Comparison of the Thermochemistry of the Difluorides and Potassium Hexafluorometallates(IV) of the Elements of the Germanium Triad with that of the Elements of the Nickel Triad: A Study of the Inert-pair Effect †

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An attempt has been made to resolve the conflict between the classical interpretation of the development of a valency two less than the group valency in Groups 3B—8B of the Periodic Table and contemporary criticism of it. This has been done by analysing the enthalpy of process (1) for M = Ni, Pd, Pt and Ge, Sn, Pb. The following standard enthalpies of formation at 25 °C were determined by

$$K_2MF_6(c) \longrightarrow MF_2(c) + 2KF(c) + F_2(g) \qquad (1)$$

solution calorimetry: $PdF_2(c)$, −495; $SnF_2(c)$, −672; $PtF_4(c)$, −681; $K_2NiF_6(c)$, −1 963; $K_2PdF_6(c)$, −2 040; $K_2PtF_6(c)$, −2 055; $K_2GeF_6(c)$, −2 603; $K_2SnF_6(c)$, −2 575; $K_2PbF_6(c)$, −2 209 kJ mol^{-1}. Other data were taken from the literature or were estimated. From the analysis it was concluded that the classical explanation of the development of a valency of two in Group 4B, that a pair of valency electrons becomes inert, is essentially correct.

The work described in this paper was carried out some time ago [1] to try to elucidate the phenomenon of the development of a valency two less than the group valency (N) in Groups 3B—8B of the Periodic Table, particularly in the heavier members of Groups 3B and 4B. This phenomenon was attributed by Grimm and Sommerfeld [2] to the ability of a group of two electrons to show stability, not only when it is by itself, as in the helium atom, but also when it forms part of a larger shell: an explanation popularised by Sidgwick,[3] who used the phrase 'inert pair' to describe the electrons concerned. This interpretation has, however, been challenged by Drago.[4] Drago showed that, contrary to the idea that the outer s electrons become more stable in going down Groups 3B, 4B, and 5B, the energy required to remove them from the isolated atoms (the sum of the ionization potentials I_{N-1} and I_N) is no greater for the heavier members than it is for those in the middle of the group. He further showed, on the basis of the data that were available, that (*a*) the factor that is most responsible for the increasing stability of the ($N-2$)-valent chloride (MCl_{N-2}) relative to the N-valent one (MCl_N) in going down Groups 3B and 4B is the fall in bond energy in MCl_N, and (*b*) the reason for the latter is not so much a rise in *s–p* promotion energy as the inert-pair hypothesis would suggest, but a fall in *intrinsic* bond energy in going down the group.

Drago's analysis has been adopted by Cotton and Wilkinson,[5] who refer also to the fact that atoms or ions that are supposed to contain an inert pair of electrons often occur in unsymmetrical environments, in which the electrons concerned assume a certain amount of p character, as first discussed by Orgel.[6] To us, however, the inert-pair effect seems too felicitous an idea to be abandoned quite so easily, and we decided to make a further analysis of the relative stabilities of the N and $N-2$ valency states. In particular, we decided to make a comparison between the fall in stability of the higher state relative to the lower one as atomic number is increased with the converse phenomenon: the *rise* in stability of higher oxidation states relative to lower ones in a transition-element group.

To make this comparison, we needed to choose a $M^N \longrightarrow M^{N-2}$ process for which a transition-element counterpart could be found, and upon which the effects of any structural differences are likely to be small. The process that we adopted was reaction (1), which allowed a comparison to be made

$$K_2MF_6(c) \longrightarrow MF_2(c) + 2KF(c) + F_2(g) \qquad (1)$$

between the germanium triad (M = Ge, Sn, or Pb) and the nickel triad (M = Ni, Pd, or Pt). The potassium hexafluorometallates(IV) of these elements are all known, and all have structures based on octahedral co-ordination of M.[7] The structures of the difluorides, however, are more varied. The nickel and palladium compounds have the rutile structure, with almost regular octahedral co-ordination of the metal atoms, while the Group 4B difluorides have much less symmetrical structures, with gross co-ordination numbers of M of four (GeF_2),[8] six (SnF_2),[9,10] and nine (α-PbF_2).[8] The existence of the platinum compound is uncertain,[11–13] but we believed that we could make it by reducing the tetrafluoride with the metal, and that it would have a similar structure to that of PdF_2. Reaction (1) is of course a hypothetical one, since KF and MF_2 combine to form mixed fluorides; but the way in which the ease of this reaction varies with M should be typical of real processes, including those studied by Drago.[4]

In considering the variations in the relative stabilities of K_2MF_6 and MF_2 according to equation (1), we assumed that the predominant factor is the enthalpy change, $\Delta_d H^\ominus$. This is given by equation (2). Some of the heats of formation in this

$$\Delta_d H^\ominus = \Delta_f H^\ominus[MF_2(c)] + 2\Delta_f H^\ominus[KF(c)] - \Delta_f H^\ominus[K_2MF_6(c)] \qquad (2)$$

equation are known, but the majority had to be determined. A brief account of these determinations is given below: further details may be obtained from ref. 1.

Experimental

Materials.—All air-sensitive materials were handled under dry nitrogen.

