QUARTERLY REVIEWS

VAPOURS OF THE ELEMENTS

By BERNARD SIEGEL

(AEROSPACE CORPORATION, EL SEGUNDO, CALIFORNIA)

THIS Review is of the bonding in those homonuclear molecules that are only observed at high temperatures, the condensed state of the element being the stable form at room temperature. Most of the elements fall into this category. Emphasis is placed on the significance of the bond strength as exemplified by the bond dissociation energy in correlating the various types of vapour molecules. However it should be noted that a comparison of chemical stabilities in terms of $D_0°$, the bond dissociation energy at 0°K, is only meaningful if the molecules are compared at a specific pressure. Because of the different pressure–temperature relationships for the various non-volatile elements, their equilibrium vapour pressures at any given temperature vary widely and this affects strongly the degree of dissociation at any specific temperature. Often the magnitudes of the degrees of dissociation for two molecules are in apparent conflict with their respective bond dissociation energies as is the case for Li_2 and Cs_2, shown in Fig. 1. As will be discussed, $D_0°$ is appreciably larger for Li_2. The larger mole fractions of Cs_2, in relation to Cs atoms, reflects merely the higher vapour pressures of cæsium than of lithium. A second point can be made from Fig. 1. The normal boiling point of lithium is 1620°K, but the mole fractions of Li_2 in the saturated lithium vapour have been computed to 3000°K, with the equilibrium vapour pressure rising to 114 atm. at that temperature. It is seen that the mole fractions of Li_2, in relation to Li atoms, rise to a maximum at 3000°K. Thus despite the fact that the $D_0°$ for Li_2 is below that of any permanent homonuclear gas molecule, Li_2 is quite stable in the saturated vapour at 3000°K. Comparison is made in Fig. 1 with the dissociation of F_2 and Cl_2 under identical conditions of temperature and pressure. It is seen that these gases exhibit similar behaviour except that association is very much greater for Cl_2 because of its considerably higher bond strength. It should also be noted that at atmospheric pressure lithium is virtually monatomic at 3000°K.*

Unless is it specified otherwise, our discussion is for the saturated vapours of the elements, *i.e.*, those vapours which are at the equilibrium vapour pressure of the element at any given temperature.

---

*A more detailed discussion, which will be published elsewhere, of the effect of the volatility-bond strength relationship in determining the degree of dissociation of homonuclear molecules has been prepared by the writer.

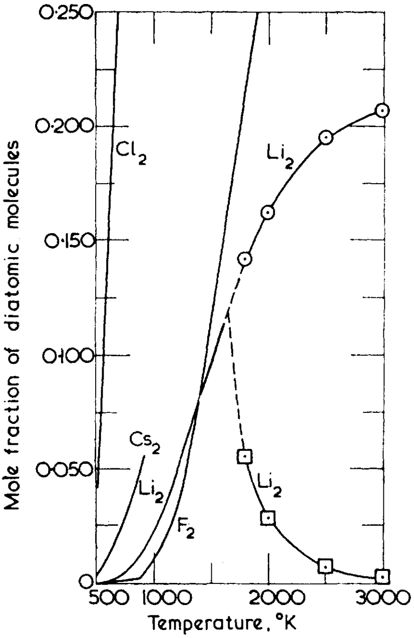

FIG. 1. *Saturated and non-saturated lithium vapour. A comparison with fluorine and Chlorine under identical conditions of temperature and pressure.*

The circles are for the saturated lithium vapour above the normal boiling point; the squares are for the unsaturated vapour at atmospheric pressure. The thermodynamic data required to compute the data in this Figure were obtained from refs. 16 *and* 64.

Group IA and IIA elements

Each of these elements forms diatomic molecules which are more weakly bonded than are any of the permanent gas molecules. The Group IIA elements must form normal diatomic molecules from atoms which have the ns^2 valence shell configuration in the ground state. Molecules of this type, having as many electrons in antibonding as in bonding molecular orbitals, do not have much chemical binding energy.[1] The latter are thus of the secondary or van der Waals type, and one would expect the bond dissociation energy to be less than 10 kcal./mole, the approximate lower limit for normal sigma bonds. The Mg_2 molecule has been observed by absorption spectroscopy in the rapid non-equilibrium sublimation of Mg_3N_2 at 1200—1400°c, but only monatomic Mg(g) was found when the sublimation was carried in an equilibrium manner; the calculated bond dissociation energy D_0° for Mg_2 from this study was 7·2 kcal./mole.[2] It

---

[1] G. Herzberg, "Spectra of Diatomic Molecules", 2nd edn., D. Van Nostrand, Princeton, 1950.

[2] J. R. Soulen, P. Sthapitanonda, and J. L. Margrave, *J. Phys. Chem.*, 1955, **59**, 132.

was concluded that Mg_2 is formed in an early step in the sublimation procedure but that only Mg(g) is stable when equilibrium is attained. Similarly in a mass spectrometric study of the saturated vapour over strontium at 500—650°C, only monatomic Sr was found,[3] and in mass spectrometric studies of the beryllium vapour in the range 1137—1347°C only monatomic beryllium was found.[4] A $D_0°$ of 16 kcal./mole has been estimated[5] for Be_2 but this value seems high for the type of bonding that is undoubtedly involved.

The above discussion is for the normal diatomic molecule. However it is conceivable that metastable molecules might form from excited states of the alkaline earth atoms. Such a situation exists for the metastable He_2 molecule, which is in a triplet sigma state and has[6] a $D_0°$ of at least 1·76 ev. However the excited states must be created by electronic excitation and metastable He_2 has only been observed to form in the emission spectrum of excited helium at low pressures. Therefore metastable He_2 is not actually a high-temperature species since the overall thermodynamic temperature at which it is formed is quite low.

Since the IA atoms have the ns^1 valence shell ground-state configurations, diatomic molecules can form simply by formation of a sigma bond by overlap of the *s* atomic orbitals. The homonuclear diatomic molecules of the IA elements should therefore be more strongly bonded than those of the IIA elements. This is in fact the case and each of the former have been studied in some detail.[7–10] The $D_0°$ values are given in Table 1. However the overlap between single electrons in the spherically symmetrical *s* atomic orbitals of the alkali-metal atoms does not lead to very strong bonding, as compared with most of the molecules to be discussed in subsequent sections. An interesting hypothesis regarding the nature of this weak bonding has been advanced. This involves a repulsion between the valence and non-bonding electrons, and was suggested because of the significantly weaker bonding[11] in Li_2 than in Li_2^+ (similarly Na_2^+ is more strongly bonded[12] than is Na_2).

TABLE 1. *Bond dissociation energies at* 0°K *of diatomic Group* IA *molecules*

Molecule	Li_2	Na_2	K_2	Rb_2	Cs_2
$D_0°$ (kcal./mole)*	25·8	17·5	11·9	11·3	10·4

* Data from Ref. 7.

