

SOLID SOLUTIONS IN THE SYSTEM:

p-DICHLORBENZENE: p-CHLORBROMBENZENE: p-DIBROMBENZENE

by

Leslie Prodan

A thesis presented to the Committee  
on Graduate Studies, University of  
Manitoba, in partial fulfillment of  
the requirements for the degree of  
Master of Science.

April 1947.



### ACKNOWLEDGMENT

Sincere thanks are extended to Dr. A. N. Campbell, under whose guidance this project was initiated and carried out, for his encouragement and many helpful suggestions.

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## INTRODUCTION

## Introduction

The origin of the term and the concept of "solid solution" must be credited to the Dutch physico-chemist J.H. van't Hoff (1). In attempting to explain deviations from the laws of dilute solutions, developed largely by himself, he was forced to assume that in cases where the depression of the freezing point of solutions by dissolved substances was too small, the solute crystallized along with the solvent. The solid obtained from such solutions he called "dilute solid solution". While van't Hoff was the first to publish his views on this subject, in 1866 Lecoq de Boisbaudran presented to the Académie des Sciences de Paris two papers in which the expressions "solid solution" and "solid solvent" were used. At this time, however, such ideas conflicted strongly with the accepted notions of most chemists and physicists and the papers were rejected. Boisbaudran's views did not reach publication until 1891 (2), twenty-five years after his initial attempt, and a year and a half after van't Hoff's fundamental paper.

By "solution" is meant, specifically, any homogeneous mixture whose composition can be varied within limits. Such a definition places no restriction whatever on the physical state, and is equally applicable to solids as to liquids and

gases. A "solid solution" is a crystalline body usually formed from a liquid solution, which retains in the solid state as intimate an admixture of solute and solvent as that existing in the liquid state. The distinguishing features of a solid solution must be rigidity and a crystalline structure. With regard to these latter properties only two exceptions need be noted: liquid crystals, which are fluid but possess a crystalline structure, and glasses, which have great rigidity but show no evidence of anisotropy.

When a chemically pure substance freezes, it does so at a definite temperature. This is not a characteristic of solid solutions; for a solution of two materials capable of forming a continuous series of solid solutions, the first solid separating upon freezing is always richer in the higher melting component of the original solution. As freezing progresses, the composition of the solid separating changes continually until, when all liquid has disappeared, the solid obtained has the same composition as the original liquid solution. A change of concentration in both liquid and solid solutions during the process of freezing entails a change of temperature, and so it is that a solid solution freezes or melts over a range of temperature. The temperature of initial deposition of solid is the "freezing point" and the temperature at which the last trace of liquid disappears upon cooling a solution is the "melting point".

The particular system to be studied, namely, the system, p-dichlorobenzene: p-dibromobenzene: p-chlorobromobenzene, has been shown by G. Bruni and F. Gorni (3) to exhibit complete miscibility in both liquid and solid states; the system forms a continuous series of solid solutions. However, two of the binary systems possess a minimum freezing point. The data of Bruni and Gorni do not indicate a minimum freezing point for the ternary system, although Bruni, in a pamphlet published in 1901 (4) says, "----- The latter (a minimum) was found experimentally in mixtures of p-dichlor-- , p-dibrom-- , and p-chlorobromobenzene, which melt at  $52.5^{\circ}$ ,  $68^{\circ}$ , and  $85^{\circ}$  respectively, and whose mixtures show a minimum zone on the freezing surface in the dichlorobenzene corner."

It was the purpose of this project to repeat the determinations of Bruni and Gorni with regard to the freezing point curves of the three possible binary systems and the freezing surface of the ternary system. Further, the melting point curves of the binary systems and the melting surface of the ternary system, which have not been examined experimentally as yet, have been determined. It was also necessary to dispel the apparent ambiguity concerning the existence of a minimum freezing point in the ternary system.

Of particular importance was the sensitive apparatus

and specialized technique employed to determine freezing and melting points. The method used was essentially a refined method of thermal analysis.

## THEORETICAL CONSIDERATIONS

## I. THE PHASE RULE

### Fundamental Definitions

Before embarking on a discussion of the Phase Rule proper, it is necessary to describe and explain a few of the basic quantities encountered in discussions of chemical thermodynamics and the Phase Rule. The essential quantities and concepts are outlined below:

System. A system may be defined as any physical body or group of bodies isolated for special consideration. If the system is uniform throughout in physical and chemical properties it is a "homogeneous system"; if the system is composed of two or more parts having different physical or chemical properties and separated by bounding surfaces, it is a "heterogeneous system".

State. The state of a system is its physical condition as defined by any combination of quantities which differentiate this condition from all others. The quantities defining the state are the properties of the system. Properties such as mass or volume, which are additive, are called "capacity factors"; those which are non-additive, such as density, pressure, or temperature, are "intensity factors". Knowledge of the capacity factors of a system enables its state to be

perfectly defined, since by the mathematical methods of thermodynamics, all intensity factors may be derived.

Equilibrium. For equilibrium to exist in a system, there must be an equal balance between the various parts of which the system is composed. Equilibrium in a heterogeneous system is "heterogeneous equilibrium"; similarly, equilibrium in a homogeneous system is known as "homogeneous equilibrium". When used by the chemist, the word "equilibrium" means "neutral equilibrium". This may be likened to a balance having equal masses on both pans. The balance will attain a position of rest, but the slightest change of mass on either pan destroys the equilibrium. In contrast to neutral equilibrium there may exist a stable equilibrium, a mechanical analogue being a balance with a ten pound weight on one pan and a one pound weight on the other. An intermediate type, a metastable equilibrium, may be encountered; the equilibrium of a system in this condition is stable with regard to very slight displacements, but is much less stable than any other condition of equilibrium.

If a system is to attain equilibrium, there is required some driving force. In chemical thermodynamics this driving force has been designated as the "thermodynamic potential", or the "Gibbs free energy". The criterion of any equilibrium condition in a system is that the

thermodynamic potentials of all individual parts composing the system be equal. If the thermodynamic potential of a system reaches a minimum invariable value, a condition of stable equilibrium has been attained.

Phase. Each physically homogeneous portion of a system separated from all other such portions by a bounding surface is a phase. For example, if a quantity of water existed partly as solid, partly as liquid and partly as vapour, the system would contain three phases. A system composed of three immiscible liquids would contain three phases, since each homogeneous liquid must be separated from its neighbors by a bounding surface. It is important to distinguish between the phases and constituents of a system; a constituent maintains a fixed recognizable structure, while a phase may be composed of several constituents.

It is now apparent that equilibrium in a system composed of one phase only is homogeneous, and where the system is composed of two or more phases, heterogeneous equilibrium must exist. Any condition of equilibrium is independent of the amounts of phases present in a system, for equilibrium is determined solely by the thermodynamic state of the system.

Components. The number of components of a system is the number of substances the masses of which in each phase

completely determine the physical condition of the phase, provided the temperature and pressure are known. As components of a system must be selected the smallest number of independently variable constituents required to express the composition of each phase participating in a state of equilibrium in the form of a chemical equation. The number of components of a system may be selected unerringly by following a simple rule. Divide the total number of elements present in a system into two groups such that knowledge of the masses of all elements in the first group enables computation of the masses of the elements in the second group; the number of elements in the first group is the number of components. In the example of water, mentioned above, the elements present are H and O. Therefore, knowing the mass of O, we can deduce the mass of H. Similarly, knowledge of the mass of H permits deduction of the mass of O. Since the mass of only one element need be known to establish the composition of the system water, this system must be a one-component, or singular system.

In an aqueous solution of sulphuric acid three elements are present, namely, H, S and O. Knowledge of the masses of any two of these elements establishes the mass of the third. Thus the system sulphuric acid-water is a two-component or binary system, the components being water and sulphuric acid. For a given system the number of

components is fixed, but there is a certain freedom of qualitative selection of the components. This is especially true in multi-component systems, when the choice of components is influenced by considerations of convenience or simplicity.

Degree of Freedom. The variability or degree of freedom of a system is the number of variable factors which must be fixed in order to completely define the condition of the system. Four sets of such factors are recognized, each set containing four independently variable quantities.

For purposes of convenience in studying equilibria experimentally, the chemist has selected the set: thermodynamic potential - pressure - temperature - composition, usually symbolized:  $G - P - T - x$ .

Since if any three of these variables are fixed, the fourth must also be fixed, it is sufficient to know  $P$ ,  $T$  and  $x$ , in order to establish the condition of a system. If the system is defined in terms of the variables  $G-P-T-x$ , it is possible to translate its condition in terms of any one of the other three fundamental sets of variables by applying the appropriate thermodynamical calculations.

Transformation. Any process of change from one physical state or from two or more physical states to a different physical state, or to two or more different physical states,

is a transformation. Thus the familiar processes of melting or freezing are transformations, the temperature at which they occur being the transformation temperature. For a transformation to occur, it is necessary that at least two phases coexist in equilibrium.

All transformations may be classified into five types:

|                 |                                     |
|-----------------|-------------------------------------|
| Solid — Liquid  | ( S — L )                           |
| Solid — Vapor   | ( S — V )                           |
| Solid — Solid   | ( S <sub>1</sub> — S <sub>2</sub> ) |
| Liquid — Vapor  | ( L — V )                           |
| Liquid — Liquid | ( L <sub>1</sub> — L <sub>2</sub> ) |

### The Phase Rule

In papers published between the years 1876 and 1878, J. W. Gibbs (5) developed a method of chemical thermodynamics which proved to be exceptionally powerful in solving problems in heterogeneous chemical equilibria. Inventing suitable mathematical functions, he established the criteria of equilibrium and showed what experimental data were necessary to solve a particular problem. By collecting experimental data in the form of a "fundamental equation" for each phase, any problem could be solved algebraically. Gibbs' methods were developed graphically by van Ryn van

Alkemade (6), and extended qualitatively by Bakhuis Roozeboom (7) and F. Schreinemakers. An important generalization resulting from Gibbs' studies was the Phase Rule, a brief derivation of which will be given.

Suppose a system to consist of  $C$  components existing in  $P$  phases. For a condition of neutral equilibrium in the system, the thermodynamic potentials of the  $P$  phases must be equal. This potential in any one phase is determined by the composition of the phase, the temperature and pressure, a total of three variables. The composition of unit mass of each phase is known if the masses of  $(C-1)$  components in each phase are known. Since there are  $P$  phases, the total number of variables possessed by the system is  $P(C-1) / 2$ ; the factor 2 accounts for the two variables temperature and pressure. Now for each phase there exists one equation defining its thermodynamic potential, so that  $(P-1)$  equations are required; and in order to fully define the state of the system there must be  $C(P-1)$  equations, as the thermodynamic potential of each phase is dependent on the masses of the components. For a complete solution there must be as many equations as variables. If there are insufficient equations, the number of deficient equations is the variability, or degree of freedom of the system. Therefore the degree of freedom of

a system is

$$F = P(C-1) / 2 - C(P-1) = C - P / 2.$$

This is the Phase Rule as first discovered by Gibbs.

It can be seen that a system of  $C$  components can exist in  $C / 2$  phases only if  $F = 0$ , that is, if temperature, pressure and concentration have fixed values. For  $C$  components in  $C / 1$  phases, there will be one degree of freedom, or one factor which may be varied without destroying the equilibrium condition.

The phase rule is able to predict the number of phases coexisting under given conditions, but does not inform us as to what phases exist or as to their relative amounts.

The relative amounts of coexisting phases are not considered as variables. If a system is subject to some variable such as a gravitational, electric, or magnetic field, the number 2 must be increased one unit for each additional variable. The Phase Rule may therefore be generalized:

$$\text{Degree of Freedom} = \text{Variables} - \text{Invariants}$$

where the Invariants are the number of phases.

## Solutions

### The Ideal Solution

A solution may be defined as any homogeneous mixture whose composition can be varied within limits (1). This definition does not make any assumption as to the state of aggregation and is therefore equally applicable to gaseous, liquid, and solid solutions. Thus, any phase of two or more components may be regarded as a solution.

The ideal solution is a convenient standard to which all other solutions may be compared, but very few solutions met with in practice compare closely to it. When two liquids form an ideal solution they do so without evolution or absorption of heat, and all properties of the solution such as vapor pressure, density and viscosity, may be calculated from the properties of the two components by applying standard relations known as the laws of ideal solutions. The most important of these laws are those of Raoult and van't Hoff.

Any pure liquid exhibits an escaping tendency, or a tendency for the liquid molecules to form a vapor. The fundamental statement of Raoult's law is that the escaping tendency of any chemical individual is proportional to its mole fraction. Addition of a solute to a pure liquid will therefore decrease the mole fraction of the liquid and

consequently decrease its escaping tendency (vapor pressure). This is evident from the relation

$$P = P_0 x$$

where  $P_0$  is the vapor pressure of the pure liquid,  $x$  its mole fraction, and  $P$  the vapor pressure of the solution.

As the vapor pressure of a pure liquid is depressed by the addition of solute, so is its freezing point. For a dilute ideal solution of two components, from which pure solvent is deposited in the freezing process, van't Hoff has formulated a law of freezing point depression which may be expressed

$$\frac{dT}{dx_a} = \frac{RT_a^2}{-L_a \cdot x_a} \quad \text{--- (1)}$$

where  $R$  is the gas constant,  $T_a$  the absolute temperature of the liquid-solid transformation of solvent  $A$ ,  $L_a$  the heat of transformation per mole of  $A$ , and  $x_a$  the mole fraction of  $A$  in solution. For practical application, this relation may be integrated provided the heat of fusion ( $L_a$ ) is assumed to remain constant over the range of temperature considered (8). Hence we obtain

$$\log x_a = \frac{-L_a}{4.579} \frac{T_a - T}{T_a T} \quad \text{--- (2)}$$

where  $4.579 = 2.303 R$  and  $T$  is the absolute transformation temperature of the solution. This expression is applicable

to more concentrated solutions, but holds strictly for ideal solutions only.

If any solution can be shown to obey Raoult's or van't Hoff's law, this is sufficient criterion to establish it as an ideal solution.

### The Non-ideal Solution

Deviations from the laws of ideal solutions must be attributed to interaction of the atoms of the components of the solution. In the non-ideal solution the force between two kinds of atoms A and B is either one of excess attraction or excess repulsion.

For an ideal solution a linear relationship exists between vapor pressure  $p$  and mole fraction  $x$ , as defined by Raoult's law; this is represented by line (1) Figure 1. In the event of excess attraction between atoms A and B, the atoms are more tightly bound and the vapor pressure of the solution is decreased. The latter condition is represented by curve (2). Conversely, an excess repulsive force manifests itself by an increased vapor pressure, as shown by curve (3). If the attractive force is sufficiently great, a compound of A and B may be formed; again, the force of repulsion between atoms A and B may become so large that a solubility gap, or a region of almost negligible solubility occurs. Figure 2 represents the latter case.

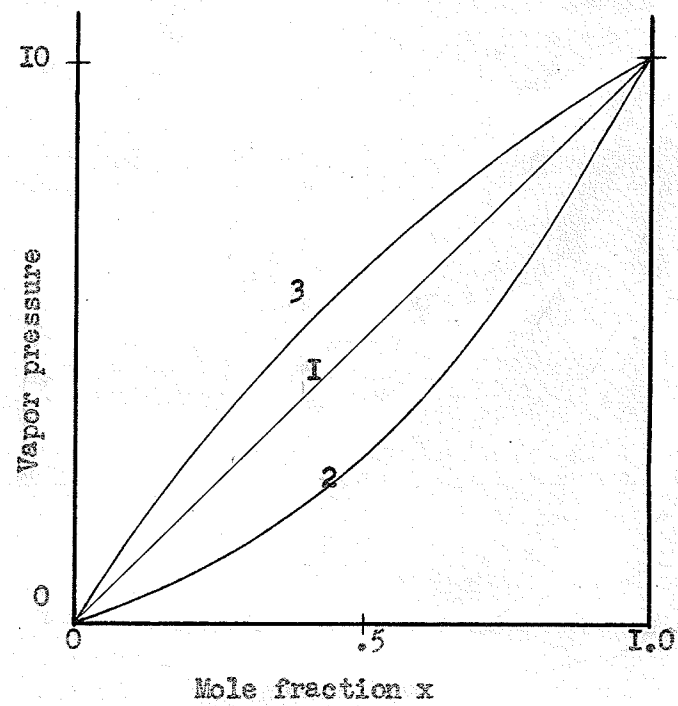


Figure 1.

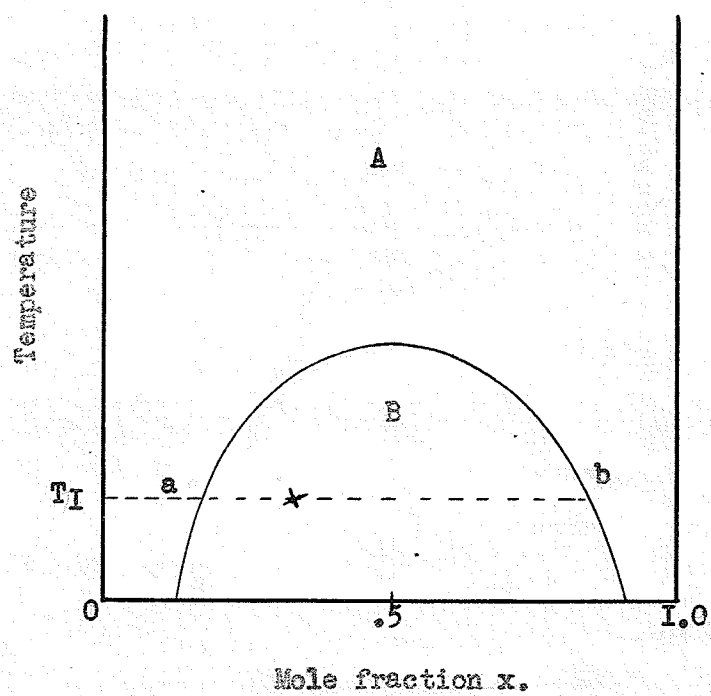


Figure 2.

Plotting the composition of the solution against temperature we obtain the "phase diagram", in this case consisting of two "fields", one representing the temperatures and concentrations for which one homogeneous phase exists and the other representing the temperatures and concentrations for which two phases exist. These fields are A and B respectively in Figure 2. In field A there are two degrees of freedom ( $F = 2 - 1 \wedge 1 = 2$ ) since pressure is fixed; therefore, temperature and concentration may be continuously and simultaneously variable without appearance or disappearance of a phase. At a point X in field B there are two liquid phases, the mole fraction  $x$  in each being given by points a and b. Thus for any given temperature the composition of the liquids must be fixed in order that there be no change in the number of phases.

To make possible the application of the exact thermodynamic relations of ideal solutions to non-ideal solutions, G.N. Lewis (9) has invented the concepts of fugacity and activity. The fugacity is a measure of the escaping tendency of a solution considered as an ideal solution; while the activity is a factor which corrects the mole fraction of a solution component to its ideal-solution value. These functions serve only to bring experimental results into agreement with the laws of ideal solutions.

## Solid Solutions

### (a) General character

All solids exhibit an escaping tendency; every solid gives rise to a vapor pressure, although it may be very small. It is conceivable, then, that a solid phase may be formed consisting of two or more components and which obeys Raoult's law. Such an association of solids is an ideal solid solution.

A solid solution may be considered analagous to a liquid solution, its distinguishing feature being the possession of a crystalline structure. The crystalline structure of solid components influences their miscibility in the solid state; only those substances having similar crystalline structure are able to form solid solutions in all proportions or what is known as an "isomorphous series". This statement has been borne out by recent X-ray crystallographic work (10). Thus, miscibility in the solid state is more limited than in the liquid state, but it is by no means a rare phenomenon. Solid solutions are common in alloys, mixtures of organic and inorganic substances, and in minerals solid solutions are the rule, a pure crystal being seldom found.

Solid solutions may be formed by freezing from a mixture of the fused components, from a solution of the

components in a common solvent, or by sublimation.

Considering deposition from a melt only, the solid phase separating is usually richer than the melt in the higher melting component. In certain cases the solid phase may have the same composition as the liquid from which it is deposited; this phenomenon is known as "congruent" freezing.

(b) Binary Systems

(i) Graphical Representation

Consider a solution of two components A and B whose freezing points are  $T_a$  and  $T_b$ , respectively, from which solid solutions may be deposited in all proportions upon freezing. The "phase diagram" of this system is obtained by plotting composition of the solution as abscissae against temperature as ordinates, as shown in Figure 3. Composition is always expressed as the number of parts or moles of one component in 100 parts or moles of the solution, called respectively "weight percent" and "mole percent". Originally, van Ryn van Alkemade plotted the thermodynamic potential (G) against concentration (G), but because of the impracticability of the method, Roozeboom (11) substituted temperature for G.

The diagram of the type shown in Figure 3 is an "isobaric section", since it represents the state of

equilibrium of the system under constant pressure, assumed, unless otherwise stated, to be atmospheric pressure.

A complete representation of the system would be a spatial diagram having three mutually perpendicular coordinate axes, one for each of the variables temperature, pressure and concentration.

In this diagram there are three fields: liquid solution, liquid and solid ( $L \neq S$ ) and solid solution. In the liquid field there exists one two-component phase and therefore this system possesses two degrees of freedom ( $F = 2 - 1 \neq 1 = 2$ ). Temperature and pressure may be simultaneously changed without the appearance or disappearance of a phase. This is also true of the solid solution field. In the lens-shaped  $L \neq S$  field two phases coexist, namely, liquid and solid. Therefore, only one degree of freedom is permissible; ( $F = 2 - 2 \neq 1 = 1$ ) either temperature or concentration must be arbitrarily fixed. The upper "liquidus" line represents the freezing points of all possible solutions of A and B; the "solidus" line represents the melting points of all possible solid solutions.

(ii) Liquid-Solid Transformation

Consider the  $L \rightleftharpoons S$  transformation of a solution of composition  $x$  (Figure 3). Upon cooling the high temperature

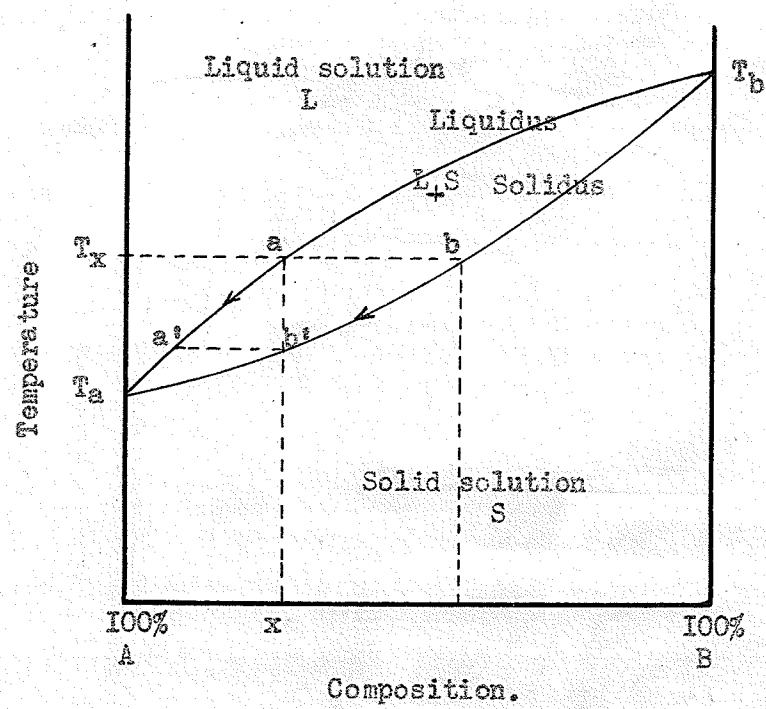


Figure 3.

phase, solid solution begins to deposit at temperature  $T_x$ , the composition of the initially separating solid phase being given by  $b$ . At this temperature liquid of composition  $a$  is in equilibrium with solid of composition  $b$ . The solid phase is richer in component B than the liquid phase, leaving the liquid impoverished in this component. Removal of the high-melting component B from the liquid causes a slight decrease in temperature, and as freezing progresses the temperature of the system drops while both liquid and solid phases change in composition. When the transformation is nearly complete, the composition of the last portion of liquid is that of  $a^1$ . The completed transformation yields a solid solution of composition  $x$ , the same as that of the original liquid solution.

