Notes from the Oesper Collections

The Search for Sulfur Iodide

William B. Jensen

Department of Chemistry, University of Cincinnati
Cincinnati, OH 53706

Our stockroom, which dates back to the origins of our department in 1874, recently disposed of the last of its older cork and glass-stoppered chemical bottles. These were given to the Oesper Museum, but required a substantial cleanup as they were covered with masking tape, computer printouts, barcodes, and various safety labels – all remnants of previous ill conceived attempts to catalog them and to make them conform to recent OSHA guidelines for the labeling and storage of chemicals. In most cases we were able to remove these modern trappings of bureaucracy and leave only the original historically significant labels, though in a few cases these had so deteriorated or had been covered over by more recent versions, that it was impossible to save them and it became necessary instead to replace them with reproductions of the originals.

A case in point was a lovely 8 ounce glass-stopper bottle labelled "sulfur iodide" (figure 1). This had

Table 1. Known halides of sulfur.

Class	Known Examples
Fluorides	$(S_n)F_2$ (n = 2-4), SF_2, SF_4, S_2F_{10}, SF_6
Chlorides	$(S_n)Cl_2$ (n = 2-8), SCl_2, SCl_4
Bromides	$(S_n)Br_2$ (n = 2-8), SBr_2
Iodides	?

come from the C. A. F. Kahlbaum Chemische Fabrik of Berlin and had probably been purchased prior to World War I. In making the replacement label for the unsalvageable German original, I wanted to be more specific as the compound's actual composition. This was because I knew that there were several known fluorides chlorides, and bromides of sulfur (table 1) and this had naturally raised the question in my mind as to which the possible iodides of sulfur was in the bottle. However, much to my surprise, most inorganic textbooks and reference works that I consulted either ignored the subject, reported that there were no known examples of sulfur iodides, or claimed that the evidence for the existence of such compounds was highly problematic at best. Typical is Sidgwick's 1950 summary in his two-volume reference work, *The Chemical Elements and their Compounds* (1):

Sulfur and Iodine – A variety of solid phases have been examined, but there is no evidence that any of them are anything more than solid solutions of iodine in sulfur ... The regularity and extent to which the affinity for a halogen falls with the increase in the atomic number of the halogen, is far greater with sulfur than with any other element.

The truth of Sidgwick's concluding comment is certainly supported by the contents of Table 1, which lists several sulfur halides that were unknown at the time of his writing (2).

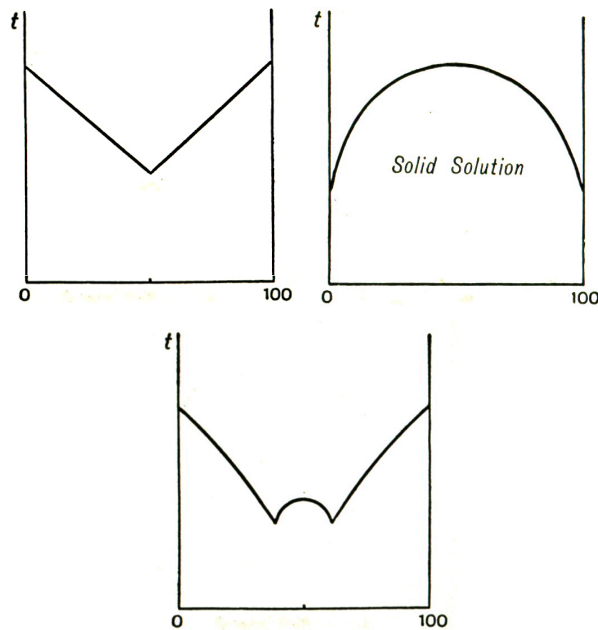Figure 1. The mysterious antique bottle of "sulfur iodide."

Figure 2. The Idealized melting point curve for a binary mixture forming a 50:50 eutectic (upper left); a solid solution displaying mutual solubility in all proportions (upper right); and a binary 1:1 compound (lower center). In practice many systems are more complex and are not only asymmetrical but show combinations of all three idealized cases

But if this is the case, then what is in the eight ounce bottle? The search for an answer to this question led me to look into the history of the various attempts to prepare these simple compounds predicted by a naive reading of the periodic table, as well as the equally fascinating history of various attempts to theoretically rationalize their nonexistence. As is often the case, the best place to start such a search was J. W. Mellor's classic 16 volume work, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, which provided a thorough review of all attempts to prepare the iodides of sulfur prior to 1930 (3).

