# Thermodynamics of the Actinoid Elements. Part V.[1] Enthalpies and Gibbs Energies of Formation of some Protactinium-(IV) and -(V) Halides

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The following enthalpies of solution (kJ mol$^{-1}$) have been measured: protactinium metal in oxygen-free 12M-HCl–0.05M-HF to yield Pa$^{IV}$, −666 ± 13, and in 12M-HCl–0.05M-HF containing oxygen to yield Pa$^{V}$, −817 ± 15; $PaCl_4$(s) in oxygen-free 12M-HCl–0.05M-HF and 12.05M-HCl, −160.9 ± 2.6 and −105.9 ± 2.5, respectively; and $PaCl_5$(s) and $PaBr_5$(s) in 12M-HCl −0.05M-HF, −203.2 ± 3.0, and −242.0 ± 5.0, respectively. Combination of these values with previously reported enthalpies of solution for other protactinium compounds and with other thermodynamic data yields the following enthalpies of formation (in kJ mol$^{-1}$) at 298 K: Pa$^{IV}$ in 1 and 6M-HCl, −620 ± 13 and −608 ± 13, respectively; Pa$^{V}$ in 12M-HCl–0.05M-HF, −672 ± 15; $PaF_4$(s), −1 918 ± 30; $PaCl_4$(s), −1 045 ± 13; $PaBr_4$(s), −827 ± 13; $PaCl_5$(s), −1 143 ± 15; $PaBr_5$(s), −865 ± 16; and $Cs_2[PaCl_6]$, −2 011 ± 13. By use of suitably interpolated entropy and heat-capacity data, thermodynamic functions associated with formation of the halides have been calculated as a function of temperature.

Most of the available data on the thermodynamics of protactinium and its compounds are based on values interpolated from corresponding thorium and uranium species. Using such interpolated values for the enthalpies of formation of $PaO_2$(s) and $PaF_4$(s), Laser and Merz [2] obtained enthalpies and entropies of formation of various oxides, fluoride oxides, and fluorides of protactinium from the behaviour of carrier-free $^{233}$Pa in the high-temperature fluorination of neutron-irradiated thorium compounds. We have previously [3,4] measured the enthalpies of solution of $PaCl_4$(s), $PaBr_4$(s), and $Cs_2[PaCl_6]$(s) in 1 and 6M-HCl and, using an estimated value for the enthalpy of formation of aqueous Pa$^{IV}$ and our enthalpy of solution of $PaCl_4$(s), Ferris [5] estimated the enthalpy of formation of $PaCl_4$(s).† From this value, and the distribution coefficients of Pa$^{IV}$ between molten lithium halides and liquid bismuth, he obtained thermodynamic functions associated with the formation of the protactinium tetrahalides together with activity coefficients of Pa$^{IV}$ in liquid bismuth. Lorenz and Scherff [6] studied the carbothermic reduction of $PaO_2$ by measuring the CO partial pressure as a function of temperature and obtained an expression for the Gibbs energy of formation of the dioxide based on an estimated function for the Gibbs energy of formation of the carbide produced in the reaction. Knoch and Schieferdecker [7] reported thermodynamic data associated with the oxidation of the dioxide into the pentaoxide at high temperature from oxygen-pressure measurements over an oxide phase of varying composition. Weigel *et al.* obtained, from vapour-pressure measurements, thermodynamic data associated with the sublimation, fusion, and vaporisation of $PaCl_5$ [8] and $PaBr_5$.[9]

The fact that no experimental enthalpy of formation of any protactinium compound has been reported so far is probably due to a combination of several factors including the relative scarcity of the element, the radioactivity of its isotopes and, above all, the hydrolytic behaviour of the quinquevalent state combined with the existence of a fairly unstable quadrivalent state. We report here direct determinations of the enthalpy of solution of protactinium metal and of $PaCl_4$, $PaCl_5$, and $PaBr_5$ in 12M-HCl–0.05M-HF solutions (oxygen-free where the quadrivalent state is involved). Combination of these data with our earlier results [3,4] yields the enthalpy of formation of Pa$^{IV}$ in 1 and 6M-HCl and of the various quadrivalent compounds studied. The enthalpy of formation of Pa$^{V}$ in 12M-HCl–0.05M-HF has also been obtained, together with the enthalpies of formation of the pentahalides. By use of suitably interpolated entropy and heat-capacity data, thermodynamic functions associated with the formation of a number of these compounds have been calculated as a function of temperature above 298 K.

## EXPERIMENTAL

*Instruments and Operating Procedure.*—The microcalorimeter has been described [10] and calibration runs have been published.[11,12] To eliminate corrosion by the 12M-HCl–0.05M-HF solutions used in this study the tantalum calorimeter chamber was covered with a thin layer of paint made of Apiezon W in toluene and the outside face of the Pyrex calorimeter sample holders was painted with a suspension

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† 1M = 1 mol dm$^{-3}$, 1 atm = 101 325 Pa.

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[9] F. Weigel, G. Hoffmann, V. Wishnevsky, and D. Brown, *J.C.S. Dalton*, 1974, 1473.

[10] J. Fuger, Annual Reports Euratom, Univ. Liège Research Contract, 011—64 TPUB, 1965—1966.

[11] J. Fuger, D. Brown, and J. F. Easey, *J. Chem. Soc.* (*A*), 1969, 2995.

[12] J. Fuger, J. C. Spirlet, and W. Muller, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 709.

of paraffin in cyclohexane. These coatings were shown to have a negligible effect on the performance of the instrument. All compounds were handled in dry oxygen-free atmospheres (argon for the metal and nitrogen for the compounds). In every case the atmosphere of the boxes used for filling and weighing the samples contained less than 10 p.p.m. water vapour (Alnor Dew-point meter, Casella, London) and less than 10 p.p.m. oxygen (potential drop across a $ZrO_2$ membrane [13]). Samples were weighed with a Cahn (Paramount, California) model Gram electric microbalance with an ultimate sensitivity of 0.1 μg. Samples weights were reduced to weights *in vacuo*.

For the experiments involving $Pa^{IV}$ the calorimetric solutions were carefully deaerated by prolonged flushing with pure argon which had been saturated with HCl and water vapour by contacting it with solutions of the same concentration, and the calorimeter was assembled in an atmosphere of pure argon. When dissolving protactinium metal to the quinquevalent state, and the pentahalides, the calorimeter was assembled in an atmosphere of pure oxygen. The acid concentrations of the calorimetric solutions were established by titration of a sample collected from each solution at the time of assembling the calorimeter. For the metal dissolution experiments, all solutions were $12.05 \pm 0.2$M. For dissolution of the halides, the average concentration of the solutions was the same but the fluctuation from run to run was kept less than $\pm 0.05$M. It was also shown by titration that the concentration of the solutions was unchanged ($\pm 0.05$M) after several hours in the calorimeter. In the case of quadrivalent species the visible–u.v. spectra of the calorimeter solutions were regularly recorded on a Cary 14 H spectrophotometer in order to confirm the absence (less than 2%) of oxidation to the quinquevalent state. It was also shown in separate experiments that on dissolution of the metal in aerated solutions the protactinium was quantitatively (uncertainty $< 2\%$) oxidised to the quinquevalent state within less than 5 min.

