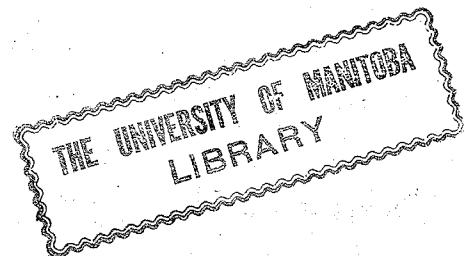


AN INVESTIGATION OF THE SYSTEM:
PICRIC ACID - 2:4-DINITROPHENOL,
AND SIMILAR SYSTEMS WITH PARTICULAR
REFERENCE TO THE PROPERTIES OF THE
EUTECTIC COMPOSITION OF EACH SYSTEM:

BY

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of the requirements for the M.Sc. degree.

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INTRODUCTION

Picric acid by itself is a violent explosive, but the pure material melts at too high a temperature (122°) for satisfactory shell-filling, 105° being the maximum temperature usually allowed. Furthermore, it is rather sensitive. By the addition of 2:4-dinitrophenol, its melting point can be lowered until it is below the maximum allowed. By this addition it is also rendered much less sensitive.

During the last war, Italy and France (1) used a mixture of picric acid and dinitrophenol in the proportions: 65% picric acid and 35% dinitrophenol. Great Britain used a similar mixture, which was called "Shellite", consisting of 60% picric acid and 40% dinitrophenol.

A search through the available literature, however, revealed only one systematic determination of the system. This had been done by Bogojawlensky (2). The original reference was not available, but his values for the eutectic composition were reported in the "International Critical Tables" (3) as: 47.5 mole per cent of picric acid (53% by weight) and a eutectic temperature of 81.5° .

Although the mixture called "Shellite" was an improvement over the pure picric acid, it was still not completely satisfactory due to the large amount of shrinkage which

the mixture showed on solidification. This shrinkage leads to the formation of cavities in the body of the explosive charge with a consequent reduction in the density of the charge and a corresponding loss of power. These cavities can not be filled by the addition of more molten explosive. If the shrinkage takes place from the sides of the shell, then there is a danger that the shell may prematurely explode when fired from a gun. It is therefore desirable that this shrinkage be overcome in some way.

Dr. G. F. Wright suggested: "this could largely be avoided if crystallisation were retarded until the melt had cooled to room temperature."

In order to accomplish this end, Dr. A. N. Campbell suggested: "that the problem appeared to be that of retaining "Shellite" in the vitreous condition, at least for a time, after it had cooled to room temperature." He had shown (4) that while it was impossible to influence the spontaneous formation of nuclei, the velocity of growth could readily be influenced by altering the viscosity of the medium, the velocity being less the more viscous the medium.

A systematic investigation was therefore carried out on the system: picric acid--2:4-dinitrophenol, as follows:

- (1) Equilibrium diagram.
- (2) Density of all mixtures at 130°.

(3)

- (3) Viscosity of all mixtures at 130°.
- (4) Velocity of crystallisation of the pure substances and of the eutectic composition for increasing degrees of supercooling.

Once these values had been obtained, the experiments were repeated using added materials which we hoped would considerably increase the viscosity, and hence decrease the velocity of crystallisation.

Since the problem is very largely one of retarding the crystallisation velocity, a consideration of work that has been done on it will be in order. This will be undertaken after a short discussion of the principles of the "Phase Rule" that are involved in the equilibrium diagrams has been given.

THEORETICAL DISCUSSION

In the last quarter of the eighteenth century, Wenzel in 1777, and Berthollet in 1799, had shown that chemical reactions proceed only to a certain point and there make a halt. Many examples of such equilibria were brought forth in the succeeding century, but it was not until Willard Gibbs put forth in 1874-78 a theorem, general in its application and employing no hypothetical assumptions as to the nature or constitution of matter, that the experimental facts were put on a sound theoretical basis.

Both Wenzel and Berthollet had recognised the influence exercised by the mass of the reacting substance on the equilibrium of the system. In 1867, Guldberg and Waage put the study of chemical equilibria on a quantitative basis in their "Law of Mass Action". But since it was based on molecular and kinetic theories, it involved certain assumptions as to the nature and condition of the substances taking part, and therefore it failed when it was applied to systems in which very little was known about the molecular complexity.

Gibbs based his theories on the laws of thermodynamics, and in deducing the law of equilibrium, he regarded a system as possessing only three independently variable factors:

temperature, pressure, and the concentration of the components. The action of gravity and other forces were excluded. His theorem, generally known as the "phase rule", defined the conditions of equilibrium as a relationship between the "phases" and "components".

A "phase" may be concisely defined as: "a homogeneous, physically distinct, and mechanically separable portion of matter. Thus ice, water, and vapor are three phases of the substance water. But a phase need not be chemically simple; for example, a solution of NaCl is homogeneous and may exist as: ice, solution, and vapor. Again there are three phases, but one of the phases, the solution, is now chemically complex. A substance having allotropic modifications exists, or may exist, in as many phases as there allotropes in addition to existing as a liquid and vapor phase. However, this does not mean that all these phases can exist together in stable equilibrium.

The "components" of a system are not synonymous with the chemical elements or compounds present, although both elements and compounds may be components. By components are meant only those constituents whose concentration can undergo independent variation in the different phases. Since the "Phase Rule" deals with the final state and not with the processes by which the final equilibrium is attained, then only those

constituents which take part in the state of real equilibrium are considered.

In choosing the components, the following considerations apply:

(1) The components are to be chosen from among the constituents which are present when the system is in a state of true equilibrium, and which take part in that equilibrium.

(2) As components are to be chosen the smallest number of such constituents necessary to express the composition of each phase participating in the equilibrium, zero and negative quantities of the components being possible.

(3) In any given system, the number of components is definite, but may alter with an alteration of the conditions of the experiment.

It is a great merit of the Phase Rule that the state of a system is defined entirely by the relation existing between the number of the components and the phases present, no account being taken of the molecular complexity of the participating substances, nor any assumption made with regard to the constitution of matter. It is further immaterial whether we deal with physical or chemical equilibria.

Gibbs' Phase Rule may be expressed by the following equation:

$$F = n - r + 2 \quad \text{or} \quad F = n + 2 - r \quad (5)$$

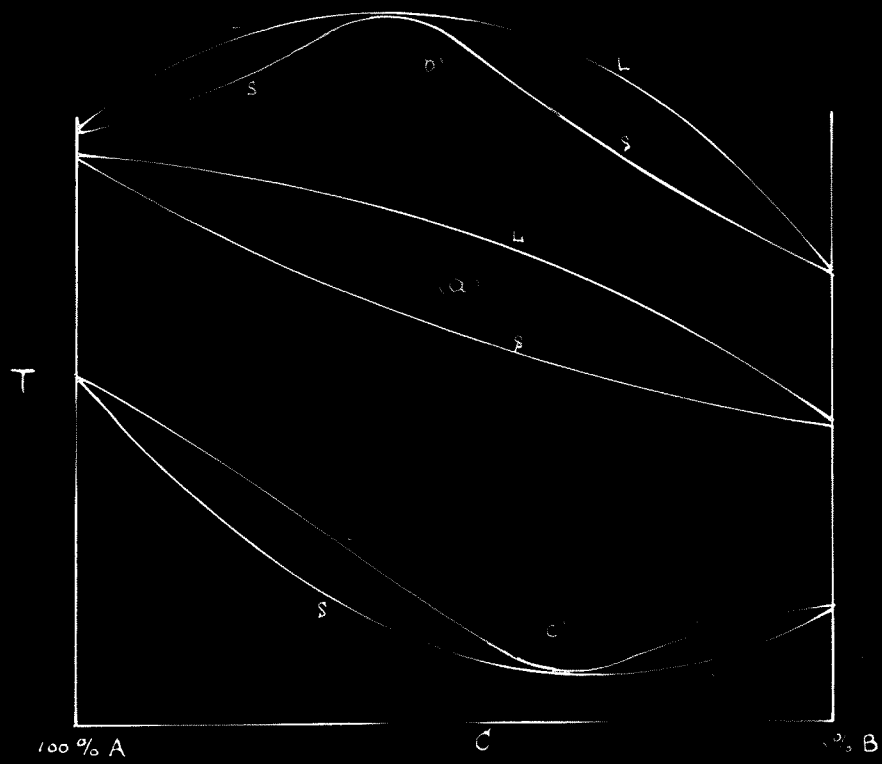


Fig. 1

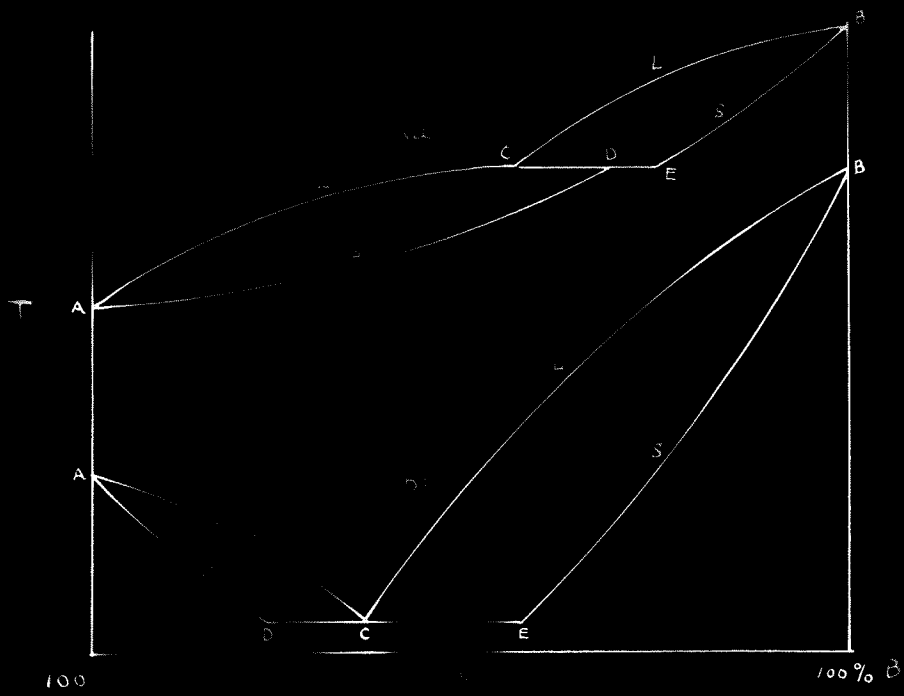


Fig. 2

where F = the degrees of freedom, or variability of a system, n = the number of components, and r = the number of phases. The degree of freedom is the number of the variables: pressure, temperature and composition which must be fixed in order to perfectly define the system.

In this investigation, two component and three component systems are dealt with and hence a short discussion of these follows.

Two Component Systems.

Let us consider the following possibilities:

- I. Two components completely miscible in both the liquid and solid phases. (see figure 1.)
 - (a) The freezing-point solubility curve has neither a maximum or a minimum.
 - (b) The freezing-point solubility curve has a maximum.
 - (c) The freezing-point solubility curve has a minimum.
- II. Two components completely miscible in the liquid phase, but only partially miscible in the solid phase; i.e., the two components do not form a continuous series of solid solutions (see figure 2).
 - (a) The freezing-point curve exhibits a transition point.
 - (b) The freezing-point curve exhibits a eutectic point.
- III. Two components completely miscible in the liquid phase, but completely immiscible in the solid phase (fig. 3)

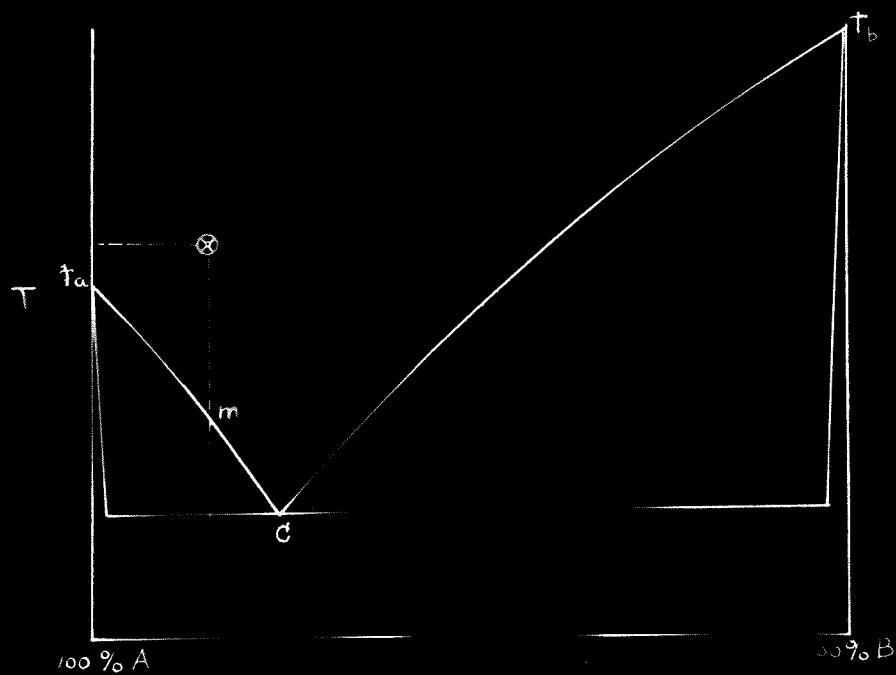


Fig 3

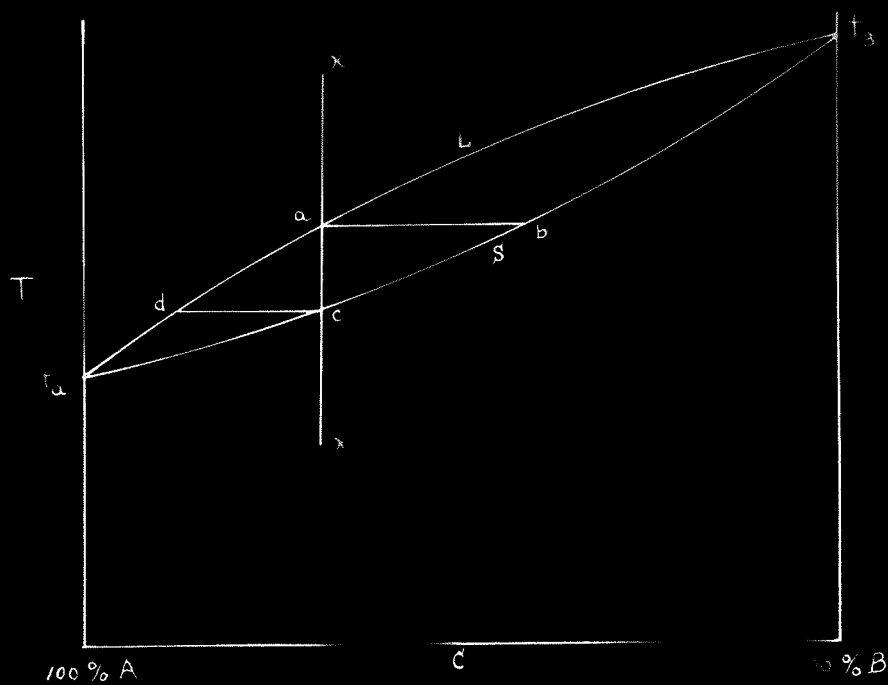


Fig 4

There are, of course, other possibilities which have been found experimentally, but these include the type of curves found in this investigation and therefore will be sufficient for the present discussion.

The curves shown in figures 1 & 2 are commonly known as the "five types of Roozeboom"; a, b, and c of figure 1 being types 1, 2, and 3 respectively; and a and b of figure 2 being types 4 and 5 respectively.

Discussion of the Curves.

Introduction

By means of the Phase Rule equation, it can be seen that for two components existing in one phase, $F = 3$; i.e., the degree of freedom of the system is three and therefore three variables must be fixed in order that the system may be perfectly defined. Therefore, in addition to temperature and pressure, a third variable, concentration, must be chosen. To represent graphically the two component system with its three possible independent variations, we should require, in order to represent all the possible conditions of equilibrium, a three coordinate diagram in space (see figure 5). This is a solid whose axes OT, OP, and OC represent temperature, pressure and composition respectively.

The surface OPMT would then represent the variation of pressure and temperature, the concentration being constant although not necessarily zero. This is called the "pt" diagram, $c = \text{a constant}$.

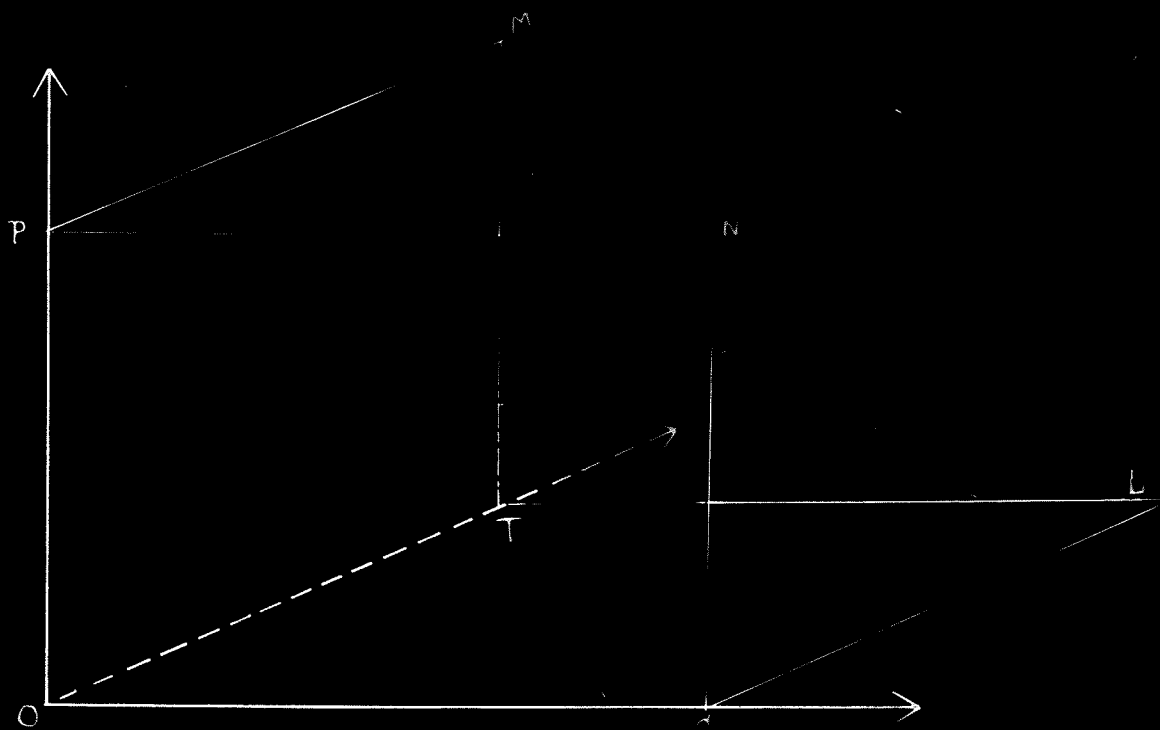


Fig 5

Similarly we have: OTLC, the t, c diagram, $p = \text{constant}$, and OPNC, the p, c diagram, $t = \text{constant}$. The most commonly used representation is the t, c diagram. The pressure in this case is considered to be constant and at atmospheric pressure. Since most of the properties of a substance require considerable changes of pressure in order to noticeably affect them; e.g., the melting point of a substance is changed only by a few hundredths of a degree by a change in pressure of one atmosphere, then the small fluctuations in atmospheric pressure can be disregarded.

