T H E S I S

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A Phase Rule Study of Mixed Derivatives of Alcohols

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A PHASE RULE STUDY OF MIXED DERIVATIVES OF ALCOHOLS

Introduction

Many attempts have been made to quantify one alcohol mixed with another on the basis of variation of some physical property of the alcohols as mixed. Numerous studies have been made on the density gradation, and refractive index changes, as two alcohols are mixed. Mixtures of alcohols have even been oxidized to their respective acids and quantified according to variation of the properties of the mixed acids derived from the alcohols. (1) (2) (3).

It was desired to study the melting point property of mixed derivatives of alcohols, using some of the commonly made alcohol derivatives such as, p- nitro methyl benzoate, p- nitro ethyl benzoate, 3-5 dinitro methyl benzoate, 3-5 dinitro ethyl benzoate, and 3-5 dinitro butyl benzoate. (4). These alcohol derivatives are quite easily made, exhibit definite melting points, and crystalline structure.

If one established phase diagrams by this study of melting points, for two component mixtures of these derivatives it might be possible to quantify a mixture of two alcohols by making mixed derivatives therefrom,

taking a melting point of the mixed derivatives and referring to the established diagrams.

If mixtures of two derivatives; for example, p- nitro methyl benzoate and p- nitro ethyl benzoate; were made and the per cent composition varied, definite mixed melting point temperatures could be obtained. By plotting the melting point ranges of these mixtures, an insight into the nature of the phases of the systems would be shown. One would have determined whether the mixed derivatives were mutually soluble in the solid state or insoluble. It is a well established fact that mixtures of solids of the type which form solid solutions, do not form eutectic mixtures but have a very definite composition at which there are only two phases present namely; liquid and solid solution yielding a minimum melting temperature. In a system exhibiting insolubility in the solid state a definite eutectic mixture of the two substances would result. (5) (6) (7).

Preparation of Derivatives

The compounds p- nitro benzoyl chloride and 3-5 dinitro benzoyl chloride are prepared by the method given in Organic Synthesis Vol. III by H. T. Clark, in which phosphorus penta chloride is added to the acid of the particular nitro compound desired, and the mixture is heated for at least one hour. At the completion of the reaction the product obtained is distilled in a vacuum to remove the excess phosphorus oxy-chloride. The product is only fairly pure but as we are going to purify our final ester product it is unnecessary to purify at this point.

The esters prepared by refluxing p- nitro benzoyl chloride with pure absolute methyl alcohol and pure absolute ethyl alcohol, 3-5 dinitro benzoyl chloride with pure absolute methyl, ethyl, and butyl alcohols in turn, would not yield sharp melting points, as purified by recrystallization from ether or petroleum ether. A mixture of ethyl alcohol and water was then tried for purification of the alcohol derivatives. The esters were dissolved in hot 95 per cent ethyl alcohol after which water was added to the hot solution to incipient precipitation. The precipitate formed was then just dissolved

with more ethyl alcohol. The solution was then filtered through a hot water filter and crystals of the ester were formed in the cold filtrate. In order to remove the liquor from the crystals the cold solution was filtered on a Buchner funnel, then placed in a vacuum desiccator and dried. It was found necessary to recrystallize by this method at least twice in order to obtain a sufficiently pure product. The following pure derivatives of the alcohols were prepared:

p- nitro methyl benzoate	M. P.	57.0-57.5° C.
p- nitro ethyl benzoate	M. P.	96.0-96.5° C.
3-5 dinitro methyl benzoate	M. P.	106.5-107° C.
3-5 dinitro ethyl benzoate	M. P.	91.5-92° C.
3-5 dinitro butyl benzoate	M. P.	63.3-63.6° C.

Mixed Melting Points

A study of the literature revealed the fact that there is very little agreement upon the melting points for the esters prepared. The following table will give an idea of the discrepancies existing:

	Malone and Reid (8)	Others (8)
3-5 dinitro methyl benzoate	107.8° C.	107.5-112° C.
3-5 dinitro ethyl benzoate	92.7° C.	90 -94° C.
3-5 dinitro butyl benzoate	62.5° C.	61 -64° C.
p- nitro ethyl benzoate		96° C.
p- nitro methyl benzoate		57 ° C.

It is to be noted that the melting points of our purified ester derivatives agree quite closely with those of Malone and Reid.

Mixtures of p- nitro ethyl and p- nitro methyl benzoates were taken and their melting points determined by means of capillary tubes. The amount of the p- nitro ethyl benzoate was fixed and the amount of p- nitro methyl benzoate varied so that the percentage of our mixtures ranged from zero per cent of p- nitro benzoate to 100 per cent of this compound. The results obtained from observation of the melting points of these mixtures will be discussed later. Mixtures of 3-5 dinitro methyl

benzoate and 3-5 dinitro ethyl benzoate were studied in a similar manner. Mixtures of 3-5 dinitro ethyl benzoate and 3-5 dinitro butyl benzoate were the third system studied in the above manner.

The results of the melting points of the mixtures are recorded in Tables I, II, and III and were plotted according to the regular method used for a two component system, using the first indication of melting as the so-called freezing point and the point at which the last of the mixture melted as the melting point. These temperatures varied within quite wide limits, depending upon the composition of the mix as can be seen from curves I, II, and III.

TABLE I

MIXTURES OF P-NITRO ETHYL BENZOATE AND P-NITRO METHYL BENZOATE

Mgms. Ethyl	Mgms. Methyl	M.P. First	M.P. Last	% Methyl
200	20	52.0	54.5	11.0
200	40	51.0	52.0	16.6
200	60	51.5	52.5	23.0
200	80	54.0	57.0	28.6
200	100	56.5	59.5	33.3
200	120	57.5	63.0	37.5
200	140	58.5	65.0	41.1
200	160	59.5	69.0	44.4
200	180	61.5	71.5	47.4
200	200	64.0	72.5	50.0
30	70	76.5	81.0	70.0

