

# The History and Development of Radiation Chemistry

Ronald Cooper

School of Chemistry, University of Melbourne, Parkville, Vic. 3010, Australia.  
Email: ronaldc@unimelb.edu.au

Stemming from the discovery and isolation of radioactive elements by the Curies came observations of chemical and physical changes produced by ‘emanations’. From ~1900 AD, observations were sporadic and spread across a range of chemical systems. Several conflicting results from irradiated water were reported – one recording no decomposition, whereas another study observed hydrogen and hydrogen peroxide formation. The field progressed slowly while the only practical source of radiation was X-rays. After the mid-1940s, the isotope output from nuclear reactors gave chemists high-activity radiation sources with which to conduct experiments. Particle accelerators were utilized and led to the pulsed radiolysis technique, which unlocked the door to the study of ultrafast solution reactions of free radicals and excited states. The radiation chemistry of water is now a qualitative and quantitative basis for the initiation and study of a wide range of chemical and physical processes. Polymeric systems, solid-state dosimeters, and gaseous plasmas are active areas of research. The radiological use of radiation has an active radiobiology field developing new biochemical processes involving DNA stability.

Manuscript received: 12 April 2011.

Manuscript accepted: 9 May 2011.

## Earliest Observations

Many early and random observations of the effects of radium ‘emanation’ rays on systems were reported.

In 1903–09, Orlov and other Russian workers<sup>[1]</sup> used radium solutions, usually with a barium salt carrier, as radiation sources and studied a range of systems but, curiously, not water. The effects of radium emanation were observed on various systems such as metals, e.g. aluminium, as well as fusible organics and fats.

Ramsay<sup>[2]</sup> observed emission of H<sub>2</sub> and O<sub>2</sub> from aqueous solutions of radium salts. Ozone production was detected in irradiated air.

In 1910, Kharichkov<sup>[3]</sup> observed the production of H<sub>2</sub>O<sub>2</sub> in radium-containing solutions.

In 1913, Duane and Scheuer<sup>[4]</sup> observed the decomposition of H<sub>2</sub>O by  $\alpha$  particles to produce H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>.

By 1920, available X-ray sources were sufficiently intense to produce detectable amounts of decomposition and revealed the challenging result that pure water free of air did not decompose under X-irradiation.

In 1927, Fricke<sup>[5]</sup> proposed a dosimeter based on the oxidation of ferrous to ferric ion.

Activated water was the accepted initiator of reactions. In solutions, it could react with solutes but in pure H<sub>2</sub>O, it dissipated without reaction.

From 1928 to 1938, Hugo Fricke at the James Laboratory for BioPhysics at Cold Spring Harbour, New York, produced an impressive volume of work. A range of products and their yields from irradiated water were identified and assayed. Ultraprecise yields of H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> from irradiated water were made then and remain now as accepted accurate base data. The work used X-rays only owing to their relevance to medical usage. The effects of pH and oxygen content were observed but unexplained.

From the mid-1940s, the need to understand the radiolysis of water became crucial. The cooling of nuclear reactors using water required that the effects of radiation on reactor components be understood. Further, the processing of nuclear fuel required knowledge of the stability of solvents and chemical reagents to ionizing radiation. The result was an intensive research program initially focussed on the radiolysis of water and aqueous solutions. The chemistry group, which was part of the original Manhattan Project, was divided into three. Groups were set up in the USA at Oak Ridge National Laboratory, Argonne National Laboratory, and Notre Dame University.

In Europe, a research group, led by J. Weiss, was active in Newcastle, UK. Weiss<sup>[6]</sup> advanced a free-radical theory and was first to publish this mechanism. Simultaneously, and independently, Burton and Franck at Notre Dame University came to the same conclusion. Frustratingly, these US workers were restricted from publication by secrecy laws!

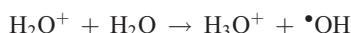
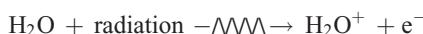
It was soon recognized that a reliable quantitative description of the yields of species produced or destroyed by radiolysis needed to be established.

