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On the Cover

Prof. H.J. Schumacher in his working desk.

Background: INIFTA, the institute in Argentina that Schumacher helped establish and directed for 25 years.

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FROM THE EDITOR

The people who make this Journal are most pleased to present this issue, which can be properly named Schumacher's festschrift.

This modest homage is made extensive to all of his collaborators and disciples who continued Schumacher's efforts to fostering basic science in Argentina. Specially Professors Castellano, Arvia, Sicre and the rest of the old guard at the Research Institute of Theoretical and Applied Physical Chemistry, INIFTA.

The successful scientific career of Prof. Schumacher has been extensively covered by Dr. Arvia and Dr. Cobos et al. in their contributions to this issue. Therefore it would be redundant to further elaborate on that matter.

Next issue, due out in mid 2006, will focus mainly on theoretical chemistry featuring contributions to honor Prof. Imre Csizmadia along with regular works on general topics.

The Journal is indexed in Chemical Abstracts and in the Scielo database (Scientific Electronic Library on Line).

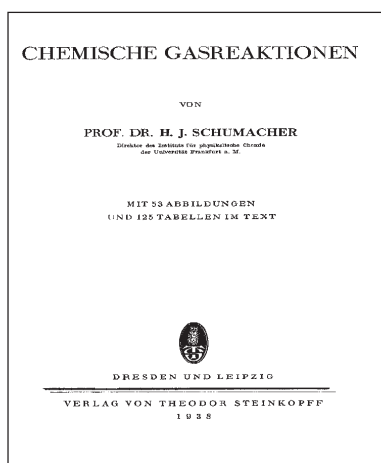
Thanks are always due to guest and associate editors plus anonymous referees who spare part of their valuable time to keep this publication on the move.

Stay tuned.

Reynaldo O. Lezna
Editor-in-Chief

PREFACE

Hans Joachim Schumacher and chemical kinetics in the gas phase



The influence of Prof. Hans Joachim Schumacher (1904-1985) on science in Argentina is well-known and his work has been several times recognized along six decades. In particular, a number of issues of the *Anales de la Asociación Química Argentina* (since 2002 *The Journal of the Argentine Chemical Society, this Journal*) were published in his honor. In 1971, on occasion of Prof. Schumacher 65th birthday, Prof. Pedro J. Carrquiriborde made a review of Prof. Schumacher's works in Argentina. More recently, in 1985, Prof. Alejandro J. Arvia described his successful academic activity in an issue published in homage to Prof. Schumacher 80th anniversary.

In 1925 Prof. Schumacher started his Ph. D. studies at the Institute of Physical Chemistry «Friedrich Wilhelm» in Berlin, Germany, under the supervision of a pioneer in the field of chemical kinetics, Prof. Max Ernst August Bodenstein, who, in turn, had been a disciple of Viktor Meyer in Heidelberg. In Schumacher thesis, concluded two years later, the study of the kinetics and mechanism of the thermal reaction between molecular chlorine and carbon monoxide was carried out along with the role played by molecular oxygen on the system. This work was the beginning of a brilliant scientific carrier devoted to research chemical kinetics in the gas phase. The above studies lead to his first paper as single author in 1927¹. Schumacher's studies of the thermal reaction of molecular chlorine with ozone and the mechanism of the decomposition of chlorine hexoxide were carried out with Prof. Bodenstein.

From his early years Prof. Schumacher made research independently and formed disciples. He published a large number of kinetic studies of thermal and photochemical reactions in the gas phase. Most of the works were carried out by using sensitive manometric and spectrophotometric techniques, analyzing complex reaction mechanisms making use of the steady-state approximation proposed by Bodenstein in 1913. Among others, the experimental research on halogen and nitrogen oxides, the reactions of halogen molecules with ozone, the important investigations on interhalogen reactions can be highlighted. Prof. Schumacher performed the first reliable studies of the low pressure fall-off regions of the thermal dissociation reactions of nitryl chloride (1931), difluorine monoxide (1934) and perfluoroperoxide (1937). The careful measurements of Schumacher and coworkers demonstrated the specific influence of added inert gases and provided the first relative collision efficiencies in unimolecular reactions. In accordance with nowadays knowledge of collisional energy transfer, the fact that absolute collision efficiencies are not smaller than about 0.01, was already pointed out in his classical book *Chemische Gasreaktionen* published in 1938. More detailed investigations in this direction did not start until the 1960's.

¹ For a list of publications see Arvia's article on page 43.

A large part of Prof. Schumacher's scientific activity was carried out in Argentina. Initially as director of the *Instituto Superior de Investigaciones* (Advanced Research Institute), *ISI*, of the Faculty of Chemistry and Pharmacy at La Plata National University and then as director (up to 1973) of the *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas* (Research Institute of Theoretical and Applied Physical Chemistry), *INIFTA*. In 1950 the first papers of Schumacher in Argentina came out. These works, dealing with the electronic absorption spectra and thermochemistry of bromine fluoride, chlorine trifluoride and chlorine fluoride were published in *this Journal*. In 1953 Schumacher published in *this Journal* an interesting set of seven papers on the behavior of the ozone-oxygen system at different pressures and temperatures. Altogether Schumacher published forty six papers in *this Journal*. The first coworkers of Prof. Schumacher at *ISI* were Profs. Alejandro J. Arvia and Juan E. Sicre. Prof. Pedro J. Aymonino was his first postgraduate student to finish a doctoral thesis (reaction of molecular fluorine and chlorine dioxide). Prof. Enrique Castellano joined Schumacher's group in 1958. Professors Sicre and Castellano were to be his closest scientific collaborators in Argentina. Both of them, as well as a number of researchers and Ph.D students, carried out a large number of kinetic and mechanistic studies, published in international journals, of thermal and photochemical reactions of a variety of fluorooxysulfurated, fluorooxynitrogenated and fluorooxycarbonated species. These investigations allowed to determine relevant kinetic and photochemical reaction parameters leading to the elucidation of complex reaction mechanisms of highly reactive species, some of them of potential importance in atmospheric chemistry. For instance, members of the FCO_x ($x=1, 2$ and 3) family postulated in the sixties by Schumacher and coworkers, were isolated and kinetically studied by real time flash photolysis techniques thirty years later at *INIFTA* and in other laboratories.

The now popular ozone molecule caught Prof. Schumacher's attention all along his scientific life. Schumacher's first study of the ozone thermal decomposition at low pressures appeared in 1928. Subsequent investigations of the ozone thermal and photochemical decompositions, as well as the reactions of ozone with fluorine, chlorine and bromine molecules investigated in the early thirties, attracted international recognition. In particular, the controversy on the chain reaction mechanism of ozone decomposition persisted by decades. The discrepancies were clarified in 1962 when Schumacher and Castellano undertook careful quantum yield determinations of ozone decomposition upon irradiation with light of 570-630 nm. This study finally allowed discarding unwanted chain reactions induced by small amounts of impurities present in previous investigations. Later studies of the photochemical decomposition of ozone by ultraviolet light carried out by Schumacher, Castellano and coworkers completed about thirty publications of Prof. Schumacher on the ozone system.

More than half of Prof. Schumacher's scientific research was done in his country of adoption, Argentina, where he left disciples, laboratories and most importantly, a school of research. Besides, quite a number of joyful stories and anecdotes about Schumacher's good humor, in his learnt Castellano, are still making the round at *INIFTA* and will certainly be passed on to future generations.

This special issue is therefore just a modest tribute to a scientist who played a relevant role in the research of chemical kinetics in the gas phase during a large part of the last century.

Carlos J. Cobos (Guest editor)
Adela E. Croce, Reynaldo O. Lezna