

# Historic landmarks in radiation chemistry since early observations by Marie Skłodowska-Curie and Pierre Curie

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**Abstract.** The origin of the radiation chemistry history is contemporary with the X-rays and uranic rays discoveries. The complexity of the phenomena induced by the radiation effects, which involve electrons, ions and free radicals and a specific spatial distribution of the energy deposit along the tracks, was progressively understood, particularly when pulse radiolysis and time-resolved detection permitted to observe the short-lived transient species and to explain the chemical or biochemical mechanisms. This short review summarizes the most important landmarks of the concepts and their applications.

**Key words:** history • radiation chemistry • mechanisms • solvated electron • theories • applications

## Introduction

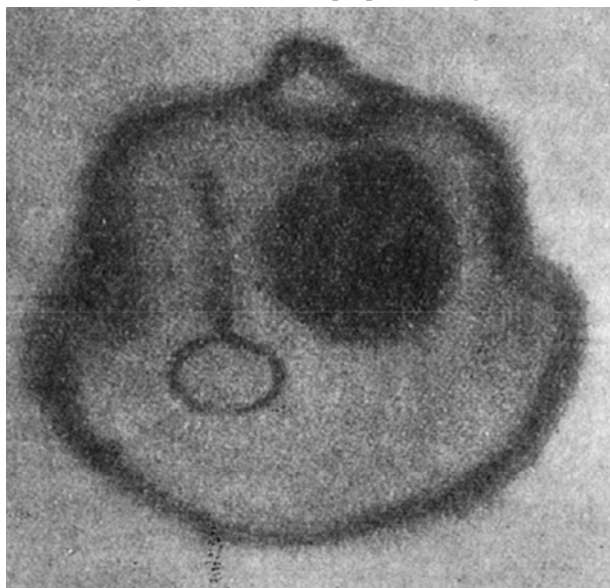
At the very end of the nineteenth century, few crucial discoveries suddenly opened a new era in Science, and their implications are not yet fully explored even today. First, the discovery by W. C. Roentgen [85] in November 1895 of an invisible and penetrating radiation, X-rays, generated by the impact of cathodic rays on the anti-cathode of a Crookes tube, extended the field of photophysics and photochemistry to much more energetic radiation. The interest raised by the new rays, which were able to induce fogging of photographic plates and fluorescence of the Crookes tube glass walls or of screens coated with barium platino-cyanide, led several scientists immediately start new studies. A possible correlation between the phenomenon of fluorescence in certain materials excited by light and the existence of X-ray emission was early postulated by Henri Poincaré [83], then rejected by Henri Becquerel [5–7] who demonstrated instead in December 1896 that the potassium uranyl sulfate spontaneously emitted, without light excitation, energetic radiation with features very similar to those of Roentgen rays. Becquerel soon observed that the uranic radiation could also reduce the silver ions of photographic plates and ionize the air so discharging an electroscope [5–7]. When the young Marie Skłodowska-Curie decided to start research on this subject at the end of 1897, she extensively used the very sensitive piezoelectric quartz electrometer perfected by Pierre and Jacques Curie [27, 91–93] to

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detect quantitatively the ionizing properties of uranic radiation. Guided by this original method, Marie Curie discovered within a few months of intensive and delicate work, successively with Pierre Curie [29], then with Pierre Curie and Gustave Bémont [31], that pitchblend and chalcocite ores contained two new elements much more «radioactive» than uranium itself. They named them polonium (Po) and radium (Ra), after Marie's fatherland and after the specific radioactive property, respectively. Henceforth, samples containing Po or Ra, prepared by Pierre and Marie Curie or according to their process, constituted the most readily available radioactive sources, and permitted an extensive study of the physical and chemical properties of the new radioactive elements, of the radioactivity laws, and of the effects of ionizing radiation on matter.

