

A Supplement of GFEDF Based on Water Splitting for Hydrogen Fuels

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Abstract—Hydrogen fuel is a kind of clean energy that can be generated by photo catalyzing water splitting. It is interesting to investigate the case contrasting to Gibbs free energy determination formula (GFEDF). Through calculation and theoretical analysis, results are: (1) there is not electric energy and other form of work consumed in photo catalyzing water splitting, hence, the work from outside environment is less than the change of Gibbs free energy; contracting to GFEDF. (2) GFEDF works with a reaction when absorbed heat is less than the heat for entropy change; GFEDF does not work with a reaction when absorbed heat is more than the heat for entropy change. Thereby, work is not always more than the change of Gibbs free energy to make a nonspontaneous reaction occur.

Keywords—hydrogen; electric energy; enthalpy; Gibbs free energy

I. INTRODUCTION

Gibbs free energy (GFE) is an endorsement of the second law of thermodynamic. It is technically used to identify the direction of a change and to calculate the reaction equilibriums [1, 2]; additional to analyze the absorption ability between the absorbent and solutes and to analyze the solvation tendency of solutes in a solvent [3, 4]. Gibbs free energy determination formula (GFEDF, $\Delta G \leq W_o$) is technically applied to quantify the minimum work for a change [5]. According to GFEDF, the absolute value of work released to environment should be less than (or equivalent to) the absolute value of the change of Gibbs free energy for a spontaneous or reversible reaction; and the work achieved from outside environment should be more than the change of Gibbs free energy for a nonspontaneous reaction.

Hydrogen fuel is a kind of clean energy that can be generated from water by utilization of solar energy [6-8]. Hydrogen fuel can be generated by photo catalyzing water splitting and thermochemical water splitting cycle [9, 10, 11]. For instance, Yin et al. [12] carried experiment on water splitting for hydrogen and oxygen evolution used Bi₃TiNbO₉ nanosheets. Liu et al. [13] designed cocatalyst loading position for photocatalytic water splitting in electrolyte solutions for hydrogen fuel. Zhao et al. [14] prepared Al-Ca master alloy and used it as catalyst for water splitting to generate hydrogen fuel. Chalcogens doped BaTiO₃ was prepared for visible light photocatalytic hydrogen production from water splitting. The

Chalcogens doped BaTiO₃ can significantly decrease the E_g of BaTiO₃, and especially true for the larger concentration of the dopant [15].

Instead of electric energy, those methods utilize heat and solar energy to generate hydrogen fuel [16-18]. Where, there is not work consumed for hydrogen fuel generation; and thereby, the work from outside environment is less than the change of Gibbs free energy in a nonspontaneous reaction [19, 20], contracting to GFEDF [21, 22, 23]. Therefore, further reinvestigate GFEDF in nonspontaneous reactions by theoretical analysis.

II. METHODS AND MATERIALS

A. Investigating the Values of “ $\Delta S - Q/T$ ” under Different Conditions

The values of $\Delta S - Q/T$ under different conditions are investigated by theoretical deduction, based on a hypothesis that it needs a sum of heat for entropy change (Q_s); which is equivalent to the multiplying of absolute temperature and entropy change, expressed as:

$$Q_s = T \Delta S. \quad (1)$$

B. Investigating the Relationships between Work and the Change of Gibbs Free Energy under Different Conditions

The relationships between work and the change of Gibbs free energy under different conditions are investigated by theoretical analysis and mathematical reasoning under different situations, based on the values of “ $\Delta S - Q/T$ ” under different conditions.

C. Verifying the Result Contracting to GFEDF

The result contracting to GFEDF is verified through examining that the final result of “ $\Delta G > W_o$ ” in nonspontaneous reactions meets the facts.

