Diffusion of helium and estimated diffusion coefficients of hydrogen dissolved in water-saturated, compacted Ca-montmorillonite

Tomohiro Higashihara[*]　Teppei Otsuka[**]　Seichi Sato[*]　Hiroshi Ohashi[*]

　　　　　The diffusion coefficients of hydrogen gas dissolved in water-saturated, compacted montmorillonite are required to estimate the performance of bentonite buffer materials for geological disposal of nuclear waste. As part of the effort to determine the diffusion coefficients, the diffusion coefficients of helium in water-saturated, compacted calcium montmorillonite (Ca-montmorillonite) were determined as a function of dry density, 0.78 to 1.37×10^3 kg m^{-3}, by a transient diffusion method. The diffusion coefficients were from 8.3×10^{-10} m^2 s^{-1} at 0.78×10^3 kg m^{-3} to 2.8×10^{-10} m^2 s^{-1} at 1.37×10^3 kg m^{-3}. The data obtained by this diffusion experiment of helium were highly reproducible. The diffusion coefficients of helium in Ca-montmorillonite were somewhat larger than those previously obtained for helium in sodium montmorillonite (Na-montmorillonite).
　　　　　The diffusion coefficients of hydrogen gas in the montmorillonites were roughly estimated using the diffusion coefficients of helium. These estimates were based on assumptions that both helium and hydrogen molecules are non-adsorptive and that the geometric factors in the compacted montmorillonites are approximately the same for diffusion of helium and diffusion of hydrogen.
Keywords: helium, hydrogen gas, diffusion coefficient, Na-montmorillonite, Ca-montmorillonite, a transient diffusion method, compacted bentonite, water-saturation, formation factor, mass spectrometry

1 Introduction

　　　　After the disposal of nuclear waste in a deep geologic formation, the compacted bentonite surrounding the waste will become water-saturated and swell to fill all residual spaces between the metallic over-pack and the surrounding host rock. Bentonite is a promising candidate material for retardation of radionuclide migration because it is an ion exchange material with a large surface area, e.g., several tens of square meters per gram as measured by the BET method. In addition, the bentonite is impermeable. Therefore the amount of hydrogen gas resulting from the corrosion of over-pack materials and the migration of this hydrogen in the compacted bentonite should be investigated to assess the long-term performance of the bentonite.

　　　　Several reports, in which breakthrough of gas has been studied using a controlled flow rate gas migration apparatus, are available[1]. But depending on the hydrogen gas production rate and the migration of gas under a pressure gradient, the pressure relaxation by the diffusion of gas possibly has an important role on the performance of the buffer materials. Few reports are available on the experimental results of gas diffusion in water-saturated, compacted clay for nuclear waste disposal. Eriksen et al.[2] and Neretnieks[3] studied steady-state diffusion of hydrogen gas in water-saturated, compacted bentonite (MX-80) by a through-diffusion method. Their data were examined by Werme et al.[4], Wikramaratna et al.[5], and Platt et al.[6] . The data reported in references (2) and (3) varied from 3.6×10^{-12} to 1.8×10^{-11} m^2 s^{-1}. As of yet, these data have not been well accepted.

　　　　In contrast to hydrogen gas, helium can be recovered from the montmorillonite at elevated temperatures without any chemical reaction loss and mass spectroscopic analysis can be performed under extremely low background condition. In our previous work, diffusion of helium in compacted Na-montmorillonite, a major mineral component of bentonite, was studied by a transient diffusion method[7] at dry densities from 0.8 to 1.6×10^3 kg m^{-3}. Quite satisfactory concentration profiles of diffusion of helium were obtained as a function of penetration depth, along with highly reproducible diffusion coefficients.

　　　　The purpose of the present study is to characterize water-saturated, compacted Ca-montmorillonite as a gas migration material. The diffusion coefficients of helium in the montmorillonite were determined as a function of dry densities from 0.8 to 1.4×10^3 kg m^{-3} by a transient diffusion method. The diffusion coefficients of hydrogen gas in the montmorillonite were roughly estimated based on the assumption that 1) both helium and hydrogen gases are non-adsorptive and 2) the geometric factors for diffusion of helium and diffusion of hydrogen are approximately the same in the montmorillonite.