Difluorides. Palladium difluoride was made by reducing the trifluoride with an excess of the metal.[14] Analysis of the product gave its composition as $0.880PdF_2 + 0.120Pd$. Apart

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† *Non-S.I. unit employed:* cal = 4.184 J.

from lines attributable to palladium, the *X*-ray powder photograph could be interpreted on the basis of the tetragonal unit cell, $a = 4.95$, $c = 3.38$ Å (± *ca.* 1%), in agreement with literature data for the ordinary form of PdF_2.[15]

Tin difluoride was prepared by evaporating a solution of SnO in 40% HF.[16] Elemental analyses were within 5 parts per 1 000 of the theoretical values for SnF_2. The *X*-ray powder photograph resembled that of the monoclinic form of SnF_2:[9,17] lines were observed corresponding to d/Å = 3.55 (m), 3.39 (m), 3.17 (s), 2.59 (w), 2.44 (w), 2.00 (vw), 1.90 (vw), 1.85 (m), and 1.75 (w). The i.r. spectrum, however, was more like that of the orthorhombic modification of Donaldson *et al.*,[10] having absorption maxima at 540 and 360 cm^{-1}. The method of preparation rules out the other known forms.[18]

Attempts were made to prepare platinum difluoride by heating 1 : 1 mixtures of the tetrafluoride and platinum. The tetrafluoride was prepared by the direct fluorination of the dichloride, and contained 99.7% of the theoretical amount of platinum. Its *X*-ray powder photograph was similar to that indexed by Bartlett and Lohmann [11] on the basis of a monoclinic unit cell. In a preliminary experiment, no signs of reaction between the tetrafluoride and platinum were observed at 100 °C, but after heating the mixture for 2 h at 300 °C, the PtF_4 lines on the *X*-ray powder photograph were found to have lost *ca.* 80% of their intensity relative to the Pt lines despite <2% loss in weight. There were no new lines on the powder photograph, and no definite changes to the platinum lines. The product was black. In a further experiment, under more rigorously dry conditions, no reaction was observed at 300 °C, but at 450 °C the PtF_4 lines disappeared completely from the powder photograph, and the product had the composition $PtF_{1.0}$. Whether a lower fluoride had been formed in these experiments is a matter of conjecture, but these results may be added to a number of others in the literature that suggest the possible existence of metallic or semi-metallic lower fluorides of the heavier transition metals, in addition to Ag_2F.[13,19]

For the purpose of the present paper, we shall assume that platinum difluoride is on the borderline of stability with respect to reaction (3). With $\Delta S^{\ominus}$ for this reaction likely to be

$$2PtF_2(c) \longrightarrow Pt(c) + PtF_4(c) \qquad (3)$$

small, this assumption means that the heat of formation of the difluoride can be approximately determined from that of the tetrafluoride [equation (4)].

$$\Delta_f H^{\ominus}[PtF_2(c)] \approx \tfrac{1}{2}\Delta_f H^{\ominus}[PtF_4(c)] \qquad (4)$$

Hexafluorometallates. Except for the germanate, these were made by direct fluorination.[7] The materials fluorinated were KCl + $KNiCl_3$, K_2PdCl_6, K_2PtCl_6, K_2SnCl_6, and K_2PbCl_4. The germanate was prepared by dissolving germanium in a mixture of 40% HF (H_2SiF_6-free) and '100 volume' hydrogen peroxide, and adding potassium carbonate.

The purity of the products was established by elemental analysis, and, in the case of those obtained by direct fluorination, from the loss in weight accompanying their formation. Results were in all cases within 5 parts per 1 000 of the theoretical values for K_2MF_6.

The hexafluorometallates were characterised by *X*-ray powder photography and i.r. spectroscopy (4 000—250 cm^{-1}). The results agree with those in the literature.[20] Cell constants obtained from the powder photographs are given in Table 1. There is some evidence that these may only refer to sub-cells of larger structural units.[21] The visible spectrum of the nickelate displayed the remarkable fine structure of the band in the green region reported by several workers.[22] The results of a more extensive study of the spectroscopy of this compound will be reported elsewhere.[23]

Table 1. Cell constants of the hexafluorometallates at room temperature

Compound	Symmetry	Cell constants (Å)
K_2NiF_6	Cubic	$a = 8.109$ [a]
K_2PdF_6	Hexagonal	$a = 5.77$, $c = 9.42$ [b]
K_2PtF_6	Trigonal	$a = 5.78$, $c = 4.66$ [b]
K_2GeF_6	Trigonal	$a = 5.63$, $c = 4.67$ [b]
K_2SnF_6	Trigonal	$a = 5.87$, $c = 4.69$ [b]
K_2PbF_6	Trigonal	$a = 6.01$, $c = 4.65$ [b]

[a] Obtained by extrapolation of high-angle doublets (accuracy *ca.* 0.1%). [b] Obtained by a least-squares fit of low-angle lines (accuracy *ca.* 1%).

Other reagents. Hydrated nickel sulphate was prepared by recrystallising the AnalaR material from dilute sulphuric acid. Analysis for nickel gave its composition as $NiSO_4{\cdot}6.95H_2O$. It was assumed to be a mixture of $NiSO_4{\cdot}6H_2O$ and $NiSO_4{\cdot}7H_2O$ (0.05 : 0.95). Germanium dioxide was purchased from Hopkin and Williams Ltd. and dried at 200 °C. Its *X*-ray powder pattern was that of the trigonal form;[24] while this does not exclude the possibility that some of the vitreous form was present, the proportion of the latter was taken to be small. Tin dichloride was made by refluxing reagent-grade material with acetic anhydride and distilling the product in hydrogen chloride. The tin content was >99.8% of the theoretical value for $SnCl_2$. Potassium hydrogendifluoride was prepared from AnalaR K_2CO_3 and 40% HF, and recrystallised from formamide.[25] Potassium fluoride was made from this by heating it. Analysis indicated that both compounds were >99.7% pure. Stock solutions of sulphuric acid (A), hydrochloric acid (B), hydrofluoric acid (C), hydrogen peroxide (D), and potassium hydroxide (E) were prepared from AnalaR reagents, and their composition determined by analysis (see below). Because of its use as a solvent for Sn^{II}, solution (B) was made up in

