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NONEXISTENT COMPOUNDS AS A GUIDE TO INNOVATION

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A study of nonexistent compounds can be a useful exercise in gaining insight into the factors that can inhibit innovation. Several reasons are suggested: lack of financial support, disinterest in preparing compounds that lack evident utility, notable synthetic challenges with inadequate rewards, inhibition by well-established contemporary knowledge, and invalid interpolations.

Key words: Argon; Autohypnosis; Innovation; Isomers; Noble gases; Xenon

INTRODUCTION

A fascinating review article, written by E. H. Appelman (4), explored the reasons certain compounds were unknown: His view was that they fit into three categories:

- Extensions of existing knowledge that no one has bothered to prepare;
- Extensions of knowledge, but attempts to prepare them were unsuccessful;
- Whole areas of chemistry that "have not been studied or have been written off as unfruitful for synthetic work" (4).

One may properly note that there is really no shortage of compounds. The Chemical Abstracts Service Registry™ of the American Chemical Society contains more than 72 million unique organic and inorganic substances (2). The list is updated daily with about 15,000 substances (2).

The reasons for concern about the absence of certain substances are, however, because they are related to inhibition of innovation. A certain unprepared substance, if found, might well have properties of value for technology. Accordingly, it seems timely to consider some current reasons for certain nonexistent substances.

LACK OF NEED, LACK OF FINANCIAL SUPPORT

Dr. Alfred Werner, a chemistry faculty member in Zurich in the last decade of the 19th century and for about 15 years of the 20th, became known as "The Father of Coordination Chemistry." In an era when conductivity was the major physical method of characterization of compounds, he was forced to use an isomer number pattern as a means of structure evaluation. For example, for the compound called dichlorodiammineplatinum(II), $[PtCl_2(NH_3)_2]$, two structures—tetrahedron or square plane—could be predicted. If the structure was a regular tetrahedron, Werner predicted the compound could exist as a single entity. If the structure was square planar, there could be two geometric isomers termed *cis* and *trans* (18). The correct structure was predicted (18). The two geometric isomers were known, and the structure corresponded to the prediction.

A more complicated example of an isomer number set of compounds can be represented as Mabcdef, where M is a transition metal ion, most likely Pt(IV),

and the other letters denoted different unidentate ligands (single bond to the metal ion), for example, Cl-, Br-, I-, H_2O, NH_3, that would be arrayed in the form of an octahedron around the central metal ion. Bailar noted that there could be no more than 30 isomers, that is, 15 pairs of optical enantiomers. He worked out a means of representing these isomers that was and remains fascinating (5).

The major point of interest is the obvious synthetic challenge, as well as what seems as an equally obvious lack of need. One can hardly imagine an administrator at the National Science Foundation seeing a need for any of the 30 compounds. Nor could one imagine an independently wealthy chemist feeling the need to undertake the incredible challenge of the synthesis. This is surely understandable, but there is always a thought: Could not a single isomer be of some significant value? It is unlikely that we shall ever know, considering over a century of avoidance of this synthetic challenge.

Related to that concern is the question of prestige. How likely would the work be cited? What major journal with a high impact factor (the number of times in a given year that articles in the journal are cited in other journals) would be likely to accept a paper describing the synthesis? The concern over journal impact factors has been criticized by Alberts (1), and while his criticism is well taken, the concern remains.

"AUTOHYPNOSIS"

Appelman (4) noted that certain compounds have "resisted discovery for long periods of time. Only to be synthesized quite painlessly once the initial breakthrough has been made." He asked an internationally renowned chemist–academician V. I. Spitzyn why this should be true, and the answer was "Autohypnosis" (4).

Based on experience, ours or others', we become convinced that certain compounds will not exist. The prime example is the so-called inert gases, Group 18 in a contemporary periodic table, later renamed the noble gases. No examples of compounds of these elements had been observed, despite some significant efforts. Therefore, it was a generally accepted conclusion that they were properly named inert gases because of a lack of credible evidence (vide infra) of the formation of any chemical compounds.

Examples of failed efforts were presented by Moeller (19).