2 Experimental

2.1 Specimens

　　　　Kunipia-F, a commercial form for Na-montmorillonite, was used to prepare Ca-montmorillonite. The procedure for the preparation of homoionized Ca-montmorillonite is given elsewhere[8]. Each Ca-montmorillonite powder specimen, dried at 378 K for 24 h, was weighed and transferred to an acrylic cell 20 mm in diameter and 20 mm in height. Sintered stainless-steel filters were placed at both ends of the cell to permit water saturation from both ends. The sintered filters were 2.0 mm in thickness with 2-μm-diameter pores. The filters were retained with stainless steel supporting plates 5.0 mm in thickness with a number of holes 2.5 mm in diameter. The dry densities of the Ca-montmorillonite specimens were 0.78, 1.00, 1.15, 1.26, and 1.37×10^3 kg m^{-3}.

　　　　To avoid helium diffusion being influenced by air occluded in the compacted montmorillonite, the specimens were prepared using the following procedure. Each cell was put in a beaker,

which was placed in a vacuum desiccator. After evacuation for half an hour, deionized water was introduced from the side of the desiccator onto the cell. Water saturation continued for 30 d.

2.2 Procedure

The diffusion of helium in the compacted montmorillonite was carried out at 298±0.1 K by a transient diffusion method. One end of each water-saturated specimen was tightly sealed using a lid with an O-ring while the other end was covered by a porous stainless-steel filter. Each specimen was then immersed in deionized water contained in a separable flask. The flask was placed in a temperature-controlled water bath, and helium was bubbled into the deionized water, as shown in Fig. 1.   Each specimen was immersed for 4.0 h.

After 4.0-h immersion to allow the helium to diffuse, each montmorillonite specimen was sectioned into 1.0-mm-thick wafer. Each wafer was quickly quenched in liquid nitrogen to avoid helium leakage. It required about one minutes to section each 1.0-mm-thick wafer. A few wafers were used to measure the dry density. This was accomplished by measuring the weight changes of the wafers before and after heating at 378 K for 24
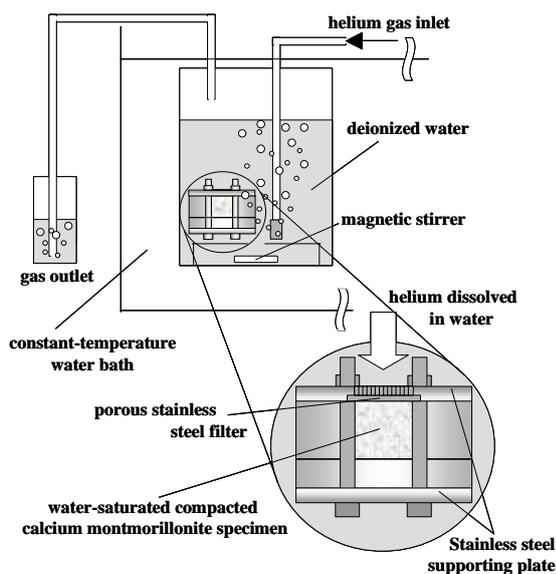

Fig. 1   Schematic view of helium diffusion in calcium montmorillonite, diffusion source is helium dissolved in deionized water by bubbling

Fig.2 Vacuum system for analysis of helium released from a montmorillonite wafer by heating

h[9].

The quantity of helium in the wafers was determined using the vacuum system shown in Fig. 2. To analyze the helium content, a wafer quenched in liquid nitrogen was placed in a silica tube immersed in liquid nitrogen. After evacuating the tube, the wafer was heated to 413 K. The helium gas released from the wafer was analyzed with a quadrupole gas analyzer (QMS, ANELVA AQA-100 MPX). The concentration profile of helium in the montmorillonite specimen was obtained as a function of penetration depth.

The apparent diffusion of helium in the compacted montmorillonite can be described by the equation,

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{1}$$

with the initial and boundary conditions,

$$C = 0 \qquad \text{in} \quad 0 < x \le L, t = 0$$
$$C = C_0 \qquad \text{at} \quad x = 0, t \ge 0$$

where,

   C : concentration of helium (mol m^{-3}) in the compacted montmorillonite per unit volume

   C_0: concentration of helium (mol m^{-3}) in the compacted montmorillonite in contact with water containing dissolved helium

   D_a: apparent diffusion coefficient (m^2 s^{-1})

   L : thickness of specimen (m)

In the experimental period, the value of L is sufficiently large to meet the boundary condition of $L = \infty$. The solution of the Eq. (1) can be described by the relation [10] ,

$$C/C_0 = 1 - erf\left(\frac{x}{2\sqrt{D_a t}}\right) \tag{2}$$

The value D_a was determined by the least-squares fit using C/C_0 and D_a as variables.