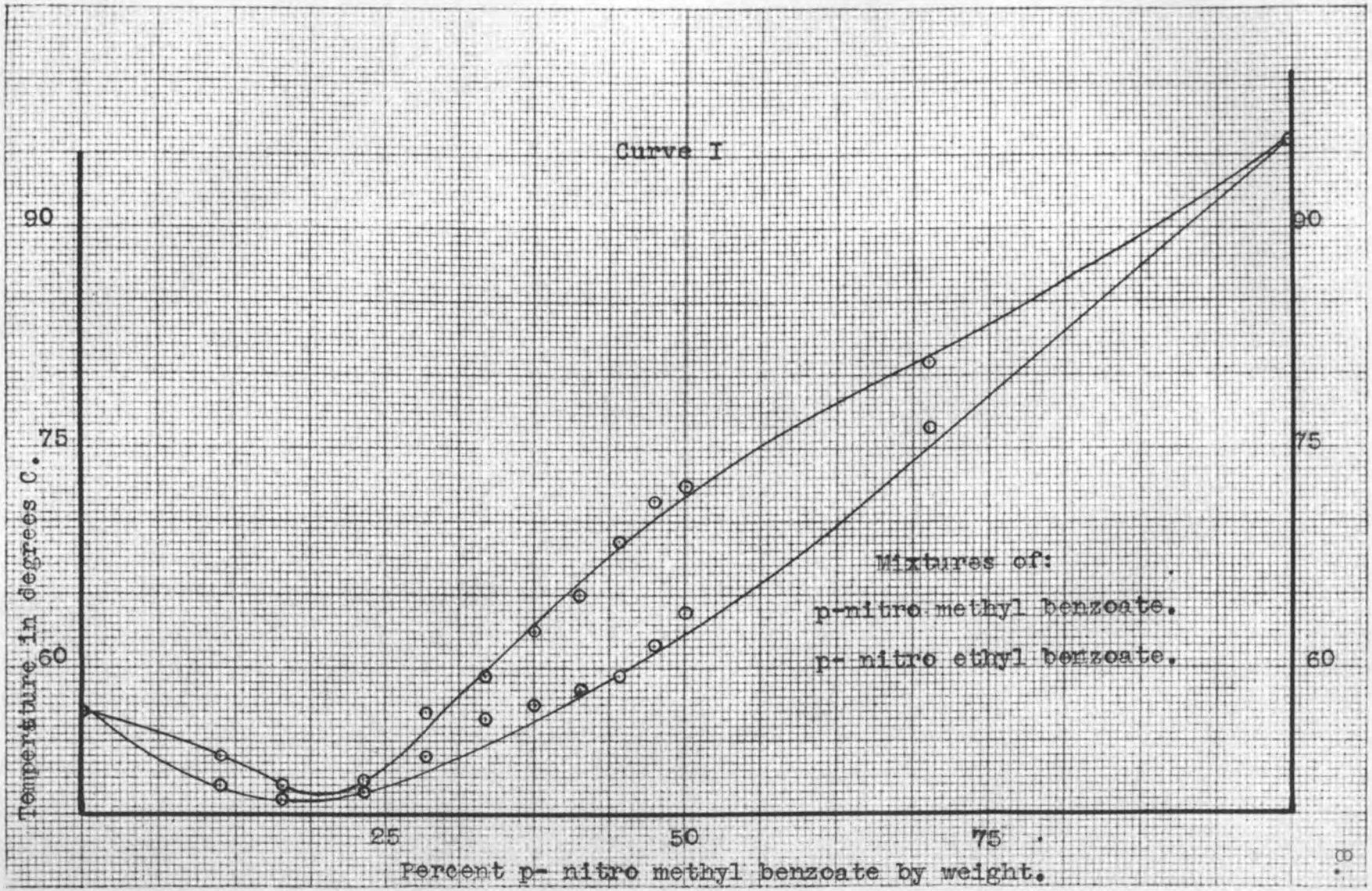

Curve I
90
75
60
Temperature in degrees C.
Mixtures of:
p-nitro methyl benzoate.
p- nitro ethyl benzoate.
25
50
75
Percent p- nitro methyl benzoate by weight.

TABLE II

MIXTURES OF 3-5 DINITRO ETHYL BENZOATE AND 3-5 DI-NITRO METHYL BENZOATE

Mgms. Ethyl	Mgms. Methyl	M.P. First	M.P. Last	% Methyl
200	0	92.5	93.0	0.0
200	20	86.0	89.0	11.0
200	40	82.5	85.0	16.6
200	60	80.5	83.8	23.0
200	80	78.5	80.5	28.6
200	100	75.0	78.5	33.3
200	120	74.0	77.5	37.5
200	140	73.0	76.5	41.1
200	160	73.0	75.5	44.4
200	180	73.0	74.7	47.4
200	200	73.0	74.3	50.0
200	250	73.5	77.0	55.5
200	300	75.0	77.5	60.0
30	90	85.0	87.0	75.0
30	120	87.0	91.5	80.0
30	170	93.0	96.0	85.0
10	90	97.5	100.0	90.0
0	200	106.0	106.5	100.0

