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THE ACCELERATION OF THE HYDROLYSIS OF MUSTARD GAS BY ALKALINE COLLOIDAL SOLUTIONS¹

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Introduction

During the war the rapid and complete removal of mustard gas² from contaminated clothing in the field laundries was a matter of prime importance. A wide variety of methods were suggested and many tried, but without going into details in this paper it may be said that none of the earlier methods fulfilled the requirements of rapidity, certainty and cheapness, without damage to the cloth. This paper discusses the results and mechanism of a method of accelerated hydrolysis which was developed to meet these requirements.

The Removal of Mustard of Gas from Clothing by Accelerated Hydrolysis

Hydrolysis, in which water acts as the destructive agent, was from the start considered a desirable method since it is obviously simple and inexpensive if it can be made effective. But, under ordinary conditions, this reaction proceeds so very slowly that the clothing would have to be soaked in water for several days or else actually boiled for an hour or more, which would be difficult, and indeed dangerous, on account of the volatility of the mustard gas with steam. An attempt was accordingly made to find some means by which this hydrolysis might be accelerated. After considerable investigation it was discovered that the addition of alkaline solutions of sulfonated animal or vegetable oils to the water, facilitated hydrolysis to a remarkable degree and made the process practicable for field use.

In order to show the necessity of accelerating the normal rate of hydrolysis and the advantages to be gained by the use of these sulfonated oils, it seems desirable to present a few typical curves showing the rate of removal of mustard gas from cloth in the presence of different solutions.

The following general procedure was used in studying the rate of hydrolysis of mustard gas on cloth.

¹ Published with the permission of General Amos A. Fries, Chief of the Chemical Warfare Service.

Much of the work described in this paper was carried out by the writers in the Research Division of the Chemical Warfare Service, at the American University, Washington, D. C. Its publication has been delayed until certain points of theoretical importance were cleared up by later investigations in the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology. The latter work was aided by a grant from the C. M. Warren Fund of the American Academy of Arts and Sciences, the assistance of which is gratefully acknowledged.

² Following the customary nomenclature used during the war, *liquid* β,β' -dichloro-di-ethyl sulfide is referred to as "mustard gas" throughout this paper.

A 25cm. square of cotton toweling weighing about 9 g., was folded and placed in the bottom of a dry 250cc. Erlenmeyer flask. Exactly 2 cc. of the liquid "mustard gas" was added from a small buret, drop by drop, care being taken to distribute the liquid uniformly over the surface of the folded cloth. In order to give the mustard gas an opportunity to soak in, the contaminated cloth was allowed to stand for at least $1\frac{1}{2}$ hours before the laundering solution was added. This solution was made up in a volumetric flask to 250 cc. at room temperature and heated to 85° . It was then added to the Erlenmeyer flask containing the cloth soaked with mustard gas and was kept in a water-bath at 85° . Aliquot samples, 15 cc. each, were withdrawn from time to time and the chloride content determined with 0.1 *N* silver nitrate solution. In calculating results allowance was made for chloride removed in previous samples and for decrease in volume due to removal of these samples. Evaporation was prevented by keeping the flasks loosely stoppered.

In the course of the experiments about 200 different solutions were used and it was not found difficult to get results which checked within 5% or, at the most, 10%, in repeating the experiments. The results obtained in a few of the more important experiments are shown in Fig. 1.

Curve 1, in Fig. 1 brings out very clearly the impracticability of using plain water to complete the hydrolysis even at 85° . It will be noted that hydrolysis is fairly rapid up to 50% of completion and then slows down, requiring over 3 hours to reach 65% of completion.

The substitution of a 2% sodium carbonate solution for the plain water raises the curve without changing its shape very greatly, but it again flattens off below 85% hydrolysis. The addition of 3% of soap to the solution already containing 2% of sodium carbonate makes a further increase in the initial rate, but this flattens off very sharply at about 90%. The sharp flattening off in this vicinity has been confirmed by repeated tests and is apparently characteristic of the presence of soap except in very strongly alkaline solutions.

Curve 4 shows clearly the great superiority over the other solutions of a

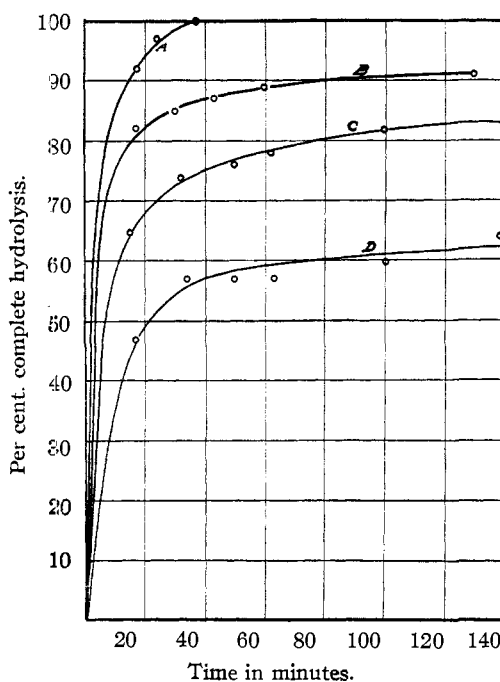


Fig. 1.—Rate of hydrolysis of mustard gas on cloth at 85° . A. H_2O ; B. 2% Na_2CO_3 . C. 2% Na_2CO_3 + 3% soap; D. 2% Na_2CO_3 + 3% sulfonated corn oil.

solution containing 2% of sodium carbonate + 3% of sulfonated corn oil, as this completes the hydrolysis within 35 minutes, as shown by repeated check tests.

A large number of experiments have been made with different concentrations and combinations of these materials, but the curves shown represent approximately the optimum concentrations for each of the combinations, although minor variations in either direction do not have a large effect.

As to the effect of other types of solutions, neutral salts and acids in concentrations up to 2 or 3% were found to have a negligible effect, although higher concentrations seemed to retard hydrolysis somewhat. Practically all of the alkaline salts had some accelerating influence when present in moderate concentration, although this was far from proportional to the hydroxyl-ion concentration; 2% of sodium carbonate is about as good as any *non-colloidal* alkaline solution which would not seriously injure fabrics.

The use of the sodium carbonate along with the soap or the sulfonated oil was found essential in order to prevent the precipitation of the respective organic acids by the free hydrochloric acid which is otherwise formed as the mustard gas hydrolyzes.

In addition to sulfonated corn oil, many other sulfonated compounds were investigated. In general it was found that only the sulfonated glycerides (animal and vegetable oils) were effective, sulfonated aromatic compounds having substantially no beneficial influence.

It was found that increased temperature and stirring were both quite beneficial—indeed, by boiling the sulfonated corn oil solution the hydrolysis may be completed in less than 5 minutes. The treatment had no more effect upon the color or strength of khaki cloth than the regular laundering procedure. The recommended method was further tested out in foreign laboratories and approved for field use.