Direct Synthesis from the Elements

The simplest and earliest approach to making an iodide of sulfur is to directly heat a mixture of the two elements, either as solids or when dissolved in a common solvent, such as carbon disulfide:

$$S_8 + 4I_2 \rightarrow 4(S_2)I_2 \qquad [1]$$

This was the approach taken by Courtois, the discoverer of iodine, in 1813 (4) and by Gay Lussac the next year in his classic exploration of the properties of this newly discovered element (5). Courtois claimed that "sulfur units with iodine, but with less energy than

phosphorus," whereas Gay Lussac concluded that the affinity between the two elements was "very feeble" and expressed doubt as to whether they formed a true chemical compound. Mellor summarizes at least eight additional attempts between 1827 and 1896 to prepare an iodide of sulfur by direct combination of the elements, most of which used detection of a finite heat of reaction as a criterion for compound formation and all of which proved to be either negative or inconclusive.

By the early 19th century chemists had conceptually differentiated between heterogenous mixtures and homogeneous solutions of variable composition, on the one hand, and compounds and simple substances of definite composition, on the other, though the operational implementation of these definitions proved difficult in the laboratory as more and more borderline cases were found. This is illustrated by the large number of spurious elements that have been reported in the chemical literature (6). Less well known is the fact that this is equally true of chemical compounds, as summarized by Le Chatelier in 1908 (7):

The inorganic chemists, less favored than their organic brethren, have too often allowed themselves to be seduced into artificially augmenting the number of real compounds. If we go through the large general treatises on chemistry we can boldly state that at least half of the compounds described there have never existed.

However, with the rise to prominence of thermal analysis and the application of the phase law in the last quarter of the century, it was thought that chemists had finally found a sound experimental criterion for differentiating between these various classes of substances (figure 2), and indeed, many of the spurious compounds mentioned by Le Chatelier were eliminated through application of these new criteria. But as the number of reported phase studies increased, it became apparent, as cautioned by Timmermans in his classic monograph on the characterization of chemical species (8), that even these newer criteria could sometimes prove ambiguous. Many chemical species are kinetically metastable and do not appear in the corresponding phase diagram, which assumes a true equilibrium between the various phases. Yet others dissociate at the temperatures being studied. And still others, such as the nonstoichoimetric intermetallic compounds studied by Kurnakov, seemed to simultaneously have properties common to both solutions and compounds.

These problems are well illustrated by the application of thermal analysis to the sulfur/iodine system, of which Mellor mentions at least eight examples done between 1863 and 1915. Three of these studies reported the formation of solid solutions, four the forma-
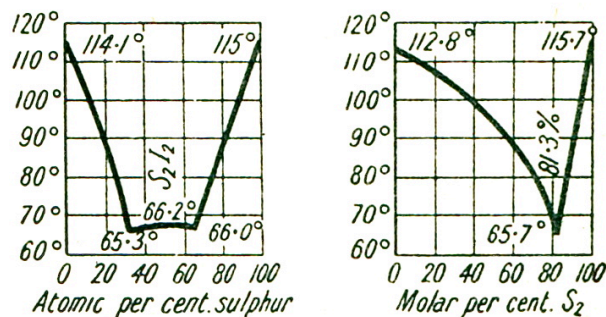
Figure 3. *Left:* Linebarger's 1895 melting point curve (9) for the S-I system indicating the formation of a 1:1 compound thought to correspond to S_2I_2. *Right:* Ephriam's 1908 freezing point curve for the S-I system showing neither compound formation nor solid solution formation, but rather a simple eutectic mixture at 81.3 mole percent S_2 (10).

tion of an eutectic (figure 3, right), and only one (figure 3, left) the formation of a compound having the relative formula SI (usually written as $(S_2)I_2$ in analogy with $(S_2)Cl_2$). On the basis of these results, Mellor himself concluded that all so-called sulfur iodides were actually heterogeneous mixtures, in contrast to the later opinion of Sidgwick, quoted above, who had concluded instead that they were solid solutions.