3 Results and Discussion

Figure 3 gives concentration profiles of diffusion of helium in water-saturated, compacted Ca-montmorillonite as a function of penetration depth at five dry densities, 0.78 to 1.37×10^3 kg m^{-3}. The solid lines are the least-squares-fit curves for the experimental data. The sintered filter might affect the experimental results, even if the thickness of the filter 2 mm in thickness with 2 μm pore size is markedly thinner than the penetration depth of helium in the compacted montmorillonite. However, the experimental data in Fig. 3, are well reproduced by the curves based on Eq. (2). In the present study, we conclude that the migration process is controlled by simple diffusion under the constant concentration of helium at the boundary of compacted montmorillonite. The diffusion coefficients obtained decrease from 8.3 to 2.8×10^{-10} m^2 s^{-1} as dry density increase from 0.78 to 1.37×10^3 kg m^{-3}.

Some diffusion coefficients of hydrogen in compacted bentonite are available in the literatures. Values of 2×10^{-11} m^2 s^{-1} and 3.6×10^{-12} to 1.8×10^{-11} m^2 s^{-1} have been reported based on the
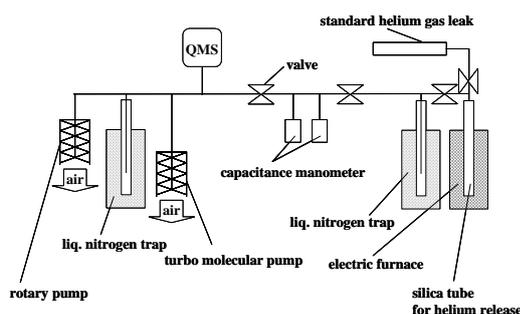
Fig. 3 Concentration profiles of helium in water-saturated compacted calcium montmorillonite
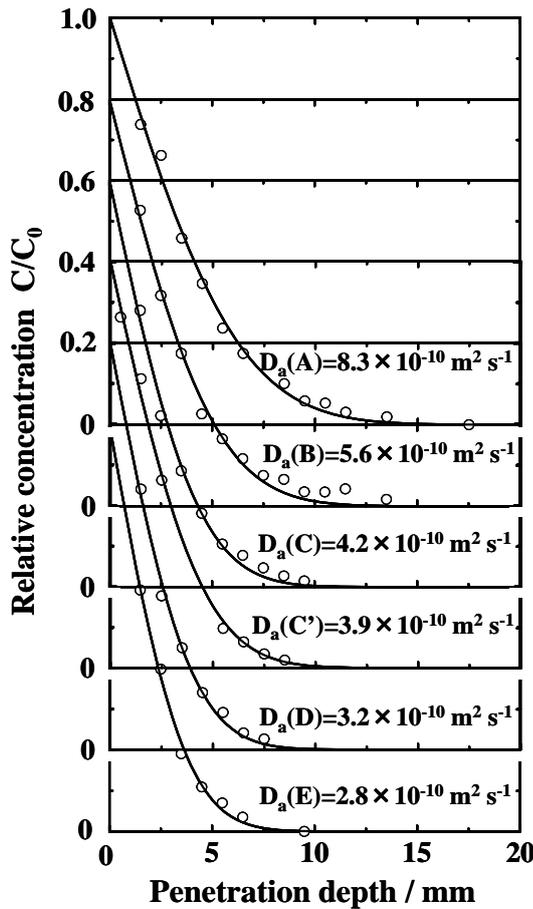Dry density, A: 0.78; B:1.00; C:1.15; C':1.15;
            D:1.26; E:1.37 ×10^3 kg m^{-3}
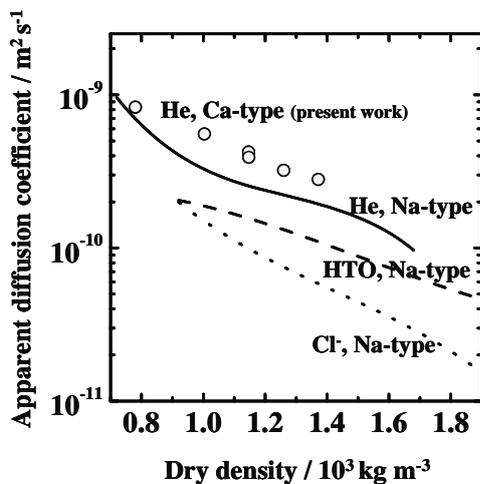**Bubbling time: 4 h; Temperature: 298 K**