Investigation of the Mechanism of the Acceleration

While the foregoing experiments demonstrated beyond question the necessity of accelerating the hydrolysis, and the value of alkaline solutions of sulfonated oils for the purpose, they afforded no clue as to why these particular solutions, at fairly definite alkalinities, should have such remarkable accelerating properties. Since this question was of both theoretical and practical interest in several connections, a detailed study has been made of the mechanism of the accelerating action. Most of the later phase of this work were carried out in this Laboratory.

When liquid mustard gas is brought into contact with water it *dissolves* as *such* at a rate that may be expressed mathematically as follows.

$$\frac{dm}{dt} = AS - \frac{(M)}{(M')} AS = AS \frac{(M') - (M)}{(M')} \quad (I)$$

where m is the total number of mols of mustard gas dissolved up to time t ;

dm/dt , therefore, is the rate of solution (moles per min.); (M) is the concentration of mustard gas *as such* (moles per liter) in the solution at time t ; (M') is the concentration of mustard gas in a saturated solution at the temperature in question; A is the area in sq. cm. of the interfacial surface between mustard gas and water; and S is the specific rate of solution, that is, the rate of solution when $M=0$, and hence $A \frac{(M'-M)}{M'}$ equals unity.

After solution, the mustard gas reacts with the water. This hydrolysis takes place in two stages, as will be shown later. The reaction may be expressed as follows.



As this paper deals with the mechanism of the acceleration of the hydrolysis in alkaline solution, the reversal of the two reactions in the presence of hydrochloric acid need not be considered for the present.³

The rates of producing hydrochloric acid by each stage of the hydrolysis may, therefore, be expressed as follows.

$$\frac{dC_1}{dt} = K_1(M) = \text{rate of formation of hydrochloric acid (moles per liter per min.)} \\ \text{due to Reaction 1} \quad (\text{II})$$

$$\frac{dC_2}{dt} = K_2(I) = \text{rate of formation of hydrochloric acid due to Reaction 2,} \quad (\text{III})$$

where (I) is the number of moles per liter of the *intermediate* hydrolysis compound present as such at time t ; K_1 is the specific rate of Reaction 1 proceeding from left to right, that is, the rate when (M) = unity; K_2 is the specific rate of Reaction 2 proceeding from left to right, that is, the rate when (I) = unity.

Equations II and III involve the assumption that the mass-action effect of the water is constant throughout the experiments, which is substantially the case in all experiments discussed herein. It is, of course, possible that K_1 and K_2 may be affected catalytically and hence not be constant under all circumstances.

The speed with which liquid mustard gas is destroyed by hydrolysis depends, then, upon two processes: first, the rate of solution of the mustard gas into the aqueous phase and, second, the rate of hydrolysis of the dissolved molecules. The fact that mustard gas hydrolyzes only after it has dissolved in the aqueous phase has been abundantly verified experimentally, for example, by showing that the rate of hydrolysis in a solution thoroughly agitated with excess of mustard gas is (at least at temperatures below 50°) independent of the amount of liquid mustard gas present. If the reaction took place to an appreciable extent at the interface or in the mustard gas phase, an increase in the quantity of the latter present should increase the rate of hydrolysis.

³ The second paper by the present authors will discuss the reverse reactions in detail.

In a 2-phase system composed of water and mustard gas, when steady conditions (temperature, area of interface, etc.) are maintained, a dynamic equilibrium is soon set up such that the rate of solution just equals the rate of hydrolysis, and the concentration M of dissolved mustard gas at a given point in the solution remains substantially constant. The time required to reach this equilibrium value is in general very small, because of the comparatively slight solubility of mustard gas in water. We may, therefore, write for steady conditions

$$\frac{dm}{dt} = K_1(M) \quad (\text{IV})$$

but as
$$\frac{dm}{dt} = AS \frac{(M') - (M)}{(M')} \quad (\text{I})$$

we have
$$M = \frac{AS(M')}{K_1(M') + AS} \quad (\text{V})$$

The rate of formation of hydrochloric acid from both reactions is equal to

$$\frac{d(C_1 + C_2)}{dt} = K_1(M) + K_2(I) \quad (\text{VI})$$

Again, under steady conditions $K_1(M) = K_2(I)$, so that substituting the value of (M) from Equation V gives

$$\frac{d(C_1 + C_2)}{dt} = \frac{dC}{dt} = \frac{2K_1 AS(M')}{K_1(M') + AS} \quad (\text{VII})$$

where $C = C_1 + C_2$, the total number of moles of hydrogen chloride produced.

The equilibrium for which these equations were derived is a stable one since any variation in (M) or (I) is automatically compensated for by slight changes in the rates of solution or of hydrolysis which quickly restore normal conditions.

Equation VII shows the relationship between the specific rate of reaction for the first stage of hydrolysis, the solubility of mustard gas in the aqueous phase, the specific rate of solution, and the area of the interface. A study of this equation shows that the rate of destruction of the mustard gas might be accelerated by any one or a combination of the following factors: (1) an increase in K_1 , the specific rate of hydrolysis; (2) an increase in (M') , the solubility of mustard gas in the water phase; (3) an increase in S , the specific rate of solution of mustard gas into the water phase; (4) an increase in A , the area of interface.

The problem of determining the mechanism of the accelerating effect of the sulfonated oils necessitates, therefore, an analysis of the effect of the presence of these materials on each of these 4 factors, which are considered in the above order.

Effect on the Specific Rate of Hydrolysis.—To determine the effect of sulfonated oils and similar compounds on the specific rate of hydrolysis of mustard gas, a comparative study was made of the hydrolysis curves of mustard gas completely dissolved in various aqueous solutions. The

slight solubility of mustard gas in water and the amount of hydrolysis which takes place while the solutions are being prepared makes this a rather difficult procedure. The presence of other electrolytes in relatively high concentrations renders the use of conductivity methods impossible. However, by working at low temperatures and thus reducing the rate of hydrolysis, the following method gave satisfactory results.

A liter of water, cooled to nearly 0° , was shaken with mustard gas crystals for about an hour and then filtered through paper in a funnel packed in ice; 300 cc. of the filtrate, cooled by ice, was collected and divided into 4 equal parts. To one, sufficient sulfonated corn oil was added to give a 3% solution; to the second, sulfonated corn oil and sodium carbonate were added so as to give a 3% and 2% solution, respectively; to the third, enough sodium carbonate to give a 2% solution; the fourth was left unchanged. These 4 solutions were kept surrounded by ice, and 25cc. samples were withdrawn from time to time, shaken at once with cold chloroform to remove all unhydrolyzed mustard gas (see next section) and then titrated for free chloride content.