It follows that when a solid solution freezes it does so over a range of temperature. Conversely, melting of a solid solution must also take place over a range of temperature. This temperature range is described as the freezing or melting interval.

Concentration change in both liquid and solid phases during freezing is achieved by a process of diffusion. In liquids, diffusion of the atoms of the components is sufficiently rapid to maintain a homogeneous solution, but in solids diffusion is impeded by the presence of the

crystal lattice and therefore it is usual to detect a composition gradient. The solid phase may alter its composition in one of two ways; either the process of diffusion in the solid is continuous, so that the solid phase is homogeneous, or the solid deposits in successive layers of different composition. In practice, neither of these extremes is observed, deposition of solid usually being a combination of the two processes. However, by cooling the melt very slowly it is possible to approach the equilibrium condition closely, the solid phase altering its composition largely by diffusion.

The exact mechanism of diffusion in the solid state is not clear, but Rosenhain (12) has explained it on the basis of "intercrystalline slips" caused by local strains in the crystal lattice.

### (iii) Quantitative Relations

Any phase transformation involves:

- (1) A change in heat content of the system ( $\Delta L$ )
- (2) A change of composition ( $\Delta x$ )
- (3) A change of volume ( $\Delta v$ )

In the phase transformation liquid solution - solid solution, it should be possible to derive a relation between composition of the liquid and solid phases in equilibrium and the heat content of the system. Such a relation would enable us to calculate the relative positions of the liquidus and

solidus curves in a phase diagram of the type shown in Figure 3.

Van't Hoff's law of freezing point depression (equation 1, page 14) is applicable only to an ideal solution from which pure solvent alone freezes out. It is therefore useless in those cases where solid solutions are formed, since solute and solvent freeze out together in this event.

For very dilute solid solutions, Rothmund (13) has derived an expression relating composition of liquid and solid phases with temperature on the assumptions that the solid solution obeys Raoult's law, and the heat of fusion of the solid is constant over the temperature range considered. In a discussion of the relative positions of liquidus and solidus curves in a system of the type shown in Figure 3, van Laar (14) introduced equations for the liquidus and solidus curves which are applicable for all concentrations in the liquid and solid solutions. Perhaps the most reliable equations for the solidus and liquidus curves are those derived more recently by Seltz (15), using the concepts of activity and fugacity introduced by G.N. Lewis (9) for ideal liquid solutions. The equations were derived for a solid solution which obeys Raoult's law, and do not take into account the change of heats of fusion (L) with temperature. They are:

$$(a) \text{ Liquidus: } x_b^l = \frac{1 - K_a \cdot e^{\frac{L_a}{RT_x}}}{\frac{L_b}{K_b \cdot e^{\frac{L_b}{RT_x}}} - K_a \cdot e^{\frac{L_a}{RT_x}}}$$

$$\text{or } x_b^l = \frac{1 - e^{\frac{L_a}{R}(\frac{1}{T_x} - \frac{1}{T_a})}}{\frac{L_b}{e^{\frac{L_b}{R}(\frac{1}{T_x} - \frac{1}{T_b})}} - e^{\frac{L_a}{R}(\frac{1}{T_x} - \frac{1}{T_a})}} \quad \text{--- (3)}$$

$$\text{where } K_a = \frac{1}{\frac{L_a}{e^{\frac{L_a}{RT_a}}}} \text{ and } K_b = \frac{1}{\frac{L_b}{e^{\frac{L_b}{RT_b}}}}$$

$$(b) \text{ Solidus: } x_b^s = x_b^l \cdot K_b \cdot e^{\frac{L_b}{RT_x}} \quad \text{--- (4)}$$

The symbols are those used in Figure 3:

R = gas constant.

L = latent heat of fusion of solid per mole.

x = concentration expressed as mole fraction.

$T_x$  = absolute freezing temperature of the solution

$T_a, T_b$  = absolute freezing temperature of pure components

A and B respectively.

The subscripts a and b refer to components A and B;

the superscripts l and s refer to the liquid and solid phases respectively.

That these equations are theoretically sound, may be demonstrated by neglecting the first term in the denomination of equation (3), that is, by assuming only pure solvent freezes from the solution. Equation (3) then reduces to the ideal solution equation (equation (2) page 14).

(iv) Classification

Binary systems forming isomorphous solid solutions have been classified qualitatively into five types by Roozeboom (16). Another type was introduced by Ruer (17) making a total of six types which are classified as follows:

A. Components form a continuous series of solid solutions corresponding to complete miscibility in the solid state:

Type I. Liquidus and solidus curves run continuously from the freezing point of pure A to the freezing point of pure B.

Type II. Liquidus and solidus curves pass through a maximum.

Type III. Liquidus and solidus curves pass through a minimum.

Type VI. Liquidus and solidus curves show a point of inflection.

B. Components do not form a continuous series of solid solutions, corresponding to limited miscibility in the solid state.

Type IV. The two series of solid solutions show a transition or peritectic.

Type V. The two series of solid solutions form a eutectic.

A. Type I (Fig.3)

This common type of binary system has been explained under "Solid Solutions".

It has been contended (18) that in such systems the solidus curve is a straight line joining the freezing points of the pure components and the solid solution separating has the same composition as the liquid solution. Such a situation is impossible however, since van Laar (14) has proved that coincidence of liquidus and solidus curves can never occur. Generally, the liquidus curve lies above the straight line joining the freezing points of the components, and the solidus below; but it is possible for the liquidus curve to coincide with this straight line, or to lie below it.

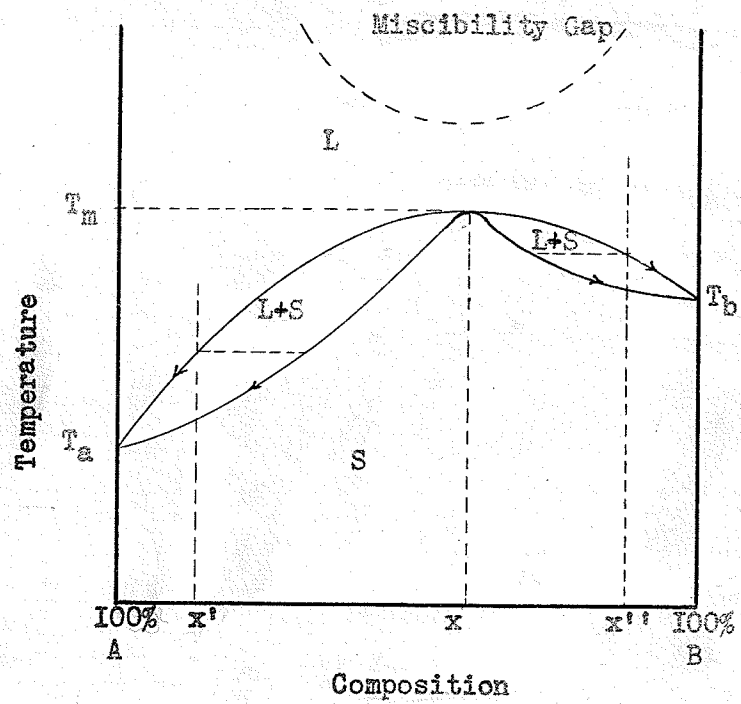


Figure 4.

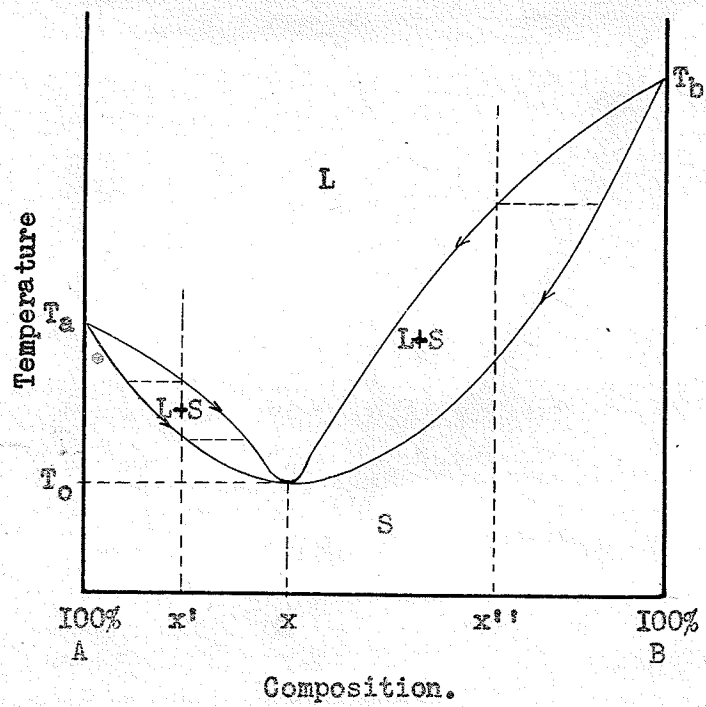


Figure 5.

Type II (Fig.4)

Such systems exhibit a tendency toward formation of a miscibility gap in the liquid phase at some higher temperature. A solution of composition  $x$  "freezes congruently" at a maximum temperature  $T_m$ , i.e., yields a solid solution of the same composition as the liquid phase. At  $T_m$  only, (excepting  $T_a$  and  $T_b$ ) the solution freezes as a chemical individual;  $T_m$  is therefore designated as a "singular point". Solutions to the right and left of  $T_m$  freeze over a temperature interval as in Type I, the solid phase being in one case richer in B than the melt, (solution  $x^I$ ) and in the other case richer in A, (solution  $x^{II}$ ). For all concentrations, the solid phase is homogeneous and of a single crystal type.

Type III (Fig.5)

The diagram of this type may be considered a derivation of Type I, the liquidus and solidus curves of which are distorted by a tendency toward formation of a miscibility gap in the solid state at some lower temperature.

As in Type II, a singular point  $T_0$  exists, at which minimum temperature a liquid of composition  $x$  freezes congruently. Solutions to the left of  $T_0$  yield upon freezing a solid phase richer in component A, while those to the right of  $T_0$  deposit a solid phase richer in B. For any given

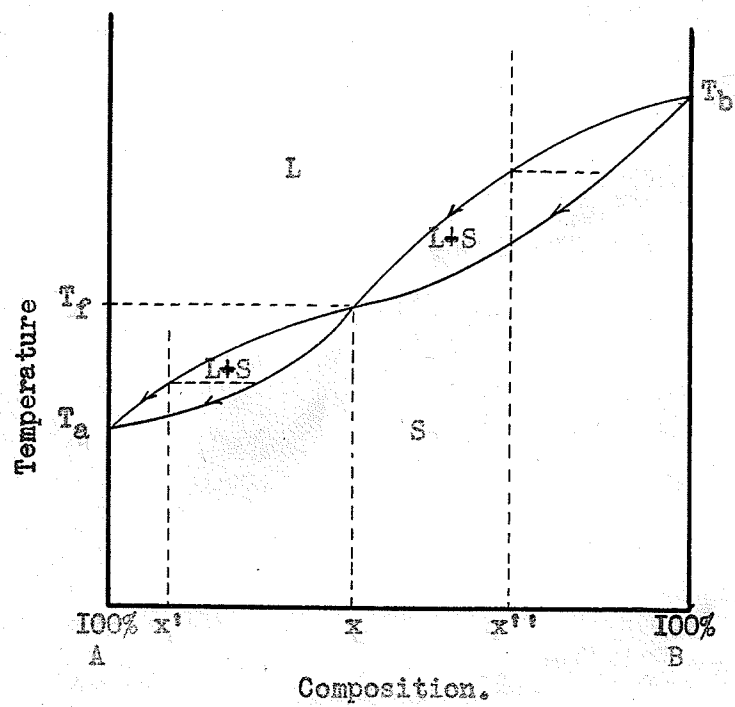


Figure 6.

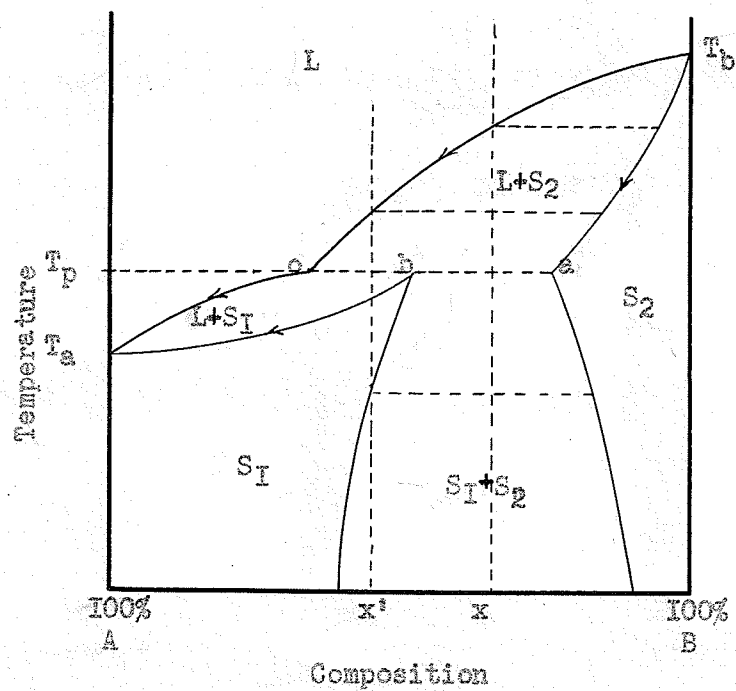


Figure 7.

temperature between  $T_a$  and  $T_o$ , therefore, there must exist two mixtures of distinctly different compositions which possess this same transformation temperature. However the crystals depositing from each mixture necessarily must be of the same crystal type.

#### Type VI (Fig.6)

A singular point ( $T_f$ ) is exhibited in this type of binary system, which is neither a maximum nor a minimum temperature, but a point of inflection. At this point a solution of composition  $x$  freezes congruently.

The diagram is a combination of Types II and III where the freezing point of B is depressed by addition of A and the freezing point of A is raised by addition of B. The solid phase deposited on freezing a solution is always richer in the higher melting component B.

The last three types considered, (II, III, VI) are physical manifestations of the theoretical requirement that at any singular point the tangent to the liquidus (and solidus) curve must be horizontal. A horizontal tangent to any curve is possible only if the curve exhibits a maximum, a minimum, or a point of inflection.

B.

Type IV (Fig.7)

Appearance of a miscibility gap in the solid phase in the range of transformation temperature of Type I gives rise to this diagram. Along  $T_{a0}$  liquid is saturated with solid phase  $S_1$ , which possesses the crystalline structure of component A; along  $T_{b0}$ , liquid is saturated with solid  $S_2$ , which is of the same crystalline type as component B. In the miscibility gap ( $S_1 / S_2$ ) the solid phase is composed of a mixture of crystals of type A and B.

Cooling a solution of composition x first yields solid  $S_2$  upon freezing. As freezing progresses, the composition of the liquid changes along  $T_{b0}$  and that of the solid along  $T_{ba}$ , until at o the liquid phase is saturated with respect to  $S_1$ . At constant temperature  $T_p$  the liquid now deposits  $S_1$  and when all is solid, a mixture of  $S_1$  and  $S_2$  is obtained. Upon cooling a solution of composition  $x^1$ , a peculiar behaviour is observed. Crystals of  $S_2$  first freeze out, but when the solution reaches the composition of o it is saturated with respect to  $S_1$  and this solid begins to precipitate. Since three phases coexist, (neglecting vapor, as the pressure is constant)  $S_1$  continues to deposit at constant temperature ( $T_p$ ) at the expense of  $S_2$ , which must now redissolve in liquid L. With the disappearance of  $S_2$ , two phases ( $L / S_1$ ) coexist, and the

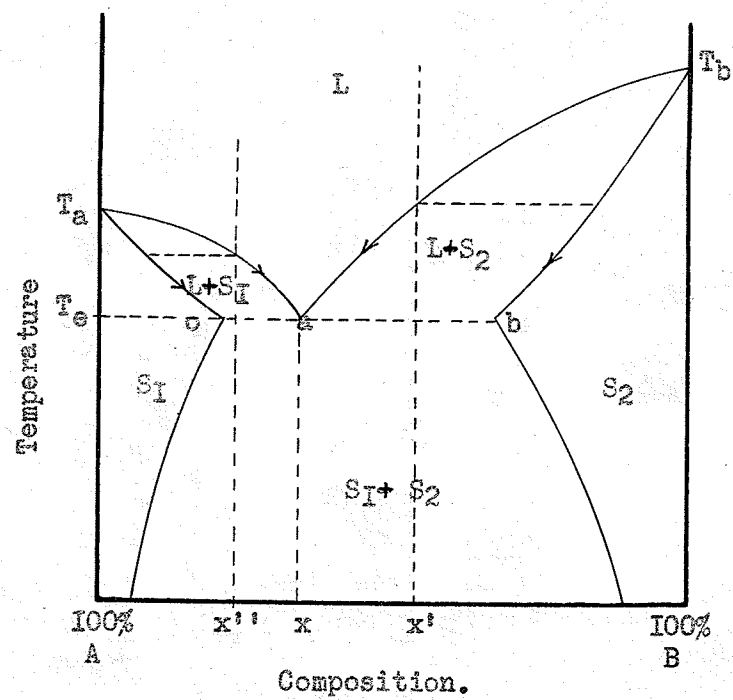


Figure 8.

temperature now falls as  $S_1$  deposits, until all is solid. Upon cooling the solid further, the limit of solid solubility (miscibility gap) will be reached, when crystals of  $S_2$  begin forming. The final solid phase obtained is a mixture of  $S_1$  and  $S_2$ . The behaviour at temperature  $T_p$  is peculiar to this type of binary system; consequently,  $T_p$  receives the particular name "peritectic temperature" and this type of diagram is known as a "peritectic diagram".

#### Type V (Fig.8)

As in Type IV, two series of solid solutions are formed here, but the miscibility gap of Type V is larger than that of Type IV.

Cooling a solution of any concentration lying between  $a$  and  $b$  will result in deposition of one or other of  $S_1$  and  $S_2$ , with the liquid eventually attaining the concentration  $x$ . At this constant temperature ( $T_e$ ) both  $S_1$  and  $S_2$  deposit simultaneously to give a solid phase consisting of a conglomerate of  $S_1$  and  $S_2$ . Point  $a$  is called the "eutectic point" since it represents the lowest freezing point of the system; the temperature  $T_e$  is therefore known as the "eutectic temperature".

The diagram of Type V is characterized by two regions of two-phase equilibrium above the temperature of three-

phase equilibrium, as compared to one such region in Type IV. Also, the freezing points of the components are widely separated in Type IV, but in Type V the interval between the freezing points of the components is usually small.

(c) Ternary Systems

(i) Graphical Representation

In a system of three components, in order to define the composition of the system, it is necessary to know the concentrations of two of the components. Therefore, a complete graphical representation of such a system requires four dimensions, one for each of the variables temperature, pressure and the two concentrations. An isobaric (constant pressure) section requires three dimensions, but by again sectioning the isobaric section it is possible to represent equilibria in a ternary system on a two-dimensional diagram. Usually the section is taken at constant temperature, leaving only the concentrations of the three components to be represented on a plane diagram.

Of the several methods proposed for representing ternary systems on a plane diagram, those of Gibbs (19) and Roozeboom (20) are the most frequently used in practice. Both authors employed an equilateral triangle, the corners of which represent the pure components, A, B and C.

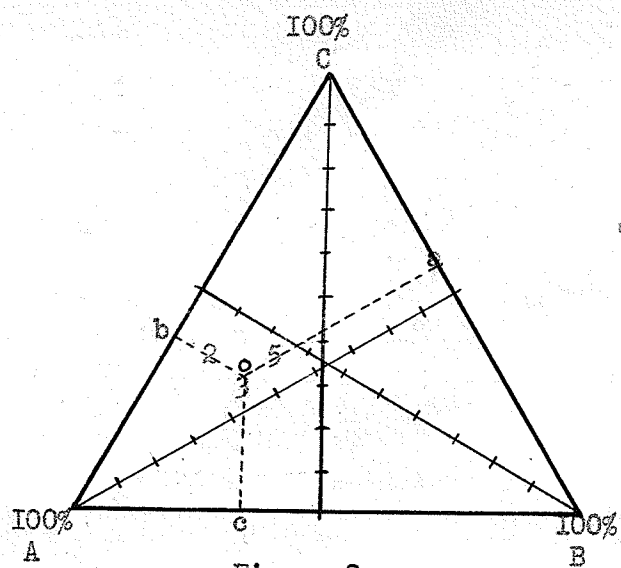


Figure 9.

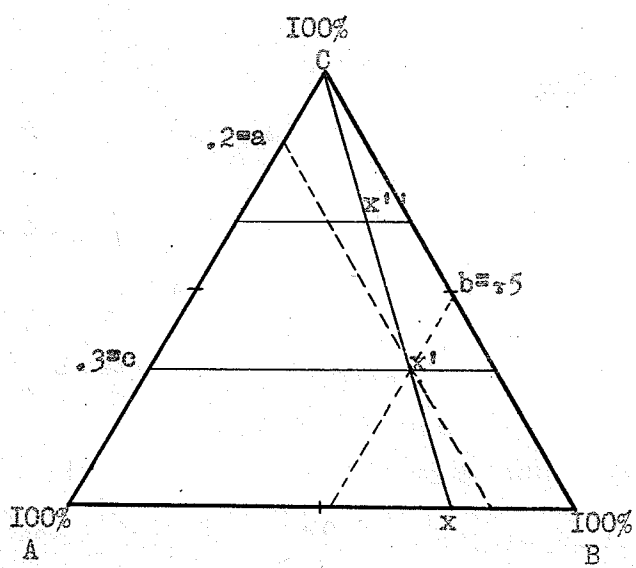


Figure 10.

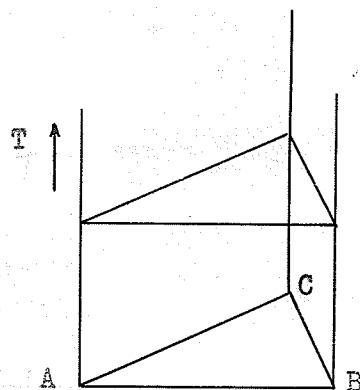


Figure 11.

A point on the side of the triangle represents a binary mixture and a point in the body of the triangle represents the composition of a ternary mixture. Gibbs employed the property of an equilateral triangle, namely, that the sum of the perpendiculars to the sides from any point is equal to the altitude of the triangle. Thus, the ratios of the components for a mixture  $o$  (Fig.9) are the ratios of the lengths  $ao$ ,  $bo$  and  $co$ ; the mixture  $o$  therefore consists of 50% A, 20% B and 30% C.

In the more popular method due to Roozeboom, the length of one side is made equal to unity. As shown in Figure 10, the composition of a ternary mixture  $x^1$  is consequently determined by measuring the distances to the sides in a direction parallel to the sides of the triangle. Ternary mixture  $x^1$  consists of 20% A, 50% B and 30% C.

