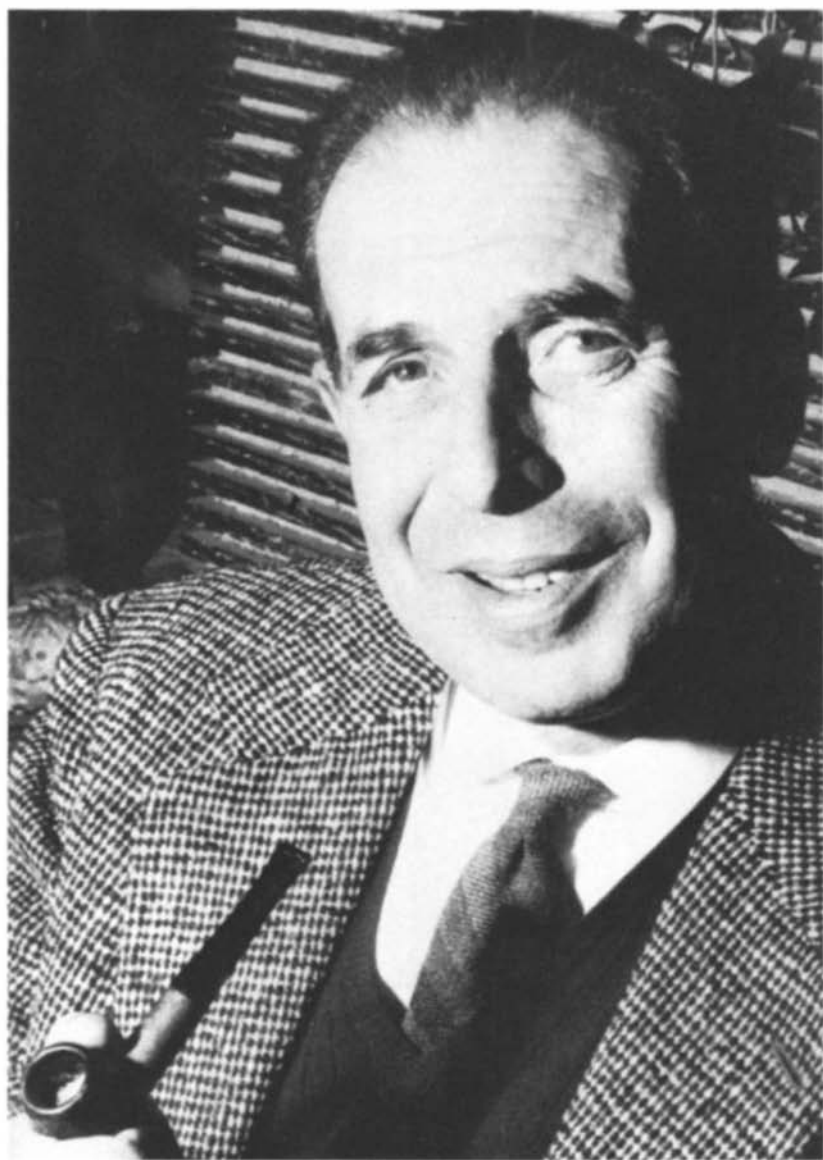




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A HISTORY OF PHYSICAL CHEMISTRY IN FRANCE 2521

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EARLY HISTORY (1775–1840)

Physical chemistry begins with the association of physical measurements to chemical events. It thus was born long before it was named, and the division of scientists into physicists and chemists became effective only in the late 1830s. If one disregards the precursors—B. Pascal who discovered atmospheric pressure (1648), Mariotte (1620–1684) of the Boyle-Mariotte law, Amontons (1663–1705) who found that the boiling temperature of water was a fixed point, Nollet (1700–1770) who discovered diffusion in liquids, and Réaumur (1683–1757)—one can say that physical chemistry as a science started in France in the last quarter of the eighteenth century.

The list of names of French scientists working between 1775 and 1840 reads like the first chapters of an elementary textbook of physical chemistry: Lavoisier (1743–1794) formulated the law of conservation of *work* in 1783 and the law of conservation of *mass* in 1789; Charles established in 1787 the first relation between the expansion of gases and the temperature, a relation that was more precisely formulated by Gay Lussac in 1802. Bertholet (1748–1822) expressed in a qualitative manner the law of mass action, Proust in 1806 the law of definite proportions in chemical species, and Gay Lussac in 1809 the law of combination of gases. In 1815 Biot studied the optical polarization of sugars. In 1818 Dulong used the thermal dilatation for measuring temperatures and in 1819, together with Petit, outlined the relationship between the specific heat and the atomic weight of solids. In 1824 Carnot established what is now called the second law of thermodynamics.¹

¹ Sadi Carnot (1796–1832) died very young from cholera after having published just his single famous paper. But more were in preparation. Unfortunately it was only in 1878 that his brother Hippolyte Carnot published his notes, which contained a large number of valuable remarks and indications.

For instance, although in his paper he considered heat as a liquid (“the caloric”), according to the consensus at that time, he wrote a few years later: “Can a movement (that of radiated heat) produce a body (the caloric)? Definitely not; it can induce only a movement. Heat is hence the result of a movement. Is heat the result of vibrational movement of molecules? If so, the quantity of heat is nothing else but the quantity of driving power used to produce vibrations. The quantity of heat must

Interestingly, Carnot's paper passed unnoticed until Clapeyron formulated his results in a more rigorous mathematical form (1834), introduced the graphic representation of thermodynamic cycles, and expressed the law of vapor pressure variation with temperature. In 1834 also, Peltier observed the effect which is still named after him.

In a different field J. B. Dumas devised a method for determining molecular weight (1826) and contributed to the atomic theory of matter, while some years later Laurent (1807–1853) clarified the relationships between the atomic and molecular weights and their equivalents.

As early as 1772 Romé de Lisle discovered that the angles between the faces of crystals are always the same for the same kind of substance, while in 1784 Haüy established the law of rational indices for crystals and laid the foundation of crystallography.

For unknown reasons the French contribution to the development of physical chemistry dropped sharply, at least in relative importance, after this firework of results and ideas, from the late 1830s on. Nevertheless one must mention the contribution of Pasteur, who related rotational isomerism to crystal shape (1848). This isomerism was explained by Le Bel in 1874 simultaneously with van t'Hoff, by the "asymmetric carbon atom" hypothesis. Bravais (1811–1863), extending Haüy's work, clearly stated that a crystal was a more or less complicated three-dimensional lattice, with ions, atoms, or molecules sitting on the corners, and established the 14 translational groups in 1849. In 1844 Poiseuille (1799–1869) derived his well-known formula for the rate of flow of liquids through capillaries.

1840–1900

Although Regnault defined in 1842 the notion of ideal gas, only towards the end of the century was work on thermodynamics revived. Following Regnault (1810–1878), Cailletet (1832–1913) and Amagat (1841–1915) worked on gases and critical phenomena. Amagat's precise measurements of pressure-volume-temperature relationships for gases (ca 1870) evidenced deviations from the Gay Lussac laws and opened the way to van der Waal's famous equation. Raoult established the laws of melting point depression (1882) and of vapor pressure decrease (1886) in solutions. At about the same time Pictet

hence remain constant as long as the driving power is used to produce vibration . . . which seems to result from calorimetric experiments; but when the amplitude of the movements becomes measurable, the quantity of heat cannot remain constant. If the heat is the result of movement it is evident it can be produced by the consumption of driving power and that it can produce this power. The production of 1 unit of mechanical power requires the destruction of 3.70 units of heat. Since the unit of 'dynamic' power is 100 mkg, the unit of heat is hence 370 mkg." (Mayer in 1842 found 365 mkg and Joule 425 mkg.)