By thus keeping one of the variables constant, the graphic representation of the system is made very much simpler. Figures 1, 2, and 3 then are only one surface of the space diagram in which the pressure is constant and the temperature and concentration may vary.

For two components in two phases, $F = 2$. Then there are only two variables which must be fixed in order that the system may be perfectly defined. If the temperature and composition are fixed, then the pressure is automatically fixed.

For two components in three phases, $F = 1$. Therefore the fixing of one of the variables perfectly defines the system.

In order that the system be invariant; i.e., $F = 0$,

no less than four phases must be present; e.g., solid₁, solid₂, liquid, and vapor.

In the formation of solid solutions from mixtures of the fused components, there are really two solutions, one completely liquid, the other completely solid. In general the concentration of the two components in these two phases will not be the same, and so two curves will be required, one referring to the solid phase (solidus curve, *s* in figure 4) and the other referring to the liquid phase (liquidus curve, *L*). The temperature at which solid begins to be deposited from the liquid solution is called the freezing point of the solution or mixture, and the temperature at which the solid solution just begins to liquefy is called the melting point of the solid solution. Therefore the liquidus curve is the freezing point curve, and the solidus curve is the melting point curve.

I. The two components are completely miscible in the liquid and solid phases.

A solid solution, being homogeneous, can constitute only one phase; and on melting, since it must melt to a homogeneous mixture, the molten solution consists of one phase only. If the vapour of the two components is considered to be present, then the maximum number of phases possible is three. Hence $F = 1$, and the system can never become in-

variant. Therefore, the equilibrium curve must be continuous; i. e., without any breaks or points of inflection.

Type I. The freezing-points of all mixtures lie between the freezing points of the pure components. (fig. 1, a)

Since we are dealing with solid solutions, the melting point curve must also be continuous, as shown. The relative positions of the two curves, which has been deduced by thermodynamics and also by experiment, is given by the rule: "At any given temperature, the concentration of that component by the addition of which the freezing-point is depressed is greater in the liquid than in the solid phase; or conversely, the concentration of that component by the addition of which the freezing point is raised, is greater in the solid than in the liquid phase.

On cooling a fused mixture of two substances capable of forming solid solutions, the temperature of solidification will not remain constant during the separation of the solid, nor will the temperature of liquefaction of the solid solution be constant.

If we take a mixture of A and B (see figure 4) of composition and temperature represented by x , and allow it to cool along the line xx' , then at a , where it strikes the liquidus curve, solid will begin to deposit whose composition is given by b on the solidus curve. (a and b are at the same

temperature.) But since b is richer in B, the composition of the liquid must move in the direction a→d. The composition of the solid solution will at the same time move from b→c, providing we allow sufficient time for the solid solution to undergo change by diffusion. When the solid solution reaches c, the liquid will have solidified completely to a solid solution of the same composition as the original liquid.

Similarly heating up a solid solution of a composition and temperature x', melting starts at c, giving a liquid of composition d, richer in A, and therefore its composition will move in the direction c→b. The composition of the liquid meanwhile will move in the direction d→a. Finally at a all the solid has melted to a liquid of the same composition as the original solid. The process of liquefaction or solidification is therefore extended over the temperature interval ac.

Type II. The freezing point curve passes through a maximum

In this curve (see figure 1, b.), the freezing point of each of the components must be raised by the addition of the other component. At the maximum point the melting and freezing curves touch, and therefore the composition of the solid and liquid phases must be identical. Therefore, solidification and liquefaction would take place completely without change of temperature. Hence a solid solution at the maximum would ex-

hibit a definite melting-point and would behave like a simple substance; i.e., like a compound A_xB_y . Each part of the curve on either side of this "singular" point behaves like type I. Van Laar showed thermodynamically that it was impossible to have a maximum unless a compound was formed. Hence type II is just type I twice over; i.e., we have the components A and A_xB_y as one system; and A_xB_y and B as the other system.

Type III. The freezing-point curve passes through a minimum.

In this case a minimum freezing-point is obtained, but it is still a continuous curve due to the existence of solid solutions. On the one side of the minimum point, the liquid phase contains relatively more, on the other side relatively less of the one component than does the solid phase. While at the minimum point, the composition of the two phases is the same. Therefore complete solidification and complete liquefaction will occur at this point without change of temperature, and the solid solution will accordingly exhibit a definite melting point.

II. The two components do not form a continuous series of solid solutions (but the liquid components are completely miscible.)

The solid components A and B are not completely miscible. Hence the solid component A can dissolve the solid component B only until the concentration has reached a certain value.

On adding a further quantity of B, the composition of the solid solution will not be altered, but there will be formed a second solid phase consisting of a solution of A in B. At this point four phases will coexist; namely, a solid solution with excess A, a solid solution with excess B, liquid and vapour. Hence $F = 0$ and an invariant point is obtained. The t_c curves will no longer be continuous, but will exhibit a discontinuity at the point at which the invariant system is formed.

Type IV. The freezing-point curve exhibits a transition point

The behavior of this type is represented in figure 2, a. The addition of B raised the melting point of A, the concentration of B being greatest in the solid solution in accordance with the rule previously given. The melting point of the solid solution is represented by AD, and the freezing-point of the liquid solution is represented by AC. The addition of A lowers the melting point of B, giving the curves BC and BE for the liquid and solid phases. At the temperature of the line CDE, the liquid solution of the composition represented by C is in equilibrium with the two different solid solutions represented by D and E. Therefore at this temperature, $F = 0$, and both the solidus and liquidus curves must exhibit a discontinuity.

Type V. The freezing-point curve exhibits an eutectic point

This behavior is represented by figure 2, b. The freez-

ing-point of each of the components is lowered by the addition of the other, until, at last, a point is reached at which the liquid solidifies to a conglomerate or mixture of the two solid solutions. This is the lowest melting point of the mixture and is called an eutectic point. At the eutectic the liquid is in equilibrium with two different solid solutions, the composition of these being represented by points D and E. Therefore for a liquid of composition C, complete solidification will take place at the temperature represented by the point C to a conglomerate of D and E.

In the extreme case of type IV, where the components A and B are completely miscible in the liquid phase and completely, or almost completely, immiscible in the solid phase, the eutectic line (or what was the solid solution line) extends completely across the tc diagram. This is shown in figure 3. There is then practically no solid solution so that the eutectic composition becomes merely a mixture or conglomerate of pure A and pure B. This is the type of behaviour found for the explosive systems we have studied.

If a mixture of composition and temperature represented by x (figure 3.) is cooled down, then when the temperature reaches that of point m, solid A will begin to separate out. This separation will be accompanied by the heat of solidification and will show up on a cooling curve as a point of in-

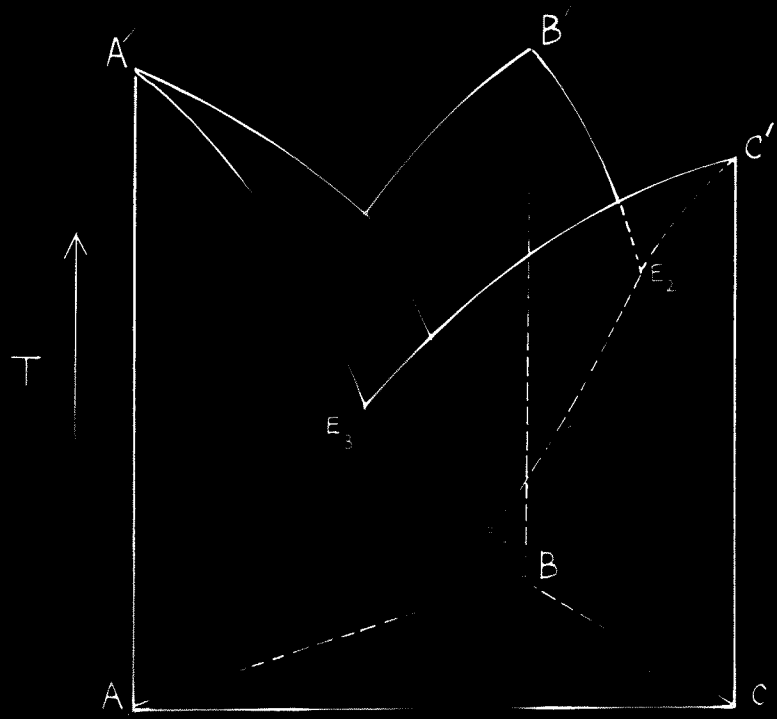


Fig 6

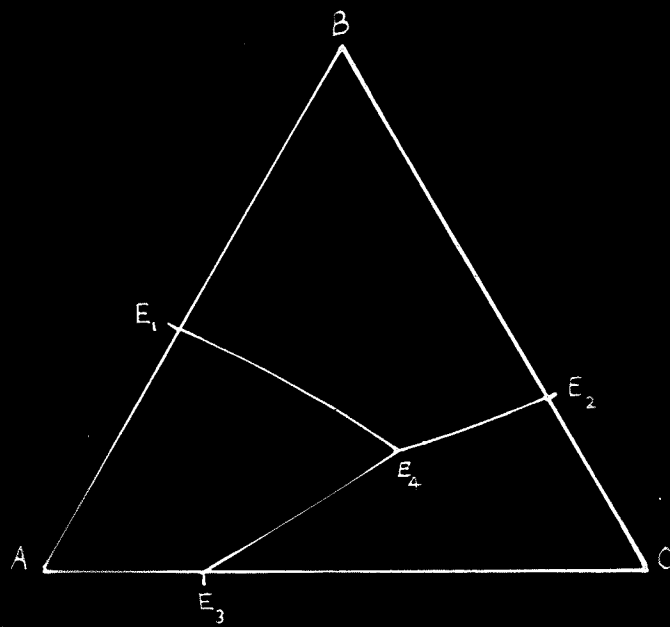


Fig 7

flection. Since there is now less A in the mixture; that is, the liquid, the composition will move in the direction $m \rightarrow c$, while solid A will be constantly deposited as the temperature falls. At point C, solid B will begin to separate and the temperature will then remain constant while solid A and solid B separate in constant proportions; i.e., the proportions represented by the composition of C, until all is solid. A similar analysis holds for a liquid on the other side of the eutectic composition. For a liquid of the exact eutectic composition, there will be no preliminary separation of A or B. Therefore, at the eutectic, all the liquid will solidify at a constant temperature as though it were a pure substance.

Three Component Systems.

Only a short discussion of the graphical representation of the case corresponding to the extreme case of type V of the two component system will be given here.

The three component system, consisting of the three components A, B, and C, can be represented by joining the three possible two component tc diagrams, A:B, A:C, and B:C, in the form of a prism, the base of the prism being an equilateral triangle. The faces of the prism (see figure 6), $AA'B'B$, $AA'C'C$, and $BB'C'C$, then represent the tc diagrams of two component systems, A:B, A:C, and B:C. The edges of the prism, AA' , BB' , and CC' represent the pure components A, B,

and C, while the interior of the prism represents the effect of the three components upon one another. Temperature is represented by the height of the prism. Thus a horizontal section through the prism will be an isothermal and will be represented by an equilateral triangle, whose sides represent the two component systems and whose interior represents the three component system. The points will, of course represent the pure components.

However, this same equilateral triangle can represent the projection of the curves inside the prism onto its base. In this case, the temperature of each point must be indicated.

E_1 , E_2 , and E_3 on both diagrams represent the eutectic compositions of the systems, A:B, B:C, and C:A respectively. E_4 is the ternary eutectic. E_1E_4 then represents the effect of adding C to the eutectic of A:B and is called an eutectic trough. It is not necessarily straight. Similarly for E_2E_4 , and E_3E_4 . E_4 is the lowest point reached for the three component system and hence is called the ternary eutectic.

For a three component system, we have: $F = 3 + 2 - r$.

Therefore the number of phases that must coexist is seen to be five. Hence at the ternary eutectic we must have: liquid, vapor, A, B, and C as solids, coexisting at a temperature and composition fixed by the nature of the system.

Theoretical Discussion on the Velocity of Crystallisation

Since the problem is primarily one of inhibiting or slowing down crystallisation until the molten explosive has cooled to room temperature; i.e., the attaining of a large degree of supercooling, a discussion of the theory and measurement of the velocity of crystallisation will be in order.

In the following discussion, the phrase "velocity of crystallisation" will be shortened to C.V. (crystallisation velocity.).

The first experiments on the velocity of crystallisation were made by Gernez in 1882 (6) and 1884 (7) on phosphorus. Further experiments were carried out by him on sulphur in 1884 (8,9).

Since the solidification of a supercooled substance is accompanied by a liberation of the heat of fusion whose effect is to raise the temperature of the adjacent layer, he said that the rapidity with which this solidification proceeds depends on this heat of fusion. Therefore, in order to get reproducible values for the C.V. it is necessary to have a thread of the supercooled liquid infinitely thin, in order that the heat of solidification may be removed as quickly as possible.

Gernez found that if the substance was poured into a

U-tube whose inner diameter did not exceed 2.7 millimetres, the influence of the heat of fusion was negligible, especially if the walls of the tube were thin. The thin wall would allow the heat to escape quickly into the supercooling bath. If the diameter of the tube exceeded 2.7 mm, he found that the C.V. increased with the diameter of the tube.

In his measurements on the C.V. of phosphorus, Gernez carried out the following treatment which is the standard procedure for measuring the C.V.:

~~He heated the~~
He heated the U-tube containing the phosphorus for from 15 to 30 minutes in a bath at a fixed temperature above the melting point of the phosphorus. The U-tube was then quickly transferred to a bath of water kept at a fixed degree of supercooling. It was allowed to remain in the bath, undisturbed, for periods of time up to an hour or even more. The crystallisation was then initiated by touching the surface of the supercooled phosphorus with the end of a capillary tube from which projected a thread of solid phosphorus. At the moment of touching, a stop-watch was started. When the crystallisation reached the second free surface, the stop-watch was stopped. The C.V. was then calculated by dividing the distance between the free surfaces by the time taken for the crystallisation to traverse this distance. The usual units are millimetres per minute.

This method of measuring the C.V., however, is now modified somewhat. Instead of measuring the distance from free surface to free surface, only the distance down one of the arms of the tube is taken. Convection currents, due to the heat liberated, make the measurements upwards in the tube unreliable.

Gernez found that no matter to what degree he heated the phosphorus above its melting point (up to a limit of 215°), the C.V. was not sensibly changed for any fixed degree of supercooling. Furthermore, he found that no matter how many previous measurements had been made on the phosphorus, the values for the C.V. remained the same.

For sulphur, however, the above results were not applicable. It was found that it might have different values at the same degree of supercooling depending on its previous treatment.

This he ascribed to the allotropic modifications of solid sulphur, and to the dynamic equilibrium of molten sulphur, (10).

The length of time during which the sulphur remained in the bath in which it was heated above its melting point, and the temperature to which it was heated, were found to have an independent, definite influence on the C.V. at any given degree of supercooling. From the results which he obtained from this series of measurements, he was able to show that liquid sulphur was able to undergo a modification which de-

pended on the duration of the action of the source of heat. This modification was found to persist for a time after the liquid was brought back to its initial conditions. It was found that the C.V. for sulphur also depended on what crystalline form had been used to inoculate the supercooled liquid.

Gernez said that the C.V. was proportional to the degree of supercooling. But his measurements were not carried to more than about 20° below the melting point.

After Gernez's work on phosphorus and sulphur, Moore (11) measured the C.V. of glacial acetic acid and some other organic compounds. He confirmed Gernez's results as to the dependence of the C.V. on the degree of supercooling, but he did not find any difference in the value of the C.V. with different methods of treatment. This he explained by saying that the materials with which he worked did not have the peculiar nature of sulphur.

At the temperature at which spontaneous crystallisation began in his supercooled liquids, Moore detected a decrease in the rate of increase in the C.V. He attempted to push his measurements to a greater degree of supercooling in order to confirm this phenomena, but in spite of his elaborate precautions, he was unable to do this because of spontaneous crystallisation.

Moore showed that with tubes of from 1 to 7 millimetres

in diameter, the C.V. did not depend on the diameter of the tube. However, his measurements did not extend to large degrees of supercooling.

He attempted to increase the possible degree of supercooling without spontaneous crystallisation by using a mixture of two similar substances; e.g., phenol and cresol. His results showed that a greater degree of supercooling could not be obtained. (I have found that it could be in my mixtures) He noticed, however, that the addition of cresol had a very marked effect in reducing the C.V. of the phenol. (I too have noticed this in the mixtures of the explosives.)

Tumlirz (12) investigated the supercooling of water and obtained the following results:

The velocity with which the solidification progressed in supercooled water, increased constantly and rapidly with the degree of supercooling. He pointed out that the C.V. at any given degree of supercooling fluctuated somewhat. This was due, he said, to the manner in which the crystallisation progressed. For example, instead of crystallising straight down the tube, it might crystallise in a twisting plane. Hence it would appear to be slower. Because of such irregularities, the velocity might vary during the course of a single experiment.

By means of a mathematical treatment, Tumlirz showed

that if liquid sulphur is made solid by supercooling until its viscosity is infinite, then it cannot be the normal, crystallised sulphur. It must be an amorphous solid.

It was Tammann, however, who made an extensive study of the C.V. and proposed a theory on it.

He claimed (13) that during the solidification process the same constant temperature, namely that of the melting point, must prevail in the boundary layer between the solid and the supercooled liquid, independently of the degree of supercooling. Thus he could not see why the C.V. should depend on the degree of supercooling.

On Tammann's suggestion, Friedländer (14) had undertaken experiments on various organic substances down to 30° of supercooling. It was found that from $0 - 15^{\circ}$ of supercooling, the C.V. increased proportionately to the degree of supercooling; but in the region of $15 - 30^{\circ}$ of supercooling, it was independent of the degree of supercooling.

