψ_{II}, since this pair of functions remains nonorthogonal even when the four carbon nuclei are infinitely far apart. All other pairs are at least asymptotically orthogonal. We might note that the projection of Ψ_J onto the corresponding Ψ_J', the fraction of Ψ_J which is not included in Ψ_I, is simply $1-S_{IJ}^2$.

Before going on to discuss the projections themselves, we should stop to comment on the use of wave functions found by diagonalizing an AIM energy matrix. Within the AIM method, the best wave function is never obtained explicitly; in fact the energy is obtained in an approximation which uses different bases for the

TABLE I. Squares of overlap integrals between valence bond functions.

	Ψ_I	Ψ_{II}	Ψ_{III}	Ψ_{IV}	Ψ_V	Ψ_{VI}
Ψ_I	1					
Ψ_{II}	0.36	1				
Ψ_{III}	0.12	0.011	1			
Ψ_{IV}	0.10	0.009	0.102	1		
Ψ_V	0.014	0.0008	0.031	0.023	1	
Ψ_{VI}	0.14	0.0006	0.066	0.062	0.065	1

unperturbed and perturbing parts of the Hamiltonian. On the other hand, one does obtain approximate coefficients for an expansion of the molecular wave function in terms of atomic stationary state functions. In a treatment such as this one, we replace the correct atomic stationary state functions with their isomorphous counterparts based on an orbital model when we project the AIM functions onto VB structures. The Pariser-Parr approach[5] can be made formally equivalent to AIM, but the interpretation of the wave function is somewhat different. Here, when intra-atomic energies are treated explicitly as parameters, the LCAO functions can be interpreted as the appropriate basis functions of the energy matrix.

Table II contains the squares of the projections of valence bond functions onto the four representations of the ground state wave function. The butadiene carbon skeleton is taken in its *trans* form, with $r_{C=C}=1.35$ A, $r_{C-C}=1.46$ A, and $<_{C=C-C}=124°$. As mentioned previously, the projections of the ionic structures onto the ASMO CI function were taken from reference 4.

First we shall look at relations between the behavior of different ASMO and AIM functions, and then go on to the more important task of relating the projections to the behavior and structure of the butadiene molecule.

It is apparent that the contribution of ionic structures to the ASMO CI function is much less than to any of the other three. This results directly from the overestimate made by the ASMO method of the energy Q necessary to form a C^+C^- ion pair.[6] The fraction that any function can contribute to a ground state function determined by configuration interaction depends inversely on the square of the difference between the energy expectation values of the two functions before CI. The function Ψ_{III} differs roughly in energy expectation from Ψ_I by the energy necessary to form an ion pair, plus the energy of a double bond, less the electrostatic attraction of the ion pair. This gives approximately 10.5 ev+5.5 ev−10.5 ev=5.5 ev

[3] R. S. Berry, J. Chem. Phys. **26**, 1660 (1957).
[4] J. Fain and F. A. Matsen, J. Chem. Phys. **26**, 376 (1957).

[5] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 767 (1953).
[6] W. Moffitt and J. Scanlan, Proc. Roy. Soc. (London) **A218**, 464 (1953).

TABLE II.

(a) Squares of projections of valence bond structure functions onto various approximate ground state wave functions of butadiene.

Valence bond function	Structure	Square of projection onto lowest state of:			
		ASMO SCF	ASMO CI	AIM SCF	AIM CI
Ψ_I	C=C—C=C	0.55	0.87	0.56	0.69
Ψ_{II}	C—C=C—C	0.07	0.20	0.08	0.11
Ψ_{III}	C=C—C⁺—C⁻	0.19	0.06ᵃ	0.28	0.24
Ψ_{IV}	C=C—C⁻—C⁺	0.26	0.08ᵃ	0.20	0.18
Ψ_V	C⁺—C=C—C⁻	0.02	0.001ᵃ	0.01	0.007
Ψ_{VI}	C⁺—C⁻—C⁺—C⁻	0.49	0.01ᵃ	0.49	0.43

(b) Squares of projections onto AIM CI ground state of renormalized parts of VB functions made orthogonal to Ψ_I.