As a matter of fact, the invisible X-rays and the radiation emitted by radioactive elements were originally discovered indeed indirectly through the detection of their effects on traversed matter: reduction of silver ions of photographic plates (Fig. 1), induced fluorescence of screens coated with barium platino-cyanide, or ion-pair formation in irradiated air. In one of the earliest reviews devoted by Pierre Curie [16, 28] to the effects of irradiation, a large variety of other physical and chemical phenomena were already described. In addition to a temperature increase whose origin was by then still a ground for discussion, Pierre and Marie Curie [30] reported already in 1899 on the numerous chemical effects of ionizing radiation (Table 1) such as the ionization of various gases, the condensation into fog of saturated water vapors [26], the production of ozone from oxygen, the colouring of glass and porcelain, the yellowing of radium-barium chloride and barium platino-cyanide crystals, the colouring of table salt, the aging of paper and the radiolysis of aqueous solutions of radioactive compounds [30]. A complete loss of crystallinity was also observed in thin films of paraffin or other organic substances [81]. The degradation of



**Fig. 1.** Radiography of a purse with a photographic plate illustrating Marie Curie's thesis [92, 93]. The radiation used are  $\gamma$ -rays emitted by a radium source contained in a glass bulb (the  $\beta$ -radiation were rejected using deviation by a magnetic field to prevent their scattering by the object).

paper cellulose was the first observation on polymeric systems [81].

We recognize in these early observations the origin of radiation chemistry although the field had not yet received its specific name by then. Owing to the complexity of the phenomena, studied also by Lind using  $\alpha$ -particles [73], their complete interpretation required several decades [67], but considering the techniques by then available the shrewdness of these pioneering observations is impressive. Biological effects were also very early investigated by Giesel [47] on the human eye and by Becquerel and Curie on the skin [8].

The aim of this short historical review is to focus on the main landmarks of radiation chemistry history [9, 13, 18, 19, 49, 50, 62, 67, 96].

### Water radiolysis

The influence of an electric field on the collection of ions formed in irradiated gases, extended to liquids [60], suggested that the initial spatial ion distribution was highly non-homogeneous and depended on the radiation type. The density of ionizations and the geometry of the different tracks governed indeed the probability of further recombinations and the nature of the chemical processes. The quantitative interpretation of these complex phenomena were long to establish.

Very soon, fruitful observations were made on the radiation chemistry of water. Giesel [46], Curie and Debiegne [32], then Kernbaum [66], reported that water was decomposed into hydrogen, oxygen and hydrogen peroxide. In her thesis [92, 93] and her textbook [27], Marie Curie reports hazards due to the production of explosive mixtures of hydrogen and oxygen in concentrated  $\alpha$ -rays emitter solutions. The mechanism of decomposition was based on the ionization of water similar to its occurrence in the gas phase. From his quantitative studies on radium solutions, Debiegne [37] proposed a dissociation mechanism as in a 'pseudo-electrolysis without electrodes' into the free radicals  $H^{\bullet}$  and  $OH^{\bullet}$  arising from the primary ions  $H_2O^+$  and  $H_2O^-$  (Table 1, reactions (1)–(5)). The mechanism was further performed by Wourzel [106].

An important conceptual jump is due to Fricke's group [45] studying the effects of X-rays which appeared to be very similar to those of  $\gamma$ -rays. He showed first in 1933 that the pure,  $O_2$ -free water undergoes no decomposition. Then Fricke demonstrated that in fact the solvent water alone was affected directly by X-rays absorption, and that the radiolytic molecular products, hydrogen peroxide and hydrogen, undergo further secondary reactions with the water radicals, so that water molecules are formed again. On the contrary, when solutes are present, they scavenge efficiently the radicals issued from water and protect hydrogen peroxide and hydrogen from decomposition. This allowed radiation chemists to rationalize a lot of further accumulated observations on various solutions submitted to different types of ionizing radiation, particularly after the advent of nuclear energy and the extensive research programme around the Manhattan Project during the 1940s. Direct visualization of  $\alpha$ -particle branch tracks in the Wilson cloud chamber demonstrated the non-

