Dynamic equations of impurity hydrogen during heavy water electrolysis

Zhou Junbo[a],[*], Wang Kuisheng[a], Shen Huitang[b], Wang Shaobo[b]

[a]*College of Mechanical and Electrical Engineering, Beijing University of the Chemical Technology, 15, Bei San Huan Dong Road, Beijing 100029, China*
[b]*Particular-energy Environment-protection Research Institute of C S I C, Handan 056027, China*

Abstract

Based on the electrolytic reaction and the balance equation of hydrogen isotope exchange in gas and liquid phases, the dynamic equation of impurity hydrogen is established during heavy water electrolysis. And combined with engineering practice, the calculation formula is drawn together with the calculation step and the calculation methods of all parameters while batch feeding heavy water electrolysis. These lay the necessary theoritical foundation for the research of heavy water electrolysis and the production of high-purity deuterium.

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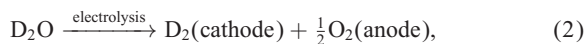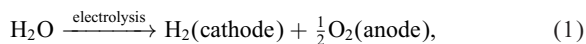*Keywords:* Heavy water; Electrolysis; Hydrogen; Deuterium; Dynamic equation

1. Introduction

Electrolysis is a technology known all over the world. Hydrogen or oxygen generation by common water electrolysis has been applied in a wide range of industries like petroleum, chemicals, energy, electronics, metallurgy and so on, while researches of deuterium generation technologies by heavy water electrolysis are relatively few. In order to gain high-purity deuterium, electrolysis of heavy water with the D_2O concentration of more than 99% is usually used. As a military material, deuterium plays a decisive role in manufacturing hydrogen bombs, neutron bombs and deuterium fluoride laser weapons. Deuterium, as a civil material, is also applied widely in the fields of controllable nuclear fusion reactions, optical fiber material manufacture, deuterium lubricant, light sources, nuclear agriculture, nuclear medical researches and medicine manufacture. However, the deuterium purity may have an inestimable influence on the effects of its applications, especially in nuclear fusion. The hydrogen content in electrolyzed deuterium is an important index to determine the deuterium purity. Therefore, we have to theoretically calculate dynamic changes of impurity hydrogen during the electrolysis to lay a necessary theoretical foundation for the research of heavy water electrolysis and the production of high-purity deuterium.

2. Electrode reactions and balance equations in electrolysis [1,2]

The following reactions occur during heavy water electrolysis

$$H_2O \xrightarrow{\text{electrolysis}} H_2(\text{cathode}) + \tfrac{1}{2}O_2(\text{anode}), \qquad (1)$$

$$D_2O \xrightarrow{\text{electrolysis}} D_2(\text{cathode}) + \tfrac{1}{2}O_2(\text{anode}), \qquad (2)$$

where D_2O is the heavy water. Oxygen is generated on the anode and released, while on the cathode, hydrogen, deuterium and mixed molecules of hydrogen and deuterium are produced (Fig. 1). Based on the balance reaction, Eq. (3), we can get Eq. (4), thus K_6 can be calculated

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* Corresponding author. Tel./fax: +86-10-6441-7994.
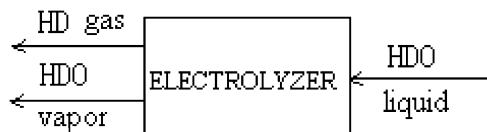*E-mail addresses:* zhogab@163.com (Z. Junbo), kuishengw@163.com (W. Kuisheng).

Fig. 1. Input and output balance of impurity hydrogen.

according to (4):

$$H_2 + D_2 \xrightarrow{K_6} 2HD, \tag{3}$$

$$K_6 = \frac{[HD]^2}{[H_2][D_2]}, \tag{4}$$

where HD is the mixed molecular hydrogen and deuterium atom, K_6 is the reactive equilibrium constant, that is 3.26 at 25° C and 1 atm pressure based on Ref. [3]; [HD], [H₂] and [D₂] are molar fractions, respectively. If the component of hydrogen atoms is 1% in cathode gases, the HD molar fraction (ratio) is calculated to be 1.976% from (4) and the molar ratio in the form of H₂ molar rate is only 0.012%. This shows that impurity hydrogen in the gas phase presents mostly in the form of HD mixture molecules. And therefore, when the heavy water (D₂O) above 99 wt% is electrolyzed, impurity hydrogen produced on the cathode presents mainly in the form of mixture molecules (HD) of hydrogen and deuterium.

In the same way, it accords with the balance equation.

$$H_2O + D_2O \xrightarrow{K_5} 2HDO, \tag{5}$$

where HDO is mixed molecular water. That is

$$K_5 = \frac{[HDO]}{[H_2O][D_2O]}, \tag{6}$$

where K_5 is the reactive equilibrium constant; [HDO], [H₂O] and [D₂O] are the molar fractions, respectively (concentration). This shows that impurity hydrogen in the liquid phase presents mainly in the form of HDO molecules when the purity of heavy water is very high, i.e. the content of light water is very small [4].