Valence bond function	Ψ_{II}'	Ψ_{III}'	Ψ_{IV}'	Ψ_V'	Ψ_{VI}'
Square of projection onto AIM CI function	0.04	0.05	0.03	0.03	0.14

ᵃ See reference 3.

if one uses empirical values for the energies.[6-9] The structure VI similarly will lie higher than III but will have an attractive dipole-dipole interaction energy, which will somewhat reduce the 5.5 ev difference. In fact, if one considers real dipoles 1.35 A apart, oriented as they are in *trans*-butadiene, the dipole-dipole attractive energy is 2.95 ev, so the energy associated with structure VI is only 2.5 ev above that of III. On the other hand, if one uses the ASMO estimate of Q, structures III and IV have energies about 12 ev above I, and VI is another 9 ev above them. Consequently the ionic functions are relatively unavailable for configuration interaction, or alternatively, their energy expectations are so high that little is gained by their inclusion. It is probable that the ASMO CI function is badly underestimating the importance of these structures, so we shall concentrate our attention henceforth on the two SCF functions and especially on the AIM CI function.

We note that the ASMO and AIM SCF functions have nearly the same projections throughout. They differ significantly only in their relative contributions from Ψ_{III} and Ψ_{IV}. The ASMO function prefers having two electrons near the double bond, while the AIM function moves them to the further carbon. These functions, Ψ_{III} and Ψ_{IV}, are the only ones considered

here which contribute to the polarity of the double bonds, and it is interesting that the two methods do tend to give opposite polarities. Evaluation of the gross atomic populations as defined by Mulliken[10] adds credence to this discrepancy: dividing the π-electron density as Mulliken does, one finds in the ASMO SCF method that a terminal carbon has 0.97 π electron associated with it, while an inner carbon has 1.03 π electrons; according to the AIM SCF wave function, the populations are 1.06 and 0.94 for the terminal and inner carbons, respectively. Chemical evidence seems to be on the side of the negative terminal carbon,[11] but the net charges are so small and the wave functions so sensitive that one can hardly say this is anything but fortuitous, and the mechanism of the addition reactions is by no means certain.

The inclusion of configuration interaction does very little to the qualitative picture of the π-electron system. The contributions of nonionic structures are increased, and the double bonds are made slightly more polar with the negative end outermost, when configuration interaction is included in the AIM method. Because of their success in the determination of the electronic spectrum of butadiene,[3] it seems reasonable that the AIM CI functions may be the most reliable ones available for the π electrons of this molecule. We proceed on this assumption in carrying out the rest of our analysis.

Turning to the physical implications of the projections, one is struck by the large contributions of ionic structures in relation to the contribution of Ψ_{II}, the classical resonance structure for butadiene. It should be especially noted that after the normal structure I, the most important contribution comes from VI, corresponding to two attracting dipoles. This is perhaps surprising at first glance, but is entirely in keeping with the satisfactory results obtained from the dispersion force model suggested by Simpson[12] and helps to substantiate his hypothesis. Furthermore the bond-length alternation of long polyenes is more understandable if the main interaction between neighboring double bonds is a dipole-dipole interaction in the form of a strong correlation effect rather than conjugation in the sense of double-bond character of the 1,3 bond.

Configuration interaction, or inclusion of resonance structures, is one way of including in a wave function the effects of the correlated motion of the electrons. In terms of resonance structures, the dipole-dipole structure VI is one of the best structures to describe correlations in the *positions* of electrons in the two double bonds. Structure II, on the other hand, accounts for correlations in the *spins* of electrons, correlating electrons on the two central carbons and on the

[7] R. S. Mulliken, J. Chem. Phys. 2, 782 (1934).
[8] R. S. Mulliken and C. C. J. Roothaan, Chem. Revs. 41, 219 (1947).
[9] R. G. Parr and B. L. Crawford, J. Chem. Phys. 26, 526 (1948).

[10] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).
[11] For example, C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, New York, 1953), especially Secs. 43b and 43d.
[12] W. T. Simpson, J. Am. Chem. Soc. 73, 5363 (1951); 77, 6164 (1955).

two terminal atoms. It seems more satisfying intuitively that spatial correlations be more important than spin correlations for electrons in adjacent double bonds. The former are directly related to the Coulomb energies and the latter, to exchanges; the Coulomb integral involving electrons on the central carbons C_2 and C_3 is more than an order of magnitude larger than the corresponding exchange integral.

