ADVANCES IN MASS SPECTROMETRY

VOLUME 5

Edited by

A. QUAYLE

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Proceedings of a Conference held in Brussels, 31 August–4 September 1970

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Editor's Foreword

At three-yearly intervals over the past 12 years international conferences on mass spectrometry have been held. The fifth conference in this series took place in Brussels from 31 August–4 September 1970, following those held at London (in 1958)*, Oxford (1961)†, Paris (1964)‡, and Berlin (1967)¶, and adopted the now familiar international pattern.

Yet, in a way, this last conference differed from all the others: it was dedicated to the memory of one renowned scientist and mass spectroscopist, the late Professor Paul Goldfinger, to whom it owed its inception and venue. After it had been decided to hold the conference in Brussels, its initial outline, the setting-up of the Belgian organizing committee, and the calling together of the international committee depended on the initiative, energy, and ideas of Professor Goldfinger. Even when stricken by illness, Professor Goldfinger continued to attend such committee meetings as he was able. The international committee, composed of representatives of the sponsoring bodies AG Massenspektroscopie der DPG, ASMS/ASTM E–14, GAMS, and the Hydrocarbon Research Group of the Institute of Petroleum, together with the Dutch and Belgian mass spectrometrists, benefited from his advice and counsel to the very end. He was sadly missed by us all.

Professor Goldfinger's untimely death some six months before the conference threw an immense burden on Professor Jean Drowart. Already shouldering much of the load, he then had the full responsibility for the conference thrust upon him. That it was so successful was due in no small measure to his individual efforts; only after the close of the conference could he relax from months of sustained hard work. In these unusual circumstances, it is only right to pay further tribute to the ladies concerned: to Madame Goldfinger, for her bravery in continuing to help with the conference organization and particularly with the ladies' programme, and to Madame Simone Drowart, not only for her support of Jean, but for her own hard work on the conference secretariat up to and throughout the conference itself. Lacking the support of a permanent organizing body, such as those arranging previous conferences in this series had enjoyed, our Belgian colleagues laboured under an onerous personal responsibility; they can be justly proud of the success they achieved.

The papers in this volume are not presented in the order in which they were given at the conference; they have been rearranged, as far as possible, to deal first with theory and fundamentals, then with instrumentation, and finally with applications. Despite the use of three parallel sessions at times, it was not possible to include in the conference all the papers submitted and, in restricting them to

* "Advances in Mass Spectrometry". Ed. J. D. Waldron, Pergamon Press, London, 1959.

† "Advances in Mass Spectrometry", Vol. 2. Ed. R. M. Elliott, Pergamon Press, London, 1963.

‡ "Advances in Mass Spectrometry", Vol. 3. Ed. W. L. Mead, Institute of Petroleum, London, 1966.

¶ "Advances in Mass Spectrometry", Vol. 4. Ed. E. Kendrick, Institute of Petroleum, London, 1968.

a total of 147, the international scientific committee was most grateful for the guidance of the referees of many nationalities who aided the final selection.

Finally, the editor is most grateful to the staff of the Institute of Petroleum, and in particular to C. H. Maynard and P. W. Hepple, for their assistance in editing this volume and in many other ways leading to the publication of these conference proceedings. Our thanks go also to the authors and contributors for their co-operation.

Shell Research Ltd
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A. QUAYLE
(*Chairman, Mass Spectrometry Panel, Hydrocarbon Research Group*)

Welcoming Address

By A. JAUMOTTE

(*Rector, Free University of Brussels*)

As you know, the Fifth Triennial International Mass Spectrometry Conference has been dedicated to the memory of the late Professor Paul Goldfinger and this opening ceremony presents to us another opportunity to honour this eminent scientific personality. Paul Goldfinger was the original organizer of this conference. Memories of him will always remain fresh in our minds. His example and achievements will continue to guide us.

How, indeed, could we forget the exceptional courage of this man, whom adversity struck on so many occasions during his life? But misfortune was never for him a cause for discouragement. On the contrary, it was for him each time a new source of energy, in which he found the determination to take up again the task he had assigned himself.