III. RESULTS

A. The Values of " $\Delta S - Q/T$ " under Different Conditions

When the absorbed heat (or released heat) is less than the heat for entropy change ($Q < Q_s$), Equation (2) and (3) are obtained by comparison; indicating that the value of $\Delta S - Q/T$ is more than zero, consistent with the expression of the second law of thermodynamic (ESLT).

$$\Delta S - Q/T > \Delta S - Q_s/T = 0. \quad (2)$$

$$\Delta S - Q/T > 0. \quad (3)$$

When the absorbed heat (or released heat) is more than the heat for entropy change ($Q > Q_s$), Equation (4) and (5) are obtained by comparison; indicating that the value of $\Delta S - Q/T$ is less than zero, contracting to ESLT.

$$\Delta S - Q/T < \Delta S - Q_s/T = 0. \quad (4)$$

$$\Delta S - Q/T < 0. \quad (5)$$

B. The Relationships between Work and the Change of Gibbs Free Energy under Different Conditions

Based on the case contracting to GFEDF, the relationships between work and the change of Gibbs free energy under different conditions are investigated by theoretical analysis and mathematical reasoning under different situations.

Shown as in Fig. 1, when the absorbed heat (Q) from outside environment is less than the heat for entropy change (Qs) in a reaction; the value of $(\Delta S - Q/T)$ is more than zero, meeting ESLT. The value of $(\Delta S - Q/T)$ is more than zero results that the change of Gibbs free energy is less than the work ($\Delta G < W_o$), consistent with GFEDF. Therefore, GFEDF works with some reactions that the absorbed heat is less than the heat for entropy change.

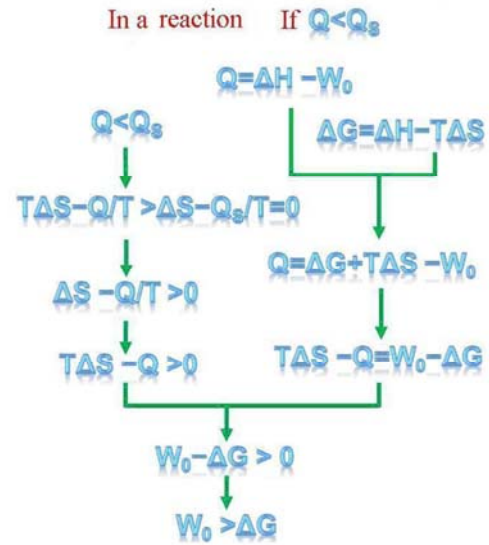


FIGURE I. DEDUCING SCHEME FOR THE RELATIONSHIP BETWEEN WORK AND GFE IN A REACTION WHEN $Q < Q_s$

Shown as in Fig. 2, when the absorbed heat (Q) from outside environment is more than the heat of entropy change (Q_s) in a reaction; the value of $(\Delta S - Q/T)$ is less than zero, contracting to ESLT. The value of $(\Delta S - Q/T)$ is less than zero results the change of Gibbs free energy is more than work ($\Delta G > W_o$), contracting to GFEDF. Therefore, GFEDF does not work with a reaction when the absorbed heat is more than the heat for entropy change.

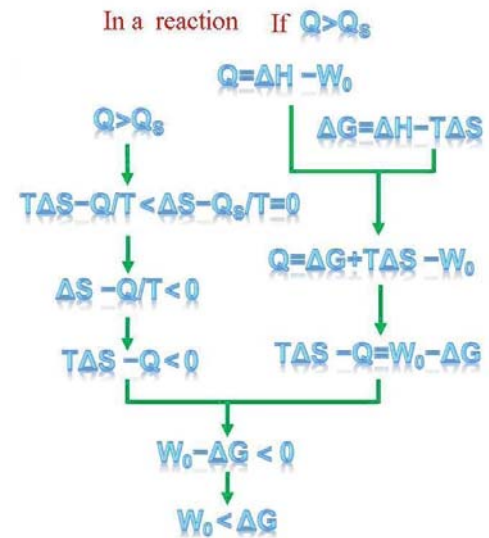


FIGURE II. DEDUCING SCHEME FOR THE RELATIONSHIP BETWEEN WORK AND GFE IN A REACTION WHEN $(Q > Q_s)$

C. Verification of the Result Contracting to GFEDF

The correctness of the result contracting to GFEDF is supported by the facts that: in the fields including artificial

