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TECHNICAL REPORT 3842

**THE KINETICS OF THE REACTION OF
LITHIUM CHLORIDE AND LEAD AZIDE
EXPOSED TO THE ATMOSPHERE**

HENRY KRAMER

APRIL 1969

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Explosives Laboratory
Feltman Research Laboratories
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Dover, New Jersey

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SUMMARY

The importance of this preliminary report is that it demonstrates that the lead azide-lithium chloride system can be treated kinetically. The study shows the optimum composition of lead azide and lithium chloride, and suggests means of accelerating the destruction of the lead azide. However, to obtain a comprehensive grasp of the reactions involved it is imperative that the interaction of lead azide, water, and carbon dioxide be studied in detail. For example, using the data of Feitknecht, it can be calculated that the equilibrium constant for the third reaction is 2.1×10^{-2} mm. The data which is suspect in the calculation appears to be (1) the solubility product of lead azide, (2) the solubility product of $\text{Pb}(\text{OH})\text{N}_3$, and (3) the distribution coefficient of hydrazoic acid between air and water as a function of temperature. Accumulation of this fundamental data is absolutely necessary because it will answer such important questions as how lead azide should be stored and how end-items using lead azide should be manufactured and stored, especially if water is integral to the system.

INTRODUCTION

The kinetics of the reaction of lead azide, lithium chloride, water, and carbon dioxide have not been intensively investigated. One of the reaction products, lead azidochloride, has been investigated by both Brickenbach (Ref 1) and Pristera (Ref 2). This report concerns the formation of other reaction products, tentatively advances a reaction mechanism, and briefly discusses the kinetics of the reactions involved.

The reaction between lead azide and lithium chloride is complex, heterogeneous, and diffusion-controlled, involving liquid, solid, and gaseous phases. Kineticists, as a rule, hesitate in dealing with problems of such complexity; this report is preliminary, as much additional work will be required to achieve a complete understanding of the details of the reaction. However, the information presented here should provide a useful physical model of the reaction. It must be understood that a real solid surface is never uniform in the kinetic and energetic sense and that heterogeneous reactions are strongly complicated by surface inhomogeneities and impurities.

PROCEDURE

Six hundred milligrams of special purpose lead azide was weighed into a small polyethylene beaker and distributed evenly on the bottom of the beaker. A weighed pellet of lithium chloride was then placed in the center of the dispersed lead azide. The samples were allowed to stand at 90°F and 85% RH for various periods of time. Duplicate samples were withdrawn and weighed to determine water pickup. Ethyl alcohol was added to quench the reactions and the alcohol/water phase was separated from the residue. This residue was washed with alcohol until chloride-free and the alcohol/water extract was diluted to volume.

The residue was dried, weighed, dissolved in ammonium acetate solution and diluted to volume. Each solution was then analyzed for chloride and azide ions by the modified Volhard procedure as described by Ribaudó (Ref 3).

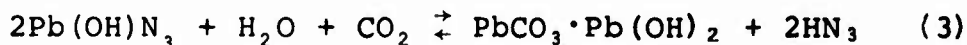
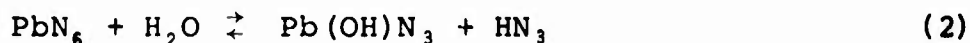
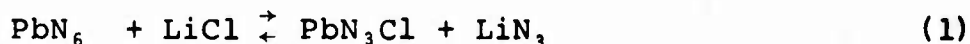
Ultraviolet and infrared spectrophotometric measurements, along with x-ray studies, were made of the alcohol/water insoluble residue to obtain more information on the

path of the reactions and to help to interpret some of the observed phenomena during the kinetic measurements.

The materials used were: Special purpose lead azide, 98.0% pure, based on the azide content, with an average particle size of 77 microns; and lithium chloride, pelletized to facilitate weighing, 99.0% pure.

RESULTS

The decomposition of lead azide-lithium chloride mixtures exposed to the atmosphere apparently proceeds in the following steps:



Reaction 1 begins rapidly and reaches a quasi-steady state in about 40 hours. The rate of reaction in relation to that of reaction 2 is about 8:1 as determined by the absorption of the azide ion in the ultraviolet. The kinetics for the formation of lead azidochloride are a function of several parameters: Weight of the lithium chloride, specific surface of the lithium chloride, and particle size of the lead azide. The data is presented in Table 1 below.

TABLE 1

Formation of lead azidochloride

Ratio of Reactants (mmoles) $\text{PbN}_6:\text{LiCl}$	Specific Surface of LiCl Pellet, mm^2	Conversion of PbN_6 to PbN_3Cl , %
2:2.4 ^a	70	25
2:4.8	107	50
2:7.2	348	90

^aA 20% excess of chloride ion is needed to form the meta-thetical product, PbN_3Cl .

