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THE EXPANDING HORIZON OF INORGANIC CHEMISTRY[1]

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IT is doubtful if the history of science has ever experienced a broader and more general advancement in an equal period of time than the world has witnessed during the years 1921–1941. Developments in all phases of science have been startling in their scope, their influence upon modern life and in the possibilities which they reveal for still further advancement.

Chemistry has produced or assisted in the production of its full share in these developments. The various branches of chemistry have been busy in expanding their own fields of endeavor and in contributing, as opportunities offer, to the sum total of human progress. So diverse has chemistry become and so technical in its diversity that no modern tries to keep himself informed concerning the developments of the science as a whole because the changes come with bewildering rapidity and in overwhelming numbers. The chemist of to-day feels well satisfied with himself if he can keep abreast of advancing thought in the definite field in which lies his major interest. He must of course be at least dimly conscious of the progress made in adjacent fields and in the realms of the sister sciences. But the modern chemist must be a highly specialized worker in an ever narrowing field in order that he may be able to keep up with his competitors whose training is likewise restricted to an intensive study of limited phases of the subject. It is true that we still insist in our graduate training on a suitable background of prerequisites and minor subjects, but it is quite evident that the background is slowly but surely fading into the remote distance. Perhaps at no time in the history of our educational

[1] President's address, Illinois Chapter of Sigma Xi, May 14, 1941.

system has it been more true that a Ph.D. is "one who knows more and more about less and less."

Chemists have been prone to regard inorganic chemistry as a worked-out field from which nothing new, nothing progressive can be expected. The expression of such a viewpoint indicates that the "background" is in actual fact becoming so dim that it gives quite erroneous impressions of relative values. It is safe to say that inorganic chemistry has made remarkable advances during recent years. Its contributions have been varied, but without these contributing factors much of the advancement in other branches of chemistry and in other sciences as well would be difficult or quite impossible. Inorganic chemistry still furnishes, as it has been doing through the years, the basic facts and theories upon which advancement in other sciences are dependent. For centuries mankind used native metals for making implements and weapons as well as clay for the fabrication of crude utensils, but during these long ages little improvement was made in the manufacture of such objects. In modern times metallurgy and ceramics have extended these processes enormously because of fundamental study concerning the chemical composition of the native materials and of the chemical reactions which take place when these raw materials are subjected to familiar age-old processes. In this intensely practical age in which we live it is easy to forget the fundamental importance of fact and theory. We should recall that few really great advancements have been made in the history of science because of pure chance. Most of our developments have come because some one has combined fact and theory to formulate a new concept, and then persistent effort has been made to convert the dream into an existing and useful product.

Another way in which inorganic chemistry is expanding its horizon is in contributing materials which are essential for progress in various other sciences. New techniques in almost any branch of science require new material with new properties and new abilities. The demands for equipment which will stand up under hitherto impossible conditions are most insistent and very necessary before some one's dream can become a reality. Many times the demand is for the present-day impossibility, but frequently the inorganic chemist has been able to suggest or supply material which will meet the required conditions. In this way chemistry has been able to contribute to the advancement of engineering, agriculture, ceramics, metallurgy, sanitation, medicine, and many other branches of human endeavor as well as to the safety, comfort and convenience of mankind. Sometimes these contributions have been diverted from the paths of the constructive and have been set to work to injure, harass and destroy. But the contributions of inorganic chemistry have shown such a wide diversification in modern life that their occasional misuse must be expected. A list of new materials made available during the past two decades would be impressive, even if its length made it tedious. Among these new materials there are few which could have been furnished without the aid, either directly or indirectly, of the inorganic chemist.

This statement may seem to be a wild and extravagant boast, but I assure you it is made in all modesty. To illustrate its meaning, permit me to cite a few examples from recent experiences. These are listed merely to illustrate the fact that progress is most rapid and most successful when the sciences work together toward a common end. The inorganic chemist is trying to prove that while his contribution may be a humble one, it is nevertheless a very essential part of the picture. In fact, the picture itself might even be wholly impossible were it not for the inorganic contribution, which is all too frequently entirely overlooked.