3. Dynamic balance equations of impurity hydrogen

According to calculations from Eqs. (4) and (6) and the above discussion, we can know if the 99.5% purity heavy water is electrolyzed to generate deuterium, and the presence of H₂ and H₂O(vapor) can be ignored, impurity hydrogen in gas and liquid phases presents, respectively, in the forms HD and HDO mixture molecules. In the electrolyzer, the change rate of HDO moles per unit time can be written as

$$\frac{d}{dt}N_{HDO}(QL) = \frac{d}{dt}N_{HDO}(F) - \frac{d}{dt}N_{HD}(G)$$
$$- \frac{d}{dt}N_{HDO}(V), \tag{7}$$

where $N_{HDO}(QL)$ is the change rate of HDO moles, $N_{HDO}(F)$ is the moles number of addition of HDO in feeding heavy water per unit time during the electrolysis, $N_{HD}(G)$ is the rate of escape of HD with gas, and the term with $N_{HDO}(V)$ is the rate of escape HDO as vapor.

The rate of escape of HD can be calculated from the electrolytic separation factor for hydrogen. Thus, N_E moles heavy water per second (N_E mol/s) are electrolyzed and S_E is the electrolytic separation factor, then for low-concentration hydrogen, S_E can be defined as

$$S_E = \frac{(D/H)_{liquid}}{(D/H)_{gas}}. \tag{8}$$

The number of HD moles escaping per second is

$$\frac{d}{dt}N_{HD} = \frac{N_E x}{S_E}, \tag{9}$$

where x is the molar fraction of HDO in the electrolyzer at time t.

The rate of escape of HDO as vapors can be calculated from the vapor pressure $P_v(P_{D_2O})$ of heavy water at the temperature of electrolysis, the pressure P in the electrolyzer, the flow rate F_g of gases evolving out of the electrolyzer and the separation factor S_V for isotopic fractionation of hydrogen due to evaporation. Thus

$$\frac{d}{dt}N_{HDO}(V) = \frac{P_v}{P - P_v}F_g\frac{x}{S_v}, \tag{10}$$

where F_g is the gas flow rate from the electrolyzer (mol/s), and due to fresh D₂O fed into the electrolyzer, the parameter can be expressed as

$$\frac{d}{dt}N_{HDO}(F) = F_L a, \tag{11}$$

where F_L is the feed rate of heavy water (mol/s), a is the molar fraction of HDO in the feed.

Thus Eq. (7) is written as

$$\frac{d}{dt}N_{HDO} = F_L\alpha - \frac{N_E x}{S_E} - \frac{P_v}{P - P_v}F_g\frac{x}{S_v}. \tag{12}$$

If the electrolyzer contains N_t moles of heavy water at time t, then

$$x = \frac{N_{HDO}}{N_t}. \tag{13}$$

Therefore,

$$\frac{dx}{dt} = \frac{1}{N_t}\frac{d}{dt}N_{HDO} - \frac{N_{HDO}}{N_t^2}\frac{d}{dt}N_t \tag{14}$$

or

$$\frac{dx}{dt} = \frac{1}{N_t}\left(\frac{d}{dt}N_{HDO} - x\frac{d}{dt}N_t\right). \tag{15}$$

Substituting $(d/dt)N_{HDO}$ Eq. (12) into (15)

$$\frac{dx}{dt} = \frac{1}{N_t}\left(F_L a - \frac{N_E x}{S_E} - \frac{P_v}{P - P_v}F_g\frac{x}{S_v} - x\frac{d}{dt}N_t\right). \tag{16}$$

This is the basic differential equation and if all the other parameters are given, x can be calculated from this equation.

For certain condition, a typical application will be discussed below.

4. Real example of electrolyzer with batch feed water

In most electrolysis experiments, deuterium, mixture gas of hydrogen and deuterium and oxygen, respectively, come out of the cathode and anode of the electrolyzer; and the cell is operated for a certain period without adding fresh heavy water. In this case, the parameter F_L in Eq. (16) is zero and then $F_g = \frac{1}{2}N_E + N_E = \frac{3}{2}N_E$. Also, N_t is no longer a constant and is given as

$$N_t = N - \left(N_E + F_g \frac{P_v}{P - P_v} \right) t, \tag{17}$$

or

$$N_t = N - N_E \left(1 + \frac{3}{2} \frac{P_v}{P - P_v} \right) t, \tag{18}$$

therefore,

$$\frac{d}{dt} N_t = -N_E \left(1 + \frac{3}{2} \frac{P_v}{P - P_v} \right). \tag{19}$$

