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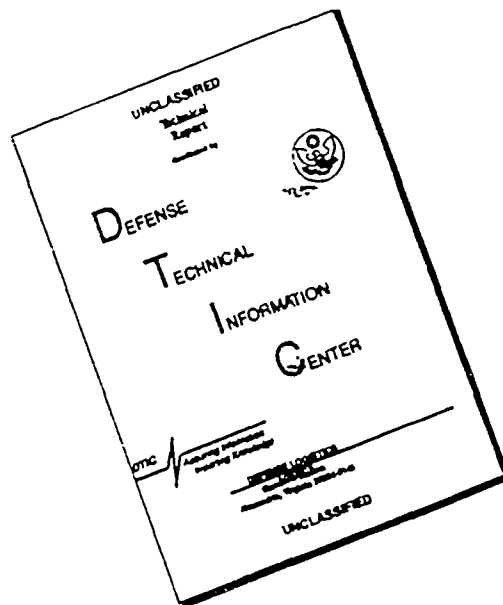
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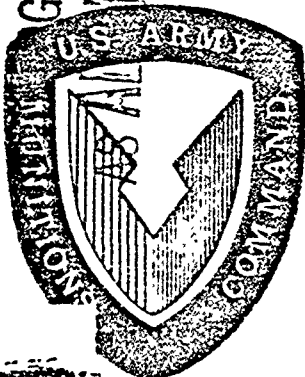PAGES WHICH DO NOT
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MECHANISM OF THE THERMAL IGNITION OF EXPLOSIVES

A. F. BELYAEV

APRIL 1965

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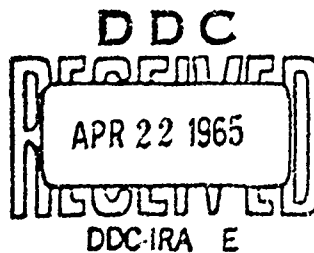
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Technical Memorandum 1481

MECHANISM OF THE THERMAL IGNITION
OF EXPLOSIVES

by

A. F. Belyaev

April 1965

MECHANISM OF THE THERMAL IGNITION OF EXPLOSIVES

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pp. 613-622

If one heats an explosive rather slowly, then at some temperature, which is characteristic for the explosive in question and depends on the conditions under which the substance is being heated, spontaneous ignition of the substance takes place. One usually refers to this phenomenon as spontaneous ignition or thermal flash. The temperature of ignition of various explosive substances, when referred to standard conditions, changes within rather wide limits.

For various substances under varying conditions the type of thermal ignition may range from a completely soundless combustion to a detonation accompanied by strong sound and mechanical action. In the case of some substances under certain conditions, heat ignition does not occur; there is a disappearance of the substance without light and flame.

On the example of nitroglycol [1] the author proved the assumption expressed earlier [2] to the effect that in the combustion of a secondary explosive the principal reaction which controls the velocity of combustion takes place in the gas phase. For the majority of secondary explosives the process of gasification consists merely in evaporation.

If in the combustion of an explosive we have primarily combustion of its vapors, then naturally the type of combustion, facility of ignition, etc., must depend on the volatility of the explosive. It is also obvious that there must be an effect of the volatility on the nature of the thermal ignition. In a very great number of investigations on the mechanism of thermal ignition, volatility was completely disregarded. One

must, however, note that the conditions for evaporation in spontaneous combustion are less favorable than in the combustion of an explosive that has been ignited rapidly. In the latter case we have combustion of a cold substance that has not been heated throughout its volume; high temperatures develop in that part of the substance which at any given moment is in contact with the combustion front and consequently is at the surface. In spontaneous combustion the substance is heated throughout its mass and consequently the chemical reaction may proceed within the whole mass, whereas evaporation at temperatures lower than that of boiling may take place only from an open surface. One may assume with complete certainty that in the spontaneous combustion of secondary explosives under any conditions (under atmospheric pressure) the temperature in the condensed phase cannot rise above that of the boiling temperature of the substance in question at atmospheric pressure. If we imagine that at some spot within the condensed phase the temperature will exceed for even a single moment that of the boiling point, then at this spot there will be boiling of the substance, i.e., intensive boiling within the volume and a drop in the temperature must occur. It will be shown below that in the investigation of thermal ignition one must definitely take into consideration the effect of volatility.