*Units and Limits of Error.*—Throughout this paper the joule (J) is used as energy unit. All literature data originally reported in calories, or its multiples, were recalculated using the conversion factor 1 cal = 4.1840 J. The $^{12}C$ scale of atomic weights was used to calculate the molecular weights; for protactinium, the atomic weight was assumed to be 231.05.

Calorimetric measurements are reported for $298.15 \pm 0.05$ K. Error limits reported on the mean of several identical measurements are based on the 95% confidence interval [14] but also include estimated systematic errors arising from the use of corrosive solutions of high vapour pressure.

For the dissolution of protactinium metal in 12M-HCl–0.05M-HF solutions the enthalpy effect associated with the saturation of the evolving hydrogen amounts to *ca.* 25 kJ per mol of dissolved protactinium if one assumes that $H_2$ evolves quantitatively and saturates fully with hydrochloric acid and water vapour at the partial pressures in tables.[15] In these calculations the partial pressure due to the small concentration of hydrofluoric acid was neglected. This effect varies rapidly with the acid concentration: it amounts to 24.2 and 25.6 kJ per mol of dissolved protactinium in 12 and 12.1M-HCl solutions, respectively. Since we had no proof of quantitative hydrogen evolution and saturation, we accepted a 30% error on this correction which leads to a 1.3% error on the enthalpy of solution of protactinium to $Pa^{IV}$ and 1% in the case of dissolution to $Pa^{V}$. This correction (as well as that for the gas contained in the sample holders, see below) was applied for each measurement according to the exact acid concentration of that run. The presence in the metal samples of a high-temperature form (discussed below) which, in addition, is not necessarily distributed homogeneously leads to accepted supplementary errors of 0.6 and 0.5% on the enthalpies of solution to $Pa^{IV}$ and $Pa^{V}$, respectively, compared to results reported for the dissolution of the standard form of the metal. No allowance was made, however, for the fact that this high-temperature form could be stabilised by non-negligible amounts of an undetected impurity.

In addition to the errors inherent in the dissolution of the metal samples, others arise which are common to the dissolution of any sample in these concentrated and corrosive media. Saturation by the solvent of the dry nitrogen and argon contained in the Pyrex sample holders (of known volume) leads to a correction which may reach 2% of the heat effect. Assuming again this gas evolution and saturation to be complete within 30%, a supplementary error of 0.6% on the total heat is introduced. Finally, the release of the sample in the solution by breaking the bottom of the Pyrex holders initiates corrosion of the inner face of the holder. Although the extrapolation procedure in calculating the heat released on dissolution of the sample accounts for this effect (assuming a constant corrosion rate), we feel it advisable to include a supplementary error of *ca.* 1% of the total heat evolved. Dissolution of $PaCl_4$ in 12.05M-HCl is distinctly slower than in the presence of hydrofluoric acid and may take several minutes, depending on the size of the pieces. This may be the cause of an additional error of *ca.* 0.5% of the measured heats.

Combination according to a standard procedure [16] of the above errors with the statistical error on the mean of each series of results leads to the reported uncertainty limits. When combining our data with those from other sources, we used the error stated by the author. The errors given for the calculated enthalpies of formation were obtained from those for the individual terms of the thermodynamic cycle used. Unless otherwise specified, auxiliary thermodynamic data used in these calculations are taken from those of Wagman *et al.*[17]

*Materials and Reagents.*—The metal samples were presented to us by the late Professor B. B. Cunningham, Lawrence Berkeley Laboratory, University of California. Their preparation, on the scale of a few milligrams, has been described in detail by Cunningham [18] and by Dod.[19] Copper-spark analysis showed that all impurities were

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[18] B. B. Cunningham, Third Internat. Protactinium Conf., Schloss Elmau bei Mittenwald, 1969, Report BMBW-FBK 71—17, p. 14.1.

[19] R. Dod, U.S. Report-LBL 659, 1972, and personal communication.

below detection limits * except for Ca and Mg in preparations (I) (LBL-337.71; 5 mg) (0.02%), (II) (LBL-337.58,59,60; 10.5 mg) (0.02%), and (III) (LBL, arc melted at LASL; 8.5 mg) (0.1% each). No analysis was made for the light elements such as H, C, O, and N and in view of the error limits accepted for our measurements no correction was made for the presence of the detected impurities. In addition to the above preparations a number of unanalysed protactinium pieces were used in the experiments made to select the dissolving medium.

As pointed out by Dod [19] most of his metal samples contain a high-temperature, quenched-in, face-centred cubic (f.c.c.) phase [20] of 20—80% abundance relative to the room-temperature, standard, body-centred (b.c.) tetragonal phase.[21] It has been reported, however, that cold working of the samples adequately converts them [19,20] into the standard form. These observations were accepted without further checking on samples (I) and (II) since it was assumed that cutting of the calorimeter samples from the main pieces would be an effective cold working. However, *X*-ray examination of a portion of sample (III) showed that neither severe deformation, nor heating to 1 075 K for 24 h (in a tantalum mesh, in a high vacuum) followed by slow cooling, nor cycling the sample from room to liquid-nitrogen temperature was adequate to eliminate completely the f.c.c. phase which remained present to the extent of *ca.* 30% in the b.c. tetragonal phase. Other authors [22] have recently made similar observations.

The halides were prepared in duplicate or triplicate according to published methods [23,24] and stored in evacuated silica tubes prior to use. The $PaCl_4$ samples were used as such but, in view of their extreme hygroscopicity, the pentahalides were resublimed in the evacuated tubes immediately prior to use. Sublimation temperatures were 510—520 K for $PaCl_5$ and 575—600 K for $PaBr_5$. The analytical procedures [23,24] have been described previously. *X*-Ray powder photographs were recorded for each compound and the absence of extraneous lines was verified. Analyses and *X*-ray data on the pentahalides were obtained immediately after preparation and not on the resublimed samples prior to use. Protactinium pentabromide is dimorphic but it has been shown that by sublimation *in vacuo* only the monoclinic β form is obtained.[25,26] This form has a dimeric structure very similar to that of $UCl_5$.[27]

All reagents used were of analytical grade. Concentrated hydrobromic acid solutions were obtained by saturating with HBr(g) commercially available analytical grade hydrobromic acid solutions. These were then adjusted by dilution to the desired concentration.