Thus, before 1832 Carnot had formulated but not published what is called the first principle of thermodynamics and had the correct view of the nature of heat.

(1876), Trouton (1884), and de Forcrand established the *Trouton rule*, valid for normal liquids, which connected the heat of vaporization and the boiling temperature. Somewhat later Daniel Berthelot proposed his equation of state of gases (1897), long before van Laar suggested that the attractive interaction between two different molecules was a geometrical mean of interactions between like molecules.

In addition to his immense work in organic synthesis Marcellin Berthelot (1827–1907) established a thermochemical system through systematic calorimetric measurements, but stopped short of connecting it fully with thermodynamics. The application of thermodynamics to chemical processes in France was due to Duhem (1861–1916) and mostly to Le Châtelier (1850–1936), who recognized the significance of Willard Gibbs' methods and results.

Although Le Châtelier's law (1888) is only a very rough approximation to the reality, it was quite useful in forecasting possible reactions, and it must be recognized that Le Châtelier, intent on applications, made thermodynamics understandable and useful to chemistry. His work and influence shaped much of the French physical chemistry up to 1940. He and his students emphasized the study of chemical equilibria rather than of chemical mechanisms and kinetics, producing an enormous amount of fundamental scientific work on systems of practical importance. They pioneered in the study of metallography (Osmond 1849–1912); of chemical equilibria involved in metallurgical processes (Boudouard, Chaudron); in the phase equilibria of various silicates—from cement to glass; in the thermodynamics of combustion and explosion phenomena (Mallet); and in phase analysis of solids (Chevenard). On a more theoretical side Jolibois studied the allotropy of phosphorus, while Guichard made the precise determination of the atomic weight of iodine at a time when the "tellurium-iodine inversion" in the periodic table was not yet understood, and introduced the use of the thermobalance for the study of gas evolution from solids.

In the use of physical methods for solving chemical problems one must not forget that Moissan (1852–1907) launched the electric furnace and used it in the first attempt at diamond synthesis. He also isolated fluorine—up to then an elusive element—by nonaqueous electrolysis, while Hérault (1863–1914) started the industrial production of aluminum by molten salt electrolysis.

At the turn of the century, by themselves and by their numerous students, by their scientific achievements and their personal and administrative influence,²

² Berthelot, appointed life "sénateur," had served a short term as foreign minister. There has always been a strong tradition of interest in public affairs by the French scientists, whether or not they held political office. The famous military engineer of Louis XIV, Vauban, in his book *La Dime Royale* was probably the first to advance the idea of what we now call the GNP. Lavoisier was a "fermier général" (tax collector) and, before being as such sentenced to death, had a key role in ordinance during the early revolutionary wars. In its early days the Paris Académie des Sciences produced, at the government's request, numerous reports on various subjects (e.g. the number of hospital beds needed in Paris). In some of these Lagrange (of the

Berthelot and Le Châtelier dominated the French chemical scene. Deserved as it was, this influence had its drawbacks: both men opposed the atomic theory because they believed that a self-consistent phenomenological system of chemistry could be developed without resorting to "the atomic hypothesis." This position, very similar to that which Ostwald upheld in Germany for a long time, was stronger and more durable in the French centralized academic and university system. Hence the late and slow start of modern atomism in France, which was mostly supported by physicists and did not fully come into its own until the late 1930s. Up to then, chemical kinetics, structural chemistry, etc were not generally favored subjects, to say the least.

Among those who advocated the opening up of chemistry, two were outstanding. G. Urbain (1872–1932) was famous for his studies of the rare earths, with his systematic use of fluorescence and phosphorescence spectra, culminating in the identification and isolation of lutetium (1907).³ He accepted the Werner theory of inorganic complexes⁴ and favored early studies (in France at least) of natural high polymers, which were not at that time considered a sensible subject for pure chemical research. This fitted his concern with the fundamentals of chemistry, such as the positive definition of elements and molecules, embodied in his book *Les disciplines d'une science: la chimie* which, beyond its relevance to the special contemporaneous circumstances of French chemistry, deserves attention by its clear and incisive analysis of the concepts discussed.

In addition to very elegant work on coupled oxidation, the labile oxidation states of cobalt and cerium, and the physical chemistry of metal organic compounds, A. Job, addressing himself in his book *La méthode en Chimie* to the atomism-energetism controversy, wrote that the problem confronting chemists was "to distribute the energies into the details of structures," a good formula (but rather heretical in France at this time) for the future development of physical chemistry.

Before turning to the French atomism of the first quarter of the twentieth century, we must briefly recall some work done at the century's turn by physi-

polynomials) anticipated methods which were to be used, 150 years later, in the early days of "operational research" during World War II. Gay Lussac, Thénard, and Dumas were members of one or the other Chambers of Parliament between 1830 and 1850. Pasteur was influential with Napoléon III. French scientists played a key role during the dark days of the Dreyfus case. The mathematicians Borel and Painlevé held ministerial posts (the latter being Prime Minister more than once); Jean Perrin and Irène Joliot-Curie were undersecretaries of state for research between 1936 and 1939. Langevin and F. Joliot were noted members of the French Communist Party during and after World War II.

³ Between the two world wars, and up to now, some of Urbain's students have kept active in rare earth work, linking with magnetochemistry and high temperature chemistry. In particular they prepared and studied many pure rare earth metals.

⁴ One of us, while a doctoral student, had occasion to see Le Châtelier's unflattering marginal notes in Urbain's book *La chimie des complexes minéraux*.

cists and chemists that was to be relevant to physical chemistry. In physics G. Lippman (1845–1921) made the first color photographs in 1891 by an interference process to which modern holography is indeed in debt; he also discovered electrocapillarity, using it to develop a simple electrometer which electronics has now made obsolete.

The discovery of piezoelectricity (1880) by Pierre Curie (1859–1906) and Jacques Curie was derived from theories on symmetry conceived by Pierre Curie.⁵ Soon after that the two brothers started their well-known studies on magnetism, which gave rise to the French school on that subject. The school soon prompted the work of P. Weiss, which resulted in an early, not altogether correct, idea of the “magneton” (1911) and the theory of paramagnetism by Curie’s assistant, P. Langevin (1872–1946). Langevin’s formula was later on shown by Debye to describe also the dielectric polarization. That atomic diamagnetism is an additive property of compounds, if one allows for increments related to molecular structure, was shown between 1908 and 1913 by P. Pascal, one of the founders of magnetochemistry.

As concerns the chemical approach to physical chemistry, the most important contribution, towards the end of the last century, was probably the work of Sabatier (1854–1941), who discovered in collaboration with Senderens in 1897 the hydrogenating and dehydrogenating properties of nickel and who later explored hundreds of catalytic reactions. On the basis of this wealth of data he could show that any catalyst was active for both direct and reverse reactions, and that catalysts could be classified according to the type of reaction they favor (hydrogenation, hydration, and so on). He can be considered the founder of modern heterogeneous organic catalysis.

Another important field opened up in France at the turn of the century, namely the discovery of radioactivity by Becquerel (1896) and the isolation of radium and polonium by Pierre and Marie Curie (1898) and of actinium by their assistant, Debierne (1899). This field has been pursued in France ever since.

1900–1914

Undoubtedly the most important personality in French physical chemistry proper, the man who for many years influenced its development in France, was Jean-Baptiste Perrin (1870–1942). He started his scientific life by demonstrating in 1895 (simultaneously with, and independently from, J. J. Thomson) that cathode rays were electrons. His interest then shifted to the newborn colloïd science, which was also the subject of research of his colleagues J. Duclaux and Victor Henri.⁶ Although he obtained some important results concerning contact electrization and colloïdal solutions (1904), his major work was the

⁵ In 1916 Langevin constructed the first “sonar,” utilizing this discovery.