Burton<sup>[7]</sup> in 1947 proposed a means to express radiation chemical yields of species produced or changed on irradiation: the *G* value – the number of molecules destroyed or produced per 100 eV of radiation energy absorbed by the medium. This unit was a ‘convenience’ unit because it gave numbers for experimental yields in the range 1–10. Using this definition, yields of free radicals and products in water were firmly established and accepted internationally.

Now the standardized unit is the *G* value, but in terms of a radiation dose of 1 gray. This is the yield in moles per joule of absorbed dose.

Using this system,  $G=1$  gives  $0.1039 \times 10^{-6}$  mole  $\text{J}^{-1}$ . In water, this translates to  $0.1039 \mu\text{M J}^{-1}$ .

The radiolytic effect on water was then thought to be that irradiation produced ionized as well as excited water, which subsequently produced  $\text{H}$  and  $\text{OH}$  radicals. These species initiated all the subsequent chemistry.



The chemistry is hence due to the subsequent redox reactions of the free radicals  $\cdot\text{H}$  and  $\cdot\text{OH}$ .

In the late 1940s to early 1950s, UK centres at Manchester (Baxendale), Newcastle (Weiss), Leeds (Dainton), and United Kingdom Atomic Energy Commission–Harwell were active as well as centres in Europe – Paris, Berlin, Vienna, and Russia. Canadian research groups were established at Chalk River, Ontario, and Pinawa in Manitoba.

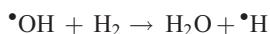
Advent of nuclear reactors gave researchers stable irradiation sources – one commonly used was  $^{60}\text{Co}$ , but electron accelerators were also useful sources of radiation. They enabled radiation chemistry studies to be conducted with safe, convenient and reliable facilities.

United Nations ‘Atoms for Peace’ programs stimulated research into uses of radioisotopes generally. Radiation chemistry was one area. Research rapidly expanded worldwide and to keep pace and regularly pool ideas, International Gordon Research Conferences began in the USA from 1953 and were annual meetings.

The concentrated work on aqueous systems soon solved several of the early puzzling observations.

Why, apparently, was there no decomposition in pure  $\text{H}_2\text{O}$  but some decomposition in aerated water?

The answer was that, in the initial stages of radiolysis,  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  accumulate by radical combination or crosscombination. Subsequently, the same radicals initiate a chain reaction in which these products are destroyed.



Thus, the products of irradiation are converted back to water.

This result was checked by deliberately adding hydrogen peroxide before radiolysis. The result was that the peroxide decomposed.

In the presence of dissolved oxygen, the  $\text{H}$  atoms are scavenged to yield the hydroperoxyl radical  $\cdot\text{HO}_2$ , which is a precursor of hydrogen peroxide. Thus, the  $\text{H}$  atoms are no longer available to participate in the above chain reaction and stable products are formed until all the oxygen is removed.

A second unexplained result was the formation of so-called molecular products  $\text{H}_2\text{O}_2$  and  $\text{H}_2$  in unscavengable yields.

Nuclear physics explains that the energy deposited by ionizing radiation is not evenly distributed throughout the medium. Spatially separate high-energy events such as Compton interactions produce secondary species of lower energy. These secondary species – electrons in the case of  $\gamma$ - or X-rays – are rapidly stopped, producing localized regions – spurs – containing a high

density of ions, excited states, and free radicals. Radical combination can compete with escape into bulk medium. This process is more important with irradiations using particles such as protons or  $\alpha$  particles, which have very short ranges and deposit their energy much more locally. The result is to produce greater yields of  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  due to the very high local concentrations of free radicals. It is estimated that locally this can be as high as 1 M.

These yields are well known in water for a range of irradiation types.

Following acceptance of the free-radical mechanisms in irradiated water, an enormous amount of experimental work was undertaken. The yields of radicals in irradiated aqueous systems for a range of radiation types were accurately established and the quantitative basis of the (now) universally used dosimeter – the Fricke or ferrous sulfate system – set as an international standard.  $G(\text{Fe}^{3+})$  in aerated acid solution was set firmly at 15.6  $\text{Fe}^{3+}$  ions per 100 eV absorbed energy. This value is strictly valid for radiations such as gamma and X-rays and also high-energy electrons. Heavy particles have slightly different but well-established values.