## RESULTS AND DISCUSSION

According to the observations of Cunningham and his co-workers [18] the selection of a medium in which protactinium dissolves rapidly and quantitatively appeared to be difficult. We examined the dissolution of protactinium samples (a few hundred micrograms) in oxygen-free hydrochloric acid solutions of various concentrations under a microscope. In 9M-HCl completion of the reaction took more than 10 min, while in 12M-HCl the piece disintegrated in *ca.* 2 min. However, as with the dissolution of other light actinoid metals [11,28—31] in hydrochloric acid, a black residue remained after reaction. Contrary to observations made with other actinoids, the addition of $Na_2[SiF_6]$ (*ca.* 0.005M) was not sufficient to eliminate the residue, but addition of 0.05M-HF was very effective. Increased HF concentration (a factor of 10) resulted in a marked decrease in the dissolution rate, possibly due to transient formation of a protective layer of protactinium tetrafluoride. In this series of preliminary experiments we also observed that $PaCl_4$ samples rapidly dissolved in 12M-HCl–0.05M-HF to yield $Pa^{IV}$ concentrations in the $10^{-3}$M range without visible residue. Similar experiments with $ThCl_4$ ($<2 \times 10^{-3}$M) resulted in an immediate precipitate of the tetrafluoride hydrate, whereas $UCl_4$ dissolved easily to reach concentrations of at least $10^{-2}$M. This marked trend is obviously related to the formation of halide complexes. Aerated 12M-HCl–0.05M-HF was found to dissolve protactinium metal to the quinquevalent state rapidly and completely and also to completely dissolve $PaCl_5$.

Table 1 shows results obtained for the dissolution of the metal in the calorimeter. In oxygen-free solutions, the reaction can be represented by equation (1) in which

$$\mathrm{Pa(s,\ \alpha\text{-}\beta)} + [a\ \mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] \xrightarrow{\Delta H_1} [\mathrm{PaCl_4},\ (a-4)\mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] + 2\mathrm{H_2}\ (g) \quad (1)$$

$b/a = 3.43$, $a/c = 240$, and $a = ca.\ 24\,000$; $\Delta H_1$ thus represents the enthalpy of formation of $Pa^{IV}$ in that medium, *viz.* $\Delta H_1 = \Delta H_f$ ($Pa^{IV}$, 12M-HCl–0.05M-HF) $= -666 \pm 13$ kJ mol$^{-1}$. It should be noted, however, that since the metal samples do not represent the pure standard form of the metal at 298 K, the various enthalpies of formation deduced will not be standard enthalpies. The difference is not expected to be large ($<4$ kJ mol$^{-1}$), unless an undetected impurity present in

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* Detection limits by this technique are: 0.01 (Ag, Al, Be, Ca, Cr, Eu, Fe, Ga, La, Mg, Mn, Mo, Nb, Ni, Sc, Si, Sr, Ti, V, Yb, Y, and Zr); 0.05 (Bi, Co, Er, Gd, Ge, Hf, Ho, In, Lu, and Rh); 0.1 (Am, Ce, Dy, Nd, Pb, Pd, Pt, Re, Sn, Ta, W, and Zn); 0.5 (As, Cd, Ir, Pr, and U); and 1 μg (Au, Ba, K, Na, and Sb). For the analyses, samples (50—100 μg) cut from the main pieces were used.

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[29] E. F. Westrum, jun., and LeRoy Eyring, *J. Amer. Chem. Soc.*, 1952, **74**, 2045.

[30] G. R. Argue, E. E. Mercer, and J. W. Cobble, *J. Phys. Chem.*, 1961, **65**, 2041.

[31] G. C. Fitzgibbon, D. Pavone, and C. E. Holley, jun., *J. Chem. Thermodynamics*, 1969, **1**, 267.

significant amounts contributes to the stabilisation of the high-temperature phase. The value of *a* above is approximately the same for all the reactions reported here, the protactinium concentration being of the same order of magnitude.

TABLE 1

Enthalpies of solution of protactinium metal ($\alpha + \beta$ phases) in 12M-HCl–0.05M-HF at 298.15 ± 0.05 K

| Preparation no. | Expt. no. | Wt. of sample mg | $10^4$ Concentration of actinoid in solution mol $l^{-1}$ | Enthalpy effect J | $\Delta H$ [a] kJ $mol^{-1}$ |
|---|---|---|---|---|---|
| (*a*) To $Pa^{IV}$ (oxygen-free solutions) | | | | | |
| (I) | (1) | 0.572 | 2.913 | 1.604 | −674 |
| (I) | (2) | 0.756 | 3.847 | 2.112 | −672 |
| (I) | (3) | 0.951 | 4.842 | 2.629 | −664 |
| (I) | (4) | 1.034 | 5.267 | 2.966 | −688 [b] |
| (I) | (5) | 1.210 | 6.161 | 3.346 | −664 |
| (II) | (6) | 1.303 | 6.637 | 3.607 | −664 |
| (II) | (7) | 1.330 | 6.775 | 3.683 | −664 |
| (II) | (8) | 1.621 | 8.254 | 4.448 | −658 |
| | | | | Average | −666 ± 13 [c] |
| (*b*) To $Pa^{V}$ | | | | | |
| (II) | (1) | 1.104 | 5.623 | 3.827 | −828 |
| (II) | (2) | 0.790 | 4.023 | 2.683 | −813 |
| (II) | (3) | 1.413 | 7.197 | 4.832 | −816 |
| (III) | (4) | 0.704 | 3.586 | 2.375 | −805 |
| (III) | (5) | 0.819 | 4.170 | 2.840 | −827 |
| (III) | (6) | 0.559 | 2.845 | 1.966 | −839 |
| (III) | (7) | 0.516 | 2.625 | 1.737 | −806 |
| (III) | (8) | 0.403 | 2.056 | 1.353 | −800 |
| | | | | Average | −817 ± 15 [c] |

[a] Corrected individually for the vaporisation of the solvent by the evolved hydrogen. [b] Discarded from average; discrepancy due to partial oxidation to $Pa^{V}$. [c] See text for error limits.

