PHYSICAL SCIENCES

PROTON TRANSFER PROCESSES IN COMPLEX CONDENSED SYSTEMS

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https://doi.org/10.5281/zenodo.16875607

Abstract

Safe development of hydrogen energy, production and storage of hydrogen are pressing issues of modern science. For the real development of hydrogen energy, one of the most important problems remains the problem of hydrogen storage. It is safer to store hydrogen in carriers, for example metal hydride storage devices. So, proton transfer in various condensed systems, such as metal hydride is of primary interest. Theoretical studies in this area primarily involve consideration of the problems of interaction of impurity particles with complex condensed systems, charge transfer in such systems and, in particular, proton transfer. Proton transfer processes in nonregular condensed systems are of great importance for the development of theoretical models of hydrogen energy problems.

To solve the problems of theoretical description of proton behavior in chemical processes, we will first consider particle transfer processes within the framework of the general theory of charge transfer processes in nonregular condensed systems, taking into account the effects of frequency and spatial dispersion of the medium. The Green function mathematical apparatus is used for analytical calculations.

Keywords: proton transfer, hydrogen storage, condensed systems, Green functions

1. Introduction

In the era of green energy development, one of the most important issues of scientific research is the problem of the safe use and development of hydrogen energy. The problems of safe development are among the main ones in many areas of obtaining, storing and using hydrogen in various sectors of the economy, and, what is especially important, in transport as an energy source. It is therefore important to develop safe methods for producing hydrogen and storing it safely in various carriers.

From the point of view of scientific development of the designated problems, individual issues of hydrogen energy have been studied for quite a long time, both in scientific terms and for practical application in various fields. For scientific research, the issue of proton transfer in various condensed systems was of primary interest. Theoretical studies in this area primarily involve consideration of the problems of interaction of impurity particles with complex condensed systems [1 – 3], charge transfer in such systems and, in particular, proton transfer. Proton transfer processes in nonregular condensed systems are of great importance for the development of theoretical models of hydrogen energy problems.

In this paper, proton transfer processes are considered within the framework of the general theory of charge transfer processes in nonregular condensed systems, taking into account the effects of frequency and spatial dispersion of the medium. Proton transfer processes in the system are described in the classical and quantum approximations, taking into account the shape of the potential energy curve of the system along the charge transfer coordinate.

2. Materials and methods

2.1 The main methods of obtaining hydrogen.

All hydrogen is not an environmentally friendly fuel, it all depends on the method of its production. According to the methods of production, hydrogen is divided into color gradations:

Brown (high-carbon) hydrogen - greenhouse gases are released during the production process of this method;

Gray (high-carbon) hydrogen - during its production, harmful waste is released into the atmosphere;

Blue (medium carbon) hydrogen - using CCS - carbon capture and storage technology;

Turquoise (low carbon) hydrogen - the carbon emissions will either be buried or used in industry;

Yellow (orange, carbon-free) hydrogen - no CO_2 emissions, but the method cannot be considered completely environmentally friendly;

Green (carbon-free) hydrogen - no CO_2 emissions into the atmosphere during the production process.

2.2 Hydrogen storage in carriers

For the real development of hydrogen energy, one of the most important problems remains the problem of hydrogen storage. It is safer to store hydrogen in carriers.

Carriers can be liquid hydrocarbons, adsorbents, metal hydrides or other hydrogen-rich compounds. Carriers must meet the following basic requirements:

• Maintain the phase state in the required range of temperatures and pressures;

• Provide high volume and mass density of hydrogen;

• Provide easy unloading of hydrogen;

• Be environmentally safe.

It is desirable that the carriers be easily rechargeable.

