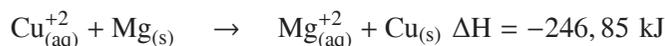


Understanding Active Metal Reaction Kinetics with Cu–Mg Replacement Reaction

Ilhami Ceyhun and
Zafer Karagölge
Atatrk University
Education Faculty
Department of Chemical
Education
Erzurum,
Turkey.
Email:
iceyhun@atauni.edu.tr

Metal substitution reactions are simple redox reactions. These reactions demonstrate the relative activity and the electrochemical series of metals. In particular, the purpose of this study is to help students comprehend the displacement reaction among, Mg metal and solutions containing Cu^{+2} , Ni^{+2} , Pb^{+2} , Cd^{+2} , Co^{+2} . This study is an important experiment towards understanding reaction kinetics.

In this experiment, particularly, the kinetics of the displacement reaction of Cu^{+2} (CuCl_2) and Mg metal has been examined. The reaction is exothermic and has been carried out by a group of students in 50–60 minutes. At a basic level, ionic reaction is;



In this reaction, Cl^- ion is insignificant. The mass calculation of copper can be ignored; however, Cl^- ions are free spectators. Interestingly, when students compared SO_4^{-2} ions with Cl^- ions, they found that Cl^- ions accelerated the reactions. In addition, students could also identify the relationship between G and K.

The article also brings out the effectiveness of cooperative learning in an experimental group where students are divided into two groups; the theoretical and the experimental.

Introduction

With its framework set against the background of usual physical chemistry course, chemical kinetics is a subject of great importance, and must necessarily be a part of chemistry curriculum.

Chemical kinetics is the study of the rates of chemical reactions.

Keywords

Chemical kinetics, rate law, replacement reaction, rate equation.



A small number of factors control how fast a reaction will occur. Investigation of these factors provide clues to the ways in which reactants are transformed into products in chemical reactions and helps in understanding their mechanism.

The chemical kinetics laboratory discussion worksheet presented here is a one-hour ready-made exercise designed to further student's understanding of chemical kinetics [1]. This discussion is suitable for pre-college and college students to help connect the macroscopic view of chemical kinetics to the particle-level – an important step that needs to be incorporated in introductory chemistry courses [2, 3].

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Magnesium is the lightest among today's construction metals and it is used as a low-density, material. Magnesium was discovered in England in 1755 by Joseph Black, but was first isolated in its pure form by Humphrey Davey in 1808 from a mixture of MgO (magnesia) and HgO.

Magnesium is abundant in seawater (0.127%). The reaction between CaO and seawater produces hydroxide ions ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{+2} + 2\text{OH}^-$). These hydroxide ions then react with magnesium ions to produce magnesium hydroxide ($\text{Mg}^{+2} + 2\text{OH}^- \rightarrow \text{Mg}(\text{OH})_2$). The reaction between $\text{Mg}(\text{OH})_2$ and HCl gives MgCl_2 and H_2O . The electrolysis of hot melted MgCl_2 produces magnesium metal ($\text{Mg}_{(s)}$) in the cathode and chlorine ($\text{Cl}_{2(g)}$) in the anode, respectively [4–7].

Cathode: $\text{Mg}^{+2} + 2\text{e}^- \rightarrow \text{Mg}_{(s)}$

Anode: $2\text{Cl}^- \rightarrow \text{Cl}_{2(g)} + 2\text{e}^-$

MgO is formed when magnesium comes in contact with air. Under acidic ($\text{pH} \leq 4$) and basic ($\text{pH} \geq 9$) conditions, the oxide layer is broken and its corrosion accelerates. Magnesium corrodes rapidly in presence of water, and hence pure magnesium is rarely used in engineering applications. Magnesium also plays a crucial role in biological systems and reduce nervous system hypersensitivity by producing a calming effect.



	Solution	E(volt)	Speed
Mg _(s) +	CuSO ₄	2.70	fast
	CuCl ₂	2.70	fast
	PbCl ₂	2.23	fast
	Pb(NO ₃) ₂	2.23	fast
	NiSO ₄	2.11	fast
	CoSO ₄	2.08	slow
	CdBr ₂	1.96	slow

Table 1. The exchange rates of oxidation reactions.

Kinetics of Cu⁺²– Mg Reaction

Student groups have investigated the kinetics of the reaction solutions in the presence and absence of Cl⁻ ions [8]. These reactions are more complex than first order homogeneous reactions [9].

In order to set up the reaction, Mg ribbon wrapped on a rotating disc was used. This ribbon prevents the contact of the disc with the solution (*Figure 1*) [10–12].