CONFLICT WITH SUCCESS AS A PROBLEM

The noble gases represented a problem from the outset. Lord Rayleigh and Sir William Ramsay had the misfortune to discover argon first. It was announced in an address in January 1895 that the new gas had a molecular weight of about 40 g/mol, and because the Mendeleev periodic table was arranged by increasing atomic mass (the atomic number concept would not be established until H. G. J. Mosely's report in 1913), the ratio of specific heats (Cp/Cv) was found to be 1.66, which was consistent with a monoatomic gas (unfortunately, the theory had only been tested for one monoatomic gas, mercury vapor). Given the atomic weight (at.wt.) of 40 g/mol, the element should logically be between potassium (at.wt.=39.09 g/mol) and calcium (at.wt.= 40.08 g/mol) or perhaps between calcium and scandium (at. wt.=44.95 g/mol).

The pair had discovered one of three examples of inversions of atomic weight. One pair, cobalt (at.wt.=58.93) and nickel (at. wt.=58.69), had not troubled Mendeleev, who placed them correctly in his table (possibly he presumed that the known atomic weights were incorrect). Ramsay had been able to isolate argon first because argon is the most abundant of the noble gases in the atmosphere (9,340 ppm vs. 0.086±0.001 ppm for Xe). The authors would have had trouble placing neon (18.18±0.04 ppm) in an 1870s periodic table because of the monoatomic nature, seemingly inert behavior, and the absence of a "column" for these gases in Mendeleev's table.

The rigidity of thought also was backed by Mendeleev's prediction of certain elements "missing" from his periodic table, as well as the fact that when these "missing" elements were discovered, their properties were in good agreement with predicted values (Table 1). The table is significantly condensed, and, in fact, the predictions included the formula of the oxide with some predicted properties, nature of the salts, formula of the anhydrous salts, how it would be discovered (spectroscopically or not). The predictions were made in 1871, and gallium was discovered by Lecoq de Boisbaudran, a

Table 1. Some Properties Predicted by Mendeleev (1871) in Comparison With Those Later Discovered (23)

Element Abbr.	Element	Date	Atomic Weight	Specific Gravity	Predicted	Observed
Ea*	Galium	1875	~68	69.7	5.9	5.94
Eb	Scandium	1879	44	44	3.5†	3.86†
Es	Germanium	1886	72	72.3	5.5	5.47

*E, eka, a sanskrit word for one. Mendeleev meant to refer to unknown. The element one above a known one in a given column Ea was eka aluminum; for Eb was eka boron; and for Es was eka silicon.
†Specific gravity for the oxide.

Frenchman, who patriotically named it gallium (23). Certainly one could see why Ramsay would have had a problem convincing scientists that he had discovered new elements given the success of Mendeleev in making his "eka predictions" (cf. Table 1). But other problems can now be recognized, including atmospheric concentration of the noble gases as an example.

CONCENTRATION AS A PROBLEM

During the 1920s and early 1930s, faced with examples of failures to form compounds with argon and helium, it occurred to chemists that size or mass might be related to the failures (11). Linus Pauling was among those who recognized xenon might be promising, and in fact he predicted compounds that were later discovered in the early 1960s.

Yost and Kay (22), colleagues of Dr. Pauling at CalTech, tried to prepare xenon fluoride and xenon chloride, but they failed. Considering the atmospheric abundance in the atmosphere is $9.2 \times 10^{-4}\%$ that of argon, it is understandable that their supply of xenon was surely limited. Since they also used a glass apparatus, of necessity, the formation of silicon tetrafluoride probably overwhelmed any xenon fluorides (11). Probably one significant result was that the failure by two qualified chemists provided documentary evidence of the inert nature of the (now) noble gases.

SUCCESS, GIVEN CRITICAL ASSISTANCE

The availability of PtF_6, a strong oxidizing agent, made it possible to oxidize the oxygen mole to form the oxygenyl ion and the synthesis of $O_2 + PtF_6-$ (cf. Equation 1) by Bartlett and Lohman (6):

$$O_2(g) + PtF_6(s) => O_2 + PtF_6-(s) \qquad (1)$$
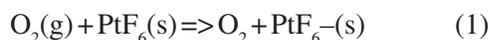
Subsequently, Bartlett noted that the first ionization potential for oxygen was similar to that of xenon (Table 2), for example, 12.2 eV and 12.13 eV, respectively. He noted that it appeared that xenon might be oxidized by the hexafluoride (7). The resulting product was an orange-yellow solid, insoluble in carbon tetrachloride, and underwent hydrolysis (Equation 2) when treated with water vapor.

$$2Xe + PtF_6-(s) + 6H_2O(l) =>$$
$$2Xe(g) + O_2(g) + 2PtO_2(s) + 12HF(g) \qquad (2)$$
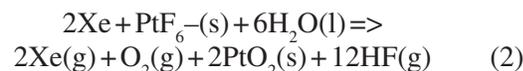
In 1962, the start of considerable progress in the field occurred. Claassen and coworkers (12) provided a "description of XeF_4 as an easily prepared, stable compound." By 1966, 10 noble gas compounds had been prepared.