In oxygenated solutions immediate oxidation to the quinquevalent state occurred, the assumed reaction being described by equation (2). However, consideration has been given to the possibility of the occurrence of other oxidation schemes. Morss and Haug [32] showed

$$[\mathrm{PaCl_4},\ \tfrac{1}{4}\mathrm{O_2},\ (a-4)\mathrm{HCl},\ b\mathrm{H_2O},\ c\ \mathrm{HF}] \xrightarrow{\Delta H_2} [\mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ (b+\tfrac{1}{2})\mathrm{H_2O},\ c\ \mathrm{HF}] \quad (2)$$

that the oxidation of $Eu^{II}$ in oxygenated 0.1M-HCl proceeds almost quantitatively through the formation of hydrogen peroxide, according to equation (3). In concentrated HCl solutions, however, $H_2O_2$, if formed,

$$\mathrm{Eu^{2+}(aq)} + \tfrac{1}{2}\mathrm{O_2(aq)} + \mathrm{H^+(aq)} \longrightarrow \mathrm{Eu^{3+}(aq)} + \tfrac{1}{2}\mathrm{H_2O_2(aq)} \quad (3)$$

would oxidise HCl to chlorine which would itself serve as oxidising agent for the $Pa^{IV}$ ions. We verified in out-of-calorimeter experiments that no oxidising agent such as $H_2O_2$ or chlorine was formed as a result of the dissolution of protactinium metal in oxygenated 12M-HCl–0.05M-HF solutions, as shown by the absence of oxidation of iodide ion to iodine. In these tests, carbon tetrachloride was used as extractant for the iodine. By adding small amounts of dilute ($<10^{-3}$M) $H_2O_2$ solutions to the HCl solutions, we ascertained that the sensitivity of the calorimetric test was such that less than 2% of the dissolving protactinium could have been oxidised by a process involving the formation of $H_2O_2$. At this level, the occurrence of such a process would have a negligible (less than 1 kJ $mol^{-1}$) effect on the measured heat.

As in the case of the quadrivalent species there is no definite information as to the ionic form of $Pa^{V}$ in 12M-HCl–0.05M-HF solutions. On the basis of the results of Guillaumont [33] one can assume the presence of a $[PaX_8]^{3-}$ species, $Pa^{V}$ being mainly co-ordinated by fluoride ions. Accepting the reaction sequence (1) and (2) above, the enthalpy of formation of $Pa^{V}$ in this medium according to equation (4) can be obtained by subtracting

$$\mathrm{Pa(s,\alpha-\beta)} + [a\ \mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] \xrightarrow{\Delta H_4} [\mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] + \tfrac{5}{2}\mathrm{H_2(g)} \quad (4)$$

from the heat of solution, $\Delta H_1 + \Delta H_2$, the partial molar enthalpy of formation of 0.5 mol of water in the medium considered, from gaseous hydrogen and dissolved oxygen, according to equation (5). For the purpose of its

$$\tfrac{1}{2}\mathrm{H_2(g)} + [\tfrac{1}{4}\mathrm{O_2},\ \mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] \xrightarrow{\Delta H_5} [\mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ (b+\tfrac{1}{2})\mathrm{H_2O},\ c\ \mathrm{HF}] \quad (5)$$

evaluation, reaction (5) can be considered as a combination of (6)—(8). Here $4\Delta H_6$ represents the enthalpy of solution of 1 mol of oxygen in 12M-HCl–0.05M-HF,

$$\tfrac{1}{4}\mathrm{O_2(g)} + [\mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] \xrightarrow{\Delta H_6} [\tfrac{1}{4}\mathrm{O_2},\ \mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] \quad (6)$$

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{4}\mathrm{O_2(g)} \xrightarrow{\Delta H_7} \tfrac{1}{2}\mathrm{H_2O\ (l)} \quad (7)$$

$$\tfrac{1}{2}\mathrm{H_2O(l)} + [\mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ b\ \mathrm{H_2O},\ c\ \mathrm{HF}] \xrightarrow{\Delta H_8} [\mathrm{PaCl_5},\ (a-5)\mathrm{HCl},\ (b+\tfrac{1}{2})\mathrm{H_2O},\ c\ \mathrm{HF}] \quad (8)$$

neglecting the influence of the small $Pa^{V}$ concentration. This value was not measured directly; we calculated it from the solubility of oxygen as a function of the acid concentration at different temperatures. Such solubility studies have been carried out by Geffcken [34] at 288 and 298 K for various media, including HCl (up to 2M), $HNO_3$ (up to 2M), and $H_2SO_4$ (up to 2.5M). It was shown that, in all these cases, the solubility decreases fairly smoothly with increasing acid concentration and that the difference in solubility between 288 and 298 K at a given acid concentration decreased also with increasing concentration. Extrapolation of the data to 12M-HCl (neglecting the effect of 0.05M-HF) yielded a solubility of *ca.* $5.8 \times 10^{-4}$ mol $l^{-1}$ $O_2$ under 1 atm of oxygen at both temperatures, giving $4\Delta H_6 = 0 \pm 8$ kJ (mol $O_2)^{-1}$. The error limits for this result arise from the uncertainty in the extrapolated solubilities. The quantity $\Delta H_7$ is the standard enthalpy of formation of 0.5 mol of water, thus

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[32] L. R. Morss and H. Haug, *J. Chem. Thermodynamics*, 1973, **5**, 513.

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[34] G. Geffcken, *Z. phys. Chem.*, 1904, **49**, 257.

$2\Delta H_7 = \Delta H_f^\ominus$ ($H_2O$, l) = −285.83 kJ (mol $H_2O$)$^{-1}$. Neglecting the influence of the HF and of the protactinium species, $2\Delta H_8$ represents the relative partial molar enthalpy of water in 12.05M-HCl. As usual this value is obtained from the relative apparent enthalpy and the relative partial molar enthalpy of HCl in that medium, thus $2\Delta H_8 = -4.58 \pm 0.05$ kJ (mol $H_2O$)$^{-1}$. Therefore, we have $2\Delta H_5 = -2\Delta H_6 + 2\Delta H_7 + 2\Delta H_8 = -290.4 \pm 4$ kJ (mol $H_2O$)$^{-1}$ (A) and $\Delta H_f$(Pa$^{V}$, 12M-HCl–0.05M-HF) = $\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_5 = -672 \pm 15$ kJ mol$^{-1}$ (B).

