

THE REACTIVITY OF SOLIDS YESTERDAY AND TODAY

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Abstract - The international meetings devoted to the reactivity of solids have their origins in the first Symposium organized by Prof. Chaudron in Paris in 1948 with the sponsorship of the French National Center of Scientific Research. At this time, the main topic was the study of reactions occurring inside a solid and between solids. The following meetings progressively include themes relating to solid-gas and solid-liquid systems in their program. In the first part of this lecture, the nature of these themes is recalled and their evolution during the 35 last years analysed. The improvements in understanding of reaction mechanisms in ceramics and metals is emphasized. In the second part, the progress in metallic surface knowledge due to new techniques : low energy electron diffraction, electron spectroscopies, radioactive tracers is evoked. Some results obtained in the laboratory of the author in this way are mentioned.

I INTRODUCTION

Perhaps the principal reason for choosing me to present the opening lecture is that in 1947 I organized, with the late Professor Georges Chaudron, the first of these meetings. We never imagined that it would be the starting point for a series of gatherings as prestigious as those that have followed. I am delighted that this tenth anniversary is being celebrated here, in Dijon, on the initiative of a team that has contributed so much to this important field.

In the first part of this talk I will recall the history of the previous nine conferences and make a brief summary of the development of concepts related to the reactivity of solids during the last decades.

Then I will mention some features of recent research that I believe, rightly or wrongly, to be significant, particularly concerning the first stages of the reactions of gases at metal surfaces.

II ORIGIN AND HISTORY OF THE CONFERENCES

For a long time, the study of reactions in the solid state and in a more general way the reactivity of solid bodies was, as you know, largely neglected. Often even the existence of such reactivity was denied as we know from the celebrated adage attributed to Aristotle : Bodies can only react if they are dissolved. However, in a paradoxical manner, there were many technologies used by the ancient civilisations that depended on the existence of such reactions - whether it was the making of objects in ceramic or the dry method preparation of numerous mineral pigments. Yet up to the beginning of this century a good number of scientists continued to think that the reactions that occur in solids or between them could take place only by material transport across a fluid phase, liquid or gaseous.

As a witness to this state of affairs, I put to you the fact that when I was a student, half a century ago..., the textbooks of physical chemistry went on at some length about reaction kinetics in gaseous milieux and perhaps liquids but they were practically silent on reactions bringing into play solid particles. The only concessions were to the famous law of Pilling and Bedworth which is known to apply to a rather special type of reaction that of the surface oxidation of metals.

Among the reasons for this ostracism one might mention on the one hand the slowness of most solid state reactions in the temperature ranges then readily accessible in the laboratory and on the other hand the precariousness of the methods available for analysing the constituents. From the 1920s one had undoubtedly access to the real atomic structure of solids as a result of the discovery of X-ray diffraction. But for quite a number of years this knowledge remained concerned more or less with static aspects, whereas the transformations of solids are by their very nature dynamic.

However, two kinds of scientists had been for a long time anxious to see some progress in fundamental research on the reactions and transformations that can arise in certain categories of solids. These were in the first place the metallographers who daily observed evidence of transformations with changes of phase in their alloys. Secondly, certain geologists and geochemists studying processes of metamorphism had to invoke the possibility of material transport in solids, sometimes over long distances, under the combined influence of high temperatures and pressures over very long periods.

Such was the situation at the end of the last World War, during which few of us had time to devote to solid state reactivity. At that moment, however, there emerged, through the quality of their work and the clarity of their points of view, some first-class scientific minds. I will mention four who make up what I will call my "personal Panthéon". My choice, which may seem arbitrary to some of you, follows partly, I will admit, from the friendships I was able to establish with each of them in the course of many scientific meetings. In alphabetical order, to avoid any hierarchy, they are :

Georges Chaudron in Paris who was the first to study in some depth, from 1920, a reversible reaction taking place entirely in the solid state : that of the decomposition of ferrous oxide.

Arvid Hedvall at Göteborg who was unquestionably the most vigorous apostle for solid state reactions, especially for the silicates.

Ivar Stranski in Berlin who analysed with remarkable prescience the role that surfaces must play in these reactions.

Carl Wagner, finally, who in Göttingen and in Cambridge (USA) was able to discern the role played by lattice defects in the thermodynamic properties of solids in general and in their transformations.

It was in 1946 that Georges Chaudron, realising the interest there would be in bringing together to focus on this topic all those who had been separated for the long and painful years, took the initiative to organise for the following year, with the support of the French Centre National de la Recherche Scientifique and the Rockefeller Foundation, a colloquium on "Reactions in the Solid State". I was dispatched to Göteborg to make contact with Arvid Hedvall. Ten nations were represented at this Colloquium by scientists whose names are, I am sure, familiar to you all, but of whom many are unfortunately no longer with us. Reading the titles of the 38 lectures and talks that were presented reveals our principal preoccupations at the time. A good number of those are still on our agenda in spite of the 37 years that have gone by : a fact that should cause us to be patient - and even more to be modest.