Let us examine the energetics of the dipole-dipole effect in more detail. It was mentioned previously that the energy of attraction of the two dipoles in structure VI is 2.95 ev or 68 kcal/mole. The net contribution to the π-electron energy due to dipole-dipole attraction will be given by the 68 kcal multiplied by the square of the projection of Ψ_{IV} onto the best approximate ground state function. This product, for the equilibrium configuration of the four carbon nuclei, is given in Table III, together with the corresponding values for two other nuclear configurations. Configuration A corresponds to bond lengths of 1.33 and 1.54 A, and structure C, to bond lengths all of 1.40 and 120° $C=C—C$ angle.

The energy values in Table III enable us to see what contribution dipole interactions make to the central carbon-carbon bond length. The dipole interaction energy is relatively large and varies considerably with distance. The net contribution of the dipole-dipole interaction, with the variation of the wave function taken into account, gives an effective potential which varies more slowly, but is actually *repulsive* in character. The contribution of the dipolar structure VI actually drops faster than the dipole-dipole attraction increases. This is perhaps an unusually explicit example of how the variation of the electronic wave function, determining the effective potential for nuclear motion, can dominate the effects of the real potential of the nuclei in any fixed position.*

We might compare the rate of change of the net dipole interaction energy with that expected for a stretching constant of about 5×10^5 dynes/cm. The latter would lead to a variation of 1.3 kcal if the C—C bond were squeezed 0.06 A from its equilibrium position; the AIM CI calculation shows that the net dipole contribution to the energy drops by 1.3 kcal when the nuclei move from nuclear configuration B to configuration C. This is all very well, but simply shows that polar interactions are probably one of several effects, all of the same order of magnitude, which determine the bond lengths and force constants.

Finally, we return to the problem of conjugation and polar character in butadiene, and to the concomitant and more general problem of the interpretation of results based on a nonorthogonal set of functions. Table II shows that the total contribution of any of the ionic

* This phenomenon might be called "dipole-dipole attractive repulsion" and the converse effect for oppositely oriented dipoles, "repulsive attraction." Dr. E. P. Geiduschek has suggested the name "dipole ambivalence" to describe the two phenomena.

TABLE III. Variation of dipole-dipole interaction energy with nuclear configuration in the AIM CI ground state function of butadiene.

Nuclear configuration	$E_{\text{dipole-dipole}}$	$[\int\Psi_{VI}\cdot\Omega_N]^2\times E_{\text{dipole-dipole}}$
A. C=C=1.33 A C—C=1.54	60.6 kcal/mole	31.7 kcal/mole
B. C=C=1.35 A C—C=1.46	68.1	29.3
C. C=C=1.40 A C—C=1.40	77.6	27.9

functions Ψ_{III}, Ψ_{IV}, or Ψ_{VI} to the best ground state function is larger than the corresponding contribution of Ψ_{II}, by a significant amount. But Table I shows that some 36% of Ψ_{II} is identical with or is included in Ψ_{I}, which contributes 69% of the ground state. It was mentioned previously that this is in large part due to the fact that Ψ_{I} and Ψ_{II} are not even orthogonal when the carbon nuclei are infinitely separated. This can be seen as follows. There are two independent singlet functions available when four electrons are assigned to four nonequivalent orbital functions. In order that the entire wave function for one singlet be orthogonal to that of the other, the two spin functions must be orthogonal to each other since the orbital parts of the functions are the same. The spin function corresponding to Ψ_{I} may be written

$$A = \tfrac{1}{2}[\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta].$$

The spin function orthogonal to this has the form

$$B = \frac{1}{\sqrt{3}}[\alpha\alpha\beta\beta+\beta\beta\alpha\alpha-\tfrac{1}{2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha+\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)],$$

while the spin function corresponding to Ψ_{II} has the form

$$C = \tfrac{1}{2}[\alpha\alpha\beta\beta+\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\beta\alpha].$$

Hence $C=(\sqrt{3}/2)B-\tfrac{1}{2}A$, and the square of the projection of A onto C is 0.25. So even when the carbon nuclei are infinitely separated, Ψ_{I} and Ψ_{II} are 25% nonorthogonal; the additional 11% that appears when the nuclei are brought together is due to the overlap of the orbital functions, and is of the same order of magnitude as the squared overlap of functions which are orthogonal at infinite separation.

