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THE COPPER–CHLORINE THERMOCHEMICAL CYCLE OF WATER SPLITTING FOR HYDROGEN PRODUCTION

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ABSTRACT

Copper dissolves in hydrochloric acid with hydrogen evolution and the formation of cuprous chloride. The latter disproportionates into metallic copper and cupric chloride which acts as a source of chlorine in the next reaction. Chlorine reacts with magnesium hydroxide at 80 °C to form magnesium chloride, oxygen, and 1 mol of water. In the next reaction 2 mol of water react with magnesium chloride to regenerate magnesium hydroxide and 2 mol of hydrogen chloride which can be recycled. The reactions were studied thermodynamically and experimentally, and optimum working conditions were established. Reference is made to computer programs for kinetic studies and to X-ray diffraction for the identification of reaction products.

INTRODUCTION

The question of manufacturing clean fuels for the future prompted attention towards the production of hydrogen. Among the various routes to this goal is the design and performance of thermochemical cycles for water splitting. The method involves carrying out a set of chemical reactions, the net result of which is the dissociation of a water molecule, but the working chemicals must be capable of regeneration. This is to bring the free energy, ΔG, of the direct thermal decomposition of water to a practical value. The reactions are initiated at temperatures which maximize the effect of a positive entropy change, ΔS, and minimize those of a negative ΔS. The object of establishing a successful thermochemical cycle is a challenge for chemists, engineers and economists. Of 54 reaction sequences, only a few are still thought to have any chance for future industrial uses [1].

The copper–chlorine thermochemical cycle [1,2] involves the following set

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of reactions

$$2\ Cu_{(s)} + HCl \overset{100\,^{\circ}C}{\rightarrow} 2\ CuCl + H_2 \tag{1}$$

$$2\ CuCl \overset{30-100\,^{\circ}C}{\rightarrow} CuCl_2 + Cu \tag{2}$$

$$CuCl_2 \overset{500\,^{\circ}C}{\rightarrow} CuCl + 0.5\ Cl_2 \tag{3}$$

$$Cl_2 + Mg(OH)_2 \overset{80\,^{\circ}C}{\rightarrow} MgCl_2 + H_2O + 0.5\ O_2 \tag{4}$$

$$MgCl_2 + 2\ H_2O \overset{350\,^{\circ}C}{\rightarrow} Mg(OH)_2 + 2\ HCl \tag{5}$$

Dokiya and Kotera [3] proposed a related hybrid cycle in which two main reactions are involved

$$2\ CuCl + 2\ HCl \rightarrow H_2 + 2\ CuCl_2 \tag{6}$$

$$2\ CuCl_2 + H_2O \rightarrow 2\ CuCl + 2\ HCl + 0.5\ O_2 \tag{7}$$

The first reaction (6) is a room temperature electrolysis. The second reaction (7) is a thermal one and can be thought of as the net of two reactions, namely, reaction (3) and the following

$$Cl_2 + H_2O \rightarrow 2\ HCl + 0.5\ O_2 \tag{8}$$

The authors [3] studied the electrolysis step thoroughly and the thermal one in brief.

The aim of the present work is to investigate the thermodynamic and experimental aspects of the copper–chlorine cycle. This choice is based on the availability of the materials, Cu, HCl, and $Mg(OH)_2$ at relatively low prices. The system does not involve difficult separation processes for hydrogen other than the removal of moisture which accompanies the gas in the the first reaction. Separation can be easily performed by condensation and excess heat is absorbed by use of a heat exchanger [4]. Further, the highest reaction temperature required within the cycle is 500 °C for the decomposition of solid cupric chloride. The latter makes the use of solar energy heaters [5] possible.

EXPERIMENTAL

Apparatus

High temperature studies (~ 500 °C) were carried out in a dual cylindrical furnace (Analis Instrument Scientific, Belgium). The furnace was calibrated with the aid of a Comark digital thermometer fitted with the mineral probe of an NiCr/NiAl thermocouple. The sample was placed in a cylindrical quartz reactor with quickfit ends. A segment at the centre of the reactor was separated by quartz discs with a 2.5 mm hole and packed with quartz balls (3-mm diameter; cf. Fig. 3).

Thermogravimetric measurements (TG) were carried out on a TA 500 Heraeus thermal analyser. The X-ray diffraction patterns were recorded on a Siemens D500 diffractometer. The rest of the apparatus was made of pyrex glass.

Materials

All chemicals were of analytical reagent grade. Doubly-distilled water was used for dilution and steam generation.