It was decided at an outcome of this Colloquium that the following meeting would take place under the presidency of Arvid Hedvall at the Chalmers Institute of Göteborg. That event took place four years later in 1952 and on a scale much more ambitious than that of the Paris meeting since some 110 lectures and contributions were presented. There succeeded the following conferences :

In 1956 in Madrid under the presidency of J.M. Albareda Herrera

In 1960 in Amsterdam under the presidency of J.H. de Boer

In 1964 in Munich under the presidency of G.M. Schwab

In 1968 in Schenectady under the presidency of J.W. Mitchell

In 1972 in Bristol under the presidency of J.S. Anderson and F.S. Stone

In 1976 in Göteborg under the presidency of A. Magneli

In 1980 in Cracovie under the presidency of J. Haber

In 1984 in Dijon under the presidency of P. Barret.

A very historical research might have been to follow the progressive appearance either of new experimental data or of new concepts over the course of the years. This I was tempted to do but found myself obliged to abandon the attempt faced with the diversity of contributions at the conferences and the very gradual development of ideas and techniques. Therefore, in what follows, I will limit myself to recalling a number of themes that I consider to be essential and which appear in more or less developed form in the records of almost all the nine conferences that have preceded this one.

III DEVELOPMENT OF THEMES AND CONCEPTS

The first theme that I want to recall is that of Diffusion in three-dimensional solids. Studied at the beginning of our meetings in a purely phenomenological manner, particularly by means of radioactive isotopes, it took on a more theoretical aspect, drawing more and more on physical speculations concerning the role played by point lattice defects, interstitials or vacancies. These speculations, very advanced in the case of metallic lattices because of their relative simplicity, were gradually extended to mineral phases : oxides, sulphides and silicates, in particular. The concept of non-stoichiometric ionic phases was developed in parallel so that they grew a form of doctrine bringing together static and dynamic aspects of crystalline structures.

The whole of these approaches eventually considered diffusion in supposedly monocrystalline solids. It was towards the 1960s that the specificity of Diffusion in intercrystalline boundaries was increasingly taken into account. There again it was the metallographers who opened up the way, but very rapidly it was realised how important was the role of these boundaries in diffusion in non-metallic polycrystalline substances : alkali halides and refractory oxides. This new theme opened up wide perspectives for researchers long preoccupied with the mechanisms of sintering of metallic powders and ceramic materials such as ferrites, alumina and zirconia. That is the second theme that I want to bring to your attention. To use a more specialist language let us say it concerns diffusion in incoherent extended defects found in most intercrystalline boundaries.

Using the same language we might consider the third theme as concerned with diffusion in coherent extended defects. I mean by those solids in which there exist planes or channels in which the binding modes, and in consequence the mobilities, are different and in general higher than for other directions : oxides, sulphides and lamellar halides, clays, graphites and zeolites. There we have a vast world of materials that our lectures have often only touched upon, since the scientists concerned with them often had their own specialist meetings, in particular for clays and carbon. One must not lose sight, however, of the fact that the mechanisms of the reactions in these materials become much clearer when they are looked at in the light of an understanding from theoretical studies and experiments based on more simple model structures. In particular it is of great interest to bring together the behaviour of what may be called internal surfaces and that of external surfaces, on which I will say a few words in a moment.

A theme that is still a current preoccupation is that of nucleation of a new solid phase at the surface or inside a three-dimensional solid. The distinction, rather theoretical when one examines it in all its details, between so-called homogeneous nucleation, that is to say nucleation that can only be attributed to fluctuations of the medium, and so-called heterogeneous nucleation which must be attributed to localized and pre-existing defects, continues to arouse ardent polemics. My feeling is that the remarkable progress made in the last decade has only pushed back the solution to this problem and it would be false to think of it as purely academic. As proof one only needs to think of the role played in the kinetics of precipitation in structurally hardened alloys.

The nucleation of a new phase at the surface of a solid leads us naturally to the theme of epitaxy which has been the subject of very many contributions at these conferences. Does this mean that the problem has become perfectly clear ? At the risk of disappointing many of you, and myself included, who have worked on it, I would think not. Nevertheless the technology of today knows how to control the factors even if the reasons for success are not always known. The production-line fabrication of numerous devices in solid state electronics bears witness to the success.