$$\text{(A) } H_2SO_4,aH_2O\ (a = 52.9) \quad \text{(B) } HCl,bH_2O\ (b = 423)$$

$$\text{(C) } HF,cH_2O\ (c = 3.22) \quad \text{(D) } H_2O_2,dH_2O\ (d = 4.90)$$

$$\text{(E) } KOH,eH_2O\ (e = 88.9)\ (+\ \delta CO_2)$$

boiled-out distilled water saturated with nitrogen. To minimize δ, (E) was made by dissolving well washed pellets in boiled-out distilled water.[26] Hydrazine solutions were made from hydrazine hydrate and analysed iodimetrically. Iodine was reagent grade. Other materials were AnalaR.

Calorimetry.—Heats were measured with the isoperibol calorimeter built by Pearse,[25] to which only minor modifications were made. To provide a more durable protection for the Dewar flask, a thin polypropylene vessel was made to fit snugly inside it. Metal parts in contact with liquid were plated with gold. Heats were measured at *ca.* 25 °C. The performance of the calorimeter was tested by measuring the heats of the same reactions as those used by Nelson and Pearse.[25] The results obtained agree with literature values to within, on average, 1.0 kJ mol^{-1}.

Heats of solution were measured in 265 (Ge) or 275 g of solvent, on *ca.* 0.002 (Pd, Pt, Ge) or *ca.* 0.003 mol (Ni, Sn, Pb) of M scale. When two substances were dissolved simultaneously, they were separated in the sample holder with a Polythene disc. If the liquid in the calorimeter was liable to aerial oxidation at any stage, the space above it was flushed with nitrogen at the beginning of the run. Results for each compound studied are presented below. They are expressed in the form $\bar{X} \pm 2s[n]$, where n is the number of determinations, $\bar{X}$ is their mean, and s the standard deviation of the mean.

Potassium hexafluoronickelate(IV). Two heats of solution were measured: (i) that of the nickelate and potassium sulphate in stock solution (A) to which some sulphuric acid and water had been added; (ii) that of hydrated nickel sulphate and KHF_2 in (A). The results (kJ mol^{-1}) are given below (n = 6.95).* The reaction taking place in (i) was assumed to be

$$K_2NiF_6(c) + \tfrac{1}{2}K_2SO_4(c) + [(x + \tfrac{1}{2})H_2SO_4,(xa + n + 1)\,H_2O] \quad \Delta H_\mathrm{i} = -159.3 \pm 0.8[3]$$

$$NiSO_4{\cdot}nH_2O(c) + 3KHF_2(c) + [xH_2SO_4,xaH_2O] \quad \Delta H_\mathrm{ii} = +129.6 \pm 0.3[3]$$

similar to that between K_3CuF_6 and dilute sulphuric acid, and its heat was corrected in the same way in which Nelson and Pearse [25] corrected the heat of the latter. The corrected heat, which is for the formation of 100% of oxygen in the reaction, is $\Delta H_\mathrm{i}' = -235.0$ kJ mol^{-1}. The heat of formation of the nickelate is given by equation (5), where ΔH_iii is the heat of

$$\begin{aligned}\Delta_f H^\ominus[K_2NiF_6(c)] = {}& 3\Delta_f H^\ominus[KHF_2(c)] + \Delta_f H^\ominus[NiSO_4{\cdot}nH_2O(c)] \\ & - \tfrac{1}{2}\Delta_f H^\ominus[K_2SO_4(c)] - \tfrac{1}{2}\Delta_f H^\ominus[H_2SO_4,2(n + 1)H_2O] \\ & - \Delta H_\mathrm{i}' + \Delta H_\mathrm{ii} - \Delta H_\mathrm{iii} \quad (5)\end{aligned}$$

mixing of $\tfrac{1}{2}[H_2SO_4,2(n + 1)H_2O]$ and $[xH_2SO_4,xaH_2O]$. This is calculated to be -0.95 kJ mol^{-1} from ref. 27.

Palladium difluoride. The heat of solution of palladium difluoride in a slight excess of aqueous hydrazine was measured. In a trial experiment, 100.8% of the Pd^{II} was found to be precipitated as the metal in this reaction. No hydrazine could be detected at the end of the calorimetric runs, and the excess was presumed to have decomposed. A correction was made for this on the assumption that the principal mode of decomposition under the conditions is reaction (6).[28] The heat of

$$3N_2H_4(aq) + 4HF(aq) \longrightarrow 4NH_4F(aq) + N_2(g) \quad (6)$$

this reaction was taken to be -224 kJ per mol of N_2H_4, from ref. 27. A correction was also made for the evaporation of water with the nitrogen evolved in the main reaction (-0.7 kJ per mol of PdF_2). The results (kJ mol^{-1}) were as follows. The heat of formation was calculated from equation (7).