**Table 1.** Advances in radiation chemistry

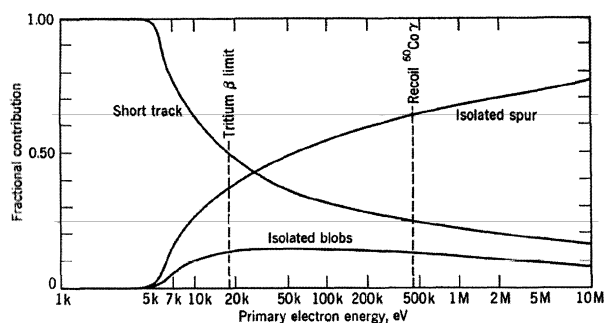
1896–1903	Radioactivity discovery. Reduction of metal ions in solids. Production of hydrogen and oxygen from radiolysis of water and radium salt solution. Colour change of irradiated solids [30].
	Mechanism of water radiolysis [37]:
1914	(1) $\text{H}_2\text{O} \xrightarrow{\nu\nu\nu} \text{H}_2\text{O}^+, \text{H}_2\text{O}^-$ (2) $\text{H}_2\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OH}^\bullet$ (3) $\text{H}_2\text{O}^- + \text{H}^+ \rightarrow \text{H}^\bullet + \text{H}_2\text{O}$ (4) $\text{OH}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O}_2$ (5) $\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$
1934	Direct action on the solvent and indirect action on solutes via the solvent primary radicals induced by irradiation [45].
1944	(6) $\text{H}_2\text{O} \xrightarrow{\nu\nu\nu} \text{H}_2\text{O}^+, e^-$ [1, 105] (7) $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^\bullet$ (8) $e^- + \text{H}_2\text{O} \rightarrow \text{H}^\bullet + \text{OH}^-$ Radical-radical reactions
1945	Water radiolysis by $\alpha$ -particles. Radiation-induced polymerization and polymer cross linking, grafting or degradation [22, 23, 34, 39, 40].
1953	(9) $\text{H}_2\text{O} \xrightarrow{\nu\nu\nu} \text{H}_2\text{O}^+, e^-, \text{H}_2\text{O}^*$ (10) $\text{H}_2\text{O}^* \rightarrow \text{H}^\bullet + \text{OH}^\bullet$ (7) $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^\bullet$ (11) Electron solvation: $e^- \rightarrow e^-_{\text{th}} \rightarrow e^-_{\text{aq}}$ [55, 82, 95]
1962	First direct observation of the hydrated electron [52, 65]. Reactivity of the hydrated electron and other primary radiolytic radicals. Energy deposition models [80].
1970–1971	Solvated electron in polar liquids, geminate recombination in non polar liquids by nanosecond pulse radiolysis [41]. Electron solvation in cold visquous alcohols [4].
1970–1975	Observation of spur reactions and time-dependent yields by picosecond pulse radiolysis [17, 59, 62]. Free radical chemistry. Cluster chemistry [38, 54].
1981	Pulse radiolysis of polymers [98]. Solvation dynamics of electron in water by femtosecond laser photoionization [76]. Non-homogeneous kinetics [44].
1986	Intramolecular and intermolecular electron transfer [24]. Time-resolved primary radical reactions after pulses of ion beams [70]. Interaction of very low-energy electrons with matter [86].
2000	Picosecond laser photocathode electron gun accelerators [10]. Picosecond radiolysis of water and alcohols at high temperature and pressure [77].

-homogeneity of the energy deposition [48]. Lea [71] first stressed the importance of taking branch tracks into account when computing the probability of interaction with biological structures.

Free radicals initially formed in reactions (6)–(8) appeared to be distributed in the small volumes of the radiation tracks, favoring radical-radical reactions (4)–(5) including  $\text{H}^\bullet$  and  $\text{OH}^\bullet$  recombination, according to the radical mechanism of Weiss [105] and of Allen [1, 35] (Table 1). Then  $\text{H}^\bullet$  and  $\text{OH}^\bullet$  radicals, not yet recombined, as well as the molecular products  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ , diffuse and react with the solute. But, the mechanisms and the primary radical yield values were still much disputed for more than a decade as appears in further reviews [51, 99]. Theoretical models gave a quantitative description of the initial energy partition and spatial distribution of the radiolytic species along the different tracks of beta- and gamma-rays and of heavy ions, which govern their reactions during their diffusion [79, 80] (Fig. 2).