### The Solvated Electron

It was soon recognized that, in comparison with acidic solutions, reduction reactions at high pH involving the assumed  $\text{H}$  atom were significantly different. Weiss and Hayon<sup>[8]</sup> observed that the radiolysis of chloracetic acid solutions over a range of pH gave  $\text{H}_2$  as a product at low pH, whereas at high pH,  $\text{Cl}^-$  was produced. They concluded that the reducing radical in alkaline solution was the solvated electron. To confirm this, Schwartz and Czapski,<sup>[9]</sup> at Brookhaven National Laboratory, examined reactions of the reducing radical with  $\text{H}_2\text{O}_2$  competing with  $\text{NO}_2^-$  or  $\text{H}^+$ . The effect of varying ionic strength on these reactions showed conclusively that the reducing species had a unit negative charge. It was identified as the solvated electron  $\text{e}_{\text{aq}}^-$ . These results were very soon confirmed by experiments by Dainton<sup>[10]</sup> at Leeds, UK.

It is interesting to note that the theoretical physicist R. L. Platzman<sup>[11]</sup> predicted such a species as early as 1952 and even predicted its visible absorption spectrum.

### Pulse Radiolysis

Following closely on the heels of the development of flash photolysis came pulse radiolysis. Electron accelerators were soon developed as very convenient sources of short-pulse radiation. In 1960, almost simultaneously, McCarthy and McLachlan<sup>[12]</sup> at Dupont and Matheson and Dorfman<sup>[13]</sup> at Argonne National Laboratory published the first papers using pulse radiolysis as the experimental technique. In England, Boag and Keene were developing the technique and soon were joined by Hart. Boag and Hart<sup>[14]</sup> used pulse radiolysis to first observe the absorption spectrum of the aqueous (or wet) electron. This showed an absorption with a maximum at  $\sim 720$  nm and with an extinction coefficient of  $15800 \text{ M}^{-1} \text{ cm}^{-1}$ . This meant that concentrations as low as  $10^{-5}$  M could accurately be detected by spectrophotometry.

The discovery and development of this technique revolutionized radiation chemistry. Initially, it could record the time-dependent spectra of reaction intermediates with a lifetime of a few microseconds. It enabled the reaction kinetics of  $\text{H}$ ,  $\text{OH}$ , and  $\text{e}_{\text{aq}}^-$  to be directly observed with ease and accuracy.

Initially, pulses of the order of a microsecond were available, but within 5 years, the pulse length was reduced to a few nanoseconds and with sufficient radiation dose to produce significant amounts of decomposition. It was of sufficient time

resolution to observe the decay of solvated electrons as they combine in the spurs. More recently, pulses as short as a few picoseconds have been generated that enable the observation of spur reactions as well as short-lived excited states of active solutes.

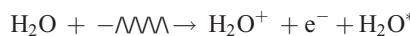
A range of detection techniques were employed to examine the extensive properties of the solvated electron. The essential properties are listed in the following Table 1.

The output from this technique was massive. The rate constants for the reaction of H atoms, solvated electrons and OH radicals with a wide range of substrates number in the many hundreds. Tabulations with critical appraisals are readily available.<sup>[15]</sup> A very extensive account of all the applied pulse radiolysis techniques has been published by Tabata.<sup>[16]</sup>

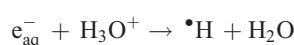
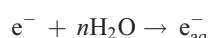
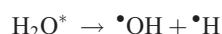
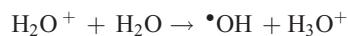
By the mid-1960s, the radiation chemistry of water was firmly consolidated.

It may be summarized as follows.

Following primary ionization and excitation,



secondary reactions, within  $10^{-12}$  s, establish the essential chemistry,



The  $\cdot\text{OH}$  radical is a powerful oxidizer;  $\text{e}_{\text{aq}}^-$  and H are reducing agents.

### Quantitative Yields

Precise dosimetry and accurate chemical analysis have produced internationally accepted standard yields from these well-defined chemical processes.

