The Goldschmidt Memorial Lecture.

DELIVERED BEFORE THE CHEMICAL SOCIETY ON MAY 20TH, 1948.

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I FEEL very sad at giving this lecture. It was from this very table nineteen years ago at a meeting of the Faraday Society that V. M. Goldschmidt gave his first account in English of the new crystal chemistry that he had done so much to found. That was published in the now historic little book * of the Faraday Society meeting of 1929—and it was there he summed up for us in England the fruit of the extraordinary work that he had been carrying out in the previous few years. It was not new to everyone there; many of us had followed the work in the " Verteilungsgesetz der Elemente," † a series of papers published some two or three years before. These were milestones in crystal chemistry and in general inorganic chemistry, and started a whole train of further work (of which I hardly dare speak here, considering that we have its ablest exponent—Professor Pauling—sitting in the front row). What I will try to do is to show you something, not only of this particular aspect of crystal chemistry, but also of the coherence and unity of the work of Goldschmidt throughout. He combined wide scope and precision in detail in a most exceptional way. He had many ideas but his ideas were not diffuse, they were concentrated on one major problem. In order to deal with something new which arose during a piece of research, he would often make an excursion on one side, but yet always came back to the central problem, which for him was the material constitution of this earth, or more generally of the stellar universe. In doing so he became the founder of modern Geochemistry and of Crystal Chemistry, sciences that will always be associated with his name.

Now the preparation which he had for this task was itself quite exceptional. He was the son of a distinguished chemist, H. Goldschmidt, was born in Zürich in 1888, and was steeped in an intellectual atmosphere from birth. He was, however, not by any means affected only by chemistry. He came very early under the influence of that great Norwegian petrologist and mineralogist, Brøgger, and from him he passed to other masters in various parts of Europe, particularly to Groth's school of crystallography in Munich. He absorbed all that was known there at the time of crystal chemistry. So he returned to Oslo, becoming a Professor at the early age of 26, to start his work essentially as a petrologist. We may divide his work into stages. His petrological period, 1907 to the middle of the first World War, 1916, was followed by a very important intermediate practical period, 1916—1922, in the service of the Norwegian government. Then came the great *X*-ray crystal-chemical period from 1923 to 1927. In 1927 he took up the chair of Mineralogy at Göttingen, combining it with his Oslo chair and travelling between the two by air; but after two years he settled in Göttingen, entered the third period of work, the chemical aspect of the distribution of the elements which he had before treated petrologically and physically, and developed an analytical laboratory of unsurpassed accuracy of determination. On his analytical work alone he would rank as an extremely fine inorganic chemist. He continued it until the first shock of events, which were to have a disastrous effect on his life, forced him out of Germany, where he lost his laboratory and all his apparatus, most of it his own personal property. He went back to Oslo in 1935 where he started all over again. This respite lasted only for a few years, for in 1940 Hitler followed him to Oslo, but even then could not stop him. He worked for the Allies underground, was just not sent to a concentration camp but was imprisoned twice, escaped, literally at the last minute, being sent to the extermination camps of Poland, and finally got to Sweden. Then he came to this country where he spent most of the rest of his life, broken in health, yet able to open a new but final phase of soil geochemistry before his death in March 1947.

The thread of his researches—his intense interest in the elements, their genesis, their affinities and successive associations—was never broken. He would change from one method to another that would promise new and fuller information. Petrology, crystallography, and chemistry themselves, though he enriched all these disciplines markedly, were to him only tools for exploring the world and its history.

Goldschmidt must have very early in his scientific life already laid his plans for this great research. He always gave the impression of a man who knew where he was going, even if it was into the unknown. When I first met him in Bad Ems in 1928 he was recovering from a

