

POSSIBLE WAYS OF PRODUCING HYDROGEN AND OXYGEN FROM WATER FOR THE PURPOSES OF A HYDROGEN ECONOMY

V. S. Bagotskii, Yu. M. Vol'fkovich,
Yu. L. Golin, A. N. Suvorov,
and Yu. S. Sherstobitov

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Possible ways of producing hydrogen and oxygen in closed cycles from water are discussed. An attempt is made to systematically arrange the different directions of exploratory work by grouping them together according to the methods used to produce oxygen. The utilization of electrochemical reactions in chemical power sources and electrolyzers is advocated for certain cycle steps. Thermodynamic criteria for selecting the most promising cycles are presented.

The chances of the so-called hydrogen economy strongly depend on man's ability to produce hydrogen and oxygen from water utilizing the energy of nuclear reactors without the expenditure of chemicals and discharge of waste materials. Any solution of this problem would vastly expand the range of application of fuel cells, and already for this reason should not be overlooked by electrochemists. It must be stressed, however, that in contrast to installations for direct energy conversion, any fuel cell-regenerator system is subject to the limitations imposed by Carnot's theorem; for a number of simple cases these limitations have been discussed in detail in [1]. It is the aim of the present communication to discuss the more complicated cases of multistep cycles, to assess the latitude of advance of the exploratory work, and to classify possible solutions of the problem according to some fundamental features, so as to facilitate the forecasting of results in the general direction examined here.

Questions of producing hydrogen and oxygen from water occupied D. I. Mendeleev as early as 1871 [2]. In his "Principles of Chemistry" he formulated the chief difficulties confronting workers in this field and predicted certain stages of cycles which today are regarded as highly promising. Amplifying these statements and making use of up-to-date handbook and literature data [1-15] we compiled a table of cycles where these cycles are divided into classes, each class being characterized by one of the following methods of producing oxygen: 1) thermal decomposition of the oxides of metals and metalloids; 2) electrochemical reaction; 3) decomposition of water by halogens; 4) sulfiding roasting of oxides; and 5) chloridizing roasting of oxides.

The list of classes does not claim to be complete, but it must be noted that by far not all the methods of producing oxygen which are known today are useful in solving the problem formulated above.* A code has been attached to each cycle; its first digit states the class, the other two digits identify the particular realization.

The conditions under which the reactions are run are indicated above the reaction equations: CPS for chemical power source, T for the supply of heat, and E for the supply of electrical energy; reactions driven by radiation are underscored by dotted lines; for most reactions the calculating temperature (in K) is stated; electrochemical reactions are followed by an indication of the voltage for reversible occurrence. Some cycles are followed by references to literature sources which directly or indirectly confirm that the cycle as a whole or particular steps of the cycle can be realized.

Some readers will possibly regard it as a debatable point that processes requiring the supply of electrical energy have been included into the table. The following arguments can be cited in defense of our position. A number of authors advocate, for the purposes of a hydrogen economy, the production of hydrogen by water electrolysis. A voltage of 1.23 V is required to conduct this process reversibly (at 298 K). In actual cells

* Examples belonging to this category of methods are the decomposition of potassium perchlorate, the decomposition of hydrogen peroxide, and the reaction of silver fluoride with water.

TABLE 1. Cycles of Chemical and Electrochemical Reactions for the Production of Hydrogen and Oxygen from Water