## Electron solvation

However, new developments, both conceptual and technological, were soon to appear in radiation

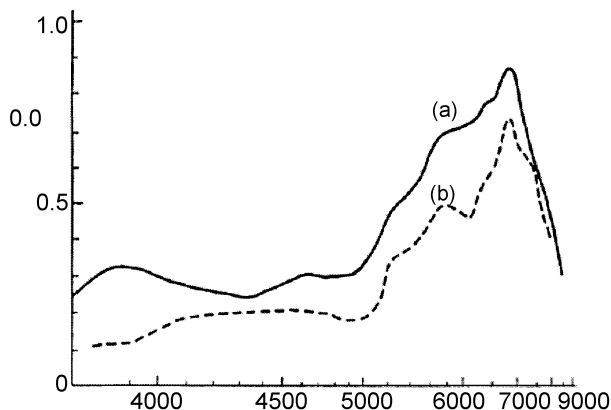


**Fig. 2.** Energy partition between spurs, blobs, and short tracks for electrons in water. Ordinate gives the fractional energy in a given form through all generation as a function of primary energy [79].

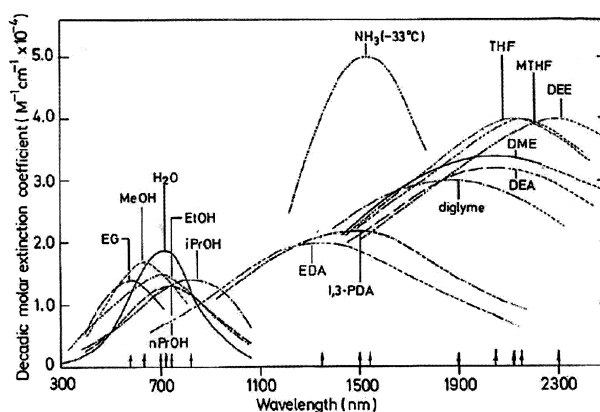
chemistry, with other more general consequences for physical chemistry, specially kinetics and radical chemistry. In fact, an increasing amount of data could not be explained by the reactions of  $H^\bullet$ ,  $OH^\bullet$ ,  $H_2$  and  $H_2O_2$  alone. During the 1950s, evidence accumulated that another transient reducing radical, distinct from  $H^\bullet$  atoms, must be generated, mainly in neutral or basic solutions. Hochanadel [55] from Allen's group and Stein [95] from Weiss's group proposed to identify the postulated species as an hydrated electron, analog to the metastable solvated electron already known in blue metal-ammonia solutions. Platzman considered in his model [82] the possibility of the primary electron formed in reaction (9) of escaping, by a thermalization and solvation process, from recombination with the parent cation (Table 1, reaction (11)). Some of the hydrated electrons were supposed to take part in the radical-radical reactions too, the rest reacting directly with the solute.

The invoked hydrated electron should exhibit, however, specific properties, particularly a much shorter life-time compared to the ammoniated electron of metal-ammonia solutions and a reactivity distinct from  $H^\bullet$  atoms according to the experimental results already available by then, but these unusual features were an object of endless debates on its real existence. Czapski and Schwarz [33] made an important contribution to the discussion in determining the effect of the ionic strength of the solution on competitive reactions of the unknown species with  $H_2O_2$  vs.  $NO_2^-$ ,  $O_2$ , or  $H^+$  in  $\gamma$ -radiolysis of water. Agreement with the variation expected from the Debye equation for a species carrying a single negative charge strongly supported the hydrated electron hypothesis. Moreover, a blue colour was observed in irradiated glassy water ice and assigned to solvated electrons [88, 89].