Tammann said that the velocity of solidification would be independent of the temperature of the supercooled liquid as long as the heat set free on solidification was sufficient to heat the solid material to its melting point. The quotient: Latent heat divided by the specific heat of the solid would give the number of degrees of supercooling over which the latent heat would be sufficient to raise the temperature to

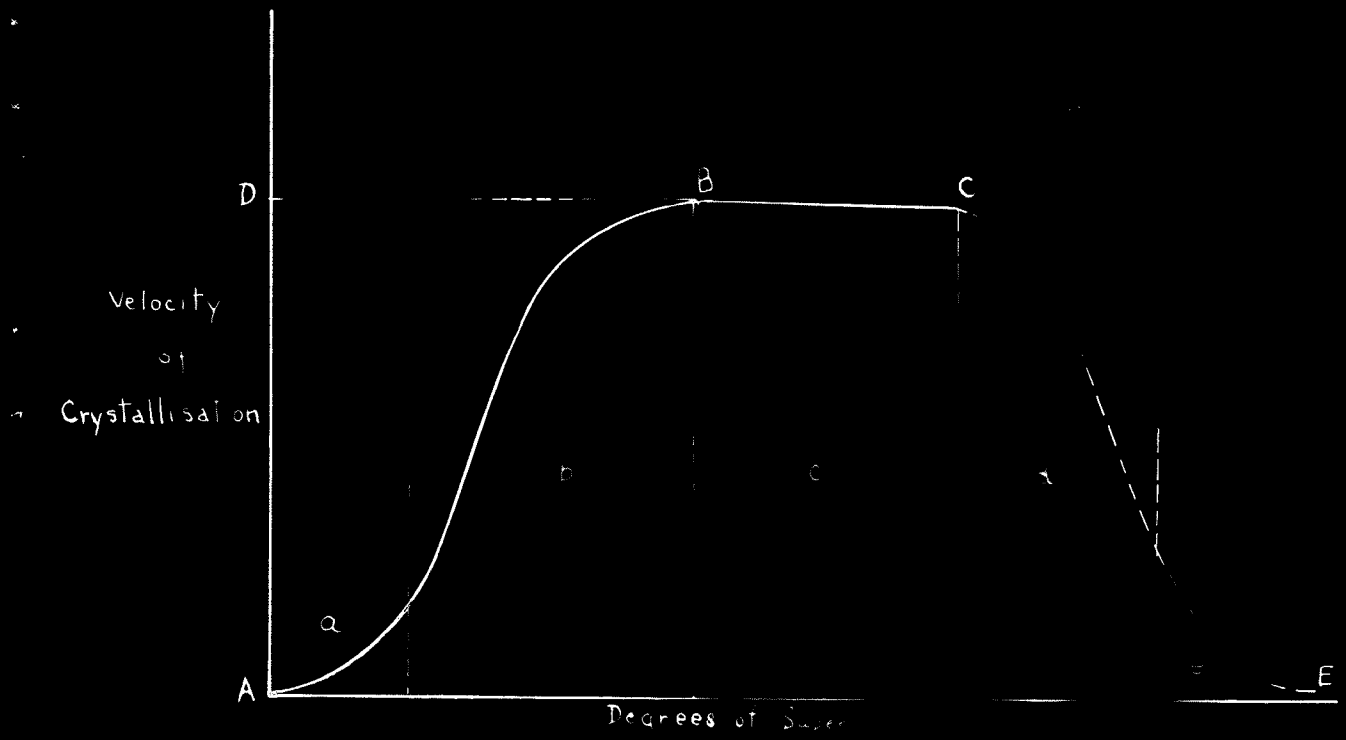


Fig 8

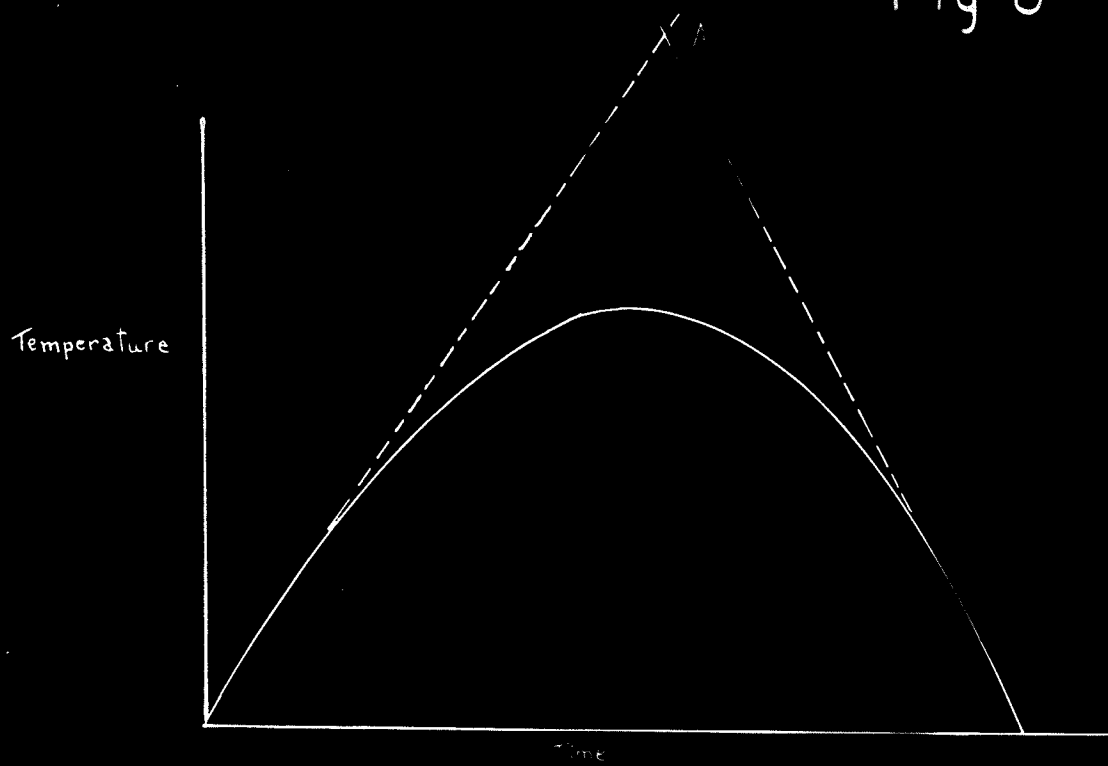


Fig 9

the melting point. On further cooling, however, he said that it was to be expected that the C.V. would decrease with the decreasing temperature of the boundary layer, as is the case for the velocity of vaporisation and the velocity of solution. This supposition was confirmed by his experimental results.

Tammann proposed that the general form of the crystallisation would be as shown in figure 8. The abscissae represent degrees of supercooling while the ordinates represent velocity of crystallisation in millimetres per minute.

Between A and B, the C.V. increases with increasing supercooling. At B it reaches a maximum which is characteristic of the pure substance. This velocity remains constant over the interval BC. At C, however, there is not enough heat set free to raise the temperature of the boundary layer to the melting point. Therefore, the C.V. begins to rapidly diminish with increasing degrees of supercooling until it becomes zero at E.

⁽¹⁵⁾
Kuster objected to Tammann's theory on the Velocity of Crystallisation. He said that Tammann had accounted for actual deviations from his ideal curve by assuming that impurities interfered, and that different arrangements of the crystals at different degrees of supercooling were formed. His main objection, however, was to Tammann's idea

that the melting point of the solid prevailed on the boundary layer of the liquid and solid, independently of the degree of supercooling. This, he said, appeared to be impossible; because, if that were so, then there was still an equilibrium between the solid and liquid phase. But since the crystallisation progressed, then the temperature of the contact layer must lie below the melting point. Furthermore, he said, every precipitation proceeded from a supersaturated condition; therefore the contact layer itself must be supersaturated; i.e., supercooled. However, Tammann's ideas prevailed.

Tammann (16) also investigated the dependence of the number of nuclei, which are formed spontaneously in supercooled liquids, on the temperature.

Tammann's work up to 1915 on the C.V. and nuclei number is collected in his book, "Kristallisieren und Schmelzen". The English translation of this appeared under the name: "The States of Aggregation" in 1925. (17)

Since this book contains most of the ideas on the subject of crystallisation velocity and nuclei number, a summary of these ideas will be given:

The tendency towards Spontaneous Crystallisation in Undercooled Liquids.

In many undercooled liquids, the number of crystallisation centres formed in a unit of mass per unit of time is so small

that it is possible to count them and to study the influence of temperature, etc., upon them. It was found that the tendency toward spontaneous crystallisation is highly sensitive to slight alterations in the supercooled liquid, and that a pronounced temperature maximum exists at which a maximum number of centres is formed. By special treatment, these centres can be made to grow without increasing their number. Thus they are made visible and so can be counted.

Foreign substances have an effect upon the tendency towards spontaneous crystallisation which varies considerably with the nature of the substance, although the temperature of the maximum itself is very little affected.

The nuclei number is influenced by insoluble powders, even though they do not act as centres for nuclei formation, as shown by microscopic examination. With both soluble and insoluble impurities, however, the nuclei number of the pure substance may be either raised or lowered, but in both cases the maximum nuclei number remains at almost the same temperature.

Tammann showed that the tendency toward spontaneous crystallisation at first increased with increasing degrees of supercooling, but it began to decrease after passing a certain temperature which was characteristic of the substance.

Therefore, if the substance is cooled very rapidly so

that this temperature is quickly passed, it should be possible to obtain the substance in the form of an amorphous solid; i.e., in the form of a glass, since the inner friction grows rapidly with decreasing temperature. By this treatment it should be possible to obtain all substances in the form of a glass. Formerly, it was assumed that only mixtures could be obtained in this condition.

From an investigation of 153 substances (18), Tammann concluded that they belonged to several wholly different groups with respect to their ability to undercool, but that with sufficiently rapid cooling, the majority could be obtained as glasses. He found that the tendency to undercool increased with the number of hydroxyl groups. (If this is universally true, then it would serve as a criterion for making mixtures of explosives which would have the desired supercooling properties.)

At one time it was thought that a region extended below the melting point of a substance, called the sphere of metastability, within which nuclei would not form spontaneously. Tammann has shown, however, that if sufficient time is allowed, spontaneous crystallisation will take place as close as 0.4° to the melting point. Although he showed that an extensive metastability did not exist, Tammann said that a metastability of a few tenths of a degree below the melting point must exist

because of the increase in the solubility resulting from a decrease in the particle size.

The temperature to which the melt was heated before undercooling had, as was to be expected, an effect on the number of nuclei formed. Under otherwise similar conditions, the higher the temperature to which the melt was heated above its melting-point, the smaller the number of nuclei which was formed on supercooling.

(I think that this was due to the fact that even above the melting point of a substance, some crystal lattices tend to persist, if not actually as such, at least as fragments of lattices, or as arrangements of molecules that can rapidly form a lattice. In other words, even though the arrangement of the molecules in a liquid is supposed to be random, it is possible that as a crystal lattice breaks up, the molecules of which it is formed do not move away from their former positions very quickly. As the temperature is raised, however, the kinetic energy of the molecules becomes greater and hence they move into a random arrangement much more quickly. From this it seems that heating for a long time at a lower temperature should have the same effect on the nuclei number as heating for a short time at a higher temperature.)

Tammann considered that the number of crystallisation centres which formed in a supercooled liquid was directly

proportional to the time the liquid was supercooled. This was not confirmed experimentally in all cases, however.

The Change in Viscosity with Supercooling.

The viscosity of a liquid first increases slowly with increasing supercooling, and then reaches a critical temperature at which the rate of increase mounts rapidly until finally a hard brittle glass is formed. However, although the viscosity increases very rapidly with falling temperature, other properties of the liquid show no abnormal change. Therefore, Tamman felt justified in considering glasses as undercooled liquids.

Tamman noted that in many cases the liquids lost their mobility exactly at temperatures where the tendency to form crystals was the greatest. In other cases, the tendency towards spontaneous crystallisation was greatest when the melt had become rigid. In still other cases, the maximum nuclei number occurred at temperatures far above the softening range of the glass. Therefore, for different substances, the greatest tendency towards spontaneous does not lie at temperatures of equal inner friction. This means that the viscosity of the substance is not the only factor in the spontaneous formation of nuclei, as is to be expected.

Viscosity has, however, a great influence on the formation of the nuclei. This may be explained as follows:

The greater the viscosity, the more difficult it is for the molecules to group themselves into a crystal lattice, and therefore the smaller the nuclei^{number} becomes. Finally when the viscosity becomes very great, the crystal lattice can not be formed and the glass becomes stable, even though, thermodynamically considered, it is in an unstable state.

The Linear Crystallisation Velocity (C.V.)

Since crystals are many-sided, the C.V. must depend on the direction in which the velocity is measured, because if the C.V. were independent of the direction, then the crystals would be bounded by spherical surfaces.

Actually any one crystal form would have different velocities of growth depending in which direction from any given face of the crystal the velocity was measured. However, it has so far been possible to determine only the greatest C.V. at any one temperature. This C.V. may be the sum of several different velocities of crystallisation.

By introducing the substance into a dilatometer and reading the change in volume in a unit of time, a "three dimensional velocity," which would take into account the crystallisation from all faces of the crystal, would be obtained. But this method is clumsy and unsatisfactory due to the occurrence of several nuclei in the supercooled liquid, and to the difficulty of withdrawing the heat of crystallisation.

Tammann criticises Gernez's and Moore's conclusions as to the direct proportionality between the C.V. and the degree of supercooling on the basis that they had not extended their measurements to a sufficient degree of supercooling. He found that the C.V. was independent of the degree of supercooling after it had exceeded 20 - 30°. His analysis of the typical behavior of the C.V. with undercooling is given below: (see figure 8)

In the range "a", 1 - 5° below the melting point, few consistent values for the C.V. can be obtained due to the growth of large crystals in directions different from that of the axis of the tube. Thermal convection currents, or currents arising from slight admixtures in the melt have a great influence on the C.V. in this range, tending to accelerate it. Therefore with tubes in which convection can easily take place (relatively large diameter), the C.V. will be higher than its true value. Moore (11) found that in the range of diameters, 1 - 7 millimetres, the C.V. was independent of the diameter. Tammann found that it was not.

In the range "b", about 5 - 30° below the melting point, the crystals grow parallel to the axis of the tube, and grow mostly from the ends, so that long crystal filaments are formed. Furthermore, they grow along the periphery of the tube since the heat is removed more quickly there.

In the range "c", however, the crystals fill the tube. In this range, the value of the C.V. is independent of the bath temperatures, because a constant temperature; i.e., the melting-point, prevails at the crystallisation boundary.

Tammann said that there was no simple explanation for the C.V. measured in the ranges "a" and "b", because in copper tubes which can conduct the heat away rapidly, the maximum velocity is reached much more quickly; i.e., with less supercooling. He claimed that with sufficiently rapid withdrawal of heat, the maximum constant velocity characteristic of the substance would be obtained at the melting point of the substance. (If we assume that this is possible, it really discredits Tammann's own assumption that the melting point prevails at the solid-liquid boundary, because he says that the faster the heat is taken away, the sooner the maximum velocity is reached. With such a rapid withdrawal of heat, how can the melting point be reached?)

Tammann assumed that the maximum C.V. will be reached at a supercooling of $20 - 30^{\circ}$, and will remain constant at this value while the supercooling increases to 80° below the melting point. But he found several exceptions to this; notably 2:4-dinitrophenol which had not reached its maximum until 40° , or approximately 73° of supercooling.

The influence of admixtures upon the maximal C.V.

The equilibrium temperature of a crystal with its melt is lowered by the addition of non-isomorphous substances. Since the reaction velocity commonly decreases with falling temperature, a diminution of the C.V. is to be expected. This was confirmed by experiment.

Since equimolecular quantities of admixtures lower the equilibrium temperature of a crystal and its melt by equivalent amounts, equivalent lowering of the C.V. by equimolecular quantities was to be expected, provided that the substances added affected the C.V. in no other way. This was found to be the case, in some cases, but in others the C.V. fell below that expected.

Bogojawlenski (19) investigated the C.V. of a number of pure substances, among them picric acid and 2:4-dinitrophenol, and a few mixtures. His findings agree with those of Tammann. He found that the C.V. of mixtures was very irregular. This he ascribed to the fact that the concentration changed as one of the components crystallised out.

Later work on the C.V.

In 1929, a doubt was cast on Tammann's theory about the temperature of the boundary between the solid and super-cooled liquid being that of the melting-point. By direct measurement, and by a mathematical treatment, Pollatschek (20)

showed that the temperature prevailing at the boundary solid-supercooled liquid, was never that of the melting-point.

He used a thermo-electric element which was placed in the tube so that the crystallisation boundary had to pass it. It was made of very thin wire in order that the heat absorbed by it would not be very great. However, no matter how small the element is, some heat will be absorbed and so the true temperature will not be reached. Again, if the melting-point is reached it cannot last more than an instant, and due to the lag of the element will not be recorded. In order to overcome this difficulty, Pollatschek extrapolated his curve (see figure 9) in order to get the true temperature "A". By a mathematical treatment, he showed that this extrapolation was justified; but the extrapolated temperature was never that of the melting-point. From this it seems that Tammann's assumption was wrong.

The effect of colloidal substances on the C.V.

Freundlich and Oppenheimer (21), working on undercooled aqueous solutions, found that colloidal particles with a spherical form lowered the C.V., but that colloidal particles with a non-spherical forms, increased it. They explained this by saying that non-spherical particles had surfaces which served to orientate the molecules of the supercooled solution. Hence, the formation of nuclei was favored.

The Nature of Glass

As has already been mentioned, Tammann considered that a glass was merely a supercooled liquid with a stability conferred upon it by virtue of its high viscosity, and not because there was any fundamental change.

Warren (22) showed by means of X-ray diffraction that glass was an amorphous solid, and therefore that the term supercooled liquid as applied to glass was quite correct, although possibly not suitable.

Shishacow (23), however, said that although X-ray diffraction indicates that glass is an amorphous solid, electron diffraction indicates a definite existence of very minute crystals. These, of course, would seem to be crystal lattices that have not had a chance to grow appreciably.

Valenkof, Boray, and Koshitz (24) offered evidence that there is not a sharp boundary between the glassy and crystalline states. This is opposed to Warren's view. (22)

Some time before this X-ray and electron evidence was submitted, (in 1927), Parks and Hoffman (25) suggested that a glass might be a fourth state of matter, or a colloid analogous to a jelly. They believed that there was a fundamental difference between the glassy and liquid states. Their belief was based on the fact that they had found that viscosity, thermal conductivity, and dielectric constant, vary

changed very rapidly at approximately the same temperature, although there was no definite "transition" temperature.

Of the several hypotheses which they propose, I believe X that the one that best fits in with the results found by Shishacow (23) and Valenkof (24) is the one which assumes that the glass is a colloid; i.e., a gel consisting of but one component. (an isocolloid.). This gel consists of two forms of the same substance, one acting as the dispersing medium, and the other as the dispersed phase. This is tantamount to saying that colloidal crystal nuclei are dispersed in a supercooled liquid, forming a gel. The changes in the properties of the substance which were found by Parks and Hoffman would then be colloidal phenomena of some sort. If this is the true explanation, then Tammann's fundamental assumption that a glass is a supercooled liquid has not been materially altered. In fact, calling glass a supercooled liquid is probably more satisfactory than calling it a gel.

The General Plan of the Work.

In order to investigate the mixture called "shellite" it seemed desirable that the exact eutectic composition of the mixture should be determined first. Thus a mixture could be obtained which would melt completely, or almost completely, at one fixed temperature. Bogojawlensky (2) had already investigated the system; but since the original references was unobtainable, it was desirable to check the values he obtained. This was done by two different methods.

Once the eutectic composition was determined, the effect on its properties of adding a third component, was tried.

X Since we thought that viscosity would be the main factor in determining the crystallisation velocity, and hence the rate of solidification in a shell, determinations of viscosity and density were done on the pure substances and several mixtures. In order to have a quantitative measurement of the suitability of these mixtures, measurements of crystallisation velocity were also made.

