

of certain indicators was not a reliable measure of the hydrogen-ion concentration, as shown by the hydrogen electrode.

### Summary

1. Glass-surface potentials are established and maintained by the passage of electricity through the glass.
2. Glass-surface potential is a linear function of hydrogen-electrode potential only through a limited range of values.
3. Variations in glass-surface potential may be used as the basis of an electrometric titration method in the presence of oxidizing agents which render the hydrogen electrode useless. In such cases the method might give data which could not be obtained in any other way.
4. The presence of certain substances (strong salt solutions or gelatin solutions) other than hydrogen ions affects glass-surface potentials.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 58]

## THE SOLUBILITY AND SPECIFIC RATES OF HYDROLYSIS OF MUSTARD GAS IN WATER<sup>1</sup>

By ROBERT E. WILSON, E. W. FULLER AND M. O. SCHUR

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### Introduction

The previous paper by the writers dealt chiefly with the accelerating effect of various alkaline colloidal solutions on the rate of hydrolysis of mustard gas. The tendency of the reactions to reverse in acid solutions was, therefore, merely mentioned in passing. This paper is devoted primarily to an analysis of the hydrolytic reactions of mustard gas in neutral and acid solutions, and presents data as to its solubility and the magnitude of the four reaction rate constants for the progress and reversal of each of the two stages of its hydrolysis.

It has been shown in the previous paper that the hydrolysis of mustard gas takes place only in the aqueous phase, and not at the interface; that the rate is constant in alkaline solutions but is retarded in acid; and that the hydrolysis eventually goes to completion in all solutions.

Throughout the first paper it was taken for granted that the hydrolysis took place in two stages, rather than that both chlorine atoms always split off simultaneously. This former assumption is the only reasonable one in view of the fact that the 2 chlorine atoms are separated by 5 intermediate atoms. It is further verified by two other independent observations.

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In the first place, as pointed out previously, there was a marked initial retardation of the rate of hydrolysis in sulfonated corn oil solutions, even in the presence of a large excess of mustard gas, and this behavior could be explained only on the basis that at the start the intermediate compound produced by the first stage of the hydrolysis dissolves in the colloidal oil globules as fast as it forms, thus preventing the splitting off of the second chlorine atom at the normal rate until the amount of the intermediate compound left in the aqueous phase reaches the normal equilibrium value. In the second place the rate of the reaction can be greatly reduced by moderate concentrations of acid, and yet under such conditions the reaction always goes to completion, eventually. The marked retardation can mean only that a reverse reaction is reaching a magnitude comparable with that of the corresponding forward reaction, and if it were only a single stage reaction, the accumulation of the reaction products would certainly stop the reaction before completion, especially if the acid concentration was increased. The observed failure to stop could be readily explained, however, if the first stage of the reaction were reversible and the second one not appreciably so, for the continued destruction of the intermediate compound by the irreversible second stage would prevent the first stage from coming to a stop, however much it might be retarded.

On the basis of these and other considerations to be mentioned later, it is unquestionably true that the reaction proceeds in two stages, substituting first one chlorine and then the other with hydroxyl groups, with the simultaneous formation of hydrochloric acid.

### Derivatives of Complete Equations for the Reaction Rates

In the previous paper, equations for the rate of hydrolysis were given for alkaline solutions where the hydrogen-ion concentrations were so low as to eliminate any tendency toward reversal. The same equations, taking into consideration the possibility of reversibility, and assuming no change in the mass-action effect of the water and no catalysis by ions, would be as follows. The net rate of formation of hydrochloric acid due to the first stage of the hydrolysis is

$$\frac{dC_1}{dt} = k_1 (M) - k_1 (I) (H^+) (Cl^-) \quad (1)$$

and the rate of formation of hydrogen chloride due to the second stage is

$$\frac{dC_2}{dt} = K_2 (I) - k_2 (G) (H^+) (Cl^-) \quad (2)$$

Once steady conditions are set up, these two rates must be substantially identical. In these equations ( $M$ ) is the moles of dissolved mustard gas present per liter of solution; ( $I$ ) is the moles of intermediate hydrolysis compound present per liter of solution; ( $G$ ) is the moles of thiodiglycol present per liter of solution;  $K_1$  and  $K_2$  are the specific rate constants

(moles per liter per minute) for the two stages of the hydrolysis; and  $k_1$  and  $k_2$  are the specific rate constants for the reversal of the two stages of the hydrolysis.

