

I Ceyhun and Z Karagölge
Atatürk University
Education Faculty,
Department of Chemical Edu-
cation, 25240
Erzurum-Türkiye
Email: iceyun@atauni.edu.tr

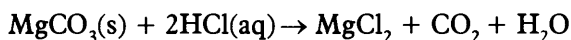
An Experiment for Teaching Chemical Kinetics in Chemical Education

This article describes an experiment in chemical kinetics that is suitable for an undergraduate laboratory course in general chemistry. Four different undergraduate student teams investigated the relation between the HCl concentration and the flow rate of CO₂ which is formed from the reaction of MgCO₃(s) + HCl(aq). About 70% of them indicated that the experimental and theoretical results were in good agreement. By plotting the experimental data, the activation energy of the reaction was found to be 26.50 kJ/mole.

1. Introduction

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

For the reaction

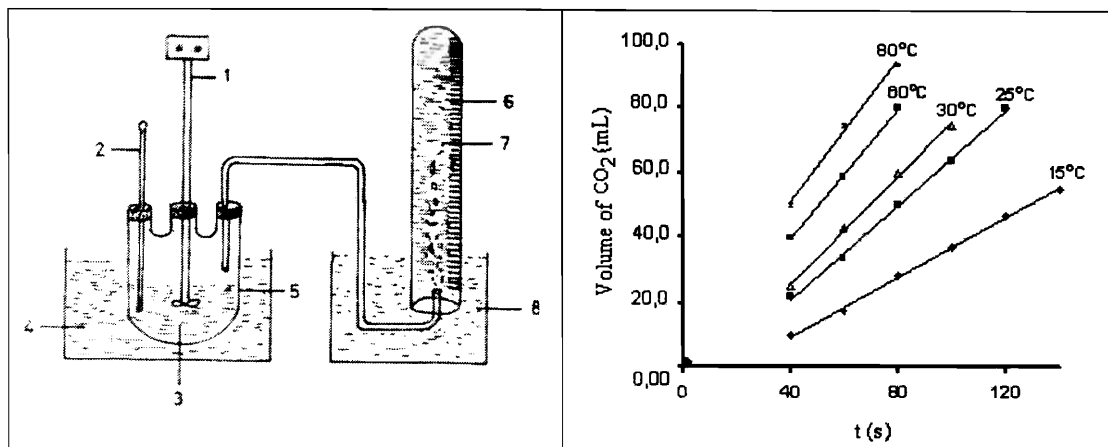


Gortikov and Nanteleeva [1], and Tominaga and his co-workers [2], reported a first order rate dependence on HCl concentration. For the reaction of calcite with hydrochloric acid, Ferrari and Sessa [3] found that a 10°C rise in temperature of a well-stirred mixture of calcite in 8% HCl solution approximately doubles the rate of calcite dissolution. Analysis of the Ferrari and Sessa data reveals, however, an abrupt slope change at 20°C, when the CaCO₃ dissolution rate is plotted against temperature. To compound the mystery, the near unanimous finding of all workers studying the CaCO₃(s) + HCl(aq) system shows a marked dependence of CaCO₃ dissolution rate on stirring speed [1, 3-7] and viscosity [2] that suggests the diffusion controlled nature of the reaction.

Keywords

Chemical kinetics, chemical education, teaching/learning kinetics, laboratory instruction.





In light of the above discussion, the kinetics of the reaction of $\text{MgCO}_3(\text{s})$ with $\text{HCl}(\text{aq})$ is found to be ideal for undergraduate chemistry kinetics experiments. Materials needed are safe, readily available, and easy to handle.

2. Experimental Procedure

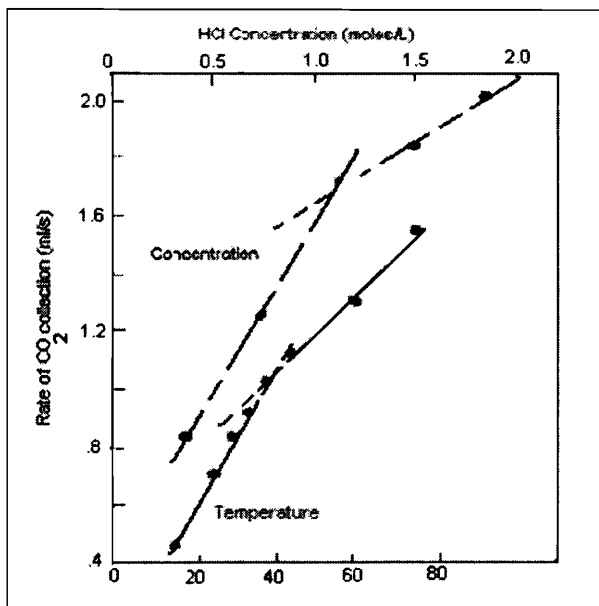
The reaction was carried out with 5 g of MgCO_3 and aq HCl. Assuming the rate of $\text{CO}_2(\text{g})$ evolution is an accurate measure of $\text{MgCO}_3(\text{s})$ dissolution rate in HCl, the three necked flask in *Figure 1* was used to determine CO_2 volume under a variety of experimental conditions. Several trial runs were performed under each set of conditions to obtain a reproducibility of 3% or better. Typical data plots are shown in *Figures 3* and *4* and a summary of findings is given in *Table 1*. Reaction rates are calculated from the slopes of graphs plotted with volume of CO_2 versus time (as read from *Figure 2*), and is expressed in moles of $\text{CO}_2(\text{g}) = 24.5 \times 10^3 \text{ ml}$.

