[CONTRIBUTION FROM THE NATIONAL FIREWORKS ORDNANCE CORP.]

THE DECOMPOSITION OF HALEITE (ETHYLENEDINITRAMINE)[1]

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As a natural part of the U. S. Army's program on explosives, it was decided to study the decomposition of Haleite in aqueous solution and in the solid state. Such a study was justified on the basis that although the compound has been known for over sixty years, it has not previously been considered for use as an explosive. The basic data to be gained from the study mentioned would be of obvious utility in the solution of manufacturing and storage problems and are also of considerable theoretical interest.

As long ago as 1887, Franchimont and Klobbie (1) reported that Haleite decomposed in aqueous media to yield nitrous oxide, ethylene glycol, and acetaldehyde. It was further stated that Haleite is resistant to the action of aqueous alkali, but decomposed readily in aqueous acids. These statements suggested that the decomposition reaction is acid-catalyzed, but not base-catalyzed. Hammett (2), however, pointed out that the decomposition of the parent substance, nitramide, exhibits general base catalysis, but that its rate is uniformly low and constant in aqueous solutions ranging from 0.001 to 0.1 N in hydrochloric acid.

It, therefore, seemed interesting to investigate this case, and at the same time to find out something concerning the nature of the decomposition of Haleite in the solid and liquid states. In addition, the hydrolysis of dinitroethylene urea, the precursor of Haleite, was studied in a cursory manner.

MATERIALS AND EXPERIMENTAL PROCEDURE

A. Materials. The *dinitroethylene urea (DNEU)* used was titrated by solution in hot caustic (0.1 N), and back titrating the excess caustic with 0.1 N sulfuric acid, using phenolphthalein as an indicator. The equivalent weight found was 58.86, which multiplied by 3 yielded 176.58 as the molecular weight compared to the theoretical of 176.09. The DNEU contained 0.4% sulfuric acid, determined as $BaSO_4$, and 0.1% nitric acid, determined using nitron.

The *Haleite* used was, in all cases but one, PA Lot 1 material recrystallized five times from dioxane. Several other solvents were tried, but dioxane gave the purest and most stable Haleite. This product had m.p. 176.5°, 0.00% moisture content on desiccation 24 hours over sulfuric acid, and was 99.95% pure by electrometric titration. The exception, Table I, Fig. I, was unrecrystallized material.

α-TNT was recrystallized twice from carbon tetrachloride and had a setting point of 80.65° (original 80.44°). *β-* and *γ-TNT* were prepared by recovery from crude TNT by four recrystallizations from alcohol; this mixture was then dissolved in alcohol and crystallized by cooling over a period of 16 hours. This resulted in separate crystallization of impure β- and γ-isomers; the former appeared as massive pale yellow crystals and the latter as dirty grey, large, thin plates. These were separated by decanting the plates, and, after drying, air-separating residual plates from the β-isomer; *i.e.*, an air stream directed against the product removed the thin, light plates. The crude β-, m.p. 110.2° was recrystallized

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[1] This work was done at Picatinny Arsenal, Dover, N. J. This paper was released for publication by the Department of Defense.

TABLE I

HYDROLYSIS OF DNEU

RUN NO.	G. DNEU PER 100 CC. WATER	SULPHURIC ACID NORMALITY	TEMP., °C.	HYDROLYSIS TIME, MIN.	YIELD, %	PURITY, %
1	32.2	0.00	98–100	14[a]	95.6	99.1
2	32.2	.50	98–100	14[a]	82.0	—
3	32.2	.00	98–100	28	95.0	99.1
4	16.1	.00	78–80	45[a]	91.0	99.0
5	16.1	.50	78–80	45[a]	82.3	—
6	16.1	.00	78–80	90	91.0	98.9

[a] The hydrolysis was discontinued as soon as visual observation indicated complete solution of DNEU.

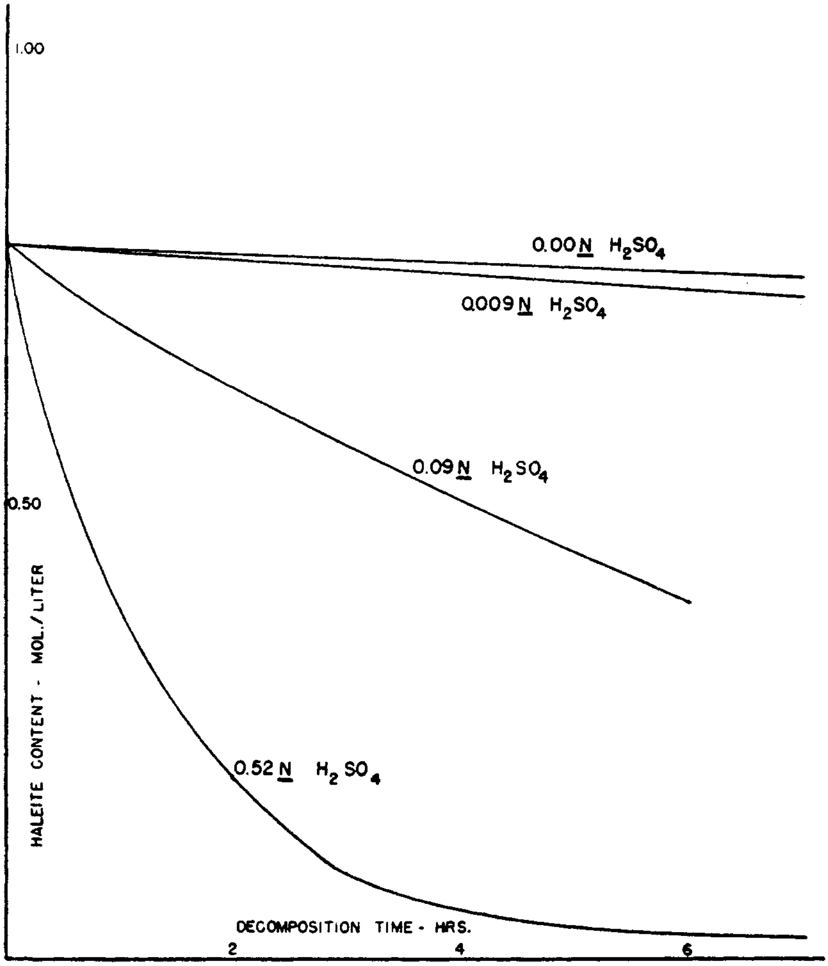


FIG. I. DECOMPOSITION OF HALEITE AT 98°

twice from alcohol, m.p. 111.0°; the crude γ-, m.p. 101.8°, was crystallized six times from alcohol, in three of which Darco was used, m.p. 103.0°. X-ray examination revealed no impurities in the β- or γ-isomers.

