THE DISSOCIATION ENERGIES OF THE GROUP VIA DIATOMIC MOLECULES

By J. DROWART and P. GOLDFINGER

(LABORATOIRE DE CHIMIE PHYSIQUE MOLÉCULAIRE, UNIVERSITÉ LIBRE DE BRUXELLES, BRUSSELS, BELGIUM)

1. Introduction

THE dissociation energies of S_2, Se_2, and Te_2 and to a lesser extent of SO have been in question for nearly 30 years.[1–4] In the last few years additional spectroscopic[5–9] and thermodynamic data,[10,11] partly obtained with use of the mass spectrometer,[12–18] have become available and seem to bring about a clarification of these problems. It is therefore desirable to discuss these as well as earlier measurements and to examine the conclusions which can be drawn at present. Recent spectroscopic results are also available for SeO,[19] TeO,[20] and TeS[21] and mass-spectrometric results on TeSe.[22] This permits one to extend the discussion to the ten inter-Group VIA diatomic molecules.

2. Sulphur and Sulphur Monoxide

A. Historical.—In their classical studies on vapour densities of inorganic substances, H. Biltz and Victor Meyer[23] had included measurements of the vapour density of sulphur, selenium, and tellurium up to a temperature of 1992°K. Within 2% they found a molecular weight of twice the atomic weight. Later measurements with V. Meyer's method, further developed

---

[1] P. Goldfinger, W. Jeunehomme, and B. Rosen, *Nature*, 1936, **138,** 205.

[2] G. Herzberg and L. Mundie, *J. Chem. Phys.*, 1940, **8,** 263.

[3] G. Herzberg, "Diatomic Molecules", Van Nostrand, New York, 1950.

[4] A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953.

[5] R. G. W. Norrish and G. A. Oldershaw, *Proc. Roy. Soc.*, 1959, *A*, **249,** 498.

[6] W. D. McGrath and J. J. McGarvey, *J. Chem. Phys.*, 1962, **37,** 1574; *Proc. Roy. Soc.*, 1964, *A*, **278,** 490.

[7] R. F. Barrow and R. P. du Parcq, in "Elemental Sulfur", ed. B. Meyer, Interscience, New York, 1965.

[8] L. Herman and P. Felenbok, *J. Quant. Spectroscopy Radiative Transfer*, 1963, **3,** 247; L. Herman and R. Herman, *Nature*, 1963, **197,** 677.

[9] G. G. Chandler, R. F. Barrow, and B. Meyer, *Phil. Trans.*, 1966, **260,** *A*, 395.

[10] G. St. Pierre and J. Chipman, *J. Amer. Chem. Soc.*, 1954, **75,** 4787; *J. Metals*, 1956, **8,** 1474.

[11] E. W. Dewing and F. D. Richardson, *Trans. Faraday Soc.*, 1958, **54,** 679.

[12] R. Colin, P. Goldfinger, and M. Jeunehomme, *Nature*, 1960, **187,** 408.

[13] R. Colin, P. Goldfinger, and M. Jeunehomme, *Trans. Faraday Soc.*, 1964, **60,** 306.

[14] J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, 1963, **39,** 283.

[15] R. Colin and J. Drowart, *J. Chem. Phys.*, 1962, **37,** 1120.

[16] R. F. Porter, *J. Chem. Phys.*, 1961, **34,** 583.

[17] R. Colin, *Ind. chim. belg.*, 1961, **26,** 57.

[18] D. Detry, *Ind. chim. belg.*, 1963, **28,** 752; M. Jeunehomme, Thesis, Bruxelles, 1962.

[19] R. F. Barrow and E. W. Deutsch, *Proc. Phys. Soc.*, 1963, **82,** 548.

[20] G. G. Chandler, H. J. Hurst, and R. F. Barrow, *Proc. Phys. Soc.*, 1965, **86,** 105.

[21] H. Mohan and K. Majumdar, *Proc. Phys. Soc.*, 1961, **77,** 147.

[22] R. F. Porter and C. W. Spencer, *J. Chem. Phys.*, 1960, **32,** 943.

[23] H. Biltz and V. Meyer, *Ber.*, 1889, **22,** 725.

by Nernst, were extended to 2290 and 2350°K,[24–26] and a value of 90 kcal. mole^{-1} was quoted for the dissociation energies of all three molecules. Measurements on S_2 using the explosion method[27,28] gave higher as well as lower values.

It was shown[1] that, if third-law calculations are used instead of the second law,* the vapour density measurements yield† $D(S_2) \simeq 74$, $D(Se_2) \simeq 71$ or 66, and $D(Te_2) \simeq 55$ or 50 kcal. mole^{-1}. These values could be reconciled with the spectroscopic values of the dissociation energies[29–31] by assuming dissociation into (^{3}P) + (^{1}D). Dissociation into normal (^{3}P) atoms would give $D(S_2) < 102$, $D(Se_2) < 82$. An alternative interpretation of the S_2 spectrum[2] gave a third "spectroscopically possible" value: $D(S_2) < 83$ kcal. mole^{-1}.

It was proposed[1] to link together the dissociation energies of SO and S_2 with the heats of combustion of SO and S_2 by a thermochemical cycle. Measurements have been performed[10–11] which are equivalent to the determination of the heat of formation of SO, $\Delta H^\circ_0 f$(SO). They were first used[10–11] as an argument for the value of $D(S_2) = 83$ kcal. mole^{-1}. As a result of the reinvestigation[5] of the SO spectrum the same measurements led to the high values[32,33] of $D(S_2)$ and D(SO). Finally, the dissociation energy of S_2 and SO were obtained by mass-spectrometric equilibrium measurements.[12–14] The vaporisation of Group IV sulphides has been studied with effusion techniques[34–38] and by mass spectro-

---

* It is interesting to note that von Wartenberg[25] made third-law (Nernst Theorem) considerations on the possibility of observing diatomic metal molecules, but did not include the $S_2 \rightleftharpoons 2S$ equilibrium in these considerations.

