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EXPERIMENTS ON IGNITION OF NITROCELLULOSE,

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EXPERIMENTS ON IGNITION OF NITROCELLULOSE

Abstract

The ignition of powder probably depends on the retention of gaseous products near the surface of the powder. The gaseous products are evolved from the powder according to the equation -

$$\frac{dy}{d\theta} = 5.2 \times 10^{17} \left(\frac{\%N}{14.2}\right)^2 \exp. -47,300/RT$$

$\frac{dy}{d\theta}$ = mols of gas per second per gram nitrocellulose.

$\%N$ = % Nitrogen in nitrocellulose

R = gas constant

T = temperature, °K

This evolution of gas is practically thermally neutral, neither absorbing nor giving off heat.

The gaseous products evolved undergo a subsequent reaction having an activation energy of 6400 cal. and liberating as much as or less than 2500 cal. per gram of gas $\leq$ 156,000 cal. per average mol of gas.

The time lag to ignition of nitrocellulose, initially at room temperature, heated by Nitrogen gas at temperature above 220° C is given by -

$$\text{seconds time lag} = \theta = 2.3 \times 10^{-4} \exp. 6400/RT$$

This report describes two experiments and a conjectural interpretation dealing with powder ignition. In the experimental part, evidence for a two step ignition process is set forth. This is followed by a discussion giving a tentative and admittedly debatable interpretation of the data.

Experimental Part

If Nitrocellulose is heated in a vacuum (5 x 10^{-4} cms. of mercury) the rate of liberation of gas in mols. per second per gram is expressed by the equation:

$$\frac{dY}{d\Theta} = 5.2 \times 10^{17} \left(\frac{\%N}{14.2}\right)^2 \text{exp.} \frac{-47,300}{RT}$$

Y = mols. of gas

Θ = time

R = gas constant

T = temperature, ° Kelvin

The apparatus pictured in Figure No. 1 was used to determine the rate. Either Nitrocellulose sticks of .16 cms. radius or thin films were placed in the heating tube, the system pumped out and closed off, and the nitrocellulose heated at constant temperature in the oil bath. The films were prepared by evaporating 10 cc of an acetone solution of nitrocellulose (containing 20 grams per liter) on the walls of the heating tube. The dimensions of the resulting film were 7 cms. length x 2 cms. diameter. A diffusion pump held the pressure in the heating tube to its initially low value throughout the run. The pressure in the large flask was measured as a function of time. The slopes of the pressure time curves were found to be practically constant up to a loss in weight of more than 20% of the nitrocellulose. These slopes are tabulated here and plotted in graph one.

FOR STICKS AND FILMS OF 13.2% NITROGEN NITROCELLULOSE

Temp., °C	1/T, °K	dp/dΘ, cms./sec.gm.		log dp/dΘ	
		stick	film	stick	film
140.2	2.419 x 10^{-3}		1.17 x 10^{-5}		-4.9318
142.8	2.403 x 10^{-3}	1.72 x 10^{-5}	1.74 x 10^{-5}	-4.7645	-4.7595
147.8	2.374 x 10^{-3}		3.07 x 10^{-5}		
150.0	2.362 x 10^{-3}	4.44 x 10^{-5}		-4.3526	
153.5	2.343 x 10^{-3}	6.22 x 10^{-5}		-4.2062	
154.8	2.335 x 10^{-3}		7.90 x 10^{-5}		-4.1024

FOR FILMS OF 11.0% NITROGEN NITROCELLULOSE

Temp.,°C	1/T	dp/dΘ	log dp/dΘ
144.4	2.394×10^{-3}	1.43×10^{-5}	-4.8447
146.0	2.369×10^{-3}	2.66×10^{-5}	-4.5751
149.0	2.386×10^{-3}	1.59×10^{-5}	-4.7986

From the Arrhenius equation;

$$\frac{d \log dp/d\Theta}{d\ 1/T} = -\frac{E}{2.303\ R}$$

E, the energy of activation, = 47,300 cal.

The difference of the two curves is .165, hence the ratio dp/dΘ for 13.2 to 11.0% N nitrocellulose is 1.46. But 1.46 is approximately the square of the ratio of 13.2 to 11.0.

$$\left(\frac{13.2}{11}\right)^2 = 1.44$$

Thus dp/dΘ is approximately proportional to the square of the Nitrogen content. This dependance is based on two points only.