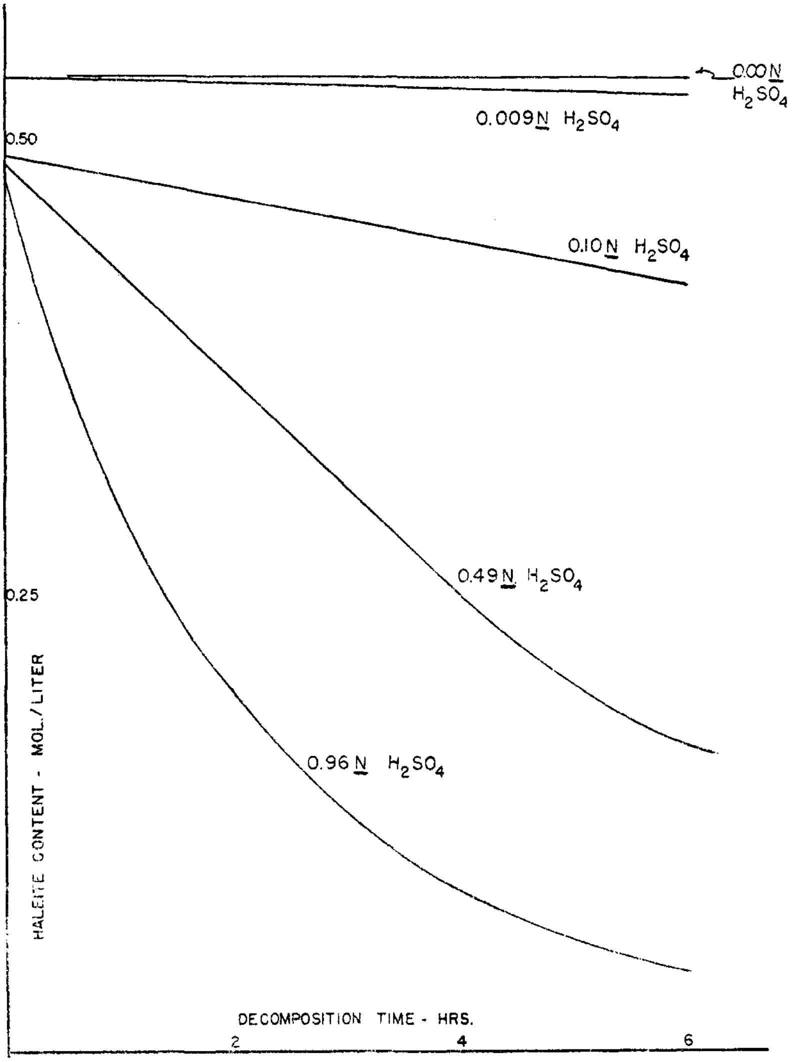
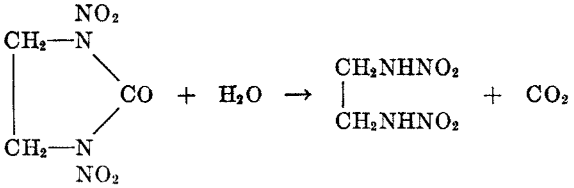


Fig. II. Decomposition of Haleite at 84°

B. Experimental procedure. 1. Aqueous decomposition. The hydrolysis of DNEU was carried out using 16.1 g. of DNEU per 100 cc. of water. The yields were determined by filtering off the Haleite formed, at room temperature, drying, and weighing. The purity of the product was determined by electrometric titration (see Fig. II) and the yield corrected for this.

The decomposition reaction is quite well known.



As carbon dioxide is titrated to bicarbonate in the presence of phenolphthalein and Haleite is dibasic, the equivalent weight 58.86 (58.86 × 3 = 176.58) bears this out admirably, as DNEU has a molecular weight of 176.09.

In the aqueous decomposition of Haleite the reactions were conducted in a three-necked, one-liter flask fitted with a mercury-sealed stirrer, a thermometer, and a water condenser. The tests at 60°, run in water alone, were, however, crudely done (in test tubes, in a constant temperature bath) and are only qualitative; 75 cc. of water were used in each run. The amount of Haleite decomposed was determined by removing a 100-cc. portion, which was weighed, cooled, and filtered. The Haleite was dried and weighed, and the filtrate made up to one liter and an aliquot titrated, to correct for Haleite remaining in solution.

The *nitrous oxide* evolved was tested for by (a) odor, (b) the glowing splinter, and (c) acid iodine solution protected by nitrogen. *Acetaldehyde* was collected from the gases evolved by the reaction mixture and identified by its ability to reduce ammoniacal silver nitrate, by the Schiff test, and finally by isolating it as the 2,4-dinitrophenyl hydrazone, m.p. 147°. The *ethylene glycol* formed was identified by reacting it with benzoyl chloride, by the Schotten-Baumann method, to produce the dibenzoate, m.p. 73°. The presence of Haleite in the reaction mixture was shown by the use of diphenylamine-sulfuric acid reagent and, after sufficient heating to destroy all the Haleite, the same reagent showed that no nitrites or nitrates were produced in the decomposition.

The nitrous oxide tests, while appearing to indicate its presence, were considered to be unreliable. A sample of the gaseous products were, therefore, sent to the General Electric Company where it was run through the mass spectrometer. Nitrous oxide and other gases were found.

COMPONENT	VOLUME %
H_2O	0.50
N_2O	32.7
N_2	64.9
O_2	.11
A	.06
CH_3CHO	1.55

2. *Reduced pressure studies.* These were carried out in a test tube attached to a mercury manometer starting at an initial pressure of 2–5 mm. of mercury. All solid samples were passed through a 50- and retained on a 100-mesh U. S. Standard Sieve, and all samples were dried 4 hours at 60° in a vacuum-oven.

3. *Atmospheric pressure studies* were conducted as par. 2 above, but regulated at 1 atmosphere by a simple mercury overflow.

EXPERIMENTAL RESULTS

A. Hydrolysis of dinitroethylene urea (DNEU). The data obtained (see Table I) show that the rate of hydrolysis of DNEU in aqueous solution is independent of acidity from 0 to 0.5 *N*, decomposition accounted for, but increases with rising temperature. It is also indicated that the rate of hydrolysis is more rapid than the rate of solution, for usual types of laboratory agitation. For this reason no kinetic studies were attempted.

As the results stated above, judging by Table I, may not be too apparent, it should be added that in none of these experiments was additional Haleite produced by further heating of the solutions involved. Further, accounting for the decomposition which results from the presence of added acid, all yields are the same, within the experimental error involved.

TABLE II

Decomposition of Haleite, 98°

REACTION TIME, HOURS	HALEITE CONTENT OF REACTION MIXTURE							
	No Sulphuric Acid Present		Solution 0.00891 *N*[a] in Sulphuric Acid		Solution 0.0936 *N*[a] in Sulphuric Acid		Solution 0.5180 *N*[a] in Sulphuric Acid	
	Mole/Liter	%	Mole/Liter	%	Mole/Liter	%	Mole/Liter	%
0	0.784	100.0	0.784	100.0	0.785	100.0	0.771	100.0
1	—	—	—	—	.700	89.1	.386	50.1
1⅙	—	—	.777	99.2	—	—	—	—
2	.771	98.5	.770	98.4	.630	80.3	.203	26.3
3	—	—	.762	97.3	.566	72.2	.0955	12.4
4	.765	97.6	.750	95.7	.502	63.9	.049	6.4
5	—	—	—	—	—	—	.029	3.8
6	—	—	—	—	.394	50.2	—	—
7	.752	96.0	.729	93.0	—	—	.023	3.0
24	.698	89.2	—	—	—	—	—	—
47	.631	80.6	—	—	—	—	—	—

[a] *N* = Normal.

TABLE III

Decomposition of Haleite, 84°

REACTION TIME, HOURS	HALEITE CONTENT OF REACTION MIXTURE									
	No Sulphuric Acid Present		Solution 0.00932 *N*[a] in Sulphuric Acid		Solution 0.0995 *N*[a] in Sulphuric Acid		Solution 0.486 *N*[a] in Sulphuric Acid		Solution 0.960 *N*[a] in Sulphuric Acid	
	Mole/Liter	%	Mole/Liter	%	Mole/Liter	%	Mole/Liter	%	Mole/Liter	%
0	0.533	100.0	0.533	100.0	0.491	100.0	0.486	100.0	0.480	100.0
1	—	—	—	—	—	—	.425	87.4	.304	63.3
2	—	—	—	—	.468	95.5	.368	75.7	.198	41.3
3	—	—	—	—	—	—	—	—	.133	27.7
3¼	—	—	—	—	—	—	.300	61.8	—	—
4	—	—	—	—	.444	90.4	.249	51.3	.088	18.3
6	—	—	—	—	.419	85.4	—	—	.043	9.0
6¼	—	—	—	—	—	—	.163	33.6	—	—
24	.526	98.8	.491	92.1	—	—	—	—	—	—
48	.517	97.0	.465	87.2	—	—	—	—	—	—
96	.490	92.0	.426	80.0	—	—	—	—	—	—

[a] *N* = Normal.