⁶ The laboratories of J. Perrin and Victor Henri were in the same building and were a meeting place of all scientists interested in physical chemistry. In particular Einstein, Nernst, and Bodenstein were frequent visitors.

study of Brownian motion and the determination of the Avogadro number, in relatively good agreement with the most recent results (7.05×10^{23} instead of 6.06×10^{23}), from which he deduced the weights of single atoms and electrons. The way he presented his results, making them accessible even to non-scientists, did much to help the triumph of atomistics over the conceptions of M. Berthelot and Le Châtelier. His lucid, extremely well-written book (*Les Atomes*, Paris 1912) stands as a masterpiece of popular but high-level scientific literature.

While Duclaux continued the study of colloids even after his retirement from Collège de France in 1946, and while Victor Henri turned to spectroscopy and photochemistry, discovering photochemical chain reactions, Perrin initiated the study of thin layers of soap solutions, thus starting the atomic aspect of surface chemistry. Perrin also turned his attention to the mechanism of chemical reactions, particularly of monomolecular ones, for which he wrongly suggested a general photochemical activation mechanism. More important, although for a long time neglected, was the contribution of one of his most brilliant students, René Marcellin, who showed (1911), at the same time as Scheffer and Kohnstamm in Holland, that besides the Arrhenius' activation energy the rate constant had to contain an activation entropy term. In his thesis, defended in 1914 just before the outbreak of World War I, he developed the general theory of absolute rates, in very much the same way as did Eyring and his co-workers later on, describing activation-dependent phenomena by the movement of representative points in a phase space. But, lacking a theory of interaction of particles, given only much later by quantum mechanics, he could of course make no numerical calculations.⁷

Another important piece of work done in the beginning of the century was the theory advanced by Gouy that the double layer between a metal and an electrolyte solution was not always limited to two condensed ionic layers, as suggested by Helmholtz, but that the ions could be distributed over a layer of finite thickness (theory of diffuse double layer).

1914–1918

In a more general way, World War I completely disrupted French science. All young men went into battle, with a tremendous loss of talent—recognized or not yet proven—which was to weigh heavily for the next half century. The scientific needs of total war had not been foreseen, and were met, particularly in the case of chemical warfare, by a combination of hard work and brilliant improvisation, including gathering back from front line duty some of the younger scientists who had survived the terrible slaughter of the first period of traditional fighting, before the “trench war” bogged down the armies.

⁷ Like Moseley in 1915, Marcellin was killed in action in the very beginning of World War I. These two men stand as symbols of the intellectual loss which Europe suffered through the indiscriminate massacre of its young and mature generations between 1914 and 1918.

1918-1939

Scientific life resumed actively in France after 1918, following the main lines mentioned earlier which derived from the strong position which France had established in optics, atomic science, nuclear science, and magnetism.

However, the main event during these years, helped by the good intuition and scientific judgment of J. Perrin and P. Langevin, was the doctoral thesis of L. de Broglie which first proposed and developed (in 1923) the idea that waves were always associated with particles and which showed that Bohr's stable electronic orbits in atoms could be considered as those which accommodated standing waves of electrons. This basic discovery provided the cornerstone of modern quantum mechanics. But it was mostly developed outside France; the only important French contributions at that period appear to be those of L. Brillouin. In particular no French scientist took any part in the very swift creation of the quantum theory of the chemical bond and of the quantum description of chemical reaction paths, which fitted so well in the general framework of Marcellin's thesis.

It was also in 1923 that Victor Henri discovered the predissociation phenomenon (actually preliminary spectroscopic indications of predissociation had already been obtained by Victor Henri before World War I, but his research was interrupted in 1914 and taken up again only several years later). Nearly at the same time another case of radiationless transition (internal conversion) was observed by Perrin's student P. Auger in the case of X rays (Auger effect). In 1924 Du Noüy calculated the Avogadro number from surface tension of dilute solutions of sodium oleates forming condensed layers in which molecules are disposed horizontally.

It was only in 1926, after receiving the Nobel prize, that Jean Perrin obtained a large building that soon became the Laboratory of Physical Chemistry. His definition of physical chemistry was the same as that of G. N. Lewis: physical chemistry was considered whatever interested Jean Perrin, and his interests were very wide. They included even cosmic rays, since it was while working in this laboratory that Auger discovered extensive air showers! On the other hand A. Marcellin, and later on Dervichian and Guastalla, made important contributions to our knowledge of monomolecular layers of higher fatty acids on water surface. Other groups were busy on other subjects: F. Perrin performed his classical work on polarizability.

Perrin and Mlle Choucroun discovered the long-distance excitation transfer in solutions; Hulubei and Mlle Y. Cauchois worked on X-ray spectra, using Cauchois' bent crystal technique; Rouault on electron diffraction by gaseous molecules; Kowarski on crystal growth from gas phase. It was, with the Radium Institute of Madame Curie and Langevin's Physics Seminar in Collège de France, by far the liveliest scientific place in France, and an invitation to the weekly tea in Perrin's laboratory was an honor and a sign of recognition.

A few years later Perrin became the head of a second laboratory. Across the courtyard from the Laboratory of Physical Chemistry another modern

laboratory building was erected, the Institute of Physicochemical Biology, a private institution endowed by Edmond de Rothschild. The work there was also done in several directions. While Wurmser was the head of the Physical Chemistry section, with L. Rapkine joining him soon after, biological oxidation processes and oxidation-reduction potentials were investigated. Aubel headed the section of Biochemistry, Ephrussi that of Genetics, and T. Kahn that of Physiology.

While Perrin's laboratory was the most important one, some physicochemical research was also done elsewhere. In the late twenties and early thirties the following laboratories and research directions should be mentioned. At the Sorbonne, P. Pascal was carrying on work on diamagnetic susceptibilities to extend and improve his previous work on the additivity rule. P. Laffitte was determining explosion and cold flame limits in oxidation reactions, while M. Prettre was interested in the kinetics of branched-chain oxidation reactions (giving the first confirmation of Semenov's theory outside the USSR), and in the difference between physical and chemical adsorptions. At the Central Ordnance Laboratory, Marcel Mathieu worked on reactions of cellulose and developed "topochemistry." In A. Cotton's laboratory at the Sorbonne, J. Lecomte built infrared spectrometers and started the determination of infrared spectra of more and more complicated molecules with the collaboration of P. Barchewitz, G. Emschwiller, R. Freymann, M. Parodi, and others.

In Montpellier Cabannes continued his work on the depolarization of scattered light, extending it from the Rayleigh line to the Raman spectra, for which he had developed a classical (i.e. nonquantum mechanical) theory. Raman spectra of gases and liquids were investigated in different universities by Rousset, Kastler, Daure, and others.

Raman spectra of electrolyte solutions were investigated by E. Bauer (1881–1965) and Silveira in Langevin's physics laboratory in Collège de France. This work was later extended, in collaboration with Magat, to liquid water, H_2O , and D_2O , and led to the discovery of intermolecular Raman frequencies, which were interpreted with the aid of the Bernal-Fowler model of water structure and a purely electrostatic theory of the hydrogen bond. In the Laboratory of Physical Chemistry of the Collège de France, Duclaux continued his work on colloids, while Mme Dobry was making the first osmotic pressure measurements of the molecular weight of a polymer, demonstrating that it was not simply an association of monomers. In Bordeaux Devaux kept experimenting with molecular films. Pioneering work towards high precision mass spectrometry, initiated by L. Cartan, died with him when he was killed as a resistance fighter. A. Tian and M. Calvet started research in microcalorimetry, a field which was to expand later. X-ray crystallography was active, with pioneering studies on thermal lattice movements (Laval) and on small-angle scattering (Guinier).