Table IIb gives some indication of the contribution to the AIM CI ground state function by those parts of $\Psi_{II}-\Psi_{VI}$ orthogonal to Ψ_{I}. Quite clearly, these contributions are considerably smaller than the contributions of the unprimed functions since each of the excited resonance structures except Ψ_{V} has a reasonably

large overlap with Ψ_I. But even after being made orthogonal to Ψ_I, the dipolar structure is still by far the most important. That the six structures chosen for this investigation are the most important can be seen immediately. Table I shows that, except for Ψ_{III} and Ψ_{IV}, the various excited functions are relatively orthogonal, so that we can get a fair estimate of the contribution of all six structures by adding S^2 for Ψ_I, $\Psi_{II}',\cdots,\Psi_{VI}'$ together. This gives 0.98, which is roughly the amount of the ground state function Ω which comes from these structures. (This is not to say that some higher structure could not be nearly parallel to one of our six functions; this could happen, and would be essentially an alternative description of the π electrons.)

It is tempting to try to divide Ψ_{II} into four parts: that part contained in Ψ_I and also Ω, the ground state function, a part excluded from Ω but parallel to Ψ_I, a part in Ω but not in Ψ_I, and a part orthogonal to both. We must be careful of our interpretations if we try this; wave functions add like vectors, and we find that the part of Ψ_{II} simultaneously parallel with Ψ_J and Ω is out of phase with the part of Ψ_{II} parallel to Ω put orthogonal to Ψ_I. The two contributions to Ω must be subtracted rather than added, and partially cancel each other. We do find that of the 36% of Ψ_{II} which is in Ψ_I, 10.6% is in the part of Ψ_I orthogonal to Ω, and the other 25.4% is in both Ψ_I and Ω. This means that the part of Ψ_{II} contained in Ψ_I is somewhat more parallel to Ω than a simple 69% of the 36% would indicate. But in general, one cannot neatly separate the contributions of Ψ_{II} or any of the VB functions into parts which retain any of the original valence bond significance and are still mutually exclusive contributions. We can only make qualitative statements, and say that, for butadiene, ionic structures probably do contribute more to the ground state than does the conjugated structure, and that more of the conjugated behavior of structure II is contained in structure I than is any other effect described by other VB structures.

The table of VB overlap integrals does at least give us one reassuring bit of information. The small overlap of Ψ_{II} with Ψ_{VI} shows that dipole-dipole interactions are essentially separable from effects of double-bonding across the middle bond. Despite the difficulty of disentangling either Ψ_{II} or Ψ_{VI} from Ψ_I, at least they can be pulled apart from each other.

We might interject a remark regarding the multiple-bond order. Using the usual molecular orbital definition,[13] Mulliken finds that most MO calculations give a double-bond order for the central C—C bond of butadiene of about 0.2 or a little over.[14] Using the definition of double-bond order for a valence bond treatment,[15] we see immediately from Table II that

the double-bond order of the central bond is 0.11. It should not be surprising that these two differ because the MO definition takes into account all contributions which tend to put electrons between the nuclei, while the VB definition includes only the contribution from the structure II.

It seems that as long as one uses the empirical bond-length bond-order curve appropriate to the chosen definition of bond order, it does not make much difference which definition one chooses. This suggests that there is some correlation between the amount of double-bond character and the total amount of overlapping electron density between two nuclei, even if the latter is somewhat different numerically from the former. Or alternatively, it suggests that bond lengths are not very sensitive functions of bond order according to either definition. A change of MO double-bond order from 0.1 to 0.2 leads to a change of predicted bond length from 1.49 to 1.46 A, according to the table given by Coulson.[16] Until relatively recently, this would still have been as good as an experimental determination. And it seems possible that interpretation of bond length measurements beyond this point may require more careful definition of the concept of bond length itself.[17] On the other hand perhaps Dewar's suggestion[2] is correct: that, after simple multiplicity, the hybridization of carbon atoms is the major determining factor of carbon-carbon and carbon-hydrogen bond lengths. Then conjugative and polar effects would presumably act as still higher order phenomena, causing changes of the order of 0.02 A or less in C—C bonds. Certainly we cannot separate these various effects exactly in any meaningful way except to try to calculate equilibrium distances for hypothetical systems of carbon atoms having only σ bonds. As the present calculation shows, one can pick any one phenomenon and see how it affects the length of some chosen bond, but one cannot suppose *a priori* that several effects under consideration are mutually exclusive. The variation of double-bond character carries with it some variation in polar character; a change of hybridization will lead to a change in bond order, and so forth.