In  $\gamma$ -, X- or  $\beta$ -irradiated water, pH 7, the  $G$  values are:

$$G(\text{e}_{\text{aq}}^-) = 2.80$$

$$G(\cdot\text{OH}) = 2.8$$

$$G(\cdot\text{H}) = 0.6$$

$$G(\text{H}_2) = 0.45$$

$$G(\text{H}_2\text{O}_2) = 0.75$$

The above  $G$  values and an established mechanism for the radiolysis of water enabled the precise prediction of  $G(\text{Fe}^{3+}) = 15.6$  for the Fricke dosimeter, which is based on

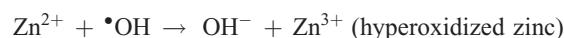
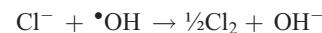
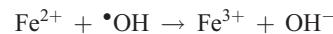
Table 1. Physical properties of the hydrated electron

Equivalent conductance	$1.85 \times 10^2 \pm 0.06 \times 10^2 \Omega^{-1} \text{cm}^2$
Mobility	$1.92 \times 10^{-3} \pm 0.06 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
Diffusion coefficient	$4.95 \times 10^{-5} \pm 0.15 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$
Molar volume	$7 \text{cm}^3 \text{mol}^{-1}$
Radius of charge distribution	0.21–0.3 nm
Standard electrode potential	−2.87 V
Optical absorption maximum	718.8 nm (1.725 eV)
Molar absorption coefficient	$18500 \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
Oscillator strength	~0.75
Free energy of hydration $\Delta G_{\text{hyd}}^\circ$	156.8 kJ mol <sup>−1</sup>

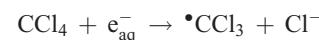
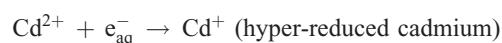
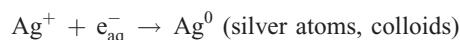
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ . This applies to irradiations using gamma or X-rays as specified earlier.

The ability to generate solvated electrons and hydroxyl radicals in water enables the widest range of selected oxidation and reduction processes to be studied. Inorganic coordination chemistry is able to probe electron-transfer processes in transition metal complexes. These molecules are considered as candidates for solar energy conversion systems as well as controlled drug release agents. Radiation chemistry can quantitatively produce and help study the redox forms of these compounds, whereas photolysis cannot.

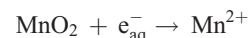
Oxidation reactions of the type:



Reducing reactions are especially facilitated:



with subsequent hydrolysis:



(reductive dissolution of insoluble manganese dioxide)

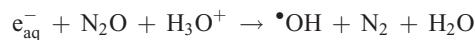


Superoxide is a generator for biologically important free radicals.

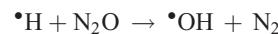
The above is a brief list of the many reactions that can be initiated in a controlled and quantitative way by using radiation chemistry techniques.

The principal control of the oxidizing or reducing quality of an irradiated solution is quite straightforward.

In water saturated with nitrous oxide gas,  $\text{N}_2\text{O}$ , the reactions



and



convert all the reducing species ( $\text{e}_{\text{aq}}^-$  and H atoms) to  $\cdot\text{OH}$  radicals, producing an oxidizing medium.

Alternatively, addition of a small trace of methanol to alkaline water effectively scavenges all the H atoms and OH radicals and the solution is left as a reducing medium i.e. containing only  $\text{e}_{\text{aq}}^-$ .

These reactions can now be used to tailor the subsequent chemistry in the solution. Oxidizing or reducing conditions can be generated as well as a library of free radicals usable in chemical synthesis.

## Organic Compounds

The radiolysis of organic compounds is far more complex than that of water. The triatomic nature of water limits the number of initial species that can be formed, charged or uncharged. In the case of organic compounds, the polyatomic nature means that a range of atomic, radical and ion species are initially produced. Attempts have been made to correlate mass spectrometric 'cracking patterns' with the free-radical distributions in irradiated hydrocarbons. Consequently, with a wide range of compounds studied, there is not the quantitative base yet established for radical and ion yields in organic media. An added factor is that molecular excited states are frequently observed, especially in aromatic compounds. In benzene and toluene, singlet states and accompanying fluorescence are observed as well as long-lived reactive triplet states. In the absence of added solutes, these species can relax back to the ground state without any chemical reaction and hence radiation damage is partially self-annealed.