Adding Equations 1 and 2, the total rate of forming HCl becomes

$$\frac{d(C_1 + C_2)}{dt} = \frac{dC}{dt} = K_1 (M) - k_1 (I) (H^-) (Cl^+) + K_2 (I) - k_2 (G) (H^+) (Cl^-) \quad (3)$$

This equation is, of course, only tentative, based on the simplest conceivable mechanism, and must be confirmed by experiment before it can be accepted.

### Reversibility of Second Stage Negligible

The hydrolysis of mustard gas in aqueous solution or in the presence of dil. hydrochloric acid proceeds substantially to completion as shown by careful experiments at various temperatures between 0° and 100°. Dilute solutions of thiodiglycol and hydrogen chloride acid produce no burns on the skin even after long exposure, and no evidence of reaction can be found by careful quantitative measurement. The regeneration of mustard gas from this thiodiglycol and hydrochloric acid can be brought about only under special conditions involving the presence of a minimum quantity of water and a maximum concentration of hydrogen chloride. Thus when 1 cc. of thiodiglycol was treated with 20 cc. of 25% hydrochloric acid at 70° no indication of the formation of mustard gas was evident and only when dry hydrogen chloride was passed through the solution for a considerable time did droplets of mustard gas appear. Evidently the tendency to regenerate mustard gas in even moderately concentrated acid solutions can be considered to be negligible.

From these facts it is apparent that either one or both of the two stages in the hydrolysis must be substantially non-reversible. On the other hand, the very marked retardation of the reaction, with increasing amounts of acid, indicates that at least one stage must be reversible to a considerable extent. It remains to determine which is reversible and which one substantially non-reversible under the conditions of these experiments.

A little consideration shows that in a 2-stage hydrolysis such as this, where the intermediate compound is quite soluble, the net rate of the first reaction really determines that of the second, once steady conditions are established, because the concentration of the intermediate compound will increase or decrease automatically until its rate of destruction just balances its rate of formation. For the same reasons, the magnitude of the second reaction rate constant or its reversal is of no moment, once steady conditions are established. The retardation of the reaction by acid must, therefore, be due to the reversibility of the first stage of the hydrolysis, while the failure to stop before completion is due to the substantial non-reversibility of the second stage.

Equation 3 then simplifies to

$$\frac{dC}{dt} = K_1 (M) - k_1 (I) (H^+) (Cl^-) + K_2 (I) \quad (4)$$

### The Reversibility of the First Stage

Since the first stage of the reaction is evidently reversible, it was desired to determine the magnitude of  $k_1$ , the specific rate of the reverse reaction. This obviously involves a knowledge of the concentrations of intermediate compound present in the solution. At first sight, it would appear that the simplest way to obtain the desired information would be to prepare some of the intermediate compound and to study the rate at which it forms mustard gas in the presence of hydrogen chloride. Some attempts were made along these lines, as described later, but the difficulty of preparing the compound in a satisfactory degree of purity, coupled with the fact that it disappears very rapidly due to the non-reversible second stage of the hydrolysis, makes it impracticable to secure accurate results by this method. Recourse was therefore had to a careful quantitative study of the magnitude of the retardation in the rate of hydrolysis in the presence of various amounts of acid and the subjection of these results to mathematical analysis.