How, indeed, could we forget the enthusiastic conviction with which he fought against the barriers that separate men of good will? This driving force made him an ardent defender of all forms of international co-operation.

How, indeed, could we forget his scientific personality? A brilliant intellect, allied with an extensive knowledge and culture, always made him realize how results of one discipline could allow one to understand another. This led him in his search for the understanding of the chemical bond, to become interested simultaneously in the study of the reactivity of free radicals, of photochemistry, of chemistry at high temperatures, of mass spectrometry, of quantum chemistry, and of optical spectroscopy.

How could we forget his pioneering work? Together with his co-workers, among whom we wish to mention our colleague Jean Drowart, he applied mass spectrometry to high temperature chemistry and thermochemistry. The results obtained in that section of his laboratory have made it a centre of excellence with a worldwide reputation.

How could we forget his generous personality? Not satisfied with being a brilliant research worker, Paul Goldfinger was also an enthusiastic teacher, concerned with the transfer of his knowledge and his passion for research to his students. This led him, in arranging the programme of this conference, to group the review papers in plenary sessions so as to enable all the participants to attend them without missing any papers of particular interest to their own field of research discussed in working sessions.

Ladies and gentlemen, it behoves us to pay a solemn tribute to the man who was so exceptional in many ways, by dedicating to his memory this conference which he had so carefully prepared and which is characterized by his influence. I wish to thank the Organizing Committee for this mark of respect and admiration for our late colleague, Paul Goldfinger, whom we all so sadly miss.

With respect to the conference itself, I am very pleased to note that it is, like

the previous ones, genuinely and, more and more, international. This applies not only to the sponsoring mass spectrometry societies, which now include that of Japan, but also to the participants, who come from all corners of the world to present, compare, and discuss the results of their experimental and theoretical investigations.

The programme shows how much mass spectrometry has developed since the initial investigations of Thompson, Dempster, Aston, and other pioneers. In appreciating the extent of the developments presented here, tribute must be paid to the late Professor Goldfinger and to the Organizing Committee for having brought together such an impressive number of distinguished scientists. The review papers, progress reports, and original contributions give, indeed, a panoramic view of the discipline of mass spectrometry, not only in fundamental studies but also in applications—applications to space and upper atmosphere research, to physics, to physical, organic, and inorganic chemistry, and to biochemistry.

The excellence of the contributions, each of which is at the frontier of its particular field of research, will ensure, we are certain, the success of this conference, as was the case for the previous ones.

It is a pleasure for me to mention, at this moment, the role played by the various laboratories of our own university in the field of mass spectrometry, the more so because, as hosts, members of the staff preferred to let their guests present their results in order to avoid having a programme that is too long. In addition to the laboratory of physical chemistry, of which the late Professor Goldfinger was the director, I mention the laboratories of geology and nuclear geochemistry, and those of organic, analytical, and general chemistry.

This conference will undoubtedly promote further progress in the understanding of the basic processes of ionization and the applications of these processes. As far as our university is concerned, we hope that additional facilities, in particular the new computer at the Centre de Calcul, will contribute to the further development of the work of our scientists.

Ladies and gentlemen, we hope that you will spend an interesting and informative week at our university. This will be for us the best reward for our efforts in organizing a conference of the scope of this one.

In conclusion, may I say that I wanted to open this conference, in person, to honour the memory of Paul Goldfinger. I now call on our colleague, Jean Drowart, to give you some details of Paul Goldfinger's career.

In Memoriam—Paul Goldfinger

By J. DROWART

(*Free University of Brussels*)

IF it had been possible to follow the original programme of this conference, Professor Goldfinger would at this moment be giving the opening address. I know how much he looked forward to it. Instead, it is with deep sorrow that I am led to pay tribute to his memory and personality.

In doing so, I wish, in the name of the Organizing Committee and in my name, to thank Rector Jaumotte for having personally given the welcoming address and for having described in such a kind and striking fashion the scientist we are honouring. Simultaneously, I would like to thank the representatives from the Ministry of National Education, from foreign and Belgian universities and research institutes, from industry, the Chairman of the Faculty of Sciences, and the colleagues and friends of the late Professor Goldfinger for attending this session, together with the conference participants, to honour his memory.