RESULTS AND DISCUSSION

The free energy of the reactions involved in the cycle have been calculated using the thermodynamic values of the enthalpy and entropy change of the formation of the basic compounds quoted from Kubascheweski and Alcock [6]. The plots of the free energy changes as a function of temperature are shown in Fig. 1. The curves 1, 2 and 3 refer to reactions (3), (4), and (5),

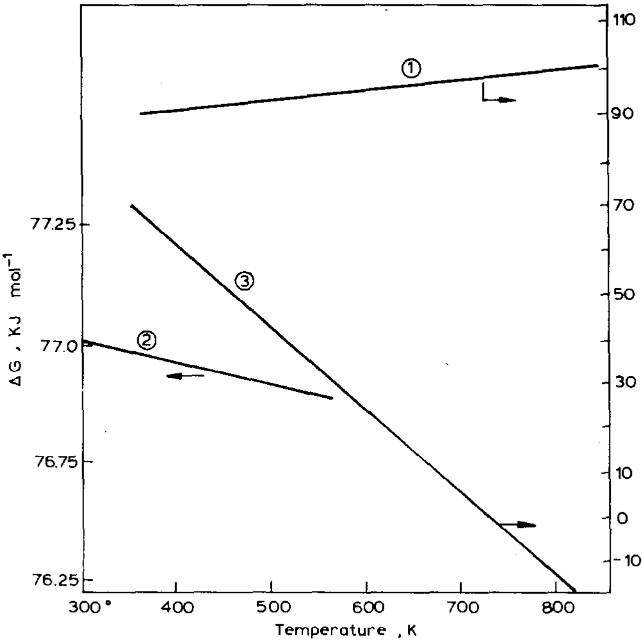

Fig. 1. Free energy change as a function of temperature for (1) reaction (3); (2) reaction (4); and (3) reaction (5).

respectively. It is clear that reaction (3) is endothermic. The reaction is more favoured at low temperatures (500–600 K) but the thermal decomposition of cupric chloride is relatively slow at this range of temperature (see below). Reaction (4) is thermodynamically possible even at room temperature (~ 300 K). However some heat is necessary for initiation. The spontaneity of reaction (5) is highly dependent on the temperature as seen from the slope of the plot of ΔG against temperature. High temperatures (~ 800 K) must not be used, despite the fact that the free energy change attains negative values because of the thermal stability of magnesium chloride [7] and the magnesium hydroxide [8].

Reaction (1), hydrogen production

Copper powder was allowed to react with hydrochloric acid (37%) under reflux. The outlet of the condenser was connected to an aqueous sodium hydroxide trap and a water trap to remove small amounts of hydrogen chloride that might evolve from the reaction mixture. The purified gas is collected over water in preparation for analysis. The system was purged with nitrogen gas prior to the addition of the acid. The system was kept at 100 °C. The evolution of the gas was slow. At 120 °C the reaction proceeded rapidly and the hydrogen content of the gas produced increased accordingly. The experimental data are given in Table 1. The experimental set up is schematically shown in Fig. 2.

Reaction (2), partial regeneration of copper

When metallic copper was completely consumed, the excess hydrochloric acid solution was washed and filtered off. The precipitated cuprous chloride

TABLE 1

Experimental parameters and results of several runs of reaction (1)

Exp. No.	Acid vol. [a] (ml)	Copper weight (g)	Time [b] (min)	Temperature range (°C)	Hydrogen vol. [c] (ml)	Efficiency [d] (%)
3	10	1.0	25	120–130	135.6	77.0
4	10	3.0	60	100–140	96.8	55.0
5	17	1.0	45	100–140	133.6	75.9
7	10	1.0	15	100–110	101.7	55.9
8	10 [e]	0.5	30	100–140	ND [f]	—

[a] 37% concentration.

[b] Until evolution of gas ceases.

[c] At 25 °C corrected for water vapour pressure.

[d] Division of the volume of hydrogen collected by the theoretically predicted value.

[e] 9% concentration.

[f] Not detectable.