The results, which are shown graphically in Fig. 2, are obviously entirely different from those observed in cloth experiments where a liquid

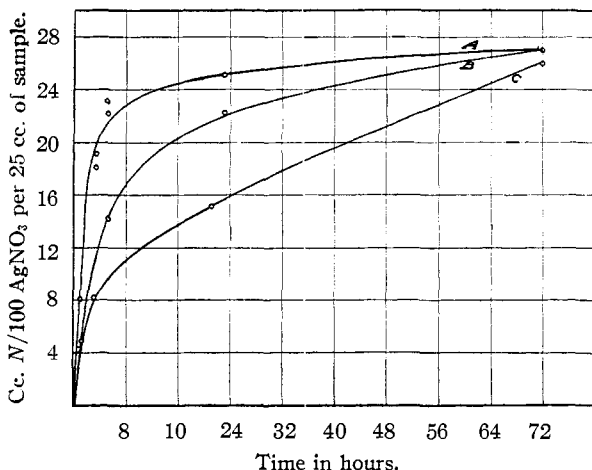


Fig. 2.—Rate of hydrolysis of mustard gas solutions saturated at start. A. Water - 2% Na_2CO_3 ; B. 3% Sulfonated corn oil + 2% Na_2CO_3 ; C. 3% Sulfonated corn oil.

mustard gas phase was present. The water and sodium carbonate runs checked very closely and gave the highest rate of hydrolysis, also checking with several other curves (not shown) for various non-colloidal alkaline and acid solutions. However, 3% sulfonated corn oil alone gave a very much slower rate of hydrolysis, although the addition of 2% sodium carbonate to this brought it back about half way to normal.

It is evident, then, that the accelerating action of the sulfonated oils in the cloth experiments cannot be explained on the basis of a change in the

specific rate of hydrolysis. Indeed, these apparently contradictory experiments must themselves be accounted for. The explanation becomes fairly obvious, however, when it is pointed out that mustard gas is quite soluble in sulfonated corn oil (about 20% by volume in 80% sulfonated oil + 20% water at room temperature). It is, therefore, entirely probable that colloidal particles of sulfonated corn oil would dissolve considerable amounts of mustard gas from solutions, thereby reducing the number of hydrolyzing molecules and giving a much lower initial rate of hydrolysis. This explanation is further confirmed by the fact that the neutral solution of the sulfonated corn oil contains many more colloidal particles than the alkaline one, and makes the greater reduction in the rate of hydrolysis. As the mustard gas in the aqueous phase disappears by hydrolysis, that in the oil phase gradually redissolves in the aqueous phase, so that the rate of hydrolysis drops off but slightly from its initial low value, and approximately complete hydrolysis is reached almost as soon as for plain water.

Similar experiments made at 25° confirmed the above results, although the difference was not so marked (due presumably to fewer colloidal particles being present), nor was the accuracy of the determinations as great. It was impractical to carry out such experiments at temperatures higher than 25° on account of the very rapid increase in the rate of hydrolysis.

In any event, in the light of these experiments, it may safely be assumed that the accelerating action of sulfonated corn oil is not to be explained on the basis of any increase in K_1 , the specific rate of hydrolysis.

Effect on the Solubility of Mustard Gas.—It is almost impossible to determine by direct measurements whether or not the solubility of mustard gas in the aqueous phase is influenced by the presence of the colloidal accelerating agents. Fairly accurate solubility determinations can be and have been made in non-colloidal solutions by working at low temperatures and filtering very rapidly to remove the excess of liquid mustard gas, thus minimizing the necessary correction for the amount of hydrolysis taking place before all the excess of liquid phase is removed. In the case of the colloidal solutions, however, complete separation of the colloidal particles containing dissolved and emulsified mustard gas is almost impossible, except possibly by using filters so dense that the amount of hydrolysis taking place during filtration would be so large as to make the result of little value.

If an aqueous solution is kept substantially saturated with mustard gas by continuous and vigorous shaking, the rate of hydrolysis will not be limited by the area of interface or by the rate of solution, but by the solubility of mustard gas in the aqueous solution, multiplied by its specific rate of hydrolysis. Since it has just been shown that the specific rate of hydrolysis is not increased by the presence of the "accelerating agents," an increase in the rate of hydrolysis under the above conditions would in-

dicating an increase in solubility. Furthermore, if the rate were found to be identical for all solutions, it would certainly indicate that neither of the two variables was affected, thus confirming the previous conclusion with respect to the specific reaction rate.

While it was readily possible to keep the aqueous phase saturated with mustard gas by efficient shaking, it was difficult to find a means of stopping the hydrolysis of dissolved and undissolved mustard gas at a definite time and thus allow the hydrolyzed mustard gas to be determined by titration of the free chloride present in the sample. The following method was eventually worked out and gave quite satisfactory results.

One cc. of mustard gas was introduced into 150 cc. of the aqueous phase at 25° contained in a 250cc. glass-stoppered bottle clamped into position in an effective shaking apparatus in a thermostat at 25° ± 0.1°. The bottle was shaken for 15 minutes, a 10cc. sample withdrawn and delivered at a noted time into 100 cc. of purified chloroform, and vigorously agitated. Similar samples were removed every 15 minutes. The func-

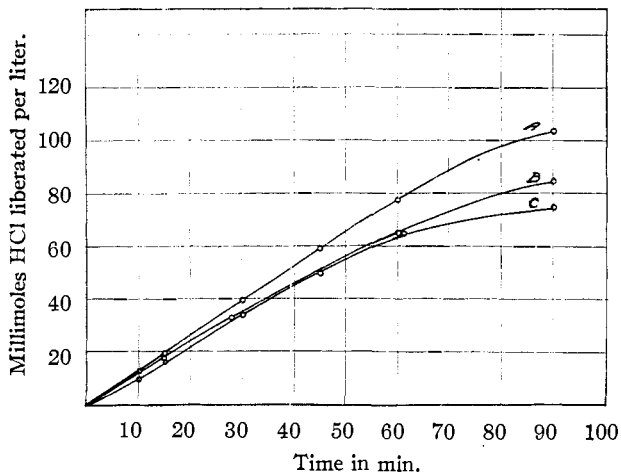


Fig. 3.—Rate of hydrolysis at 25°; solutions shaken with excess of mustard gas. A. 2% Na₂CO₃; B. Water; C. 2% Na₂CO₃ + 3% sulfonated corn oil.

tion of the chloroform was to remove unhydrolyzed mustard gas from the sample (the mustard gas being enormously more soluble in the chloroform) and thus prevent further hydrolysis of dissolved or suspended mustard gas after the noted time of delivery of the sample. Experiments showed that none of the free chloride was removed by the chloroform. The samples were then titrated for chloride content by means of the Volhard method. These experiments were found to have a high degree of reproducibility.

Typical results are shown in Fig. 3. It will be noted that the curve for hydrolysis in the presence of 2% sodium carbonate is accurately represented by a straight line passing through the origin, up to the point where 85% of the mustard gas has hydrolyzed, after which the amount of liquid phase remaining is insufficient to keep the water fully saturated. The

same characteristic straight line with the same slope has been found for all other non-colloidal alkaline solutions and it has been continued for as long as 3 or 4 hours by starting with more liquid mustard gas.

