turally unrelated dye, fluorescein.   The results obtained with this series of compounds are especially striking because the dyes differ only in the nature of the alkyl groups.   Still more pronounced effects would be expected in studies of compounds having greater structural differences.

Many obvious applications and extensions of these ideas are now being investigated and detailed results will be published later.   Of particular interest are an investigation of the possibility that optical isomers can be separated with such adsorbents and an attempt to demonstrate "specific catalysis," analogous to the action of enzymes, by specific adsorbents for the reactants or products of various reactions.

[1] Pauling, L., *J. Am. Chem. Soc.*, **62**, 2643–2657 (1940).
[2] Pauling, L., and Campbell, D. H., *J. Exptl. Med.*, **76**, 211–220 (1942).

THE VALENCE-STATE ENERGY OF THE BIVALENT OXYGEN ATOM

By LINUS PAULING

CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA*

A significant simplification in the discussion of the structure of molecules can be achieved by referring the energies of molecules not to the energies of their constituent atoms in any one of the stationary spectroscopic states of the isolated atoms, but instead to a hypothetical valence state of each atom.[1]   The valence state of an atom is defined as that state in which it has the same electronic structure as it has in the molecule. Thus in the valence state the spins of the electrons that are used for forming bonds in a molecule are considered to resonate between positive and negative values, corresponding to the resonance of each bonding electron with another electron of opposite spin in the atom with which the bond is formed.   For the bivalent oxygen atom, with six L electrons, two orbitals, one mainly $2s$ in character and one $2p$, are occupied by unshared pairs, and the other two orbitals, mainly $2p$ but with a small amount of s hybridization, are occupied by one bonding electron apiece, the spins of which are parallel 50 per cent of the time and antiparallel 50 per cent of the time. In the following paragraphs values of the energy of this bivalent state of the oxygen atom relative to the normal state of the isolated atom, ^3P, are derived by four different methods.   It is found that the four values agree

reasonably well with one another, and their average value, 0.74 v.e., is indicated to be reliable to about 0.05 v.e.

According to the Slater theory, the energy values of the three Russell-Saunders states based upon the normal configuration of the oxygen atom are $F^0 - \dfrac{5}{25} F^2$, $F^0 + \dfrac{1}{25} F^2$, and $F^0 + \dfrac{10}{25} F^2$, for ^3P, ^1D, and ^1S, respectively. The spectrum of oxygen shows that the ^1D state lies 9239 cm.$^{-1}$ above ^3P and ^1S 9739 cm.$^{-1}$ above ^1D. These differences in energy are not in the ratio $2:3$ predicted by simple spectroscopic theory. For the valence state of the atom, neglecting hybridization, the energy is predicted to be equal to the Coulomb interaction of two p electrons occupying different orbitals directed along two mutually orthogonal axes, $F^0 - \dfrac{2}{25} F^2$, and one-half of the resonance integral between these two orbitals, that is, $-\dfrac{3}{50} F^2$, a total of $F^0 - \dfrac{7}{50} F^2$. F^2 is indicated to have the value 6.16 v.e. by the $^1S - {}^1D$ separation, and 8.21 v.e. by the $^1D - {}^3P$ separation. If the ^3P state is considered to be depressed in energy through resonance with a ^3P state based on a higher configuration, then the energy of the valence state relative to ^3P is predicted to be 0.86 v.e., which is the energy of ^1D corrected by the quantity $-\dfrac{9}{50} F^2$ with F^2 given by the $^1S - {}^1D$ separation. Similarly if ^1S is considered to be depressed by resonance, the energy of the valence state is predicted to be 0.49 v.e. In the absence of knowledge about the nature of the cause of the deviation of the intervals from the theoretical ratio the best that we can do is to take the average, 0.68 v.e., as the spectroscopic value of the energy of the valence state.[2] The true value would be expected to be slightly higher because of hybridization of the bond orbitals; s-p hybridization in the alkali-metal diatomic molecules gives rise to a valence-state energy of 0.1 to 0.2 v.e. for the alkali atoms,[3] and similar effects of hybridization may be expected for other atoms.

A second, independent value of this energy quantity can be obtained by use of the postulate that the Morse function represents correctly the bond energy of two atoms in their valence states, and that the energy of a molecule obtained by extrapolation from the low-lying vibrational energy levels corresponds to the valence states of the atoms in the molecule. Linear extrapolation of the vibrational energy levels of the normal state of the oxygen molecule, $O_2 X\,^3\sum_g^-$, with use of the values 1580 cm.$^{-1}$ for ω_e and 11.35 cm.$^{-1}$ for $\omega_e x_e$ (as given by the slope of the best straight line for $\Delta G(v + {}^1\!/_2)$ to $v = 17$), leads to 6.69 v.e. for the energy of dissociation to two oxygen atoms in the valence state. The dissociation energy of the normal oxygen molecule into oxygen atoms in the normal state is 5.084 v.e., and in conse-

quence the energy of the valence state of the oxygen atom is indicated to be 0.80 v.e., one-half the difference of these two quantities.