† The alternative values for Se_2 and Te_2 were obtained with $^1\Sigma$ or $^3\Sigma$ ground states, respectively; the results assuming the latter are 3 kcal. higher than in the original paper[1] which apparently contains an error.

[24] W. Nernst, *Z. Elektrochem.*, 1903, **9**, 607.

[25] H. von Wartenberg, *Z. anorg. Chem.*, 1908, **56**, 320.

[26] H. von Wartenberg, *Ber.*, 1906, **39**, 381.

[27] H. Budde, *Z. anorg. Chem.*, 1912, **78**, 169.

[28] N. Bjerrum, *Z. phys. Chem.*, 1913, **81**, 281.

[29] B. Rosen, *Z. Physik*, 1927, **43**, 69.

[30] S. M. Naudé and A. Christy, *Phys. Rev.*, 1931, **37**, 903.

[31] E. Olson, *Z. Physik*, 1937, **108**, 40.

[32] L. Brewer, *J. Chem. Phys.*, 1959, **31**, 1143,

[33] D. G. H. Marsden, *J. Chem. Phys.*, 1959, **31**, 1144.

[34] R. F. Barrow, P. G. Dodsworth, G. Drummond and E. A. Jeffries, *Trans. Faraday Soc.*, 1955, **51**, 1480; V. I. Davydov and N. P. Diev, *Zhur. neorg. Khim.*, 1957, **2**, 2003.

[35] K. Sudo, *Sci. Reports Res. Inst. Tôhoku Univ.*, 1960, **A**, **12**, 54; E. Shimazaki and T. Wada, *Bull. Chem. Soc. Japan*, 1956, **29**, 294.

[36] H. Spandau and F. Klanberg, *Z. anorg. Chem.*, 1958, **295**, 291; M. D. Galinov and A. I. Okunev, *Trudy Ural'sk Nauchn Issled. i. Proektn Inst. Medn. Prom.*, 1963, 375 (*Chem. Abs.*, 1965, **62**, 7176).

[37] W. H. St. Clair, B. K. Shibler, and I. S. Solet, *U.S. Bur. Mines Rept. Invest.*, 1954, 5095; A. W. Richards, *Trans. Faraday Soc.*, 1955, **51**, 1193; D. N. Klushin and V. Ya. Chernykh, *Zhur. neorg. Khim.*, 1960, **5**, 1409; H. Rau, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 731.

[38] R. Schenck and A. Albers, *Z. anorg. Chem.*, 1919, **105**, 145; V. K. Veselowski, *Zhur. priklad. Khim.*, 1942, **15**, 422; R. A. Isakowa, V. N. Nesterov, and A. S. Shendyapin, *Zhur. neorg. Khim.*, 1963, **8**, 18; O. G. Miller and M. A. Abdeev, *Trudy Altaisk Gorno Nauch Issledovatel Inst. Akad. Nauk Kazakh* S.S.R., 1958, **7**, 182 (*Chem. Abs.*, 1960, **54**, 4297f); K. Sudo, *Sci. Repts. Res. Inst. Tohoku Univ.*, 1960, **A**, **12**, 54.

metry.[15,39] The combination of these results with accurate spectroscopic values for the dissociation energies[40–42] of these molecules can be used in thermochemical cycles to determine $D^\circ_0(S_2)$.

B. Spectroscopic Data.—1. The spectroscopic observations of the dissociation of S_2 have been discussed several times.[2–4,30,31,43] It is generally accepted that in the main band system ($B^3\Sigma^-_u$–$X^3\Sigma^-_g$), a predissociation[29–31,43] sets in at $v' = 10$ at 35,713 cm.$^{-1}$ = 4·43 ev = 102·1 kcal. mole^{-1}. According to Rosen, Désirant, and Duchesne[43] this is a predissociation case I*b* (see ref. 3, p. 422) which yields an exact limit. These authors have observed predissociation[7] not only in $v' = 10$, but also in $v' = 9$ and 8 at higher rotational quantum numbers: however no rotational analysis was carried out. Herzberg and Mundie[2] criticised these conclusions since violent perturbations in the $v' = 8$ and 9 levels do not permit one to apply Herzberg's method[44] for obtaining an exact predissociation limit. The predissociation could therefore belong to case I*c*. The latter authors further discussed the broadening of fine-structure lines for higher values of v' and concluded that at about 4·7 ev a second predissociation occurs, which belongs to case I*c* and leads to $S(^1D) + S(^3P)$, and thus arrived at $D^\circ_0(S_2) \leqslant 3{\cdot}6$ ev = 83 kcal. mole^{-1}. This interpretation also takes into account the assumption that a pressure-dependent line-broadening[45] and a broadening in a magnetic field[46] in $v' = 5$ at 4·2 ev are genuine induced predissociations and not a pressure broadening (see also ref. 8). Recent investigations[7] set the predissociation limit at 35,590 cm.$^{-1}$ = 101·8 kcal. mole^{-1}.

The extrapolation of the vibrational levels of the ground state fits with any value of $D^\circ_0(S_2)$ (see ref. 4, p. 208); unfortunately the excited $B^3\Sigma^-_u$ state is so violently perturbed that no reasonable extrapolation can be made: since levels are known above 41,000 cm.$^{-1}$ if, as is probable, dissociation yields $^3P + {}^1D_1$, a reasonable limit may be $D^\circ_0(S_2)$ = 43,000 − 9,239 cm.$^{-1}$ = 97 kcal. mole^{-1}.

2. The predissociation[47] in SO belongs to case I*b*. Norrish and Oldershaw[5] have produced SO by flash photolysis and have observed the SO absorption spectrum. They found new vibrational levels, correcting the numbering of v'' which has been confirmed by microwave studies.[48] The new numbering of v'' leads to a value of 43,219 cm.$^{-1}$ = 5·357 ev =

---

[39] J. Drowart, *Bull. Soc. chim. belges*, 1964, **73**, 451.

[40] G. Drummond and R. F. Barrow, *Proc. Phys. Soc.*, 1952, A, **65**, 277.