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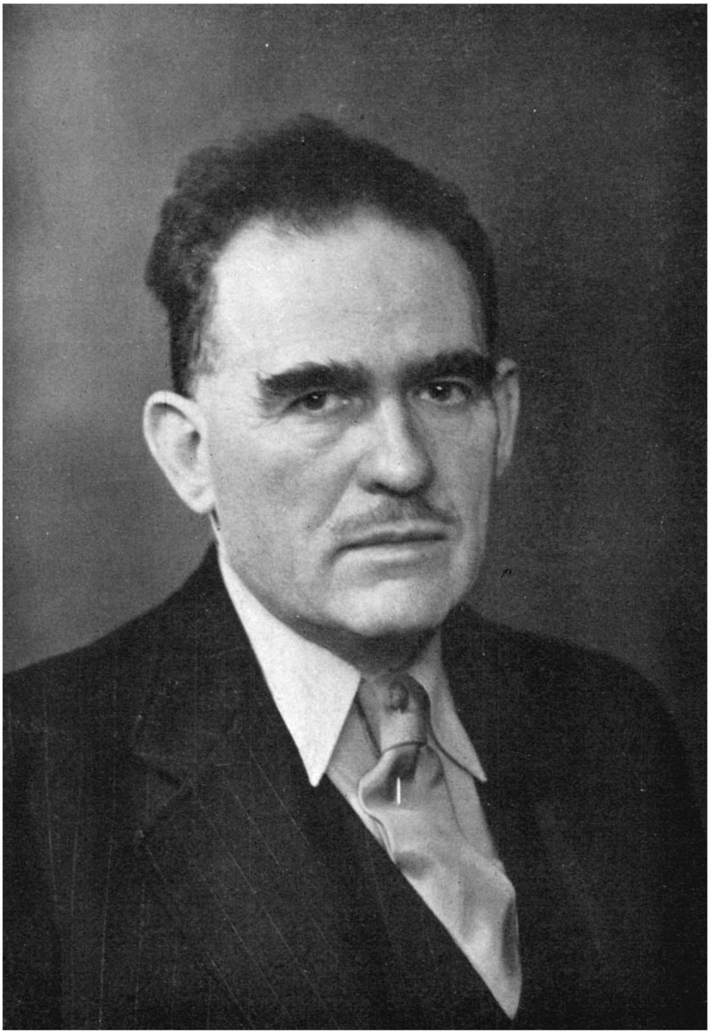
* " Crystal Structure and Chemical Constitution," The Faraday Society, March, 1929.

† *Skrifter Norske Vidensk. Akad.*, I., 1923, No. 2; 1924, No. 5; 1925, No. 5; 1926, Nos. 1, 2, 8; 1937, No. 4.



V M Goldschmidt

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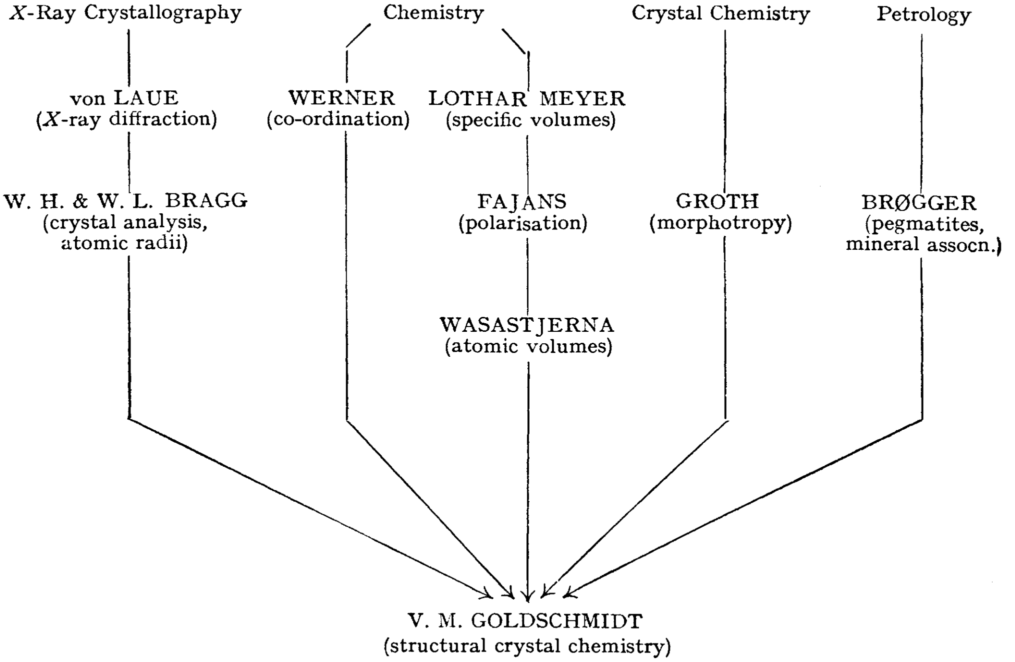
[*To face p.* 2108.

bad attack of fluorine poisoning, owing to having been too enthusiastic in watching an analysis. (This may condemn him from the point of view of chemists.) In spite of the fact that he had practically no voice, he spoke of what he wanted to do in geochemistry and what he would actually achieve. An astonishing amount of this he did manage to do in the next 20 years. The sum of his work was going to appear in his great book on Geochemistry, but unfortunately he died just before this was finished; we may yet hope to see this edited, though without the final touch of his master hand.