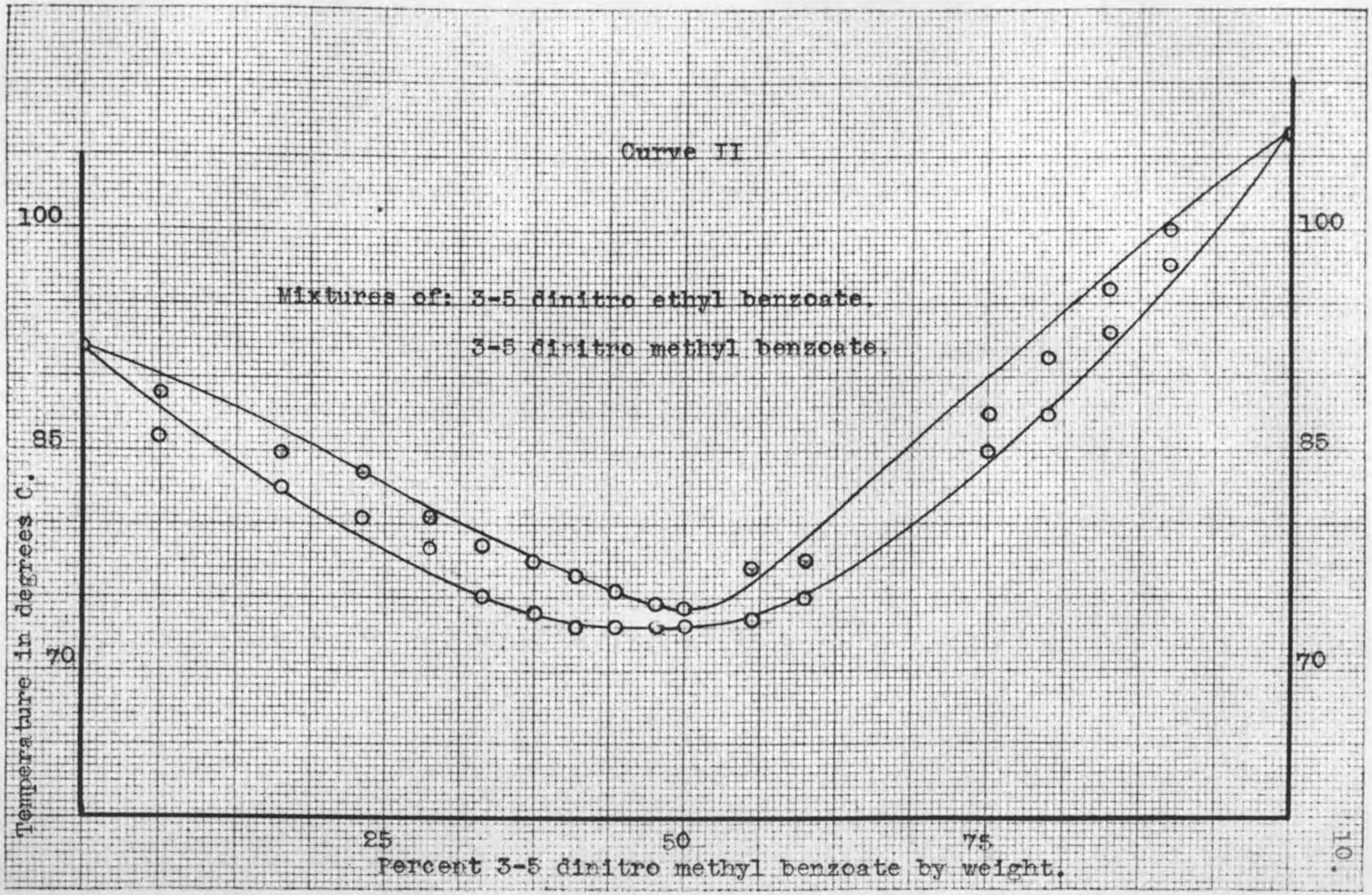
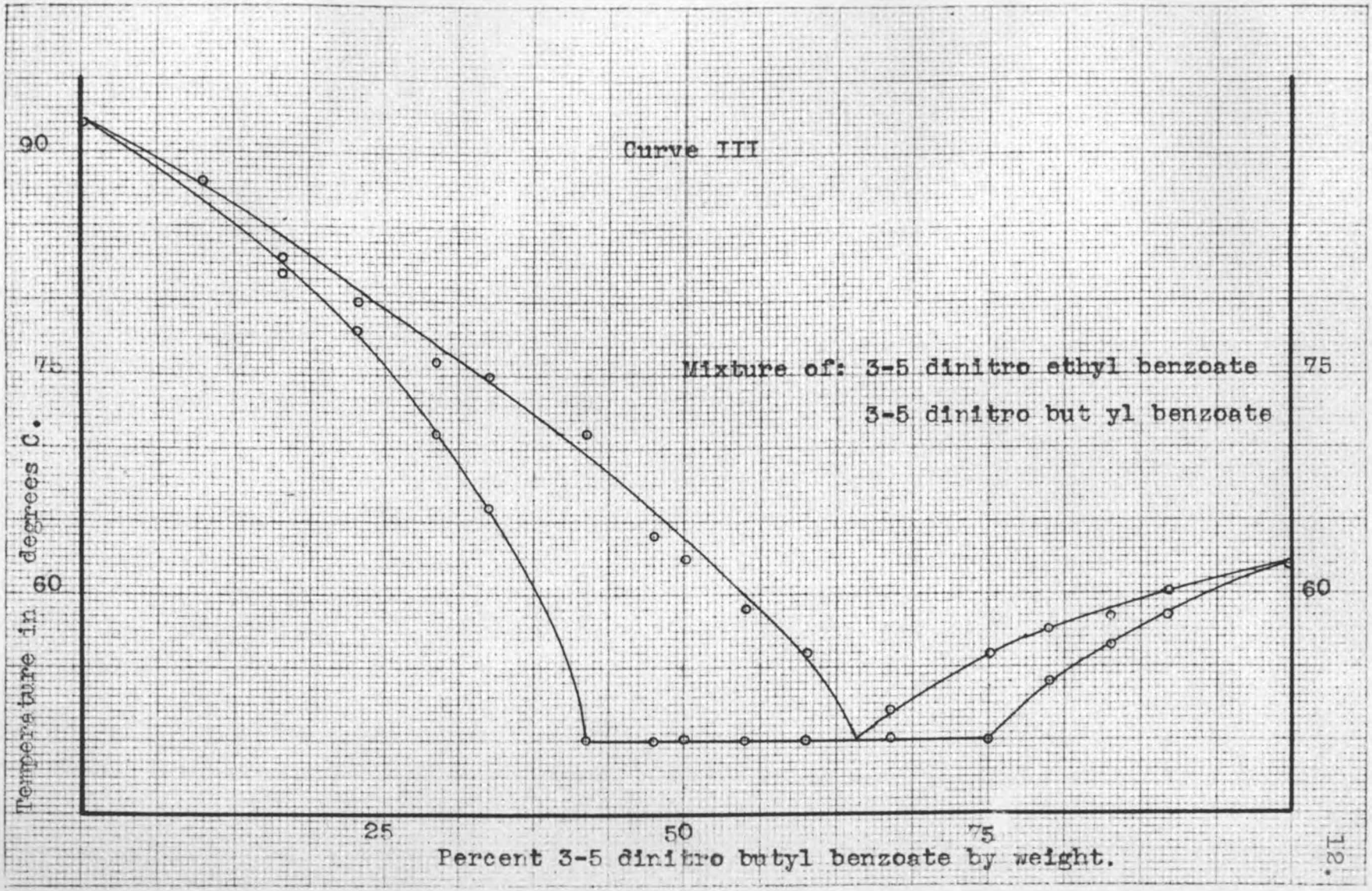

Curve II
Mixtures of: 3-5 dinitro ethyl benzoate.
3-5 dinitro methyl benzoate.
100
85
70
Temperature in degrees C.
25
50
75
Percent 3-5 dinitro methyl benzoate by weight.