B. Decomposition of Haleite (ethylenedinitramine) in aqueous solution. Haleite is generally known to be quite stable in alkaline solution but to decompose in

TABLE IV

Decomposition of Haleite, 60°

REACTION TIME, HOURS	HALEITE CONTENT OF REACTION MIXTURE			
	No Sulphuric Acid Present		Solution 0.0977 N[a] in Sulphuric Acid	
	Mole/Liter	%	Mole/Liter	%
0	0.1042	100.0	0.1035	100.0
24	.1038	99.5	.0979	94.5
48	.1033	99.2	.0936	90.5
72	—	—	.0885	85.5
96	—	—	.0845	81.5
120	.1020	97.8	.0800	77.4
168	.1012	97.1	—	—

[a] N = Normal.

TABLE V

Reaction Velocity Constants for the Decomposition of Haleite

TEMP., °C.	CONC. OF SULPHURIC ACID Equivalent/Liter	REACTION VELOCITY CONSTANT[a] k, PER HOUR
98	0.0000	0.00201
98	.0089	.00475
98	.0936	.0490
98	.5180	.2551
84	.0000	.000367
84	.0093	.00101
84	.0995	.0115
84	.4860	.0757
84	.9600	.1749
60	.0000	.0000567
60	.0977	.000922

[a] The Velocity constants listed are for use with the equation:

$\log_{10} C = \log_{10} C_0 - kt$

C = concentration at time t in the unit of C_0

C_0 = initial concentration in any units

k = reaction velocity in reciprocal hours

t = the reaction or decomposition time in hours

TABLE VI

Decomposition of Haleite under Reduced Pressure (5-g. Samples)

HOURS	AT 100° GAS EVOLVED, CC.	AT 120° GAS EVOLVED, CC.
20	—	0.70
40	0.64	1.40
60	—	2.15
80	.76	3.00
100	—	4.40
120	.87	—

neutral and acid solution. The products of decomposition are given in the literature as nitrous oxide, ethylene glycol, and acetaldehyde. This information was confirmed.

TABLE VII

Decomposition of Haleite under Reduced Pressure in the Presence of Impurities (5-g. Samples)

HOURS	GAS EVOLVED AT 120°, CC.			
	Addend → None	0.1% H_2O	0.1% Glycol	50% Glycol
16	—	—	—	11+
45	3.87	3.78	3.87	—
71	5.45	5.55	5.89	—
92	6.87	7.14	9.62	—
97	—	—	11+	—
119	8.97	9.96	—	—
123	—	11+	—	—
145	11+	—	—	—

TABLE VIII A

Decomposition of 50/50-Haleite/TNT under Reduced Pressure (5-g. Samples)

AT 80°		AT 100°		AT 120°	
Hours	cc.	Hours	cc.	Hours	cc.
552	0.68	24	0.75	10	1.12
1176	.86	40	.85	20	3.10
1563	1.05	65	1.06	30	7.00
2012	1.42	90	1.15	37	11+
2252	1.70	123	1.43		
2687	2.05				
3350	2.51				
4145	3.52				
4817	4.74				

TABLE VIII B

Decomposition of 50/50-Haleite/TNT under Reduced Pressure (5-g. Samples)

TYPE OF TNT	GAS EVOLVED, CC.			HOURS TO 11+ CC.
	Hours → 10	20	30	
α	1.12	3.10	7.00	37
β	—	4.00	7.50	37
γ	—	—	—	22

The rate data collected in this study (Tables II, III, and IV) show that Haleite decomposes more rapidly in more acidic and in hotter solutions. The decomposition is first order, at constant acidity, with an activation energy in the neighborhood of 28,000 cal/mole (Figures I, II, III, IV, and V) in 0 to 0.5 *N* sulfuric acid. The activation energy of the decomposition decreases with increasing acidity.

C. Decomposition of solid Haleite under reduced pressure. The rate of decomposition of solid Haleite was determined at 100 and 120° under reduced pressure (Table VI, Fig. VI). At 120° the reaction was autocatalytic and was accelerated by the products. It was also accelerated by the impurities present. This is illustrated in Table VII, Fig. VII, for one product, glycol, and one impurity, moisture.

TABLE IX

DECOMPOSITION OF HALEITE UNDER REDUCED PRESSURE AT 120° (2.5-g. Samples)

HOURS	CC.	CC. + 4.0
0	0	4.0
45	1.89	5.9
71	2.52	6.5
92	3.11	7.1
119	4.86	8.9
149	5.76	9.8
178	8.41	12.4
226	9.76	13.8
232	11+	15+

TABLE X

DECOMPOSITION OF HALEITE AT 1 ATMOSPHERE AND 120° (2.5-g. Samples)

HOURS	CC.	CC. + 0.46
0	0	0.46
60	.2	.66
100	.8	1.26
150	8	8.5
175	19	19.5
200	35	35.5
225	60	60.5
250	104	104.5

TABLE XI

DECOMPOSITION OF 50/50-HALEITE/TNT AT 1 ATMOSPHERE AND 120° (5-g. Sample)

HOURS	CC.	CC. + 1.0
0	0	1
20	4	5
40	11	12
60	34	35
65	50	51
70	81	82
75	132	133
80	204	205
85	282	283
90	400	401

TABLE XII

ACTIVATION ENERGIES (E) FOR THE DECOMPOSITION OF HALEITE IN VARIOUS ENVIRONMENTS; K cal/mole

TEMP. RANGE, °C.	SOLID HALEITE[d]			AQUEOUS				TNT
	NDRC[a]		Vacuo	Water	N H_2SO_4			
	Vacuo	1 Atm.			0.01	0.1	0.5	
60–80				18[b]		25		
80–100			[c]	32.5	29.5	26	23	32
100–120	37		36					34
120–135	41.5	43.5						
135–145	51.5	59.5						

[a] OSRD Report No. 1734. [b] Low due to the qualitative nature of this experiment. [c] Does not decompose detectably in 4 months. [d] For liquid Haleite from 184–254°, E = 30.5 [Robertson, *Trans. Faraday Soc.*, **44,** 677–682 (1948)].

TABLE XIII

FREQUENCY FACTORS (LOG Z[a]) FOR THE HALEITE DECOMPOSITION

T., °C.	SOLID HALEITE[e]		AQUEOUS				TNT
	NDRC[b]	Vacuo	Water	N H_2SO_4			
	1 Atmos.			0.01	0.1	0.5	
60			12[d]		10		
80							11.5
84		[c]	13	11.5	10.5	9.5	
98			13	11.5	10.5	9.5	
100–145	12						
100		13					11.5
120		12.5					11.5
180–250	13						

[a] From $k = Ze^{-ER/T}$, Z in sec^{-1}. [b] OSRD Report No. 1734. [c] Does not decompose perceptibly in 4 months at 80°. [d] Calculated for E = 32.5. [e] For liquid Haleite, log Z = 13, see footnote [d], Table XII.