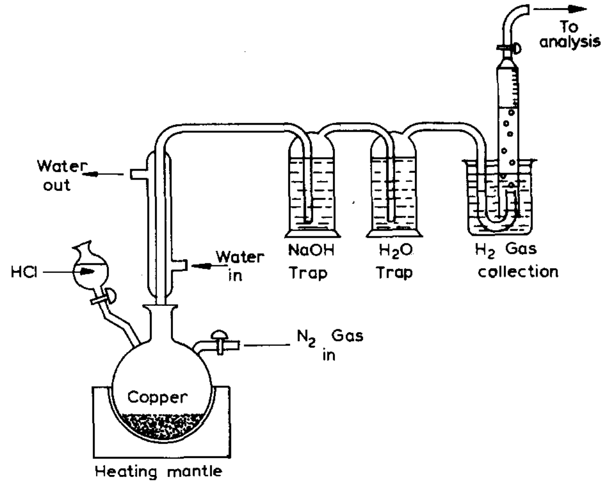

Fig. 2. Experimental apparatus used for reaction (1).

was washed with water. A slight excess of water was maintained above the precipitate and the heating was continued at 70–90 °C for a short interval. Copper lumps began to separate and the mother liquor turned blue with time. Water is essential for this reaction because it thermodynamically assists the disproportionation of cuprous into copper and cupric species by the enthalpy of solvation of cupric chloride. This is due to the positive values of the free energy corresponding to the conversion in the solid state [3] and the potential of the conversion

$$Cu + Cu^{2+} \rightarrow 2\ Cu^{+} \qquad (9)$$

which is −0.37 V [9].

Reaction (3), dechlorination of cupric chloride

The thermogravimetric (TG) curve of $CuCl_2 \cdot 2\ H_2O$ is illustrated in Fig. 3. Cupric chloride loses the water of hydration between 71 and 133 °C in one step. The transition into cuprous chloride begins slowly at 345 °C and the maximum rate of dechlorination was observed at 447 °C. The process is terminated at 521 °C where the product (CuCl) starts to sublime [7]. The TG curve does not show a horizontal plateau at the end of the dechlorination, i.e., the last stages of the reaction overlap with the sublimation of CuCl. The TG data presented in Fig. 3 have been used for the estimation of the reaction order, n, and activation energy, E_a, using the method of Coats and Redfern [10]. This method employs the following expressions

$$\ln\left[\frac{\ln(1-\alpha)}{T^2}\right] = \ln\frac{ZR}{E_a}\left(1-\frac{2RT}{E_a}\right) - \frac{E}{R}\frac{1}{T} \qquad (n = 1)$$

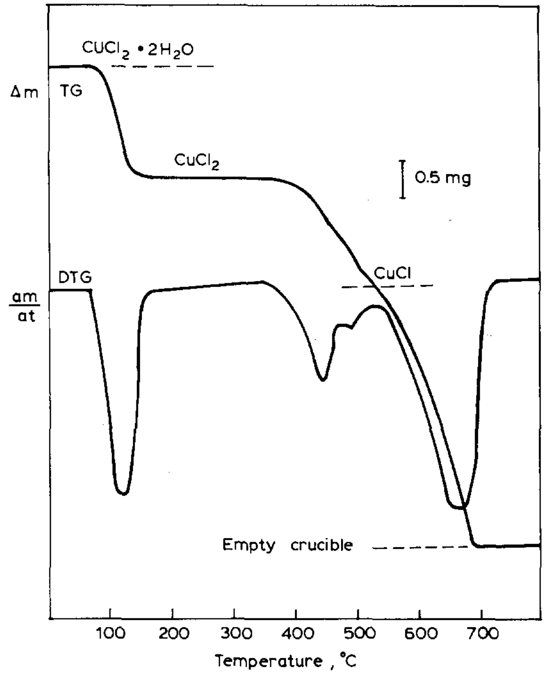

Fig. 3. TG and DTG curves of copper(II) chloride dihydrate.

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\frac{ZR}{E_a}\left(1-\frac{2RT}{E_a}\right)-\frac{E}{R}\frac{1}{T} \qquad (n \neq 1)$$

where α is the fraction decomposed; T is the absolute temperature; R is the gas constant (8.3 J mol^{-1} K^{-1}); and Z is the pre-exponential factor (s^{-1} mol^{-1}). Previously, n was changed by increments of 0.3 or 0.25 until the most linear plot was obtained which was used for the estimation of E_a and Z. A computer program was recently used by Barbooti and co-workers [11] to perform these tedious calculations, which plotted the f(α) values vs. $1/T$ using the relatively smaller increment of 0.01 of n values. The computerized method has been used here and the following kinetic parameters have been obtained: $n = 1.093$ and $E_a = 98.59$ kJ mol^{-1}, with a correlation coefficient of 0.99408.

The selection of the dechlorination temperature, therefore, is important and a value of 500 °C which has been recommended [2] is higher than necessary. This temperature is high enough to bring about the sublimation of CuCl which has to be recycled. Thus, it is recommended that a temperature range of 440–450 °C must be used.