The existence of this straight line is of importance from several aspects. In the first place, it obviously means that the rate of the reaction is not influenced by changes in hydroxyl-ion concentration, and that, under these conditions, there is no appreciable tendency to reverse the hydrolysis, even though considerable amounts of the reaction products are formed. This lack of reversibility is, of course, due to the substantial absence of hydrogen ions which are required for the reverse reactions.

The fact that, within the accuracy of the experiments, the straight line passes through the origin is especially significant, because the hydrochloric acid is formed in 2 stages, and hence it cannot be produced at a steady rate until the intermediate hydrolysis compound produced by the first stage in the hydrolysis has reached its equilibrium concentration, at which it hydrolyzes to produce hydrogen chloride just as fast as it is itself produced. Since there is no noticeable period during which the rate of hydrolysis is gradually increasing from half to the full final value, it follows that the equilibrium concentration of the intermediate compound must be extremely small or, in other words, that its specific rate of hydrolysis must be much greater than that of the first stage of the hydrolysis. This is confirmed by later experiments.

Each of the other two curves shown in Fig. 3 is in striking contrast with the sodium carbonate curve in one of these two respects. In the case of the hydrolysis in plain water, the initial rate of hydrolysis is apparently identical with that for sodium carbonate, but decreases markedly as time goes on, on account of a reversing tendency in the presence of hydrogen ions. The precise mechanism of this retarding action is discussed in detail in the following paper, but it has no bearing on the accelerating action of the alkaline solutions under consideration.

In the case of the sulfonated corn oil solution, the initial rate is obviously quite appreciably slower than that in sodium carbonate solutions. This initial retardation can scarcely be due to the solution of mustard gas in the colloidal oil particles because in the present case there is a large excess of liquid mustard gas present. Furthermore, the rate of hydrolysis actually increases as time goes on. The more reasonable explanation is that the initial slowness of the reaction is due to the removal of the intermediate hydrolysis compound from the aqueous phase by solution in the colloidal oil particles, so that the initial rate of hydrolysis is not much more than half that in sodium carbonate solutions, but rapidly increases to nearly the normal value as the colloidal oil particles accumulate enough intermediate compound to be in equilibrium with its normal concentration in the aqueous phase.

It is also observed that the sulfonated corn oil curve flattens off much more quickly than does the sodium carbonate curve. This decrease is probably due to the solution of the last 30 or 40% of the mustard gas in the colloidal particles of sulfonated corn oil. This conclusion is borne out by the fact that liquid drops of mustard gas, which were always visible in the non-colloidal solutions until 90% or more had been hydrolyzed, disappeared in the sulfonated corn oil solution when about 60 or 70% had hydrolyzed. Furthermore, this final flattening off can be delayed indefinitely by the addition of more liquid mustard gas at the start of the reaction.

These experiments, therefore, indicate that the various "accelerating agents" do not increase the solubility of mustard gas in the aqueous phase, and furthermore confirm the previous indication that they do not increase the specific rates of hydrolysis. They also add much weight to the evidence that colloidal particles of sulfonated corn oil dissolve considerable amounts of mustard gas and of the intermediate hydrolysis compound, and that under many conditions this results in a *decreased* rate of hydrolysis on account of the removal of these materials from the zone of action in the aqueous phase.

Attention must, therefore, be turned to the other two possible factors in the acceleration of the hydrolysis, namely, the specific rate of solution and the area of interface exposed.

Effect on the Specific Rate of Solution.—In order to study the effect of the various "accelerating agents" on the specific rate of solution, experiments were conducted in which the area of interfacial surface between water and mustard gas was kept small and constant, while the rate of hydrolysis was speeded up so that it was no longer the limiting factor, thus making possible the detection of any variations in the magnitude of the specific rate of solution. A preliminary set of investigations was carried out by blowing a small cylindrical cup in the bottom of a Pyrex flask, filling this with mustard gas, and then filling the flask with the various hydrolyzing solutions. The results obtained in this way were extremely interesting, in that they indicated a slight accelerating action by ordinary alkaline solutions and a very marked accelerating action, similar to that in the cloth experiments for the colloidal alkaline solutions, such as those of soap and sulfonated corn oil.

It was found difficult, however, to obtain a satisfactory degree of reproducibility in these results, especially with the accelerating agents, and the whole series was accordingly repeated in a much more accurate manner by Mr. C. E. Ronneberg, of this Laboratory, who used a special apparatus designed to insure constancy of the interfacial area, very accurate temperature control, and a reproducible method of stirring. The apparatus is shown diagrammatically in Fig. 4, constant temperature being maintained by placing the whole system in the vapors of boiling carbon tetrachloride.

The method of carrying out the experiments was as follows. Seventy-five cc. of water or other hydrolyzing medium was placed in the inner compartment of the thermostat and the carbon tetrachloride brought to a boil at atmospheric pressure. As soon as the apparatus and solution had reached the equilibrium temperature (76°) about 25 cc. of mustard gas, which had previously been heated to about 100° in a vacuum to remove dissolved air and then allowed to cool to 70–80°, was introduced into the apparatus under such conditions that no particles of mustard gas were left floating on the top. This brought the level of the oil to the mark "F," whose cross-section, 8.688 sq. cm. had been carefully determined. By means of a special motor, the propeller stirrer could be rotated at any desired speed. The time of adding the oil was carefully noted. At half-hour intervals a 10cc. sample was withdrawn with a pipet through opening D, and titrated for total chloride.

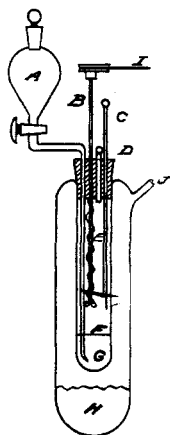


Fig. 4.—Apparatus for constant surface experiments. A. Funnel for mustard gas; B. Stirrer; C. Thermometer; D. Opening for sampling; E. Hydrolysis medium; F. Constant surface; G. Mustard gas; H. Boiling CCl_4 (76°); I. Belt to motor; J. Vapor to reflux condenser.

Preliminary experiments indicated that, at least in the non-colloidal solutions, there was no appreciable amount of unhydrolyzed mustard gas present in the aqueous layer, on account of the very rapid rate of hydrolysis at the high temperature. The use of chloroform to remove such dissolved material was, therefore, unnecessary.

The level of water in the flask was kept constant by adding portions of the original solution to make up for each sample removed, correction being made for the amount of chlorides removed with each sample.

The assumption that the interface was constant in all the experiments is not strictly true, because the shape of the meniscus changed slightly, depending upon the interfacial tension between the mustard gas and the various aqueous solutions. This change, however, was not appreciable except in the case of the soap solutions discussed later, where the mustard gas did not completely displace the soap solution from the side walls of the tube. Even in this case, the increase in the area exposed could not possibly account for the large amount of acceleration which was observed.

Before undertaking the study of different solutions, experiments were made to determine the effect of the rate of stirring on the rate of solution into water alone.