In 1921 indium was a mere name upon the list of known chemical elements. A certain book, devoted to the chemistry of the so-called "rare" elements, was published in 1923. A most illuminating statement in this book reads: "Indium, one of the rarest of metals, is found in minute amounts in a large number of minerals. The amount never exceeds 1/10 of 1 per cent." Surely an element so rare, so inaccessible, so costly can never expect to become useful outside of the museum collections of the curious and unapproachable. But in 1941 we find a great majority of the dentists in our land using a gold filling containing from $\frac{1}{2}$ to 5 per cent. indium, because this alloy has the most suitable melting range, hardness and strength and is superior in resisting tarnish. Surprising as this change is, it is nowhere near as spectacular as to find full-page advertisements in the engineering magazines lauding the advantages of indium-treated bearings in heavy duty machinery. Such bearings are now easily made by a simple electrolytic deposition from a water solution of the sulfate. By heat-treating the deposit, the indium shows the remarkable property of diffusing into the base metal, thus forming a hard smooth surface which will not peel or chip and which shows remarkable ability to resist the corrosive effects of the free organic acids which are so commonly present in lubricating oils. Only a thin layer of indium is required, a fact which makes it possible to use a metal which still sells for $12 to $15 an ounce. But this price is less than one fifth that asked a few years ago, and further reductions may be expected since the producers of zinc, cadmium, iron, arsenic, antimony, aluminum, magnesium, lead, copper, silver and many other metals are finding it profitable to save their indium residues, since now these find a ready sale at a good price. As knowledge concerning the handling of indium increases, economies may be expected so that still greater reductions in price will be in order. It is a fact to-day that indium has ceased to be a curiosity and it is now rapidly taking its place as a useful metal.

In 1921 the only useful purpose served by columbium was to fill one space in the Periodic Table. To-day ferro-columbium is a valued article of commerce, highly prized in the production of stainless steel because the presence of one per cent. of columbium "fixes" the small amount of carbon which is unavoidable and permits welding, spinning and drawing of the metal as well as its use in chemical processes at high temperatures. This fact, coupled with the recent development of case-hardening of stainless steel by the so-called nitriding process, has made possible an enormous expansion in the uses of high chromium steels, and it is safe to predict that the future holds numerous possibilities for still greater expansions in the usefulness of these epoch-making materials.

Titanium and its compounds had begun to attract some attention in 1921 and these materials were beginning to be used in the treatment of steel, in various lighting devices, in the dye and ceramic industries, as reagents in analytical chemistry and in the production of smoke screens. Titanium paints had just begun to attract attention. But these uses were largely experimental in character, and none of them except the treatment of steel could be spoken of as having any considerable commercial importance. According to *Mineral Industry,* the production of titanium material in the United States for 1920 amounted to 545 tons of ore and 2 tons of ferrotitanium were imported. In 1939 this country imported over 287,000 tons of ore, an increase of more than 500 fold in the amount of available titanium material. At present TiO_2 finds a rapidly expanding use in making glass, enamels, lacquers, paper, rayon, linoleum, white rubber, printers ink, plastics, tooth paste and face powder. By far the greatest development has come in the production of paints which was begun in Europe about 1919. In 1939 one firm in this country was producing 70 tons of TiO_2 daily, while a rival producer was increasing its output three fold. It is a significant fact that lead paint has been supreme through the centuries, while to-day its leadership is being seriously challenged by titanium.

Beryllium has been pretty much of a problem metal during recent years. Interest in its development has risen at intervals, but the scarcity of the metal and the difficulties connected with its preparation for use have prevented any advancement of a spectacular nature. There has been extensive growth in the utilization of its alloys, especially with copper for both the automobile and the airplane. The hardness, corrosion resistance and non-sparking properties of beryllium alloys have attracted favorable comment in a variety of industries. The use of beryllium metal, which is remarkably hard and elastic, as armor plate for air craft has been so satisfactory that beryllium has been mentioned among the critical materials of modern warfare.

These are a few examples of metals selected from a list of our less familiar elements which have risen from a state of partial or complete obscurity to a point of commercial importance within the past two decades. Many other examples might be given, but a mere enumeration of a few will suffice:

Lithium compounds have gained prominence in ceramics, in air-conditioning systems and in storage batteries. Cesium is considered essential in the manufacture of high-grade radio tubes. Radium is vastly more abundant to-day than it was 20 years ago and its price is a fraction of that which formerly prevailed. Gallium is finding use in high temperature thermometers, in dentistry, and in numerous alloys. The alloys of thallium are among the most resistant metallic substances in the presence of sulfuric, nitric and hydrochloric acids, while its compounds are successful poisons. Zirconium powder is almost ideal as an ammunition primer and it is doubtless playing an important role at the present time in our own preparations for national defense. Molybdenum, formerly regarded as an adulterant in tungsten steel, has now become one of our most important materials in the production of alloy steels. Tantalum, tungsten, vanadium and selenium have all found greater usefulness, while tellurium, long regarded as useless and a nuisance, is gradually finding ways of entering the service of mankind. Neon, a very rare component of the atmosphere, is now in such common use in lighting devices that it can with difficulty retain its position as one of the less familiar elements, although the atmosphere, its only source, contains only 12 ten thousandths of one per cent.