TABLE III

MIXTURES OF 3-5 DINITRO ETHYL BENZOATE AND 3-5 DI-NITRO BUTYL BENZOATE

Mgms. Ethyl	Mgms. Butyl	M.P. First	M.P. Last	% Butyl
200	0	92.5	92.5	0.0
200	20	88.0	88.0	11.0
200	40	82.0	83.0	16.6
200	60	78.0	80.0	23.0
200	80	71.0	76.0	28.6
200	100	70.0	75.0	33.3
200	140	64.0	71.0	41.1
200	160	51.0	66.0	44.4
200	180	51.0	64.0	47.4
200	200	51.0	62.5	50.0
200	250	51.5	59.0	55.5
200	300	51.0	56.0	60.0
30	90	51.0	56.0	75.0
30	120	54.0	57.5	80.0
30	170	56.5	58.5	85.0
10	90	58.0	59.5	90.0
0	200	63.5	63.5	100.0


Curve III
Mixture of: 3-5 dinitro ethyl benzoate
3-5 dinitro but yl benzoate
90
75
60
Temperature in degrees C.
25
50
75
Percent 3-5 dinitro butyl benzoate by weight.

Discussion of Results

From a study of the phase diagram curve I, for p-nitro methyl benzoate and p- nitro ethyl benzoate, it will be noted that the minimum melting point temperature is at 52 degrees C. The schematic diagram in this case shows a true type of solid solutions. This curve indicates the formation of a continuous system of mixed crystals in the solid phase and at the low point all of the crystals should either melt or freeze at a definite temperature (9). The difference in temperature between these two points, as shown, is no greater than the small range of about one-half degree encountered in obtaining the melting point of a purified organic compound. Intermediate mixtures between the eutectic and pure compounds showed somewhat greater range of temperature between the temperatures of first to complete melting. The low point on the diagram does not really represent true eutectic inasmuch as no invariant point is possible with complete solubility in the solid.

In the system 3-5 dinitro ethyl benzoate and 3-5 dinitro methyl benzoate the low point was found to be nearly at the 50 per cent mix. It can be seen from Curve II that within about five per cent on each side of the 50 per cent mark, the melting points are all at

about the same temperature. This may be due to the fact that it was not possible to read melting temperatures more accurately than one-half of one degree; or it may be of the same type as the 3-5 dinitro ethyl benzoate and 3-5 dinitro butyl benzoate (Curve III) showing partial solubility in the solid state. If any insolubility in the solid state exists, it is only in narrow range near the mid point as to composition. However, it appears to be of the type first mentioned, in which there occurs a continuous system of mixed crystals with the low point at 73 degrees C.

The low melting mixture of 3-5 dinitro ethyl benzoate and 3-5 dinitro methyl benzoate by close inspection appears to be at 48 rather than at 50 per cent. If the 48 per cent mix is the low melting mixture, it would seem to bring out the fact that these compounds form a minimum melting temperature mix at approximately a mole for a mole ratio.

In the mixture of 3-5 dinitro ethyl benzoate and 3-5 dinitro butyl benzoate we have a system that exhibits a eutectic at 64 per cent butyl derivative; it differs considerably from the two previous systems studied in that it shows only partial solubility of the solids in the solid state. This system

exhibits an invariant point at 64 per cent butyl derivative and a temperature of 51 degrees C.

At 51 degrees C. 3-5 dinitro butyl benzoate is soluble in solid 3-5 dinitro ethyl benzoate to the extent of about 45 per cent; the ethyl 3-5 dinitro benzoate is about 25 per cent soluble in the 3-5 dinitro butyl benzoate. No knowledge of transformation lines in the solid was obtained.

If one takes a 44 per cent butyl derivative mix, first melting takes place at 51 degrees C. ranging to complete melting at 72 degrees C. A 33 per cent mix, however, will exhibit first melting at about 70 degrees C., and complete melting at 75 degrees C., showing that solubility in the solid state is had for this mixture.

Melting Points Using a Thermocouple

A copper-constantan thermocouple was used in the apparatus for determining melting temperature, because this couple gives a relatively high voltage between the temperatures of zero and one hundred degrees centigrade. (10) The couple was made by fusing the wires in a carbon arc to prevent oxidation of the metals.

A beam of light was focused on the mirror of a d' Arcinal galvanometer. Leads of the thermocouple were attached to the galvanometer and changes in the position of the mirror due to the flow of current in the wire caused the reflected spot of light to move along a fixed meter stick. A small ice-water filled Dewar flask was used as the cold junction bath. A Dewar flask of about 500 cc. capacity was used as the hot temperature bath for standardization of the thermocouple.

In order to standardize the thermocouple, hot water was placed in the large Dewar flask, the thermocouple twisted around the bulb of a German standard thermometer and inserted in the flask. The position of the light beam on the meter stick was read, at the same time that corrected temperature of the thermometer was noted. This operation was repeated with water at different temperatures giving temperatures over a wide range.

The readings of the meter stick were plotted as ordinates and the thermometer temperature plotted as abscissa, the resultant curve was a straight line. From this curve temperatures could be read from extent of galvanometer deflection over the whole range of temperatures in which we were interested. In order to make this still more useful the diagram was plotted on 16" x 11" paper and kept for the conversion of galvanometer scale deflections in cm. into degrees centigrade. These temperatures were of course corrected temperatures since the thermocouple was calibrated with a standard thermometer, corrected for emergent stem.

We attempted to determine the freezing point of 3-5 dinitro ethyl benzoate and 3-5 dinitro butyl benzoate with this thermocouple arrangement, but due to the fact that these compounds formed a glass-like supercooled liquid instead of crystallizing normally, and we were using such small quantities, we were unable to get a time lag at the freezing point. Therefore it was decided to take the melting points during the slow heating of the crystals, particularly since melting point information is more useable than freezing point for organic derivatives. By the use of time-temperature

diagrams, curves IV to VIII, the inflection points, indicating a change of phase, and also the melting points of the pure compounds could be determined.