A most important geometrical property of the composition triangle is that a straight line from any vertex to the opposite side represents a constant ratio of the components represented by the two remaining vertices. Adding component C to a binary mixture of A and B of composition  $x$  (Fig.10) results in a series of solutions in which the ratio of A to B remains the same as in the original mixture  $x$ . All solutions such as  $x$ ,  $x^1$ ,  $x^{11}$  contain components A and B in the same proportion.

A complete isobaric section of a ternary system is represented graphically by a prism, (Fig.11) the temperature axis being erected perpendicular to the composition triangle. In representing ternary systems, especially those in which solid solutions are formed, it is customary to represent several isothermal sections superposed on one basal plane.

(ii) Some Examples

It has been shown that binary systems forming solid solutions can be classified into six types. In a ternary system, however, addition of one component greatly increases the number of different ternary systems possible, since for one ternary system there may be three different binary systems, represented by the sides of the composition triangle.

Ternary systems involving Roozeboom's Types I, II and III have been classified into ten types by Schreinemakers (21). Only two of these ternary systems will be considered here.

Type I.I.I. The three components are completely soluble in both liquid and solid states, the binary systems all being of Roozeboom's Type I.

The isobaric section of this system is illustrated in Fig.12; component A has the lowest freezing point and C the

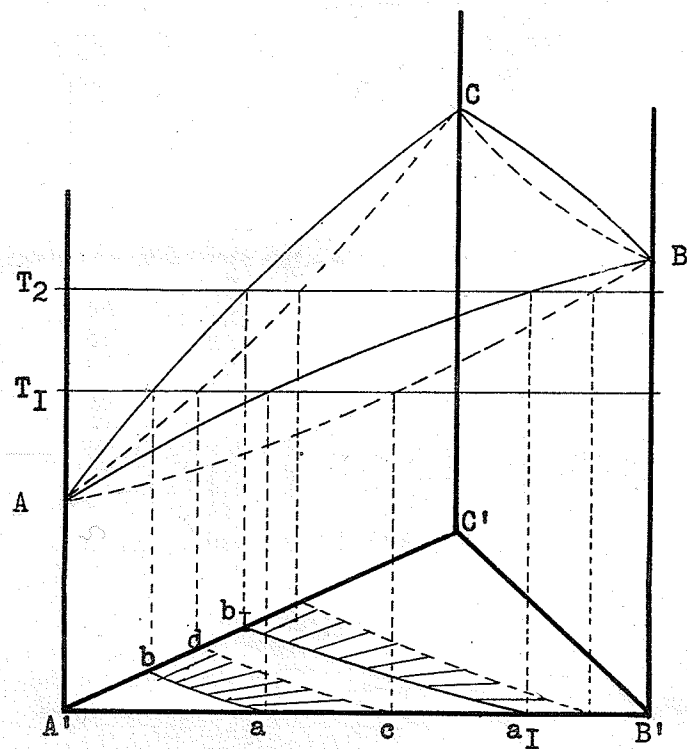


Figure I2.

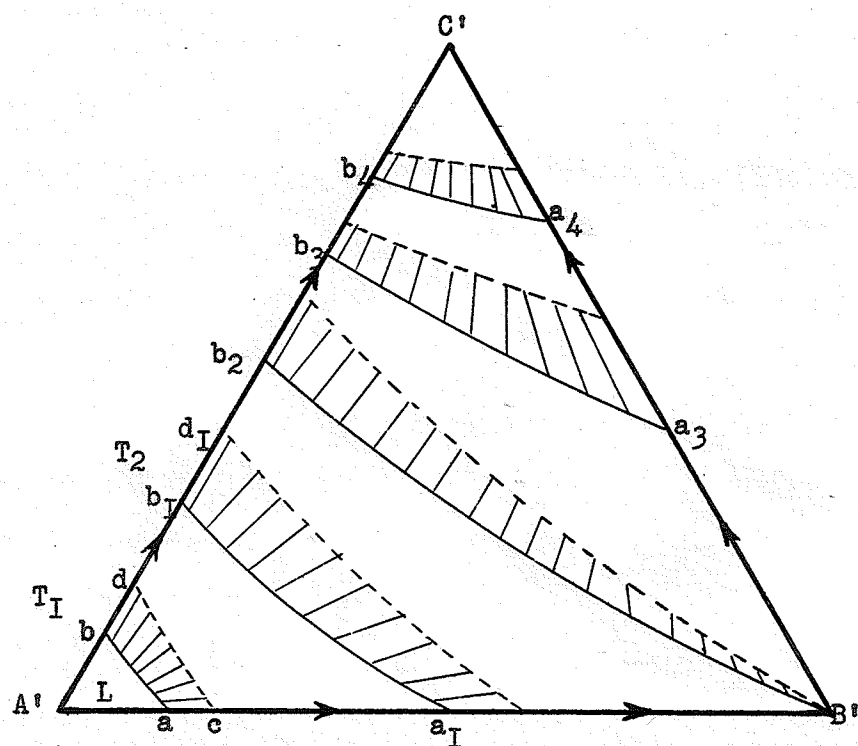


Figure I3.

highest. Two surfaces coinciding at the freezing points of the components enclose the liquid-plus-solid region, the upper liquidus or freezing surface being concave toward the basal plane  $A^1B^1C^1$  and the lower solidus or melting surface being concave upward. Above the surface ABC all is liquid, while below the solidus surface only homogeneous solid solutions exist.

Suppose the isobaric section of Fig.12 is sectioned at constant temperature  $T_1$ . The intersection of the isothermal plane  $T_1$  with the liquidus surface will yield a curve ab projected on the basal plane  $A^1B^1C^1$ . Similarly, the intersection of this plane with the solidus surface produces curve cd. The isothermal section at temperature  $T_1$  will therefore be similar to Fig.13, possessing three fields: the liquid (L) field  $A^1ab$ , one heterogeneous solid-plus-liquid ( $L \text{ / } S$ ) field abcd and the solid (S) field  $B^1C^1cd$ . The short lines running from liquidus curve ab to solidus curve cd are "tie-lines", their intersections with the solidus curves representing the compositions of the solid phases in equilibrium with the liquid phases whose compositions are given by the intersections with the liquidus curves. It is clear that the direction of the tie-lines near the edges of the diagram must be approximately parallel to the sides of the triangle, since the tie-lines of the binary systems lie in the plane of the sides.

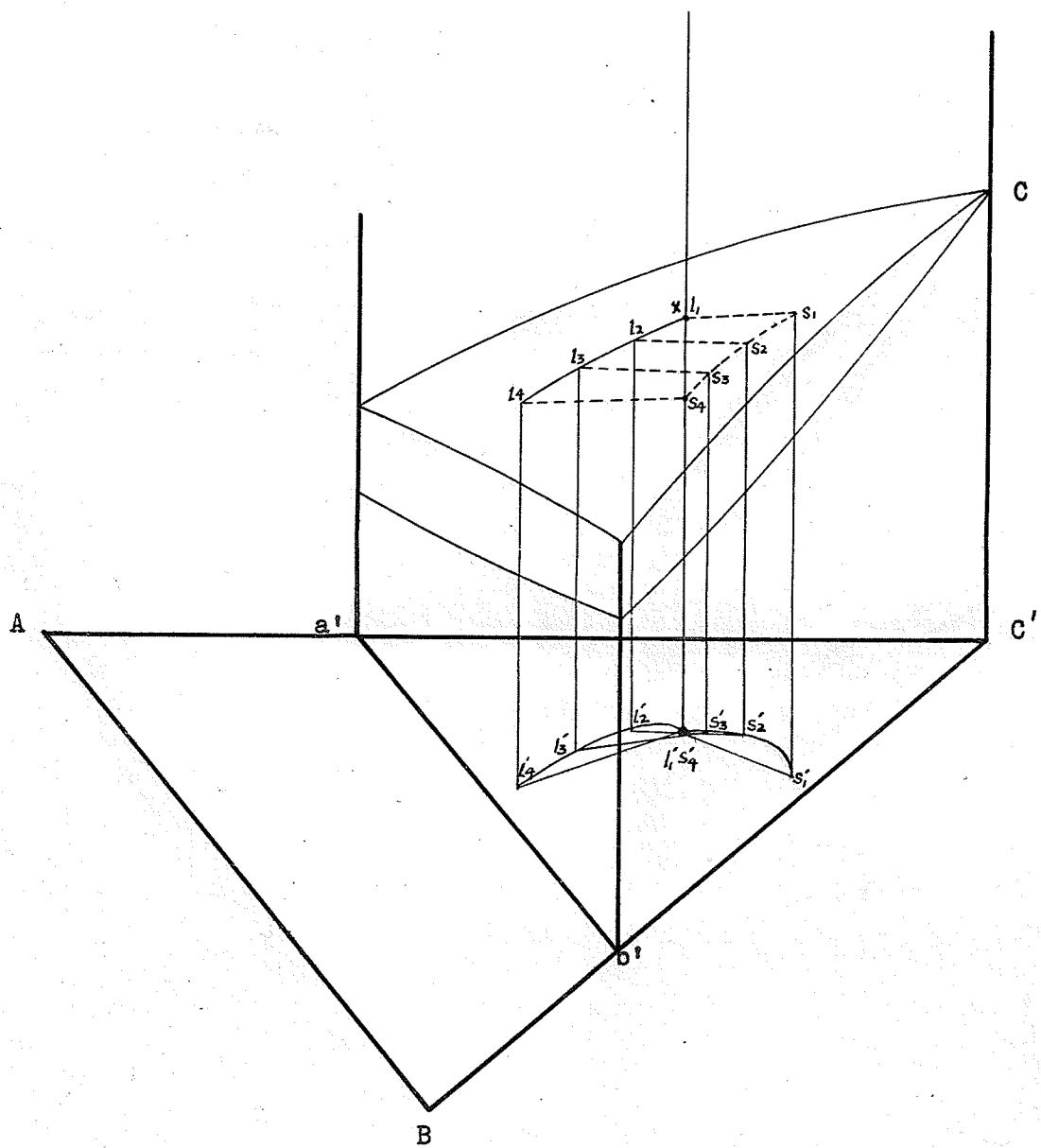


Figure 14.



An isothermal section at a higher temperature  $T_2$  will produce a heterogeneous band  $a^1b^1c^1d^1$  shifted toward the higher temperatures of B and C, and successive isothermal sections will give a series of heterogeneous bands, which, when projected on the basal plane  $A^1B^1C^1$ , complete the diagram represented in Fig.13. One heterogeneous band at the freezing temperature of pure B has been drawn to illustrate the fact that the solidus and liquidus curves must coincide at any point at which congruent freezing occurs. In this diagram and those to follow, the arrows along the sides indicate the direction of increasing temperatures in the binary systems.

The solid-liquid transformation in a ternary system is analogous to the same process in a binary system, the only difference being that a spatial representation is necessary to describe it completely. Fig.14 represents a portion of the isobaric section in the corner of C. Consider a liquid of composition  $x$  which is being cooled so slowly that the solid phase precipitating is in equilibrium with the liquid phase at all times. At point  $l_1$ , the liquid phase is saturated with respect to the solid phase of composition  $s_1$ . The line  $l_1s_1$  is therefore a tie-line. Upon reducing the temperature of the system solid deposits from the melt, the composition of the liquid

following path  $l_1l_4$  on the liquidus surface and that of the solid phase following path  $s_1s_4$  on the solidus surface. The composition of the solid phase in equilibrium with liquid at any instant during the freezing process is given by a series of tie-lines which must pass through the total composition vertical  $xl_1^1$ . Thus, the tie-lines generate a helical surface in space because their direction changes continually as the transformation proceeds. This is shown by the projection of the tie-lines and composition paths on the basal plane  $ab^1Cl$ . The transformation is complete when the last portion of liquid of composition  $l_4$  solidifies to give a solid phase of composition  $s_4$ , the same as that of the original solution  $x$ . ( $x$ ,  $l_1$  and  $s_4$  represent the same total composition.)

The crystallization path  $s_1^1xl_4^1$  may also be derived from a consideration of the heterogeneous band in an isothermal section. For this purpose Fig.15 is given; the solid lines represent liquidus isotherms and the broken lines represent the corresponding solidus isotherms. When a liquid of composition  $x$  is cooled to the temperature of isotherm 1, the solid separating has an initial composition  $s_1^1$ . As the temperature continues to fall, the heterogeneous band shifts toward the lower temperature of A, until at the temperature of isotherm 2, solid phase  $s_2^1$  is in equilibrium



Figure 16.

with liquid phase  $l_2^1$ , as given by the tie-line  $l_2^1 x s_2^1$ . The transformation is complete when the temperature of isotherm 4 is reached.

Comparison of Figs.14 and 15 gives the complete picture of the solid-liquid transformation in a ternary system forming a continuous series of solid solutions.

Type 1.3.3. One binary system of Type I; two binary systems of Type III.

Assume that a minimum freezing point occurs in binary systems AC and BC, that of AC being lower than the minimum of system BC; component C has the highest freezing point and A the lowest.

In general three cases may be considered:

- (a) A ternary minimum freezing point exists.
- (b) No ternary minimum freezing point exists.
- (c) A congruent freezing point occurs in the ternary system which is neither a maximum nor a minimum freezing point.

Type 1.3.3.(a).(Fig.16)

In this system,  $m$  is the minimum freezing point of binary system AC,  $m_1$  is the minimum freezing point of binary system AB, and  $m_2$  is the ternary minimum. The points  $m$ ,  $m_1$ , and  $m_2$  therefore represent the only possible mixtures which will freeze congruently. The three dimensional isothermal

section is not shown for this system, but may be visualized with the aid of Fig.12.

Upon raising an isothermal plane, first contact with the heterogeneous region will be made at  $m_2$  (Fig.16). At a slightly higher temperature the intersection of the isothermal plane with the heterogeneous region produces a circular heterogeneous band which moves outward from  $m_2$  as the isothermal plane is raised, until at the temperature of  $m$ , the liquidus and solidus curves coincide as shown in the figure. At a temperature slightly above that of  $m$ , the closed heterogeneous band breaks at  $m$  into two branches which move outward from  $m$  as the isothermal plane is raised, the liquidus and solidus curves again coinciding at the temperature of  $m_1$ . At  $m_1$  the heterogeneous band again breaks, forming two separate heterogeneous bands 1 and 2, band 1 moving toward A and disappearing at that temperature, band 2 moving through B toward C and disappearing at this highest temperature of the heterogeneous region.

The solid-liquid transformation for this system and those to follow is exactly analogous to that described for Type I.I.I., except that when a liquid phase attains the composition of  $m$ ,  $m_1$  or  $m_2$ , the transformation temperature remains constant (as required by the Phase Rule) while solid of the same composition as the liquid precipitates.

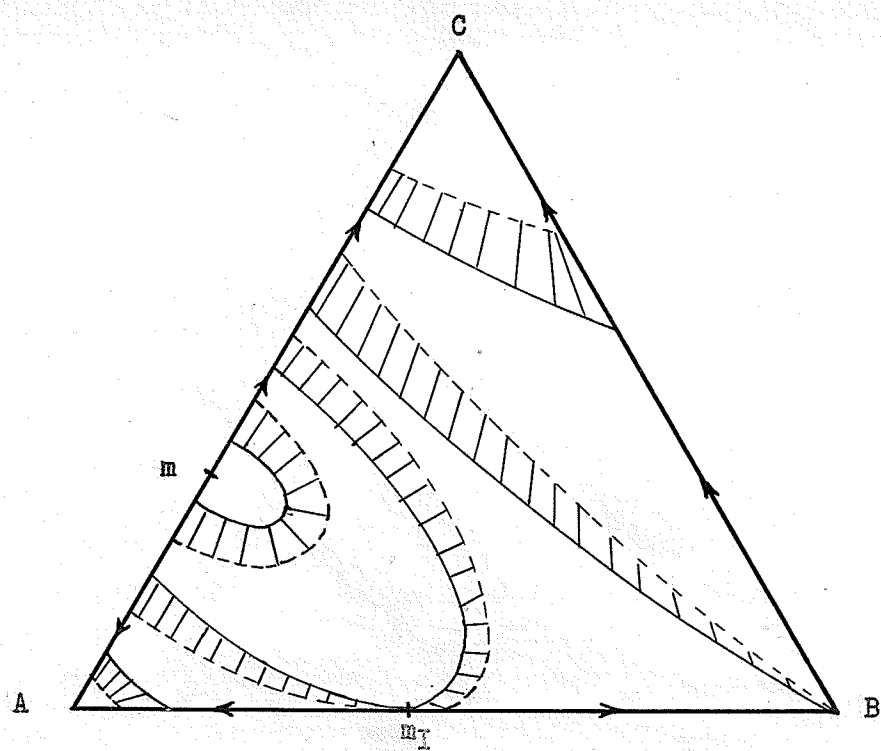


Figure 17.

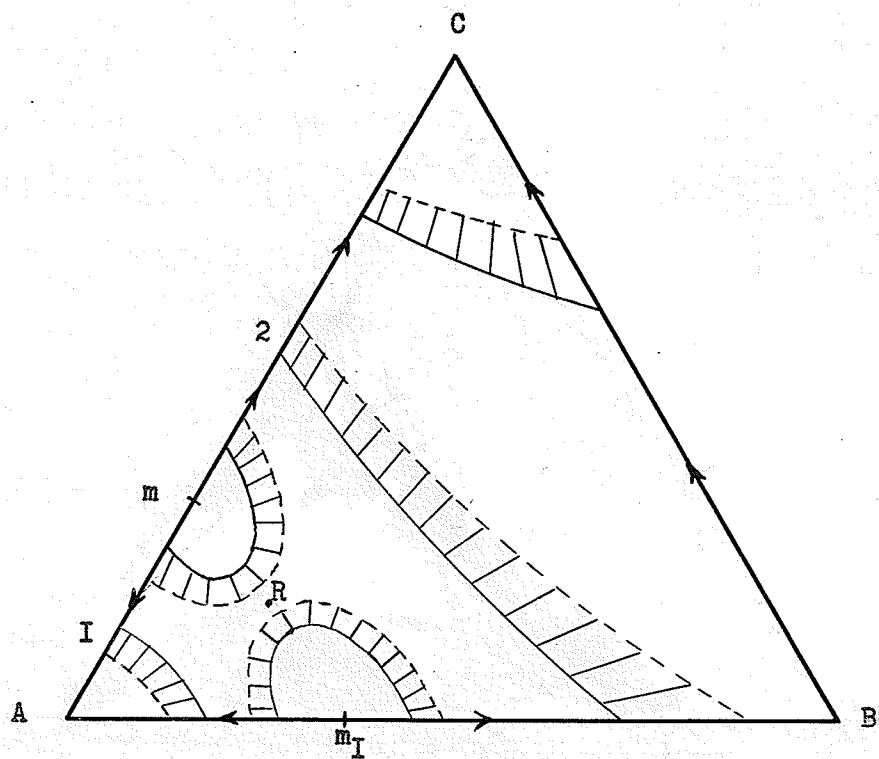


Figure 18.

Type 1.3.3.(b) (Fig.17)

Here, binary minimum  $m$  represents the lowest temperature of the heterogeneous region and therefore, as an isothermal plane is raised its intersections with the heterogeneous region will produce closed heterogeneous bands growing from  $m$  and ending on side  $AC$ . At  $m_1$ , solidus and liquidus curves must coincide; raising the isothermal plane further causes the band to break at  $m_1$ , forming two separate bands, one progressing to  $A$  and the other to  $C$ .

Type 1.3.3.(c) (Fig.18)

Point  $R$  in this system represents a mixture which freezes congruently at a temperature slightly above that of  $m$  or  $m_1$ , but below the freezing point of the lowest freezing component  $A$ .

Upon raising an isothermal plane, contact with the heterogeneous region is made initially at  $m$  then at  $m_1$ , the two bands growing from  $m$  and  $m_1$  finally merging at  $R$ . At a temperature very slightly above that of  $R$ , the two bands break and pair off, forming two separate bands 1 and 2 which proceed toward  $A$  and  $C$  respectively.

A detailed account of the solid-liquid transformations in these systems would be superfluous, but it should be noted that while the heterogeneous bands represent isothermal areas, the solidus curves always lie on the higher temperature side of the corresponding liquidus isotherms.

### THERMAL ANALYSIS

A transformation process in a pure substance or a system of substances involves a change of energy content; usually the energy change of the system is manifested either by evolution or absorption of heat. It is fortunate that nearly all transformations involve a considerable amount of heat, so that the transformation temperature may be measured experimentally by thermometric means. Any thermometric method for obtaining the temperature of a transformation is a method of "thermal analysis".

#### Cooling Curves

Suppose a liquid is heated  $50^{\circ}$  above room temperature, a thermometer is immersed in it, and the liquid is then allowed to cool under room conditions. The rate of cooling of the liquid will be proportional to the difference between room temperature and the temperature of the liquid, according to Newton's law of cooling, and if the temperature of the liquid is measured at regular time intervals, the plot of temperature versus time will have the appearance of Fig.19(a), in the absence of transformation. Such a graphical plot is a "cooling curve". Should a transformation occur, (e.g. deposition of solid) it will be marked by a sudden change in the rate of cooling. In the case of the solid-liquid transformation of a pure substance, the first

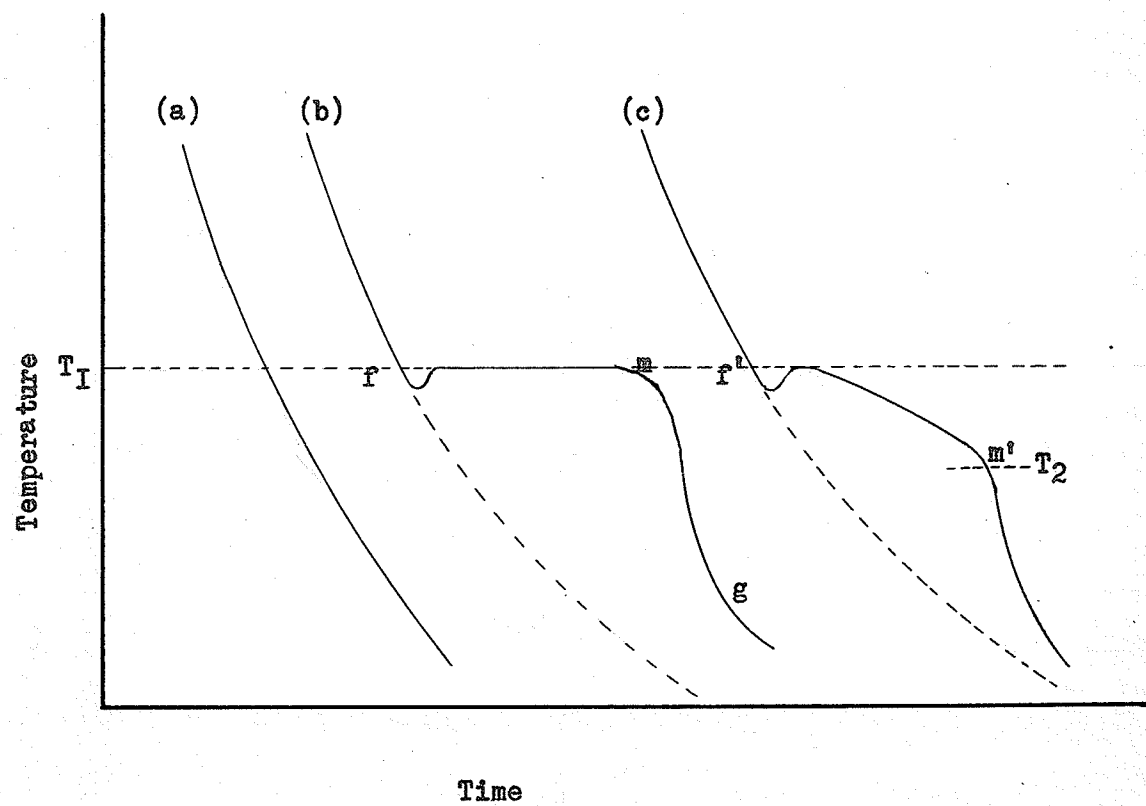


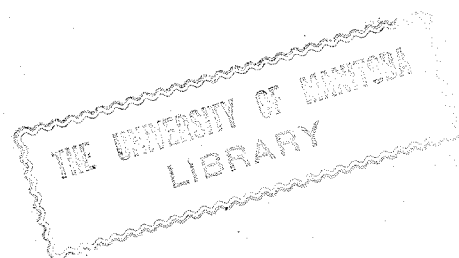
Figure I9.

appearance of solid marks the freezing point, and the temperature of the liquid must remain constant until all is solid. This "invariant point" is indicated on the cooling curve by a "halt", represented by the horizontal portion fm in Fig.19(b). When the transformation is complete, the system is no longer invariant; the solid begins cooling rapidly along mg and then more slowly in accordance with Newton's law. That the "halt" on the temperature-time graph serves to accurately determine the freezing point of a substance has been established by the experiments of Le Chatelier (22). For a fused mixture of two or more components from which a solid solution is deposited on freezing, the transformation temperature does not remain constant because of the continuous composition change in the solid and liquid phases. Therefore, the cooling curve will have the form of Fig.19(c), the initial transformation temperature  $T_1$  (freezing point) being given by  $f^1$  and the final transformation temperature  $T_2$  (melting point) by  $m^1$ . At the freezing point, the phenomenon of "supercooling" usually is observed; the temperature of the melt falls slightly below the true freezing point, then rises to a maximum value. This effect is represented by the small depressions at f and  $f^1$  on curves (b) and (c), Fig.19. The precision of such a freezing point determination is greatly affected by the extent of supercooling, particularly

in viscous melts and those possessing poor thermal conductivity. Supercooling may be completely avoided in most cases by "inoculating" the melt, that is, by introducing a tiny crystalline fragment of the substance into the melt at the freezing point to induce crystallization.

