exist and the money spent on uranium activities could be better spent in other areas.

In fact, it is possible that the opposite is the case. Because of the drop in uranium exploration activities, the IAEA's role has become more important in the preservation of data and "know-how" acquired in the past boom period. The broad range of information and its value in other areas offer attractive opportunities to provide significant assistance to other areas of the environmental sciences. At the same time, the opportunity is there to help to preserve the expertise and skills of the uranium exploration community against the needs of the future. In addition, the techniques and skills of uranium explorers have been demonstrated to offer the potential for rapid response in times of nuclear emergency unavailable from any other quarter.

As the only international organization with activities in uranium exploration and development and a center of expertise in the wider application of the data and techniques of uranium exploration, should the IAEA be subject solely to current uranium market forces? Or does it have an obligation to encourage and assist in the wider and fuller use of the expenditures made for uranium exploration by its Member States?

Answers to such questions will be key forces in themselves for the future of international co-operation in this field.

Radiation chemistry: Little known branch of science

A largely unrecognized branch of chemistry has had far-reaching effects

by Vitomir Markovic

Radiation chemistry is a branch of chemistry (some say physical chemistry) that studies chemical transformations in materials exposed to high-energy radiations. It uses radiation as the initiator of chemical reactions, as a source of energy that disrupts the sensitive energy balance in stable systems. In that way it is a younger sister of photochemistry, which does the same, but uses another type of electromagnetic energy — light — as the initiator. Radiation chemistry does not deal with radioactive elements (as radiochemistry does), except to use them as a source of radiation, always physically separated from the irradiated system.

Practical applications of radiation chemistry today extend to many fields, including health care, food and agriculture, manufacturing, and telecommunications. Relatively few people are aware of the range of contributions from this largely hidden branch of science.

Origins and development

The origins of radiation chemistry, as a new science, can be traced back to the end of the 19th century, just a few years after the discovery of X-rays. It is not surprising that chemical effects of X-rays were observed so soon, if one recalls that even soft X-rays (low energy, 100–200 kiloelectron-volts) are made of quanta having the capacity to excite or ionize atoms and molecules and break tens of thousands of molecular bonds. Early attempts to understand the nature of chemical reactions induced by radiation were hindered by the lack of sufficiently strong radiation sources to produce changes that could be measured by what, in retrospect, were very rough and insensitive analytical techniques.

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Much pioneering work was done in those early years. Yet the existence of this new science was only recognized in the early 1940s when radiation and nuclear sciences went through rapid developments and numerous breakthroughs. Machines that produce radiation and radioactive isotope sources were produced with outputs not even dreamed of before. At first, chemists were invited to assist other programmes, such as studying radiation effects on living cells.

Some chemists soon discovered that, besides solving practical problems, radiation chemistry could open new doors of knowledge of fundamental value in chemistry. An important achievement was the discovery of the most powerful chemical reducing agents, known as solvated (or hydrated) electrons. The arrival of a technique known as pulse radiolysis in the 1960s extended frontiers of chemical kinetics even farther. The fastest diffusion-controlled reactions were directly observed. A recent compilation (1988) lists, for example, about 3500 rate constants for reactions of main free radicals produced in irradiated systems. This rate information is highly important to researchers applying radiation in studies of environmental and biological problems, in medical therapy (radiotherapy), and in modelling problems in industrial processing and reactor technology.

Indubitably, radiation chemistry has evolved into a broad discipline of chemistry. The methods employed and knowledge acquired have a broad range of applications in other scientific disciplines and industries. However, is it adequately recognized, even by professionals in corresponding areas? There is a general feeling that relatively few scientists realize that radiation chemistry has yielded an array of benefits for major fields of basic and applied chemistry, physical chemistry, and biology.

Radiation chemistry

Radiation chemists are interested in different types of radiations:

- electromagnetic (X-rays, gamma rays)
- charged particles (including electrons, positrons, protons, heavy ions)
- neutral particles (neutrons).

