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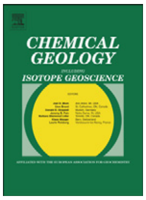

Calcium carbonate and calcium sulfate precipitation, crystallization and dissolution: Evidence for the activated steps and the mechanisms from the enthalpy and entropy of activation values

Athinoula L. Petrou *, Athina Terzidaki

Laboratory of Inorganic Chemistry, Department of Chemistry, University of Athens, Panepistimioupolis, 15771 Athens, Greece

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ABSTRACT

Calculation of the thermodynamic parameters E_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the precipitation, crystallization and dissolution processes of the salts $CaCO_3$ and $CaSO_4$, leads to very important conclusions about the activated steps and the mechanisms. The $\Delta G^{\neq}$ values are almost the same for all the processes at the same temperature, suggesting that the electrostatic forces between the ions Ca^{2+} and CO_3^{2-} ($CaCO_3$) and Ca^{2+} and SO_4^{2-} ($CaSO_4$) are the most important factors governing the above processes. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ differ but the values of $\Delta G^{\neq}$ which refer to the overall transformations are the same and are independent of the various steps that take place as well as the mechanisms (associative, dissociative). Dehydration and aquation of the ions are revealed by the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The precipitation of the two salts may take place both by a dissociative mechanism ($\Delta S^{\neq} > 0$) or by an associative mechanism ($\Delta S^{\neq} < 0$). For processes taking place without the need for diffusion of the ions, (Ca^{2+}, CO_3^{2-}, SO_4^{2-}), the free energy of activation is about 85 kJ mol^{-1}, whereas when diffusion of the ions is necessary, an additional amount of ~20 kJ mol^{-1} is required. This amount is the activation energy for the diffusion. In the case of $CaCO_3$, a wide range of values is found for $\Delta H^{\neq}$ from −66.00 to 162.00 kJ mol^{-1}, and for $\Delta S^{\neq}$ from −501.00 to +248.00 J K^{-1} mol^{-1} while the $\Delta G^{\neq}$ values cover only a small range from 75 to 90 kJ mol^{-1}. Values of 120, 131 and 132 kJ mol^{-1} are reported for cases where retardation is caused due to the presence of foreign compounds. In the case of $CaSO_4$, a wide range of values is found for $\Delta H^{\neq}$ from 6.00 to 122.00 kJ mol^{-1} and for $\Delta S^{\neq}$ from −342.00 to +117.00 J K^{-1} mol^{-1} while the $\Delta G^{\neq}$ values fall in the narrow range from 80.00 to 89.00 kJ mol^{-1}. A value of 126 kJ mol^{-1} is reported for cases where retardation is caused due to the presence of foreign compounds. The E_{act} values vary between −63 and 164 kJ mol^{-1} for $CaCO_3$ and between 8 and 184 kJ mol^{-1} for $CaSO_4$, demonstrating once again that the $\Delta G^{\neq}$ value is more realistic, being almost the same for similar processes. The various small differences for the values of $\Delta G^{\neq}$ arise from the different ionic strengths due to the concentration and charge of the foreign ions affecting the rate constants and thus the activation parameters. The pH also has an effect, as does the nature of the solvent. The very large and very small absolute values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ suggest composite reactions. Composite reactions in the precipitation, crystallization and dissolution processes are the ones where dehydration takes place (positive values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$) followed by association of the ions (negative values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$). The algebraic sum of the relevant $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values gives the total value of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Activation energy values reported in the literature for certain cases compared to the values reported in the presence of adducts do not indicate retardation. On the contrary, they suggest acceleration of the reactions. The use of $\Delta G^{\neq}$ instead of the E_{act} values is more realistic in showing the large retardation effect. The presence of salt, for example NaCl, causes retardation of the crystallization process.