On the theoretical side very important contributions were made by Yvon and by L. Brillouin; Yvon's work concerned the kinetic theory of liquids and related the density fluctuations to light scattering. When published it passed largely unnoticed, until 10 or 12 years later when the same results were ob-

tained independently by Kirkwood, who later recognized the importance of Yvon's contribution. Brillouin treated the fine structure of Rayleigh wings in light scattering as related to the diffraction by local standing waves.

Contrary to some other countries, French science profited very little from the German scientists leaving Germany after the arrival of Hitler to power, as very few of them attempted to establish themselves in France, and any such attempt was interrupted by the war and the German occupation. This was due to a large extent to the rigidity of the French system for obtaining positions: In 1932 practically the only stable situations were positions in University teaching, which carried the status of civil servants. To become a civil servant a foreign-born applicant had to be naturalized at least 5 years. Naturalization required at least a year after the 3 years residence needed to introduce an application. This meant that a foreign scientist wishing to settle in France had to wait 9–10 years before he could get a stable position. In the meantime, he could obtain a fellowship from Caisse des Sciences, but the number of such fellowships was limited and their amount rather small.

Nevertheless, some outstanding scientists did come to France; F. London, L. Tisza, and Guggenheim joined Langevin's laboratory, and it was there that London gave the interpretation of the diamagnetic anisotropy of benzene and treated the problem of helium at very low temperatures, while Tisza worked out his theory of He II and Guggenheim (partly in collaboration with Elsasser, who, like Friedlander, had joined J. Perrin's laboratory) proposed the first shell theory of nuclei. A few others (e.g. Chargaff and Nachmansohn) joined the biochemistry laboratories at the Pasteur Institute and the Sorbonne, while E. Lederer, now professor in Orsay, joined the Rothschild Institute.

During the 1914–1918 war, chemical warfare, the key role of ammonia and nitric acid synthesis in maintaining the German war machine against the allied maritime blockade, had already awakened France to the importance of science-based industry, with its ultimate dependence on fundamental research. This gave rise to a rather active campaign launched by the nationalist writer M. Barrès to enlist public support for science. But only in 1936 was there substantial public action. The new "Popular Front" government chaired by Léon Blum gave Jean Perrin a vice-ministerial appointment (he was succeeded by Irène Joliot Curie in 1937) during which Perrin managed to create the CNRS (National Center for Scientific Research) which became, and remains, the main public agency supporting fundamental science.

1939–1945

The CNRS had hardly had time to get going before World War II dealt a new and heavier blow to French science. In particular, it drastically reduced the work in physical chemistry. Much more than the diversion of effort towards war research in the first year of the war, the occupation period was specially destructive.

First, most of the senior staff of Perrin's laboratory left France. Jean Perrin, Francis Perrin, Auger, Mlle Choucroun, Rogozinsky, and S. Winter managed

to reach the USA, where most of them participated in the war effort. This was made possible by Louis Rapkine, who, after efficiently contributing to the rescue of scientists fleeing the fascist regimes before the war, followed up this task in favor of French scientists and succeeded in obtaining financial support from the Rockefeller Foundation, invitations from American Universities (mostly from New York's New School for Economics), and visas from the State Department. Upon arrival in the USA all of them enlisted in de Gaulle's Free French Army and were placed at the disposal of the American government. One of the two authors joined Princeton (Magat). The other (Guéron), who managed to reach Great Britain at the time of the armistice, worked first there and then in Canada on the atomic project together with others, mostly from the Radium Institute and from Joliot's laboratory at the Collège de France. H. H. v. Halban and L. Kowarski had performed in Cambridge the key experiment planned in France by Joliot on uranium-heavy water systems, demonstrating that these could sustain a fission chain reaction. This result was to be developed in the Canadian project, which was joined also by P. Auger and B. L. Goldschmidt.

From all Perrin's Institute only a few remained in France: Mlle Cauchois, at the time Assistant Professor, had the great merit of preventing the laboratory from falling into the hands of collaborationists; A. Marcellin did applied research; Dervichian soon transferred to the Pasteur Institute, while Rouault was appointed Professor in Lille. Others like E. Bauer were forced to hide and managed to escape to Switzerland; some like Yvon, Sadron, and Hering (with nearly all the staff from the Strasbourg University) were deported to a German concentration camp. Some, like the physicists Abraham and E. Bloch, never came back. Among others (like Joliot, R. Audubert, M. Mathieu, and J. P. Mathieu) who joined the Resistance, many were arrested and some executed (Solomon, L. Cartan, Hollweck, Mlle Bloch).

Nevertheless some important research was done, quite paralleling work published in unoccupied countries; for example, Sadron developed the theory of hydrodynamic properties of coiled polymers in solution and arrived at the same results as did Werner Kuhn, while Bauer's "absolute rate" theory of dielectric dispersion gave results very close to those obtained in the USA by Henry Eyring and W. Kauzmann.

Those who could keep working (e.g. in Pascal's laboratory or in Audubert's Laboratory of Electrochemistry) had practically little or no chance to carry out research; they were completely cut off from the world scientific community: no journals, no possibility of buying new equipment, tremendous difficulties in repairing or maintaining apparatus. The problems to work on had to be selected so as to provide no valuable new information to the Germans; otherwise the scientists refrained from publishing their results. The only way of getting equipment and spare parts was to take them from the apparatus of absent colleagues. This was natural under the circumstances, and was done on a large scale. At the end of the war when Bauer became Director of the former Perrin's laboratory he found, apart from the equipment of Mlle Cau-

chois, one test tube with a cork and a few lenses. Of course during all that period practically no students or research workers could be trained in physical chemistry.

1945–1955

At the war's end all had to start from scratch once more. The total number of senior physical chemists actually at work in universities and in industry did not exceed 30! Some laboratories, like that of Prettre in Lyon, were destroyed by bombing.

Some old, unfavorable features of the prewar organization persisted: physical chemistry above the sophomore level was taught as a separate subject in only four universities out of seventeen and some of the teaching was anything but modern. The subject was optional, and not included in the curricula leading to the degrees required from future high school or university teachers. On the positive side was the existence of CNRS with Joliot as Director and a Rockefeller grant of some \$15,000 for equipment, to be divided among the physical chemists, which gave the opportunity to buy a little modern equipment, US army stocks, some equipment recovered from the Germans, and last but not least, tremendous good will and friendly relations among the physical chemists, particularly those in their 30s and 40s.

The provisional government was rather favorable to scientific research. But in a country where nearly all bridges, harbors, and railway switchyards were destroyed, that was half starving and half freezing, with most of the industry obsolete, with many cities badly damaged, there were plenty of far more urgent problems than research and the part of the budget devoted to the latter could but be rather small. Those responsible for research had to decide on priorities. Joliot's decision was extremely wise: most of the money was to be spent on fellowships for young research workers, since, of all pending tasks, their training required the longest time—7 to 10 years—and had thus to be started as early as possible. A small amount of money was provided for equipment and practically none for buildings, except for reconstruction.

Research workers in their productive years were also faced with a difficult decision: should they work alone or with a small group, trying to do as high-level work as possible, or should they put aside their personal work and the recognition they could have achieved, for the sake of training as many people as they could handle? They practically all adopted the second choice, in agreement with Joliot's policy. Several research groups started at that time are still in existence, having developed into rather large Institutes. They were located in Nancy (chemical kinetics under M. Letort), in Strasbourg (macromolecular physics and chemistry under Sadron), and in Lyon (catalysis under M. Prettre).

