High Pressure Chemistry

Synthetic, Mechanistic, and Supercritical Applications

Edited by Rudi van Eldik and Frank-Gerrit Klärner

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Preface

High pressure chemistry is an area that has developed a vigorous activity over the past decades. Although most of the earlier work was mainly performed in the area of organic chemistry, a major contribution from inorganic chemists over the past two to three decades resulted in the development of sophisticated instrumentation that enables the study of fast chemical reactions under high pressure. More recently, the application of supercritical fluids has received much attention especially in chemical industry. Numerous reviews have reported on the progress made in these areas over the past years.

The monograph consists of fourteen contributions based on oral presentations at the European High Pressure Research Group Meeting held at Kloster Banz, Germany, in September 2000. The theme of the meeting was High Pressure Chemistry. It covers contributions from high pressure inorganic and organic chemistry, as well as the application of supercritical fluids in chemical synthesis and processes. The monograph is subdivided into three sections. The first three chapters are devoted to basic principles involved in the application of high pressure techniques in inorganic and organic chemistry. The subsequent eight chapters are devoted to mechanistic and synthetic applications of high pressure in inorganic, organometallic, organic, and supramolecular chemistry. The final three chapters are devoted to chemical reactions in supercritical fluids and cover catalytic reactions, applications in the fine chemical industry and the application of super critical water. All in all, the individual chapters reveal the present status of high pressure chemistry and its application in a variety of areas.

The editors appreciate the co-operative support they received from the individual authors of the chapters, as well as the effective interaction with Wiley-VCH. The efforts of numerous scientific coworkers and the financial support from many funding agencies have all contributed to bringing high pressure chemistry to where it stands at present. May we all in future benefit from these developments and stimulate further activities of the next generation in this area of chemistry.

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I
Basic Principles

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1
Effect of Pressure on Inorganic Reactions: Introduction and Mechanistic Applications

Rudi van Eldik and Colin D. Hubbard*

1.1
Introduction

Chemistry literature is to a large extent concerned with preparative work and the structural and spectroscopic characterization of reaction products. The velocity of the reactions and efficiency of product formation as manifested in the reaction yield, are also of importance in synthetic studies, particularly when the products are of direct use or are intermediates in commercially relevant activities. The kinetics of reactions can be very informative in combination with other information for revealing the details of the reaction mechanism. Once a chemical reaction mechanism is fully understood, the insight gained can be used to tune the chemical process in any desired direction. The evidence for a particular mechanism is often circumstantial, and therefore kineticists try to employ the widest set of experimental variables available in an effort to interpret the resulting kinetic data in the least equivocal manner possible.

The value of the mechanistic information that emerges from kinetics measurements over a series of elevated pressures for solution reactions in inorganic and organic chemistry has been realized for some time [1–3]. However, many inorganic reactions are too fast to follow using conventional instrumentation. Hence the momentum regarding investigations at high pressures *vis-a-vis* organic reactions was delayed somewhat until adaptation of rapid reaction techniques for operation at high pressures had been achieved, mostly in the period from 1975 to 1985. This fertile period has been recorded in reviews, in conference proceedings, and in monographs, and readers may obtain a thorough background and sense of historical development by consulting this literature [4–11]. Even until quite recently, suitable instrumentation was not widely available.

The purpose of this chapter is to familiarize the reader with the current status of activities in the application of hydrostatic pressure to mechanistic studies in the areas of inorganic and organometallic chemistry, as well as in the blossoming field of bioinorganic chemistry. Although the basic principles involved in high pressure kinetics for reactions in general have been the subject of many reports [12–14], some essential aspects and the most frequently used methods will be presented

here to form a basis for the subsequent chapters dealing with the effect of pressure on particular types of reactions in inorganic and organic chemistry.