---

[3] A. J. H. Boerboom, H. W. Reyn, and J. Kistemaker, *Physica*, 1964, **30**, 254.

[4] O. T. Nikitin and L. N. Gorokhov, *Zhur. neorg. Khim.*, 1961, **6**, 224.

[5] J. Drowart and R. E. Honig, *J. Phys. Chem.*, 1957, **61**, 980.

[6] P. N. Reagan, J. C. Browne, and F. A. Matsen, *Phys. Rev.*, 1963, **132**, 304.

[7] W. H. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman, *J. Res. Nat. Bur. Stand.*, 1955, **55**, 83.

[8] R. J. Thorn and G. H. Winslow, *J. Phys. Chem.*, 1961, **65**, 1297.

[9] T. A. Coultas, *J. Chem. Eng. Data*, 1963, **8**, 527.

[10] M. M. Makansi, W. A. Selke, and C. F. Bonilla, *J. Chem. Eng. Data*, 1960, **5**, 441.

[11] E. W. Robertson and R. F. Barrow, *Proc. Chem. Soc.*, 1961, 329.

[12] R. F. Barrow, N. Travis, and C. V. Wright, *Nature*, 1960, **187**, 141.

Although the diatomic homonuclear molecules of the alkali metals have been deduced by other means, they have not yet been observed mass spectrometrically. In fact, one such study reports the absence of Na_2 and K_2 at temperatures above and below 1000°C by non-equilibrium heating from a filament.[13]

Group IIIB elements

Boron.—The Group IIIB elements have the ns^2np^1 valence shell configurations in the ground-state atoms, but bond formation in their homonuclear diatomic molecules does not apparently involve only the simple overlap of the *p* electrons. The B_2 molecule in the ground state has a triplet sigma electronic configuration, indicating that the molecule has a double bond.[1] Nevertheless this double bond is not very strong (probably because of repulsions from the non-bonding valence electrons) since $D_0°$ is undoubtedly less than 70 kcal./mole. A value of 69 ± 11·5 kcal./mole has been reported from spectroscopic data,[14] while 65·5 ± 5·5 kcal./mole has been obtained from mass spectrometry.[15] The B_2 found by the latter method was observed in the sublimation of boron at 2330°K although it was shown to be present in extremely small amounts in comparison with B(g) at that temperature. However boron is similar to the alkali metals in that the mole fraction of B_2 increases substantially with temperature in the saturated boron vapour. From data in the JANAF Tables on B(g) and B_2(g), the mole fraction of the latter increases from $7{\cdot}3 \times 10^{-5}$ to $3{\cdot}7 \times 10^{-3}$ in the temperature range 2500—3900°K.[16] Accordingly, the observed absence of B_2 in a mass spectrometric study of boron vapour at 2100°K[17] should not be surprising since at that temperature the mole fraction of B_2 would be probably below the detection limits of mass spectrometers. Recent studies of the vapour of boron carbide by the torsion–effusion[18] and Knudsen-cell[19] techniques at temperatures up to 2522 and 2615°K reported only B(g).

Heavier Diatomic Molecules.—Very little is known about Al_2. In a mass spectrometric study of the equilibrium vapour over aluminium carbide at 2100°K, a trace mass peak was noted[20] for Al_2^+, but it is not clear whether the latter is due to ionisation of Al_2 or fragmentation of gaseous aluminium carbide upon electron impact. Since the aluminium vapour pressure at 2100°K has the appreciable value[16] of 0·0188 atm., the Al_2 molecule should be observable at this temperature if its bond strength is at all appreciable.

---

[13] T. Yuasa, *Bull. Chem. Soc. Japan*, 1962, **35**, 211.

[14] A. G. Gaydon, "Dissociation Energies", 2nd edn., Chapman and Hall, London, 1953.

[15] G. Verhaegen and J. Drowart, *J. Chem. Phys.*, 1962, **37**, 1367.

[16] JANAF Thermochemical Tables, Dow Chem. Co., Midland, Michigan, 1963.

[17] P. A. Akishin, O. T. Nikitin, and L. N. Gorokhov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **129**, 1077.

[18] D. L. Hildenbrand and W. F. Hall, *J. Phys. Chem.*, 1964, **68**, 989.

[19] H. E. Robson and P. W. Gilles, *J. Phys. Chem.*, 1964, **68**, 983.

[20] W. A. Chupka, J. Berkowitz, C. F. Giese, and M. G. Inghram, *J. Phys. Chem.*, 1958, **62**, 611.

A value for the $D_0°$ of this molecule has been estimated[5] as 39 kcal./mole. Under these conditions fluorine, which has a comparable dissociation energy, would have a mole fraction of F_2 of 0·001, a value which is detectable by mass spectrometry.

A mass spectrometric study[21] of gallium vapour at 865—1025°C produced the mass spectral ions Ga^+ and Ga_2^+ in the ratio of 100 to 1. However Ga_2O^+ was also found and the ratio of the latter to Ga_2^+ was constant as both species decreased with time, leading to the conclusion that the Ga_2^+ was probably formed by fragmentation of the oxide impurity rather than from a primary Ga_2 molecule. A Ga_2^+ mass peak was also found in the vapour over gallium carbide[20] at 1600°K, the ratio Ga^+/Ga_2^+ being 1890. Here also there is no assurance that the Ga_2^+ is attributable to Ga_2 since it could have arisen from fragmentation of gaseous gallium carbide. An upper limit of 32—34·5 kcal./mole has been estimated[5,20] for the $D_0°$ of Ga_2.

Values of 22·4 ± 2·5[22] and 30 ± 14 kcal./mole[23] have been calculated for the $D_0°$ of In_2 on the basis of mass spectrometric data. From data on the saturated vapour over indium antimonides, it was shown that the mole fraction of In_2 relative to In(g) rises with increasing temperature in the range 1220—1381°K, although at 1381°K the mole fraction of In_2 is[22] only $4·5 \times 10^{-5}$, since this temperature is almost 1000° below the normal boiling point of indium.

TABLE 2. *Dissociation energies at* 0°K *for the Group* IIIB *diatomic molecules*

Molecule	B_2	Al_2	Ga_2	In_2	Tl_2
$D_0°$ (kcal./mole)*	~66[15]	(39)[5]	(<32 to 34·5)[5,20]	22[22]	(14)[5]

* Data in parentheses are estimated values.

The dimeric ion Tl_2^+ has been found at 429—700°C in the saturated vapour of thallium,[24] the ratio Tl^+/Tl_2^+ being 100. However the Tl_2^+ was attributed to fragmentation of a thallium oxide film on the metal rather than as indicative of Tl_2, for reasons similar to those described above for Ga_2. An estimated $D_0°$ of 14 kcal./mole has been advanced[5] for Tl_2.