[41] R. F. Barrow, G. Drummond, and H. C. Rowlinson, *Proc. Phys. Soc.*, 1953, A, **66**, 885.

[42] E. E. Vago, and R. F. Barrow, *Proc. Phys. Soc.*, 1947, **59**, 449.

[43] B. Rosen, M. Désirant, and J. Duchesne, *Phys. Rev.*, 1935, **48**, 916.

[44] G. Herzberg, *Ann. Physik*, 1932, **15**, 677; G. Büttenbender and G. Herzberg, *Ann. Physik*, 1935, **21**, 577.

[45] V. N. Kondratiev and E. Olson, *Z. Phys.*, 1936, **103**, 395.

[46] J. Genard, *Mém. Soc. roy. Liège*, 1937, **4**, No. 2.

[47] E. V. Martin, *Phys. Rev.*, 1932, **41**, 167.

[48] F. X. Powell and D. R. Lide, jun., *J. Chem. Phys.*, 1964, **41**, 1413.

123·5 kcal. mole^{-1} for the predissociation observed by Martin. As in the case of S_2, some authors[4] favoured the assumption that the predissociation yields atoms in the ground state ($^3P + {}^3P$), others[3] that the oxygen atom is in the ground state and the sulphur atom in the excited ^1D state. The value of D°_0(SO) could therefore be 123·5 or 97·1 kcal. mole^{-1}.

McGrath and McGarvey[6] have observed in flash photolysis the $B^3\Sigma^-$ level up to $v' = 29$ at 52,379 cm.$^{-1}$ and by a short extrapolation gave a limit at 53,677 cm.$^{-1}$. If one assumes that the predissociation observed by Martin[47] yields atoms in the ground state and takes the v'' numbering of Norrish and Oldershaw, S(^1D) + O(^3P) should lie at 43,219 + 9,239 = 52,458 cm.$^{-1}$. In spite of a pronounced discontinuity in the vibrational intervals between $v' = 14$ and $v' = 17$, it seems that the extrapolation of the observed levels leads more easily to this value than to 53,677 cm.$^{-1}$, as also suggested by Abadie and Herman[49] and by a recent examination of the SO spectrum by Colin and Herzberg[50] who observed the convergence at *ca.* 52,465 cm.$^{-1}$ It seems most likely that the predissociation observed by Martin gives the dissociation energy of SO, D°_0(SO) = 123·5 kcal. mole^{-1}.

3. Walsh has studied the glow of CS_2[51] and observed SO, S_2 and CS band emission. He explained them by reactions (1) and (2).

$$S(^3P) + O(^3P) + SO(X^3\Sigma^-) \rightarrow SO(X^3\Sigma^-) + SO(B^3\Sigma^-) \quad (1)$$

$$S(^3P) + S(^3P) + S_2(X^3\Sigma^-_g) \rightarrow S_2(X^3\Sigma^-_g) + S_2(B^3\Sigma^-_u) \quad (2)$$

CS can also act as third body in reaction (1) or as an energy acceptor from SO($B^3\Sigma^-$): CS is then transferred into the $A^1\Pi$ state. CS bands appear up to $v' = 2$ lying at 41,523 cm.$^{-1}$; SO bands up to $v' = 2$ at 42,610 cm.$^{-1}$ (according to the new numbering[5] of v'') of the $B^3\Sigma^-$ state and S_2 bands up to $v' = 9$ at 35,710 cm.$^{-1}$ of the $B^3\Sigma^-$ state. It seems very probable that energy transfer to CS, S_2, and SO can result only from recombination according to (1) or (2). This is therefore an important confirmation of the existence of stable vibrational states up to the above-mentioned wave numbers and a probable break at or near the following vibrational level of the excited state and, in the case of SO, also that reaction (1) yields the necessary energy.

In the case of S_2 however, other processes,[52] especially S + O recombination, could yield the necessary energy and it may be difficult to draw conclusions from Walsh's experiments alone as to the value of $D(S_2)$.

C. Equilibrium Measurements.—1. As mentioned above, Biltz and Meyer[22] obtained at 1992°K (measured with a gas thermometer) within 2% the correct molecular weight for S_2, Se_2, and Te_2. The extension

---

[49] D. Abadie and R. Herman, *Compt. rend.*, 1963, **257**, 2820.

[50] R. Colin and G. Herzberg, personal communication.

[51] A. D. Walsh, in "The Threshold of Space", ed. M. Zelikoff, Pergamon Press, Oxford,1957.

[52] T. M. Sugden and A. Demerdache, *Nature*, 1962, **195**, 596.

of V. Meyer's method by Nernst[24] and von Wartenberg[25,26] to 2350°K using an iridium vessel seemed to show noticeable dissociation for all three molecules. As appears below, however, S_2 and Se_2 are practically diatomic at this temperature and only Te_2 is sufficiently dissociated. Comparison of results for other elements leads also to contradictions with modern data.

2. Budde[27] and Bjerrum[28] applied the explosion method to the study of the $S_2 \rightleftharpoons 2S$ equilibrium. Bjerrum considered oxidation of sulphur to SO_2, but owing to the complexity of this case he considered his measurements as well as those of Budde as not conclusive. Obviously in such experiments complex equilibria occur and in order to use the results they should be recalculated from modern values of thermodynamic functions with allowance especially for the formation of SO and S_2O. It is doubtful however whether such a tedious recalculation would really improve our knowledge.

3. St Pierre and Chipman[10] as well as Dewing and Richardson[11] have equilibrated $S_2 + SO_2$ or S_2 and a source of oxygen (CO_2, etc) on slags or silver beads. A difference in material balance was attributed to the formation of SO. The equilibrium

$$\tfrac{1}{2}\, S_2 + \tfrac{1}{2}\, O_2 \rightleftharpoons SO; \qquad -\Delta H^\circ{}_0 f(SO) \tag{3}$$

was thus calculated, which is directly related with $D^\circ{}_0(O_2)$, $D^\circ{}_0(S_2)$, and $D^\circ{}_0(SO)$.