Paul Goldfinger was born in Szasregen, Rumania (then Hungary) on 10 January 1905. After attending grade school in Budapest and high school in Rol, near Geneva, he obtained the degree of chemical engineer in 1927 and the Ph.D degree

in sciences in 1929 at the Federal Technical University in Zurich. From 1929 to 1933, Dr Goldfinger was research assistant at the Kaiser Wilhelm Institute for Physical Chemistry in Berlin, directed by Nobel Laureate Professor F. Haber. In 1933, Dr Goldfinger joined the Physical Chemistry Group of Professor V. Henri at the University of Liège. From 1936 to 1940, he worked at the Laboratoire de Recherche Gasparcolor in Brussels. During World War II, Paul Goldfinger interrupted his scientific activities and played an active role in the Belgian Underground Army, in recognition of which he received the Belgian Commemorative War Medal 1940–45 and the Belgian Medal of the Resistance. From 1946 to 1948, he was Research Associate at the University of Nancy, after which he was Lecturer, later Professor in Physical Chemistry, and Director of the Laboratory for Molecular Physical Chemistry at the Free University of Brussels until his death on 25 March 1970.

Already with his thesis, directed by Nobel Laureate Professor R. Kuhn, entitled "An Attempt to Generalize Stereochemistry", the scientific activity of Dr Goldfinger was in the field of physical chemistry. He rapidly orientated his research in different complementary directions in the areas of chemical kinetics, photochemistry, and thermochemistry concerned with the nature, the stability, and the reactivity of free radicals and high temperature molecules.

In chemical kinetics and photochemistry, Professor Goldfinger studied chain reactions in the gas phase,[1] auto-oxidation in relation to absorption spectra,[2] and isotopic exchange reactions.[3] In industry, he investigated and made important contributions to photochemical problems in the colour film industry. Thereafter he studied the mechanism of chemiluminescent reactions in solution[4] and simultaneously developed a well-known treatment of the relation between the order and the mechanism of pyrolytic relations[5] and attempted the chemical and spectroscopic identification of the methylene radical.[6] Professor Goldfinger next systematically studied gas phase photochlorinations[7] and photochemically initiated oxidations,[8] their mechanism,[9] activation energies, rate constants, and theoretical interpretation.[10]

In organic and high temperature chemistry, Professor Goldfinger's interests included the heat of sublimation of carbon and its relation to the dissociation energy of CO, CN, and other related molecules[11] and the dissociation energy of the molecules S_2, Se_2, and Te_2,[12] problems to which in 1936 he already applied the third law principle. Also here he developed generalizations such as those between the stability of gaseous molecules and of the corresponding condensed phases[13] and stimulated the study of such species by spectroscopic and quantum chemical methods.

In mass spectrometry, Professor Goldfinger again had widespread interests. One was its application to the study of inorganic vapours,[14] which was realized[15] with the help of Dr R. E. Honig, who is present at this conference. While studying the composition and thermodynamic properties of the gaseous phases of Group III–V and II–VI compounds,[16] of Group VI elements,[17] of their compounds,[18] and of ternary molecules such as ammonium chloride,[19] Professor Goldfinger keenly encouraged and helped us in the investigation of many other inorganic systems at high temperatures. Other directions, related to his interests in kinetics, were the investigation of ion-molecule and second-order processes[20] and the study of fast reactions at high pressures.[21]

Over 100 publications authored or co-authored by Professor Goldfinger and

another 100 and more papers by his associates materialize his productive and varied activity. The latter was recognized in many other fashions. Recipient of several national distinctions, Officier de l'Ordre de Léopold, Commandeur de l'Ordre de la Couronne, and Grand Officier de l'Ordre de Léopold II, Professor Goldfinger was made Doctor Honoris Causa of the University of Nancy in 1963 and appointed Visiting Professor at the National Research Council of Canada in 1961, at the University of Rome in 1964, and at the University of Oregon in 1968. Member of the Société Chimique de Belgique, of the Société Belge de Physique, of the Faraday Society, of the American Association for the Advancement of Sciences, of the American Institute of Physics, of the American Society for Testing and Materials, he was Chairman of the Brussels section of the Société Chimique de Belgique from 1961 to 1963. Chairman of many sessions at international conferences, Professor Goldfinger was elected as member of the editorial boards of *Chemical Physics Letters*, *Comprehensive Kinetics*, *Current Contents*, *High Temperature Science*, *International Journal of Chemical Kinetics*, and *Revue de Chimie Minérale*, as well as being photochemistry expert at the Council of Europe in Strasbourg. He was chairman of the Photochemistry Meeting held in Brussels in 1962 and, as you know, Chairman of the Organizing Committee of this conference.