The generally decreasing $D_0°$ values with molecular weight for the Group IIIB homonuclear diatomic molecules are given in Table 2.

Group IVB elements

The change from ns^2np^1 to ns^2np^2 valence shell ground-state configurations of the elements makes a substantial difference in the types of homonuclear molecules formed in the vapours of these elements. The diatomic molecules of the Group IVB elements are appreciably more strongly bonded

---

[21] S. Antkiv and V. H. Dibeler, *J. Chem. Phys.*, 1953, **21**, 1890.

[22] G. DeMaria, J. Drowart, and M. G. Inghram, *J. Chem. Phys.*, 1959, **31**, 1076.

[23] E. G. Shvidkovskii, *Doklady Akad. Nauk S.S.S.R.*, 1963, **149**, 816.

[24] S. A. Shchukarev, G. A. Semenov, and I. A. Ratkovskii, *Zhur. neorg. Khim.*, 1962, **7**, 469.

than the corresponding Group IIIB diatomic molecules of the same period. Further the Group IVB elements (with the exception of lead) form higher polymeric molecules of variable chain lengths, a behaviour not observed with the elements considered heretofore.

Diatomic Molecules.—The diatomic C_2 molecule is listed in Herzberg's compilation[1] as having a triplet pi ground electronic configuration, but it has been shown that the latter is a low-lying excited state and that the actual ground state is a singlet sigma state.[25] Accordingly, the ground state C_2 molecule has a double bond, as is evidenced by its r_e of 1·312 Å, which is considerably shorter than the 1·54 Å bond distance of the typical C–C single bond.[26] A number of values, ranging from 140—150 kcal./mole, have been reported[5,27–31] in recent years for the $D_0°$ of C_2, but the preferred value is about 144 kcal./mole. It has been claimed that the probable ground state of the Si_2 molecule is a triplet sigma state.[32] If so, Si_2 is different from C_2 in that Si_2 has a single rather than a double bond in the ground-state molecule. This is reflected in the very much weaker bonding in Si_2. A value of about 75 kcal./mole has been reported in several places[5,31,33] for the $D_0°$ of Si_2, as well as 69 kcal./mole.[32] The overlap is within the experimental uncertainties and the actual value is probably near 75 kcal./mole. Values of about 64 kcal./mole,[5,34] 46 kcal./mole,[5,35] and 23 kcal./mole[5] have been computed for the $D_0°$ of Ge_2, Sn_2, and Pb_2, respectively. The $D_0°$ values for the Group IVB homonuclear diatomic molecules are given in Table 3.

TABLE 3. *Bond dissociation energies at* 0°K *for the Group* IVB *diatomic molecules*

Molecule	C_2	Si_2	Ge_2	Sn_2	Pb_2
$D_0°$ (kcal./mole)	~144[27,28,31]	~75[5,31,33]	~64[5,34]	~46[5,35]	~23[5]

Higher Molecules.—With the exception of lead the vapours of each of the elements in this Group have been reported to consist not only of atoms and diatomic molecules, but a number of higher polymers as well. These will be discussed in turn commencing with the lightest element, carbon.

A linear triatomic C_3 molecule has been found spectroscopically in

[25] E. A. Ballik and D. A. Ramsay, *J. Chem. Phys.*, 1959, **31,** 1128.
[26] T. L. Cottrell, "Strengths of Chemical Bonds", Butterworths, London, 1958.
[27] S. M. Reed and J. T. Vanderslice, *J. Chem. Phys.*, 1962, **36,** 2366.
[28] L. Brewer, W. T. Hicks, and O. H. Krikorian, *J. Chem. Phys.*, 1962, **36,** 182.
[29] D. Steele, *Spectrochim. Acta*, 1963, **19,** 411.
[30] W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, 1955, **59,** 100.
[31] J. Drowart, G. DeMaria, and M. G. Inghram, *J. Chem. Phys.*, 1958, **29,** 1015.
[32] R. D. Verma and P. A. Warsop, *Canad. J. Phys.*, 1963, **41,** 152.
[33] R. E. Honig, *J. Chem. Phys.*, 1954, **22,** 1610.
[34] J. Drowart, G. DeMaria, A. J. H. Boerboom, and M. G. Inghram, *J. Chem. Phys.*, 1959, **30,** 308.
[35] M. Ackerman, J. Drowart, F. E. Stafford, and G. Verhaegen, *J. Chem. Phys.*, 1962, **36,** 1557.

carbon vapour.[36–38] Trapping out of such vapours, generated at 2300—2600°K, in inert-gas matrices at very low temperatures has also shown the presence of C_3 by spectroscopy.[39] In early mass spectrometric studies of carbon vapour C, C_2, and C_3 gases were found at about 2400°K, with C_3 the most abundant.[39,40] In a later mass spectrometric study, C_4 and C_5 were identified in this vapour, along with C, C_2, and C_3;[41] however, at 4100°K, C_4 and C_5 were reported to be less abundant than C_3, C_2, or C. Based on heats of formation,[16,38,41,42] the $\Delta H_{298}°$ of the reaction $C_3(g) \rightarrow C_2(g) + C(g)$ is $\sim$ 182 kcal./mole, a value substantially higher than that for the simple dissociation of $C_2(g)$ to $2C(g)$. The corresponding value for $C_4(g) \rightarrow C_3(g) + C(g)$ is $\sim$ 124 kcal./mole, making C_3 more stable than C_4. However C_5 is somewhat more stable thermodynamically than C_4. This increased stability of the odd-numbered molecules, as compared with the even-numbered molecules has been found by mass spectrometry[41] and by a theoretical molecular orbital approach.[42] In the former, only trace amounts of the higher polymeric molecules C_6 and C_7 were observed, but the latter[42] predicts that C_6 and C_7 should be more abundant. At 2000°K this analysis predicts C_5 to be the most abundant species in the saturated carbon vapour, with C_7 becoming comparably abundant in the 2500—3000°K range, and even higher polymers important at higher temperatures. Thus, at 2000°K the average numbers of atoms per molecule is 4·8 while at 3000° it is 8·1, and at 4000° it is 13·5. These polymeric molecules are predicted to be linear rather than ring-shaped, and bonded solely through double bonds.[42,43]

In the vapour over silicon at 1660°K, mass spectral peaks ranging from $Si^+(g)$ to $Si_7^+(g)$ were found;[33] these may each represent neutral molecules, especially in view of the fact that carbon is known to form such polymers. From reported data[16,34] the dissociation energies at 298°K for the reactions $Si_4(g) \rightarrow Si_3(g) + Si(g)$ and $Si_3(g) \rightarrow Si_2(g) + Si(g)$ are about 95 and 104 kcal./mole. As was found for C_3 and C_2, the primary dissociation of Si_3 to $Si_2 + Si$ is considerably more endothermic than that for $Si_2 \rightarrow 2Si(g)$. The shape of the Si_3 molecule is unknown but it has been assumed to be linear, by analogy[31] with C_3.