Cycle code	Reactions	$\Sigma \Delta Z_T^0$	T_{max} (K)	$(\Sigma \Delta Z^0)_{comp}$	Place of the cycles according to the criteria stated in columns		
					3	4	5
1	2	3	4	5	6	7	8
1.1	$SO_3 \xrightarrow{T} SO_2 + \frac{1}{2} O_2$; $H_2SO_3 \div H_2O \xrightarrow{E} H_2 + H_2SO_4(0,17V)$; $H_2SO_4 \xrightarrow{T} H_2O + SO_3(900 K)$; $SO_2 \div H_2O = H_2SO_3$	—	—	—	—	—	—
1.2	$3Mn_2O_3 \xrightarrow{T} 2Mn_2O_4 + \frac{1}{2} O_2(1100 K)$; $2Mn_2O_4 + H_2O \xrightarrow{E} 3Mn_2O_3(0,69 V)$	—36,1	—	—35,3	—	—	—
1.3	$SnO_2 \xrightarrow{T} SnO + \frac{1}{2} O_2(2500 K)$; $Pb \div H_2O \xrightarrow{E} PbO + H_2(0,25V)[6]$; $PbO \div Sn \xrightarrow{E} Pb \div SnO$; $2SnO = SnO_2 + Sn [6]$ CPS (0,36 V)	—65,2	2500	—17,9	4	8	8
1.4	$Ag_2O \xrightarrow{T} 2Ag + \frac{1}{2} O_2(1400 K)$; $2Ag + H_2O \xrightarrow{E} Ag_2O + H_2(1,17 V) [2, 9]$	—15,9	—	—10,3	—	—	—
1.5	$Pb_2O_4 \xrightarrow{T} PbO + \frac{1}{2} O_2(1000 K)$; $3PbO + H_2O \xrightarrow{E} Pb_2O_4 + H_2(0,97 V *)$	—15,2	—	—15,2	—	—	—
1.6	$2Cu(OH)_2 \xrightarrow{T} Cu_2O + 2H_2O + \frac{1}{2} O_2$; $Cu_2O + 3H_2O \xrightarrow{E} 2Cu(OH)_2 + H_2(0,75V)$	—	—	—	—	—	—
1.7	$HgO \xrightarrow{T} Hg + \frac{1}{2} O_2(600 K)$; $2HBr + Hg \xrightarrow{T} HgBr_2 + H_2$; $CaBr_2 + H_2O = Ca(OH)_2 + 2HBr$; $HBr_2 + Ca(OH)_2 = CaBr_2 + H_2O + HgO [4]$	—17,3	—	—25,3	—	—	—
1.8	$3Fe_2O_3 \xrightarrow{T} 2Fe_3O_4 + \frac{1}{2} O_2(1770 K)$; $\frac{1}{2} C + H_2O = \frac{1}{2} CO_2 + H_2(1000 K)$; $\frac{1}{2} CO_2 + 2Fe_3O_4 = \frac{1}{2} C + 3Fe_2O_3 [7, 10]$	—63,7	1770	—35,0	7	6	6
2.1	$3Fe_2O_3 \xrightarrow{E} 2Fe_3O_4 + \frac{1}{2} O_2 (V > 1,0 V)$; $\frac{1}{2} C + H_2O \xrightarrow{T} \frac{1}{2} CO_2 + H_2(1000 K)$; $\frac{1}{2} CO_2 + 2Fe_3O_4 = \frac{1}{2} C + 3Fe_2O_3 [7]$	—12,3	—	—12,3	—	—	—
2.2	$2CuCl + H_2O \xrightarrow{E} 2Cu + 2HCl + \frac{1}{2} O_2(1,09 V)$; $2Cu + 2HCl = 2CuCl + H_2 [3]$	0	—	—19,5	—	—	—

TABLE 1 (cont'd)