The parameter that is derived from high pressure kinetic experiments in solution is the difference in partial molar volume between the activated complex of transition state theory and the reactant state, and is known as the volume of activation, $\Delta V^{\neq}$. If the particular reaction is reversible and the system experimentally accessible, $\Delta V^{\neq}$ for the reverse reaction can also be obtained and the difference between these two quantities results in the reaction volume, ΔV°. The latter quantity may also be determined by measuring the equilibrium constant (K) for the reaction as a function of pressure, or from the partial molar volumes of the reactants and products, derived from solution density measurements. The volume of activation itself is determined from measurements of the reaction rate constant k at different hydrostatic pressures p at a given absolute temperature T, since $(\partial \ln k/\partial \mathrm{p})_{\mathrm{T}} = -\Delta V^{\neq}/\mathrm{RT}$ (R is the ideal gas constant), an equation was developed within transition state theory based upon the analogous equilibrium constant relationship, $(\partial \ln K/\partial \mathrm{p})_{\mathrm{T}} = -\Delta V^{\circ}/\mathrm{RT}$. The former equation, upon integration, can be employed to determine $\Delta V^{\neq}$ from a plot of ln k versus p. Providing the pressure is no higher than 200 MPa, in the vast majority of cases $\Delta V^{\neq}$ is pressure independent and the plot is linear. A non-linear behaviour is usually encountered when dealing with a compressible solvent where both the reaction and activation volume become pressure sensitive. For such cases often encountered in organic systems (see Chapter 2), where it is necessary to consider the pressure dependence of $\Delta V^{\neq}$, i.e. to extrapolate the data to ambient pressure, there are various treatments available for processing the primary data [5, 15]. In this introductory chapter the focus will be on reactions in which there is a negligible or absence of pressure dependence of the volume of activation. In general, volume of activation data quoted in this report will refer to ambient conditions, i.e. close to room temperature, and readers are advised to consult the cited literature for more detailed information on the exact experimental conditions employed.

Equilibrium and kinetic parameters obtained as a function of temperature permit the drawing of diagrams illustrating the Gibbs free energy (G), enthalpy (H) and entropy (S) changes in proceeding in the sequence reactant state/transition state/product state, and including intermediates when they are formed. Correspondingly, a volume diagram or volume profile can chart the respective volume changes along the reaction coordinate, and when appropriate actual partial molar volumes are known, on an absolute rather than a relative basis, something that cannot realized for G, H or S. Hence if reactants A and B form a product AB and no intermediates are formed, i.e. there is a single step reaction, a volume profile in which the reaction volume is, for example, negative and the volume of activation is such that the transition state is almost halfway between reactant and product states, is depicted in Fig. 1.1.

As shown in Fig. 1.1, other forms of the volume profile are possible depending on the particular character of the system. Thus, in principle, a volume profile represents a simple and lucid way of describing a reaction and diagnosing the mechanism, but with the caveat that mechanistic diagnosis is uncomplicated when only intrinsic changes (changes in bond lengths, bond angles for example) occur. In

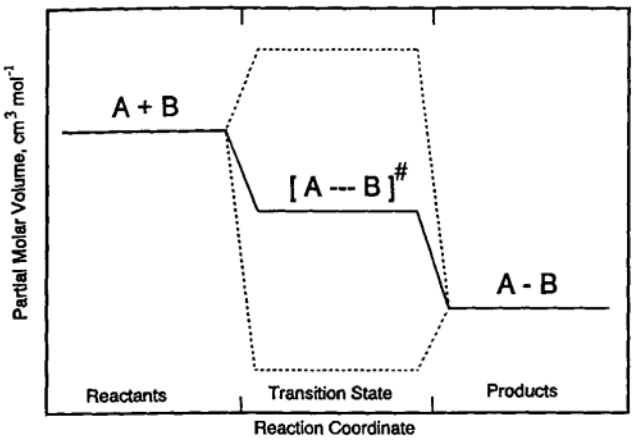

Fig. 1.1. Volume profile for the overall reaction A + B → AB. The activated complex is $[A\text{---}B]^{\neq}$.

many actual reactions, when charged species are produced or neutralized during the reaction, or increases or decreases in polarity occur, then there is also a change in the volume occupied by the solvent molecules surrounding the system by virtue of an increase or decrease in (at least) the first solvation layer. Volume reduction of solvent from this source is known as electrostriction. Thus the facile interpretation of measured values of ΔV° or $\Delta V^{\neq}$ can be compromised by the existence of the two contributions which are difficult to quantify. The intrinsic and solvational contributions to $\Delta V^{\neq}$ can schematically be visualized as shown in Fig. 1.2.