One of the most promising substances for using as a third component was suggested by Dr. A. N. Campbell. He suggested X that since nitro-cotton of low nitration (colloidion) dissolved to very viscous solutions and was itself an explosive, the addition of it might increase the viscosity of the shellite sufficiently for the C.V. to be greatly reduced, or even brought to zero. The viscous liquid, or glass, obtained would then

cool completely before it solidified.

Only the highly nitrated cotton used for manufacturing "cordite" was obtainable however. This was used in lieu of the collodion, although it is not as soluble as collodion. Very viscous solution of the nitro-cotton in the shellite were obtained with as little as 5% of the gun-cotton. The desired reduction in the C.V. was not obtained, however. This method was then abandoned.

Another method of attack was suggested by the work of Morey (29) on glasses. He pointed out that an ordinary glass (in fact all glasses) devitrifies or crystallises below a certain temperature, but not above it. This is really the melting-point of the mixture of substances from which the glass is made, although at this temperature the glass may be very viscous or even rigid. Some glasses easily devitrify, others do not. He said that any successful composition for a glass must have, among other things, a high viscosity at its liquidus temperature in order that crystal nuclei will not be able to grow and thereby cause the glass to devitrify.

An hypothetical illustration will illustrate how this viscosity can be obtained:

Let us say that a glass consisting of two components has an eutectic temperature of 800° . Its viscosity is considerable yet not sufficient to prevent crystallisation from start-

ing as the temperature drops below 800° . However, if it can be quickly cooled to 700° , the viscosity will now be increased so greatly (due to the lowered temperature) that the crystallisation can not proceed. Rapid cooling would give a glass in this case, but it would be an uncertain and difficult procedure.

Morey said that by adding as little as 1-5% of another component, miscible with the other two, the eutectic temperature could be lowered as much as 100° . Our glass, after the addition of such a third component, could be cooled to 700° without any crystallisation being possible. Below 700° , the increased viscosity, which would be little affected by the addition of the third component, would prevent the growth of crystal nuclei. A 'stable' glass would thus be obtained without recourse to rapid cooling.

I thought that by adding a third component (not a colloidal one like nitro-cotton) to shellite, somewhat the same effect should take place. With a greatly diminished C.V., the explosive could be kept as a liquid until it had completely cooled.

Dr. Campbell suggested that T.N.T. would be a suitable third component. The system Picric Acid- T.N.T. had already been determined ⁽²⁸⁾ (30, 31), leaving the systems: T.N.T.- dinitrophenol and picric acid-~~TNT~~-dinitrophenol, to be determined. The determination of these systems and their properties constituted the rest of the work undertaken.

Description and Use of the Apparatus.

Thermometers:

The various thermometers which were used were each compared with a standard thermometer, and the corrections to be applied to their readings were determined. In some cases the corrections were negligible and were ignored. However, the values given in the various tables can be considered to be correct within the experimental error.

Viscosimeters.

Two of these were made from hard glass tubing. They were slightly modified Ostwald viscometers designed to hold about two cubic centimeters of the liquid to be measured. Aniline was used to calibrate the one with the longer "run" time, while a mixture of the explosive whose viscosity was known was used to calibrate the other. This latter one was used for the viscosity of the supercooled liquids in order that the run time would not be excessive. A cathetometer was used to follow the progress of the liquid in the viscometer.

Specific Gravity Bottle.

This was made from hard-glass tubing and resembled an ordinary specific gravity bottle. Its volume, however, was only 1 - 2 cc. This volume was determined by calibration with aniline and mercury at the temperature at which it was used. The stopper was made from capillary tubing to allow

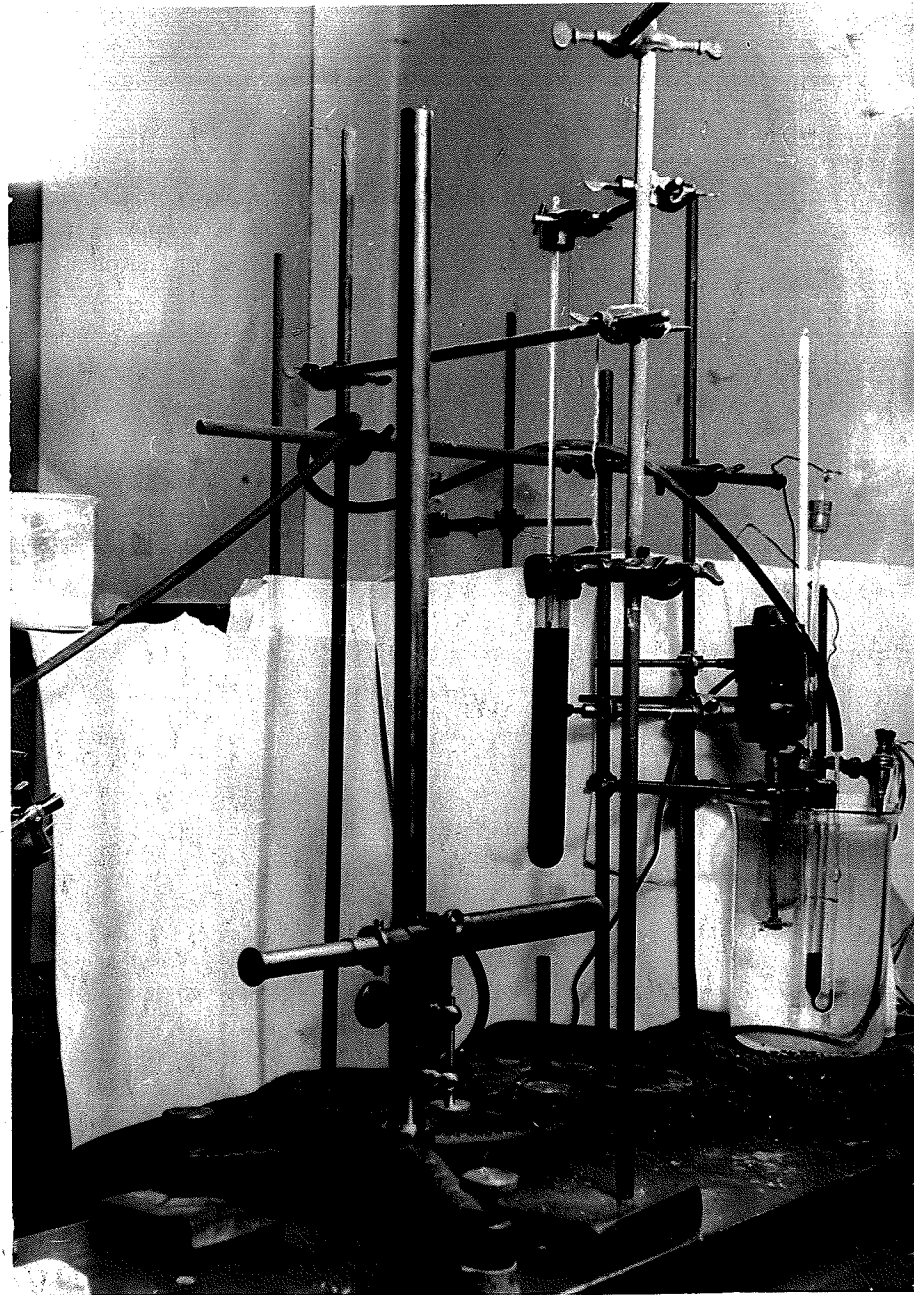


Plate 1

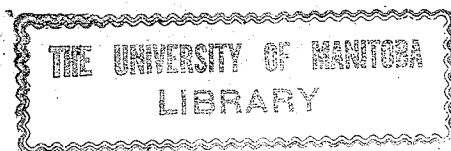
excess liquid to escape, while preventing evaporation.

Velocity of Crystallisation Apparatus.

This was made from hard glass, wide walled, capillary tubing of 1-2 mm internal diameter. It was bent in the standard U-tube shape and was fitted with wide glass tubing on one arm to facilitate filling with the liquid to be supercooled. Inoculation of the supercooled liquid with the solid phase was carried out on this side. The other arm of the tube was terminated by smaller tubing. This allowed a water pump to be attached to the apparatus for rapid emptying and cleaning. The length of one arm was about twelve centimeters.

The apparatus was held vertically in the thermostat by means of a clamp. A cathetometer placed some distance away was used to measure the distance the crystallisation had progressed down the one arm during a certain time. The cathetometer recorded to 0.1 mm by means of a vernier.

The first measurement of the C.V. were taken by noting the time taken for the crystallisation to progress from one mark on the side-tube to another ten centimeters away. This was satisfactory if spontaneous crystallisation did not take place. When spontaneous crystallisation did take place, it was found to be more satisfactory to follow the progress of crystallisation from one spontaneously induced nucleus by means of the cathetometer. The bulk of the measurements were done this way.



Thermostat (see plate 1.)

This consisted of a large glass beaker in which an electric heater, which might only be a cylindrical light bulb, or a 100 watt or 750 watt heater, depending on the temperature required, a xylene-mercury regulator, an electric stirrer, and a thermometer were inserted. This left sufficient room for the apparatus which was to be kept at constant temperature. The regulator actuated a relay which in turn controlled the heater current.

The first liquid used in the beaker was paraffin oil, but it was found to be unsuitable due to its rapid darkening at the temperatures employed. A very concentrated solution of CaCl_2 in water was found to be suitable because it did not boil even at 140° . At temperatures below 90° , pure water was used because the CaCl_2 solution crystallised. A layer of paraffin oil on the surface of the solution prevented too rapid evaporation of the water.

At 130° the thermostat remained constant to about $\pm 0.5^\circ$. At temperatures nearer room temperature, the constancy was much better, being $\pm 0.2^\circ$ or less.

Thaw-point, Melting-point Furnace. (see plate 2) (26)

This consisted of a heavy cylinder of brass with a central opening for the thermometer and melting-point tube. At right angles to this central opening and at 45° to one another, two

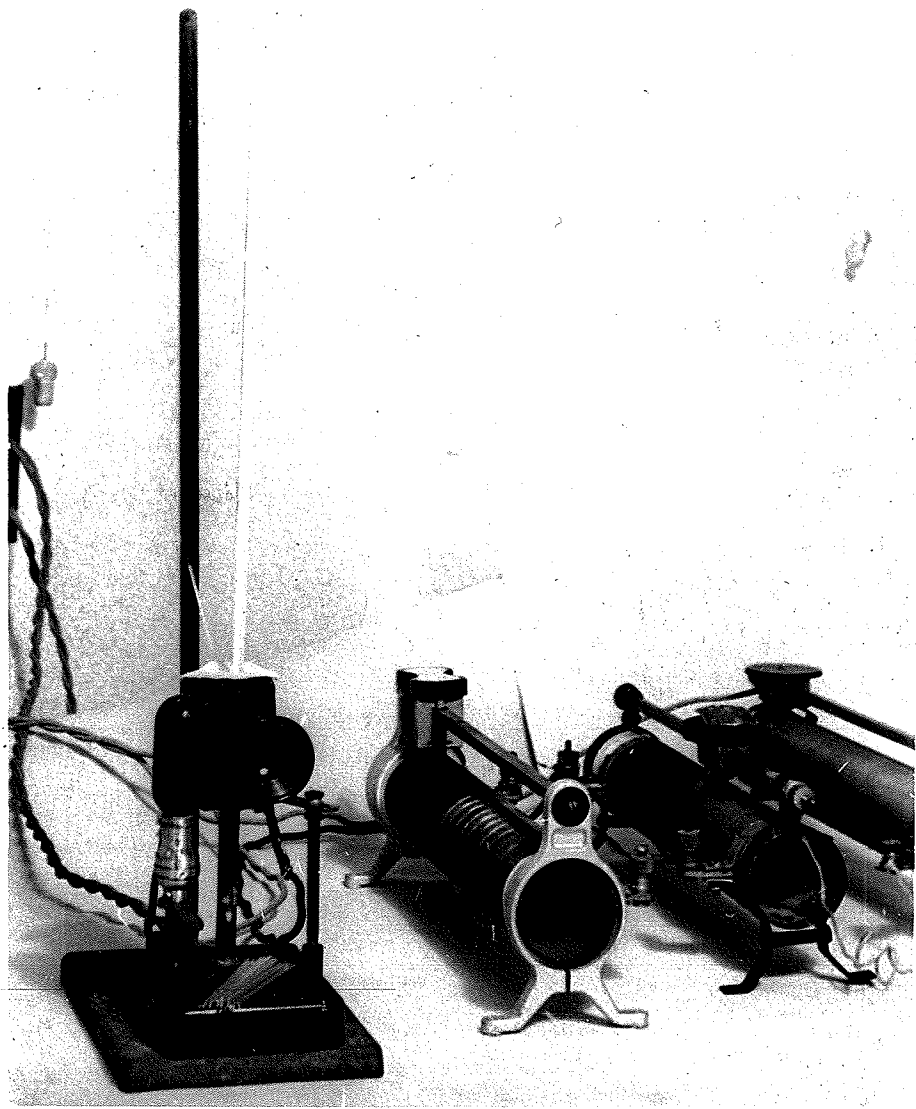


Plate .2

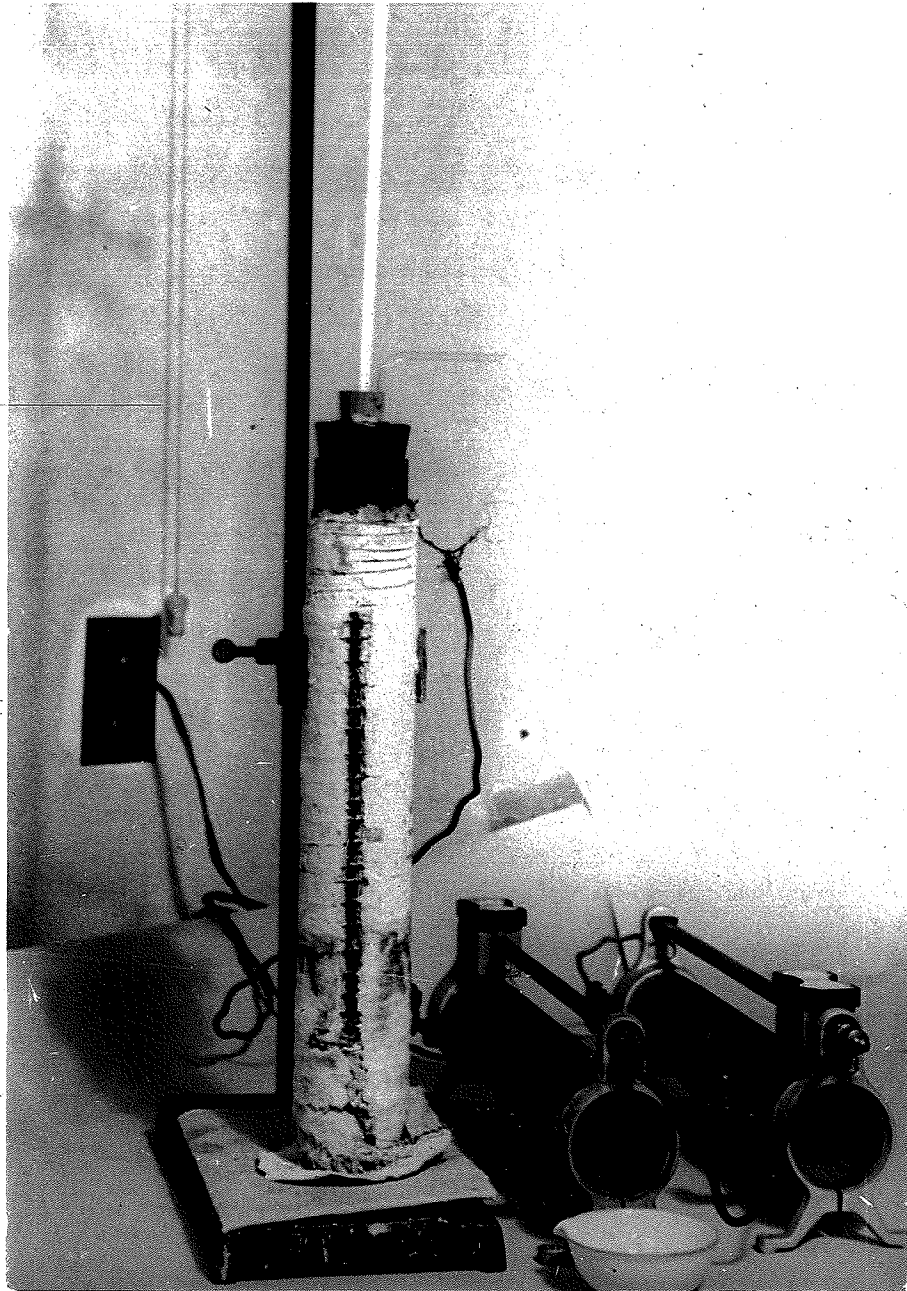


Plate 3

holes were drilled in the side of the cylinder. One of these served to let a source of light illuminate the melting-point tube, the other was used for observation. The source of light and a magnifying glass to facilitate the observations were mounted on the same stand. The brass cylinder was covered with a layer of asbestos paper, wound with nichrome wire, a second layer of asbestos paper, and a second layer of nichrome wire. The two wire windings were connected in series, and the furnace was finally covered with several layers of asbestos paper, using water glass as an adhesive.

In order to control the temperature of the furnace, several rheostats were placed in series with it. The temperature could then be kept constant, or could be slowly raised or lowered. The circuit was connected to 110 volts A.C.

Freezing-point Furnace. (see plate 3)

This was used in determining cooling curves. It was constructed of glass tubing wound with asbestos paper and nichrome wire. Slit windows were left on opposite sides of the apparatus (one is shown in figure 3.) in order that a source of light might be shone through one in order to allow inspection of the melt through the other.

The mixture being investigated was contained in a hard glass test tube in which a stirrer and a thermometer were placed along with the mixture. The tube was placed centrally in the furnace by means of a rubber stopper. Thus it was surrounded

by an air space and did not come in direct contact with the furnace.

In order to control the temperature of the furnace, the furnace winding was put in series with two rheostats, the whole circuit was then connected to 110 volts a.c. One of the rheostats was marked directly in temperatures of the interior of the furnace. This had been determined by a separated experiment. Thus, by setting the rheostat, the temperature of the furnace could be brought to the desired value.

The usual method of determining a cooling curve is to place the hot liquid, contained in a test-tube, into an air-space surrounded by a water or oil bath at a constant temperature below the melting point of the mixture. The temperature of the liquid is taken every minute, or half minute, and a graph is plotted of temperature against time. The curve obtained, called Newton's cooling curve, is hyperbolic in form. Freezing-points show up on such a curve as a jog or discontinuity; but if the heat effect is small, or if it takes place when the loss of heat is rapid, there may be no noticeable discontinuity.