The formation of excited states can result from geminate ion recombination in the localized spur regions or in the bulk. Some ions may escape into the bulk to become 'free ions'. The escaping tendencies vary widely with the particular system.

A few generalizations can be made. Alcohols produce only a few free radicals and can solvate the electron with accessible IR absorption spectra. At low temperatures, glassy alcohols have been used to measure electron tunnelling phenomena to test Marcus' theories.

## Polymers

One of the major worldwide success stories in radiation research has been the industrial application of radiation chemistry to polymerization and polymer structure creation and properties.

In 1929, Newton<sup>[17]</sup> managed to vulcanize rubber using 'cathode rays'. During and after World War II, many studies looked at the stability of polymers that could be used as insulators in high radiation fields. The study of radiation and polymers has become an increasingly active area of research, leading to extensive industrial development. Two general areas may be identified: radiation-induced polymerization and radiation effects on polymers.

In the 1930s, it was found that vinyl monomers underwent chain polymerization when irradiated with gamma rays. In the 1940s, the advent of high-strength radiation sources pointed towards potential industrial processing. Early workers such as Magat<sup>[18]</sup> assumed a free-radical mechanism for polymer initiation until the work of Talrose et al.<sup>[19]</sup> showed that ionic species could also be responsible via ion-molecule reactions. Later, in 1957, Davidson et al.<sup>[20]</sup> showed that liquid isobutene would not polymerize with free-radical initiation but underwent ionic chain polymerization when irradiated.

A large number of systems have been studied and classified into free-radical or ionic polymerizations. It seems that ionic processes are favoured in ultradry monomers.

Radiation effects on existing polymers attracted a wide interest. This followed on from Charlesby's<sup>[21]</sup> discovery that polyethylene was converted by irradiation into an insoluble, non-melting, cross-linked material. Subsequently materials such as silicones, rubber, polyvinyl chloride, polyacrylates, and polystyrene were cross-linked under radiation. Industry looked to radiation chemistry to be the tailor of new polymeric materials. Later, processes such as grafting were explored and resulted in the production of polymer coatings on paper, wood, metals, and fabrics. A particular obvious application was the

formation of cross-linked polytetrafluoroethylene (PTFE or 'Teflon') as a protective coating on metals – non-stick fry-pans.

Radiolytic curing of polymers such as hydrogels enables biocompatible materials for use in contact lens manufacture, wound dressings and 'patches' for slow-release drugs.

Oxidation-reduction processes in irradiated water are being used by Queensland workers to generate antiglare coatings for windscreens of cars. Radiation and polymers have been a long-time forte of the chemistry schools at the Universities of Sydney and Queensland. Conducting polymers, radiation-stable polymers, surface coatings for space technology, grafted polymers for biocompatibility and insulators in fusion reactors are just a few examples of this widespread field. Controlled growth of latex particles for paints and drug release is also a radiation-induced process.

Radiation chemistry and polymers are and have been a highly active field of study and application.

The reader is referred to extensive reviews in refs [22] and [23].

## Solids

The electrical and mechanical stability of materials in high-radiation fields stimulated the attention of radiation chemists to the study of defects in solids. This had a direct relevance to the use of materials in nuclear reactors and in other systems operating in high-radiation fields.

The coupled use of radiation and electron spin resonance enabled the identity of defect structures to be probed. This research led to the development of the sensitive ThermoLuminescent Dosimeters, TLDs, for personal monitoring and a technique for dating of archaeological pottery artefacts. More recently, the electron spin resonance detection of free radicals has been used to determine the extent of irradiation in food preservation.

The electrical breakdown of insulators has also been a cross-discipline study by radiation chemists and solid-state physicists. Recently, a workshop in Germany examined the use of ultra-high-purity sapphire ( $\text{Al}_2\text{O}_3$ ) as the electrical insulator and first wall material in a high-temperature fusion reactor. Measurement of the radiation-induced conductivity by pulse radiolysis was a significant factor in the decision by electrical engineers to use sapphire for this purpose.