The volume of the system was 13.6 litres, accordingly

$$\frac{1\ \text{cm. P}}{\text{sec., gm.}} = 7.32 \times 10^{-3} \text{ mols./sec., gm., at room T}$$

and $$\frac{dY}{d\Theta} = 5.2 \times 10^{17} \left(\frac{\%N}{14.2}\right)^2 \text{exp.} - 47{,}300/RT$$

This expression may be fitted to a first order reaction equation rather easily. For a first order reaction;

$$\frac{dY}{d\Theta} = kY$$

gives the rate of appearance of gas. If the mols. of gas liberated be plotted against loss in weight of the reacting piece, and this initial slope extrapolated to$_2$100% loss in weight - we obtain a value of ^{1} of 1.58×10^{-2} mols./gram.

Hence,

$$k = 3.3 \times 10^{19}\ \frac{\%N}{14.2}^{2}\ \text{exp.} -47{,}300/RT$$

The fact that approximately the same decomposition rates are obtained for films and sticks means that the reaction is thermally neutral - assuming the thermal conductivity of nitrocellulose to be independent of temperature.

This may be shown as follows:

The equation of heat flow is -

$$C\rho \frac{\partial T}{\partial \theta} = \nabla^2 k'T+P$$

k' = conductivity

P = rate of production of heat per unit vol.

In this steady state experiment, $\partial T/\partial\theta = 0$

hence, if k' is independent of T,

$$k' \Delta^2 T = -P$$

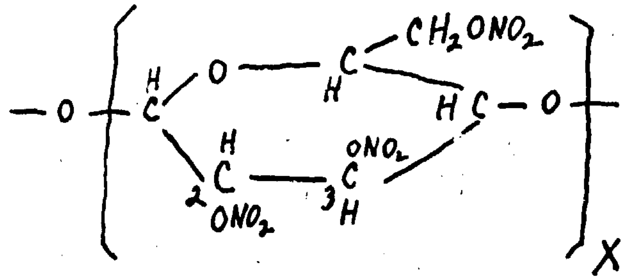
But since the rate was independent of thickness of the piece $\Delta^2 T$ must have been zero, and therefore $P=0$. The reaction is therefore thermally neutral. In addition, the identity of decomposition rates demonstrates that changing the surface/mass ratio of the nitrocellulose by a factor of 32 does not appreciably alter the decomposition rate.

The permanent gases given off during heating consist largely of carbon monoxide and nitrous oxide. In addition, a very reactive, highly oxidizing gas is evolved. Its reactivity is demonstrated by its occasionally exploding under 1-2 mm. pressure with such force as to shatter the glass apparatus - its oxidizing power by its forming a layer of red mercuric oxide on the mercury in the diffusion pump on standing over night.

The presence of heavier gas molecules is demonstrated also by the fact that average molecular weight of the gas evolved is about 63, whereas N_2O has a molecular weight of only 44 and CO a still smaller weight. This average molecular weight is obtained from the observation that 1 gram of gas averages 1.58×10^{-2} mols.

A quantitative analysis of the permanent gases and an identification of the extremely reactive gas has not yet been carried out.

The nitrogen dependence of the decomposition rate and the fact that N_2O is the only nitrogen oxide found in the gaseous products of this process can be interpreted to mean that the decomposition of nitrocellulose initiates on groups containing two neighboring nitrogen atoms. The two secondary carbon atoms, numbers 2 and 3 in the formula



are the only positions conforming to this requirement, but the nitrate groups in question need not be on the same glucose unit.

The reaction of nitrocellulose need not immediately result in gasification of all reacting nitrogen. Analyses of the nitrocellulose residues after heating, prove the nitrogen to have been reduced partly to non-ester nitrogen in the solid phase. Data illustrating this fact are given here:

NITROCELLULOSE STICKS HEATED AT 120° C

UNDER 5×10^{-4} CMS. OF MERCURY PRESSURE

% loss in weight of stick	Total N in residue	Ester N in res.
1.51	11.77	11.79
1.88	11.77	10.91
3.58	11.56	10.57
5.65	11.77	10.34

That the evolution of gas from the powder actually may be involved in the ignition of powder is demonstrated by the following ignition experiment on 13.2% N nitrocellulose sticks. The experiments were conducted in the apparatus illustrated in Figure No. 2. Nitrocellulose sticks were mounted on bakelite sticks of equal diameter, (thus no irregularities in gas flow occurred at the upstream end of the nitrocellulose) the entire stick was shoved longitudinally into the hot gas stream, and the time lag to ignition measured as a function of gas velocity and temperature.

The data are plotted in graph two, and tabulated here.