If a weighed quantity of an explosive is heated to temperature T (above some minimum temperature T_0), then ignition will not take place immediately, but after passage of some time τ. This time is referred to as the period of ignition delay.

Between T and τ, the following simple relationship applies in many cases:

$$\lg \tau = \frac{0.434 A}{RT} + c; \qquad (1)$$

It follows from the theory of chain reactions [4], that the value A must represent the activation energy of molecules of the explosive in question. Thus, equation (1) makes it possible to determine the value of A and has been repeatedly used for this purpose. Occasionally the value of A determined in this manner actually coincided from the practical standpoint with the value of the activation energy determined by other methods [3, 4, 5]. In other cases the value obtained had nothing in common with the actual magnitude of the activation energy.

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Temperature T in equation (1) has the physical meaning of the temperature of the explosive. However, one usually inserts for T the temperature of the furnace, assuming that the weighed-in quantity of the explosive thrown into a furnace with temperature T will rapidly assume this temperature. We shall see below that this substitution of the temperature of the substance with the temperature of the furnace is permissible only under the condition that the substance remains in the furnace for a long time (i.e., τ is great) and under the condition that the temperature of the furnace is lower than the boiling point of the explosive. A number of investigations in which the actual temperature of the explosive was compared with the temperature of the furnace [3, 7, 5] indicated that even at considerable delays and temperatures lower than that of the boiling point there was a certain difference between the temperature of the substance and the temperature of the furnace. This difference, which is usually small, may become very significant if, for instance, the temperature of the furnace exceeds considerably the boiling point of the substance. In this case the temperature of the condensed phase will be considerably lower than that of the furnace. It is true that the vapors of the explosive may be heated up to temperatures higher than that corresponding to the boiling point. We shall return to this question later.

We have carried out a number of experiments in which the temperature of the explosive was measured directly (or, more precisely, the temperature of that part of the explosive which was in the condensed phase) while the explosive was in the furnace. The purpose of the experiments in question was determination of the actual temperatures of the explosive during the whole time of the experiment, beginning with 3--5 seconds after placing the explosive in the furnace and ending with the moment of ignition. The distinction between these experiments and published investigations [6, 7] which were similar as far as the conception and methods were concerned consisted in the fact that in our experiments the temperature of the furnace was as a rule higher than that of the boiling of the explosive.

Trotyl was used as the explosive substance. A weighed quantity (0.1 g) was thrown into an open test tube at the bottom of which was a sensitive thermocouple with low inertia. The thermocouple was connected with a galvanometer. The deflections of the galvanometer were observed visually.

Two variations of the experiments were carried out. In the first variation, the test tube was placed into the opening of the furnace and was heated by the surrounding air. In the

second variation, the test tube was submerged to one third into a furnace containing Wood alloy. Let us first cite the data obtained in the experiments with the air furnace. In all tables the time was counted from the moment when the weighed quantity of the explosive was thrown in. The heading of every table indicates the temperature of the furnace on the basis of the indications of a thermometer placed in the furnace and the temperature at the bottom of the test tube immediately before the explosive was thrown in -- on the basis of the indications of the galvanometer. In some experiments these temperatures coincided, while they differed to some extent in other experiments.

Table 1	Table 2
Temperature of the furnace 340°C. Temperature according to the galvanometer 336°C.	Temperature of the furnace 360°C. Temperature according to the galvanometer 360°C.

① время в сек.	температура взрыва в °C ②		① время в сек.	температура взрыва в °C ②
5	295		3	306
10	305		5	314
15	314		13	325
25	323		16	323
33	328		22	332
			27	335

③ Вспышка   ③ Вспышка

1--Time in sec; 2--temperature of the explosive in °C; 3--ignition.

1--Time in sec; 2--temperature of the explosive, °C; 3--ignition.