The advent of pulse radiolysis techniques [2, 15, 63, 65, 75, 96, 102] permitted the direct observation of transient radiolytic species. For the first time, Matheson and Dorfman observed by this method short-lived radicals such as  $I_2^-$  or the benzyl radical [75]. An important result was then the direct observation of the hydrated



**Fig. 3.** Absorption band due to the hydrated electron as observed in 1962 in irradiated aqueous solutions; (a) 0.05 M solution of  $Na_2CO_3$  (de-aerated) given a mean dose of 7 krad; (b) pure water (de-aerated) exposed to the same mean dose [52]. To overcome the low intensity of the absorbance signal due to the nanomolar concentration of  $e_{aq}^-$ , the total optical path was increased by placing the cell of 4 cm in a multiple reflection assembly.



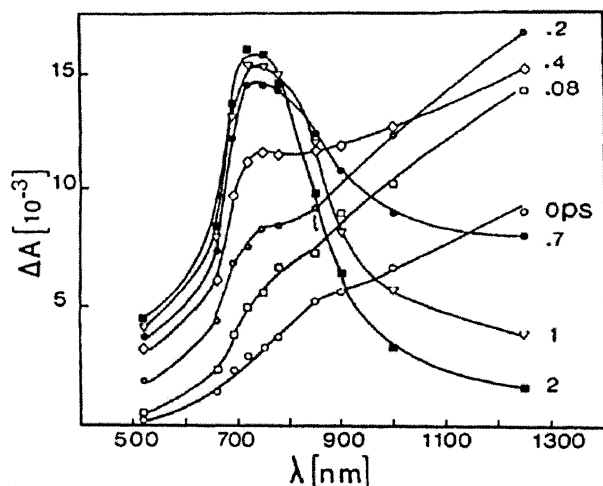
**Fig. 4.** Absorption spectra of the solvated electron in various pure solvents at room temperature. The arrows on the abscissa (nm) indicate the position of the maxima [41].

electron in liquid water, independently evidenced by Hart and Boag at Gray laboratory near London [52] and Keene in Manchester [65] (Fig. 3), and also of the electrons solvated in a long series of other liquids under various conditions of temperature and pressure [41, 77] (Fig. 4). In particular, solvated electrons generated by irradiation in neat liquid ammonia are as short-lived as in water, owing to their recombination with other radicals. In contrast, they are day-long stable and easily observable even after  $\gamma$ -radiolysis when produced in ammonia containing proton and  $NH_2^\bullet$  radical scavengers, so that their similarity with solvated electrons of metastable metal solutions was definitely demonstrated [11]. Electron accelerators with shorter pulses, installed in Toronto [17, 59] and in Argonne [62], permitted the time-resolved observation of early processes in water and various alcohols a few picoseconds only after the initial deposition of the energy.

Despite its transient character, the solvated electron is the only species which could be studied in such very different media, from the highest to the lowest polarity liquids, through the properties of solvation dynamics, optical absorption spectrum, mobility, reactivity, ESR spectrum in glasses, etc. The solvation dynamics studies of electrons generated in viscous alcohols by electron pulse irradiation [4] or in water by multiphoton ionization using femtosecond laser pulses [76] provide the spectral evolution step-by-step and the kinetics of the electron during solvation (Table 1, reaction (11) and Fig. 5).

All the above data were precious for theoreticians to propose a solvation shell structure and to validate models of the solvation for the electrons and other charged species. In particular, the important contributions of J. Jortner, L. Kevan, M. Newton, B. Webster, P. Rossky were at the center of the discussions in Colloques Weyl [36, 43, 64, 68, 72, 100, 104].

Pulse techniques give direct access to the fate of the solvated electrons as a monitor of early processes following radiation absorption. New impulse was given to theoretical fundamental models on the non-homogeneous distribution of the ion pairs in the early tracks, which governs the kinetics of their recombination or escape, and on the time-dependence of the radiolytic yields expected in different liquids [44, 58, 79, 87]. Another experimental approach was to study the strong interaction with matter of slow electrons of very



**Fig. 5.** Absorption spectra of the electron at different delays after photoionization of liquid water by two-photon UV excitation [76].

low and selected energy ( $< 20$  eV), comparable with the energy of secondary electrons which are produced in tracks of high-energy radiation and responsible of most of energy deposit [86].