Practical considerations dictated the conditions chosen. The 950 rpm stirring speed was easy to monitor and control, gave reproducible results and the reaction was fast enough to permit several trials during the 40 min work period. Mesh size seemed to be the simplest way to measure the $\text{MgCO}_3(\text{s})$ surface area, a technique not previously reported in the literature. HCl molarity

Figure 1 (left). Schematic of experimental apparatus. 1. Mechanic stirrer, 2. Thermometer, 3. Reactants, 4. Bath water, 5. Reactor, 6. Gas collection tube, 7 and 8. Acidic solution.

Figure 2 (right). Data plots of $\text{CO}_2(\text{g})$ collected per-second, for 20 mesh MgCO_3 in 0.040 M HCl at the indicated temperatures, at 950 rpm stirring speed.

Figure 3. Plots of $\text{CO}_2(\text{g})$ collection rates in aqueous HCl, for 20 mesh MgCO_3 , at 950rpm stirring speed. Each 'data' point is the slope of a corresponding volume of $\text{CO}_2(\text{g})$ collected, versus HCl concentration (not shown), or HCl temperature (Figure 2), as reported in the table. Note abrupt slope changes at 0.116M HCl (upper plot, using upper horizontal scale), and 37°C (lower plot, using bottom horizontal scale).

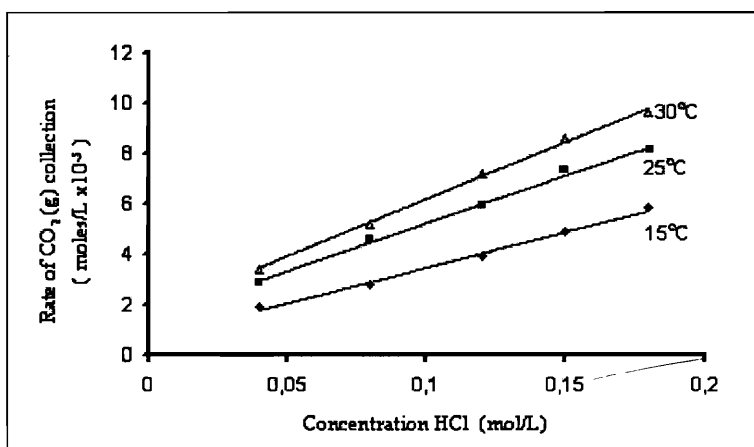


ranges were those that would keep the reaction rate measurably slow. Finally assuming that the net reaction equation is,



it can be shown that the maximum possible HCl concentration change, using 800 ml of 0.04 molar acid, is about 2% during the evolution of 100 ml of $\text{CO}_2(\text{g})$. This figure is well within the above-reported reproducibility, and its calculation provides an example of the way in which the $\text{MgCO}_3(\text{s}) + \text{HCl}(\text{aq})$ system

Figure 4. Rate of $\text{CO}_2(\text{g})$ collection (moles/L) versus HCl concentration for 20 mesh MgCO_3 in HCl solution at the indicated temperatures and 950 rpm stirring speed.



Concentration of HCl (mole/L)	Temperature (°C)	Rate of CO ₂ (g) X (mL/sec)	Collection (± 3%) Y (mole/sec)*
0.040	15	0.480	1.96×10^{-5}
	25	0.720	2.94×10^{-5}
	30	0.840	3.43×10^{-5}
	60	1.340	5.47×10^{-5}
	80	1.580	6.45×10^{-5}
	30	1.200a	4.90×10^{-5}
0.080	30	1.770b	7.22×10^{-5}
	15	0.690	2.82×10^{-5}
	25	1.140	4.65×10^{-5}
0.120	30	1.280	5.22×10^{-5}
	15	0.980	4.00×10^{-5}
	25	1.460	5.96×10^{-5}
0.150	30	1.740	7.10×10^{-5}
	30	1.840	7.51×10^{-5}
0.180	30	2.100	8.57×10^{-5}

950 rpm stirring speed and 20 mesh MgCO₃(s), unless otherwise indicated
a: 40 mesh, b: 60 mesh, * Y = X / 0.245 × 10⁵

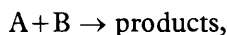
allows the students to plan the experimental details. One need only to find the number of moles of HCl initially present, reacting, and remaining, to arrive at the 2% figure.

Table 1. Collected volume of CO₂(g) versus time.

