Preface

Most organic molecules retain their integrity when dissolved, and even though in such cases the effects exerted by solvents are, in the language of the coordination chemist, of the “outer sphere” kind, the choice of solvent can be critical to the successful outcome of an operation or preparation. Solubilities of reactants and products must be taken into account, and even if the organic principals in the reactions retain their integrity, many of the reagents are electrolytes, and their state of aggregation will affect their reactivity. In testifying to the importance of understanding solute-solvent interactions I draw attention to a large class of inorganic species for which the involvement in the chemical and physical properties by the solvent is even more deeply seated. It is comprised by the large body of metal atoms in low oxidation states for which solvent molecules intervene as reagents. At the same time, because the ions carry charges, the effects arising from outer sphere interactions are usually greater than they are for neutral molecules. To cite an example: when $FeCl_3(s)$ is dissolved in water to form a dilute – say $0.010\,M$ – solution there is a complete reorganization of the coordination sphere of the cation. Whereas in the solid each cation is surrounded by six chloride ions, in the solution the dominant form is $[Fe(H_2O)_6]^{3+}$ followed by $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_4Cl_2]^{+}$, *etc*. in rapidly decreasing abundance. I infer from the titles of the contributions by *Ohtaki* and *Marcus* to the volume that some of the consequences of this kind of solvent intervention in the behaviour of the solutions are dealt with in their papers. Perhaps the considerations which follow complement what appears in these articles.

To understand the properties of such solutions, a description of the molecules present is essential. In addressing the systems by experiment, a critical item of information is just how rapidly the adjustments in the composition of the coordination sphere of the ions take place. By contrast to the behaviour of $FeCl_3(s)$, though, the driving force for the reorganization of $CrCl_3(s)$ to the hexaquo ion and $3Cl^-(aq)$ is somewhat greater than it is for $FeCl_3(s)$, when $CrCl_3(s)$ is introduced to water. Even wetting of the solid is a slow process, let alone its dissolution. This example illustrates the disparity between thermodynamic and kinetic stability which prevails in the chemistry of the metal species being considered. As exemplified by the exchange of water between the inner coordination sphere of the tripositive ions, the rates span a range of about 10^{19}. A change of the oxidation state by one unit can also affect the lability profoundly: for example, the $1e^-$ reduction of $Cr(H_2O)_6^{3+}$ increases the rate of exchange of the bound water by a factor of about 10^{14}. Whereas solutions of cations which undergo substitution slowly can be investigated using traditional experimental approaches, those which undergo substitution very rapidly require more sophisticated methods.

As defined in my ready-to-hand dictionary the facets which comprise the science of chemistry are ‘‘the structure, composition, and properties of substances and of their transformations’’. The central position of chemistry among the other physical sciences, resulting from the extensive overlap of its subject matter with them, is often referred to, especially by chemists. Of the four facets mentioned, the last stands apart as being most particularly the province of the chemist. In carrying out reactions, whether for the purpose of changing compositions or for harnessing the energy associated with them, the most important arena is the liquid state, especially as a liquid acting as a solvent provides the required mobility for the components of the reaction. Understanding solvent interactions, affecting as they do both the equilibrium state and the rates of reaction, is vital to developing the kind of understanding which is needed to optimize the desired outcome of the chemical change.

Near the end of the 4th decade of the last century, progress began to be made toward understanding the reactions of inorganic species in solution, beginning with those involving substitution. Data on the stability of inorganic complexes began to appear in the literature, and somewhat later reports devoted to understanding rates and mechanisms of substitution reactions. Whereas such rates are easy to measure when they are slow – unless of course they are very slow – those posed by the substitution of labile complexes were a serious challenge which was met by *Eigen* and coworkers. Despite this important advance and other early rapid progress, our understanding of basic issues, such as the extent of bond making as against bond breaking in the activated complexes for diverse systems, or of the electron redistribution factors which affect them, is far from satisfactory. While this state of affairs might be expected to result in continued research activity, interest in the field relative to other preoccupations has seriously declined. This is true also of the other major reaction class, that of redox reactions, taken as an important subject in its own right. Great advances were made early in the 5th decade by virtue of theoretical advances by *Hush*, *Marcus*, *Sutin*, and others for the simplest of such reactions, those involving $1e^-$ changes during which the coordination spheres of the reactants remain intact. Thanks to their success in dealing with the inner and outer sphere barriers to electron transfer imposed by the requirements of the *Franck-Condon* restriction, a *semi*-quantitative understanding of such reactions has been arrived at. By contrast, understanding redox reactions in the course of which primary bonds are ruptured, among them the important class involving oxygen transfer in the oxidation of organic molecules, has languished. The realization by the reader that understanding solvent-solute interactions is basic to progress in understanding the reactions of the substitution labile cations in solution will contribute to the survival of research activity in the subject.

Henry Taube, Stanford, July 2001
Nobel Laureate in Chemistry 1983