In order to obtain the enthalpy of formation of $PaCl_4$(s), according to equation (9), the enthalpy of solution of

$$\text{Pa(s, }\alpha\text{—}\beta) + 2Cl_2\text{ (g)} \xrightarrow{\Delta H_9} PaCl_4\text{(s)} \qquad (9)$$

this compound in 12M-HCl–0.05M-HF according to (10)

$$PaCl_4\text{(s)} + [a\text{ HCl, }b\text{ }H_2O\text{, }c\text{ HF}] \xrightarrow{\Delta H_{10}} [PaCl_4\text{, }a\text{ HCl, }b\text{ }H_2O\text{, }c\text{ HF}] \qquad (10)$$

was measured. These results are reported in Table 2 together with those for the enthalpy of solution of the same compound in 12.05M-HCl. Using equation (11),

$$2H_2\text{(g)} + 2Cl_2\text{(g)} + [PaCl_4\text{, }(a-4)\text{HCl, }b\text{ }H_2O\text{, }c\text{ HF}] \xrightarrow{\Delta H_{11}} [PaCl_4\text{, }a\text{ HCl, }b\text{ }H_2O\text{, }c\text{ HF}] \qquad (11)$$

the enthalpy of formation of $PaCl_4$(s) is obtained as (C),$\Delta H_f$($PaCl_4$,s) = $\Delta H_9 = \Delta H_1 - \Delta H_{10} + \Delta H_{11}$: $\frac{1}{4}\Delta H_{11}$ thus represents the partial molar enthalpy of formation of HCl in 12M-HCl–0.05M-HF. Neglecting the influence of low HF and actinoid concentrations, we used the partial molar enthalpy of formation in 12.05M-HCl. As usual, this value is obtained from the enthalpy of formation of infinitely dilute acid and the relative apparent molar enthalpy of the 12.05M-acid. Thus we assumed $\frac{1}{4}\Delta H_{11} = H_f$ (HCl, 12.05M-HCl) = $-134.88 \pm 0.30$ kJ mol$^{-1}$.

TABLE 2

Enthalpies of solution of $PaCl_4$ at 298.15 ± 0.05 K

| Preparation no. | Expt. no. | Wt. of sample / mg | $10^3$ Concentration of compound in solution / mol l$^{-1}$ | Enthalpy effect / J | $\Delta H$ / kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| (*a*) In 12M-HCl–0.05M-HF ($O_2$-free) | | | | | |
| (I) | (1) | 4.864 | 1.535 | 2.074 | −159.0 |
| (I) | (2) | 4.129 | 1.303 | 1.809 | −163.3 |
| (I) | (3) | 7.112 | 2.244 | 3.050 | −159.9 |
| (II) | (4) | 3.026 | 0.955 | 1.308 | −161.2 |
| (II) | (5) | 2.658 | 0.839 | 1.149 | −161.1 |
| | | | | Average | −160.9 ± 2.6 * |
| (*b*) In 12.05M-HCl ($O_2$-free) | | | | | |
| (I) | (1) | 6.077 | 1.917 | 1.733 | −106.4 |
| (II) | (2) | 4.419 | 1.394 | 1.247 | −105.2 |
| (III) | (3) | 3.760 | 1.186 | 1.060 | −105.1 |
| (III) | (4) | 3.656 | 1.153 | 1.048 | −106.9 |
| | | | | Average | −105.9 ± 2.5 * |

* See text for error limits.

Using the previously reported[3] enthalpies of solution of $PaCl_4$(s) in 1 and 6M-HCl and the partial molar enthalpies of formation of HCl in these media, the enthalpies of formation of Pa$^{IV}$ in 1 and 6M-HCl were obtained. Combination of these values with the enthalpies of solution of $PaBr_4$ in 1 and 6M-HCl yields the enthalpy of formation of this compound. In the calculations, we used values as previously[1] for the partial molar enthalpies of formation of HCl and HBr. The enthalpy of formation of $Cs_2[PaCl_6]$(s) can also be obtained from the enthalpy of solution of this compound in 1 and 6M-HCl, previously reported,[4] and the enthalpy of formation of $PaCl_4$ according to a thermodynamic cycle used for the other dicaesium actinoid hexachloro-complexes. The results of these calculations are in Table 3. Agreement between the enthalpies of formation obtained from different media is quite satisfactory. For $PaBr_4$(s), we obtain −824 and −830 kJ mol$^{-1}$ from 1 and 6M-HCl, respectively, while for $Cs_2[PaCl_6]$(s) the agreement of the individual data is better than 1 kJ mol$^{-1}$.

TABLE 3

Enthalpies of formation * of various Pa$^{IV}$ species at 298.15 ± 0.05 K

| Species | $\Delta H_f$/kJ mol$^{-1}$ |
|---|---|
| (Pa$^{IV}$, 12M-HCl–0.05M-HF) | −666 ± 13 |
| ($PaCl_4$, s) | −1 045 ± 13 |
| (Pa$^{IV}$, 1M-HCl) | −620 ± 13 |
| (Pa$^{IV}$, 6M-HCl) | −608 ± 13 |
| ($PaBr_4$, s) | −827 ± 13 |
| ($Cs_2[PaCl_6]$, s) | −2 011 ± 13 |

* From the halogens in their standard state at 298.15 K.

Comparison of the enthalpy of formation of $Pa^{4+}$ in 1M-HCl, $\Delta H_f$ ($Pa^{4+}$, 1M-HCl) = $-620 \pm 13$ kJ mol$^{-1}$, with those of the neighbouring actinoid quadrivalent ions[1] [$\Delta H_f$($Th^{4+}$, 1M-HCl) = $-768.6 \pm 1.7$, $\Delta H_f$ ($U^{4+}$, 1M-HCl) = $-588.7 \pm 3.3$, and $\Delta H_f$($Np^{4+}$, 1M-HCl) = $-553.5 \pm 1.3$ kJ mol$^{-1}$] shows that the value for $Pa^{4+}$ lies closer to that of $U^{4+}$ than of $Th^{4+}$, thus differing largely from the value obtained by averaging data on thorium and uranium. The same remark applies, of course, to $\Delta H_f$ values for all the quadrivalent compounds: to take only one example, the enthalpy of formation of $PaCl_4$(s) has been interpolated by Maslov and Maslov[35] who accept a value of 1 121 kJ compared with our present determination of $-1\,045 \pm 13$ kJ mol$^{-1}$.

The potential of the Pa$^0$–Pa$^{IV}$ couple in 1M-HCl can now be calculated by using suitable entropy estimates. Taking for Pa(s) an entropy of $51.8 \pm 1$ J K$^{-1}$ mol$^{-1}$ obtained by averaging the accepted values for Th(s, α) (53.39 J K$^{-1}$ mol$^{-1}$)[36] and U(s, α) (50.21 J K$^{-1}$ mol$^{-1}$),[37] and for $S$($Pa^{4+}$, 1M-HCl) a value of $-397 \pm 40$ J K$^{-1}$ mol$^{-1}$ consistent with accepted values * for other

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* Based on a new assessment of thermodynamic data (J. Fuger and F. L. Oetting, 'Chemical Thermodynamics of the Actinide Elements and Their Compounds,' ch. 2 'Aqueous Ions,' Atomic Energy Rev., in the press).

[35] P. G. Maslov and Yu. P. Maslov, *J. Gen. Chem.* (*U.S.S.R.*), 1965, **35**, 2112.

