Metasequoia has long been a member of the forest of the temperate zone, and has commonly ranged southward into latitudinal ecotones with the forests of the subtropical zone.   During the Eocene epoch this conifer extended still farther south in the uplands, where it lived in an altitudinal ecotone bordering the Clarno flora of the John Day Basin. It has survived in the high valleys of central China under conditions which seem to resemble closely its Tertiary environment in Oregon.   The modern occurrence of *Metasequoia glyptostroboides* in the mixed deciduous and evergreen forest of Szechuan and Hupeh therefore becomes a key to our understanding of many forests of the past in which this deciduous conifer was a member of similar ecotones.

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THE DISSOCIATION ENERGY OF CARBON MONOXIDE AND THE HEAT OF SUBLIMATION OF GRAPHITE

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For a number of years there has existed doubt about the value of the dissociation energy of carbon monoxide and about the heat of sublimation of graphite, a directly related quantity.   The most popular values for the dissociation energy of carbon monoxide are 9.144 electron-volts, suggested by Herzberg[1] on the basis of predissociation phenomena in band spectra, 9.61 e. v., suggested by Hagstrum and Tate[2] on the basis of electron impact experiments (or the value 9.85 e. v. derivable from predissociation data[3]), and 11.11 e. v., suggested by Gaydon and Penney[4] from an analysis of spectroscopic data.   These values together with thermochemical data lead to the values 124.9, 141.4, and 170.3 kcal./mole, respectively, for the heat of sublimation of graphite.   Strong evidence for the last of these values has been presented by Brewer, Gilles, and Jenkins,[4] who have reported 170.4 kcal./mole from a direct experimental determination.   The value has, however, been criticized by other investigators,[6, 7] and has been defended by Brewer.[8]

In this paper we communicate an argument which indicates that the high values of about 170 kcal./mole for the heat of sublimation of carbon to $C_{(g)}(^3P)$ and 11.11 e. v. for the dissociation energy of carbon monoxide are not correct, and which leads instead to the values 140 kcal./mole and 9.77 e. v., respectively.

The argument is based on the postulate that the linear extrapolation of the vibrational levels for the lower vibrational states of a molecule (a linear Birge-Sponer extrapolation) leads to an energy value corresponding to the dissociated atoms in a hypothetical electronic state called the valence state. An atom in the valence state, as defined in this paper, is an isolated atom with the same electronic structure as that which the atom has in the molecule under consideration. It is the state that would result if the atoms in the molecule were to be pulled apart without change in the electronic structures that exist in the molecule in the lower vibrational levels of the lower electronic state. The wave function for the valence state of an atom may of course be formed by linear combination of those for its spectroscopic states, and the energy of the valence state is somewhat higher than that of the normal spectroscopic state, by an amount, the valence-state energy, that is reasonably constant for a given atom from molecule to molecule.[9, 10]

The valence-state energy of the oxygen atom has been evaluated as 0.74 ± 0.05 e. v.[10] A rough value for the valence-state energy of nitrogen can be calculated from spectroscopic data for the three low-energy levels of the atom, all based on the configuration $2s^2 2p^3$. These levels, ^4S, ^2D, and ^2P, have energy values F°, $F^\circ - 6/25\, F^2$, and $F^\circ - 15/25\, F^2$, respectively, according to simple spectroscopic theory. The states ^2D and ^2P are observed to lie at energies 2.38 e. v. and 3.57 e. v. above the normal state ^4S. These values are not in the ratio 3:5 given by the simple theory, and accordingly there is uncertainty as to the value of the resonance integral F^2. The normal valence state of nitrogen to the extent that it is based on the normal configuration $2s^2 2p^3$ is the state in which each of three electrons occupying separate p orbitals has its spin oriented independently of the other two electrons, the corresponding energy being $F^\circ - 21/50\, F^2$. Because of the uncertainty in the value of F^2, the energy of the valence state cannot be predicted precisely. If the ^4S level is considered to be depressed by resonance with a similar state based on an excited configuration of the atom the valence-state energy would be calculated to be 1.39 e. v., whereas if the ^2P level is considered to be depressed by resonance the valence-state energy would be 1.19 e. v. A value somewhat larger than either of these values might be expected to result from contributions of higher spectroscopic states to the valence state.

A more reliable value for the valence-state energy of the nitrogen atom can be obtained from the consideration of nitric oxide. The energy of

dissociation of the normal nitric oxide molecule to a nitrogen atom and an oxygen atom in their valence states is found by linear extrapolation of the low-lying vibrational levels to be 7.87 e. v.   If we subtract from this quantity the sum of the valence-state energy of oxygen, 0.74 e. v., and that of nitrogen, approximately 1.5 e. v., the dissociation energy D_0 is predicted to be approximately 5.6 e. v.   This argument hence favors the value $D_0 = 5.29$ e. v. proposed by Mulliken[11] and supported by Wulf[12] and Hagstrum,[13] rather than the value 6.49 e. v. supported by Gaydon.[14] If we accept the value 5.29, the valence-state energy of the nitrogen atom is calculated to be 1.84 e. v.

Some substantiation of this value is provided by the consideration of the normal state and the first excited state of the nitrogen molecule.   The energy of dissociation of N_2 in its normal state $X^1\sum_g^+$ into two nitrogen atoms in their valence states is found by linear extrapolation to be 11.60 e. v., and the value of this quantity given by the first excited state $A^3\sum_u^+$ is 10.58 e. v.   On subtracting the dissociation energy of the nitrogen molecule, 7.38 e. v. (the alternative spectroscopic value 9.76 e. v. is to be eliminated as not leading to sufficiently large values for the valence-state energy and being incompatible with the results of electron-impact experiments[13]), and dividing by 2, we obtain 2.11 and 1.60 e. v., respectively, for the valence-state energy of the nitrogen atom.   The value 2.11 e. v. given by the normal state of the nitrogen molecule is probably high because of a large amount of s character in the orbital of the σ bond for this molecule. We conclude that the normal valence-state energy of the nitrogen atom is approximately 1.84 e. v., and that variation of a few tenths of an electron-volt may be expected.

