A STUDY OF THE BINARY SYSTEMS
SALICYLIC ACID-BIPHENYL AND SALICYLIC ACID-DIPHENYLAMINE

By

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INTRODUCTION

In the course of the investigation of the solubility equilibrium in binary mixtures, it was found by Andrews, Kohman and Johnston (1) that the method and apparatus commonly used for this type of work was insufficiently accurate for this study. It was necessary to re-design the whole apparatus and to consider the theory underlying the method as a means of evaluating the results correctly. A detailed discussion is given by Andrews, Kohman and Johnston in their study of solubility relation of isomeric organic compounds.

The familiar method of taking time-temperature curves was used. A thermocouple was used as the heat measuring instrument instead of the usual mercury thermometer, since it has a small heat capacity, a small lag, and conducts as little heat away from the solution as is possible. Another advantage of the thermocouple is that smaller amounts of material may be used. With a large amount of material there will be differences of temperature throughout the mass, and the heat set free by the transition of the outer layers is transferred slowly to the thermometer. A Leeds and Northrup type K potentiometer and standard cell were used for voltage measurements.

Since in this experiment it was found that salicylic acid has a tendency to volatilize when heated, it was necessary to analyze each sample after the cooling curve had been determined.

THE RELATION BETWEEN COMPOSITION AND MELTING POINT OF MIXTURES

In this study the solubilities, eutectic temperatures and eutectic compositions are compared with values calculated for perfect solutions from the equation given by Washburn (14):

$$dT = \frac{RT^2}{\Delta H_f} \frac{dN}{N} \quad \text{or} \quad \frac{d \log_e N}{dT} = \frac{\Delta H_f}{RT^2} \qquad (1)$$

where ΔH_f is the molecular heat of fusion of the solvent at absolute temperature T, R is the gas constant, and N is the mole fraction of the solvent.

This same equation has been also derived by LeChatelier (7) and Schreder (10). In deriving this equation, it is assumed that there is no association or dissociation of the components and that there is no formation of a compound or solid solution. It is also assumed that the laws of ideal solutions are valid. Bell and Sawyer (5) show the validity of this relationship with a study of lowering of the freezing point by tri-nitro-m-xylene by the nitrotoluenes. It is assumed that this equation is used under conditions when ΔH_f is constant. However, as pointed out by Vant Hoff that at the melting point the liquid has a greater specific heat than the solid. If we assumed that this difference is faily constant over moderate temperature ranges, then

$$\Delta H = \Delta H_o + \Delta C \cdot \Delta T \qquad (2)$$

where ΔH is the heat of fusion at any temperature, ΔH_o the heat of fusion at the melting point of the pure component, ΔC is the difference in the molecular heat contents of liquid and solid, and ΔT the depression of the freezing point due to the addition of the second component.

If it is assumed that ΔH is constant, the above differential equation may be integrated and we get

$$\log_e N = -\frac{\Delta H_f(T_0 - T)}{RT_0 T} \qquad (3)$$

where T_0 is melting point of pure substance and T the melting point in the presence of the second component.

This formula is given by Baud and Gay (3) in another form.

$$T = - kT \log_{10} N \qquad (4)$$

which becomes identical with Equation 3 if

$$K = \frac{RT_0}{\Delta H_f \log_{10} e} \qquad (5)$$

Washburn (13) has tested the validity of the formula by studies of binary mixtures of benzene, biphenyl and naphthalene.

Since the literature presents no data for the heat of fusion of salicylic acid, a calculated value was used ($\Delta H_f = 7570$ cal.)*. This value was calculated by Equation 3 by using an observed value of T at N mole fraction. The heat of fusion for biphenyl is 4020 cal. (14) and the heat of fusion for diphenylamine is 4263.6 cal. (6). The freezing points for the mixtures containing salicylic acid are calculated, using Equation 3, and shown in Tables I and II.

Equation 3 has also been derived thermodynamically by Lewis and Randall (8).

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* See Appendix I for calculation.

INTERPRETATION OF TIME-TEMPERATURE CURVES

For a Single Substance

The form of the time-temperature curve for the period of freezing of a single pure substance is given in Fig. 1, the dotted part representing the case where there is no supercooling of the material.

The temperature of a mass of a pure liquid, surrounded by a shield cooling at a uniform rate (RS), falls along AB to C, at which crystallization begins to take place. The heat of crystallization raises the temperature to that of the true equilibrium between solid and liquid; and the curve is horizontal along DE. When the mass is completely crystallized at E, the effective temperature head is relatively large, and the mass begins to cool rapidly, until it reaches the point F, and gradually becomes parallel again to RS.

It is interesting to note here that the degree of purity of the sample can be observed due to the fact that the pure component will follow the theoretical curve unusually closely. In this case the diphenylamine and biphenyl freezing points remained relatively constant over an interval of four to five minutes. If the sample contains an impurity, the initial temperature of freezing will likely be depressed, the temperature falls off as freezing progresses and the concentration of the impurity in the solution increases. White (15) has given a thorough discussion of this matter and of its usefulness as a means of estimating the amount of the impurity.