In Paris, the former Perrin's laboratory took up work on dielectrics, molecular spectroscopy, chemical kinetics, monomolecular layers, high polymer solutions and, later on, radiation chemistry and radiation polymerization under E. Bauer in collaboration with Guastalla and M. Magat; X-ray spectroscopy kept on under Y. Cauchois who later succeeded Bauer. Other Paris laboratories

were devoted to electrochemistry under R. Audubert and Mlle M. Quintin; synthesis of high polymers under G. Champetier; X-ray structure of polymers under Marcel Mathieu and Mehring, soon joined from England by Rosalind Franklin; and kinetics of explosion reactions under P. Laffitte. About the same time as in Bauer's laboratory, radiation chemistry of water and aqueous solutions began to be investigated in the Radium Institute under M. Haissinsky. A few years later new research groups started (magnetochemistry under Pacault and infrared spectroscopy under Mlle M. L. Josien in Bordeaux), or were extended (microcalorimetry under Calvet in Marseille; gas-metal reactions under Chaudron in Lille).

In this list are included only the largest of the laboratories that considered themselves laboratories of physical chemistry and were supervised by the Committee on Physical Chemistry of the CNRS. But some work done in chemistry and physics university departments also belonged to physical chemistry. Such was the case, in Paris, of electrochemistry under E. Darmois, of infrared spectroscopy under P. Barchewitz, and of dielectrics under R. Freymann in Rennes and under Arnoult in Lille.

The situation was particularly poor on the theoretical side. Apart from Bauer, nobody was engaged in work on the theoretical aspects of physical chemistry, with the exception of quantum chemistry, where a group, started by Daudel towards the end of the war, later developed into what one can call the French school of quantum chemistry. All the other theoreticians went into quantum field theory, or neutron and high energy physics, the latter mostly in the framework of the Commissariat à l'Energie Atomique (the French AEC). It is something of a paradox that the creation of the Commissariat à l'Energie Atomique in 1946⁸ added to the difficulty of restarting research in fundamental physical chemistry, because it attracted several well-trained physical chemists and a larger number of the half-trained younger ones and put them to work, at least at the start, on applied rather than on fundamental problems.

The governments which succeeded the 1945–1946 provisional government were much less interested in scientific research. For example, the first 5 years development plan did not include scientific research, and one of the Ministers of Finance stated that research was just a passing fashion!⁹ Apart from a few large scientific institutions (CEA, Office for Aeronautical Research, Office for Telecommunication Research) which were created or actively favored from 1947 on, it was only in 1954, with Mendès-France as Prime Minister, that the

⁸ Joliot, after having been General Director of the CNRS, was the scientific executive head of the CEA (High Commissioner for Atomic Energy) with a General Administrator on the same level of authority.

⁹ This difference between the consecutive governments is probably due to the fact that a large fraction of Ministers in the provisional government had spent a large part of the war in Great Britain and the USA and realized the importance of the contribution of science to the war effort, while most of the influential Ministers of the governments that followed were active in the Resistance in France and were not aware of that point.

government showed concern for scientific research and started to provide increasing financial support, until in 1969, as everywhere else, the appropriations for fundamental science leveled off.

1955–1970

It is clear that under these conditions a general “take off,” of postwar French science, and of physical chemistry in particular, took place only in the early fifties. It was at that time that the building of new large research laboratories began, to house the new Institutes or Research centers, the first one being the Research Center on Macromolecules in Strasbourg with Sadron as its first Director. Until then, the different research groups were housed in pre-war laboratories, in a space foreseen for 5–10 times less people than their actual staff. Most of the new institutes were located outside the Paris area, in keeping with the general policy of counteracting the long prevailing trend of having most of the up-to-date research done in Paris, with the provincial universities mostly second grade.

But physical chemistry was still considered a minor subject, as compared to organic or inorganic chemistry. This did not change until the university reform called “Réforme Fouchet” (after the name of the Minister of Education who implemented it in 1966). This reform organized on a wider national basis the university curricula, increased the duration of undergraduate studies to four years instead of three, and created as final diploma the master’s degree. It provided for such a *dégré* in physical chemistry, on the same level as in chemistry (organic or inorganic) and biochemistry. As a result physical chemistry is now taught in its own right in ten or twelve universities.

Scientific and technical expansion with its administrative and organizational aspects has thus been an important feature of the last 10–15 years, in France as everywhere else. Universities increased in numbers, partly through internal reorganizations, from 17 to 65 at the present date. The total student population increased from roughly 200,000 to some 650,000–700,000 now, with over 110,000 majoring in scientific studies. Their research laboratories, as well as those of the top engineering schools, were very much enlarged, as were those of the big industrial firms. Many great public or semipublic research establishments were created. In addition to those already mentioned for atomic energy, high energy physics, aeronautical science and engineering, and telecommunications, which were enlarged, there now exist institutes for space research and development, medical research, oceanography, and metals research and development, among others, all of which carry out much work in physical chemistry, at least some of it highly fundamental.

It would be foolhardy to select, from the very large number of publications and results, those that in the long run will prove the most important. All the more as no real scientific breakthrough occurred in physical chemistry,¹⁰

¹⁰ Contrary to physics where L. Néel discovered antiferromagnetism and A. Kastler the optical pump.

either in France or elsewhere, during the last 25 years. We have therefore chosen to list some typical results and research subjects, indicating where the research is being done. They will be presented by subject matter, quoting laboratories and groups rather than individuals, although we shall give the names of the laboratory heads and sometimes those of group leaders.¹¹

CHEMICAL KINETICS

In Nancy, Letort and his co-workers studied the mechanism of polymerization of acetaldehyde in the immediate vicinity of, but below, the melting temperature, and related it to the crystal structure. The same group contributed also to disentangling the problem of low temperature oxidation of hydrocarbons. Interesting work was also done on the identification of intermediate free radicals by mass spectrometry, and on oxidation of graphite.

An important advance in the theory of branched-chain reactions was achieved in Laffitte's laboratory by Ben Aïm. Kinetics of heterogeneous reactions is actively studied in Dijon in the laboratory of Barret. A theory of steric hindrance of the "second type," which influences the activation entropy, was developed in Bauer's laboratory in Paris.

HETEROGENEOUS CATALYSIS

Heterogeneous catalysis was studied in two laboratories: in Lyon at the University and later on (1960) in the Research Institute of Catalysis (RIC) of the CNRS (under Prettre, with Imelik, Teichner, and Trambouze) and the other in Lille under Germain.¹² The latter, small in size, did essentially pioneering work on the relation between the activity and semiconducting properties of the catalysts, while RIC treated the problem of heterogeneous catalysis on a much broader basis. For instance, it has disentangled the complex mechanism of controlled oxidation of methane to produce water-gas, developed catalysts for this reaction, and determined the optimum conditions of their utilization. This laboratory also developed very precise equipment to study the texture of finely divided or porous solids, using essentially small-angle scattering of X rays.

It was shown also that, on catalysts that are insulators, two types of active centers do exist: Lewis' acids and electron donors or acceptors. Methods were developed that allow the identification of these centers and the determination of their number on a given catalyst. Their chemisorptive properties were measured using infrared and ESR techniques. The acid-base and oxidation-reduction properties of numerous catalysts used in contact catalysis were determined.