While the freezing point is relatively easy to determine from a cooling curve, the melting point cannot be evaluated with certainty because the cooling curve at this point is rounded; the problem is to select the correct point, as  $T_2$  in Fig.19 (c). The reason that a sharp break in the cooling curve is not observed when the liquid-solid transformation is complete, is that the amount of heat liberated by the last small portion of solidifying liquid is insufficient to compensate for the heat lost to the environment by radiation. Furthermore, by this time the thermometer bulb is surrounded by solid which cools faster than the liquid by virtue of its lower specific heat.

The inherent weaknesses of the temperature-time plot have been overcome in some degree by employing slightly different experimental techniques and plotting the data so obtained in a manner which most accentuates the observed phenomenon.



### Types of Cooling Curves.

Cooling curves obtained by allowing a substance to cool of its own accord may assume a variety of shapes depending on the quantities chosen in plotting abscissae and ordinates. The relative merits of the various types have been discussed by G.K. Burgess (23) and W. Rosenhain (24).

#### (1) Temperature-Time Curves (T versus t)

Fig.19 represents this type of plot. Its chief disadvantage lies in its inability to detect very small heat effects. It is sensitive when applied over a small temperature range, but is useless over large temperature intervals.

#### (2) T versus t, T' versus t (or T versus T')

In the event that small transformations cannot be detected by the temperature-time method due to irregularities in cooling, it is advantageous to place a second temperature measuring device in the furnace near the sample. Readings of the temperature of the melt (T) and of the furnace (T') are taken alternately at regular time intervals, and the two curves T vs.t and T' vs.t are plotted side by side.

(3) T versus t, (T - T') versus t

The plot of furnace temperature ( $T'$ ) versus time ( $t$ ) may show deviations caused by slight variations in the furnace temperature. To avoid these a neutral body having as closely as possible the same heat capacity as the sample melt is placed in the furnace and its temperature ( $T'$ ) is measured at regular time intervals. The plot of ( $T - T'$ ) versus  $t$  clearly shows any small transformations, but the method is difficult to apply because of the careful adjustments needed to make the sample and neutral body cool at the same rate.

(4) T versus (T-T')

Such a plot does not involve the time variable. It is susceptible to the application of mechanical recording instruments and therein lies its only advantage.

(5) T versus (T-T') / T.

When cooling is rapid, and when the heat capacities of melt and neutral body differ considerably, this method should be applied. This is a differential curve,  $(T-T')/T$  being a measure of the difference in temperature between the furnace and the melt for a decrement of temperature  $T$  in the sample.

(6) T versus  $\frac{dT}{dt}$

This plot suffers from the same disadvantages possessed by the simple T versus t cooling curve. It is invaluable, however, when the rate of a transformation must be determined.

(7) T versus  $\frac{dt}{dT}$

The "inverse rate" curve is of particular value in studying critical regions in metallic systems. A halt is shown by a very conspicuous cusp and a change in the rate of cooling is represented by a bulge in the curve. The method is applicable only for very slow cooling.

Any one of the seven methods of plotting cooling curves as outlined above may be selected to suit a specific case. Most of these methods can be adapted to the use of photographic or mechanical recording machines, thus eliminating a large amount of tedious work for the observer. However, recording machines have a limit of sensibility and when very precise measurements are required, there is no substitute for the constant presence of the experimenter.

Linear Cooling

Free-cooling curves are satisfactory in most cases when great sensitivity is not required over a large range of

temperature; but when one wishes to attain a high degree of precision in measurements over a comparatively small temperature interval, they are inadequate. For such requirements the simple temperature versus time plot is undoubtedly the best to use. However, this fails to give an accurate melting point as is required, for example, in the study of a system forming solid solutions, in which case the interval between freezing point and melting point is likely to be small. A refinement of the simple temperature - time plot of cooling curves has been introduced by W. Plato (25), the use of which increases the accuracy of a freezing point determination and yields much more reliable melting point data. A law of cooling was sought which would make the cooling rate independent of the nature of the material examined and the difference in temperature between the melt and environment. The most useful cooling law specifies a linear relationship between temperature and time.

If a melt with thermometer immersed in it is placed in a furnace, the temperature of which may be altered at will, and the furnace is made to cool by subtracting equal portions of heat from it in equal time intervals, the temperature of the melt will follow that of the furnace. In the absence of transformation in the melt, the plot of temperature versus time has the appearance of Fig.20 (a), namely, a straight

line. For a pure substance in which a transformation occurs at a temperature  $T_1$ , linear cooling produces the cooling curve shown in Fig.20 (b). The temperature of the melt follows that of the furnace linearly to f, (the freezing point) where the first appearance of solid phase produces a halt in the cooling rate of the melt. During the time interval represented by the straight horizontal portion fm, solid deposits continuously, until at m, (the melting point) where the material is completely solid, the rate of cooling increases abruptly. Cooling of the solid is very rapid along mb, since during the time of freezing (fm) the furnace has cooled along fb, while the temperature of transformation has remained constant at  $T_1$ . At the time instant m, therefore, the difference in temperature between the solid and the furnace is considerable. At point b, the solid once more resumes the cooling rate of the furnace and cooling proceeds linearly along the original path.

During the liquid-solid transformation of a system which forms solid solutions, the temperature does not remain invariable, but gradually decreases as the solid solution deposits. The ideal linear cooling curve for such a system is shown in Fig.20 (c). The cooling gradient remains constant along  $f^1m^1$  from the freezing point ( $T_1$ ) to the melting point ( $T_2$ ), where a sharp break in the cooling

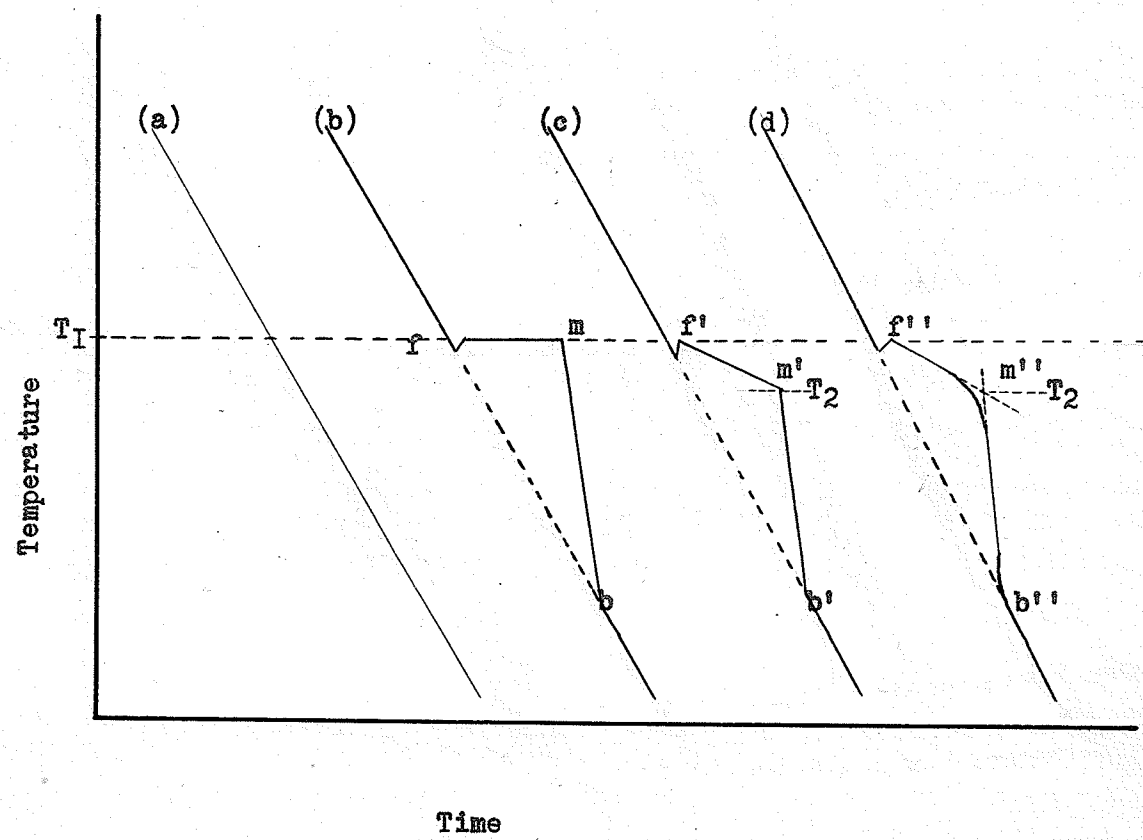


Figure 20.

curve marks the disappearance of the liquid phase. The solid solution cools rapidly from  $m^1$ , finally assuming the cooling rate of the furnace.

Comparison of the linear cooling curves, Fig.20 (b) and (c), with the analogous free cooling curves, Fig.19 (b) and (c), indicates the advantages to be gained by employing linear cooling in thermal analysis. With a suitable apparatus, a melt may be made to adopt any rate of cooling desired. Furthermore, the areas  $fmb$  (Fig.20(b)) and  $f'm'b'$  (Fig.20(c)) are directly proportional to the respective heats of fusion of the systems concerned. Such a relationship enables calculation of heats of fusion and specific heats of materials from linear cooling curves. The immediate advantage of the linear cooling curve over the free cooling curve lies in the ease and accuracy with which the melting point may be determined using the former. In the ideal curve the intersection of the portions  $f'm'$  and  $m'b'$  give the melting point unambiguously (Fig.20(c)). However, the curve obtained in any experiment usually shows a pronounced curvature as the freezing process approaches completion; the last portion of freezing liquid does not release enough heat to maintain a constant temperature gradient. Fig.20(d) represents an experimentally determined curve where the melting point is not defined by a sharp break in the cooling curve. Tammann (26) has shown that the

extensions of portions of the curve  $f''m''$  and  $m''b''$  intersect at the true melting point. Therefore, as long as  $f''m''$  and  $m''b''$  have a reasonably linear portion, it is possible to arrive at melting points which may be duplicated.

Super-cooling is not eliminated merely by employing linear cooling. By "seeding" or inoculating the melt with a tiny crystal of the solid material immediately above the true freezing point, a sharp break in the cooling curve results, marking the true freezing point.

#### Binary Systems

Thermal analysis of any system may be carried out on a microscopic or macroscopic scale, depending on the amounts of the components available and the degree of precision of measurements desired. For systems of organic compounds, most of which are volatile in the region of their melting points, it is best to use as large a quantity of the components as possible in order to minimize the change in total composition due to volatilization.

Assuming a suitable apparatus is available, the procedure for thermal analysis of a binary system consists in first determining the freezing point of one of the purified components. Successive portions of the second component are added to the melt and the freezing point of each new mixture is determined until a composition of 50%

is reached. The procedure is repeated, starting with the second pure component and adding to it the first in successive definite amounts. Plotting the freezing points obtained on a temperature-concentration diagram and joining them, the curves starting from each point representing the pure components should meet at the centre of the diagram.

Should solid solutions be formed from the melt, the melting points of the mixtures are determined from the cooling curves and plotted simultaneously with the freezing points. For each mixture analyzed there will therefore be two points and joining the freezing points and melting points yields the freezing curve and melting curve respectively.

Using a mercury thermometer as a temperature measuring device, it is necessary to use at least 20 grams of material in order to measure a freezing point to a precision of  $\pm 0.02^{\circ}$ . For a system which forms a continuous series of solid solutions, (Type I) about 15 to 20 mixtures should be analyzed. The occurrence of a maximum or a minimum freezing point necessitates a greater number of analyses in order to determine the temperature of the invariant point.

### Ternary Systems

Preparing ternary mixtures of random compositions and carrying out thermal analyses on them results in data which are not easily correlated; a great deal of interpolation is required. Since experimental results are plotted on an equilateral triangle, use may be made of the property of such a triangle, namely, that a straight line from one vertex to the opposite side represents a constant ratio of the components represented by the two remaining vertices. Therefore, by making up a mixture of two components A and B and adding to it portions of a third component C, the mixtures will be represented by points on a line running from vertex C to the point on side AC representing the composition of the binary mixture  $A_xB_y$ : construction of freezing and melting curves in the plane coinciding with this line constitutes a "quasi-binary" section of the isobaric model. By determining several such quasi-binary sections for a given ternary system, the complete isobaric model may be constructed.

The method outlined is convenient because of the ease with which the mixtures may be prepared. Since the experimentally determined freezing and melting points lie in one plane, the average smooth curves drawn through the plotted points represent the most probable freezing and melting curves. Thus individual erroneous analyses can be instantly recognized.

## PREVIOUS INVESTIGATIONS

The freezing curves of the three possible binary systems composed of two of the three components p-Dichlor- , p-Chlorbrom- and p-Dibrombenzene have been determined by G. Bruni and F. Gorni (27). The freezing points of the materials are given as 52.7°, 67.0° and 85.9°C respectively. All binary systems are shown to form a continuous series of solid solutions, the two systems containing dichlorbenzene as one component each exhibiting a minimum freezing point. Adding chlorbrombenzene to dichlorbenzene produces a depression in the freezing point of the mixture up to a concentration of 3.5 percent, after which the freezing point of the mixture rises continuously to the freezing point of pure chlorbrombenzene; the minimum freezing temperature is 52.60°. Similarly, the system dichlorbenzene: dibrombenzene exhibits a minimum congruent freezing point of 52.55° at a concentration of 2.5 percent. In all three systems the freezing curves lie below the straight line joining the freezing points of the components, but the liquidus curve for the system chlorbrom: dibrombenzene approaches very closely to a straight line. F.W. Kuster (28) has examined the freezing curve of the system dichlorbenzene: dibrombenzene, but appears to have overlooked the minimum freezing point with complete disregard for the earlier work of Bruni and Gorni.

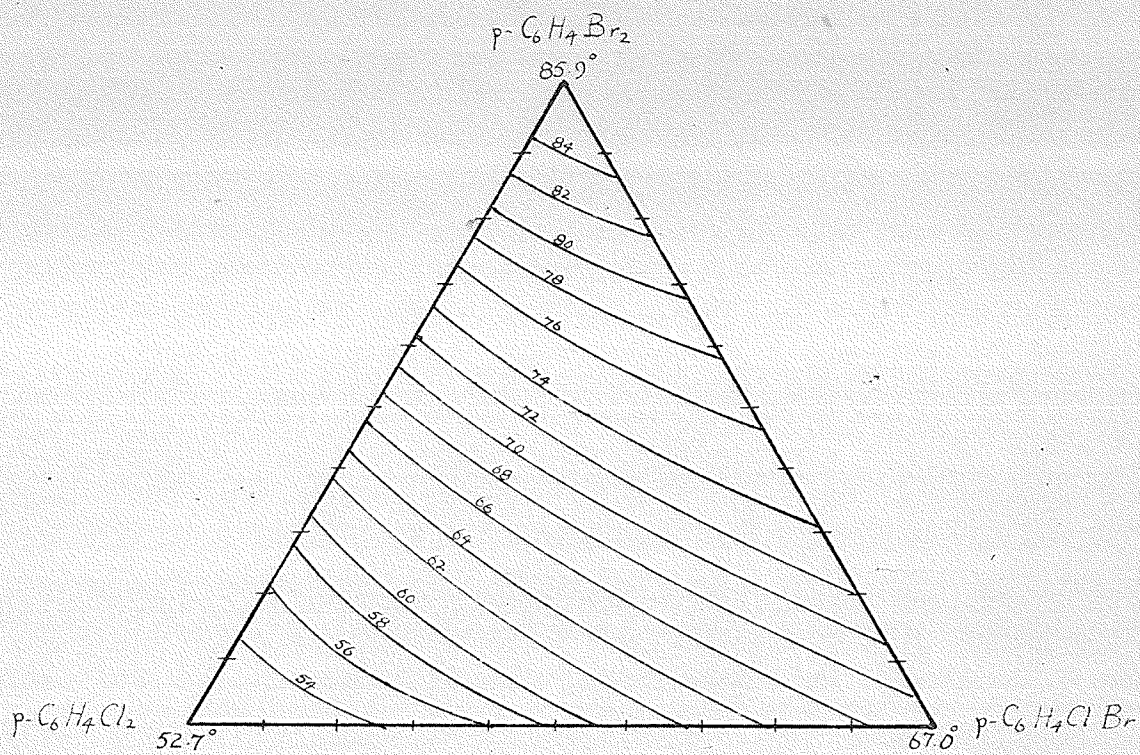


Figure 21.

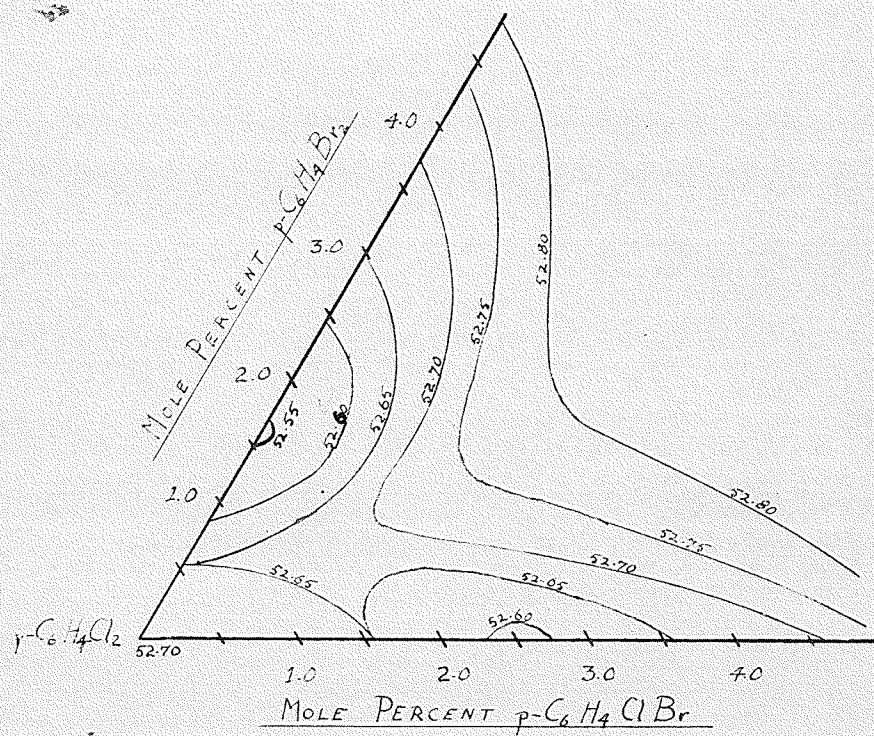


Figure 22.

The latter authors also constructed the ternary freezing surface; their results are plotted in Fig.21. The liquidus isotherms are all convex toward the lower temperature, indicating that the freezing surface of the isobaric model is concave downward. Also, the surface lies completely below the plane passing through the freezing points of the three pure components. The freezing surface assumes a more interesting form in the corner of the dichlorobenzene and consequently the results are shown on a larger scale in Fig.22. The shape of the isotherms clearly characterizes the system as an example of Schreinemaker's Type 133 (c); (c.f. Fig.18. loc.cit.) therefore a ternary congruent freezing point which is neither a maximum nor a minimum must be expected. Bruni and Gorni did not report such a congruent freezing point.

Data relevant to the solidus curves of the binary systems and the solidus surface of the ternary systems appears to be lacking. H.R. Kruyt (29) has determined the approximate position of the melting curve for the system dichlorobenzene: dibromobenzene; his results indicate a maximum freezing interval of approximately  $14^{\circ}$ .

## EXPERIMENTAL

(a) Construction of the Apparatus

The Environment

In order to obtain regulated cooling entirely independent of the external conditions, an arrangement must be constructed whereby the loss of heat by radiation from the furnace is made constant. The apparatus designed for this purpose is shown in Fig.23.

A circular tank 45 cm. in diameter was constructed from #24-gauge copper-sheet (1). In the centre of this tank a cylinder 15 cm. in diameter was soldered, giving the completed tank the appearance of a large doughnut cutter. The central opening was lined with asbestos paper and the annular space was filled with water, the total capacity being about 20 litres. The tank was set on a 1/2 inch thick soft asbestos sheet (10), which served as insulation while the side surface was insulated with two layers of felt cloth (3). Inlet (4) and outlet (5) pipes for the water circulation system were located at the top and bottom respectively, the latter pipe being provided with a stop-cock for controlling the rate of flow of the water. A circular top (2) for the tank was cut from 5/8 inch Transite asbestos board. This material is hard, easily worked and is both an excellent thermal and electrical insulator. The cover was cut 2 cm.

larger than the tank so that it rested tightly against the felt insulation on the top outer edge of the tank. A hole 4 cm. in diameter cut in the centre of the cover was the only means of access to the interior of the furnace (8), which was fastened to the cover by means of three Transite blocks bolted in place, as shown in the top view of the tank (fig.23).

As it was required to maintain the temperature of the water in the tank at a constant value, a circulation and thermostat system had to be constructed. The desired working range of the apparatus was intended to be from  $20^{\circ}$  to  $100^{\circ}$ ; to obtain linear cooling at a reasonably rapid rate necessitated an environment temperature  $20^{\circ}$ - $30^{\circ}$  below the lower working limit (viz.  $20^{\circ}$ ). An environment temperature of  $10^{\circ}\text{C}$  was found by later experiment to be adequate; a lower temperature would have been preferable, but a circulating liquid other than water was required, for reasons to be explained.