TABLE V

3-5 DINITRO ETHYL BENZOATE (RUN I)

Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)	Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)
0	58.6	85.7	22	62.7	91.5
1	58.8	86.0	23	62.8	91.7
2	59.0	86.3	24	63.0	91.9
3	59.2	86.5	25	63.3	92.4
4	59.3	86.7	26	63.5	92.7
5	59.5	87.0	27	63.6	92.9
6	59.7	87.3	28	63.7	93.0
7	60.0	87.7	29	63.9	93.3
8	60.2	88.0	30	63.9	93.3
9	60.4	88.3	31	64.2	93.7
10	60.6	88.6	32	64.6	94.3
11	60.8	88.9	33	65.2	95.1
12	61.1	89.2	34	65.8	96.0
13	61.4	89.7	35	66.3	96.7
14	61.6	90.0	36	66.7	97.3
15	61.8	90.3	37	66.9	97.6
16	62.0	90.6	38	67.0	97.8
17	62.2	90.9	39	67.2	98.0
18	62.3	91.0	40	67.4	98.3
19	62.5	91.3	41	67.6	98.6
20	62.6	91.4			
21	62.7	91.5			

TABLE IV

3-5 DINITRO ETHYL BENZOATE

Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)	Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)
0	40.0	59.0	27	61.7	90.1
5	45.0	66.1	28	62.1	90.7
10	49.7	72.9	29	62.4	91.1
15	53.9	79.1	30	62.7	91.5
16	54.7	80.1	31	62.9	91.9
17	55.4	81.0	32	63.2	92.2
18	56.1	82.0	33	63.6	92.9
19	56.8	83.1	34	64.2	93.5
20	57.5	84.1	35	65.4	95.4
21	58.2	85.1	36	66.6	96.6
22	58.9	86.1	37	66.9	97.5
23	59.5	87.0	38	67.1	97.9
24	60.1	87.9			
25	60.7	88.7			
26	61.2	89.4			

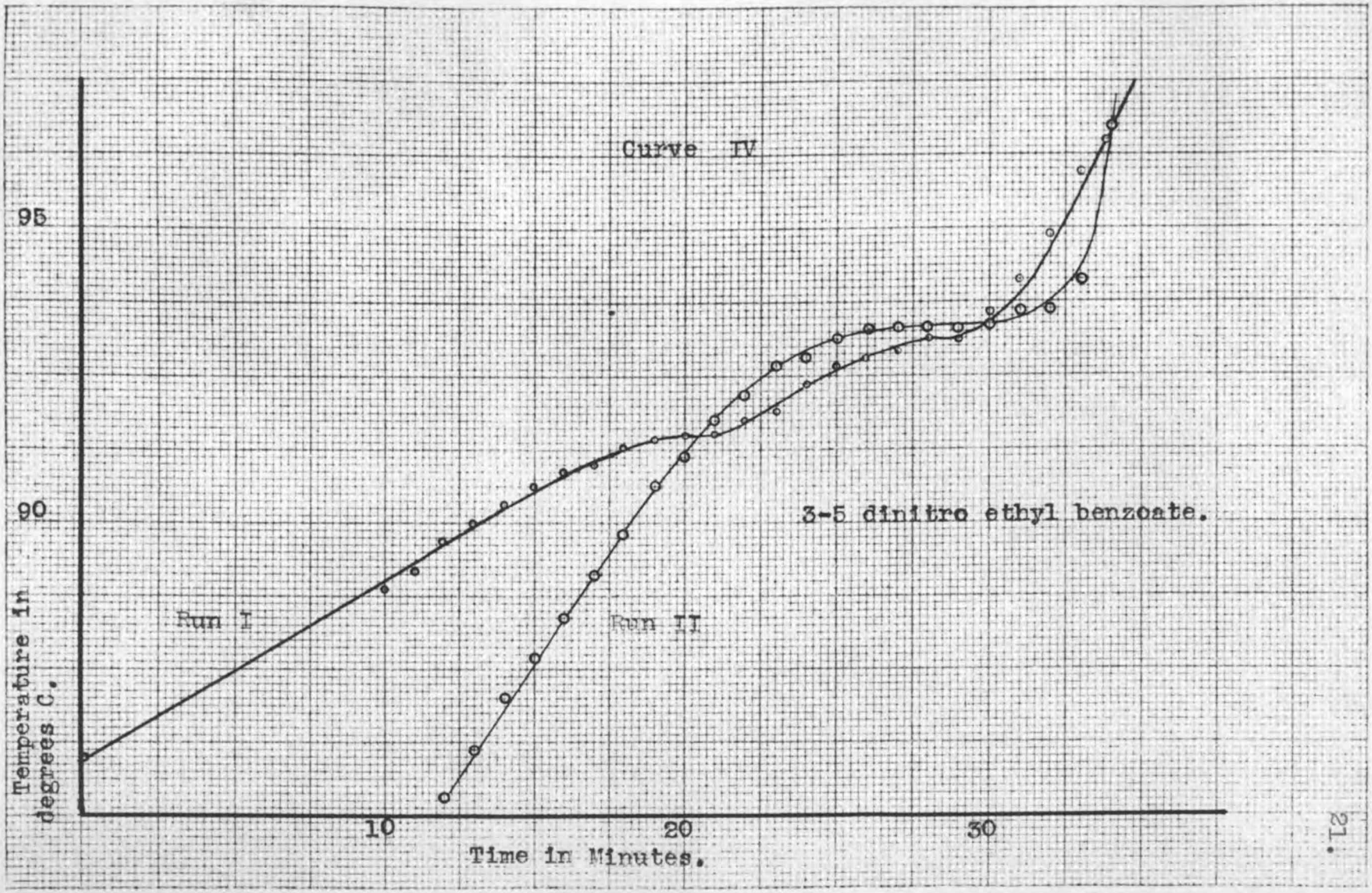

Curve IV
95
90
3-5 dinitro ethyl benzoate.
Run I
Run II
Temperature in degrees C.
10
20
30
Time in Minutes.