In Figures 1, 2, and 3, the chloride and azide concentration are presented as a function of time for both the liquid phase and the solid phase. After the initial formation of lead azidochloride, little more is formed with time except for the mixture in Figure 2, which barely develops a liquid phase. Reducing the particle size of the lead azide to the micron range (1-5) resulted in complete conversion of lead azide to lead azidochloride within ten hours using a 2.4:8 mmolar ratio of lead azide to lithium chloride.

The loss of azide ion, as shown in Figures 1 and 2, is independent of the chloride concentration and water pickup. The slope of the decrease in azide concentration suggests a zero order, diffusion-controlled reaction apparently caused by exposure to the atmosphere. To verify this point, samples were examined microscopically; they showed a central nodule of lead azide surrounded by a fragmented layer of lead azidochloride. In addition, samples containing 0.600 g lead azide, 0.200 g lithium chloride, and 1.00 g water were prepared in vacuum. No nitrogen was found in the gas phase, indicating that no redox reaction had occurred. However, 6.6×10^{-6} moles of HN_3 were found in the gas phase on replicate samples. Assuming that all the HN_3 goes into the gas phase because of the high ionic strength of the solution, the equilibrium constant for reaction 2 is 5.06×10^{-3} mm. Two samples with this composition were stored in vacuo for 1500 hours, a period long enough, according to theory, to completely destroy lead azide exposed to the air at 90°F and 85% RH. Analysis of the samples indicated only a 50% conversion to lead azidochloride, and a sharp detonation resulted when the sample residues were heated, indicating residual lead azide.

Evidence for this was shown by preparing several samples in vacuum and adding either solid carbon dioxide or sodium bicarbonate and connecting the apparatus to an evacuated infrared gas cell. The reaction vessel was heated to 40°C to accelerate the reaction. There was an immediate release of HN_3 and a continual buildup with time at a wavelength of 4.76 microns in the infrared. These experiments clearly indicated that carbon dioxide plays an important part in the atmospheric decomposition of lead azide.

In all the compositions studied, the liquid phase consisted of lithium chloride and lithium azide. Lead could not be detected. The pH of this solution goes from 6.4

to 8.8 within 24 hours and then remains constant. The solid phase consists of lead azidochloride, basic lead carbonate, and unreacted lead azide. A tentative identification of basic lead azide was made by x-ray diffraction. No low temperature form of the basic salt has been observed.

Physically, after the initial phases of reaction, a kernel of lead azide covered with lead azidochloride remains. Diffusion then controls the reaction as water and carbon dioxide diffuse through the shell. Basic lead salts are formed, the first probably being basic lead azide, which is the partial hydrolysis product of lead azide, followed by the formation of basic lead carbonate. Infrared spectra using the potassium bromide technique show an increase of carbonate at a wavelength of 7.14 microns with time. From the invariance of chloride and azide concentrations in the solid phase, it is likely that lead azidochloride is not attacked. The lead azide and basic lead azide are attacked as is indicated in reactions 3 and 4.

Material balance of the weighed alcohol/water insoluble residue is obtained by (a) calculating the quantity of lead azidochloride from the chloride in the residue, (b) calculating the quantity of basic lead carbonate from the HN_3 lost, or (c) calculating the quantity of unreacted lead azide (or basic lead azide) from the difference between the azide content of the residue and that of the liquid. The sum of these weights agrees within $\pm 5\%$ with the weight of the alcohol-insoluble residue. Thus, we may conclude that no significant quantities of other products are formed.

The effects of additives on the system were examined for two reasons. The first was to determine the precision of the experimental data and the second to accelerate the destruction of lead azide, preferably at a controlled rate.

From Figure 4, it can be seen that the variation in azide concentration in the residue, which is of greatest interest to us, falls well within the experimental precision of a complex heterogeneous reaction on a nonuniform surface. Adding a water-soluble surface-active agent did not speed up the reaction. Adding fluoride ion did not lead to the formation of the more insoluble lead fluorochloride. Zinc and aluminum accelerated the decomposition of lead azide under the experimental conditions, but it

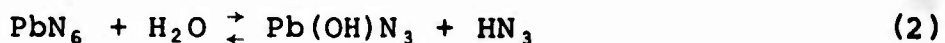
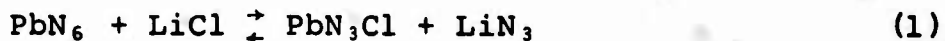
was felt that galvanic action might prove hazardous. As has been noted earlier in this report, carbon dioxide accelerates the decomposition of lead azide. Therefore, sodium bicarbonate was added to the lead azide-lithium chloride mixture. In Figure 5, the data is plotted as before. It is evident that the azide ion concentration increases much more rapidly in the liquid phase than Figures 1 and 2 indicate. Reactions 2, 3, and 4 are accelerated by the introduction of an adsorbent for the HN_3 , which shifts the equilibrium to the right and thereby accelerates the decomposition of lead azide. The equilibrium is shifted even further by the formation of the more insoluble basic lead carbonate. The increase of chloride ion in the residue is probably not due to an increase in concentration of lead azidochloride but rather to the formation of a basic lead chloride. The reason for this is that, for each gram atom of azide in the liquid, there can be only one gram atom of chloride in the residue if the sole product is to be lead azidochloride.