A similar calculation can be made for the OH molecule. This molecule is to be considered as containing a bivalent oxygen atom with one valence free. The extrapolated energy of dissociation into a hydrogen atom and an oxygen atom in its valence state is 5.03 v.e., corresponding to the observed values $\omega_e = 3735$ cm.$^{-1}$ and $\omega_e x_e = 82.6$ cm.$^{-1}$. The dissociation energy into a hydrogen atom and a normal oxygen atom is 4.34 v.e., as given by the work of Dwyer and Oldenberg.[4] The difference between these values, 0.69 v.e., is the energy of the valence state of oxygen in this molecule.

It is very interesting to note that the difference between the energy of removal of the first hydrogen atom from a water molecule, involving breaking one oxygen-hydrogen bond, and the energy of removal of the second hydrogen atom vanishes when the valence state of oxygen is used as the point of reference. The energy of removal of the first hydrogen atom is found by combining thermochemical data with Dwyer and Oldenberg's value for the dissociation energy of OH to be 5.12 v.e., whereas that for the second hydrogen atom is 4.34, relative to the normal state of the oxygen atom. If the valence state of oxygen is used as a point of reference, the second of these values is to be increased by the energy of the valence state, which has been shown above to be approximately 0.7 v.e., and it is thus brought into approximate equality with the first bond energy. The equality of these two energy quantities to within 2 per cent is a striking illustration of the significance of the chemist's picture of the molecule as involving chemical bonds between pairs of atoms.

If the assumption is made that in this molecule the energy of breaking the first bond is exactly equal to the energy of breaking the second bond, when the valence state of oxygen is taken as the point of reference, an independent value can be derived for the energy of the valence state of oxygen. This value, 0.78 v.e., the difference of the two dissociation energies, agrees reasonably well with the others.

The agreement between the values of the valence-state energy of the oxygen atom in three different molecules, O_2, OH, and H_2O, suggests that the same value will hold for other molecules also, and this suggestion is supported by the agreement with the range of values given by the simple theory of atomic spectroscopic states. The average of the four independent values of the energy of the bivalent state of the oxygen atom relative to the normal spectroscopic state, 0.74 v.e. or 17.1 kcal./mole, is presumably reliable to about 0.05 v.e.

* Contribution No. 1283 from the Gates and Crellin Laboratories of Chemistry.
[1] Pauling, L., *Sommerfeld Festschrift, Z. Naturforsch.*, **3a**, 438–447 (1948).

[2] In the discussion of the valence state of oxygen in reference 1 the energy of the valence state was given incorrectly as $F^0 - \dfrac{11}{100} F^2$.

[3] Pauling, L., *Proc. Roy. Soc., London*, **A196**, 343–362 (1949).

[4] Dwyer, R. J., and Oldenberg, O., *J. Chem. Phys.*, **12**, 351–361 (1944).

ACQUISITION OF THE J SUBSTANCE BY THE BOVINE ERYTHROCYTE*

BY CLYDE STORMONT[†]

DEPARTMENT OF GENETICS, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The antigenic pattern of the bovine erythrocyte is genetically conditioned by numerous genes on at least nine of the thirty pairs of chromosomes.[1, 2] The combinations of these genes permit well over a million blood types. Any two animals taken at random, therefore, will almost invariably possess distinct blood types. A study of bovine twins, however, disclosed a much higher proportion of identical blood types than is expected in view of the relatively low frequency of monozygotous twinning in cattle.[3] Owen pointed out that this high proportion of identical blood types could be accounted for as a consequence of the known frequent union of chorionic blood vessels of twin fetuses, as demonstrated by Lillie.[4] Apparently, embryonal blood cells are interchanged by those twins having a common circulatory system and these primordial cells settle in the hematopoietic tissues where they serve as a source of erythrocytes throughout the life of each twin. The identity of blood types in otherwise genetically dissimilar twins would thus result from a mixture of two kinds of erythrocytes, namely, those produced by (*a*) the twin's own cells and (*b*) cells transplanted from the co-twin. Several lines of evidence, including the *in vitro* separation of the two kinds of erythrocytes comprising the mosaic of blood cells, afford proof of this explanation. It is now found that the cellular character called J constitutes an exception to the general rule in that twins possessing a blood admixture nevertheless may differ in respect to the presence or absence of this blood factor. The present report is concerned with the reasons for this non-conformity in behavior of character J.

Each of the numerous antigenic factors of cattle erythrocytes is recognized by the reaction (hemolysis) of these cells produced by a corresponding reagent (antibodies) and complement (fresh rabbit serum). For example, erythrocytes of an individual that possesses a gene for antigen A are sensitized by the action of A reagent and subsequently destroyed (hemolysed) by the action of the complement, while those of an animal that lacks gene A