Preliminary experiments showed that with rates of stirring as low as 100 r.p.m. the chlorides were not uniformly distributed throughout the solutions and the samples were, therefore, not representative. On the other hand, at rates above 400 r.p.m. the surface of the mustard gas showed slight ripples which were considered undesirable. The accurate studies of the effect of the rate of stirring on the hydrolysis were, therefore, carried out with the satisfactory intermediate stirring rates of 200 and 300 r.p.m. The results of three such runs are shown in Fig. 5; these,

together with similar data for sodium carbonate solutions, prove that within these limits the rate of stirring does not affect the rate of solution for non-colloidal solutions. At 400 r.p.m. there was slight acceleration.

Using this apparatus, the relative rates of solution at 76° were determined for a wide variety of hydrolyzing media, the most important of which are shown in Fig. 6. From a study of these results the following conclusions may be drawn.

(1) The rate of solution in acid solutions appears to be very slightly less than that in water, the difference being but little greater than the experimental error.

(2) In non-colloidal alkaline solutions, the rate is slightly greater than for water, the difference being quite reproducible and well beyond the experimental error.

(3) In the colloidal alkaline solutions the rate is very much greater than that for any of the non-colloidal solutions, the rate of solution into 3% sulfonated corn oil plus 2% sodium carbonate being nearly 3 times that for plain water.

On the whole, therefore, the results are a striking confirmation of those obtained in the cloth experiments, though they still fail to make clear the mechanism by which the various solutions bring about the remarkable acceleration in the rate of solution. It is possible to note a parallelism between the rate of solution and the interfacial tension of mustard gas against the different solutions, but it is difficult to believe that this has any direct significance. It has also been suggested that the results might be due to the spontaneous peptization of tiny particles from the mustard layer by the solutions of low interfacial tension, aided by the stirring, but this explanation scarcely seems tenable in view of the amount of energy which would have to be supplied in producing such tiny colloidal particles.

Considering first the relatively slight retardation by acid, and acceleration by non-colloidal alkaline solutions the explanation is fairly obvious. It has been shown by a number of investigations⁴ that the principal obstacle to the solution of a compound from one phase into another lies, not at the interface itself, but in a stationary film of fluid through which the

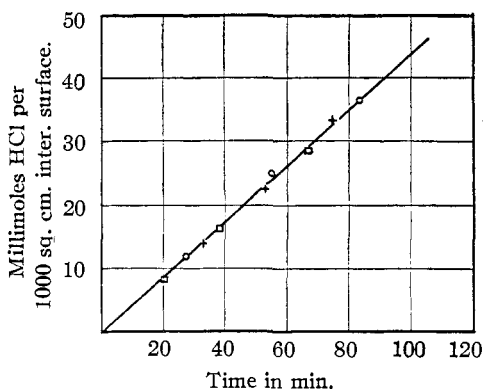


Fig. 5.—Constant surface experiments. Effect of rate of stirring on rate of solution. \circ , r.p.m. = 300; \times , r.p.m. = 200; \square , r.p.m. = 200 (2nd run).

⁴ See Nernst and Brunner, *Z. physik. Chem.*, **47**, 52 (1904).

compound must diffuse before it reaches a portion of the solution where the concentration of the diffusing material is kept relatively low by convection currents, etc. The thickness of this stationary film has been shown to be quite appreciable, but it can be diminished, and the rate of solution increased, by various means, such as stirring.

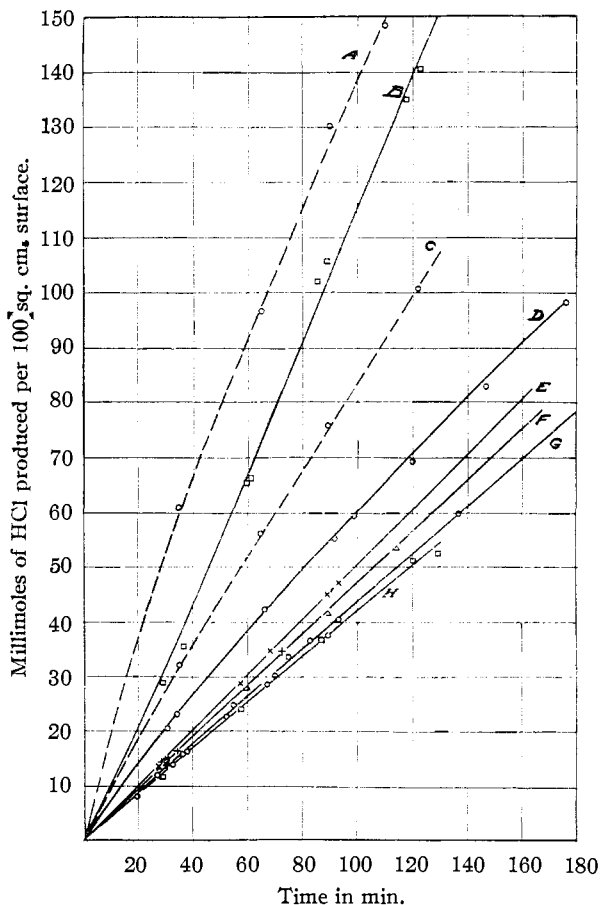


Fig. 6.—Effect of hydrolyzing medium on rate of solution. Constant surface experiments. A. 3% soap + 2% Na_2CO_3 (apparent); B. 3% Sulfonated corn oil + 2% Na_2CO_3 ; C. 3% Soap + 2% Na_2CO_3 (corr.); D. 2% Turkey red oil — 2% Na_2CO_3 ; E. 0.23 N KOH; F. 2% Na_2CO_3 and 0.10 N KOH; G. H_2O ; H. 0.20 N H_2SO_4 .

The case of mustard gas diffusing into *hot* aqueous solutions is similar, but the film is probably much thinner than usual, because the dissolved mustard gas is being used up by hydrolysis in the film itself. The effective

film thickness is accordingly determined, not by the distance the mustard gas must diffuse until it reaches a point in the solution where convection is taking place freely, but merely a distance sufficient to give time for practically complete hydrolysis. A rough calculation based on an approximate determination of the rate of hydrolysis of a saturated solution at 76° indicates that the film thickness required for this purpose is of the order of magnitude of 1 micron, much less than that of the usual stationary diffusion film. This conclusion is borne out by the facts that no appreciable amount of mustard gas is ever found in the main body of the non-colloidal aqueous solutions, and that moderate changes in the rate of stirring do not appreciably affect the results.

In the light of these facts, the effect of acid (either added as such, or produced by the hydrolysis) is undoubtedly to slow down the rate of hydrolysis as in the shaking experiments, and thus increase the effective thickness of the film through which diffusion must take place, while dil. alkali prevents this retardation. As would be anticipated, the magnitude of these effects is comparatively small.