This difficulty is overcome by keeping a constant difference of temperature between the cooling body and its surroundings. A straight line is thus obtained, and discontinuities due to small heat effects readily show up. This is "Plato's method". It is effected, in this case, by decreasing the temperature of

the furnace by approximately equal amounts at intervals of time from one to five minutes. The temperature is decreased by increasing the external resistance. The hot liquid then cools at a constant rate, the rate of cooling depending on the difference of temperature between the hot liquid and its surroundings. By keeping a difference of temperature of $5-10^{\circ}$ between the hot body and the furnace, a cooling rate of $0,1^{\circ}$ per minute is obtained. With such a slow rate, heat effects were readily obtained for the binary systems, but not for the ternary system. This was due to the exceedingly slow evolution of heat by the crystallisation of the ternary, which in turn was due to the slow rate of crystallisation.

Experimental ProceduresThe System: Picric Acid - 2:4-dinitrophenol1. By the Thaw-point, Meltingpoint method.

Since this is a semi-micro method, it was thought that it would be a suitable method for determining explosive systems.

In this determination, the picric acid and 2:4-dinitrophenol were used as supplied.

Mixtures of about one gram each, representing 0, 10, etc., up to 100% picric acid, were made up, melted to a homogeneous mixture on the water bath, rapidly cooled with stirring to obtain a homogeneous solid, and finally pulverized in an agate mortar. A uniform mix was thus obtained.

Melting-point tubes were then filled to a depth of about 4 millimetres with the powdered mixture, a thin glass stirring rod was then introduced, and the miniature apparatus was then heated in the melting-point furnace, described above. (see plate 2)

The first noticeable appearance of melting was taken as the softening or thaw-point. This was determined by means of the stirring rod as well as by visual observation. The temperature at which the last crystal in the liquid disappeared was taken as the melting-point. In order to ensure accuracy, the temperature of the furnace was raised at the rate of one degree every three minutes, or even slower.

The values for the softening and melting-points are given in table 1, and plotted in figure 10. The deduction of the eutectic values for temperature and composition is given below the table.

Since the values obtained were not in agreement with those found by Bogojawlenski, the system was redetermined by the following method:

2. By the Freezing-point method.

For this and subsequent determinations, picric acid and dinitrophenol which had been recrystallised twice from hot water, and dried on a water bath and in a sulphuric acid dessicator, were used.

Twenty grams of pure picric acid were introduced into a hard glass test tube, melted and heated to about $10-20^{\circ}$ above its melting point, and then placed in the freezing-point furnace (see plate 3) which was kept at about 10° below the melting point. The cooling curve was then determined in the manner described above, and from this curve the freezing-point was obtained. A similar procedure was carried out on various mixtures up to 50% picric acid, but for the mixtures the eutectic temperature was also determined. The mixtures were made by adding the required amount of dinitrophenol to the twenty grams of picric acid already in the test tube. This was then repeated, starting with pure dinitrophenol and adding

the required amounts of picric acid, up to 50%.

As a check on the freezing-points which were taken as the highest temperatures of several determinations for each mixture, the point where crystals first appeared in the liquid (seen through the window) was also recorded. If the visual and cooling curve values did not agree, the higher of the two was taken. This was usually the temperature obtained at the appearance of the crystals because these usually appeared before the cooling curve showed a halt. The heat liberated by the crystallisation was not sufficient, even at the slow rate of cooling employed, to raise the temperature to the true freezing-point, in many cases.

The values obtained by this method are given in table 2 (a) and are plotted in figure 11. The deductions from the curve are given below the table.

In table 2 (b) Bogojawlenski's and my results are given.

3. The system: Trinitrotoluene - 2:4:-dinitrophenol by the freezing-point method.

A similar procedure to that followed for picric acid - dinitrophenol was used. The values obtained for the freezing and eutectic points are given in table 3 and plotted in figure 12. Deductions from the curve are given below the table.

4. The system: Picric acid - Trinitrotoluene.

This system was not done by me. The values given in table 4 (a) are those of Taylor and Rinckenbach (30) who used the ordinary Newton cooling curve method, but who found the temperature of freezing by extrapolation back to the original curve. The values given in table 4 (b) are those found by Guia (31). His method was to take the temperature of initial crystallisation. All these results are given in figure 13. From the figure it can easily be seen that Taylor and Rinckenbach's results are more consistent. Therefore the curve is drawn through their results and the eutectic composition and temperature are deduced from it.

5. The systems: Picric acid - Gun cotton. and:

Dinitrophenol - Gun cotton.

The melting-points of various mixtures are given in table 5. The gun cotton was incorporated in the dinitrophenol by heating it in the molten dinitrophenol for one hour at 130°. After this time, no gun cotton was detected in the mixture by examination under the polarising microscope for the 1% mixture, but gun cotton was still present in the form of threads in the 10% mixture. In making the gun cotton-picric acid mixture, the required quantities were dissolved in acetone to secure a homogeneous mixture. The acetone was then evaporated off, and the resulting mixture was heated at 130° for one hour in order to get rid of as much acetone as possible. Although

all the acetone should come off above its boiling-point, (56°) it seems to be held by the viscous gun-cotton solutions.

6. The system: Picric acid - DNP - TNT. (see figure 14.)

The approximate composition of this system was found by assuming that the eutectic troughs were straight and could be represented by drawing straight lines from one pure component to the eutectic composition of the other two components. The three lines thus drawn met in a small triangle (see fig. 14). One of the points of this triangle would, it was hoped, be the ternary composition, or at least not far from it. The approximate ternary melting-point was determined by the micro method, but both the freezing-point and melting-point methods were used in determining the system. It was found, however, that owing to the exceedingly slow growth of the crystals, the freezing-point method did not give a definite heat effect, even with the slow rate of cooling employed, until many degrees after the first appearance of crystals. Therefore only the visual determinations were considered accurate enough to be used.

The compositions represented by the points of the triangle were first investigated. Since it was found that point 1 was higher than 2 and 3, and that point 3 had a higher melting-point than 2, it was thought that the eutectic would be found along the line AB in the direction A → B. Several determinations were then made along this line (4, 5, 6.). The lowest one did not have a melting point coincident with that found for the ternary

eutectic by the thaw-point of various of these mixtures. Therefore, although this point (point C on the graph), must be on a eutectic trough since the compositions on both sides of it have higher melting-points, it was not the ternary. The supposed eutectic trough, DC, was then drawn and the melting points of compositions on this line on both sides of C were determined. "C" however, was the lowest melting composition, and was called the ternary eutectic, since it was not thought worth-while to make further determinations. This "ternary" was then used for further experiments. All the values obtained for the system are given in table 6.

7. Densities.

The specific gravity bottle filled with the explosive mixture to be measured was allowed to stand for about ten minutes in the thermostat (less time was allowed for mixtures which were at temperatures representing supercooling of the mixture.), at the end of this time the stopper was put in, excess liquid was removed by means of shreds of filter paper, and the bottle was dried and weighed. The values obtained were used in determining viscosities. For mixtures, the temperature of the determination was approximately ten degrees above its melting-point.

The values for the complete system: picric acid - dinitrophenol at 130° are given in table 7 (a) along with the

the equation deduced from the data by the method of averages. The experimental and calculated values are plotted in fig. 15.

In tables 7 (b, c, d), the densities of various other mixtures are given.

8. Viscosities.

The viscosity and fluidity ($= 1/\text{viscosity}$) for the system picric acid - dinitrophenol were determined. The results are given in table 8 (a). The viscosity versus weight per cent of picric acid is plotted in figure 16, and the fluidity versus mole per cent of picric acid is plotted in figure 17.

The viscosity of various mixtures at various temperatures is given in table 8 (b).

In table 8 (c), the viscosity of the ternary eutectic at various degrees of supercooling is given. These values are plotted in figure 18.

9. Velocity of Crystallisation.

Owing to spontaneous crystallisation, it was found impossible to follow the velocity of crystallisation of pure picric acid and pure dinitrophenol to many degrees of supercooling. The results obtained, however, agree closely with those found by Bogojawlenski. (19) These are given in table 9 (a), and are plotted in figure 19.

The C.V. for TNT had not, as far as I know, been done before. By following one spontaneously induced nucleus with

a cathetometer, it was found to be possible to extend the measurements to room temperature. The results are given in table 9 (b) and are plotted in figure 19.

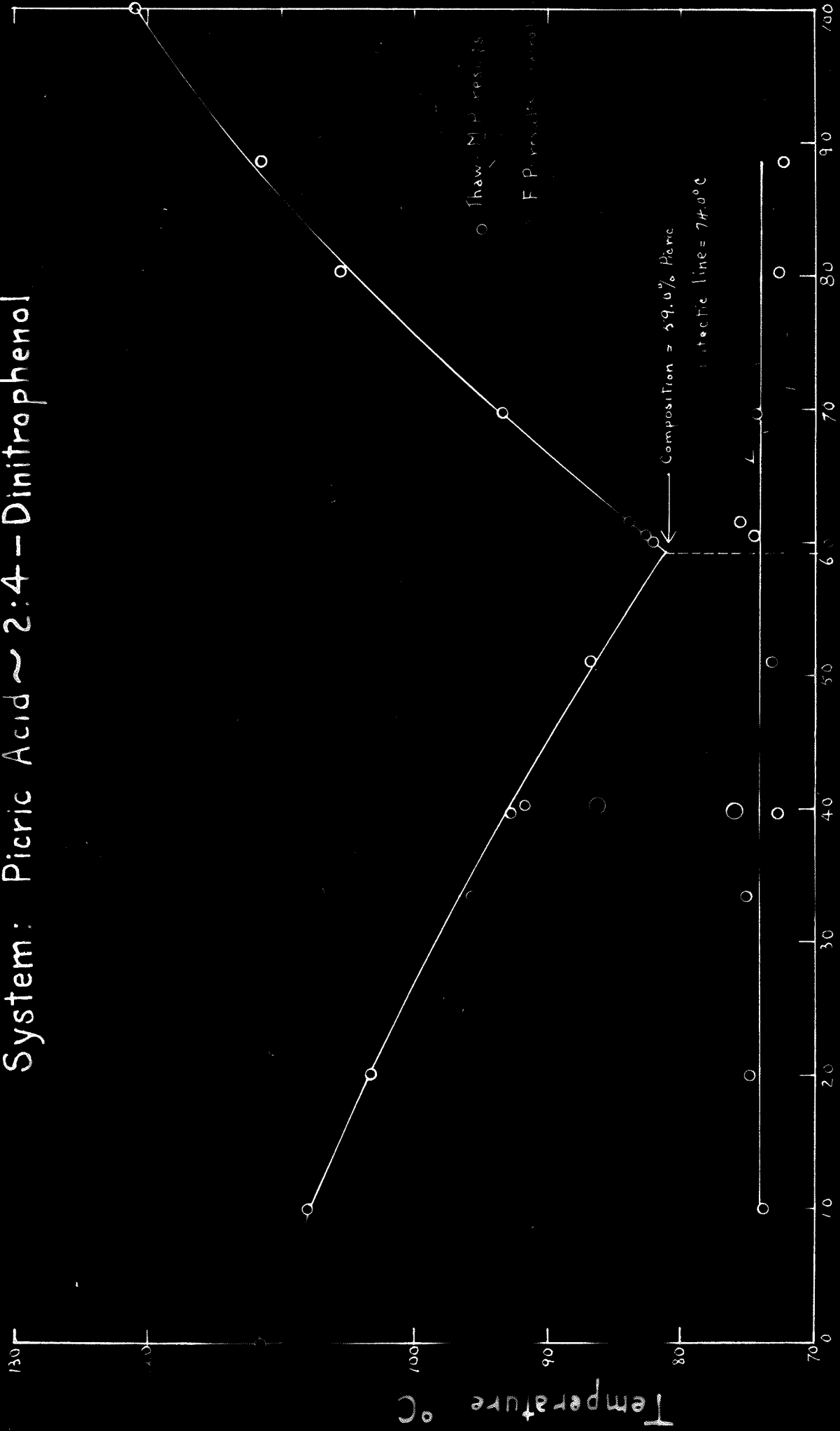
If the C.V. had been determined by following the progress of the crystallisation between fixed marks on the tube, as it had been for picric acid and dinitrophenol, it would not have been possible to extend the measurements on TNT to as many degrees of supercooling. Therefore, it seems that picric acid and dinitrophenol could have been more fully determined by following spontaneously induced nuclei as was done with TNT.

The C.V. for 55% picric acid + 0%, 1%, and 3% gun cotton in the system picric acid - dinitrophenol are given in table 9 (d) and plotted in figure 20. The C.V. for a 60% picric acid mixture are given in table 9 (c).

The velocity for the eutectic composition of the system: DNP - TNT is given in table 9 (e), while the values for the ternary eutectic are given in table 9 (f).

A number of these curves are plotted in figure 21. This was done in order that the various mixtures could be compared.

System: Picric Acid ~ 2:4 - Dinitrophenol



Weight % Picric Acid

Fig. 10

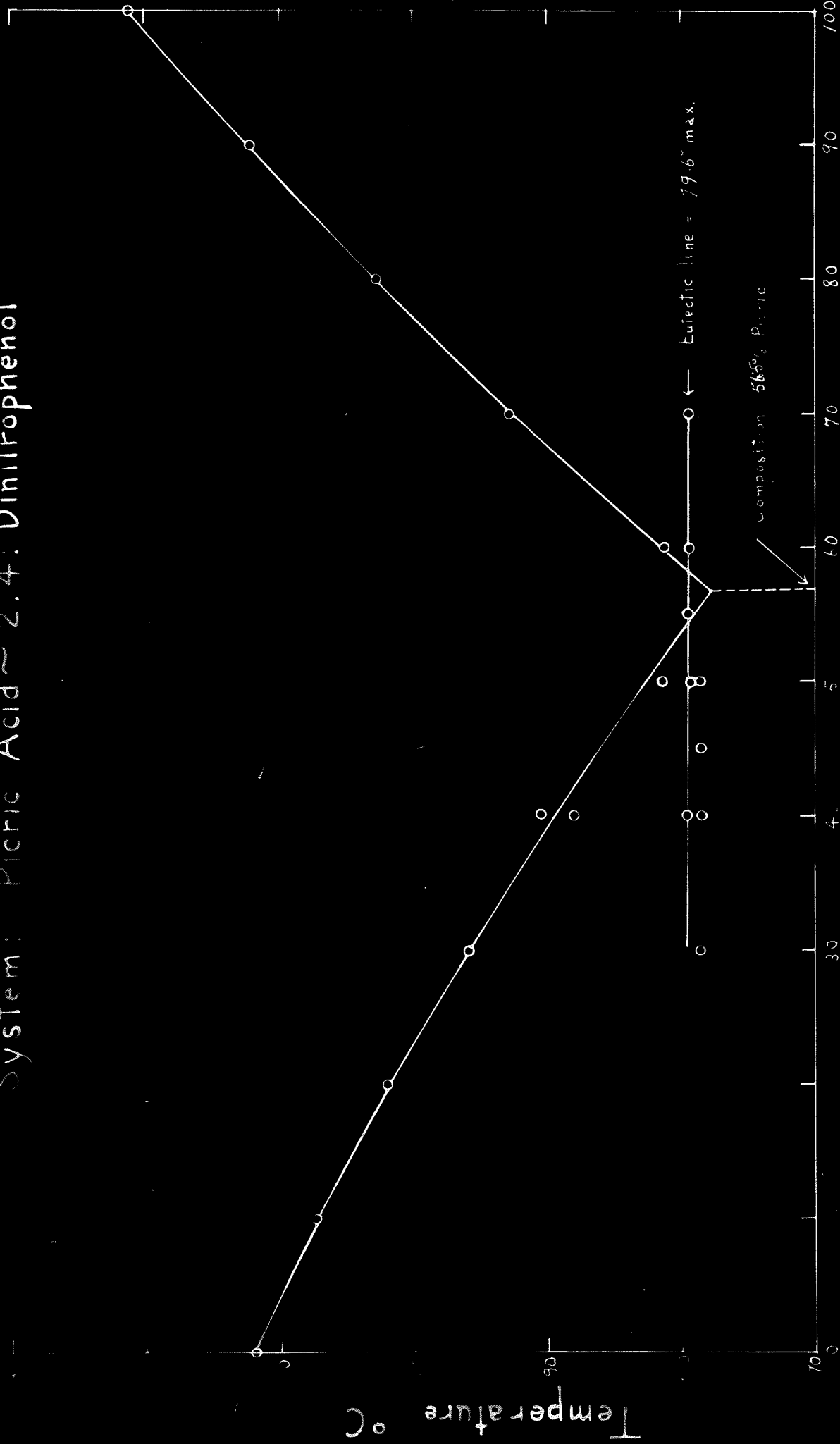
DATA

Table 1. The system: picric acid - dinitrophenol, by the thaw-point, melting-point method.

Composition % picric.	Softening point.	Melting point.
0.0 ^o	109.0 ^o	111.5 ^o
10.0	73.7	108.0
20.0	74.8	103.2
(21.6 by F.P method	none	95.7)
33.4	75.0	95.6
39.6	72.5	92.7
40.4	76.2	91.6
(same mix by F.P.	76.0 eutectic	86.3)
51.1	73.1	86.7
60.0	----	82.0
60.5	74.4	82.5
61.5	75.4	83.7
69.6	74.2	93.4
80.2	72.5	105.5
88.5	72.3	111.5
100.0	119.0	121.0

The eutectic temperature indicated by the thaw-points is approximately 74^o; by the ordinary cooling curve, it is 76^o, and from the graph (fig. 10), it is 81^o. From the graph, the

System: Picric Acid ~ 2.4: Dinitrophenol



Weight % Picric Acid
Fig. 11

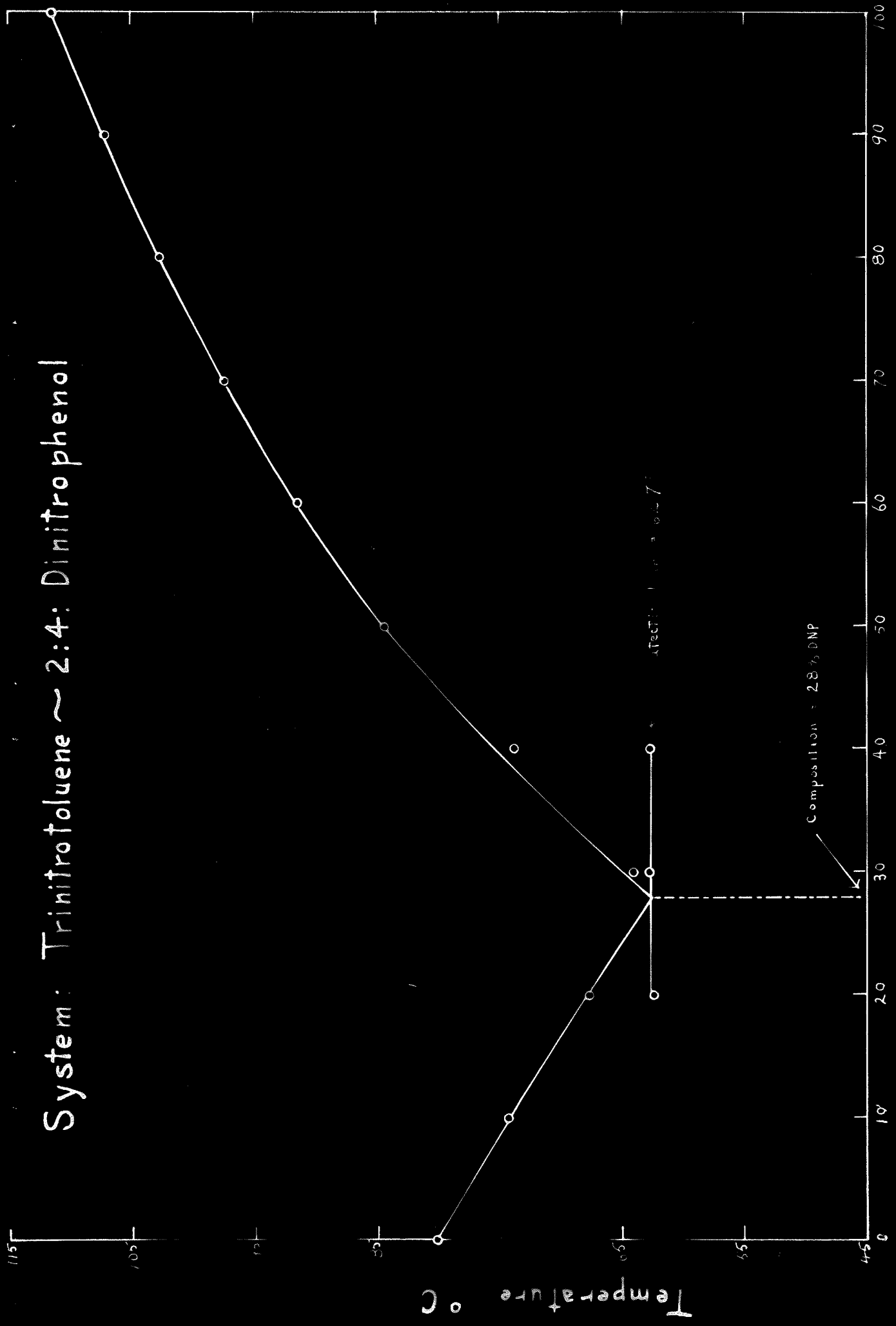
composition of the eutectic was 59% picric acid. A 60% mixture was thought to be close enough for making tests.