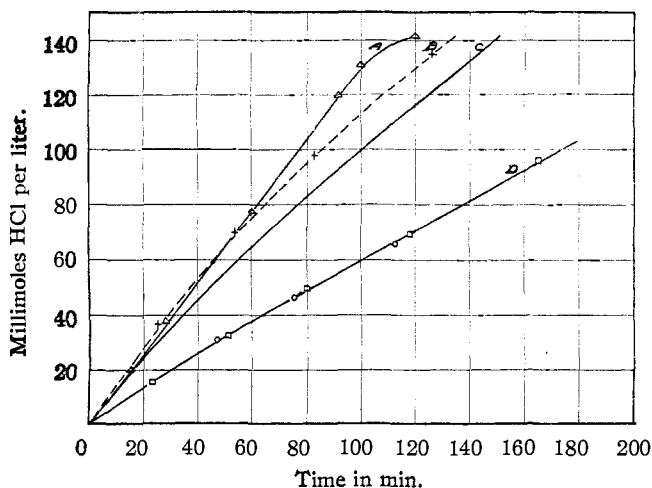


Fig. 1.—Rate of hydrolysis of saturated mustard gas solutions in the presence of various other compounds. A. Na<sub>2</sub>CO<sub>3</sub>; B. HNO<sub>3</sub> (0.1 N); C. H<sub>2</sub>O; D.  $\circ$  = HCl (0.106 N at start);  $\square$  = NaCl (0.099 N at start).

In order to hold the first and most important term of the reaction,  $K_1(M)$ , constant throughout the experiments, the aqueous phase was always kept saturated with mustard gas, as in the shaking experiments described in the previous paper. These were carried out in a thermostat

at a temperature of  $25^{\circ} \pm 0.1^{\circ}$ . Efficient shaking thus kept ( $M$ ) substantially equal to ( $M'$ ), the saturation value, which was previously shown to be the same for water as for dil. acids and alkalis.

The results of a series of these experiments are shown in Fig. 1. The fact that the sodium carbonate line is straight until 90% of the mustard gas is hydrolyzed, establishes two points of importance. In the first place, with the degree of shaking employed, not more than 10% of the mustard gas used was required to keep the solution saturated.

The other significance of the curve arises from a consideration of what must happen at the start of a 2-stage hydrolysis. At first no intermediate compound is present, so the chloride ion produced from the second stage of the reaction is initially zero. The total rate of producing hydrogen chloride, as indicated by the slope of the lines plotted in Fig. 1, would therefore start at half the normal value, and gradually increase to the full normal value as the intermediate compound built up to its equilibrium concentration under a given set of conditions. Beyond this point, the rate of hydrolysis should be constant as long as the solution remains saturated with mustard gas. The extrapolation of this straight line back to the ordinate axis should cut it at a point below the origin, the distance below being a direct measure of the equilibrium concentration of intermediate compound which must be built up before hydrochloric acid is formed at a normal rate.

Actually, the lines for both acid and alkaline solutions pass directly through the origin within the limits of error, indicating that the equilibrium concentration of the intermediate compound is extremely small, for if it were even a fifth as large as the solubility of mustard gas, it would be readily detectable. On the other hand, in the case of colloidal solutions such as those of sulfonated corn oil, discussed in the previous article, appreciable amounts of intermediate compound were apparently removed from the aqueous phase by solution in the colloidal oil globules, thus retarding the initial rate of hydrolysis.

It follows from the above that the rate of hydrolysis of the intermediate, at a given concentration, must be *at least* five times as great as that of mustard gas under the specified conditions.

The gradual decrease in the slope of the curve for plain water (Fig. 1) is obviously a measure of the reversal of the first stage of the hydrolysis, which is now under consideration. In order to make possible a detailed mathematical analysis of the results and a reasonably accurate determination of the values of the constants involved, several runs were made with great precision and covering a much longer time than those shown in Fig. 1. The results thus secured were put on a large scale plot and measurements of the slopes (instantaneous rates of hydrolysis corresponding to a given concentration of hydrogen chloride) carefully made. Fig. 2

gives the slopes found for the water curve plotted against the corresponding concentration of hydrogen chloride. The slope of the curve for sodium carbonate solutions is constant and equal to that of the water curve at the start, namely 1.31 millimoles of hydrogen chloride formed per liter per min. The difference between this value and the instantaneous value  $S$  (in millimoles) corresponding to any given concentration of hydrogen chloride is evidently a measure of the amount of retardation of the reaction from its normal value in alkaline solutions.

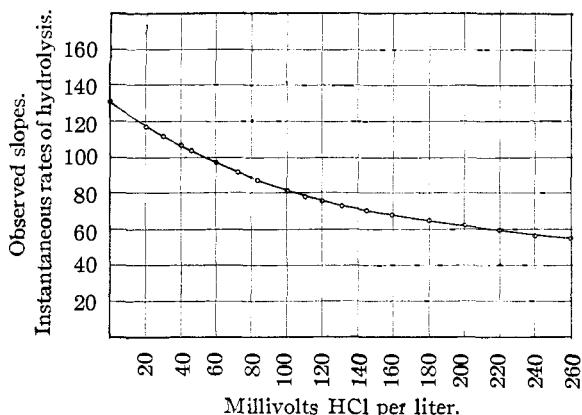


Fig. 2.—Instantaneous rates of hydrolysis of saturated solutions of mustard gas in various concentrations of HCl.