Reaction (4), generation of oxygen

Chlorine gas was allowed to react with solid magnesium hydroxide in accordance with eqn. (4). Reactors of various sizes and geometries were tried until the design shown in Fig. 4 was reached. The design allows the immersion of the reactor in an oil bath to affect homogeneous heating. The reactor was packed with glass rings (3 mm thick) to ensure a high contact area of the flowing gas with the solid $Mg(OH)_2$ distributed within the reactor. The inlet of the reactor was plugged with glass wool and the upper surface of the reactant was covered with a 2-mm layer of glass wool. The oil bath guarantees a constant temperature throughout the experiment ($\pm 3°C$). At the end of each experiment the extent of the reaction was estimated by X-ray diffraction analysis of the solid product. The percentage of magnesium chloride present in the product gives a direct measure of the degree of the reaction after the passage of a stoichiometric amount of chlorine through the reactor. IR spectra of the solid product were used as a preliminary qualitative test. Chlorine was generated by the action of hydrochloric acid on manganese dioxide.

When chlorine was flowing naturally, as a result of the pressure increase in the reaction vessel, the yield of $MgCl_2$ was very small ($\sim 4\%$). The yield was improved when nitrogen was used to drive chlorine through the system (total flow rate, 50 ml min^{-1}). The average value of the yield was 27%. Further studies are to be carried out to increase the rate and yield of the reaction. It is important to note that the surface of the $Mg(OH)_2$ particles is increasingly coated with a layer of $MgCl_2$ which prevents chlorine interaction with the material at the core of the particle. This explains the limited yield of the reaction. However, gas–solid reactions frequently suffer from the build up of a protective layer of the products on the surface of the reactant particle when the rate of the reaction depends on the porosity of the products [12].

In another set of experiments, reactions (3) and (4) were combined. Cupric chloride was placed in a horizontal quartz reactor heated by an electric furnace. Nitrogen was allowed to pass through the reactor to carry the gaseous products. The outlet of the reactor was connected to the inlet of the glass reactor, described above, which contains magnesium hydroxide.

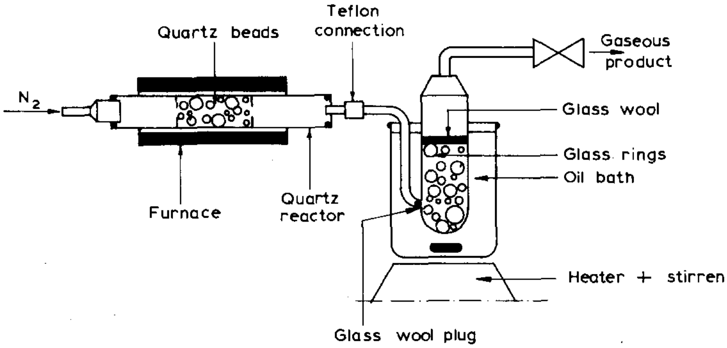

Fig. 4. Composite apparatus for the combination of reactions (3) and (4).

The composite system is shown in Fig. 4. The reaction yield, in the best cases, did not exceed the average value mentioned previously. The aim of this combination was to prove the possibility of carrying out two steps of the process simultaneously, a matter which is of importance to chemical engineers.

Reaction (5), regeneration of hydrogen chloride

Steam reacts with magnesium chloride to produce magnesium hydroxide together with gaseous hydrogen chloride as in eqn. (5). The free energy of the reaction assumes a value of 4.9 kcal mol^{-1} at the recommended temperature, 350 °C (see above). The reaction was carried out in two differently shaped reactors. Magnesium chloride was distributed over a wide-area silica tubular reactor and heated by the furnace. In another set of experiments the reaction was done in the reactor shown in Fig. 4 where magnesium chloride was distributed within the glass rings to obtain a high contact area. Steam was transferred by thermally insulated pyrex pipes into the reactors. The flow rate of the steam was measured by condensing the steam and measuring the collected water vs. time. A rate of 0.2 g min^{-1} was maintained throughout the experiments. The exit of the reactor was connected to a trap of sodium hydroxide solution of an exactly known quantity to assess the estimation of the hydrogen chloride produced by back titration with the acid. Further, the material was analysed by X-ray diffraction to detect the formation of magnesium hydroxide.

The yield was low ($< 5\%$) with the silica horizontal reactor whilst a higher yield could be obtained with the fixed bed vertical reactor ($18 \pm 4\%$). The yield was estimated after the passage of the stoichiometric amount of steam. However, when excess steam was used the reaction yield could only be slightly improved because of the expected shielding by $Mg(OH)_2$ on the surface of $MgCl_2$ particles.