Mass spectral peaks ranging from Ge^+ to Ge_7^+ has also been found[34,44] for germanium vapour, with the polymeric species accounting for about 20% of the vapour at 1370°K. The polymeric ions have been attributed to parent molecules.[34] At 1800°K the relative partial pressures of the polymeric molecules decrease with increasing molecular weight, the vapour

---

[36] K. Clusius and A. E. Douglas, *J. Chem. Phys.*, 1954, **32,** 319.

[37] W. R. S. Garton, *Proc. Phys. Soc.*, 1953, *A*, **66,** 848.

[38] L. Brewer and J. L. Engelke, *J. Chem. Phys.*, 1962, **36,** 992.

[39] W. Weltner, jun., P. N. Walsh, and C. L. Angell, *J. Chem. Phys.*, 1964, **40,** 1299.

[40] R. Honig, *J. Chem. Phys.*, 1954, **22,** 126.

[41] J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *J. Chem. Phys.*, 1959, **31,** 1131.

[42] K. S. Pitzer and E. Clementi, *J. Amer. Chem. Soc.*, 1959, **81,** 4477.

[43] E. Clementi, *J. Amer. Chem. Soc.*, 1961, **83,** 4501.

[44] R. E. Honig, *J. Chem. Phys.*, 1953, **21,** 573.

being predominantly atomic germanium. The $\Delta H_0°$ for $Ge_3(g) \rightarrow Ge_2(g) + Ge(g)$ is ~ 89 kcal./mole,[34] maintaining the trend established for carbon and silicon. At about 1200°K clusters of Sn mass peaks up to Sn_5^+ have been found,[44] but the fraction of molecules is much smaller than for germanium, actually less than 1 %. In the tin vapour the relative abundances of polymeric species decrease with increasing molecular weight.

The evaporation of lead at 800°K has been studied mass spectrometrically.[44] No molecule higher than Pb_2 was found, and at this temperature even the Pb_2 molecules are in very small concentration, the Pb_2^+/Pb^+ ratio being 3×10^{-5}.

Group VB elements

The one additional electron in N, as compared with C, drastically changes the bonding in the homonuclear molecules of these elements, so the gaseous N_2 is the stable form of nitrogen at ordinary temperatures, in contrast to crystalline diamond or graphite. This extra electron permits the formation of a triple bond in N_2 as compared with the weaker double bond in C_2. Furthermore it prevents the nitrogen atom from forming hybridised orbitals only with bonding electrons. The repulsions due to the non-bonding electron pair which must be associated with each nitrogen atom in higher nitrogen molecules or stable crystalline configurations based on bonds other than van der Waals forces, reduces the strength of N–N bonds are compared with C–C bonds. Thus the dissociation energy for N_2 is 225 kcal./mole, while the N–N and N=N bond energies are 39 and 100 kcal./mole; the dissociation energy for C_2 is 144 kcal./mole, while the C–C and C=C bond energies are 82·6 and 145·8 kcal./mole.[26] It is easily seen from these data that there is a far smaller difference in bond energy for the carbon system between the C_2 molecule and individual bonds in diamond or the conjugated graphite structure, than is characteristic of nitrogen. This prevents the formation of a stable condensed state of tervalent nitrogen at ordinary temperatures.

However, as Table 4 shows, the strengths of the bonds in the homopolar diatomic molecules of the heavier Group VB elements progressively diminish with increasing weight, the most significant drop occurring between N_2 and P_2. This very much alters the relative bond strengths between the diatomic molecules and the elements in condensed states. Further, although N cannot make appreciable use of its high-lying 2*d* orbitals, the heavier group VB elements have lower-lying *d* orbitals which can be used for significant increase in bond strength of individual bonds. These factors contribute to making phosphorus and the other Group VB elements form

TABLE 4. *Dissociation energies at* 0°K *of Group* VB *diatomic molecules*

Molecule	N_2	P_2	As_2	Sb_2	Bi_2
Dissociation energy (kcal./mole)	225[14]	116[14]	91[14]	70[14,22]	47[47,48]

stable crystalline modifications at normal temperatures. Thus the gaseous molecules of these elements are only observed at elevated temperatures. However, the crystalline states of the Group IVB elements, relative to their gaseous molecules, are more firmly bound than are the corresponding Group VB solids, as is evidenced by the generally higher boiling points and sublimation energies of the Group IVB elements. This leads to volatilisation of the Group VB homonuclear elements at considerably lower temperatures than is characteristic of the Group IVB elements. At such lower temperatures one might expect to find molecules more complex than simply diatomic molecules, especially since P, As, and Sb in tervalent states can conceivably form tetra-atomic molecules with each atom at the corner of a regular tetrahedron; it should be noted that such molecules require distortion from the mutually perpendicular pi orbitals of the elements in their ground states since the bond angles in the tetrahedral molecules would be each 60°. It should also be noted that this tetrahedron is different from that based on quadrivalent carbon in which the latter is at the centre of the tetrahedron forming bond angles of 109° 28′ with four atoms at the corners of the tetrahedron. The conditions of temperature and type of sublimation procedure which permit observation of Group VB homonuclear gaseous molecules that are more complex than diatomic molecules are discussed below, after the discussion of bonding in the diatomic molecules.

Diatomic Molecules.—The emission spectra of the diatomic molecules of this group have long been known.[1] The dissociation energies for N_2, P_2, and As_2, given in Table 4, were obtained from such data[14] and appear to be quite reliable. The approximate validity of the spectroscopic value of 69 kcal./mole[14] for Sb_2 has been confirmed by a value of 70·6 kcal./mole obtained by mass spectrometry.[22] The value of 70 kcal./mole is selected for Table 4.

The dissociation energy for Bi_2 is somewhat more controversial. A spectroscopic value of 39 kcal./mole is recommended by Gaydon but this value is questionable in view of more recent work. By combining vapour-pressure data obtained by effusion with the degree of dissociation of the vapour obtained from the molecular beam velocity spectrum, Ko[45] deduced the relative abundances of Bi and Bi_2 in the temperature range 1100—1220°K. This led to a dissociation energy of Bi_2 of 77·1 kcal./mole. By a combined Knudsen and torsion–effusion technique at 913—971°K, Yosiyama[46] obtained a value of 70 kcal./mole. However a more recent recalculation of Ko's and Yosiyama's data by Brackett and Brewer[47] has reduced the value to 47 ± 1 kcal./mole. Furthermore, a recent combined Knudsen–torsion effusion study[48] of bismuth vapour at

[45] C. C. Ko, *J. Franklin Inst.*, 1934, **217,** 173.