The mechanism of this reaction involves three steps:

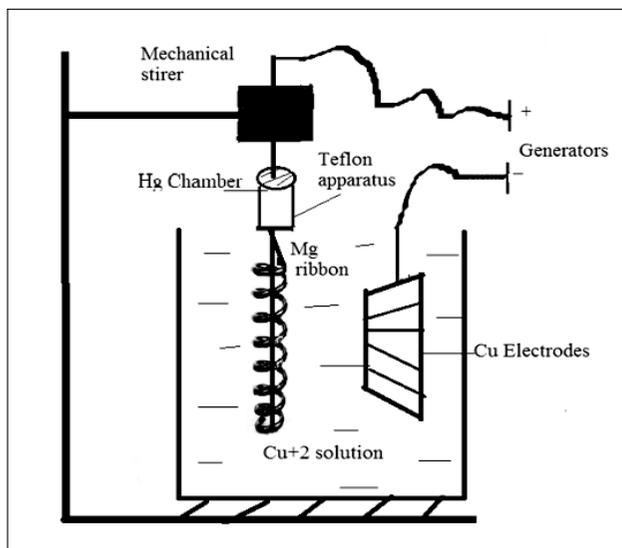


Figure 1. Experimental setup.

1. Diffusion of Cu^{+2} to the Mg surface (mass transfer and adsorption of Cu^{+2} ions).
2. Electron transfer from Mg to Cu^{+2} (surface reaction).
3. Desorption of Mg^{+2} ions, and diffusion of Mg^{+2} ions away from the surface.

Generally, step 1 and step 2 are considered the rate determining steps.

Reaction of Mg Metal with the Solution

Processes that must take place before copper deposition include oxide dissolution, copper nucleation on the surface, and an increase in the surface roughness, which are all dependent on the surface area of Mg. These processes cause the reaction to have an induction time during which reaction of Mg is slow.

The integrated rate equation [13] for this reaction is,

$$\ln \frac{[\text{Cu}^{+2}]_0}{[\text{Cu}^{+2}]} = \left(k \frac{x}{v} \right) \{ t - t_{\text{ind}}(1 - \theta_0)[1 - \exp(-t/t_{\text{ind}})] \}.$$

In the integrated rate equation, X is the surface area of Mg, θ_0 is the bare surface that is not a function of Mg content of MgO, $[\text{Cu}^{+2}]_0$ is the Cu concentration of the first solution; V is the volume of Cu solution, and t_{ind} is the induction time. When t is large, $[1 - \exp(-t/t_{\text{ind}})]$ approaches one, and the best fit to experimental data assumes $\theta_0 = 0$.

$$\ln \frac{[\text{Cu}^{+2}]_0}{[\text{Cu}^{+2}]} = \left(k \frac{x}{v} \right) \{ t - t_{\text{ind}} \}.$$

The obtained data is plotted between $\ln \frac{[\text{Cu}^{+2}]_0}{[\text{Cu}^{+2}]}$ and t and a line is obtained. The x -axis of the rectangle is fixed at the point t_{ind} and $k \frac{x}{v}$ is calculated from the slope.



	Solution	ΔG	Reaction	
$Mg_{(s)}^{+2}$	Cu^{+2}	-2.70 nF	fast	↑ rate increases
	Pb^{+2}	-2.23 nF	fast	
	Ni^{+2}	-2.11 nF	fast	
	Co^{+2}	-2.08 nF	slow	
	Cd^{+2}	-1.96 nF	slow	

Table 2. Change in ΔG and reaction rate of each reaction.

Experimental Part

In order to teach the concept of chemical kinetics, the class was first divided into two groups. While the first group was taught the theoretical aspects, the second group was introduced to experimental activities. A week later, comprehension levels were determined through interactive questions and quiz. Low comprehension levels (around 40%) were observed. Further, 12 students were divided into four groups of three each, and test sheets were provided.

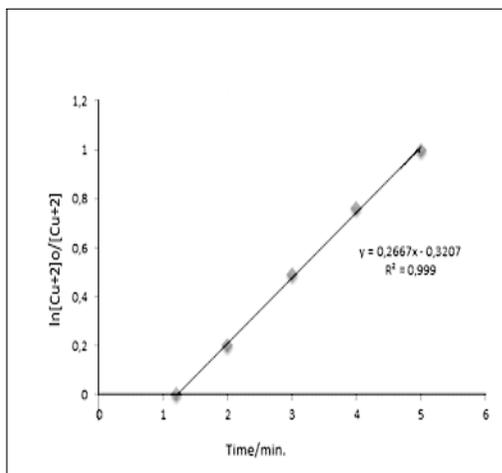
Pure water was used for all the solutions in the experiments. 100 ml 0.20 M $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $PbCl_2$, $NiSO_4$, $CoSO_4$, and $CdBr_2$ solutions were used for the experiment. As shown in *Figure 1*, Mg strips with a thickness of 0.15 – 0.30 mm and width of 3 mm were wrapped on a steel bar which acts as the anode and pure Cu metal was used as the cathode. Both were immersed in Cu^{+2} solution [14].