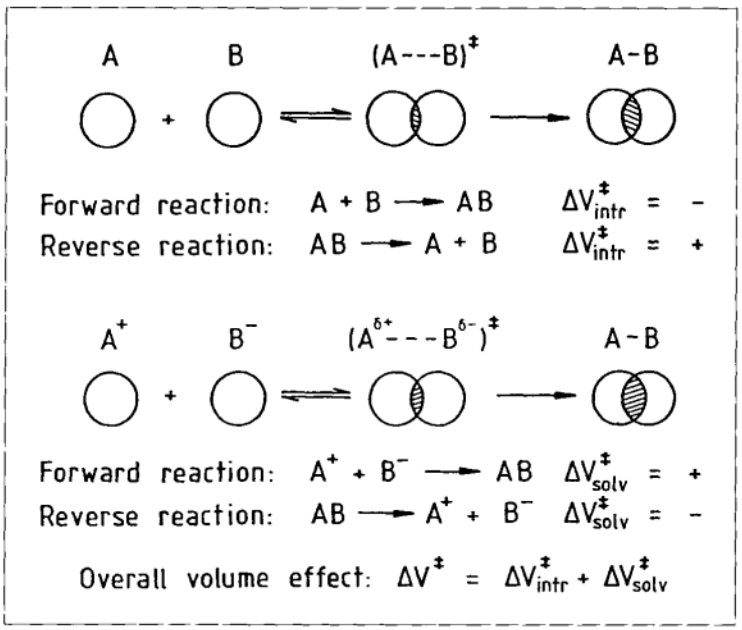

Fig. 1.2. Intrinsic and solvational contributions to the volume of activation.

Clearly a reaction accelerated by pressure has a negative volume of activation and one retarded by pressure, a positive volume of activation. Most inorganic reactions that have been studied yield $\Delta V^{\neq}$ values within the range of +30 to −30 $cm^3\ mol^{-1}$, which corresponds to retardation and acceleration respectively of a factor of about 4 at 100 MPa (1 kbar) compared to 0.1 MPa (atmospheric pressure). In the absence of solvational contributions, positive $\Delta V^{\neq}$ values are indicative of the commencement of bond breakage, whereas negative $\Delta V^{\neq}$ values are indicative of reactions in which a bond is beginning to be established upon reaching the transition state. Further classification of reaction types will be presented later.

A brief account of experimental methods follows with illustrations in some cases. Thereafter thermal reactions grouped by reaction type from inorganic, organometallic and bioinorganic chemistry will be described from the perspective of the mechanistic insight gained from the application of high pressure techniques. A section on photo- and radiation-induced chemical reactions is also included. At this stage readers are referred to more detailed reports on water exchange processes in Chapter 4, application of electrochemical techniques in Chapter 5, and photochemical processes in Chapter 6.

1.2 Determination of Volumes of Activation

The scope of activity in the overall field in question may be gauged by the number of pertinent papers published or the number of volume parameters reported. Up to 1978 about 170 of the latter values had been published, while in the subsequent two decades approximately 1000 and 1600 values of the activation volume, respectively, have been reported [8, 16, 17]. The most frequently used method of monitoring a reaction in coordination chemistry is by following changes in the UV/Vis spectrum either with a conventional spectrophotometer or with a stopped-flow instrument. For conventional time range reactions (reaction times longer than a few minutes) using UV/Vis spectroscopy, a two-window cell (Fig. 1.3) and a pressurizable cuvette (pill-box) (Fig. 1.4) may be used for high pressure measurements [18]. The advantage of the pill-box cuvette is that pressure can be transmitted through the compression of the movable, closely fitting cylindrical parts; it can be easily filled using a syringe needle technique, after which the two cylindrical parts are turned 180° to seal the cuvette. When the cell is pressurized, the two cylindrical parts move closer together as a result of the compression of the solvent used in the sample solution within the cell, and therefore the pressure from the pressurizing medium is transmitted to the sample solution. The cell is pressurized with a pressure generating system which typically consists of the components shown in Fig. 1.5. An hydraulic pump is used to generate an oil pressure, which is then transmitted by the separator to the pressurizing medium (for instance water) used within the optical cell. Compression and expansion can be controlled with the series of mechanical valves and monitored with a pressure gauge.