[46] M. Yosiyama, *J. Chem. Soc. Japan*, 1941, **62,** 204.

[47] E. Brackett and L. Brewer, U.S.A.E.C., UCRL-3712 (1957).

[48] A. T. Alred and J. N. Pratt, *J. Chem. Phys.*, 1963, **38,** 1085.

824—970°K has led to a D_{298} of 47·9 ± 2·7 kcal./mole. Accordingly the value of 47 kcal./mole is given in Table 4.

Each of the diatomic molecules in the normal ground state is in a singlet sigma electronic state,[1] indicating that the bonding is by a triple bond. However the bond strengths of these triple bonds fall markedly with increasing molecular weight.

Tetra-atomic Molecules.—Most data indicate that phosphorus, arsenic, and antimony evaporate under equilibrium conditions at temperatures below about 1000°C to form the corresponding P_4, As_4, and Sb_4 molecules, with a virtual absence of the corresponding diatomic molecules under these conditions. This has been shown for phosphorus by vapour density measurements[49] and mass spectrometry;[50] for arsenic by vapour density,[51] torsion momentum,[52] and mass spectrometry;[53] and similarly for antimony.[54–56] In the case of phosphorus it was shown mass spectrometrically[50] that mass peaks attributable to both P_2^+ and P_4^+ could be found but that the former originated by collisions of P_4 molecules with the hot spectrometer filament.

Studies with cadmium arsenide in the temperature range 220—280°C[57] and 434—695°C[58] have also demonstrated that As_4 is the only appreciable gaseous molecule containing arsenic in the vapour. The latter study was by dew point measurements combined with direct pressure measurements, while the former was by mass spectrometry. It was concluded that the As_3^+ and As_2^+ mass peaks were fragments from As_4 ionisation, although a small amount of As_2 could not be ruled out.

Despite the virtual absence of diatomic molecules in the equilibrium vapour of phosphorus, arsenic, and antimony at moderately high temperatures, these diatomic molecules have been found at such temperatures when the evaporations were carried out in a non-equilibrium manner. Under such conditions mass spectrometric studies[54,59] of the sublimation of alloys of P, As, and Sb with indium and gallium at temperatures to 1200°K, demonstrated that P_2, As_2, and Sb_2, were formed, along with P_4, As_4, and Sb_4. This was proved by the observed variation of the ion-intensity ratios corresponding to tetrameric and dimeric molecules as a function of temperature, the tetramers increasing with temperature. Similarly it has been shown[52] by torsion momentum data that whereas As_4 is

[49] D. P. Stevenson and D. M. Yost, *J. Chem. Phys.*, 1941, **9**, 403.

[50] J. S. Kane and J. H. Reynolds, *J. Chem. Phys.*, 1956, **25**, 342.

[51] P. J. McGonigal and A. V. Grosse, *J. Phys. Chem.*, 1963, **67**, 924.

[52] F. Metzger, *Helv. Phys. Acta*, 1943, **16**, 323.

[53] L. Brewer and J. S. Kane, *J. Phys. Chem.*, 1955, **59**, 105.

[54] P. Goldfinger and M. Jeunehomme, "Advances in Mass Spectrometry," ed. J. D. Waldron, Pergamon Press, pp. 534-546, New York, 1959.

[55] V. V. Illarionov and A. S. Cherepanova, *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, 1086.

[56] G. M. Rosenblatt and C. E. Birchenall, *J. Chem. Phys.*, 1961, **35**, 788.

[57] J. B. Westmore, K. H. Mann, and A. W. Tickner, *J. Phys. Chem.*, 1964, **68**, 606.

[58] V. J. Lyons and V. J. Silvestri, *J. Phys. Chem.*, 1960, **64**, 266.

[59] J. Drowart and P. Goldfinger, *J. Chim. phys.*, 1958, **55**, 721.

the only significant species in the equilibrium arsenic vapour, non-equilibrium evaporation leads to mainly As_2. Clearly in this temperature range the equilibrium between the tetra-atomic and diatomic molecules favours the tetra-atomic molecules. This has been disputed by a mass spectrometric study of phosphorus vapour, which was interpreted,[60] on the basis of ionisation curves at various electron energies, as forming P_2 and P_3 in addition to P_4. While the latter study used an alumina crucible with a 0·5 mm. hole, the puzzling conclusions may have been due to non-equilibrium conditions. Another conclusion of this sort has been advanced[22] regarding the presence of Sb_2 as well as Sb_4 in the equilibrium vapour over indium antimonide at 800—1150°K. In the latter it was claimed that the relative amounts of Sb_2 as compared with Sb_4 increase with increasing temperature.

The formation of P_2, As_2, and Sb_2 when non-equilibrium conditions were employed strongly implies that these diatomic molecules are the primary species evaporating from the condensed states. Although at equilibrium the tetra-atomic molecules appear to be favoured energetically in the temperature range below 1000°C, these tetra-atomic species conceivably could result from precursor diatomic molecules which would then be observed if measurements were made before sufficient time was allowed for equilibrium to be attained. In this connection it should prove informative to inquire into the structure of red phosphorus, which is the form generally used in the phosphorus experiments. Although the structure of red phosphorus is not known definitely, Pauling and Simonetta[61] have suggested that it is formed thermally from white phosphorus, which is believed to consist of weakly joined tetrahedral P_4 units, by the rupture of one P–P bond in each P_4 unit, giving chain structures with opened tetrahedra. Sublimation of the latter need not result in primary P_4 molecules but might possibly sublime as P_2 molecules. As for arsenic and antimony, these elements form metastable crystalline forms which contain tetrahedral units, but heating of the latter converts them into metallic modifications in which each atom is tervalent but specific units such as As_4 and Sb_4 are not present.[62]

Electron diffraction studies[63] of phosphorus and arsenic vapours have delineated the structures of P_4 and As_4. These molecules are tetrahedral with three 60° bond angles per atom; presumably Sb_4 is also tetrahedral. These short bond angles are quite unusual for these elements and reflect considerable steric strain. In view of the tervalences of these elements in the tetra-atomic molecules, the bonds should be essentially single bonds rather than the triple bonds characteristic of the diatomic molecules. This is indicated by the bond distances in P_4 and P_2: [63] 2·21 Å in P_4; 1·894 Å in P_2. Accordingly the bond dissociation energies of the diatomic molecules

---

[60] J. Carette and L. Kerwin, *Canad. J. Phys.*, 1961, **39**, 1300.

[61] L. Pauling and M. Simonetta, *J. Chem. Phys.*, 1952, **20**, 29.

[62] A. F. Wells, "Structural Inorganic Chemistry," 3rd edn., Oxford Univ. Press, London, 1962.