TABLE VI

3-5 DINITRO BUTYL BENZOATE

Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)	Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)
0	21.9	33.2	26	41.6	61.3
5	26.7	40.0	27	41.9	61.7
10	31.3	46.6	28	42.0	61.9
15	35.3	52.4	29	42.2	62.1
16	35.9	53.2	30	42.4	62.4
17	36.5	54.0	31	42.8	63.0
18	37.0	54.7	32	43.2	63.6
19	37.5	55.4	33	43.8	64.5
20	38.1	56.3	34	45.2	66.4
21	38.6	57.0	35	46.5	68.3
22	39.3	58.0	36	47.0	69.0
23	40.0	59.0	37	47.4	69.6
24	40.7	60.0	38	47.8	70.2
25	41.2	60.7	39	48.1	70.6

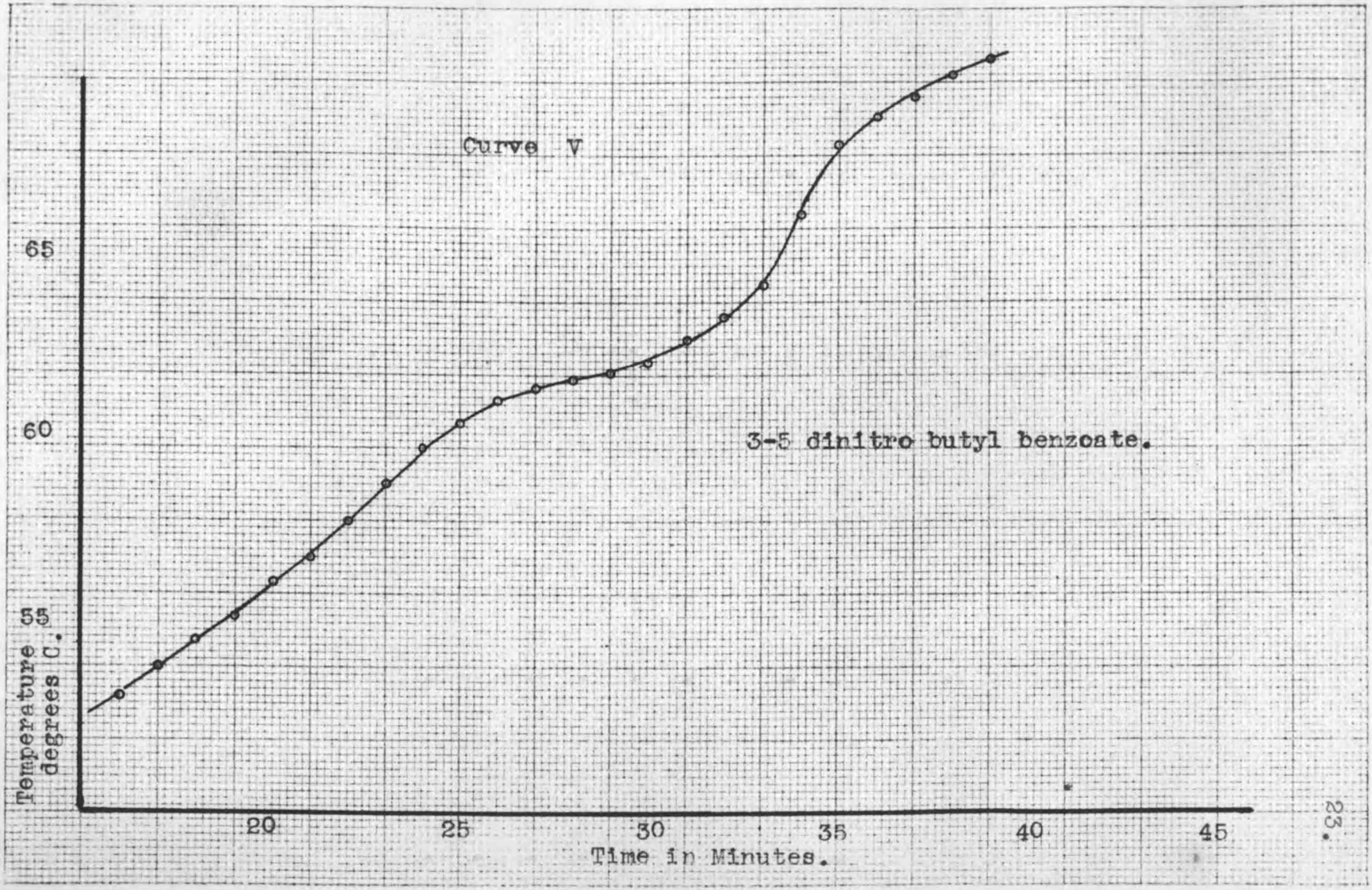

Curve V
65
60
55
Temperature degrees C.
3-5 dinitro butyl benzoate.
20
25
30
35
40
45
Time in Minutes.

TABLE VII

MIXTURE OF 44.4 % 3-5 DINITRO BUTYL BENZOATE AND

55.6 % 3-5 DINITRO ETHYL BENZOATE

Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)	Time (Min.)	Thermo-couple (Cm.)	Temp. (°C)
0.0	26.9	40.3	11.5	38.4	56.7
1.0	27.9	41.8	12.0	39.2	57.8
2.0	28.9	43.2	12.5	39.9	58.9
3.0	30.0	44.6	13.0	40.3	59.4
4.0	31.0	46.1	13.5	41.5	61.1
5.0	32.0	47.7	14.0	42.2	62.2
6.0	32.9	48.9	14.5	42.8	63.0
7.0	33.6	49.9	15.0	43.4	63.9
7.5	33.9	50.9	15.5	44.0	64.7
8.0	34.2	50.8	16.0	44.6	65.5
8.5	34.6	51.4	16.5	45.2	66.5
9.0	34.8	51.6	17.0	45.8	67.3
9.5	35.1	52.1	18.0	47.0	69.0
10.0	35.2	52.2	19.0	48.2	70.7
10.5	36.2	53.6	20.0	49.8	73.0
11.0	37.4	55.3	21.0	50.4	75.3