The type of high pressure cell in Fig. 1.3 can also be used to construct a three-

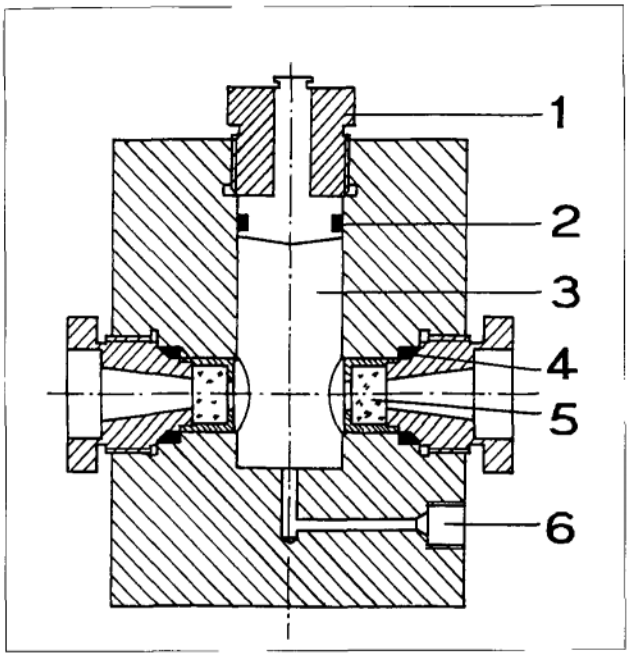

Fig. 1.3. Schematic view of a two-window high-pressure cell: 1 – pressure plug; 2 – O-ring; 3 – reaction compartment; 4 – Δ- and O-ring; 5 – sapphire window; 6 – pressure connection.

or four-window cell which may be used for flash photolysis and pulse radiolysis applications. Technical details of these cells and methods of use may be found in recent literature [18–20].

The development of high pressure stopped-flow instruments opened up the possibility to study reactions in the millisecond and second time range as a function of pressure [21–27]. A stopped-flow instrument is designed to enable the rapid

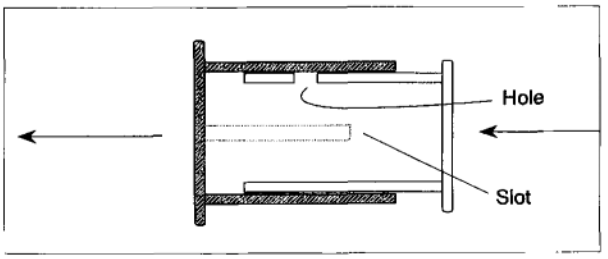

Fig. 1.4. Schematic presentation of a "pill-box" optical cell for measurements in a high pressure optical cell. The slot and hole allow the pill-box cell to be filled and extra liquid to be released on closing the cell.

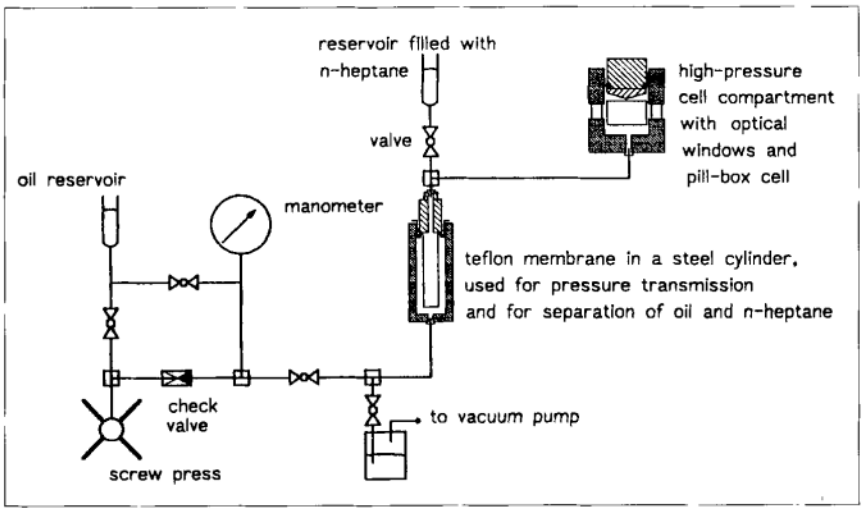

Fig. 1.5. Typical system to generate high pressure.

mixing of two solutions containing the reactants, followed by the monitoring of the reaction progress when mixing is completed. Two high pressure versions of stopped-flow instruments are shown in Figs 1.6 and 1.7, with the difference that in the first case (Fig. 1.6) the activation of the syringes occurs by means of a motor inside the high pressure cell, whereas in the second case (Fig. 1.7) the syringes are activated from outside the cell. Activation of the sample syringes causes a flow of the two reagent solutions through a mixing jet and optical path into a receiver syringe, which is followed by the activation of the optical detection system that then monitors the reaction progress of the rapidly mixed reagents occurring in the optical path. The deadtime of the mixing process is between 2 and 10 ms.