CONVERGENCE AS A FACTOR IN SUCCESS

Several factors were helpful in the synthesis of the first noble gas compound and others. Chief among these was work that was done at Argonne National Laboratory. The discovery of the first noble gas compound was the convergence of several events/factors.

The Manhattan Project of World War II

An interest in UF_6 occurred because of a desire for gaseous separation of 235U from the more abundant 238U. A resulting interest in other metal

Table 2. Ionization Energies for Oxygen and the Noble Gases, kJ/mol (13)

Oxygen	Helium	Argon	Krypton	Xenon
1313.9	2372.3	1520.4	1350.7	1170.4

hexafluorides led to the discovery of the hexafluorides of platinum, technicium, ruthenium, and rhodium (10).

Development began of a group of workers experienced in handling chemically reactive materials, including those at Argonne National Laboratory, near Chicago. These workers confirmed Bartlett's result "almost as soon as they learned of his experiments" (10). Confirmation was an essential event because in some places there was significant disbelief about Bartlett's discovery (10).

An Argonne group speculated that his result was not necessarily the result of the strong attraction of PtF_6 for electrons; rather it was an ability of PtF_6 to serve as a fluoridating agent. This led to the discovery of XeF_4 and several other xenon fluorides (10,11,14). Most of the first year's work following Bartlett's discovery was reported in a meeting held at Argonne in April 1963 and published in a 400-page book (14).

FLAWED EXTRAPOLATION

As Appelman noted (4), early attempts to prepare perbromates were unsuccessful. Perchlorates were first synthesized in 1816 by von Stadien, who successfully oxidized chlorates with sulfuric acid (4). Paraperiodates, for example, $Na_3H_2IO_6$, were first synthesized in 1833 (4) by passing chlorine through alkaline sodium iodate. Perbromate was not effectively synthesized (in 10% yield) until 1963 when a noble gas compound, XeF_2, was caused to react with bromate ion (4).

Appelman wrote, "next to the perchlorates, perbromates are the least reactive of the oxyhalogen compounds" (4). As a consequence, perhaps early investigators may have prepared perbromates, but they overlooked them because they were expecting a reactive product instead of an inert one (4). They may have been hampered by a flawed extrapolation. This may not happen often, but a single time may have been an obstacle to progress.

FEAR OF THE UNKNOWN

We can be inhibited, understandably, by a reasonable fear of the unknown that may be based on a reasonable suspicion that prevents us from proceeding with a problem or a possible invention.

Mercury compounds can be both familiar and fearsome. Calomel, Hg_2Cl_2, was famous as a household remedy as well as a member of Group I anions in classical qualitative analysis courses. On the other hand, it has long been recognized that mercury–nitrogen compounds are explosive, which limited the number of persons willing to study them (17).

Accordingly, the report of the synthesis of a new mercury azide was surely a fascinating exception to the inhibition. Millon's base, $[Hg_2N]OH.2H_2O$, had been known since Millon's discovery (1830–1850), but the azide derivative was unknown until 2013. Shultz, Villinger, and coworkers (17) prepared a saturated solution of mercury azide, $Hg(N_3)_2$, then combined it with aqueous ammonia to produce a new azide, $[Hg_2N]N_3$. Using extra care and safety gear, the team managed to analyze the yellow solid that exists in two crystalline forms, both of which were produced and analyzed (X-ray diffraction as well as IR, Raman, and optical emission spectroscopy).

The precautions were impressive because the samples were sensitive to rapid heating, shock, and especially friction, and detonation could occur even in solution. The syntheses were affected in the absence of light. Appropriate precautions included "safety shields, face masks, leather gloves, and protective clothing." Of course, mercury compounds are highly toxic (17). One may well ask "how many times does understandable caution/fear limit progress?"

Fluoronium Ion—An Exception to the Rules

Hypervalent or fluorine cations called fluoronium ions have been proposed by analogy with bromonium, iodonium, and chloronium. The latter three can be significant intermediates in organic reactions, but as Dr. Tom Lectka noted in 2013, you never saw fluoronium quoted (8). Lectka prepared several candidate compounds that would show the existence of a fluoronium ion, but the project failed each time over a period of several years. When he reached 50, he decided that it was time to work on a project he enjoyed, rather than trying to satisfy some funding agency (8). Lectka and some interested chemistry students tried a different approach: generate fluoronium in solution as a reactive intermediate and use indirect physical chemistry to infer its existence from reaction products. They were successful (21), and the list of halonium ions was complete.