Making these substitutions in Eq. (16) and simplifying, we get

$$\frac{dx}{dt} = \frac{N_E}{N - N_E \left(1 + \frac{3}{2} P_v/(P - P_v) \right) t}$$
$$\times \left(\frac{S_E - 1}{S_E} + \frac{3}{2} \frac{S_v - 1}{S_v} \frac{P_v}{P - P_v} \right) x. \tag{20}$$

Integrating and putting the condition $x = x_0$ at $t = 0$,

$$\ln \frac{x}{x_0} = -\frac{(S_E - 1)/S_E + \frac{3}{2}(S_v - 1)/S_v\, P_v/(P - P_v)}{1 + \frac{3}{2} P_v/(P - P_v)}$$
$$\times \ln \left[1 - \frac{N_E}{N} \left(1 + \frac{3}{2} \frac{P_v}{P - P_v} \right) t \right]. \tag{21}$$

Eq. (21) can be used to calculate the hydrogen content during the electrolysis in terms of electrolysis . Alternatively, this equation can also be written in terms of N_t. Thus,

$$\ln \frac{x}{x_0} = \frac{(S_E - 1)/S_E + \frac{3}{2}(S_v - 1)/S_v\, P_v/(P - P_v)}{1 + \frac{3}{2} P_v/(P - P_v)} \ln \frac{N_0}{N_t}. \tag{22}$$

Using Eq. (22), the hydrogen content can be calculated with the initial and final electrolyte.

Now, let us consider the other parameters in Eqs. (21) and (22). They are electrolysis rate N_E, electrolytic separation factor S_E, distillation separation factor S_V and D_2O vapor pressure P_v.

Given the current, the electrolysis rate N_E can be calculated from Faraday's laws of electrolysis. The electrolytic separation factor S_E depends on the temperature of electrolysis and on the electrode materials [5]. Not many data are available for the electrolytic separation factors of hydrogen
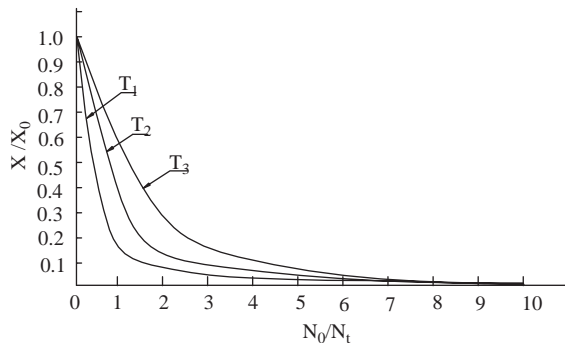

Fig. 2. x/x_0 aganist N_0/N_t changes sketch drawing ($T_1 < T_2 < T_3$).

and deuterium. As known from the experiment of Zhang Qinglian, an academician [6], the value range is from 9.1 to 10.6. For heavy water above 90% high concentration, the value S_E is 9.1 ± 0.1.

Based on Raoult's vapor-pressure law and Dalton's partial-pressure law [8], the separation factor S_V of distillation can be directly calculated from vapor pressures of D_2O and HDO. That is

$$S_v = \frac{P_{D_2O}}{P_{HDO}}. \tag{23}$$

The vapor pressure of D_2O and HDO can be calculated in accordance with Antoine Equation or Riedel Equation [9] and it can also be found from relative documents [9,10]. It is noted that here the P_{D_2O} found is just the P_V in Eq. (21) and (22). Fig. 2 shows the diagram of x/x_0 against changes of N_0/N_t. This means that the smaller the x/x_0, the less amount of HDO with the increasing time for electrolysis; T_1, T_2 and T_3 express changed curves at three temperatures, respectively, and it is seen in the figure that the more rapidly the impurity hydrogen reduces, the higher the purity of deuterium by subsequent electrolysis with temperature reduction. The specific value can be calculated based on Eq. (22), Raoult's vapor-pressure law and Dalton's partial-pressure law.

In addition, it is illustrated from our experimental results and experimental studies of Ivenchuk et al. [7] that the electrolytic separation factor of hydrogen and deuterium depends inversely on the temperature of high-concentration heavy water electrolysis. That is the lower the temperature, the more easily the impurity hydrogen is separated, although the electrolytic current has no effect on the separation, since the current increase causes temperature to rise. Therefore, during the high-purity deuterium generation by heavy water electrolysis, the process is generally performed at a low temperature and a small current to ensure light water (H_2O) to be preferably electrolyzed and released. The longer it is, the higher purity of subsequent deuterium. It is obvious that the conclusion is identical with results calculated by theoretic derivation Eq. (22) (seen in Fig. 2).

5. Conclusion

After the analysis of the above theoretic derivation and experimental results, it can be proved that our theoretic calculation accords with the experimental data. Thus, we can calculate HDO changes at any moment by using Eq. (22) and other equations to determine changes of impurity hydrogen, which lays a necessary theoretical foundation for the research of heavy water electrolysis and the production of high purity deuterium.

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