The data of Tables 1, 2, 3 are plotted in the form of solid curves in the graph on Figure 1, where time in seconds is plotted along the axis of abscissa while the temperature of the explosive is plotted along the axis of ordinate. The initial temperatures are indicated on the left. The moments of ignition are shown by circles. The number of the curve corresponds to the number of the table.

Let us cite the data for a test tube submerged in a furnace with Wood alloy.

The data of Tables 4 and 5 (furnace with Wood alloy) are plotted in Figure 1 in the form of dotted curves.

4

Table 3

Temperature of the furnace 400°C.
Temperature according to the galvanometer 405°C.

① время в сек.	температура навески в °C ②
3	306
5	323
10	332
14	337
16	333
18	338

③ Вспышка

1--Time in sec; 2--temperature of
the explosive; 3--ignition.

Table 4

Temperature of the furnace 340°C.
Temperature according to the galvanometer 337°C.

① время в сек.	температура навески в °C ②
3	268
8	314
14	322
19	329

③ Вспышка

1--Time in sec;
2--temperature of the
explosive; 3--ignition.

Table 5

Temperature of the furnace 380°C.
Temperature according to the galvanometer 375°C.

① время в сек.	температура навески в °C ②
3	315
7	337
8	337
12	350
14	350

③ Вспышки не было

1--Time in sec;
2--temperature of the
explosive, °C; 3--ig-
nition.

If we consider the course of curves 1, 2, 3 (air furnace)
we can see that although the temperature of the furnace was
changed from 340 to 400°, the actual temperatures of the ex-
plosive at the time of ignition were close to each other.

The course and type of the curves clearly indicate a
general tendency of the temperature of the condensed phase to

approach a certain limit within the 335--338° range, even in the case when the temperature of the furnace was 400°. Curve 4 is of approximately the same type, except that heating took place more rapidly in the furnace with the alloy.
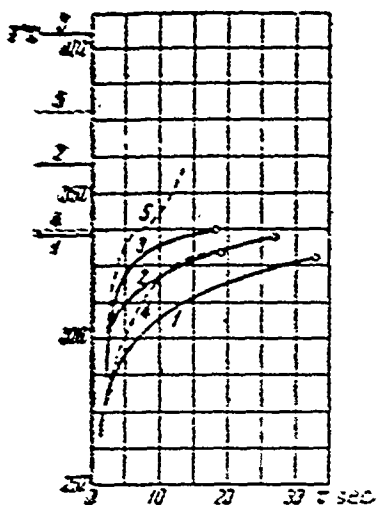

Fig. 1.

According to data obtained by the author earlier the boiling point of trotyl must be 315--320° [8]. This figure is close to the value of the maximum temperature which the explosive has a tendency to approach; however, the latter is somewhat higher.

It is natural to assume that the value of the boiling point of trotyl (315--320°) determined earlier is somewhat too low and that actually the boiling point of this substance is 335--340°. This assumption makes understandable the course and type of all curves, including curve 5, which we haven't discussed yet.

On curve 5 the temperature clearly forms a plateau at 337° and then rises further; no ignition took place and no trotyl remained at the bottom of the test tube in this case. Apparently, the point at which the increase of the temperature stopped corresponded to violent boiling of the trotyl (the presence of the alloy and the fact that the temperature was high ensured an intensive supply of heat).

Thus, the experiment confirmed that in the condensed phase of the explosive the temperature cannot exceed that corresponding to the boiling point. The latter must be regarded as equal to 335--340° rather than 315--320°, as assumed earlier by the author.

Ahrens [9] pointed out that correlation of the heat of evaporation calculated by the author with the boiling point of the explosive resulted in a systematic deviation from Trouton's rule for the majority of the substances. We cannot discuss in detail the reasons for this deviation within the scope of the present article; they will be discussed in another communication. We shall only note that for some classes of chemical compounds there is a systematic deviation from Trouton's rule. It is obvious, however, that in the case of ten, hexogen, and tetryl, the author's data require thorough revisions.