Considering two possible spectroscopic values of $D^\circ{}_0(SO)$ and three values of $D^\circ{}_0(S_2)$ one obtains Table 1. The results of St Pierre and Chipman, $\Delta H^\circ{}_0 f(SO) = -18{\cdot}3$ or $-19{\cdot}2$ kcal. mole^{-1}, would fit approximately in Table 1 for $D^\circ{}_0(SO) = 123{\cdot}5$ and $D^\circ{}_0(S_2) = 83{\cdot}0$ kcal.; they yield $D^\circ{}_0(S_2) = 92{\cdot}4$ or $90{\cdot}6$ kcal. mole^{-1} if the high value of $D^\circ{}_0(SO)$ is accepted as exact. Dewing and Richardson's results $\Delta H^\circ{}_0 f(SO) = -15{\cdot}4$ or $-15{\cdot}6$ kcal. mole^{-1} give a good fit for both the high values of $D^\circ{}_0(SO)$ and $D^\circ{}_0(S_2)$. The results yield $D^\circ{}_0(S_2) = 98{\cdot}2$ or $97{\cdot}8$ kcal. mole^{-1}, with $D^\circ{}_0(SO) = 123{\cdot}5$ kcal. mole^{-1}.

TABLE 1. *Heat of formation of SO (kcal. mole^{-1})*

$D^\circ{}_0(SO)$ \ $D^\circ{}_0(S_2)$	101·8	83·0	75·4
123·5	−13·6	−23·0	−26·8
97·1	+12·8	+ 3·4	− 0·4

As appears in the next section, Dewing and Richardson's[11] results are in excellent agreement with the final conclusions, and those of St Pierre and Chipman[10] could be considered as "not disagreeing" if some allowance is made for experimental uncertainty. The difficulty in both experiments is however much more fundamental in that other components could be present in such complicated systems at high temperatures. In particular attention has been drawn to the likely formation of disulphur monoxide, S_2O.[53] "Side reactions" were indeed observed and corrections for pick-up of sulphur by the mullite tube, for volatilisation of platinum oxides, and for other causes applied. Other effects could escape observation.

4*a*. In mass-spectrometric investigations,[12–14] sulphides (MeS) of Ca, Sr, and Ba were evaporated in order to observe at sufficiently high temperatures and low pressures the equilibrium $2S \rightleftharpoons S_2$. The crucial point is the so-called pressure-sensitivity calibration,[54,55] which relates observed ion intensities to partial pressures. Initially the weight-loss calibration was used;[12] later[13] it was considered that side reactions could cause errors in this method and the pressure-independent equilibrium (4)

$$\tfrac{2}{3}\,\mathrm{MeS(s)} + 2\mathrm{S(g)} \rightleftharpoons \tfrac{2}{3}\,\mathrm{MeS(g)} + \tfrac{4}{3}\,\mathrm{S_2(g)} \qquad (4)$$

was considered for calculations. This is equivalent to considering the S_2 pressures known from thermodynamic data for the equilibrium (5).

$$\mathrm{MeS(s)} \rightleftharpoons \mathrm{Me(g)} + \tfrac{1}{2}\,\mathrm{S_2(g)} \qquad (5)$$

The error limits of both methods were carefully examined*; the latter procedure which yields $D°_0(S_2) = 96{\cdot}4 \pm 5$ kcal. mole^{-1} was considered to be most reliable even though the former yields values which are only 2 to 3 kcal. lower. Berkowitz and Marquart[14] have measured ion-intensity ratios in the evaporation of CaS, SrS, and FeS but have not performed pressure-sensitivity calibrations.

4*b*. From the equilibrium (6) and use of

$$\mathrm{MeO} + \mathrm{S} \rightleftharpoons \mathrm{Me} + \mathrm{SO} \qquad (6)$$

$D°_0(SO) = 123{\cdot}5$ kcal. mole^{-1}, $D°_0(MeO)$ values were obtained[13] in agreement with measurements of Drowart, Exsteen, and Verhaegen[56] for CaO and SrO and with values of Inghram, Chupka, and Porter[57] for BaO.

The mass-spectrometric measurements for S_2 and for SO thus unambiguously exclude the values $D°_0(S_2) = 74$ or 83 and $D°_0(SO) = 97{\cdot}1$ kcal. mole^{-1}.

5. The vaporisation of oxides, sulphides, and selenides has been investigated extensively by mass spectrometry.[54,58] In some cases, decomposition to solid or gaseous metal and chalcogenide atoms or mole-

---

[53] U. Blukis and R. J. Myers, *J. Phys. Chem.*, 1965, **69**, 1155; see also R. Steudel and P. W. Schenk, *Z. physik. Chem.*, 1964, **43**, 33.

[54] M. G. Inghram and J. Drowart, in "High Temperature Technology", Proceedings of a Symposium, McGraw-Hill Book Co., New York, 1960.

[55] J. Drowart and P. Goldfinger, *Angew. Chem.*,

* For a general discussion of error limits in mass spectrometric equilibrium measurements, see ref. 55.

[56] J. Drowart, G. Exsteen, and G. Verhaegen, *Trans. Faraday Soc.*, 1964, **60**, 1920.

[57] M. G. Inghram, W. A. Chupka, and R. F. Porter, *J. Chem. Phys.*, 1955, **23**, 2159.