There remains, however, the problem of explaining the great acceleration by the alkaline colloidal solutions. The clue which led to a satisfactory explanation of the mechanism of this acceleration lay in the observation of the behavior of the solutions of 3% sulfonated corn oil and 2% sodium carbonate in the "constant surface" experiments. At this alkalinity, the solution is at the start apparently quite clear, though of a peculiar pale orange color. As soon as the hydrolysis starts, however, a slight cloudiness develops just above the interface and the circulation currents produced by the stirring soon form a thin, slowly ascending wavy column of colloidal material which gradually disappears in the upper part of the solution.

From this it would appear that the acid produced near the mustard gas surface by the hydrolysis is sufficient to form the oil globules characteristic of slightly alkaline or acid solutions of sulfonated corn oil. The average size of these globules is probably much greater than the thickness of the layer through which mustard gas is diffusing, but many of them undoubtedly extend into this layer until only an infinitesimal film of solution separates them from the mustard gas phase. Since, as has been shown, mustard gas is quite soluble in these oil globules, they would dissolve fairly large quantities, and thus accelerate the apparent rate of solution by decreasing the average distance through which the mustard gas had to diffuse. The slow circulation of the solution would gradually sweep these particles along and up into the main body of the solution where the alkalinity would redissolve the colloidal particles, resulting in the very rapid hydrolysis of the mustard gas which they carried.

A number of crucial experiments suggested themselves as a means of determining the validity of this explanation. For example, this theory

would predict that the rate of solution in the presence of these colloidal solutions would increase markedly with the rate of stirring, in contrast to the results of the previous determination on non-colloidal solutions, and this was found to be the case. Again, if the theory be true, it should be possible to detect the presence of traces of undissolved mustard gas in the samples withdrawn from the colloidal solutions, and this was again verified. In the third place, it would be expected that the amount of sodium carbonate present in the sulfonated corn oil solution should greatly affect the results; if too little were present, the oil particles would not completely redissolve in the upper part of the solution and the acceleration would

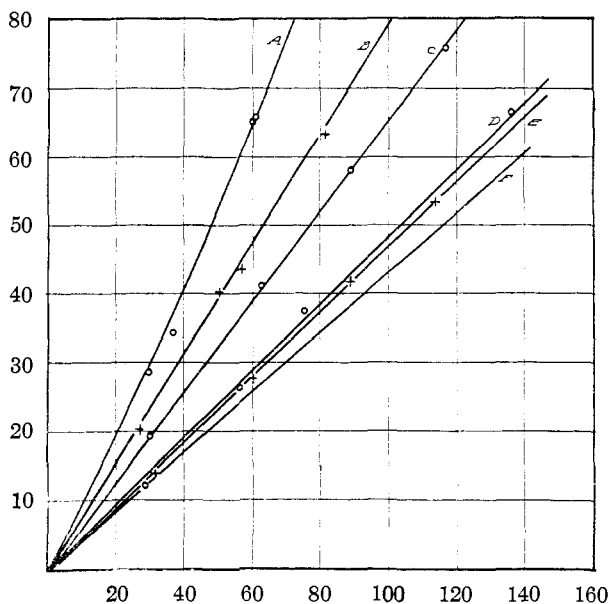


Fig. 7.—Effect of amount of Na_2CO_3 on accelerating effect of sulfonated corn oil. A. 2% Na_2CO_3 + 3% sulfonated corn oil; B. 1% Na_2CO_3 + 3% sulfonated corn oil; C. 4% Na_2CO_3 + 3% sulfonated corn oil; D. 6% Na_2CO_3 + 3% sulfonated corn oil; E. 2% Na_2CO_3 ; F. H_2O .

probably be somewhat decreased, while if large amounts of sodium carbonate were present, this would prevent the formation of the colloidal particles even in the layer next to the mustard gas, and the acceleration produced by such solutions should be much less, approaching the normal rate for non-colloidal solutions.

A series of experiments, using the same concentration of sulfonated corn oil, but concentrations of sodium carbonate varying from 1 to 6% were, therefore, carefully made, and the results are presented in Fig. 7. The results show clearly that the optimum concentration of sodium carbonate

is about 2% (as indicated previously by the cloth experiments) and that the amount of acceleration drops off on either side, and especially at the higher alkalinities.

One further interesting experiment was carried out in order to distinguish clearly between the mechanism as predicted by the above hypothesis, and the suggestion that mustard gas particles might be spontaneously peptized or, in some way, taken up by the colloidal particles by mechanical contact with the mustard gas phase itself. An oil-soluble, water-insoluble, red dye was dissolved in the mustard layer to the extent of about 2%. If the acceleration is due to the detachment of particles from the mustard gas phase, or to direct contact of the colloidal oil particles with the mustard gas phase, an amount of dye should be carried into the solution, corresponding to the amount of increase in the mustard gas hydrolyzed. It was found, however, that less than 1% as much dye was carried into the solution during a normal "constant surface" run with sulfonated corn oil, as when an equal amount of the same dyed mustard gas was shaken with the solution. It was further shown, by shaking a small amount of dyed mustard gas with these colloidal solutions, that under the conditions of these experiments, the dye did not return to the mustard layer in appreciable quantities if it was once brought into the colloidal solution. The dye was determined colorimetrically after extraction by prolonged shaking with an equal volume of chloroform.

In the light of this experiment, the hypothesis of spontaneous peptization or of mechanical contact between oil globules and mustard gas must give way to the above theory, which involves the absorption of mustard gas by the oil globules after the former has gone into molecular solution. Only in this event would the water-insoluble dye be expected to remain behind in the mustard gas phase.

The fundamental validity of the theory is, therefore, considered to be well substantiated, at least for the most important case, that of sulfonated corn oil. No such extensive tests have been carried out on the other alkaline colloidal accelerating agents, but there is every reason to believe that essentially the same mechanism is effective in these cases. The turkey red oil gives less acceleration and less formation of a cloud at the interface. In the case of soap, colloidal particles are always present, regardless of the concentration of alkali, and it was found that the acceleration is not markedly affected by changing the concentration of alkali as is the case for sulfonated corn oil. Whether the colloidal "micelles," shown by McBain to be present in such solutions, dissolve the mustard gas or merely adsorb it, is an academic question which it is almost impossible to determine, but the essential mechanism would be identical in either case.

In the case of the soap solutions, however, there was another factor which undoubtedly affected the results, namely, the inability of the mustard

gas to displace the soap solution completely from the sides of the "constant surface" tube, and there was a wide ring, extending about 6 mm. below the normal interface, where soap solution was in contact with the mustard phase, thus increasing the total interfacial area by about 65%. It is rather improbable that this extra surface is as effective in hydrolyzing mustard gas as the upper surface exposed to circulation, but even making the maximum possible correction on this assumption, as is done in Fig. 6, it is apparent that the soap itself has a marked accelerating action, though probably somewhat less than that of the sulfonated corn oil.

There is one other point which has not been entirely explained. Concentrations of potassium hydroxide in the neighborhood of 0.02 *N* gave a somewhat greater acceleration than the other alkaline solutions and also showed a tendency to produce scum in spite of precautions to purify both the mustard gas and the caustic potash. The acceleration is, however, almost negligibly small compared with that found for the sulfonated corn oil, etc.

