

1961

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Recommended Citation

Woods, Joe D. and Rider, Thomas J. (1961) "Effect of Negative Ions Upon Rates of Reaction of Zinc With Hydrochloric and Perchloric Acids," *Proceedings of the Iowa Academy of Science*, 68(1), 182-188.

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Effect of Negative Ions Upon Rates of Reaction of Zinc With Hydrochloric and Perchloric Acids

JOE D. WOODS¹ AND THOMAS J. RIDER

Abstract. The rate of evolution of hydrogen by the action hydrochloric acid and perchloric acid on zinc was measured volumetrically as a function of various negative ion concentrations. Increasing zinc ion concentration retards the rate of the reaction. A four to one ratio of chloride to zinc ion reaccelerates the rate, suggesting the formation of $ZnCl_4^{2-}$ which removes the excess zinc ion from the reaction. Other complexing ions, thiocyanate, bromide and iodide ion, accelerate the reaction as does chloride. Sulfate, like perchlorate, has little effect. The results explain the fact that hydrochloric acid reacts with zinc at a higher rate than does perchloric acid of equal concentration and similar strength.

Although hydrochloric and perchloric acids are both strong acids, in the sense that they are almost completely ionized in aqueous solution, they do not evolve hydrogen at the same rate when reacting with zinc metal. Zinc dissolves in hydrochloric acid at a faster rate than in perchloric acid.

It is known that when hydrochloric acid acts on zinc the rate of hydrogen evolution is proportional to the hydrogen ion concentration (1). Also the activity of hydrogen ion is practically the same for hydrochloric and perchloric acids of equal concentrations (2). Some other factor is responsible for the different reaction rates with zinc. The purpose of this study was to investigate the effect of the negative ion on the rate of reaction of zinc with hydrochloric and perchloric acids, respectively.

EXPERIMENTAL

The rate of reaction of various systems involving either HCl or $HClO_4$ and the sodium salts of various anions was measured to determine what effect, if any, these anions might have on the rate of reaction of the acid with zinc metal. These anions were also varied in concentration to determine the effect of concentration of anion upon the rate. Since temperature has an influence on reaction rates, data were collected at various temperatures. It was assumed, and later shown to be true, that the influence of the sodium ion was constant in all cases.

A closed gas measuring system was constructed so that the

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rate of reaction could be observed according to the amount of hydrogen gas evolved in a given unit of time using a fixed amount of zinc metal.

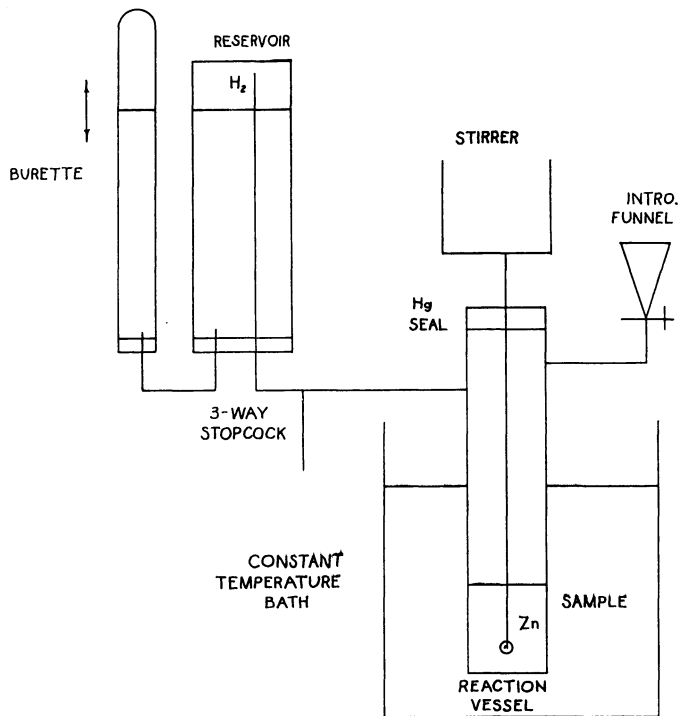


Figure 1. Apparatus.