[63] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.*, 1935, 3, 699.

of this group should be far greater than those for individual bonds in the tetrahedral molecules. The dissociation energies for the reactions $X_4(g) \rightarrow 2X_2(g)$ are given in Table 5; these data were obtained by mass spectrometry.[22,54] In dissociation X_4 to $2X_2$, six single bonds are broken to form two triple bonds. It can be seen from Table 5 that the heavier X_4 molecules are somewhat more stable relative to $2X_2$ than is P_4. In view of the weakness of the "triple" bond in Bi_2 the single bonds in Bi_4 would be weaker still and it should not be surprising that Bi_4 has not been reported as a stable gaseous molecule. This is especially true in view of the 1832°K boiling point for bismuth.[64]

TABLE 5. *Dissociation energies of Group* VB *tetra-atomic to diatomic molecules at* 298°K

Reaction	$\Delta H_{298}°$ (kcal./mole)
$P_4(g) \rightarrow 2P_2(g)$	55·7[54]
$As_4(g) \rightarrow 2As_2(g)$	69·6[54]
$Sb_4(g) \rightarrow 2Sb_2(g)$	62·4[22], 63·4[54]

Higher Molecules.—Without specifying temperatures, Kerwin[65] found that the evaporation of red phosphorus leads to a small P_8^+ mass peak, with a ratio of ion intensities P_4^+/P_8^+ of 200. In a more detailed study, Carette and Kerwin[60] again reported the presence of P_8^+ in the vapour above red phosphorus, with an ion-intensity ratio Pt^+/P_8^+ of 500 at 320°C. This indicates the formation of small amounts of P_8. Kane and Reynolds[50] were unable to detect such a P_8 species but did find traces of As_8 in arsenic vapour. Carette and Kerwin report that the thermal treatment of the sample prior to mass spectral analysis plays a role in this phenomenon.[60]

Group VIB elements

The first of the Group VIB elements resembles nitrogen in that oxygen forms a permanent diatomic gas. However the resemblance between the Group VB and VIB elements stops here. Whereas phosphorus, arsenic, and antimony form equilibrium vapours, at temperatures below 1000°C, consisting primarily of tetrahedral molecules, under comparable conditions sulphur and selenium form complex vapours of ring-shaped molecleus with an entire spectrum of ring sizes. Moreover the distribution of molecules of various ring sizes is different for sulphur than for selenium. Whereas antimony forms a stable tetrahedral molecule, there is no evidence that the comparable Group VIB element, tellurium, forms polymeric rings. At much higher temperatures, however, sulphur and selenium resemble the corresponding Group VB elements in that they form predominantly diatomic molecules.

---

[64] D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chem. Soc. ,Washington, D.C., 1956.

[65] L. Kerwin, *Canad. J. Phys.*, 1954, **32**, 757.

Diatomic Molecules.—It has been difficult to definitively assign a dissociation energy for the S_2 molecule from spectroscopic data; values of 3·3, 3·6, and 4·4 ev are cited by Gaydon,[14] who recommends the highest value of 101 kcal./mole, while Cottrell[26] has recommended the middle value of 83 kcal./mole. However the preponderance of evidence now favours 101 kcal./mole. This has been proved by mass spectrometry[66-68] and by recalculated vapour-pressure data.[69] The spectroscopic value for the dissociation energy of Se_2 is 65 kcal./mole,[14] but a higher value of 75 kcal./mole has also been reported from a mass spectrometric study.[70] The spectroscopic value for the dissociation energy of Te_2 is 53 kcal./mole,[14] in good agreement with a value of 52·0 kcal./mole obtained mass spectrometrically.[71] These values are given in Table 6, along with the spectroscopic value for O_2. The mass spectrometric value for Se_2 is given in parentheses, while the value for Te_2 as given in Table 6 is the average between the two values cited above.

TABLE 6. *Dissociation energies at* 0°K *of Group* VIB *diatomic molecules*

Molecule	O_2	S_2	Se_2	Te_2
Dissociation energy (kcal./mole)	118·0[14]	101[66-69]	65[15](75)[70]	52·5[14,71]

The ground-state diatomic O_2 and S_2 molecules are known to be in triplet sigma electronic states, and are thus diradicals. Although this assignment is less certain for Se_2 it is probable that this molecule resembles O_2 and S_2 in its bonding.[14] That S_2 is a diradical has been proven by its magnetic susceptibility.[72] One can also assume that these Group VIB diatomic molecules have the double bond characteristic of oxygen. As can be seen from Table 6, the bond strengths decrease regularly with increasing weight in this group of molecules, reflecting the fact that in the unsaturated vapours the heavier molecules dissociate to the atoms at lower temperatures than do the lighter molecules.

Since S_2 and Se_2 are present only as minor constituents in the equilibrium vapours of these elements at temperatures below 700—800°K, investigations of the properties of these diatomic molecules have usually been carried out at temperatures exceeding 1000°K. Thus, an electron-diffraction study of the molecular parameters of S_2 has been carried out[73] at 1123°K, the equilibrium reaction between S_2 and SO_2 has been studied[74] at 1523°K, while the thermodynamics of S_2 have been studied by the sublimation of sulphides that give S_2 at numerous temperatures over 1000°K.[54,66-68]

[66] J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, 1963, **39**, 275.
[67] R. Colin, P. Goldfinger and M. Jeunehomme, *Nature*, 1960, **187**, 408.
[68] R. Colin, P. Goldfinger, and M. Jeunehomme, *Trans. Faraday Soc.*, 1964, **60**, 306.
[69] L. Brewer, *J. Chem. Phys.*, 1959, **31**, 1143.
[70] D. Detry, *Ind. Chim. belge*, 1963, **28**, 752.
[71] R. F. Porter, *J. Chem. Phys.*, 1961, **34**, 583.
[72] J. A. Paulis, C. H. Massen, and P. v. d. Leeden, *Trans. Faraday Soc.*, 1962, **58**, 52.
[73] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *Phys. Rev.*, 1931, **49**, 199.
[74] E. W. Dewing and F. D. Richardson, *Trans. Faraday Soc.*, 1958, **54**, 679.

Unlike sulphur and selenium, tellurium apparently does not form ring-shaped molecules, even at lower temperatures. The only gaseous molecule thus far observed for tellurium is Te_2. The latter has been observed mass spectrometrically by sublimation of germanium telluride[75] and lead telluride,[71] and by its absorption spectrum from the sublimation of tin and lead tellurides.[76]

Ring-shaped Molecules.—A number of vapour-density studies for sulphur covering the temperature range 300—1000 °C have clearly indicated that the vapour is complex in this temperature range, and that the composition varies with temperature. Mixtures of S_8, S_6, and S_2,[77–79] and also S_4,[80] were deduced from the data. Electron diffraction studies[81,82] have established that the S_8 molecule is a puckered ring with S–S bond distances of 2·07—2·08 Å, a value considerably longer than the 1·889 Å[26] double bond distance in S_2. In the electron diffraction study by Maxwell *et al.*[73] it was observed that the S–S bond distance increased with decreasing temperature, representing increased polymerisation of S_2 to higher ring-shaped molecules as the temperature was lowered.