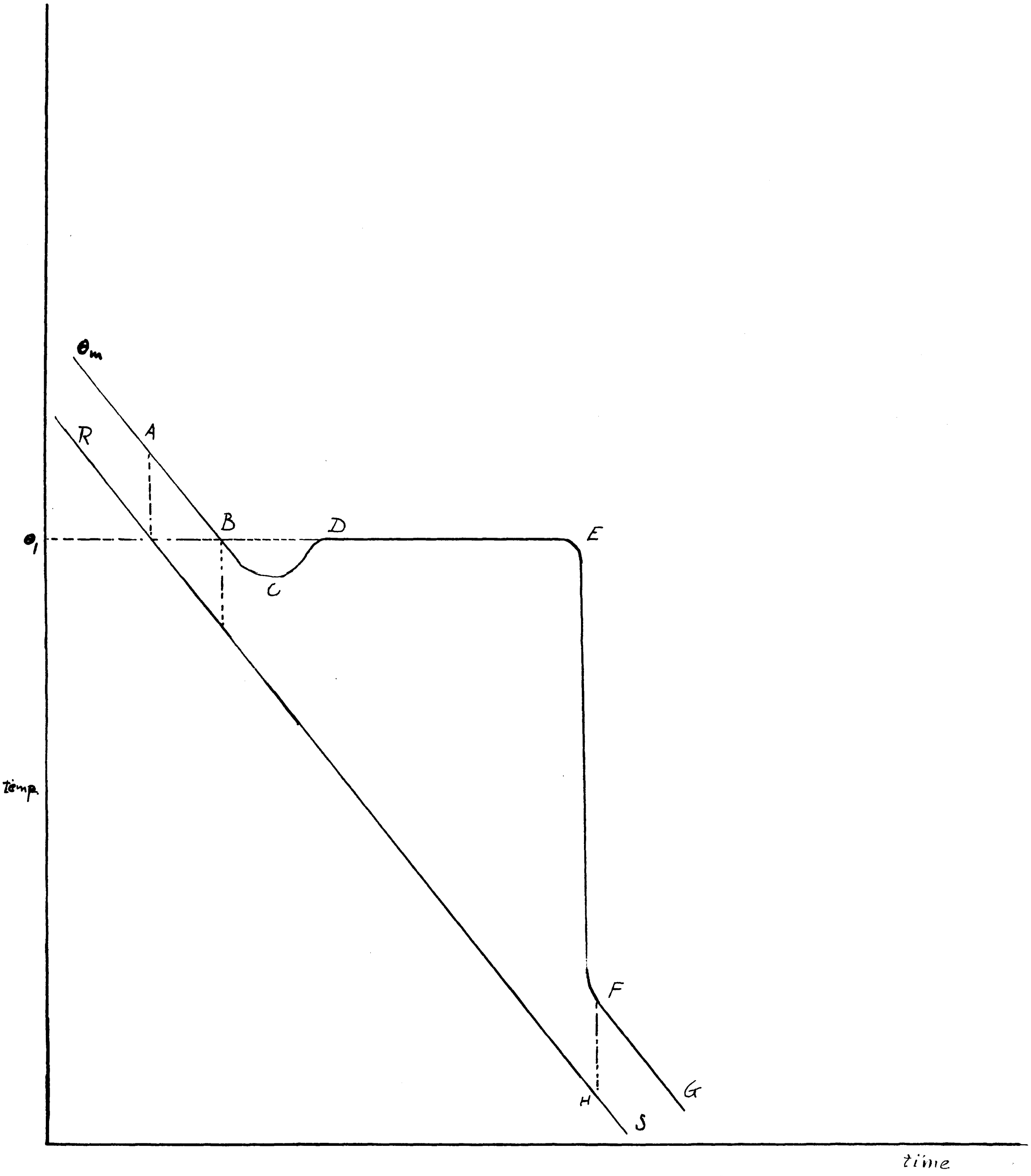

Figure 1.- Time-temperature curve for single substance.

During the last quarter of freezing interval, the temperature may fall off more rapidly, but this is to be attributed partially to non-ideal conditions. It is likely that the last fraction crystallizing cannot supply heat to the thermoelement and its surroundings fast enough to maintain the true equilibrium temperature.

Andrews, Kohman and Johnston (1) showed that the time rate of heat loss by the material in similar apparatus is proportional to the effective temperature head, in accordance with Newton's law, by making observations of the cooling rate of liquid naphthalene under various heads. It was, therefore, justifiable to use this law in the interpretation of time-temperature curves observed in this type of apparatus.

Newton's law may be written:

$$\frac{d\Theta m}{dt} = K' (\Theta_s - \Theta_m)$$

where Θ_s is temperature of shield, Θ_m is the temperature of the melt, t is time, and K' is a constant for the particular set-up and material. If H is the heat content of the melt, and C is the heat capacity, $dH = Cd\Theta$ by definition, and $\frac{dH}{dt} = CK' (\Theta_s - \Theta_m)$. In this case under discussion, C can be considered to be constant over the temperature interval, and taking the heat capacity of the solid to be equal to that of the liquid; therefore, the heat of melting is independent of the temperature. Therefore, we can use K in the place of CK', the heat loss