[36] M. H. Rand, 'Thorium: Physico-chemical Properties of Its Compounds and Alloys,' Atomic Energy Rev., Special Issue No. 5, 1975, p. 7.

[37] M. H. Rand and O. Kubaschewski, 'Thermochemical Properties of Uranium Compounds,' Oliver and Boyd, London, 1963.

quadrivalent actinoid ions, we obtain for the $\mathrm{Pa^0}$–$\mathrm{Pa^{IV}}$ couple in 1M-HCl a value of 1.46 ± 0.06 V.

From the known values [1] of the enthalpies of formation of thorium and uranium tetra-chlorides and -bromides and the present data on $\mathrm{PaCl_4(s)}$ and $\mathrm{PaBr_4(s)}$, we observe that the ratio $[\Delta H_f(\mathrm{PaX_4,\ s}) - \Delta H_f^{\ominus}(\mathrm{UX_4,\ s})] : [\Delta H_f^{\ominus}(\mathrm{ThX_4,\ s}) - \Delta H_f^{\ominus}(\mathrm{UX_4,\ s})]$ is 0.16 : 1 for the two series of compounds. Assuming this constant ratio to hold for the fluorides, we can estimate $\Delta H_f(\mathrm{PaF_4,s})$ from $\Delta H_f^{\ominus}(\mathrm{ThF_4,\ s}) = -2\,111.5 \pm 7.5$ kJ $\mathrm{mol^{-1}}$ (ref. 38) and $\Delta H_f^{\ominus}(\mathrm{UF_4,\ s}) = -1\,883 \pm 20$ kJ $\mathrm{mol^{-1}}$.[37] This procedure, which appears to us more sound than a linear interpolation, yields $\Delta H_f(\mathrm{PaF_4,\ s}) = -1\,918 \pm 30$ kJ $\mathrm{mol^{-1}}$. This value is markedly different from an early estimate [39] ($-1\,997$ kJ $\mathrm{mol^{-1}}$) deduced from a consideration of the experimental conditions used to reduce $\mathrm{PaF_4}$ by barium vapour at 1 773 K. It differs still more from that given by Ferris,[5] $-2\,017 \pm 25$ kJ $\mathrm{mol^{-1}}$, and is in only *apparent* agreement with the estimates of Laser and Merz,[2] $-1\,947$ kJ $\mathrm{mol^{-1}}$, and of Maslov and Maslov,[35] $-1\,925$ kJ $\mathrm{mol^{-1}}$, since these were based on a now obsolete value for the enthalpy of formation of $\mathrm{ThF_4(s)}$.

As shown in Table 2, the enthalpy of solution of $\mathrm{PaCl_4(s)}$ in 12.05M-HCl is 55 kJ $\mathrm{mol^{-1}}$ less negative than in 12M-HCl–0.05M-HF. This effect, due to complexing of $\mathrm{Pa^{IV}}$ by fluoride ions, is accompanied by important spectral changes on addition of 0.05—0.1M-HF to 12M-HCl solutions. Thus, in 12M-HCl the major absorption band was at 417 nm with another at 298 nm in agreement with earlier observations,[40] whereas the same solution containing 0.1M-HF displayed two bands at 381 and 287 nm, the second being by far the more intense. Similar spectral differences have been noted on fluoride complexing of $\mathrm{U^{IV}}$ in concentrated HCl.[41]

TABLE 4

Enthalpies of solution of $\mathrm{PaCl_5}$ and $\mathrm{PaBr_5}$ in 12M-HCl–0.05M-HF at 298.15 ± 0.05 K

| Preparation no. | Expt. no. | Wt. of sample / mg | $10^3$ Concentration of compound in solution / mol $\mathrm{l^{-1}}$ | Enthalpy effect / J | $\Delta H$ / kJ $\mathrm{mol^{-1}}$ |
|---|---|---|---|---|---|
| (*a*) $\mathrm{PaCl_5}$ | | | | | |
| (I) | (1) | 2.672 | 0.770 | 1.313 | −200.6 |
| (I) | (2) | 3.725 | 1.073 | 1.887 | −206.9 |
| (I) | (3) | 3.434 | 0.989 | 1.718 | −204.3 |
| (I) | (4) | 3.339 | 0.962 | 1.667 | −203.9 |
| (I) | (5) | 5.128 | 1.477 | 2.510 | −199.9 |
| (II) | (6) | 4.718 | 1.359 | 2.377 | −205.7 |
| (II) | (7) | 7.399 | 2.132 | 3.647 | −201.3 |
| (II) | (8) | 4.694 | 1.352 | 2.338 | −203.4 |
| | | | | Average | −203.2 ± 3 * |
| (*b*) $\mathrm{PaBr_5}$ | | | | | |
| (I) | (1) | 2.498 | 0.466 | 0.941 | −237.5 |
| (I) | (2) | 4.921 | 0.918 | 1.894 | −242.6 |
| (I) | (3) | 3.364 | 0.627 | 1.277 | −239.5 |
| (I) | (4) | 4.242 | 0.791 | 1.650 | −245.3 |
| (I) | (5) | 5.257 | 0.981 | 2.042 | −245.0 |
| | | | | Average | −242.0 ± 5 * |

* See text for error limits.

The enthalpies of solution obtained for $\mathrm{PaCl_5}$ and $\mathrm{PaBr_5}$ in 12M-HCl–0.05M-HF are in Table 4. Combination of these values with the enthalpy of formation of $\mathrm{Pa^V}$ in the same medium ($\Delta H_4$) in a cycle similar to that described for $\mathrm{PaCl_4(s)}$, using the partial molar enthalpies of formation of HCl and HBr, respectively, yields enthalpies of formation of the pentahalides (Table 5). For the partial molar enthalpy of formation of HCl, we assumed, as above, $H_f$ (HCl, 12.05M-HCl) $= -134.88 \pm 0.30$ kJ $\mathrm{mol^{-1}}$. To obtain the partial molar enthalpy of formation of HBr in 12.05M-HCl (neglecting again the influence of fluoride ion), we assumed its partial molar enthalpy of formation in HBr of the same molality (16.24 mol $\mathrm{kg^{-1}}$) as 12.05M-HCl to be $H_f$(HBr, 11.34M-HBr) $= -86.68 \pm 0.30$ kJ $\mathrm{mol^{-1}}$, and added to it the enthalpy of dilution of 11.33M (or 16.24 mol $\mathrm{kg^{-1}}$) HBr into HCl of the same molality, according to equation (12),

$$[\mathrm{HBr},\ 3.42\ \mathrm{H_2O}] + [a\ \mathrm{HCl},\ b\ \mathrm{H_2O}] \xrightarrow{\Delta H_{12}} [\mathrm{HBr},\ a\ \mathrm{HCl},\ (b + 3.42)\mathrm{H_2O}] \qquad (12)$$