Energies of these radiations are usually of the order of kiloelectron volts (KeV = 10^3 eV) or millions of electron volts (MeV = 10^6 eV). These are many orders of magnitude higher than the ionization and excitation energies of electrons in atoms and molecules (tens of eV), or bonding energies of atoms in molecules (several eV). One particle, or quantum, of electromagnetic radiation can ionize or excite a multitude of molecules — hence, the high efficiency of conversion of radiation energy into chemical effects.

Most radiation chemical experiments are done using gamma rays (from the isotope cobalt-60) or high-energy electrons (from electron beam accelerators with energies of several MeV). The same types of radiations are used in industrial applications. Interacting with matter, these types of radiations dislocate only orbital electrons and produce excited atomic species, free radicals, and ions. These radiation energies do not induce radioactivity in matter exposed to them.

Lately, interest has grown in the use of neutron beams, heavy ion beams, and electrons of very low energy (much less than 0.1 MeV).

Impact on other sciences

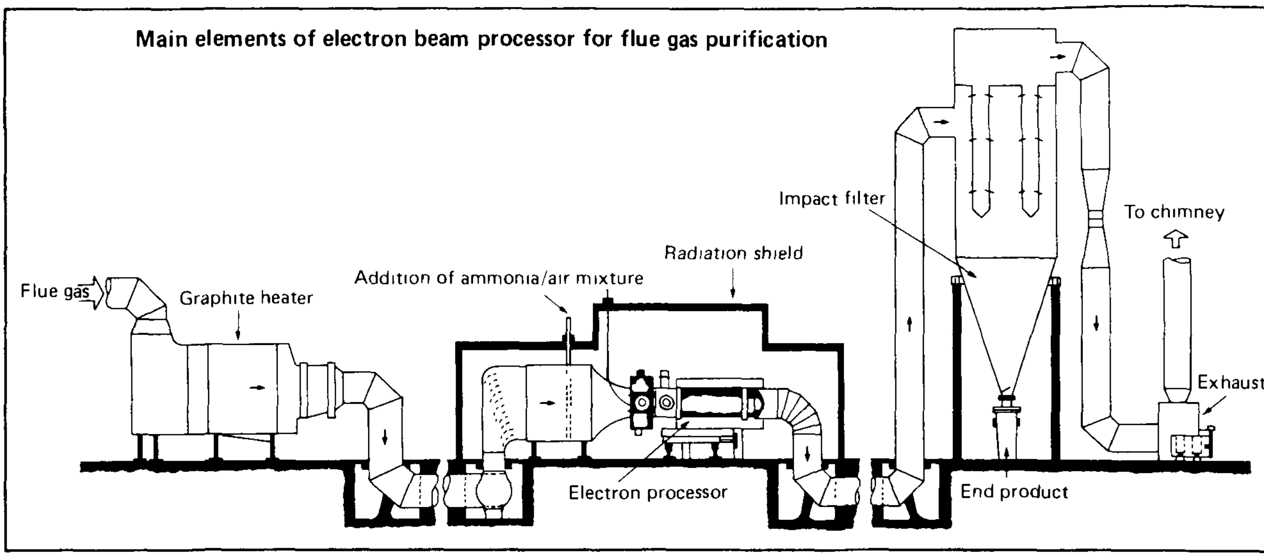
The important advantage of radiation chemistry lies in its ability to be used to produce, and study, almost any reactive atomic species playing a part in chemical reactions, synthesis, industrial processes, or in biological systems. The techniques are applicable to gaseous, liquid, solid, and heterogeneous systems. By combining different techniques of radiation chemistry with analytical chemistry, the reaction mechanism and kinetics of chemical reactions are studied.

Some examples of applications in other sciences include:

Free radical chemistry. Free radicals are short-lived, reactive atomic species, and common intermediates of chemical reactions. They play an important role in our environment, including the atmosphere (ozone depletion, acid rain, smog) and industrial processes. Free radical reactions take place in living cells (plants, animals, human beings) and may have both harmful and beneficial effects. Of special importance are oxy- and peroxy-radicals formed in aqueous and organic systems in the presence of oxygen. Free radicals produced by radiation kill tumor cells and our bodies use free radicals to kill invading organisms. It is easily understandable that knowledge of free radical reactions is essential in such diverse areas as biology, biochemistry, medicine, nutritional sciences, food preservation, and industry. Although free radicals can be produced by other means as well, radiation chemistry remains an important source of information.