Table 2 (a) The system: picric acid - dinitrophenol, by the freezing-point method. (see figure 11)

Composition % picric	Eutectic halt	Freezing point
0.0	---	111.9
10.0	---	107.3
20.0	---	102.0
30.0	78.4	95.9
40.0	78.5	88.0
50.0	78.6	81.0
<hr/>		
40.0	79.3	90.2
50.0	78.8	80.9
55.0	79.2	----
60.0	79.0	80.8
70.0	79.1	92.5
80.0	----	102.4
90.0	----	111.7
100.0	----	120.7

The eutectic composition and temperature from the graph (figure 11) are: 56.5% picric acid and 79.3°. A 55% mixture was used for making the tests. These values were thought to be more reliable and were used instead of those found by

System: Trinitrotoluene ~ 2:4: Dinitrophenol



Reaction: $100 + 0.77$

Composition = 28% DNP

Weight % Dinitrophenol

Fig. 2

by the other method. The eutectic composition and temperature for this system, as determined by Bogojawlenski and myself, are given in the following table:

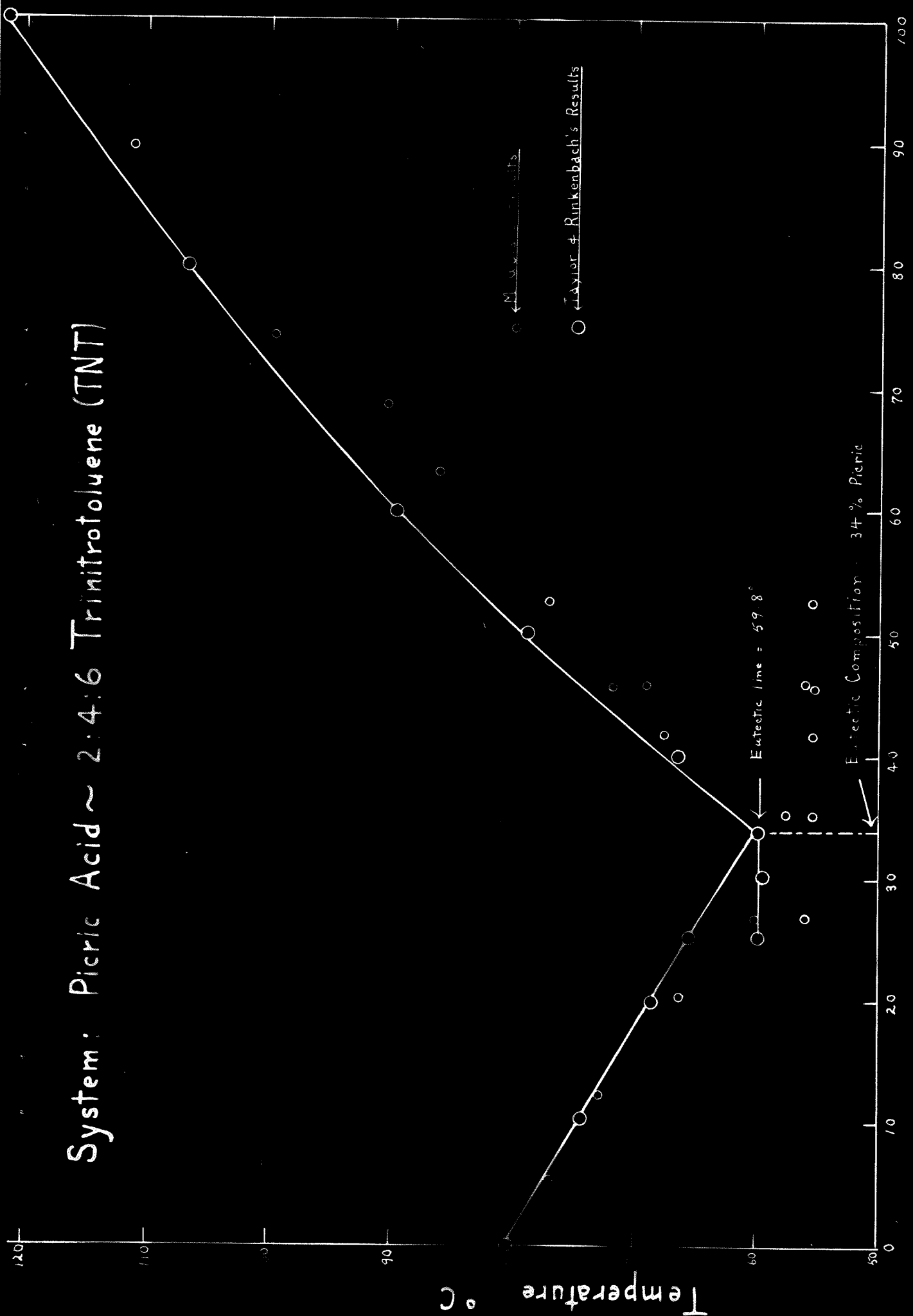
Table 2 (b). The eutectic temperature and composition of the system: picric acid - dinitrophenol.

Observer	Method	Melting-point	Composition wt. % picric.
Bogojawlenski	-?-	81.0	53.0
Britchard	M.P. (micro)	74.0 observed 81.0 from graph.	59.0
"	F.P. (macro)	79.3 (highest)	56.5

Table 3. The system: TNT - DNP by the freezing-point method.

Composition % DNP	Eutectic halt	Freezing- point	Method used to find the F.P.
0.0	----	80.1	heat effect.
10.0	----	74.2	" "
20.0	62.4	67.7	" "
30.0	62.7	64.0	heat and visual
40.0	62.7	73.7 73.4	visual heat effect.
50.0	----	84.3 83.6	visual heat effect
50.0	----	84.7	heat and visual
60.0	----	91.4 91.2	visual heat effect
70.0	-----	97.4 97.1	visual heat effect
80.0	----	102.6 102.1	visual heat effect
90.0	-----	107.0	visual and heat
100.0	----	111.2	heat effect.

System: Picric Acid ~ 2:4:6 Trinitrotoluene (TNT)



Weight % Picric Acid

Eutectic line = 59.8°

Eutectic Composition = 34% Picric

Maxwell's Results

Taylor & Rinkenbach's Results

These values are plotted in figure 12. From this graph, the eutectic temperature and composition is given as: 62.7° and 28% by weight of dinitrophenol.

Table 4 (a) The system: picric acid - TNT (literature values)

Composition % picric	Eutectic halt	Freezing-point (by extrapolation)
100.00	----	121.8
80.03	----	106.7
60.09	----	88.5
50.08	----	78.85
40.09	----	66.3
33.70	59.8	----
30.20	59.4	----
25.24	59.8	65.35
19.99	----	68.4
10.45	----	74.35
0.00	----	80.27

The above results are those of Taylor and Rinkenbach (30). They are plotted in figure 13.

Guia's results are given below in table 4 (b):

Table 4 (b). Same system. Also plotted in figure 13.

Composition % picric	Eutectic halt	Freezing-point (initial cryst.)
0.0	----	80.6
5.53	----	76.9
12.38	----	72.7
20.37	----	66.2
26.97	-56.0	60.0
35.31	55.4	57.5
41.91	55.4	67.5
45.56	55.3	71.7
45.95	56.0	69.0
52.62	55.3	77.0
63.12	----	86.1
68.69	----	90.2
74.34	----	99.5
89.90	----	111.2
100.00	----	121.7

Taylor and Rinkenbach's results can be seen to be better than those of Guia from the graph. (figure 13.) Therefore, the eutectic composition and temperature were deduced from their results. These values are 34% picric and 59.8°. The values used in plotting the ternary, however, were those given by the "Critical Tables". These were: 59.7° and 36 mole per cent (or 36.2 weight %) of picric acid.

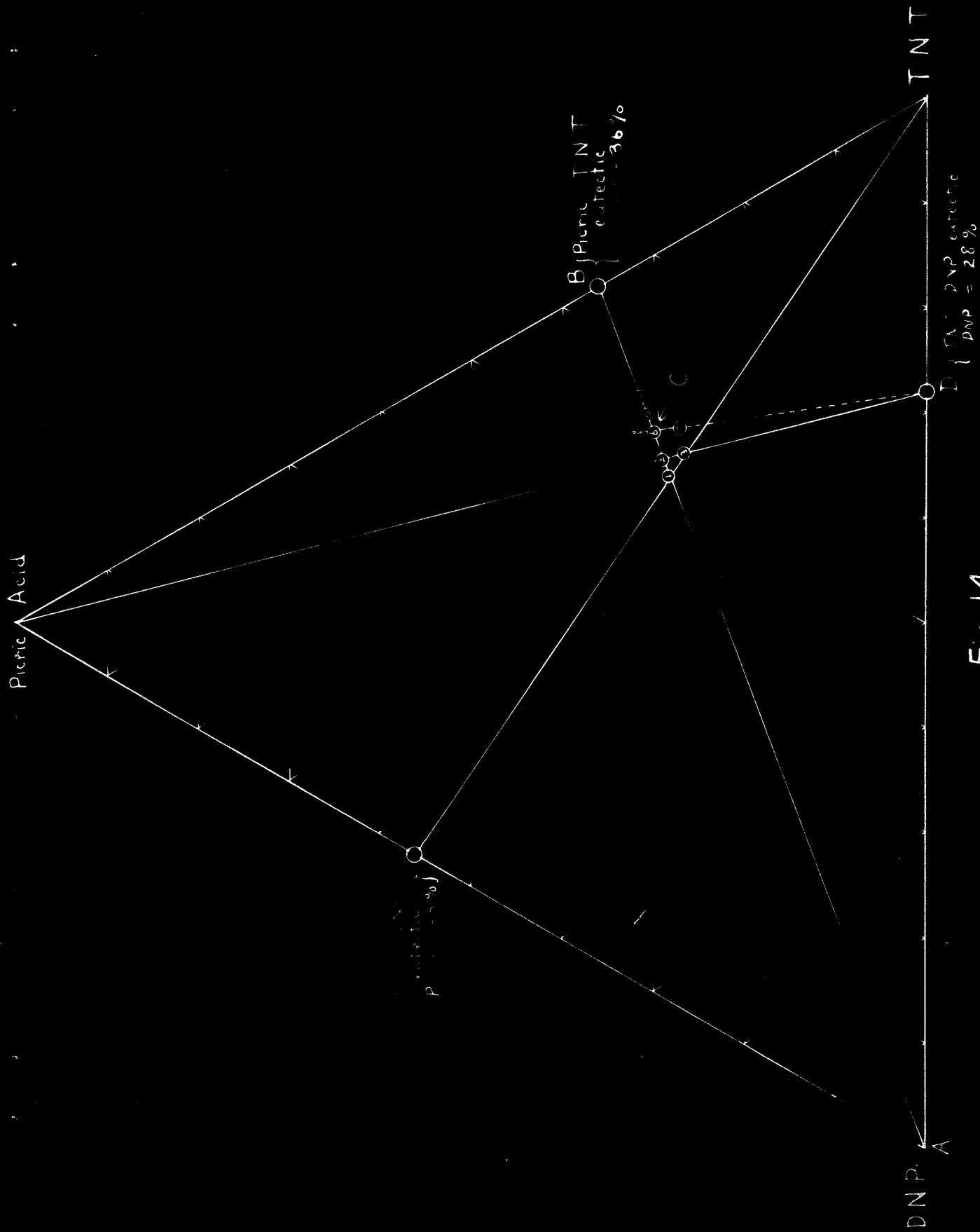


Fig. 14.

Table 5. The effect of gun cotton on the melting-point.

Composition	Melting-point.
DNP alone	111.5
DNP + 1% G.C.	112.0 - 112.5
DNP + 10% G.C.	112.0
Picric acid alone	120.5 - 121.0
Picric + 5% G.C.	118 - 122

The viscosity of the mixtures prevented accurate determinations, but it was concluded that in the concentrations of gun cotton that were used, there was no measurable effect.

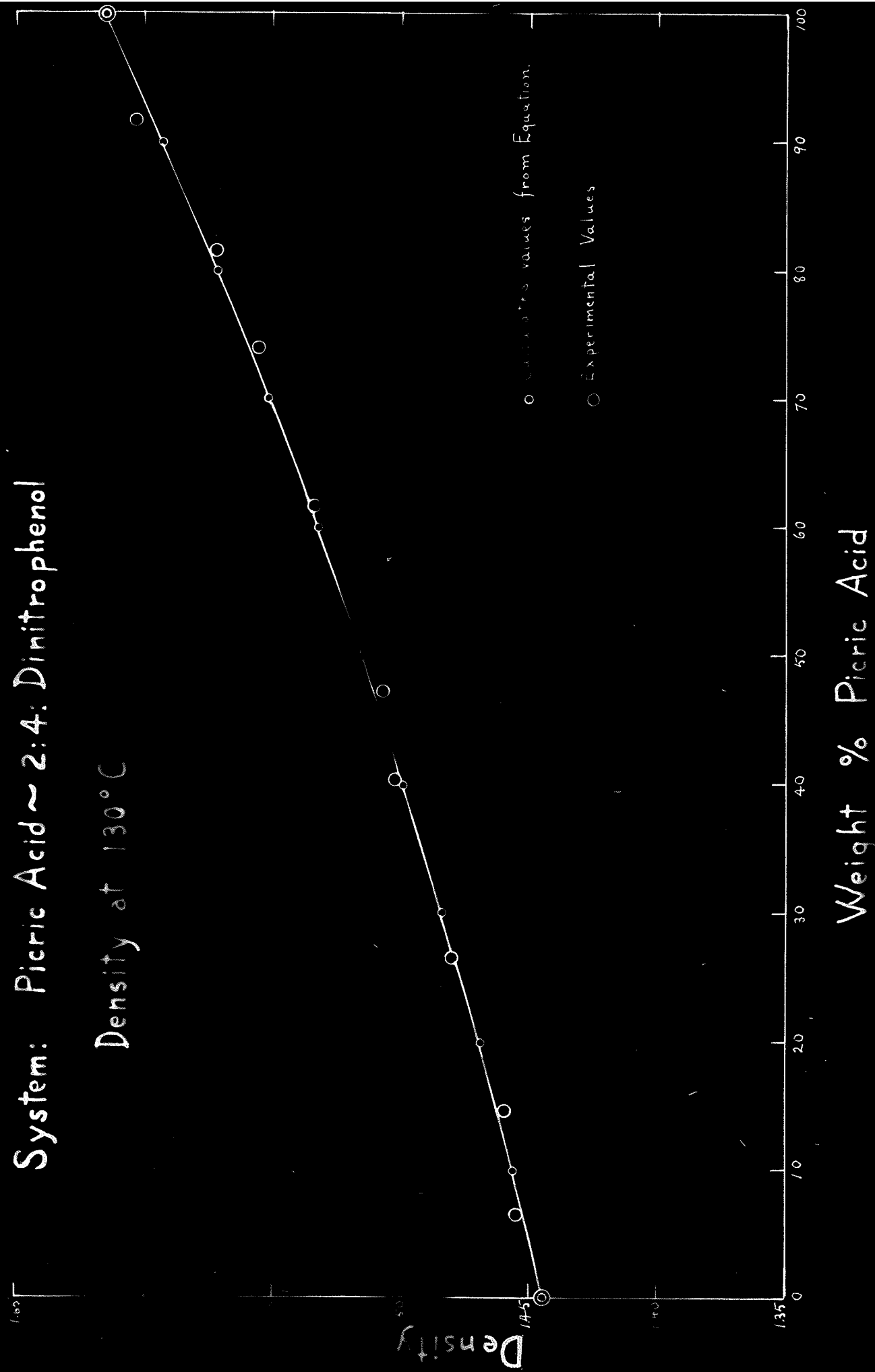
Table 6. The system: picric acid - DNP - TNT, (see fig.14.)

Number on graph	Composition.			Ternary eutectic	Melting-point	Method
	picric	TNT	DNP			
1	28	50	22	45.4	52.5	micro
2	29	51	20	45.7 - 47.0	49.2	micro
	same			40.6?	46.8	macro (heat)
3	27	52.5	20.5	45.6	49.5	micro
4	31	56	13	----	52.5	macro (visual)
5	same proport.15			----	49.3	" "
6	30	53	17	----	48.5	" "
7	27	55	18	----	49.5	" "
8	32	same proportions			51.0	" "

The composition of the ternary was taken as that of number 6: 30% picric, 53% TNT, and 17% DNP. The true ternary temperature was taken as 45 -46, not 48.5.

System: Picric Acid ~ 2:4: Dinitrophenol

Density at 130°C



Weight % Picric Acid

Fig. 1

Table 7 (a) Density of the system: picric acid - dinitrophenol,
at 130°. (see figure 15)

Composition % picric	Density gm/cc.
0.00	1.445
6.49	1.455
14.63	1.458
19.92	1.470
26.50	1.480
40.36	1.502
47.20	1.506
61.60	1.533
74.06	1.555
81.50	1.572
91.55	1.603
100.00	1.614

The equation deduced from the above, by the method of averages is:

$$D_{130} = 1.445 + 1.078 \times 10^{-3} p + 6.24 \times 10^{-6} p^2$$

where D = the density, and p = weight % picric acid.