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It follows from our experiments that if the activation energy is calculated on the basis of relationship (1), using the temperature of the furnace as T, the following two conditions must be observed, at least:

1. The temperature of the furnace must be considerably lower than the boiling point of the substance.

2. The period of ignition delay should not be too small: at delays of the order of 20--30 sec and smaller, a considerable time passes before the substance has been heated. In some investigations both of these conditions were practically fulfilled and the values of activation energy obtained were reliable [3, 5, 10]; in other investigations both conditions (or one of them) were not fulfilled and the values of the temperature coefficient obtained did not correspond to the activation energy.

Because the temperature of the condensed phase cannot be higher than the boiling point, further heating (and consequently the spontaneous ignition connected with this heating) may take place only in the gas phase. Not only the pure vapor but also vapor diluted with products of decomposition and air may ignite; for this reason spontaneous ignition may take place at temperatures lower than the boiling point. Let us note further that ignition of the vapors must not necessarily take place above the surface of the condensed phase; in very intensive decomposition, although the temperature of the condensed phase does not significantly exceed the boiling point, violent foaming of the liquid may occur and ignition may take place in the foam bubbles.

Let us consider in greater detail the conditions under which ignition originates in vapors. One must bear in mind that in the investigation of ignition by the usual method, the upper part of the test tube has a considerably lower temperature than the lower part. The vapors that form (or their mixture with the decomposition products) will move to the upper part of the test tube and condense there or come out of the test tube into the surrounding air. The conditions of ignition of the vapors must therefore depend on the temperature of the furnace, the boiling point (the initial temperature of the vapors will not be higher than the boiling point), and the rate of flow of the vapors. Ignition may take place at a relatively low temperature when the rate of vapor formation is low and the vapors move relatively slowly, so that they have time to be heated sufficiently. This case is represented by curves 1, 2, 4. On the other hand, ignition may not take place

even at a high temperature if the high rate at which heat is supplied to the condensed phase will lead to energetic evaporation and consequently to a rapid motion of the vapors in a direction to the colder parts of the test tube and the opening of the test tube. If this velocity will be sufficiently high, the vapors will pass the critical high-temperature zone of the lower part of the test tube without having been heated to a sufficient degree and brought to ignition. An intensive supply of heat at conditions of a high rate of evaporation can therefore bring about distillation of the substance from the lower part of the test tube to the upper rather than spontaneous ignition.

Andreev, who conducted an extensive investigation [11] pertaining to the dependence of the period of ignition delay on the temperature for various explosives, established [11, 12] that for some explosives (trotyl, picric acid) an increase of the furnace temperature above a certain limit reduces the probability of ignition up to the point that ignitions do not take place at all. Andreev was of the opinion that this phenomenon is related to some kind of autocatalytic or chain process. One must, however, assume that the existence of an upper limit under the conditions in question is related first of all to the rapid rate of flow of vapors which do not have time to be heated to a sufficient degree. Among the curves given by us, curve 5 corresponds precisely to the case of an upper limit of this type.

Table 6

Ignition of Trotyl in the Presence of a Wire

Temperature, °C	Results of experiments in the presence of a glowing wire in the upper part of the test tube	Results of experiments without a wire (usual technique)
330	Ignition within 46, 45, -6 sec	Ignition within 51, 40, 49, 51 sec
3-0	Ignition within 35, 15, 3 3 sec	Ignition within 49, 44, 41, 50 sec
360	Ignition within 3, 2, 4 3 sec	Ignition within 18, 23, 25, 34 sec
380	Ignition within 2, 12, 2 1 sec	Ignition within 24, 23, 16 sec No ignition in 1 instance
400	Ignition within 1.5, 2.1, 5, 10 sec	Ignition within 18, 22 sec; No ignition in 2 instances.