Here is a great life's work all but complete. To trace how Goldschmidt came to undertake it we have to consider a number of different influences that were acting on him at that period. I have mentioned his law studies; his family and his travels exposed him to nearly all the influences that could lead to a new synthesis of geochemistry and inorganic chemistry. The clue to that synthesis he was to find in *X*-ray crystallography and in the new crystal chemistry which his experience, training, and vision enabled him to found.

Here is another case in the history of science where the genius of a great discovery lies in the ability to effect a junction between widely separated scientific disciplines. It is one of particular interest because, unlike those of Newton or Franklin, Goldschmidt's discovery was based on extensive rather than intensive studies.



The major ideas which he combined are shown in the diagram, but the work of combination was not something to be achieved by any flash of inspiration; it required systematic survey and experiment.

The first work Goldschmidt did was in petrography. He combined an extremely able field geological training with excellent petrographical techniques and a knowledge of physical chemistry, and introduced the latter into his studies of igneous metamorphosis. As a result of his investigations in the Southern Norwegian mountains he developed a reasoned account of changes in igneous rocks, and especially of the pegmatites where the rare elements tended to accumulate. He became particularly interested in the minerals of the rare elements, especially the rare-earth and uranium series, and this interest he never lost. His first paper was on uranium and his last on neptunium and plutonium. He studied the complexes of minerals formed by magmatic differentiation, and was reaching for an analysis of the chemistry that lay behind them. He knew perfectly well the curious laws of replacement and isomorphism which the minerals seemed to have, which did not fit in with the ordinary laws of chemistry, but the new tool, *X*-ray crystallography, which in his hands was to provide a new basis for far more general laws, only came to him as the result of an altogether external event, the outbreak of the first World War.

Goldschmidt was an intensely practical character, and was concerned to see that his science was used for the benefit of his country. Norway was cut off by German submarines from what had been considered essential supplies. The Norwegian government formed a Materials Supply Committee—and Goldschmidt became its Chairman at the age of 28. It was extremely active and did some remarkable work, particularly in finding local sources for previously imported chemicals. One of these problems was that of extracting potassium from mica, which led him into the very interesting field of the clay mineral studies. This in turn led him to investigate more closely the chemical nature of economic materials, and thus to the study of crystal chemistry. I cannot do better than repeat his own words :

> " The experimental work in the field of crystal chemistry which in recent years the Mineralogical Institute of the University has undertaken had as objective to throw light on the geochemical distribution and technical properties of practically important materials. During the carrying out of these researches which for the most part was by means provided by the Raw Materials Committee of the Norwegian State there appeared a series of generally crystallochemical relationships which made possible a notable deepening of the principles and data of crystal chemistry."

He then describes the state of crystal chemistry in mineralogy when he took it up :

> " For the miner and for the practical chemists crystallography was a purely descriptive auxiliary science which made possible the recognition and distinction of crystalline materials whether they were minerals or technical products."

It was in fact a determinative science, much as spectroscopy was from the time of Kirchoff to that of Bohr.

The actual story as he told it to me—I don't know whether it is true or not, but it is a good Goldschmidt story—was that it all came about through a lawsuit. At the end of the first World War the then government of this country, feeling it had to protect the British chemical industry which had been left so undeveloped before the war, produced a tariff on the import of organic chemicals. Among those referred to was calcium carbide. The chemical interests in this country claimed it was an organic chemical; the Norwegian government maintained it was not. A test case was to be fought in London. Goldschmidt was briefed by the Norwegian government to be the expert witness on the subject. He certainly was not an organic chemist, but he read a text-book on the boat going across and set forth bravely for the law court. When he learned on arrival that the British government expert was Sir William Pope, he decided after all it would not do and he would have to fight him on another ground. Luckily he knew Sir William Bragg, so he took a crystal of calcium carbide and asked him to work out the structure (incidentally he got it completely wrong, but no one could know that at the time) and Goldschmidt fought the case on the basis that this was the structure of an inorganic crystal. There could be no argument against this on chemical grounds, and calcium carbide was finally exempted. The Norwegian Government were naturally pleased and asked how it was done. He put it all down to *X*-rays and on the strength of this obtained an *X*-ray tube and a powder camera.

