Mass-spectrometric Determination of the Bond Energies of the Molecules AuS, BS, and BS_2

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Summary Mass-spectrometric evidence and experimental values for the bond energies are reported for the molecules AuS, BS, and BS_2.

IN further mass spectrometric investigations of the Au–Ce–CeS–BN–C system[1] from a tungsten Knudsen effusion cell we have observed the molecules BS, BS_2, and AuS for which we report thermochemical properties. Previous m.s. studies of the vaporization products of B_2S_3 by Gilles and his collaborators[2] at temperatures between 300—500° have revealed the existence of a large number of gaseous polyatomic boron sulphides. Sommer, Walsh, and White[3] have observed the molecules B_2S_3, B_2S_2, and possibly BS_2 in the vapour produced by the reaction between ZnS(s) and B(s) at 700—900°. Ficalora *et al.*[4] have investigated the reaction between sulphur vapour, generated through the decomposition of Cr_2S_3, and a boron crystal rod at temperatures around 1400°K, and report evidence for several low molecular weight polyatomic boron sulphides, including BS_2 and B_2S. In none of these investigations[2–4] could diatomic boron sulphide be observed as a parent molecule. This molecule has, however, been identified in optical spectroscopic measurements.[5,6]

For the present system the molecule BS becomes the predominant gaseous boron sulphide in the saturated vapour above 2000°K, due to the tightly-bonded sulphur

Third-law enthalpies of reactions involving the molecules AuS, BS, *and* BS_2

Reaction	Number of data sets	Temperature interval (T°K)	ΔH^0_0 (kcal mol^{-1})	D^0_0(M)[a] (kcal mol^{-1})	Molecule(M)
CeS(g) + Au(g) = AuS(g) + Ce(g) ..	5	2154—2268	37·3 ± 1·0	98·7 ± 6[b]	AuS
CS(g) + B(g) = BS(g) + C(g)	5	2230—2330	40·1 ± 2·0	140·4 ± 6[c]	BS
CeS(g) + B(g) = BS(g) + Ce(g) ..	8	2057—2344	−9·4 ± 1·5	145·4 ± 6[b]	BS
2CeS(g) + B(g) = BS_2(g) + 2Ce(g) ..	3	2279—2319	7·7 ± 0·8	264·3 ± 8[b]	BS_2
2BS(g) = BS_2(g) + B(g)	3	2279—2319	21·6 ± 1·8	264·4 ± 8[d]	BS_2

[a] Dissociation energy for AuS(g) and BS(g) and heat of atomization for BS_2(g).

[b] Using D_0(CeS) = 136·0 ± 3·0 kcal mol^{-1} (ref. 7).

[c] Using D^0_0(CS) = 180·5 ± 5·0 kcal mol^{-1} (ref. 9).

[d] Using D^0_0(BS) = 143 ± 6 kcal mol^{-1}, this investigation.

in condensed and gaseous cerium monosulphide[7] and the decreased activity of boron in the condensed system used. At these temperatures while gold was still present, conditions were also favourable for investigating the molecule AuS. Smoes and Drowart[8] have previously reported the presence of the molecules AuS and Au_2S over MnS(s) + Au(l), but did not present any data or thermodynamic evaluation for these molecules.

The reaction enthalpies for the gaseous equilibria listed in the Table have been evaluated by the Third-law method, using the relation $\Delta H^0_0 = -\boldsymbol{R}T\ln K_p - T\,\Delta[(G^0_T - H^0_0)/T]$.

The equilibrium constant, K_p, was directly obtained from the corresponding ion currents measured with 20 ev ionizing electrons. It was assumed that the effects of the relative ionization cross sections and multiplier gains of the reactants and products compensate each other. A typical set of relative ion currents involving the AuS molecule is $I(AuS^+)$, $4{\cdot}03 \times 10^{-11}$; $I(Au^+)$, $3{\cdot}50 \times 10^{-8}$; $I(CeS^+)$, $8{\cdot}50 \times 10^{-8}$; $I(Ce^+)$, $4{\cdot}50 \times 10^{-7}$ (all measured at 2268°K). A corresponding set measured at 2279°K for the participants of the reactions involving the molecules BS and BS_2 is $I(BS^+)$, $2{\cdot}06 \times 10^{-10}$; $I(B^+)$, $2{\cdot}20 \times 10^{-11}$; $I(CeS^+)$, $3{\cdot}81 \times 10^{-7}$; $I(Ce^+)$, $3{\cdot}38 \times 10^{-7}$; $I(BS_2^+)$ $3{\cdot}41 \times 10^{-12}$; $I(CS^+)$, $4{\cdot}82 \times 10^{-9}$; $I(C^+)$, $1{\cdot}9 \times 10^{-13}$. The values given correspond to the most abundant mass number of the respective molecule and have been, in the case of B^+ and C^+, corrected for fragment contributions.

The numerical values of the free energy functions, $-(GT^0_T - H^0_0)/T$ were taken from literature for CeS,[7] BS,[9] CS,[9] C,[9] B,[9] Ce,[10] and Au.[11] Those for AuS and BS_2 were estimated according to commonly used procedures.[9] For AuS the analogy to AuO(g)[12] was used resulting in 71·6, 72·4, and 73·3 (in e.u.) for 2000, 2200, and 2400°K, respectively. The values of 74·2, 74·9, and 75·5 for 2000, 2200, and 2400°K, respectively, were calculated for BS_2(g) in analogy to the molecules BO_2, BS, CS, and CS_2.[9]

The averages of the various experimental reaction enthalpies (Table) have been combined with the appropriate literature values of the dissociation energy for the respective reaction participants (Table). The resulting dissociation energy for gaseous gold monosulphide, D^0_0 = 99 ± 6 kcal mol^{-1}, is rather high and indicates a bond order of more than one, involving *d*-orbital participation. The experimental value for the dissociation energy of gaseous boron monosulphide, D^0_0 = 143 ± 6 kcal mol^{-1}, compares with the value D^0_0 = 118 ± 19 that has been estimated by Gaydon[13] on the basis of spectroscopic data.[5] The calculated ratio $D^0_0(BO)/D^0_0(BS)$ of 1·34[12] is identical with the value for $D^0_0(AlO)/D^0_0(AlS)$[14] and also compares well with the corresponding ratios found for many other diatomic sulphides.[7,15] The heat of atomization of the molecule BS_2 is 264·4 ± 8 kcal mol^{-1}.

The apparent discrepancy between the spectroscopic value for D^0_0(BS) and the thermochemical value obtained in the present investigation may possibly be caused by an ionic contribution to the bonding in the BS molecule which would tend to produce too low dissociation energies in graphical Birge–Sponer extrapolations.[13] McDonald and Innes[16] have recently explained in a similar way the too low spectroscopic values that were previously obtained for the AlO molecule, which is isoelectronic with BS.

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