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To confirm the correctness of this assumption, we conducted experiments with trotyl, inserting into the opening of a test tube to the depth of 1 cm a thin tungsten wire that was heated to a weak glow. Especially conducted experiments showed that this wire did not exert any effect on the thermal conditions within the central and lower part of the test tube. However, the wire had to ignite the vapors in the case when they rose to the top without being ignited in the lower or middle part of the test tube. The amounts of trotyl weighed in amounted to 0.1 g. The results obtained are given in Table 6. The periods of delay of ignition at various temperatures in the presence and absence of the glowing fire in the upper part of the test tube are also given for experiments carried out at various temperatures. As a rule, four experiments were carried out at every temperature.

We can see that at 330°, a temperature lower than the boiling point of trotyl, the presence of the wire did not change the length of the ignition delay. The ignition (of a mixture of vapors with air and with decomposition products) took place in the lower part of the test tube because of heat supplied by the walls of the test tube. The situation was entirely different at a temperature higher than the boiling point (340° and higher). At this temperature there was a significant difference between the length of the ignition delay in the presence of a wire and the absence of a wire. Ignition failures at high temperatures were not observed in the presence of the wire. The experiments carried out are an indirect proof of the correctness of the assumption made above in regard to the reason for the existence of an upper limit. In the presence of the wire the vapors which did not ignite because of their rapid flow after passing the critical zone, were ignited by the wire. In the absence of the wire, the substance condensed in the upper, cold part of the test tube; the drops of condensate flowed downwards (depending on the conditions they could reach the bottom, completing a full cycle, or evaporate underway). As a result of this prolonged distillation accompanied by continuous motion of the condensed phase downwards and the vapors upwards, ignition could have taken place at a definite moment; however, the substance would also have partially evaporated from the test tube or partially decomposed without ignition.

In addition to the experiments on trotyl described above, similar experiments were conducted on picric acid. The results obtained were very similar, so that we shall refrain from reporting them.

According to Andreev's data [12], no ignition failures occurred in the case of tetryl; thus, if one disregards certain changes in type of ignition, the phenomenon of the upper limit is absent in this case. Table 7 lists data on the effect of a glowing wire placed in the upper part of the test tube on the length of the ignition delay for tetryl at two temperatures. The experiments were carried out in exactly the same manner as those with trotyl.

Table 7

Ignition of Tetryl in the Presence of a Wire

Temperature, °C	Results obtained in the presence of a glowing wire in the upper part of the test tube	Results obtained without a wire (usual technique)
224	Ignition within 36, 37, 40, 43 sec	Ignition within 47, 42, 43, 43 sec
290	Ignition within 7, 9, 2, 9 sec	Ignition within 4, 6, 13, 9 sec

In the case of tetryl, the wire had no effect. The reactivity of the tetryl vapors was apparently relatively high, so that in the vicinity of the boiling point an intensive reaction could originate even at a high rate of flow of the vapors; ignition always took place in the vicinity of the surface of the condensed phase or possibly in the bubbles of the foam that formed during intensive decomposition.

Under the condition of the usual determination of the ignition delay, the weighed-in quantity of explosive that has been thrown in cools at the first moment the volume of glass with which it comes into contact. Additional quantities of heat are supplied rather slowly by conduction through the glass. We carried out experiments in which the intensity of the boiling was raised considerably. This was achieved by placing 5 g of tin into the test tube before inserting it into the furnace. After the test tube had been heated, the tin served as a reservoir of heat and contributed to more rapid heating and more intensive boiling of the substance. The weighed-in amount of the explosive (0.1 g) was thrown into the heated test tube, as before. The experiments were conducted with trotyl. Table 8 lists the results obtained. Just as before, several tests were conducted at every temperature.