NITROCELLULOSE PIECES 2.4 - 2.5 CMS. LONG, IN N_2 GAS

Gas flow (L/sec,23°)	Time, seconds	Average of
261° C		
.54	25	6 runs
.36	27	3 "
.23	25	2 "
.18	33	2 "
.14	33	3 "
0.00	9.5	4 "
210° C		
.7	55	6 "
.54	52	4 "
.36	85	3 "
.23	106	2 "
.12	223	4 "
.09	72	2 "
.00	41.6	4 "
199° C		
.8	79	3 "
.4	132	3 "
.2	276	3 "
186° C		
.7	280	6 "
.62	294	2 "
.54	378	2 "
.46	448	3 "
.36	>2380	2 "
.18	1160	2 "
.12	345	3 "
.00	92	4 "

Under identical conditions of temperature and L/sec. gas flow, ignition times varied as follows:

Time, secs.	Gas
29.1	N_2
17.9	H_2
41.1	O_2

These differences probably should be ascribed altogether to the differences in heat and material transfer of the three gases. Oxygen has no chemical effect in hastening ignition. Similarly, there is no appreciable change in time lag if the Nitrogen contains small amounts of NO_2, Br_2, HI, benzaldehyde, alcohol or water. The ignition time is independent of length of the nitrocellulose pieces between 1.25 cms. and 7.5 cms. in length. The inside diameter of the burning tube was .25 cms., in most runs, but the same time lags were obtained with burning tubes of .4 cms. radius.

Discussion

Since the coefficient of heat transfer from the gas to the solid phase is either constant or increasing with increasing gas velocities, the initially increasing ignition time lag with increasing gas velocity appears as fairly conclusive evidence that the retention of gaseous products near the surface of the powder is a determining factor in the ignition process. However, the independence of ignition time and length of piece probably means only the gaseous products contained in a narrow quasi-stagnant film serve towards ignition.

One recalls the highly reactive, oxidizing gas particles mentioned before in the low pressure experiments. These, if present at higher pressures, might be the reactant particles which could ignite the piece either by their own heat of decomposition or by serving as initial centers for a gas phase chain reaction. With increasing Nitrogen flow, the effect of increased heat transfer from the hot Nitrogen to the piece (consequently the increased rate of evolution of gas from the piece) and of decreased thickness of the film contiguous to the piece (thus less retention of evolved gas) might so interact as to give the observed curves. In addition, this interaction might well be complicated by a development of the gas reaction in time.

A discussion of the data will be facilitated by a plot of log Θ, the logarithm of the time lag, against the reciprocal of the absolute temperature. To this end graph three was constructed from the data given above. It is seen that the temperature coefficient of the time lag, at higher rates of flow of gas has two limiting values. For low temperatures, $d(\log\Theta)/d(1/T) = 6520$. At high temperatures $d(\log\Theta)/d(1/T) = 1390$. These values ought to be proportionate to the activation energies of two different rate processes. If they were consecutive processes we would expect to find the observed change in $d(\log\Theta)/d(1/T)$. For of two consecutive processes, the slower one would always set the observed rate for the over all reaction. Thus, we would measure primarily the temperature coefficient of the slower process and this would be the process with the greater temperature coefficient at low temperatures, the other process at high temperatures.

The following very conjectural treatment is suggested. We already know that one process is the evolution of powder gas from the stick. Since the retention of this evolved gas near the stick is necessary to ignition, the other process must be a reaction involving the gas in the film. Such a reaction would be expected to develop in time according to the relation

$$W = Be^{\varphi\Theta},$$

in which $\varphi = CP^n \exp -E/RT$

Θ = time

P = pressure of reactants.

(See Semenoff, "Chemical Kinetics and Chain Reactions", page 454, Oxford 1935).

The assumption that W must reach a critical value for ignition to take place is sufficient to account for the changing temperature coefficient.

$$W = W_{crit.} = \text{constant},$$

then since constant = $\ln B + \varphi\Theta$

$$\ln \Theta = -\ln \varphi - \ln \ln B + \text{constant}.$$

B is in part a concentration factor. it cannot be much greater in magnitude than the concentration of reactants. φ contains the same factor, since P is a pressure of reactants. Consequently, $\ln \ln B$ is small compared to $\ln P$ and may be neglected.

Actually in most explosive reactions, the condition for explosion may be stated $\varphi\Theta$=constant, which is what is assumed above.

Then, $\frac{d(\ln\theta)}{d(1/T)} = \frac{E}{R} - n\,\frac{d(\ln P)}{d(1/T)} - \ln P \;\frac{dn}{d(1/T)}$

Now gas is generated from the powder in accordance with the experimentally determined rate:

$$\frac{dY}{d\theta} = 5.2 \times 10^{17}\left(\frac{\%N}{14.2}\right)^2 \text{exp. } -47{,}300/RT$$

And we should expect P to be proportional to this.