TABLE XIV

SOLUBILITY OF HALEITE IN WATER AND TNT

TNT		WATER	
Temp., °C.	g. Haleite/100 g. TNT	Temp., °C.	g. Haleite/100 g. Water
79.8	0.48	20	0.23
85	.58	30	.47
90	.77	60	2.13
95	1.12	70	3.63
100	1.62	90	10.82
105	2.45	95	16.40

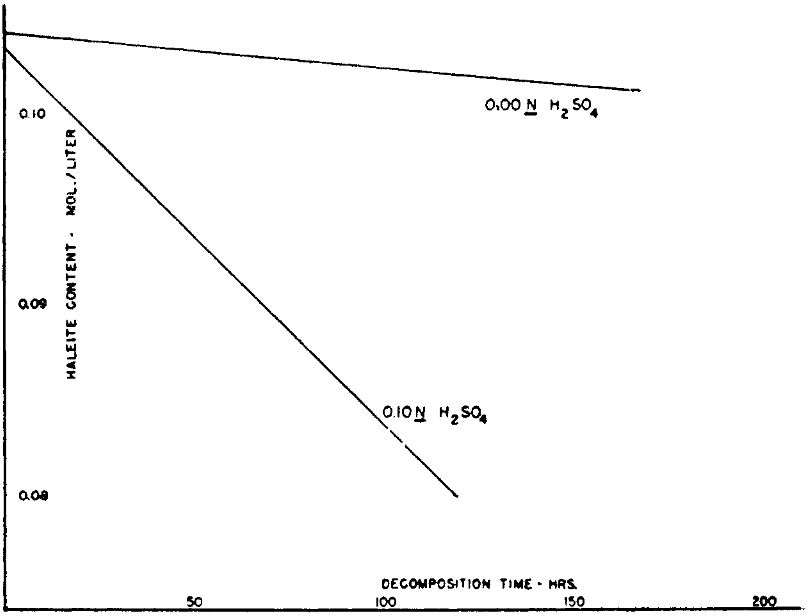


FIG. III. DECOMPOSITION OF HALEITE AT 60°

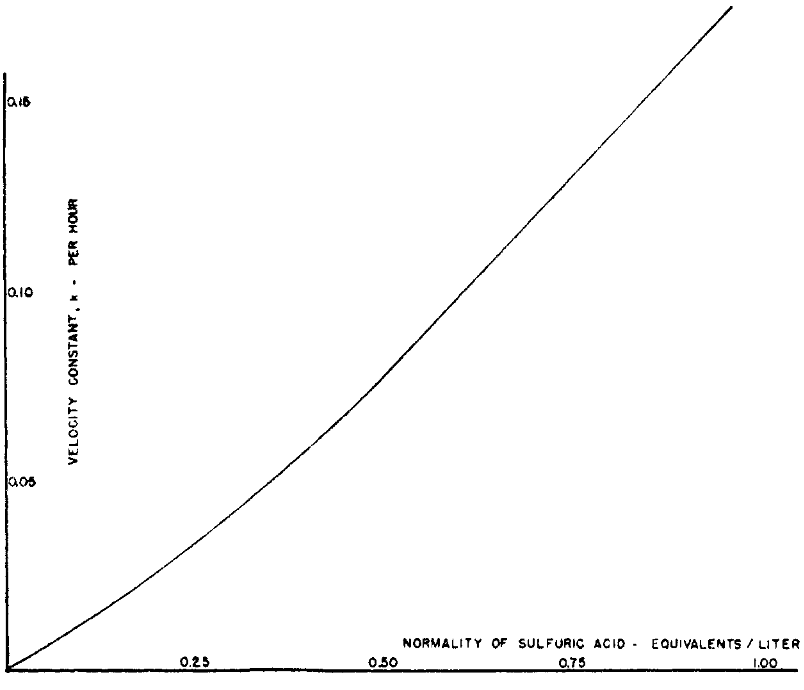


FIG. IV. VELOCITY CONSTANT FOR THE ACID DECOMPOSITION OF HALEITE AT 84°

Another interesting addend, TNT, also increases the decomposition rate (Tables VIII A and VIII B; Figures VIII A and VIII B). This process has an activation energy of about 32,000 cal/mole near 100°.

The decomposition of Haleite at 120° follows a chain mechanism, up to about 2–3% reaction (Table IX, Figure IX A, B).

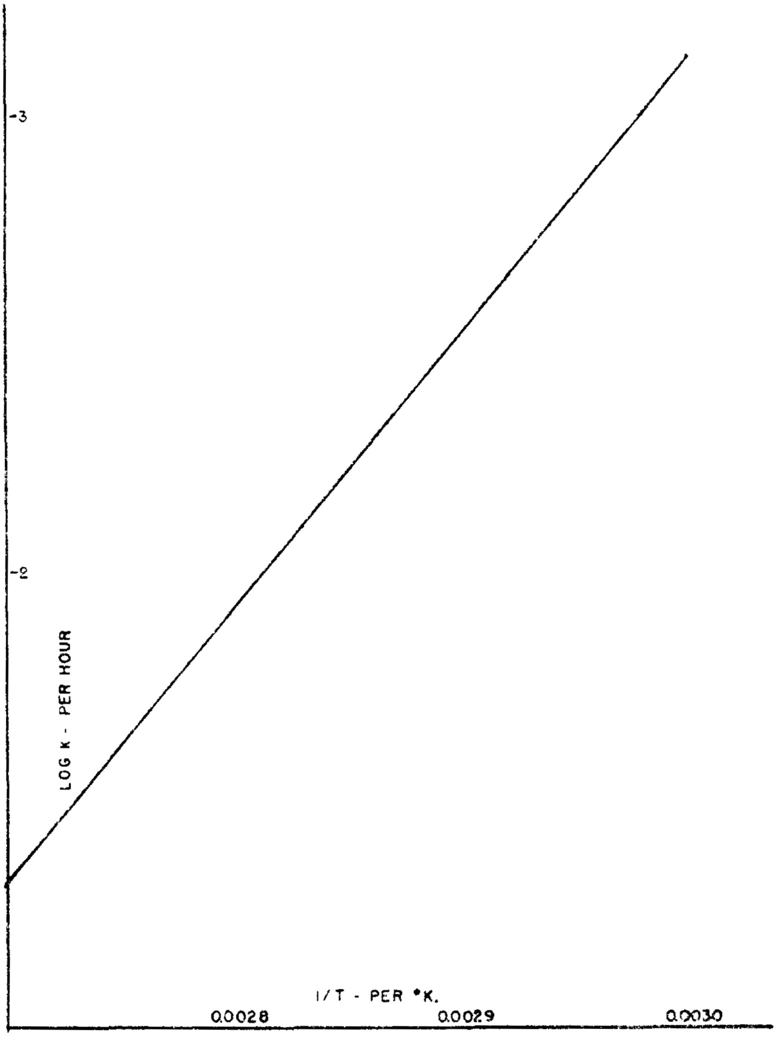


FIG. V. Temperature (T) Dependence of the Reaction Velocity Constant (*k*) for the Decomposition of Haleite in 0.10 Normal Sulfuric Acid.

Decomposition of solid Haleite at atmospheric pressure. At 120° Haleite exhibited an induction of 100–150 hours and its decomposition appeared to follow a chain mechanism after this up to 25% decomposition (Table X, Fig. X A, B). In TNT the chain mechanism appeared to hold over the entire decomposition (Table XI, Fig. XI A, B) of Haleite.