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Table 8

Ignition of Trotyl in the Presence of Tin

Temperature, °C	Results obtained in the presence of tin in the test tube	Results obtained in the absence of tin (usual technique)
316	Ignition within 26, 52, 43 sec	Ignition within 38, 63, 60, 54 sec
332	Ignition within 24, 28, 14 sec . No ignition in one instance	Ignition within 31, 36, 40, 38 sec
350	Ignition within 19 sec No ignition in three instances	Ignition within 20, 26, 24, 35 sec
366	Ignition within 12 sec No ignition in three instances	Ignition within 27, 25, 23 sec
376	Ignition within 7 sec No ignition in three instances	Ignition within 22 sec No ignition in three instances
390	No ignition in four instances	Ignition within 17 sec No ignition in three instances
400	No ignition in four instances	Ignition in 8 sec No ignition in three instances

The data in Table 8 indicate that the presence of tin in the test tube, first, reduced the time required for heating the explosive, which led to a considerable reduction of the length of ignition delay, and, secondly, increased the intensity of boiling, so that the rate of evolution of vapors was increased. The latter circumstance made the phenomenon of the upper limit more pronounced, so that it was evident at relatively low temperatures. One might add to what has been said above that distillation of the substance into the upper part of the equipment and partial escape of the vapor outside were readily observed in all experiments at sufficiently high temperatures, being particularly prominent in the presence of tin.

Let us assume that the experiments are conducted at a reduced pressure, say 50--100 mm Hg, rather than at atmospheric

pressure. At reduced pressures the boiling point is lowered. As a result distillation of the substance into the colder part of the equipment is facilitated and ignition must become more difficult.

Indeed, according to the data of Ahrens [8] both trotyl and ten at pressures below 100 mm boil energetically and are distilled to colder parts of the equipment without initiation of ignition and even without noticeable decomposition at any temperature of the furnace up to 370°.

It will not be out of place to make the following comments. Ahrens ascribes to this author the assertion that the boiling point of an explosive is identical with its ignition temperature and is of the opinion that the fact established by him to the effect that there is no ignition at reduced pressures contradicts the thesis of this author. It is not known where Ahrens found this assertion. It is true that the author and Yuzefovich [13] stated in work cited by Ahrens that for some explosives the temperature of ignition determined by the standard method is close to the boiling point at atmospheric pressure. This fact followed from a direct comparison of the ignition temperatures with the boiling points. Perhaps, taking into consideration the corrections which must be introduced into the author's data pertaining to boiling points, it is more accurate to state that for a number of substances the ignition takes place at a considerable vapor tension above the surface of the substance. However, the author and Yuzefovich did not conclude from this that in general the temperature of ignition corresponds to the boiling point. Any such conclusion would be in conflict with the fundamental theoretical concepts advanced by the author and there should be no necessity to carry out special experiments for disproving it. If Ahrens had familiarized himself more thoroughly with the work by the author and Yuzefovich [13] cited by him, he would have realized that the fundamental thesis of the work in question did not consist in the absurd assertion that the ignition temperature is equal to the boiling point, but in the assumption that the nature of thermal ignition (specifically, the fact whether or not ignition takes place) depends to a major extent on the volatility of the substance. Actually, Ahrens' data on the radical change in the behavior of substances (with reference to thermal ignition) on lowering of the boiling point because of a reduction of the pressure not only do not contradict the fundamental concept of the author but, on the contrary, are a good illustration confirming this concept.

All facts mentioned above demonstrate convincingly that one cannot leave out of consideration volatility when one investigates thermal ignition. The boiling point of an explosive, the conditions of vapor formation, and those of vapor flow determine to a significant extent the nature of thermal ignition and the fact whether or not thermal ignition is possible. It is precisely the conditions of vapor formation and vapor flow which are responsible for the existence of an upper limit of thermal ignition. Without consideration of the factors mentioned, one cannot satisfactorily explain the reasons for the existence of the upper limit.

Some explosives have a very pronounced upper limit. As an example of substances of this type one may mention trinitrobenzene; it is very difficult to bring about thermal ignition of trinitrobenzene under the conditions usually applied in tests. This can be explained by the fact that the boiling point of trinitrobenzene is relatively low, while the reactivity of this substance as well as of its vapors at the boiling temperature is also low. Trinitrobenzene corresponds to trotyl tested at a reduced pressure.

In the cases when the ignition temperature is considerably lower than the boiling point intensive decomposition accompanied by foaming takes place in the condensed phase. Under these conditions ignition of a rather violent type occurs. A similar effect may take place when the ignition temperature is higher than the boiling point.