Consequently, $\ln P = -23{,}600/T + f(L,\theta)$,

(L=liters/sec.flow)

and $\frac{d(\ln P)}{d(1/T)} = -23{,}600$

At high flow rates and high T,

$$\frac{d(\ln\theta)}{d(1/T)} = 6{,}400 \quad .$$

Bearing in mind the discussion of temperature coefficients, this must represent the temperature coefficient for the slower process. Hence, E/R= 6,400, and -

$$\frac{d(\ln\theta)}{d(1/T)} = 6{,}400 + 23{,}600\,n - f(L,\theta) - \frac{23{,}600}{T}\;\frac{dn}{d(1/T)}.$$

$f(L,\theta)$ may be approximated as follows:

By definition, $\ln P = f(L,\theta) - 23{,}600/T$

$$\text{or } P = e^{\,f(L\theta)}\; I_{lim}$$

where I is the integral proportional to the rate of gas evolution and I_{lim} is proportional to the limiting maximum rate.

If we approximate the gas film by an infinite flat film bounded at one surface by the powder surface, then the concentration of gas at a distance y measured out from the powder surface is (see Barrer, "Diffusion In and Through Solids," page 9, Cambridge, 1941).

$$C(y) = I\left[1 - \frac{2}{\pi}\int_0^{y/2\sqrt{D\theta}} e^{-v^2}\,dv\right]$$

D = diffusion coefficient.

The pressure is proportional to this concentration, whence

$$P(y) \propto C(y) \propto I\left[1 - {}^{y}/\sqrt{\pi\ D\Theta} + y^{3}/24\ (\sqrt{\pi\ D\Theta}^{3} - \ldots.\right]$$

And the average pressure through the film of thickness d

$$= \frac{1}{d}\int_{0}^{d} P(y)\ dy \propto I\left[1 - \frac{d}{\sqrt{\pi\ D\Theta}} + \ldots.\right]$$

Equating P and this average P gives -

$$f(L,\Theta) = \ln\left[\frac{I}{I_{lim}}\ (1 - {}^{d}/\sqrt{\pi\ D\Theta})\right] + \text{constant}$$

The film thickness d varies with velocity of the heating gas:
If $d = d_oL^{-m}$, L = Liters/second -

$$\frac{d(\ln\theta)}{d(1/T} = 6400+\ 23{,}600\ n- \left[\text{In}\left\{\frac{I}{I_{lim}}(1 - \frac{d_o l^{-m}}{\sqrt{\pi\ D\Theta}}\right\} -23{,}600/T+\text{const.}\right]\frac{dn}{d(\frac{1}{T})}$$

If n=0 at high temperatures, 1 at low temperatures, and dn/d(1/T) = 0 at both high and low temperatures, the main features of the curves for higher rates of flow are obtained. We can also see (because the larger L, the sooner I/I_{lim} approaches unity) that the factor multiplying dn/d(1/T) will go through a minimum with increasing L, and thus qualitatively account for the variation in d(ln Θ)/d(1/T) with changing L.

The heat evolved by this assumed gas reaction may be large. The heat of combustion of nitrocellulose is about 2500 cal./gm. The powder has approximately this same heat of combustion per gram after having lost over 20% by weight in the low pressure gas evolution experiments. Since the heat effect accompanying the evolution of gases from the piece is approximately zero, the heat of combustion of the evolved gases is therefore about 2500 cal./gm., or (since 1 gram of evolved gases = 1.58×10^{-2} mols.) about 156 large calories per average mol. If the gases carried oxygen sufficient to yield completely oxidized products, CO_2, N_2, the heat of reaction would be equal to this heat of combustion.

From the curves at higher temperature, where the effect of changing gas velocity is slight, we determine the time lag to ignition at higher temperatures, where

$n = dn/d(1/T = 0$, to be $\Theta = 2.3 \times 10^{-4}$ exp. 6400/RT.

Summary

The ignition of nitrocellulose is probably a two step process involving first, the evolution of gas from the solid; second, the reaction of this gas near the powder surface.