Mathematically, we may write for steady conditions, as shown above,

$$\frac{S}{1000} = \frac{2dC}{dt} = \frac{2dC_2}{dt} = 2K_1(M') - 2k_1(I)(H^+)(Cl^-) = 2K_2(I), \text{ and}$$

$2K_1(M') = \frac{1.31}{1000}$  (value determined in alkaline solutions); whence

$$\frac{1.31 - S}{1000} = 2k_1(I)(H^+)(Cl^-) \quad (5)$$

and substituting a value for  $(I)$  from Equation 1 above

$$\frac{1.31 - S}{S} = \frac{k_1}{K_2}(H^+)(Cl^-) \quad (6)$$

Hence, if the observed values of  $\frac{1.31 - S}{S}$  are plotted against the corresponding concentrations of hydrogen chloride the values should all be proportional to the product of  $(H^+)(Cl^-)$  calculated for the same concentrations. Better still, by multiplying  $(H^+)(Cl^-)$  by a value of the proportionality constant  $k/K_2$ , determined by substituting in Equation 5 the observed values at one concentration (say 50 millimoles of hydrogen chloride per liter) and plotting this against the concentration of hy-

drogen chloride, the two curves should approximately coincide throughout their length.

Inspection of Fig. 3 indicates, however, that this is far from being true. Evidently the rate of the reverse reaction increases much less rapidly than the product,  $(\text{H}^+)(\text{Cl}^-)$ . Two similar curves were then drawn to see whether  $\frac{1.31-S}{S}$  was proportional to the concentration of a single ion<sup>2</sup> ( $\text{H}^+$ ) or ( $\text{Cl}^-$ ) again selecting the proportionality constant so as to make

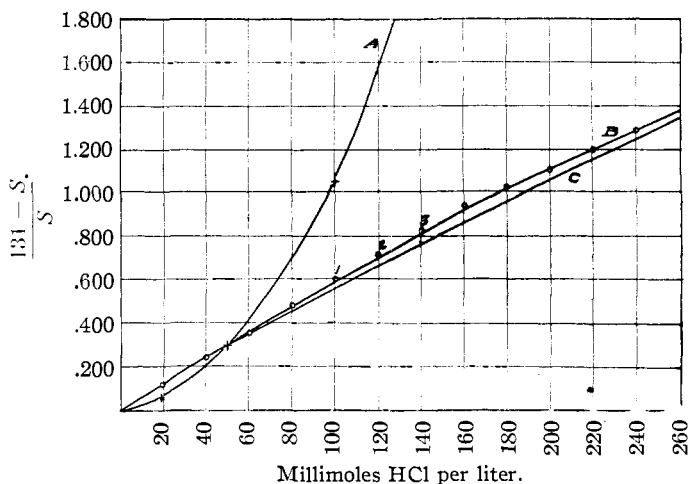


Fig. 3.—Observed values of  $(1.31 - S)/S$  compared with calculated curves, assuming proportionality to  $(\text{H}^+) \times (\text{Cl}^-)$  and to  $(\text{H}^+)$  or  $(\text{Cl}^-)$  alone. A. Calc. for  $\propto (\text{H}^+) \times (\text{Cl}^-)$ ; B. Calc. for  $\propto (\text{H}^+)$ ; C. Calc. for  $\propto (\text{Cl}^-)$ ; 1, 2, 3, etc., observed points.

the curves coincide at one point (50 millimoles). Very surprisingly, the values of  $\frac{1.31 - S}{S}$  were found to correspond well within the limits of experimental error throughout the whole range of observations. The slightly better correspondence of the hydrogen-ion curve is not significant, since a very slight change in the proportionality constant calculated at the 50 millimole point would make the chloride ion correspond equally well.