1. Introduction

Calcium carbonate ($CaCO_3$) is an important material that occurs in the natural environment as a constituent of many biological, geological and ecological systems, while it is also involved in many industrial processes, for example in scale formation. For these reasons, precipitation, crystallization and dissolution of calcium carbonate in aqueous solutions has attracted the interest of many investigators in a wide variety of fields. Many studies have focused on the problems that are related to the mechanism of its formation, and the role that various parameters play in its formation in aqueous solutions has been studied (Koutsoukos and Kontoyannis, 1984). Thermal decomposition has also been studied by several investigators and various mechanisms have been reported (Rajeswara Rao, 1993, and refs. therein).

Calcium sulfate ($CaSO_4$) has also been intensively investigated since many aspects of its reaction mechanisms remain unanswered (Klepetsanis et al., 1999). Solution chemistry helps greatly in the

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* Corresponding author.
E-mail address: athpetrou@chem.uoa.gr (A.L. Petrou).

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elucidation of the reaction mechanisms of the various calcium sulfate forms (hydrates) that are formed in aqueous media. The precipitation process includes nucleation and crystal growth that are two mechanistically different steps. A knowledge of the calcium sulfate precipitation mechanism has also been very important for the effective prevention of calcium sulfate scale (Klepetsanis and Koutsoukos, 1991). A kinetic study has been conducted to measure and model the rate of calcium sulfate precipitation within porous media (Merdhah and Yassin, 2008).

In this work we aim to contribute to the efforts to solve the serious problems that are related to $CaCO_3$ and $CaSO_4$ precipitation, crystallization and dissolution by providing values for the thermodynamic parameters in order to assist in the clarification of the corresponding mechanisms. These parameters are obtained by the treatment of literature kinetic data using the Eyring–Polanyi equation. Thus we will provide an alternative analysis of well-documented examples from the literature on calcium carbonate and calcium sulfate precipitation, crystallization and dissolution. Based on the values for enthalpy and entropy of activation ($\Delta H^{\neq}$ and $\Delta S^{\neq}$), we will provide evidence for the existence of dehydration and aquation (hydration) steps and we will also show that some processes of the mechanisms are composite. We will also show that in some cases (depending on the experimental conditions) the diffusion of the ions is one of the controlling factors in the activation step, adding approximately 20 kJ mol^{-1} to the value of the free energy of activation. From the values of the free energy of activation ($\Delta G^{\neq}$), we draw conclusions concerning the true energy requirements of the processes.

It has been shown (Petrou, 2012) that the combination of enthalpy and entropy of activation in the free energy of activation gives a more realistic value of the energy requirements of the activation step that the processes need in order to take place. The analysis has also shown that similar processes have similar $\Delta G^{\neq}$ values (Petrou, 2012). A detailed analysis has also been presented on how the values of $\Delta S^{\neq}$ may be used to suggest a mechanism for a process (Petrou and Economou-Eliopoulos, 2009b).

Our suggestion (Petrou, 2012) of using the "corrected" energy value that is critical for geochemical processes, the $\Delta G^{\neq}$ value, instead of the E_{act} value, provides a way to address unexplained or queried geochemical results, and to give solutions to existing problems: (a) Based on the E_{act} values authors suggest mechanisms. As we have already shown (Petrou, 2012), the E_{act} value is not a realistic value, i.e. it does not give the true energy requirements in geochemical processes. This implies that the mechanisms that have been proposed based on the E_{act} values (or the rate constants) may not be correct [Table 2, case (o)]. This problem has been solved by introducing the $\Delta G^{\neq}$ values. (b) An explanation has also been given of why calculated activation energy values (that are related only to the enthalpy of activation values) for certain transformations deviate from the expected and observed energy requirements that characterize the processes when the entropic component is substantial. Values of E_{act} that are intended to explain retardation of processes indicate acceleration instead [Table 1, case (e), Table 2, case (q)]. This has also been solved by introducing $\Delta G^{\neq}$. (c) Different values of E_{act} have been proposed in the literature for the various processes (precipitation, crystallization, dissolution) leading to various conclusions. However, the values of $\Delta G^{\neq}$ are similar and point to the same conclusions. From the entropies of activation an insight into the degrees of freedom of the activated complexes can be obtained and hence information about the mechanisms of the processes may be extracted (Petrou and Economou-Eliopoulos, 2009b).