A second important method for determining $\Delta V^{\#}$ is by application of NMR spectroscopy. Progress in NMR instrumentation from electromagnets to superconducting magnets and higher field strengths has largely been matched by developments in construction of suitable high pressure probes for newer instruments in individual laboratories [29–38]. Investigations of solvent exchange (see Chapter 4) and electron self-exchange reactions have been the principal beneficiaries of progress in high pressure NMR techniques. A typical example of an NMR high pressure probe developed in our laboratories, is shown schematically in Fig. 1.8. The operation principle of both these high pressure probes is that the NMR sample tube is placed within a high pressure cell and is pressurized with a suitable fluid by a movable stopper that transmits the pressure from the pressurizing fluid to the sample solution by moving down the NMR tube, which is controlled by the compressibility of the solvent used in the sample solution. With the aid of these high pressure probes practically all possible NMR measurements can be performed as a function of pressure up to 200–300 MPa (i.e. 2 to 3 kbar) at a fixed

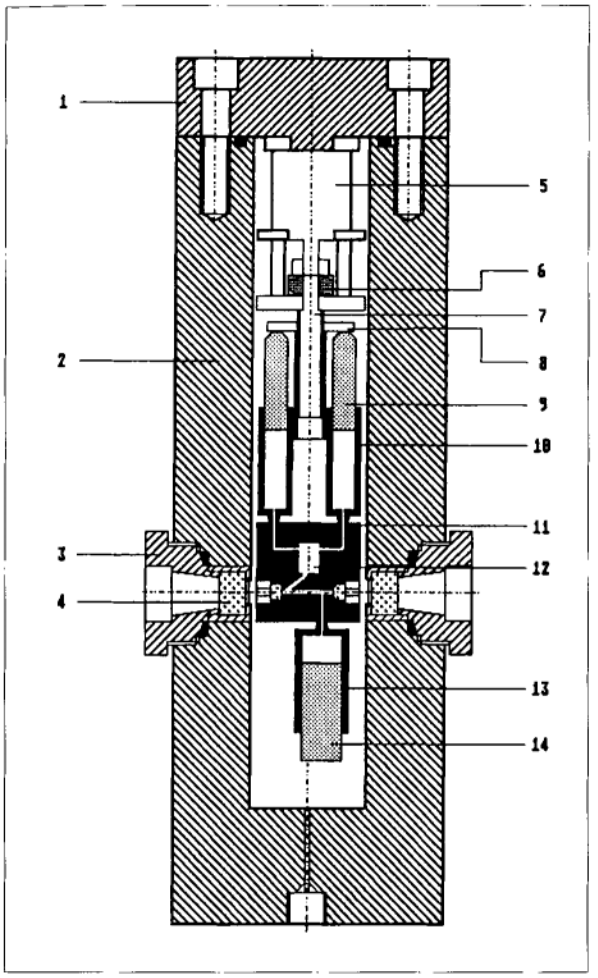

Fig. 1.6. Schematic representation of a high pressure stopped-flow unit: 1 – lid to overall unit; 2 – outer vessel; 3 – window holder; 4 – quartz windows; 5 – electric motor; 6 – motor actuator; 7 – stopped-flow unit positioning rod; 8 – syringe-driving plate; 9 – drive syringe (inner); 10 – drive syringe (outer); 11 – block holding windows, mixer and syringe attachment points; 12 – mixing jet; 13 – stop syringe (outer); 14 – stop syringe (inner).

temperature. The only restriction is that the sample tube within the high pressure probe cannot be spun.

The temperature-jump technique [39, 40] is frequently used to study the kinetics of rapidly equilibrating processes in solution on a microsecond time scale. This technique can only be applied to equilibria that are sensitive to temperature, such that a rapid temperature jump of a few degrees will result in a relaxation of the system to the new temperature, a process that can be followed on a micro- or millisecond time scale.