It follows from what has been said above that the initiation of ignition in the latter case is difficult. However, if ignition still takes place at a moment when the substance has not yet distilled into the upper part of the test tube, it will be violent, because the substance will be in a state of boiling.

It has often been pointed out that if the temperature of the furnace is much higher than that of ignition (in the case of trotyl at a temperature of 450--500°) almost instantaneous inflammation takes place followed by a quiet combustion. The fact that at a high temperature of the furnace combustion is much calmer than in ordinary ignition was often found surprising. It was even assumed [12] that in this case an upper limit is again exhibited, but this limit is not expressed in the complete absence of ignition, but a calmer course of the combustion process. Actually, it is quite natural that combustion will be calm under the conditions mentioned.

If the temperature of the furnace considerably exceeds the temperature of the ignition, the surface of the substance will be heated rapidly. Vapors will then be evolved and rapid ignition of these vapors will take place.

Combustion will occur under conditions in which the principal mass of the substance has not had time to be heated: a cold substance will burn. Any turbulization produced by rapid decomposition or intensive boiling will be absent. If the temperature of the furnace is much higher than the temperature of ignition, it is more accurate to speak of ignition of the substance by a heated surface rather than of spontaneous ignition (a flash). The precise difference between spontaneous ignition and ignition of the explosive after fire has been set to it is that prolonged heating of the whole volume of this substance precedes spontaneous ignition and that this heating is accompanied by chemical changes and turbulization of liquid.

By asserting that the volatility of the substance has a definite effect on the nature of thermal ignition, the author did not mean to deny in any manner that other factors also have an effect, specifically autocatalysis.

The process of ignition on heating is very complex and it would be entirely incorrect to reduce the process of spontaneous ignition to any single factor.

It is certain that autocatalysis may significantly change the nature of the process and alter the intensity of the reaction in the condensed phase as well as reactivity of the gas phase and its capacity to undergo ignition.

It was the intention of the author to demonstrate that one cannot, for example, consider autocatalytic effects without considering the effects due to evaporation. Explosives have a number of characteristic properties which distinguish them from ordinary substances. However, explosives are not substances to which fundamental physico-chemical laws do not apply. Therefore, one must take into consideration the vapor tension of explosives and their boiling point, although the substance may not be capable of existing for a long time at this temperature. The fact that the boiling point of an explosive is not pure fiction can be proved by direct experiments with nitroglycol [1] and trotyl (as has been done in the present work). The fact that strong prejudices existed in this respect is demonstrated by the fact that nobody was even interested in the problem of the boiling point of explosives; the term boiling point of explosives was studiously avoided.

Experiments were often carried out with explosives above their boiling point on the assumption that the temperature of the substance must be equal, or very close, to that of the temperature of the furnace.

A theory of thermal ignition, i.e., spontaneous ignition of volatile explosives (a class of substances to which the great majority of secondary explosives belongs), can be formulated only if the effect of evaporation is considered, in view of the fact that ignition arises in the gas phase. Such factors as the existence of a temperature corresponding to the boiling point, the flow of vapor to the cold parts of the equipment, and the flow of condensate downward into the equipment affect the probability of ignition and its nature as well as the length of the delay of ignition. Obviously, it is not necessary to consider factors related to evaporation if the explosive even in the vicinity of the ignition temperature does not have a perceptible volatility. This condition applies to the majority of initial explosives.

CONCLUSIONS

1. The temperature of an explosive placed into a furnace having any temperature cannot perceptibly exceed the boiling point of the explosive. A more rapid supply or evolution of heat will only lead to more intensive boiling. If the temperature of the furnace is considerably higher than the boiling point, the maximum temperature in the condensed phase will differ significantly from the temperature of the furnace. Intensive local heating that leads to the development of a flame and ignition can therefore arise only in the vapor of the substance (or a mixture of the vapor with air and products of decomposition). Ignition may arise either at a considerable distance from the condensed phase or in the immediate vicinity of this phase within bubbles of foam that form during intensive decomposition.