It may not be surprising to find that the usefulness of newcomers among the metals increases rapidly, once methods of utilization have been established. But if we extend our survey to include the most important and best known among commercial metals we shall find some equally impressive developments within the past 20-year period.

Iron is still the giant among the metals, since the latest production figures show that its total world production is more than 25 times that of all other of the common commercial metals combined. Iron has been used since prehistoric times, and there is no metal whose adaptability to an endless variety of purposes has been more thoroughly studied through the ages than has iron. If any metal deserved to have the reputation in 1920 of offering no inviting problems for the research student, surely it must be iron. But the developments of stainless steel have almost all come since 1920. The use of columbium to permit welding has already been mentioned. Recently the adaptation of the nitriding process to stainless steel produces a metal of outstanding strength, toughness and resistance to corrosion, together with surface hardness and wear resistance of the highest order. This is a material so useful that it is essentially a new metal, capable of innumerable applications. It is doubtful if there has been any more epoch-making development since the introduction of the open hearth than we are now witnessing in the phenomenal growth of stainless steel.

In 1920 the world produced 257,000 metric tons of aluminium. In 1939 the production was nearly three times this amount. During the intervening years, in spite of business depressions and labor disputes, the uses of aluminum have increased at a very rapid rate. Aluminum and its alloys are now used for purposes reaching from kitchen utensils to parlor furniture, from speed boats to airplanes, from truck bodies to stream-lined trains and skyscrapers, from insulating materials to Christmas tree decorations, from food wrappers to electric cables, from paint to high explosives, and from mirrors to permanent magnets. So important has aluminum become in modern life that it was listed in 1939 as one of the 17 strategic materials in United States defense, even though we have for some time ranked second in production and have supplied more than one fifth of the world's aluminum.

In 1921 there were produced in this country a trifle more than 10,000 pounds of the metal magnesium valued at $2.25 per pound; in 1939 there were actually sold more than a thousand times as much and the price had fallen to 27 cents per pound. Because of the rapidly increasing demand for this very light metal, there has recently been put into operation at Freeport, Texas, a $5,000,000 plant for recovering magnesium from sea water. In addition the United States government is investing nine and a quarter million dollars in the building of a magnesium plant upon the west coast for the production of metallic magnesium from Nevada brucite by an entirely new process. When these facilities are completed and if production is equal to prediction the total capacity in this country will approach 25,000 tons per year. This is four times our 1940 production. Magnesium is no longer to be considered as a "rare" metal to be used in small quantities, since now if metals are priced by volume rather than by weight it is the cheapest metal that we know with the exception of zinc and iron.

The production of compact metal from a powder has been practiced for over a century, and the use of powder metallurgy in the preparation of such metals as tungsten, molybdenum and platinum has been practiced for years. But within the past few years these methods have been extended to many other metals and their alloys. Powder metallurgy is found to be convenient if not essential in the working of metals whose melting points are excessive, when metals do not alloy conveniently because of too great differences in melting points, when casting of the metals is not desired and when the product must retain certain properties of the components. This process is now used in making such modern appliances as porous bronze bearings, bearings of high tensile and compressive strength, cemented cutting tools, such as carboloy, and ramet, and the preparation of commutators of flaky copper powder. The use of metal powders in paints, in printers inks, in explosives and in the reduction of refractory oxides may safely be regarded merely as a good beginning in a new type of commercial process.

Gold and silver have been used since time beyond the memory or record of man. They have been symbols of wealth, of exclusiveness and of extremes of selfishness. Their high cost has prevented commercial applications except in a very restricted manner. But present market conditions have brought startling changes in the status of these two metals. Silver at 35 cents per ounce is no longer a precious metal, and as a result it is daily finding new applications which are startling because they are so unexpected. Silver has long been known to possess outstanding properties such as ductility, electrical conductivity and germicidal properties, and we are not surprised to find these uses expanding materially. It is quite natural also to find silver used in the production of metal coatings of various types and thicknesses, including vaporized films and electrolytic deposits. But we are surprised to find silver bearings in our automobiles, and to find the metal used in welding, soldering and in catalysis, sterilization and various other applications. It is perhaps quite significant to note that if our supply of tin is cut off by disturbed foreign commerce a metal commonly suggested as a lining for our food containers is silver. The suggestion seems entirely impractical, but the present price and supply of silver forces upon us the conclusion that this change may come in the not very distant future.