A closely related theme has led to observations that are fascinating in that they establish an interaction between the structural and thermodynamic aspects of solid state transformations : the study of successive stages of these transformations when they take place at not very high temperatures. Under such conditions, the transition to the final thermodynamically stable state occurs via discrete and transitory structures that can sometimes be isolated and which sometimes have very interesting physical or chemical properties. There again it was the metallographers who opened up this path following the discovery of Guinier-Preston zones observed during the recovery of certain alloys. We have there in particular one of the main causes of memory effects exhibited so often by reactions taking place in the interior of solids and therefore often difficult to study.

Finally I will be careful not to forget all the work that has been done, in particular by Professor P. Barret's group, on reactivity in powdered solids. In fact, it is most often on this kind of medium that in practical systems one is constrained to work.

It would serve no purpose to make efforts to understand the extremely idealised systems if one could not profit from them to try to control what happens in real systems. No doubt this tenth conference will bear once again a harvest of results that can benefit industry.

IV REACTIVITY OF SOLIDS AND SURFACE SCIENCE

This aspect of the reactions in which solids take part had long been neglected but in recent years it has aroused considerable interest. It is concerned with the very first stages of a reaction during which the first atomic layer of the surface is modified. The neglect of this subject was largely due to a lack of structural information in the absence of methods of investigation sensitive enough to receive signals from that single layer without being drowned in signals from deeper levels.

And yet we are dealing with an essential stage in any reaction with a solid since it is across the first atomic layer that there is contact with the external medium, whether that be solid, liquid or gaseous. Faced, as one used to be, with the impossibility of having direct experience of the nature of this layer, two attitudes were possible and were effectively adopted. The first, taking a simplistic position, was to deny that it was a factor to be taken into consideration. What role could there be for a layer a few angstroms thick in comparison with the thousands of layers that would be involved a few moments later by the progress of the reaction? The second attitude was to turn to speculations which ran the risk of contradiction only at some future time when appropriate experimental methods became available. Well, that moment came and for one or two decades it has been possible to base working hypotheses on reliable observations.

A number of physical methods for studying surfaces, for which the principles had long been known, but for which the technology for routine experimental work had not been perfected, became available: low-energy electron diffraction, Auger spectroscopy, work function measurements, spectral analysis of ions, high-resolution microscopy, etc... The possibilities for visualising surface details, although essentially qualitative, brought a new dimension to our knowledge not only of atomic-scale topography, but also the distribution of components. Thus a new era opened up in our intimate knowledge of surfaces, from which our understanding of the reactivity of solids is beginning to benefit. Professor Haber will treat this aspect of solid reactivity in detail and I will limit myself to some general remarks based essentially on the experience gained with Jacques Oudar and our coworkers during more than twenty years of research on chemisorption on the surfaces of metals.

One unknown factor troubled and still sometimes troubles much research on solid reactivity: the absence of precise measurements of the chemical composition of the external atomic layer. Imagery by ion emission and Auger electron spectroscopy have certainly brought valuable information in many cases. But it is incontestably the use of reactants marked with radioactive isotopes that have provided the most precise quantitative data.

Let me recall that from 1960 it became possible by this method to trace with a precision not previously achieved isotherms for the reversible chemisorption of radioactive sulphur on copper, the first step in the sulphidation of the metal. There followed descriptions by our group of the chemisorption of sulphur on numerous polycrystalline and monocrystalline metals in a series of publications probably known to you. I will mention here only information arising from the precise knowledge of the composition. One sees for example important differences between the behaviour of different crystalline faces with respect to chemisorption. The values of the thermodynamic quantities that characterise the interaction - enthalpy, free enthalpy - depend on the crystalline orientation. The two-dimensional surface compounds that belong to each orientation thus have distinct personalities corresponding to specific structural forms. Thus there appears the foundations of a physical chemistry of interfaces in a quasi-two-dimensional space, which can be followed up by the principles, if not by the methods, of the physical chemistry of three-dimensional solids.

It is easy to imagine the consequences of these considerations on the mechanisms of the first stage of the reaction of a solid with its environment. In particular, it is known that in very many instances the presence of a particular two-dimensional compound is likely to inhibit completely the transfer of material across the surface. Besides the studies just mentioned, which have an essentially static nature, it is important to carry out dynamic studies of the properties of these layers. Thus one comes back, while better defining them, to the concepts used currently to explain the poisoning of surfaces in heterogeneous catalysis or the passivation of electrodes.

I come to the end of my talk. I had wanted to summarise the evolution of ideas during the 35 years for which we have met every four years. I am aware of only partially succeeding and of disappointing some of you. Nevertheless I believe that what is the most important now is to imagine what will be the future. After those two chapters: the Reactivity of Solids Yesterday and the Reactivity of Solids Today, the third remains to be written - the Reactivity of Solids Tomorrow. To you all, and especially to our young colleagues, I leave the writing of that chapter.