The identity of chemisorptive properties on the (100) and (110) faces of monocrystals of Ni for H_2 and C_2H_4 was demonstrated by using slow electron

¹¹ We apologize to those colleagues whose work will not be quoted or will be only incompletely quoted; as stated above, we have chosen to list a certain number of typical examples of the work done in France and our selection does not imply any judgment of the scientific value of individual contributions.

¹² Now at the University of Lyon.

scattering, and the hydrogenation of C_2H_4 under these conditions was studied. This work was extended to divided Ni on a silica support prepared by decomposition and reduction of two nickel hydrosilicates (talc and antigorite of Ni)¹³ which showed the same properties. Finally, different semiconducting catalysts (NiO , ZnO , TiO_2 , ThO_2) and their catalytic properties were investigated; ThO_2 , because of its thermal stability, was the only one in quantitative agreement with the theoretical predictions of Wolkenstein when used for oxidation of carbon monoxide.

CALORIMETRY

The isothermal microcalorimeter of Calvet (Marseille) that can be used over a very wide range of temperatures is well enough known to make it unnecessary to say more on this subject. Some calorimetry research is also being done in Orsay under Dodé (very high temperature region) and in the laboratory directed by Magat (low temperatures).

COLLOIDAL PHYSICAL CHEMISTRY

Most of the work in this field is done in the CNRS laboratory in Montpellier, where Guastalla expanded research started before the war in Perrin's laboratory and continued there under Bauer. It concerns the adsorption of tensioactive substances on the surfaces of solutions and on solid-solution interfaces, electrophoresis of colloidal particles, and electrochemical properties of nonmiscible liquid phase systems.¹⁴ Finally, some work was done on the relation between the tensioactivity and the bacteriostatic properties of certain soaps.

ELECTROCHEMISTRY

Several laboratories are engaged in electrochemical research, two of them resulting from a split of Audubert's laboratory after his death. At the Paris University Mlle Quintin continued, until her retirement, work on electrolyte solutions, particularly in nonaqueous media; Bonnemay and co-workers in the CNRS Laboratory in Bellevue worked on problems concerning electrode-electrolyte contacts. But the most important part of the work of this group appears to be their contribution to the realization of fuel cells. Lepoutre (in Lille) contributed significantly to the understanding of alkaline metal solutions in liquid ammonia. Electrochemical research is being done also by Bonnier (Grenoble), Valensi (Poitiers), Brenet (Strasbourg), and Epelboin (Paris).

MAGNETOCHEMISTRY

As already mentioned, magnetochemistry was started in France by P. Pascal and was carried on in recent years by A. Pacault at the University of

¹³ The nickel crystallites of the catalysts prepared from talc developed preferentially (100) planes; those prepared from antigorite developed (110) planes.

¹⁴ Part of this last work is being carried out by Mme Dupeyrat in the Laboratory of Physical Chemistry of the Paris university (Mlle Cauchois, Director).

Bordeaux and since 1966 in the CNRS Institute near that city. One of the most striking achievements of that laboratory was the construction of a torsion balance that allows the measurement of the susceptibility of a compound in its paramagnetic excited state under intensive illumination (triplet states), the sensitivity being of the same order of magnitude as that of current ESR equipment. Research is also being carried on in ESR, spin-echo, and NMR. But this group did not limit itself to magnetochemistry and soon extended its interests to various topics, from the precise study of Rayleigh scattering to the study of the kinetics of formation of graphite. Among others, specific heats between 1.3° and 4.2°K are measured in strong magnetic fields and the existence of a negative anisotropic magnetoresistance of amorphous pyrocarbons between 1.6 and 77°K was demonstrated.

SPECTROSCOPY

Vibrational spectroscopy.—While Lecomte still pursues his work at the Paris University, two of his former students founded schools working in very different directions. Mlle Josien and her co-workers (CNRS Laboratory in Thiais) are essentially interested in the analysis of vibrational spectra of more and more complicated molecules and the frequency shifts by substitution as well as those produced in solutions and mixtures through intermolecular forces, using infrared and Raman laser spectroscopy. The same type of studies is carried out by Josien's former student Lascombe in Bordeaux. Barchewitz (Laboratory of Physical Chemistry of Paris University) is particularly interested in high dispersion spectroscopy (rotational fine structure, CO₂ and N₂O gas lasers, and equipment construction). Vibrational frequencies and their fine structures in monocrystals of HCl, DCl, and HBr down to helium temperatures were studied by Peyron in Lyon.

As far as intermolecular movements are concerned, the study of dielectric dispersion was started immediately after the end of the war, as mentioned, first in Paris by Bauer, followed by Arnoult in Lille, by Freymann in Rennes, and by Barriol in Nancy. After Bauer's retirement, work on this line was continued in Orsay by Brot. In recent years, thanks to the development of far infrared equipment, this type of work was extended to smaller wavenumbers (100–20 cm⁻¹) in different laboratories: by Novak in Josien's laboratory, by Hadni in Nancy, by Lascombe in Bordeaux, and by Brot in Orsay. In most of these places the results of far infrared are completed by data from Raman lasers. In all cases the main matters of concern are organic crystals and their phase changes, as a part of a CNRS cooperative project. The nonmolecular crystals are being studied by physicists (e.g. J. P. Mathieu).

Spectroscopic information is usually completed by broadband NMR studies, calorimetry, and X-ray diffraction work (Meinzel in Rennes and Renaud in Paris). For these studies X-ray equipment was developed that allows diffraction measurements to be made at liquid air temperatures and under pressures of 5–10 kbar (Renaud in Cauchois' laboratory).

Electronic spectroscopy.—Contrary to the atomic spectroscopy, electronic molecular spectroscopy is not very highly developed in France. The only important laboratory in this field is that of Leach, a former student of Bauer's, in Orsay and that of his student, Mme Kahane-Paillous (Grenoble). The work was at the beginning essentially directed towards the vibrational analysis of polyatomic molecules and radicals in excited states, in gas phase as well as in matrices. The influence of the matrix structure on the electronic and vibrational frequencies of benzene in crystalline cyclohexane was particularly investigated. The subject matter was later extended to the excitation of molecules by low energy electrons of controlled velocity, energy transfer problems, high resolution spectroscopy of small molecules, and, after Lindqvist joined the laboratory, flash and laser techniques. By use of 10^{-8} sec laser pulses, spectra corresponding to singlet-singlet transitions began to be investigated.

Some work in the field of molecular spectroscopy, particularly in the far uv (1000–150 Å), has been going on for several years at the CNRS high pressure laboratory in Bellevue under Vodar; most of the work pertains, however, to diatomic molecules (O_2 , NO, etc). The effect of pressures on rotational lines was also investigated.

X-ray spectroscopy.—The laboratory of Mlle Cauchois continues to be very active in this field. Its work was extended some years ago into the Hollweck region (10–1000 Å).

MACROMOLECULAR PHYSICAL CHEMISTRY

This subject is treated in a large number of laboratories, since a systematic effort has been made in that direction. The most important ones are the Macromolecular Research Center (CRM) of the CNRS in Strasbourg, created around Sadron, with H. Benoit now its Director; the combined laboratories of Champetier and Sigwalt at the Paris University; the laboratory of J. Néel in Nancy; those of Selegny and of Maréchal in Rouen; and those of Guyot, Vallet, and Golé in Lyon. One could add to this list the CNRS Laboratory of Radiation Chemistry in Bellevue, under A. Chapiro, which specializes in the application of radiation methods to macromolecular compounds. For historical reasons we shall treat it in the Radiation Chemistry section.

The original idea that led to the creation of CRM was to bring under one roof chemists, physical chemists, and biochemists interested in high polymers. However, a few years ago the biological group under Sadron split off and started a new Center of Molecular Biophysics in Orleans in 1967. The chemical section (under Parrod and Rempp), besides doing research work on ionic polymerization, made a great effort to prepare structurally well-defined polymers and copolymers for the physical chemistry section.