The extent of reactions (4) and (5) is limited because the of hindered interaction of the flowing gas with the reactants by the product formed on the surface. This hindrance, however, could be utilized by using the whole product material of reaction (4) as a reactant in reaction (5). The efficiency, therefore, will be relatively high as the material reacts to almost the same depth, i.e., 20 wt% $MgCl_2$ forming the outer surface of an $Mg(OH)_2$ particle will interact with steam in the last reaction of the cycle, to be reconverted entirely into $Mg(OH)_2$, where only the surface material undergoes reaction.

PROCESS DESIGN

A thermochemical process has been developed for the reference and improved versions of the copper–chlorine cycle. The goal of the design was

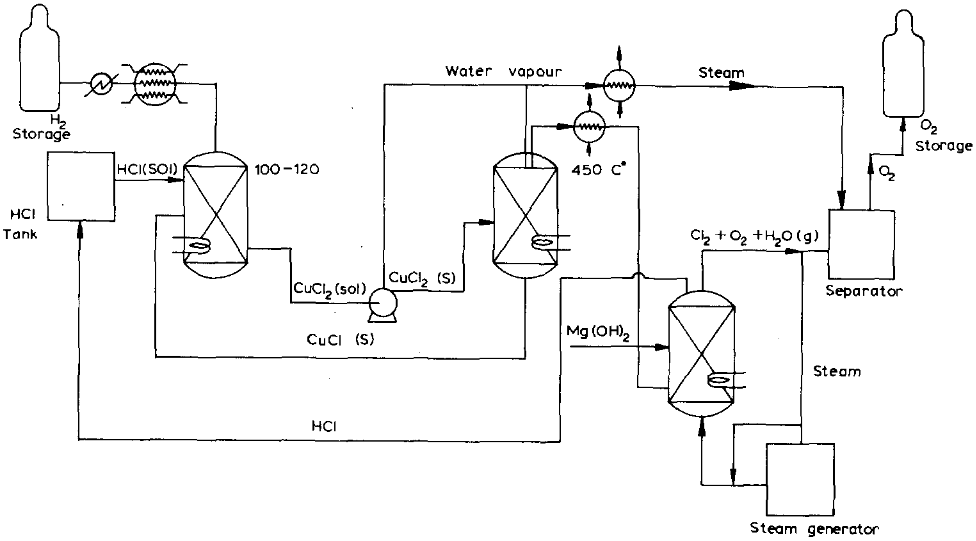

Fig. 5. Flow sheet of the copper–chlorine thermochemical cycle.

to produce an engineering flow sheet. The flow sheet takes into account the source of energy (possibly solar energy) and the rejection of waste heat as shown in Fig. 5. The design suggests that the production of hydrogen can be carried out in the first reactor, where the cuprous chloride later disproportionates into copper and cupric chloride.

The second reactor is used only for the dehydration and dechlorination of the cupric chloride. Reactor (3), however, can be used for the generation of oxygen by the chlorination of magnesium hydroxide and also the regeneration of hydrogen chloride by the action of steam on magnesium chloride produced. Reactors (1) and (2) can, therefore, be operated at constant temperature conditions, namely, 100 and 450 °C in batchwise mode, whilst reactor (3) must be operated in an alternating thermal environment (80 and 350 °C). The gases may be recycled as indicated in Fig. 5.

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REFERENCES

1 L.O. Williams, Hydrogen Power, Pergamon, London, 1980, Chap. 4.
2 C.A. McAuliffe, Hydrogen Energy, MacMillan, Hong Kong, 1980, Chap. 2.

3 M. Dokiya and Y. Kotera, Int. J. Hydrogen Energy, 1 (1976) 117.
4 K.E. Cox, Proc. 2nd World Hydrogen Energy Conf., Zurich, Aug. 1978, Vol. 2, p. 471.
5 H.S. Gurev, R.E. Hahn and K.D. Masterson, Int. J. Hydrogen Energy, 2 (1977) 259.
6 O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, 5th edn., Pergamon, Oxford, 1979.
7 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, London, 1963.
8 P.H. Fong and D.T.Y. Chen, Thermochim. Acta, 18 (1977) 273.
9 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th edn., Wiley, New York, 1980, pp. 800–801.
10 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
11 F. Jasim, M.M. Barbooti and K.I. Hussain, Thermochim. Acta, 58 (1982) 289.
12 N.B. Hannay, Treatise on Solid State Chemistry, Vol. 4, Plenum, New York, 1976, Chap. 2.