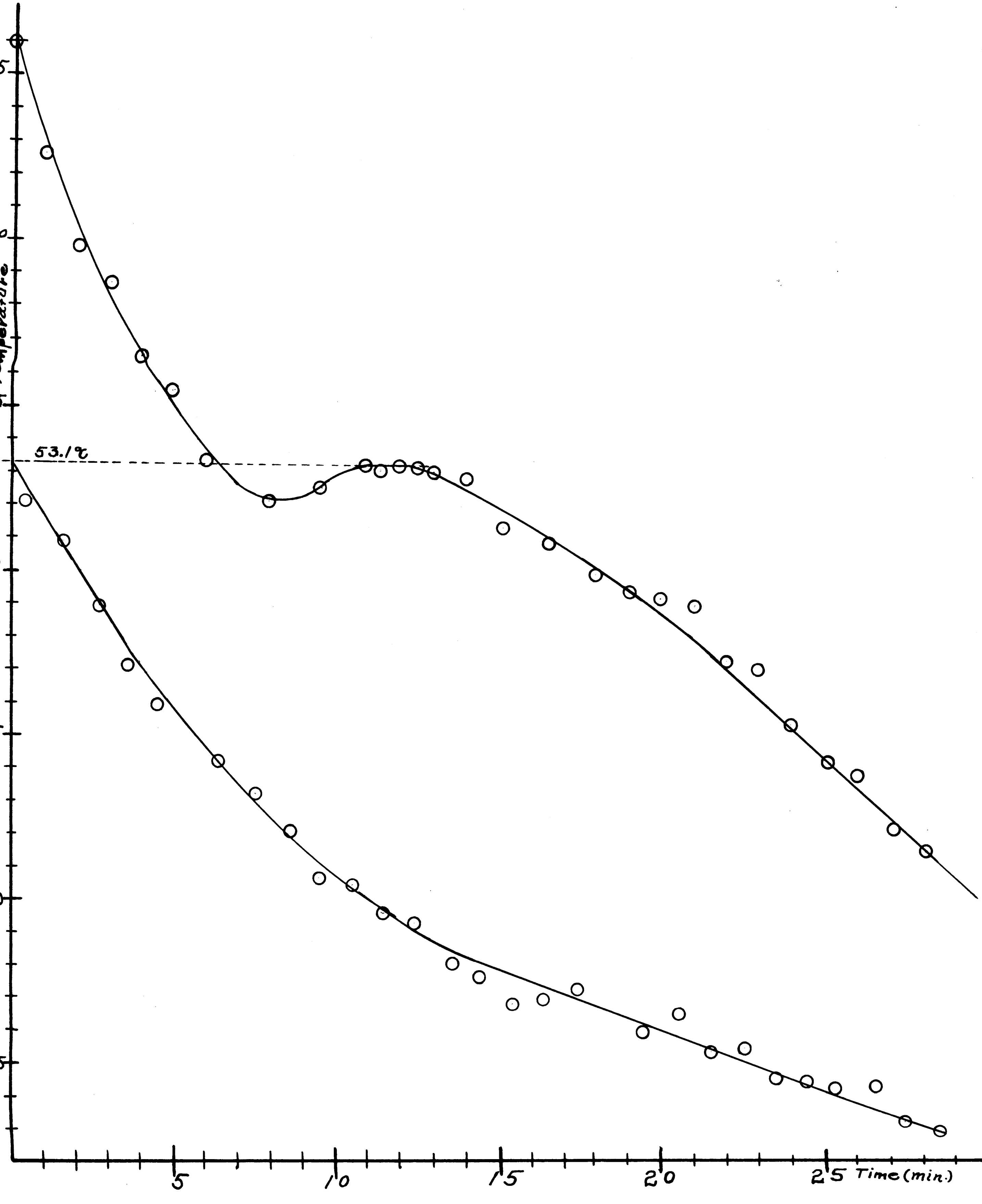

Figure 2.- Time-temperature curve for pure diphenylamine.

from A to B is

$$-\Delta H = H_B - H_A = K\int (\theta_s - \theta_m)dt$$

The temperature of the shield θ_s and the temperature of the material θ_m are recorded at regular intervals of time, and plotted as shown in Fig. 1; the area under the curve ABLM represents the integral, and, therefore, the heat loss of the material. Also, its heat capacity, in cooling from A to B, is proportional to ABLM. By similar reasoning, the heat loss from B to F is proportional to the area BCDEFHL; here again area BFHL corresponds to the heat capacity, and BCDEF to its latent heat of freezing.

Thus, it is possible to calculate the heat capacity and heat of fusion from time-temperature curves, if desired.

As an example, the data for pure diphenylamine are plotted as shown in Fig. 2. The data was obtained from this experiment.

<u>For a Binary Mixture</u>

A binary mixture cools similarly along AP (Fig. 3) until the component X begins (in absence of undercooling) to separate at P, when there is a change in direction (along the curve PD) but no horizontal portion of the curve. The heat set free now causes the rate of cooling of the melt to change in a perfectly definite way, because to any temperature below P there corresponds a definite composition of the residual liquid, hence a definite amount of the component has crystallised and a definite total amount of heat has been set free. The composition of the residual liquid approaches that of the eutectic as

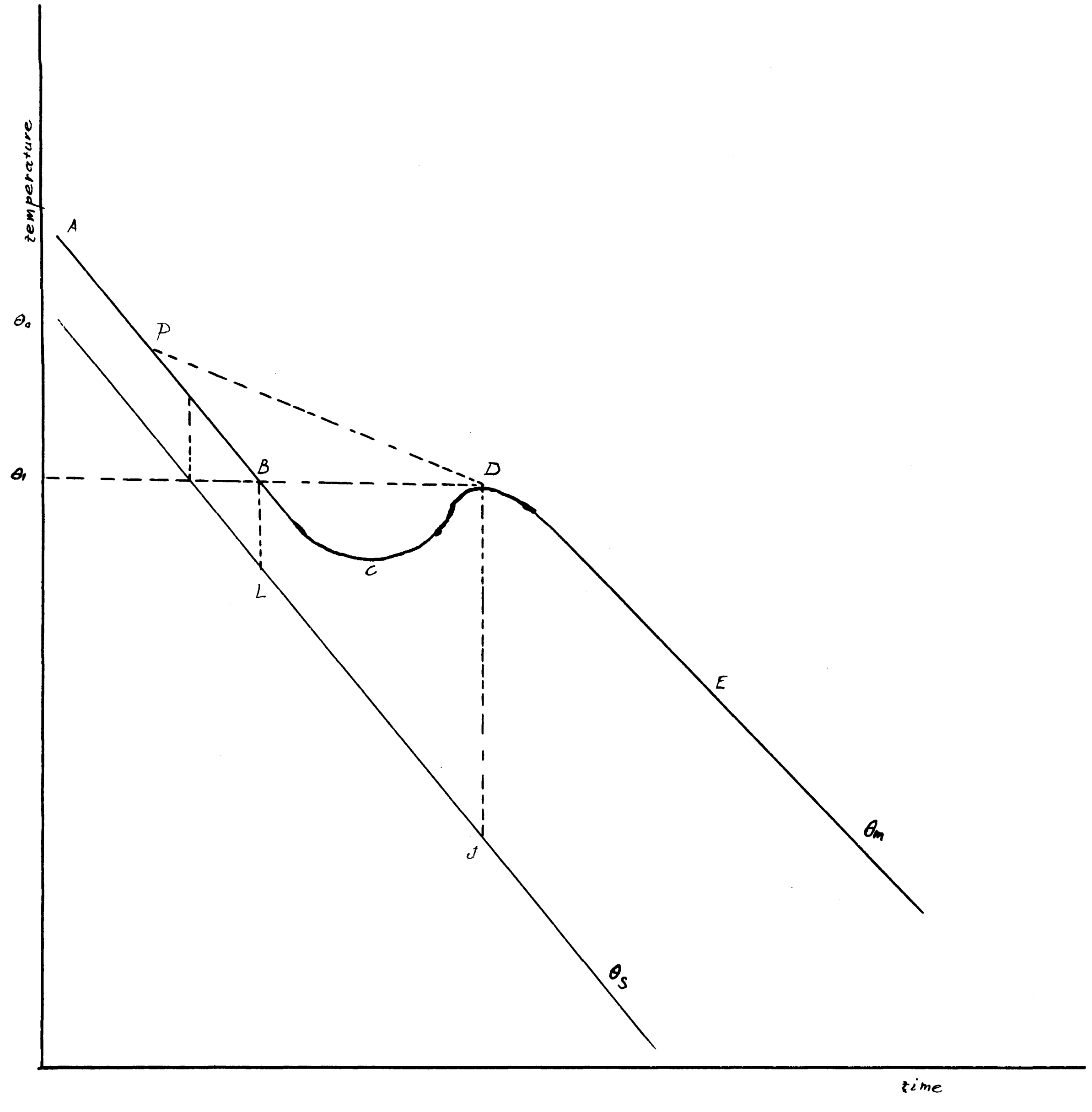

Figure 3.- Time-temperature curve for binary mixture.

the eutectic temperature is approached; at that temperature the liquid still remaining behaves as a pure substance.

