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Position Paper on Hot-Atom Chemistry in Inorganic Solids

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The present Panel has been charged with the task of providing the Agency and its member States a Report which will embody on the one hand a summary of the status of research in Hot Atom Chemistry in 1974 and on the other, advice and recommendation for appropriate further research and developmental activities in this field. Such panel reports have often been useful in aiding the Director General, the Scientific Advisory Committee and Agency staff in guiding the future program of the Agency into particular directions where need is greatest.

The work of the present Panel should be viewed not only in the context of the two previous Agency Symposia in Hot Atom Chemistry (Prague 1960 and Vienna 1964) but also in the line of continuing Agency interest in Research Reactor Utilization, as typified by, for example, the Panel in Vienna (4-8 March 1963, STI/DOC/10/17) and the IAEA Study Group meeting in Manila (17-20 March 1969). Although there are many ways of generating particular hot atoms that do not involve reactors (for example, fast neutron or proton beams from cyclotrons, beta or positron decays leading to radioactive daughters, etc.), in many laboratories, especially in developing countries, the reactor center remains the focus of present and potential hot atom research. In such areas, the Manila Study Group pointed out, programs in Hot Atom Chemistry could be expected to include topics such as

1. Development of methods for the preparation of certain highly enriched radioisotopes and labelled compounds.
2. Accumulation of practical data useful for actual production.
3. Fundamental research to understand mechanism of hot atom reactions useful for isotope production and preparation of labelled compounds.
4. Training of radiochemists.

The emphasis in actual Hot Atom research, it was felt in Manila, should be along the following lines

1. Development of new methods for the production of certain radioisotopes and labelled compounds.
2. Low temperature studies and studies on annealing processes.
3. Relationship between physico-chemical properties and annealing behavior.
4. Identification of charged states, chemical species and chemical forms.

It is interesting that the program proposed by the Study Group strongly emphasized the practical applications of hot atom chemistry, and the fundamental research necessary to prepare the basis for practical studies. Several years ago, as part of the IAEA publication "Radioisotope Production and Quality Control" (Tech. Reports Series No. 128, 1971) the author (with M. Hillman) presented a chapter on "Szilard-Chalmers Processes for Isotope Production".

With this as background, the aim of the present paper will be to describe the present status of research in solid-state hot atom chemistry, with emphasis on the theory, and to indicate the connections this could have to further research and development.

When a "hot atom" is generated in a solid, by whatever means, if it has an initial kinetic energy greater than about 30-50 eV, it will on the average escape from its original crystal lattice site, move off into the lattice, leaving behind a vacancy, and lose energy through collisions until it again comes to rest. During this flight it can knock other atoms out of their lattice sites, if sufficient initial energy is available. It can also, in crystals made up of molecules or complex ions, leave behind a trail of radicals, other molecular fragments, or ligand-deficient complexes. When the fast atom comes to rest, if the crystal is analyzed chemically, or examined by non-chemical ("in-situ") techniques, it is found that the (radioactive) recoil atom may be in the original, or in an altered, chemical state: for example in crystalline potassium chromate (K_2CrO_4) irradiated with thermal neutrons, the "hot atom" ^{51}Cr, when the crystal is dissolved and analyzed, may be found as CrVI, (chromate) or in monomeric, dimeric or polymeric CrIII forms.

But the story does not end there. If the K_2CrO_4 crystal containing ^{51}Cr atoms is heated ("thermally annealed") before analysis, it will be found that even though no gross chemical change has occurred the relative percentages of activity in the different chemical forms mentioned earlier will have altered in a complex pattern. These percentages, or "yields", in different hot atom systems have also been found to be affected by the application of light, pressure, or ultrasonic energy, by the levels of trace impurities present in the crystal, type of atmosphere surrounding the crystal during annealing, conditions of analysis, etc. It is obvious that there is a broad field for research here, the very complexity of the system serving as a challenge to scientists.

To simplify matters we may distinguish several logical temporal subdivisions in the study of solid-state hot atom chemistry, as follows:

1) The period of time initiated by the nuclear event leading to the formation of the hot atom at the starting point of its crystal trajectory. This is 10^{-14} sec or less.
2) The period of flight through the crystal itself, until the atom is essentially at rest. This is about 10^{-13} to 10^{-12} seconds.

3) A period of time including the former but extending onward from the stopping of the fast atom, for about 10^{-6} to 10^{-7} seconds, during which the electronic and thermal excitation of the hot atom and its surrounding neighbors subsides.

4) The long-term period, from a few seconds upward, during which laboratory experiments involving annealing or the application of other stresses, physical measurements or chemical analysis may be applied.

Using this as a framework, we may now examine the theoretical and experimental knowledge which we presently possess, define what is lacking, and how experimental and theoretical research can be brought to bear to fill in the gaps. The same numbering used above is followed here.

1) In the period around the nuclear event we are dealing with nuclear physics. The energy of the incoming nucleon, the type and spectral distribution and angular correlations of the gamma rays or emitted particles such as electrons, other nucleons etc. determine the energy and initial physical state of the hot atom. The probability of internal conversion of gamma radiation emitted during the nuclear event is a datum of great importance, especially since the internal conversion process a) leads to highly charged, and consequently violently reactive atoms and b) may be delayed to times extending past the slowing-down period — in other words, may constitute a kind of "second activation".

Given the relevant nuclear data, there is no theoretical problem in calculating the initial energy and charge distributions of the hot atoms. What is needed is more complete data on neutron capture gamma ray spectra, and on the difficult problem of estimating the probability and time-scale of the concomitant internal conversion events. The first of these is under active investigation, with substantial production of new data. The second problem has hardly been touched. Here a theoretical study, for example of charge relaxation in different crystals, is badly needed as well.