He wanted to start work straight away, but, realising that with his limited knowledge and apparatus he could not compete with the Braggs in the analysis of complex minerals like the silicates, he began on simple structures—the AX and AX_2 compounds which were mostly of the rock salt, cæsium chloride, rutile, corundum, and calcium fluoride types. The structures of all these were already known. Goldschmidt's original approach was to examine systematically binary compounds of most of the elements. What he did was a model of extensive work. In that sense he was a real chemist; a physicist would spend years working out one structure, but he spent a few months working out a very large number. In two years he and his co-workers, several of whom like Barth, Oftedal, and Zachariasen were to become noted geochemists and crystallographers, worked out structures of 200 compounds of 75 elements and in that way established the extensive basis on which to found general laws.

The sequence of the work is rather interesting. He started on the uranium compounds, with which he was already familiar, to get his hand in. Then he went on to another set of compounds, also of geochemical interest, the rare earth sesquioxides (A_2X_3 compounds). The significance of this choice, probably a deliberate one, was that it was here he began to make comparative studies of compounds of the same type of formula, $A_xB_yC_z$ . . . and not as he and others had done before, either of compounds of a limited group of chemical elements or of one of isomorphous compounds. He had here the advantage of possessing a unique and almost complete collection of rare earths. He showed that the sesquioxides occurred in three overlapping structures which he called A, B, and C. $_{51}$La showed A only, $_{58}$Ce to $_{60}$Nd A and B, $_{61}$Sm alone A, B and C, $_{62}$Eu to $_{66}$Dy B and C, and $_{67}$Ho to $_{71}$Lu only C. The reason for these transitions could not be chemical, it must depend on some physical property. Goldschmidt had the genius to seize on the simplest of these, the size of the atoms, guided by the clue of the small but steady diminution of the lattice parameters in going towards the higher atomic numbers, the celebrated lanthanide contraction.

At that time arguments about atomic sizes were hopelessly confused owing to a quite natural misreading of the meaning of the Lothar-Meyer curve. Specific volumes had been identified with atomic and even with ionic volumes and, as the largest specific volumes were associated with metals, it was assumed that the metal ions were the largest. Early *X*-ray work had apparently substantiated this view as it was possible to account for the lattice dimensions of the alkali halides by assuming large cations and small anions. Already, however, doubts about this view had arisen because it failed to explain the high polarisability of the anions. Fajans and after him Wasastjerna demonstrated on these grounds that the properties of ions could best be understood by reversing the accepted procedure and making the cations small and the anions large.

Goldschmidt's characteristic contribution was that of using this new view of ionic size to explain the morphotropy, or the changes of structure, which occurred in passing along any series of similar compounds on changing the atomic number. He noticed that this transition from one crystal type to another occurred when the radius of one or other of its constituent ions was altered, and, by considering groups of compounds with ions of different charge such as the halides and the oxides, that it was the radius ratio that determined the structure. This led him directly to the most fundamental concept of crystal chemistry, the importance of co-ordination.

Now co-ordination was nothing new in chemistry. It had been introduced by Werner fifty years before to account for the peculiarities of the ions of complex salts. What Goldschmidt did was to point to its crucial role in determining the structure of the simplest crystalline compounds. In spite of the enormously wide variety of crystal structures known even in the inorganic sphere, the varieties of co-ordination are absolutely limited and are derivable from the simplest geometrical considerations. Goldschmidt took the small positive cations as the co-ordinating ions. As they increased in size relatively to the large negative non-metallic anions the co-ordination number increased : beginning with two in a line, passing on to three in a triangle, to four in a tetrahedron, to six in an octahedron, and finally to eight in a cube. The cube marked the turning point. A larger ratio, implying a cation larger than an anion, led to inverted structures. Goldschmidt applied and tested this rule on most of the structures of the simple ionic compounds, those of the types AX, AX_2, A_2X_3, ABX_3, A_2BX_3, and A_2BX_4.