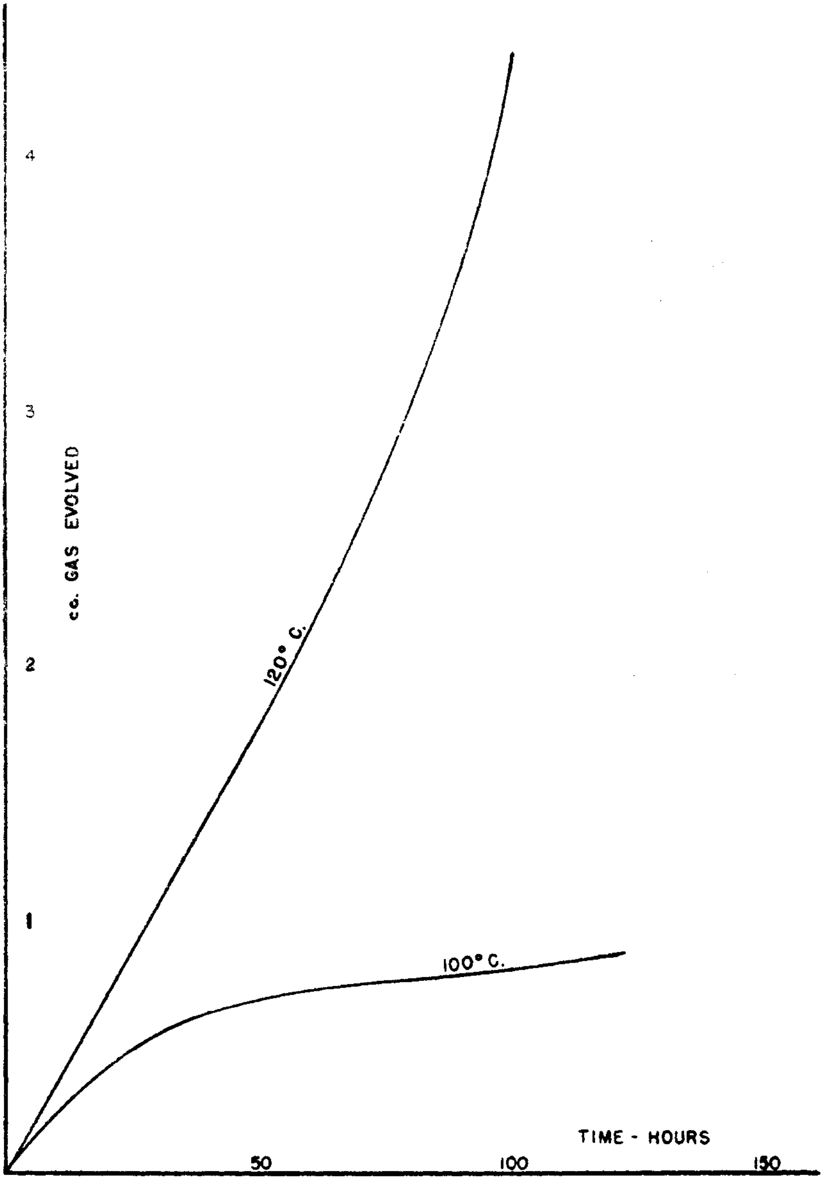


FIG. VI. DECOMPOSITION OF HALEITE UNDER REDUCED PRESSURE

Discussion of Results

A. Hydrolysis of DNEU. This reaction seems quite straightforward and appears to proceed quantitatively to produce Haleite and carbon dioxide. The data of Table I, considering the solubility of Haleite in water and the decomposition of Haleite, bear this out, as does the titration equivalent found.

B. Decomposition of Haleite in aqueous solution. From a purely practical stand point it is obvious from the data presented that excellent yields of Haleite can

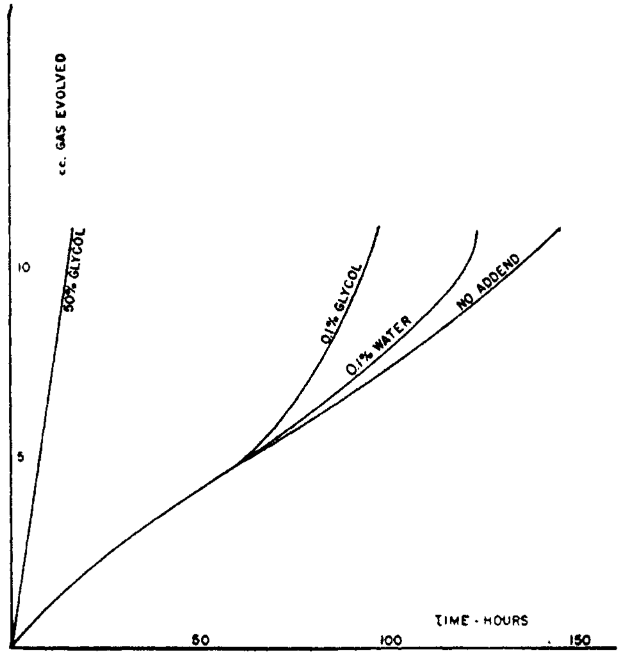


FIG. VII. DECOMPOSITION OF HALEITE UNDER REDUCED PRESSURE AT 120°

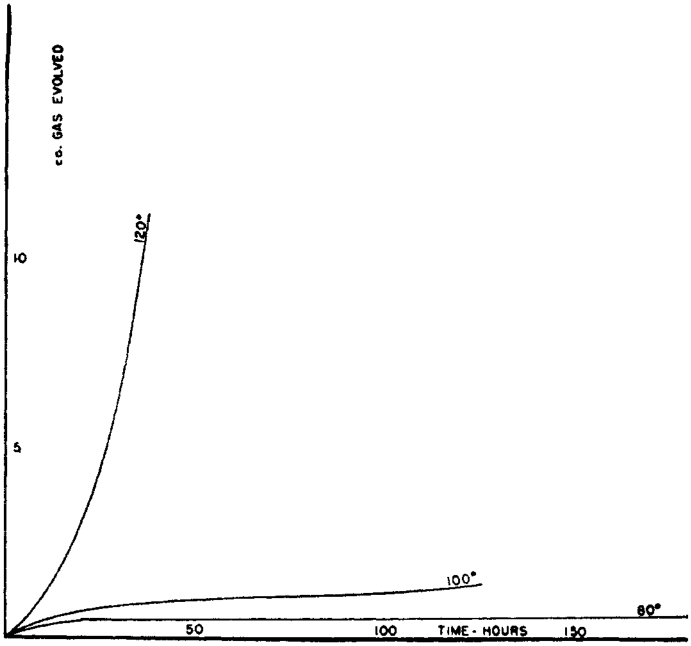


FIG. VIIIA. DECOMPOSITION OF 50/50-HALEITE/TNT UNDER REDUCED PRESSURE

be obtained in a short time by hydrolyzing DNEU at 100°. As might be suspected the yield loss due to said decomposition of Haleite can be practically eliminated

