

Commentary

Is Mercury Now a Transition Element?

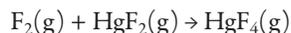
by William B. Jensen

Even before the issue of *Angewante Chemie* containing the actual paper by Wang, Andrews, Riedel, and Kaupp was officially published, the October 8, 2007 issue of *Chemical & Engineering News* was announcing the reported synthesis of mercury tetrafluoride in bold quarter inch font type and describing it as “a fundamental advance that opens new possibilities for mercury compounds” (1). And indeed a no less bold claim appears in the title of the original paper itself, which leads off with the proclamation that “Mercury Is a Transition Element” (2). Yet an actual reading of the paper reveals that a more accurate title might be “A Possible Detection of Minute Quantities of HgF_4 at 4 K Under Extreme Nonequilibrium Conditions” since the synthesis in question was done using matrix isolation techniques and the authors have in fact neither experimental compositional data nor experimental structural data to support their claim, but rather a single match between a weak infrared absorption peak and the value of one of the calculated stretching modes for a hypothetical square-planar HgF_4 molecule.

But the purpose of this commentary is not to cast doubts on the experimental evidence, but rather to call attention to two important issues that this purported synthesis will pose for teachers of both general and inorganic chemistry should it ultimately prove to be correct—namely, what is the proper ontological status in a descriptive inorganic course of highly reactive transient species formed under extreme conditions and how should one evaluate their importance relative to the periodic table? Before confronting these questions, however, it is important to be clear about several facts concerning this supposed synthesis.

First, the theoretical calculations that predict HgF_4 reveal that its possible existence is due to the strong relativistic effects found for Hg—effects that also account for its liquid state at ambient temperatures and for the atypical structures of many of its compounds (3). Though similar effects are expected for the largely unknown chemistry of mercury’s heavier analog, element 112, a similar relativistic breach of the d^{10} subshell is very unlikely in the case of Zn and Cd (2).

Second, it is also extremely unlikely that macro quantities of HgF_4 will ever be prepared under ambient conditions. Though theoretical calculations predict that the further fluorination at 0 K of a gaseous HgF_2 monomer to generate the hypothetical HgF_4 monomer is exothermic by -27.4 kJ/mol:



real HgF_2 is not a molecular monomer under these conditions but rather an 8/4 nonmolecular solid ($\Delta H_f = -422.6$ kJ/mol) for which the corresponding reaction is strongly endothermic. $\text{HgF}_2(\text{s})$ does not significantly vaporize until 919 K, by which point unfavorable entropy and other thermal effects have long since negated any favorable enthalpy changes for the reaction in question.¹ Indeed calculations show that already by 10 K the hypothetical gas-phase reaction has an unfavorable free energy of

+6.3 kJ/mole and that by 298.15 K this has further increased to an unfavorable value of +44.5 kJ/mol (2). Only by minimizing entropy effects and by kinetically restricting the formation of polymeric $\text{HgF}_2(\text{s})$ by imposing a diffusion barrier in the form of the noble gas matrix is it possible to generate small quantities of the monomer under conditions favorable to the reaction—whence the use of extremely low temperatures and matrix isolation techniques. Even then, the experimental data reveal that the incipient polymerization of HgF_2 is competitive with the peak tentatively assigned to HgF_4 .

Exactly what are we to make of potentially aberrant species formed under nonequilibrium conditions and the imposition of extreme kinetic constraints? Are the regularities of conventional inorganic systematics and valence an artifact of allowing the reacting species competitive alternatives and do these regularities disappear when access to these alternatives is eliminated? Thus while transient molecules of HgF_4 may well be formed whenever F_2 and Hg react under ambient conditions, there is no doubt that they are competitively eliminated almost instantaneously relative to the formation of polymeric $\text{HgF}_2(\text{s})$ and so play no role in the normally observed chemistry of Hg. Likewise, what criteria determine whether a species is or is not discussed in a typical inorganic textbook? As the study of the chemistry of the radioactive elements has long demonstrated, neither life span nor the ability to prepare macro quantities are necessarily the determining factors. On the other hand, the chemistry of the radioactive elements seldom challenges conventional systematics in the same way as many of the species prepared by matrix isolation techniques or observed as transient species in mass spectrometers, ionization chambers, or the interior of stars. I ask these questions rather than answer them because I do not necessarily know the answers, only that the questions have become increasingly pertinent as modern instrumentation has increased our ability to detect ever smaller quantities persisting over ever briefer time frames and over an ever increasing range of extreme conditions (4).