2. The phenomenon of the upper limit of thermal ignition, which has been discovered by Andreev, is due first of all to the fact that at high temperatures under definite conditions the vapors of the explosvie flow rapidly into the upper, relatively cold part of the test tube, and do not have time to ignite.

3. The conditions of evaporation, conditions pertaining to the flow of vapor, and the magnitude of the boiling temperature are factors that play an important part in the initiation of thermal ignition. Without considering these factors, it is

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impossible to formulate a completely valid theory of spontaneous ignition of volatile explosives, to which almost all secondary explosives belong.

4. In the case of non-volative explosives at high values of the length of ignition delay, the linear dependence of the logarithms of ignition delay on the inverse temperature may yield reliable values for the activation energy.

If this method is applied for the determination of the activation energy of volatile substances (to which the majority of secondary explosives belong), considerable errors will result. This problem requires further study.

BIBLIOGRAPHY

1. Belyaev A. F., ZhFKh (Journal of Physical Chemistry), 14, 1009-25, 1940; Acta Physicochim., 14, 523-46, 1941.
2. Belyaev A. F., ZhFKh, 12, 93-9, 1938; Acta Physicochim., 763-72, 1938.
3. Garner W. and Hailes H., Proc. Roy. Soc., 139 A, 576, 1933.
4. Semenov N. N., in the symposium: Initsiiruyushchie vzryvchatye veshchestva (Initial Explosives), No. 2, pp 47-62, ONTI, 1935.
5. Appin A. Ya., in the symposium: Sbornik statei po teorii vzryvchatykh veshchestv (Collection of Articles on the Theory of Explosives), pp. 106-120, Oborongiz (State Publishing House of Nat. Defense), 1940.
6. Tamman G. and Kroger C., Z. Anorg. Chemie, 169, 1-32, 1928.
7. Micevicz and Majkowski, Z. f. d. ges. Schiess. u. Sprengst., 23, 422-27, 1928.
8. Belyaev A. F., DAN (Reports Acad. Sci. USSR), 29, 466-68, 1940.
9. Ahrens H., Z. f. d. ges. Schiess. u. Sprengst., 38, 159, 1943.
10. Patri M., in the book: Gorenie in detonatsiya vzryvchatykh veshchestv (Combustion and Detonation of Explosives), pp. 46-49 (editorial supplement), Oborongiz, 1938.
11. Andreev K. K., in the symposium: Sbornik statei po teorii vzryvchatykh veshchestv, pp. 134-136, Oborongiz, 1940.
12. Andreev K. K., in the symposium: Sbornik statei po teorii vzryvchatykh veshchestv, pp. 137-143, Oborongiz, 1940.
13. Belyaev A. F. and Yuzefovich N. A., DAN, 27, 131-3, 1940.

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13 ABSTRACT

The temperature of an explosive placed into a furnace having any temperature cannot perceptibly exceed the boiling point of the explosive. If the temperature of the furnace is considerably higher than the boiling point, the maximum temperature in the condensed phase will differ significantly from the temperature of the furnace. Intensive local heating that leads to the development of a flame and ignition can therefore arise only in the vapor of the substance (or a mixture of the vapor with air and products of decomposition). Ignition may arise either at a considerable distance from the condensed phase or in the immediate vicinity of this phase within bubbles of foam that form during intensive decomposition.

The phenomenon of the upper limit of thermal ignition is due first of all to the fact that at high temperatures under definite conditions the vapors of the explosive flow rapidly into the upper, relatively cold part of the test tube, and do not have time to ignite.

The conditions of evaporation, conditions pertaining to the flow of vapor, and the magnitude of the boiling temperature play an important part in the initiation of thermal ignition. Without considering these factors, it is impossible to formulate a valid theory of spontaneous ignition of volatile explosives, to which almost all secondary explosives belong.

With non-volatile explosives at high values of the length of ignition delay, the linear dependence of the logarithms of ignition delay on the inverse temperature may yield reliable values for the activation energy.

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14 KEY WORDS	LINK A		LINK B		LINK C	
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Explosive						
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