It seems, however, inconceivable that the reverse reaction is in itself proportional to the concentration of a single ion, rather than to the product of both concentrations as demanded by the mass-action law. A more reasonable assumption would be that one of the forward reactions was

<sup>2</sup> All the values used in this paper as ionic concentrations are calculated, sometimes by extrapolation, from the data of Lewis and Randall on the activity coefficients of individual ions as a function of the "ionic strength" of the solutions. See THIS JOURNAL, 43, 1112 (1921).

catalyzed in direct proportion to the concentration of hydrogen ions, so that the net retarding effect became proportional to the chloride ions only.

### The Catalysis of the Second Stage by Hydrogen Ion

A little consideration shows that the first stage of the hydrolysis is certainly not catalyzed appreciably by hydrogen ions, for, if it were, the initial rate of hydrolysis in saturated solutions would be very much higher in the presence of small amounts of acids, whereas it is actually the same as in the alkaline solutions. Furthermore, an equation derived on this assumption would not make  $\frac{1.31-S}{S}$  proportional to  $(Cl^-)$ . If, however, the second reaction were catalyzed by hydrogen ions, the only observable effect would be the change in the equilibrium concentration of the intermediate compound, which would, in turn, affect the reversal of Stage 1.

Mathematically, for such a case  $\frac{S}{1000} = 2 \frac{dC_2}{dt} = 2K_2' (I) (H^+)$ . Substituting this value of  $(I)$  in Equation 5 would give

$$\frac{1.31-S}{S} = \frac{k_1}{K_2} (Cl^-) \quad (7)$$

which is precisely the relationship found experimentally.

As a crucial test of this explanation, it will be noted that, according to Equation 7, the retarding influence of hydrochloric acid should be substantially identical with that of an equal concentration of sodium chloride, whereas any other acid but hydrochloric should give a curve corresponding fairly closely to that for water. Both of these predictions would be entirely contradictory to the ordinary deductions from the mass-action law, in the absence of an assumption that the second stage of the hydrolysis is catalyzed by hydrogen ions. Both, however, were subsequently verified by experiments as shown by the curves for nitric acid, hydrochloric acid, and sodium chloride solutions in Fig. 1. Furthermore, the observed retardations by the sodium chloride and hydrochloric acid correspond quite reasonably well with that calculated from their chloride-ion concentrations, as indicated by Table I following. Thorough going attempts to develop some other reasonable hypothesis as to the mechanism of the reaction which would fit the observed facts were fruitless.

We may, therefore, write as a fundamental equation for the rate of hydrolysis of mustard gas *in acid solutions*

$$\frac{dC}{dt} = K_1 (M) - k_1 (I) (H^+) (Cl^-) + K_2' (I) (H^+) \quad (8)$$

or its simpler equivalent for *saturated* acid solutions, from (7),

$$\frac{S}{1000} = \frac{dC}{dt} = \frac{0.00131}{1 + k_3 (Cl^-)} \quad (9)$$

where  $k_3 = \frac{k_1}{k_2}$ .



From 4 points on the water curve (Fig. 2), the average value of  $k_3$  was calculated to be 6.14. Substituting this value in Equation 9, it was possible to compare the observed and calculated values of  $S$  for a wide variety of solutions, as shown in Table I below.

TABLE I  
COMPARISON OF CALCULATED AND OBSERVED VALUES OF  $S$  IN VARIOUS ACID SOLUTIONS  
All concentrations expressed in equivalents per liter

Conc. of HCl by hydrolysis	Conc. of electrolytes present	Original solution	Calc. conc. ( $\text{Cl}^-$ )	Obs. $S$	Calc. $S$
0.05	0	Water	0.048	1.02	1.02
0.10	0	Water	0.094	0.81	0.83
0.17	0	Water	0.158	0.66	0.66
0.26	0	Water	0.237	0.55	0.54
0.06	0.100	$\text{HNO}_3$	0.056	1.13	0.98
0.12	0.100	$\text{HNO}_3$	0.110	0.86	0.78
0.04	0.106	HCl	0.136	0.71	0.71
0.08	0.106	HCl	0.171	0.66	0.64
0.04	0.099	NaCl	0.129	0.71	0.73
0.08	0.099	NaCl	0.165	0.66	0.65

It will be noted that the correspondence between the observed and calculated values is excellent in all cases, except for the single run with nitric acid which gave rather high results at the start, a fact which might be explained in several ways. At any rate, in the light of these results there can be little doubt as to the validity of Equation 9 above, and the mechanism of the reaction in acid solutions which it indicates. In alkaline solutions, regardless of the chloride-ion concentration, the reaction is, of course, irreversible.