Cycle code	Reactions	$\Sigma \Delta Z_T^0$	$T_{\max}$ (K)	$(\Sigma \Delta Z_T^0)_{\text{comp}}$	Place of the cycles according to the criteria stated in columns		
					3	4	5
1	2	3	4	5	6	7	8
3.1.1	$\text{Cl}_2 + \text{H}_2\text{O} \xrightarrow{T} 2\text{HCl} + \frac{1}{2} \text{O}_2$ (1000 K); $2\text{Ag} + 2\text{HCl} = 2\text{AgCl} + \text{H}_2$ (800 K) $2\text{AgCl} = 2\text{Ag} + \text{Cl}_2$	-57,3	1000	-57,3	8	3	4
3.1.2	$\text{Cl}_2 + \text{H}_2\text{O} \xrightarrow{T} 2\text{HCl} + \frac{1}{2} \text{O}_2$; $\text{SnCl}_2 + 2\text{HCl} \xrightarrow{E} \text{SnCl}_4 + \text{H}_2$ ($V > 0,15$ V); $\text{SnCl}_4 = \text{SnCl}_2 + \text{Cl}_2$ (1970 K)	-64,9	1970	-30,6	5	7	7
3.1.3	$\text{Cl}_2 + \text{H}_2\text{O} \xrightarrow{T} 2\text{HCl} + \frac{1}{2} \text{O}_2$ †; $\text{Fe} + 2\text{HCl} \xrightarrow{\text{CPS}(0,44\text{V})} \text{FeCl}_2 + \text{H}_2$; $3\text{FeCl}_2 \xrightarrow{E} \text{Fe} + 2\text{FeCl}_3$ (1,2 V); $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ [6]	-13,4	—	-13,4	—	—	—
3.1.4	$2\text{Cu} + 2\text{HCl} \xrightarrow{T} 2\text{CuCl} + \text{H}_2$; $2\text{CuCl}_2 = 2\text{CuCl} + \text{Cl}_2$; $4\text{CuCl} + 4\text{HCl} = 2\text{Cu} + 2\text{CuR}_2 + 4\text{HCl}$; $2\text{CuR}_2 + 4\text{HCl} = 4\text{HR} + 2\text{CuCl}_2$; $\text{Cl}_2 + \frac{1}{2} \text{Mg}(\text{OH})_2 = \frac{1}{2} \text{Mg}(\text{OCl})_2 + \text{HCl}$; $\frac{1}{2} \text{Mg}(\text{OH})_2 + \text{HCl} = \frac{1}{2} \text{MgCl}_2 + \text{H}_2\text{O}$; $\frac{1}{2} \text{Mg}(\text{OCl})_2 = \frac{1}{2} \text{MgCl}_2 + \frac{1}{2} \text{O}_2$; $\text{MgCl}_2 + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{HCl}$ [1]	—	—	—	—	—	—
3.2	$\text{Br}_2 + \text{H}_2\text{O} = 2\text{HBr} + \frac{1}{2} \text{O}_2$; $2\text{Ag} + 2\text{HBr} \xrightarrow{E} 2\text{AgBr} + \text{H}_2$ ($V > 0,03$ B); $2\text{AgBr} = 2\text{Ag} + \text{Br}_2$	-55,3	—	—	—	—	—
3.3.1	$\text{I}_2 + \text{H}_2\text{O} = 2\text{HI} + \frac{1}{2} \text{O}_2$; $\text{Cr} + 2\text{HI} = \text{CrI}_2 + \text{H}_2$; $\text{CrI}_2 = \text{Cr} + \text{I}_2$ (1070 K; 0,55 V)	-75	1070	-74,3	2	4	2
3.3.2	$\text{I}_2 + \text{H}_2\text{O} = 2\text{HI} + \frac{1}{2} \text{O}_2$; $2\text{Ag} + 2\text{HI} \xrightarrow{E} 2\text{AgI} + \text{H}_2$; $2\text{AgI} = 2\text{Ag} + \text{I}_2$ (1000 K; 0,41 V)	-69,9	1000	-69,9	3	2	3
3.3.3	$\text{I}_2 + \text{H}_2\text{O} = 2\text{HI} + \frac{1}{2} \text{O}_2$; $2\text{Cu} + 2\text{HI} \xrightarrow{E} 2\text{CuI} + \text{H}_2$ (620 K); $2\text{CuI} = 2\text{Cu} + \text{I}_2$ (1170 K; 0,36 V)	-64,4	1170	-49,9	6	5	5
3.3.4	$\text{I}_2 + \text{H}_2\text{O} = 2\text{HI} + \frac{1}{2} \text{O}_2$; $2\text{CrI}_2 + 2\text{HI} = \text{H}_2 + 2\text{CrI}_3$; $2\text{CrI}_3 = 2\text{CrI}_2 + \text{I}_2$ (1100 K)	—	—	—	—	—	—
4	$2\text{CuO} + \text{H}_2\text{S} \xrightarrow{T} \text{Cu}_2\text{S} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$ ‡; $2\text{CuCl} + 2\text{H}_2\text{O} \xrightarrow{E} 2\text{CuO} + 2\text{HCl} + \text{H}_2$ (0,62 V at 298 K) $\text{Cu}_2\text{S} + 2\text{HCl} = \text{H}_2\text{S} + 2\text{CuCl}$	-75,2	1000	-75,2	1	1	1
5	$\text{CuO} + \text{Cl}_2 = \text{CuCl}_2 + \frac{1}{2} \text{O}_2$ *; $\text{Cu} + \text{H}_2\text{O} \xrightarrow{E} \text{CuO} + \text{H}_2$ ($V > 0,57$ V); $\text{CuCl}_2 = \text{Cu} + \text{Cl}_2$ (870 K; 0,5 V)	-20	—	-23	—	—	—

Note: V) Voltage.

* At a temperature of 298 K, $E = 0.79$ V.

† The reaction can be run in a CPS (0.13 V).

‡ $\log K_p = 1 - (350/T) + 6.26$.** $\log K_p = 1.12$ ($T = 700$ K); $\log K_p = 0$ ($T = 1000$ K).

the voltage is substantially higher than this figure, particularly because of the large oxygen evolution overpotential. However, the simplicity of organization of the process proves to be the dominating factor in this case. Similarly, electrochemical steps when used in certain complicated cycles will: i) decrease the total number of steps; ii) simplify their technical implementation; iii) decrease the operating temperature; and iv) make reactions feasible which cannot be carried out in conventional ways. It is known, e.g., that the high dissociation temperature of Fe_2O_3 (1800 K) interferes with a practical realization of cycle 1.8. But the theoretical emf of the corresponding reaction falls off quite rapidly with increasing temperature (0.98 V at 298 K, 0.65 V at 770 K, and 0.443 V at 1070 K). Electrolysis at 800 K may be easier to practice than thermal dissociation at 1800 K.