But associating bond lengths with hybridization rather than with bond orders does gain one great advantage: it allows the direct correlation of two observable properties, the bond length and the symmetry of the local field about each carbon atom in a bond. Although hybridization and fractional bond orders may be directly connected, we must rely on an LCAO model to define either; by ostensibly correlating bond length and hybridization, Dewar has actually bypassed this limitation. Perhaps this will lead to a more powerful approach to the theoretical determination of bond lengths from electronic wave functions.

[13] C. A. Coulson, Proc. Roy. Soc. (London) **A169**, 413 (1939).
[14] R. S. Mulliken (private communication).
[15] Pauling, Brockway, and Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

[16] C. A. Coulson, *Valence* (Oxford University Press, London, 1952), p. 253.
[17] See, for example, L. S. Bartell and R. A. Bonham, J. Chem. Phys. **27**, 1414 (1957).

We may summarize our investigation as follows. The nonorthogonal valence bond representation has proved helpful in giving a qualitative picture of the importance of ionic contributions to the wave function of the π electrons of butadiene. These ionic contributions seem to enter primarily as a means of introducing correlations between the motion of electrons in different double bonds. Care must be taken if any quantitative interpretation is to be given to the valence structures, particularly in the case of conjugation. The valence bond approach is not particularly helpful in studying bond lengths because it seems to break the problem into one of several phenomena of comparable magnitude, rather than providing a viewpoint in which one effect is dominant. In addition, its nonorthogonal functions do not even correspond to complete separation of the effects which the method selects.

Experimental Test of the Volmer Theory of Heterogeneous Nucleation

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The prediction of the Volmer theory that the critical supersaturation for nucleation from the vapor phase on a flat surface depends upon $(1- \cos\phi^2)(2+ \cos\phi)$, where ϕ is the contact angle of the condensate on the surface, has been tested experimentally. Critical supersaturations for visible fogging on test surfaces coated with various transparent plastics were found to agree within observational error with the theoretical values computed for the observed contact angles.

INTRODUCTION

IT is well known that a high supersaturation is necessary before homogeneous condensation is initiated in a pure vapor, whereas condensation commences upon foreign particles or "nuclei" at much more modest degrees of supersaturation.

If the nucleus is a droplet of the liquid phase, then condensation will proceed if the free energy of the vapor is sufficient to provide for the increasing surface energy of the growing droplet. The growth of droplets in this way is determined by the Gibbs-Thomson equation

$$\log(p_r/p_\infty) = (2\sigma M/\rho RT)\cdot(1/r), \qquad (1)$$

which relates the vapor pressure p, at which a liquid surface of radius r is in equilibrium, with the vapor pressure p_∞ of a plane surface under the same conditions. In this equation σ, M, and ρ are the surface tension, molecular weight, and density of the liquid, R is the universal gas constant, and T the temperature (°K).

If the nucleus is a solid perfectly wetted by the condensed liquid, no change in surface free energy is involved when the solid-vapor interface is replaced by solid-liquid and liquid-vapor interfaces. From the point of view of nucleation, therefore, an insoluble but perfectly wettable particle is equivalent to a droplet of the same radius. Hence condensation will take place on either liquid droplets or perfectly wettable insoluble nuclei providing the supersaturation exceeds a certain critical value. If supersaturation is defined as $(p-p_\infty)/p_\infty$, then from Eq. (1), the critical supersaturation for a droplet or wettable particle of radius r is given by

$$S_r = \exp[(2\sigma M/\rho RT)\cdot(1/r)]-1. \qquad (2)$$

If the nucleus is soluble, allowance must be made for the lowering of the vapor pressure, in accordance with Raoult's law. Thus for a soluble nucleus, the critical supersaturation will be somewhat less than that given by Eq. (2). The fundamental Gibbs-Thomson equation has been universally accepted as rigorously true, but direct experimental verification has been obtained only recently.[1]

If the nucleating particle is not perfectly wettable, then replacing the solid-vapor interface with solid-liquid and liquid-vapor interfaces alters the surface free energy. Such nuclei should not therefore be taken as equivalent to liquid nuclei. The problem of heterogeneous nucleation was examined in detail by Volmer,[2]

[1] V. K. La Mer and R. Gruen, Trans. Faraday Soc. **48**, 410 (1952).

[2] M. Volmer, *Kinetik der Phasenbildung*. (Th. Steinkopff, Dresden and Leipzig, 1939).