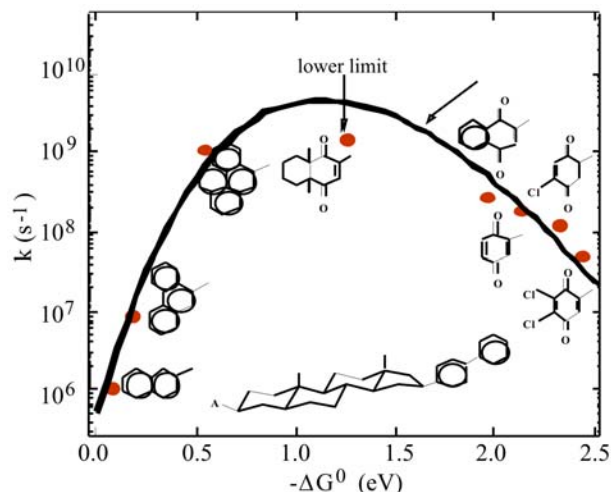
### Electron transfer processes

Electron transfer is the fundamental event underlying a range of critically important chemical and biological processes, both in homogeneous and heterogeneous systems. The primary radicals issued from the solvent radiolysis are electron donors or acceptors. By choosing proper scavenging solutes, they may be either selected by removing the unwanted ones or converted into a single kind of secondary one-electron reducing or oxidizing radicals. Thus, pulse radiolysis, including the most recent developments [10], contribute to improve our understanding of a lot of chemical and biochemical mechanisms, some of them of difficult approach so far.

Tables of reaction rate constants of solvated electrons,  $H^{\bullet}$  atoms or  $\bullet OH$  radicals with a very large variety of solutes have been established in water and alcohols [20, 21, 97, 103]. Also a great deal of data was collected on short-lived charged or neutral radicals formed after irradiation. Time-resolved kinetic studies allowed the determination of their spectroscopic properties, their absolute rate constants, and the mechanism of their reactions, all of high interest to explain chemical, and also biochemical or electrochemical processes [9, 13, 19, 96]. The kinetic method consisting in measuring the electron transfer rate constant was also used to determine the one-electron reduction potential of couples involving short-lived species such as free radicals [101].

Newly available facilities of pulsed heavy ion-beams and the increasing power of simulation approaches provide today a more accurate description of the fast early processes including the complex spatial distribution of species formed in tracks of the highest density of ionization [69, 70], which is helpful to the understanding of nuclear and space chemistry and of radiobiological effects.

The intramolecular electron transfer along rigid molecules between a donor at one end produced by the



**Fig. 6.** Intramolecular electron transfer rate constants from the 4-biphenyl ion radical to various compounds as a function of free energy change [24].

scavenging of the solvated electron and at the other end a series of acceptors was experimentally investigated [24] (Fig. 6). The dependence of the rate constant on the free energy changes of the reaction, specially in the inverted region where the rate constant decreases with increasing the free energy as predicted by Marcus theory, was found for the first time.

The electron transfer reactions occur in most biological processes. An intramolecular electron transfer was observed first by the group of Land and Swallow [84] from the tyrosine to the tryptophyl radical, through peptides as spacers, which is a model system of crucial importance for mechanisms in living cells. This pioneering work opened the route to the study of innumerable electron transfer mechanisms in biological systems, despite their complexity, as a function of their conformational structure and the location of active groups [57, 94]. The mechanisms of the irreversible break and of the possible repair of the DNA double strand after indirect action of radiolytic free radicals [42] or direct radiation-excitation [90] are at the center of research in radiobiology and radiotherapy, also born with the discovery of radioactivity [8].

### Polymer radiation chemistry

It has been known since the studies by W. D. Coolidge in 1925 [22] that polymerization and polymer cross-linking [22, 23, 34, 39, 40, 56, 61] were chain reactions initiated by radicals and electrons and ions, which are all provided by irradiation. More recent pulse radiolysis observations permit measurement of electron transfer in the polymeric chain [98].