with $b/a = 3.42$ and $a$ varying from *ca.* 60 to 120. A value of $\Delta H_{12} = +0.17 \pm 0.01$ kJ $\mathrm{mol^{-1}}$ was obtained from a series of eight measurements. In this series the final bromide concentration varied from 0.1 to 0.2M without observable (within 0.01 kJ $\mathrm{mol^{-1}}$) change in the value of $\Delta H_{12}$. It was therefore assumed that the enthalpy change on going to a medium infinitely dilute in bromide ions is negligible. The absolute error in the value of $\Delta H_{12}$ is believed to be within 0.06 kJ $\mathrm{mol^{-1}}$ since great care was exerted to titrate very accurately (within ± 0.02M) the HCl and HBr solutions used. Thus, $H_f$(HBr, 12.05M-HCl) $= H_f$(HBr, 11.33M-HBr) $+ \Delta H_{12} = -(86.68 \pm 0.06) + (0.17 \pm 0.06) = -86.51 \pm 0.31$ kJ $\mathrm{mol^{-1}}$ (D).

TABLE 5

Enthalpies of formation * of various $\mathrm{Pa^V}$ species at 298.15 ± 0.05 K

| Species | $\Delta H_f$/kJ $\mathrm{mol^{-1}}$ |
|---|---|
| ($\mathrm{Pa^V}$, 12M-HCl–0.05M-HF) | −672 ± 15 |
| ($\mathrm{PaCl_5}$, s) | −1 143 ± 13 |
| ($\mathrm{PaBr_5}$, s) | −863 ± 13 |

* From the halogens in their standard state at 298.15 K.

Combination of our results for the pentahalides with enthalpies of formation of the corresponding tetrahalides yields for reaction (13), where the halogens are in their

$$\mathrm{PaX_4(s)} + \tfrac{1}{2}\mathrm{X_2}(\mathrm{g,\ l,\ or\ s}) \xrightarrow{\Delta H_{13}} \mathrm{PaX_5} \qquad (13)$$

standard state at 298.15 K, $-98 \pm 20$ kJ $\mathrm{mol^{-1}}$ for the chlorides and $-36 \pm 21$ kJ $\mathrm{mol^{-1}}$ for the bromides,

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[38] E. H. Van Deventer, E. Rudzitis, and W. N. Hubbard, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3233.

[39] B. B. Cunningham, *Proc. First Internat. Conf. Peaceful Uses At. Energy*, Geneva, 1955, vol. 7, p. 225.

[40] K. W. Bagnall and D. Brown, *J. Chem. Soc.* (*A*), 1967, 275.

[41] J. Fuger and D. Brown, unpublished work.

illustrating the large decrease in stability of the pentahalides relative to the tetrahalides for the heavier halide ion. Such a trend, together with the decrease in stability of higher valency halides with increasing atomic number, is also displayed for other elements in the actinoid series. For the corresponding equation (13) with uranium chlorides, Rand and Kubaschewski[37] assessed a value of $-43 \pm 8$ kJ mol$^{-1}$, whilst a value of $-17 \pm 3$ kJ mol$^{-1}$ was deduced from the more recent determination of the enthalpy of formation of $UCl_5$(s) by combustion calorimetry[42] in chlorine ($-1\,036.4 \pm 2.1$ kJ mol$^{-1}$) and that of $UCl_4$(s) obtained by solution calorimetry ($-1\,019.2 \pm 2.5$ kJ mol$^{-1}$).[31] Blair and Ihle[43] studied the thermal decomposition of $UBr_5$(s) to $UBr_4$(s). They report for reaction (13) an enthalpy change of $0 \pm 1.3$ kJ mol$^{-1}$ from a third-law calculation and $-7$ kJ mol$^{-1}$ from a second-law treatment of the decomposition process as a function of temperature. However, the value used by these authors in the third-law calculation for the entropy of $UBr_5$(s) at 298 K ($-324$ J K$^{-1}$ mol$^{-1}$) rested on early estimates of Brewer *et al.*[44] on transition-metal pentabromides. When, in combination with Blair and Ihle's experimental results, an entropy value for $UBr_5$(s) at 298 K of $-280$ J K$^{-1}$ mol$^{-1}$ is used, which, we believe, is more consistent with the assessment of Rand and Kubaschewski on the various uranium halides, we calculate for $\Delta H_{13}$ a value of $-12$ kJ mol$^{-1}$ for uranium bromides.

Thermodynamic functions associated with the formation of various protactinium halides can be calculated as a function of temperature by combination of the experimental enthalpies of formation with the appropriate entropies and heat capacities. Since none of these latter values is known experimentally, suitably interpolated data must be used. In order to allow comparison of the results, the formation reactions from *gaseous* halogens according to equations (14) and (15) will be considered.

$$\mathrm{Pa(s)} + 2\mathrm{X_2(g)} \longrightarrow \mathrm{PaX_4\ (s)} \qquad (14)$$

$$\mathrm{Pa(s)} + \tfrac{5}{2}\mathrm{X_2(g)} \longrightarrow \mathrm{PaX_5\ (s)} \qquad (15)$$

In the case of $PaCl_5$ and $PaBr_5$, since thermodynamic data corresponding to the sublimation and vaporisation are known,[8,9] we also report the thermodynamic functions for reaction (16). The fundamental equations are

$$\mathrm{Pa(s)} + \tfrac{5}{2}\mathrm{X_2(g)} \longrightarrow \mathrm{PaX_5(g)} \qquad (16)$$

well known. Assuming, as is customary,[37] the heat-capacity change to be constant as a function of temperature, the thermodynamic functions can be expressed by equations (17)—(19), in which $\Delta H$, $\Delta S$, and $\Delta G$ are, respectively, the molar enthalpy, entropy, and Gibbs energy for the reaction under consideration. The same formulation, which is usual, has been used in a previous publication[1] on other actinoid tetrahalides, thus allowing comparison of the data.