However, in actual experimentation there is usually some undercooling. When crystallization is induced, at C, equilibrium between X and solution is soon attained and maintained thereafter, and the heat set free raises the temperature rapidly to a maximum D, beyond which it then falls off as before, a state of equilibrium being maintained. The composition of the liquid phase at D differs from that of the original solution by the proportion of X which has been crystallized; this must be corrected. The usual methods of making this correction are not based upon sound principles and are unsatisfactory. Since this method is based upon Newton's law, it must be interpreted accordingly.

In proceeding along the curve from B to D the system passes from solution at Θ_1 to mixture of solution with n mols solid X, again at Θ_1; and the heat lost by the cooling mixture is nL, where L is the molal heat of fusion of X. But the heat lost is also, as we have seen, proportional to the area BCDJL. If, for the given mixture of X and Y, Θ_o be the real equilibrium temperature, the system passes from a state of equilibrium at F (Θ_o) through an unstable region to equilibrium again at D (Θ_1). For this small range of composition the equilibrium concentration of X is practically a linear function of the temperature; that is, the lowering of equilibrium temperature is proportional to n, the (small) number of mols of X which then have separated. Hence, this lowering; namely $(\theta_0 - \theta_1)$, is proportional to nL and, therefore, to the area BCDJL. Hence, by varying slightly the point C at which the mixture begins to crystallise, both this area and the maximum D (θ_1) will change correspondingly; and, the several values of θ plotted against those of the area will lie on a straight line; and, also it can be seen that this line extrapolated to zero area corresponds to $n = 0$; that is, the particular point so obtained is the equilibrium temperature θ_0 corresponding to the known initial composition of the solution.

This method has been used in the determination of the solubility diagram of a number of systems (1) and its accuracy has been proven by comparison with other methods of attack.

The older method of interpretation, such as used by Bell and Herty (4), is not as accurate. They considered the line DE to be linear, then produced it back to meet AB, then assumed that this point of intersection represented the freezing point of this solution. As shown in Fig. 4, with different degrees of undercooling of a solution, varying values are obtained. This method has been questioned in several papers (1)(9)(11).

TEMPERATURE HEAT-LOSS CURVES

In order to obtain an accurate value of θ_o the temperature at which X tends first to crystallise, for any given solution, it suffices to take two or three cooling curves on that solution, inoculating it at slightly different temperatures, to note in each case the maximum temperature θ_1; to measure the area BCDJL in each case; to plot this area against θ_1 and then extrapolate to zero area which corresponds to the true value θ_o, as in Fig. 5.

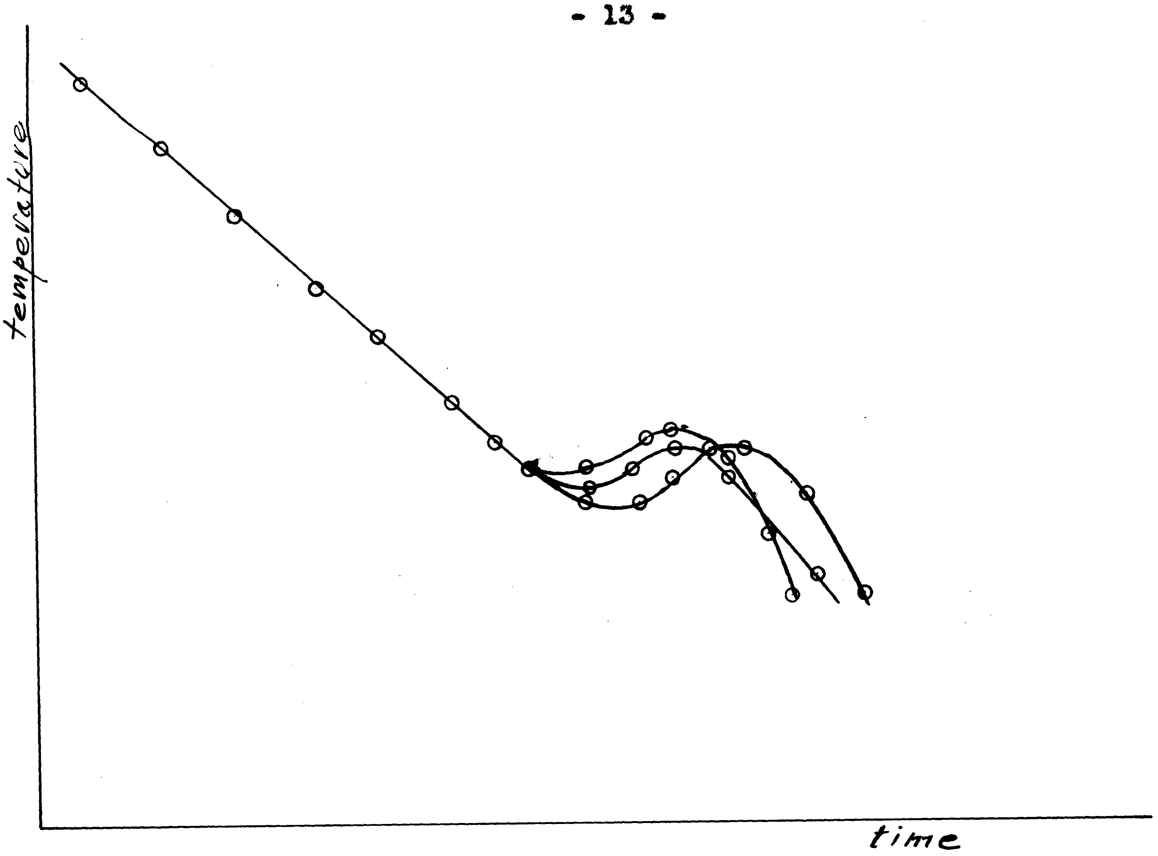

Figure 4.- Time-temperature curve.