It was at about this period that he moved to Göttingen and renewed his contact with Max Born who was then elaborating the precise quantitative theory of the lattice energy of simple ionic compounds. Goldschmidt's work was complementary to that of Born, the one following the line of intensive study, the other of extensive exploration. Once he had realised that the physical basis for the simple crystallochemical laws lay in the electrostatic attraction between ions of different signs and different sizes, he was able to go further and search for the limits of the applicability of these laws. These, he found, in two different directions, one that of the polarisability of the anions and the other that of the non-electrostatic character of the interatomic bond. He was able to show that the structures of the sulphides and some of the higher halides of small, highly charged, and consequently highly polarising cations, were not of a fully ionic character, for although the anions were co-ordinated round the cations in a normal manner the reverse was not the case. The anions were so polarised by the cations that they had become dipoles on their own account and that structure was composed of rods or sheets held together by relatively weak dipole and van der Waals forces. It was from this that he was able to evolve the first general law of crystal chemistry, his law that *the structure of a crystal is determined by the numerical proportions, the ratio of radii, and the polarisability of its ions.*

The other exception was to be found in the neighbourhood of the fourth column of the periodic table, compounds such as zinc selenide, gallium arsenide, or germanium metal, where the interatomic distance hardly varied with the type of compound, and where simple additive laws no longer held. These compounds Goldschmidt talked of as being commensurable with ionic compounds. They are, in fact, the group that we now recognise as being held together by covalent bonds, making the whole structure a gigantic molecule, in the semi-metallic or adamantine compounds whose electronic and particularly whose semi-conducting properties are now receiving so much attention. These non-ionic compounds he recognised as incommensurable with the ionic compounds and intermediate between them and the metals.

As the result of his extensive studies on ionic compounds Goldschmidt was able to draw up the first tables of empirical atomic radii for most of the ions in the periodic table. He was thus able to understand clearly for the first time the significance of the replacement laws that had made mineralogical chemistry such a confusing subject. The extremely complex formulæ of such minerals as tourmaline and mica, for example, he showed to be due to the apparent indifference of any crystal structure to the particular character or even to the charge of its constituent ions if the total charges of positive and negative ions were balanced. He had earlier shown, by studying the isomorphism of calcium difluoride and yttrium trifluoride, that this balance could be achieved by simply leaving out a certain number of ions from their possible positions in the structure, thus opening the field to the concepts of defect structures. This observation is of the most fundamental importance to the whole theory of chemistry, because it shows that the laws of constant and multiple proportions of Dalton apply strictly only for covalent compounds, that is, for molecular compounds. The reason they appear to hold for ionic compounds or salts is simply that of the equivalence of positive and negative charges, and they lose all meaning in the case of metallic compounds. Goldschmidt did not confine himself to the explanation of the actual structure of the ionic crystals. He was also concerned with their physical properties. He showed in particular how the characteristic hardness of the minerals is associated with the relative charges and interatomic distances of the compounds, and he introduced the extremely ingenious idea of model substances, that is, of substances with the same radii of positive and negative ions but with half the charges. Beryllium fluoride is in this way a model for quartz, and rubidium borofluoride for barium sulphate, compounds resembling each other crystallographically but differing in their melting points and hardness.

It was at this point that the work of Goldschmidt merged into the far more detailed analysis of ionic compounds which was being carried out particularly by the school of Sir Lawrence Bragg in Manchester. The structures of the silicates, far more complex than any that Goldschmidt had attacked, were being determined by precise and absolute physical methods. As the results of one structure after another came out, the fundamental difference, recognised in an empirical way by the mineralogical chemists, between the acid and the basic silicates began to appear, the latter containing isolated SiO_4 ions and these polymerising into rings, chains, and sheets as the ultimate limit of pure crystalline silica itself was reached. Working in Bragg's laboratory, Pauling was able to combine this new knowledge with Goldschmidt's generalisation, to provide the first explicit series of laws of ionic crystal chemistry, the celebrated Pauling Rules, which enabled the possible types of crystal structure to be deduced from the knowledge of the relative numbers, charges, and sizes of the constituent ions. The works of Goldschmidt, Bragg, and Pauling are therefore inextricably combined in this foundation of modern inorganic chemistry.