$$\begin{aligned} &\Delta H_T = A + \Delta C_P T, \\ \text{with}\quad &A = \Delta H_{298} - 298\,\Delta C_P \qquad (17) \end{aligned}$$

$$\begin{aligned} &\Delta S_T = B + C \log_{10} T, \\ \text{with}\quad &B = \Delta S_{298} - 2.3026\,\Delta C_P \log_{10} 298 \\ \text{and}\quad &C = 2.3026\,\Delta C_P \qquad (18) \end{aligned}$$

$$\Delta G_T = A - (B - \Delta C_P)T - CT \log_{10} T \qquad (19)$$

In the absence of experimental results on entropies and heat capacities of protactinium compounds and since data available for thorium[36] and uranium[37] compounds have been thoroughly assessed, we used values for protactinium metal and the tetrahalides obtained by averaging the corresponding values for the thorium and uranium analogues. The $C_P$ values were evaluated at 600 K. The entropy difference between the solid penta- and tetra-halides is assumed to be 46 J K$^{-1}$ mol$^{-1}$ by analogy with the values assessed by Rand and Kubaschewski[37] for the entropies of the various uranium halides and the $C_P$ values of $PaCl_5$(s) and $PaBr_5$(s) were obtained in a similar way. For the enthalpies and entropies of sublimation of $PaCl_5$(s) and $PaBr_5$(s), Weigel *et al.*[8,9] obtained $\Delta H_s(PaCl_5) = 92.8$ kJ mol$^{-1}$ and $\Delta S_s\,(PaCl_5) = 143.1$ J K$^{-1}$ mol$^{-1}$ in the range 509—579 K (m.p.) and $\Delta H_S(PaBr_5) = 103.1 \pm 0.4$ kJ mol$^{-1}$, and $\Delta S_S(PaBr_5) = 160.2 \pm 0.8$ J K$^{-1}$ mol$^{-1}$ in the range 491—556 K (m.p.). Using a reasonable $\Delta C_P$ value of $-25$ J K$^{-1}$ mol$^{-1}$ for the sublimation process, we recalculated these values at 298 K and incorporate the results in Table 6 together with all the other data required for calculation of the coefficients of equations (17)—(19) for the enthalpy, entropy, and Gibbs energy of formation of the halides. These coefficients are shown in Table 7. In these calculations we used 298 instead of 298.15 K. As the m.p.s of the tetrahalides are not known, we used an estimated value for the limit of validity of the thermodynamic functions corresponding to the tetrahalides.

TABLE 6

Data used in the calculation of various thermodynamic functions associated with formation of protactinium tetra- and penta-halides from the gaseous halogens

| Compound | $S$ at 298 K<br>J K$^{-1}$ mol$^{-1}$ | Ref. | $\Delta H_f$ at 298 K<br>kJ mol$^{-1}$ | Ref. | $C_P$ at 600 K<br>J K$^{-1}$ mol$^{-1}$ | Ref. |
|---|---|---|---|---|---|---|
| Pa(s) | 51.8 | *a* | 0 | | 32.39 | *a* |
| $F_2$(g) | 202.67 | 17 | 0 | | 35.27 | *b* |
| $Cl_2$(g) | 222.96 | 17 | 0 | | 36.61 | *b* |
| $Br_2$(g) | 245.35 | 17 | 30.907 | | 37.28 | *b* |
| $PaF_4$(s) | 147.0 | *a* | $-1\,918$ | *c* | 124.8 | *a* |
| $PaCl_4$(s) | 194.3 | *a* | $-1\,045$ | *c* | 133.5 | *a* |
| $PaBr_4$(s) | 231.1 | *a* | $-889$ | *c* | 139.1 | *a* |
| $PaCl_5$(s) | 240 | *a* | $-1\,143$ | *c* | 156 | *a* |
| $PaBr_5$(s) | 277 | *a* | $-940$ | *c* | 162 | *a* |
| $PaCl_5$(g) | 398 | *a* | $-1\,044$ | *a* | 131 | *a* |
| $PaBr_5$(g) | 451 | *a* | $-833$ | *a* | 137 | *a* |

[a] See text. [b] JANAF Thermodynamic Tables, Ref. NSRDS-NBS-37, June 1971. [c] This work.

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[42] P. Gross, C. Hayman, and G. L. Wilson, *Monatsh.*, 1971, **102**, 924.

[43] A. Blair and H. Ihle, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3795.

[44] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in 'The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics,' ed. L. L. Quill, NNES Plutonium Project Record, McGraw-Hill, New York, 1950, div. IV, vol. 19B, paper 6.

TABLE 7

Coefficients for the calculation of thermodynamic functions associated with the formation of protactinium halides

$$\Delta H_T = A + \Delta C_P T$$
$$\Delta S_T = B + C \log_{10} T$$
$$\Delta G_T = A - (B - \Delta C_P)T - CT \log_{10} T$$

| | $A$ / kJ mol$^{-1}$ | $B$ / J K$^{-1}$ mol$^{-1}$ | $\Delta C_P$ / J K$^{-1}$ mol$^{-1}$ | $C$ / J K$^{-1}$ mol$^{-1}$ | $T$/$K$ |
|---|---|---|---|---|---|
| (*a*) $Pa(s) + 2X_2(g) \longrightarrow PaX_4(s)$ | | | | | |
| $PaF_4(s)$ | −1 925 | −435 | 21.9 | 50.4 | 298—*ca.* 1 350 |
| $PaCl_4(s)$ | −1 053 | −462 | 27.9 | 64.2 | 298—*ca.* 950 |
| $PaBr_4(s)$ | −899 | −495 | 32.2 | 74.0 | 298—*ca.* 875 |
| (*b*) $Pa(s) + \frac{5}{2}X_2(g) \longrightarrow PaX_5$ (s or g) | | | | | |
| $PaCl_5(s)$ | −1 153 | −552 | 32 | 74 | 298—579 |
| $PaBr_5(s)$ | −951 | −593 | 36 | 84 | 298—556 |
| $PaCl_5(g)$ | −1 046 | −251 | 7 | 16 | 298—*ca.* 950 |
| $PaBr_5(g)$ | −834 | −277 | 11 | 26 | 298—*ca.* 875 |

We have also assumed the estimated m.p.s of $PaCl_4$ and $PaBr_4$ for the limiting temperature of validity of the functions corresponding to the formation of $PaCl_5(g)$ and $PaBr_5(g)$, respectively. It is felt that the assumptions made on entropies and $C_P$ values do not amount, over the range of applicability of the functions, to more than 30% of the accepted errors in the enthalpies of formation values. These error limits, however, have to be kept in mind when using the thermodynamic functions. This is particularly true when comparing thermodynamic functions associated with the formation of $PaBr_5$ with those of $PaBr_4$, since the error limits obtained for reaction (13) amount already to more than 50% of the reported enthalpy effect.

We thank the late Professor B. B. Cunningham and his co-workers, Drs. R. Dod, T. C. Parsons, and G. V. Shalimoff (Lawrence Berkeley Laboratory, University of California), for preparation and analysis of the metal samples, Mr. F. Watelet for help in the operation of the calorimeter, Dr. M. H. Rand (Materials Development Division, A.E.R.E. Harwell) for discussion, and the Institut Interuniversitaire des Sciences Nucléaires (Brussels) for support of the Laboratory of Radiochemistry (Liège).

[5/041 *Received, 8th January, 1975*]