Enthalpy of Formation of Rhenium Heptafluoride

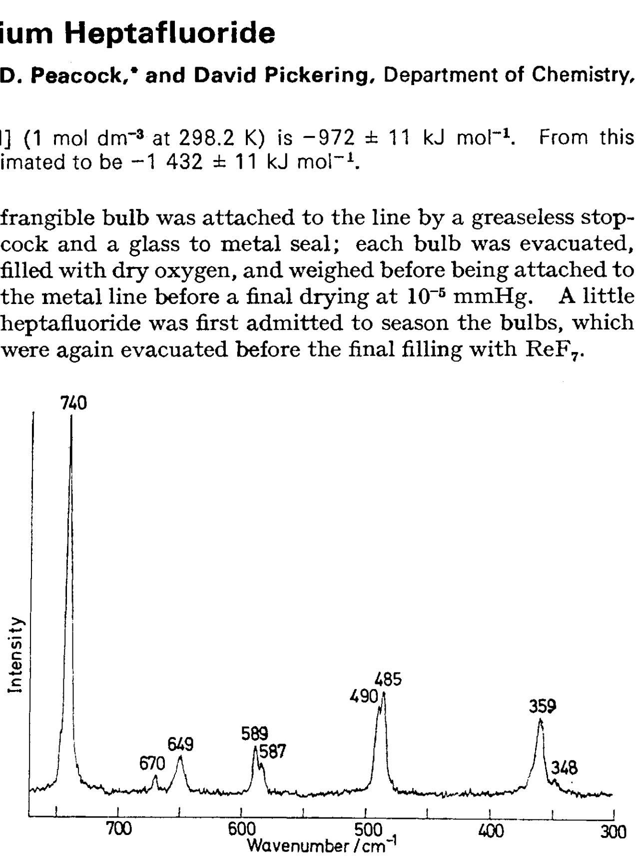
By **John Burgess, John Fawcett, Raymond D. Peacock,* and David Pickering,** Department of Chemistry, The University, Leicester LE1 7RH

The enthalpy of hydrolysis of ReF_7(c) in Na[OH] (1 mol dm^{-3} at 298.2 K) is -972 ± 11 kJ mol^{-1}. From this result the enthalpy of formation of ReF_7(c) is estimated to be $-1\,432 \pm 11$ kJ mol^{-1}.

ALTHOUGH rhenium heptafluoride has been known for nearly twenty years,[1] its enthalpy of formation has still not been reported. Because of the difficulty in obtaining the compound free from the hexafluoride, or of converting the hexafluoride into the heptafluoride in a sufficiently high yield, the fluorine bomb-calorimetry approach, which has been used with considerable success for determining enthalpies of formation of a number of higher fluorides (*e.g.* MoF_6 and WF_6 [2]), is less suited to ReF_7, and in consequence we have estimated this quantity from hydrolysis data.

EXPERIMENTAL

Rhenium Heptafluoride.—This was prepared from the elements in a metal vacuum system. The nickel reaction and storage cans were pretreated with hydrogen at elevated temperatures. The rhenium sponge was treated with hydrogen at red heat in order to reduce oxides to metal before transfer to the reaction can. After thorough drying under a high vacuum, fluorination was effected by addition of fluorine at 6 atm ($>2:1$ excess over rhenium) and increasing the temperature to 640 K for 4 h.† The reaction can was cooled to 190 K, the excess of fluorine was pumped away, and the rhenium heptafluoride was transferred *in vacuo* to the storage can. The purity of the sample (*ca.* 95—99%) was assessed from its Raman spectrum,[3] measured at several temperatures between 90 and 190 K, which showed it to be free from ReF_6 and ReF_5O. The spectrum of the pure solid, which has not been previously reported, is reproduced in the Figure. Transfer from the storage can to frangible bulbs [4] was made through a section of metal line which had been carefully seasoned with fluorine. Each frangible bulb was attached to the line by a greaseless stopcock and a glass to metal seal; each bulb was evacuated, filled with dry oxygen, and weighed before being attached to the metal line before a final drying at 10^{-5} mmHg. A little heptafluoride was first admitted to season the bulbs, which were again evacuated before the final filling with ReF_7.



Raman spectrum of solid ReF_7

Raman Spectra.—These were recorded on a Coderg T800 instrument using the Kr^+ line at 6 471 Å.

Thermochemical Measurements.—Enthalpies of hydrolysis in sodium hydroxide (1 mol dm^{-3}) were measured by methods similar to those described for ReF_6.[4] The performance of the apparatus was checked periodically against the well

---

† 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] J. G. Malm and H. Selig, *J. Inorg. Nuclear Chem.*, 1961, **20**, 189.

[2] J. Burgess, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1974, 1062.

[3] H. Selig and E. L. Gasner, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1659.