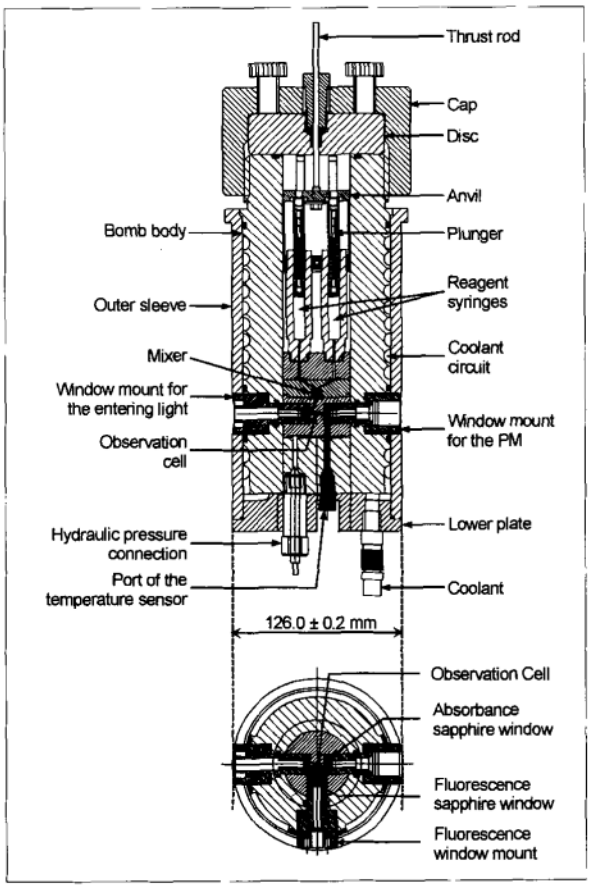

Fig. 1.7. Schematic representation of the commercially available Hi-Tech HPSF-56 high pressure stopped-flow unit [28].

Electrochemical methods have also been adopted for application of high pressure [41–43] (see Chapter 5). Correlations emerging from these investigations have valuable application in the interpretation of partial molar volume changes associated with electron transfer reactions (see Sect. 1.3.4). A potential future interest is in reactions carried out at elevated pressures in a supercritical fluid medium; in view of this a special optical cell has been developed for studying organometallic reactions initiated by flash photolysis in supercritical fluids [20] (see Chapters 12 to 14).

The principles and instrumentation outlined above have been applied to numerous types of reactions in inorganic chemistry. A systematic treatment of the different reaction types and specific examples to illustrate the role of high pressure measurements in such studies, now follows.