Indirect Synthesis Through Double Displacement

The failure of the above attempts to prepare sulfur iodides via direct reaction of the elements does not, of course, preclude either their possible existence or the use of alternative methods of preparation, though they seem to show that such compounds, should they exist, must either be of low thermodynamic stability or are kinetically metastable.

One commonly used method of indirectly synthesizing such compounds was recognized as early as 1764 by the French chemist, Pierre Macquer, who suggested use of a double displacement reaction in which a highly stable by-product was formed at the same time as the desired product of low stability (11):

A body, which of itself cannot decompose a compound consisting of two substances, because, as we just now said, they have a greater affinity for with each other than it has with either of them, becomes nevertheless capable of separating the two by uniting with one of them, when it is itself combined with another body, having a degree of affinity with [the other] sufficient to compensate for its own want thereof. In that case there are two affinities, and thence ensues a double decomposition and a double combination.

In other word, in modern terms, a compound AD

of low thermodynamic stability can be prepared via the the double decomposition reaction:

$$AB + CD \rightarrow AD + CB \qquad [2]$$

provided that the by-product, CB, is of sufficiently high thermodynamic stability to compensate for AD's lack thereof. Many many examples of the application of this often implicit principle are known in both the fields of inorganic and organic synthesis. However, such an approach will only work if AD, once formed, still has sufficient thermodynamic stability in and of itself or, if it is thermodynamically unstable, sufficient kinetic metastability, to avoid subsequent dissociation into its component elements:

$$AD \rightarrow A + D \qquad [3]$$

and it is precisely this necessary caveat that has plagued the various attempts to apply this approach to the synthesis of the sulfur iodides.

Mellor summarizes at least six attempts between 1833 and 1886 to apply Macquer's principle to the synthesis of sulfur iodide, including the reaction of polydisulfur dichloride with hydrogen iodide:
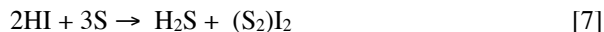
$$(S_2)Cl_2 + 2HI \rightarrow (S_2)I_2 + 2HCl \qquad [4]$$
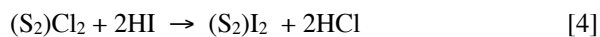
the reaction of dihydrogen sulfide with potassium tetrachloroiodate:

$$4H_2S + 4K(ICl_4) \rightarrow 2(S_2)I_2 + 8HCl + 4KCl + 2Cl_2 \quad [5]$$
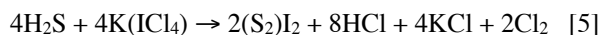
the reaction of dihydrogen sulfide with iodine trichloride:

$$3H_2S + 2ICl_3 \rightarrow (S_3)I_2 + 6HCl \qquad [6]$$

the reaction of hydrogen iodide with sulfur:

$$2HI + 3S \rightarrow H_2S + (S_2)I_2 \qquad [7]$$

the reaction of polydisulfur dichloride with various alkyl iodides:

$$(S_2)Cl_2 + 2RI \rightarrow (S_2)I_2 + 2RCl \qquad [8]$$
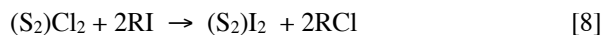
and the reaction of hydrogen iodide with sulfur dioxide:

$$8HI + 2SO_2 \rightarrow 4H_2O + 3I_2 + (S_2)I_2 \qquad [9]$$
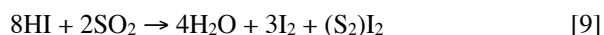
Of these, reaction 4, first suggested by Inglis in 1835 (12) and based on the relative stabilities of HI versus HCl, is both the simplest and the most plausible. Continuing Mellor's review through 1962, Fehér and

Münzner (13) cite at least eight more attempts to prepare these compounds, the most promising of which are based on the double displacement reaction:

$$(S_2)Cl_2 + 2KI \rightarrow (S_2)I_2 + 2KCl \qquad [10]$$
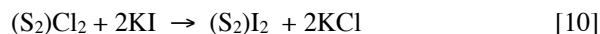
first used by the Indian chemist, M. R. A. Rao, in 1940 (14) in which the superior lattice energy of KCl versus KI supposedly compensates for the low stability of $(S_2)I_2$ versus $(S_2)Cl_2$.