In conclusion, the constant-surface experiments afforded the real clue to the accelerating action of the alkaline colloidal solutions in the cloth experiments, and the mechanism by which the specific rate of solution is increased has apparently been demonstrated beyond serious question.

Effect on Area of Interface.—The only important observation in the cloth experiments which remains unexplained by the constant-surface experiments is the very sharp decrease in the rates of hydrolysis which occurs between 20 and 30 minutes, in the case of practically all solutions (See Fig. 1) except those of alkaline sulfonated corn oil. This is especially remarkable in the case of the soap solutions which showed up well in the constant-surface experiments. The rapid change in rate cannot be due to the liberation of hydrochloric acid by hydrolysis, since the same effect is observed in the alkaline solutions. Indeed, the only factor which has not been eliminated by the results described in the foregoing sections is the possibility of a change in the *area of the interface* between mustard gas and the hydrolyzing solutions. Any variation in this factor must, however, be far greater in magnitude than the normal decrease due to the destruction of part of the mustard gas, if it is to account for the very sharp observed changes in the rate of hydrolysis, beginning at about 20 minutes from the start of the experiments.

The observed results might, however, be accounted for on the assumption that the mustard gas in these cases is gradually forced out of the capillaries of the cloth, gathering into small globules, producing a great reduction in the area of interfacial surface between the solution and the mustard gas. As a matter of fact, once attention was focused on the possibility, it was not difficult to observe the formation of such droplets as the cloth experiments proceeded. In the case of the solution of sulfonated corn oil sodium carbon-

ate, this globulizing tendency of the mustard gas appeared to have been overcome, and consequently there is only a slight decrease in the rate of destruction.

It is, of course, obvious that the tendency of the mustard gas to form globules, instead of staying spread out in thin films, would be largely a function of the surface tension between the mustard gas and the aqueous phase. In order to verify this hypothesis, the writers, during the war, requested Dr. W. D. Harkins to make determinations of these interfacial tensions. The results, which he has already published,⁵ are summarized in the following table.

Mustard gas in contact with	Interfacial surface Tension at 20° Degrees per cm.
Mustard vapor.....	42.82
Water.....	28.36
HCl, 0.1 <i>N</i>	28.90
Na ₂ CO ₃ 0.1 <i>N</i>	18.82
NaOH.....	12.78
1% Turkey red oil.....	14.47
1% Turkey red oil in 0.1 <i>N</i> Na ₂ CO ₃	8.35
1% Twitchell's reagent (commercial).....	12.32
1% Twitchell's reagent in 0.1 <i>N</i> Na ₂ CO ₃	12.89
1% Sulfonated corn oil.....	12.94
1% Sulfonated corn oil in 0.1 <i>N</i> Na ₂ CO ₃	10.91

While the results were not obtained at the same temperature, nor with precisely the same concentrations as were used in the cloth experiments, they do account qualitatively for the observed differences between the globulizing tendencies of water, sodium carbonate, and alkaline sulfonated corn oil.

The only discrepancy remaining is the peculiarly sharp slowing up of the hydrolysis in the cloth experiments with soap solutions, which cannot be explained on the basis of this tendency to globulize, since the interfacial tension in this case is undoubtedly very low. It was noted, however, that as hydrolysis proceeds in the presence of soap, a white, finely divided substance makes its appearance in the solution and gradually increases in quantity. The turbidity due to the presence of this substance does not disappear when alkali is added and hence it is not precipitated fatty acid. The substance was isolated by cooling the soap solution and skimming off the greasy white layer that formed on top. It was dissolved in hot alcohol and reprecipitated by the addition of water and then dried. The dried material melted rather sharply at 30° and yielded on analysis 6.2% of sulfur. It was thought that this substance might be an ester of thiodiglycol and the fatty acid of the soap. Such an ester would have the composition, C₁₇H₃₅OOC₂H₄SC₂H₄OOC₁₇H₃₅, and would contain 5.1% of sulfur.

⁵ Harkins and Ewing, *THIS JOURNAL*, **41**, 1977 (1919).

A substance of similar appearance and melting point was obtained by refluxing mustard gas and sodium stearate in alcohol and also by refluxing thiodiglycol and stearic acid in acetone. The possibility of an ester of thiodiglycol forming in the soap solution is, therefore, reasonably well established.

The consequence of the formation of such an ester in the cloth experiments would undoubtedly be to precipitate a considerable proportion thereof in the pores of the contaminated cloth, forming a gummy, insoluble film which would prevent the aqueous solution from coming into close contact with the remaining unhydrolyzed mustard gas. Rosin dissolved in sodium carbonate solution gives results very similar to those obtained with ordinary Ivory soap, and furthermore deposits a sticky yellow substance on the cloth which, unlike the original rosin, does not dissolve in dil. sodium hydroxide solution.

In the constant-surface experiments, although the formation of the ester takes place in the soap solution, there is no cloth present to hold a film of the ester, and consequently diffusion takes place freely, making it possible to observe the full effect of the increase in the specific rate of solution occasioned by the "transport service" of the colloidal particles of soap.

Extension of the Results to the Hydrolysis of Fats and Acid Chlorides

Considerable preliminary work has recently been done in this Laboratory to determine whether or not it is possible to accelerate the hydrolysis of fats, or of organic acid chlorides, by similar means, or at least to see what light would be thrown on the mechanism of these hydrolyses by the methods developed for studying the mustard gas reaction. The results of this work will probably be published in more detail later, but the essential conclusions up to the present time may profitably be summarized in this connection.

In the case of fats (specifically, pure olive oil) it was found impractical to carry out shaking experiments at 25° because the rate of hydrolysis was entirely too slow. At 75°, the shaking experiments revealed an important difference between fats and mustard gas, in that the rate of hydrolysis under such conditions is not *independent of*, but roughly *proportional to* the amount of interface exposed. Apparently, either the hydrolysis takes place *at* the interface, or else (which practically amounts to the same thing) at this temperature the rate of solution is so very much slower than the rate of hydrolysis of the dissolved molecules, that it is impossible to keep the entire solution saturated, all the hydrolysis taking place in an almost infinitesimal aqueous film surrounding each fat globule.

In view of this, and the fact that the product of the hydrolysis is itself a colloid which greatly aids in dispersing the fat, it is almost impossible to use the shaking method of studying the effect of various known accelerating agents, but it is significant that most, if not all of them, do lower the interfacial tension between the fat and the oil.

Attempts to carry out constant-surface experiments were unsuccessful because even at 76° the rate of solution, or hydrolysis, at the small interface was too low to permit of accurate measurement in view of the limits of error of the analytical methods which must be used in this case. The situation is also complicated by the fact that the hydrolysis of a glyceride is a 3-stage reaction.