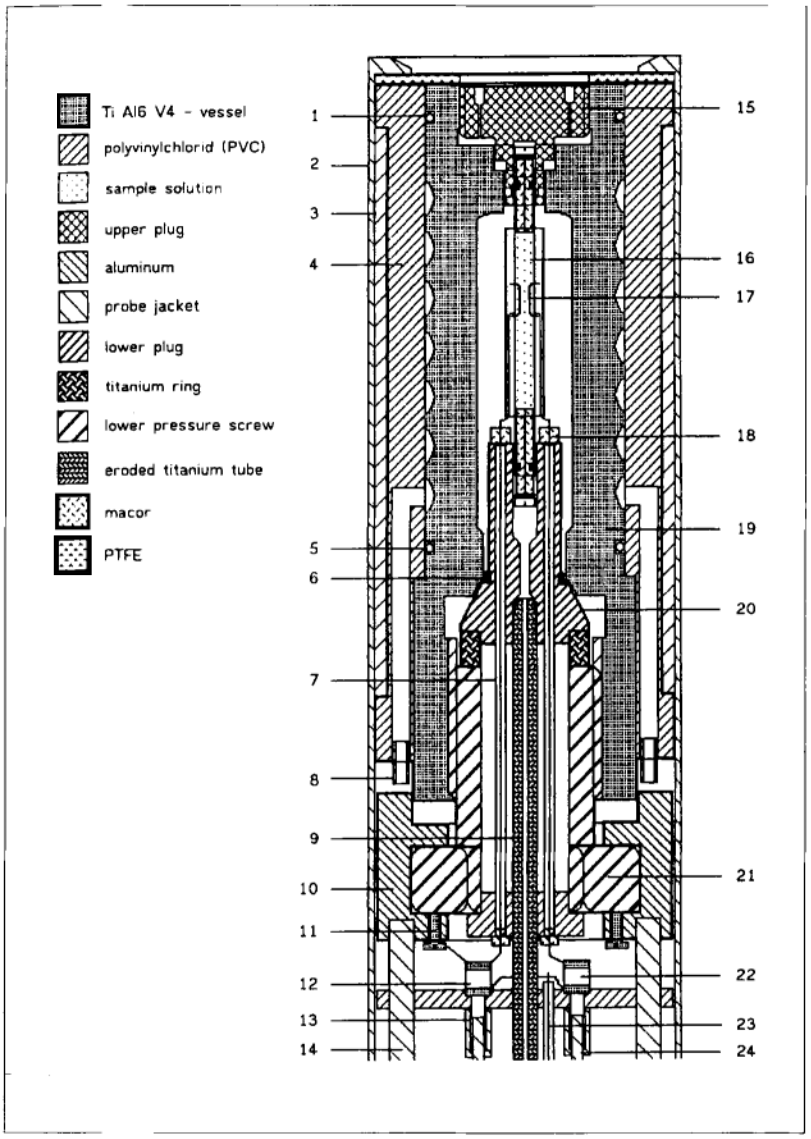

Fig. 1.8. Design features of a probe head for high-pressure NMR (400 MHz) measurements: 1 – O-ring; 2 – probe jacket; 3 – thermal insulation; 4 – polyvinyl chloride; 5 – O-ring; 6 – O-ring; 7 – semi-rigid coaxial cable; 8 – connection to thermostat; 9 – titanium tube; 10 – lid; 11 – screw; 12 – capacitor; 13 – capacitor holder; 14 – aluminum tube; 15 – upper plug; 16 – sample tube; 17 – saddle coil; 18 – Macor; 19 – TiAl6V4 vessel; 20 – lower plug; 21 – lower pressure screw; 22 – capacitor; 23 – coaxial cable; 24 – capacitor holder.

1.3 Thermal-Induced Reactions

In this section of our presentation we will focus on different types of reactions in inorganic chemistry that occur thermally. In Sect. 1.4 we will present an account of radiation-induced inorganic reactions. Photo-induced inorganic reactions are dealt with in Chapter 6.

1.3.1 Ligand Substitution Reactions

Ligand substitution reactions of metal complexes have been the topic of many mechanistic studies in coordination chemistry because of the fundamental role of such reactions in many chemical, biological and catalytic processes. For a general ligand substitution reaction as shown in Eq. (1.1),

$$ML_nX + Y \rightarrow ML_nY + X \tag{1.1}$$

where X is the leaving group, Y the entering ligand, and L_n the spectator ligand(s) (charges are omitted for clarity), there are basically three simple pathways: (i) the dissociative (D) process with an intermediate of lower coordination number; (ii) the associative (A) process with an intermediate of higher coordination number; (iii) the interchange (I) process, in which no intermediate of lower or higher coordination number is involved. The interchange of the ligands X and Y can be more dissociative (I_d) or more associative (I_a) in nature, depending on whether bond breakage or bond formation is more important, respectively. These mechanisms are outlined schematically in Fig. 1.9.

Such ligand substitution reactions should exhibit very characteristic $\Delta V^{\neq}$ values depending on the degree of bond breakage or bond formation in the transition state. The most simple type of ligand substitution reaction involves the symmetrical exchange of coordinated solvent or ligand with bulk solvent or ligand molecules, respectively.

$$[M(S)_x]^{n+} + S^* \rightarrow [M(S)_{x-1}(S^*)]^{n+} + S \tag{1.2}$$

Exchange of a unidentate solvent molecule (S) between the first coordination sphere of a solvated metal ion (M^{n+}) and the bulk solvent (Eq. (1.2)) has been studied for cations of many elements of the Periodic Table. The incoming solvent molecule S* is denoted with an * to distinguish it from the initially coordinated molecule with which it exchanges. Such reactions are very important and a knowledge of the kinetic and associated activation parameters represents important background to the understanding and tuning of substitution of a solvent by other ligands [44]. The focus has frequently been, but by no means exclusively, on water as solvent. There is no reaction volume and the solvent exchange process is assumed to have zero solvational change. Thus $\Delta V^{\neq}$ should be a direct measure of the intrinsic volume changes that occur, such that a continuous spectrum of tran-