Birth and Death of a Myth

Henry A. Bent

The year 1962 saw a noble myth die, laid to rest by a few colorless crystals in a nickel can. The formula of the lethal crystals—XeF_4. The news of their synthesis spread like wildfire. Professional mythologists, trained in the backwash of the early successes of quantum mechanics to use, not to abuse, received myths, were astonished. The core of chemical theory had crumpled. Or had it? Some thought so and rushed in with rescue operations. Others subjected the compounds—soon prepared with the noble gas in several oxidation states—to a battery of tests. Interesting facts quickly began to appear.

Kinetic and thermodynamic measurements indicated respectable bond energies, reasonable heats of vaporization, and normal heat capacities. X-ray and neutron diffraction studies (three within a year on XeF_4 alone, one of the best characterized of all crystals) showed normal inter- and intramolecular interatomic distances. Electron spin resonance, nuclear magnetic resonance, Mössbauer, infrared, and Raman spectroscopy revealed some large coupling constants but otherwise normal molecular parameters. Ex post facto molecular-orbital studies showed what such studies usually show—that a qualitative description of the electron cloud of a molecule can be formulated in terms of molecular orbitals.

Within a year these results had been established, published in the periodical literature, and discussed at a conference, from which emerged with enterprising promptness a book—**Noble-Gas Compounds** (University of Chicago Press, Chicago, Ill., 1963. 418 pp. $12.50), edited by H. Hyman.

This book carries a twin billing. It is described as a complete summary of research in the field of noble-gas compounds and as "a pedagogical tool with a value well beyond that of a simple collection of current research. . . . Here in a single volume the student will find how modern chemists study inorganic chemistry—the questions that are asked and the way answers are found." Among the 58 contributions there is something for everyone, but not a lot for anyone. Nearly half the papers are less than four pages in length, too short, I believe, to be of much value to most students, for whom these papers were probably not intended in the first place, with the notable exception, perhaps, of the opening chapter, E. N. Hiebert's charming 18-page "Historical remarks on the discovery or argon: The first noble gas." Affluent libraries may wish to acquire the volume for this chapter alone. The following excerpts are typical.

> Rayleigh's next step was to try to exaggerate the discrepancy. Concerning this decision, he wrote two years later: "One's instinct at first is to try to get rid of a discrepancy, but I believe that experience shows such an endeavour to be a mistake. What one ought to do is to magnify a small discrepancy with a view to finding out the explanation."
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> Ramsay wrote the following year, "The statement [that air contained another gas even more inert than nitrogen] was received with surprise and interest; chemists were naturally somewhat incredulous that air, a substance of which the composition had been so long and so carefully studied, should yield anything new."
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> Rayleigh and Ramsay concluded, "We do not claim to have exhausted the possible reagents. But this much is certain, that the gas deserves the name 'argon,' for it is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character . . . . It will be interesting to see if fluorine also is without action, but for the present that experiment must be postponed, on account of difficulties of manipulation."

Difficulties of manipulation persisted for several decades. In 1933 a report entitled "An attempt to prepare a chloride or fluoride of xenon," by Yost and Kaye, concludes with this sentence: "It does not follow, of course, that xenon fluoride is incapable of existing."

For nearly 30 years the Inert-Gas Myth continued to serve chemistry as a convenient approximation to the truth. The vantage point of present knowledge makes clear, however, that to accommodate the myth it was increasingly necessary to strain chemical theory and ignore chemical facts. Interestingly, more than one chemist evidently had contemplated the series, which begins with two well-known compounds, SF_6, BrF_5, XeF_4, FrF_3, and idly had wondered if there was anything to it. Now that we know there is, where do we stand? What have we learned from the Great Mistake?

We have learned that out of test-tubes may still come surprising things. Now one often hears the statement made that with the discovery of quantum mechanics the possibility exists of making chemistry entirely theoretical. A recent note adds that 30 years, however, is not nearly enough time to determine whether or not this is so. Yet, during these 30 years, the skill of theoretical chemists augmented by computer efficiency has produced an effort of mind and matter which, in terms of the pre-1930 level of scientific activity, would be equivalent to a computational labor of many thousands of years. This labor has produced not one firm prediction about even the simplest test-tube experiment.

If this judgement is harsh, it is harsh because inordinate emphasis has been placed on the predictive component of quantum theory, a component, incidentally, that is not particularly prominent in several widely acclaimed theories in other fields—for example, the theory of evolution and absolute rate theory. What the noble-gas experiment did was to dramatize a present limitation of quantum mechanics, a limitation that may or may not be merely computational, by illustrating in striking fashion the generally acknowledged fact that chemistry is still an experimental science.

It also dramatized the usefulness of the isoelectronic principle. An elegant example is given in the chapter on the crystal and molecular structures of XeO_3 and HIO_3. In a similar vein, the comparison of the vibrational spectra of XeF_4 and $XeOF_4$ recalls the structural similarities found for SF_4 and SOF_4.

All in all, the chemical bond appears to have survived the critical year 1962–1963 essentially unchanged. The contending views forwarded in this volume for bonding in XeF_2 and XeF_4 are not as different as they appear on the surface. If the molecular orbital descriptions—which deal with energy

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eigenfunctions (of fictitious Hamiltonians) and which as they stand give no information about the electron density distribution—are subjected to equivalent orbital transformations to give orbitals that so far as possible satisfy the strong orthogonality condition, one finds that the various descriptions are in essential agreement about the answer to this question: Are there or are there not in XeF_2 and XeF_4 five and six electron pairs, respectively, in the valence shell of xenon?