DISCUSSION

It is useful to summarize some of the known data regarding the effects of water on lead azide. At room temperature, lead azide is soluble to the extent of 0.02%. From a knowledge of the dissociation constants of lead hydroxide and hydrazoic acid, only 1.5×10^{-5} grams of lead hydroxide per 100 grams of water are present at equilibrium. One hundred grams of water at room temperature can dissolve 1.5×10^{-2} grams of lead hydroxide, some 1500 times more than results from hydrolysis; hence, a considerable loss of hydrazoic acid must occur to shift the reaction far enough to the right for lead hydroxide to be precipitated. This seldom happens in actual practice because basic lead azides intervene, as has been noted by the work of Feitknecht (Ref 4) and Todd (Ref 5). Basic lead azide is known to be a hydrolysis product obtained by using either base or water at relatively high temperatures, but has not been seen at room temperatures. Although unequivocal identification has not been possible, it is a likely precursor to the basic carbonate in view of the high pH, 8.8, of the supernatant solution. It is also likely that the basic lead azide may be destroyed in the long x-ray exposures required for its identification in the lead azide-lead azidochloride matrix.

Water in equilibrium with carbon dioxide has a pH of about 5.5, which drops to 3.9 as the carbon dioxide concentration increases to 100%. These pH figures (neglecting the bicarbonate ion) mean that water in contact with normal to highly carbon dioxide enriched air may contain 10^{-6} to 10^{-4} gram ions of carbonate per liter. The lead azide content of a saturated solution is 0.02% or 6.4×10^{-4} gram ions of lead per liter. Since the solubility product of lead carbonate is 1×10^{-14} it follows that the carbonate has to rise only above 10^{-10} gram ions per liter for lead carbonate to be precipitated.

The sequence of decomposition reactions postulated is:



It is interesting to note that lead azidochloride is about five times as soluble as lead azide; nevertheless, the reaction goes to the right. A possible explanation for this phenomenon is the formation of an ion pair which is sufficiently long lived to be recognizable as a kinetic entity. Other evidence is that the lead azidochloride species in aqueous media has a different absorption spectra than the azide ion in the ultraviolet. The absence of lead in the aqueous phase also suggests that the absorbing species may be $[\text{PbN}_3]^+$.

Rigorous kinetic treatment of the data is not yet possible. Reaction 1 is homogeneous and first order, but the subsequent reactions are diffusion-controlled, as Figure 6 shows. A plot of $(1 - \alpha)^{1/2}$ versus time gives a straight line, where α is the fraction of unreacted azide. Crystals in condensed media undergoing this type of decomposition have been represented by a "contracting sphere" model. We should expect diffusion to take place parallel to the closely packed planes of the metal atoms, and the interface to be formed perpendicular to the layers around the edge of the crystal. The kinetics of this model follow the equation (Ref 6):

$$(1 - \alpha)^{1/2} = (1 - kt)/R$$

where α is the fraction of unreacted azide

R is the initial radius of the undecomposed crystal
t is time.

The rate constant k is equal to dr/dt , where r is the radius of the undecomposed crystal at time t. Thus, a plot of $(1 - \alpha)^{1/2}$ against t should give a straight line for a diffusion-controlled reaction.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. H. J. Matsuguma and Dr. N. Slagg for their helpful discussions, and to J. Campisi, Propellants Laboratory, for the x-ray diffraction studies.