One of the processes leading to mechanical and electrical breakdown in solids is the creation of displacement or F centres. Here, the irradiating particle transfers momentum to the nucleus of a lattice ion or atom in a crystal. The resultant vacancy can be filled with free electrons liberated by conventional radiolytic processes. These trapped electrons are the source of radioluminescence, colour centres and thermally activated conductivity. Suitably 'doped' F-centre lasers are produced by irradiation. This doping technique has much to offer the field of solid-state physics.

## Radiosensitization-protection in Radiotherapy

Complex structures can be synthesized such that they specifically bind in the minor groove of DNA. These molecules can act as traps for species generated by the radiolysis of the ambient water. These trapped free radicals adsorbed onto the DNA chain can react directly with nearby DNA components, leading to DNA strand breakage. Alternatively, the adsorbed ligands can react with free radicals created directly on the DNA, thus resulting in repair. Consequently, the whole topic of electron transfer is one of intense importance and activity. The collaboration between organic chemists, radiation- and photochemists

and molecular biologists is crucial. In Australasia, collaborations involving Melbourne University, the Peter MacCallum Cancer Institute and the University of Auckland are typical of the interdisciplinary approach needed for this work.

See detailed articles in ref. [23].

## Gases

Gaseous systems have received only slight attention. Ionizing radiation is a convenient way to generate free radicals and the reaction kinetics of radicals such as H, O, OH, CH, HO<sub>2</sub>, NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, and CCl<sub>3</sub> have been thoroughly measured by pulsed radiolysis.<sup>[24]</sup>

The production of electronic excited states has enabled the electronic processes in gas lasers (KrF, XeCl, etc.) to be assayed. Ion recombination processes at ambient gas pressures of over an atmosphere have been monitored both by fluorescence and microwave conductivity techniques. This has contributed to the field of plasma physics where ion recombination processes can only be observed at low pressures – 1.33 Pa (10 Torr) and less. Theories of three-body assisted ion recombination have had to be extended. See Mezyk in ref. [23].

These studies have had an impact on the design and modelling of a range of plasma-related applications.

## Food Irradiation

This has been one area of serious research and much political reaction. Irradiation has been cleared for usage by the World Health Organizations and the US Food and Drug Administration. The free-radical species generated by irradiation have been shown to produce a range of beneficial effects. In vegetables and fruit, irradiation can prevent sprouting and delay ripening. It can disinfest food of insects and parasites. Its most often-used purpose is to reduce or completely eliminate pathogenic or spoilage micro-organisms. With doses in excess of 44 kgray, frozen precooked foods are considered to be sterilized and can be stored at room temperatures. Taub<sup>[25]</sup> has given an extensive review of this field.

## Present Status and Future Prospects

Radiation chemistry has explored the fundamental chemical physics of the action of radiation. It can now introduce precisely known amounts of ions, free radicals and electronic excited states into gases, liquids, and solids. Further, the development of time-resolved analytical techniques has made pulse radiolysis a powerful tool with which to measure the rates at which the entities derived from radiation action react with their surroundings. Reaction mechanisms can be proposed and modelled with confidence from the large data banks of radiolysis measurements. The following is a list of some of the areas currently under active study using radiation chemistry methods.

- Flue gas clean-up of NO<sub>x</sub> and SO<sub>x</sub> by low-energy electron-beam treatment
- Rate coefficient measurement for reactions in gaseous electronics. Crucial processes in describing and modelling electrical discharge phenomena such as lighting, welding, gas lasers, atmospheric electrical storms, and surface etching
- Chemistry of the storage of radioactive waste from the nuclear fuel cycle
- Pulsed irradiation techniques enabling the direct observation of the reaction of species important in atmospheric and combustion chemistry
- Radiation-induced degradation of pesticides and intractable materials, e.g. halocarbons, PolyChloroBiphenyls

- Electron-transfer processes in organometallic arrays leading to new concepts in producing bio-switches and conducting films
- Nano-sized colloidal particles for use in solar cells, electrochromic devices, non-linear optical switches, conducting and fluorescent coatings
- Curing of paints, resins and surface coatings
- Production and property modification to produce novel polymers

## Epilogue

Radiation chemistry and chemists have spread into a very wide range of applications. It is due to the early careful fundamental work that this field offers a precise qualitative and quantitative base from which to work.