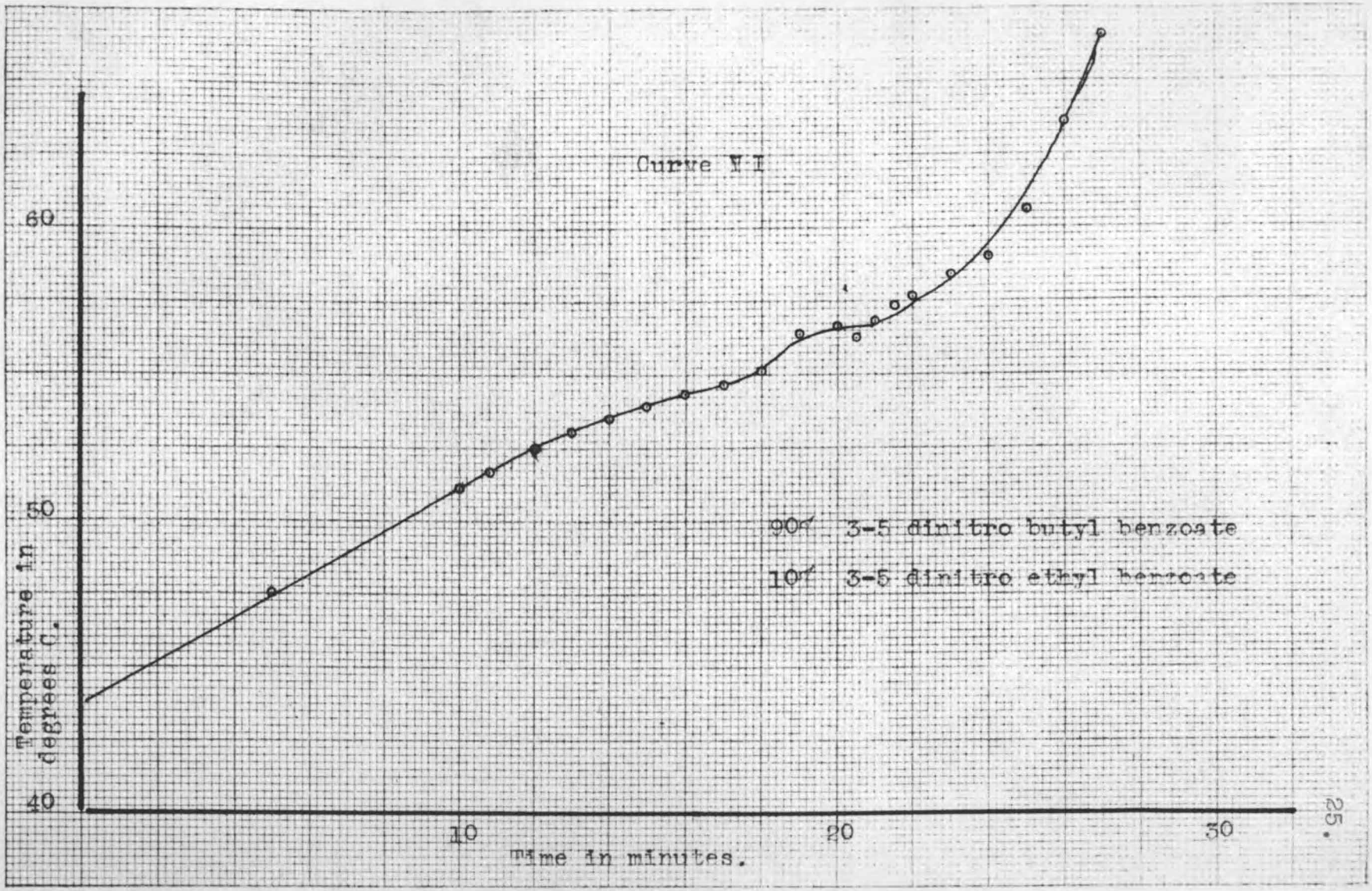
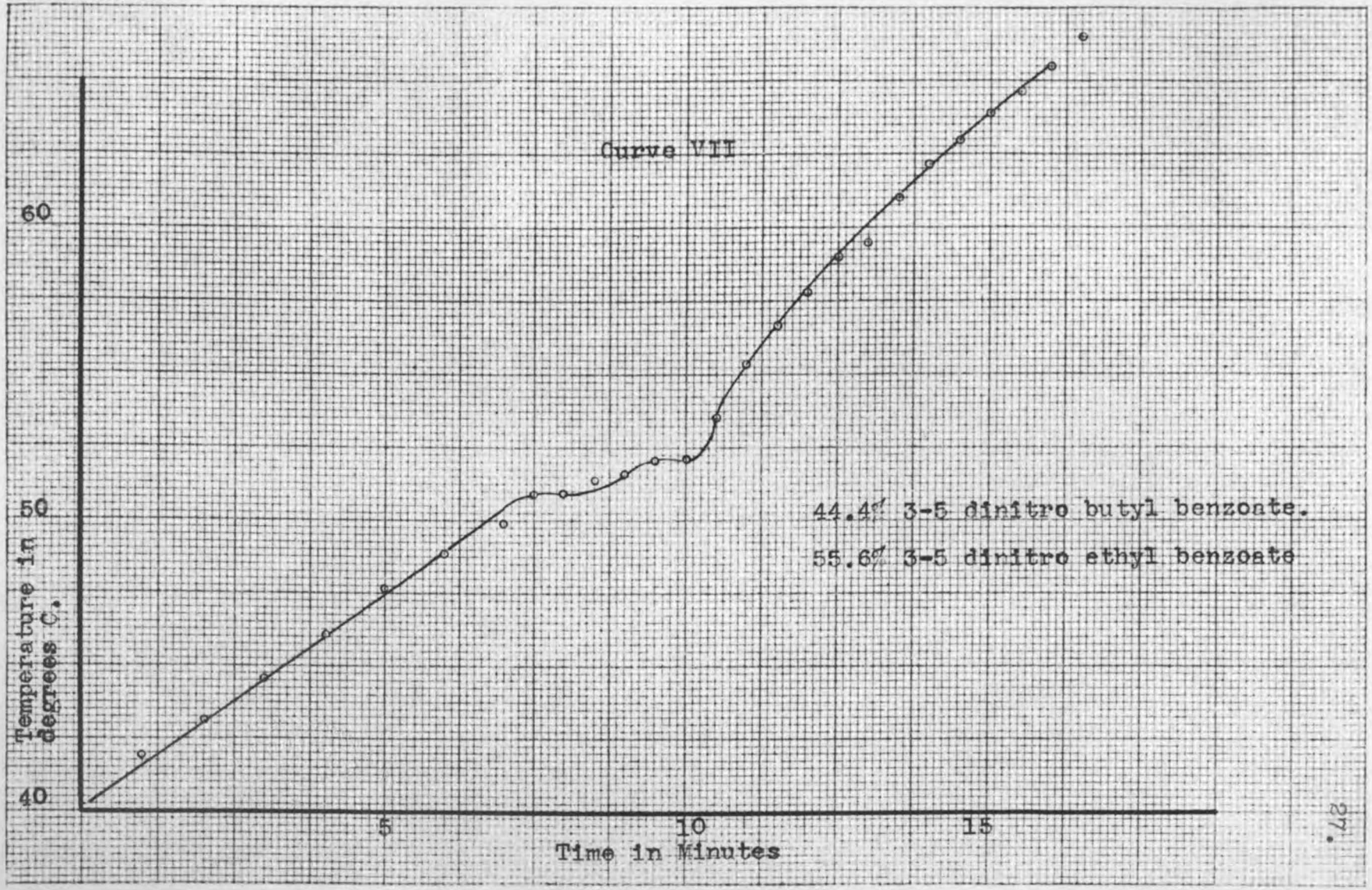