Radiation-induced polymerization or grafting is more than ever an active field of research as an alternative to other methods because it does not require any additive and the polymerization is as homogeneous as the penetration of radiation itself [25]. It is widely applied to the synthesis of new materials, grafted polymers or block copolymers, biocompatible polymers,...., each tailored for its special use. Generally, the irradiation induces a chain reaction which requires quite small doses. The radiation type used is chosen according to

the penetration features, the reaction selected: polymerization and crosslinking in the bulk, or polymer-grafting just at the surface of another material in order to confer it functionalizing and specific properties (for example, plasticity, hardness, biocompatibility, hydrophobicity, adhesion).

Applications represent a massive industrial output [25]. The domains are as various as packaging industry, construction with composite materials, polyethylene foam systems and varnish coatings, paper and textile industries, rubber vulcanization in tyre industry,... Other specific applications of radiation-induced polymerization or polymer degradation concern medical prostheses, magnetic pastes for tapes, gels for paints, adhesives, inks, resins for electron microlithography, nanoporous membranes, heat-shrinkable tubings used, for example, for wire insulation.

### Cluster chemistry

The radiation-induced reduction of silver ions into atoms in photographic silver bromide plates was indeed at the origin of the X-rays and radioactivity discoveries [5–7, 91]. The phenomenon was then used in nuclear silver bromide emulsions for imaging the tracks and until today in some radiographic dosimeters. Metal ions in solution have been also widely used in reduction or oxidation processes as indicators to calibrate the yields of primary radiolytic radicals as a function of the nature of the radiation and of the solution composition [18, 49]. Some of these scavengers, such as gold or silver ions, undergo reduction under gamma-irradiation up to the zero-valence metal, in the form of colloids or of precipitates. However, pulse radiolysis studies on the reduction of silver ions also concluded to a spontaneous oxidation of silver atoms by oxygen which was a matter of hot discussions as far as such an oxidation of this noble metal was contradicting the classical chemical knowledge [3].

In fact, it appeared from other experiments on the radiolysis of monovalent copper ions in liquid ammonia, based on the complete analysis of the end-products, that the metal copper was indeed not eventually formed and instead an equivalent amount of hydrogen gas was found [38]. These observations suggested that, despite the bulk metal is stable under the same conditions, the nascent metal atoms were able as soon as formed to be spontaneously corroded by the solvent. In order to explain this puzzling results, it was for the first time concluded that isolated metal atoms and very small clusters display indeed a reduction potential much lower than that of the bulk metal, thus implying new size-dependent thermodynamical properties of metal clusters [38]. They were further understood as resulting from quantum-size effects [12]. The radiolytic method was immediately exploited to synthesize stable metal clusters for catalysis and to study their formation mechanism and their specific properties [12]. It was confirmed [53, 54] that the reduction potential of isolated silver atoms in water must be indeed lowered, relative to that of the silver electrode, by the sublimation energy of the metal (equal to 2.6 V for silver), so making them easily oxidized.

Pulse radiolysis has then been used to determine kinetically the redox potential of metal clusters of different nuclearities as an extension of the method developed for short-lived radicals, by checking their reactivity towards species of known reduction potential [78]. In the case of clusters progressively growing by a cascade of coalescence reactions of initial atoms, a series of transient clusters of increasing nuclearity is successively in contact with the reference system. The method consists in observing, by time-resolved techniques, at which critical nuclearity (that is after which induction time) electrons are transferred from an electron donor of known potential to metal cations fixed on the growing clusters. The reduction potential of clusters of critical nuclearity predominant at this induction time is, therefore, derived since it is slightly higher than the reference donor potential [78]. Using a series of electron donors of various potentials, the nuclearity-dependence of the reduction potential of silver clusters in water was obtained [12] (Fig. 7). The trend is expected to be similar for all metal clusters in solution since their potential always differ from that of their atoms by the sublimation energy, but quantitative data on metals other than silver are very rare [12].