Gaseous hydrogen is capable of entering into a chemical reaction with many metals (Mg) or metal alloys (FeTi, $TiMn_2$, $LaNi_5$, Mg_2Ni), forming solid compounds. This reaction is reversible, which allows for the implementation of loading and unloading cycles of metal hydride storage devices. The binding of gaseous hydrogen to form a metal hydride is accompanied by the release of heat (an exothermic process), and, as a rule, occurs at ambient temperature and pressure. After adsorption on the metal surface, hydrogen dissociates and diffuses into the metal crystal lattice. First, hydrogen is adsorbed on the metal surface, then the H_2 molecules dissociate, hydrogen atoms are introduced into the crystal lattice, and finally the metal hydride is formed. The reverse process (dehydrogenation), accompanied by the release of hydrogen gas from the metal hydride, requires the supply of a sufficient amount of heat (endothermic process).

3. Particle transfer reactions in nonregular condensed media

To solve the problems of theoretical description of proton behavior in chemical processes, we will first consider particle transfer processes within the framework of the general theory of charge transfer processes in nonregular condensed systems, taking into account the effects of frequency and spatial dispersion of the medium.

For a particle transfer reaction, the number of normal coordinates of intramolecular vibrations for individual reagents before and after the reaction can be different. In general, the rate constant of the transfer process can be represented as:

$$K_a = \frac{1}{ikT} e^{\beta \text{Ғ}_i} \int_{-i\infty}^{i\infty} d\theta [f_{00}(\theta) + f_{10}(\theta) + f_{01}(\theta)] \quad (1)$$

where k is the Boltzmann constant, T is the temperature in the Kelvin scale, and Ғ_i is the free energy of the system, independent of the volume of the system. The functions $f_{00}(\theta)$, $f_{10}(\theta)$, $f_{01}(\theta)$ are defined by the relations:

$$f_{00}(\theta) = \exp\left[\beta\left(F_i - F_f\right) + \beta\theta\left(F_i^s - F_f^s\right)\right]\langle exp\left(\beta\theta H_i^p\right) \cdot exp\left[\beta\theta\left(H_i^m + H_{int}^i\right)\right] \cdot exp\left[-\beta\theta\left(H_f^m + H_{int}^f\right)\right] \cdot exp\left(-\beta\theta H_f^p\right)\rangle.$$

$$f_{10}(\theta) = \langle T_\tau \int_{\beta\theta}^{\beta} d\tau \int d\vec{r}\, v_{s\alpha}^i(\vec{r}) \delta P_\alpha(\vec{r}\tau) \delta Q_s^i(\tau) exp\left(\beta\theta H_i^p\right) \cdot exp\left[\beta\theta\left(H_i^m + H_{int}^i\right)\right] \cdot exp\left[-\beta\theta\left(H_f^m + H_{int}^f\right)\right] \cdot exp\left(-\beta\theta H_f^p\right)\rangle \cdot exp\left[\beta\left(F_i - F_f\right) + \beta\theta\left(F_i^s - F_f^s\right)\right].$$

$$f_{01}(\theta) = \langle T_\tau \int_0^{\beta} d\tau \int d\vec{r}\, v_{s\alpha}^f(\vec{r}) \delta P_\alpha(\vec{r}\tau) \cdot exp\left[\beta\theta\left(H_i^m + H_{int}^i\right)\right] \cdot exp\left[-\beta\theta\left(H_f^m + H_{int}^f\right)\right] \cdot \delta Q_s^f(\tau) exp\left(-\beta\theta H_i^p\right)\rangle \cdot exp\left[\beta\left(F_i - F_f\right) + \beta\theta\left(F_i^s - F_f^s\right)\right]. \quad (2)$$

Here H_i^m and H_f^m are the Hamiltonians of the medium at the beginning and at the end of the process, respectively, H_i^p and H_f^p are the Hamiltonians of the reactants at the beginning and at the end of the process; F_i^s and F_f^s are the solvation energies of the reactants at the beginning and at the end of the transfer process, F_i and F_f the free energies of the system at the beginning and end of the transfer process, and the normal coordinates of the reactants at the beginning and end of the transfer process.