Curve V I
60
50
40
Temperature in degrees C.
10
20
30
time in minutes.
90% 3-5 dinitro butyl benzoate
10% 3-5 dinitro ethyl benzoate

TABLE VIII

Mixture of: 3-5 dinitro ethyl benzoate, 10%
3-5 dinitro butyl benzoate, 90%.

Tine in Minutes.	Thermo. in cm.	Temperature in degrees C.
00.0	29.3	43.8
5.0	31.4	46.8
10.0	34.4	51.1
11.0	34.9	51.7
12.0	35.4	52.5
13.0	35.8	53.1
14.0	36.1	53.5
15.0	36.4	53.9
16.0	36.7	54.3
17.0	37.0	54.7
18.0	37.4	55.1
19.0	38.2	56.4
20.0	38.4	56.7
20.5	38.1	56.3
21.0	38.5	56.9
22.0	39.1	57.7
23.0	39.6	58.4
24.0	40.0	59.0
25.0	41.1	60.6
26.0	43.2	63.6
27.0	45.3	66.6


Curve VII
60
50
40
Temperature in degrees C.
5
10
15
Time in Minutes
44.4% 3-5 dinitro butyl benzoate.
55.6% 3-5 dinitro ethyl benzoate

Discussion of Thermocouple Melting Points

From a study of the melting point curves for 3-5 dinitro ethyl benzoate it will be noted that run II, Curve IV, gave a typical curve for a pure compound, and this curve shows that the compound, as prepared, has a melting point range of not more than .4 of a degree C. In this run the rate of heating was regulated properly and consequently the resulting curve is quite regular and does not present the irregularities presented by run I on the same diagram. In the case of run I it will be noted that there is quite a lag recorded in the temperature at approximately 91.5 degrees C; and then a fairly sharp rise in temperature with another lag near the true melting point 92.8 degrees C. The first lag in temperature is probably due to the fact that these organic compounds, similar to other organic crystalline compounds, are poor conductors of heat and, since no mode of stirring was possible, there will consequently result this lag in temperature. The upper break in the curve for run I coincides within one-half degree with the melting point obtained in run II. This will show that if the rate of heating is closely governed, that results may be duplicated by the use of a thermocouple for melting point determinations.

The curve for 3-5 dinitro butyl benzoate does not exhibit the same accuracy of results that was shown by one of the curves for pure ethyl benzoate. This is due in part to the control of the rate of heating and also to inherent difficulties in the method. However, the range of melting for this compound is about one degree, 61.6 degrees C. to 62.8 degrees C., which would give the mean melting point for the pure compound as 62.2 degrees C. This temperature agrees quite well with that obtained with the capillary tubes.

Two curves of mixtures of 3-5 dinitro ethyl benzoate and 3-5 dinitro butyl benzoate have been included as representative of the degree of success obtained with the use of the thermocouple for the study of melting points of mixtures of organic compounds which form crystalline systems.

In the curve for 90 per cent 3-5 dinitro butyl benzoate it will be noted that there is a break at 57 degrees C. indicating a transition point or a change of phase, and another break in the curve at 59.6 degrees C. indicating point of complete melting. If the curve III is studied it will be noted that this 90 per cent mix is outside the range of insolubility of the solids

in each other, and should not give indication of a eutectic break at the 51 degree C. temperature.

In the curve given for 44.4 per cent 3-5 dinitro butyl benzoate and 55.6 per cent 3-5 dinitro ethyl benzoate, it will be noted that there is evidence of a break at 51 degrees C. which would indicate the presence of a eutectic. The next break is somewhat indefinite but the curve does seem to substantiate the point of first melting as previously determined with thermometer and capillary melting point tubes, which temperatures are listed in table III and plotted on curve III.

Further work in developing the use of thermocouples for making melting point determinations on organic substances and checking melting points as determined by thermometer, recording visual melting, is being carried on.

Practical Application

Desiring to see if we could estimate mixed alcohol percentages we experimented as follows: A known mixture of ethyl and butyl alcohol was converted into mixed ester derivatives by refluxing with 3-5 dinitro benzoyl chloride. The mixed derivative was washed with a one per cent sodium hydroxide solution to decompose the excess 3-5 dinitro benzoyl chloride and dissolve any free acid formed. A melting point was made on the mixed alcohol derivative. On referring to the curve III to compare our melting points with that obtained by mechanical mixing of corresponding amounts of pure derivative, we found some variance, but not enough to discourage further work along this line, to establish the method as practical. In the work just described we checked the melting points obtained with the thermocouple against those obtained by use of a capillary melting point tube. The agreement was very good.

Summary

1.) A temperature composition phase diagram has been established for p- nitro methyl benzoate and p- nitro ethyl benzoate.

2.) A temperature-composition phase diagram has been established for 3-5 dinitro methyl and ethyl benzoates.

3.) A temperature-composition phase diagram has been established for 3-5 dinitro ethyl benzoate and 3-5 dinitro butyl benzoate.

4.) Some melting points of pure organic substances and of mixtures of organic substances have been determined by use of the thermocouple and practicality of the thermocouples in such analysis investigated.

5.) A possible method of estimating the percentages of one alcohol in another is presented.

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