How then should we assess the importance of the possible preparation of HgF_4 for the periodic table? Ignoring the irony that many U.S. textbooks are already under the incorrect impression that mercury is a transition element (5, 6), I would suggest two possible approaches, which, for our present purposes, may be denoted as statistical and functional respectively. From the statistical point of view, we note that only one of the three important members of Group 12 shows a possible involvement of the $(n-1)d$ subshell in its chemistry and then for only 1/1000th of its known chemistry under extremely atypical conditions. Our choice then is between labeling this group as transitional and treating the behavior of 2/3 of its members and of 99.9% of their known chemistry as exceptions to this label or continuing to treat this group as main-group with only 1/1000 of the known chemistry of one of them as an exception. I think the optimal choice is rather obvious.

The functional criterion is based on the seldom emphasized fact that most of the divisions in the periodic table are actually temperature- and pressure-dependent. The most obvious of these is the so-called diagonal line separating the metals from the nonmetals. Thus Sn changes from the 6/6 metallic white form to the 4/4 nonmetallic grey form on lowering the temperature to 13.2 °C (7). Likewise S becomes a metal at pressures of 48 GPa and Br at 100 GPa (8). In other words, the metal/nonmetal boundary shifts with temperature and pressure and the particular version we choose to display on our periodic tables represents the case corresponding to the most typical range of temperatures and pressures encountered in day-to-day laboratory and industrial practice. In a similar fashion, we can interpret the presumed preparation of HgF₄ as meaning that far more fundamental distinctions, such as the difference between transition and main-block elements, are also ultimately temperature and pressure dependent.² But are we going to choose the boundary that applies at 4 K or that which corresponds to the typical range of temperatures and pressures encountered in the laboratory and industry? Again I think that the optimal choice is obvious. In short, whether this synthesis is or is not confirmed, for the present at least (since history teaches us that chemistry always has its unpredictable surprises), its practical consequences for how we view and use the periodic table are essentially negligible.

Notes

1. Some sources report that HgF₂(s) decomposes at this temperature, though this does not appear to be consistent with the reported thermodynamic data.
2. This analogy is somewhat artificial as the temperature and pressure shifts in the metal/nonmetal boundary are thermodynamic whereas the assumed detection of HgF₄ also requires the use of extreme kinetic constraints.

Literature Cited

1. Mercury Tetrafluoride Synthesized. *Chem. Eng. News* **2007**, *85* (41), 11.
2. Wang, X.; Andrews, L.; Riedel, S.; Kaupp, M. Mercury Is a Transition Element: The First Experimental Evidence for HgF₄. *Angew. Chem. Int. Ed.* **2007**, *46*, 8371–8375.
3. Norrby, L. J. Why is Mercury Liquid? Or Why Do Relativistic Effects Not Get into Chemistry Textbooks? *J. Chem. Educ.* **1991**, *68*, 110–113.
4. One of the few attempts to deal with this problem is found in Wiberg, N. *Inorganic Chemistry*; Academic Press: New York, NY, 2001, where the author consistently distinguishes between stable compounds and transient reaction intermediates.
5. For the correct definition see Larsen, E. M. *Transitional Elements*; Benjamin: New York, NY, 1965; pp 1–2.
6. For a discussion of this textbook error, see Jensen, W. B. The Place of Zinc, Cadmium, and Mercury in the Periodic Table. *J. Chem. Educ.* **2003**, *80*, 952–961.
7. Addison, W. E. *The Allotropy of the Elements*; Elsevier: New York, NY, 1964, pp 94–96.
8. Young, D. A. *Phase Diagrams of the Elements*; University of California Press: Berkeley, 1991, pp 131, 142.

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