$$PdF_2(c) + [\tfrac{1}{2}N_2H_4,zH_2O] \quad \Delta H = -170.9 \pm 10.7[3]$$

$$\begin{aligned}\Delta_f H^\ominus[PdF_2(c)] = {}& 2\Delta_f H^\ominus[HF(\text{in } \tfrac{1}{2}zH_2O)] - \\ & \tfrac{1}{2}\Delta_f H^\ominus[N_2H_4(\text{in } 2zH_2O)] - \Delta H \quad (7)\end{aligned}$$

Potassium hexafluoropalladate(IV). Two heats of solution were measured: (i) that of the palladate in a slight excess of aqueous hydrazine; (ii) that of KHF_2 in dilute hydrofluoric acid. In a trial experiment the proportion of palladium precipitated as the metal in reaction (i) was found to be 100.4%, and the composition of the gas evolved *ca.* 100% N_2. The solutions at the end of the calorimetric runs had no reducing power. The heats of reaction (i) were corrected in the same way as the heats for PdF_2, with an evaporation correction of -1.4 kJ per mol of K_2PdF_6. The results (kJ mol^{-1}) were as follows. The heat of formation of the palladate was calculated from equation (8).

$$K_2PdF_6(c) + [N_2H_4,zH_2O] \quad \Delta H_\mathrm{i} = -458.9 \pm 3.0[3]$$
$$2KHF_2(c) + [2HF,zH_2O] \quad \Delta H_\mathrm{ii} = +50.4 \pm 2.3[3]$$

$$\begin{aligned}\Delta_f H^\ominus[K_2PdF_6(c)] = {}& 2\Delta_f H^\ominus[KHF_2(c)] + 2\Delta_f H^\ominus[HF(\text{in } \tfrac{1}{2}zH_2O)] \\ & - \Delta_f H^\ominus[N_2H_4(\text{in } zH_2O)] - \Delta H_\mathrm{i} + \Delta H_\mathrm{ii} \quad (8)\end{aligned}$$

Platinum tetrafluoride. Two heats of solution were measured: (i) that of the fluoride and potassium fluoride in (B); (ii) that of K_2PtF_6 in (B). The resulting solutions (containing $PtCl_6^{2-}$ ions, see ref. 29) were assumed to be identical. The results (kJ mol^{-1}) were as follows. The heat of formation was calculated from equation (9).

$$PtF_4(c) + 2KF(c) + [xHCl,xbH_2O] \quad \Delta H_\mathrm{i} = -381.0 \pm 0.2[2]$$
$$K_2PtF_6(c) + [xHCl,xbH_2O] \quad \Delta H_\mathrm{ii} = -146.6 \pm 2.9[2]$$

$$\begin{aligned}\Delta_f H^\ominus[PtF_4(c)] = {}& \Delta_f H^\ominus[K_2PtF_6(c)] \\ & - 2\Delta_f H^\ominus[KF(c)] - \Delta H_\mathrm{i} + \Delta H_\mathrm{ii} \quad (9)\end{aligned}$$

Potassium hexafluoroplatinate(IV). The same procedure was used as for the palladate. In trial experiments, the proportion of the platinum precipitated as the metal in the reaction with hydrazine was found to be 99.8—100.3% and the gas evolved *ca.* 100% N_2. The slight excess of hydrazine used in the experiments was found to be destroyed. The corrected heat of reduction was $-443.9 \pm 3.3[3]$ kJ per mol of K_2PtF_6.

Potassium hexafluorogermanate(IV). Heats of solution were measured in a mixture (m) of (C) (260 g) and (D) (4.6 g). Three heats were measured: (i) that of germanium dioxide in (m) to which some (C) had been added; (ii) that of KHF_2 in solutions obtained as in (i); (iii) that of the germanate in (m) to which some water had been added. The hydrogen peroxide in (m) served no purpose in the calorimetry: it had been added with a view to the subsequent determination of $\Delta_f H^\ominus[GeF_2(c)]$. Tests showed that it did not decompose under the conditions used.[30] The results (kJ mol^{-1}) were as follows, where S_i is the solution from (i). The heat of formation of the germanate was calculated from equation (10), where ΔH_iv

$$GeO_2(c) + [xH_2O_2,(y + 2)HF,(z + 2c)H_2O] \quad \Delta H_\mathrm{i} = -118.6 \pm 1.3[3]$$
$$2KHF_2(c) + S_\mathrm{i} \quad \Delta H_\mathrm{ii} = +26.7 \pm 1.7[3]$$
$$K_2GeF_6(c) + [xH_2O_2,yHF,(z + 2c + 2)H_2O] \quad \Delta H_\mathrm{iii} = +24.2 \pm 1.0[3]$$

$$\begin{aligned}\Delta_f H^\ominus[K_2GeF_6(c)] = {}& 2\Delta_f H^\ominus[KHF_2(c)] + \Delta_f H^\ominus[GeO_2(c)] + \\ & 2\Delta_f H^\ominus[HF(\text{in } cH_2O)] - 2\Delta_f H^\ominus[H_2O(l)] - \\ & \Delta H_\mathrm{i} + \Delta H_\mathrm{ii} - \Delta H_\mathrm{iii} - \Delta H_\mathrm{iv} - \Delta H_\mathrm{v} \quad (10)\end{aligned}$$

is the heat of dilution of $[xH_2O_2,yHF,zH_2O]$ with $(2c + 2)H_2O$ and ΔH_v is the heat of mixing of the former with 2[HF, cH_2O]. On the assumption that $xH_2O_2 \equiv xH_2O$,[30] ΔH_iv and ΔH_v were calculated to be -3.8 and 0.0 kJ mol^{-1} respectively from the data of Johnson *et al.*[31]

Tin difluoride. Two heats of solution were measured: (i) that of SnF_2 and KCl in (B); (ii) that of $SnCl_2$ and KF in (B). The results (kJ mol^{-1}) were as follows. The heat of formation was calculated from equation (11).