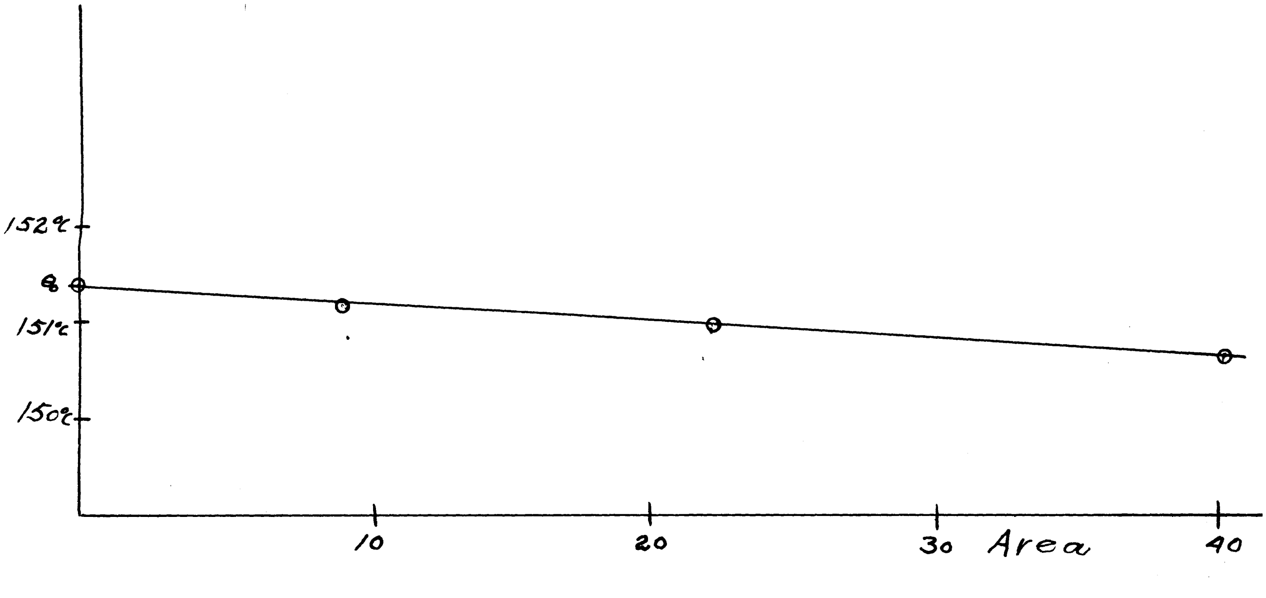

Figure 5.- Temperature- heat-loss curve.

OBJECT OF INVESTIGATION

This study was undertaken in order to investigate the systems salicylic acid-biphenyl and salicylic acid-diphenylamine. It was desired to know whether there is any compound formation in either of the two systems, and if simple solutions result, to determine the ideality of such solutions.

EXPERIMENTAL PROCEDURE

Purification of Materials

Diphenylamine was recrystallized several times from 95% ethyl alcohol. The final product melts at 53.1° C which conforms with the accepted value. The salicylic acid was C.P. grade from Baker Chemical Company and did not require further purification, having a melting point of 159.2° C. The biphenyl was purified by recrystallization from alcohol until a melting point of 69.4° C was finally obtained.

Apparatus

The apparatus as illustrated in Fig. 6 consists of a 2 x 18 cm test tube (T) which contains the sample (M). This is enclosed in air jacket (A) which is suspended in the oil-bath (O) in beaker (B). The electrical motor (E) turns the glass stirrer (G) in order to keep the oil-bath at an even temperature throughout. Into the test tube (T) is placed the thermocouple element (θ_m) which is to measure the temperature of the melt. The thermo-element (θ_s) is in the air jacket (A). The leads of the hot junction of two thermocouples go to the two-way switch (S) which is inserted for the convenience of making alternate readings swiftly. The cold junction of each of the thermocouples is placed in the thermos bottle (C) in cracked ice, and kept at 0° C., these leads fastened directly to the negative pole of the potentiometer (P).

Readings were taken at one-minute intervals until within the range of the freezing point and then taken at one-half-minute intervals. For each sample, three "runs" were made.

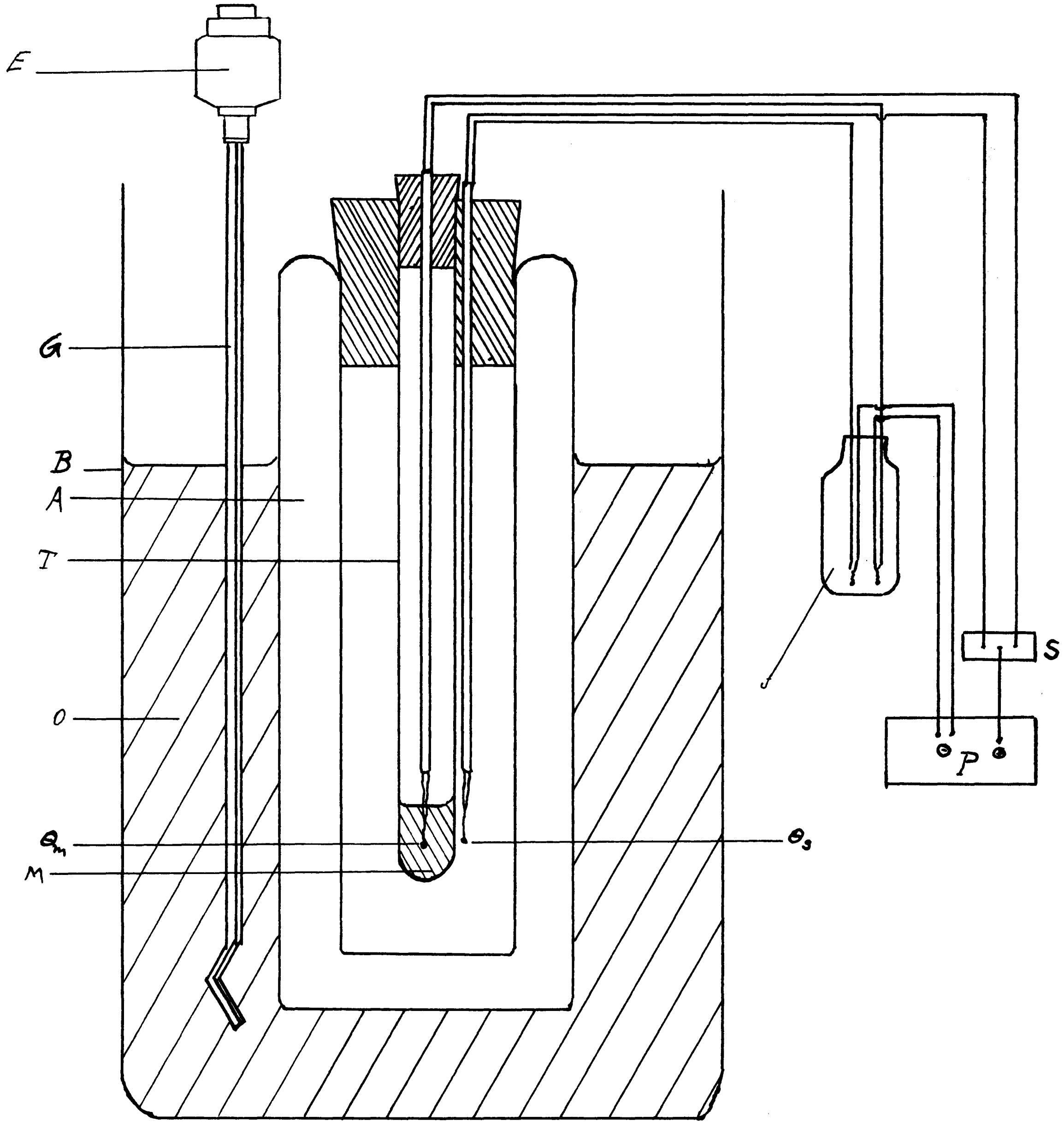

Figure 6.- Freezing point apparatus.