A very interesting result, obtained by a collaboration between these two sections, concerns the so-called organized polymers: when block copolymers are brought in contact with a liquid dissolving preferentially one of the copolymers under certain conditions of temperature and concentration, the

macromolecules associate, producing regular mesomorphic structures, e.g. alternate layers of "soluble" and "insoluble" segments, or else parallel cylinders with the soluble part outside and the insoluble inside. If now one uses as solvent a polymerizable monomer and induces its polymerization, one obtains a solid polymer that keeps the initial structure. In other words, one obtains in this way a polymeric composite material with internal microheterogeneity of various geometry.

In the physical chemistry section (under Sadron and Benoit) a large portion of the research was devoted to the theoretical development and experimental checking of a coil model in which interactions between short segments impose different probabilities to different relative positions of consecutive units. Nearly all available techniques were used, going from viscosity to light scattering, to dipole movement, and to the deformation of the coil by a hydrodynamic force field. Now, block copolymers constitute an important fraction of compounds investigated. Interestingly, some synthetic polymers, usually coiled in solution, can also exist as a helix, the transition from one conformation to the other depending on the solvent and on the temperature. In recent years important contributions were also made to the properties of polymers in the solid state by Kovacs.

The Champetier-Sigwalt group, at first mainly interested in cellulose and polycondensation polymers, shifted slowly towards the mechanism of cationic polymerization and block copolymerization, and to the polymerization of sulfur compounds, while another group became interested in semiconducting polymers and, more recently, in problems of life genesis.

J. Néel worked initially on thermodynamic properties but shifted more recently towards the study of polypeptides. Guyot succeeded in preparing highly crystalline polyvinyl chloride but unfortunately only of short-chain length. He has also explored the influence of the penultimate monomer of a growing copolymer chain on the reactivity of the endgroup.

Some experimental and theoretical research on polymers was also done in Magat's group in Bauer's laboratory: application of fluorescence to the study of segment movements in macromolecules, later developed in CRM, problems of solubility, polymerization in precipitating media, polycondensation of the second type, properties of graft copolymers in solutions, and exact solution of the self-avoiding random-walk problem (see also under radiation chemistry).¹⁵

THEORETICAL CHEMISTRY

As already mentioned, quantum chemistry started rather late in France; it was only towards the end of World War II that Daudel started a group in this direction, investigating with A. and B. Pullman the charge distribution in polyaromatic compounds and relating it to their carcinogenic activity. Two important groups developed then, one under Pullman working on the physico-chemical properties of biologically active compounds and relating them to the

¹⁵ This group completely left the high polymer field a few years ago.

delocalization of electrons. A large amount of work is now being done on the purine and pyrimidine bases and on the problem of selecting the best approximations for the calculation of different properties. The other group under Daudel is interested in more general questions, such as molecular interactions, including hydrogen bonding, NMR and ESR spectroscopy, and spin relaxation. A third group was started in the late sixties by Salem in Orsay. After some work concerning the rotational barrier around single bonds and intermolecular interaction, this group studied the reaction paths for the two possible isomerizations of cyclopropane. Other smaller groups are active in Bordeaux, Marseille, Strasbourg, and Lyon.

PHOTOCHEMISTRY

The physical chemistry aspects of photochemistry (as distinct from the organic, more preparative, photochemistry) is relatively little developed in France. In the late 1950s Leach, Matheson, and Vermeil demonstrated by far uv photoionization that the ionization potential of isobutene was lower by some 1.5 eV in the liquid, as compared to the gas, phase. This led Mme Vermeil and her group (Paris) to investigate the far uv photolysis of simple compounds and to show the importance of "hot" hydrogen atoms in secondary reactions, while Leach and his group (Orsay) discovered the opening up of the benzene ring followed by chemical stabilization of the product in the solid state, when irradiated at 2537 Å.

Joussot Dubien (Bordeaux) was one of the first to demonstrate the possibility of biphotonic ionization, and in collaboration with Bensasson (Paris), using a nanosecond laser, has observed the first singlet-singlet transition between excited states of benzene.

Ivanoff's group in Orsay has studied the photoisomerization of diazine in the gas phase as function of vibronic levels of two possible singlet states. Dufraisse, before the war, was one of the initiators of the photochemistry of complicated organic compounds and, while this work was continued by some of his students, this field, for a long time rather dormant in France, is now developing exponentially.

PHYSICAL CHEMISTRY OF ISOTOPES

Stable and radioactive isotopes are extensively used in France in all branches of fundamental and applied physical chemistry. We shall mention work relating only to the fundamentals of isotope effects or to particularly important or original applications.

Isotopic effects in molten salts were studied by Chemla (Paris). In molten metals the Saclay group (CEA) showed a temperature reversal (so far unexplained) of the isotopic effect linked to the passage of dc current. In the CEA (under E. Roth) much work was done on the H-D system. In cooperation with industrial firms a pilot plant for preparing pure D₂ (and D₂O) by liquid hydrogen distillation was built and efficiently operated for over a year. The NH₃-H₂ exchange was extensively studied, with homogeneous catalysts of the KNH₂ type, resulting in a demonstration plant built in cooperation with

industry. This plant has been operating without trouble for the last three years, and a bigger one is to be built in India. The same group has made extensive studies of the D contents of antarctic ice cores, and very elegant experiments on the variation of the D/H ratio in successive layers of hailstones. Another CEA group (under C. Fréjaques) has done all the research and development necessary for setting up the Pierrelatte uranium separation (by gaseous diffusion) plant, and is experimenting with the ultracentrifuge separation of uranium isotopes.

RADIATION CHEMISTRY

One of us having been closely connected with this field, we shall expand it more than the other aspects, as a typical example of the development of physical chemistry in France after the war.

One could claim that radiation chemistry was born in France together with radioactivity, since the latter was discovered by Becquerel through a chemical reaction—blackening of a photographic plate by pitchblende. The radiolysis of water was studied as far back as 1914 by Debierne, who at that time suggested that a large part of the consecutive reactions was due to what we now call radicals H and OH. But no other work known to us was carried out before 1940 when Joliot polymerized methylmethacrylate by radiation at room temperature but in the presence of a chemical catalyst. This observation was never published, since it was anticipated by a few weeks by Philipps and Hopwood. During and immediately after the war Bonet-Maury and co-workers made their well-known experiments on the difference between final products of α and γ irradiation water (LET effect).

But the main development of radiation chemistry in France began in 1948 when two groups, Haïssinsky's in the Radium Institute and Magat's in Bauer's laboratory (formerly Perrin's laboratory), started work in this field; the subject was divided between them. Haïssinsky's group worked on water and aqueous solutions using the classical technique of scavenging the oxidizing and reducing species by electrolytes at various, particularly basic, pHs and on the LET effects (Pucheault). The work was extended in more recent years to liquid ammonia (Belloni) and dimethyl sulfoxide (Koulekès).

Magat's group chose to work on organic compounds, using in the beginning the polymerization of monomers with well-established rate constants as a kind of chemical amplifier to determine the numbers of radicals produced by a given amount of radiation. The sources used were, in the beginning, the first French atomic pile Zoe (soon abandoned because of the complexity of the radiation) and 1 Ci of radium kindly lent by Mme Joliot-Curie. It is with the latter source that, in collaboration with Chapiro, the kinetics of radiation polymerization was established and was shown to proceed by a radical mechanism. The first G values for monomers and solvents could hence be evaluated from rates of initiation. These were crosschecked soon after by using diphenylpicrylhydrazyl as radical scavenger.