Before leaving this field, however, Goldschmidt entered the last remaining large area of chemical ignorance, that of the metals and alloys. Here he early realised that the effective diameters of atoms were quite different from those in the ionic state and were always larger. The differences varied very much between the alkali metals, where they were more than twice, and the transition metals, where they were hardly anything at all. He was able to draw up the first table of metallic radii and was even able to make allowance for the different effects of co-ordination by persuading atoms which are normally of fairly low co-ordination, such as bismuth (6), to show twelve-fold co-ordination by alloying them with others such as silver in which this is the natural co-ordination and observing the proportionate charge in parameter. As Hume Rothery showed, the atomic size is not the only determinant of alloy structure; where these do not differ much, the ratio of electrons to atoms is as important. Nevertheless the work of Goldschmidt marks him here also as one of the founders of modern alloy chemistry.

After his brilliant and now historic excursion into the field of crystal chemistry, Goldschmidt in 1928 returned to his first and lifelong interest, that of geochemistry. He had at the outset set himself the problem of how the elements are distributed in the crust of the earth. This was the " Verteilungsgesetz der Elemente," those classical monographs in which he summed up the major part of his life's work. He had found in crystal chemistry the clue to this distribution as determined by the size, charge, and polarisability of the respective ions they formed. He saw that the very nature of the spheres into which the earth was divided was determined by the ionic character of the major elements, those of oxygen, silicon, iron, and magnesium. The core, he thought, was made of iron in which a number of elements such as platinum and siderophilic elements were dissolved. Next to that he postulated an intermediate layer containing the elements allied to sulphur, arsenic, etc., the so-called chalcophilic elements such as lead and copper.

These inner layers of the earth must always remain somewhat hypothetical, but Goldschmidt was on much safer ground in coming to the next main sphere of the earth's interior, the lithosphere. The lithophilic elements are predominantly the silicates of iron, magnesium, calcium, aluminium, and the alkalis, in that order passing upwards. The density of a rock and consequently its height from the earth's centre will depend on the degree of effective packing of its ions rather than on the specific gravity of the ions themselves; thus uranium, though a very heavy ion, forms, on account of its large size, silicates which are relatively light and thus is found in the more acid and higher rocks. Goldschmidt was particularly interested in the distribution of the rare elements, not on any pedantic grounds but because he used them consciously as tracers for the physical and chemical reactions that went on in rock formation and metamorphosis. It was for this purpose that he established at Göttingen the analytical laboratory in which he analysed thousands of rock and mineral specimens and developed new analytical methods of great refinement. I remember his telling me that it was necessary to remove any jewellery from visitors to his laboratory for fear they would contaminate his gold and silver analyses.

Anaylsis was however for him only a means to an end. He was really concerned with the logic of the interchange of elements; as he liked to put it himself, he felt himself in charge of the account-books of the universe. One fascinating piece of research which he carried out was that by which he found the concentrations of germanium in the ash from certain kinds of Newcastle coal.* The argument was briefly this : in a forest, the roots of the trees draw up with the water the elements contained in solution at very high dilution as salts. These pass to the leaves where most of the water is evaporated. Consequently the leaves at the end of the season contain a relatively high proportion of a large number of elements. The leaves fall to the ground and in a well-established or primitive forest the soil to a considerable depth is formed entirely of them. They in turn are subject to leaching, which removes the majority of soluble salts. The result is the gradual accumulation of the insoluble salts of very rare metals often in toxic strength. He made analyses of the soil of some very old forests and showed, for instance, that some of them contained enough arsenic to prevent the effective growth of anything with shallow roots between the trees. Ultimately the forest bed is converted into coal, but the rare elements and particularly the germanium remain in it.

Another example of his powers of interpretation was provided in the case of certain nodules found very generally in red sandstone. Very fine examples of these were collected by Mr. G. E. L. Carter from Budleigh Salterton, and were shown by him to be radioactive. Dr. Perutz † in my laboratory studied these in detail and found they consisted almost entirely of vanadium salts with isolated crystals of uranium salts. Goldschmidt explained their occurrence as follows : all iron-bearing rocks contain a small amount of tervalent vanadium replacing iron. Under conditions of extreme oxidation such as occur in deserts, some of this vanadium is oxidised to the quinquevalent state. In this state it is soluble and washes down into the clay pans which are found dispersed in all desert formations. Here the vanadium salts are concentrated by biological action into concretions which are ultimately consolidated and recrystallised by metamorphic action.