photosynthesis [24, 25], photo catalyst reaction [19, 20, 26, 27], enzyme catalyzed reaction [28] and electrocatalytic reaction [29, 30], many nonspontaneous reactions can be achieved without work from outside environment. Instead of work, light and heat are the energy to make the reactions occur under catalyst. Taking water splitting as an example [27], it can occur under catalysts by photonic energy, consuming not any work from outside environment. Where, the work is zero, and the change of Gibbs free energy is greater than zero; getting the result of “ $\Delta G > W_0$ ” by comparison. Thereby, the correctness of the deducing result contracting to GFEDF is verified.

IV. DISCUSSIONS

A. Energy Conversions in Nonspontaneous Reactions

Based on the first law of thermodynamic, enough energy should be supplied to meet the change of enthalpy. The enough energy includes heat and work, expressed as Equation (6); and thereby both heat and work are the energy to make a reaction occur. Additionally, the change of Gibbs free energy is expressed as Equation (7). As assuming $Q_s = T \Delta S$, the change of enthalpy also can be expressed as Equation (8); which indicates that the change of enthalpy is the sum of the change of Gibbs free energy and the heat for entropy change.

$$\Delta H = Q + W_0. \quad (6)$$

$$\Delta G = \Delta H - T \Delta S. \quad (7)$$

$$\Delta H = \Delta G + Q_s. \quad (8)$$

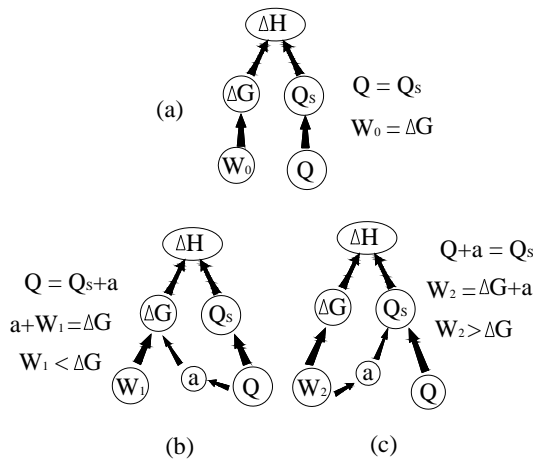


FIGURE III. ENERGY CONVERSION IN NONSPONTANEOUS REACTIONS

As shown in Fig.3 (a), when the absorbed heat is equivalent to the heat for entropy change; the absorbed heat is completely

consumed for entropy change, not any heat remaining. Thus, a sum of work is needed from outside environment for the change of Gibbs free energy; the sum of work is equivalent to the change of Gibbs free energy under the situation. As shown in Fig.3 (b), when the absorbed heat is more than the heat for entropy change, beside a part of heat is consumed for entropy change; there is another sum of heat remaining. The remaining heat acts as a part of energy to supply the change of Gibbs free energy. Thus, additional to the remaining heat, it needs a sum of work from outside environment to meet the change of Gibbs free energy. The sum of work is less than the change of Gibbs free energy under the situations, contracting to GFEDF; but consistent with the facts of the special case of photo catalyzing water splitting. As shown in Fig.3 (c), when the absorbed heat is less than the heat for entropy change, the absorbed heat is not enough for entropy change. Thus, beside the work for the change of Gibbs free energy, another sum of work is needed to act as a supplement of heat for entropy change. Thereby, the total work is more than the change of Gibbs free energy, consistent with GFEDF.