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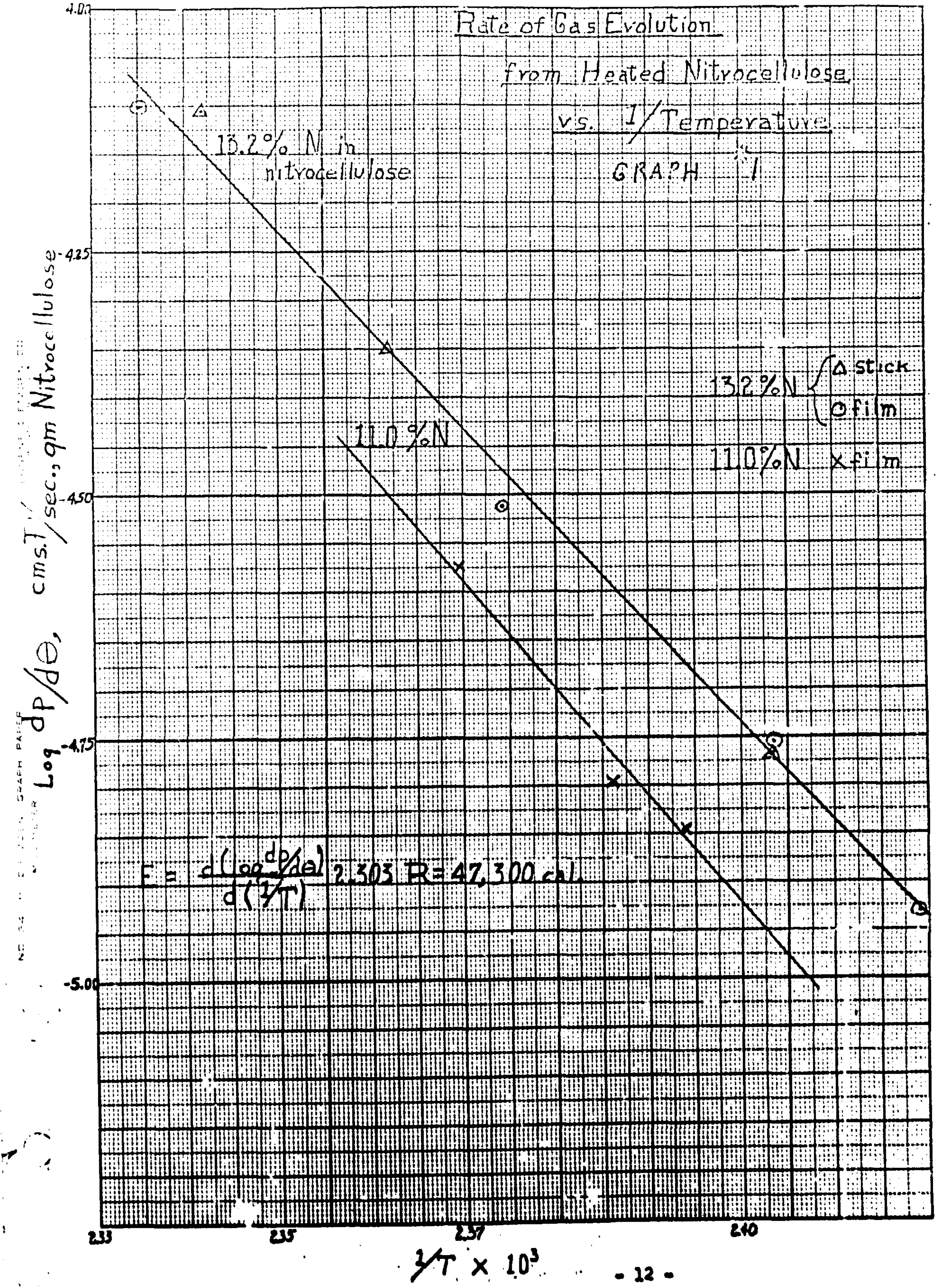
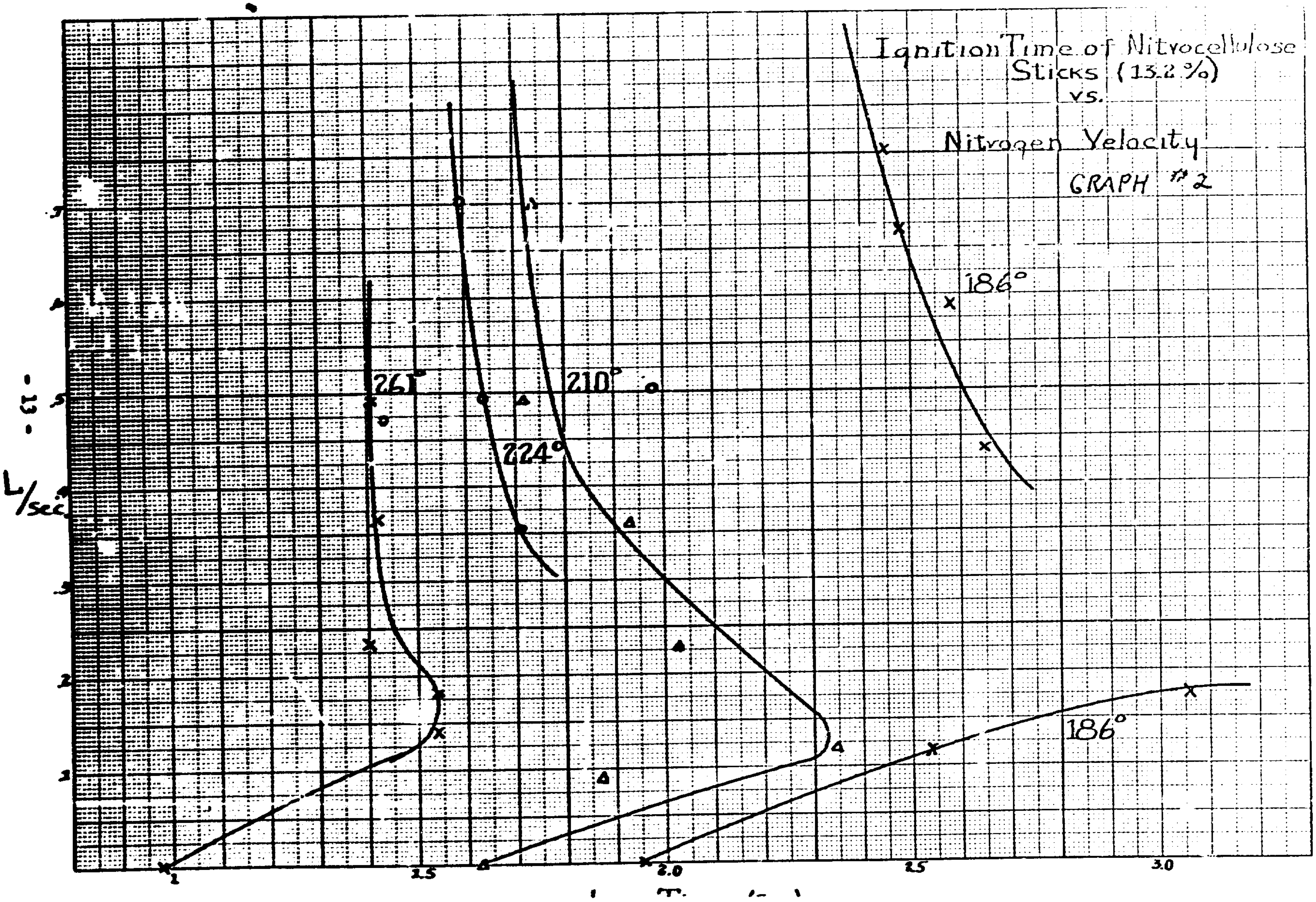