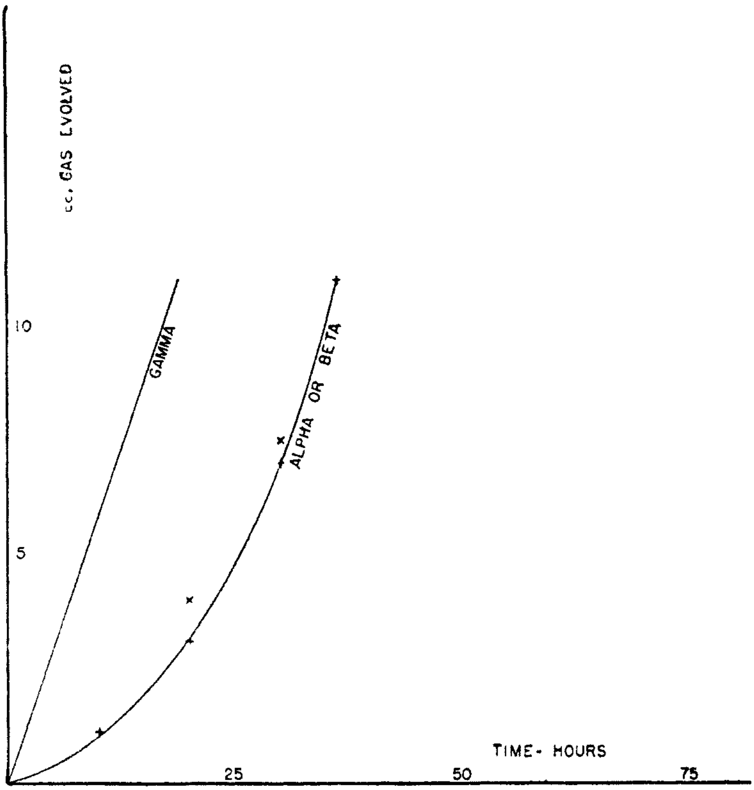


FIG. VIIIB. DECOMPOSITION OF 50/50-HALEITE/TNT UNDER REDUCED PRESSURE AT 120°

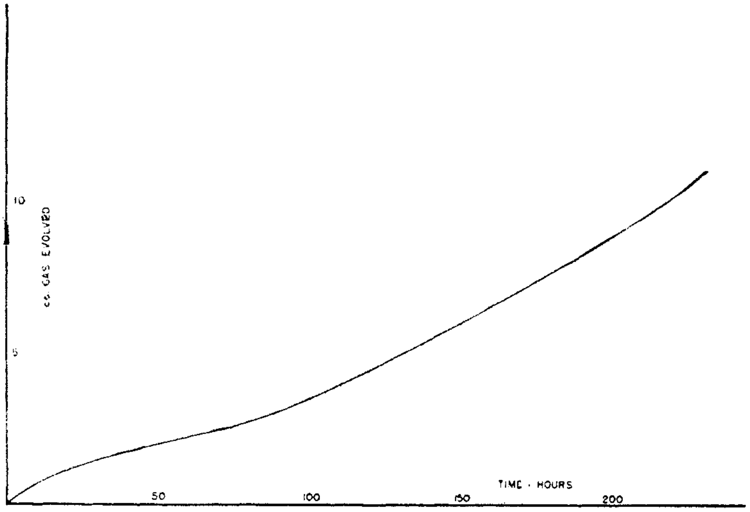


FIG. IXA. DECOMPOSITION OF HALEITE UNDER REDUCED PRESSURE AT 120°

by buffering the hydrolysis solution. As an exaggerated example of this, digestion of a Haleite solution 0.49 *N* in sulfuric acid and 0.74 *M* in sodium acetate for 6

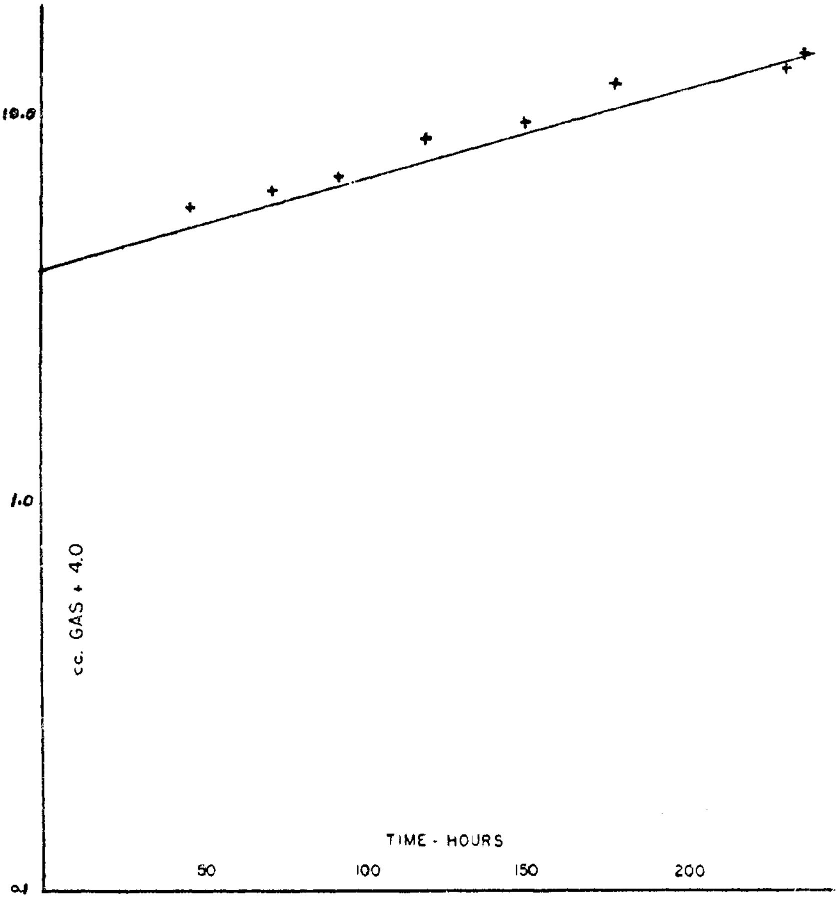


FIG. IXB. DECOMPOSITION OF HALEITE UNDER REDUCED PRESSURE AT 120°

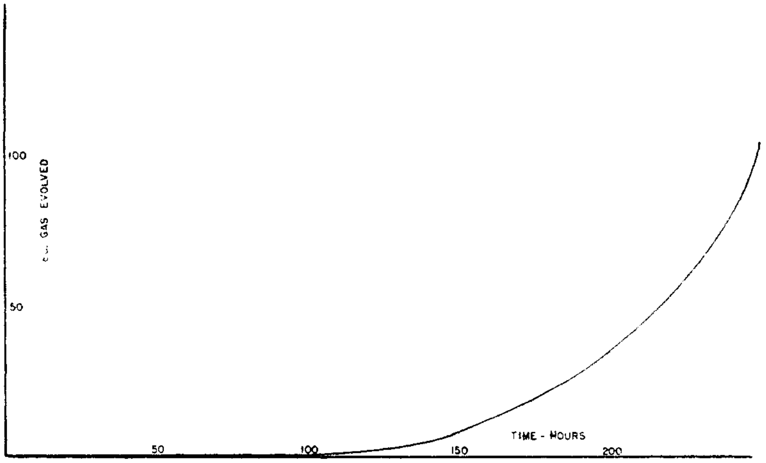


FIG. XA. DECOMPOSITION OF HALEITE AT ONE ATM. AT 120°

hours at 84° produced no detectable decomposition; if no sodium acetate had been added about 65% of the dissolved Haleite would have decomposed.