General chemistry (organic, inorganic). Radiation chemistry allowed the first detailed identification and studies of many short-lived intermediates in chemical reactions. It produced a large body of data that enabled better understanding of some complex reaction paths and made possible modelling of different systems. Basic chemical and physical processes, known as charge transfer, exciton transfer, radical-radical, and radical-molecule reactions, have been extensively studied.

Chemical kinetics. Pulse radiolysis enabled spectral identification of extremely reactive and short-lived free radicals, radical ions, and excited atomic species. Very fast processes routinely occurring over nanoseconds (10^{-9} s) and microseconds (10^{-6} s), and even as short as several picoseconds (10^{-12} s), are being observed by pulse radiolysis. Short pulses of intense electron beams are used along with fast and sensitive detection techniques; these include techniques known as light absorp-



One emerging application based on radiation chemistry is directed at removal of toxic gases from emissions at fossil-fuelled power plants. Flue gases are irradiated in the presence of ammonia; the electron beam process removes sulphur dioxide and nitrogen oxide and additionally creates a by-product that can be converted into agricultural fertilizer.

tion, emission and scattering, conductivity (for charged species), electron spin resonance (ESR) spectra (for free radicals), and Raman spectra.

Nuclear chemistry and nuclear applications. Radiation chemistry is essential for understanding and control of processes in nuclear reactors where water is used as moderator and coolant and, of course, subject to radiolysis. Other problems including corrosion, control of acidity, and degradation of organic materials are also related to radiation chemical effects.

Practical applications

Practical applications of radiation chemistry have become far-reaching, particularly in industry.* One specific area of interest has been in radiation modification of polymers for different uses.

Radiation crosslinking of polymers is commercially used in the wire and cable industry to improve high-temperature performances of insulating materials as well as in the rubber tire industry. Materials are used in a wide range of industries, including space and aviation, automobile, electronics, telecommunications, and civil engineering. Heat-shrinkable products (film, tape, tubing, connectors) are most easily made using radiation.

Radiation sterilization of disposable medical products is becoming the preferred method in the medical industry. The decontamination of cosmetic products, some pharmaceuticals, as well as raw materials in the pharmaceutical industry, is also gaining wider acceptance. These applications depend extensively on the knowledge of radiation effects on materials.

Radiation curing is based on radiation-induced polymerization. It produces superior quality products, as compared with thermal and ultraviolet curing, while reducing or eliminating environmental pollution, and lowering overall costs. It is used for surface coating, curing of adhesives, laminates, and printing, for example.

Food irradiation is a process whose acceptance is based on biological and organoleptic tests, but also on the knowledge of chemical effects of radiation on food products and their components. It is safe to say that more is known about the chemistry of irradiated food than of food cooked or otherwise treated.

New emerging applications include radiation treatment of flue gases from coal- and oil-fired power plants to remove toxic components, sulphur dioxide, and nitrogen oxide, for purposes of environmental protection. Treated products can be converted into agricultural fertilizer.* In other areas of research, a series of biomedical applications are being developed using radiation modification of polymer surfaces or immobilization of different biologically active materials.**

Trends and developments

In November 1988 in Bologna, Italy, the IAEA convened an advisory group of experts in radiation chemistry to assess trends and developments in 17 countries. Experts attended from Austria, Canada, China, Denmark, Federal Republic of Germany, France, German Democratic Republic, Hungary, India, Israel, Italy, Japan, Netherlands, Poland, United Kingdom, United States, and USSR.

Reports at the meeting reviewed a number of developing applications of radiation chemistry. They include polymeric systems for photochemical storage of energy; radiation sensitive/resistant polymers; environmental applications (for example, treatment of pollutants in

* See, for example, the *IAEA Bulletin*, Vol. 27, No. 1 (1985) p. 33.

* See the *IAEA Bulletin*, Vol. 29, No 2 (1987) p 25, and IAEA TECDOC-428 (1987).

** See IAEA TECDOC-486 (1988).

water); the effect of irradiation on corrosion; and immobilization of drugs and biologically active materials.