Success at Last?

On the basis of reaction 10, Rao appears to have made the first 20th-century claim to have successfully made a sulfur iodide – albeit as a transient reaction intermediate. On shaking a solution of $(S_2)Cl_2$ in carbon tetrachloride with powdered KI, he observed that the solution underwent a series of color changes from yellowish brown through various shades of reddish brown and finally to violet. He assumed this was evidence for the transient formation of polydisulfur diiodide and sulfur diiodide followed by their gradual dissociation into sulfur and iodine (whence the final violet color) – a conclusion that he attempted to verify spectroscopically.

Rao's synthesis was repeated by Fehér and Münzner in 1961 using a nitrogen atmosphere and cyclohexane rather than carbon tetrachloride as the solvent (13). Once again UV-visible spectroscopy was used to characterize the resulting color changes and the various transient sulfur iodides identified using analogies with the known spectra of the various sulfur chlorides. On this basis, the authors reported the transient formation of a series of polysulfur diiodides $[(S_n)I_2, n = 2-6]$ prior to the final complete dissociation into octasulfur and diiodine.

In 1953 the Indian chemist, A. R. V. Murthy, used reaction 4 to prepared a mixture of transient sulfur iodides essentially identical to those reported by Rao (15, 16). This synthesis was repeated by Padma *et al* in 1974 (17) and in much greater deal in a series of papers by Minkwitz and collaborators in the late 1970s (18-20). They were able to isolate the reddish brown intermediate as a solid using pentane as the solvent, a nitrogen atmosphere, and working temperatures as low as -90°C in order to prolong the lifetime of the intermediates. This change in solvent was prompted by the low working temperatures, since the freezing point of pentane (-130.5°C) is much lower than that of either the carbon tetrachloride (-22.92°C) or cyclohexane (6.47°C) used in previous work.

Minkwitz *et al* found that the brown product was amorphous. Though its composition approximated a
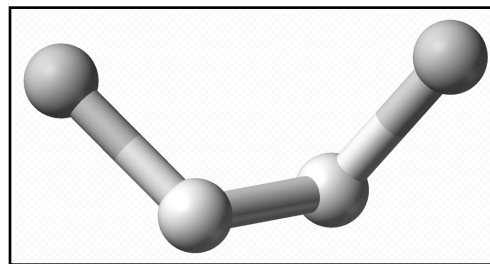

Figure 4. The proposed structure of $(S_2)I_2$, similar to that of $(S_2)F_2$, $(S_2)Cl_2$, and $(S_2)Br_2$.

1:1 ratio of sulfur to iodine, it was variable, thus suggesting that it was contaminated by various competing intermediates and decomposition products. Indeed, not only did the composition vary from one preparation to the next, it also differed depending on whether reaction 4 or reaction 10 was used for the synthesis. These authors also reported both an IR and a UV-visible spectrum for the solid and, based on analogies with the spectra of the known sulfur chlorides, concluded that it was composed mostly of polydisulfur diiodide with a structure identical to that of the corresponding polydisulfur difluorides, dichlorides and dibromides (figure 4).

On the basis of the above work, most German textbooks of inorganic chemistry (2, 21) now acknowledge the existence of polydisulfur diiodide, which is usually described as a dark brown solid stable below -31°C, though its existence continues to be ignored by most British and American textbooks. As for the sulfur diiodide (SI_2) postulated by Rao, from analysis of their spectra Minkwitz *et al* concluded that it did not exist, though in 1980 Feuerhahn and Vahl claimed to have detected it as a transient reaction intermediate in an argon matrix at 9°K (22). However, even the German textbooks have ignored this claim, in part because the formation of one or two molecules of a transient species under the highly atypical conditions employed in matrix isolation severely strains the traditional concept of what it means to have successfully synthesized a chemical compound (23).

As a final historical irony, the above results also show that neither the 20th-century Indian chemists nor the 20th-century German chemists involved in this work were the first to observe the formation of polydisulfur diiodide, since in fact it was first made, using reaction 4, by an English chemist named Inglis as early as 1835, who described it as follows (12):

I caused hydriodic [sic] acid to come into contact with the chloride of sulfur; instant reaction took place, muriatic acid [i.e. HCl] was formed and a dark compound, which was probably an iodide of sulfur, presented itself.