The temperature of the environment was set and checked from time to time by means of the thermometer (7). A mercury thermo-regulator (6) (American Instrument Co.) mounted on the cover served to control the circulating system. This regulator could detect temperature changes of  $\pm 0.02^{\circ}$ .

## The Cooling Circuit

### (a) Description

Since the environment temperature was at least  $10^{\circ}$  below room temperature, a cooling system was designed as shown diagrammatically in Fig.24. Here, tank A represents the environment already described. Tank B, containing kerosene, was 30 inches in height and 10 inches in diameter. It was provided with a thick tight-fitting wooden cover and was insulated with felt. Part (14) was a coil of  $3/8$  inch copper tubing. This coil was connected directly to a methyl chloride refrigerating unit; it was actually an immersion type of freezing coil connected by a flexible coupling to the refrigerator compressor. The outlet pipe (5) from the tank A directed the water through copper tubing coil (15), which was immersed in the kerosene, to water pump (12). This pump was a double geared type, which supplies considerable pressure and was belt driven by a  $1/4$  H.P. electric motor (13). The optimum operating speed of the pump was found to be approximately 400 r.p.m. The outlet pipe from the pump was connected to the inlet (4) of tank A. A rubber tube, not shown in any of the drawings, was connected to the inner end of the inlet pipe (4); its purpose was to conduct the forceful incoming stream of water to the bottom of the tank, thereby producing a rotary circulation of the water

in the annular space. This method of stirring proved to be so satisfactory that no mechanical stirrer was required in tank A.

The kerosene was maintained at a temperature of  $\pm 1.0^{\circ}\text{C}$  by means of a bimetallic thermo-regulator (16) connected in series with the A.C. line and the refrigerator motor.

(b) Operation

An increase of temperature of the kerosene bath caused the regulator (16) to close the refrigerator electrical circuit. Coil 14 absorbed heat from the kerosene, thereby depressing the temperature of the liquid to the original value. At this point the regulator broke the circuit, and the refrigerator ceased operating. With vigorous stirring by means of a current of air introduced through a tube reaching to the bottom of the tank, the kerosene could be maintained at  $\pm 0.5^{\circ}\text{C}$ .

The temperature of bath A was kept constant at  $\pm 0.02^{\circ}\text{C}$  by means of regulator (6). This regulator was connected in series with a 6V D.C. source of current and a relay of the mercury contact type (American Instrument Co.). Increased bath temperature activated the mercury regulator which closed the relay circuit; closing of the relay tilted the mercury capsule (18) which, in turn, closed the

pump motor circuit. Operation of the pump drew the warm water from bath A through the cooling coil (15), where the water lost a portion of heat, returning the cooled water to the bath through the inlet (4). Water circulated in this manner until bath A was cooled to the proper temperature, when regulator (6) opened the electrical circuit and stopped the pump.

The cooling arrangements for the baths A and B were entirely independent, the two motors being controlled by separate thermo-regulators. The temperature of bath B could not be allowed to reach 0°C since the water passing through coil (15), although with considerable velocity, froze in the coil. In the early adjustments of the arrangements this occurred several times. It was a time-consuming failure to remedy, because in the time required to thaw out the coil, bath A had increased its temperature by about 5°, particularly when the furnace was operating at 90°.

The temperature of bath B defined the lower operating temperature limit of bath A. Due to heat absorption in the connecting lines and pump, bath A could not be operated below 10°C without placing undue strain on the pump and its motor. Insulating the connecting lines and pump with heavy felt minimized the heat absorption, but even with this assistance the pump operated almost continuously when the

furnace was set for  $90^{\circ}\text{C}$ . With a cold furnace, the pump operated for approximately 1 minute every 5 to 10 minutes. Since the apparatus ran continuously day and night, considerable strain was placed on the pump motor. The starting current of this motor was 25 amperes, therefore the mercury switch operating the motor circuit had to have this current carrying capacity as a minimum. The 40 ampere capsule marketed by the Canadian General Electric Company was satisfactory.

When the apparatus was idle for any period of time, the water was drained from bath A. Upon starting the cooling circuit again, cold tap water (temperature approximately  $12^{\circ}$ ) was used to fill the tank. This procedure saved time, since it required a minimum of 2 hours to cool the large quantity of water from room temperature down to  $10^{\circ}$ .

### The Furnace

#### (a) Construction

The furnace was designed to operate up to approximately  $120^{\circ}$  as a high temperature limit. Hard glass was therefore a satisfactory material for use as a heating coil form. A 14.5 cm. length of 5 cm. diameter tubing was cut from standard stock tubing. The wall thickness of the piece chosen was 2 mm. The tube was wrapped with two layers of

asbestos paper which had been soaked in an aqueous sodium silicate solution, and while still wet, 50 tightly wound and evenly spaced turns of #22 B&S nichrome wire were applied to the form. The ends of the coil were fastened securely, sufficient wire being left for leads to the terminals on the cover of the water bath. By winding the coil tightly, the wire sank into the soft asbestos and when the silicate hardened, the coil was held rigidly in place.

This electric furnace coil was found to produce an even heating of a melt along the sides of the containing tube, but since the open lower end of the furnace tube reached almost to the bottom of the water bath (Fig.23), melts tended to solidify from the bottom upwards. To obtain a more uniform heating of a melt, a flat heating coil was provided at the lower end of the furnace tube. For this purpose a circular flanged plug of Transite was fitted to the lower end of the furnace tube. On the upper surface a series of zigzag saw cuts were made to a depth of about 1/8 inch and spaced at the open ends the same distance. Into the resulting grooves nichrome wire was pressed and sealed in with porcelain cement. A disc of hard glass 5 cm. in diameter was cemented over the flat coil and the whole auxiliary element was fastened on the

lower end of the furnace tube with porcelain cement. It was wired in series with the main coil. The completed furnace was lined with two layers of asbestos paper and was fastened to the water bath cover as shown in Fig.23, the leads being brought out to two binding posts.

The total resistance of the furnace, measured on a Wheatstone bridge, amounted to 49 ohms. This agreed with the resistance calculated from the value of the wire's resistance given by the manufacturer.

#### The Electrical Circuit

The electrical furnace control circuit is shown in Fig.24. A means of accurate temperature control was required; this was accomplished by adjustments of an external resistance (R) in series with the furnace and source of current. The resistance consisted of six wire wound rheostats in series, having a total resistance of 850 ohms and a maximum current carrying capacity of 3 amperes. The 110 volt A.C. line supplied a sufficiently steady current source, obviating any need for a battery of storage cells, which was the current source used by Plato (25). A D.P.D.T. switch (Sw.) was wired into the circuit in such a way that in one position the 110 volt A.C. line was connected to the furnace coil and resistance R in series, and in the other position the external resistance alone was

connected to a Wheatstone Bridge circuit. The bridge employed a sensitive needle type galvanometer (Leeds and Northrup Co.) as a null point indicator; it was capable of measuring resistance to  $\pm 0.2$  ohms.

(b) Temperature Measurement

All measurements of temperature were carried out using a mercury in glass thermometer having a scale of  $0^{\circ}$  to  $110^{\circ}$  divided in tenths of a degree (Central Scientific Co.). The thermometer was carefully calibrated against an identical type of National Bureau of Standards certified thermometer. A small reading lens clamped to the thermometer enabled estimation of tenths of one scale division so that the scale could be read to  $\pm 0.01^{\circ}$  with precision. In practice, an auxiliary thermometer was suspended close to the stem of the calibrated thermometer; this thermometer indicated the temperature of the emergent stem. The stem correction was applied to all thermometer readings.

(c) Calibration of the Apparatus

A Pyrex test-tube 4 cm. in diameter and 13 cm. long was selected as a containing vessel for the melts. This tube fitted the furnace opening snugly and was supported by its flange. It was fitted with a rubber stopper on which were mounted the centrally located stirrer and the thermometer.

The arrangement is shown in Fig.25 (a). The stirrer (1) was a rotary glass up-draft type, running in a glass tube bearing (2). The upper end of the stirrer was cemented to a brass cap (3) which was attached to a flexible cable driven by a worm-gearred stirring motor. The method of mounting the motor is shown in Plate I (a). Since the motor was geared down to a ratio of 20:1, even at its highest speed the stirrer rotated approximately 3 times per second. This rate was satisfactory, however.

With the cooling system and electrical circuit functioning properly, the furnace was allowed to heat to a temperature of approximately  $95^{\circ}$ , indicated by a thermometer inserted in the furnace. The tube containing paraffin oil was placed in the furnace and with the stirrer running continuously, the apparatus was left operating overnight to reach an equilibrium temperature. The external resistance in the circuit was measured on the Wheatstone Bridge and the thermometer reading was recorded. Inserting more resistance in series with the furnace caused the furnace temperature to fall to a new constant value, determined as before, by allowing the apparatus to run overnight. Continuing in this manner down to  $20^{\circ}$  a series of ten determinations at intervals of approximately  $10^{\circ}$  were obtained. Plotting temperature versus external resistance gave the

initial calibration curve, from which the required external resistance for any given equilibrium temperature could be read.

As a calibrating fluid, paraffin oil was most satisfactory, since it has no transitions in the temperature range examined, is relatively non-volatile and its specific heat is reasonably close to that of the organic melts which later replaced it.

With the primary calibration completed, the furnace was now calibrated for a particular linear cooling rate. Selection of the proper rate was quite important. A very slow rate of cooling, while desirable from the standpoint of composition change by diffusion in the solid phases, was to be avoided because of the long time required to determine a single cooling curve; too rapid a cooling rate did not permit attainment of equilibrium between solid and liquid phases. Furthermore, it was discovered by experiment that a linear cooling rate could not be obtained at the lower temperatures with this apparatus when cooling was too rapid. As the furnace temperature approached within  $50^{\circ}$  of the environment temperature, Newtonian cooling began to take prominence. It was imperative that a perfectly linear cooling rate be produced over the entire temperature range of the apparatus.

From the results of a large number of trials using paraffin oil and the organic melts, a cooling rate of  $1.5^{\circ}$  in 5 minutes was decided upon. With paraffin oil as the calibrating fluid, the circuit resistance was adjusted so that the thermometer registered  $95^{\circ}$  with the stirrer running. Then, largely by trial and error, and using the initial calibration curve as a guide, resistance was slowly inserted into the furnace circuit in steps; each increment of resistance was measured by quickly throwing the D.P.D.T. switch to the Wheatstone Bridge circuit. The thermometer scale was observed constantly, readings being taken every minute to assure a constant cooling rate of  $0.3^{\circ}$  per minute. Often it was necessary to remove resistance from the circuit in order to maintain the linear cooling rate, but all adjustments were recorded. When the temperature range of  $95^{\circ}$  to  $20^{\circ}$  had been covered in this manner, temperatures were plotted against resistances. The points so obtained were scattered but it was possible to draw a rough curve. A second calibration run was carried out in a similar manner using the rough calibration curve as a guide. The results of this run were plotted with the data from the first run on the same graph, the rough calibration curve being appropriately modified. A third calibration run based on the modified curve produced the final refined calibration curve. From this curve could be read the exact resistance

to be inserted in series with the furnace every  $2\frac{1}{2}$  minutes to produce a linear cooling rate of  $0.3^{\circ}$  per minute.

The final test of the calibration curve was carried out as follows. At least one hour was allowed to permit the stirred paraffin oil to attain the same temperature as the furnace, which was set for  $95^{\circ}$ . Resistance was inserted in the furnace circuit until the rate of cooling approached  $0.3^{\circ}$  per minute, and at intervals of exactly  $2\frac{1}{2}$  minutes thereafter, the exact values of resistance being read from the calibration curve. Each increment of resistance was measured by quickly switching in the Wheatstone Bridge, adjusting the rheostats for the proper value, then again throwing the switch to the furnace circuit. During the measurement of resistance the furnace was momentarily disconnected from the current source, but as the time interval was no greater than 15 seconds the temperature decrement did not deviate perceptibly from the established cooling rate.

Thermometer readings were taken every minute until the entire range of the apparatus had been covered ( $95^{\circ}$ - $20^{\circ}$ ). Plotting temperatures as ordinates against time in minutes as abscissae resulted in a straight line deviating from perfect linearity by no more than  $0.2^{\circ}$ .

Below  $20^{\circ}$  the selected cooling rate could not be

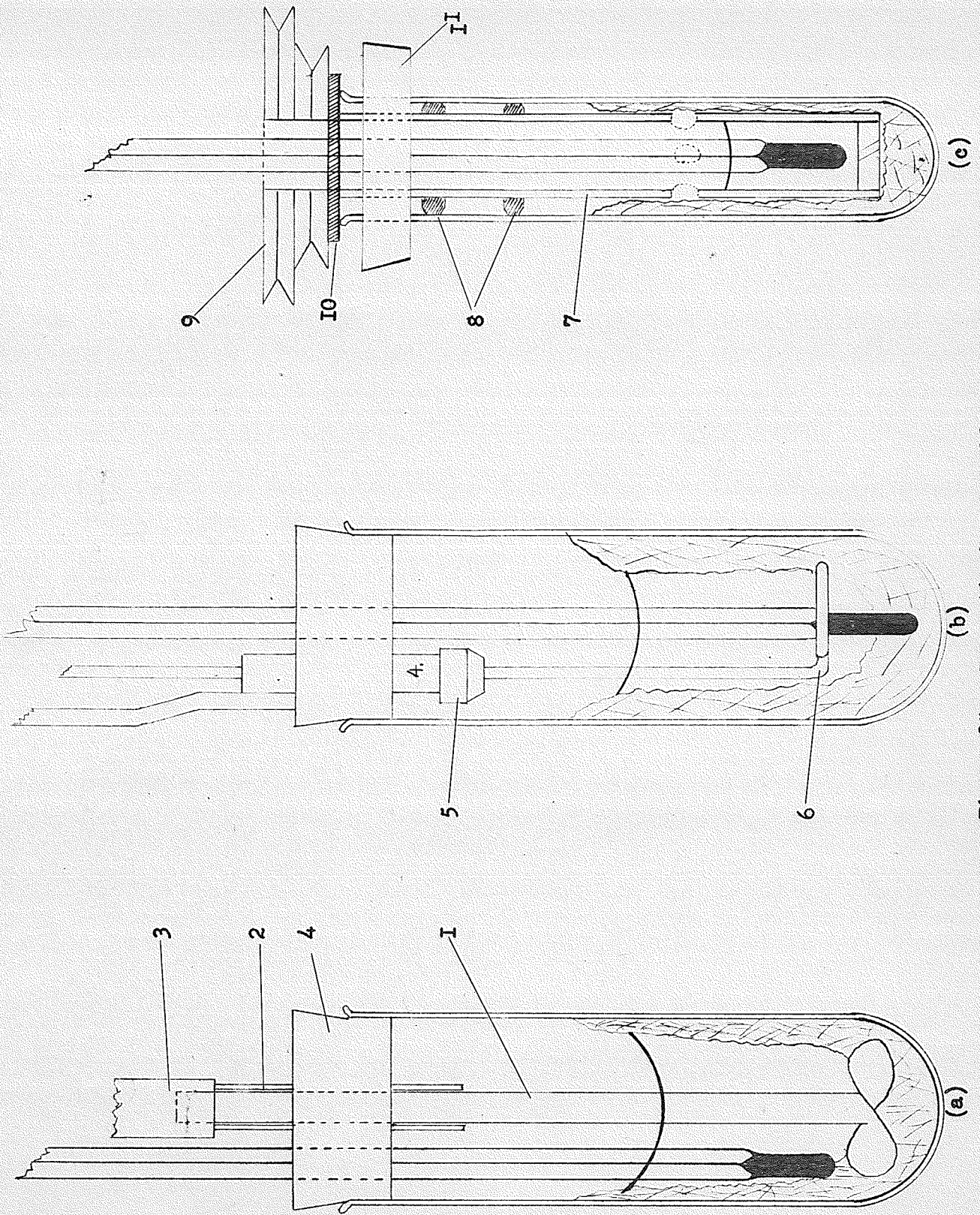


Figure 25.--Some stirring assemblies.

maintained, for the temperature of the furnace and melt was not far removed from that of the environment. Consequently, instead of following a linear cooling law, the furnace tended to cool more slowly in accordance with Newton's law of cooling. Choosing a slower rate of linear cooling would have extended the lower limit of the range of the apparatus, but this was impractical; using the cooling rate of  $0.3^{\circ}$  per minute required 4 hours to cover the entire range of the apparatus, during which time the constant attention of the operator was required.

#### (d) Stirring

The greatest of practical difficulties was encountered in attempting to devise a flawless stirring mechanism. The rotary stirring apparatus shown in Fig.25 (a) was unsatisfactory when used with the organic melts because deposition of solid began on the walls of the tube; the solid layer grew toward the centre of the mass until the stirrer froze and was unable to operate. At this point a large amount of liquid still remained unsolidified. An adequate cooling curve could not be obtained, since cessation of stirring produced a change in the cooling rate of the melt. The latter was evidenced by a break in the curve followed by temperature fluctuations. Also, since the thermometer bulb was not centrally located, it became encrusted with solid before

solidification was half completed. The net result was a cooling curve from which only a freezing point determination could be obtained.

To provide more vigorous stirring with a centred thermometer, a mechanical vertical stirrer was designed. The assembly is represented in Fig.25 (b). A nickel-steel ring stirrer (6) reciprocated in a bearing (4) which was sealed at its lower end by a packing gland (5) stuffed with cotton. The purpose of the gland was to prevent escape of any vapors, as the organic melts were quite volatile and sublimed readily. The vertical action of the ring stirrer was provided by a mechanical reciprocating mechanism shown in full scale in Fig.26. The body of this device (1) was made of brass bent to shape. The steel drive shaft (3) running in a bronze bearing (4) was fixed to a brass flywheel (2). A connecting rod (5) pivoted on the flywheel (6) and on the vertical shaft (7), transmitted the power from the flywheel to the stirrer shaft. The stirrer bearing was made by first soldering a thin-walled brass tube (8) to the body, then with the shaft in position, filling it with molten high-speed babbit metal. The resulting bearing was close-fitting but worked smoothly.

The reciprocating mechanism was inserted through a hole in the rubber stopper close to the thermometer. The

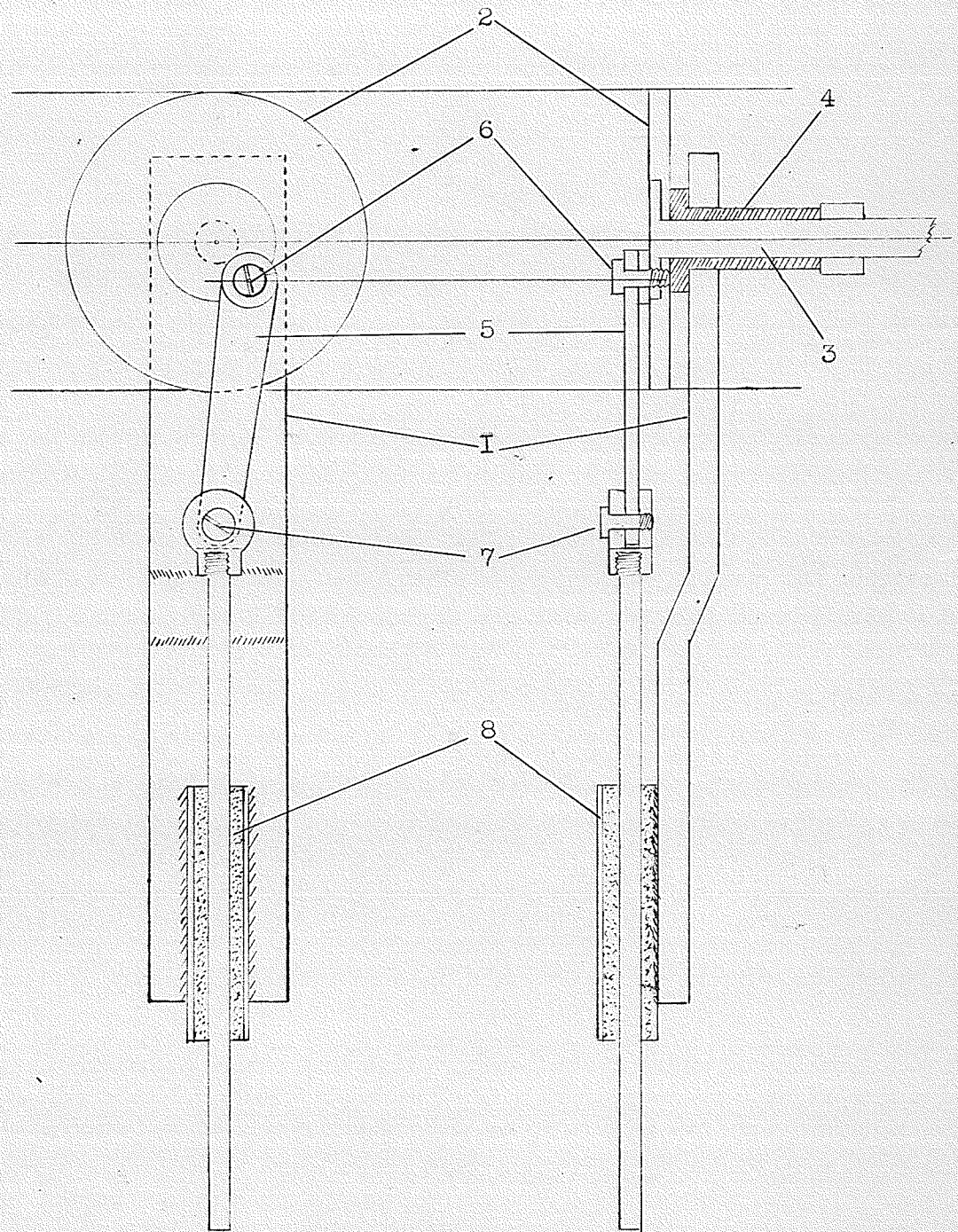


Figure 26.

Scale-1 in. = 1 in.

drive shaft was connected to a flexible cable driven by the geared stirring motor and the throw of the flywheel was so fixed that the ring had a total vertical action of approximately  $1\frac{1}{2}$  inches. Plate I (a) is a photograph of the complete assembly.

This stirrer was better than the rotary glass stirrer but still suffered from several disadvantages. The ring operated at a rate of approximately 5 strokes per second, a speed sufficient to maintain an equal distribution of crystallized material in the liquid. Eventually, however, the ring froze into the solid growing from the walls of the tube, leaving a portion of liquid unstirred. Trouble was also experienced with the vertical bearing. Vapor managed to escape through the packing into the body of the bearing where it sublimed, preventing the stirrer from functioning.

Far more satisfactory results were obtained with the stirring arrangement shown in Fig.25 (c). A narrower tube was selected for the container so that smaller amounts of materials could be used to maintain a sufficient depth of liquid to keep the thermometer bulb immersed at all times. This tube was a 1 inch Pyrex test-tube cut to a length of 5 inches. The stirrer was of the de Witt type, consisting of a hollow glass tube (7) fitted with fibre ring bearings (8) rotating concentrically with respect to the container.

Four glass blades fastened at angles of  $45^{\circ}$  in the lower end of the stirring tube served to propel the liquid from the bottom of the container upward into the tube. Liquid and crystals drawn into the tube passed the thermometer bulb and escaped through four holes spaced approximately  $1\frac{1}{2}$  inches from the lower end. To the upper end of the stirring tube was cemented a two-step wooden pulley which was belt-driven from a small stirring motor. A fibre disc (10) running on the fire-polished rim of the container supported the stirring tube longitudinally. The entire apparatus was fixed in the furnace by means of a rubber stopper (11) which fitted tightly in the furnace opening.