2) The behavior of the energetic hot atom, while slowing-down in a crystal, properly is a study in Solid State Physics. Some experiments, utilizing nuclear resonance fluorescence, have permitted us to examine the actual kinematics of deceleration: it is my view that such experiments, which are not particularly difficult to perform, could be made to reveal much valuable additional information on this time period in the life of the hot atom. Most reactor centers have this capability.

On the theoretical side, computer studies have dominated. In a number of excellent papers, the interactions of a hot atom, starting out in various directions, with its host crystal have been simulated: the slowing-down trajectories, production of "channelons" and "focussing collisions" as well as interstitial and vacancy sites have been studied in detail. Many more of such computer "experiments" are needed, especially in more complex crystals in which molecules or complex ions are embedded: the first attempts have recently appeared. For example, the trajectories of Br atoms in $KBrO_3$ could be contrasted with those in KBr. But such studies already require large computers: extension to more complex (and consequently more interesting to the hot atom chemist) crystals would demand even more memory and higher speed. Also, the computer algorithms could be made to be more realistic to the chemistry involved.

Quite clearly, in this important time period there is great opportunity for new and interesting work in both theory and experiment, in which hot atom chemistry and solid state physics must each play a role. Such efforts have the greatest chance of success if the project is interdisciplinary, spanning the two sciences. The results of nuclear resonance fluorescence experiments can serve as a check on the theories.

3) The third time period, involving the just-stopped recoil atom surrounded and trapped by the atoms of the lattice with which it made its final few energetic collisions, brings us squarely into the realm of chemistry. If we realize that the mean free path of the energetic atom is short -- in fact, only of atomic sizes -- then it follows that the end of the track marks a "dumping" of a substantial amount of energy, rapidly, into a very restricted volume. The result is, of course, a momentary pulse of high "temperature", the so-called "thermal spike" of solid state physics.

When a delayed internal conversion event takes place, with the momentary ejection of a number of electrons from the hot atom followed by the immediate relaxation of the large plus charge through electron depletion of neighboring atoms, then a powerful "spike" of both a thermal and electronic nature must be formed. There has been little or no theoretical work on the properties of these electron-depletion spikes, formed as mentioned above.

There is much theoretical discussion on the possible results of the thermal spike, both in solid state physics, where it relates to defect production, and in hot atom chemistry, where it has been postulated as an explanation for the observed distributions of yields, in some cases. Quite clearly there is more work to be done: both chemical and physical techniques need to be applied. For example, the time-resolved Mössbauer effect, especially with shorter-lived species, needs to be reinvestigated, to shed light on this region. Another valuable physical technique is time-differential angular correlation: both of these sample the chemical environment rapidly enough to give us a look at short-term hot atom chemistry. But, as equipment is costly and complex, and experiments are long, very little work has to date been done.

The purely chemical investigation of hot atom reactions in the "hot zone" or thermal spike ought to continue, but with very careful planning, so that the results can be more decisive than those obtained in the past. Again, "experiments" on the computer, simulating events in complex-ion or molecular crystals, would give us a better idea of the size, duration, and temperature history of the hot zone or spike.

4) The long-term investigation of the hot atom chemistry which follows the thermal spike, has accounted for most of the published literature. Dissolution of irradiated crystals, chemical separations, measurement of yields, and the observation of annealing effects of many kinds has constituted the classical approach to recoil chemistry. The mathematical analysis of annealing curves (of the isochronal as well as isothermal variety) has given us some insight into the activation energies, and perhaps the mechanisms, of many annealing reactions. In-situ methods such as perturbed angular correlation and (perhaps) half-life variation may also be applicable although it is not yet clear how closely these methods can identify the chemistry of the recoil atom.

There is ample opportunity and need for a closer theoretical examination of annealing mechanisms. If a mechanism for oxidative annealing has been postulated, for example the recombination of an oxygen atom with a reduced fragment, or the diffusion of a hole onto a trapping site, it ought to be possible to make at least a rough calculation of the activation energy from first principles, and compare this with experiment. The same ought to be true of ligand-fragment recombinations.

Another type of experiment carries out hot atom reactions in host crystals deliberately "doped" with, for instance, low levels of foreign atoms which are electron acceptors (traps) -- an example would be silver ions in alkali halide lattices. Other types of doping can lead to other lattice defects -- an interesting one is the aliovalent dopant which requires cation or anion vacancies to maintain charge balance. In all these experiments the collaboration of a solid-state physicist is very desirable.

Another field which shows promise of yielding some information on annealing mechanisms is the study of "transfer annealing", i.e. exchange reactions in the solid state. Here again, there is little or no background of theory available.

In conclusion it can be said that through careful planning of experiments, work in the classic, post-irradiation period of hot atom chemistry can still produce interesting data and needs to be extended. Particularly desirable are single-crystal investigations in which thermal or photo annealing are carried out with careful temperature or wavelength control so as to resolve most clearly the particular absorption peaks or activation energy groups that may be present. A very powerful combination is the collaborative research between a hot atom chemist and a solid-state physicist who is equipped to make color-center, thermoluminescence, or ESR measurements. In this way it is sometimes possible to identify quite directly the mechanisms involved in hot atom annealing and to verify the theory.

Although the classic era of hot atom chemistry is clearly behind us, it does seem possible that these investigations could provide a new point of departure into the study of a far more complex range of crystal defect structures than those presently known. And it is surely true that, just as these measurements can help us better understand the statics of crystal defect structures, the physical techniques of time-differential angular correlation, nuclear resonance fluorescence and perhaps Mössbauer effect can shape our understanding of the dynamics of their production.

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