The angle brackets denote quantum-statistical averaging over the states of the corresponding Hamiltonian.

When calculating quantum-statistical averages in the functions $f_{00}(\theta)$, $f_{10}(\theta)$, $f_{01}(\theta)$, factorization will occur into quantum-statistical averages over the coordinates of the medium and over the normal coordinates Q_s^i and Q_s^f of the intramolecular oscillations of the particles participating in the transfer process.

In general, the calculations of the K_a functions are quite cumbersome. Therefore, it is more convenient to calculate the kinetic parameters of the charge transfer process for maximally simplified models, taking into account the possibility of using approximate methods for certain degrees of freedom. For example, when calculating the function K_a, one can use the decoupling of quantum-statistical averages from the medium polarization operators into paired averages.

For a more detailed simplification of the analytical expressions for the rate constant of the process, one can use the classical approximation for the vibrational degrees of freedom of the reactants.

As a result, for the rate constant of the process of a-partial reaction we obtain

$$K_a = \frac{\beta}{i} \int_{-i\infty}^{i\infty} d\theta exp\left[-\beta\theta\left(F_f^s - F_i^s + E_r^m\right) + \beta\left(\text{Ғ}_i - F_i^m\right) - \psi^m(\theta)\right] \cdot \left|V_{fi}\right|^2 \times exp\left[-\beta \sum_{n=1}^{N} E_{rn} \frac{\theta(1-\theta)\omega_n^i \omega_n^f}{(1-\theta)\left(\omega_n^i\right)^2 + \theta\left(\omega_n^f\right)^2}\right] \cdot \left[\prod_{s=1}^{N} \beta(1-\theta)(\omega_s^i)^2 + \theta\left(\omega_s^f\right)^2\right]^{-1/2} \cdot \left[1 + \sum_{k=1}^{N}\left(G_k + \frac{\omega_k^f}{\omega_k^i} \cdot G'_k\right) \cdot \left(\beta\theta - F_\omega(\theta)\right)\left(2E_{rk}\omega_k^i\right)^{1/2} \cdot \theta\left(\omega_k^f\right)^2 \left[(1-\theta)(\omega_n^i)^2 + \theta\left(\omega_n^f\right)^2\right]^{-\frac{3}{2}}\right] \quad (3)$$

where E_{rn} is the reorganization energy of the system's n-th intramolecular degree of freedom:

$$E_{rs} = \frac{1}{2}(q_{s0})^2 \omega_s^n \quad (4)$$

where ω_s^n is the oscillation frequency, of the n-th degree of freedom , q_{s0} is the equilibrium value of the coordinate of the corresponding degree of freedom.

In formula (3) G_k and G'_k are expressed as:

$$G_k = \int d\vec{r}\, d\vec{r}' \frac{\partial E_\alpha(\vec{r})}{q_s} g_{\alpha\beta}^m\left(\vec{r}, \vec{r'}; \omega = 0\right) \Delta E_\beta\left(\vec{r'}\right), q_s = 0$$

$$G'_k = \int d\vec{r}\, d\vec{r}' \Delta E_\alpha\left(\vec{r'}\right) g_{\alpha\beta}^m\left(\vec{r}, \vec{r'}; \omega = 0\right) \frac{\partial E_\beta(\vec{r})}{q_s}, q_s = 0 \quad (5)$$

where $g_{\alpha\beta}^m$is the Green's function of the medium polarization fluctuation operators, ΔE_α, ΔE_β is the change in the electric field strength of impurities during the charge transfer process.

Integration over $\vec{r}$ and $\vec{r'}$ for the functions G_k and $G_k{}'$ can be carried out using the saddle-point method.

As a result, we obtain that the value of the maximum of the integrand over θ in formula (3) has the form:

$$\theta^* = -kT\frac{\partial lnK_a}{\partial \Delta F} \quad (6)$$

where ΔF is the free energy of the process.