The cycles presented in Table 1 contain different numbers of steps which differ drastically in the equilibrium constants, rate constants, optimum temperatures, and other parameters, so that it is difficult to unambiguously select the most promising versions. It is proposed in a first stage to use as the criterion the

overall change $\sum_j \Delta Z_{T_j}^0$ of the isobaric-isothermal potential of all reactions of the cycle* at their individual

temperatures T_j , including the reaction of water synthesis for which $\Delta Z_{298}^0 = -56.7 \text{ kcal/mole}$. Assuming cheap thermal energy to be available in the future from nuclear or thermonuclear reactors one can omit from this sum any expenditure for the heating (or cooling) of the reactants. The cycle for which the above criterion has the smallest (algebraic) value must be regarded as the most preferable one. The cycles fall into three groups, according to the value of this criterion (see Table 1, column 3). The first group, that of the "ideal" cycles, takes up the versions for which $\sum \Delta Z_{T_j}^0 < -56.7 \text{ kcal/mole}$. When this condition is met (within the assumptions mentioned above, of course), this implies that the reaction of water decomposition proceeds spontaneously, i.e., water as it were ceases to be a stable compound. The codes of cycles of this group are underscored with a double line. The codes of cycles for which the above criterion is between about 0 and -56.7 kcal/mole are underscored with a single line. These cycles can be called "favorable," in contrast to the cycles of the third group which have values of $\sum \Delta Z_{T_j}^0$ close to zero ("possible" cycles).

The features of the group of ideal cycles demand more detailed comment. Column 6 of Table 1 indicates the placement of the cycles of this group according to the value of $\sum \Delta Z_{T_j}^0$ (the most preferable cycles take the first places). It can be seen from the table that the cycles resting on a utilization of sulfiding roasting of cupric oxide and of water decomposition by iodine can be regarded as the most profitable ones. It can also be seen that this group consists chiefly of cycles of the third class. The cycles contained in the group presently considered can also be arranged in the order of decreasing maximum temperature (see columns 4 and 7 of the table), which allows the chances of their being used in present-day reactors to be estimated.

But the most correct way of comparing the cycles appears to be that using the criterion of $(\sum \Delta Z_{T_j}^0)_{\text{comp}}$ (Table 1, column 5); this is computed just like the first criterion, except that for all the high-temperature reactions, $\Delta Z_{T_j}^0$ is calculated for a temperature of 1000 K, which today is of the greatest practical interest. The placement of the cycles according to the value of this criterion is basically the same as that obtained when comparing the maximum temperatures (cf. columns 7 and 8).

According to the full set of criteria, cycles 4, 3.3.1, and 3.3.2 (the copper-chloride-sulfide, the iodine-chromium, and the iodine-silver cycle) are revealed as the most preferable ones. This provides certain arguments for regarding them as in principle more promising than the cycle 1.7, which is under development at the present time [4]. Also worth mentioning are the chlorine-silver and the iodine-copper cycle (3.1.1 and 3.3.3). The iron-carbon cycle (1.8) following them already enjoys an adequate reputation [7].

It must be stressed in conclusion that it will only become possible to make a definite selection of a particular version of hydrogen and oxygen production from water after careful analysis of data on the reaction kinetics and of engineering and economic questions.

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* In the following outline this sum will be written as $\sum \Delta Z_{T_j}^0$.

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ESTIMATE OF THE PERCOLATION PROBLEM

VII. THE HONEYCOMB LATTICE OF BONDS: ESTIMATE OF THE PERCOLATION THRESHOLD

Yu. G. Chirkov

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It is shown how by estimating upper and lower values of the percolation threshold one can gradually decrease the interval within which the percolation threshold of the honeycomb lattice of bonds is located. These calculations rest on an application of the asymptotic method of estimating percolation thresholds and of the diagram technique with which one can calculate the percolation probability of two-terminal networks.

The percolation behavior of lattices of bonds in the percolation point (percolation threshold) is qualitatively special in character: here (and only here) does the lattice of bonds become similar to pseudolattices (the Bethe lattice, cacti) [1-3]. This hypothesis was made the basis of percolation-threshold calculations using "percolation graphs" [3] and also of the asymptotic method of percolation-threshold estimates with which it had been possible to obtain accurate values for the percolation points of the square and triangular lattice of bonds [1]. We shall show how by using the same ideas one can also estimate the percolation point for the honeycomb lattice of bonds with a high (apparently, with any) degree of accuracy.

A site wetted by the fluid which, in a honeycomb lattice, is asymptotically far away from the source site, and located in the n -th layer of sites, can be connected with the $(n+1)$ -th layer of sites, either by two bonds or (with equal probability) by one bond [1] (Fig. 1).

As in [1], we shall estimate the value of the percolation point using the relation

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