METHODS OF ANALYSES

Determination of Salicylic Acid

The sample containing salicylic acid was first dissolved in ethyl alcohol and then five drops of thymol blue indicator were added. The sample was titrated to a bluish green "end point", using N/10 NaOH. This gave the grams of salicylic acid present (1 cc N/10 NaOH = .013808 grams salicylic acid).

Determination of Diphenylamine

In this method, the total nitrogen (2) was determined and then the grams of diphenylamine calculated. First, the sample was weighed and transferred to a Kjedahl flask. 30 cc of H_2SO_4 containing 1 g. of salicylic acid were added and shaken until thoroughly mixed and allowed to stand, shaking frequently, for at least 30 minutes or until complete soln resulted. 5 g. of $Na_2S_2O_3$ were added and the soln heated for 5 minutes; it was then cooled, 10 g. K_2SO_4 added, and heated very gently until foaming ceased. The heat was increased until the acid boiled briskly and digested for a time after the mixing was colorless or nearly so.

After cooling, it was diluted with about 200 cc of H_2O and a little granulated zinc added to prevent bumping. Sufficient NaOH solution was added to make the reaction strongly alkaline, pouring it down the side of the flask so that it did not mix at once with the acid solution. The flask was connected to the condenser by means of a kjeldahl connecting bulb, taking care that the tip of the condenser extended below the surface of the standard acid in the receiver; the contents were mixed by shaking and distilled until all NH_3 had passed over into a measured quantity of the standard acid. This was then titrated with standard alkali solution, using methyl red as indicator. 1 cc of standard N/10 HCl soln is equivalent to .016919 gms. of diphenylamine. From this, the percent or mole fraction of the sample may be easily calculated.

TREATMENT OF DATA

The data, both observed and calculated values, for the systems salicylic acid-biphenyl, and salicylic acid-diphenylamine are shown respectively in Tables I and II.

The theoretical solubility curves for salicylic acid, biphenyl and diphenylamine (14) are plotted in Fig. 7. Figs. 8 and 9 are the curves for the experimental values of Tables I and II.

There is no compound formation in either system. It is noted that the experimental curve for the salicylic acid-biphenyl system followed very closely to the theoretical curve. The salicylic acid-diphenylamine curve does not act as ideally as did the salicylic acid-biphenyl system. While the theoretical eutectic for salicylic acid-biphenyl is 65.1° C at a mole fraction of .923, the observed eutectic was found to be 67.6° C at .903 mole fraction. For the system salicylic acid-diphenylamine is 52.4° C at .976 mole fraction, the observed eutectic was 48.6° C at .923 mole fraction.

Table I. The System: Salicylic Acid-Diphenyl

Mole Fraction	Freezing Point		Eutectic
	Observed °C	Calculated °C	
1.000	69.3	69.3	
.976	68.8	67.6	67.8
.894	68.2	71.5	
.881	69.7	75.2	
.748	99.4	100.8	67.6
.641	115.3	114.2	67.4
.551	124.9	123.2	
.318	142.1	141.3	
.177	149.8	151.1	
0.	159.2	159.2	

Table II. The System: Salicylic Acid-Diphenylamine

Mole Fraction	Freezing Point		Eutectic
	Observed °C	Calculated °C	
1.000	53.1	53.1	
.963	51.6	50.1	48.4
.882	62.6	75.8	48.5
.863	72.6	79.7	
.777	93.8	96.8	48.7
.598	117.2	118.3	
.487	125.7	127.8	
.388	132.6	136.4	
.358	135.8	138.5	
.287	140.3	143.3	
.254	143.2	145.2	
.114	151.4	153.3	
.038	157.3	157.3	
0.	159.2	159.2	