[58] J. Drowart, in "Condensation and Evaporation of Solids", Gordon and Breach Inc., New York, 1964, p. 255.

cules is observed; in other cases, diatomic molecules or polymers are predominant. The latter has been observed for Group IV oxides.[39,59,60]

In the vapour of Group IV sulphides,[39,15] selenides,[39,61] and tellurides,[16,39,62] by far the predominant molecule is the MeX monomer and therefore the numerous total-pressure measurements permit one to calculate the heats of vaporisation with good precision. For SnS and PbS the standard heat of formation is also well known and accurate convergence limits have been observed for the gaseous molecules. Provided the correlation of the limits with atomic products is known, the results can be used in thermochemical cycles to derive $D^\circ_0(S_2)$. For PbS, the rotational analysis indicates[63] the electronically excited E state to be O^+. Hence, provided the non-crossing rule is applicable, the most likely dissociation products are $Pb(^3P_1)$ and $S(^3P_1)$.[63] The observed convergence limit is at 2715 Å.[42] The dissociation energy of PbS in its ground state is then $D^\circ_0(PbS) = 81{\cdot}81 \pm 0{\cdot}40$ kcal. mole^{-1}. For SnS, for which the electronically excited E state is most probably the analogue of that for PbS and PbO,[64] the convergence limit[41] is obtained by a short extrapolation at 40,850 cm.$^{-1}$. There are in addition one other limit at *ca.* 56,100 cm.$^{-1}$ and a continuum at 56,470 cm.$^{-1}$, both attributed to the products $Sn(^1D_2) + S(^1D_2)$. These three observations yield respectively $D^\circ_0(SnS) = 110{\cdot}8$, 109·3, and 110·4 kcal. mole^{-1}, of which the average $110{\cdot}2 \pm 0{\cdot}8$ is used in the subsequent calculations.

The thermochemical cycle considered is given in Table 2. The enthalpies of the different reactions were recalculated using the third law and the original data referred to in the Table. The free-energy functions were taken from the literature[65] or recalculated with more recent spectroscopic data. It is worthwhile to point out that possible systematic errors in the free-energy functions for condensed MeS have little influence on the result. They cancel out in the calculation of the heat of formation and the heat of sublimation, except for the incidence of the heat-content differences between the average temperatures at which both were measured. Therefore the uncertainties for the corresponding enthalpies quoted in Table 2 are statistical rather than absolute errors. For $D^\circ_0(S_2)$ an estimated absolute uncertainty is quoted.

For GeS, there is an accurate convergence limit in the E state[42] at 2140 Å (46,729 cm.$^{-1}$). A recent mass spectrometric measurement[66] of the

[59] R. F. Porter, W. A. Chupka, and M. G. Inghram, *J. Chem. Phys.*, 1955, **23**, 216.

[60] J. Drowart, F. Degrève, G. Verhaegen, and R. Colin, *Trans. Faraday Soc.*, 1965, **61**, 1072; R. Colin, J. Drowart, and G. Verhaegen, *Trans. Faraday Soc.*, 1965, **61**, 1364; J. Drowart, R. Colin, and G. Exsteen, *Trans. Faraday Soc.*, 1965, **61**, 1376

[61] R. Colin and J. Drowart, *Trans. Faraday Soc.*, 1964, **60**, 673.

[62] R. Colin and J. Drowart, *J. Phys. Chem.*, 1964, **68**, 428.

[63] R. F. Barrow, P. W. Fry, and R. C. Le Bargy, *Proc. Phys. Soc.*, 1963, **81**, 697.

[64] R. F. Barrow, J. L. Deutsch, and D. N. Travis, *Nature*, 1961, **191**, 374.

[65] K. K. Kelley, *U.S. Bur. Mines Bull.*, 1960, 584; K. K. Kelley and E. G. King, *U.S. Bur. Mines Bull.*, 1961, 592. Janaf Thermochemical Tables; D. R. Stull and G. C. Sinke, *Adv. Chem. Ser.*, No. 18 (Amer. Chem. Soc. Washington DC, 1956).

[66] P. Coppens, Licence Thesis, University of Brussels, July 1966.

TABLE 2. *Dissociation energy* $D^\circ_0(S_2)$ *from the thermochemical cycles*

Reaction	ΔH°_{298} Reaction/enthalpy (kcal. mole^{-1})		
	Ge	Sn	Pb
MeS(c) → MeS(g)	40·3 ± 0·5[a]	53·0 ± 0·2[b]	55·3 ± 0·7[c]
MeS(g) → Me(g) + S(g)	132·1 ± 0·6[d]	111·1 ± 0·8[e]	82·6 ± 0·4[f]
Me(c) → Me(g)	89·5 ± 0·5[g]	72·0 ± 0·5[h]	46·8 ± 0·3[i]
S(rh) → ½ S_2(g)	15·4 ± 0·1[j]	15·4 ± 0·1	15·4 ± 0·1
S(rh) + Me(c) → MeS(c)	−17·7 ± 1·5[k]	−25·8 ± 0·3[l]	−23·4 ± 0·1[m]
S_2(g) → 2S(g)	99·4	101·9 ± 2·5	104·6 ± 2·5
$D^\circ_0(S_2)$	98·4	100·9 ± 2·5	103·6 ± 2·5

[a] Refs. 34, 35, 36. [b] Ref. 37. [c] Ref. 38. [d] Ref. 40, 66. [e] Ref. 41. [f] Ref. 42. [g] A. W. Searcy, *J. Amer. Chem. Soc.*, 1952, **74**, 4789; A. W. Searcy and R. D. Freeman, *J. Chem. Phys.*, 1955, **23**, 88; C. B. Alcock and P. Grieveson, *J. Inst. Metals*, 1962, **90**, 304 [h] P. Harteck, *Z. phys. Chem.*, 1928, **134**, 1; L. Brewer and R. F. Porter, *J. Chem. Phys.*, 1953, **21**, 2012; A. W. Searcy and R. D. Freeman, *J. Amer. Chem. Soc.*, 1954, **76**, 5229; C. B. Alcock and P. Grieveson, ref. *g*. [i] A. T. Aldred and J. N. Pratt, *Trans. Faraday Soc.*, 1961, **57**, 611 and refs. therein; J. H. Kim and A. Cosgarea, jun., *J. Chem. Phys.*, 1966, **44**, 806; P. Goldfinger and M. Jeunehomme, *Trans. Faraday Soc.*, 1963, **59**, 2851. [j] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Nat. Bur. Stand. Circular 500, 1952. [k] Ref. 67 [l] A. W. Richards, see ref. 37; K. Sudo, *Sci. Reports Res. Inst. Tohoku Univ.*, 1951, A, **3**, 187; H. Rau, ref. 37. [m] K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, 1957, **104**, 379; K. Sudo, *Sci. Reports Res. Inst. Tohoku Univ.*, 1950, **A**, **2**, 305; J. R. Stubbles and C. E. Birchenall, *Trans. AIME*, 1959, **215**, 535.