Goldschmidt must rank after Vernadsky as the founder of modern geochemistry. Not only did he establish an enormous amount of factual data in geochemistry, but he also gave all geochemical problems that he touched a rational interpretation in terms of crystal chemistry and ultimately of physics.

It was at this stage that Goldschmidt's work was first seriously interrupted by political events. The advent of Hitler forced him to leave his great laboratory at Göttingen with all the apparatus most of which he had purchased with his private fortune. He was, however, with indomitable energy, able to reconstruct it at Oslo and there, for the last hectic years before the war, continue his work. The war saw him in hiding, arrested, in prison, escaping, and finally reaching Britain. Here at the Macaulay Institute and at Rothamsted he started a field of study which, if he had lived, would have equalled that of the others in importance. This was the application of geochemical methods to soil science or, as he would put it, the chemistry of the biosphere.

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* Coal Research (B.C.U.R.A.), London, June 1944.

† *Min. Petr. Mitt.*, 1939, **51**, 141.

He was, however, already broken in health and hardly survived by a year his return to Norway.

With Goldschmidt there died a great man as well as a great scientist. He was a man of extraordinary courage and self-sufficiency. He was solitary but was extremely friendly and sympathetic to others. He possessed an enormous fund of intellectual energy and a determination which carried him through to the end of his comprehensive scientific projects. He was at his best in adversity and was never defeated by all the hard blows which fate served out to him. I remember his telling me after his first expulsion from Germany how thankful he was to Hitler. " If it had not been for Hitler," he said, " I should have remained a Geheimrat Professor at Göttingen, more and more honoured and more and more bored. Now I am an exile, I have no laboratory, no position, no money, and so life is starting all over again, more exciting than ever, and," he added, " I have found out how really good people are. In ordinary life you can never find whether people are genuinely good, because it pays to be good. Under Hitler, everything is reversed. It pays to be as nasty as possible, and it is surprising, in spite of that, how many good people I have found—even among the educated classes." Another typical story of him is of the days just after Hitler's coming to power when he arrived in the Senate of the University with his short hair cut even more closely than ever. When he was asked why, he answered, " Damit es besser rollen kann," for Hitler had always promised that " heads must roll." But Goldschmidt outlived Hitler and outdid him. All through the early part of the war he used his abilities to deceive the Nazis as to the mineral resources of his country, leading them to waste enormous efforts where there was nothing useful to be found. At first with characteristic stupidity, they failed to recognise his existence at all. When he was had up before the Gestapo and accused of having been dismissed from the Professorship at Göttingen, he asserted he had resigned and produced in proof a certificate to that effect signed by Goering as Minister of Education and Hitler as Vice-Chancellor; the Gestapo official said that it was a forgery; Goldschmidt answered, " That may be so, but when I receive documents signed by the heads of the German state I cannot assume that they are forgeries." For this sally he received two months' imprisonment. But his real crime, of being a Jew, was not then discovered. He was fortunate at the last moment to avoid deportation to Poland and a death camp. Instead he escaped, hid in the woods, and finally found his way to Sweden where, he said, he was delighted to find that at last he was among people who knew who he was.

Goldschmidt was, indeed, one of the really great men of science, one with that rare combination of comprehensive grasp of a complex subject and deep penetration which revealed its underlying structure. We know already that his work will last, that it has taken its place in the permanent structure of science. His work in geochemistry and crystal chemistry would each by themselves suffice to give him an outstanding place in the history of science, to say nothing of his contribution to petrology, of which I am not competent to speak, but which was of the highest order. It is to Goldschmidt more than to anyone else that we owe the picture of atoms and ions of definite measurable sizes, and of their combination at least in organic and metal chemistry as a function of their size. In a few years' time, Goldschmidt's crystal chemistry will take a place beside, if it does not replace, the work of Lavoisier in the merit of not being merely true, but also extremely simple and beautiful. His work on geochemistry cannot expect to have the same finality, but here again the concepts of atomic radii and co-ordination will provide a clue for the complex transformations that have accounted for the history of the earth on which we live.