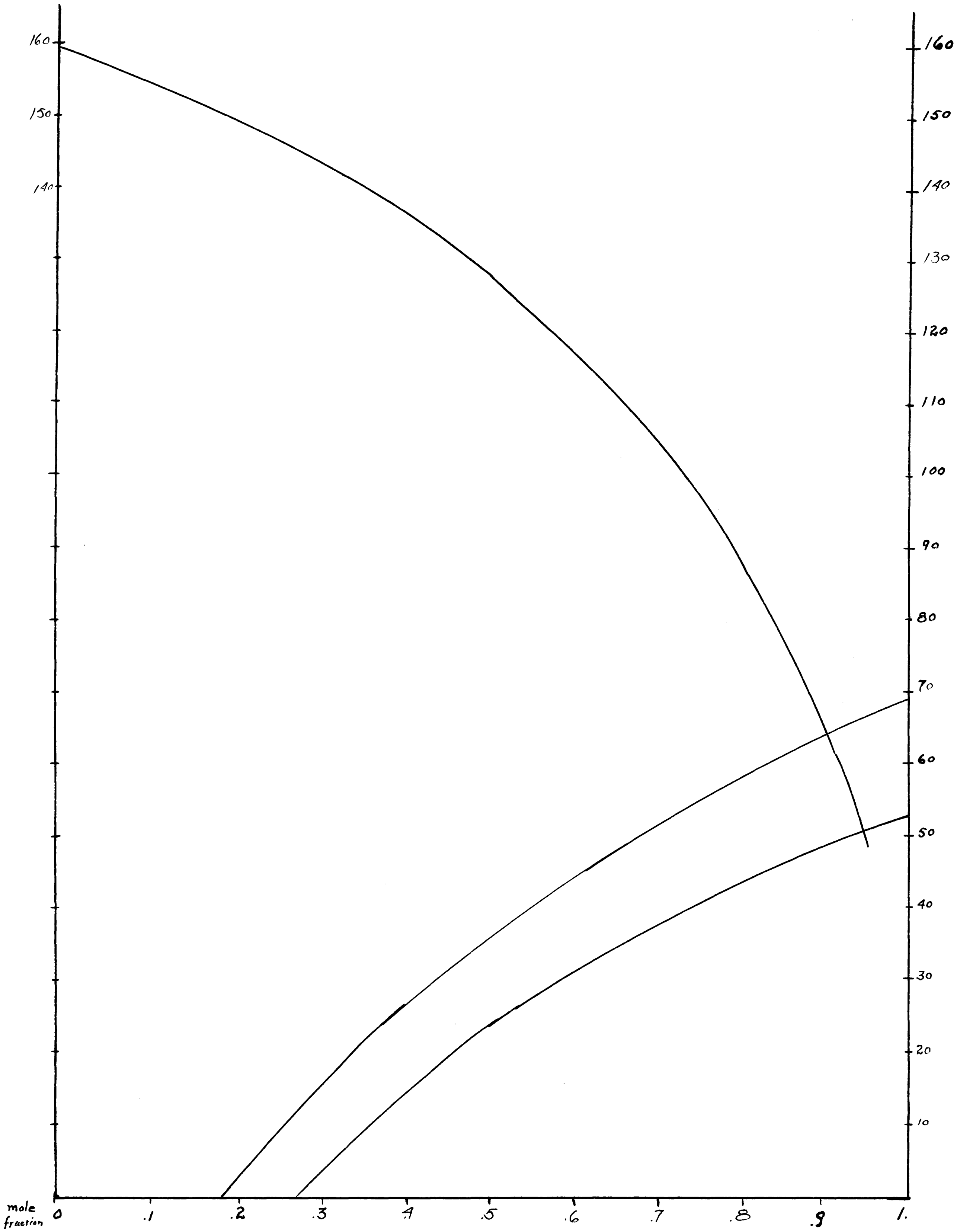

Figure 7.- Solubility curves.

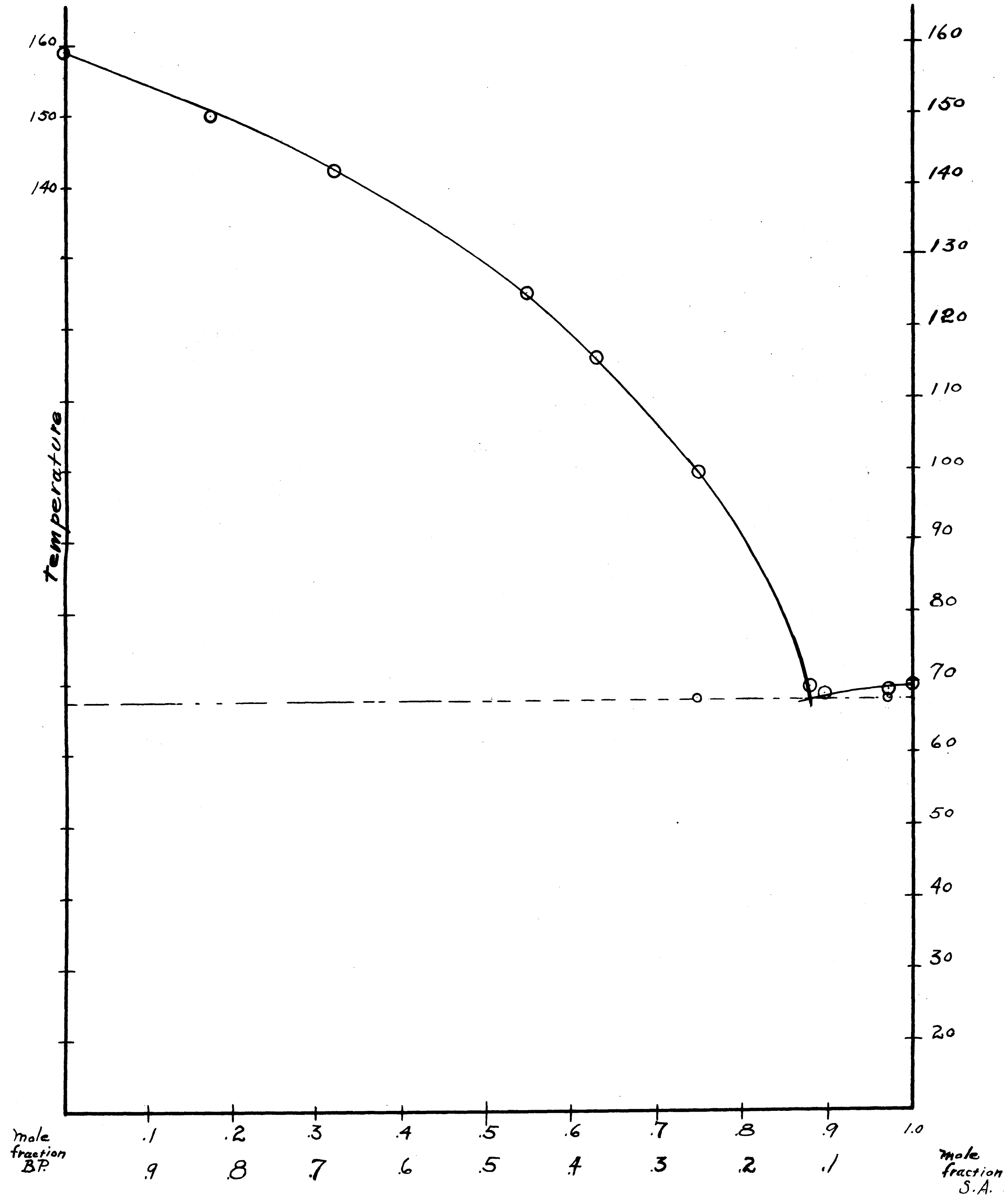

Figure 8.- The System: Salicylic Acid-Biphenyl.