Fig. 4 Apparent diffusion coefficients of helium in water-saturated, compacted calcium montmorillonite, ○ ; and helium, ——[7]; tritium in HTO,‒ ‒ [11]; chloride ion,·····[12]; in compacted sodium montmorillonite

data by Eriksen and Jacobsson[2], and Neretnieks[3].

The present values for Ca-montmorillonite are slightly greater than the previously obtained values[7] for Na-montmorillonite. Our diffusion coefficient data for the present Ca- and the Na-montmorillonite studies are one to two orders of magnitude greater than those previously reported [3,4], although the present diffusion data are for helium rather than hydrogen, for Kunipia-F rather than MX-80, and for apparent diffusion coefficients rather than effective diffusion coefficients. The effective diffusion coefficients of helium in the montmorillonite are not straightforwardly available from the present apparent diffusion coefficient of helium. Further discussions on the comparison between the previous data[3,4] and the present ones are not carried out.

In Fig. 4, the apparent diffusion coefficients of helium obtained in the present work are plotted together with those of tritium[11] in the form of HTO, and chloride ions[12] in compacted Na-montmorillonite. The diffusion coefficients of helium decrease monotonously, in a similar manner as those of HTO and Cl$^-$, with increasing dry density, although the values of helium in Ca-montmorillonite are somewhat larger than those of helium, HTO, and Cl$^-$ in Na-montmorillonite.

Pores will exist in compacted montmorillonite through which ions can migrate. From a thermodynamic point of view, the pore is filled with the water having high ionic strength[9], e.g., the gel filling void. Helium is more mobile in the larger pores of Ca-montmorillonite than in the pores of Na-montmorillonite, because 1) the layer expansibility in Ca-montmorillonite, which has a hydrate having a maximum three layers, is weaker than that in Na-montmorillonite, which can have higher hydrate state (more than three-layers), and 2) it is quite possible that the number of layers per quasi-crystalline grain of Ca-montmorillnite is much larger than that of Na-montmorillonite[13]. Therefore, the migration path in Ca-montmorillonite is less restricted than in Na-montmorillonite, which suggests the diffusion of helium in these materials is geometrically favorable in the former than the latter. On the other hand, the diffusion of helium in either form of montmorillonite does not depend on the electrostatic potential arising from the montmorillonite sheet. The diffusion behavior of helium differs from a positively charged and negatively charged chemical species. It is quite possible that the diffusion path in montmorillonite is geometrically dissimilar among helium, HTO, and Cl$^-$. Besides, the diffusion coefficient of helium in bulk water is the largest, then HTO and Cl$^-$ among He, HTO and Cl$^-$. That contributes to the largest apparent diffusion coefficient of helium in compacted Na-montmorillonite in Fig. 4. Both the geometric factor of compacted montmorillonite and the diffusion coefficient in bulk water influence the diffusion data of the chemical species.

The geometric factors of diffusion in the montmorillonites are considered, using a formation factor, $1\big/\left(\frac{\delta}{\tau^2}\right)$. The experimentally determined apparent diffusion coefficient of
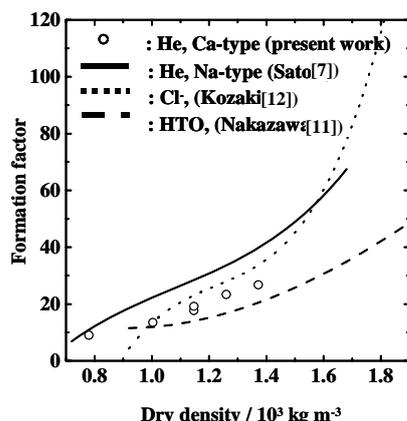
Fig. 5 Formation factor of helium diffusion in water-saturated, compacted calcium montmorillonite, together with that of helium, HTO and Cl⁻ in sodium montmorillonite

helium, D_a(He), can be described by

$$D_a(He) = \frac{\delta}{\tau^2} D_b(He) \qquad (3)$$

where D_b(He) is the diffusion coefficient of helium in bulk water.