2. The Eyring or activated complex theory relation — free energy of activation

The *transition state or activated complex theory* states that upon approach of reactant molecules some bonds start to lengthen while other bonds start to form. These changes are accompanied by energy changes and, finally, the reacting molecules achieve a specific arrangement before they can be transformed into the products of the reaction. The specific, transient, arrangement that possesses a definite energy is known as the *transition state*. The "transition state" or "activated complex" theory postulates that the reaction proceeds through formation of an "activated complex" that is in equilibrium with the reactants (Petrou and Economou-Eliopoulos, 2009b; Petrou, 2012), and the rate constant is given by:

$$k = \kappa(RT/Nh)\exp\left(-\Delta G^{\neq}/RT\right). \tag{1}$$

The transmission coefficient κ is generally close to unity and may be ignored (Espenson, 1981). $\Delta G^{\neq}$ is the Gibbs free energy of activation, h is Planck's constant, R is the Universal gas constant and N is the Avogadro's number. The term RT/Nh is independent of the nature of the reactants and, at a given temperature, the rate of any reaction is determined by $\Delta G^{\neq}$. By applying the thermodynamic relationship

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}. \tag{2}$$

Eq. (1) can be expressed in terms of the activation enthalpy, $\Delta H^{\neq}$, and the activation entropy, $\Delta S^{\neq}$, thus:

$$k = \kappa(RT/Nh)\exp\left(\Delta S^{\neq}/R\right)\exp\left(-\Delta H^{\neq}/RT\right). \tag{3}$$

The above Eq. (3) is the general form of the Eyring equation or Activated Complex Theory equation, which is also known as Eyring–Polanyi equation in chemical kinetics. It relates the reaction rate constant to temperature and its linear form is:

$$\ln(k/T) = -\left(\Delta H^{\neq}/R\right)(1/T) + \ln(\kappa R/Nh) + \left(\Delta S^{\neq}/R\right). \tag{4}$$

This linear form is usually used for the suggestion of a mechanism of a certain reaction in the following way: the reaction is performed at various temperatures and the reaction rate constant is measured. The plot of ln (k/T) versus 1/T gives a straight line with slope $-\Delta H^{\neq}/R$ from which the Enthalpy of Activation is derived and with intercept $\ln(\kappa R/Nh) + \Delta S^{\neq}/R$ from which the Entropy of Activation is calculated. The term ln (κR/Nh) has a known constant value 23.76. The calculated value of the Entropy of Activation suggests an Associative mechanism when $\Delta S^{\neq}$ is negative, a Dissociative mechanism when $\Delta S^{\neq}$ is positive, an Interchange mechanism when $\Delta S^{\neq}$ is equal to zero (when the rate constants refer to replacement reactions) (Petrou and Economou-Eliopoulos, 2009b). Calculation of $\Delta G^{\neq}$ is possible for the appropriate reaction temperatures according to the Eq. (2).

3. Diffusion-controlled reactions

Reactions in solution in which every collision of the reacting molecules leads to products are called diffusion-controlled reactions. Their rates are limited only by diffusion that has activation energy values ranging from 10 to 20 kJ mol^{-1}. The rate-constants for such (second order) reactions range from 10^9 to 10^{10} M^{-1} s^{-1} and are dependent on the nature of the solvent (Katakis and Gordon, 1987).

Alkattan et al. (1998), have reported an apparent activation energy for diffusion of 19 ± 4 kJ mol^{-1} which is somewhat higher than the 13.2 kJ mol^{-1} obtained by Oelkers and Helgeson (1988) for the apparent activation energy of HCl diffusion. The differences between these results were assigned to the hydrodynamics of the different experimental setups used to obtain the rates (Alkattan et al., 1998).