Arguments about whether xenon utilizes *d*-character in its bonding orbitals are probably specious. The suggestion made in one study that changes in nuclear repulsion may be balanced by changes in electron repulsion reenforces my prejudice that the results of molecular orbital studies are to be viewed as, at best approximate, *descriptions* of electronic structure, not as *explanations*.

In summary, the noble-gas episode has been chiefly a domestic affair—one for chemists by chemists. Simultaneously, however, it has been an impressive illustration of the congency of an observation about science made 38 years ago by Gilbert N. Lewis. Scientific theories, Lewis wrote, "are not those beautiful structures so delicately designed that a single flaw may cause the collapse of the whole. The scientist builds slowly and with a gross but solid kind of masonry. If dissatisfied with any of his work, even if it be near the very foundations, he can replace that part without damage to the remainder. On the whole he is satisfied with his work, for while science may never be wholly right, it certainly is never wholly wrong; and it seems to be improving from decade to decade."

Human Engineering

Anthropometric Survey of Turkey, Greece, and Italy. H. T. E. Hertzberg, Edmund Churchill, C. Wesley Dupertuis, Robert M. White, and Albert Damon. Published for NATO by Pergamon, London; Macmillan, New York, 1963. Illus. $15.

No previous study of as many as 3356 men has been as thorough as this description of the pilots and enlisted men of three Mediterranean countries; the study was prepared for NATO. Data include social background, body-build photographs, skinfold and body composition measurements, and 150 measurements of the diameters and circumferences of body, limbs, and head. The primary purpose was to ensure functional fit of the men's equipment, clothing, and workspace, but the somatotype and body composition records are intended for much wider use in comparing populations, in aging studies, and in study of constitution.

A complete visual index for all measurements is given in chapter 7B, and chapter 8 devotes one page to each measurement, including an exact diagram, a photograph, and a description of technique, the usual statistical parameters (M, σ, V, N) for all subgroups (country total, pilots, cadets, ground forces, Army, Navy enlisted man), and percentiles for Turkey, Greece, Italy, and the U.S. Air Force. Together with these, the succinct descriptions of instruments and methods (Hertzberg, chapter 2), of somatotyping (Dupertuis, chapter 4), of measuring skinfold or subcutaneous fat (White, chapter 5), and of statistical methods and sampling (Churchill, chapters 3 and 7A) make up the ultimate encyclopedia for objectively describing body shape. This elaborate set of standards will be invaluable to everyone working in descriptive human engineering. But it will also be most useful to physicians and public health officers who, in making surveys, intend to use a few critical measures for nutritional status or growth. The many uses of such data are made apparent in chapter 6 where Damon gives a critical worldwide outline of such surveys, from 1869 to the present, and considers the evolution of the use of body-build methods and studies in such fields as nutrition, physiology, disease susceptibility, and race and population differences. This discussion saves the book from being a purely technical manual.

The style is laconic and clear throughout. There are very few obvious errors—on pages 136 and 137 the diagrams for patella height (bottom) and for calf height are interchanged. Some purists will object to use of "nasal root depression" rather than "nasion" (naso-frontal suture) for face, nose, and forehead heights. But an interesting discussion of anatomic variability in vertebral spine protrusion (for the landmark cervicale) applies by inference to nasion and other bony landmarks.

The population conclusions (p. 275) are limited to the major trend—body size increases from Turks to Greeks to Italians (to Americans). But the data indicate much more. Weight-stature ratios show that Turks are relatively lightest, Italians stoutest, with Greeks and U.S. Air Force personnel intermediate. Greeks and Italians tend to be stocky in build and Turks thin and muscular in comparison with more elongated Americans. All four populations are more alike in bony dimensions of the trunk than in limb lengths and proportions, in fat, or in head and face proportions. One of the most creative possibilities mentioned in Appendix III, "Future plans," is the proposed sale, three or more years hence, of the coded data cards to qualified scholars in NATO countries. This will stimulate comparison with local civilian samples, analyses of growth and health trends, and genetic studies.

The most surprising thing about this book is that the entire collecting, processing, and publishing of these data took only 3 years. This speed and competence is a tribute to the ability of the American team and to the enthusiastic cooperation they inspired and received in more than a dozen different Mediterranean Air Force centers. The human contribution made by this work to knowledge and to friendship contrasts with current political tensions.

Competent fieldwork in physical anthropology is not easy with respect to techniques or human relations. This effort, under the leadership of Hertzberg, clarifies both.

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German-English Dictionary

Dictionary of Pure and Applied Physics. vol. 1, *German-English*. Compiled by Louis de Vries and W. E. Clason. Elsevier, New York, 1963. viii + 367 pp. $9.95.

It might be assumed that the cooperation of two distinguished lexicographers would result in a nearly impeccable product; regrettably, this dictionary falls short of the high standards set by De Vries and Clason in their other volumes.

Certain aspects of the dictionary suggest an undue delegation of authority or inadequate editorial responsibility. Although I acknowledge the merit of including ". . . also . . . the most useful and commonly used technical