The valence-state energy of the carbon atom can be similarly derived from spectroscopic data for the molecules CH and C_2.   For the normal state of CH the energy of dissociation to a carbon atom and a hydrogen atom in their valence states is 5.20 e. v., as given by linear extrapolation, and the dissociation energy D_0 to the atoms in their normal states is 3.47 e. v.   The difference, 1.73 e. v., can be taken as the valence-state energy of the carbon atom, inasmuch as the valence state and the normal spectroscopic state of the hydrogen atom are essentially the same.   For the normal C_2 molecule the energy of dissociation to two carbon atoms in their valence states is found by linear extrapolation to be 7.05 e. v., and the dissociation energy D_0 is 3.6 e. v.   These quantities lead to 1.73 e. v. for the valence-state energy of carbon, in exact agreement with the preceding value.

The energy of a carbon atom in its valence state and an oxygen atom in its valence state relative to the normal state of the carbon monoxide molecule is found to be 11.23 e. v. by linear extrapolation for the normal state, and the values 12.33, 11.87, and 12.10 e. v. are similarly obtained for

the first three excited states of the molecule, a $^3\Pi$, a' $^3\sum$, and A $^1\Pi$. If we subtract from these numbers the quantity 2.47 e. v., the sum of the valence-state energies for carbon and oxygen, as evaluated above, we obtain 8.76, 9.86, 9.40 and 9.63 e. v. for the dissociation energy of the normal carbon monoxide molecule to atoms in their normal spectroscopic states. These values are incompatible with the high value 11.11 e. v. for $D_0(CO)$, and may be considered to support either the value 9.14 or the value 9.61–9.85.

Evidence indicating that the second of these values, 9.6–9.85, is correct is obtained from the discussion of the cyanogen molecule and the cyanide radical. Linear extrapolation of the vibrational levels of the lowest state of the CN molecule, X $^2\sum{}^+$, leads to 9.85 e. v. for the energy of a carbon atom and a nitrogen atom in their valence states relative to the normal state of the molecule. On subtracting 1.73 for the valence-state energy of carbon and 1.84 for that of nitrogen, we obtain 6.28 e. v. for $D_0(CN)$. This value strongly supports the spectroscopic value 6.24 e. v. for this molecule,[14] rather than the alternative spectroscopic value 7.50 e. v. From thermochemical data and the accepted dissociation energy of the oxygen molecule, 5.08 e. v., it can be calculated[15] that the dissociation energy of cyanogen, C_2N_2, into two CN molecules is given by the equation

$$D_0(NC\text{---}CN) = 2D_0(CO) + D_0(N_2) - 2D_0(CN) - 10.7 \text{ e. v.} \quad (1)$$

The dissociation energy of cyanogen has been reported by Kistiakowsky and Gershinowitz[16] to be 77 $\pm$ 4 kcal./mole, and by White[17] to be 146 $\pm$ 4 kcal./mole. A chemical argument can be given that leads to an intermediate value. The dissociation energy of cyanogen may be expected to be greater than the carbon-carbon single-bond energy in diamond (one-half the heat of sublimation of diamond) by an amount equal to the conjugation energy of the two triple bonds in the molecule. This conjugation energy is twice that of two conjugated double bonds, with theoretical value[18] 8 kcal./mole. The value of $D_0(NC\text{---}CN)$ may hence be taken as 16 kcal./mole (0.70 e. v.) greater than one-half the heat of sublimation of diamond, and if this heat of sublimation lies between 125 and 170 kcal./mole the value of $D_0(NC\text{---}CN)$ is calculated to be 90 $\pm$ 11 kcal./mole Instead of using this value, with its large uncertainty, we may adopt the following procedure. Thermochemical data require that the value of $D_0(CO)$ be 3.70 e. v. greater than the heat of sublimation of diamond, and hence, with the resonance energy 0.70 e. v. in cyanogen, we obtain the equation

$$D_0(NC\text{---}CN) = \frac{1}{2}D_0(CO) - 1.15 \text{ e. v.} \quad (2)$$

From (1) and (2) we obtain the equation

$$3/2\, D_0(CO) = 2D_0(CN) - D_0(N_2) + 9.55 \text{ e. v.} \quad (3)$$

This equation with the values given above for $D_0(CN)$ and $D_0(N_2)$ leads to 9.77 e. v. for $D_0(CO)$, and hence to 140 kcal/mole for the heat of sublimation of graphite and 86 kcal./mole for the dissociation energy of cyanogen.

The methods that we have used in reaching these values involve some novel ideas—the concept of valence-state energy and the postulate that the valence-state energy is usually nearly the same for an atom in different molecules, the use of linear extrapolation of vibrational levels to obtain the dissociation energies of molecules into atoms in their valence states, the use of conjugation energy for expressing a difference in dissociation energies—and their reliability and accuracy have not been extensively tested. From internal evidence it seems likely, however, that these methods when cautiously applied yield energy values that involve no larger errors than a few tenths of an electron-volt, and that they may be used with considerable confidence, as in the present paper, to select the correct ones from among alternative widely differing possible values of dissociation energies of molecules.

* Contribution No. 1297.

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