Table 7 (b) Density of some mixtures of the above system
at 90°.

Composition % picric	Density gm/cc.
60%	1.58
55%	1.54
55% + 5% G.C.	1.54 (gun cotton has little effect, if any.)

System: Picric Acid ~ 2,4-Dinitrophenol
Fluidity at 130°C

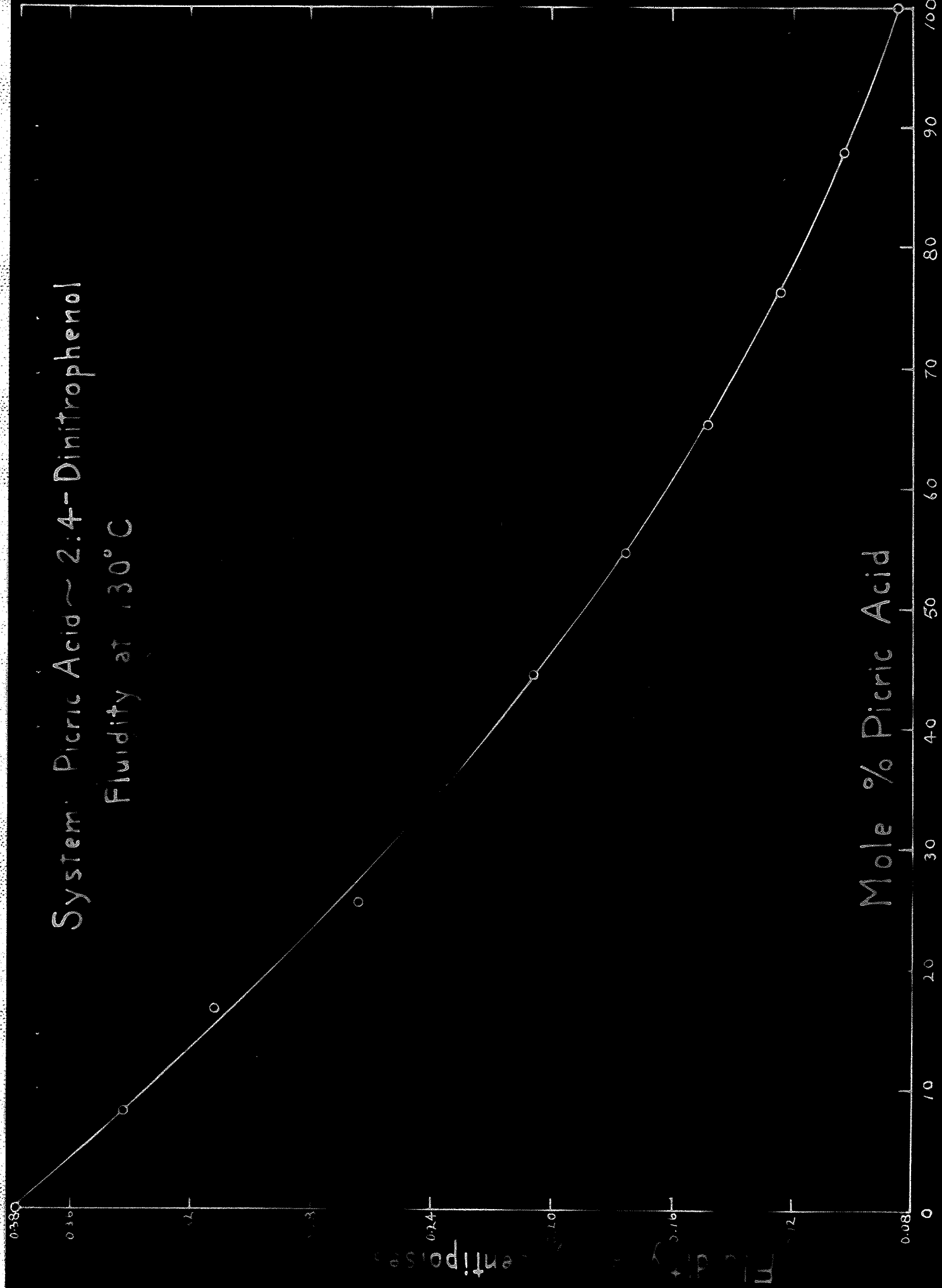
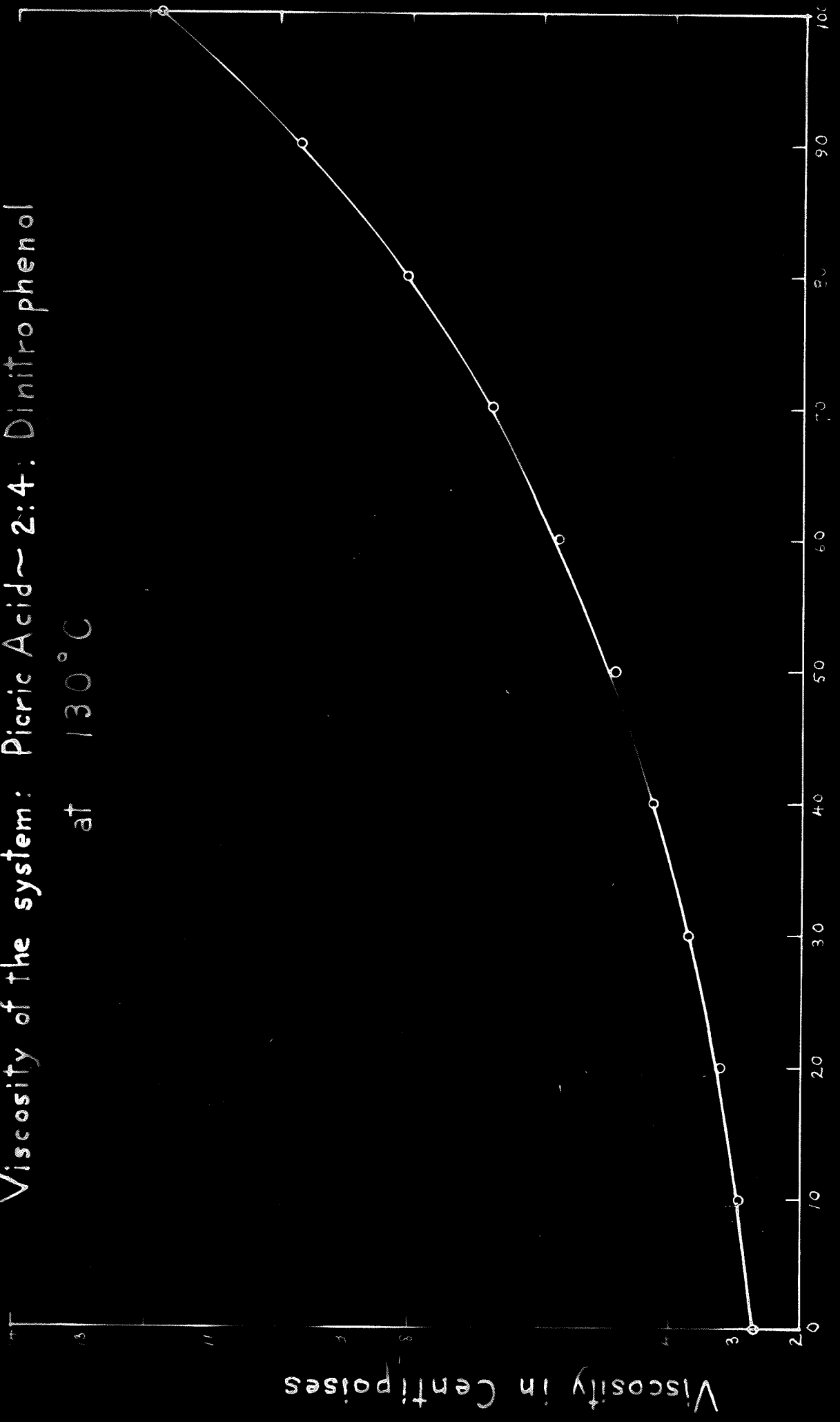


Fig. 17

Viscosity of the system: Picric Acid ~ 2:4: Dinitrophenol
at 130°C



Weight % Picric Acid
Fig. 16

Table 7 (c). Eutectic composition of TNT - DNP (28% DNP)

Density at 72.8° = 1.47

Table 7 (d). Density of the ternary composition.

Temperature	Density.
56.0	1.54
26.0	1.56

Table 8 (a). Viscosity of the system: Picric acid - DNP

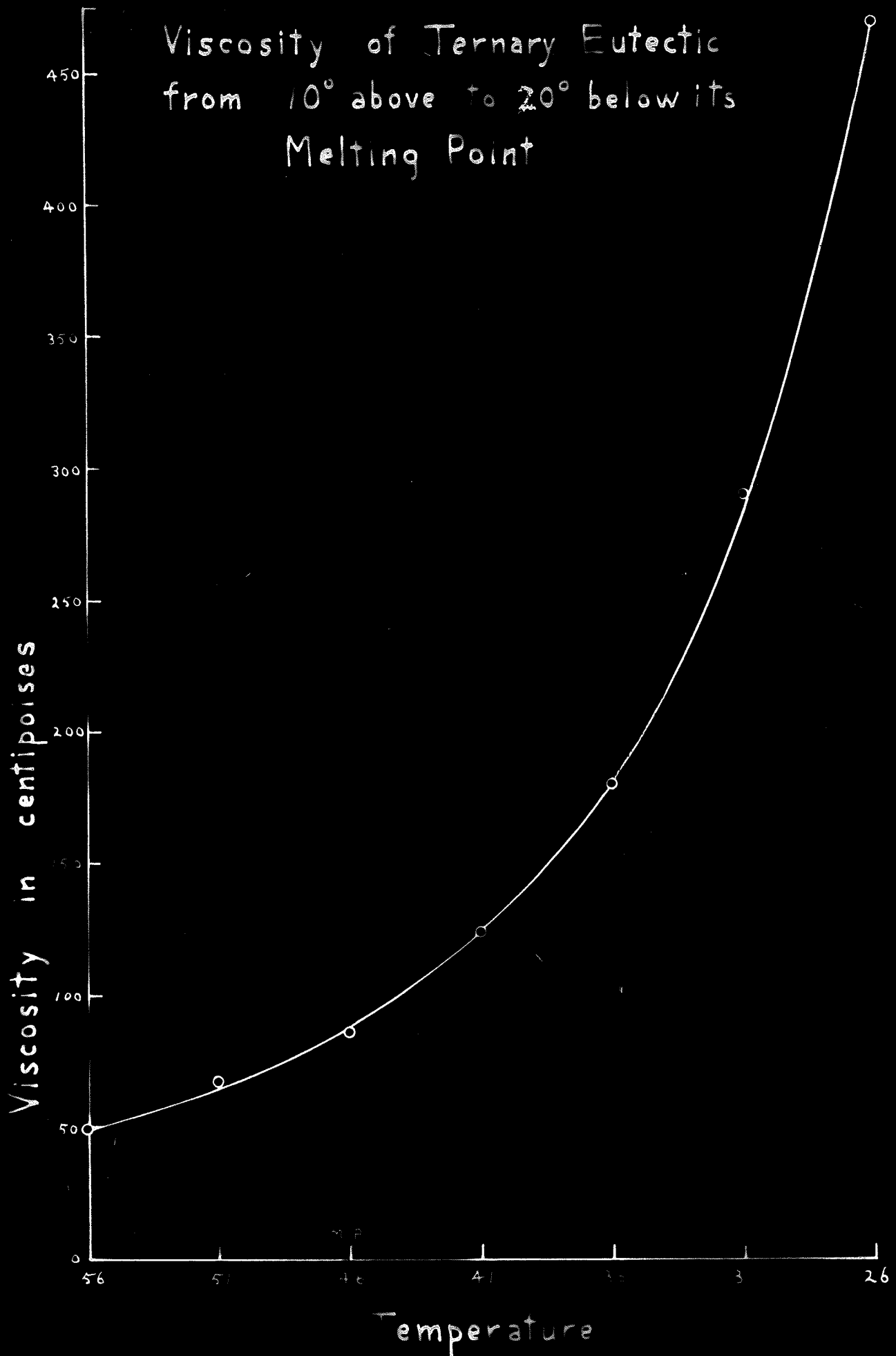
at 130° (see figures 16 & 17)

Composition		Viscosity in centipoises	Fluidity = 1/viscosity.
Wt. % picric	Mole % picric		
0.0	0.0	2.64	0.379
10.0	8.19	2.93	0.342
20.0	16.72	3.22	0.311
30.0	25.62	3.71	0.269
40.0	34.90	4.25	0.235
50.0	44.54	4.85	0.206
60.0	54.64	5.73	0.175
70.0	65.21	6.74	0.148
80.0	76.20	8.04	0.124
90.0	87.80	9.68	0.103
100.0	100.00	11.78	0.085

Table 8 (b).

System	Composition	Temperature	Viscosity in centipoises.
picric-DNP	60% picric	90°	17.96
"	55% "	90	15.14
"	55% + 1% GC.	90	113.7
"	" + 5% GC.	90	acts like glue
TNT - DNP	28% DNP	72.8	12.96

Viscosity of Ternary Eutectic
from 10° above to 20° below its
Melting Point



Temperature

Fig. 18

Table 8 (c). Viscosity of Ternary eutectic from approximately 10 degrees above to 20 degrees below its M.P.

Temperature	Viscosity in centipoises.
56	49.3
51	67.4
46	86.5
41	124.2
36	180.2
31	290.0
26	470.0
0	26,600.0 (not a true viscosity due to sticking to the sides of the viscosimeter:)

These values are plotted in figure 18.

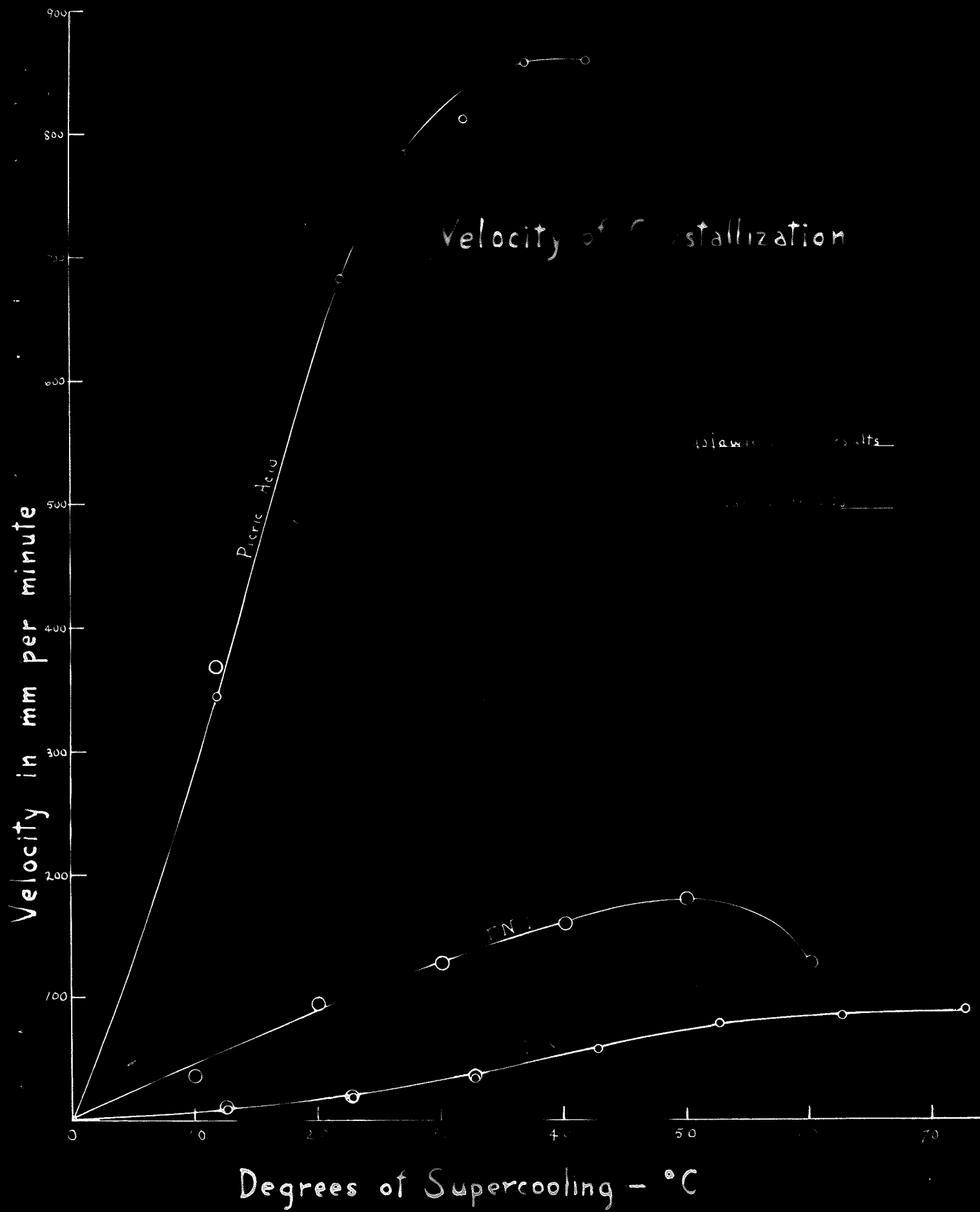
Table 9 (a). Velocity of Crystallisation of picric acid and 2:4-dinitrophenol.

Picric Acid.

Temperature	Degrees of Supercooling	Velocity in mm/minute	With Gun cotton
		Bogojawlenski. Pritchard.	
110	12	343	366 ±18
100	22	681	
95	27	783	
90	32	811	
85	37	858	
80	42	858	

Dinitrophenol

100	12.8	6.35	7.52	5.8
90	22.8	16.2	18.0	15.3



Degrees of Supercooling - °C
Fig. 19

Dinitrophenol (con't)

Temperature	Degrees of supercooling	Velocity in mm/min. Bogojawlenski Pritchard.	
80	32.8	30.3	35.4
70	42.8	55.7	
60	52.8	76.8	
50	62.8	83.2	
40	72.8	88.3	

All the above values are plotted in ~~the~~ figure 19.

Table 9 (b). C.V. for T.N.T.

Temperature	Degrees of Supercooling	Velocity in mm/minute.
22.0	58.1	127
30.0	50.1	171
40.0	40.1	158
50.0	30.1	126
60.0	20.1	94
70.0	10.1	35

These values are also plotted in figure 19.

Table 9 (c). C.V. for 60% picric acid in the system picric acid - dinitrophenol. (see figure 21, A.)