B. Acting as a Supplement of GFEDF

GFEDF is derived from the principle of Carnot cycle that only physical process involved. Therefore, it remains a huge space to researchers to study the relationship between the real work needed and the change of Gibbs free energy in special reactions. This paper discovers that the values of “ $\Delta S - Q/T$ ” is not always more than zero in chemical reactions, and work is not necessary more than the change of Gibbs free energy to make a nonspontaneous reaction occur. These new discoveries are some what different to the traditional explanation of GFEDF. Thereby, it might be an important supplement of GFEDF and even the second law of thermodynamic. These new discoveries can well explain the facts that some nonspontaneous reactions can be achieved without work or with a work less than the change of Gibbs free energy.

V. CONCLUSIONS

Based on the calculation and theoretical analysis, the conclusions are: (1) there is not electric energy and other form of work consumed in the reaction of photo catalyzing water splitting for hydrogen fuel. Hence, work from outside environment is less than the change of Gibbs free energy in the case, contracting to GFEDF. (2) GFEDF works with a reaction when absorbed heat is less than the heat of entropy change; GFEDF does not work with a reaction when absorbed heat is more than the heat for entropy change. Thereby, work is not always more than the change of Gibbs free energy to make a nonspontaneous reaction occur.

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REFERENCES

- [1] Shabbar, S, Janajreh I. Thermodynamic equilibrium analysis of coal gasification using Gibbs energy minimization method. *Energ Convers Manage* 2013; 65: 755–763.
- [2] Demidov D V, Mishin I V, Mikhailov M N. Gibbs free energy minimization as a way to optimize the combined steam and carbon dioxide reforming of methane. *Int J Hydrogen Energy* 2011; 36: 5941–5950.
- [3] Chashchikhin V, Rykova E, Bagaturyants A. Calculations of the Gibbs free energy of Adsorption of Some Small Molecules and Amino Acid Decomposition Products on MCM-41 Mesoporous Silica. *J. Phys. Chem. Lett.* 2013; 4 (14): 2298–2302.
- [4] Sergiievskiy V. P., Jeannmairret G, Levesque M., Borgis D. Fast computation of solvation free energies with molecular density functional theory: thermodynamic-ensemble partial molar volume corrections. *J. Phys. Chem. Lett.* 2014; 5 (11): 1935–1942.
- [5] Jin Y, Jin D, Zhuang Y. Physical chemistry. P300, second edition, Higher education press, Beijing, April 1998.
- [6] Mbah J, Weaver E, Srinivasan S, Krakow B, Wolan J, Goswami Y, et al. Low voltage H₂O electrolysis for enhanced hydrogen production. *Energy* 2010; 35: 5008–5012.
- [7] Yoong L S, Chong F K, Dutta K B. Development of copper-doped TiO₂ photocatalyst for hydrogen production under visible light. *Energy* 2009; 34: 1652–1661.
- [8] Li W, Zhu X, Cao Z, Wang W, Yang W. Mixed ionic-electronic conducting (MIEC) membranes for hydrogen production from water splitting. *Int J Hydrogen Energy* 2015; 40: 3452–3461.
- [9] Waskasi M M, Hashemianzadeh S M, Sarhangi O S M, Harzandi A P. Computational model of hydrogen production by Coumarin-dye-sensitized water splitting to absorb the visible light in a local electric field. *Energ Convers Manage* 2012, 62: 154–164.
- [10] Bhosale R R, Kumar A, Sutar P. Thermodynamic analysis of solar driven SnO₂/SnO based thermochemical water splitting cycle. *Energ Convers Manage* 135 (2017) 226–235.