When calculating the kinetic parameters of various adiabatic reactions, adiabatic terms can be used instead of channel terms. In this case, the probability of transition between two potential energy surfaces will be determined by the transmission coefficient:

$$æ = (1 - e^{-\gamma_e})(1 - 0.5e^{-\gamma_e}) \quad (7)$$

where parameter γ_e determines the nature of the process

$$\gamma_e = {2\pi L^2}/{(|v| \cdot |\Delta F|)} \quad (8)$$

Here v is the velocity of the system near the transition configuration, ΔF is the difference in the slopes of the potential energy terms near the point of their intersection, L is the electron resonance integral of the process, which in many ways determines the nature of the process. If the value of L is small, so that the condition $\gamma_e \ll 1$ is satisfied, then the process is of an electron-nonadiabatic nature and when describing the system it is sufficient to use the channel terms of the initial and final channels as potential energy terms. If the value of L is large, so that the condition $\gamma_e \gg 1$ is satisfied, then the reaction is of an electron-adiabatic character and adiabatic terms should be used as potential energy terms.

4. Proton transfer reactions in nonregular condensed medium

The above general correlations for the process of charge transfer in a nonregular condensed medium can be significantly simplified for specific processes, in particular for the process of proton transfer. For proton transfer reactions, it should be taken into account that the number of normal coordinates of intramolecular vibrations of individual reactants before and after the reaction will be different. Accordingly, calculations of the functions $f_{00}(\theta), f_{10}(\theta), f_{01}(\theta)$, included in the expression for the rate constant of the process (see formula (1)) can be carried out only for specific processes.

The calculations can be significantly simplified if we neglect the interaction of fluctuations of the medium polarization with intramolecular vibrations of the reactants and reaction products.

The proton transfer reaction is an interesting object for determining the classical and quantum behavior of a system. The solution to this question depends on the form of the potential energy of the system. If the quasi-classical approximation is used for the density matrix, then the criterion of classical approximation has the form

$$\frac{\hbar}{\sqrt{24}(kT)^2}\sum_n \left|\dot{x_n}\frac{\partial u(x)}{\partial x_n}\right| \ll 1 \quad (9)$$

where $\dot{x_n}$ is the speed of the system along the n-th degree of freedom with thermal energy.

As can be seen from this condition, the system behaves classically in the region of coordinate values x in which the steepness of the potential energy curve along the corresponding degree of freedom is small (enough to ensure the smallness of the derivative $\partial u(x)/(\partial x_n)$). Accordingly, where the steepness of this curve is large, the behavior of the system will be quantum.

As an example, calculations of kinetic parameters for the proton transfer process in a hydroxonium ion at room temperature were also carried out. The Morse potential was used as the potential of the field in which the proton moves:

$$U = D(1 - e^{-\alpha x})^2 \quad (10)$$

where D is the dissociation energy, which is equal to 710 kilojoule/mol, for hydroxonium ion; α is the steepness parameter of the potential energy curve. This parameter can be expressed through the proton oscillation frequency ω_p in this potential at small oscillations:

$$\alpha = \omega_p\left(m_p/2D\right)^{1/2} \quad (11)$$

Here, m_p is the reduced mass of the proton oscillation.

Calculations show that the classical or quantum behaviour of a proton in a system is determined by the parameter A:

$$A = (4KT/\hbar\omega_p) \times (3KT/D)^{1/2} = (4KT/\hbar\alpha D) \times (3KT/2)^{1/2} \quad (12)$$

where T is the temperature in the Kelvin scale.

If the values of the parameter P are large, then the movement in this region is of a classical nature, except for a certain region on the steep (repulsive) branch of potential energy, which separates the regions of classical and quantum nature, determined from the condition $P = 1$.

For a proton, as a rule, the condition $P \ll 1$ is realized. In this case, the point x^* lies on a gently sloping branch of potential energy and the motion near the minimum is of a quantum nature.