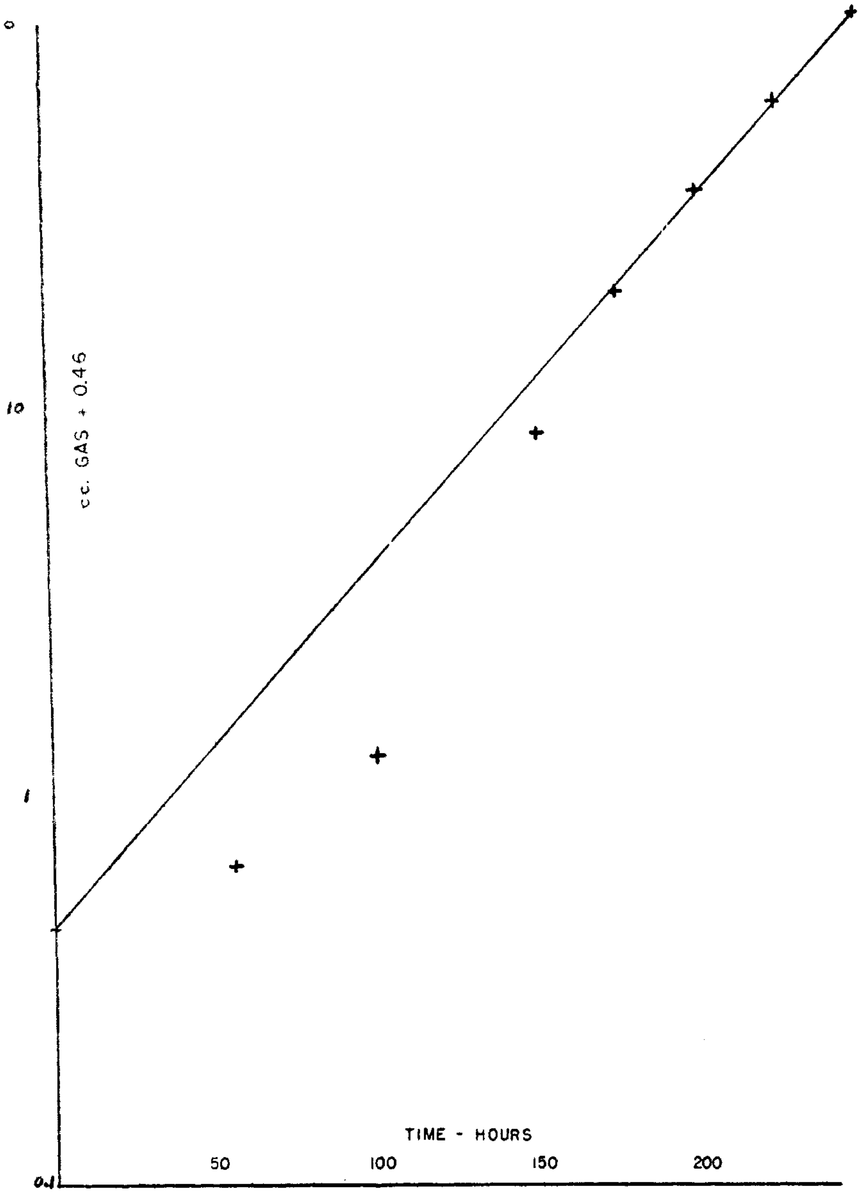


FIG. XB. DECOMPOSITION OF HALEITE AT ONE ATM. AT 120°

Reasonable quantities of buffer (~0.2% of the water weight) substantially reduce losses and yield a more stable product. Further, in view of the fact that the rate of hydrolysis is faster than the rate of solution using normal laboratory apparatus, it is also obvious that the process can be expedited by using efficient down-draft stirring and improving the wettability of the DNEU (wetting agents).

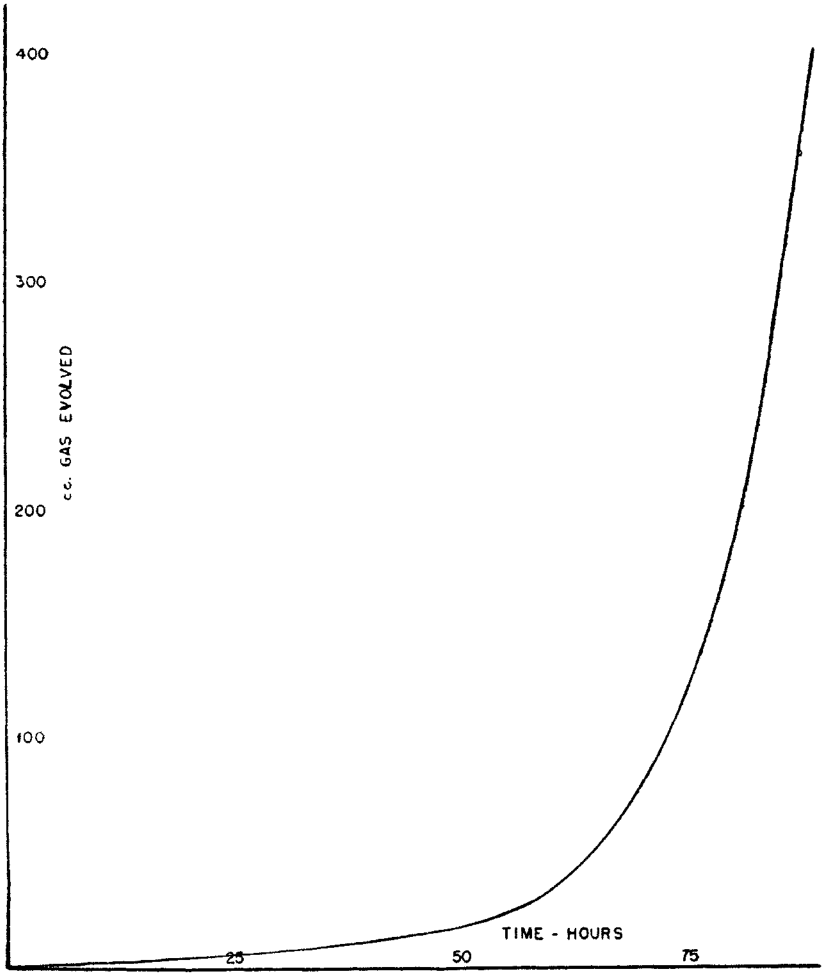


FIG. XIA. DECOMPOSITION OF 50/50-HALEITE/TNT AT ONE ATM. AT 120°

It is quite apparent from Fig. IV that the Haleite decomposition is really a second order reaction and can be expressed as

$$1. \qquad -\frac{dc}{dt} = k\{\log^{-1}(-H_0)\}c = kAc,$$

or

$$2. \qquad c = c_0 e^{-kAt},$$

where H_0 is Hammett's acidity function. Equation 2 holds only above 0.5 *N* H_2SO_4; below this value the term in H_0 would have to account for the acidity of Haleite itself. Above 0.5 *N* it holds (see Fig. II, lines from 0.5 to 1 *N*) because $[H_2SO_4]$ remains constant. This was shown by decomposing completely an aqueous Haleite solution and determining the acidity and sulfate content of the final solution.