Temperature	Degrees of Supercooling	Velocity in mm/minute.
70	9.3	1.28
60	19.3	2.05
50	29.3	1.89
40	39.3	1.02
30	49.3	0.47

Effect on the velocity of Crystallization of Adding Gun Cotton to the Eutectic Composition

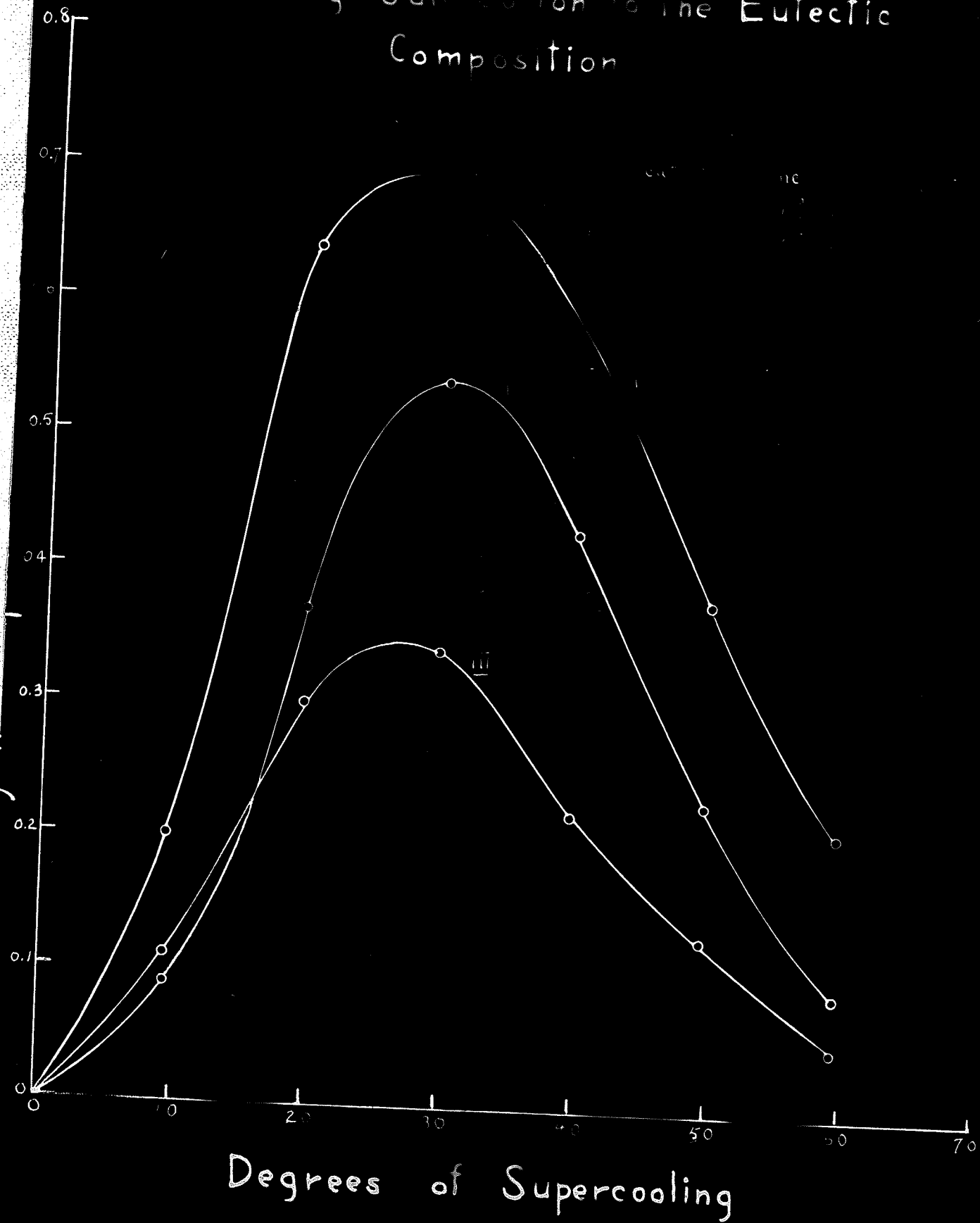


Fig 20

Table 9 (c) con't.

Temperature	Degrees of Supercooling	Velocity in mm/minute.
20	59.3	0.14
13	66.3	0.075.

Table 9 (d) C.V. of 55% picric acid in the system:

picric acid - dinitrophenol (see figures 20 & 21)

Temperature	Degrees of Supercooling	Velocity in mm/minute		
		0% GC	1% GC	3% GC.
70	9.3	0.09	0.20	0.11
60	19.3	0.37	0.64	0.30
50	29.3	0.54	0.69	0.34
40	39.3	0.43	0.44*	0.22
30	49.3	0.23	0.38	0.13
21	58.3	0.09	0.21	0.05

Table 9 (e) C.V. for the eutectic composition of the system:

TNP - DNP. (28% DNP) (see figure 21,B)

Temperature	Degrees of Supercooling	Velocity in mm/minute.
60	2.7	0.13
50	12.7	0.77
40	22.7	0.76
30	32.7	1.81

Table 9 (f) C.V. for the ternary eutectic. (see fig. 21, D.)

Temperature	Degrees of Supercooling	Velocity in mm/minute.
36	10	0.051
26	20	0.052
0	46	0.014

* Not plotted.

Velocity of Crystallisation of Two and Three Component Systems

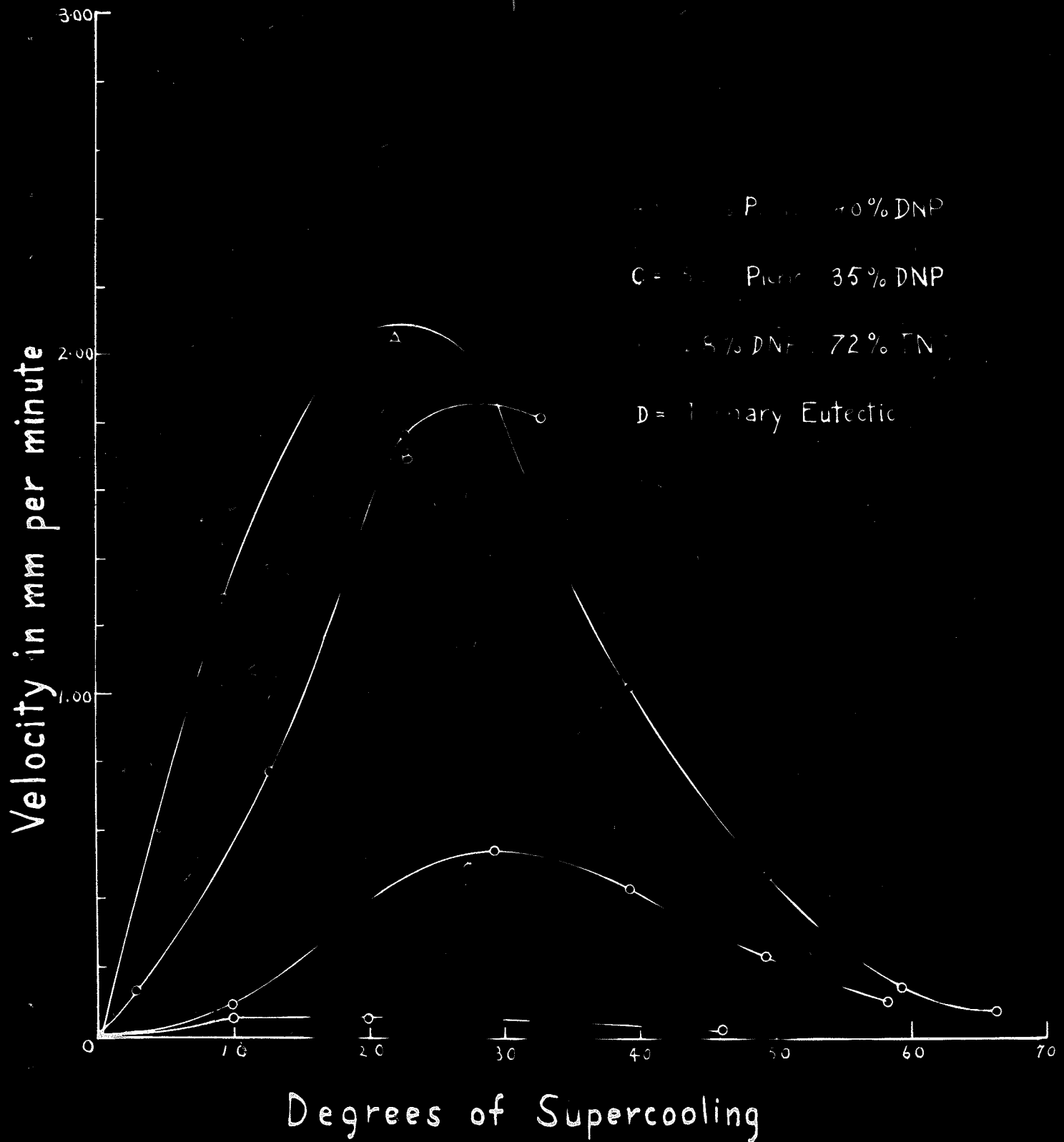


Fig. 21

Discussion of the Results

The system: Picric acid - 2:4 - dinitrophenol.

Owing to the discrepancy between the results obtained for the eutectic by the two methods (see table 2 b), no definite composition can be deduced for it. It seems, however, that the composition should be closer to 60% picric acid than to 50% (as Bogojawlenski's results would indicate); because the C.V. for DNP is very much slower than that of picric acid and therefore the freezing-point method (fig. 11) would tend to give results that are too low on the DNP side of the diagram. The C.V. would not affect the melting-point method, however. Therefore, this method might be the more accurate of the two. From the two different methods, the eutectic composition would seem to lie between the limits 55% and 60% picric acid, with 59% being favored since this value is given by the melting-point curve (fig. 10) and also by the intersection of the freezing-point curve with the eutectic line on the picric acid side of the diagram (fig. 11). The eutectic temperature given in figure 10 is not a reliable one because it does not coincide with intersection of the melting-point curve at the eutectic ~~xxxxx~~ composition, and also because it could be easily lowered (first appearance of thawing) by the presence of even small amounts of impurities. The value given in figure 11 is more reliable because it was obtained by the heat effect.

When we consider Bogojawlenski's results for this system, it seems that the eutectic temperature which he obtained (81°) is reasonable, but the value for the composition is not in agreement with those obtained in this investigation. A mean value of the three determinations would probably be satisfactory. This would then give:

56

56% picric acid and a temperature of 80° .

With sufficient care, it seems that the thaw-point, melting point method should give accurate results for the melting-points, but unless the components are very pure, the eutectic temperature would be too low.

System: Trinitrotoluene - Dinitrophenol.

The equilibrium diagram for this system is much more satisfactory than that for picric acid - dinitrophenol. This may be due to the fact that a visual check (first appearance of crystals) was made on the freezing-points. Although this method is subjective, it can not give values that are too high because crystals must appear before they can be seen. These visual values, if they are carefully observed, serve as a check on determinations which depend on the heat effect.

System: Picric acid - Trinitrotoluene.

By inspection of figure 13, it is easily seen that the results of Taylor and Rinkenbach are the better. Their method of determining the freezing-points; i.e., by extrapolating

from the maximum obtained on the cooling curve back to the original curve, is claimed to be justified (see ref.) and would seem to be so from the consistent results they obtained (c.f. those of Guia.):

System: Picric acid - Dinitrophenol - Trinitrotoluene.

It was found to be impossible to determine the freezing-point of this system by the heat effect. Even the visual method was uncertain due to a natural opalescence of the melt. However, the composition which was called the ternary may be the true one. The discrepancy between its melting point and the thaw-point may be due, as in the picric acid - dinitrophenol system (see fig. 10), to impurities which cause the melting-point to be lowered below the true value. These impurities could easily be present since none of the components was absolutely pure, as indicated by its melting-point.

Viscosity and Velocity of Crystallisation

From figure 16, it can be seen that the viscosity of all mixtures of the system: picric acid - dinitrophenol, lies between the viscosities of the pure substances, on a smooth curve. A similar curve is given for the fluidity versus mole % picric acid, but it is not the straight line required by Bingham. But then, he required fluidity to be plotted against temperature. At any rate, there is no doubt that the lowest and highest viscosities of the system

(and also the lowest and highest fluidities of the system) lie between those of the pure substances.

From table 8 (a) and figure 16, it can be seen that picric acid is approximately 4.5 times as viscous as dinitrophenol at the same temperature. But its velocity of crystallisation is about 10 times as great as that of DNP at comparable degrees of supercooling. Although the viscosity and C.V. were done at different temperatures, it is probably safe to assume that at the same temperatures the same ratios between the viscosities would hold. Therefore, although viscosity may have an effect on the C.V., we can not compare different substances in this way because the C.V. clearly depends on the nature of the substance also. Thus all the comparisons that are made here will be rather loose ones.

It was mentioned in the introduction (theoretical) , that the C.V. of mixtures was irregular due to concentration changes. If the eutectic composition is used, however, there should be no concentration changes, and constant values of the C.V. should be obtained.

When picric acid and dinitrophenol are mixed, it might be expected that the C.V. would lie on a curve between the values of the pure substances, as in the case of viscosities. But this was not the case. A 60% picric acid mixture, which might be expected to have a velocity higher than that of DNP,

at the same temperature (i.e., at the same fixed temperature, not at the same degree of supercooling.), is actually found to be only 1/85 that of DNP. Thus there must be some other effect which takes place, notably the tendency of the molecules of DNP to interfere with the formation of the crystal lattice of picric acid, and vice versa. A second component, then, acts as though it increases the 'internal' viscosity, without the measured viscosity being appreciably altered.

The concentration of the second component also has an effect on the C.V., as is to be expected. For example, a mixture containing 60% picric acid (Shellite) has a maximum C.V. of almost 4 times that for a 55% mixture. Thus, for this system, the C.V. seems to depend on which side of the eutectic one chooses a mixture. If instead of 60% picric acid, a 55% mixture had been used, "Shellite" would have been much more suitable for pouring into shells.

By adding 1% of gun cotton to the 55% picric acid mixture, its viscosity is increased approximately 8 times, but its C.V. is also increased about 1.2 times. However, this can be explained on the basis of the work of Freundlich and Oppenheimer (21). They showed that non-spherical colloidal particles increased the C.V. Since gun cotton has been shown to be a long chain molecule of probably colloidal dimensions, then the increase in the C.V. is readily explained. 3% of gun cotton increases the

viscosity beyond the practical limit (30 poises) without reducing the C.V. very much. (see figure 20).

Using colloidal materials to increase the viscosity of a mixture in order to reduce the C.V. will probably never succeed because although the viscosity is increased, the crystals can still grow between the colloidal particles just as though the crystal nuclei were in the original liquid, unless the concentration of the colloidal particles is great enough to prevent growth between them. By adding truly dissolved substances, however, even though the viscosity may not be materially increased (it may even be decreased), a so called "Internal Viscosity" is created; i. e., the different molecules get in one another's way and slow down or prevent the formation and growth of lattices. This can not be just the effect of lowering the melting-point of the substance and therefore increasing the viscosity as the lower temperatures are reached; because the ternary mixture, at the same temperature, has only 1/8 the C.V. of 55% picric + 1% gun cotton, yet its viscosity at the same temperature is less than 1/2 that of the shellite-gun cotton system. The comparison is a loose one since the ternary had over 50% TNT, which the other system does not have. However, as can be seen from figures 19 and 21, TNT acts in much the same way as DNP.

An examination of figure 21, will show that the two component systems have C.V.'s that are much higher than those of the three component system made from them. These are all at different temperatures, although at the same degree of supercooling, therefore there is no doubt that since the ternary has the lowest melting-point, its viscosity must be greater than that of the other systems. However, this is not the only reason for its having a low C.V., because an examination of figures 18 and 21 shows that the viscosity may increase tremendously without the C.V. being materially affected. Thus, although there can be no doubt that a greatly increased viscosity lowers the C.V., the relation is not a direct one. If one could measure what I have called the internal viscosity, a closer relation might be found.

It is to be noted that none of the curves which I have obtained, even for TNT, shows an extended maximum for the C.V. Thus Tammann's ideal curve has not been found for these systems. However, the existence of a maximum at 20 - 30 degrees of supercooling has been found, but it immediately falls again.

It seems to me, that the C.V. will be found to depend, not on the heat liberated on solidification, and viscosity alone, as Tammann's has suggested, but also on other factors such as surface tension, dipole moment and other such expressions of attractive or repulsive forces. The C.V. curve would, in

short, be a curve representing a balance between the forces tending to form the crystal lattice, and those tending to prevent its formation; e.g., viscosity, kinetic movement, etc. Different rates of change in these forces with falling temperature would then explain the form of the C.V. curve. If this is true, then in order to explain Tammann's curve for the C.V., systematic measurements of many more properties in the region of supercooling would have to be ~~made~~ made.

Conclusions

1. The equilibrium diagram of picric acid - 2:4-dinitrophenol has been determined. Its eutectic composition probably lies between the limits of 55% and 60% picric acid by weight, with a melting-point of about 80°.
2. The equilibrium diagram of Trinitrotoluene - 2:4 - dinitrophenol has been determined. It has a eutectic composition of 28% dinitrophenol by weight and a melting point of 62.7°.
3. Determinations were made on several compositions of the system: Picric acid - dinitrophenol - trinitrotoluene. These indicated a possible ternary eutectic at 30% picric acid, 53% TNT, and 17% DNP by weight, with a melting point of 45 - 48°.
4. A number of densities were determined for use in calculating the viscosities of various mixtures.
5. The viscosities of the system: picric acid - dinitrophenol were found to lie on a smooth curve between maximum and minimum values which were those of the pure substances. However, from

the contour of the viscosity curve, but more especially from that of the fluidity curve, it can be seen that the viscosities are not strictly additive, indicating that possibly the two components have some effect upon one another.

6. Although the viscosities were nearly additive, the c.v.'s were not; i.e., the crystallisation velocity of the mixture was always less than that of the pure components.

7. Tamman's C.V. curve was not realized for the pure substances and mixtures studied, although a maximum C.V. was obtained in most cases, but not all, at about 20 - 30° of supercooling.

8. Comparisons of viscosities and C.V.s showed that a direct relation between them did not exist, although there can be no doubt that increasing the viscosity considerably, reduces the C.V.

9. The addition of gun cotton, and presumably other colloidal materials would act somewhat the same, increased the viscosity of the system called Shellite considerably, but it did not have the desired effect on the C.V.

10. Addition of a third component (non-colloidal), lowered both the melting-point and the C.V. It was the more promising of the two methods.

11. The ternary eutectic mixture can no longer be considered to be Shellite, owing to the large proportion of TNT that was used. However, by adding a high melting-point, third component

such as picramide, somewhat the same reduction in the C.V. may be effected without unduly changing the Shellite mixture.

12. Since the lowest allowable melting-point for an explosive of mixture of explosives is 62° , the ternary mixture melting at 45° would not be suitable, but other mixtures of higher melting-point might be.

13. By changing the composition of the Shellite from 60% picric acid to 55% picric acid, a considerable improvement in its shell-filling properties might be effected.

14. Qualitative tests showed that the ternary mixture would completely cool (supercool) to room temperature and would remain liquid, or as a liquid - solid mixture for six hours or more. There is no doubt then that such a mixture would have desirable shell-filling properties if its low melting-point were not objectionable.

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