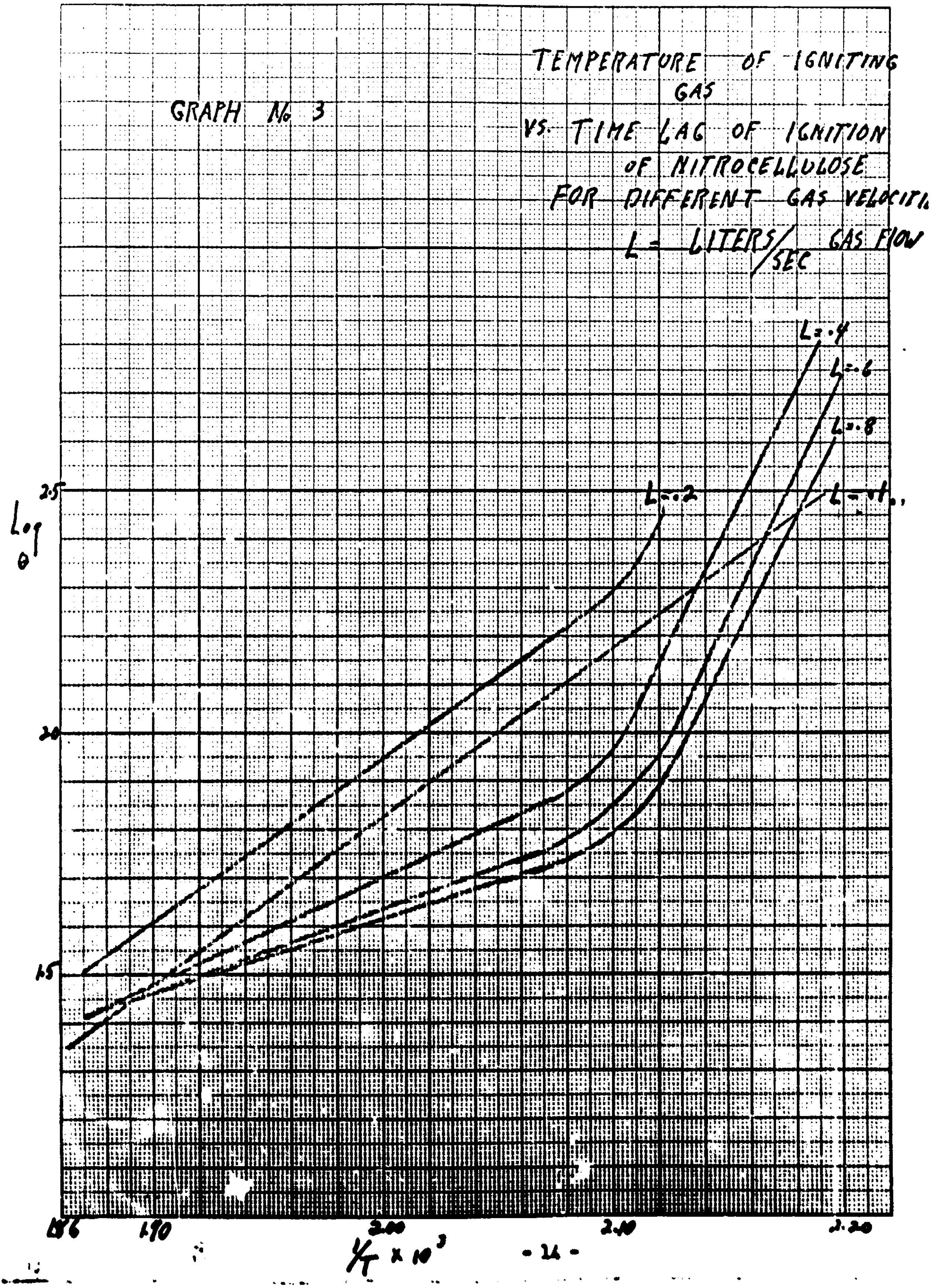
Capt. Ord. Dept.