In the case of the acid chlorides, some difficulty was experienced in finding one with a solubility and rate of hydrolysis which would lend itself to accurate measurement over suitable periods of time. Benzene-sulfonchloride was, however, found to be quite suitable in this respect. A comparable series of experiments was therefore carried out by Mr. C. E. Ronneberg which showed that this compound was surprisingly similar to mustard gas in its solubility and mechanism and rate of hydrolysis in water, but that it differed in apparently being catalyzed by hydroxyl ions, the rate being roughly proportionate to the fourth root of the hydroxyl-ion concentration. In order to measure accurately the acceleration by colloidal solutions, it was, therefore, necessary to work in acid solutions, where the rate of hydrolysis was found to be independent of the acid concentration, and showed no tendency to reverse. Under these conditions it was found that sulfonated corn oil, and especially Twitchell's reagent⁶ made marked increases in the specific rate of solution in constant-surface experiments. The effect of stirring, the formation of a cloudy layer near the interface, etc., all indicated that these colloidal droplets in which the chloride was soluble, accelerated the rate of solution in a manner exactly similar to that demonstrated for the case of mustard gas.

In conclusion the writers desire to express their indebtedness to the helpful suggestions of Dr. A. B. Lamb, under whose general direction this work was begun at the American University; to Mr. N. D. Thatcher, who aided greatly in the preliminary investigations along these lines during the war; to Mr. C. E. Ronneberg for the portions of the work acknowledged in the text; and to Dr. A. D. Macallum, who did the preliminary work on the hydrolysis of fats.

Summary

1. The problem of the rapid removal of mustard gas from contaminated clothing, without injury to the fabric or danger to the operators, was satisfactorily solved during the war by the discovery that the rate of hydrolysis under such conditions could be markedly accelerated by the use of certain alkaline colloidal solutions, particularly those of sulfonated corn oil.

2. Using a solution containing 3% of sulfonated corn oil and 2% of sodium carbonate, it is possible to complete the hydrolysis of mustard gas on cloth

⁶ "Kontakt Saponifer," kindly furnished by the Twitchell Process Co.

in 35 minutes at 85°, as compared with a matter of many hours for water or non-colloidal alkaline solutions under identical conditions.

3. Preliminary investigation proved that the hydrolysis does not take place in the mustard gas phase nor at the interface, but rather in the aqueous phase after the mustard gas has gone into solution *as such*. It can, therefore, readily be proved that the hydrolysis could be accelerated only by increasing one or more of the following 4 factors: (1) the specific rate of hydrolysis in the aqueous phase; (2) the solubility of mustard gas in the aqueous phase; (3) the specific rate of solution per unit area of interface; (4) the interfacial area between the mustard gas and the water.

4. A series of experiments was carried out to determine the effect of alkaline colloidal agents on each of these 4 factors. It was found that solutions such as those of alkaline sulfonated corn oil had no tendency to increase the specific rate of hydrolysis, nor the solubility of mustard gas in the aqueous phase, although the colloidal oil particles did tend to dissolve mustard gas from the aqueous phase and thereby *decrease* the effective rate of hydrolysis in a solution initially saturated with mustard gas, but containing no excess liquid phase.

5. It was found that the alkaline colloidal solutions did accelerate the specific rate of solution per unit area of interface, by acting as carriers to transport mustard gas from the very thin aqueous layer through which the mustard gas was diffusing before hydrolysis was complete. The action was especially effective in the case of moderately alkaline sulfonated corn oil solutions, where the acid released by the hydrolysis in the film near the mustard gas surface precipitated oil globules therein, which rapidly dissolved a large amount of mustard gas and were then carried up by circulation currents into the main body of the solution where they redissolved and released the mustard gas in such form that it was very rapidly hydrolyzed.

6. In the case of the cloth experiments, the alkaline colloidal solutions were also helpful (due to their low interfacial tensions against mustard gas) in overcoming the tendency of the mustard gas to be displaced from the capillaries of the cloth and to form globules which hydrolyzed very slowly.

7. The behavior of alkaline soap solutions, which showed marked accelerating action in contact with a constant surface of liquid mustard gas, but which, in the cloth experiments, were not able to complete the hydrolysis within a reasonable period, was found to be due to the formation of a compound between the hydrolysis product of mustard gas and the soap, which was of a gummy consistency and deposited on the fibers of the cloth. Tests indicated that the compound was probably a fatty acid ester of thiodiglycol.

8. A preliminary attempt was made to apply the foregoing methods to a study of the hydrolysis of fats (specifically, olive oil). It was found that in this case hydrolysis takes place either at the interface or in an infi-

tesimal aqueous film surrounding the fat globules, and that anything which increases the degree of peptization of the fat, and hence the amount of interface exposed, accelerates the hydrolysis.

9. The mechanism of the hydrolysis of benzene-sulfone-chloride was found to be similar in practically every respect to that of mustard gas, except that it was apparently catalyzed in the aqueous phase by the presence of hydroxyl ions, and showed no evidence of reversal in acid solutions. Acid solutions of various colloids showed a similar accelerating tendency in cases where benzene-sulfone-chloride was soluble in the colloidal phase.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 22]

A STUDY OF THE CONDUCTION PROCESS IN ORDINARY SODA-LIME GLASS

BY CHARLES A. KRAUS AND EDWARD H. DARBY

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Introduction

While the fact that glass is a conductor of the electric current was known at a very early date, none of the earlier investigators seems to have had a clear notion of the nature of the conduction process.

It was Warburg¹ who, for the first time, showed definitely that this process in glasses is an electrolytic one, and that the passage of the electric current through glass is due to the motion of sodium present in the glass. On passing a direct current through glass, using mercury electrodes, he found that a thin layer of very high resistance is formed at the anode.

Le Blanc and Kerschbaum² repeated Warburg's work using a mercury anode. They concluded that conduction is due entirely to the motion of the sodium present in the glass and that the glass is ionized to the extent of about 80% at 250°, the temperature at which they carried out their experiments. They also observed the formation of the poorly conducting layer at the anode. In this layer, Ohm's law does not hold, the current apparently varying as the square of the resistance. According to these writers, the passage of the current through this layer is not accompanied by a transfer of matter. They give the migration velocity of the sodium ion in glass as 1×10^{-8} cm. per sec. at the temperature in question. They showed, too, that at the anode the original glass may be regenerated by reversing the current, while, if a sodium amalgam is employed as anode, the layer is not formed.

Warburg and Tegetmeier³ studied both glass and quartz crystals, using amalgams and, in some cases, coatings of plumbago or gold. They showed that in these substances conductance is due to the presence of sodium. Tegetmeier⁴ worked with both sodium and lithium amalgams. He states that lithium may be completely electrolyzed through quartz and glass, the metal appearing at the cathode. The glass is brittle and goes to pieces easily. The passage of lithium through glass could be followed by the

¹ Warburg, *Ann. Physik*, **21**, 622 (1884).

² Le Blanc and Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910).

³ Warburg and Tegetmeier, *Ann. Physik*, **35**, 455 (1888).

⁴ Tegetmeier, *ibid.*, **41**, 18 (1890).