$Mg_{(s)} + Cu_{(aq)}^{+2} \rightarrow Mg_{(aq)}^{+2} + Cu_{(s)}$. By the reaction, $\Delta G = -nFE$, $\Delta G = -2 \times 96500 \text{ coulomb} \times 2.7 \text{ volts} = -521.100 \text{ kJ}$. So there is a spontaneously occurring reaction. The reaction is very fast ($E_{\text{cell}} = 2.70 \text{ volts}$). According to the obtained data, the reaction rate increases as $-\Delta G$ increases in spontaneous reactions (*Tables 1–3*).

At specific time intervals, the reaction was stopped, and the electrode was dried to find the amount of substance collected at the cathode. This weighing was done at 20-minute intervals. Then the reaction was terminated. As shown in *Figure 2*, a graph is obtained between $CuCl_2$ and the amount of Mg added. The rate



Figure 2. The result for the reaction of CuCl_2 solution with $\text{Mg}_{(s)}$.



constant ‘K’ can be determined from this graph with $K = 0.13$ cm/sec and $t_{\text{initial}} = 1.22$ sec. The same process was repeated using CuBr_2 and Mg , where $K = 0.106$ cm/sec and $t_{\text{initial}} = 1.87$ sec. This results show that CuBr_2 shows a slower reaction rate than CuCl_2 .

However, when repeated with CuSO_4 , it is seen that SO_4 slows down the reaction further. Here $K = 4.7 \times 10^{-4}$ cm/sec and induction time is 7.91 sec (Figure 3) [15]. These experimental values are average values of the four groups.

Reaction	ΔG (kJ)	K
$\text{Mg}_k + \text{Cu}^{+3}$	521.100	2.79×10^{91}
$\text{Mg}_k + \text{Pb}^{+3}$	430.390	3.37×10^{75}
$\text{Mg}_k + \text{Ni}^{+2}$	407.200	2.87×10^{71}
$\text{Mg}_k + \text{Co}^{+2}$	401.440	2.75×10^{70}
$\text{Mg}_k + \text{Cd}^{+2}$	378.280	2.41×10^{66}

Table 3. Change in ΔG and K of each reaction.



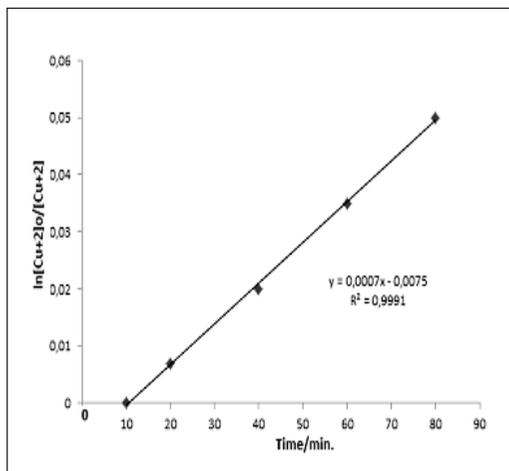


Figure 3. The result for the reaction of $CuSO_4$ solution with $Mg_{(s)}$.

Results and Discussions

This kinetic model of $Cu_{(aq)}^{+2}$ reaction was developed with rotating Mg disk [16, 17]. In this simple system, high Cl^- concentration and high ionic strength of the environment (such as sea water ($[Cl^-] =$ from 0.50 to 0.55 M) is applied [18].

$Cu^{+2} - Mg$ exchange reaction is accelerated by Cl^- and Br^- , while SO_4^{-2} has been shown to slow down the reaction. Here-with, a more general term, the 'halide-acceleration effect', should be used instead of the 'chloride-acceleration effect' [8]. The rate determining step is achieved by increasing the transfer of electrons from the Mg to Cu^{+2} .

Following this, when interactive questions were asked to the students, better comprehension levels were observed (about 90%). It was seen that learning was more effective through experimenting and they understood the concept of chemical kinetics better. At the same time, students also understood the relationship between ΔG and K. As K grows, speed increases.

Figures 2 and 3 which charts the reaction with solutions containing the Cl^- and SO_4^{-2} ions provide information on the speed of the reaction. The displacement reaction of Mg and Cu^{+2} ions has been influential towards understanding and learning chemical kinetics.



Suggested Reading

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