This stirrer was efficient and operated smoothly. Stirring was continuous until solid grew from the walls of the container, encrusting the stirring tube. By this time only a very small amount of liquid surrounding the thermometer bulb remained unsolidified. This last portion froze within a few minutes enabling the attainment of a smooth idealized cooling curve from which reproducible melting point determinations could be obtained.

The principal disadvantages of this arrangement were the necessity for external suspension of the thermometer in the exact centre of the stirring tube and the loss of materials through sublimation. Each determination required

a freshly prepared mixture, because of the composition change brought about by the volatilization of the components.

Efficient stirring in a closed system finally was obtained by employing a fluctuating current of dry air. A continuous current could not be used because of the volatility of the organic substances. The complete stirring assembly is shown diagrammatically in Fig.27. The motor-driven reciprocating mechanism (1) was coupled to a piston (2) working in a  $3/8$  inch bore glass cylinder (3). The piston consisted of a  $1/4$  inch glass rod 12 inches long, over one end of which a piece of soft rubber tubing was fastened. This piston was a very loose fit in the cylinder. A piece of rubber pressure tubing (4) connected the cylinder to a second piece of glass tubing (5) which, in turn, was joined to a long tube of smaller bore having an outlet closed by a clamp on an attached length of rubber tubing (7). When the U-tube and reciprocating mechanism were clamped to a suitable stand, the U-tube was filled with clean, dry mercury. The top end of tube (6) was connected by means of rubber tubing to the stirring tube (8), located adjacent to the thermometer (11) which was centred in the main container (9). The stirring tube was merely a piece of  $3/8$  inch bore glass tubing, the immersed orifice of which was constricted slightly. An outlet tube (10) consisting of

a 6 inch length of 3/16 inch bore glass tubing, was connected to the U-tube (12) by a short length of rubber tubing. Sulphuric acid was used to fill U-tube (12) because of its hygroscopic nature and because it offered less resistance to the oscillating air current within the closed system than did mercury.

As the piston oscillated in the cylinder at a rate of approximately 4 strokes per second, the mercury in the U-tube was forced to oscillate in resonance with it. The oscillation of the mercury column in tube (6) produced a sympathetic oscillation of the air in the system which was transferred to the liquid in the stirring tube (8). The throw of the reciprocating mechanism was fixed so that the fused melt oscillated a distance of  $1\frac{1}{2}$  inches in the stirring tube. The position of the liquid level in tube (8) could be quickly adjusted by altering the air pressure within the system through tube (7). Usually, when the piston reached bottom dead-centre, the liquid level was at the orifice of the stirring tube. As the piston rose, the melt was forced into the tube. On the piston's down-stroke, the liquid spurted from the tube's orifice with sufficient velocity to disturb the crystalline sediment on the bottom of the container. This disturbance recurring 4 times per second produced a

vigorous and efficient agitation of the melt and depositing crystals.

The stirring process and progress of crystallization could not be observed directly in practice, but the oscillation and relative positions of the levels in tube (12) were sufficient indication. As the freezing process approached completion, the liquid in the stirring tube slowly solidified and finally sealed the orifice. The cessation of stirring action was detected by the gradually diminishing amplitude of the oscillations in tube (12) and their ultimate disappearance.

The position of the orifice of the stirring tube was critical. For best results, it was immersed  $2/3$  of the total depth of the melt. The thermometer bulb then was placed  $1/4$  inch below the orifice.

Smooth, efficient stirring was obtained with this apparatus. Contrasted with the abrupt cessation of the mechanical stirrers and the attendant break in the cooling curve, the stirring action stopped gradually; the cooling curves showed no evidence of a break when the stirring ceased completely. Employment of the closed system was also advantageous, since losses by evaporation were minimized. Loss through the stirring tube was very slight. The outlet tube (10), however, usually collected a

sublimate which was easily returned to the body of the melt by breaking the connection (13), and scraping the deposit down with a glass rod. Collection of a sublimate in tube (10) was actually an advantage, since by scraping the tube at the proper instant, the melt in the container could be seeded, and supercooling avoided.

(e) General Procedure

For the determination of a cooling curve of a pure substance or a mixture forming a solid solution, two satisfactory procedures were developed:

Procedure I. About 30 grams of a mixture were introduced into the container and fused over a Bunsen flame. When the stirring apparatus was functioning properly, a determination of the freezing point of the mixture was made by allowing the melt to cool freely outside the furnace. Then the furnace was set for a temperature 10 degrees above this freezing point; the container was inserted and left for one hour to attain temperature equilibrium. By inserting the proper resistance into the furnace circuit every  $2\frac{1}{2}$  minutes, according to the calibration curve, the furnace and contained melt were induced to cool at the predetermined rate of  $0.3^{\circ}$  per minute. As cooling progressed, thermometer readings were taken every minute and plotted on rectangular

coordinate paper: 2.5 cm. on the ordinate represented 1 degree and 0.5 cm. on the abscissa was equivalent to 1 minute. Approximately  $0.1^{\circ}$  above the predetermined freezing point, the melt was seeded by quickly scraping down the outlet tube with a glass rod. Temperatures were recorded until a complete cooling curve was plotted. The freezing and melting points of the mixture were obtained from the curve and corrected for the thermometer error and emergent mercury column.

While this procedure yielded quite satisfactory results, it consumed considerable time in the determination of a single cooling curve. To obtain a complete cooling curve, a range of at least 30 degrees had to be examined; this process required a minimum of 3 hours, depending on the amount of mixture in the container. In an attempt to diminish the time required for a determination, there was conceived a second procedure, which proved to be very successful.

Procedure II. As a mixture was being prepared, the furnace was allowed to heat. A free-cooling freezing point determination was carried out as in Procedure I. When the furnace reached a temperature (indicated by an inserted thermometer) approximately 15 degrees above the freezing point of the mixture, linear cooling was initiated.

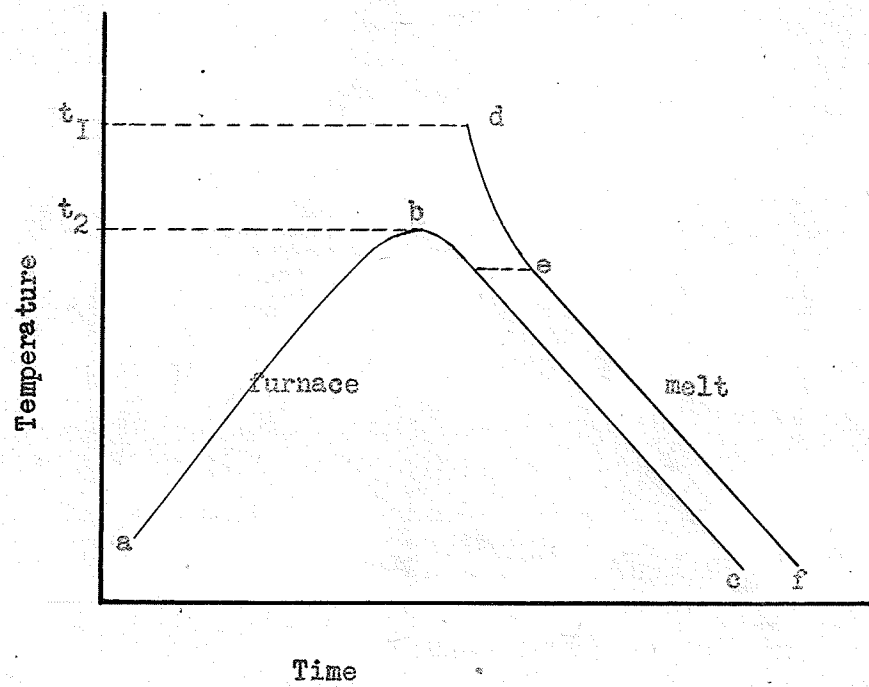


Figure 28 (a).

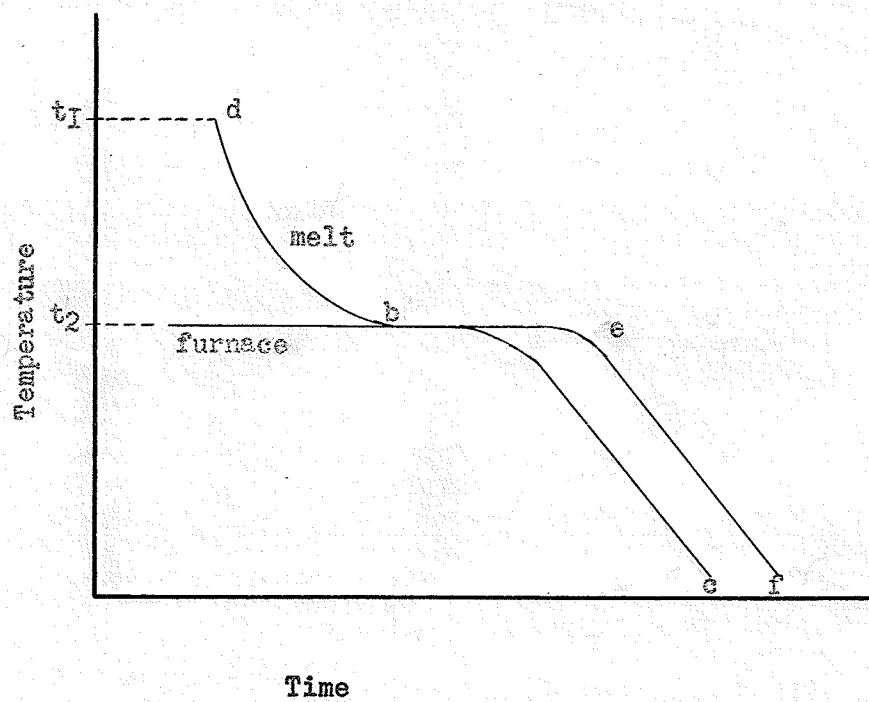


Figure 28 (b).

Meanwhile, the melt was heated over a Bunsen flame to a temperature 15 degrees above the freezing point, then was allowed to cool slowly until its temperature lay about 5 degrees above the furnace temperature. The container was inserted quickly into the furnace and Procedure I was continued thereafter.

The temperature-time relationships of furnace and melt are shown qualitatively in Fig.28 (a). The curve abc represents heating of the furnace along ab to a maximum temperature  $t_2$ , followed by linear cooling along bc. The melt, initially at temperature  $t_1$ , cooled freely to e, where the linear cooling of the furnace induced linear cooling along ef.

Temperature-time relationships of Procedure II may be contrasted with those of Procedure I, represented in Fig.28 (b). In the latter case, one hour was required for attainment of equilibrium between furnace and melt, indicated by b. Application of Procedure II entirely eliminated this "fore-period".

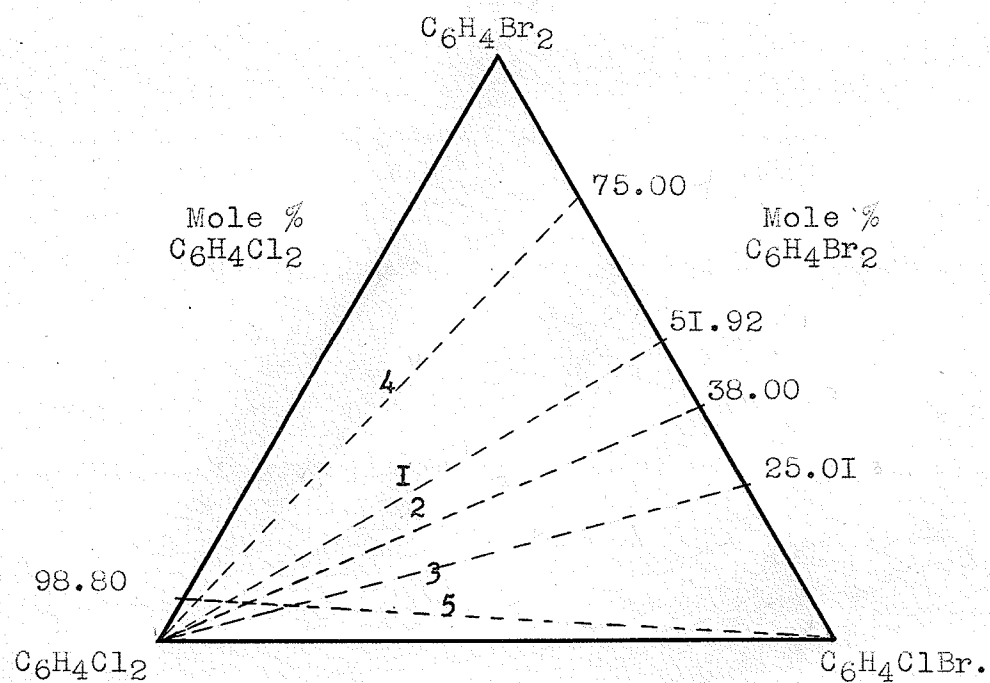
The diagrams indicate that the temperatures of the melt and furnace during cooling were not the same. For the selected rate of cooling, the constant temperature differential amounted to about 8 degrees, but varied depending on the specific heats of the various

mixtures. This principle has been employed in a method of radiation calorimetry for calculating specific heats and heats of fusion from cooling curves (30).

#### Thermal Analysis of the Binary and Ternary Systems

The liquidus and solidus curves of the binary systems were determined by employing the usual procedure of beginning with one pure component and adding consecutive amounts of a second component up to a concentration of 50 percent. Then, starting with the second component, the first component was added up to a concentration of 50 percent. The resulting data were plotted on a temperature-concentration diagram and if the determination was accurate, the two branches of the curves met exactly at the 50 percent point.

In the study of the ternary system, five quasi-binary systems were determined, as shown in Fig.29. Binary mixtures of the compositions indicated were carefully weighed out, fused and thoroughly mixed in glass stoppered bottles. The procedure in the determination of the quasi-binary systems was the same as that employed for the binary systems of the pure components; a mixture replaced one of the pure components. Plotting the data on a rectangular diagram produced the quasi-binary sections of the ternary isobaric section.



-Figure 29.-

By graphical interpolation, the solidus and liquidus isotherms of the ternary system could be derived.

(f) Purification of Materials

The materials used, namely p-dichlorobenzene, p-dibromobenzene and p-chlorobromobenzene, were obtained from the British Drug Houses. The supply of dichlorobenzene was augmented by some Merck dichlorobenzene, sold commercially as an insecticide. When the stock of chlorobromobenzene diminished, additional material was prepared by bromination of chlorobenzene according to the method of Cohen and Dakin (31).

Each of the materials was steam distilled once from dilute sulphuric acid, once from dilute sodium hydroxide and finally fractionated using a short column. The dichlorobenzene obtained melted at  $52.5^{\circ}$ , but a cooling curve determined on a portion showed a freezing interval of  $0.8^{\circ}$ , indicating an impure state. The ortho isomer (b.p.  $179^{\circ}$ ) was separated from the desired para isomer (b.p.  $173^{\circ}$ ) by crystallization from ethyl alcohol. After six crystallizations, the material froze at  $53.08^{\circ}$  with no detectable freezing interval.

The dibromobenzene was treated in a similar manner. Fractionation as a means of purification was useless since the meta isomer (an oil at room temperature)

boiled at exactly the same temperature as the para isomer, viz.,  $219^{\circ}$ . Six crystallizations from ethyl alcohol yielded a product freezing at  $87.30^{\circ}$ , a freezing interval being completely lacking.

Greater difficulty was experienced in preparing a pure sample of chlorbrombenzene. The meta and para isomers both boiled at  $196^{\circ}$ , while the ortho isomer boiled slightly higher at  $199^{\circ}$ . However, purification by crystallization was effective, as the ortho and meta isomers, both oils at room temperature, were removed from the solid p-chlorbrombenzene by ethyl alcohol. The product obtained after six crystallizations froze at  $64.7^{\circ}$ , but the cooling curve showed a freezing interval of  $0.6^{\circ}$ . That this material was still relatively impure was proven further by the fact that after storing it for one week over concentrated sulphuric acid in a clean vacuum desiccator, a few droplets of an oil were deposited on the cover of the desiccator. Two additional crystallizations from ethyl alcohol yielded a sample which froze at  $64.58^{\circ}$  and had a freezing interval of  $0.07^{\circ}$ . This was considered pure enough for the present purposes.

All three substances were stored over concentrated sulphuric acid in vacuum desiccators. Most of the material used had stood under vacuum for at least two months.

## RESULTS

# The Pure Materials

Some properties of the substances studied are given in the table below.

TABLE I

## CRYSTALLOGRAPHIC AND THERMAL PROPERTIES OF SOME DI-HALOGEN BENZENES

|                                                              | $p\text{-C}_6\text{H}_4\text{Cl}_2$ | $p\text{-C}_6\text{H}_4\text{ClBr}$ | $p\text{-C}_6\text{H}_4\text{Br}_2$ |
|--------------------------------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Crystal System                                               | monoclinic<br>prismatic             | monoclinic<br>prismatic             | monoclinic<br>prismatic             |
| Axial Ratio<br>$a : b : c =$<br>B                            | 2.5196:1:1.3920<br>112030'<br>(010) | 2.6077:1:1.4242<br>113000'<br>(010) | 2.6660:1:1.4179<br>112038'<br>(010) |
| Optic Axis                                                   |                                     |                                     |                                     |
| Lattice Dimensions<br>$a =$<br>$b =$<br>$c =$<br>$d_{100} =$ | 14.83A°<br>4.10<br>5.88<br>13.70    | 15.15A°<br>4.13<br>5.81             | 15.46A°<br>4.11<br>5.80<br>14.29    |
| Unit Structure                                               | 2 molecules                         | 2 molecules                         | 2 molecules                         |
| Heat of fusion (cal./gm.)<br>(cal./mole)                     | 29.50 $\pm$ 0.11<br>4340            | 23.42 $\pm$ 0.09<br>4484            | 20.80 $\pm$ 0.08<br>4908            |
| Specific Heat<br>of Liquid (cal./gm.)                        | 0.298 $\pm$ 0.004<br>(99.10-52.90)  | 0.239 $\pm$ 0.004<br>(99.80-64.60)  | 0.200 $\pm$ 0.004<br>(87.0°-130.0°) |

Examination of the table makes apparent the great similarity of crystalline structure in the three compounds. The crystallographic data were taken from the most recent publication by S.B. Hendricks (32).

According to J. Narbutt (33), the heat of fusion and specific heat of dibrombenzene are the most accurately determined values. Here also, the thermal properties do not vary greatly from one compound to the next, but there is an increasing gradation from the highest to the lowest molecular weights.

#### Freezing Points

The freezing point of p-dichlorobenzene has been reported by various authors: Bruni (34) gives the freezing point as  $52.7^{\circ}$ ; Kuster (28),  $52.7^{\circ}$ ; Nagornow (35),  $52.8^{\circ}$ ; Narbutt (36),  $52.9^{\circ}$ ; Speranski (37),  $53.1^{\circ}$ ; Kruyt (29),  $53.0^{\circ}$ . An accurate freezing point determination was reported by Cooper (38). As large quantities of pure material were at his disposal, he determined the freezing point of a large mass contained in a tall cylinder using a totally immersed National Bureau of Standards certified thermometer. His value is  $53.13 \pm 0.02^{\circ}$ , which is in fair agreement with our value of  $53.08 \pm .02^{\circ}$ , given in Table II below. The slight difference in results is probably due to a small difference in the purity of the substances, since the precision of the determinations is the same.

With regard to the freezing point of p-chlorbrombenzene the literature is not unanimous. By bromination of chlorobenzene, Auwers (39) and Bruni (34) obtained products melting at  $67^{\circ}$ . However Speranski (37), employing the same method, obtained for his material a freezing point of  $64.7^{\circ}$ . Analysis by the Carius method indicated a purity of 99.68 percent. The latter author also prepared a quantity of chlorbrombenzene by diazotization of p-bromaniline; the product froze at  $64.7^{\circ}$ . Taking great precautions in his purification procedure, Narbutt (36) prepared a quantity of chlorbrombenzene which froze sharply at  $64.6^{\circ}$  without visible evidence of a freezing interval. Our freezing point of  $64.58^{\circ}$  corresponds well with this value.

In Table II, experiments 13 and 14 are the results of cooling curves taken on the material finally purified by two crystallizations of the material used in 12. The effect of this purification was to raise the freezing point only slightly, but to reduce the freezing interval markedly.

G. Bruni worked with a sample of dibrombenzene freezing at  $85.9^{\circ}$ . This value is the lowest of any freezing temperatures reported for the substance. Kuster (28) and Narbutt (36) report  $86.4^{\circ}$  and  $86.9^{\circ}$ , respectively, while later reports by Kruyt (29) and Nagornow (35) give even higher values:  $87.2^{\circ}$  and  $87.1^{\circ}$  respectively. The freezing point determined from

cooling curves (experiments 6-10, Table II) was found to be  $87.30^{\circ}$ , a value higher than any previously reported. As the data indicate, the precision of the determination was  $\pm 0.02^{\circ}$ . The material did not freeze over a temperature interval, so that it was unquestionably pure.

TABLE II

FREEZING POINTS OF PURE COMPONENTS

| Experiment | Weight<br>Dichlor-<br>benzene<br>(gms.) | Weight<br>Dibrom-<br>benzene<br>(gms.) | Weight<br>Chlorbrom-<br>benzene<br>(gms.) | Freezing<br>Point<br>( $^{\circ}\text{C}$ ) | Melting<br>Point<br>( $^{\circ}\text{C}$ ) | Freezing<br>Interval<br>( $^{\circ}\text{C}$ ) |
|------------|-----------------------------------------|----------------------------------------|-------------------------------------------|---------------------------------------------|--------------------------------------------|------------------------------------------------|
| 1          | 20.00                                   |                                        |                                           | 53.09                                       | 53.08                                      | 0.01                                           |
| 2          | 18.09                                   |                                        |                                           | 53.09                                       | 53.08                                      | 0.01                                           |
| 3          | 21.15                                   |                                        |                                           | 53.08                                       | 53.08                                      | 0.00                                           |
| 4          | 30.00                                   |                                        |                                           | 53.09                                       | 53.09                                      | 0.00                                           |
| 5          | 21.16                                   |                                        |                                           | 53.08                                       | 53.08                                      | 0.00                                           |
| 6          |                                         | 43.36                                  |                                           | 87.29                                       | 87.29                                      | 0.00                                           |
| 7          |                                         | 43.36                                  |                                           | 87.30                                       | 87.30                                      | 0.00                                           |
| 8          |                                         | 44.00                                  |                                           | 87.30                                       | 87.30                                      | 0.00                                           |
| 9          |                                         | 38.00                                  |                                           | 87.31                                       | 87.31                                      | 0.00                                           |
| 10         |                                         | 30.00                                  |                                           | 87.34                                       | 87.32                                      | 0.02                                           |
| 11         |                                         |                                        | 25.67                                     | 64.53                                       | 64.35                                      | 0.18                                           |
| 12         |                                         |                                        | 25.67                                     | 64.52                                       | 64.31                                      | 0.21                                           |
| 13         |                                         |                                        | 21.55                                     | 64.58                                       | 64.51                                      | 0.07                                           |
| 14         |                                         |                                        | 18.00                                     | 64.57                                       | 64.48                                      | 0.09                                           |

The freezing points obtained here do not agree too well with Bruni's. Therefore it is to be expected that our results for the various systems, while they may correspond qualitatively, will not in general agree quantitatively with his.

