there was serious asymmetry of the peak resulting from a pronounced reflection minimum on the high-frequency side from effects of the very high indexes of AuCN ($n_0=2.47$, $n_\epsilon=2.41$).[1] However, when examined in oil of index 1.8 or 2.0, AuCN gave a symmetrical peak without discontinuity of the adjacent background.

We are at a loss to explain the earlier AuCN result, unless it was from some mixed species like $ClAuCN^-$, since the frequencies of the most likely contaminants in the other preparation are $KAu(CN)_2$, 2141 cm^{-1},[2] and $HAu(CN)_2$, 2146 cm^{-1}.[3]

As a further example of the anomalous results obtained using the pressed disk technique, the maximum of AuCN when dispersed in a TlBR disk (chosen to match the AuCN indexes) was shifted to 2232 ± 2 cm^{-1}.

* This work was sponsored by the U. S. Atomic Energy Commission.

[1] E. Staritzky, Los Alamos Scientific Laboratory (unpublished work).

[2] L. H. Jones, J. Chem. Phys. **27**, 468 (1957).

[3] Penneman, Staritzky, and Jones, J. Am. Chem. Soc. **78**, 62 (1956).

"Deposition"—a Proposed Antonym for "Sublimation"

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PRESENT terminology of physics and chemistry includes just *five* terms for use in specifying the *six* possible types of phase transition that can occur between the three ordinary states of matter. In contrast to the antonymous pairs, "freezing-melting" and "condensation-evaporation," we have for the solid-vapor transition only the single term, "sublimation."

When one systematically examines usages in the literature of heat, thermodynamics, and physical chemistry, one finds the currently employed terminology for the solid-vapor transitions confusing and contradictory. Physicists almost invariably use sublimation to mean only the solid-to-vapor change. Chemists may mean that or, about equally frequently, may imply a cyclic change that also embraces the subsequent return to the solid phase, as in the phrase, "purification by sublimation." Meteorologists, who took over the term from physics and chemistry decades ago, have evolved still another usage: they employ sublimation to mean either the solid-to-vapor transition alone, *or* the vapor-to-solid transition alone, and most frequently the latter! Thus, the meteorologist has come to speak of sublimation nuclei, clearly a contradiction in terms from the viewpoint of the physicist; but the latter has nothing better to offer at present.

From consideration of several possible solutions to this nomenclatural problem, I conclude that the chemist and the meteorologist should be urged to follow the physicist in restricting sublimation to just the solid-to-vapor transition, while for the inverse transition I recommend adoption of a new term, "deposition." Readers of this journal who may have some doubt as to the appropriateness of such a new usage should refer to a more complete discussion of this problem I have given elsewhere,[1] wherein I cite a variety of passages from the literature of physics, chemistry, and physical meteorology to show that informal usage has, in fact, already given some currency to this meaning for deposition.

In terms of the proposed usage, one would speak of the growth of crystals from the vapor as growth by deposition, or depositional growth. The latent heat of deposition would become the analog of latent heat of condensation. The meteorologist would abandon the highly confusing term nucleus of sublimation and would speak of a nucleus of deposition, and the ambiguous practice of using "condensation" to refer to a vapor-to-solid transition (a common practice in the current literature of solid-state physics) could be stopped.

In all, it seems clear that adoption by physicists, chemists, and meteorologists of this recommendation would eliminate a terminological difficulty that should have been corrected long ago by introduction of a distinct sixth term in the nomenclature of phase transitions. For this reason I am making the present recommendation in notes to several journals in the fields concerned.

[1] J. E. McDonald, J. Meteorol. (to be published).

Notes

Molecular Orbitals in the $B_4H_7^-$ and $B_6H_{11}^+$ Ions

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THE close analogy of the filled molecular orbitals[1] of B_5H_9 to those of benzene, has suggested the possible occurrence of $B_4H_7^-$ having C_{3v} symmetry and $B_6H_{11}^+$ having C_{5v} symmetry. These ions are related to B_5H_9 in the same way that cyclopentadienyl ion, $C_5H_5^-$, and tropylium ion, $C_7H_7^+$, are related to benzene.