Since this brief description appeared in a summary review article on the chemistry of iodine, Inglis provided no further experimental details and made no attempt to compositionally verify his assumption that the dark compound was, as we now know, an iodide of sulfur.

Theoretical Rationales

The only theoretical rationale for the low stability of the sulfur iodides that I could locate occurs in Dasent's 1965 monograph, *Nonexistent Compounds* (24), where he rearranges Pauling's equation for the calculation of thermochemical electronegativity values so as to solve for a compound's average bond energy:

$$E_{A-B} = 0.5(E_{A-A} + E_{B-B}) + 23(\Delta EN)^2 \qquad [11]$$

Applying this to a S–I bond and using the electronegativity values reported by Pauling in the 3rd edition of the *Nature of the Chemical Bond* (25), which assigns both I and S a value of 2.5, reduces equation 11 to:

$$E_{S-I} = 0.5(E_{S-S} + E_{I-I}) \qquad [12]$$

Further assuming that the enthalpy of reaction is the stoichiometrically weighted difference in the bond energies of the bonds broken in the reactants versus those formed in products then leads one to the conclusion that the enthalpy of formation, for example, of a hypothetical SI_2, as given by the equation:

$$S_8 + 8I_2 \rightarrow 8SI_2 \qquad [13]$$

would essentially be zero as it involves the breaking of eight S–S bonds and eight I–I bonds and the making of 16 S–I bonds.

Questions of the purely empirical and highly approximate nature of Pauling's equation aside, one problem with using electronegativity arguments is that their values can change over time as the scales are further refined. Thus, in Allred's 1961 reassessment of Pauling's scale, S and I no longer have identical *EN* values (26). Even more confusing is that the relative *EN* order of these two elements can vary from one electronegativity scale to another. For example, on the Allred-Rochow force scale, S at 2.44 is more electronegative than I at 2.21, thus suggesting that we should be talking about iodine sulfides rather than sulfur iodides (27). Indeed, this point of view was partially adopted by Fehér and Münzner (13), who referred to their compounds as iodosulfanes (i.e. iodine substituted sulfane or hydrogen sulfide) rather than as sulfur iodides, though they continued to write their formulas as

if iodine was the more electronegative component.

A Final Twist

In 1989 the Canadian chemist, John Passmore, co-authored a review article with the provocative title "Sulfur and Selenium Iodine Compounds: From Nonexistence to Significance" (28). While admitting that neutral molecular $(S_2)I_2$, as described earlier, was only stable at low temperatures and that, in keeping with Dasent's electronegativity argument, the sulfur-iodine bond was extremely weak, Passmore was nevertheless able to report the isolation of series of sulfur iodine polycations that were stable at room temperature, including S_7I^+, $S_2I_4^{2+}$, and $[(S_7I)_2I]^{3+}$. These were prepared in either liquid SO_2 or liquid AsF_3 and stabilized by the presence of large counter-anions, such as $(AsF_6)^-$ and $(SbF_6)^-$.

Passmore attributed the stability of these cations, relative to the weakly stable neutral iodide, not to an enhancement of the stability of the S–I bond, but rather to the added lattice energy of the resulting complex salt. This seems to be a reflection of another important rule of chemical synthesis known as Basolo's rule. This states that the stabilization of large complex cations in the solid state is best achieved by using a large counter-anion of equal but opposite charge (29):

Solid metal complexes are stabilized by large counter-ions, preferably ions of the same but opposite charge.

Basolo based his rule on the isolation of conventional solid metal coordination complexes, such as $Co(NH_3)_6^{3+}$, but it should be equally applicable to the large polycations isolated by Passmore and coworkers. Unhappily, only one compound – $(S_7I)(AsF_6)$ – conforms completely to the rule as the other compounds isolated by Passmore *et al* have complex stoichiometries due to a mismatch in the magnitude of the charges on the cation versus the anion.

Conclusions

To return to the question that prompted this essay in the first place: just what does our antique bottle of sulfur iodide contain and how should I label it? Is it a compound, a solid solution, or a eutectic mixture? After considering the above historical facts I have finally settled on the compromise choice:

"So-called Sulfur Iodide"

References and Notes

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