The take-home message may be to follow one's dream and not be guided by goals of funding agencies. That is easily enough said, provided able volunteers and resources are available; they were at The Johns Hopkins University.

RIGHT TEAM, RIGHT TARGET

Fullerenes are allotropic forms of carbon, for example, C_{60}, whose molecules exist as empty spheres, elipsoides, tubes, and other forms (3). The spheres are often called buckyballs in tribute to a noted architect, Buckminster Fuller, who was responsible for buildings having the unique shape called a Geodesic dome. Allotropes are substances that have the same composition but exist as different forms. Diamonds (tetrahedral carbon) were known from antiquity, graphite (planar of the critical discovery), but did not share in the Nobel Prize (3).

In 1985, a five-person team (Harold Kroto, James Heath, Sean O'Brien, Robert Curl, and Richard Smalley) reported that mass spectrometry had identified a unique peak, corresponding to C_{60} (16). Sir Harry described the significance of this observation in a communication to *Nature* (16). Subsequently, it was observed that fullerenes were fairly ubiquitous, being found in candle soot. They have been produced in various laboratories and commercially (3). The team effort was recognized as Smalley, Curl, and Kroto were corecipients of the Nobel Prize in Chemistry (1996) "for their discovery of fullerenes" (20).

Fullerenes have been studied in fair detail, and various uses have been suggested, but this may not be the essential question. Why were they not discovered earlier? The C_{60} structure was proposed but with insufficient evidence, evidently, to be convincing, and Russian workers proposed the spherical structure based on theoretical calculations, but their report was evidently overlooked in the West. All this occurred before the 1985 report (3).

Considering that the C_{60} molecule was discovered in stardust many light years away, it may be successfully argued that the third form of carbon has been around almost forever but not acceptably discovered. A reviewer suggested that the 1996 prize may well have been awarded more for "Why didn't we find that sooner" than for some useful application of this allotrope of carbon.

Why, indeed, is it plausible to suggest that teamwork made the difference, and the team had not been created previously. If this hypothesis is valid, it would suggest the utter importance of good teamwork in science and perhaps the end of the lone creative individual working alone in a laboratory. There seems to be ample evidence of this in terms of government-funding practices. One problem associated with teamwork is the apportionment of credit, and this becomes significant for those in academe in tenure-track positions. Apportionment of credit, based on position in the author list and the journal impact, is an interesting approach to the quandary (1).

SUMMARY

There may well be an inhibition of innovation because of what might be called the "shoulders-of-giants" syndrome. ("If I have been able to see further, it is because I stood on the shoulders of giants.") Ramsay faced the problem of convincing fellow scientists of a new discovery in major part because it was not compatible with the periodic table of a scientific giant, Dimitri Mendeleev.

The syndrome may well have delayed the discovery of fullerenes. How many persons with a major analytical instrument would use it to examine soot? But stardust was surely a more serious subject, and the collaboration was a great success.

The syndrome reminds us the giants not only have high, but wide, shoulders. Henry Gwyn Jeffreys Moseley, who is given the credit for discovery of the atomic number, chose to move away from a major research center headed by Ernest Rutherford at Manchester perhaps in favor of a more independent existence at Oxford, where he had laboratory facilities but no financial support. On the other hand, Hans Geiger found it profitable to spend time associated with Rutherford at Manchester. Moseley recognized the importance of independence; Geiger, however, benefited from collaboration with Rutherford.

Surely investigators have needed an internal resilience to be successful in any age of science, but perhaps now, more than ever, the experience of failure can enhance that resilience. It is curious that Alfred Werner, who was the father of the chemistry of coordination compounds, may have done harm to his doctoral advisees because of his compassion. Kauffman noted that each research problem was

tested by a very capable research associate before being assigned to a student (15). Werner was a Nobel laureate, but only one of his students, Paul Karrer, was (9,20). In this time of increasing tradition of teamwork for the sake of funding, as well as overcoming individual inadequacies, it is important to acquire that internal resilience.

The patterns that have been described show some failures, some lost opportunities, but more examples of problems being solved through cooperative efforts and an absence of "autohypnosis." A significant question, especially in academe, is how much credit does each team member receive? Finding a satisfactory answer to that question may remain an ongoing challenge.

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