A simplified molecular orbital treatment, similar to that given[1] for B_5H_9, suggests that these ions should be stable. Assuming hybridization as in B_5H_9 we use an *sp* hybrid for the apex B—H bond, and tetrahedral hybrids for the basal boron atoms. In $B_4H_7^-$ three basal BH units are linked by three bridge hydrogen atoms (H_b), in B_5H_9 four BH's are linked by 4 H_b's, and in $B_6H_{11}^+$ five BH's are linked by 5 H_b's. The molecular orbitals bonding the boron framework then are formed from one hybrid orbital from each basal boron atom (*D*, *E*, *F*, etc., respectively), one *sp* orbital (*A*), and two *p* orbitals (*B*, *C*) from the apex boron atom.

The three orbitals from the three basal atoms in $B_4H_7^-$ form one totally symmetric orbital which combines with the *sp* hybrid of the apex boron atom, and these three orbitals also form a doubly degenerate pair which interacts with the *p* orbitals of the apex boron atom. Thus in $B_4H_7^-$ the linear combinations separate strongly into bonding and antibonding orbitals, with no intermediate nonbonding molecular orbital. These orbitals, reduced to the $2a+2e$ representation, are

$$\phi_1=2^{-\frac{1}{2}}\mathrm{A}+6^{-\frac{1}{2}}(\mathrm{D}+\mathrm{E}+\mathrm{F})$$

$$\phi_2=2^{-\frac{1}{2}}\mathrm{A}-6^{-\frac{1}{2}}(\mathrm{D}+\mathrm{E}+\mathrm{F})$$

$$\begin{cases}\phi_3=2^{-\frac{1}{2}}\mathrm{B}+(12)^{-\frac{1}{2}}(2\mathrm{D}-\mathrm{E}-\mathrm{F})\\ \phi_{3'}=2^{-\frac{1}{2}}\mathrm{C}+\frac{1}{2}(\mathrm{E}-\mathrm{F})\end{cases}$$

$$\begin{cases}\phi_4=2^{-\frac{1}{2}}\mathrm{B}-(12)^{-\frac{1}{2}}(2\mathrm{D}-\mathrm{E}-\mathrm{F})\\ \phi_{4'}=2^{-\frac{1}{2}}\mathrm{C}-\frac{1}{2}(\mathrm{E}-\mathrm{F}),\end{cases}$$

where overlap is neglected. The orbital ϕ_1 and the pair, ϕ_3, $\phi_{3'}$, are bonding and have energies of $H_0+3^{\frac{1}{2}}\alpha$ and $H_0+(\frac{3}{2})^{\frac{1}{2}}\beta$ in the approximation and notation of the previous study.[1] Orbitals for $B_6H_{11}^+$ in the $2a+2e_1+e_2$ representation are, in similar notation,

$$\phi_1=2^{-\frac{1}{2}}\mathrm{A}+(10)^{-\frac{1}{2}}(\mathrm{D}+\mathrm{E}+\mathrm{F}+\mathrm{G}+\mathrm{H})$$

$$\phi_2=2^{-\frac{1}{2}}\mathrm{A}-(10)^{-\frac{1}{2}}(\mathrm{D}+\mathrm{E}+\mathrm{F}+\mathrm{G}+\mathrm{H})$$

$$\begin{cases}\phi_3=2^{-\frac{1}{2}}\mathrm{B}+5^{-\frac{1}{2}}(\mathrm{D}+\mathrm{E}\cos x+\mathrm{F}\cos 2x\\ \qquad\qquad\qquad\qquad +\mathrm{G}\cos 3x+\mathrm{H}\cos 4x)\\ \phi_{3'}=2^{-\frac{1}{2}}\mathrm{C}+3^{\frac{1}{2}}/4(\mathrm{E}-\mathrm{H})+\frac{1}{4}(\mathrm{F}-\mathrm{G})\end{cases}$$

$$\begin{cases}\phi_4=2^{-\frac{1}{2}}\mathrm{B}-5^{-\frac{1}{2}}(\mathrm{D}+\mathrm{E}\cos x+\mathrm{F}\cos 2x\\ \qquad\qquad\qquad\qquad +\mathrm{G}\cos 3x+\mathrm{H}\cos 4x)\\ \phi_{4'}=2^{-\frac{1}{2}}\mathrm{C}-3^{\frac{1}{2}}/4(\mathrm{E}-\mathrm{H})-\frac{1}{4}(\mathrm{F}-\mathrm{G})\end{cases}$$

$$\begin{cases}\phi_5=(\frac{2}{5})^{\frac{1}{2}}(\mathrm{D}+\mathrm{E}\cos 2x+\mathrm{F}\cos 4x+\mathrm{G}\cos 6x+\mathrm{H}\cos 8x)\\ \phi_{5'}=2^{\frac{1}{2}}/4(\mathrm{E}-\mathrm{H})-6^{\frac{1}{2}}/4(\mathrm{F}-\mathrm{G}),\quad \text{where}\quad x=2\pi/5.\end{cases}$$