The utilization of gold has been limited through the years to coinage, jewelry and ornamental purposes. This metal has been so useful in these ways that little attention has been given to the discovery of any other commercial applications. But gold and its alloys have some remarkable properties which could be put to use on short notice if the single handicap of high cost could be overcome. Gold is the most malleable, the most ductile and the most resistant to acid corrosion of all our metals. These properties could be put to work to-morrow. If so large a proportion of the world's gold supply finds its way into American vaults that its use as the basis of exchange between the nations is no longer practical and the European dictators make good their threat to force the world to abandon the gold standard permanently, there need be no fear of gold becoming a useless metal or of finding its only application in cheap jewelry. Chemical industry and our architects would be able to put the entire amount to immediate use and it is safe to predict that once the metal becomes available for commercial uses the demand for its unusual properties will prevent a collapse of the gold market.

Time does not permit consideration of the advances made in the last two decades in the chemistry of hydrogen, of oxygen, or sulfur, of phosphorus, of nitrogen, of chlorine, of bromine, of iodine, of fluorine, of silicon, of boron and of many other materials used by the inorganic chemist. The advances have been, in most cases, gradual and substantial rather than sudden and spectacular. But these changes have made material contributions to modern life. We live longer, we travel more rapidly, we move about more safely, we are more secure, more comfortable, better fed and more effectively protected from contagion and more efficiently cured of disease because the research worker has been busily engaged in expanding the horizons of human knowledge.

Perhaps the most significant fact of all is the knowledge that each of these advances has opened out a new field which is ripe for the investigator. None of these developments must be regarded as complete, but as offering a new avenue for driving back the regions of superstition and ignorance. Inorganic chemistry, then, is not a worked-out field lacking worth-while problems for the research worker, but an area of ever widening interest, which is teeming with opportunity.

In closing may I call your attention to the fact that a survey of this type must either be incomplete or unbearably long. Perhaps it can be provocative without coming too close to either of these undesirable characteristics. If our minds have been stimulated and we are now willing to admit that inorganic chemistry has really made some worth-while advances within recent years and does actually contain some attractive problems which are still waiting solution, then perhaps we are ready to draw the conclusion that the golden age of research lies in the future and not in the past.

THE CONTROLLED EXPERIMENT AND THE FOUR-FOLD TABLE

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SUPPOSE that we are testing the potency of two viruses A and B by injecting dosages of each into six mice and find this result: Five of the mice receiving virus A die and one lives; one of the mice receiving virus B dies and five live. The question is regarding the statistical significance of the result judged by the usual criterion that $P = .05$ is the dividing line between significance and non-significance. Diagrammatically we may draw up the table

	died	lived	total
A	5	1	6
B	1	5	6
Total	6	6	12

As the numbers of mice in the A and in the B series are the same, as is often, if not usually, the case in such experiments, we may compare the numbers $n_A = 5$ and $n_B = 1$ which died by taking the difference $n_A - n_B = 4$. As the number which died in both series together is the same, namely 6, the assumption is made that the chance of death is $p = \frac{1}{2}$ and the chance of survival is $q = \frac{1}{2}$. The question is asked: If $p = \frac{1}{2}$, is the chance for a difference $n_A - n_B$ so great as 4 (without regard to sign) less than .05? The usual method of answering this question is to find the standard deviation of $n_A - n_B$ as $\frac{1}{2}\sqrt{6+6} = \sqrt{3}$, and to consider that the difference is normally distributed with this standard deviation. Since the difference can take only integral values it is assumed[1] that the sum of the probabilities for $n_A - n_B$ as great as 4 is to be found from a table of the probability integral by considering the total area in the two tails beyond 3.5 (not beyond 4) when the standard deviation is $\sqrt{3}$. The ratio of 3.5 to $\sqrt{3}$ is 2.031 and the table gives $P = .0433$. The result is significant, though barely so.

A more careful calculation may be made by actually computing the probabilities for all the combinations of n_A and n_B which will make the difference numerically as great as 4. The chances for various values of n_A and n_B, when multiplied by $(1/2)^{12}$ are:

[1] See, P. R. Rider, "An Introduction to Modern Statistical Methods," pp. 71–72.