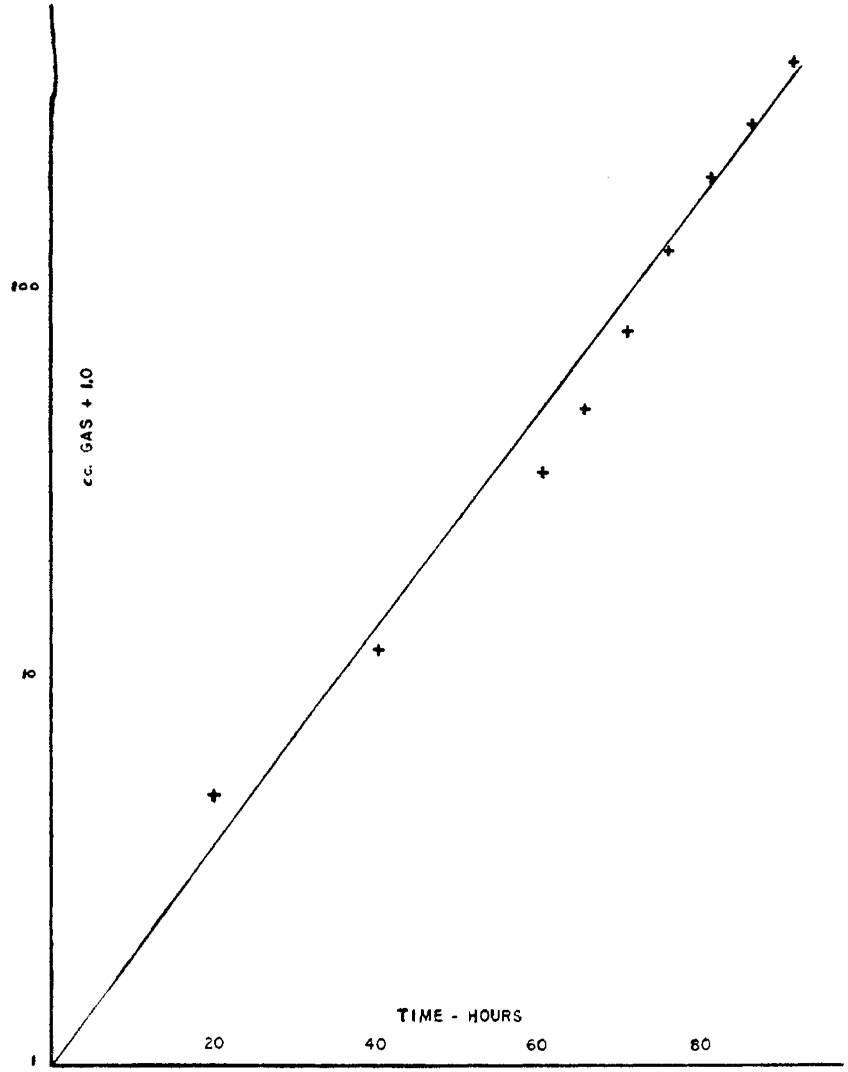


FIG. XIB. DECOMPOSITION OF 50/50-HALEITE/TNT AY ONE ATM. AT 120°

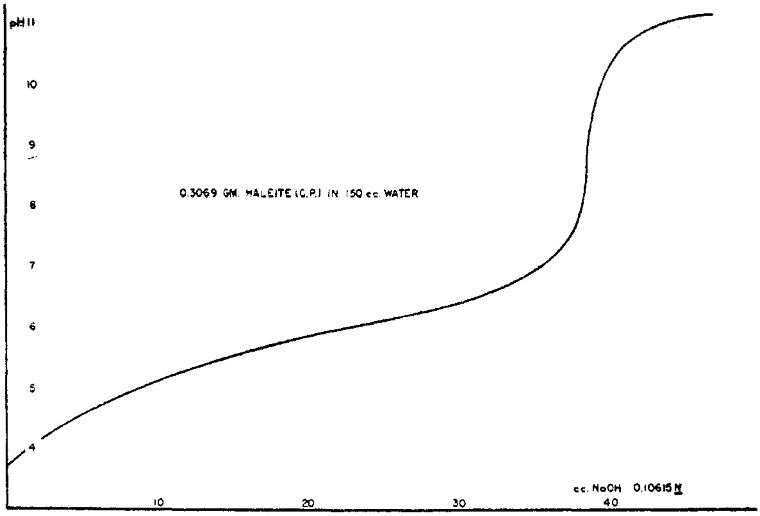
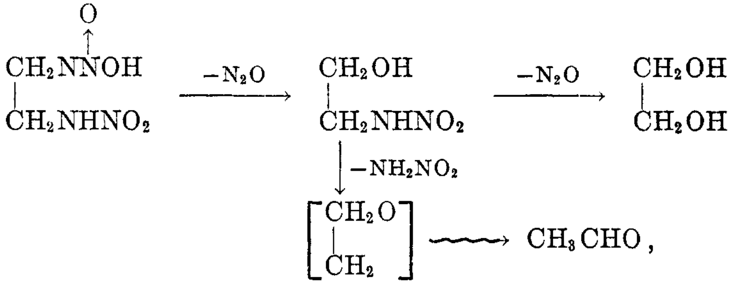


FIG. XII. ELECTROMETRIC TITRATION

The above seems most interesting and considered in the light of the known products indicates the following decomposition reactions:

3.



$$\begin{array}{l} \overset{\overset{O}{\uparrow}}{CH_2NNOH} \\ | \\ CH_2NHNO_2 \end{array} \xrightarrow{-N_2O} \begin{array}{l} CH_2OH \\ | \\ CH_2NHNO_2 \end{array} \xrightarrow{-N_2O} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

$$\downarrow -NH_2NO_2$$

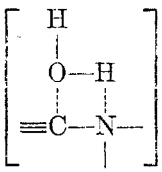
$$\left[\begin{array}{l} CH_2O \\ | \\ CH_2 \end{array}\right] \rightsquigarrow CH_3CHO,$$

and, of course,

4. $$NH_2NO_2 \longrightarrow N_2O + H_2O$$

This decomposition is reasonable for an activation energy of 30 Kcal/mole as the bonds broken are about of the same strength as those made. Thus, a critical complex, such as

5.



is probably involved. This is in harmony with the fact that in acetic acid the reaction is much faster, and the C—O bond is 29 Kcal weaker than the O—H bond.

C. Decomposition of solid Haleite under reduced and atmospheric pressures. In a very neat study of the same subject, at atmospheric pressure (3), the decomposition of Haleite was shown to follow a chain mechanism. The data reported here appear to bear this out. Hankin and Salwin also showed that the decomposition was not catalyzed by the gaseous decomposition products and increases with increasing sample size and specific surface.

This study showed that Haleite decomposition very definitely is catalyzed by the non-gaseous decomposition products and impurities. Further, as seems most reasonable, if the molecule is mobilized by solution the decomposition rate is increased. Thus solution in water or TNT markedly raises the decomposition rate (Table XIV details the solubilities in water and TNT). This is also shown by the E and Z values (Tables XII, XIII) of the Arrhenius equation

$$k = Ze^{-E/RT} \tag{6}$$

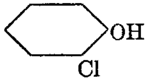
Robertson (4) also found that liquid Haleite decomposed at a much more rapid rate than the solid; for the liquid

$$k(\text{sec}^{-1}) = 10^{12.8}e^{-30,500/RT} \tag{7}$$

Again the decomposition, like that in aqueous media, was unimolecular as opposed to the chain mechanism. This information is quite interesting in relation to the Haleite decomposition in TNT. Table IV shows that Heleite is only slightly soluble in TNT, and thus as the decomposition of the system Haleite-TNT follows a chain mechanism, the solid must be more important to the decomposition than the dissolved material which must decompose by a first order reaction. This is reasonable as only about 5% of the Haleite present is in solution.

As an added point of interest, it might be mentioned that solid Haleite should be expected to exhibit greater stability than liquid Haleite, or Haleite in solution. This is so for two reasons. First, in the solid or crystalline state, the atoms involved in the decomposition reactions are held in relatively fixed or immobile positions; thus these reactions are inhibited since they obviously require sufficiently close approach of participants to permit the breaking of old and the formation of new bonds. Second, in the solid state, Haleite exists in the normal form. Thus, while the hydrogen bonding involved in the structure of the Haleite crystal must tend to distort the stable normal form somewhat in the direction of the unstable form, its effects can not be too serious. This is indicated by the hydrogen bond strengths and distances shown below.

HYDROGEN BOND STRENGTHS

BOND	HYDROGEN BOND ENERGY, KCAL/MOLE	SUBSTANCE
F—H—F	6.7	$(HF)_6$
O··H—O	4.5	Ice, H_2O_2
	6.2	MeOH, EtOH
	7.1	HCOOH
	8.2	CH_3COOH
C—H···N	3.28	$(HCN)_2$
	4.36	$(HCN)_3$
N—H···N	1.36	NH_3
N—H···F	5	NH_4F
O—H···Cl	3.9	 (g)

HYDROGEN BOND STRENGTHS BETWEEN OXYGEN ATOMS AND INTER OXYGEN DISTANCES

R—COOH	Kcal/mole	A°
H—	7.06	2.67
CH_3—	8.2	
	4.3	
HOOC—		2.6

The bond lengths of Haleite lie in the range 1.21 (H—O) to 1.52 Å (C—C).

SUMMARY

It has been demonstrated that (a) in solution Haleite decomposes by a second order mechanism, with an activation energy in the range 20–35 Kcal/mole depending on the nature of the medium; high acidity favors low E; (b) in the solid state the decomposition follows a chain mechanism E = 40–50 Kcal/mole depending on the temperature.

Haleite decomposes, principally through the *aci*-form to yield glycol, acetaldehyde, and nitrous oxide.

West Hanover, Mass.

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(2) Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, pp. 215–218.

(3) Hankin and Salwin, *Stability of Ethylenedinitramine (Haleite) and Related Nitramines*, OSRD Report No. 1734 (1943).

(4) Robertson, *Trans. Faraday Soc.*, **44**, 677–682 (1948).