### Cooling Curves

For the pure substances, cooling curves were obtained which closely approached the ideal curve. Fig.30 is a plot of the data taken from experiment 2. The broken straight line indicates the trace which would have been obtained in the absence of a transformation. Except for the regions A, where the last trace of liquid was freezing, and B, where the solid began to assume the cooling rate of the furnace, the experimental curve corresponded with the theoretical construction shown in the diagram by the projected straight lines.

All curves obtained possessed the same general form as that shown in Fig.30, the area C enclosed by the curve depending only on the mass of material used and the quantity of heat liberated in the transformation. These curves were the analogues of those obtained by Steiner and Johnson (30), who employed an electrically heated radiation calorimeter in their experiments on some organic materials.

### Transition Temperature

Upon examining the cooling curves of p-dichlorobenzene

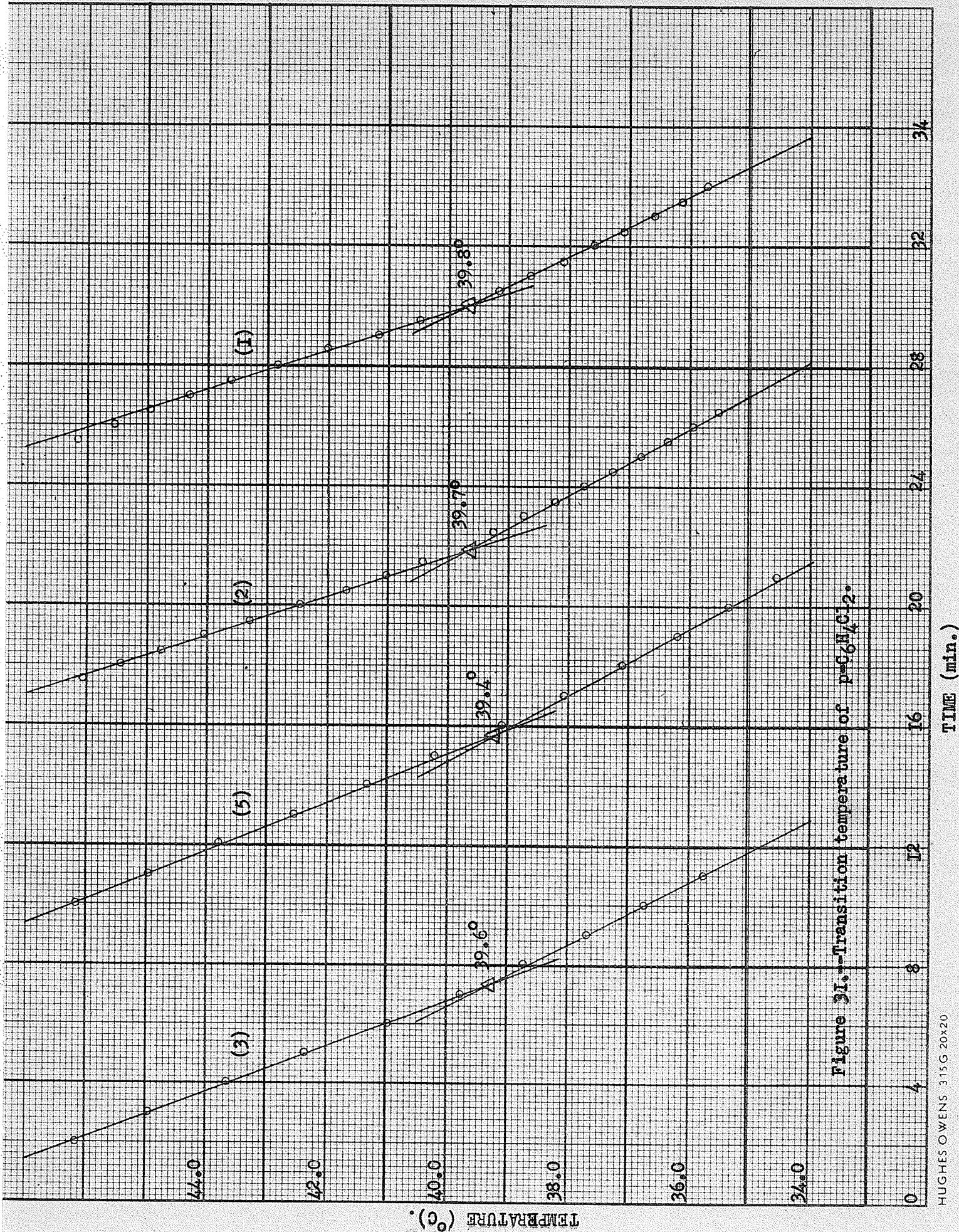


Figure 31. Transition temperature of p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>.

# I. THE BINARY SYSTEM

p-Dibromobenzene: p-Chlorbromobenzene

closely, a break in the line representing cooling of the solid was discovered. Experiments, 1, 2, 3 and 5 gave cooling curves exhibiting a break at  $39.8^{\circ}$ ,  $39.7^{\circ}$ ,  $39.6^{\circ}$  and  $39.4^{\circ}$ , respectively. Experiment 4 was not continued long enough to enable a determination of the temperature of the break. The portions of the cooling curves in the transition range are represented in Fig.31.

The change in slope at  $39^{\circ}$  was not abrupt, however, and at first it was believed that the results were due to some flaw in the calibration of the apparatus. A search of the literature revealed that a determination of the transition temperature of p-dichlorobenzene had been carried out by Beck and Ebbinghaus (40), who reported the temperature as  $39.5^{\circ}$ . This was in excellent agreement with the mean of the above results,  $39.6^{\circ}$ .

Conflicting data has been reported by Wallerant (41). From the results of microscopic studies of p-dichlorobenzene, he concluded that under atmospheric pressure this material is trimorphic, the reversible transitions occurring at  $29^{\circ}$  and  $25^{\circ}$ .

That p-dichlorobenzene does exist in at least two forms under atmospheric pressure appears to be an undisputed fact. From the results obtained by thermal analysis, it must be concluded that a transformation in the solid state occurs at  $39.6^{\circ}$ .

The complete data for the system dibromobenzene: chlorbromobenzene are compiled in Table III. It was chosen to express concentrations in terms of mole percent, since in this form the results could be more easily compared with those of the earlier workers. Also, calculations based on the equations for ideal solutions required concentrations expressed as mole fractions.

The phase diagram for this binary system is plotted in Fig.32. The liquidus curve appears to be almost a straight line. Actually, it is S-shaped, the high temperature portion lying above, and the low temperature portion lying below the straight line joining the freezing points of the pure components. This system is an example of Roozeboom's Type I, in which the freezing points of all mixtures lie between those of the pure components.

Employing the thermal data in Table I, the theoretical liquidus and solidus curves were calculated from Seltz's equations (15). The resulting diagram was of Roozeboom's familiar Type I, the liquidus and solidus curves straddling the straight line joining the freezing points of the pure components.

TABLE III

THE SYSTEM p-DIBROMBENZENE: p-CHLORBROMBENZENE

| Experiment | Weight Dibrom-benzene (gms.) | Weight Chlorbrom-benzene (gms.) | Mole % Dibrom-benzene | Mole % Chlorbrom-benzene | Freezing Point (°C) | Melting Point (°C) | Freezing Interval (°C) |
|------------|------------------------------|---------------------------------|-----------------------|--------------------------|---------------------|--------------------|------------------------|
| 15         | 0.7450                       | 20.00                           | 2.92                  | 97.08                    | 65.11               | 64.89              | 0.22                   |
| 16         | 1.886                        | 20.00                           | 7.09                  | 92.91                    | 65.97               | 65.34              | 0.63                   |
| 17         | 4.767                        | 20.00                           | 16.21                 | 83.79                    | 67.88               | 66.98              | 0.90                   |
| 18         | 8.220                        | 20.00                           | 25.01                 | 74.99                    | 69.89               | 68.43              | 1.56                   |
| 19         | 15.11                        | 20.00                           | 38.00                 | 62.00                    | 72.97               | 71.37              | 1.60                   |
| 20         | 20.00                        | 0.6792                          | 95.98                 | 4.02                     | 86.50               | 86.14              | 0.36                   |
| 21         | 20.00                        | 2.213                           | 88.00                 | 12.00                    | 84.76               | 83.96              | 0.80                   |
| 22         | 20.00                        | 5.409                           | 75.00                 | 25.00                    | 81.75               | 80.54              | 1.21                   |
| 23         | 20.00                        | 9.945                           | 62.00                 | 38.00                    | 78.67               | 77.14              | 1.53                   |
| 24         | 20.00                        | 15.03                           | 51.92                 | 48.08                    | 76.25               | 74.53              | 1.72                   |
| 25         | 1.133                        | 30.87                           | 2.89                  | 97.11                    | 65.01               | 64.46              | 0.55                   |
| 26         | 3.684                        | "                               | 8.84                  | 91.16                    | 66.32               | 65.60              | 0.72                   |
| 27         | 12.56                        | "                               | 24.89                 | 75.21                    | 70.00               | 68.40              | 1.60                   |
| 28         | 20.35                        | "                               | 34.89                 | 65.18                    | 72.42               | 70.80              | 1.62                   |
| 29         | 37.73                        | 0.7562                          | 97.59                 | 2.41                     | 86.95               | 86.40              | .55                    |
| 30         | "                            | 1.928                           | 94.08                 | 5.92                     | 86.26               | 84.95              | 1.31                   |
| 31         | "                            | 6.181                           | 83.21                 | 16.79                    | 84.07               | 81.59              | 2.48                   |
| 32         | "                            | 13.55                           | 69.25                 | 30.75                    | 80.70               | 77.96              | 2.74                   |
| 33         | "                            | 13.55                           | 69.25                 | 30.75                    | 80.68               | 77.91              | 2.77                   |
| 34         | "                            | 27.68                           | 52.52                 | 47.48                    | 76.47               | 73.52              | 2.95                   |
| 35         | 0.9142                       | 25.18                           | 2.85                  | 97.15                    | 65.10               | 64.60              | 0.50                   |
| 36         | 5.933                        | "                               | 16.06                 | 83.94                    | 67.90               | 66.61              | 1.29                   |
| 37         | 11.02                        | "                               | 26.21                 | 73.79                    | 70.11               | 68.55              | 1.56                   |
| 38         | 19.99                        | "                               | 39.18                 | 60.82                    | 73.44               | 71.08              | 2.36                   |
| 39         | 26.85                        | 0.3696                          | 98.30                 | 1.70                     | 87.12               | 86.55              | 0.57                   |
| 40         | "                            | 1.120                           | 95.11                 | 4.89                     | 86.33               | 85.37              | 0.96                   |
| 41         | "                            | 2.483                           | 89.76                 | 10.24                    | 85.24               | 83.60              | 1.64                   |
| 42         | "                            | 5.437                           | 80.01                 | 19.99                    | 83.16               | 80.85              | 2.31                   |
| 43         | "                            | 11.68                           | 65.08                 | 34.92                    | 79.55               | 77.00              | 2.55                   |
| 44         | "                            | 18.03                           | 54.70                 | 45.30                    | 77.06               | 74.32              | 2.74                   |
| 45         | "                            | 23.74                           | 47.83                 | 52.17                    | 75.39               | 72.42              | 2.97                   |

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TABLE III A

COMPARISON OF EXPERIMENTAL AND CALCULATED DATA

in System: *p*-Dibromobenzene — *p*-Chlorobromobenzene

| Freezing Point (°C) | Experimental $x_B^L$ | Calculated $x_B^L$ | Experimental $x_B^S$ | Calculated $x_B^S$ |
|---------------------|----------------------|--------------------|----------------------|--------------------|
| 65.11               | 0.971                | 0.981              | 0.949                | 0.970              |
| 65.97               | .939                 | .949               | .890                 | .921               |
| 67.88               | .838                 | .883               | .778                 | .827               |
| 69.89               | .750                 | .808               | .682                 | .729               |
| 72.97               | .620                 | .679               | .497                 | .576               |
| 76.25               | .483                 | .540               | .415                 | .431               |
| 78.67               | .380                 | .432               | .321                 | .330               |
| 81.75               | .251                 | .282               | .204                 | .204               |
| 84.76               | .120                 | .127               | .089                 | .087               |
| 86.50               | .040                 | .037               | .020                 | .025               |

The concentrations in the above table are expressed in mole fraction of component B, chlorbrombenzene.

## II. THE BINARY SYSTEM

p-Dichlorobenzene: p-Dibromobenzene

In our classification of binary systems forming solid solutions, the system p-dichlorobenzene: p-dibromobenzene falls under Type III . (Data relevant to the system are given in Tables IV and IV A.) A distinct minimum congruent freezing temperature of  $52.90^{\circ}$  was detected at a concentration of 1.22 mole percent of dibromobenzene. As this minimum freezing mixture contained so little dibromobenzene, particular care was exercised in establishing the positions of liquidus and solidus curves in this region.

Fig.33 represents the complete binary system, with the region of the minimum greatly enlarged in a separate diagram.

Seltz's equations would not be expected to apply in this example, since near the minimum, for a given value of the transformation temperature there should be two mathematical solutions. The equations do not predict this behaviour. However, the calculated curve representing the idealized system serves as an interesting comparison.

The experimentally determined liquidus and solidus curves are both straight lines over a restricted concentration range of approximately 40 to 80 percent of dibromobenzene. As in the system chlorobromobenzene: dibromobenzene, the liquidus curve of this system is S-shaped but the effect is more pronounced than in the former system. However, at no point does the liquidus curve lie above the straight line joining the freezing points of the pure components.

TABLE IV

THE SYSTEM p-DICHLORBENZENE: p-DIBROMBENZENE

| Experi-<br>ment | Weight<br>Dichlor-<br>benzene<br>(gms.) | Weight<br>Dibrom-<br>benzene<br>(gms.) | Mole %<br>Dichlor-<br>benzene | Mole %<br>Dibrom-<br>benzene | Freezing<br>Point<br>(°C) | Melting<br>Point<br>(°C) | Freezing<br>Interval<br>(°C) |
|-----------------|-----------------------------------------|----------------------------------------|-------------------------------|------------------------------|---------------------------|--------------------------|------------------------------|
| 46              | 21.15                                   | 0.1017                                 | 99.70                         | 0.30                         | 53.06                     | 53.01                    | 0.05                         |
| 47              | "                                       | .2034                                  | 99.38                         | 0.62                         | 53.02                     | 52.95                    | 0.07                         |
| 48              | "                                       | .3461                                  | 98.99                         | 1.01                         | 52.93                     | 52.91                    | 0.02                         |
| 49              | "                                       | .5555                                  | 98.40                         | 1.60                         | 52.94                     | 52.90                    | 0.04                         |
| 50              | "                                       | .6871                                  | 98.02                         | 1.98                         | 52.96                     | 52.91                    | 0.05                         |
| 51              | "                                       | .8920                                  | 97.44                         | 2.56                         | 53.00                     | 52.94                    | 0.06                         |
| 52              | "                                       | 1.062                                  | 96.97                         | 3.03                         | 53.03                     | 52.95                    | 0.08                         |
| 53              | 20.17                                   | 0.3952                                 | 98.78                         | 1.22                         | 52.90                     | 52.90                    | 0.00                         |
| 54              | "                                       | 1.671                                  | 95.09                         | 4.91                         | 53.15                     | 53.01                    | 0.04                         |
| 55              | "                                       | 3.599                                  | 90.10                         | 9.90                         | 53.68                     | 53.37                    | 0.31                         |
| 56              | "                                       | 8.162                                  | 79.87                         | 20.13                        | 55.95                     | 54.37                    | 1.58                         |
| 57              | "                                       | 13.93                                  | 69.97                         | 30.03                        | 59.49                     | 55.20                    | 4.29                         |
| 58              | "                                       | 21.64                                  | 59.92                         | 40.08                        | 13.81                     | 59.14                    | 4.67                         |
| 59              | 0.8865                                  | 27.22                                  | 4.97                          | 95.03                        | 85.70                     | 84.59                    | 1.11                         |
| 60              | 2.988                                   | "                                      | 14.99                         | 85.01                        | 82.11                     | 80.09                    | 2.02                         |
| 61              | 5.674                                   | "                                      | 25.07                         | 74.93                        | 78.26                     | 75.62                    | 2.64                         |
| 62              | 9.171                                   | "                                      | 35.11                         | 64.89                        | 74.18                     | 70.66                    | 3.52                         |
| 63              | 12.76                                   | "                                      | 42.94                         | 57.06                        | 71.13                     | 67.09                    | 4.04                         |
| 64              | 18.39                                   | "                                      | 52.04                         | 47.96                        | 67.05                     | 62.93                    | 4.12                         |
| 65              | 20.00                                   | 0.3900                                 | 98.80                         | 1.20                         | 52.90                     | 52.90                    | 0.00                         |

TABLE IV A

COMPARISON OF EXPERIMENTAL AND CALCULATED DATA

for the system: *p*-Dichlorobenzene - *p*-chlorobenzene

| Freezing<br>Point (°C) | Experimental<br>$x_B^L$ | Calculated<br>$x_B^L$ | Experimental<br>$x_B^S$ | Calculated<br>$x_B^S$ |
|------------------------|-------------------------|-----------------------|-------------------------|-----------------------|
| 53.15                  | 0.943                   | 0.996                 | 0.933                   | 0.992                 |
| 53.68                  | .902                    | .988                  | .860                    | .975                  |
| 55.95                  | .799                    | .934                  | .711                    | .873                  |
| 59.49                  | .700                    | .862                  | .593                    | .756                  |
| 63.81                  | .597                    | .758                  | .500                    | .611                  |
| 67.05                  | .521                    | .674                  | .430                    | .510                  |
| 71.13                  | .424                    | .557                  | .343                    | .391                  |
| 74.18                  | .352                    | .462                  | .276                    | .306                  |
| 78.26                  | .253                    | .331                  | .189                    | .204                  |
| 82.11                  | .150                    | .193                  | .105                    | .111                  |
| 85.70                  | .050                    | .060                  | .030                    | .032                  |

In the Table,  $x_B$  is the mole fraction of dichlorobenzene in the liquid and solid phases, designated by superscripts L and S, respectively.

### III. THE BINARY SYSTEM

p-DICHLORBENZENE: p-CHLORBROMBENZENE

Examination of the data in Tables V and V A and the plot of these data in Fig.34, shows that the experimental curves for both liquidus and solidus lines lie far below the straight line joining the freezing points of the pure components. Also, the experimental curves lie considerably below the calculated curves, which straddle the aforementioned straight line. The theoretical and observed curves compare only in that the freezing intervals are approximately the same.

As in the system dichlorobenzene: dibromobenzene, this binary system possesses a minimum congruent freezing temperature. However, the minimum lies at the slightly higher temperature of  $52.96^{\circ}$  and at a higher concentration of chlorbrombenzene, viz., 2.57 mole percent.

#### The Effect of Slow Cooling

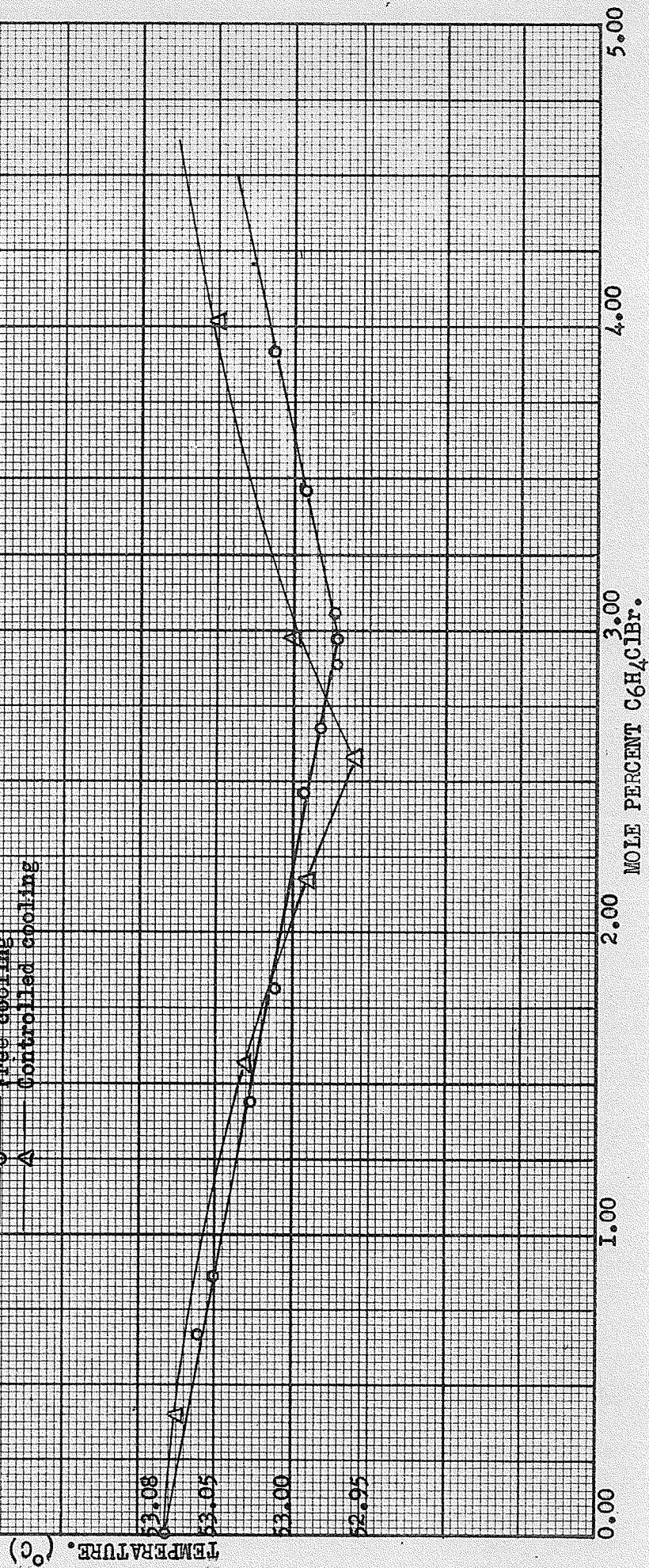
It was of interest to determine the effect, if any, of slow cooling and rapid cooling in causing a shift in the minimum freezing point of the system. That such a shift actually was effected, is shown by Fig.35. The liquidus curve determined by free cooling was a straight line extending to a minimum temperature of  $52.97^{\circ}$  at a concentration of 3% chlorbrombenzene. By employing very slow controlled cooling at the rate of  $0.3^{\circ}$  per minute, slightly higher freezing points, and a sharper minimum at 2.57% chlorbrombenzene were obtained. The general effect of the slow cooling was to produce higher freezing points. At higher concentrations, of the

Figure 35.

The effect of slow cooling on  
the liquidus curve in the system:



○ Free cooling  
△ Controlled cooling



order of 40 percent of one of the components, the determined freezing points were as much as  $0.4^{\circ}$  higher than the freezing points observed for free cooling.