Analysis of *Figure 3* shows abrupt slope changes at 0.116 M HCl concentration, and 37°C. Chemical control of rate is likely at low concentration and temperature, small MgCO₃(s) particle size and high stirring speeds. Diffusion control is favored by high HCl concentration and temperature, large MgCO₃(s) particle size and low stirring speeds. The above analysis thus suggests change from chemical to diffusion control of rate at 0.116 M HCl and 37°C, using 20 mesh size MgCO₃(s) and 950 rpm stirring speed.

3. Rate Law and Activation Energy Determination

For the general reaction



the rate can be written as

$$\text{rate} \propto [A]^x[B]^y. \quad (1)$$

In this example, the overall order is the sum $x + y$, where, x and y can have whole number, fractional, negative or even zero values. When one of the exponents is zero, the rate of the reaction does not depend on the concentration of that substance. For example, if the exponent y in equation (1) were zero, the equation would become

$$\text{rate} \propto [A]^x[B]^0$$

or

$$\text{rate} \propto [A]^x.$$

The data obtained in the present study show that the rate law can be expressed by the equation

$$\text{rate} = k [\text{HCl}].$$

This is illustrated in *Figure 4*, where k is first order rate constant. The rate constants are evaluated from the plots of rate $\text{CO}_2(\text{g})$ collection versus HCl concentration at various temperatures.

Assuming that Eyring's modification of Arrhenius equation [6] is applicable to our work, rate constant was found for HCl concentrations up to 0.11 M, and temperatures up to 30°C, which were found to be upper limits of the diffusion barriers. The rate constants were found as indicated in the preceding paragraph.

The empirical equation proposed by Arrhenius states that

$$k = A \cdot e^{-E_a / RT}$$

where k is the rate constant; A , Arrhenius factor; E_a , the activation energy; R , the universal gas constant; and T , the absolute temperature. Taking the natural logs the equation becomes,

$$\ln k = \ln A - E_a / RT,$$

which means that a plot of $\ln k$ versus $1/T$ has a slope equal to $-E_a/R$. Hence the Arrhenius activation energy, E_a , equals the



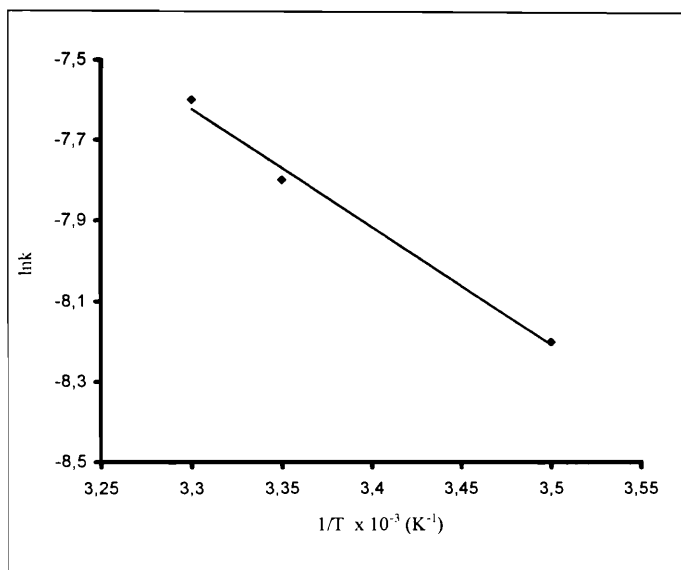


Figure 5. Arrhenius plot for $\text{MgCO}_3 + \text{HCl}$ reaction.

numerical value of this slope times R . Our data gave a slope of $-3.22 \times 10^3 \text{ K}$ (Figure 5) for the $\ln k$ versus $1/T$ plot. Thus $E_a = 8.23 \text{ J/mole K} \times 3.22 \times 10^3 \text{ K}$, that is $E_a = 26.50 \text{ kJ/mole}$.

Since the data is reproducible within 5%, we can report a E_a value of 26.50 kJ/mole of $\text{CO}_2(\text{g})$, in good agreement with Moelwyn-Hughes [7] value of 26.33 kJ/mole , where viscosity effect was neglected in both studies. Tominaga and his co-workers [2] corrected for such effects, and reported an E_a value of 22.57 kJ/mole .

4. Conclusion

In this study, it was found that 70% of the students understood the meaning of chemical kinetics, and it helped them analyse the data. The experimental yield of $\text{CO}_2(\text{g})$ obtained by the students and the yield calculated were found to match. The exercise is a good example for constructive teaching of several aspects of chemical kinetics.

Suggested Reading

- [1] Gortikov and Nanteleeva, *J. Gen. Chem. (USSR)*, Vol.7, p.56, 1973.
- [2] Tominaga, Adzumi, and Isobe, *Bull. Chem. Soc. Japan*, Vol.14, p.348, 1939.
- [3] Ferrari and Sessa, *Gazz. Chim. Ital.*, Vol.67, p.501, 1937.
- [4] Z Klein, *Anorg. Allgem. Chem.*, Vol.56, p.137, 1924.
- [5] H Eyring, *J. Chem. Phys.* Vol.3, p.107, 1935.
- [6] H Eyring, S Glasstone, and KLaidler, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York, 1941.
- [7] Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, Oxford University Press, Oxford, p.284, 1933.