The ϕ_5, $\phi_{5'}$ pair is nonbonding because there are no orbitals of e_2 symmetry in the valence shell of the apex boron atom. Energies of the bonding orbitals are $H_0+5^{\frac{1}{2}}\alpha$ for the ϕ_1 orbital and $H_0+(\frac{5}{2})^{\frac{1}{2}}\beta$ for the degenerate pair ϕ_3, $\phi_{3'}$.

The question of existence of these ions is closely related to the structures of known compounds. Thus the $B_6H_{11}^+$ ion could be derived from the B_6H_{10} structure[2] by no other change than the addition of a proton across the strained single bond. Preparation of the $B_4H_7^-$ ion is not so obvious, but this ion might exist along with BH_4^- in the salt $Na_2B_5H_{11}$. Finally, a new type of hydride of the ionic type $B_6H_{11}^+\cdot B_4H_7^-$ might exist, as might the analogous $C_7H_7^+\cdot C_5H_5^-$.

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[1] Eberhardt, Crawford, and Lipscomb, J. Chem. Phys. 22, 985 (1954).

[2] Hirshfeld, Dickerson, Lippert, and Lipscomb, J. Chem. Phys. (to be published).

Self-Diffusion of Oxygen in Uranium Dioxide*

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INVESTIGATION of the self-diffusion of oxygen and uranium in UO_2 and nonstoichiometric uranium oxides is in progress at this laboratory. This note presents results on the first phase of this study, the measurement of oxygen self-diffusion coefficients in nearly stoichiometric UO_2 ($UO_{2.00}-UO_{2.01}$).

Solid-gas isotopic exchange was used. This method is applicable for diffusion coefficient measurements when the rate of the surface exchange reaction between gas and solid is much faster than the rate of diffusion of the exchanging ion through the lattice. Solutions to the diffusion equation for measurements of this type are discussed by Carman and Haul[1] and by Crank.[2]

In these experiments, the exchange reaction is that between O^{18} enriched uranium dioxide and CO_2 gas of natural O^{18} content. The O^{18} enriched uranium dioxide is prepared by the high pressure (2200 psig and 340°C) steam oxidation of uranium metal with O^{18} enriched water. As prepared, the enrichment in O^{18} of the uranium dioxide is seven times the natural content, and the O/U ratio of the uranium dioxide is 2.004 ± 0.004. Exchange data were obtained with an apparatus modified from that described by Cameron *et al.*[3]

The diffusion process is followed by determining the change in O^{18} concentration in the gas phase. The gas is analyzed mass spectrographically by comparing the relative intensities of the $C^{12}O^{16}O^{16}$ and $C^{12}O^{16}O^{18}$ peaks. Only small quantities of gas are taken for analysis, so the experiments proceed under essentially a constant quantity of CO_2.

The appropriate diffusion equation solution[1] is the

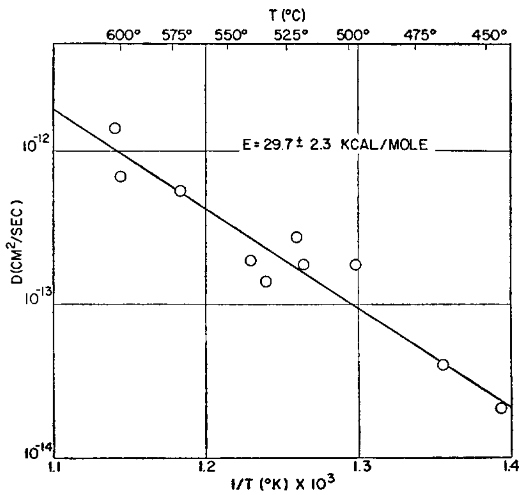

FIG. 1. Variation of diffusion coefficient with temperature.