The question naturally arises as to the proper equation for the second stage of the hydrolysis in *alkaline* solutions, where the hydrogen-ion concentration is exceedingly low. As pointed out previously, there is no convenient way of determining accurately the values of  $K_2$  in alkaline solutions, since variations in  $k_2$  affect only the time required to build up the equilibrium concentration of the intermediate compound. Since this period has been shown to be very short for both acid and alkaline solutions, it seems certain that the reaction is much faster than that of the first stage, even if no hydrogen ions are present to catalyze it. It is, therefore, quite possible that this stage of the reaction is catalyzed to some extent by hydroxyl ions as well as hydrogen ions, as has frequently been found to be the case in such hydrolytic reactions.

#### The Solubility of Mustard Gas in Water at 25°

The specific rate constant for the first stage of the hydrolysis can be calculated from the equation,  $2K_1(M') = 0.00131$ , by first determining ( $M'$ ), the solubility of mustard gas in water at 25°. This is difficult to determine accurately because the solubility is very low, and because of

the rapid hydrolysis of the mustard gas during shaking and filtration at 25°. The most serious problem is to assure filtration which is rapid and yet efficient enough to remove all tiny suspended drops. The following method was finally used and found to be satisfactory.

Mustard gas was vigorously shaken with water at 25° for 30 seconds and then filtered during the next 20 seconds with the aid of suction. The filtering medium consisted of paper pulp previously moistened with a completely hydrolyzed filtrate from a preliminary determination. A 100cc. portion of the filtrate was allowed to stand for 24 hours and then treated with an excess of sodium carbonate and warmed for a few minutes to insure complete hydrolysis. The average of 3 fairly closely agreeing determinations gave a chloride content of 9.5 milli-equivalents of chloride per liter. If it is assumed that during the preparation of the solution the mustard gas hydrolyzed according to the water curve in Fig. 1, a small correction corresponding to the total time of shaking, plus half the time of filtration, should be made. This gives a corrected value of 9.5-0.9 or 8.6 milli-equivalents, or  $8.6/2 = 4.3$  millimoles, of mustard gas per liter as the solubility value (= 1000  $M'$ ) at 25°. This is considerably higher than the approximate value of 3, determined during the war by the French, but the value 4.3 is believed to be substantially correct.

Substituting this value in the previously derived equation

$$K_1 = \frac{1.31}{2 \times 4.3} = 0.152.$$

This value checks reasonably well with a value of 0.13, determined during the war by Keyes and Russell<sup>3</sup> by a conductivity method. The value which they determined for  $K_2$  is apparently greatly in error, due to the failure to take into account the catalytic effect of hydrogen ion on this stage of the reaction, which was, of course, not suspected at that time. This source of error would also affect somewhat the value of  $K_1$ .

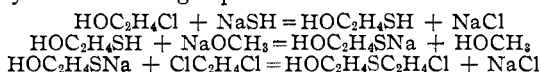
### Experiments with the Intermediate Hydrolysis Compound

The foregoing experiments have given all the constants really needed for calculating the net rates of hydrolysis of mustard gas in practically any type of solution at 25° by using the relationship  $\frac{dC}{dt} = 2K_1(M)$  for alkaline solutions and simplified equations such as (9) for acid solutions. The  $k_3$  in this equation is, however, really a combination of constants from the more fundamental equation (8), and it was considered desirable to determine these separately, if possible, and also to check up directly the effect of  $H^+$  on the second stage of the reaction.

The attempt was, therefore, made to prepare the intermediate hydrolysis compound in a fairly pure state and to study its rate of hydrolysis thus

<sup>3</sup> Unpublished *Report* of the Paris Laboratory, C. W. S., 1919.

obtaining a numerical value for  $K_2$ . The method used for its preparation is indicated by the following equations



This work was carried out by Dr. M. A. Youtz of this Laboratory. The substance secured was a thick oil, soluble in water, only very slightly volatile, with an odor resembling that of mustard gas. When applied to the skin it gave a burn considerably less than that produced by a like amount of mustard gas. The substance was not secured in a pure condition because of experimental difficulties, but it contained no inorganic chlorides. It was prepared and kept under anhydrous conditions.

