Erratum: The Chain Photolysis of Acetaldehyde in Intermittent Light

W. L. Haden Jr. and O. K. Rice

Errata : On the Statistical Mechanics of Liquids, and the Gas of Hard Elastic Spheres

[J. Chem. Phys. **12**, 1 (1944)]

O. K. RICE

University of North Carolina, Chapel Hill, North Carolina
November 2, 1944

PAGE 4: Third and fourth lines above Eq. (3) and elsewhere on the page. The "dodecahedron" is actually a figure with twelve vertices but fourteen sides (six squares and eight triangles). The volumes are given correctly.

Page 11: Eq. (24). Second term in bracket,

$$-\frac{1}{2}\frac{\sigma^3}{r_1{}^3\sigma^3}, \quad \text{should be} \quad -\frac{1}{2}\frac{\sigma^3}{r_1{}^3\zeta^3}.$$

Page 16: Left-hand side of displayed unnumbered equation should be

$$[e^{1/3}T/\Theta(a_0)](2^{1/2}/2^{1/6}).$$

Page 18: In line following first equation in Appendix, "free space" should read "portion of the total length."

Note: It may be remarked that the term "cubic close-packed" and derivatives thereof are used in two senses. Sometimes they refer to a cubic close-packed array of hard spheres in mutual contact, which thus occupy the smallest possible volume. In other cases they refer rather to the type of lattice, without demanding that the spheres be in actual contact, the possibility of displacements about the average positions which form the lattice points being visualized. The actual usage in any given instance should be clear from the context.

Erratum: The Chain Photolysis of Acetaldehyde in Intermittent Light

[J. Chem. Phys. **10**, 445 (1942)]

W. L. HADEN, JR., AND O. K. RICE
University of North Carolina, Chapel Hill, North Carolina
November 2, 1944

IN the abstract the energies of activation for reactions (2) and (3) are interchanged. They are given correctly in Table III.

Bond Moments of Higher Valence States

R. SAMUEL
The Illinois Institute of Technology, Chicago, Illinois, and the Hebrew Institute of Technology, Haifa, Palestine
November 10, 1944

IN a recent article[1] additive bond moments have been calculated for non-aromatic first-order molecules formed by a central atom in its maximal state of valency. This has been done on the basis of classical formulae. One point apparently has not been made sufficiently clear, as it has subsequently been raised in a number of discussions. This is, whether the new values in reality are not those of the semipolar double bonds. In other words, whether, for example, the value of 4.4D ascribed to the bond between pentacovalent nitrogen and oxygen in the nitro group,

does not constitute in reality the value for the semipolar double bond between the same two atoms. In this letter it will be shown that this is not so.

On the basis of the resonance interpretation of the semipolar double bond, the nitro group is a hybrid of the two forms

$$\overset{+}{O}\!=\!\overset{-}{N}\!-\!O \tag{1a}$$

and

$$\overset{-}{O}\!-\!\overset{+}{N}\!=\!O. \tag{1b}$$

On account of the rigorous energetical degeneracy each form contributes 50 percent. Indeed, if no other similar molecule existed, the value of 4.4D could easily be associated with this mixture.

But in the azoxy compounds the two corresponding forms are

$$-N\!=\!\overset{+}{N}\!-\!\overset{-}{O} \tag{2a}$$

and

$$-\overset{-}{N}\!-\!\overset{+}{N}\!=\!O. \tag{2b}$$

These constitute two different terms of the molecule, and according to their energetical difference (2a) will contribute x_1 percent and (2b) y_1 percent. To obtain the value of 4.4D for the mixture, the energy difference must be such that x_1 and y_1 just have the required values. This would be an entirely fortuitous coincidence, as this energy of excitation depends on both parts of the molecule equally and not on the nitrogen-oxygen part alone.

Again the N-ethers of oximes would be mixtures of x_2 percent of
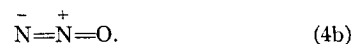
$$>\!C\!=\!\overset{+}{N}\!-\!\overset{-}{O} \tag{3a}$$

and y_2 percent of

$$>\!\overset{-}{C}\!-\!\overset{+}{N}\!=\!O, \tag{3b}$$

and if fortuitously the energy difference between these two terms is such that x_2 and y_2 obtain the required ratio the value of 4.4D may result for the moment of this bond. The same would be true of nitrous oxide, which would be a mixture of x_3 percent of

$$N\!\equiv\!\overset{+}{N}\!-\!\overset{-}{O} \tag{4a}$$

and y_3 percent of

$$\overset{-}{N}\!=\!\overset{+}{N}\!=\!O. \tag{4b}$$

This is only half of the problem. A very great number of molecules are interconnected by having one or the other bond in common. Thus, the same bond between C and N of the N-ethers occurs again with the same moment in the

diazo compounds which would be mixtures of x_4 percent and y_4 percent of two forms. The ratio of x_4 and y_4 must be such as to obtain the same value of 2.6 D for the bond between C and N as in the N-ethers. But for the latter the percentage ratio of x_2 and y_2 has already been fixed according to the requirements of the bond between N and O. The difference between the two energy levels of the N-ethers and hence the ratio of x_2 and y_2 must be such as to obtain for this mixture of two forms the same moment of the nitrogen-oxygen bond as in the nitro group, of the nitrogen-carbon (double) bond the same as in the diazo compounds, and of the nitrogen-carbon (single) bond the same as in the nitrates. The argument must not be elaborated. But it is very difficult to see how the excitation energies of the molecules can be consistent with so many different and simultaneous conditions.

To sum up: The problem which confronts us cannot be solved by means of philology but is a genuine problem in the realm of physics. On the basis of the classical formulae we expect in first approximation constant and additive moments of the individual bonds, and we find them. On the basis of the resonance interpretation of the theory of the semipolar double bond we really cannot expect additive and constant bond moments, but we find them nevertheless. Hence we have to explain each of them by a whole series of fortuitous coincidences, which in the framework of this theory remain unexplained freaks of nature. As has been pointed out, such a state of affairs cannot be directly disproved by a physico-chemical experiment, because the percentage ratio is a variable factor in the latter theory. But it would appear that the classical concepts are superior by virtue of the principle of economy of hypotheses.

[1] R. Samuel, J. Chem. Phys. **12**, 380 (1944).