The gas measuring system consisted of a reaction vessel immersed in a constant temperature bath, and fitted with a heavy stirrer connected to it through a mercury seal. The reaction vessel was connected by a three-way stopcock to an inverted graduated cylinder, which served as a water reservoir. This reservoir was connected to a burette, which was used as a device for measuring the volume of water displaced from the reservoir. This volume of water was then the volume of hydrogen gas liberated, provided that the water levels were equalized in both the reservoir and burette to bring the inside of the closed system to atmospheric pressure.

Samples of various systems involving 1 M HCl and 1 M HClO₄ with sodium anion salts were run at various concentrations and temperatures using a constant weight of granular zinc. Alge-

braic and graphical analyses of the data obtained yielded certain qualitative and quantitative relationships.

RESULTS

It was found that 1 M NaCNS, 1 M NaCl, and 1 M NaBr accelerated the rate of reaction of zinc with 1 M HCl. One molar NaClO₄ and 1 M Na₂SO₄ were found to give about the same rate of hydrogen evolution as 1 M HCl. One molar NaNO₃ and 1 M Na₃PO₄ seemed to render the zinc metal passive, possibly due to the formation of protective coatings on the metal surface. One molar ZnCl₂ and 1 M Zn(ClO₄)₂ greatly retarded the rate of reaction. The results are summarized in Figure 2.

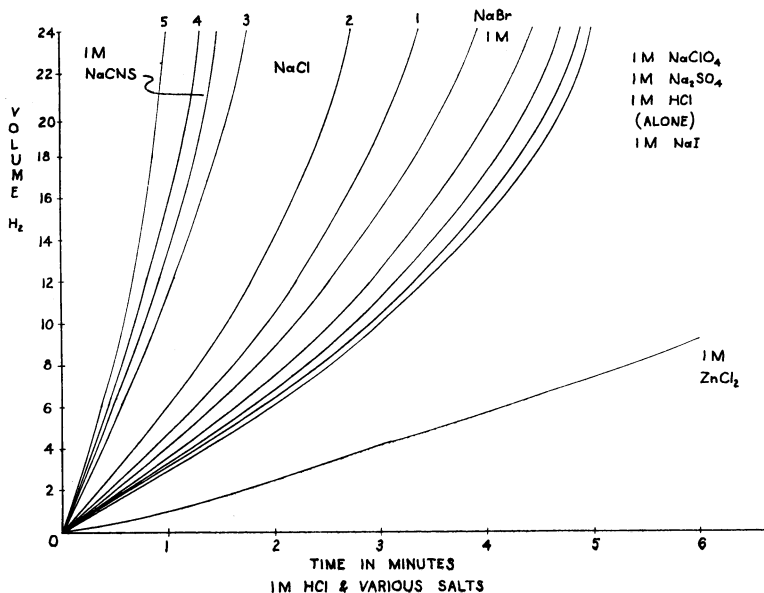


Figure 2. Rate of hydrogen evolution, 1 M HCl and various salts.

Since 1 M NaCl accelerates the rate of reaction of zinc with 1 M HCl, it was decided to measure the effect on the rate of concentrations of sodium chloride greater than one molar. The results of these determinations are also included in Figure 2. It is evident that a progressive increase in chloride ion concentration produces a progressive increase in the rate of hydrogen evolution. An investigation was made to determine if a mathematical relationship for this phenomenon could be found. If rate of hydrogen evolution is plotted versus total chloride ion concentration squared at various temperatures as in Figure 3, a nearly straight line is obtained at each temperature.