The complex equilibrium vapour of sulphur has been elucidated most completely by mass spectrometry.[66] Berkowitz and Marquart's equilibrium data are shown in Fig. 2. It can be seen that at 350°K the preponderant

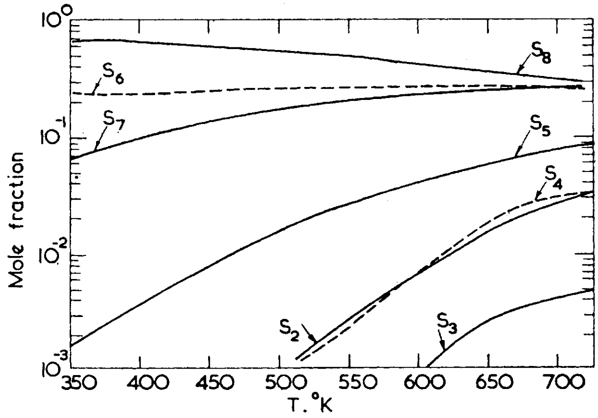

FIG. 2. *Saturated sulphur vapour below* 700°K. Reproduced, with permission, from J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, 1963, **39**, 275.

---

[75] R. Colin and J. Drowart, *J. Phys. Chem.*, 1964, **68**, 428.
[76] R. F. Brebrick and A. J. Strauss, *J. Chem. Phys.*, 1964, **41**, 197; 1964, **40**, 3230.
[77] G. Preuner and W. Schupp, *Z. phys. Chem.*, 1909, **68**, 219.
[78] G. Preuner and I. Brockmöller, *Z. phys. Chem.*, 1912, **81**, 129.
[79] W. Klemm and H. Kilian, *Z. phys. Chem.*, 1941, **49**, *B*, 279.
[80] H. Braune, S. Peter, and V. Neveling, *Z. Naturforsch.*, 1951, **6a**, 32.
[81] J. D. Howe and K. Lark-Horovitz, *Phys. Rev.*, 1937, **51**, 380.
[82] Chiu-Li Lu and J. Donohue, *J. Amer. Chem. Soc.*, 1944, **66**, 818.

species is S_8 with some S_6 and S_7. At somewhat higher temperatures S_5 becomes a minor constituent of the vapour, with S_4 and S_2 doing so at even higher temperatures. Traces of S_9 and S_{10} have also been observed. These S_n molecules appear to be ring-shaped rather than linear.[83] Bond energy data for the polyatomic sulphur molecules are given in Table 7. It can be seen that these sulphur–sulphur single bonds are not particularly strong.

TABLE 7. *Bond energies for polyatomic sulphur molecules*

Molecule	Energy per bond (kcal./mole)*	Molecule	Energy per bond (kcal./mole)*
S_3	55·5	S_7	62·2
S_4	58·0	S_8	62·8
S_5	60·2	S_9	62·2
S_6	61·7	S_{10}	62·8

* Data taken from ref. 66.

In free-evaporation studies at slightly elevated temperatures it has been shown by mass spectrometry that the actual vapour species subliming from the surface of sulphur is S_8(g) from rhombic sulphur, which consists of S_8 units in the crystal, and S_6(g) from an allotropic form of sulphur, which is known to consist of S_6 units in the crystal.[84] This demonstrates the importance of ascertaining whether equilibrium is obtained. Undoubtedly the S_6(g) species will equilibrate to form mainly S_6(g) at these temperatures if sufficient time is allowed for the attainment of equilibrium.

The molecular weight of the equilibrium vapour over selenium at about 200°C has been shown to be nearly Se_6 by vapour-pressurestudies.[85,86] At 550—800°C, both Se_6 and Se_2 have been interpreted from vapour-pressure studies as the principal gas species in selenium vapour.[78] Electron diffraction patterns of selenium vapour best fit a Se_6 model.[81] There has only been an incomplete mass spectometric study of this vapour.[54] In the latter, carried out at 177—237°C, Se_6^+ was by far the principal ion formed mass spectrometrically and Se_6 is clearly the principal gaseous species in this temperature range. However, ions ranging from Se_2^+ to Se_8^+ were also found and it may be assumed that the vapour is as complex as that of sulphur.

The bond energy per bond for Se_6(g) at 298°K, as calculated from data in Stull and Sinke's compilation,[64] is 43·5 kcal./mole. This reflects weaker bonding than in the analogous S_6 or S_8 molecules.

---

[83] L. Pauling, *Proc. Nat. Acad. Sci.*, 1949, **35**, 495.

[84] J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, 1964, **40**, 287.

[85] K. Neumann and E. Lichtenberg, *Z. phys. Chem.*, 1939, **184**, *A*, 89.

[86] A. A. Kuliev and M. G. Shakhtakhtiaskii, *Doklady, Akad. Nauk S.S.S.R.*, 1958, **120**, 1284.

Transition metals

The IB elements form homonuclear diatomic molecules which are more strongly bonded than those of the IA elements. The ground state of Cu_2 has been identified as a singlet sigma state with a rather short bond distance.[87] This was attributed to the greater binding energy obtainable *via* hybridisation. Mass spectrometric values for $D_0°$ of Cu_2 ranging from 46 to 51 kcal./mole have been reported,[88-90] while the value obtained by the Birge–Sponer extrapolation of spectroscopic data is 48 kcal./mole.[89] Ackerman *et al.*[88] have compared these data with common heats of vaporisation of the elements and free energy functions and have found that the agreement is thereby improved, the $D_0°$ being about 46 kcal./mole. For Ag_2 the $D_0°$ obtained from mass spectrometry is about 38 kcal./mole;[88,89,91] a higher value of 41·4 kcal./mole was obtained spectroscopically.[89] For Au_2 the mass spectrometric $D_0°$ is 50—53 kcal./mole,[88-90] with the preferred value being about 52 kcal./mole;[88] the $D_0°$ obtained by the Birge–Sponer extrapolation[89] is very much higher and is probably in error.

The data for copper vapour between 1440 and 1730°K[88,89] indicate a generally rising mole fraction of Cu_2, as compared with Cu, with increasing temperature, as is characteristic of the IA molecules. This is also the case for Ag_2 and Au_2. While the mole fractions of diatomic molecules in the saturated vapours of the alkali metals are considerably higher than those of Cu_2, Ag_2, or Au_2, it must be remembered that the normal boiling points of the IB elements are much higher than those of the alkali metals and thus the total vapour pressures are considerably higher for the latter elements. For example, the mole fraction of Cu_2 in copper vapour is only about 3×10^{-3} at 1700°K, but the total copper vapour pressure at this temperature is only $1{\cdot}3 \times 10^{-4}$ atm.;[64] at this temperature each of the alkali metals has a saturated vapour pressure in excess of one atm.