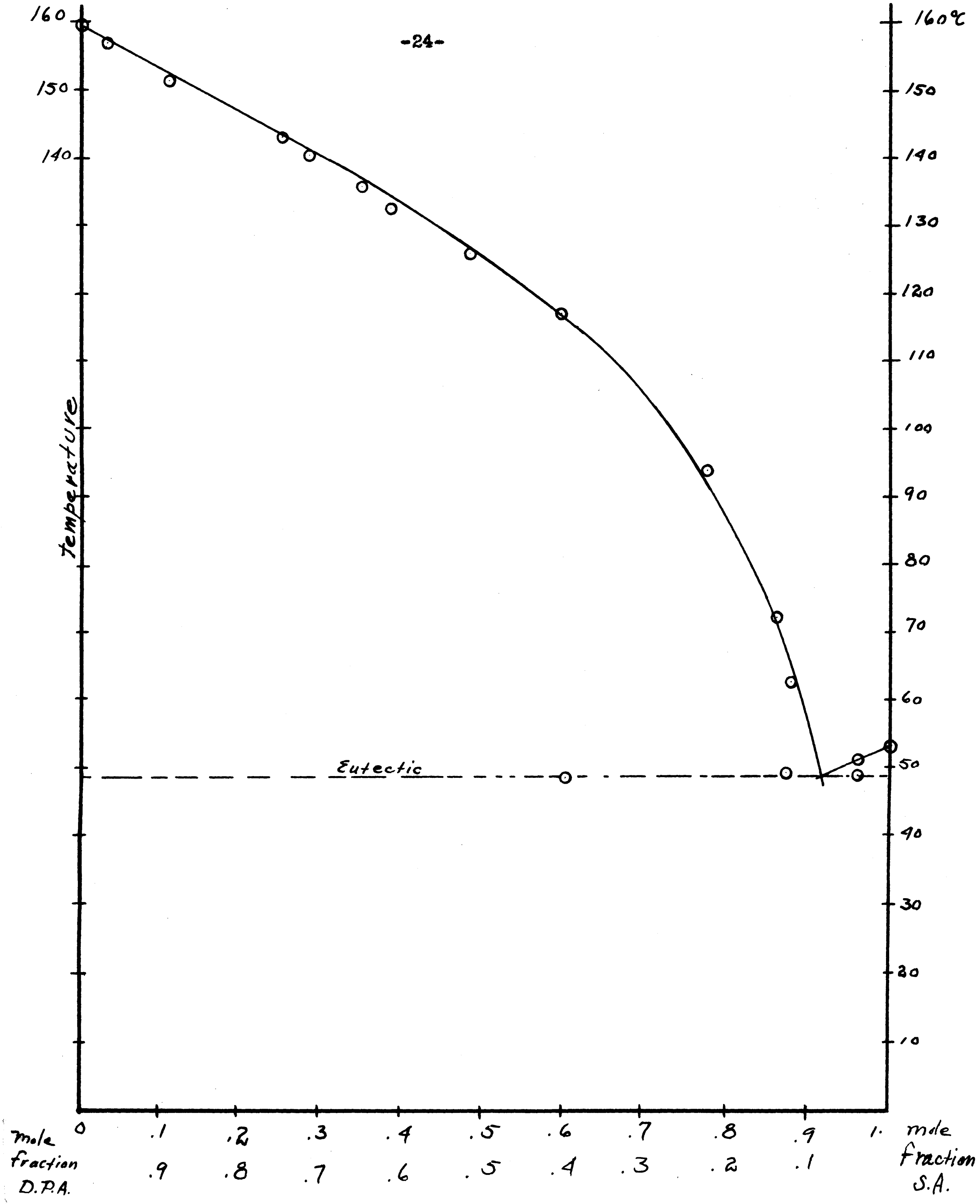

Figure 9.- The System: Salicylic Acid-Diphenylamine.

SUMMARY AND CONCLUSIONS

1. From a study of the system salicylic acid-biphenyl it was concluded that there was no compound formation in the system. The solution is very nearly ideal, having an eutectic temperature of 67.6° C at a mole fraction of .903 for the biphenyl.

2. The system salicylic acid-diphenylamine was studied and no compound formation was found to be present. The system is not as ideal as the salicylic acid-biphenyl system, but follows the ideal solution curve fairly well. The system has an eutectic temperature of 48.5° C at .926 mole fraction of diphenylamine.

APPENDIX I

The Calculation of the Molecular Heat of Fusion for Salicylic Acid

Equation 3, page 3, was used in the calculation of the molecular heat of fusion of salicylic acid.

$$\log_e N = \frac{-\Delta H_f \, (T_0 - T)}{R \, T_0 \, T}$$

where T_0 is the melting point of the pure salicylic and T the observed melting point in the presence of the second component. R is the gas constant and N is mole fraction of the salicylic acid. From observations it was found that the melting point is 157.3° C at a mole fraction of .962; therefore substituting these values in equation 3

$T_0 = 159.2^\circ \text{ C} = 432.2^\circ \text{ K}$ $\quad R = 1.985$

$T = 157.3^\circ \text{ C} = 430.3^\circ \text{ K}$ $\quad N = .962$

$$\log_e (.962) = -\frac{\Delta H_f \, (432.2 - 430.3)}{1.985 \, (432.2) \, (430.3)}$$

changing to the base 10

$$\log_{10} (.962) = -\frac{\Delta H_f \, (432.2 - 430.3) \, .4343}{1.985 \, (432.2)(430.3)}$$

$\Delta H_f = 7570$ cal.

Therefore, the molecular heat of fusion for salicylic acid is found to be 7570 cal. from an observed melting point.

APPENDIX II

THE DATA FOR THE FREEZING-POINT CURVE OF DIPHENYLAMINE AS PLOTTED IN FIGURE 2

Time (Min.)	θ_m ° C	θ_s ° C	Time (Min.)	θ_m ° C	θ_s ° C
0	66.0		15	51.5	
0.5		52.2			36.8
1	63.5		16	50.5	
1.5		50.8			37.0
2	59.7		17	50.8	
2.5		48.9			37.3
3	58.7		18	49.9	
3.5		47.2			
4	56.5		19	49.4	
4.5		45.9			36.00
5	55.5		20	49.4	
5.5					36.5
6	53.2		21	48.9	
6.5		44.3			35.5
7			22	47.3	
7.5		43.2			35.5
8	52.0		23	47.0	
8.5		42.0			34.6
9			24	45.4	
9.5		40.7			34.6
10	52.5		25	44.3	
10.5		40.4			34.4
11	53.1		26	43.8	
11.5	53.0	39.5			34.4
12	53.1		27	42.2	
12.5	53.1	39.3			33.5
13	53.1		28	41.5	
13.5		38.1			33.0
14	52.8	37.8			

APPENDIX III

THE DATA FOR THE HEAT-LOSS CURVES OF SALICYLIC ACID, SAMPLE CONTAINING .114 MOLE GRACTION DIPHENYLAMINE AS PLOTTED IN FIGURE 5.

Run	Heat Loss (Area)	θ_m ° C
1	9	151.2
2	40	150.6
3	23	150.8

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