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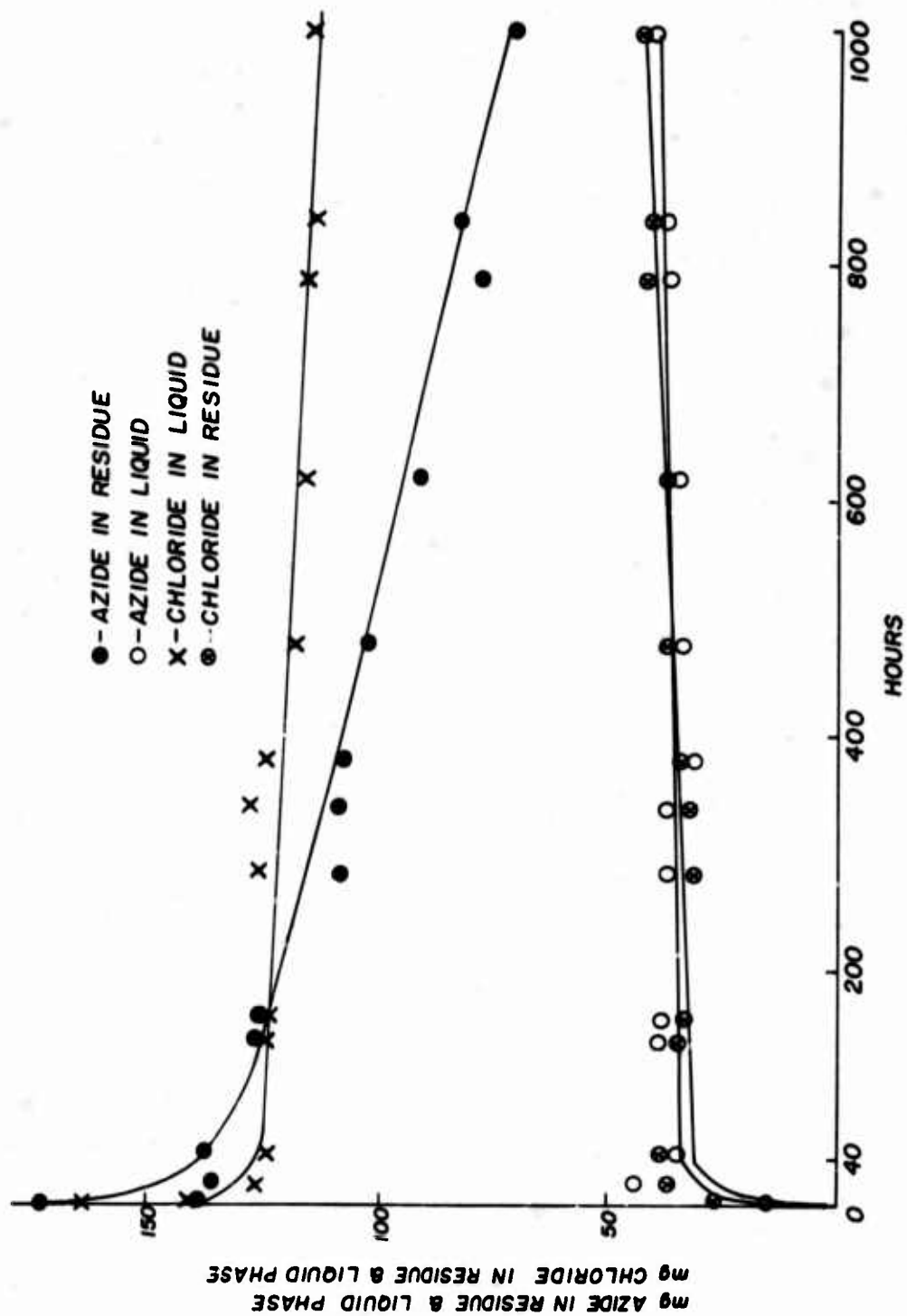


Fig 1 Reaction of PbN_6 and $LiCl$ 600 mg/200 mg. Surface area of $LiCl$, 107 mm^2