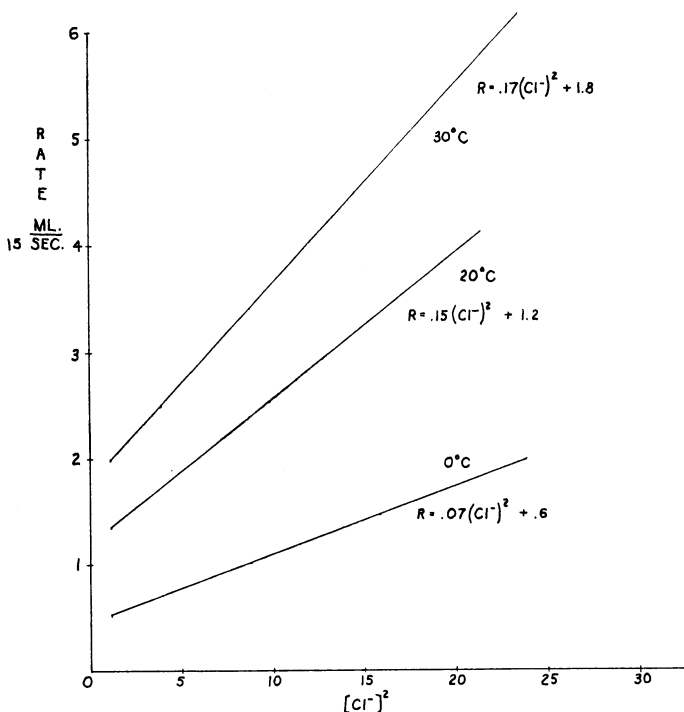


Figure 3. Rate of hydrogen evolution vs. $(\text{Cl}^-)^2$.

Using the slope-intercept form of a line, the following empirical rate laws were found:

$$R_{00}(\text{ml}/15 \text{ sec}) = .07 (\text{Cl}^-)^2 + .6$$

$$R_{200}(\text{ml}/15 \text{ sec}) = .15 (\text{Cl}^-)^2 + 1.2$$

$$R_{300}(\text{ml}/15 \text{ sec}) = .17 (\text{Cl}^-)^2 + 1.8$$

These rate equations were checked using a known concentration of chloride. From rates thus produced, the calculated chloride ion concentration agreed with the actual chloride concentration within approximately 3 percent. An empirical rate equation for bromide ion was also developed at 20°C.

$$R_{20}(\text{ml}/15 \text{ sec}) = .13 (\text{Br}^-)^2 + 1.4$$

It was found that iodide ion had to be present in concentrations above 2 molar to accelerate the rate of hydrogen evolution.

After increasing concentrations of chloride and bromide ions were shown to accelerate the rate of reaction, the effect of varying the concentration of perchlorate ion in hydrochloric acid was investigated to determine if there was any dependence of rate

on this ion. Table 1 contains the results of these determinations. It is seen that the rate does not increase with increased perchlorate, but in fact decreases slightly. This contrasts with the increased rate with increased chloride shown in Figure 3.

Table 1. Rate of H_2 evolution from 1 M HCl and $NaClO_4$ at $20^\circ C$.

Conc. $NaClO_4$ (Moles/Liter)	Rate (ML/15 sec)
0	1.4
1	1.4
3	1.4
6	1.2
Saturated	1.0

Preliminary experiments showed that the rate of hydrogen evolution, by the action of hydrochloric or perchloric acids on zinc, was decreased as the concentration of zinc ions were increased. Since high concentrations of chloride ion are able to accelerate the rate of reaction, a check was run to determine whether a high concentration of chloride could re-accelerate the rate of reaction in a rate-retarded system containing 1 M $ZnCl_2$ and 1 M $Zn(ClO_4)_2$, respectively. Figure 4 contains the results of these determinations.

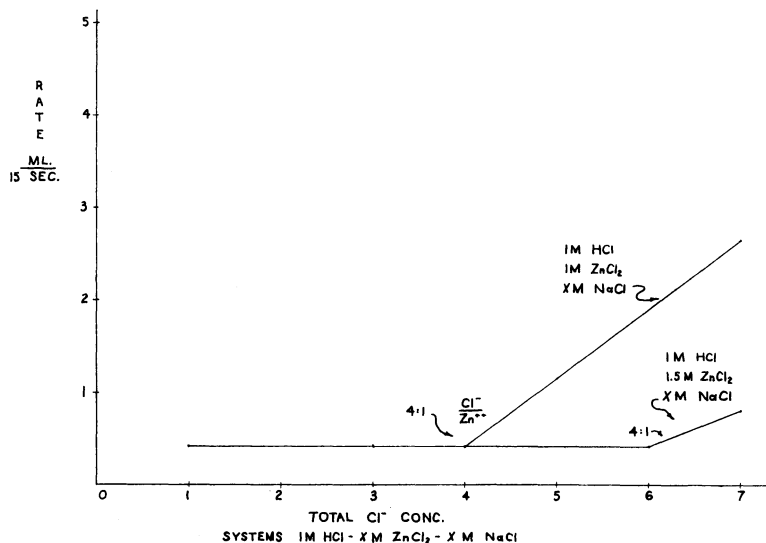


Figure 4. Rate of hydrogen evolution vs. total chloride.