Rate of Gas Evolution
from Heated Nitrocellulose
vs. 1/Temperature
GRAPH I
13.2% N in nitrocellulose
11.0%N
13.2%N { △ stick
⊙ film
11.0%N × film
Log dP/dΘ, cms.T/sec., gm Nitrocellulose
-4.00
-4.25
-4.50
-4.75
-5.00
2.33
2.35
2.37
2.40
1/T × 10³
E = d(log dp/dΘ) / d(1/T) 2.303 R = 47,300 cal.


Ignition Time of Nitrocellulose Sticks (13.2 %)
vs.
Nitrogen Velocity
GRAPH #2
186°
210°
261°
224°
186°
L/sec
7
6
5
4
3
2
1
1
1.5
2.0
2.5
3.0


GRAPH No 3
TEMPERATURE OF IGNITING GAS
VS. TIME LAG OF IGNITION OF NITROCELLULOSE
FOR DIFFERENT GAS VELOCITI
L = LITERS/SEC GAS FLOW
L=.4
L=.6
L=.8
L=.2
L=1
Log θ
2.5
2.0
1.5
1.86
1.90
2.00
2.10
2.20
1/T × 10^3

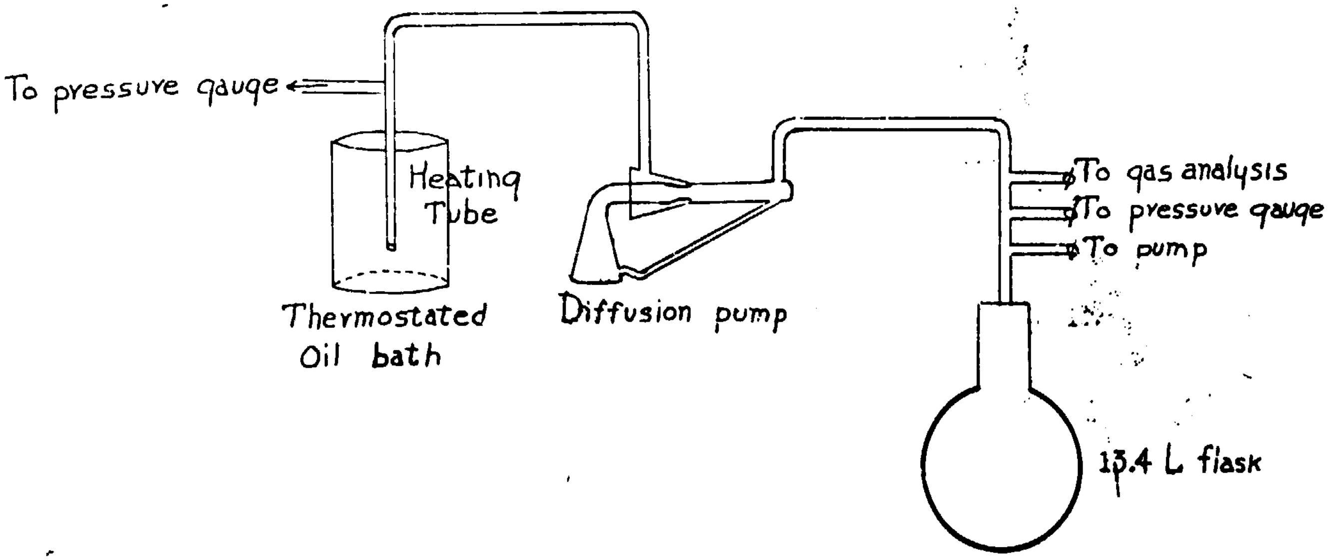


Figure #1

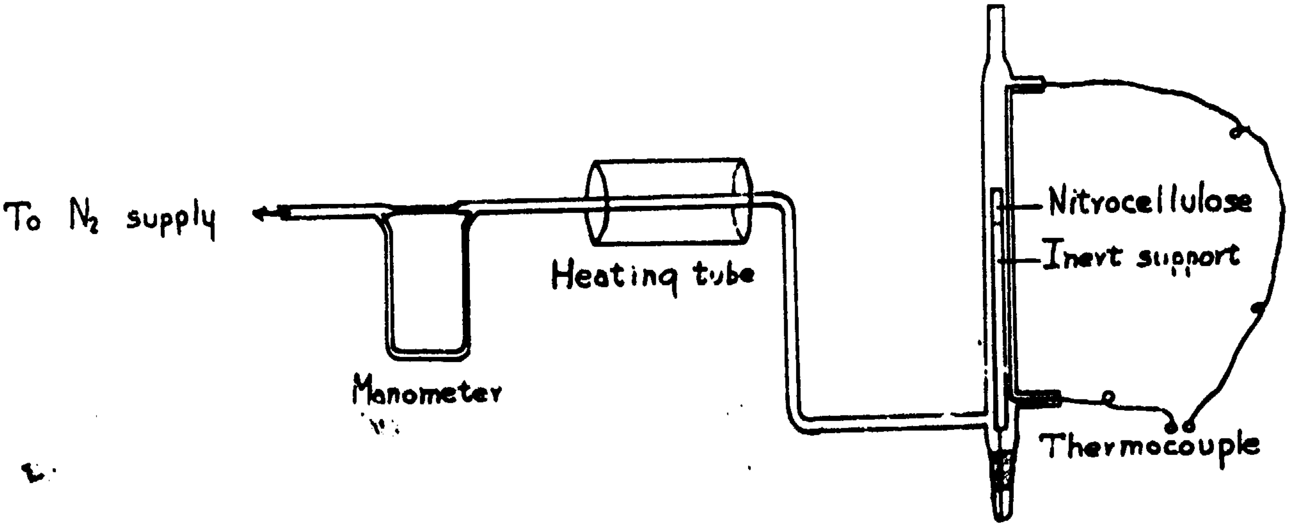


Figure #2

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1. References:

a. BRL Report 339, "On the Use of CO_2 as a Propellant in Guns", by J. H. Frazer and J. R. Lane, March 1943, UNCLASSIFIED.

b. BRL Report ~~391~~ 343, "Heats of Explosion of Nitrocellulose in Indifferent Atmospheres (Part 1 of Mechanism of Powder Burning)", by J. H. Frazer and C. P. Fenimore, August 1943, UNCLASSIFIED.

c. BRL Report 353, "Report on Temperature Dependence on Rocket Behavior," by J. H. Frazer et. al., May 1943, UNCLASSIFIED.

d. BRL Report 465, "Experiments on Ignition of Nitrocellulose", by C. P. Fenimore and J. H. Frazer, May 1944, UNCLASSIFIED.

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