As a scientist and teacher, Paul Goldfinger was enthusiastic but reasoned, with a broad knowledge and interest in varied fields of sciences, who realized how the results of one area enable one to understand those of another, how new techniques make it possible to solve problems left unanswered by others, and who conveyed to his students the desire for fundamental research, for new and accurate results. As an experimentalist, he was able, by dexterous measurements and intuition, to distinguish rapidly the essential features among complex data and next, by a judicious choice of the experimental conditions and logical reasoning, to obtain the results and their interpretation.

As laboratory director, Professor Goldfinger, whom we called "Le Patron" with this mixture of respect and irreverence characteristic of European universities, which he actually liked, allied a strong personality with a deeply humane and stimulating interest in his associates and students, their lives, interests, and careers.

As a man, Paul Goldfinger was a cultivated and broadminded person, interested in a world and society with better justice, defender of co-operation between people of good will, irrespective of their background. An exceptional courage and will power enabled him to overcome the adversity that struck him on too many occasions during his life and career and to find, without bitterness, each time the energy to take up again and to continue the task he assigned to himself. It is this same courage that enabled him to face serenely, for several months, a disease whose outcome, he knew, was most likely to be fatal and, for instance, to work until the very last day on the preparation of this conference, every phase of which he followed and influenced.

In interpreting the feelings of those who have known and appreciated Paul Goldfinger, our thoughts go also to Mrs K. Goldfinger, to his daughter, and to his grandson, present here, who, by their faith and dedication, assisted him during his life. May they also find here the expression of our deep esteem.