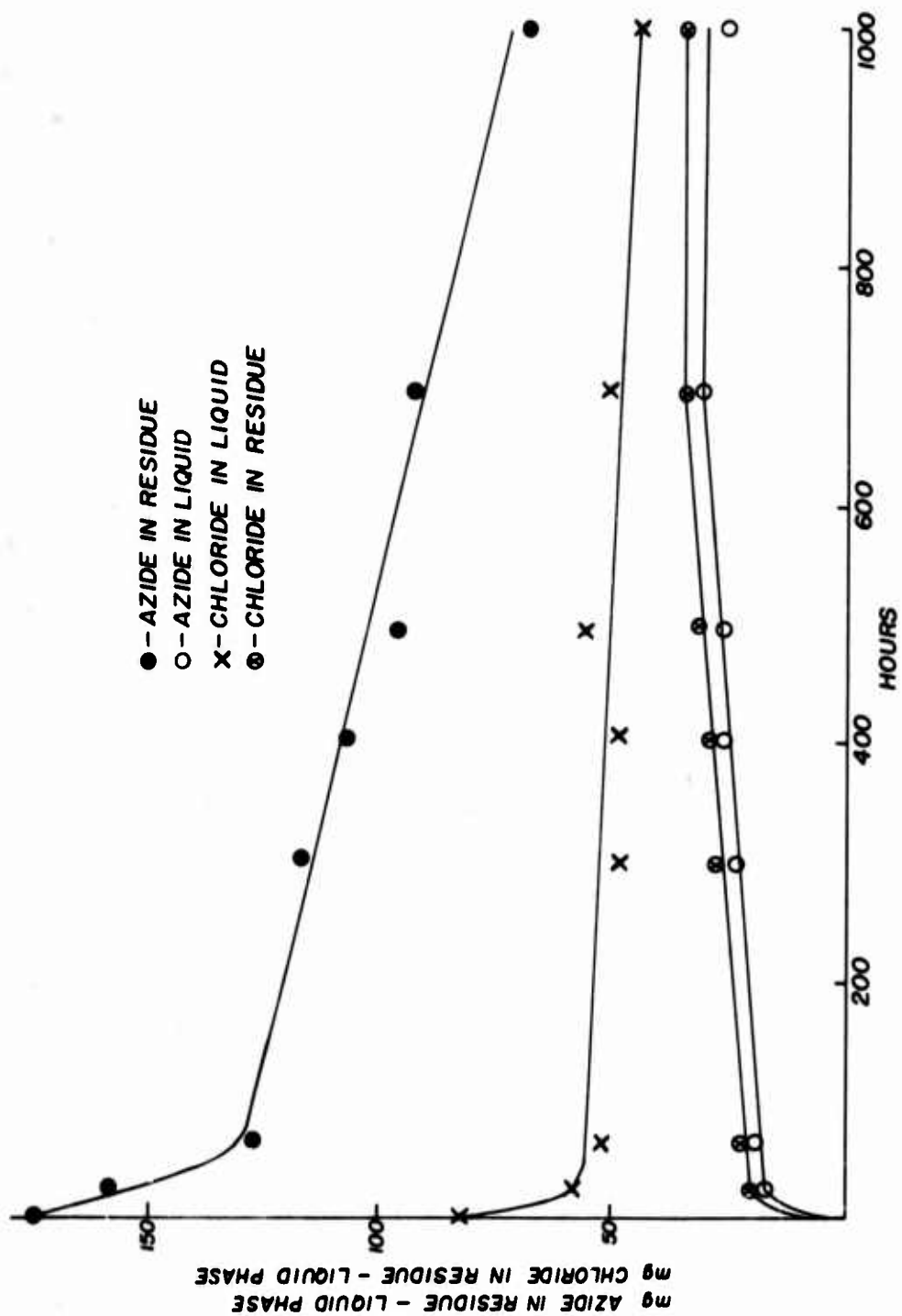


Fig 2 Reaction of PbN_6 - $LiCl$ 600/100 mg. Surface area of $LiCl$, 70 mm^2

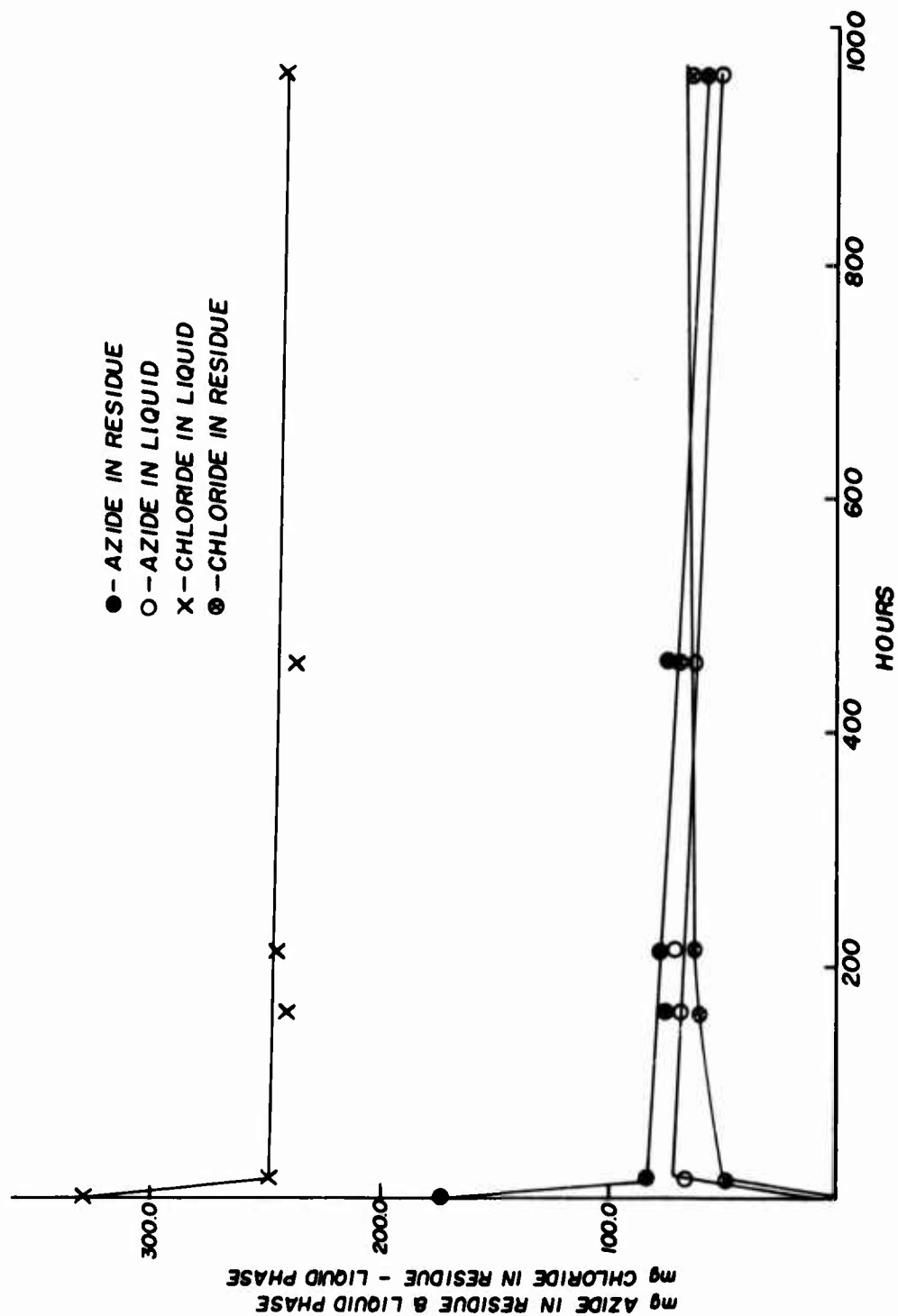


Fig 3 Reaction of PbN_6 - LiCl 600/400 mg. Surface area of LiCl, 348 mm²

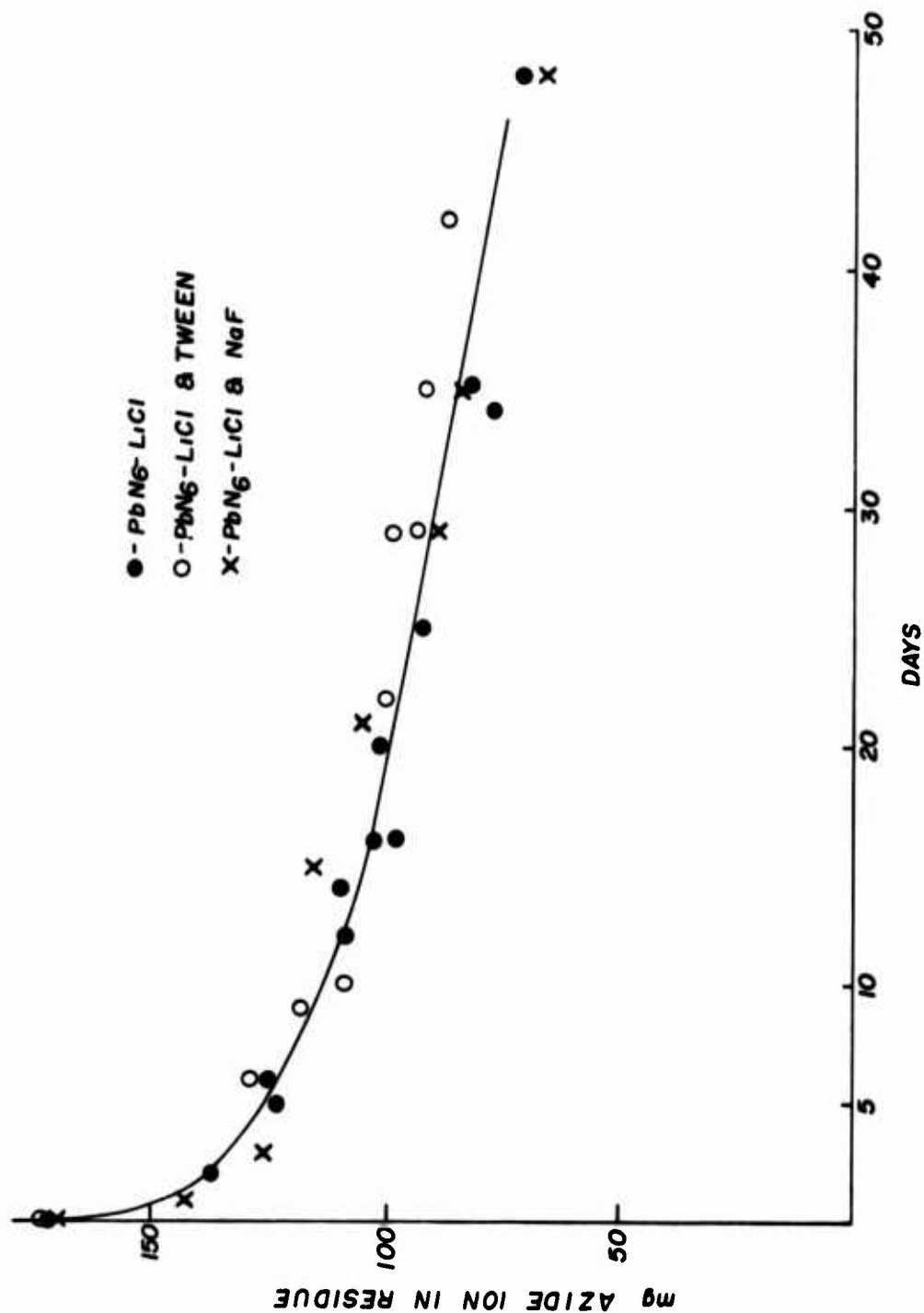


Fig 4 A comparison of N_3^- ion in residue for mixture PbN_6-LiCl

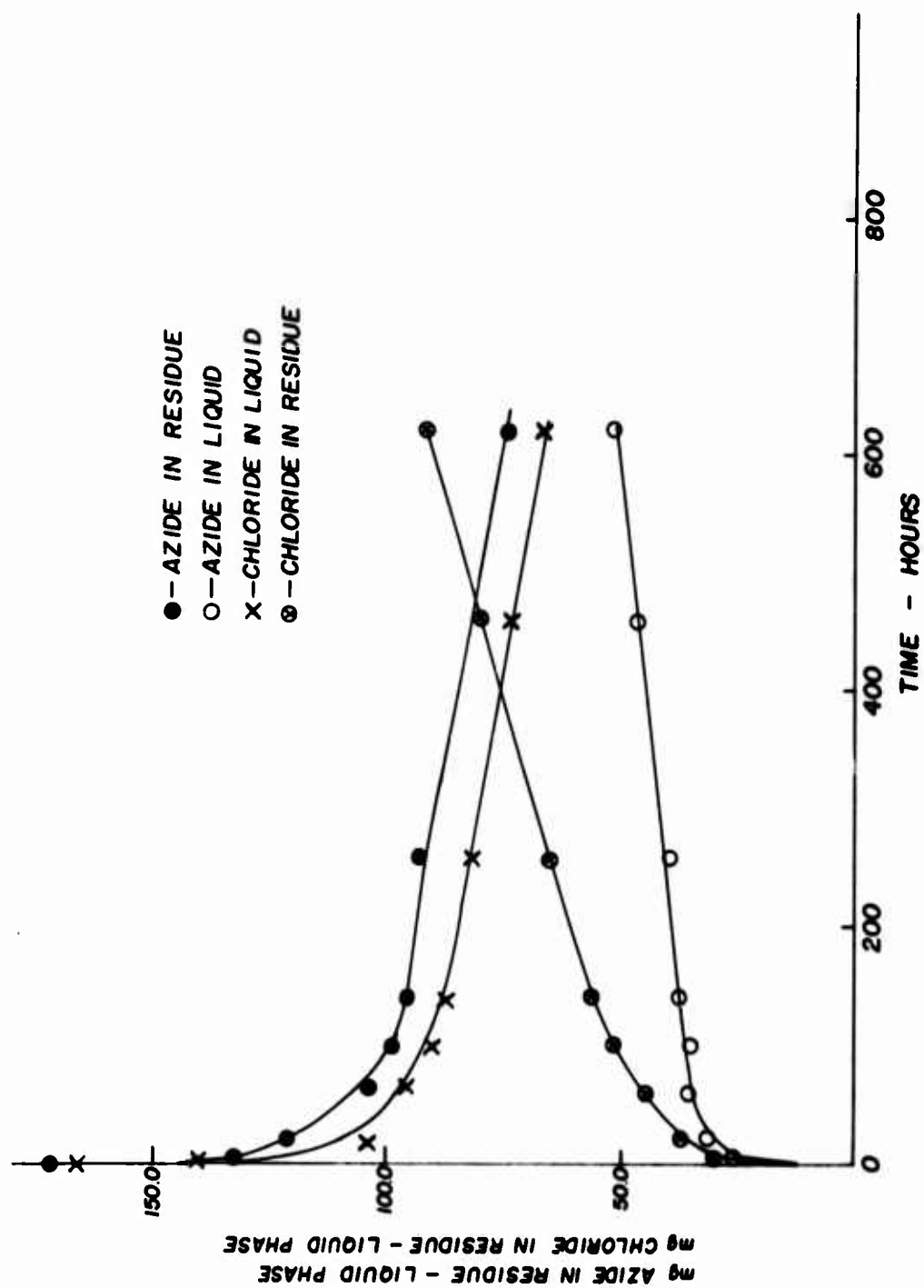


Fig 5 Reaction of PbN_3 , 600 mg, $LiCl$ 200 mg, 100 mg $NaHCO_3$