enthalpy of the reaction GeS(g) + Sn(g) → Ge(g) + SnS(g) gives ΔH°_0 = 20·6 ± kcal. mole^{-1}. With the above value for D°_0(SnS), these results there from give D°_0(GeS) = 130·8 ± 1·3 kcal. mole^{-1}. This suggests that also for GeS the *E* state limit corresponds to Ge($^3P_1$) + S($^3P_1$), which gives D°_0(GeS) = 130·9 ± 0·6 kcal. mole^{-1}. There is however apparently only one determination of the heat of formation of GeS,[67] for which the uncertainty must therefore be taken appreciably higher than for the other two Group IVA sulphides. Nevertheless the cycle again rules out the low value of $D^\circ_0(S_2)$.

The three cycles, spectroscopic arguments being combined with thermodynamic data, thus show independently that the predissociation in S_2 at 35,590 cm.$^{-1}$ = 101·8 kcal. mole^{-1} leads to atoms in the ground state. Further the cycle involving PbS and to a lesser extent that of SnS indicate that this predissociation is an exact one or very close to it and that higher combinations of the $^3P_{2,1,0}$ sublevels are improbable.

3. Selenium and Tellurium

(a) Se_2.—Earlier spectroscopic observations[68] led to the identification of a number of predissociations at 28,680,[68,69] about 29,500, and 30,864 cm.$^{-1}$. Generally speaking, these were not used to deduce dissociation energies. The difficulty resulted in part from the fact that the rotational

---

[67] K. Ono and K. Sudo, *Sci. Reports Res. Inst. Tôhoku Univ.*, 1955, **7**, 385.
[68] B. Rosen, *Physica*, 1939, **6**, 205.
[69] S. P. Davis and F. A. Jenkins, *Phys. Rev.*, 1951, **83**, 1269.

analysis suggested that the ground state is $^1\Sigma$ in contrast to a $^3\Sigma$ state expected by analogy with O_2, SO, and S_2. The dissociation energy usually adopted was $D°_0 = 65$ kcal. mole^{-1}, obtained from the Birge–Sponer extrapolation of the upper state of the main band system, correlated by analogy with the other members of the group with Se(^1D) + Se(^3P).[4] Recalculated[1] thermochemical measurements of von Wartenberg in agreement with this value now appear to be unreliable as discussed above.

Thermochemical measurements by mass spectrometry[18,70] give $D°_0(Se_2) = 74{\cdot}5 \pm 2{\cdot}0$ kcal. mole^{-1}, calculated with a $^3\Sigma$ ground state, in which the triplet splitting λ'' was assumed to be small, with the same hypothesis, a cycle for PbSe similar to that for PbS gives $D°_0(Se_2) = 75{\cdot}4$ kcal. mole $^{-1}$, with $\Delta H°_{298,\text{sub}}(PbSe) = 53{\cdot}5$;[71] $\Delta H°_{298,f}(PbSe) = -23{\cdot}9$,[72] and $D°_0(PbSe) = 71{\cdot}5$ kcal. mole^{-1} derived from the convergence limit of the E state[73] by assuming a correlation with atomic products as for PbS.

On the basis of these results it was suggested[70] that the above predissociations correlate with $^3P_2 + {}^3P_1$, $^3P_2 + {}^3P_0$ and $^3P_1 + {}^3P_1$ respectively, and the maximum in the continuous absorption[74] at 31,557 cm.$^{-1}$ with $^3P_1 + {}^3P_0$.

In a very extensive recent spectroscopic investigation[9] carried out with isotopically pure Se_2 it was shown that the v'' and v' numbering must be revised. Two exact predissociations were observed at 27,518 cm.$^{-1}$ and at 29,498 cm.$^{-1}$. The separation corresponds to the energy difference between the $J = 2$ and $J = 1$ sublevels of the ^3P ground state of the Se atom. Spectroscopic arguments make the products $^3P_2 + {}^3P_1$ and $^3P_2 + {}^3P_2$ unlikely and favour the products $^3P_2 + {}^3P_1$ and $^3P_1 + {}^3P_1$ or $^3P_2 + {}^3P_0$ and $^3P_1 + {}^3P_0$. Therefore the spectroscopic value for the dissociation energy is $72{\cdot}94 \pm 0{\cdot}05$ or $71{\cdot}39$ rather than $78{\cdot}63$ kcal. mole^{-1}. Of the two alternative figures, the value $72{\cdot}94 \pm 0{\cdot}05$ was selected[9] on the basis of the non-crossing rule.

The rotational analysis[9] resolved the problem of the electronic state of Se_2. The ground state as well as the excited B state approximate Hund's case c coupling and are composed of $\Omega = 0^+$ and $\Omega = 1$ sublevels instead of the $^3\Sigma$ states of 0_2 and S_2. The band system BO^+_u–XO^+_g is stronger and more developed than BI_u–XI_g; other transitions between the B and X level have not been observed. Therefore previous rotational analyses considered the ground state as $^1\Sigma$. The separation XI_g–XO^+_g is estimated very roughly to be about 1450 cm.$^{-1}$. Such a high value would be in essential agreement with older[75] measurements of the magnetic

---

[70] J. Drowart, Annual Summary Report No. 3, Contract AF 61(052)-225, 1962; D. Detry, Concours Universitaire, 1963-64, University of Brussels.

[71] V. P. Zlomanov, B. A. Popovkin, and A. N. Novoselova, *Zhur. neorg. Khim.*, 1959, **4**, 2661.

[72] C. B. Finch and J. B. Wagner, *J. Electrochem. Soc.*, 1960, **107**, 932.

[73] E. E. Vago and R. F. Barrow, *Proc. Phys. Soc.*, 1947, **59**, 449.

[74] R. K. Asundi and Y. P. Parti, *Proc. Indian Acad. Sci.*, 1937, **6**, 207.