The origins of this science lie in the new chemical effects that were observed ‘emanating’ from solutions of radium and its accompanying radiations. The Curie discovery led to scientific Curiosity!!! and an extensive chain of chemical processes.

## References

- [1] N. A. Orlov, *Zh. Russ. Fiz. Khim. Chast. Fiz.* **1904**, 36, 41.
- [2] K. V. Kharichkov, *Zh. Russ. Fiz. Khim. Chast. Fiz.* **1910**, 42, 902.
- [3] W. J. Ramsay, *Chem. Soc.* **1907**, 91, 931.
- [4] W. Duane, O. Scheuer, *Le Radium* **1913**, 10, 33. doi:10.1051/RADIUM:0191300100203300
- [5] H. Fricke, S. Morse, *Philos. Mag.* **1929**, 7, 129.
- [6] J. Weiss, *Nature* **1944**, 153, 748. doi:10.1038/153748A0
- [7] M. I. Burton, *Phys. Colloid Chem.* **1947**, 51, 611. doi:10.1021/J150452A029
- [8] J. Weiss, E. Hayon, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy Geneva* **1958**, Vol. 29, p. 80 (UNESCO: Geneva).
- [9] G. J. Czapski, H. A. Schwartz, *Phys. Chem.* **1962**, 66, 471. doi:10.1021/J100809A024
- [10] F. S. Dainton, E. Collinson, *Proc. Chem. Soc.* **1962**, 140.
- [11] R. L. Platzman. *Basic Mechanisms in Radiobiology NRC Publication no. 305* **1953** (Eds J. L. Magee, R. L. Platzman) (National Research Council: Washington, DC).
- [12] R. L. McCarthy, A. McLachlan, *Trans. Far. Soc.* **1960**, 56, 1187. doi:10.1039/TF9605601187
- [13] M. S. Matheson, L. Dorfman, *J. Chem. Phys.* **1960**, 32, 1870. doi:10.1063/1.1731035
- [14] E. J. Hart, J. J. Boag, *Am. Chem. Soc.* **1962**, 84, 4090. doi:10.1021/JA00880A025
- [15] *Handbook of Radiation Chemistry* **1991**, pp. 340–370 (Eds Y. Tabata, Y. Ito, S. Tagawa) (CRC Press: Boca Raton, FL).
- [16] *Pulse Radiolysis of Irradiated Systems* **1991** (Ed. Y. Tabata) (CRC Press: Boca Raton, FL).
- [17] E. B. Newton, *U.S. Patent 1 906 402* **1929**.
- [18] A. Chapiro, C. Cousin, Y. Landler, M. Magat, *Rec. Trav. Chim.* **1949**, 68, 1037. doi:10.1002/RECL.19490681107
- [19] V. L. Talrose, A. K. Lyubimova, *Dokl. Akad. Nauk SSSR* **1952**, 86, 909.
- [20] W. H. T. Davidson, S. H. Pinner, R. Worrall, *Chem. Ind.* **1957**, 1274.
- [21] A. Charlesby, *Proc. R. Soc. Lond.* **1952**, 215, 187. doi:10.1098/RSPA.1952.0206
- [22] *Early Developments in Radiation Chemistry* **1989** (Ed. J. Kroh) (Royal Society of Chemistry: Cambridge, UK).
- [23] *Radiation Chemistry: Present Status and Future Trends* **2001** (Eds C. D. Jonah, B. S. M. Rao) (Elsevier: Amsterdam).
- [24] S. Gordon, in *Early Developments in Radiation Chemistry* **1989**, Ch. 11 (Ed. J. Kroh) (Royal Society of Chemistry: Cambridge, UK).
- [25] L.A. Taub, in *Radiation Chemistry: Present Status and Future Trends* **2001**, Ch. 25, pp. 705–728 (Eds C. D. Jonah, B. S. M. Rao) (Elsevier: Amsterdam).