

THERMODYNAMICS OF WATER SPLITTING

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Summary

Since the water decomposition reaction has a large positive free energy change, exergy equal to ΔG , as well as thermal energy $T\Delta S$, should be supplied to shift the equilibrium of a water-splitting reaction.

1. Introduction: Fundamentals

The energy required for the endothermic reaction is equal to the enthalpy change of reaction, ΔH , and consists of two parts: a thermal energy requirement, ΔQ , and a useful work requirement, ΔW . In the case of a reversible chemical reaction at constant temperature and pressure the following conditions hold:

$$\Delta W = -\Delta G \quad (1)$$

$$T\Delta S = \Delta Q \quad (2)$$

Where ΔG and ΔS represent changes in Gibbs free energy and reaction entropy respectively. Thus, we write:

$$-\Delta H = -\Delta G - T\Delta S \quad (3)$$

The equilibrium constant K is related to the Gibbs free energy change ΔG for the chemical reaction as the follows:

$$\Delta G^\circ = -RT \ln K \quad (4)$$

With the decrease in ΔG the equilibrium constant of chemical reaction increases. At

$\Delta G = 0$ the value of K becomes unity. If ΔG has a negative value, it is possible that the chemical reaction proceeds spontaneously.

The temperature dependence of the equilibrium constant can be given as follows:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (5)$$

The sign of the derivative is seen to depend only on ΔH° . Therefore, for endothermic reactions, $\Delta H^\circ < 0$, K decreases with increasing T , while for endothermic reactions, $\Delta H^\circ > 0$, K increases with increasing T .

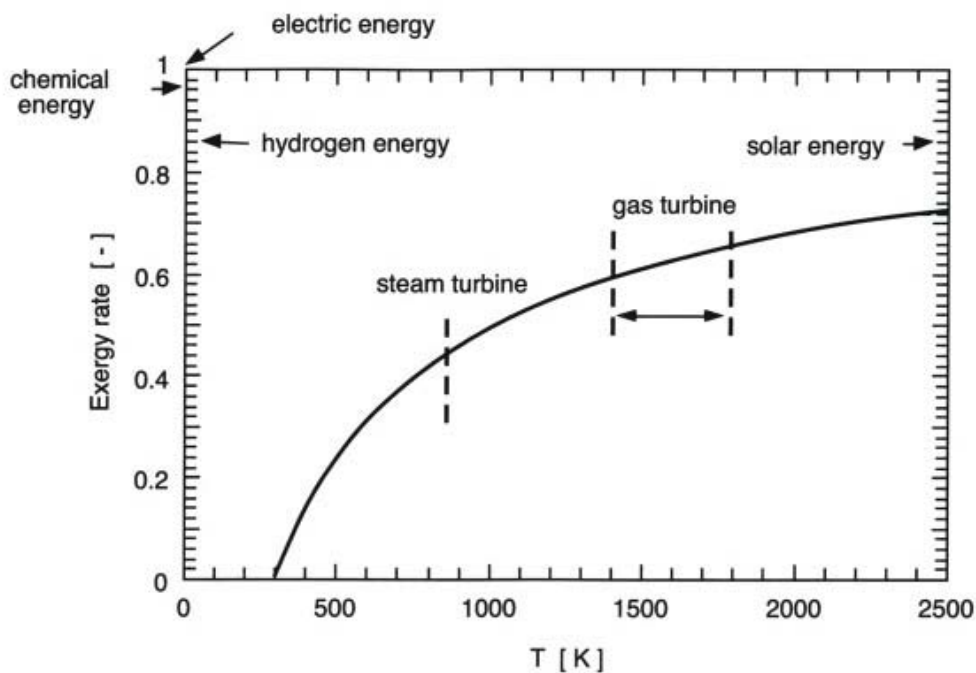


Figure 1. Exergy rate of air at 1 atm.

Exergy is a thermodynamic quantity, which encapsulates the energy and the entropy of a flow through a system and can be thought of as quantifying the thermodynamic quality of these flows. The thermodynamic definition of the exergy of a system is the maximum work that can be delivered by that system when it is brought into equilibrium with its environment. Both the physical and chemical exergies must be considered. Exergy ε can be expressed as:

$$\varepsilon = H - H_0 - T_0(S - S_0) \quad (6)$$

where T_0 is the temperature of the environment. The exergy rate is defined as the ratio of exergy to enthalpy. The exergy rate represents the quality of the energy. Figure 1 shows the exergy rate of thermal energy in the air. The exergy of electric energy and

mechanical energy is unity, while the thermal energy at 1000 °C and 2000 °C has an exergy rate of 0.5 and 0.7, respectively. The exergy loss is generated throughout the process by the irreversibility. Hydrogen has a relatively low exergy rate (0.83), while the exergy rate of conventional fuels ranges from 0.92 to 0.96. Therefore, hydrogen combustion can reduce the exergy loss in an irreversible combustion process.