[75] S. S. Bhatnagar, H. Lessheim, and M. L. Khanna, *Nature*, 1937, **140**, 152,

susceptibility, but not with more recent ones.[76,77] Taking it into account in the thermochemical measurements referred to above, one obtains $D°_0$ (Se_2) = 76·5 kcal. mole^{-1}. There would then be a small difference between the spectroscopic and thermochemical values, of the dissociation energy unless the spectroscopically unlikely value ultimately appeared to be correct.

(**b**) Te_2.—The Birge–Sponer extrapolation of the ground-state vibrational levels gives[4] $D°_0(Te_2) = 80$ kcal., whereas for the upper level of the main band system a limit at 29,300 cm.$^{-1}$ is obtained by the same method; this has generally been correlated with $Te(^3P_2) + Te(^1D_2)$. From this $D°_0(Te_2) = 18{,}700$ cm.$^{-1}$ = 53 kcal. mole^{-1}, which has usually been retained.

Predissociation has been observed[78] in the upper state of the main band system at 25,700 cm.$^{-1}$. This value roughly corresponds with the limit of continuous absorption (26,100 cm.$^{-1}$). Since this probably corresponds to a potential maximum[79] as now established for Se_2,[9] apparently little information can be deduced from these data. Collisionally induced predissociation[80] affects levels below about $v' = 8$ in the B state (about 23,900 cm.$^{-1}$). Predissociations induced by magnetic fields[81] go through a maximum around $v' = 11$ (about 24,300 cm.$^{-1}$). By assuming the predissociation to lead to $Te(^3P_2) + Te(^3P_0)$ (4707 cm.$^{-1}$), $D°_0 \simeq 19{,}400$ cm.$^{-1}$ = 55·5 kcal. mole^{-1} is obtained. This value is in agreement with the interpretation of a continuum as due to a two-body recombination[82] giving $D°_0 = 19{,}200$ cm.$^{-1}$ = 55 kcal. mole^{-1}.

The thermochemical value deduced[1] from the vapour-density measurements of von Wartenberg[25] is 50 kcal. mole^{-1}. As pointed out above, Te_2 is the only molecule of this group for which these measurements lead to a value that is in essential and perhaps fortuitous agreement with presently available information.

The dissociation equilibrium $Te_2 \rightleftharpoons 2Te$ has been studied by mass-spectrometry.[16,17] The result, calculated by assuming a $^3\Sigma$ ground state, is $D°_0 = 53$ kcal. mole^{-1}. The spectroscopic results of Barrow's group[20] show however that for SeO, Se_2, and TeO the splitting of the multiplets increases rapidly, λ'' varying from 85 to 1375 cm.$^{-1}$. This suggests a high value of λ'' for Te_2 and practically an electronic degeneracy of unity. Magnetic-susceptibility measurements[75] seem to be in essential agreement with this view. Therefore the above value may have to be increased by as much as 3 kcal. mole^{-1}.

The value of $D°_0(Te_2) = 55 \pm 2$ kcal. mole^{-1} is suggested.

[76] S. Tobishawa, *Bull. Chem. Soc. Japan*, 1960, **33,** 889.

[77] C. H. Massen, A. G. L. M. Weyts, and J. A. Poulis, *Trans. Faraday Soc.*, 1964, **60,** 317.

[78] B. Rosen, ref. 29, L. C. 31; E. Hirschlaff, *Z. Phys.*, 1932, **75,** 315.

[79] B. Rosen, *Acta phys. Polon.*, 1936, **5,** 203.

[80] V. N. Kondratiev and A. Lauris, *Z. Phys.*, 1934, **92,** 741.

[81] E. Olsson, *Z. Phys.*, 1935, **95,** 215.

[82] R. Rompe, *Z. Physik*, 1936, **101,** 214; see also ref. 3, p. 402.

4. Inter-Group VIA Molecules

(a) **SeO.**—The linear Birge–Sponer extrapolation[83] of the vibrational levels of the ground state gives $D^\circ_0 = 44{,}170$ cm.$^{-1}$ or 126 kcal. mole^{-1}. By analogy with other members of the group this is probably about 25% too high. The suggestion[4] that vibrational levels above $v' = 2$ around 34,160 cm.$^{-1}$ = 97·7 kcal. mole^{-1} are predissociated is supported by more recent results[19] which indicate predissociation for $v' < 3$, which gives $D''_0 < 35{,}540$ cm.$^{-1}$ = 102 kcal. mole^{-1}. By analogy with SO, the predissociation is attributed[19] to states arising from the ground-state atoms. From this, D''_0(SeO) $\simeq$ 100 kcal. mole^{-1}, a value also expected by analogy with the other members of the group.

(b) **TeO.**—The upper state of the main band system of TeO, studied in emission and absorption,[83] was shown to converge at *ca.* 32,542 cm.$^{-1}$, whereas there is a predissociation at about 31,600 cm.$^{-1}$.The upper state was correlated[83] with O(^3P) + Te(^1D) whence $D^\circ_0 = 21{,}983$ cm.$^{-1}$ = 62·8 kcal. mole^{-1}. The observation of additional systems[84] led to the suggestion that the above convergence corresponds to Te($^3P_0$) + O(^3P) giving $D^\circ_0 = 27{,}835$ cm.$^{-1}$ = 79·6 kcal. mole^{-1}. A rotational analysis[20] with separated isotopes for the A–X system of this molecule has shown that the ground state belongs to case *c*, with pronounced splitting of the $\Omega = 0$ and $\Omega = 1$ terms ($\lambda'' = 1375$ cm.$^{-1}$). The Birge–Sponer extrapolation of the vibrational levels of the ground state gives $D^\circ_0 = 112{\cdot}4$ kcal. mole^{-1}. By analogy with O_2 and S_2, where the extrapolation gives values too high by a factor of 1·25, the authors[20] retain D°_0(TeO) = 90 kcal. mole^{-1}. Predissociation in two levels of the upper state at *ca.* 31,450 cm.$^{-1}$ give $D^\circ_0 = 90$ kcal. mole^{-1} as above, whereas the extrapolation of the vibrational levels of the upper state, correlated with Te($^3P_0$) + O(^3P), gives $D^\circ_0 = 35{,}220 - 4{,}707 = 30{,}513$ cm.$^{-1}$ or 87·2 kcal. mole^{-1}.