Considerations for the future. Given the extent of radiation chemistry's contribution to scientific knowledge and industrial processes, what lies ahead? Is its potential being fully recognized and exploited? Where is radiation chemistry as a scientific discipline today? Where will it be in the near future?

There are some troubling signs.

In contrast to radiation chemistry's established role, the radiation chemical community is relatively small. Worldwide, there are only a few hundred active investigators in basic research and, perhaps, a similar number in the radiation processing industry.

With few exceptions, there is a continuing decline of resources being allocated to radiation chemistry in most countries. Most importantly, radiation chemistry does not exist, or has almost disappeared, from academic curricula at most universities.

This unfortunate state results from the fact that active research requires the availability of expensive radiation sources, such as electron accelerators, or less expensive, but also less flexible and limited in use, cobalt-60 gamma radiation sources. In addition, sophisticated and expensive analytical equipment may be required. Because of this, most workers in radiation chemistry are either based in nuclear science-oriented institutions, or they have to use facilities at these institutions in their work. In one sense this can be construed as a strength, since it has provided excellent instrumental backing and access to radiation sources. It has also proved a weakness, since it has isolated radiation chemists from the mainstream of chemistry. In fact, in recent years there has been a decline rather than an expansion of interest in universities. Most chemistry faculty members and students are, therefore, unaware, or only distantly aware, of the contributions that radiation chemistry can make to their efforts. In some measure, this is understandable, since the impact of radiation chemistry is quite diffuse and many times information obtained by radiation chemical methodology is not recognized as such.

In many cases, the benefits of successful industrial applications of radiation technology have been directly derived from the wider investment in radiation chemical investigation. In developing countries, however, the transfer of radiation technology is not always adequately complemented by an established fundamental research base. And in industrialized countries, once a technology is adopted by industry, there is a tendency to reduce associated fundamental investigations. Unless these trends are reversed and corrected, continuing benefits from radiation technology may not be fully realized.

Some positive developments

There are some indications of positive developments. Malaysia, for example, is giving high priority to new technologies, among them radiation technology. In the medical industry, gamma radiation sterilization of surgical gloves has been practised for many years. A second gamma irradiator for industrial service recently has been installed at the Nuclear Center near Kuala Lumpur. Efforts are also being taken to introduce ultraviolet and electron beam curing to local industry, and radiation vulcanization of rubber latex is being considered. Realizing the need to strengthen the fundamental base, the Nuclear Center in 1988 organized a national training course on fundamental radiation chemistry and its applications with the assistance of the IAEA. Four foreign lecturers and domestic staff conducted the 80-hour course for 18 participants and a number of observers.

In Japan, the Takasaki Radiation Chemistry Research Establishment (TRCRE) of the Japan Atomic Energy Research Institute is efficiently linking applied radiation chemistry with industries. As a result of co-operative efforts, new applications of radiation chemistry are still appearing for polymer materials. Application of radiation processing for environmental protection has been extensively studied. One new project at TRCRE is the application of ion beams in material science and biology. A set of facilities for ion beams is planned that will be used to further international co-operation in the field.

Elsewhere, as well, the base of technical knowledge about radiation chemistry techniques and applications is being expanded through the exchange of information. A major symposium held at Marly-le-Roi, France, in 1988 attracted about 100 French-speaking scientists, either fundamental or applied researchers, involved in the field of radiation chemistry. The meeting provided an opportunity to review research and to consider the future of radiation chemistry in France. The country has a particularly long and productive history in the field.

In the USSR, an excellent and comprehensive monograph on modern radiation chemistry, edited by A.K. Pikaev, has been published recently (in Russian only) by Nauka in Moscow. The three volumes focus on fundamental principles and experimental techniques and methods; radiolysis of gases and liquids; and solid state and polymers, including applied aspects.

Future steps

To ensure the effective transfer of radiation technology to interested countries, it seems necessary to provide stronger support to fundamental radiation research.

In the near term, one step may be to accelerate efforts at integrating the information derived from radiation chemical investigations into the various traditional branches of chemistry. In that way, radiation chemistry could be placed alongside radiochemistry and photochemistry in the curricula of chemistry departments. It is hoped that the Agency, in co-operation with its Member States, might play a visible role in these efforts, as part of its work in this important field.