There has been a report[92] of even higher molecules in the vapour of silver, with Ag_3 and Ag_4 being present in appreciable amounts at temperatures below 1500°K. However this has not been observed in any of the studies described above, or indeed in other mass spectrometric studies of silver vapour,[30,93] and probably must be discounted.

The diatomic molecules of the IIB elements Zn_2, Cd_2, and Hg_2 have been observed spectroscopically. The $D_0°$ values for these molecules are even lower than those for the IIA elements. Gaydon cites 6, 2, and 1·4 kcal./mole for Zn_2, Cd_2, and Hg_2, respectively, with the value for

---

[87] D. N. Travis and R. F. Barrow, *Proc. Chem. Soc.*, 1962, 64.

[88] M. Ackerman, F. E. Stafford, and J. Drowart, *J. Chem. Phys.*, 1960, **33**, 1784.

[89] J. Drowart and R. E. Honig, *J. Chem. Phys.*, 1956, **25**, 581.

[90] P. Schissel, *J. Chem. Phys.*, 1957, **26**, 1276.

[91] D. White, A. Sommer, P. N. Walsh, and H. W. Goldstein, "Advances in Mass Spectrometry," Proc. Second Conf., ed. R. M. Elliott, Macmillan Co., N.Y., 1963.

[92] A. W. Searcy, R. D. Freeman, and M. C. Michel, *J. Amer. Chem. Soc.*, 1954, **76**, 4050.

[93] M. B. Panish, *J. Chem. Eng. Data*, 1961, **6**, 592.

Zn_2 very much in doubt.[14] A somewhat smaller value of 0·6 ± 0·2 kcal./mole has recently also been found for Cd_2.[94] In view of the extreme weakness of these bonds it is not surprising that these molecules have not been observed mass spectrometrically, despite efforts to find such molecules.[95]

There is no known diatomic molecule for the transition metals of Groups III to VII, despite several mass spectrometric searches for such molecules (for example, scandium, yttrium, lanthanum[96] and tantalum[97])*. The problem is particularly complicated for metals with very high boiling points, such as tantalum, because studies carried out at temperatures even as high as 3000°K[97] are still very far from the normal boiling point (5700°K). Even at 3000°K the vapour pressure of tantalum is less than 10^{-6} atm.[64] and it would take a very strong bond indeed to form a stable molecule at this very high temperature and very low pressure.

Among the Group VIII metals a homonuclear diatomic molecule is known presently only for nickel. This Ni_2 molecule was observed mass spectrometrically, and a $D_0°$ of ~ 54·5 kcal./mole was computed from the data.[98] Since cobalt and iron have normal boiling points very close to that of nickel,[64] the Co_2 and Fe_2 molecules will probably also be found.† Diatomic molecules in the vapours of rhodium, iridium, osmium, and ruthenium could not be found, however, in mass spectrometric studies.[99,100] In these cases the metals have considerably higher boiling points than Fe, Co, or Ni. Thus, the calculated vapour pressures at which the vapours were studied are as follows: $2{\cdot}5 \times 10^{-4}$ mm. at 2353°K for Ru,[99] $8{\cdot}5 \times 10^{-5}$ mm. at 2715°K for Os,[99] $3{\cdot}05 \times 10^{-3}$ mm. at 2205°K for Rh,[100] and $3{\cdot}8 \times 10^{-3}$ mm. at 2630°K for Ir.[100] At these temperatures and pressures the $D_0°$ required for the stable existence of the respective diatomic molecules would probably be in excess of that found for Ni_2, and it is thus unlikely that the diatomic molecules will be observed for these heavier

---

*It has come to the attention of the writer that the molecules Sc_2, Y_2, and La_2 have been recently identified mass spectrometrically in the vapours above the corresponding metals. The reported $D_0°$ values are 25·9 ± 5, 37·3 ± 5 and 57·6 ± 5 kcal./mole, for Sc_2, Y_2 and La_2, respectively. (G. Verhaegen, S. Smoes and J. Drowart, U.S. Atomic Energy Commission Report WADD-TR-60-782, 1963).

† [*Note Added in Proof:*—Since this review was prepared there has been a reported mass spectrometric observation of Co_2 (A. Kant and B. Strauss, *J. Chem. Phys.*, 1964, **41**, 3806). The $D_0°$ obtained in that study was 39 ± 6 kcal./mole. Although Ti_2, Cr_2 and Mn_2 could not be actually obtained, upper limits were set for their $D_0°$ values. Some more recent data will shortly be available on the composition of the sulphur vapour. These data however, are only slightly different than those in Fig. 2 (J. Berkowitz, *Molecular Composition of Sulfur Vapor*, in "Elemental Sulfur", ed. C. B. Meyer, John Wiley and Sons, New York, in the press)].

[94] B. L. Bruner and J. D. Corbett, *J. Phys. Chem.*, 1964, **68**, 1115.

[95] K. H. Mann and A. W. Tickner, *J. Phys. Chem.*, 1960, **64**, 251.

[96] R. J. Ackermann and E. G. Rauh, *J. Chem. Phys.*, 1962, **36**, 448.

[97] T. P. Babeliowsky and A. J. H. Boerboom, "Advances in Mass Spectrometry," Proc. Second Conf., ed. R. M. Elliott, Macmillan Co., N.Y., 1963.

[98] A. Kant, *J. Chem. Phys.*, 1964, **41**, 1872.

[99] M. B. Panish and L. Reif, *J. Chem. Phys.*, 1962, **37**, 128.

[100] M. B. Panish and L. Reif, *J. Chem. Phys.*, 1961, **34**, 1915.

Group VIII metals at such temperatures. The possibility of observing such molecules is enhanced if the temperatures are nearer the boiling points of the metals. If the bond strengths of such molecules are not sufficiently high to withstand dissociation at temperatures exceeding 4000°K and pressures below one atm., these molecules might exist in significant concentrations only at temperatures considerably in excess of the normal boiling points in their saturated vapours.

The $D_0°$ values for the homonuclear diatomic molecules of transition metals are given in Table 8.

TABLE 8. *Bond dissociation energies at* 0°K *for the diatomic molecules of transition metals*

Molecule	$D_0°$ (kcal./mole)	Molecule	$D_0°$ (kcal./mole)
Cu_2	46[88–90]	Zn_2	6[14]
Ag_2	38[88,89,91]	Cd_2	0·6[94], 2[14]
Au_2	52[88–90]	Hg_2	1·4[14]
		Ni_2	~54·5[98]