The formation factors for the diffusion of helium shown in Fig. 5 were obtained as a function of the dry density from the D_a of helium and D_b(He), 7.5×10^{-9} m² s⁻¹ [14], based on Eq. (3). The formation factor of tritium (HTO)[11] and Cl⁻ [12] are also shown in Fig. 5. The formation factors of three non-adsorptive chemical species, He, HTO and Cl⁻ are not always same, because He is neutral species without hydration, HTO is not always restricted in pore water but in surface and interlayer water[9], and Cl⁻ is hydrated and negatively charged species. The diffusion path for charged chemical species is affected by the surface charge of the montmorillonite, and the path for H₂O is changed due to occurrence of surface and interlayer water. The formation factors in Fig. 5 suggest the following three points. First, the value of the formation factor of helium for Ca-montmorillonite increases as a function of dry density from 9 at 0.78×10^3 kg m⁻³ to

27 at 1.37×10^3 kg m⁻³. This clearly indicates that the diffusion path of helium in compacted Ca-montmorillonite, as well as in Na-montmorillonite[7], is geometrically limited by an increase in dry density. Second, the geometric factor for helium in Ca-montmorillonite is smaller than that in Na-montmorillonite, so helium is more mobile in Ca-montmorillonite than in Na-montmorillonite. This is plausible as was mentioned above. Third, the values of formation factors for helium in Na-montmorillonite are greater than those for HTO and Cl⁻ in the lower dry densities, less than 1.2×10^3 kg m⁻³. Specifically, at these densities, the migration path of helium is apparently more limited than for those of HTO and Cl⁻. Therefore, it is likely that restricted diffusion paths for helium differing from HTO and Cl⁻ exist in the Na-montmorillonite.

On the other hand, at dry densities higher than 1.2×10^3 kg m⁻³, the formation factors for helium and Cl⁻ in Na-montmorillonite tend to be larger than those for HTO. It is possible that the diffusion of Cl⁻ at increased dry densities is affected by conventional anion exclusion. This suggests that the diffusion path of helium is limited to the pore or grain boundary among particles.

Diffusion data for hydrogen gas in the compacted montmorillonites are important to assess the long-term integrity of buffer materials, but the data are very scarce as was mentioned. The diffusion coefficient of hydrogen gas in bulk water is slightly smaller than helium, but is definitely larger than H₂O[15] and Cl⁻ [16]. This means hydrogen gas diffuses in the vacant free volume among water molecules in liquid state, differing from the diffusion of H₂O in hydrogen bond and Cl⁻ in hydration state. In an attempt to estimate the diffusion data in compacted montmorillonite, we assumed that 1) the formation factors for hydrogen gas in the montmorillonite are different from those of H₂O and Cl⁻ but similar to those of helium as mentioned above about formation factors, and 2) hydrogen molecule is non-adsorptive. Then the apparent diffusion coefficients of hydrogen gas dissolved in compacted Na- and Ca-montmorillonite can be estimated by Eq. (3) using the diffusion coefficient of hydrogen in the bulk water, 6.1×10^{-9}

Table. 1 Estimated diffusion coefficients of hydrogen in water-saturated compacted sodium and calcium montmorillonite

Exchangeable cation	Dry density	Diffusion coefficient of helium	Formation factor	Diffusion coefficient of hydrogen
	10^3 kg m⁻³	10^{-10} m² s⁻¹		10^{-10} m² s⁻¹
Na⁺	0.8	6.7	11	5.4
	0.9	4.0	19	3.3
	1	3.3	23	2.6
	1.2	2.5	30	2.0
	1.4	2.0	37	1.6
	1.5	1.3	56	1.1
	1.6	1.4	56	1.1
Ca²⁺	0.78	8.3	9.0	6.7
	1.00	5.6	14	4.5
	1.15	4.2	18	3.4
	1.15	3.9	19	3.2
	1.26	3.2	23	2.6
	1.37	2.8	27	2.3

The diffusion coefficient of hydrogen in bulk water: 6.1×10^{-9} m²s⁻¹ [14]

$m^2 s^{-1}$ [14]. The estimated diffusion coefficients of hydrogen gas are given in Table 1. The present data are useful to describe the long-term performance of compacted bentonite and hydrogen behavior, together with the diffusion process of fission products and TRU elements in bentonite.