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* Here and throughout this paper, species enclosed in square brackets represent the composition of a calorimetric solution.

$SnF_2(c) + 2KCl(c) + [xHCl,xbH_2O]\ \Delta H_i = +46.3 \pm 1.0[3]$
$SnCl_2(c) + 2KF(c) + [xHCl,xbH_2O]\ \Delta H_{ii} = -31.2 \pm 1.1[3]$

$$\Delta_f H^\ominus[SnF_2(c)] = \Delta_f H^\ominus[SnCl_2(c)] + 2\Delta_f H^\ominus[KF(c)] - 2\Delta_f H^\ominus[KCl(c)] - \Delta H_i + \Delta H_{ii} \quad (11)$$

Potassium hexafluorostannate(IV). Four heats of solution were measured: (i) that of KF and iodine in (B) containing KI [25 g per 275 g of (B)]; (ii) that of KF and $SnCl_2$ in solutions obtained as in (i); (iii) that of KCl and KI in the solvent used in (i); (iv) that of K_2SnF_6 in solutions obtained as in (iii). In (ii), a slight excess of iodine was used to make up the solvent. In trial runs, the iodine consumed was 99.4—99.9% of the theoretical amount required to oxidise the $SnCl_2$. The results (kJ mol^{-1}) were as follows, where S_i is the solution

$4KF(c) + I_2(c) + [xKI,yHCl,ybH_2O]$
$\Delta H_i \quad -22.1 \pm 0.7[3]$

$2KF(c) + SnCl_2(c) + S_i \quad \Delta H_{ii} = -203.5 \pm 1.4[3]$

$2KCl(c) + 2KI(c) + [xKI,yHCl,ybH_2O]$
$\Delta H_{iii} \quad +71.3 \pm 0.6[3]$

$K_2SnF_6(c) + S_{iii} \quad \Delta H_{iv} \quad -63.4 \pm 1.3[3]$

from (i) and S_{iii} from (iii). The heat of formation of the stannate was calculated from equation (12).

$$\Delta_f H^\ominus[K_2SnF_6(c)] = 6\Delta_f H^\ominus[KF(c)] + \Delta_f H^\ominus[SnCl_2(c)] - - 2\Delta_f H^\ominus[KCl(c)] - 2\Delta_f H^\ominus[KI(c)] - \Delta H_i - \Delta H_{ii} - \Delta H_{iii} - \Delta H_{iv} \quad (12)$$

Potassium hexafluoroplumbate(IV). Two heats of solution were measured: (i) that of the plumbate in (E) to which potassium hydroxide and water had been added; (ii) that of KHF_2 in (E) to which potassium hydroxide had been added. The precipitation of lead dioxide in (i) was fairly slow, but at the end of the calorimetric runs no lead could be found in the aqueous phase, and 99.3—99.4% of the lead in the plumbate could be found in the precipitate. The results (kJ mol^{-1}) were as follows [note that the addition of KOH in (ii) and of three

$K_2PbF_6(c) + [(x + 4)KOH,(xe - 1)H_2O]$
$\Delta H_i = -232.9 \pm 2.7[4]$

$3KHF_2(c) + [(x + 3)KOH,\ xeH_2O]$
$\Delta H_{ii} = -135.2 \pm 0.9[3]$

of the moles per mole of K_2PbF_6 in (i) was unnecessary]. The heat of formation was calculated from equation (13), where

$$\Delta_f H^\ominus[K_2PbF_6(c)] = 3\Delta_f H^\ominus[KHF_2(c)] - \Delta_f H^\ominus[PbO_2(c)] - \Delta_f H^\ominus[KOH(c)] - \Delta_f H^\ominus[H_2O(l)] - \Delta H_i - \Delta H_{ii} - \Delta H_{iii} \quad (13)$$

ΔH_{iii} is the heat of solution of $KOH(c) + H_2O(l)$ in $[(x + 3)KOH,xeH_2O]$. This was calculated to be −56.7 kJ mol^{-1}, from ref. 32. The lead dioxide formed in (i) was assumed to be similar to that used by Espada *et al.*[33] to determine $\Delta_f H^\ominus$.

Heats of Formation.—The values obtained for $\Delta_f H^\ominus[MF_2(c)]$ and $\Delta_f H^\ominus[K_2MF_6(c)]$ are given in Table 2, along with literature values for NiF_2,[34] GeF_2,[34] and PbF_2.[35] The heat of formation of $PtF_4(c)$ was found to be −681 kJ mol^{-1}. Ancillary values of $\Delta_f H^\ominus$ were taken from ref. 36, supplemented with values from refs. 25 [$KHF_2(c)$], 27 [$N_2H_4(aq)$, $NiSO_4\cdot 6H_2O(\alpha)$, $NiSO_4\cdot 7H_2O(c)$, $KOH(c)$], 33 [$PbO_2(c)$], and 37 [$GeO_2(c)$]. Values from ref. 27 were adjusted to make them consistent with the values for $OH^-(aq)$, $SO_4^{2-}(aq)$, and $K^+(aq)$ given in ref. 36. The heats of dilution of hydrazine solutions were taken to be small at the concentrations used.[38] For the heat of formation of $SnCl_2(c)$ the value of Vasil'ev *et al.*[39] was adopted.