Hydrogen is produced by direct water decomposition as:



Supposing that water is initially in the gas phase, the standard thermodynamic functions are as follows:

$$\Delta H^\circ = 241.93 \text{ kJ/mol} \quad (8)$$

$$\Delta G^\circ = 228.71 \text{ kJ/mol} \quad (9)$$

$$\Delta S^\circ = 44.333 \text{ kJ/mol} \cdot \text{K} \quad (10)$$

$$\Delta C_p = 9.68 \text{ kJ/mol} \cdot \text{K} \quad (11)$$

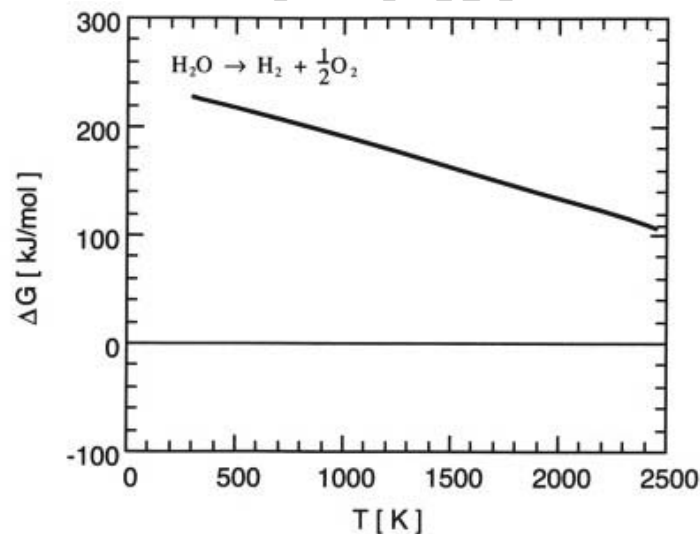


Figure 2. ΔG - T diagram of water splitting.

Because of the endothermic reaction the energy that is equal to ΔH should be provided to split water into hydrogen and oxygen; ΔG as a useful work and $T\Delta S$ as a thermal energy. The $\Delta G - T$ diagram for the water splitting reaction is shown in Figure 2. The water decomposition reaction has a large positive free energy change and a small positive entropy change, as can be seen in Figure 2. Thus, the equilibrium for the reaction is unfavorable for hydrogen production. The water decomposition reaction is

non-spontaneous except at higher temperature than turning temperature (4500 K). Exergy equal to ΔG as well as thermal energy $T\Delta S$ is required to be supplied to the reaction system. In direct water decomposition, the useful work for the separation of product (hydrogen or oxygen) is supplied to shift the reaction equilibrium.

The dissociation of water proceeds in two steps:

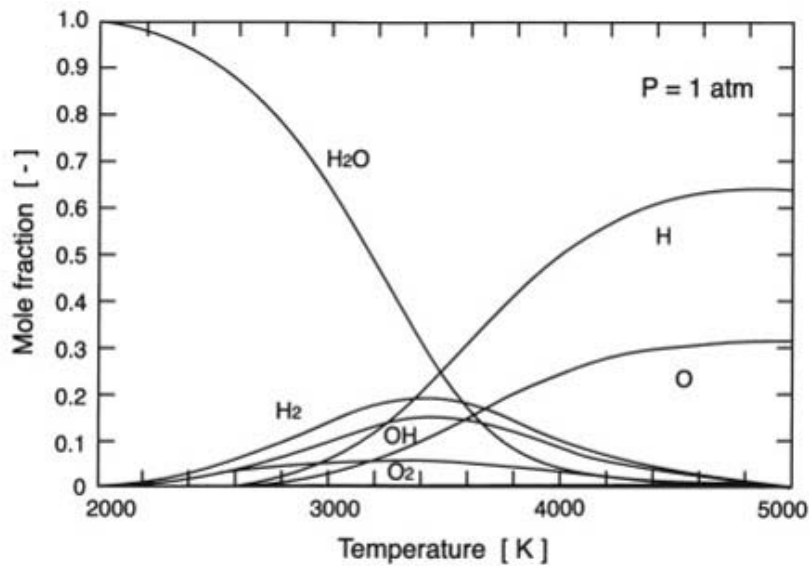
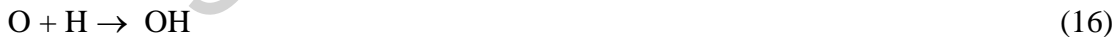


Figure 3. Equilibrium composition of dissociated water vapour.

The recombination of H and O atoms produces molecules of hydrogen and oxygen and OH as follows:



The theoretical mole fractions of six components (H_2O , H_2 , H , O_2 , O , OH) for a total pressure of 1 atm are shown in Figure 3. It is seen that about 35% of water vapor dissociates at the temperature of 3000 K, and that the mole fractions of atoms of hydrogen and oxygen are dominant in the reaction system at temperatures higher than around 3500 K. Primary heat can be used in the water decomposition process only if the temperature level is very high (at least 2500 K). This direct thermal decomposition of water is not feasible at an industrial level with present technology.

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Biographical Sketch

Atsushi Tsutsumi, born November 2, 1956, in Japan, is an Associate Professor of Chemical System Engineering at University of Tokyo. He received his Doctorate of Engineering from the University of Tokyo in 1986. He has been active in research on innovative thermochemical energy technology and nonlinear dynamics and chaos scale-up methodology development for multi-phase reactors for the last ten years. He has published over 70 scientific publications and 100 proceedings in international journals and conferences.