In 1953 a more powerful 30 Ci of cobalt source became available, and part

of the preliminary research concerning radiation degradation of polymers in solution in the presence and absence of oxygen was carried out using this source. The problems of oxidation and of oxidative degradation of polymers were studied by M. Durup and J. Durup.¹⁶

Work by Chapiro on crosslinking of polyethylene in the presence and absence of oxygen led to the idea that some of the crosslinking was due to easily breakable oxygen bridges, and initiated a long series of research on radiation grafting of different monomers on polymers using two different methods (1955). The kinetics of grafting under different conditions and the properties of grafted materials (e.g. membranes) was, and still is, investigated in Chapiro's CNRS laboratory in Bellevue.

The possibility of cationic polymerization of isobutene was demonstrated nearly simultaneously with the group headed by Davisson in Great Britain, and several cases of cationic and anionic polymerization were later investigated.

After the announcement by Mesrobian and co-workers (USA) of the possibility of polymerization in the crystalline state, work was initiated in this direction mostly on monomers which are liquid at room temperature. Chapiro and his group studied carefully the kinetics of solid state polymerization of a great number of different monomers (showing for instance that the reaction was particularly fast a few degrees below the melting point). In Magat's laboratory work was centered on two monomers, formaldehyde and acrylonitrile. In formaldehyde under certain conditions at liquid air temperature the polymerization becomes explosive, obeying the laws of Semenov's theory of thermal explosions. In the case of acrylonitrile (studied partly in collaboration with Bernas and Bensasson from Mlle Cauchois' laboratory) it was shown by calorimetric measurements (Dworkin) and later by X-ray diffraction (Renaud) that two distinct phases exist in solid state and that the kinetics of polymerization is different in the two phases and becomes reproducible only if the solid is carefully annealed. Later the possibility of a slow polymerization during irradiation at 4.2°K was shown by calorimetric measurements.

In experiments in Chapiro's laboratory some monomers polymerized very fast when dissolved in substances forming glasses at not too low temperatures, the polymerization taking place in small droplets of monomer which remain liquid, because of their size, far below the normal melting point. In other words the situation was somewhat analogous to suspension polymerization.

In 1958 home-built ESR equipment with a permanent magnet allowed Mme Marx to identify primary radicals in polymerization reactions and Szwarc to investigate the recombination of radicals in annealed and quenched solids. It appeared that in annealed crystals this recombination was particularly fast at phase transition temperatures.¹⁷

¹⁶ This type of work is now continued by Marchal and co-workers in CRM.

¹⁷ This originated interest in molecular movements in solids and led to the development of the group headed by Brot, whose work was partly mentioned previously. One interesting result was the explanation of the fact that in certain cases phase transitions observed by NMR are not observable by calorimetry.

These results were the beginning of a turn in the research direction of Magat's laboratory because of several factors: the move out to Orsay (1960) where more space was available and a 3000 Ci source could be installed, the increase of the research budget that made it possible to buy or build more expensive and sensitive equipment, and particularly the fact that several research workers reached maturity and could attack more complex problems. The work on radiation-induced chain reaction and on scavenging techniques was progressively abandoned, and research was centered on primary acts and reactions.

Durup started work on the kinetic energy of ionic fragments and on the detailed mechanism of ion-molecule reactions using mass spectroscopic techniques. Mme Fayard initiated research on isotope effects in the fragmentation of small molecular ions and on the electron capture by gaseous molecules. Leach developed work on spectroscopic properties of trapped molecules and radicals and on energy transfer¹⁸ as well as on far uv photolysis.¹⁹

Another problem was that of charge recombination followed by light emission (Kieffer and associates). This recombination was slowed down by using crystalline or glassy matrices of saturated hydrocarbons containing various amounts of different aromatics. Warming the matrices led to the liberation of the charges; and thermoluminescence peaks, particularly those corresponding to recombinations of anions with cations, as distinct from cation-trapped electron recombinations, occurred near phase transition temperatures (like radical recombinations), which indicates a rapid molecular diffusion at these temperatures. Differences between the emission spectra of the two types of recombinations were observed and interpreted. An analogous type of work, but essentially using photoionization, was and is being carried out by the group of Mme Bernas in Mlle Cauchois' laboratory.²⁰

Further developments occurred in Magat's laboratory in the last 2-3 years when investigations began on two other lines: 1. chemical effects of slow electrons (5-10 eV) of controlled energy, with radical appearance potentials studied in Mme Marx's group and overall chemical reactions by Mme Danon

¹⁸ Some time later the last two groups split off and are now independent research laboratories in Orsay.

¹⁹ As already mentioned, this group is now working in Paris under Mme Vermeil.

²⁰ Interestingly, no radiation chemical work was conducted in France using electron accelerators, neither in Haissinsky's nor Magat's laboratories and not even in the CEA laboratory on radiation chemistry in Saclay, since no such equipment had been made available. Indeed this type of work was important at a period when the emphasis was on fellowships rather than on equipment. For the same reason no work on microsecond pulse radiolysis was done in France, and the French scientists contributed neither to the kinetics of radical reactions nor to the kinetics of solvated electrons. At present three accelerators delivering nanosecond pulses are available between Orsay and the CEA laboratory in Saclay. A parallel situation exists in photochemistry—there was very little flash photolysis equipment in France, with just one in the uv region, while several short-pulse (10^{-8} – 10^{-9} sec) lasers are now in use.

and colleagues; and 2. spectroscopic emission and absorption studies using a nanosecond electron pulse generator.²¹

Another important group in radiation chemistry is that of the Atomic Energy Commission in Saclay. This group used for a long period essentially scavenging techniques for radicals and solvated electrons, first in water, then in alcohols and nitrocompounds. Later ESR was introduced and in the last years a large and successful effort was made in the direction of pulse radiolysis (10^{-8} – 10^{-9} sec pulses), particularly in the gas phase where absorption spectra of primary excited ions were observed for the first time.

The effects of different types of radiation on inorganic crystals are studied mostly by physicists. However, a group under Lucasson is investigating in Mlle Cauchois' laboratory atom displacements in metals by electron impact, and the "healing" process of the defects so introduced.

MOLECULAR BIOPHYSICS

If we exclude biophotochemistry and enzyme kinetics studies of more biological than physicochemical interest, research in molecular biophysics was until recently confined to CRM (Strasbourg). Three years ago the group directed by Sadron moved to a new laboratory in Orleans, where work on conformations of biological polymers and on energy transfer is in progress. A smaller group under Selegny (Rouen) is working on membrane problems. They succeeded in grafting an active enzyme on a synthetic membrane, and could observe an active transfer of glucose.

CONCLUDING REMARKS

We hope to have shown that, after a brilliant beginning followed by a relatively dull period in the nineteenth century, a first revival of physical chemistry in France took place in the beginning of this century, stopped by the First and then by the Second World War, which annihilated a large part of the previous effort. After the last war a new and powerful development took place and at present the scientific production of physical chemists is neither better nor worse in France than in other countries of the same importance.

²¹ We repeat that we have developed the postwar history of Magat's laboratory not because we think that particularly important work was done there, but because it is a good example of the development of the overall physicochemical research in France with its difficulties, setbacks, and advances. It is for instance typical that the number of research workers grew from 2–3 in 1948 to some 60 now, although as already mentioned, three groups—those of Leach, Fayard, and Vermeil—have split off. This growth is not unique; many of the laboratories mentioned above (CRM in Strasbourg, RIC in Lyon) are very large when compared to the American University Laboratories. This is the consequence of the small number of active physical chemists available by the end of the war.