Table 2. Standard enthalpies of formation at 25 °C of the difluorides and the potassium hexafluorometallates(IV) of the elements of the nickel triad and the germanium triad, and the standard enthalpies of dissociation of the hexafluorometallates at 25 °C according to equation (1)

M	$\Delta_f H^\ominus[MF_2(c)]$/ kJ mol^{-1}	$\Delta_f H^\ominus[K_2MF_6(c)]$/ kJ mol^{-1}	$\Delta_d H^\ominus$/ kJ mol^{-1}
Ni	−657.3 [a]	−1 963 [b]	+166 [c]
Pd	−495 [b]	−2 040 [b]	+405 [c]
Pt	(−340) [b,d]	−2 055 [b]	(+575) [c]
Ge	−658.6 [a]	−2 603 [b]	+805 [c]
Sn	−672 [b]	−2 575 [b]	+763 [c]
Pb	−677 [e]	−2 209 [b]	+392 [c]

[a] Ref. 34. [b] This work. [c] From equation (2). [d] Estimated from the heat of formation of $PtF_4(c)$ given in the text by means of equation (4). [e] Orthorhombic (α) form; from ref. 35 (*cf.* ref. 41*b*).

There are few determinations of $\Delta_f H^\ominus$ in the literature with which our values in Table 2 may be compared. Richards and Woolf[40] obtained a value of −2 528 kJ mol^{-1} for K_2SnF_6 by solution calorimetry in BrF_3; Richards[41a] obtained respectively −671 and −595 kJ mol^{-1} for monoclinic and orthorhombic[10] SnF_2 by the same method; Thourey *et al.*[41b] obtained −736 kJ mol^{-1} for SnF_2 by solution calorimetry in aqueous NaOH. From these and other comparisons we would judge that our values are accurate to within about ±50 kJ mol^{-1}.

Discussion

The values obtained for the standard enthalpy of dissociation of the potassium hexafluorometallates(IV) according to equation (1) ($\Delta_d H^\ominus$) are given in Table 2. These vary in the order Ni < Pd < Pt in the nickel triad and Ge > Sn > Pb in the germanium triad. The corresponding standard free energies are expected to vary in a similar way. Latimer's method[42] for the estimation of entropies gives $\Delta_d S^\ominus \approx 170$ J K^{-1} mol^{-1} for all M, from which $\Delta_d G^\ominus \approx \Delta_d H^\ominus - 51$ kJ mol^{-1} throughout. The sequences Ni < Pd < Pt and Ge > Sn > Pb correspond to the orders of stability generally observed in the two triads, and confirm the suitability of the reaction chosen for the study of these orders.

Consideration of Drago's First Argument.—Our task now is to re-express the variations in $\Delta_d H^\ominus$ in terms of the quantities employed by Drago.[4] In his first argument, he uses the sum of the ionization potentials for the removal of the outer *s* electrons of the atoms concerned, which for the atoms of the germanium triad is $I_3 + I_4$. An equation relating $\Delta_d H^\ominus$ to $I_3 + I_4$ may be derived from the cycle below. This gives

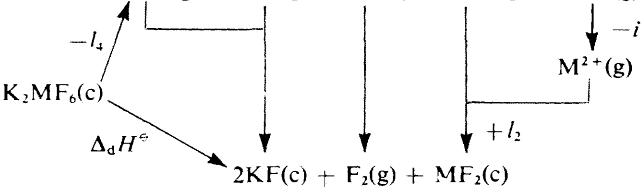

Table 3. Values of i, l_2, and l_4 for the elements of the nickel triad and the germanium triad

M	i^a/kJ mol^{-1}	l_2^b/kJ mol^{-1}	l_4^c/kJ mol^{-1}
Ni	(8 770)^d	−3 080	(−13 160)^d
Pd	(7 740)^d	−3 050	(−12 350)^d
Pt	(7 190)^d	(−3 060)^d	(−11 980)^d
Ge	7 725	−2 838	−12 520
Sn	6 886	−2 600	−11 400
Pb	7 178	−2 541	−11 260

[a] Calculated from equation (16). Ionization potentials (i.p.) were taken from the compilations of C. E. Moore ('Atomic Energy Levels,' Circular 467, Nat. Bur. Stand., Washington, 1949—1958, vols. I—III; 'Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra,' NSRDS-NBS 34, Nat. Bur. Stand., Washington, 1970) or estimated from data therein as follows. The fourth i.p. of nickel was obtained by comparing i.p.s for the manganese isoelectronic sequence with those for the potassium and the nickel sequence by the method of W. Lotz (*J. Opt. Soc. Am.*, 1967, **57**, 873). The fourth i.p. of palladium was obtained similarly by comparing the technetium sequence with the rubidium and the palladium sequence. The third i.p. of platinum was estimated by comparing the third i.p.s in the nickel group with those in the zinc group, and the fourth i.p. was obtained by a similar comparison with i.p.s in the gallium group. The results (I/hc) were: I_4(Ni), 448 000; I_4(Pd), 380 000; I_3(Pt), 239 000; I_4(Pt), 361 000 cm^{-1}. Some of the other ionization potentials involve an element of estimation, as an examination of their origin shows. [b] Calculated from equation (2.1) of ref. 43, p. 31. In this equation, the quantity corresponding to l_2 is $-[L_{298}(MX_n) + (n + 1)RT]$ ($X = F$, $n = 2$). The heats of formation of the difluorides were taken from Table 2, the heats of atomization of the elements from refs. 36 and 27, the ionization potentials from the same source as that used for i (footnote *a*), and the electron affinity of fluorine from H. Hotop and W. C. Lineberger (*J. Phys. Chem. Ref. Data*, 1975, **4**, 539). [c] Calculated in a similar way to l_2 (footnote *b*). Since K_2NiF_6, K_2PdF_6, and K_2PtF_6 are spin-paired (see, for example, A. G. Sharpe, *Adv. Fluorine Chem.*, 1960, **1**, 29), their formation from ordinary M^{4+} ions (^5D) involves a change of spin. The energy associated with this is included in l_4. [d] Value involves a major element of estimation. Approximate uncertainty ±100—200 kJ mol^{-1}.