4 Conclusions

Diffusion coefficients of helium in water-saturated, compacted Ca-montmorillonite were determined as a function of dry densities from 0.78 to 1.37×10^3 kg m^{-3} by a transient diffusion method. Diffusion coefficients from 8.3×10^{-10} m^2 s^{-1} at 0.78×10^3 kg m^{-3} to 2.8×10^{-10} m^2 s^{-1} at 1.37×10^3 kg m^{-3} were obtained. The values for diffusion of helium in Ca-montmorillonite were somewhat larger than those in Na-montmorillonite.

The diffusion coefficients of hydrogen in montmorillonite were estimated based on the assumption that the geometric factor for diffusion of helium in compacted montmorillonite is the same as that for diffusion of hydrogen.

The authors believe that this new experimental approach to determine the diffusion coefficient of hydrogen gas in water-saturated, compacted montmorillonite is a very promising method.

References

[1] Horseman, S. T., Harrington, J. F. and Sellin, P.: Gas migration in clay barriers. *Eng. Geol.* **54**, 139-149(1999).

[2] Eriksen, T. E. and Jacobsson, A.: Diffusion of hydrogen, hydrogen sulfide, and large molecular weight anions in bentonite, *SKBF/KBS Technical Report* 82-17(1982).

[3] Neretnieks, I.: Diffusivities of some constituents in compacted wet bentonite clay and the impact on radionuclide migration in the buffer. *Nucl. Technol.* **71**, 458-470(1985).

[4] Werme, L. O., Salo, J-P.: Near field performance of the advanced cold process canister. *Mat. Res. Soc. Symp. Proc.* **212**, 343-350(1991).

[5] Wikramaratna, R. S., Goodfield, M., Rodwell, W. S., Nash, P. J., Agg, P. J. : A preliminary assessment of gas migration from the copper/steel canister, *SKB Technical Report,* 93-31(1993).

[6] Platt, N., Blackwood, D. J., Naish, C. C.: Anaerobic oxidation of carbon steel in granitic groundwaters: A review of the relevant literature, *SKB Technical Report,* 94-01(1994).

[7] Sato, S., Otsuka, T. , Kuroda, Y. , Higashihara, T., Ohashi, H.: Diffusion of helium in water-saturated compacted sodium montmorillonite, (to be publishied).

[8] Kozaki, T., Sato, H., Sato, S., Ohashi, H.: Diffusion mechanism of cesium ion in compacted montmorillonite. *Eng. Geol.* **54**, 223-230(1999).

[9] Torikai, Y., Sato, S., Ohashi, H.: Thermodynamic propaties of water in compacted sodium montmorillonite. *Nucl. Technol.* **115**, 73-80(1996).

[10] Crank, J. : *The Mathematics of Diffusion*, 2nd ed., Oxford Univ. Press(1975).

[11] Nakazawa, T., Takano, M., Nobuhara, A., Torikai, Y., Sato, S., Ohashi, H.: Activation energies of diffusion of tritium and electrical conduction in water-saturated compacted sodium montmorillonite in radioactive waste management and Environmental Remediation, ASME (1999).

[12] Kozaki, T., Saito, N., Fujishima, A., Sato, S., Ohashi, H.: Activation energy for diffusion of chloride ions in compacted sodium montmorillonite. *J. Contam. Hydrol.* **35**, 67-75(1998).

[13] Choi, J. -W. and Oscarson, D. W.: Diffusive transport through compacted Na- and Ca-bentonite. *J. Contam. Hydrol.* **22**, 189-202(1996).

[14] Wise, D. L. and Houghton, G.: The diffusion coefficient of ten slightly soluble gases in water at 10-60 °C. *Chem. Eng. Sci.* **21**, 999-1010(1966).

[15] Eisenberg, D. and Kauzmann, W.: *The Structure and Properties of Water*, Oxford Univ. Press p.218. (1969).

[16] Parsons, R.: *Handbook of Electrochemical Constants*, Butterworths Science Pub. London p.79. (1959).