The nuclearity-dependent properties of metal clusters explains their specific role in the synthesis mechanisms of mono- and multi-metallic core-shell or alloyed nanoparticles [12, 74], in catalysis, and in photography. Indeed, the above experiments on the electron transfer to silver clusters [78] permitted to directly mimic and to explain the photographic development mechanism where the requirement of a critical nuclearity was not understood so far: the potential of the developer, as an electron donor, behaves as a thermodynamical threshold which prevents electron transfer towards photo- or radio-generated clusters of lower potential (subcritically-sized clusters in underexposed crystals). In contrast, the population of photo-generated clusters having a reduction potential higher than the developer (supercritical clusters in enough exposed crystals) are able to accept an electron forming a new atom, to fix another silver ion and to constitute, via this sequence repetition, an autocatalytic germ of development until the complete reduction of the supporting silver halide crystal [78]. The same method has been applied to the

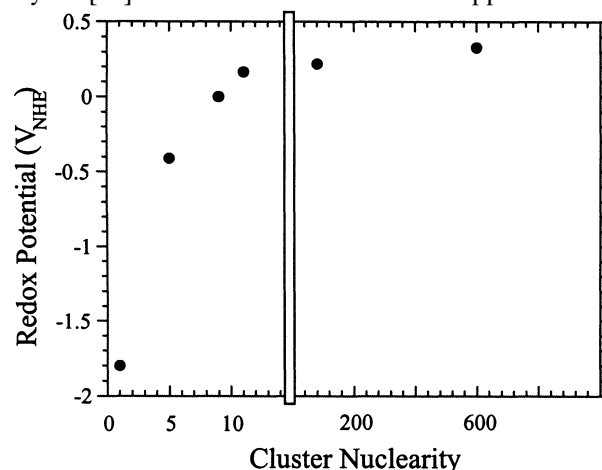


Fig. 7. Size-dependence of the reduction potential of the silver cluster couple  $\text{Ag}_n^+/\text{Ag}_n$  in water relative to the normal hydrogen electrode [12, 78].

metal nanoparticle synthesis by using metal seeds generated through  $\gamma$ -radiolysis, then developed to various final sizes depending on the amount of ions chemically reduced at the seed surface [12, 78].

Another application directly inspired from radiation chemistry is a huge enhancement of the sensitivity of photographic films. An important factor of the sensitivity limitation in all the silver-imaging systems is indeed the fast recombination of the initial electron-hole pairs induced by the light absorption in AgBr crystals. An original approach [14] thus consisted in doping the AgBr crystals with the ions formate which behave as efficient and selective scavengers of the holes as soon as they are generated inside the crystal and which produce in addition strong reducing radicals as in the radiolysis of liquids. Hence, the scavenging of the holes is complete, the loss of electrons by recombination is totally suppressed and each initial photoelectron yields an atom. Moreover, the radical issued from the formate-hole reaction produces a second silver atom per photon absorbed, so increasing the sensitivity by ten times [14]. The process is applicable to all kinds of silver imaging.

The concept of nuclearity-dependent properties and quantum size effects of clusters is now widely accepted in physics and chemistry, and more generally in nanosciences. Radiation chemistry has contributed markedly to demonstrate for the first time this important feature, to improve the understanding of the specific role of clusters in various critical phenomena and to guide their synthesis for special applications.

## Conclusion

As shown in this short review, the radiation effects which were first observed by Marie and Pierre Curie as pioneers are to-day extensively studied. The dual purpose of radiation chemistry is on the one hand to explain the interaction of high-energy radiation with matter in order to determine the initial non-homogeneous distribution of the energy of different kinds of radiation which are of increasing importance in heterogeneous and specifically biological systems. On the other hand, the purpose is also to take advantage of the strong reactivity of radiolytic species generated within ultrafast pulses as selected sources of electron donors or acceptors, to initiate and study, through direct time-resolved observation, a high variety of chemical or biochemical processes so giving access to their step-by-step mechanism.

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