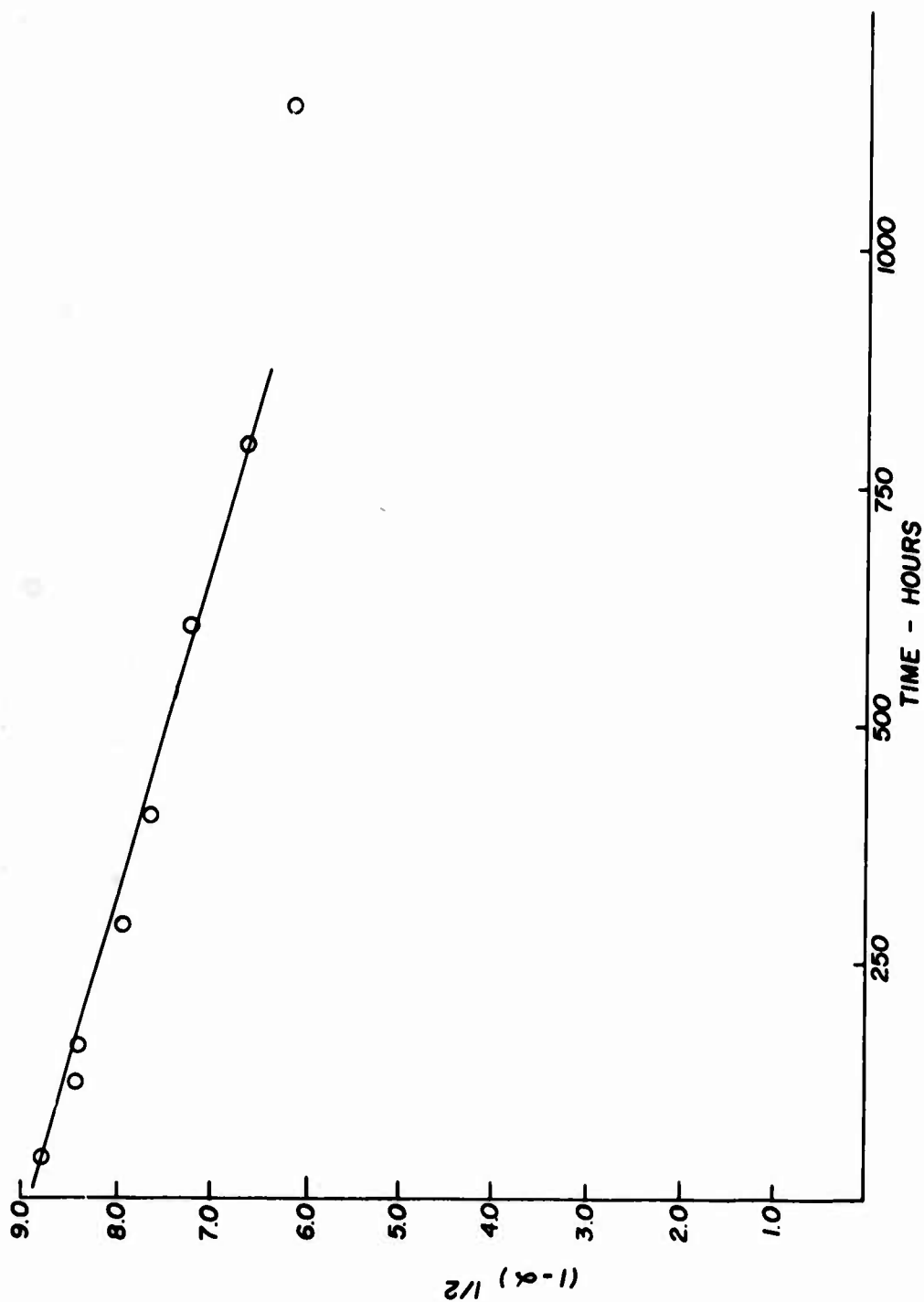


Fig 6 Test of kinetic equation for lead azide decomposition

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The importance of this preliminary report is that it demonstrates that the lead azide-lithium chloride system can be treated kinetically. The study shows the optimum composition of lead azide and lithium chloride, and suggests means of accelerating the destruction of the lead azide. However, to obtain a comprehensive grasp of the reactions involved it is imperative that the interaction of lead azide, water, and carbon dioxide be studied in detail. For example, using the data of Feitknecht, it can be calculated that the equilibrium constant for the third reaction is 2.1×10^{-2} mm. The data which is suspect in the calculation appears to be (1) the solubility product of lead azide, (2) the solubility product of $Pb(OH)N_3$, and (3) the distribution coefficient of hydrazoic acid between air and water as a function of temperature. Accumulation of this fundamental data is absolutely necessary because it will answer such important questions as how lead azide should be stored and how end-items using lead azide should be manufactured and stored, especially if water is integral to the system.		

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