Using for estimates the numerical parameters D = 710 kJ/mol, $\mu_v = 1.63\ Å^{-1}$, (for the stretching vibration of a proton in a hydroxonium ion) and $\mu_\delta = 0.86\ Å^{-1}$ (for the deformation vibration), we find that at room temperature for the stretching vibration $P_v = 0.025$, and for the deformation vibration $P_\delta = 0.047$.

As shown by numerical estimates of the parameters of proton oscillation in the hydronium ion, at room temperature the point at which the classical behavior of the system changes for the valence oscillation to the quantum one is located at a distance of $x^* = 2.2\ Å$ from the point of minimum potential energy of the system. The activation energy for reaching this point is 698 kJ/mol (in this case, by activation energy we mean the energy value that is necessary to reach the point x^* in the classical way without tunneling). The situation does not change much for deformation vibration even for the heaviest isotope – tritium, for which $x^* = 2.74\ Å$, and the activation energy is 581 kJ/mol.

For real systems, the proton transfer distance is smaller and usually amounts to several tenths of an angstrom. For such small transfer distances, the splitting of the electron terms, equal to doubled electron resonance integral L, is very large. In particular, at very small distances, the potential energy curve will have not two minima, but one. So, the criterion for the clas-

sical or quantum behavior of the proton depends significantly on the transfer distance and on the value of the electron resonance integral of the transfer process.

Proton transfer can be of either an electron-nonadiabatic or electron-adiabatic nature. For electron-adiabatic reactions with not too large values of L, at which the motion has a quantum nature, both adiabatic and nonadiabatic proton transfer can take place.

If we adopt a harmonic model for the medium and assume that ω_m is the characteristic frequency of fluctuations of the medium polarization, then for the characteristic parameter of the proton transfer process γ_P we obtain:

$$\gamma_P = \frac{\pi(\Delta E_P)^2}{\hbar\omega\sqrt{2kTE_r^m}} \quad (13)$$

where ΔE_P is the value of splitting of vibrational levels of the proton in the potential well.

In the semiclassical approximation for one-dimensional motion, one can estimate the value of ΔE_P

$$\Delta E_P = \frac{\hbar\omega_P}{\pi} e^{-\sigma} \quad (14)$$

where ω_P is the proton oscillation frequency, σ is the tunneling factor.

Depending on the proton transfer distance and the ratio of the parameters L and ΔE_P

one of three cases can occur:

- $\gamma_e \ll 1$; $\acute{æ} = 2\gamma_e \cdot e \ll 1$ - transfer occurs by a completely non-adiabatic mechanism;
- $\gamma_e \gg 1, \gamma_P \ll 1, \acute{æ} = 2\gamma_P \ll 1$ - transfer occurs partially (electronically) by an adiabatic mechanism;
- $\gamma_e \gg 1, \gamma_P \gg 1, \acute{æ} \approx 1$ - transfer occurs by a completely adiabatic mechanism.

5. Conclusion.

The paper presents the results of analytical calculations of kinetic parameters of charge transfer processes in nonregular condensed systems taking into account the effects of frequency and spatial dispersion. Within the framework of the general theory of charge transfer processes in nonregular condensed systems, proton transfer processes are considered taking into account the effects of frequency and spatial dispersion of the medium. It is shown that the process of proton transfer in the system can be described in the classical or quantum approximation depending on the shape of the potential energy curve of the system along the charge transfer coordinate - with a flat shape the process is classical, with a steep shape - quantum. Analytical expressions for the kinetic parameters of the proton transfer process in complex condensed systems (energy of medium reorganization, probability of proton transfer, electron-resonance integral, dissociation energy) are obtained.

Acknowledgment and/or disclaimers, if any

This paper was based on the presentation made in 8th International Symposium on Materials for Energy Storage and Conversion, mESC-IS 24, held in Baku 07-10 October 2024.

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