- [11] Abanades S, Charvin P, Lemont F, Flamant G. Novel two-step SnO₂/SnO water-splitting cycle for solar thermochemical production of hydrogen. *Int J Hydrogen Energy* 2008, 33 (21): 6021–6030.
- [12] Yin X, Li X, Liu H, Gu W, Zou W, Zhu L, et al. Realizing selective water splitting hydrogen/oxygen evolution on ferroelectric Bi₃TiNbO₉ nanosheets. *Nano Energy* 2018, 49: 489–497.
- [13] Liu Y, Yang S, Zhang S, Wang H, Yu H, Cao Y, et al. Design of cocatalyst loading position for photocatalytic water splitting into hydrogen in electrolyte solutions. *Int. J. Hydrogen Energy* 2018, 43: 5551–5560
- [14] Zhao Z, Chen X, Hao M. Hydrogen generation by splitting water with Al-Ca alloy. *Energy* 2011, 36: 2782–2787.
- [15] Huang H C, Yang C L, Wang M S, Ma X G. Chalcogens doped BaTiO₃ for visible light photocatalytic hydrogen production from water splitting. *Spectrochim Acta Part A* 2019, 208: 65–72.
- [16] Fang W, Qin Z, Liu J, Wei Z, Jiang Z, Shangguan W. Photo-switchable pure water splitting under visible light over nano-Pt@P25 by recycling scattered photons. *Appl Catal B* 2018, 236: 140–146.
- [17] Gao W, Zhang W, Lu G. A two-pronged strategy to enhance visible-light-driven overall water splitting via visible-to-ultraviolet upconversion coupling with hydrogen-oxygen recombination inhibition. *Appl Catal B* 2017, 212: 23–31.
- [18] Chou LY, Liu R, He W, Geh N, Lin Y, Hou E Y F, et al. Direct oxygen and hydrogen production by photo water splitting using a robust bioinspired manganese-oxo oligomer complex/tungsten oxide catalytic system. *Int J hydrogen energy* 2012, 37: 8889–8896.
- [19] Liu M. Chen Y, Su J, Shi J, Wang X, Guo L. photocatalytic hydrogen production using twined nanocrystals and an unanchored NiS_x co-catalyst. *Nat energ* 2016; 1 (11), 16151, DOI: 10. 1038/nenergy.2016.151 (2016).
- [20] Wang Q, Hisatomi T, Jia Q, Tokudome H, Zhong M, Wang C, et al. Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nat mat* 2017; 15 (6): 611–615. DOI: 10.1038/nmat4589.
- [21] Han D, Gao C, Gao P. Physical chemistry. P47, first edition, Higher education press, Beijing, May 2005.
- [22] The editorial team of Wikipedia, Gibbs free energy, Wikipedia, 29 October 2015, online, https://en.wikipedia.org/wiki/Gibbs_free_energy.
- [23] Wang Z, Zhou Y. Physical chemistry. P107, first edition, Higher education press, Beijing, April 2005.
- [24] Nong G, Chen S, Xu Y, L Huang, Zou Q, et al. Artificial photosynthesis of oxalate and oxalate-based polymer by a photovoltaic reactor. *Sci Rep* 2014; 4: 3572, DOI: 10.1038/srep03572.
- [25] Nong G., Liu Y., Zhu H, Li Y, Li P. Energy analysis for an artificial tree generating polymer fuels from water and CO₂. *Energ Convers Manage* 2017; 151: 465–471.
- [26] Wakerley D W, Kuehnelt M F, Orchard K L, Ly K H, Rosse T E, Reisne E. Solar-driven reforming of lignocellulose to H₂ with a CdS/CdOx photocatalyst. *Nat energ* 2017, 2 (4), 17021, DOI: 10.1038/nenergy.2017.21.
- [27] Nong G, Li M, Chen Y, Zhou Z, Wang S. Simulation of energy conversion in a plant of photocatalysts water splitting for hydrogen fuel. *Energy* 2015; 81: 471–476.
- [28] Barber J. A mechanism for water splitting and oxygen production in photosynthesis, *Nat plan* 2017; 3 (4): 17041, DOI: 10.1038/nplants2017.41.
- [29] Nong G, Chen Y, Li M, Zhou Z. Generation of hydrogen free radicals from water for fuels by electric field induction. *Energ Convers Manage* 2015; 105: 545–551.
- [30] Schreier M, Héroguel F, Steier L, Ahmad S, Luterbacher J S, Mayer M T, et al. Solar conversion of CO₂ to CO using earth-abundant electrocatalysis atomic layer modification CuO. *Nat Energ* 2017, 2 (6), 17087, DOI: 10.1038/energy. 2017.87.