equation (14), where l_4 is the enthalpy of dissociation of K_2MF_6 into gaseous ions, l_2 is the lattice enthalpy of MF_2,

$$\Delta_d H^\ominus = -l_4 + l_2 - i + \text{constant} \qquad (14)$$

and i is the enthalpy of ionization of M^{2+} to M^{4+} [equation (15)]. If electronic contributions to $H^\ominus_{298} - H^\ominus_0$ are neg-

$$i = N(I_3 + I_4) + (H^\ominus_{298} - H^\ominus_0)M^{4+}(g) - 2(H^\ominus_{298} - H^\ominus_0)e^-(g) - (H^\ominus_{298} - H^\ominus_0)M^{2+}(g) \qquad (15)$$

lected,[43] equation (15) reduces to equation (16), where $T = 298.15$ K.

$$i \approx N(I_3 + I_4) + 5RT \qquad (16)$$

Values for the quantities on the right-hand side of equation (14) are given in Table 3, and plotted in the Figure, along with the values of $\Delta_d H^\ominus$. The Figure shows that, if we confine our attention to the germanium triad alone, the data largely support Drago's conclusion that the stability order $Ge^{IV} > Sn^{IV} > Pb^{IV}$ does not derive from any inertness of the outer *s* electrons. The energy required to remove them, i, is smaller for lead than it is for germanium, and it is the fall in $-l_4$ that makes K_2PbF_6 less stable than K_2GeF_6. Only for the tin/lead pair is there any sign of i contributing to the fall in $\Delta_d H^\ominus$.

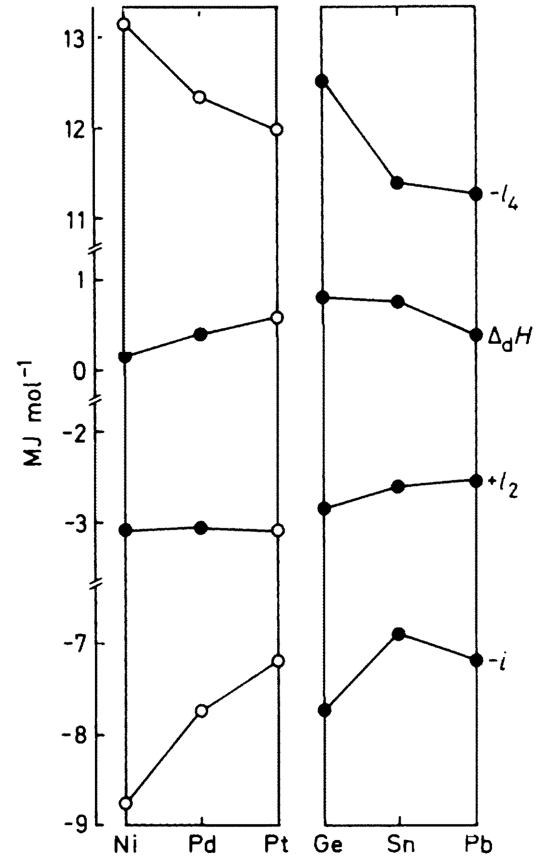

Figure. Plots of $\Delta_d H^\ominus$ and the variable quantities on the right-hand side of equation (14) for the elements of the nickel triad and the germanium triad. Values involving a major degree of estimation are indicated by open circles

When, however, we compare the data for the germanium triad with those for the nickel triad, we come to a very different conclusion. As the Figure shows, the fall in $-l_4$ is similar in the two cases. The difference between the stability orders in the two groups cannot therefore be associated with this term, and must be located somewhere else. The Figure shows that it lies in $-i$. In the nickel group, $-i$ rises steeply, and more than compensates for the fall in $-l_4$, whereas in the germanium group, it does not rise as much, and allows the fall in $-l_4$ to predominate. On this analysis, therefore, the stability order $Ge^{IV} > Sn^{IV} > Pb^{IV}$ is associated with the fact that i does not fall in the germanium group as severely as it does in the nickel group. That is, it is associated with the fact that *the outer* s *electrons do not become easier to remove to the extent that might have been expected.* Indeed, in going from tin to lead they become harder. The relative values of i, therefore, far from disproving the inert-pair effect, are precisely an expression of it.