(c) **SeS and TeSe.**—The observation of the molecule SeS has not hitherto been specifically reported although in a mass-spectrometric study of the Se–S system[85] different mixed Se–S molecules have been identified. By comparison with the other molecules of the group, the dissociation energy is estimated as 90 kcal. mole^{-1}.

The molecule TeS has been observed spectroscopically.[21] The Birge–Sponer extrapolation of the vibrational levels of the ground state D°_0 = 113 kcal. mole^{-1} which by analogy with Se_2 is probably about 40% too high, whence $D^\circ_0 = 80$ kcal. mole^{-1}.

The molecule TeSe has been identified mass spectroscopically.[22] The thermochemical value of its dissociation energy derived from the iso-

---

[83] C. S. Piaw, *Ann. Physik*, 1938, **10,** 173.

[84] P. B. V. Haranath, P. T. Rao, and V. Sivaramamurty, *Z. Physik*, 1959, **155,** 507.

[85] V. A. Umilin, I. L. Agafonov, L. N. Kornev, and G. G. Devyatykh, *Zhur. neorg. Khim.*, 1964, **9,** 2492.

molecular exchange reaction $\frac{1}{2}Se_2(g) + \frac{1}{2}Te_2(g) \rightarrow TeSe$, is $D^\circ_0 = 62{\cdot}5 \pm 3$ kcal. mole^{-1}.

Summary

Table 3 summarises available values for the dissociation energies of the Group VIA diatomic molecules.

The value for O_2, $D^\circ_0(O_2) = 117{\cdot}96 \pm 0{\cdot}04$ kcal. mole^{-1}, is based entirely on spectroscopic data.[86]

The value for Se_2, $D^\circ_0(Se_2) = 72{\cdot}94 \pm 0{\cdot}05$ kcal. mole^{-1}, is based mainly on spectroscopic data.[9] It is confirmed by the mass-spectrometric determination which gives $D^\circ_0(Se_2) = 74{\cdot}5 \pm 2$ kcal. mole^{-1}.[18]

TABLE 3. *Dissociation energies of the Group VIA molecules (kcal. mole^{-1}).*

	O	S	Se	Te
O	117·96	123·5	100	90
S		101·0	(90)	(80)
Se			72·94	63
Te				54·0

The value[5] for SO, $D^\circ_0(SO) = 123{\cdot}5 \pm 0{\cdot}3$ kcal. mole^{-1} takes into account the uncertainty associated with the predissociation limit. Further the ^3P sublevels of the atoms formed are not known. It is therefore possible that the dissociation energy could be lowered by as much as 2·3 kcal. mole^{-1}. This value is derived from spectroscopic data,[47,5] supplemented by the results[51] from chemiluminescence due to the $S + O \rightarrow SO$ recombination and from mass spectrometric measurements[12,13] of the SO dissociation energy. Either or both latter arguments were here necessary, together with the observation of an additional convergence limit,[6,50] to establish that the dissociation products are atoms in their ^3P states and not $S(^1D) + O(^3P)$.

The values for SeO[19,83] and TeO[20,83] are based exclusively on spectroscopic data, predissociations in particular. The values are however not very accurate since no detailed analysis has yet been performed. No thermodynamic datum is available to supplement the results. The error limits are estimated to be $+0{\cdot}5$, -3 kcal. mole^{-1}.

The dissociation energy of the remaining molecules is in contrast largely based on thermochemical data. For S_2, the predissociation[43,7] whose interpretation is complicated by perturbations and collision- or magnetic field-induced effects fixes an upper limit at[7] $D^\circ_0(S_2) = 101{\cdot}8$ kcal. mole^{-1}. The direct $S_2 \rightleftharpoons 2S$ equilibrium measurement[12,13] definitely identifies the products as atoms in their ^3P states. The sublevels involved however remain unidentified. The indirect thermochemical data involving the spectroscopically established dissociation energies of the molecules SnS and PbS fix the dissociation energy $D^\circ_0(S_2) = 101{\cdot}1 \pm 1{\cdot}0$ kcal. mole^{-1}.

[86] P. Brix and G. Herzberg, *Canad. J. Phys.*, 1954, **32**, 110.

For Te_2, the dissociation energy is presently practically based on the mass spectrometric study of the $Te_2 \rightleftharpoons 2Te$ equilibrium.[16,17] The accuracy of the result $D°_0(Te_2) = 55 \pm 2$ kcal. mole^{-1} is limited to a large extent by the incomplete knowledge of the electronic ground state.

The value for TeSe, $D°_0(TeSe) = 62{\cdot}5 \pm 3$ kcal. mole^{-1}, is based only on mass-spectrometric data.[22] The uncertainty results partly from the same reasons as for Te_2.

The dissociation energies of SeS and TeS are essentially estimated by analogy with the other members of the group. The uncertainty is ±5 kcal. mole^{-1}.

For several of the above molecules (*e.g.*, S_2, SO, SeO, TeO) the "high" value of the dissociation energy which for so long had been questioned appears to be essentially correct. Simultaneously the similarity in the nature of the electronic states of the Group VIA molecules is experimentally proved. This applies in particular to the relative position of the potential-energy curves and their intersection leading to predissociations. A detailed discussion of these questions is beyond the scope of this Review.

It appears that, as for many other questions, progress concerning the above problems has been rather slow in spite of many valuable contributions, all of which have not been quoted and that much further work still needs to be done for about half of these molecules. As often, the answer has only been obtained by combination of several methods and then for each of them by using the most discriminating techniques. In optical spectroscopy, high resolving power and the use of separated isotopes was necessary. In thermochemistry, complete analysis of the composition of the vapour phase by mass-spectrometry was required.

The authors thank Drs. R. F. Barrow and G. Herzberg for comments.