REFERENCES

1. Goldfinger, P., Haber, F., and Farkas, L. *Naturw.*, 1929, 17, 674; 1930, 18, 266.

2. Albu, H. W., and Goldfinger, P. *Z. Physik. Chem.*, 1932, **16**, 338; Goldfinger, P., and Graf von Schweinitz, H. D. *Z. Physik. Chem.*, 1933, **22**, 241.
3. Goldfinger, P., and Lasareff, W. *C. R. Acad. Sci.*, 1935, **200**, 1671.
4. Goldfinger, P., Bernanos, A., and Bremer, Th. *Bull. Soc. Chim. Belg.*, 1947, **56**, 259.
5. Goldfinger, P., Letort, M., and Niclause, M. "Relation Entre le Mécanisme et l'Ordre d'une Pyrolyse". Volume Commemoratif V. Henri, Maison Desoer, Liège, 1948, p. 263.
6. Goldfinger, P., Le Goff, P., and Letort, M. *C.R. Acad. Sci.*, 1948, **227**, 632.
7. Gosselain, P. A., Adam, J., and Goldfinger, P. *Bull Soc. Chim. Belg.*, 1956, **65**, 533.
8. Goldfinger, P., and Huybrechts, G., N. N. Semenov's 70th Anniversary Volume, Nauka, Moscow, 1956, p. 323.
9. Chiltz, G., Goldfinger, P., Huybrechts, G., Martens, G., and Verbeke, G. *Chem. Rev.*, 1963, **63**, 355.
10. Johnston, H. S., and Goldfinger, P. *J. chem. Phys.*, 1962, **37**, 700.
11. Goldfinger, P., and Lasareff, W. *Nature, Lond.*, 1935, **135**, 1077; Goldfinger, P., and Jeunehomme, W. *Trans. Faraday Soc.*, 1935, **32**, 1591; Doehaerd, Th., Goldfinger, P., and Waelbroeck, F. *Bull. Soc. Chim. Belg.*, 1953, **62**, 498.
12. Goldfinger, P., Jeunehomme, W., and Rosen, B. *Nature, Lond.*, 1936, **138**, 205; Colin, R., Goldfinger, P., and Jeunehomme, M. *Nature, Lond.*, 1960, **187**, 408; *Trans. Faraday Soc.*, 1964, **60**, 306; Drowart, J., and Goldfinger, P. *Quart. Rev.*, 1966, **20**, 545.
13. Verhaegen, G., Stafford, F. E., Goldfinger, P., and Ackerman, M. *Trans. Faraday Soc.*, 1962, **58**, 1926; Colin, R., and Goldfinger, P. *in* "Condensation and Evaporation of Solids", *ed.* E. Rutner, P. Goldfinger, and J. P. Hirth, Gordon and Breach Inc., New York, 1964, p. 165. Goldfinger, P. *Adv. High Temp. Chem.*, 1967, **1**, 1; Drowart, J., Goldfinger, P., and Verhaegen, G. *in* "High Temperature Technology" Butterworths, London, 1969, p. 159.
14. Goldfinger, P., *in* "Mass Spectrometry", *ed.* R. I. Reed, Academic Press, London, 1965, p. 265; Drowart, J., and Goldfinger, P. *Angew. Chem., Intl. Ed.*, 1967, **6**, 581.
15. Drowart, J., and Honig, R. E. *J. phys. Chem.*, 1957, **61**, 860.
16. Drowart, J., and Goldfinger, P. *J. chim. phys.*, 1958, **55**, 721.
17. Goldfinger, P., and Jeunehomme, M. *in* "Advances in Mass Spectrometry", Vol. 1, 1959, p. 534.
18. de Maria, G., Goldfinger, P., Malaspina, L., and Piaccente, V. *Trans. Faraday Soc.*, 1965, **61**, 2146.
19. Goldfinger, P., and Verhaegen, G. *J. chem. Phys.*, 1969, **50**, 1467.
20. Ackerman, M., Drowart, J., Goldfinger, P., and Jeunehomme, M. 3rd International Congress on Ionization Phenomena in Gases, Venice, 1957.
21. Goldfinger, P., Huybrechts, G., and Verbeke, G., *in* "Advances in Mass Spectrometry", Vol. 2, 1962, p. 360.

Opening Address

By J. DROWART and J. KISTEMAKER

THIS international conference, as did the preceding ones, is showing the ever-increasing desire throughout the scientific community to discuss the subject of mass spectrometry, the fundamental bases thereof, the instrumentation, and the more and more widespread applications.

It is most stimulating to notice the presence of participants from all corners of the world and a particular pleasure to welcome these here.

The organization of this conference greatly benefited from the untiring co-operation of the committee members representing AG Massenspektroskopie der DPG (Germany), American Society for Mass Spectrometry (U.S.A.), American Society for Testing and Materials Committee E14 (U.S.A.), Groupement pour l'Avancement des Méthodes Spectroscopiques (France), Institute of Petroleum, Hydrocarbon Research Group (Great Britain), and the Mass Spectroscopy Society (Japan), and of all the other members of the Organizing Committee.

Special thanks are further due to the scientific secretaries and to the administrative and technical personnel of the Free University of Brussels for their assistance during the sessions.

It is a particular pleasure to acknowledge the assistance and encouragement given us by the President and the Rector of the Free University of Brussels and by the CEN/SCK Center for the Study of Nuclear Energy, and to acknowledge the financial assistance received from the Belgian Ministry of National Education, Administration of Scientific Research, from the Euratom Commission of the European Community, and from the Belgian and Dutch research organizations or industrial firms: Belgian Shell, S.A., Continental Pharma, S.A., European Research Associates, S.A., Gevaert-Agfa, N.V., Labaz, S.A., Manufacture Belge de Lampes et de Matériel Electronique, S.A., Métallurgie Hoboken Overpelt, S.A., Nederlandse Staatsmijnen, Philips Gloeilampenfabrieken, N.V., Procter and Gamble European Technical Center, S.A., Solvay & Cie, S.A., Unilever, N.V., Union Minière, S.A., Union Chimique-Chemische Bedrijven, S.A., and Vielle Montagne, S.A.

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