[4] J. Burgess, C. J. W. Fraser, I. Haigh, and R. D. Peacock, *J.C.S. Dalton*, 1973, 501.

established enthalpies of solution of potassium chloride[5] and of neutralisation of tris[(hydroxymethyl)methyl]amine.[6]

RESULTS

Nine determinations of the enthalpy of hydrolysis of rhenium heptafluoride with sodium hydroxide (1 mol dm^{-3}) were made, using five portions and four portions respectively from two independently prepared samples of the compound. Between 0.04 and 0.13 g of the fluoride was used in each determination; the volume of sodium hydroxide used was 150 cm^3 in each case. The mean value for the enthalpy of alkaline hydrolysis of ReF_7 (solid), equation (1), was -972 kJ mol^{-1}. The 90% confidence limits[7] for this result were calculated to be ± 11 kJ mol^{-1}. The mean values corresponding to the two different samples of compound were sufficiently close for these to be considered to come from the same population at a high confidence level.

$$ReF_7(c) + 8[OH]^-(aq) \longrightarrow [ReO_4]^-(aq) + 7F^-(aq) + 4H_2O(l) \quad (1)$$

The enthalpy of formation of solid rhenium heptafluoride, $\Delta H_f^\ominus [ReF_7(c)]$, was calculated from the measured enthalpy corresponding to equation (1) and the known enthalpies of the other species in the equation. Values used for the latter ancillary data were: $\Delta H_f^\ominus [ReO_4^-(aq)] = -791.6$;[8] $\Delta H_f^\ominus [F^-(aq)] = -332.6$[9] (*cf.* the recent figure[10] of -333.0); $\Delta H_f^\ominus [H_2O(l)] = -285.8$;[9] and $\Delta H_f^\ominus [OH^-(aq)] = -230.0$ kJ mol^{-1}.[9] Thence $\Delta H_f^\ominus [ReF_7(c)] = -1\,452 \pm 11$ kJ mol^{-1}, where the uncertainty is expressed as the 90% confidence limit. $\Delta H_{sub}(ReF_7)$, estimated from the temperature variation of vapour pressure,[1] is 42 kJ mol^{-1}. Hence $\Delta H^\ominus [ReF_7(g)]$ is $-1\,410 \pm 11$ kJ mol^{-1}. Assuming $S^\ominus [ReF_7(g)]$ to be *ca.* 360 J K^{-1} mol^{-1}, $\Delta G_f^\ominus [ReF_7(g)]$ is *ca.* $-1\,295$ kJ mol^{-1}.

DISCUSSION

Rhenium(VII) fluoride is the only stable heptafluoride of the transition elements. For reaction (2), $\Delta H = -61 \pm 21$ kJ mol^{-1}. The corresponding free-energy

$$ReF_6(g) + \tfrac{1}{2}F_2(g) \longrightarrow ReF_7(g) \quad (2)$$

change [using values of $S^\ominus$: $ReF_6(g)$, 343; F_2, 202.6;[9] ReF_7, 360 (estimated) J K mol^{-1}] is calculated to be *ca.* -36 kJ mol^{-1}. The average bond strengths for higher fluorides of some transition elements of the third series are given in the Table. There appears to be a sufficiently regular change in bond strengths between the highest fluoride of each element between Hf and Re to be able to make rough estimates of the enthalpies of formation of $OsF_6(g)$, $OsF_7(g)$, and the hypothetical $OsF_8(c)$ of $-1\,080$, $-1\,140$, and -980 kJ mol^{-1} respectively. These figures are in agreement with the observed[11] low stability of OsF_7 and the non-existence of OsF_8.

Enthalpies of formation and average bond strengths in some higher fluorides

Compound	$-\Delta H_f^\ominus$/kJ mol^{-1}	$\bar{D}$/kJ mol^{-1}
$LaF_3(c)$	1 694 [a]	787.3 [b]
$HfF_4(c)$	1 930 [c]	716.3 [b]
$TaF_5(c)$	1 903 [c]	616.0 [b]
$WF_5(c)$	1 450 [d]	525.4 [b]
$WF_6(g)$	1 721 [e]	507.3
$ReF_6(g)$	1 349 [f]	435.5
$ReF_7(c)$	1 452 [g]	396.4[b]

[a] O. G. Polyachenok, *Russ. J. Inorg. Chem.*, 1967, **12**, 449. [b] Referring to the solid state. [c] N.B.S. Technical Note, 270/5, 1973. [d] J. Schröder and F. Sieben, *Chem. Ber.*, 1970, **103**, 76. [e] N.B.S. Technical Note, 270/4, 1969. [f] Ref. 4. [g] This work.

We thank the S.R.C. for the awards of a research grant and a studentship (to D. P.).

[6/297 *Received*, 12*th February*, 1976]

---

[5] V. B. Parker, 'Thermal Properties of Aqueous Uni-univalent Electrolytes,' U.S. Department of Commerce, 1965, NSRDS-NBS 2, table 18.

[6] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 195; J. O. Hill, G. Ojelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111; E. J. Prosen and M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 581.

[7] E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, ch. 1.

[8] R. H. Busey, K. H. Gayer, R. A. Gilbert, and R. B. Bevan, *J. Phys. Chem.*, 1966, **70**, 2609.

[9] N.B.S. Technical Note 270/3, 1969.

[10] V. P. Vasile and E. V. Kozlovskii, *Russ. J. Inorg. Chem.*, 1974, **19**, 147.

[11] O. Glemser, H. W. Roesky, K. H. Hillberg, and H. U. Werther, *Ber.*, 1966, **99**, 2652.