On the current theory of many-electron atoms, the reason for the relatively small fall in i in the germanium group lies in the relatively high degree to which the outer *s* electrons penetrate the core. For all three elements, the just completed *d* shell is particularly highly penetrated, and for lead, the *f* shell also.[44] Indeed, it would seem to be the extra nuclear charge associated with the latter, coupled with the greater effect of relativity when the nuclear charge is higher (retarding the motion of electrons as they get near the nucleus, and causing them to spend longer in its vicinity), that lies behind the increase in i in going from tin to lead.[45]

Table 4. Heats of formation of the gaseous trichlorides of Group 3B elements at 25 °C, (*a*) from metal atoms in their ordinary state ($\Delta H^{\ominus}$), (*b*) from metal atoms in their sp^2 valence state (ΔH^*), as given by Drago [4] (normal type) and revised (italic)

Compound	$-\Delta H^{\ominus}$/ kcal mol^{-1}	P/ kcal mol^{-1}	$-\Delta H^*$/ kcal mol^{-1}
$AlCl_3$	213.2	83.67	296.9
	217.4 [a]	*108.2* [b]	*325.6*
$GaCl_3$	172.4	109.5	281.9
	173.2 [a]	*136.2* [b]	*309.4*
$InCl_3$	147.6	100.8	248.4
	147.6 [a]	*126.8* [b]	*274.4*
$TlCl_3$	109.4	108	217.4
	100.5 [a]	*169.8* [b]	*270.3*

[a] Ref. 27. The heat of sublimation of $TlCl_3$ was estimated in the same way as in ref. 4. [b] Calculated from the energy of the ^4P, the ^2D, and the ^2P level of the sp^2 configuration by the formula of W. Moffitt (*Rep. Prog. Phys.*, 1954, **17**, 173). Energy levels were taken from C. E. Moore ('Atomic Energy Levels,' Circular 467, Nat. Bur. Stand., Washington, 1949—1958, vols. I—III). For Al, Ga, and In, the position of the ^2D level relative to the ^4P and ^2P was taken to be the same as for Si^+, Ge^+, and Sn^+ respectively. For Tl, the splitting of the ^2D and the ^2P level relative to that of ^4P was taken to be the same as for Pb^+. An allowance was made for thermal population of states above the ground state in the ordinary atoms at 25 °C (Al, 0.2; Ga, 0.1; In, 0.0; Tl, 0.0 kcal mol^{-1}). This was obtained from the value of $(H^{\ominus}_{298}-H^{\ominus}_{0})$M(g) given in ref. 27. Similar values of P have been given by H. O. Pritchard and H. A. Skinner (*Chem. Rev.*, 1955, **55**, 745).

Consideration of Drago's Second Argument.—Drago's second argument is based on an analysis of the heats of formation of the gaseous trichlorides of Group 3B elements from metal atoms and chlorine molecules [equation (17)]. Apart from a

$$M(g) + \tfrac{3}{2}Cl_2(g) \xrightarrow{\Delta H^{\ominus}} MCl_3(g) \qquad (17)$$

constant, $-\Delta H^{\ominus}$ is three times the bond energy (B) in MCl_3 [equation (18)]. Drago divided $\Delta H^{\ominus}$ into two components,

$$-\Delta H^{\ominus} = 3B - 3\Delta_f H^{\ominus}[Cl(g)] \qquad (18)$$

the energy required to promote the metal atoms into their sp^2 valence state (P), and the heat of formation of the trichloride from atoms in this state (ΔH^*). The latter is related to the intrinsic bond energy (B^*) by a similar equation to (18). Drago's results are shown in Table 4 (ordinary type). Since the values of P change relatively little in going down the group, he concluded that the fall in bond energy cannot be due to any inertness of the s electrons.

There are two problems with Drago's analysis, however. The first is that he did not have available the spectroscopic data needed to calculate P for thallium, and the estimate he used was too low. Revised values of P are given in Table 4,† along with more recent values of $-\Delta H^{\ominus}$ (in italic type). On the new data, the variation in P makes a significant contribution to the variation in $-\Delta H^{\ominus}$. Indeed, about half the fall in $-\Delta H^{\ominus}$ now comes from the increase in $s^2p \rightarrow sp^2$ promotion energy.

A second problem with the analysis is that the assumption that the intrinsic bond energies are unaffected by any inertness of the s electrons is not necessarily correct. Inertness of these electrons implies a smaller orbital than would otherwise have been expected, and this could mean that the outer s and p orbitals are less compatible for bonding conjointly than they usually are. The fall in intrinsic bond energy in the trivalent state may thus include some of the effect of the inert pair.

Drago's Third Argument.—In addition to the two arguments already discussed, Drago presents an analysis of the standard electrode potentials for the M^{3+}/M couples of Group 3B elements. As he points out, however, the relevant potentials for the consideration of the inert-pair effect are those for M^{3+}/M^+. An analysis of these might be expected to lead to the same conclusion as that reached from a study of reaction (1).

Conclusions

From the above discussion, the classical rationalisation of the development of a valency two less than the group valency among the heavier members of Groups 3B—8B of the Periodic Table would seem to be essentially correct. The outer s electrons of the atoms of these elements do seem to be relatively tightly bound, and this does seem to lie behind the stability of the lower valency. This does not mean that these electrons are completely inactive; they can affect the stereochemistry of lower-valent compounds, and contribute to the bonding in the higher-valent ones. Even so, they are inactive enough to have an effect on valency, and thus may be fairly described as a 'reluctant' pair, if not a positively 'inert' one.

Acknowledgements

We thank the S.E.R.C. for a research studentship (to K. G. G. H.), I.C.I. for the gift of a fluorine generator, Dr. R. V. Pearse for developing the calorimeter and some of the techniques used, Mr. G. Collier for help with the spectroscopic measurements, and Drs. A. B. Blake, P. G. Francis, and Charlotte E. Moore (Sitterly) for advice. We also thank the referees for drawing our attention to ref. 41.

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Received 21*st September* 1983; *Paper* 3/1664