TABLE V

THE SYSTEM p-DICHLORBENZENE: p-CHLORBROMBENZENE

| Experiment | Weight<br>Dichlor-<br>benzene<br>(gms.) | Weight<br>Chlorbrom-<br>benzene<br>(gms.) | Mole %<br>Dichlor-<br>benzene | Mole %<br>Chlorbrom-<br>benzene | Freezing<br>Point<br>( $^{\circ}\text{C}$ ) | Melting<br>Point<br>( $^{\circ}\text{C}$ ) | Freezing<br>Interval<br>( $^{\circ}\text{C}$ ) |
|------------|-----------------------------------------|-------------------------------------------|-------------------------------|---------------------------------|---------------------------------------------|--------------------------------------------|------------------------------------------------|
| 66         | 19.02                                   | 0.3867                                    | 98.46                         | 1.54                            | 53.03                                       | 52.99                                      | 0.04                                           |
| 67         | "                                       | 0.5477                                    | 97.84                         | 2.16                            | 52.99                                       | 52.96                                      | 0.03                                           |
| 68         | "                                       | 0.8123                                    | 97.04                         | 2.96                            | 53.00                                       | 52.97                                      | 0.03                                           |
| 69         | "                                       | 1.177                                     | 95.47                         | 4.53                            | 53.09                                       | 53.00                                      | 0.09                                           |
| 70         | "                                       | 1.569                                     | 94.04                         | 5.96                            | 53.16                                       | 53.10                                      | 0.06                                           |
| 71         | 18.09                                   | 0.0930                                    | 99.59                         | 0.41                            | 53.08                                       | 53.03                                      | 0.05                                           |
| 72         | "                                       | 0.9570                                    | 96.09                         | 3.91                            | 53.05                                       | 53.00                                      | 0.05                                           |
| 73         | 0.5155                                  | 21.55                                     | 3.00                          | 97.00                           | 64.06                                       | 63.85                                      | 0.21                                           |
| 74         | 1.895                                   | "                                         | 9.27                          | 90.73                           | 62.91                                       | 62.61                                      | 0.30                                           |
| 75         | 5.512                                   | "                                         | 25.01                         | 74.99                           | 60.67                                       | 60.15                                      | 0.52                                           |
| 76         | 11.02                                   | "                                         | 39.97                         | 60.03                           | 58.50                                       | 57.78                                      | 0.72                                           |
| 77         | 17.69                                   | 0.2288                                    | 99.02                         | 0.98                            | 53.05                                       | 53.01                                      | 0.04                                           |
| 78         | "                                       | 0.6046                                    | 97.43                         | 2.57                            | 52.96                                       | 52.96                                      | 0.00                                           |
| 79         | "                                       | 0.7026                                    | 97.03                         | 2.97                            | 53.00                                       | 52.96                                      | 0.04                                           |
| 80         | "                                       | 0.9680                                    | 95.97                         | 4.03                            | 53.05                                       | 52.99                                      | 0.06                                           |
| 81         | "                                       | 1.224                                     | 94.96                         | 5.04                            | 53.11                                       | 53.03                                      | 0.08                                           |
| 82         | "                                       | 2.559                                     | 90.00                         | 10.00                           | 53.48                                       | 53.26                                      | 0.22                                           |
| 83         | "                                       | 7.698                                     | 74.96                         | 25.04                           | 54.55                                       | 54.26                                      | 0.29                                           |
| 84         | 12.22                                   | 9.759                                     | 62.00                         | 38.00                           | 55.83                                       | 55.37                                      | 0.46                                           |
| 85         | 12.22                                   | 15.94                                     | 49.97                         | 50.03                           | 57.36                                       | 56.61                                      | 0.75                                           |

TABLE <sup>VI</sup> ~~V~~A

COMPARISON OF EXPERIMENTAL AND CALCULATED DATA <sup>44</sup>

for all System *p*-Dichlorobenzene - *p*-Chlorobenzene

| Freezing<br>Point (°C) | Experimental<br>$x_B^L$ | Calculated<br>$x_B^L$ | Experimental<br>$x_B^S$ | Calculated<br>$x_B^S$ |
|------------------------|-------------------------|-----------------------|-------------------------|-----------------------|
| 53.16                  | .958                    | 0.985                 | .921                    | 0.981                 |
| 53.48                  | .899                    | .959                  | .858                    | .949                  |
| 54.55                  | .751                    | .869                  | .709                    | .839                  |
| 55.83                  | .620                    | .774                  | .572                    | .730                  |
| 57.36                  | .493                    | .648                  | .433                    | .592                  |
| 58.50                  | .406                    | .555                  | .345                    | .497                  |
| 60.67                  | .250                    | .363                  | .203                    | .311                  |
| 62.91                  | .094                    | .163                  | .078                    | .134                  |
| 64.06                  | .019                    | .048                  | .022                    | .039                  |

In the Table,  $x_B$  is the mole fraction of dichlorobenzene.

#### IV. THE TERNARY SYSTEM

p-DICHLORBENZENE: p-CHLORBROMBENZENE: p-DIBROMBENZENE

Table VI contains all data relevant to the freezing and melting points of the ternary mixtures examined. The data have been classified into five sections, each corresponding to one of the numbered quasi-binary sections indicated in Fig.29.

Construction of some of the isotherms of the ternary system by graphical interpolation from the quasi-binary sections gave the resulting diagram of Fig.36. The isotherms shown are those lying on the solidus surface at the indicated temperatures. In general, they are all curved slightly, but the isotherm of  $58^{\circ}$  is practically a straight line. At lower temperatures than this, the isotherms change their direction of curvature.

A very similar diagram for the liquidus isotherms was obtained, differing from Fig.36 only in that the isotherms all curved toward the lower temperatures. In the body of the diagram the isotherms were substantially straight lines. This can be seen from Fig.37, which illustrates the relations between the solidus and liquidus isotherms. Each liquidus isotherm (full line) with its corresponding solidus isotherm (broken line) constitutes the boundary of a heterogeneous liquid-plus-solid region. Tie lines have been inserted qualitatively into the diagram to illustrate the direction of crystallization and composition change in the ternary system. The exact directions of the tie-lines are not known. They could be determined only by analysis of the first portion of

solid phase separating from a liquid solution of known composition.

If it were not known that minimum freezing points existed in the two binary systems containing dichlorobenzene, it might be concluded that the ternary system belongs to Type 1.1.1. of Schreinemakers' classification: the three components are miscible in all proportions in both liquid and solid phases. However, the existence of such minima prevents this deduction, and the isotherms in the dichlorobenzene corner assume a more interesting form.

The liquidus and solidus isotherms in the dichlorobenzene corner are represented on a larger scale in Figs.38 and 39, respectively. The location of the isotherms and their shape preclude any possibility of the existence of a ternary minimum freezing point, as was suggested by Bruni (4). Plotting selected liquidus and corresponding solidus isotherms, the unusual diagram of Fig.40 was obtained. Tie-lines have been inserted in order that the heterogeneous bands may be easily distinguished. More bands than the three shown were not plotted because of the complexity introduced by overlapping of the very wide bands in this region.

TABLE VI

THE TERNARY SYSTEM p-DICHLOROBENZENE: p-CHLOROBROMOBENZENE: p-DIBROMOBENZENE

| Experiment | Weight<br>Dichloro-<br>benzene<br>(gms.) | Weight<br>Chlorbrom-<br>benzene<br>(gms.) | Weight<br>Dibrom-<br>benzene<br>(gms.) | Mole %<br>Dichloro-<br>benzene | Mole %<br>Chlorbrom-<br>benzene | Mole %<br>Dibrom-<br>benzene | Freezing<br>Point<br>(°C) | Melting<br>Point<br>(°C) | Freezing<br>Interval<br>(°C) |
|------------|------------------------------------------|-------------------------------------------|----------------------------------------|--------------------------------|---------------------------------|------------------------------|---------------------------|--------------------------|------------------------------|
| Section 1  |                                          |                                           |                                        |                                |                                 |                              |                           |                          |                              |
| 86         | 0.00                                     | 25.53                                     | 33.97                                  | 0.00                           | 48.08                           | 51.92                        | 76.25                     | 74.53                    | 1.72                         |
| 87         | 1.381                                    | 7.236                                     | 9.634                                  | 10.65                          | 42.84                           | 46.51                        | 73.54                     | 70.86                    | 2.68                         |
| 88         | 3.885                                    | 7.236                                     | 9.634                                  | 25.10                          | 35.90                           | 39.00                        | 69.33                     | 66.47                    | 2.86                         |
| 89         | 7.246                                    | 7.236                                     | 9.634                                  | 38.47                          | 29.50                           | 32.03                        | 65.32                     | 62.42                    | 2.90                         |
| 90         | 10.53                                    | 7.236                                     | 9.634                                  | 47.61                          | 25.11                           | 27.28                        | 62.57                     | 59.69                    | 2.88                         |
| 91         | 13.40                                    | 0.0586                                    | 0.0781                                 | 99.32                          | 0.33                            | 0.35                         | 53.02                     | 52.98                    | 0.04                         |
| 92         | 13.40                                    | 0.1021                                    | 0.1362                                 | 98.80                          | 0.63                            | 0.57                         | 52.95                     | 52.92                    | 0.03                         |
| 93         | 13.40                                    | 0.1512                                    | 0.2014                                 | 98.24                          | 0.85                            | 0.91                         | 52.97                     | 52.94                    | 0.03                         |
| 94         | 13.40                                    | 0.2426                                    | 0.3230                                 | 97.18                          | 1.35                            | 1.47                         | 53.01                     | 52.95                    | 0.06                         |
| 95         | 13.40                                    | 0.3151                                    | 0.4197                                 | 96.39                          | 1.74                            | 1.87                         | 53.05                     | 52.98                    | 0.07                         |
| 96         | 13.40                                    | 0.6901                                    | 0.9186                                 | 92.38                          | 3.65                            | 3.97                         | 53.34                     | 53.22                    | 0.12                         |
| 97         | 13.40                                    | 1.923                                     | 2.561                                  | 81.35                          | 8.96                            | 9.69                         | 54.67                     | 54.19                    | 0.48                         |
| 98         | 13.40                                    | 3.197                                     | 4.259                                  | 72.41                          | 13.27                           | 14.32                        | 56.42                     | 55.20                    | 1.22                         |
| 99         | 13.40                                    | 4.984                                     | 6.637                                  | 62.74                          | 17.92                           | 19.34                        | 58.72                     | 56.38                    | 2.34                         |
| 100        | 1.170                                    | 8.581                                     | 11.419                                 | 7.87                           | 44.31                           | 47.82                        | 74.22                     | 72.15                    | 2.07                         |
| 101        | 3.773                                    | 8.581                                     | 11.419                                 | 21.59                          | 37.72                           | 41.69                        | 70.35                     | 67.14                    | 3.21                         |
| 102        | 8.160                                    | 8.581                                     | 11.419                                 | 37.33                          | 30.13                           | 32.54                        | 65.67                     | 62.73                    | 2.94                         |
| Section 2  |                                          |                                           |                                        |                                |                                 |                              |                           |                          |                              |
| 103        | 0.00                                     | 30.00                                     | 22.66                                  | 0.00                           | 62.00                           | 38.00                        | 72.97                     | 71.37                    | 1.60                         |
| 104        | 25.04                                    | 0.0897                                    | 0.0678                                 | 99.55                          | 0.25                            | 0.20                         | 53.08                     | 53.00                    | 0.08                         |
| 105        | 25.04                                    | 0.1855                                    | 0.1402                                 | 99.09                          | 0.56                            | 0.35                         | 53.03                     | 53.97                    | 0.06                         |
| 106        | 25.04                                    | 0.3640                                    | 0.2749                                 | 98.22                          | 1.09                            | 0.69                         | 52.94                     | 52.90                    | 0.04                         |
| 107        | 25.04                                    | 0.5500                                    | 0.4154                                 | 97.36                          | 1.63                            | 1.01                         | 52.99                     | 52.93                    | 0.06                         |
| 108        | 20.00                                    | 0.8504                                    | 0.6423                                 | 95.00                          | 3.10                            | 1.90                         | 53.10                     | 53.03                    | 0.07                         |
| 109        | 20.00                                    | 1.795                                     | 1.356                                  | 90.00                          | 6.20                            | 3.80                         | 53.46                     | 53.30                    | 0.16                         |
| 110        | 20.00                                    | 4.040                                     | 3.051                                  | 80.00                          | 12.40                           | 7.60                         | 54.55                     | 54.06                    | 0.49                         |

|                  |       |        |        |       |       |       |       |       |      |
|------------------|-------|--------|--------|-------|-------|-------|-------|-------|------|
| 111              | 20.00 | 8.701  | 6.571  | 65.00 | 21.70 | 13.30 | 57.10 | 55.60 | 1.50 |
| 112              | 1.567 | 11.39  | 8.606  | 10.00 | 55.80 | 34.20 | 70.47 | 68.29 | 2.18 |
| 113              | 4.701 | 11.39  | 8.606  | 25.00 | 46.50 | 28.50 | 66.30 | 63.01 | 3.29 |
| 114              | 9.403 | 11.39  | 8.606  | 40.00 | 37.20 | 22.80 | 62.82 | 60.76 | 2.06 |
| 115              | 14.11 | 11.39  | 8.606  | 50.00 | 31.00 | 19.00 | 60.37 | 58.29 | 2.08 |
| <u>Section 3</u> |       |        |        |       |       |       |       |       |      |
| 116              | 0.00  | 29.77  | 12.23  | 74.99 | 25.01 | 0.00  | 69.89 | 68.43 | 1.46 |
| 117              | 1.629 | 13.96  | 5.73   | 67.34 | 22.42 | 10.24 | 67.58 | 66.24 | 1.34 |
| 118              | 4.832 | 13.96  | 5.73   | 56.05 | 18.67 | 25.28 | 64.39 | 63.09 | 1.30 |
| 119              | 9.517 | 13.96  | 5.73   | 45.02 | 14.99 | 39.99 | 61.12 | 59.42 | 1.70 |
| 120              | 17.20 | 0.1357 | 0.0558 | 0.61  | 0.20  | 99.19 | 53.06 | 53.01 | 0.05 |
| 121              | 17.20 | 0.2777 | 0.1141 | 1.22  | 0.41  | 98.37 | 53.00 | 52.95 | 0.05 |
| 122              | 17.20 | 0.4411 | 0.1813 | 1.94  | 0.62  | 97.44 | 52.97 | 52.93 | 0.04 |
| 123              | 17.20 | 0.6100 | 0.2507 | 2.63  | 0.86  | 96.51 | 52.99 | 52.94 | 0.05 |
| 124              | 17.20 | 0.8935 | 0.3674 | 3.80  | 1.26  | 94.94 | 53.11 | 53.03 | 0.08 |
| 125              | 17.20 | 1.605  | 0.6600 | 6.54  | 2.18  | 91.28 | 53.35 | 53.27 | 0.08 |
| 126              | 17.20 | 3.780  | 1.552  | 13.77 | 4.59  | 81.64 | 54.20 | 53.89 | 0.31 |
| 127              | 17.20 | 6.611  | 2.717  | 21.15 | 7.08  | 71.77 | 55.49 | 54.92 | 0.57 |
| 128              | 17.20 | 8.672  | 3.564  | 25.44 | 8.82  | 65.74 | 56.44 | 55.46 | 0.98 |
| 129              | 6.401 | 9.000  | 3.699  | 44.24 | 14.76 | 41.00 | 60.99 | 59.32 | 1.67 |
| 130              | 9.290 | 9.000  | 3.699  | 37.34 | 12.44 | 50.22 | 59.10 | 57.72 | 1.38 |
| <u>Section 4</u> |       |        |        |       |       |       |       |       |      |
| 131              | 0.00  | 9.468  | 35.00  | 0.00  | 25.00 | 75.00 | 81.75 | 80.54 | 1.21 |
| 132              | 20.00 | 0.0327 | 0.1210 | 99.50 | 0.13  | 0.37  | 53.05 | 52.98 | 0.07 |
| 133              | 20.00 | 0.0791 | 0.2925 | 98.80 | 0.30  | 0.90  | 52.96 | 52.92 | 0.04 |
| 134              | 20.00 | 0.1671 | 0.6175 | 97.50 | 0.63  | 1.87  | 52.99 | 52.93 | 0.05 |
| 135              | 20.00 | 0.3429 | 1.2675 | 95.00 | 1.25  | 3.75  | 53.15 | 53.08 | 0.07 |
| 136              | 20.00 | 0.6443 | 2.3817 | 91.00 | 2.25  | 6.75  | 53.51 | 53.30 | 0.21 |
| 137              | 20.00 | 1.6286 | 6.0205 | 80.00 | 5.00  | 15.00 | 55.28 | 54.39 | 0.89 |
| 138              | 20.00 | 3.508  | 12.97  | 65.00 | 8.75  | 26.25 | 59.49 | 57.35 | 2.14 |
| 139              | 1.453 | 4.258  | 15.74  | 10.00 | 22.50 | 67.50 | 78.96 | 78.04 | 0.92 |
| 140              | 4.358 | 4.258  | 15.74  | 25.00 | 18.75 | 56.25 | 73.87 | 71.47 | 2.40 |
| 141              | 8.716 | 4.258  | 15.74  | 40.00 | 15.00 | 45.00 | 68.49 | 65.39 | 3.10 |
| 142              | 13.07 | 4.258  | 15.74  | 50.00 | 12.50 | 37.50 | 64.82 | 60.86 | 3.96 |

Section 5

|     |       |        |        |       |      |      |       |       |      |
|-----|-------|--------|--------|-------|------|------|-------|-------|------|
| 143 | 20.00 | 0.00   | 0.3900 | 98.80 | 0.00 | 1.20 | 52.90 | 52.90 | 0.00 |
| 144 | 20.00 | 0.1079 | 0.3900 | 98.40 | 0.41 | 1.19 | 52.93 | 52.91 | 0.02 |
| 145 | 20.00 | 0.1665 | 0.3900 | 98.18 | 0.63 | 1.19 | 52.94 | 52.91 | 0.03 |
| 146 | 20.00 | 0.2653 | 0.3900 | 97.82 | 2.00 | 1.18 | 52.95 | 52.92 | 0.03 |
| 147 | 20.00 | 1.095  | 0.3900 | 95.15 | 3.99 | 1.16 | 53.11 | 52.99 | 0.12 |
| 148 | 20.00 | 2.284  | 0.3900 | 90.93 | 7.97 | 1.10 | 53.35 | 53.21 | 0.14 |

## GENERAL DISCUSSION

The experimental results indicate a temperature of reversible transition of  $39.6^{\circ}$  for p-dichlorobenzene. Cooling curves of those binary mixtures containing this material as one of the components were examined carefully in this temperature region for any evidence of a break. For those mixtures containing from 95 to 100 percent p-dichlorobenzene a change in slope of the cooling curve was actually detected. The effect of addition of p-dibromobenzene or p-chlorobromobenzene to the pure p-dichlorobenzene was to depress the transition temperature of the latter. Beck and Ebbinghaus (40) have determined the transition curve for the system: p-dichlorobenzene: p-dibromobenzene and find it to be a straight line running from  $39.5^{\circ}$ , the transition temperature of p-dichlorobenzene, to  $-8^{\circ}$ , the transition temperature of p-dibromobenzene. Since the break in the cooling curve for the pure dichlorobenzene alone was barely detectable, it disappeared completely when mixtures containing either of the other two components in excess of 5 percent were examined. Also, limitations of the apparatus prevented the determination of the transition curves.

In view of the great similarity in molecular and crystallographic structures, it is not surprising that these dihalogen benzenes are miscible in all proportions in both liquid and solid phases. All three binary systems, however, exhibit a decided tendency toward negative deviation from Raoult's law; at some lower temperature there may exist a

miscibility gap in the solid solution region.

The p-dichlorobenzene molecule which is the lightest of the three, is perfectly symmetrical and has no dipole moment. Apparently this molecule possesses properties not associated with the asymmetrical chlorbrombenzene molecule or even the symmetrical dibrombenzene molecule. Addition of a higher melting foreign material of similar structure such as p-chlorbrombenzene or p-dibrombenzene produces a depression in the freezing point of the pure dichlorobenzene. Adding the heavier, higher melting dibrombenzene produces the greatest and most rapid depression. There is required more of the lighter chlorbrombenzene molecule, relative to the quantity of dibrombenzene, to produce a given freezing point depression. The solution of dichlorobenzene and chlorbrombenzene freezing at  $53.08^{\circ}$ , the freezing point of pure dichlorobenzene, contains 4.4 percent chlorbrombenzene. The analogous solution of dichlorobenzene and dibrombenzene contains only 3.8 percent of the latter, again indicating that relatively less of the heavier molecule is required to produce a specific effect. It is also of interest to note that in the system dichlorobenzene: dibrombenzene, composed of two perfectly symmetrical molecules, the freezing intervals were quite large in comparison with those of the systems composed of one symmetrical and one asymmetrical molecule.

That the binary systems are not representative of the ideal solution is shown by the lack of correspondence of calculated and experimental curves. Such correspondence would not be expected in those systems containing dichlorobenzene, but even in the system chlorbrombenzene: dibrombenzene to which Seltz's equations should apply exactly, agreement of calculated and experimental results was not good. Assuming erroneous values for the heats of fusion of the components as given by Narbutt (Table I), experimental results were employed to calculate the heats of fusion from Seltz's equations. It was found that the calculated values for the heats of fusion varied depending on the range of temperature selected. A finite heat of solution must therefore be associated with these binary solutions.

The solidus isotherms of the ternary system are very nearly perfectly straight lines; the solidus surface is but slightly convex toward the lower temperatures. At approximately  $58^{\circ}$  the direction of concavity of the surface changes, so that at temperatures below  $58^{\circ}$  the solidus surface is concave toward the lower temperatures. This temperature of  $58^{\circ}$  is very closely the average of the freezing temperatures of dichlorobenzene ( $53.08^{\circ}$ ) and chlorbrombenzene ( $64.58^{\circ}$ ).

Experimental results prove conclusively that the ternary system is representative of Schreinemakers' Type 1.3.3.,

(shown qualitatively in Fig.17) having neither a ternary congruently freezing solution nor a ternary minimum freezing point. These results contradict those of Bruni and Gorni (3), which indicate the existence of a ternary congruently freezing solution. The results of these authors were examined carefully, quasi-binary sections were plotted, and the ternary isotherms were constructed by interpolation. Data relevant to the isotherms in the dichlorobenzene corner was insufficient and the three quasi-binary sections did not agree very well within themselves, so that these authors were justified in constructing the diagram represented in Fig.22. By rejecting one series of their measurements, a diagram qualitatively similar to Fig.38 was obtained. However, no true comparison of results may be obtained, since it is evident that the materials used by Bruni and Gorni were not absolutely pure.

## SUMMARY

1. The freezing points of pure p-dichlorobenzene, p-chlorobromobenzene and p-dibromobenzene are  $53.08^{\circ}$ ,  $64.58^{\circ}$  and  $87.30^{\circ}$ , respectively.
2. Pure p-dichlorobenzene exists in at least two forms under atmospheric pressure, the reversible transformation occurring at  $39.6^{\circ}$ .
3. p-dibromobenzene and p-chlorobromobenzene are miscible in all proportions in both liquid and solid phases; the freezing points of all solutions lie between the freezing points of the pure components.
4. The binary system: p-dichlorobenzene: p-dibromobenzene exhibits a minimum temperature of congruent freezing of  $52.90^{\circ}$  at a concentration of 1.22 mole percent of dibromobenzene. The components are miscible in all proportions in both liquid and solid phases.
5. The binary system: p-dichlorobenzene: p-chlorobromobenzene exhibits a minimum temperature of congruent freezing of  $52.96^{\circ}$  at a concentration of 2.57 mole percent chlorobromobenzene. The components are miscible in all proportions in both liquid and solid phases.
6. p-dichlorobenzene, p-chlorobromobenzene and p-dibromobenzene are miscible in all proportions in both liquid and solid phases. A continuous series of solid solutions is formed. There exists no ternary congruently freezing solution.

7. Slow cooling of liquid solutions from which solid solutions are deposited in the freezing process results in higher freezing points and smaller freezing intervals than those obtained experimentally when liquid and solid phases are not in equilibrium due to too rapid a rate of cooling.

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