When attempts were made to follow its rate of hydrolysis in water at room temperature, it was found to be so rapid that the reaction was substantially complete before samples could be removed and titrated. By working at  $0^\circ$  and using a variety of devices to follow the rate with sufficient rapidity, enough results were obtained to indicate that the hydrolysis is extremely rapid, being 50% complete in less than a minute. It appeared to be accelerated in acid solutions, as predicted from the previous study, but it was not found possible, with the limited amounts and doubtful purity of the material available, to determine definite values for the constants.

### Summary

1. The hydrolysis of mustard gas in contact with water is a 2-stage reaction which affects only the molecules dissolved in the aqueous phase.
2. The rate of the first stage of the reaction determines that of the second. Once steady conditions are established, the concentration of the intermediate compound automatically increases or decreases keeping the rate of the second stage just equal to that of the first. The amount of intermediate compound present at any time is extremely small, and the time required to build up the equilibrium concentration is generally negligible.
3. The simplest expression for the rate of hydrolysis at  $25^\circ$  in alkaline solutions, where there is no tendency toward reversal, is  $\frac{dC}{dt} = 2K_1(M) = 0.304(M)$ , where  $dC/dt$  is the rate of hydrolysis in millimols of hydrogen chloride produced per liter per minute and  $(M)$  is the concentration of mustard gas in millimoles per liter.
4. The second stage of the hydrolysis reaction is substantially non-reversible except in very strong hydrochloric acid solutions. The first stage is, however, reversible to a considerable extent in the presence of even dil. acids. This reversibility of one stage serves to retard but not to stop the reaction because the intermediate hydrolysis compound is being continually destroyed by the irreversible second stage.

5. Indirect, but apparently indisputable, evidence indicates that the second stage of the reaction is catalyzed in direct proportion to the hydrogen-ion concentration in acid solutions. Since the rate is also very rapid in alkaline solutions it is very likely catalyzed by hydroxyl ions as well.

6. The mathematical expression for the rate of hydrolysis in acid solutions is, therefore,  $\frac{dC}{dt} = K_1(M) - k_1(I)(H^+)(Cl^-) + K_2'(I)(H^+)$ . A simpler, but less obviously rational form of this equation is  $\frac{dC}{dt} = \frac{2k_1(M)}{1 + k_3(Cl^-)} = \frac{0.304(M)}{1 + 6.14(Cl^-)}$ . This equation has been found to hold with satisfactory accuracy for a wide variety of acid solutions.

7. The solubility of mustard gas in water at 25° is 0.0043 mole per liter. Substituting this value in the above equations gives the rate of hydrolysis in solutions saturated with mustard gas.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

## THE ABSORPTION OF CARBON MONOXIDE BY CUPROUS AMMONIUM CARBONATE AND FORMATE SOLUTIONS

BY ALFRED T. LARSON AND CLARK S. TEITSWORTH

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### Introduction

When hydrogen is made by the interaction of carbon monoxide and steam in the presence of a catalyst there is usually about 2-4% of carbon monoxide remaining in the gas produced. If this hydrogen is to be used in the synthesis of ammonia, a fairly complete removal of the carbon monoxide becomes necessary, since all ammonia catalysts so far suggested suffer a loss in efficiency if this gas is present. Thus, at low temperatures the loss due to 0.1% of carbon monoxide may become as much as 60-70% of the conversion of pure gas. This effect becomes very much less at higher temperatures but, unfortunately, the percentage of ammonia produced decreases rapidly as the temperature is raised. It is of importance, therefore, to operate at as low a temperature as possible, which means that the nitrogen-hydrogen mixture should be quite free from such catalyst poisons as carbon monoxide.

In practice the last traces of carbon monoxide are usually removed by passing the gas under pressure through ammoniacal copper solutions. At low temperatures it forms with cuprous solutions complex or possibly addition compounds which are readily decomposed when the temperature of the solution is raised. These solutions may therefore be regenerated by