It can be seen that the rate is accelerated when the ratio of total chloride (from HCl, NaCl, and $ZnCl_2$) to zinc ion concentration is at least four to one.

The effect of changes in temperature on the rate of hydrogen evolution was also determined by running samples of 1 M HCl +

1 M NaCl and 1 M HClO₄+1 M NaClO₄ at various temperatures. Figure 5 contains the results of these determinations. It is

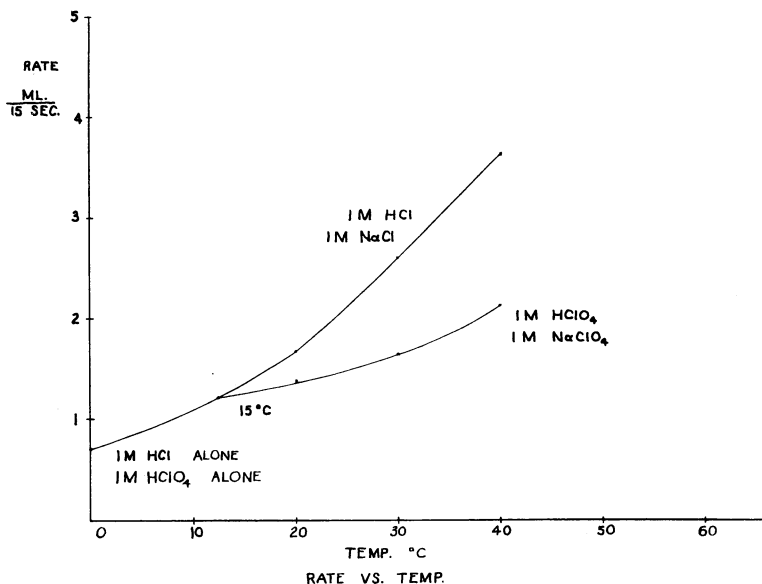


Figure 5. Effect of temperature on rate of H₂ evolution.

evident that the rate of reaction is accelerated in both systems by a rise in temperature, but the degree of acceleration in the HCl-NaCl system is higher. Below 15° the two curves seem to meet. One molar HCl and 1 M NaClO₄ alone were run at 0°C and it was found that they gave the same rate as the systems containing the extra anions. This suggests that below 15°C the anion has little or no effect on the rate.

DISCUSSIONS AND CONCLUSIONS

It is apparent from this study that the negative ion does affect the rate of reaction of zinc metal with acids, although it is realized that the effect has been clearly shown only with high concentrations of chloride ions. Those ions which can form complex ions with zinc, for example, Cl⁻, Br⁻, I⁻, CNS⁻, may tend to accelerate the rate by removing excess zinc ion from the reaction as it is formed. It is known (3) that chlorozincate complexes are the most stable, iodozincates the least stable of the halozincates. Since this study shows that chloride ion has the greatest accelerating effect and iodide the least, this stability trend is verified.

Perchlorate and sulfate ions do not complex with zinc ion

to any great extent, due to the lack of an available electron pair. This study shows that perchlorate and sulfate ions do not accelerate the rate. This suggests further that a zinc complex is the rate determining factor.

The four to one ratio of chloride ion to zinc ion that is necessary before the rate is accelerated suggests the possibility that the halozincate complex involved is ZnCl_4^{--} . It was not determined, however, whether or not this ion is involved at lower chloride concentrations starting with HCl, alone.

Below 15°C the halozincate complex apparently does not form and the rate of reaction is not affected by the presence of excess chloride ion.

Results of this study suggest that zinc dissolves at a faster rate in 1 M HCl than in 1 M HClO_4 because of the formation of a chlorozincate complex by the anion of 1 M HCl, as opposed to little or no complex formation by the anion of 1 M HClO_4 .

ACKNOWLEDGMENTS

The authors wish to acknowledge the help of Dr. F. R. Duke of Iowa State University, who originally suggested this problem. Dr. F. E. Jacob of Drake University also gave advice during this study.

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